Proc. NIPR Symp. Antarct. Meteorites, 8, 97–122, 1995

ANHYDROUS ALTERATION OF ALLENDE CHONDRULES IN THE SOLAR NEBULA I: DESCRIPTION AND ALTERATION OF CHONDRULES WITH KNOWN OXYGEN-ISOTOPIC COMPOSITIONS

Yukio IKEDA and Makoto KIMURA

Department of Earth Sciences, Ibaraki University, 1-1, Bunkyo 2-chome, Mito 310

Abstract: Anhydrous alteration of eleven Allende chondrules with already-known oxygen isotopic compositions were studied in detail with reference to a dark inclusion and the matrix from Allende. Anhydrous alteration of chondrules includes three processes different from each other, formation of secondary olivine zonation, replacement of groundmassic plagioclase or glass by nepheline and/or sodalite, and replacement of phenocrystic enstatite by ferroan olivine. The degrees of each process are different among chondrules. A positive correlation in degrees between replacement of groundmassic plagioclase or glass and phenocrystic enstatite is recognized, suggesting that these two processes took place at the same time by reactions with a nebular gas at temperatures probably lower than 800 K. The secondary olivine zonation may have formed prior to and in the early stage of the replacement of groundmassic plagioclase and phenocrystic enstatite. The anhydrous alteration of Allende dark inclusions was caused in a nebular gas having an oxygen isotopic composition along the Allende inclusion mixing line, but Allende chondrules have experienced the anhydrous alteration in a gas reservoir having an oxygen isotopic composition along the Allende chondrule mixing line. Therefore, the anhydrous alteration of chondules and dark inclusions took place in different nebular gas reservoirs prior to the accretion of the Allende parent body.

1. Introduction

Most of the chondrules in unequilibrated ordinary chondrites contain clean igneous glass within the mesostasis, and the chemical compositions of the clean glass are indigenous to the chondrules. However, most of the chondrules in unequilibrated carbonaceous chondrites include black devitrified and porous groundmasses, suggesting that they are secondarily altered groundmasses and the chemical compositions have changed by anhydrous alteration after the lithification of chondrules. IKEDA (1982) and IKEDA and KIMURA (1985) found several alkali-zoned chondrules in carbonaceous chondrites, which show remarkable alkali increase from clean glass in chondrule cores to devitrified glass in chondrule rims. They concluded that the alkalis in the devitrified glass were introduced from outside of chondrules by exchange of Ca by 2Na under a subsolidus condition; Ca contents were expelled from the original clean glass during anhydrous alteration, and 2Na were introduced instead of Ca.

Most of the Ca- and Al-rich inclusions (CAI's) and amoeboid olivine inclusions

(AOI's) in carbonaceous chondrites also experienced various degrees of anhydrous alteration similar to that of chondrules (IKEDA, 1982; BISCHOFF and KEIL, 1984; MACPHERSON *et al.*, 1988; TOMEOKA *et al.*, 1992).

Olivine in Allende chondrules sometimes shows compositional zoning from magnesian cores to ferroan rims. The zonation is more remarkable in chondrule rims than in chondrule cores, and most of the ferroan rims have the MgO/(MgO+FeO) ratios (hereafter, mg ratios) far smaller than those of the coexisting pyroxene. These suggest that the olivine zonation is not primary but was secondarily produced by anhydrous alteration under subsolidus conditions (HUA *et al.*, 1988; WEINBRUCH *et al.*, 1990).

Enstatite in Allende chondrules is sometimes replaced by ferroan olivine after the chondrule formation, indicating that anhydrous alteration took place in chondrules under subsolidus conditions (HOUSLEY and CIRLIN, 1983).

The problem we are interested in is whether the anhydrous alteration reactions took place in the solar nebula or in their parent body. In order to clarify this problem, we studied eleven Allende chondrules, one dark inclusion, and the Allende matrix. The oxygen-isotopic compositions of these components were already measured (CLAYTON *et al.*, 1983). Allende chondrules form an oxygen-isotope mixing line in the three isotope diagram, which differs from the Allende inclusion line (CLAYTON *et al.*, 1983). If alteration of Allende chondrules took place in the Allende parent body at the same time as that of Allende inclusions, then the chondrules with higher degrees of alteration should have oxygen-isotopic compositions which deviate more from the Allende chondrule line, and are nearer to the Allende inclusion line than those with lower degrees of alteration.

2. Analytical Methods

An electron-probe microanalyzer (EPMA, JEOL-733, an accelerating voltage of 15 kV and a sample current of 3 nA) was used for analyses of minerals, clean glass, and cryptocrystalline groundmasses, with the correction method of Bence and Albee for silicate and oxide.

3. Description of Chondrules

Eleven chondrules, one dark inclusion, and the matrix were separated from Allende, half of each sample was used for analyses of oxygen isotopic compositions (CLAYTON *et al.*, 1983), and the other halves were used for polished thin sections. The numbers of chondrules, the dark inclusion, and the matrix studied in this paper are the same as those in CLAYTON *et al.* (1983). The detailed petrography and mineralogy of them are given in this section, and a brief summary is shown in Table 1.

3.1. Chondrule No. 1

Chondrule No. 1 is a porphyritic Ol-Px chondrule with a diameter of 3 mm (Fig. 1-1), consisting of low-Ca pyroxene, olivine, high-Ca pyroxene, troilite, and holocrystalline groundmass. Low-Ca pyroxene is the most abundant, and it is

Table 1. Chondrule texture and crystallinity of groundmasses in Allende chondrules.

Chondrule	Texture	Crystallinity of groundmass
No. 1	Ol-Px porphyritic	Holocrystalline
No. 2	Ol-Px porphyritic	Holocrystalline
No. 4	Ol-Px porphyritic	Cryptocrystalline
No. 6	Barred Ol	Glassy
No. 7	Ol-Px granular	Holocrystalline
No. 8	Ol-Px porphyritic	Holocrystalline
No. 9	Matrix	—
No. 10	Dark inclusion	—
No. 11	Barred Ol	Holocrystalline
No. 12	Ol porphyritic	Cryptocrystalline
No. 13	Barred Ol	Cryptocrystalline
No. 14	Ol-Px granular	Holocrystalline
No. 15 core	Ol-Px porphyritic	Holocrystalline
mantle	Ol-Px granular	Holocrystalline

Abbreviation; Olivine (Ol), pyroxene (Px).

enstatite with mg ratios of about 0.98. Enstatite in the chondrule rim is locally replaced by ferroan olivine with mg ratios of about 0.6–0.74 (Fig. 2a). Most olivines occur as corroded grains included in enstatite and as small (a few tens of microns across) euhedral to subhedral grains in the groundmass. Olivine shows chemical zoning from magnesian cores with mg ratios of 0.98–0.97 to ferroan rims with mg ratios of about 0.80 (Fig. 2a). High-Ca pyroxene occurs as rims on low-Ca pyroxene with mg ratios of 0.98–0.95. The groundmass consists mainly of needles or laths of high-Ca pyroxene and interstitial grains of nepheline and sodalite (Fig. 1-2). The high-Ca pyroxene in the groundmass has mg ratios of about 0.95. These crystals are primary and crystallized from residual liquid in this chondrule. On the other hand, nepheline and sodalite in the groundmass are irregularly-shaped and loosely packed, and probably secondary crystals. They seem to have replaced primary cryptocrystalline materials which crystallized as interstitial phases (probably plagioclase) between needles or laths of high-Ca pyroxene in the groundmass.

3.2. Chondrule No. 2

Chondrule No. 2 is a porphyritic Ol-Px chondrule (Fig. 1-3), 3 mm×2.5 mm in size, similar to chondrule No. 1, but olivine occurs more abundantly than in the latter. Low-Ca pyroxene is enstatite with mg ratios of 0.98–0.97, and sometimes has magnesian high-Ca pyroxene rims. Some spherules of troilite, up to 100 microns across, occur in large low-Ca pyroxene and in the groundmass (Fig. 1-3). Olivine shows weak zoning from magnesian cores with mg ratios of about 0.99 to ferroan rims with mg ratios smaller than 0.85 (Fig. 2a). The groundmass in the chondrule core consists mainly of magnesian high-Ca pyroxene, plagioclase, and nepheline (Fig. 1-4). The plagioclase and magnesian high-Ca pyroxene are primary crystals which crystallized directly from residual melts in the chondrule, but nepheline occurs, replacing the primary plagioclase, indicating its secondary origin. The groundmass in

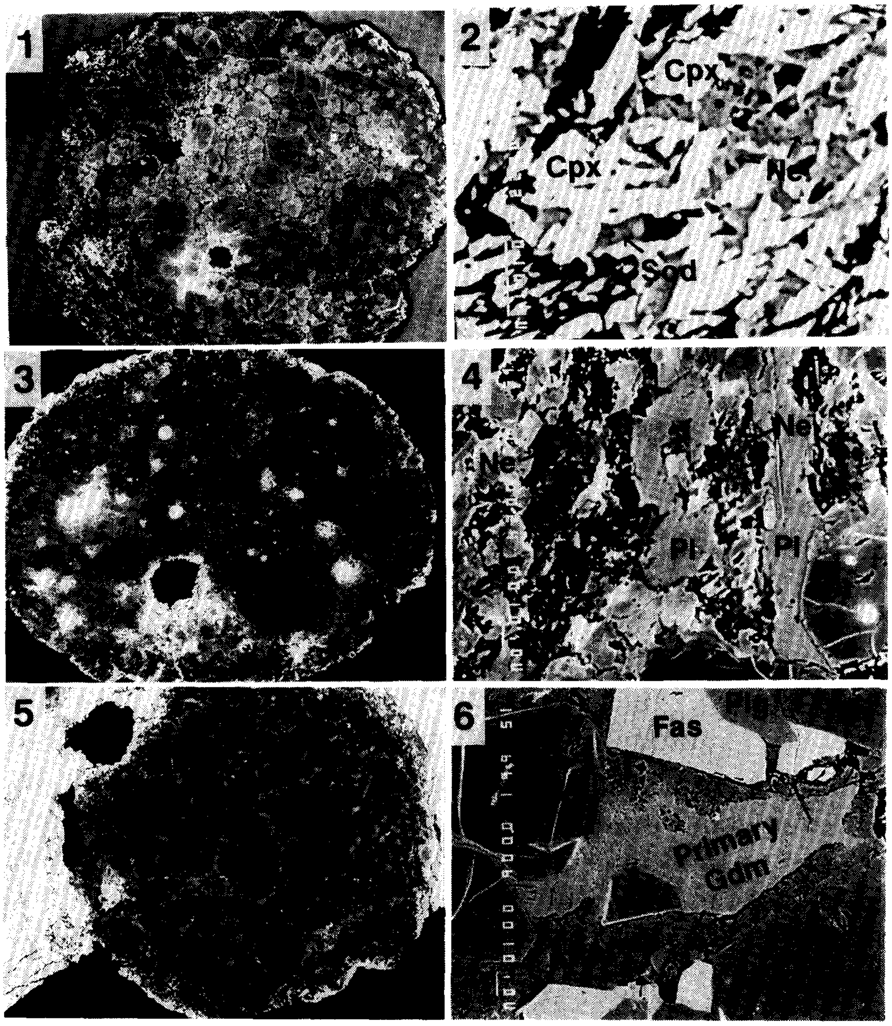

Fig. 1. Back-scattered electron images of eleven chondrules (No. 1, 2, 4, 6, 7, 8, 11, 12, 13, 14, and 15), the matrix (No. 9), and a dark inclusion (No. 10) from Allende and a run product of heating experiments of a plagioclase crystal.

