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RELICT MINERALS AND THEIR ASSEMBLAGES IN YAMATO-691 (EH3)

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Abstract: Four relict minerals; olivine, pyroxene, a silica mineral and metallic (Fe, Ni) were found in the chondrules and as the mineral fragments of Yamato-691 (EH3). Two mineral assemblages of the relict minerals were found; (a) olivine+pyroxene+metallic (Fe, Ni), and (b) pyroxene+silica mineral. The relict pyroxene in assemblage (a) was formed from the reaction of olivine and silica-rich phase (gas or liquid). These two assemblages cannot coexist under an equilibrium condition. The compositional difference of pyroxene between assemblages (a) and (b) suggests the fractionation which occurred before the chondrule formation.

1. Introduction

Chondrules were formed by a rapid cooling of silicate melts. These silicate melts had been considered to have condensed directly from the solar gas. However, after the findings of the relict olivine which survived the melting during the chondrule formation (NAGAHARA, 1981; RAMBALDI, 1981), at least some of the precursors of chondrules have been proposed to be the solid materials larger than several microns in diameter. Relict pyroxene has also been reported from electron microscopic studies (WATANABE *et al.*, 1984; KITAMURA *et al.*, 1986). While these precursor materials appeared as separated grains, WATANABE *et al.* (1987) recently proposed that the clusters of the fine materials (smaller than several microns) had also been the precursor materials. On the other hand, the mineral assemblages of the coarse-grained relict minerals have not been clarified, because the relict minerals were only found not coexisting with each other. Therefore, more detailed study on the precursor materials such as their mineral assemblages of the coarse grains is now one of the main subjects to clarify the origin of the precursor materials of chondrules.

Enstatite chondrites have been given much attention because of the highly reduced condition of the formation process. The relict minerals in the chondrules in the Qingzhen chondrite (EH3) have been found as olivine and pyroxene with the composition much more ferrous than the minerals formed during the chondrule formation under highly reduced condition (RAMBALDI *et al.*, 1983, 1984). Olivine and pyroxene with dusty fine-grained inclusions of metallic Fe blebs in the Yamato (Y)-691 chondrite (EH3) have also been found as relict (NAGAHARA, 1985a, b). These relict minerals indicate existence of oxidized components in precursors of these two enstatite chondrites.

The precursor materials of chondrules have also been studied by the variation of bulk composition of chondrules (*e.g.*, GROSSMAN and WASSON, 1982; IKEDA, 1983).

On the other hand, one of the best ways to understand the origin of precursor materials is to clarify the mineral assemblage of the relict minerals which survived the chondrule formation. If the relict minerals include other minerals which were not formed during the chondrule formation, the inclusions can also be considered to be relict. In the present study, relict pyroxene and olivine in the enstatite chondrite (Y-691; EH3) have been subjected to a detailed analysis program including back-scattered electron imaging (BEI) technique and quantitative electron probe microanalyses (EPMA) to find the relict inclusions. As the result, the relict pyroxenes which include olivine and metallic (Fe, Ni) and those which coexist with SiO_2 minerals were first found. The genetic relations among the four minerals indicate that there are two distinct mineral assemblages: (a) olivine + pyroxene + metallic (Fe, Ni) and (b) pyroxene + silica mineral.

In the present paper, the details of the relict minerals and their assemblages in our specimen of Y-691,78–6 are described. And then, the origin of these two mineral assemblages is attributed to a fractionation process before the chondrule formation.

2. Experiments

Specimen: Recovery, curation and allocation of Y-691 (EH3) have been reported by YANAI and KOJIMA (1986). Bulk chemical composition of chondrules in Y-691 has been studied by IKEDA (1988). A thin section provided from NIPR is 1.2×0.3 cm. The Y-691 chondrite consists of chondrules, lithic fragments, mineral fragments and matrix. Since some of the chondrules were not in a spherical shape but in a brecciated shape, distinction between chondrules and lithic fragments was difficult in many cases. In the present paper the term chondrules is used for both chondrules and lithic fragments in an original sense, when the cluster has a distinctive igneous texture.

After optical microscopic observation of the thin section, about thirty chondrules and several fragments were studied in detail by BEI and EPMA. For pyroxenes with Ca-poor and Fe-poor composition in this study, the terms orthoenstatite and clinoenstatite were used only when the symmetry was clear from the extinction angle. The pyroxene with ferrous composition is expressed as orthopyroxene. Otherwise, enstatite was used based only on the chemical composition.

Identification of relict mineral: Almost all of the chondrules in Y-691 include phenocrysts of enstatite as the major constituent and a few chondrules include phenocrysts of diopside and silica minerals (KITAMURA *et al.*, 1987). The less ferrous composition of these pyroxenes suggests the highly reduced condition of the chondrule formation. However, some significantly ferrous pyroxenes were found as mineral fragments and in chondrules. These pyroxenes are considered to be too ferrous to have formed during the chondrule formation, and are here identified as relict. The minerals which are included in the relict pyroxene were also identified as relict. A separated grain of olivine including metallic Fe blebs which indicates the reduction during the chondrule formation is also considered to be relict.

