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ANHYDROUS ALTERATION OF ALLENDE CHONDRULES IN THE SOLAR NEBULA II: ALKALI-Ca EXCHANGE REACTIONS AND FORMATION OF NEPHELINE, SODALITE AND Ca-RICH PHASES IN CHONDRULES

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Abstract: Fifty-eight Allende chondrules were studied to investigate secondary anhydrous alteration of chondrules. Nepheline and sodalite replace anorthite-normative cryptocrystalline groundmass and plagioclase. These reactions presumably took place by replacement of Ca of the anorthite component by 2(Na,K) introduced from chondrules, and are called alkali-Ca exchange reactions. The degree of the reaction is variable among chondrules; a few chondrules display the reaction in the peripheral parts only. In contrast, the primary groundmass in some other chondrules was totally replaced by nepheline and sodalite. Most of the Allende chondrules were subjected to the alkali-Ca exchange reaction. Some Ca-rich phases such as hedenbergite, andradite, grossular, kirschsteinite and wollastonite, rarely occur intimately with nepheline and sodalite in groundmass. These Ca-rich phases are also secondary products in chondrules. During the alkali-Ca exchange reaction, part of the CaO released from anorthite was used to form the Ca-rich phases in chondrules. Since the abundance of the Ca-rich phases is too low, CaO was mostly lost from chondrules during the alkali-Ca exchange reaction. CAIs and chondrules in oxidized CV chondrites include similar secondary minerals, suggesting that both of them were subjected to the alkali-Ca exchange reaction under similar conditions.

1. Introduction

IKEDA (1982), and IKEDA and KIMURA (1985), found four "zoned chondrules" in the ALH-77003 (CO3) and Allende (CV3) meteorites; the glassy groundmass of these chondrules shows textural and chemical zonation, from the primary and CaO-enriched glass in the center to the devitrified and Na_2O-rich margin. These authors suggested that such zoning was formed by the secondary introduction of Na_2O from solar gas, accompanied by loss of CaO from the chondrules. Later KIMURA and IKEDA (1992) discovered sodalite in devitrified groundmass in some Allende chondrules.

On the other hand, it is well known that Ca-Al-rich inclusions (CAIs) in not only Allende but other carbonaceous chondrites experienced alteration reactions to form secondary minerals such as nepheline, sodalite, grossular, hedenbergite and others (*e.g.*, WARK, 1981; MACPHERSON *et al.*, 1988). The most important alteration reaction for the CAIs is the introduction of Na and loss of Ca (*e.g.*, IKEDA, 1982; HASHIMOTO and GROSSMAN, 1987). Thus, similar alteration reactions may have also occurred in chondrules.

Here we did a detailed mineralogical and petrological study of 58 Allende chondrules. The purposes of this study are (1) detailed scrutiny of primary and secondary minerals, (2) to investigate whether the alteration reaction took place commonly in chondrules or not, and (3) to explore the reactions for alteration processes. Especially, we focus on the problem of where CaO went during the alteration processes. Our companion paper (IKEDA and KIMURA, 1995) discusses FeO reactions, oxygen isotopic compositions of altered chondrules, and physical conditions of the reactions.

2. Samples and Experimental Methods

We studied fifteen polished thin sections of the Allende chondrite (CV3). Detailed SEM-petrography and phase analysis were carried out on 58 chondrules selected from these thin sections. The chemical compositions of the constituent phases were determined with a JEOL 733 electron-probe microanalyzer. The accelerating voltage and beam current were 15 kV and 3 to 10 nA, respectively. The Bence-Albee correction method was used for the analysis of silicates. A special deconvolution program was applied to correct for X-ray overlaps of K_β on K_α lines of some successive elements such as Ti-V.

3. Petrography

3.1. General features of chondrules

Chondrules studied here cover various types of texture (46 porphyritic and 12 barred chondrules), size (0.4–2.2 mm in diameter), shape (spherical to fragmental) and chemistry (57 magnesian and 1 ferroan chondrules). Some chondrules have fine to coarse-grained rims. Table 1 displays the mineral assemblages of the chondrules.

Phenocrystic phases are usually olivine and low-Ca pyroxene ($Wo_{15}>$) with high-Ca pyroxene. Olivine is generally the most abundant phase in chondrules. Fifteen chondrules contain pale to dark brown cryptocrystalline groundmass (Fig. 1-1). Plagioclase occurs in 32 holocrystalline chondrules as fine-grained groundmass phase, or rarely as phenocryst. Hereafter, cryptocrystalline groundmass and plagioclase are designated primary groundmass.

Almost all chondrules studied include opaque spherules, consisting of awaruite, pyrrhotite, pentlandite, heazlewoodite and magnetite. Their abundance is usually less than 1–2 vol% of chondrules. Small amounts of whitlockite, apatite and brianite commonly exist in the spherules.

3.2. Altered groundmass

Devitrified groundmass appears to be dark brown to black in color under an optical microscope (Fig. 1-1). The devitrified groundmass will be called altered. The boundary between primary and altered groundmasses is always sharp (Figs. 1-1 and 1-2). The abundance and mode of occurrence of the altered groundmass seem to be different in chondrules. "Zoned chondrules", reported by IKEDA and KIMURA (1985), abundantly contain the primary groundmass in the centers of these chondrules. The altered groundmass is encountered only in the peripheral parts of these chondrules

Fig. 1-1. A "zoned chondrule" in Allende. It consists of barred olivine phenocrysts (Oli), cryptocrystalline groundmass (cGm), and dark and altered groundmass in the peripheral part of the chondrule (aGm). Transmitted light, open nicols, and width of 0.6 mm.

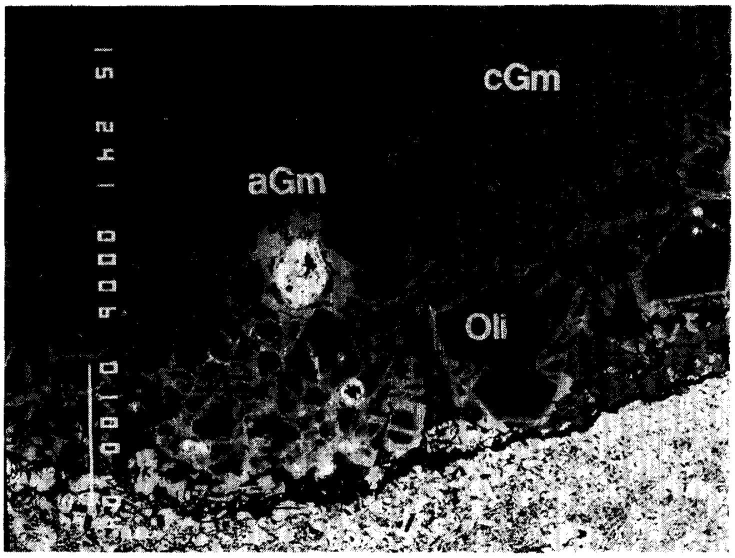

Fig. 1-2. Back-scattered electron (BSE) image of the zoned chondrule (Fig. 1-1). Olivine phenocrysts (Oli) in cryptocrystalline groundmass (cGm) are not zoned, whereas those in altered groundmass (aGm) are zoned. Width of 480 microns.