(1) Chondrule No. 1 showing a porphyritic texture. The width is about 3 mm.

(2) Holocrystalline groundmass of chondrule No. 1. Nepheline (Ne) and sodalite (Sod) are secondary minerals which have replaced groundmassic plagioclase. Clinopyroxene (Cpx) grains are primary crystals. The width is about 60 microns.

(3) Chondrule No. 2 showing a porphyritic texture with spherules of troilite (white). The width is about 3 mm.

(4) Holocrystalline groundmass of chondrule 2. Nepheline locally replaced groundmassic plagioclase (Pl). Olivine (Ol) shows weak zoning with ferroan rims. The width is about 110 microns.

(5) chondrule No. 4 showing a porphyritic texture. The width is about 3 mm.

(6) Cryptocrystalline groundmass of chondrule No. 4. Primary cryptocrystalline groundmass (Gdm) is locally replaced by secondary groundmass (Altered). Enstatite (En) sometimes has rims of pigeonite (Pig) and fassaite (Fas), and these rims are primary. The width is about 180 microns.

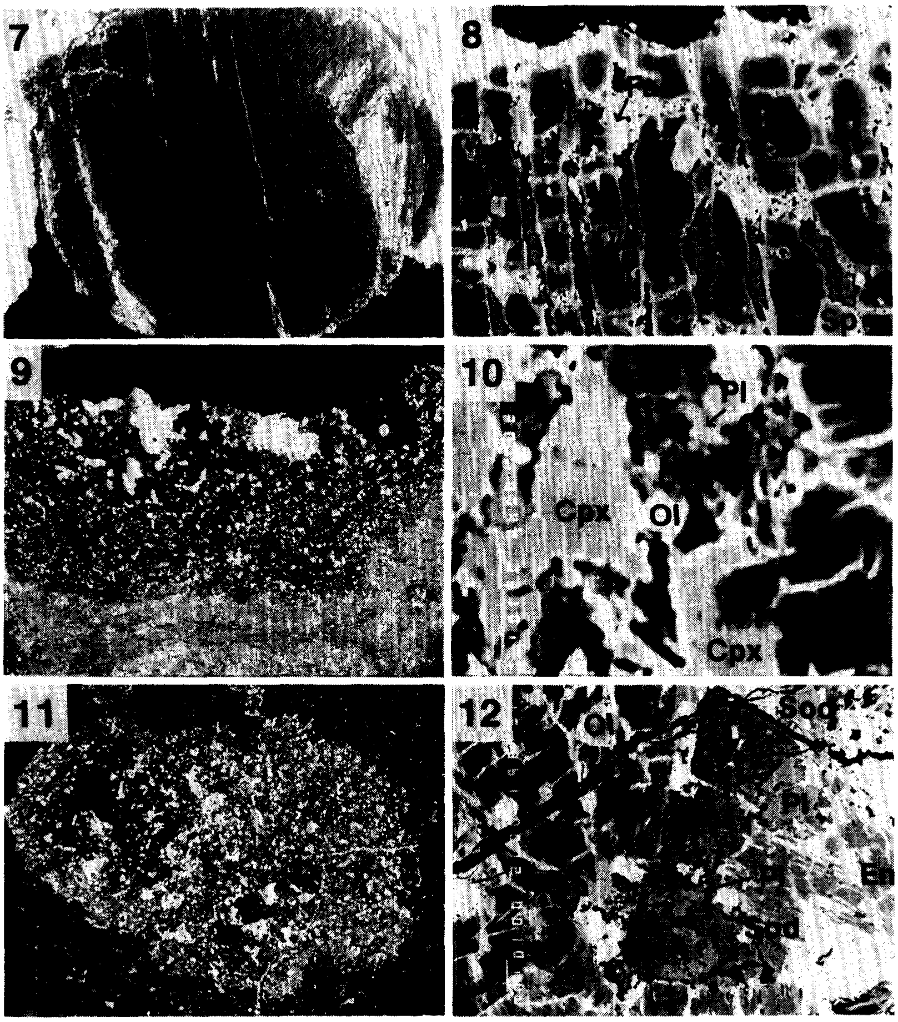

Fig. 1. (Continued)

(7) Chondrule No. 6 showing a barred olivine texture. The white is troilite. The width is about 3 mm.

(8) Enlarged image of a rim of chondrule No. 6. Groundmassic glass (Gl) remains unaltered. Spinel (Sp), fassaite, and olivine are primary. Spinel and olivine have ferroan rims, but fassaite does not. The width is about 120 microns.

(9) Chondrule No. 7 showing a granular texture. The width is about 3 mm.

(10) Holocrystalline groundmass of chondrule No. 7. Nepheline has replaced plagioclase, and plagioclase occurs as small relic grains in nepheline. Other phases include enstatite (En), olivine (Ol), and clinopyroxene (Cpx). The width is about 40 microns.

(11) Chondrule No. 8 showing porphyritic and granular textures. The dark portion in the left half of this chondrule has an original porphyritic texture and includes abundant phenocrystic enstatite. However, the light portion has a granular texture, where most of the original enstatite was replaced by ferroan olivine. The width is about 3 mm.

(12) Enlarged image of the porphyritic portion of chondrule No. 8. Nepheline (Ne) and sodalite (Sod) have replaced plagioclase (Pl), and small plagioclase grains occur as relic minerals in them. Phenocrystic enstatite (En) was locally replaced along fractures by ferroan olivine, and small olivine grains (Ol) included in enstatite show secondary zoning from magnesian cores to ferroan rims. The width is about 140 microns.

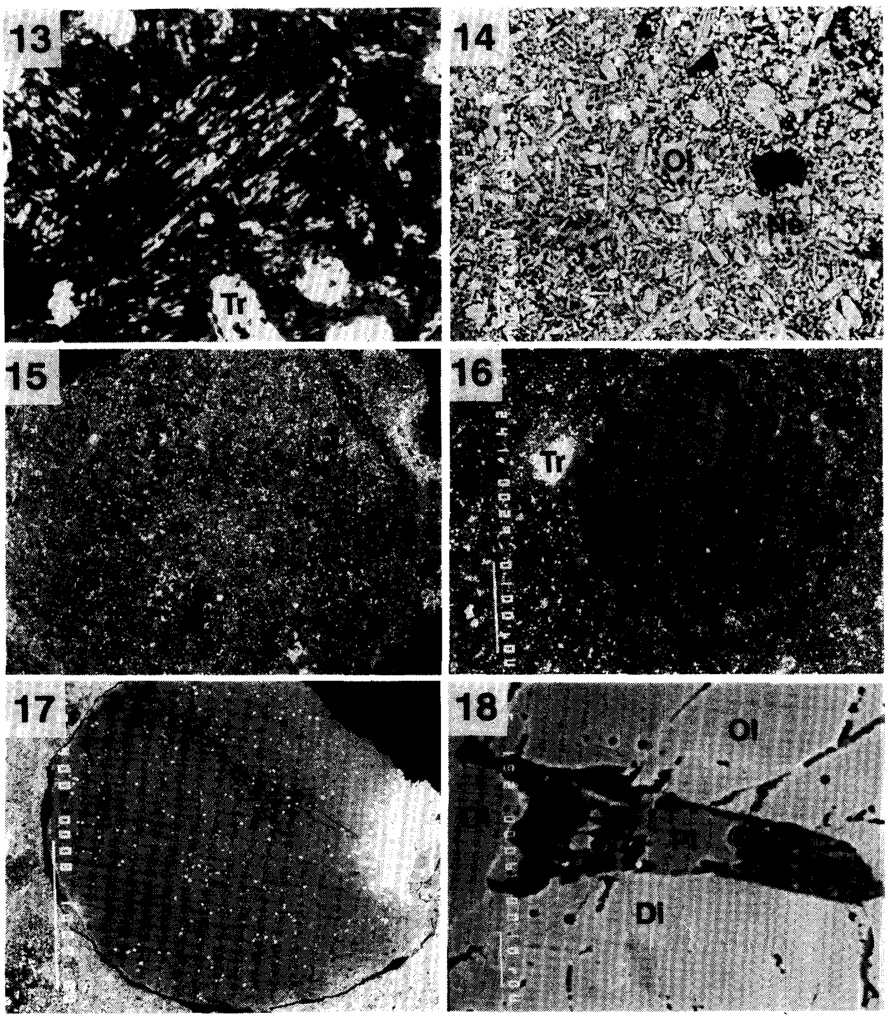

Fig. 1. (Continued)

(13) Enlarged image of the granular portion of chondrule No. 8. All enstatites were replaced by ferroan olivine with strings of troilite (Tr). The width is about 90 microns.

(14) The Allende matrix No. 9. Olivine (Ol) occurs abundantly as small euhedral or subhedral grains, and nepheline (Ne) occurs in a minor amount. The width is about 140 microns.

(15) Dark inclusion No. 10. The upper right and lower left corners are the Allende matrix. The width is about 3 mm.

(16) A small chondrule in dark inclusion No. 10, consisting mainly of ferroan olivine (Ol), although magnesian olivine cores occur in the peripheral portions of this chondrule. Tr is troilite. The chondrule diameter is about 300 microns.

(17) Chondrule No. 11 showing a barred olivine texture. The width is about 3 mm.

(18) Groundmass of chondrule No. 11. Nepheline replaced groundmassic plagioclase on the chondrule rim. Other phases are olivine (Ol) and diopside (Di). The width is about 80 microns.

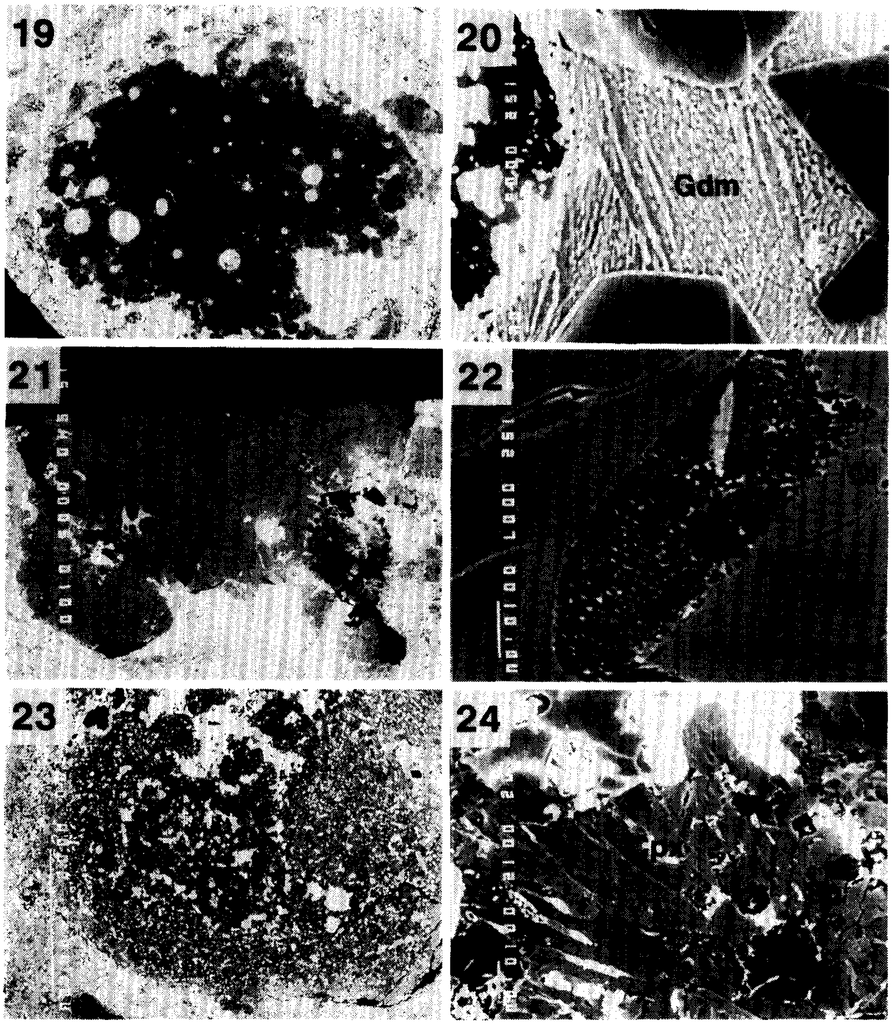

Fig. 1. (Continued)

(19) Chondrule No. 12 showing a porphyritic texture with opaque spherules of troilite and magnetite. The width is about 3 mm.