3. Results and Discussion

3.1. Relict minerals

The relict olivine and pyroxene with metallic Fe blebs and the relict pyroxene with ferrous composition were found in our specimen as well as the other specimen of Y-691 (NAGAHARA, 1985a, b). The inclusions of olivine, silica mineral and metallic (Fe, Ni) in the relict pyroxene were found and also identified as relict. The occurrence of four minerals is described and the origin is discussed as follows.

a. Olivine

As mineral fragments, single crystals of olivine often include iron-metal blebs as observed previously in Qingzhen (RAMBALDI *et al.*, 1983, 1984) and in Y-691 (NAGAHARA 1985a, b). In some cases, the metal blebs appear in a row (Fig. 1).

One of the fragments shows the partly reduced texture of olivine (Fig. 2). Unreacted olivine with $Fo_{89}Fa_{11}$ is on the right side of the figure. On the left side is olivine including metallic Fe, probably pyroxene and silica mineral. The Fe/(Mg+Fe) ratio of this mixture is 0.05–0.07. The difference in the Fe/(Mg+Fe) ratio between the unreacted and reacted zones suggests the escape of some amounts of metallic Fe from olivine during the reduction.

The other type of the relict olivine appeared to be included poikilitically in the relict pyroxene, which is described below. However, no relict olivines as phenocrysts have been found in clearly defined chondrules in our specimen, while NAGAHARA (1985a, b) reported them in her specimen.

b. Pyroxene

(A) Pyroxene with reverse zoning in a chondrule

Pyroxene with the reverse zoning (NAGAHARA, 1985a) was found only in one chondrule. The chondrule consists of phenocrysts of clinoenstatite ($Wo_{0.6}En_{99}Fs_{0.6}$). One orthopyroxene has a ferrous core ($Wo_1En_{91}Fs_8$) and metallic Fe inclusions (Fig. 3). The analyses including the metal inclusion give $Wo_{1.5}En_{90-91}Fs_{8-9}$. The core of the orthopyroxene is concluded as relict.

(B) Relict pyroxene poikilitically including olivine

Relict pyroxenes in two chondrules (B-1 and B-2) poikilitically include olivine grains which in turn include metallic Fe blebs.

(B-1) A chondrule consisting of a large orthopyroxene grain ($Wo_{3-4}En_{89-90}Fs_7$) in the central portion, and enstatite ($Wo_3En_{94}Fs_3$), pigeonite (around $Wo_{19}En_{76}Fs_5$) and mesostasis in the outer portion (Fig. 4a). The orthopyroxene includes olivine (Fa_3Fo_{97}) with metallic Fe blebs (Fig. 4b). The bulk composition of the olivines and metallic Fe blebs obtained by the plane analysis of EPMA is $Fa_{6-8}Fo_{92-94}$.

(B-2) A chondrule consisting of three large pigeonite grains ($Wo_{6-8}En_{86-89}Fs_{4-7}$) including olivine with lamellar metallic Fe blebs. The Fe/(Mg+Fe) ratio of the bulk composition of olivine including metallic Fe blebs is 0.07. Enstatite grains ($Wo_1En_{99}Fs_0$) and pigeonite are in mesostasis (Figs. 5a and 5b). The metallic Fe blebs are in rows, different from those in (B-1). The orientation of the row in olivine grains is almost constant within each large pigeonite, suggesting that the olivine grains are also in the common orientation within each pyroxene.

These two types of large pyroxene ((B-1) and (B-2)) have ferrous compositions

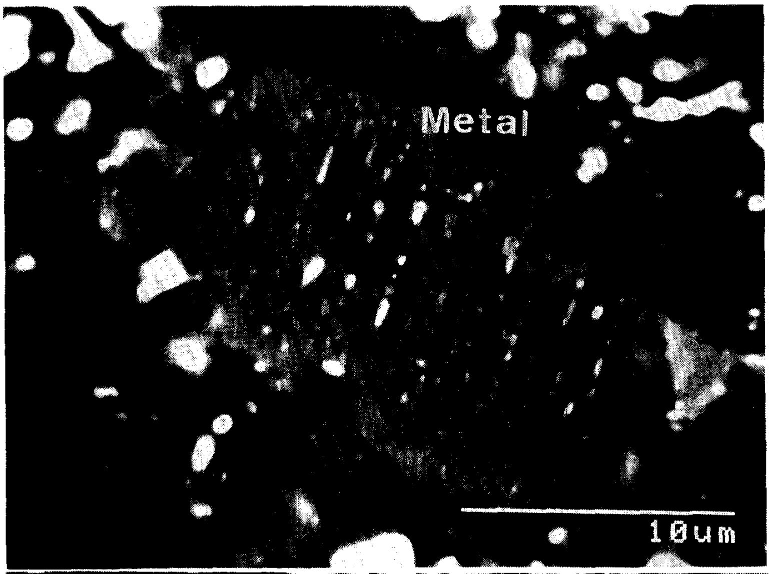

Fig. 1. BEI of a mineral fragment of olivine (Ol) with metallic Fe blebs (Metal) in rows.