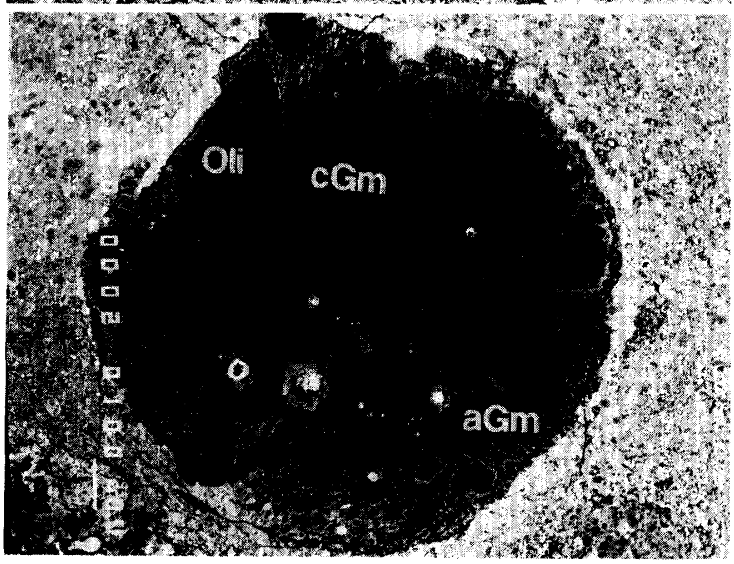

Fig. 1-3. BSE image of an altered chondrule. Cryptocrystalline groundmass (cGm) remains in the center of this chondrule, whereas groundmass is abundantly devitrified (aGm). This chondrule has olivine (Oli) phenocrysts. Width of 1300 microns.

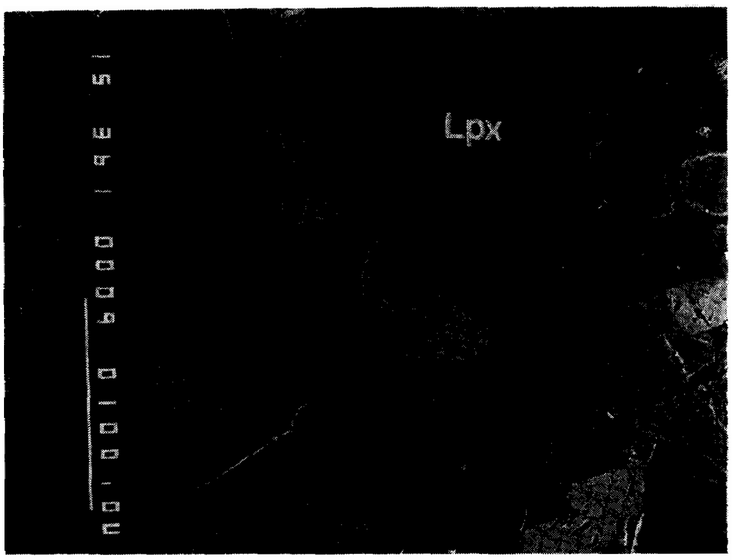

Fig. 1-4. Cryptocrystalline groundmass (cGm) in the center of a chondrule. Along the boundary between groundmass and phenocrysts, nepheline (Nep) is generated. BSE image. Width of 320 microns.

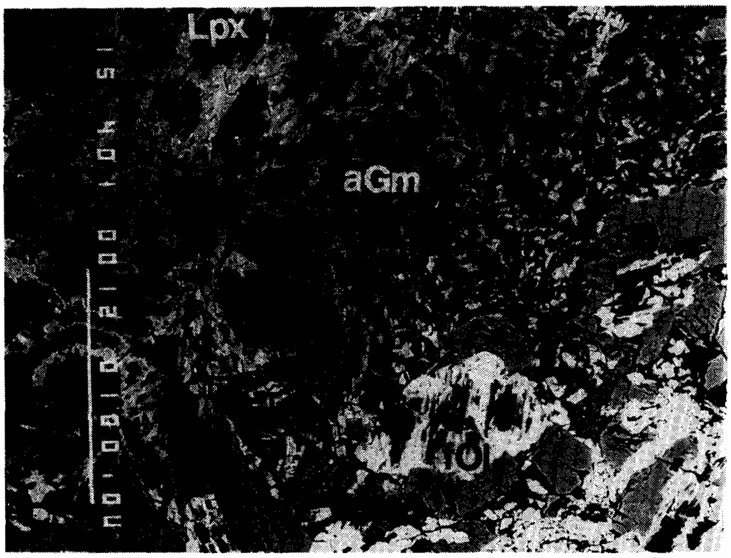

Fig. 1-5. An altered groundmass (aGm) enriched in sodalite. This chondrule has no primary groundmass. Low-Ca pyroxene phenocrysts (Lpx) are abundantly replaced by ferroan olivine (fOl), whereas high-Ca pyroxene (Hpx) does not show reaction texture. BSE image. Width of 290 microns.

Fig. 1-6. Sodalite (Sod) directly replaces plagioclase (Pla) in a chondrule. BSE image. Width of 80 microns.

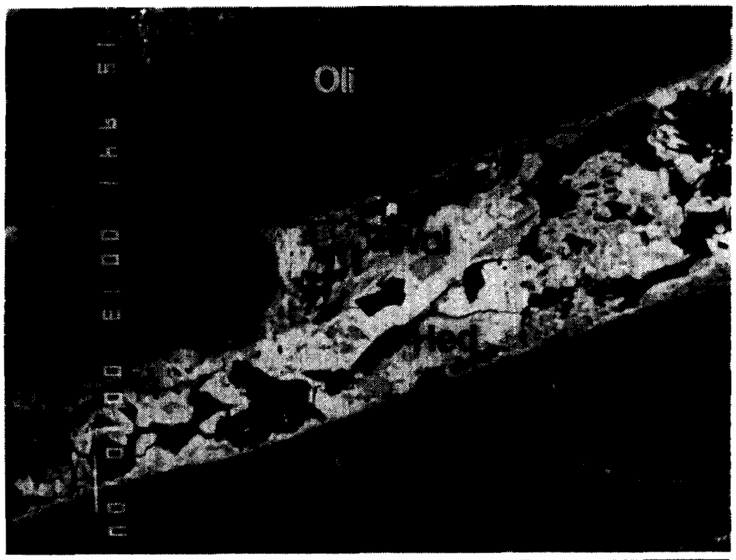

Fig. 1-7. BSE image of an occurrence of hedenbergite (Hed) with wollastonite (Wol) in the altered groundmass of a barred-olivine chondrule. Width of 100 microns.