(20) Primary groundmass (Gdm) of chondrule No. 12, consisting mainly of cryptocrystalline plagioclase (gray) and clinopyroxene (white). The groundmass is unaltered in the chondrule core, but olivine (Ol) shows secondary zoning. The width is about 80 microns.

(21) Chondrule No. 13 shows a barred olivine texture including Cr-rich spinel with irregular outlines (gray). The width is about 2 mm.

(22) Cryptocrystalline groundmass of chondrule No. 13. Primary groundmass (Primary Gdm with arrow) was locally replaced by secondary ones (Altered Gdm with arrow). Other phases are olivine (Ol) and clinopyroxene (Cpx with arrow). The width is about 80 microns.

(23) Chondrule No. 14 showing a granular texture in the mantle and a porphyritic texture in the core. The width is about 3 mm.

(24) Enlarged image of groundmass in the mantle of chondrule No. 14. Plagioclase (Pl) and enstatite (En) remain unlatered although olivine (Ol) shows secondary zoning. Cpx is clinopyroxene. The width is about 120 microns.

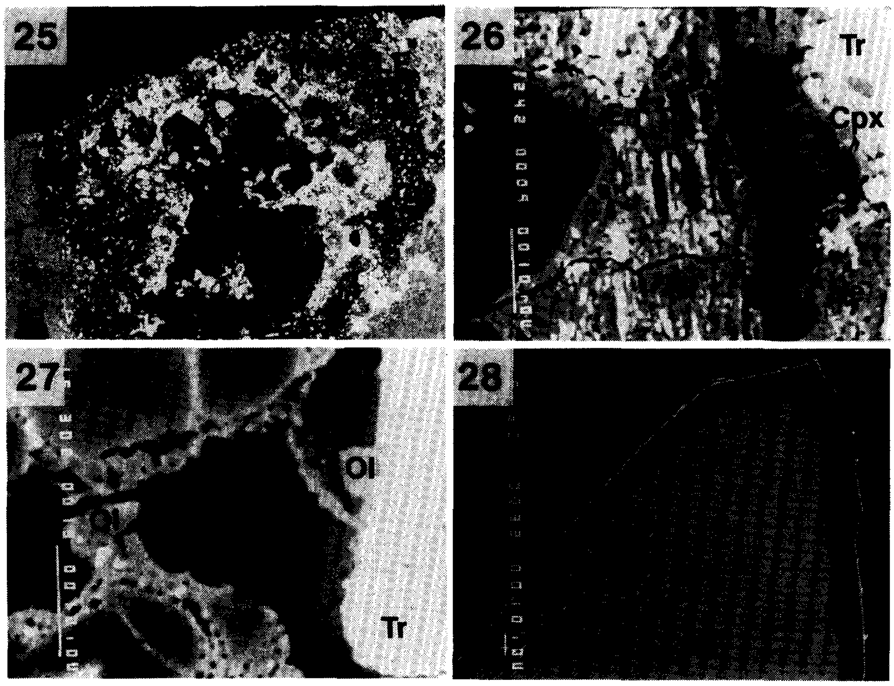

Fig. 1. (Continued)

(25) Chondrule No. 15 showing a granular texture in the mantle and a porphyritic texture in the core. There is a magnetite-rich zone (white) between the core and mantle. The width is about 3 mm.

(26) Enlarged image of the mantle of chondrule No. 15. Most enstatites were replaced by ferroan olivine (Ol) with strings of troilite (Tr, white), but a small amount of enstatite (En) occurs as small relic grains included in ferroan olivine. Note that secondarily-zoned olivine contacts by a sharp boundary with ferroan olivine replacing enstatite. Cpx is clinopyroxene. The width is about 50 microns.

(27) Another enlarged image of the mantle of chondrule No. 15. Nepheline (Ne) replaced plagioclase (Pl), and the latter occurs as relic grains. Ferroan olivine (Ol) grains occur in close association with nepheline (Ne). Tr is troilite. The width is about 40 microns.

(28) An example of a heating experiment. A single crystal of plagioclase (An) with a composition of An_{97} from a terrestial basalt was heated within NaCl powder in a Pt crucible at a temperature of 800°C for 320 hours under atmospheric conditions. In the run, nepheline (Ne) was produced by replacing the rims of plagioclase with width of about 10 microns. Minor Ca-rich phases occur at the outermost rims (bright). The width is about 190 microns.

the chondrule rim consists mainly of magnesian high-Ca pyroxene, nepheline, and sodalite, and is similar to that in the chondrule core except that all plagioclase is replaced by nepheline and sodalite.

3.3. Chondrule No. 4

Chondrule No. 4, with a diameter of about 2.5 mm, is a porphyritic Ol-Px chondrule (Fig. 1-5), consisting of olivine, low-Ca pyroxene, high-Ca pyroxene, and cryptocrystalline groundmass. Corroded olivine grains are included in large low-Ca pyroxene, and euhedral to subhedral olivine occurs in the groundmass (Fig. 1-6). They show weak zoning from magnesian cores with mg ratios of 0.98–0.97 to ferroan rims with mg ratios of about 0.9 (Fig. 2a). In the peripheral portion of this chondrule, magnesian low-Ca pyroxene is replaced by ferroan olivine with mg ratios of about 0.5–0.7. Low-Ca pyroxene is enstatite, occurring as large euhedral grains, and shows

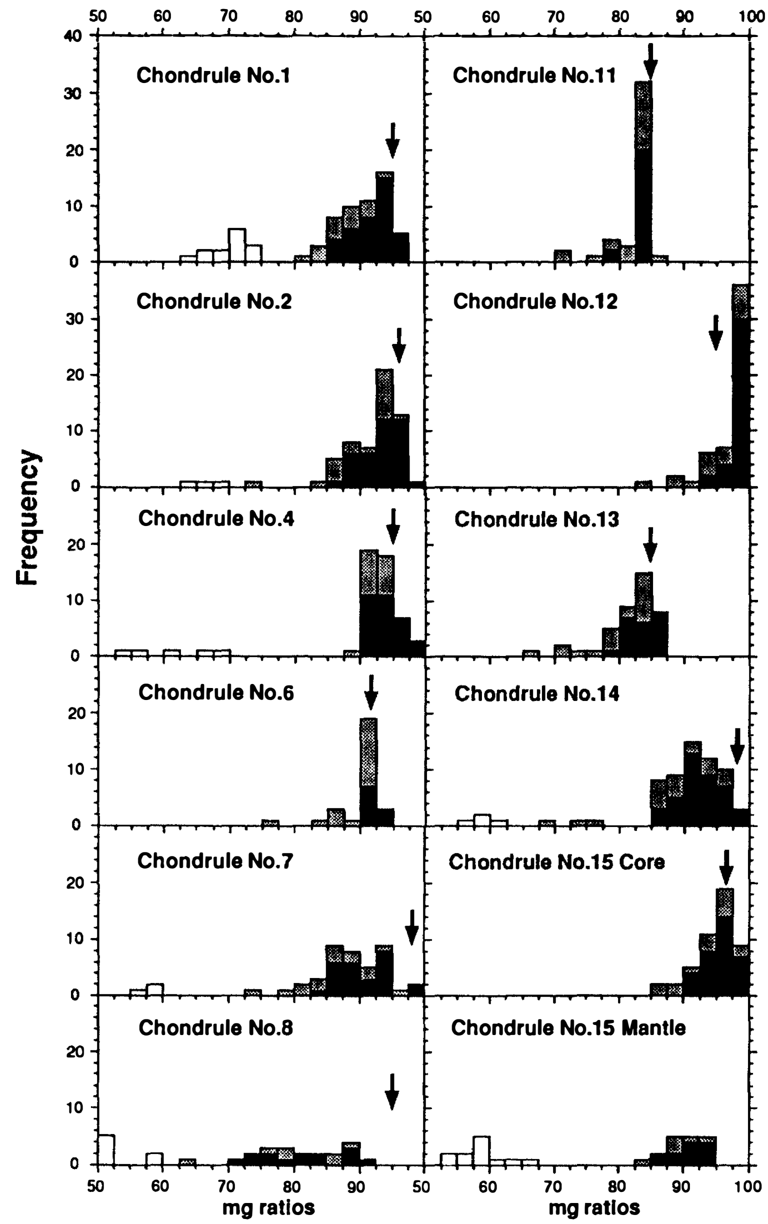

Fig. 2a. Histograms of Mg/(Mg+Fe) atomic ratios (mg ratios) of olivines in chondrules. Black bars are the compositions of olivine cores and intermediate points between the core and rim of olivine grains, hatched bars are olivine rims, and open bars are ferroan olivine replacing enstatite. The arrows show the compositions of clinopyroxenes which are a primary groundmassic mineral and thus indicate primary mg ratios of residual melts in the late stage crystallization of chondrule melts.

weak zoning from cores of $En_{97.5}Fs_2Wo_{0.5}$ to rims of $En_{96}Fs_3Wo_1$. It locally has rims of pigeonite with mg ratios of 0.96–0.95 and Wo contents of 5–8 mol%. Fassaitic pyroxene, with high Al_2O_3 contents up to 12 wt%, occurs as an outermost rim overgrown on pigeonite or directly on enstatite (Fig. 1-6). The boundaries between enstatite and pigeonite and between pigeonite and fassaitic pyroxene are very sharp.

There are two types of groundmass in this chondrule, primary and secondary (Fig. 1-6). The primary groundmass consists of massive cryptocrystalline materials, but secondary groundmass is a fine-grained porous substance which replaced the primary one (Fig. 1-6). The secondary one is too fine-grained to determine the constituent minerals, but in the slightly coarser-grained area at the chondrule rim, the major constituent appears to be nepheline.