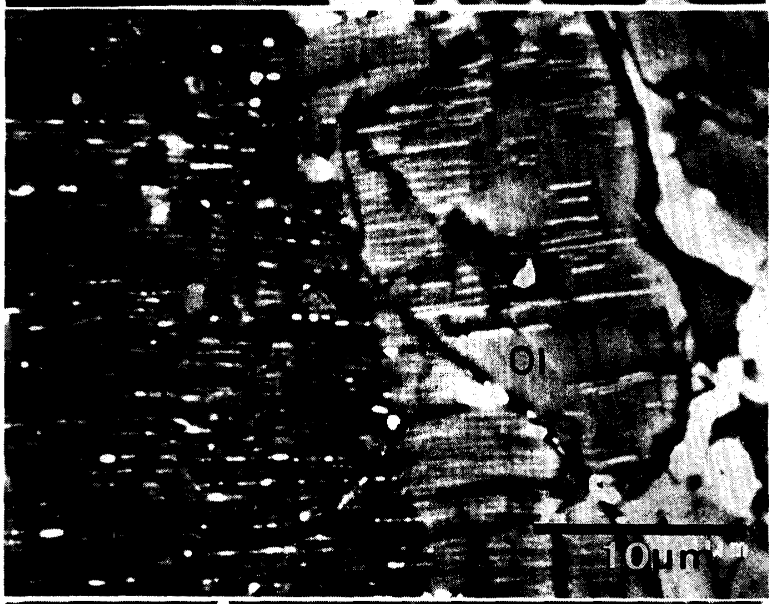

Fig. 2. BEI of a mineral fragment of olivine. The dark, left side of the olivine is the reduced zone consisting of olivine, metallic Fe blebs and SiO_2 mineral. The right-hand side is a poorly reduced zone.

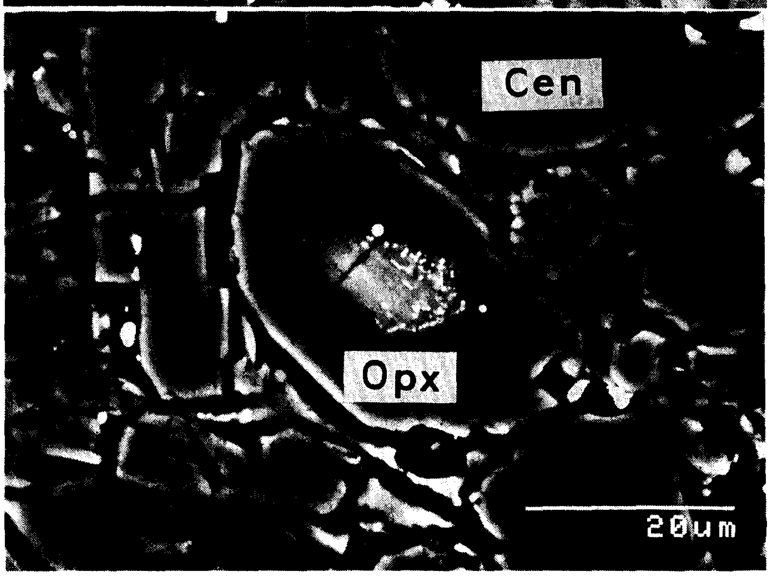

Fig. 3. BEI of the relict pyroxene in a porphyritic pyroxene chondrule. The grain with the relict ferrous core and metallic Fe inclusions is orthopyroxene (Opx). The other grains of pyroxene are clinoenstatite (Cen).

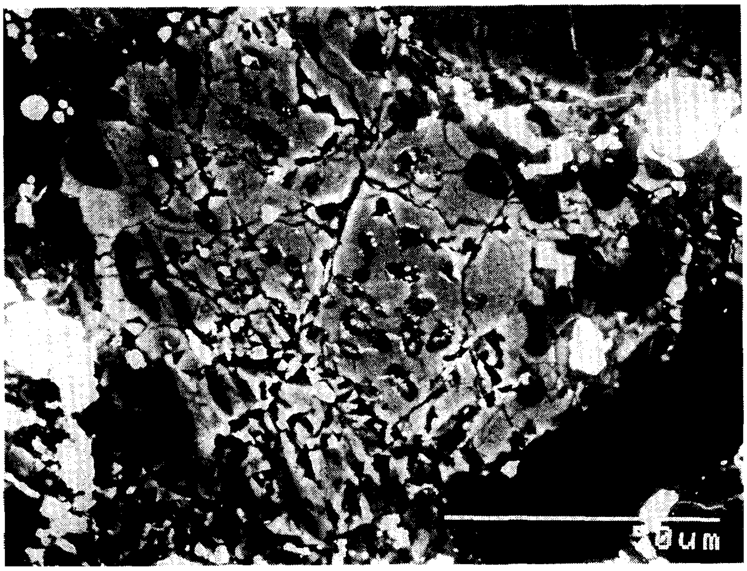

Fig. 4a. BEI of a chondrule consisting mostly of a single grain of orthopyroxene which poikilitically includes olivine grains with metallic Fe blebs. The pyroxene is rimmed by pigeonite. Enstatite is also observed around large orthopyroxene and in mesostasis.

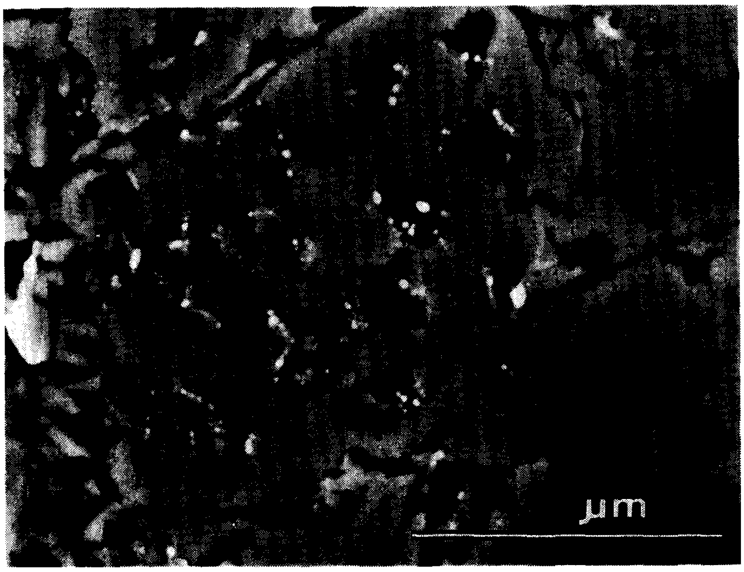

Fig. 4b. An enlarged view of (a). Metallic Fe grains (Fe) are dispersed in and around olivine grains (Ol).