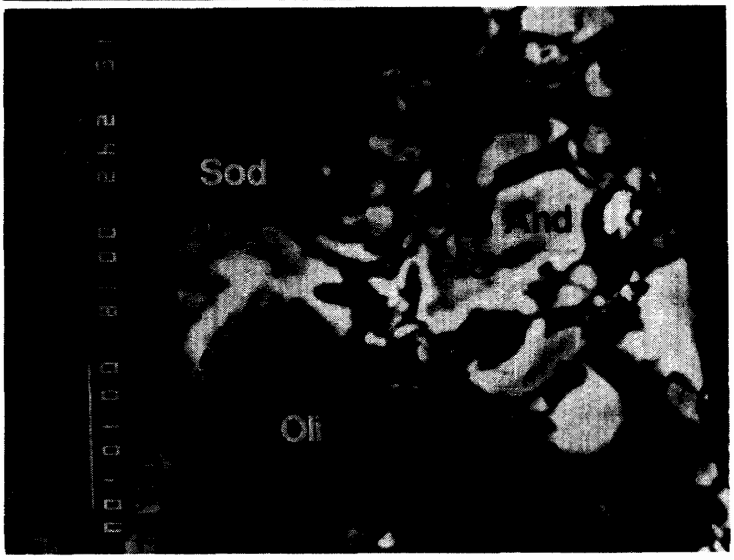

Fig. 1-8. Fine-grained grossular (Gro) occurs in intimate association with andradite (And) and sodalite (Sod) in the altered groundmass of a chondrule. BSE image. Width of 40 microns.

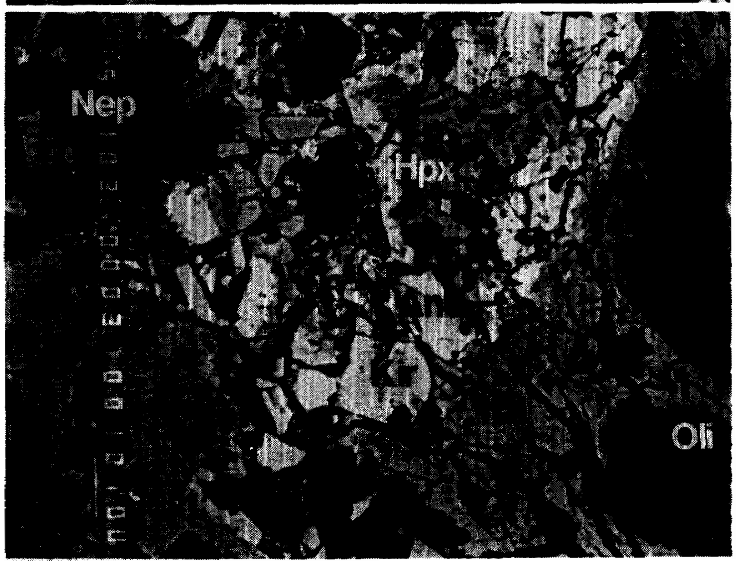

Fig. 1-9. An occurrence of kirschsteinite (Kir) with andradite (And) in the altered groundmass consisting of nepheline (Nep), ferroan olivine (fOl) and high-Ca pyroxene (Hpx) in a chondrule. BSE image. Width of 100 microns.

(Fig. 1-2). Only two zoned chondrules are encountered in our 15 thin sections.

The altered groundmass is more abundant than the primary groundmass in most of the Allende chondrules. The groundmass of a chondrule is mostly devitrified, and the primary groundmass remains only in the center (Fig. 1-3). In the central part of a chondrule, the altered groundmass is encountered along the boundaries between the primary groundmass and pyroxene phenocrysts (Fig. 1-4). Seventeen chondrules include only the altered groundmass in their central parts (Fig. 1-5).

The altered groundmass displays various textures from aggregate of fibrous crystals of submicron-scale, to aggregate of fine-grained crystals up to 10 microns in size. Nepheline is usually the predominant component in the altered groundmasses of all chondrules studied (Table 1). These nepheline grains are less than 10 microns in size. Sodalite is also a common constituent in the altered groundmass. This is the first report of sodalite from Allende chondrules. Sodalite occurs in 43 chondrules that also contain nepheline (Table 1). Sodalite and nepheline abundantly replace primary cryptocrystalline groundmass and plagioclase (Fig. 1-6).

The altered groundmass contains abundant fine-grained ferroan olivines, 2–10 microns in size. Olivine phenocrysts in the altered groundmass do not show any decomposition texture, yet they usually display normal Fe-Mg zoning. High-Ca pyroxenes show neither reaction texture nor Fe-Mg zoning. Although low-Ca pyroxene phenocrysts do not display Fe-Mg zoning, they usually show a texture reminiscent of replacement by fine-grained ferroan olivines in the altered groundmasses (Fig. 1-5).

Table 1. Mineral assemblage groups of 58 chondrules based on secondary minerals.

Group	nepheline-only	nephleine + sodalite	nepheline + sodalite + secondary Ca-rich phase					
No. of chondrules	15	14	18	4	4	1	1	1
Olivine	+	+	+	+	+	+	+	+
Low-Ca pyroxene	+	+	+	+	+	+	+	
High-Ca pyroxene*	+	+	+	+	+	+	+	+
Plagioclase	+	+	+	+	+		+	
Cryptocrystalline groundmass	+	+	+	+			+	
Nepheline	+	+	+	+	+	+	+	+
Sodalite		+	+	+	+	+	+	+
Hedenbergite			+	+	+	+		+
Wollastonite								+
Andradite				+	+	+	+	+
Grossular					+			
Kirschsteinite						+	+	
Phosphate	+	+	+	+	+	+	+	+

*"High-Ca pyroxene" excludes hedenbergitic pyroxene.