3.4. *Chondrule No. 6*

Chondrule No. 6 is a barred-Ol chondrule with a diameter of about 2.5 mm (Fig. 1-7). Each bar of olivine is 10–30 microns in width and magnesian with mg ratios of 0.94–0.90. Clean glass occurs between the olivine bars (Fig. 1-8). Sometimes fassaite with Al_2O_3 up to 15 wt% and mg ratios of about 0.92 occurs as rims on olivine bars. Small Mg-Al spinel grains with diameters smaller than 20 microns are commonly included in olivine bars and clean glass. Troilite is also observed. In the peripheral zone (about 100 microns) of this chondrule, olivine has ferroan rims with mg ratios down to 0.76, but glass remains clean. Rarely nepheline occurs, replacing the clean glass in a rim portion protruding into the Allende matrix.

3.5. *Chondrule No. 7*

Chondrule No. 7 is a granular Ol-Px chondrule with a diameter of about 3.5 mm (Fig. 1-9). The major portion of this chondrule consists mainly of granular grains of low-Ca pyroxene, olivine, and magnetite with minor amounts of groundmassic plagioclase and high-Ca pyroxene. Low-Ca pyroxene is predominant. The rim portion of this chondrule, about a few hundred microns in width, consists mainly of olivine, magnetite, and groundmassic plagioclase and high-Ca pyroxene, with minor low-Ca pyroxene. Although most of the core of this chondrule shows a granular texture, the center has a porphyritic texture where large low-Ca pyroxene crystals include small corroded olivine grains. Low-Ca pyroxene is enstatite with mg ratios of 0.99–0.98, and high-Ca pyroxene is also magnesian with the mg ratios similar to those of enstatite. Olivine shows weak zoning from magnesian core with mg of about 0.98 to ferroan rims with mg of 0.72 (Fig. 2a). Plagioclase is $An_{90-80}Ab_{10-20}$ in composition, and nepheline occurs, replacing the plagioclase (Fig. 1-10). Rarely small (a few microns across) ferroan olivine grains with mg of 0.5–0.6 occur in close association with nepheline (Fig. 1-10).

3.6. *Chondrule No. 8*

Chondrule No. 8 is a granular Ol-Px chondrule with a size of 2×3 mm (Fig. 1-11). This chondrule is highly altered, but the original texture remains as relic in the core of this chondrule. The area of the relic core is about 20% of this chondrule. In the relic core, large low-Ca pyroxene is enstatite with mg ratios of 0.98–0.96 and includes corroded olivine with mg of about 0.9, but most of the groundmassic plagioclase is replaced by nepheline and sodalite, although small irregular plagioclase grains still remain as a relic mineral in nepheline (Fig. 1-12). The major and altered portion of this chondrule consists mainly of ferroan olivine with mg of 0.5–0.6, with minor amounts of nepheline, sodalite, and magnesian high-Ca pyroxene. This ferroan olivine includes many tiny troilite grains (Fig. 1-13) and sometimes small laths of enstatite as relic minerals. It was produced secondarily by replacement of enstatite. The magnesian high-Ca pyroxene has mg ratios of 0.95–0.93 and the same chemical composition as that in the relic core of the chondrule, indicating that it is a primary phase. All plagioclases were replaced by nepheline and sodalite in the altered portion.

3.7. Chondrule No. 11

Chondrule No.11 is a holocrystalline barred Ol chondrule with a size of 3×2.5 mm (Fig. 1-17). Each Ol bar is several tens of microns in width, and the interstitial space is filled by plagioclase. The mg ratios of olivine are 0.86–0.83, although they decrease to 0.70 at the chondrule rim (Fig. 2a). Sometimes pigeonite and high-Ca pyroxene occur in contact with plagioclase, and their mg ratios are 0.85–0.82. Small grains of Cr-rich spinel, with Cr/(Cr+Al) atomic ratios of 0.45–0.50, are included in olivine or plagioclase. The chemical composition of plagioclase is An_{85-90}. In the peripheral portion of this chondrule, a few hundreds of microns in width, plagioclase is partly replaced by nepheline (Fig. 1-18), although it remains unaltered in the chondrule core.

3.8. Chondrule No. 12

Chondrule No. 12 is a microporphyritic Ol chondrule with a size of 3×2.5 mm (Fig. 1-19). Most of the olivine phenocrysts are smaller than 200 microns across. Olivine in the chondrule rim shows weak zoning from magnesian cores with mg ratios of about 0.99 to ferroan rims with mg ratios down to 0.85 (Fig. 2a), but in the chondrule core it is relatively homogeneous and magnesian with mg ratios of about 0.99. This chondrule includes small opaque spherules, 10–200 microns across, in olivine or groundmass (Fig. 1-19). They are aggregates of troilite and/or magnetite with rare whitlockite. The groundmass is fine-grained, consisting mainly of high-Ca pyroxene and cryptocrystalline plagioclase (Fig. 1-20). The high-Ca pyroxene shows a parallel-growth texture with cryptocrystalline plagioclase; each bar of pyroxene is about 1 micron wide, and plagioclase between pyroxene bars is about 1–2 microns wide (Fig. 1-20). Cryptocrystalline plagioclase of the groundmass in the chondrule rim is replaced by nepheline, but the replacement is weak in the chondrule core. The normative compositions are An_{75-80}. The groundmassic high-Ca pyroxene bars remain unaltered, and the mg ratios are about 0.95.

3.9. Chondrule No. 13

Chondrule 13 is a barred Ol chondrule with a diameter of about 2 mm (Fig. 1-21), each bar being several tens of microns in width. Olivine shows weak zoning with mg ratios of 0.87–0.82 in the chondrule core, but it has more ferroan rims in the chondrule rim than in the core, the mg ratios being down to 0.66 (Fig. 2a). Large Cr-rich spinel grains with Cr/(Cr+Al) atomic ratios of 0.30–0.35, having irregular outline up to 100 microns in size, occur in olivine and groundmass (Fig. 1-21). Large fassaitic pyroxene with mg ratios of about 0.85 and Al_2O_3 contents of 12–13 wt% also occurs between olivine bars. The groundmass is fine-grained and consists of parallel growth of high-Ca pyroxene and cryptocrystalline plagioclase (Fig. 1-22), which is similar in texture to the groundmass in chondrule No. 12. The replacement of cryptocrystalline plagioclase by nepheline is more remarkable in this chondrule than in chondrule No. 12; plagioclase is wholly replaced by nepheline in the chondrule rim, and partly replaced in the chondrule core, but groundmassic high-Ca pyroxene remains unaltered (Fig. 1-22).

3.10. Chondrule No. 14

Chondrule No. 14 is a holocrystalline granular Ol-Px chondrule (Fig. 1-23), 4×3.5 mm in size, similar to chondrule No. 7. It consists mainly of olivine, low-Ca pyroxene, plagioclase, high-Ca pyroxene, and magnetite. In the chondrule core, low-Ca pyroxene is predominant, and occurs as large euhedral or subhedral crystals or as granular grains, including corroded olivine grains and magnetite spherules. Minor plagioclase and high-Ca pyroxene occur as interstitial minerals. In the chondrule rim, granular olivine is predominant, and low-Ca pyroxene is minor. Olivine in this chondrule shows weak zoning with mg ratios of 0.98–0.85, although olivine rims become more ferroan in the chondrule rim than in the chondrule core, the mg ratios being smaller than 0.70. Low-Ca pyroxene is enstatite in the chondrule core, and enstatite and pigeonite in the chondrule rim. Their mg ratios are about 0.99. The groundmass mainly consists of holocrystalline high-Ca pyroxene and plagioclase (Fig. 1-24). The plagioclase is An_{80-92} and fresh in the chondrule core, but it is locally replaced by nepheline in the chondrule rim. The high-Ca pyroxene in the groundmass is fresh and has mg ratios of 0.99–0.98.

3.11. Chondrule No. 15

This is a holocrystalline Ol-Px chondrule (Fig. 1-25), 3×2.5 mm in size, consisting of porphyritic core and granular mantle. There is a magnetite-rich zone between the core and mantle. In the porphyritic core, phenocrystic enstatite is predominant and includes olivine grains. Plagioclase, high-Ca pyroxene, and olivine occur in the groundmass. In the granular mantle, olivine is predominant, being partly included by enstatite. Plagioclase and high-Ca pyroxene occur in the groundmass. Olivine is magnesian with mg ratios of 0.99–0.95 in the porphyritic core, but it shows remarkable zoning to ferroan rims with mg ratios down to 0.75 in the granular mantle. Enstatite is magnesian and has mg ratios of about 0.99. It is replaced by ferroan olivine with mg ratios of about 0.6 in the granular mantle and especially near the chondrule rim (Fig. 1-26). Plagioclase is An_{86-82} and is fresh in the porphyritic core, but it is partially replaced by nepheline in the granular mantle (Fig. 1-27). High-Ca pyroxene has mg ratios of 0.99–0.97.

3.12. Allende matrix No. 9

Matrix No. 9 is a typical Allende matrix (Fig. 1-14), which fills the interstitial space between Allende chondrules, inclusions, and large (>10 microns) mineral fragments. Ferroan olivine is predominant and occurs as small but elongated grains several microns in size. Nepheline also occurs as small grains, and its chemical composition is nearly the same as those in Allende chondrules.

3.13. Dark inclusion No. 10

Inclusion No. 10, with a diameter of about 2.5 mm, consists mainly of fine-grained materials (Fig. 1-15) similar to the Allende matrix, but it includes small chondrules and amoeboid Ol inclusion (AOI)-like substances. A small chondrule with a diameter of about 300 microns consists mainly of ferroan olivine with minor high-Ca pyroxene and nepheline (Fig. 1-16). Most of the olivine in the chondrule is ferroan with mg ratios of 0.6–0.5 (Fig. 2b), and seems to have been produced by replacement of enstatite by ferroan olivine, because the texture of olivine is similar to that of ferroan olivine which replaced enstatite in the Allende chondrules mentioned above. Some olivine grains in the small chondrule have magnesian cores with mg ratios of 0.85–0.80 which change abruptly to ferroan olivine rims. Fine-grained materials similar to the Allende matrix are predominant in this dark inclusion, and consist mainly of ferroan olivine, salite, magnesian high-Ca pyroxene, nepheline, andradite, magnetite, and troilite. Olivine is predominant there and has mg ratios of 0.60–0.50. Salite has a constant Wo content of about 50% with variable mg ratios of 0.80–0.50. The Al_2O_3 of the salite is lower than 0.5 wt%, and its Cr_2O_3 and TiO_2 contents are very low (<0.1 wt%). Magnesian high-Ca pyroxene has mg ratios of 0.98–0.95 which are similar to those of primary high-Ca pyroxene in Allende chondrules, indicating that it was derived from chondrules by disaggregation. Andradite occurs as small grains, about 10 microns across, and has a stoichiometric composition of $Ca_3Fe_2Si_3O_{12}$. Nepheline also occurs as small grains and has chemical compositions similar to those in Allende chondrules.