Fig. 5a. Three large pigeonite grains include olivine with lamellar metal grains. Enstatite and pigeonite are in the mesostasis surrounding large pigeonite.

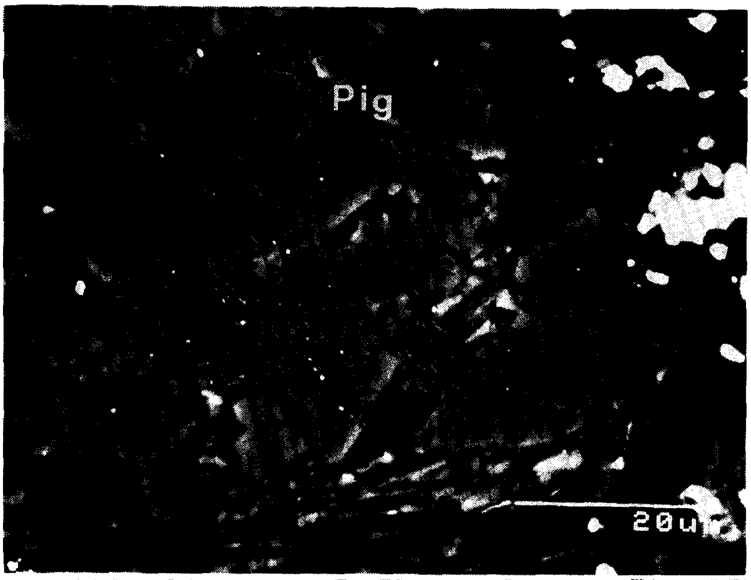

Fig. 5b. An enlarged view of pigeonite (Pig) in (Fig. 5a). Lamellar metal grains are observed in olivine.

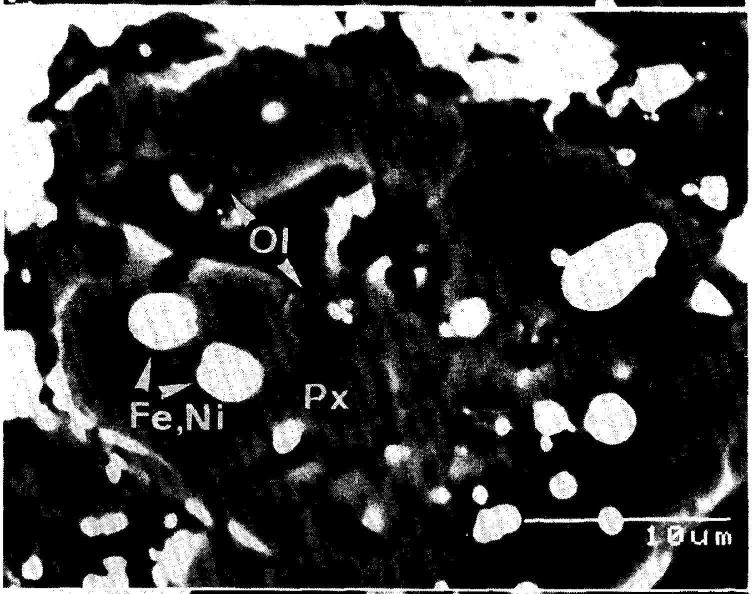

Fig. 6. A mineral fragment of ferrous pyroxene (Px) including olivine (Ol) and metallic (Fe, Ni) spherules (Fe, Ni). The olivine grains further include metallic Fe blebs which precipitated during chondrule formation.

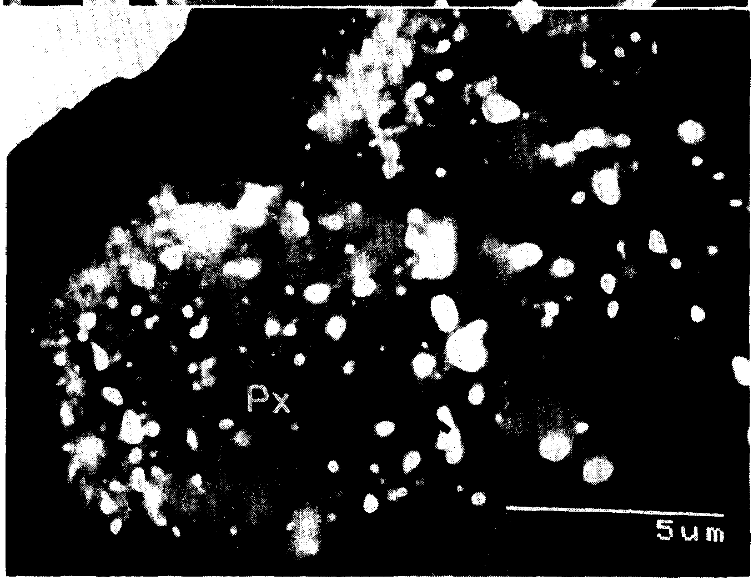

Fig. 7. Rim of a ferrous pyroxene fragment with metallic Fe blebs. The dark regions (indicated by an arrow) along the cracks and the metallic Fe blebs are pyroxene with less ferrous composition.