3.3. *Occurrence of secondary Ca-rich phases*

In addition to the high-Ca pyroxenes mentioned above, five kinds of Ca-rich silicate phases were encountered in the altered groundmass: hedenbergite, andradite, grossular, kirschsteinite and wollastonite. This is the first report of these phases from Allende chondrules. We shall call them secondary Ca-rich phases. Twenty-nine of the 58 chondrules studied have some of the secondary Ca-rich phases. The Ca-rich phases always occur in sodalite-bearing chondrules (Table 1). The abundance is less than about 1–2 vol% of the altered groundmass. They are typically smaller than 10 microns in size, and show anhedral outlines. These Ca-rich phases usually occur in close association with nepheline, sodalite and fine-grained ferroan olivine.

Table 1 summarizes the mineral assemblage groups of the Ca-rich phases in chondrules. Hedenbergite is the most common secondary Ca-rich phase, and 29 chondrules contain hedenbergite. Wollastonite was encountered in close association with hedenbergite only in a barred-olivine chondrule (Fig. 1-7). Andradite occurs in 11 chondrules, in association with hedenbergite, grossular, kirschsteinite or wollastonite. Four chondrules contain grossular that always occurs with andradite (Fig. 1-8). Two chondrules have kirschsteinite associated with andradite (Fig. 1-9) or hedenbergite.

4. Mineralogy

Olivine: Three types of olivine occurrence were noticed in magnesian chondrules: phenocrysts (Fo_{54-99}), fine grains replacing low-Ca pyroxene (Fo_{55-72}), and fine grains in altered groundmass (Fo_{51-73}). Olivine phenocrysts occurring in primary groundmass are magnesian (Fo_{90-99}), whereas those in altered groundmass are normally zoned (Fo_{54} to Fo_{99}). Ferroan rims of the phenocrysts have compositions similar to olivines in altered groundmass and olivines replacing low-Ca pyroxene. All these ferroan olivines contain 0.05–0.7 wt% MnO (Table 2). Olivine compositions range from Fo_{66-72} in a ferroan chondrule.

Pyroxene: Low-Ca pyroxenes occur as phenocrysts, and are magnesian ($En_{85-99}Fs_{0.2-7}Wo_{0.5-14}$), except those ($En_{57-61}Fs_{25-30}Wo_{11-19}$) in a ferroan chondrule (Fig. 2). Magnesian high-Ca pyroxenes occur as phenocrysts ($En_{44-84}Fs_{0.2-6.6}Wo_{15-55}$) and as elongated laths in primary and altered groundmasses ($En_{24-78}Fs_{0.1-23}Wo_{19-64}$). These high-Ca pyroxenes contain 0.0–3.1 wt% TiO_2, 0.7–22.5% Al_2O_3, 0.1–2.9% Cr_2O_3 and 0.0–1. 4% MnO (Table 2). On the other hand, hedenbergites ($En_{0-10}Fs_{40-50}Wo_{49-50}$) occur as fine grains only in altered groundmass. They are depleted in TiO_2 (0.0–0.2%), Al_2O_3 (0.0–3.3%) and Cr_2O_3 (0.0–0.2%), and contain 0.0–2.9% MnO.

Plagioclase: Plagioclase is enriched in anorthite molecule (An_{74-95}). The K_2O content is always low (<0.1 wt%).

Cryptocrystalline and altered groundmasses: Primary cryptocrystalline groundmass contains 45.4–54.5 wt% SiO_2, 18.4–29.4% Al_2O_3, 0.1–5.5% FeO, 1.8–12.6% MgO, 10.3–20.9% CaO, 0.8–5.4% Na_2O and 0.0–0.3% K_2O (Table 3). The Cl-content is below the detection limit (<0.07%). In comparison, altered groundmass is enriched in FeO (0.2–8.5 wt%), Na_2O (5.6–19.7%), K_2O (0.0–2.0%) and Cl

Table 2. Representative compositions of olivine, pyroxene and plagioclase.

Phase	Occurrence	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	NiO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl	Total	Fo	Wo/An	En/Ab	Fs/Or
Olivine	Phenocryst-core	42.36	0.07	0.23	0.07	0.62	0.00	0.00	56.56	0.59	0.04	0.00	0.00	0.00	0.00	100.54	99.4			
Olivine	Phenocryst-rim	35.54	0.00	0.00	0.00	38.56	0.18	0.18	25.35	0.10	0.06	0.00	0.06	0.00	0.00	100.03	54.0			
Olivine	Phenocryst-core	41.73	0.01	0.12	0.16	0.95	0.06	0.00	56.69	0.53	0.05	0.00	0.00	0.00	0.00	100.30	99.1			
Olivine	Phenocryst-rim	39.63	0.00	0.00	0.00	15.65	0.00	0.26	45.11	0.22	0.04	0.00	0.00	0.00	0.00	100.91	83.7			
Olivine	Phenocryst in ferroan chondrule	36.87	0.09	0.04	0.08	29.65	0.17	0.17	32.81	0.17	0.00	0.00	0.00	0.00	0.00	100.05	66.4			
Olivine	Fine-grain in groundmass	35.14	0.00	0.03	0.11	38.02	0.06	0.25	24.92	0.00	0.04	0.00	0.00	0.09	0.00	98.66	53.9			
Olivine	Fine-grain in groundmass	37.35	0.00	0.00	0.10	26.97	0.00	0.17	34.35	0.10	0.07	0.00	0.00	0.00	0.01	99.12	69.4			
Olivine	Fine-grain in groundmass	35.57	0.00	0.00	0.28	35.30	0.08	0.47	27.79	0.00	0.02	0.00	0.00	0.00	0.00	99.51	58.4			
Olivine	Replacing low-Ca pyroxene	36.45	0.00	0.25	0.36	34.16	0.14	0.31	28.58	0.06	0.08	0.01	0.00	0.00	0.00	100.40	59.9			
Low-Ca pyroxene	Phenocryst	58.60	0.16	1.05	0.65	0.48	0.07	0.32	38.12	0.46	0.02	0.02	0.01	0.00	0.00	99.96		0.9	98.4	0.7
Low-Ca pyroxene	Phenocryst	55.07	0.54	4.49	1.24	1.13	0.00	0.21	31.34	5.77	0.04	0.00	0.00	0.09	0.00	99.92		11.5	86.8	1.7
Low-Ca pyroxene	Phenocryst replaced by olivine	58.98	0.02	0.28	0.33	0.50	0.02	0.00	39.48	0.31	0.00	0.00	0.00	0.06	0.00	99.98		0.8	98.8	0.7
Low-Ca pyroxene	Phenocryst in ferroan chondrule	51.58	0.58	3.62	1.02	15.15	0.02	0.33	20.78	6.39	0.04	0.01	0.04	0.06	0.00	99.62		13.6	61.3	25.1
High-Ca pyroxene	Phenocryst	53.48	1.11	3.73	0.56	0.27	0.04	0.11	21.85	18.83	0.03	0.00	0.00	0.00	0.00	100.01		38.1	61.5	0.4
High-Ca pyroxene	Phenocryst	48.31	1.25	10.63	1.55	0.30	0.00	0.18	16.23	21.86	0.00	0.00	0.06	0.00	0.00	100.37		48.9	50.6	0.5
High-Ca pyroxene	Lath in groundmass	52.38	1.48	5.25	1.87	1.10	0.00	0.31	21.74	16.57	0.19	0.00	0.00	0.00	0.00	100.89		34.8	63.5	1.8
Plagioclase	Phenocryst	45.62	0.05	32.45	0.00	0.88	0.00	0.07	0.41	18.15	1.75	0.04	0.08	0.00	0.00	99.50		85.0	14.8	0.2
Plagioclase	Anhedral grain in groundmass	44.60	0.00	33.81	0.00	0.63	0.00	0.07	0.37	18.57	1.10	0.00	0.00	0.00	0.00	99.15		90.4	9.6	0.0
Plagioclase	Anhedral grain in groundmass	44.71	0.06	34.18	0.00	0.30	0.00	0.00	0.25	18.35	1.18	0.00	0.00	0.07	0.05	99.14		89.6	10.5	0.0
Plagioclase	Anhedral grain in groundmass	43.91	0.00	35.75	0.00	0.28	0.00	0.00	0.30	19.44	0.59	0.00	0.00	0.00	0.00	100.27		94.8	5.2	0.0