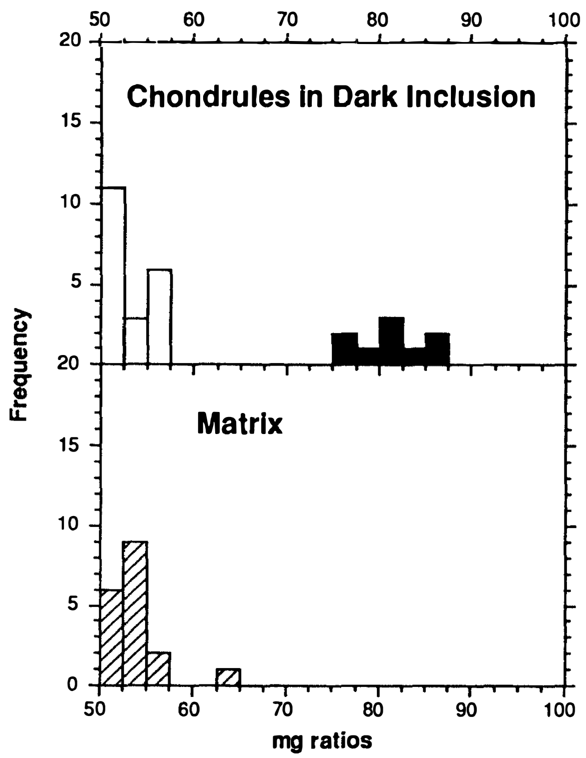

Fig. 2b. Histograms of olivines in chondrules within dark inclusion No. 10 and in Allende matrix No. 9. Most of chondrule olivines in dark inclusion No. 10 are ferroan (open bars), but minor magnesian olivine (black bars)occur in the cores of secondarily-zoned olivine (Fig. 1-16).

4. Anhydrous Alteration Reactions

Anhydrous alteration of Allende chondrules implies three processes different from each other, (I) alteration of glassy or cryptocrystalline groundmasses or groundmassic plagioclase, (II) formation of secondary ferroan olivine rims to produce normal zoning, and (III) replacement of enstatite by ferroan olivine. These three processes are discussed separately in the following sections.

(I-a) Alteration of glassy groundmasses

Chondrule No. 6 has a glassy groundmass. Most of the glass remains unaltered even in the chondrule rim, but the glass in the rim portion, which protrudes into the Allende matrix, is locally replaced by nepheline. Chemical compositions of the glass in this chondrule are represented by normative plagioclase with a negligible amount of normative pyroxene, and the normative plagioclase is $An_{90-97}Ab_{10-3}Or_0$. The main reaction to produce nepheline from the glass is:

$$\underset{\text{Glass}}{CaSi_2Al_2O_8} + \underset{\text{Gas}}{(Na,K)_2O} \longrightarrow \underset{\text{Nepheline}}{2(Na,K)SiAlO_4} + CaO, \qquad (1)$$

where alkalies with K/(Na+K) atomic ratio of about 0.065 were introduced into the chondrule, and CaO on the right hand side was lost from the chondrule or used to form Ca-rich minerals elsewhere in the chondrule.

(I-b) Alteration of cryptocrystalline groundmasses

Chondrules Nos. 4, 12, and 13 have cryptocrystalline groundmasses. Their groundmasses are similar in texture to each other, but the degree of replacement of the primary groumdmasses by altered groundmasses differs among them; the degree is small for chondrule No. 12, and large for chondrules Nos. 4 and 13.

In chondrules Nos. 4 and 13, the primary cryptocrystalline groundmasses are wholly replaced by the altered groundmasses in the chondrule rims, although they locally remain as relicts in the chondrule cores. The chemical compositions of the primary and altered groundmasses are shown in Table 2, which shows that the compositional difference between the two is remarkable for SiO_2, CaO and alkalies; SiO_2 and CaO decrease from the primary groundmass to the altered one, and alkalies increase. The average compositions of the primary and altered ones are shown in Fig. 3a, where the primary groundmasses are plotted in the compositional range of unaltered glassy groundmasses in other unaltered chondrules. However, the altered groundmasses are plotted outside the range of unaltered glassy groundmasses and deviate toward the SiO_2-poor direction (Fig. 3a). This deviation suggests that some SiO_2 was lost from the primary groundmasses to produce the altered ones and that the other components, Al_2O_3, MgO, and FeO, did not change during the alteration. The loss of SiO_2 may be expressed by the following reaction:

$$\underset{\text{Albite}}{NaSi_3AlO_8} \longrightarrow \underset{\text{Nepheline}}{NaSiAlO_4} + \underset{\text{Silica}}{2SiO_2}, \qquad (2)$$

where the albite on the left hand side is the normative albite component of the primary groundmasses, and the silica on the right hand side was lost from the chondrules or used to form other silicates elsewhere in the chondrules. In addition to

Table 2. Average chemical compositions and compositional ranges of primary and altered groundmasses (Gdm) in chondrules Nos. 4 and 13.

	Chondrule No. 4				Chondrule No. 13			
	Primary Gdm	(Range)	Altered Gdm	(Range)	Primary Gdm	(Range)	Altered Gdm	(Range)
SiO_2	52.01	(51.4–52.4)	44.26	(41.8–45.1)	49.26	(46.5–54.0)	45.81	(43.2–47.8)
TiO_2	0.62	(0.5–0.7)	0.64	(0.3–0.9)	0.65	(0.3–1.3)	0.43	(0.2–0.7)
Al_2O_3	21.67	(20.0–22.7)	25.07	(20.3–28.5)	21.53	(21.0–25.3)	22.58	(17.8–25.1)
Cr_2O_3	0.34	(0.1–0.7)	0.28	(0.04–0.6)	0.04	(0.0–0.1)	0.02	(0.0–0.08)
FeO	1.96	(1.5–2.8)	1.87	(1.1–2.6)	4.26	(1.7–5.0)	4.37	(2.1–6.1)
MnO	0.45	(0.3–0.6)	0.44	(0.2–0.8)	0.11	(0.0–0.2)	0.18	(0.1–0.3)
MgO	5.10	(4.5–5.8)	6.40	(4.6–9.3)	7.94	(3.6–8.1)	8.29	(3.8–12.7)
CaO	11.61	(10.8–12.8)	6.62	(3.4–9.4)	12.58	(11.8–14.9)	5.43	(4.3–7.6)
Na_2O	4.60	(4.2–5.1)	12.75	(10.3–15.3)	1.69	(1.6–2.2)	11.34	(8.8–14.6)
K_2O	0.04	(0.01–0.09)	1.40	(0.2–1.7)	0.01	(0.0–0.05)	1.05	(0.7–1.4)
P_2O_5	0.00		0.00		0.27	(0.1–0.9)	0.25	(0.06–0.35)
Cl	0.00		0.11	(0.0–2.0)	0.04	(0.0–0.08)	0.03	(0.0–0.08)
S	0.10	(0.0–0.3)	0.03	(0.0–0.2)	0.03	(0.0–0.1)	0.03	(0.0–0.22)
Total	98.50		99.89		98.40		99.80	

eq. (2), the silica loss from the primary groundmasses may have been caused by decomposition of the normative quartz component of the primary groundmasses; the SiO_2 loss is larger for chondrule No. 4 than for chondrule No. 13 (Fig. 3a), and this may be explained by the fact that the primary groundmass in chondrule No. 4 includes a normative quartz content which was lost during the alteration, although the primary groundmass in chondrule No. 13 has no normative quartz.

The Al-alkalies-Ca ratios of primary and altered groundmasses in chondrules Nos. 4 and 13 are plotted in Fig. 3b. The difference in average compositions between the two is explained by a simple exchange reaction:

$$\underset{\text{Anorthite}}{CaSi_2Al_2O_8} + \underset{\text{Gas}}{(Na,K)_2O} \longrightarrow \underset{\text{Nepheline}}{2(Na,K)SiAlO_4} + CaO, \qquad (1')$$

which is similar to eq. (1), but the reactant is cryptocrystalline plagioclase for eq. (1′), whereas it is a normative plagioclase component of glass for eq. (1).

(I-c) Alteration of groundmassic plagioclase

Chondrules Nos. 1, 2, 7, 8, 11, 14, and 15 have holocrystalline groundmasses which consist mainly of plagioclase and magnesian high-Ca pyroxene. Magnesian high-Ca pyroxene remains unaltered, but plagioclase has experienced alteration in various degrees. Their degrees of alteration differ among chondrules; most plagioclases are replaced by nepheline in chondrules Nos. 1 and 8, groundmassic plagioclase remains as relic grains in the chondrule cores for chondrule No. 2, and most of the plagioclase remains unaltered except the chondrule rims where plagioclase is locally replaced by nepheline in chondrules Nos. 7, 11, 14, and 15. As shown in Fig. 1 (Figs. 1-4, 1-10, 1-12, 1-18, and 1-27), replacement of plagioclase by nepheline is evident, and it may have taken place under a subsolidus condition. The

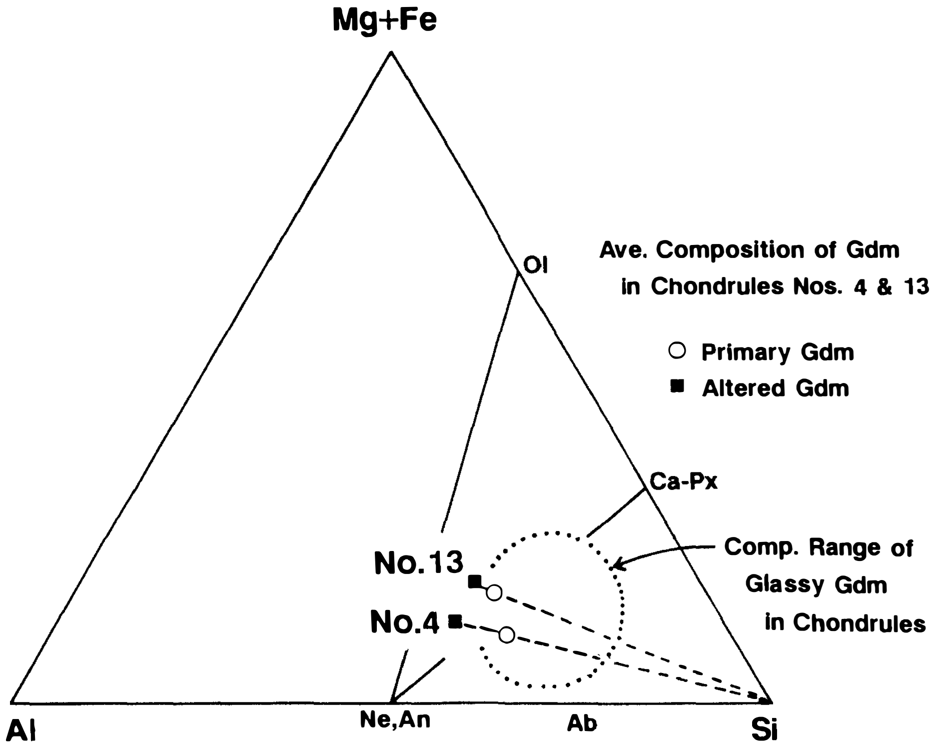

Fig. 3a. Average compositions of primary and altered groundmasses in chondrules Nos. 4 and 13 (Table 2)are plotted in (Mg+Fe)-Al-Si atomic ratios. Compositional range of unaltered glassy groundmasses of chondrules in ordinary and carbonaceous chondrites (IKEDA, 1983) is shown for reference. Note that the altered grondmasses are depleted in Si component in comparison to the primary groundmasses. Ol, Ca-Px, Ne, An, and Ab are olivine, high-Ca pyroxene, nepheline, anorthite, and albite, respectively.

reaction is caused by eqs. (1′) and (2).