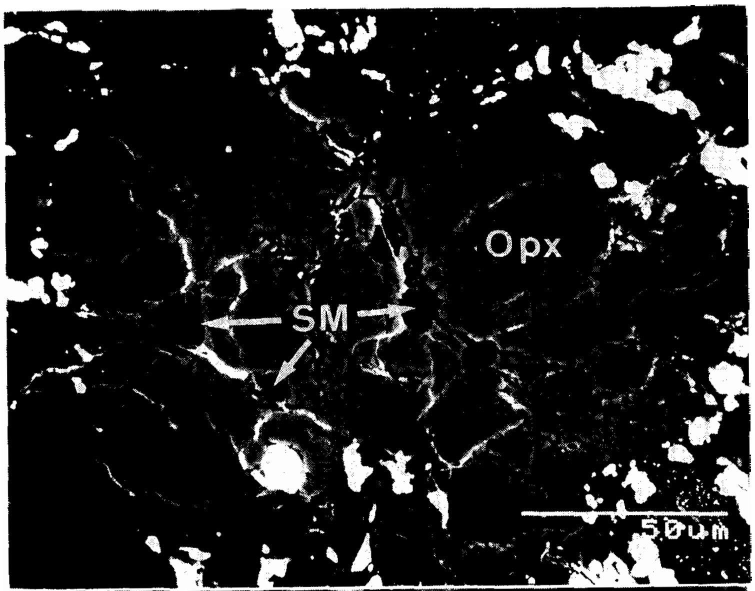

Fig. 8a. A ferrous orthopyroxene grain (Opx) with silica minerals (SM).

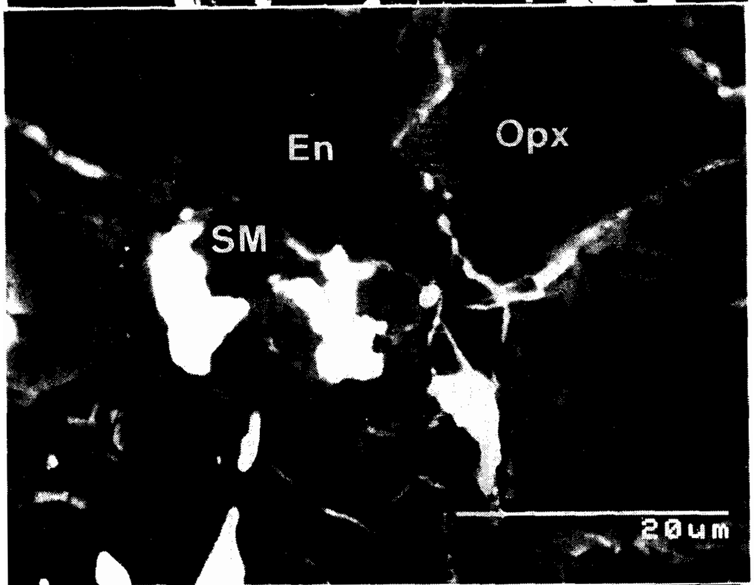

Fig. 8b. An enlarged view of the lower part of the pyroxene. Enstatite (En), SiO_2 minerals (SM) and metallic Fe are observed, which were formed during the chondrule formation.

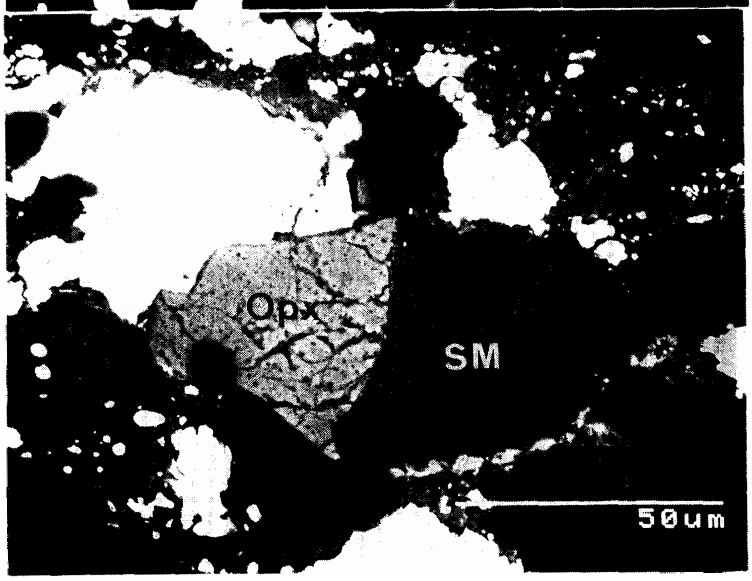

Fig. 9a. A mineral fragment consisting of orthopyroxene (Opx) and silica mineral (SM).