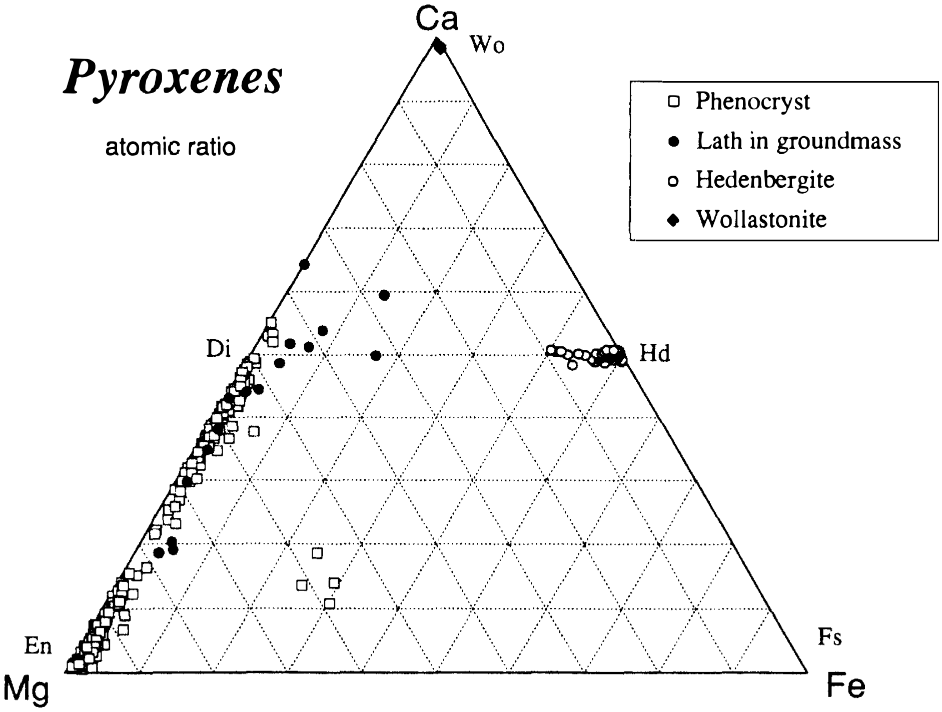

Fig. 2. Plot of atomic Ca-Mg-Fe ratio for pyroxene in chondrules. Pyroxenes of phenocrysts and elongated laths in groundmass are magnesian, except in a ferroan chondrule. Hedenbergites occur as fine grains in altered groundmass. The compositions of wollastonites in a chondrule are also plotted. Wo, Di, Hd, En and Fs are wollastonite, diopside, hedenbergite, enstatite and ferrosilite, respectively.

(0.0–6.0%), and depleted in SiO_2 (37.9–47.1%) and CaO (1.1–14.5%). The primary groundmass abundantly contains normative plagioclase (42–85 mol%, 65% on average) with augite (8–44%, 23%), hypersthene (0–20%, 2%), olivine (0–29%, 5%) and nepheline (0–9%, 1%) (Fig. 3). The anorthite molecule of the normative plagioclase is high, 0.70–0.95, in the primary groundmass. On the other hand, the altered groundmass is enriched in normative nepheline (0–81 mol%, 47% on average), sodalite (0–70%, 4%) and olivine (0–47%, 12%), but depleted in plagioclase (1–40%, 15%) and hypersthene (0%).

Nepheline: Nepheline contains 1.0–4.4 wt% CaO (Table 3). It also contains excess Si (2.00–2.11 for 8 oxygens). This suggests about 0–10% albite components in the nepheline, which is within the solubility limit of the albite component in synthetic nepheline (SCHAIRER and BOWEN, 1956). The nepheline usually contains 1.3–2.4 wt% K_2O.

Sodalite: Sodalite is stoichiometric in composition, and contains <0.5 wt% CaO, and K_2O and SO_3 less than 0.1% (Table 3).

Wollastonite: Wollastonite contains 0.5–0.9 wt% FeO, 0.0–0.2% MnO and 0.1–0.2% MgO (Table 3).

Andradite and grossular: Garnets display a wide compositional variation between grossular and andradite (Fig. 4). We probably analyzed fine-grained

Table 3. Representative compositions of silicate phases in groundmass.