Sodalite occurs in close association with nepheline in highly altered groundmasses of chondrules Nos. 1, 2, and 8. The K_2O content of sodalite is very low and less than 0.1 wt%, but the coexisting nepheline has a high K_2O content of about 1.8–2.0 wt%. Although sodalite is sometimes included by nepheline, it often occurs directly in contact with plagioclase. Sodalite seems to have formed from plagioclase by the following reaction:

$$\underset{\text{Anorthite}}{3CaSi_2Al_2O_8}+\underset{\text{Gas}}{3Na_2O}+\underset{\text{Gas}}{2NaCl} \longrightarrow \underset{\text{Sodalite}}{6NaSiAlO_4\cdot 2NaCl}+3CaO, \quad (3)$$

where Na_2O and NaCl were introduced into the chondrules, and CaO was lost from the chondrules or used to form Ca-rich phases elsewhere in the chondrules. In addition to eq. (3), sodalite may have been produced from the albite component of primary groundmasses:

$$\underset{\text{Albite}}{3NaSi_3AlO_8}+\underset{\text{Gas}}{NaCl} \longrightarrow \underset{\text{Sodalite}}{3NaSiAlO_4\cdot NaCl}+6SiO_2, \quad (3')$$

where silica on the right hand side was lost or used elsewhere in the chondrule.

In summary, the anhydrous alteration of groundmasses was caused mainly by decomposition of plagioclase or the plagioclase component of glass, and the reactions

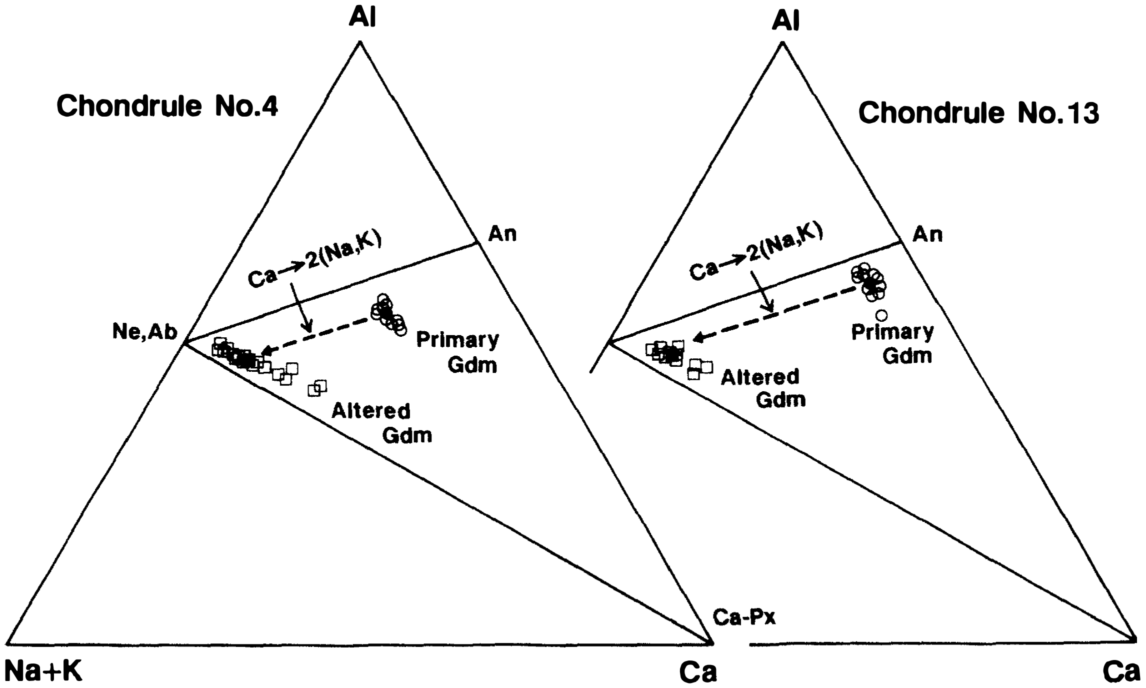

Fig. 3b. Chemical compositions of primary (open circles) and altered (open squares) groundmasses (Gdm) in chondrules Nos. 4 and 13 and their average compositions (solid symbols) are plotted in Al-(Na+K)-Ca atomic ratios. The altered groundmasses were produced from the primary groundmasses by replacement of Ca by 2(Na+K).

are expressed by eqs. (1), (1′), (2), (3), and (3′). The alkalies must have been introduced from outside of the chondrules. The CaO and SiO_2 components were expelled from the chondrules or used to form Ca-rich silicates (hedenbergite, kirschsteinite, andradite, grossular, and wollastonite) elsewhere in the chondrules (see the companion paper by KIMURA and IKEDA, 1995). However, magnesian high-Ca pyroxene remains unaltered in spite of extensive alteration of plagioclase.

(II) Formation of secondary olivine zonation

All chondrules studied here include both olivine and pyroxene. Most of the olivine in chondrules show weak or remarkable zoning from magnesian cores to ferroan rims (Fig. 2a), whereas all pyroxenes remain magnesian and have nearly constant mg ratios. This suggests that ferroan olivine of the rims cannot be in equilibrium with the coexisting magnesian pyroxene, and that the ferroan olivine was secondarily produced after lithification of chondrules (HUA *et al.*, 1988; WEINBRUCH *et al.*, 1990).

In general, olivine in chondrules crystallizes prior to pyroxene (IKEDA, 1980, 1982). First, olivine crystallizes; second, low-Ca pyroxene precipitates by reaction of olivine with the coexisting melts to include corroded olivine in the newly-formed phenocrystic low-Ca pyroxene; and finally, high-Ca pyroxene crystallizes as rims of the low-Ca pyroxene or as groundmassic grains with or without plagioclase. The partition coefficient of MgO and FeO between olivine and low-Ca pyroxene is 1/1.3 at magmatic temperatures (LARIMER, 1968), and we obtain the equilibrium relation of mg ratios between olivine and pyroxene, $mg^{Ol}=mg^{Opx}/(1.3–0.3\ mg^{Opx})$. On the other hand, the partition coefficient between olivine and high-Ca pyroxene is about 1.0 at magmatic temperatures (Obata *et al.*, 1974), indicating that mg^{Ol} nearly equals mg^{Cpx}. The magnesian cores of olivine in chondrules studied here often have mg ratios similar to the mg^{Ol} obtained from the equilibrated relation with the coexisting pyroxene, but the ferroan rims of olivine often have mg ratios far smaller than the mg^{Ol} obtained from the equilibrium relation with the coexisting pyroxene. For example, chondrule No. 1 includes olivine which zones from magnesian cores with mg ratios of 0.975 to ferroan rims with mg ratios of about 0.80 (Fig. 2a), and the coexisting low-Ca and high-Ca pyroxenes have mg ratios of about 0.98 and 0.98–0.95, respectively. For this case, the mg ratios of the rim olivine are far smaller than the mg ratios of the coexisting pyroxene. This ferroan rim olivine, with mg ratios smaller than the mg^{Ol} obtained from the equilibrium relation with the coexisting pyroxene, cannot be in equilibrium with the pyroxene at magmatic temperatures, and may have formed under a subsolidus condition by an exchange reaction of MgO and FeO in olivine; body diffusion of MgO and FeO components took place in olivine after lithification of chondrules in nebula or in parent bodies, although it did not in pyroxene, because the diffusión coefficient for pyroxene is very small at subsolidus temperatures.

The FeO components to produce ferroan olivine rims by body diffusion of FeO and MgO may have been supplied by oxidation of metal inside or outside the chondrule, and the MgO components which were released from primary magnesian olivine may have been used elsewhere inside or outside the chondrule. For this case, the MnO contents of ferroan olivine rims may be similar to those of magnesian olivine cores (Kimura and Ikeda, 1995). In addition, Ni-rich metal (awaruite) is sometimes observed in Allende chondrules (Kimura and Ikeda, 1995), supporting the oxidation of metal inside or outside the chondrules.

The reaction to form the ferroan rims of olivine in chondrules may be expressed by the equation:

$$\underset{\text{Forsterite}}{Mg_2SiO_4}+FeO=\underset{\text{Ferroan Ol}}{MgFeSiO_4}+MgO, \quad (4)$$

where FeO on the left hand side was produced by oxidation of metal inside or outside chondrules, and MgO on the right hand side was lost from the chondrules or used to form MgO-bearing silicates elsewhere in the chondrules. For the latter case, a possible reaction is:

$$MgO+FeO+SiO_2=\underset{\text{Ferroan Ol}}{MgFeSiO_4}, \quad (5)$$

where MgO may be supplied from eq. (4), FeO from the relation for oxidation of metal, and SiO_2 from eqs. (2), (3′) and/or decomposition of the normative quartz component of primary groundmasses. The ferroan olivine on the right hand side of eq. (5) may precipitate as overgrown rims on phenocrystic olivine in the chondrules so that the ferroan olivine produced by eq. (5) can hardly be distinguished from the ferroan olivine produced by eq. (4). Alternatively, some chondrules (for example, chondrule No. 7; Fig. 1-10) include small isolated grains of ferroan olivine with mg ratios of 0.5–0.7 in the groundmasses, and these ferroan olivine grains may have been produced by eq. (5).

(III) Replacement of enstatite by ferroan olivine

Enstatite in chondrules is sometimes replaced by ferroan olivine (HOUSLEY and CIRLIN, 1983; HOUSLEY, 1986). The enstatites in chondrule No. 8 are almost replaced by ferroan olivine; those in chondrules Nos. 4 and 15 are also replaced in the chondrule rims; those in chondrule No. 1 are replaced only in a chondrule rim protruding into the Allende matrix. The reaction to produce the ferroan olivine by replacement of enstatite is (HOUSLEY and CIRLIN, 1983):

$$\underset{\text{Enstatite}}{MgSiO_3} + FeO = \underset{\text{Ferroan Ol}}{MgFeSiO_4}, \quad (6)$$

where FeO on the left hand side is introduced by oxidation of metal inside or outside the chondrules. The ferroan olivine replacing enstatite has mg ratios of 0.5–0.75 (Fig. 2a), which are more ferroan than those of the ferroan rims (mg=0.9–0.7) of the secondarily zoned olivine discussed in the previous section. Secondary zonation of olivine may have formed prior to and in the early stage of the replacement of enstatite by eq. (6).

5. Alteration Degrees

Most of the Allende chondrules experienced more or less anhydrous alteration, but the degree differs among chondrules. As already discussed in the previous sections, the anhydrous alteration comprises three processes, groundmass alteration, formation of secondary olivine zonation, and replacement of enstatite. Generally speaking, the anhydrous alteration is more remarkable in chondrule rims than in chondrule cores. But, we define the degrees of alteration for whole chondrules, and they are grouped into the following three categories: Slight (0–5%), Moderate (5–50%), and Intense (50–100%). These categories will be used in the following sections.

5.1. Degree of groundmass alteration

In chondrules having glassy groundmasses, the glass is sometimes replaced by nepheline, and the degree of replacement is presented by the area % of nepheline to the total area of unaltered glass and nepheline. For the case of chondrules having cryptocrystalline groundmaases, the degree is defined by the area % of secondary altered groundmass to the total area of primary and altered groundmasses. In chondrules having holocrystalline groundmasses, the groundmassic plagioclase is sometimes replaced by nepheline and/or sodalite, and the degree is presented by the area % of nepheline and sodalite to the total area of plagioclase, nepheline, and sodalite.