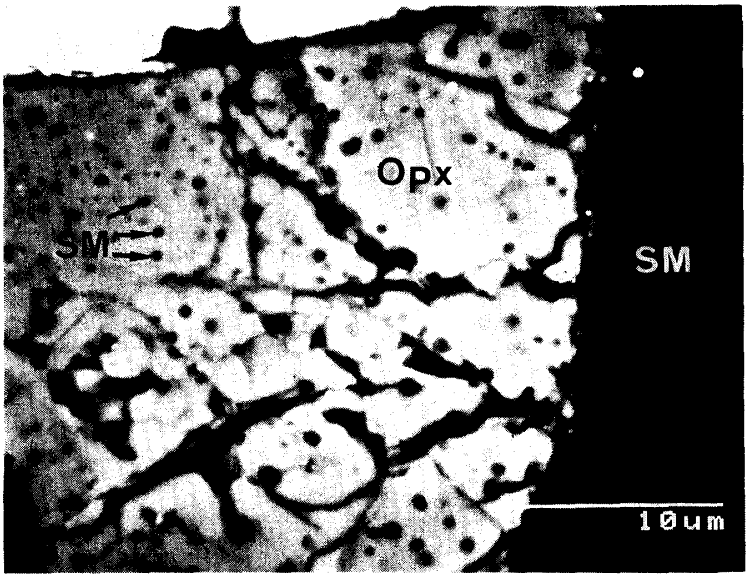

Fig. 9b. An enlarged view of the boundary region of the minerals. Lots of tiny blebs of silica mineral were included in the orthopyroxene grain.

Fig. 10. BEI of two large pyroxene chondrules. In both (a) and (b), the large orthopyroxene (Opx) phenocrysts in glass have the ferrous core and the Ca-rich rim. (a) and (b) correspond to (F-1) and (F-2) in the text.

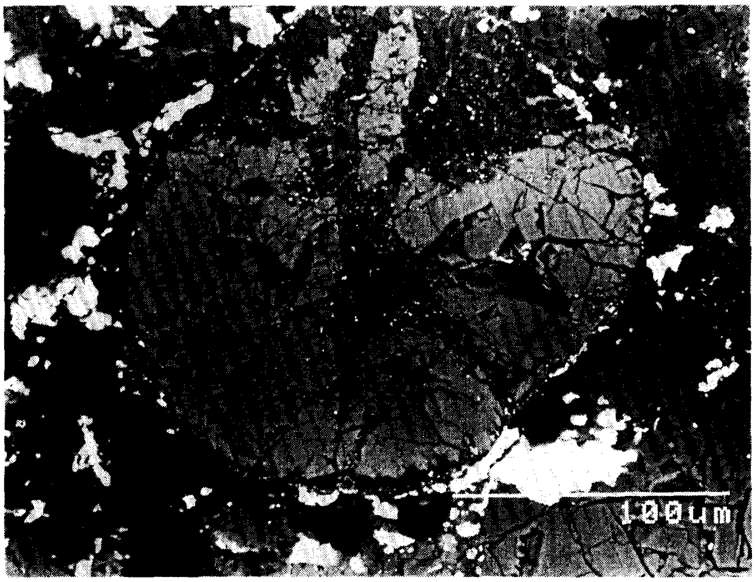

Fig. 10a.

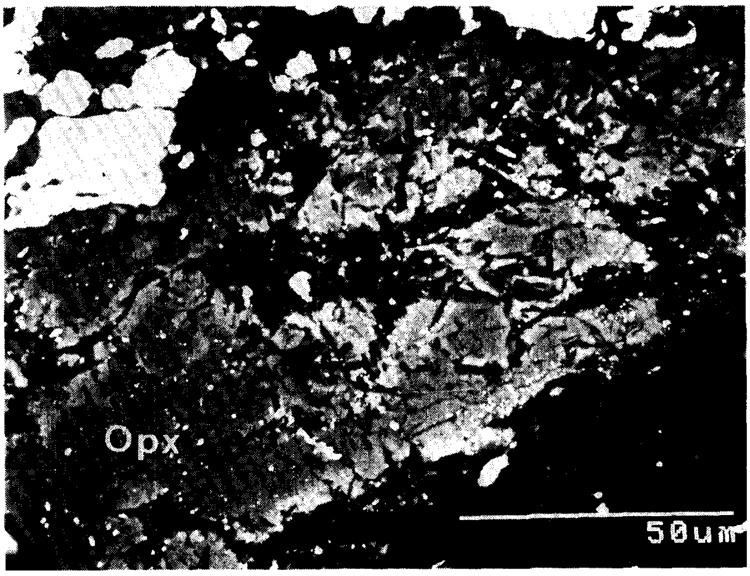

Fig. 10b.

which are different from those of surrounding enstatite in the same chondrules. Enstatite can be explained by crystallization during the chondrule formation, suggesting that the large ferrous pyroxenes are relict. This conclusion is consistent with the fact that olivine inclusions contain metallic Fe blebs which are characteristic of relict olivine grains.

(C) Relict pyroxene including olivine and metallic (Fe, Ni) spherules

This relict pyroxene appeared as a mineral fragment (Fig. 6). The pyroxene ($Wo_{1.8-2.0}En_{88.7-91.0}Fs_{7.2-9.4}$) has similar texture to (B) in that it includes olivine with metallic Fe blebs. The Fe/(Mg+Fe) ratio of olivine including metallic Fe blebs is 0.07–0.13. Although this pyroxene does not coexist with enstatite, the similarity to (B) suggests that this pyroxene is relict.

In addition to the olivine blebs, the pyroxene includes metallic (Fe, Ni) spherules with the Ni/(Fe+Ni) ratio around 0.05. Since the metallic Fe which precipitates from olivine or pyroxene by reduction should be free from Ni, the metal spherules are also considered to be relict.