Phase	Occurrence	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	NiO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl	Total	Wo	En	Fs
Cryptocrystalline groundmass	Groundmass	48.62	0.97	23.34	0.41	0.62	0.08	0.11	5.06	16.88	3.01	0.07	0.09	0.04	0.00	99.30			
Cryptocrystalline groundmass	Groundmass	48.92	0.69	20.11	0.41	1.05	0.04	0.21	7.17	19.08	2.28	0.00	0.04	0.05	0.02	100.07			
Cryptocrystalline groundmass	Groundmass	46.99	0.91	23.61	0.18	0.50	0.00	0.11	6.59	18.55	1.12	0.00	0.00	0.00	0.01	98.57			
Altered groundmass	Groundmass	44.87	0.27	26.29	0.65	1.45	0.00	0.03	3.49	8.33	13.18	1.27	0.09	0.00	0.00	99.92			
Altered groundmass	Groundmass	41.73	0.32	28.21	0.09	4.77	0.00	0.00	5.89	2.04	14.61	1.56	0.00	0.19	0.00	99.41			
Altered groundmass	Groundmass	38.15	0.36	27.30	0.25	4.19	0.35	0.14	4.83	4.88	14.20	0.01	0.00	0.06	4.66	98.43			
Altered groundmass	Groundmass	46.98	0.83	19.59	0.00	3.33	0.09	0.00	7.25	14.00	5.64	0.64	0.00	0.00	0.54	98.85			
Nepheline	Fine-grain in groundmass	42.50	0.00	34.55	0.00	0.24	0.03	0.07	0.20	2.10	17.92	2.09	0.00	0.00	0.02	99.72			
Nepheline	Fine-grain in groundmass	42.18	0.00	32.76	0.16	0.13	0.00	0.06	0.19	2.18	18.21	1.82	0.02	0.00	0.00	98.71			
Nepheline	Fine-grain in groundmass	42.77	0.00	33.68	0.00	0.27	0.00	0.00	0.01	1.08	19.18	1.93	0.00	0.00	0.00	98.92			
Sodalite	Fine-grain in groundmass	36.25	0.00	30.91	0.10	0.74	0.10	0.00	0.10	0.08	25.36	0.04	0.00	0.18	6.68	100.54			
Sodalite	Fine-grain in groundmass	36.04	0.00	31.07	0.07	0.70	0.00	0.00	0.60	0.17	24.40	0.02	0.00	0.07	7.03	100.17			
Hedenbergite	Fine-grain in groundmass	48.39	0.00	0.00	0.15	28.59	0.00	0.03	0.04	22.58	0.00	0.00	0.00	0.05	0.05	99.88	50.2	0.1	49.7
Hedenbergite	Fine-grain in groundmass	47.34	0.00	0.20	0.07	28.09	0.00	0.71	0.17	22.09	0.08	0.00	0.00	0.00	0.01	98.76	49.9	0.5	49.6
Wollastonite	Fine-grain in groundmass	50.23	0.00	0.05	0.00	0.89	0.00	0.00	0.16	46.83	0.00	0.02	0.00	0.00	0.03	98.21			
Andradite	Fine-grain in groundmass	36.19	0.00	0.00	0.06	27.83	0.10	0.00	0.00	32.50	0.00	0.00	0.05	0.09	0.00	96.82			
Andradite	Fine-grain in groundmass	35.21	0.00	1.54	0.00	25.28	0.00	0.00	0.05	33.15	0.01	0.00	0.00	0.00	0.01	95.25			
Grossular	Fine-grain in groundmass	38.29	0.00	13.36	0.00	12.57	0.00	0.54	0.22	33.15	0.02	0.03	0.00	0.00	0.00	98.18			
Kirschsteinite	Fine-grain in groundmass	33.12	0.00	0.19	0.00	29.97	0.00	0.06	4.51	30.59	0.00	0.00	0.00	0.00	0.00	98.44			
Kirschsteinite	Fine-grain in groundmass	32.75	0.00	0.31	0.00	33.35	0.02	0.03	1.93	30.96	0.00	0.00	0.00	0.00	0.00	99.35			

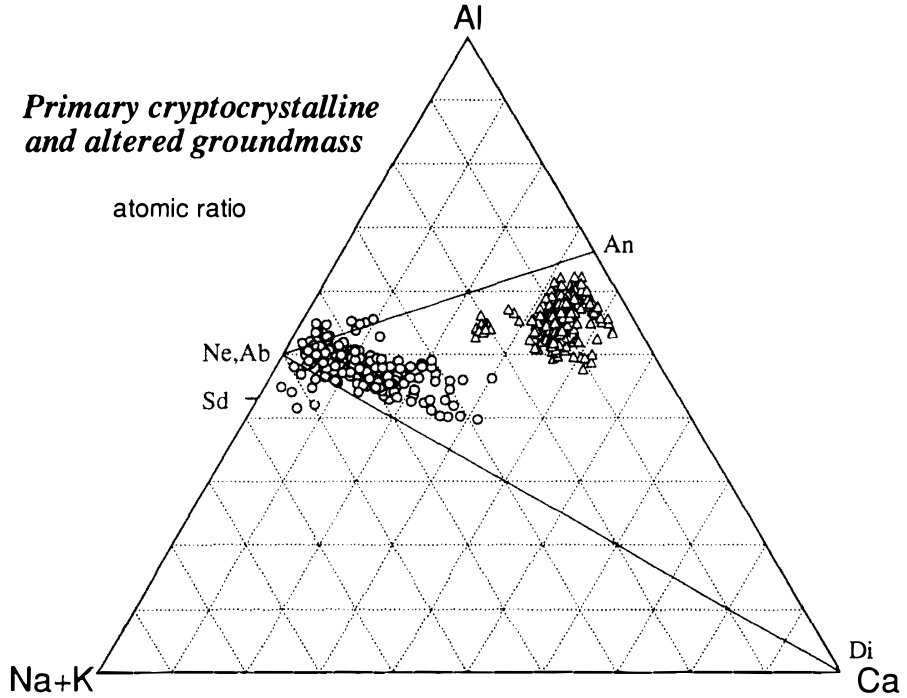

Fig. 3. *Plot of atomic Al-(Na+K)-Ca ratio for primary cryptocrystalline (triangle) and altered groundmass (circle). Note that primary groundmass is enriched in anorthite component. On the other hand, altered groundmass is enriched in nepheline component. Some altered groundmasses are plotted near sodalite. An, Ne, Ab, Sd and Di are anorthite, nepheline, albite, sodalite and diopside, respectively.*