Chondrule No. 6 has clean glass, and most of the glass remains unaltered although glass in a rim protruding into the Allende matrix is replaced by nepheline. The area % of the nepheline to the total area of glass and nepheline in the chondrule is less than a few %, and the degree of groundmass alteration is classified into the category of "Slight" (Table 3).

Chondrules No. 4, 12, and 13 have cryprocrystalline groundmasses. The altered groundmasses in chondrules No. 12 and 13 are about 10–20% of the total

Table 3. Degrees of groundmass alteration, enstatite (En) replacement, and secondary olivine (Ol) zoning in Allende chondrules, and overall degree of anhydrous alteration for the chondrules with oxygen isotopic compositions (CLAYTON et al., 1983). Nos. 9 and 10 are the Allende matrix and a dark inclusion, respectively.

Chondrule	Groundmass alteration	Enstatite replacement	Secondary Ol zoning	Overall degree	Oxygen isotop. comp. delta O^{18}	& O^{17}
No. 1	Intense	Slight	Intense	Slightly	0.84	−2.87
No. 2	Intense	Slight	Intense	Slightly	1.20	−2.42
No. 4	Intense	Moderate	Intense	Moderately	1.47	−2.12
No. 6	Slight	no En	Intense	Slightly	3.13	0.14
No. 7	Moderate	Slight	Intense	Slightly	0.22	−3.54
No. 8	Intense	Intense	Intense	Highly	1.40	−2.42
No. 9	—	—	—	—	3.72	−0.89
No. 10	—	—	—	—	5.24	0.81
No. 11	Moderate	no En	Intense	Slightly	3.77	1.45
No. 12	Moderate	no En	Moderate	Slightly	0.11	−3.32
No. 13	Moderate	no En	Intense	Slightly	3.68	1.50
No. 14	Slight	Slight	Intense	Slightly	0.99	−2.47
No. 15 core	Slight	Slight	Moderate	Slightly	−1.31	−4.77
mantle	Intense	Moderate	Intense	Moderately	0.74	−2.42

groundmassic area, and the degree is "Moderate". Altered groundmass is predominant in chondrule No. 4, and the unaltered primary groundmass is hardly observed there. Therefore, the degree is "Intense" (Table 3).

Chondrules No. 1, 2, 7, 8, 11, 14, and 15 have holocrystalline groundmasses. Most of the groundmassic plagioclase in chondrule No. 14 and in the core of chondrule No. 15 remains unaltered, and they are classified into "Slight". The plagioclases in chondrules Nos. 7 and 11 are replaced by nepheline with an area of about 10%, and the degree is "Moderate". More than half of groundmassic plagioclase is replaced by nepheline and sodalite in chondrules No. 1, 2, 8, and the mantle of chondrule No. 15, and their degrees are "Intense" (Table 3).

5.2. *Degree of secondary olivine zonation*

Most of the olivine in Allende chondrules studied here shows weak or remarkable zoning from magnesian cores to ferroan rims. The ferroan rims often have mg ratios smaller than the mg^{Ol} calculated from the equilibrium relation with coexisting pyroxenes, and they were produced by body diffusion of Mg and Fe after the lithification of chondrules, as already discussed in the previous section. The degree of olivine zonation is defined for chondrules including both olivine and pyroxene as follows: (i) a few tens of large olivine grains are sampled randomly in a chondrule; (ii) the core, rim, and intermediate point between the core and rim are analyzed for each olivine grain; (iii) the number of analytical points having mg ratios smaller than mg^{Ol}, which equals mg^{Cpx} for Cpx-bearing chondrules or $mg^{Opx}/(1.3–0.3\ mg^{Opx})$ for Cpx-free chondrules, is counted and divided by the total analytical number to obtain the percentage. The percentage is taken to be the degree of secondary olivine zonation. Figure 2 shows the histograms of olivine obtained according to the method of (i) and (ii), and the degrees of secondary olivine zonation are summarized in Table 3, where the same three categories stated above are used.

5.3. *Degree of enstatite replacement*

Enstatite in chondrules is often replaced by ferroan olivine with mg ratios of 0.5–0.75 (Fig. 2a). The areal % of the replacement was measured under a microscope.

In chondrules No. 1, 2, 7, and 14, and the core of chondrule No. 15, most enstatite occurs as unaltered grains; less than a few % of enstatite, mostly in chondrule rims, is replaced by ferroan olivine. For these cases, the degrees of enstatite replacement are taken as "Slight" (Table 3).

In chondrule No. 4 and the mantle of chondrule No. 15, 10–20% of enstatite is replaced, and the degree is "Moderate". In chondrule No. 8, most of the enstatite is replaced by ferroan olivine; less than 20% of the enstatite remains as relic in the chondrule core. This case is classified in the "Intense" category (Table 3).

In chondrules Nos. 6, 11, 12, and 13, there is no enstatite nor secondarily formed olivine, and the degree cannot be defined for them.

5.4. *Overall degree of anhydrous alteration of a chondrule*

The degrees of groundmass alteration, secondary olivine zonation, and enstatite replacement are summarized in Table 3, which indicates that there is a weak correlation in degree of alteration between secondary olivine zonation and enstatite replacement. This suggests that the two processes are related; first, secondary olivine zonation was produced by Mg-Fe diffusion forming ferroan olivine rims of mg ratios down to 0.65, and then enstatite was replaced by ferroan olivine with mg ratios of 0.75–0.50 (Fig. 2a). On the other hand, there is a good correlation in the degree of alteration between groundmass alteration and enstatite replacement (Table 3), suggesting that they took place at the same time.

The overall degree of anhydrous alteration of a chondrule is defined as follows. Chondrule No. 8 has "Intense" groundmass alteration and enstatite replacement. This is defined to be a highly-altered chondrule (Table 3). Chondrule No. 4 and the mantle of chondrule No. 15 have "Intense" groundmass alteration, and the enstatite replacement is in the "Moderate" category. The two are defined to be moderately-altered chondrules or mantles. The other chondrules have the groundmass alteration of "Moderate" or "Slight" categories, and the enstatite replacement is "Slight". These are defined to be slightly-altered chondrules (Table 3).

5.5. *Rates of alkali-Ca exchange reactions*

In order to estimate the rates of the alkali-Ca exchange reactions, which have altered groundmassic plagioclase in Allende chondrules, we conducted heating experiments using plagioclase from terrestrial basalts. The starting materials were homogeneous plagioclase single crystals, 1–2 mm across, with An_{75} and An_{97}. They were held within NaCl powder in a Pt crucible, and were heated isothermally in an electric furnace. Temperatures were 700° and 800°C, and the heating duration was 5–320 hours. The details of the heating experiments will be given elsewhere.

The peripheral portions of the starting materials reacted with the surrounding NaCl to produce nepheline rims ranging from a few to several tens of microns in width. An example of the results is shown in Fig. 1-28. The rates of reactions to produce nepheline seem not to differ largely between the starting materials An_{75} and An_{97}. The reactions which took place in the heating experiments are exactly the same as those of eqs. (1′) and (2) given in the previous section. The durations to produce nepheline rims with 10 micron width were calculated on the assumption that the width increases linearly with the duration, and are shown in Fig. 4. The reaction rates of plagioclase alteration to produce nepheline seem to intersect the curve of Mg-Fe

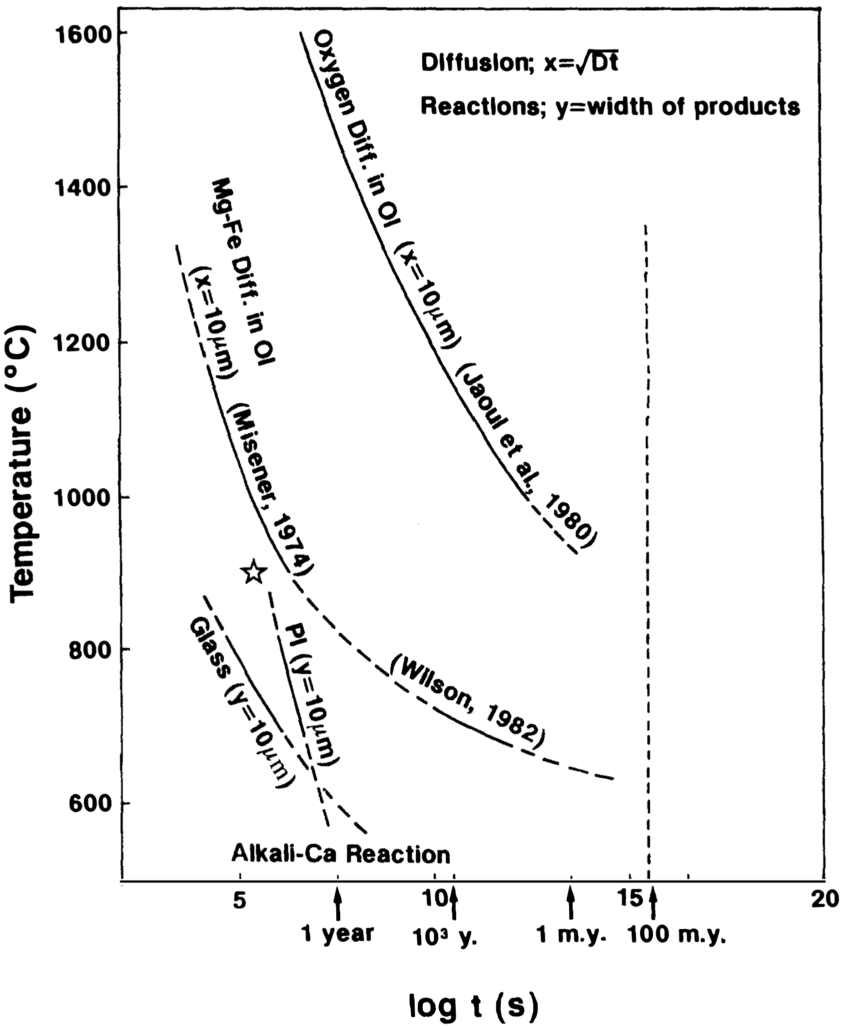

Fig. 4. *Temperature and time relations for oxygen and Mg-Fe diffusion in olivine. Diffusion distance (x) is taken as $(Dt)^{1/2}$, where D and t are diffusion coefficients (JAOUL et al., 1980; MISENER, 1974; WILSON, 1982) and time. Open star is the results of heating experiments for bronzite mixed with wustite to produce ferroan olivine at a temperature of 900°C (HOUSLEY, 1986). Solid line with Alkali-Ca Reaction is the results of heating experiments of plagioclase (Pl) or glass mixed with NaCl to produce nepheline (see text). The nebular life time is taken as 100 million years.*

diffusion of olivine with $x=10$ microns at temperatures around 1000°C (Fig. 4), indicating that calcic plagioclase in chondrules was able to react with a gas to produce nepheline at temperatures lower than 1000°C without remarkable homogenization of secondary olivine zonation. This is consistent with the fact that nepheline replacing plagioclase always coexists with secondarily-zoned olivine in Allende chondrules. KIMURA and IKEDA (1995) also suggested that the anhydrous alkali-Ca exchange reaction took place at temperatures lower than 1100 K. FEGLEY and LEWIS (1980) showed that nepheline and sodalite become stable at temperatures lower than 800–900 K in a solar nebular gas. Under such a condition the replacement of plagiolcase should take place more easily than the Mg-Fe diffusion of olivine (Fig. 4).