(D) Relict pyroxene including metallic Fe blebs

A pyroxene ($Wo_1En_{69}Fs_{30}$) as a mineral fragment is characterized by metallic Fe blebs and the heterogeneity in Fe/(Mg+Fe) within a grain (Fig. 7). No silica minerals but less ferrous regions (down to $Wo_3En_{80}Fs_{17}$), dark in the figure, were observed along the cracks of the pyroxene and around metallic Fe blebs. This texture is considered to have been formed by the reduction probably during the chondrule formation and the escape of some amount of the silica component from the grain.

(E) Relict pyroxene poikilitically including silica mineral

Ferrous pyroxene grains including silica mineral were found in a chondrule and as mineral fragments.

The orthopyroxene grain ($Wo_{0.1-0.6}En_{82.5-87.7}Fs_{12.2-16.9}$) in the chondrule includes a few of SiO_2 grains (Fig. 8a). Enstatite, silica and metallic Fe exist in an edge of the grain, which probably crystallized during the chondrule formation (Fig. 8b). The ferrous composition indicates that the orthopyroxene is the relict mineral. However, it is very unlikely that the silica mineral is a relict because it can be produced by the reduction of pyroxene with the escape of metallic Fe into the melt phase during the chondrule formation (H. NAGAHARA, private communication).

A pyroxene grain ($Wo_{1.0-2.2}En_{72.5-73.8}Fs_{24.6-25.9}$) includes a lot of silica mineral less than 1 μm in size (Figs. 9a and 9b). A fairly large silica mineral coexists with the pyroxene grain. This silica grain shows strong wavy extinction under the optical microscope, so its phase could not be identified. Even if the tiny grains of the silica mineral in the ferrous pyroxene might be formed from the pyroxene during the chondrule formation, the coarse silica mineral is too large to have been formed by reduction or sulfidation of pyroxene during the chondrule formation. The texture strongly suggests that the coarse-grained silica mineral existed as the precursor material before the chondrule formation.

(F) Pyroxene with significant Fs-contents

Two chondrules (Figs. 10a and 10b) are characterized by pyroxenes more ferrous than those of other chondrules. Mesostasis consists mainly of glass and always contains small blebs of metallic Fe.

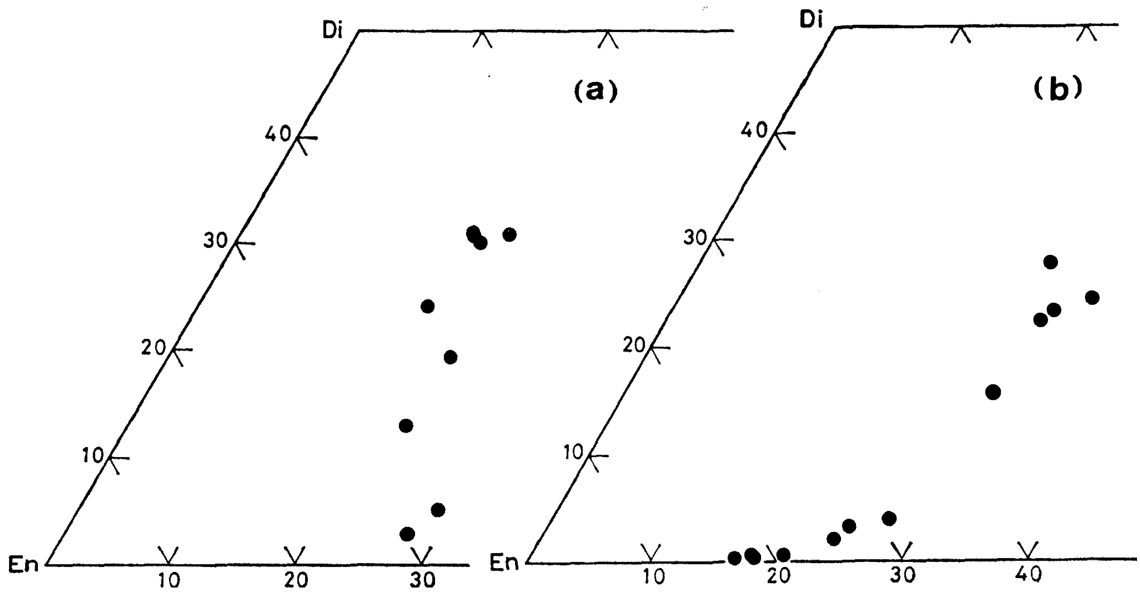

Fig. 11. The compositional trends of two large pyroxenes of (F-1) (a) and (F-2) (b) in Fig. 10, which are plotted in the pyroxene quadrilateral.

(F-1) A chondrule consists of orthopyroxene and mesostasis of glass (Fig. 10a). The orthopyroxene is of $Wo_{3-4}En_{67-70}Fs_{28-29}$ (Fig. 11a) and is rimmed by ferrous pigeonite and augite (up to $Wo_{30-31}En_{48-50}Fs_{19-22}$). The rims of pigeonite and augite contain many small metallic Fe blebs. Metallic Fe blebs also surround the chondrule.

(F-2) A chondrule (Fig. 10b) has the similar texture to that of (F-1), and pyroxenes have ferrous composition. However, the chemical trend in pyroxene is quite different in Fe/(Mg+Fe) from (F-1). The core of the pyroxene grain is orthopyroxene with $Wo_0En_{84}Fs_{16}$-$Wo_4En_{69}Fs_{27}$ and the rim is pigeonite-augite with the composition ranging from $Wo_{16}En_{54}Fs_{30}$ to $Wo_{28}En_{42}Fs_{30}$ (Fig. 11b).