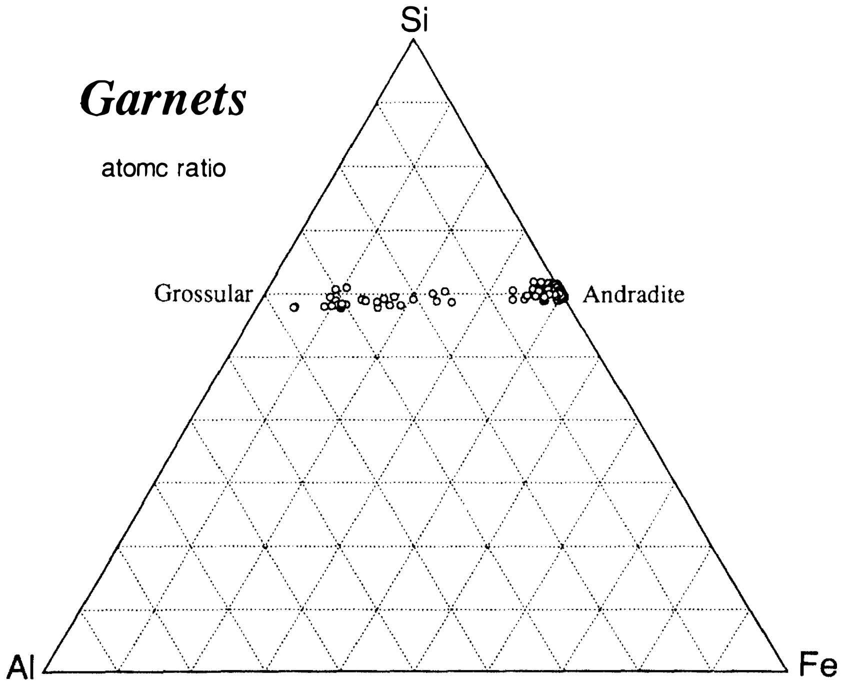

Fig. 4. *Plot of the atomic Si-Al-Fe ratio for garnets in chondrules. It is noticed that the garnets display wide compositional variation between grossular and andradite, which may be due to the analytical problem for fine intergrowth of both garnets.*

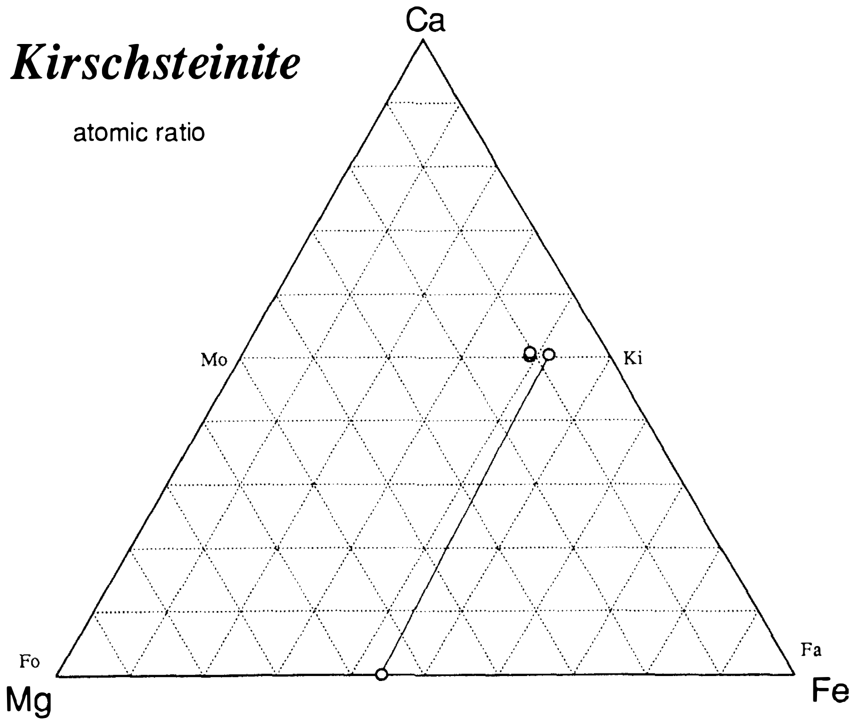

Fig. 5. Atomic plot of Ca-Mg-Fe ratio for kirschsteinites and a coexisting olivine. The kirschsteinites do not contain a (Mg, Fe)-olivine component. Mo, Ki, Fo and Fa are monticellite, kirschsteinite, forsterite and fayalite, respectively.

andradite and grossular often mixed with each other (Fig. 1-8).

Kirschsteinite: Kirschsteinite contains 29.6–33.4 wt% FeO, <0.1% MnO and 1.9–4.6% MgO (Table 3). The kirschsteinite does not contain (Mg, Fe)-olivine component (Fig. 5).

5. Discussion

5.1. Formation of nepheline and sodalite

The igneous crystallization process can not explain the occurrence of nepheline coexisting with low-Ca pyroxene in chondrules. Nepheline and sodalite do not occur in the igneous fabric, but seem to replace plagioclase and cryptocrystalline groundmass enriched in the plagioclase component. This observation indicates that nepheline and sodalite are secondary products from primary groundmass, after solidification of chondrules. We shall call the alteration reaction an alkali-Ca exchange reaction.

Plagioclase is enriched in the anorthite component that is the most abundant reactant to form nepheline and sodalite. The possible formation reaction of nepheline from primary anorthite component is as follows:

$$CaAl_2Si_2O_8 + Na_2O \rightarrow 2NaAlSiO_4 + CaO. \qquad (1)$$

During the reaction, CaO was released by decomposition of anorthite. Although nephelines in Allende chondrules contain a small amount of CaO, the contents are too low to explain CaO released by the reaction (1). This problem will be discussed later.

Plagioclases are completely or almost decomposed, and no albite was formed in chondrules. Thus, the albite component must have also decomposed to form nepheline. The possible reaction is written as follows:

$$NaAlSi_3O_8 \rightarrow NaAlSiO_4 + 2SiO_2. \qquad (2)$$

Some albite components (<10%) are present in solid solution in nephelines. However, primary groundmasses contain albite components up to 20%. Therefore, albite components alone dissolved in nephelines cannot explain SiO_2-contents released by the reaction (2). The released SiO_2 may have been redistributed into the other phases, as discussed later.

Sodalite as well as nepheline directly replaces primary groundmass. Therefore, sodalite was also generated from the plagioclase component, probably according to the following reactions:

$$3CaAl_2Si_2O_8 + 3Na_2O + 2NaCl \rightarrow 2Na_3Al_3Si_3O_{12}NaCl + 3CaO, \qquad (3)$$
$$3NaAlSi_3O_8 + NaCl \rightarrow Na_3Al_3Si_3O_{12}NaCl + 6SiO_2. \qquad (4)$$

Compositional change from primary to altered groundmass also supports the reactions (1) to (4). The plagioclase component and CaO content display an inverse correlation with the degree of alteration of the groundmass. Nepheline and sodalite, and Na_2O-, K_2O- and Cl-contents, increase with increase of alteration of groundmass. The contents of K_2O of primary cryptocrystalline groundmass and plagioclase are quite low, whereas nephelines contain K_2O as mentioned above. Therefore, almost all K_2O contents must have been secondarily introduced to chondrules with Na_2O during the alkali-Ca exchange reactions.