HOUSLEY (1986) performed heating experiments on bronzite particles mixed with wustite powder to produce ferroan olivine for 100 hours at 900°C, and extensive ferroan olivine rims surrounding the bronzite particles tens of microns thick were produced. This result is shown in Fig. 4, suggesting that the replacement of bronzite by ferroan olivine was able to take place at the same time as the replacement of plagioclase by nepheline in the Allende chondrules.

6. Correlation Between Alteration Degree and Oxygen Isotopic Composition

The oxygen isotopic compositions of chondrules studied here are shown in Table 3, and are plotted in Fig. 5. The figure indicates that all chondrules, including heavily-, moderately-, and slightly-altered ones, are plotted along the chondrule mixing line. Chondrule No. 8 is a heavily-altered one, but it never deviates from the chondrule mixing line toward the inclusion mixing line. The mantle of chondrule No. 15 has no tendency to move toward the inclusion mixing line and is plotted on the same line together with the chondrule core (Fig. 5). These facts suggest that the anhydrous alteration of Allende chondrules took place in a chondrule-gas reservoir, which was different from an inclusion-gas reservoir. The heavily and moderately altered chondrules, No. 8, 4, and 15 mantle, seem to be concentrated in the range from 1 to 2 permil of delta ^{18}O and from -2 to -3 of delta ^{17}O (Fig. 5), indicating that the gas reservoir, which altered these chondrules, had the oxygen isotopic composition of the range. The oxygen isotopic compositions of Allende matrix No. 9 and dark inclusion No. 10 are plotted along the inclusion mixing line. BISCHOFF *et al.* (1988) reported four Allende dark inclusions; they have oxygen isotopic compositions along the inclusion mixing line near dark inclusion No. 10 and matrix No. 9. They are far heavier in oxygen isotopic composition than those of the gas reservoir for chondrule alteration.

Mg-Fe diffusion in olivine (MISENER, 1974; WILSON, 1982) is much easier than oxygen diffusion in olivine (JAOUL *et al.*, 1980), as shown in Fig. 4. Therefore, the formation of secondary olivine zonation can be produced without any detectable oxygen isotope exchange. However, enstatite replacement by ferroan olivine and alkali-Ca exchange reactions for groundmass alteration, as shown by eqs. (1), (1′), (3), and (6), are reconstructive reactions, and their reaction rates may be controlled not by body diffusion but by boundary diffusion. Then, oxygen may have been easily exchangeable during the reactions between the gas reservoir and the products of the

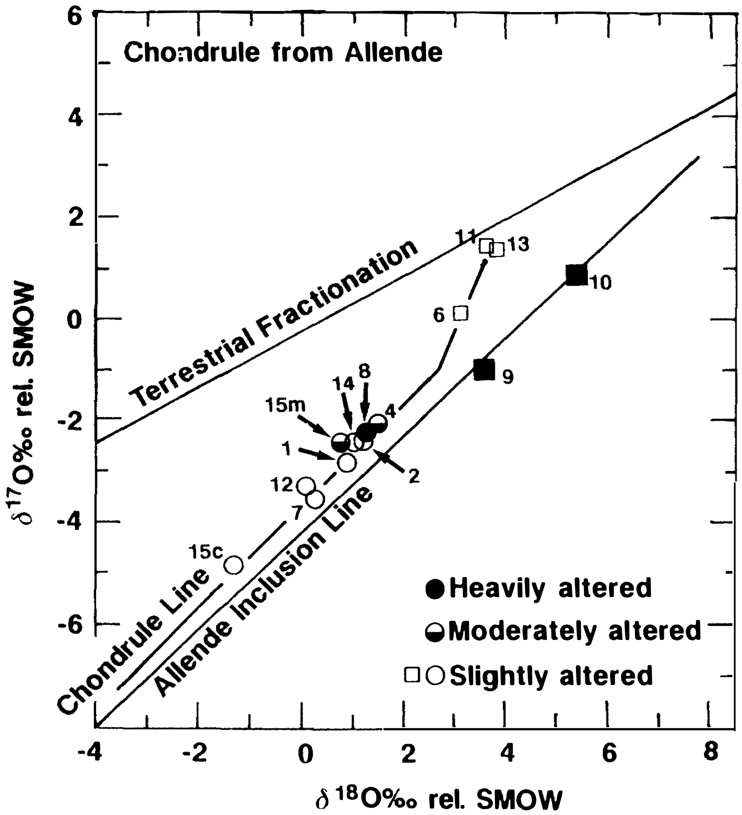

Fig. 5. Oxygen isotopic compositions of eleven Allende chondrules Nos. 1, 2, 4, 6, 7, 8, 11, 12, 13, 14, 15 core, and 15 mantle (circles: porphyritic or granular chondrules; small squares: barred-Ol chondrules), Allende matrix No. 9 (large solid square), and Allende dark inclusion No. 10 (large solid square). Allende inclusion and chondrule lines (Clayton et al., 1983) are shown for reference.

reactions. Chondrule No. 8 includes an abundant amount of ferroan olivine which was produced by replacement of enstatite at subsolidus temperatures, and the areal percent of the relic magnesian portion is about 20% of this chondrule (see Section 3.6). This indicates that most of the original oxygen in enstatite may have experienced oxygen exchange by eq. (6) with the gas reservoir which surrounded the chondrule. In spite of the extensive oxygen exchange, the oxygen isotopic composition of chondrule No. 8 never deviates from the Allende chondrule mixing line. Therefore, we conclude that the anhydrous alteration of chondrules may have taken place in a nebula prior to the accretion onto the Allende parent body.

7. Conclusions

(1) Allende chondrules have experienced anhydrous alteration in various degrees. The alteration includes three processes: secondary olivine zonation, replacement of groundmassic plagioclase or glass by nepheline and/or sodalite, and replacement of enstatite by ferroan olivine.

(2) The replacement of plagioclase or glass in Allende chondrules has a positive correlation in degree with the replacement of enstatite, suggesting that the two processes took place at the same time at temperatures lower than 1000°C, probably lower than 800 K. Secondary olivine zonation may have formed, both prior to and in the early stage of this replacement of enstatite and plagioclase.

(3) Anhydrous alteration of chondrules took place in a gas reservoir having

oxygen isotopic composition along the Allende chondrule mixing line prior to the accretion onto the Allende parent body; a dark inclusion and matrix were produced in a nebular gas along the Allende inclusion line. After anhydrous alteration, they were mixed to form the Allende parent body.

Acknowledgments

We thank Dr. TSUCHIYAMA for supply of plagioclase samples in our heating experiments.

References

BISCHOFF, A. and KEIL, K. (1984): Al-rich objects in ordinary chondrites: Related origin of carbonaceous and ordinary chondrites and their constituents. Geochim. Cosmochim. Acta, **48**, 693–709.

BISCHOFF, A., PALME, H., SPETTEL, B., CLAYTON, R. N. and MAYEDA, T. K. (1988): The chemical composition of dark inclusions from the Allende meteorite. Lunar and Planetary Science XIX. Houston, Lunar Planet Inst., 88–89.

CLAYTON, R. N., ONUMA, N., IKEDA, Y., MAYEDA, T. K., HUTCHEON, I. D., OLSEN, E. J. AND MOLINI-VELSKO, C. (1983): Oxygen isotopic compositions of chondrules in Allende and ordinary chondrites. Chondrules and Their Origins, ed. by E. A. KING. Houston, Lunar Planet. Inst., 37–43.

FEGLEY, B., Jr. and LEWIS, J.S. (1980): Volatile element chemistry in the solar nebula: Na, K, Cl, Br, and P. Icarus, **41**, 439–455.

HOUSLEY, R. M. (1986): Laboratory simulations relevant to CV parent body alteration. Lunar and Planetary Science XVII. Houston, Lunar Planet Inst., 364–365.

HOUSLEY, R. M. and CIRLIN, E. H. (1983): On the alteration of Allende chondrules and the formation of matrix. Chondrules and Their Origins, ed. by E. A. KING. Houston, Lunar Planet. Inst., 145–161.

HUA, X., ADAM, J., PALME, H. and EL GORESY, A. (1988): Fayalite-rich rims, veins, and halos around and in forsteritic olivines in CAIs and chondrules in carbonaceous chondrites: Types, compositional profiles and constraints of their formation. Geochim. Cosmochim. Acta, **52**, 1389–1408.

IKEDA, Y. (1980): Petorology of Allan Hills-764 chonderite (LL3). Mem. Natl Inst. Polar Res., Spec. Issue, **17**, 50–82.

IKEDA, Y. (1982): Petrology of the ALH-77003 chondrite (C3). Mem. Natl. Inst. Polar Res., Spec. Issue, **25**, 34–65.

IKEDA, Y. (1983): Alteration of chondrules and matrices in the four Antarctic carbonaceous chondrites ALH-77003(C3), Y-790123(C2), Y-75293(C2), and Y-74662(C2). Mem. Natl Inst. Polae Res., Spec. Issue, **30**, 93–108.

IKEDA, Y. and KIMURA, M. (1985): Na-Ca zoning of chondrules in Allende and ALHA-77003 carbonaceous chondrites (abstract). Meteoritics, **20**, 670–671.

JAOUL, O., FROIDEVAUX, C., DRUHAM, W.B. and MICHAUT, M. (1980): Oxygen self-diffusion in forsterite: Implications for the high-temperature creep mechanism. Earth Planet. Sci. Lett., **47**, 391–397.

KIMURA, M. and IKEDA, Y. (1995): 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. Proc. NIPR Symp. Antarct. Meteorites, 8, 123–138.

LARIMER, J.W. (1968): Experimental studies on the system Fe-MgO-SiO_2-O_2 and their bearing on the petrology of chondritic meteorites. Geochim. Cosmochim. Acta, **32**, 1187–1208.

MACPHERSON, G. J., WARK, D. A. and ARMSTRONG, J. T. (1988): Primitive material surviving in chondrules: Refractory inclusions. Meteorites and the Early Solar System, ed. by J. K. KERRIDGE and M. S. MATTHEWS. Tucson, Univ. Arizona Press, 746–807.

MISENER, D. J. (1974): Cation diffusion in olivine to 1400°C and 35 kilobars. Geochemical Transport and Kinetics, ed. by A. W. HOFMANN *et al.* Washington, Carnegie Inst. Washington, 117–129.

OBATA, M., BANNO, S. and MORI, T. (1974): The iron-magnesium partitioning between naturally occuring coexisting olivine and Ca-rich clinopyroxene: An application of the sample mixture model of olivine solid solution. Bull. Soc. Mineral. Cristallogr., **97**, 101–107.

TOMEOKA, K., NOMURA, K. and TAKEDA, H. (1992): Na-bearing Ca-Al-rich inclusions in the Yamato-791717 CO carbonaceous chondrite. Meteoritics, **27**, 136–143.

WEINBRUCH, S., PALME, H., MULLER, W. F. and EL GORESY, A. (1990): FeO-rich rims and veins in Allende forsterite: Evidence for high temperature condensation at oxidizing conditions. Meteoritics, **25**, 115–125.

WILSON, A. H. (1982): The geology of the Great "Dyke", Zimbabwe: The ultramafic rocks. J. Petrol., **23**, 240–292.

(*Received November 1, 1994; Revised manuscript received January 9, 1995*)