The pyroxene grains (F-1 and F-2) have more ferrous composition than the relict pyroxenes in (A), (B) and (C), but similar to the pyroxene in (D) and (E). The crystallization trends of these two pyroxenes (Figs. 11a and 11b) are different from those of enstatite in common chondrules in Y-691 (Fig. 3 in KITAMURA *et al.*, 1987) and also different from each other.

The compositional zoning of these pyroxenes indicates a rapid crystallization. Furthermore, the difference between the trends of (F-1) and (F-2) may be explained by that (F-2) pyroxene crystallized under the more oxidized condition than (F-1). There are two possible interpretations of (F-1) and (F-2): (1) the whole chondrules are the relicts of the igneous fragment formed before the chondrule formation, because no enstatite exists within them, and (2) the pyroxene was formed during the chondrule formation, but the redox condition was different in time and/or space.

3.2. *Mineral assemblages of the relict minerals*

Four kinds of the relict minerals; olivine, pyroxene, silica mineral and metallic (Fe, Ni), were found as the mineral fragments and in the chondrules of our specimen. Two assemblages of these relict minerals were found.

a. Assemblage of pyroxene + olivine + metallic (Fe, Ni)

The mineral assemblage of pyroxene + olivine + metallic (Fe, Ni) appeared in (C), but lacking metallic (Fe, Ni) in (B). The Fe/(Mg + Fe) ratio of the pyroxene and the average ratio of the olivine and the metal precipitates is coincident in (B-1)(Fe/(Mg + Fe) = 0.07), in (B-2) (Fe/(Mg + Fe) = 0.06) and in (C) (Fe/(Mg + Fe) = 0.07–0.13). Therefore, it is considered that olivine and pyroxene in this mineral assemblage were equilibrated at high temperatures retained before the chondrule formation. Since the pyroxene in (B-2) is pigeonite which is stable at more than 1300°C (LINDSLEY, 1983), the temperature for (B-2) should be at least higher than 1300°C.

It is not clear whether the precursor materials were direct condensates or igneous-processed rocks (DODD, 1981). One of the most interesting characteristics of (B-2) is that the olivine grains seem to be in the same orientation within each pyroxene. Olivine grains in pyroxenes in terrestrial igneous rocks, which are incorporated by the growth of pyroxene as inclusions, have no crystallographic relation with each other. Therefore, the pyroxene in (B-2) is considered to have been formed by the reaction of a pre-existing olivine grain with SiO_2-rich gas or liquid. However, the SiO_2 phase cannot be sepcified now, since no details in both reactions have been obtained neither theoretically nor experimentally.

b. Assemblage of pyroxene + silica mineral

The coarse silica mineral in (E) suggests an assemblage pyroxene + silica mineral as the precursor. The fact that some chondrules in Y-691 have the silica-saturated bulk composition (IKEDA, 1983, 1988) and the phenocrysts of silica mineral (KITAMURA *et al.*, 1987) is consistent with the existence of silica mineral in the precursor material.

The pyroxenes of this assemblage commonly have significantly ferrous composition, more ferrous than those of assemblage (a). Silica mineral in the precursor may form by the loss of Mg and Fe from pyroxene by reduction and/or sulfidation. However, the ferrous composition of pyroxene indicates that reduction and sulfidation were not strong enough to consume Fe^{2+}. Therefore, the formation of silica in this precursor is difficult to be explained by reduction and sulfidation.

c. Relation between two mineral assemblages

These two mineral assemblages cannot coexist under the equilibrium condition, because olivine should react with SiO_2 mineral to form pyroxene. This fact suggests that the fractionation should have occurred to form these two assemblages from gas or liquid with the solar composition, and that the two assemblages were separated in space or kept at very low temperature after the solidification.

The Fe/(Mg + Fe) ratio of pyroxene in the assemblage of Ol + Px + metallic (Fe, Ni) is significantly lower than that in the assemblage of Px + SiO_2. This difference in composition can also be explained by that these two mineral assemblages had been formed by the fractional condensation from gas or fractional crystallization from liquid. Recently WATANABE *et al.* (1987) suggested that the fine-grained aggregates in the L3 chondrites were formed from the cluster of fine-grained precursor materials. These clusters have the quasi-solar composition. In contrast with the fine-grained aggregates, the two mineral assemblages in our specimen clearly indicate the fractional process before the chondrule formation.

4. Concluding Remarks

(1) Four relict minerals; olivine, pyroxene, silica mineral and metallic (Fe, Ni) were found in the chondrules and as the mineral fragments of Y-691.

(2) Large orthopyroxene and pigeonite grains which poikilitically include olivine grains and iron-metal blebs appeared as the relict minerals in the chondrules. These pyroxenes are considered to have been formed by the reaction of olivine and silica-rich phase (gas or liquid), before the chondrule formation.

(3) The pyroxenes much more ferrous than the common relict pyroxene were observed in two chondrules. These pyroxenes show different metastable crystallization trend from each other. These trends indicate either (a) the igneous fragment formed under oxidized condition or (b) the heterogeneity of the reduced condition in time or space during the chondrule formation.

(4) Two mineral assemblages of the relict minerals were found; (a) olivine + pyroxene + metallic (Fe, Ni), and (b) pyroxene + silica mineral. These two assemblages cannot coexist under an equilibrium condition, suggesting the fractionation from the solar abundance before the chondrule formation.

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