Nepheline and sodalite occur only in the peripheral parts of some chondrules, suggesting that Na_2O was introduced out of the chondrules. IKEDA (1982), and IKEDA and KIMURA (1985) observed that the unaltered glasses in chondrule fragments directly contact the matrices in ALH-77003 and Allende. These observations suggest that the alteration reaction did not occur during metamorphism in the parent body. Alternatively, the reaction occurred before accretion to the final parent body.

5.2. *Formation of Ca-rich phases*

Hedenbergite, andradite, grossular, kirschsteinite and wollastonite usually occur in close association with nepheline and sodalite. This observation suggests that these Ca-rich phases are also secondary minerals. They may have formed by consumption of CaO and SiO_2 released by the reactions (1) to (4). However, the abundance of the Ca-rich phases is too low to explain the amount of CaO released from primary groundmass. Moreover, the twenty-nine chondrules do not include any secondary Ca-rich phases, but nepheline and sodalite occur in these chondrules. Although most of the chondrules include Ca-phosphates in opaque spherules, the abundance of Ca-phosphates is negligible. Therefore, most of the CaO released must have been lost from chondrules during the alkali-Ca exchange reaction.

When hedenbergite, kirschsteinite and andradite were formed, FeO or Fe_2O_3

must have also been supplied. We abundantly observed Fe-Mg zoning of olivine phenocryst, ferroan olivine replacing low-Ca pyroxene, and fine-grained ferroan olivine in altered groundmass. IKEDA and KIMURA (1995) suggested that these ferroan olivines may have been generated simultaneously with the alkali-Ca exchange reaction, based on a positive correlation of degrees between replacement of primary groundmass by nepheline and replacement of low-Ca pyroxene by olivine. This is consistent with the compositional change from primary to altered groundmasses: FeO contents increase in altered groundmass. FeO may have been supplied either by oxidation of metal inside chondrules, or introduction out of chondrules.

Grossular decomposes to wollastonite, gehlenite and anorthite at 798°C (HUCKENHOLZ *et al.*, 1974). This temperature gives an upper limit of the alteration temperature. Kirschsteinites in Allende chondrules do not contain the (Mg,Fe)-olivine component. An olivine-kirschsteinite pair in a chondrule gives an equilibration temperature much lower than 800°C (DAVIDSON and MUKHOPADHYAY, 1984). Thus, the alteration reactions for secondary silicates probably occurred below 1100 K. IKEDA and KIMURA (1995) suggested that the alkali-Ca exchange reaction and formation of ferroan olivine in chondrules took place probably below 800 K, based on the rates of these two reactions.

5.3. *Alkali-Ca exchange reaction in CV chondrites*

Secondary minerals of CAIs include nepheline, sodalite, grossular, andradite, wollastonite, hedenbergite, kirschsteinite and others (MACPHERSON *et al.*, 1988). These minerals are also encountered as secondary minerals in Allende chondrules. Chemical compositions of the minerals in altered chondrules are similar to those in altered Allende CAIs, respectively; nearly pure hedenbergite and andradite, grossular with small contents of andradite molecule, Ca- and K-bearing nepheline, and ferroan olivine (WARK, 1981; KORNACKI and WOOD, 1985; HASHIMOTO and GROSSMAN, 1987; MCGUIRE and HASHIMOTO, 1989). During the alteration reactions, FeO, Na_2O, K_2O and Cl were introduced, and CaO was lost from CAIs (IKEDA, 1982; HASHIMOTO and GROSSMAN, 1987). Such chemical reactions are also noticed in the alteration reactions of chondrules. It is, thus, probable that chondrules and CAIs experienced similar alteration reactions. However, melilite and fassaite are the phases most susceptible to the alteration in CAIs (HASHIMOTO and GROSSMAN, 1987). In contrast, the anorthite component is mainly decomposed in chondrules.

The temperature necessary for alteration of CAIs was estimated to be below about 1000 K (*e.g.*, HUTCHEON and NEWTON, 1981; MCGUIRE and HASHIMOTO, 1989). These temperatures overlap with those deduced for Allende chondrules in this paper.

IKEDA and KIMURA (1995) and NAKAMURA *et al.* (1993) investigated 11 and 17 chondrules separated from Allende, respectively. All of these chondrules also experienced the alkali-Ca exchange reaction to generate nepheline and sodalite. Samples by all these authors and this study came from different Allende specimens. We, therefore, conclude that almost all Allende chondrules commonly experienced the alkali-Ca exchange reactions in various degrees.

Chondrules in Ningqiang (an oxidized CV) were also subjected to the alkali-Ca exchange reaction (KIMURA *et al.*, 1995). MURAKAMI and IKEDA (1994) reported nepheline and sodalite in chondrules of Y-86751 (an oxidized CV). Accordingly, it is possible that chondrules in oxidized CVs are commonly subjected to the alkali-Ca exchange reaction. On the other hand, chondrules in Efremovka (a reduced CV) have low Na_2O content, and seem to include no nepheline (NOGUCHI, 1994). PALME and WARK (1988) summarized characteristic features of CAIs in reduced and oxidized CV chondrites: CAIs in oxidized CVs are enriched in Na, K, Cl and Fe, whereas CAIs in reduced CVs hardly contain these elements. Therefore, we argue that the alkali-Ca exchange reactions were very common for chondrules and CAIs, in oxidized CV chondrites, whereas the reaction hardly occurred in the constituents of reduced CVs.

6. Summary

1) All of the 58 Allende chondrules studied here contain nepheline in secondary devitrified groundmass. About 66% of the chondrules contain sodalite. Nepheline and sodalite replace primary cryptocrystalline groundmass and plagioclase. Half of the chondrules have some secondary Ca-rich silicate phases: hedenbergite, wollastonite, kirschsteinite, grossular and andradite. They occur in association with nepheline and sodalite.

2) Nepheline and sodalite formed secondarily by an alkali-Ca exchange reaction: Na_2O, K_2O and Cl were introduced out of chondrules, and CaO was released by breakdown of the anorthite component. Most of the Allende chondrules were subjected to this reaction.

3) The secondary Ca-rich phases were generated from CaO and SiO_2 released from the plagioclase component. However, most of the CaO from primary phases was lost from the chondrules. The reaction of the Allende chondrules may have occurred at temperatures lower than 1100 K. Ferroan olivine in altered groundmass also formed together with the alkali-Ca exchange reaction.

4) The similar secondary mineralogy of CAIs and chondrules suggests that both CAIs and chondrules in oxidized CV chondrites were subjected to the alkali-Ca exchange reactions under similar physical conditions.

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