

DIOPSIDE IN CHONDRULES OF YAMATO-691 (EH3)

Masao KITAMURA, Seiko WATANABE, Hiroshi ISOBE
and Nobuo MORIMOTO

*Department of Geology and Mineralogy, Faculty of Science,
Kyoto University, Sakyo-ku, Kyoto 606*

Abstract: Diopside in the chondrules in Y-691 (EH3), most of which include enstatite as phenocrysts, occurs in three different modes; (1) diopside rimming some of the enstatite crystals, (2) single crystals as phenocrysts of the chondrules, and (3) single crystals of diopside enriched in aluminum in one chondrule.

The finding of the single crystals of diopside, since that in Qingzhen, indicates their common existence in the E3 chondrites. Common appearance of the single crystals, in contrast with the equilibrated E and the unequilibrated ordinary chondrites, is considered to be related with the reducing condition during the chondrule formation. Crystallization temperature of the crystals is roughly estimated to be 1300–1200°C.

Coexistence of aluminum-rich and aluminum-poor diopside in a chondrule implies high pressure episode by shock process.

1. Introduction

Enstatite chondrites are unique in that they record the most reduced condition among all of the chondrites, and that they have almost the same oxygen isotope composition as the earth.

Consortium of Y-691 (EH3) has been organized by the National Institute of Polar Research (NIPR) of Japan. 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 OKADA (1975) and IKEDA (1983).

Pyroxenes are one of the major constituents of the chondrites. They are distributed in chondrules, mineral fragments and matrix. Diopside appears as the rims of Ca-poor pyroxenes in chondrules of the unequilibrated ordinary chondrites (UOC's) and the equilibrated ordinary chondrites (EOC's). Single crystals of diopside in chondrules occur rarely in UOC's, but are commonly encountered in EOC's. On the other hand, single crystals of diopside were recently found in chondrules of the unequilibrated E chondrite, Qingzhen (E3) (GROSSMAN *et al.*, 1985), while they have not been reported in the equilibrated E chondrites. The different occurrence of diopside between chondrules in unequilibrated E chondrites and UOC's, therefore, gives a constraint to the conditions of the chondrule formation of these chondrites.

In the present study, diopside crystals, in a polished thin section of Y-691, have been examined by an optical microscope (OM), a back-scattered electron image technique (BSE) and an X-ray microprobe analyzer with an energy dispersive method (EDX).

2. Experiments

A thin section provided from NIPR was mounted by PMC wax to be demounted for the transmission electron microscopic study. However, the section is too thick to be observed under OM. Therefore, the section was repolished. Since a small part of the specimen was lost, the polishing procedure was stopped. Nevertheless, the remaining part of the section was still not thin enough for detailed OM observation of the fine textures. The resultant section measured 1.2×0.3 cm after polishing. After OM observation of the thin section, about thirty chondrules and several fragments were studied in detail by BSE and EDX. In this study, pyroxenes with the enstatite composition, whose symmetry was distinct in view of the extinction angle, were denoted as orthoenstatite and clinoenstatite. Otherwise, the term enstatite was used based only on the chemical composition.

3. Results

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, chondrules are used for both chondrules and lithic fragments in an original sense, when the cluster has a distinctive igneous texture.

Most of the chondrules in our section of Y-691 include phenocrysts of enstatite as the most common constituents. The enstatite appears as clino- and orthoenstatites.

Diopside in the chondrules occurs in three different modes; diopside surrounding some of the enstatite crystals as the rims (group I), single crystals as phenocrysts of the chondrules (group II), single crystals of diopside enriched in aluminum in one chondrule (group III). Diopside-bearing chondrules are described in detail below, depending on the mineral assemblages. Chondrules not containing diopside are also described briefly as group IV, for reference.

I. Chondrules including diopside rimming enstatite

I-1: Chondrules of this type are large and most common. Phenocrysts are enstatite, some of which are identified to be clinoenstatite, and mesostasis is glass or plagioclase+silica minerals. Some of the chondrules of this group include iron-metal and/or troilite. In one of the chondrules, an enstatite grain poikilitically includes forsterite. Some of the enstatite crystals have rims of diopside (Fig. 1) but some do not. Thickness of the rims differs from grain to grain. The composition changes abruptly at the boundary between the enstatite core and the diopside rim (Fig. 3a). The Fs component of the enstatite varies from $Fs_{0.5}$ to Fs_5 . The Cr_2O_3 content is 0.5–1.2 wt% in enstatite with more than 2 mol% of Fs. The Cr content decreases with decrease of the Fs component in enstatite with less than 2 mol% of Fs. The chemical compositions of diopside are in the range of Wo_{25} – Wo_{45} (Fig. 3a).

I-2: Five radial pyroxene chondrules are included in our thin section, where both clinoenstatite and orthoenstatite were found. Thin rims of pigeonite or augite on clinoenstatite were observed in one of the radial pyroxene chondrules.

Fig. 1. Back-scattered electron image of a chondrule consists of enstatite phenocrysts (En) rimmed by diopside (Di). One enstatite grain includes forsterite (Fo). Mesostasis is glass.

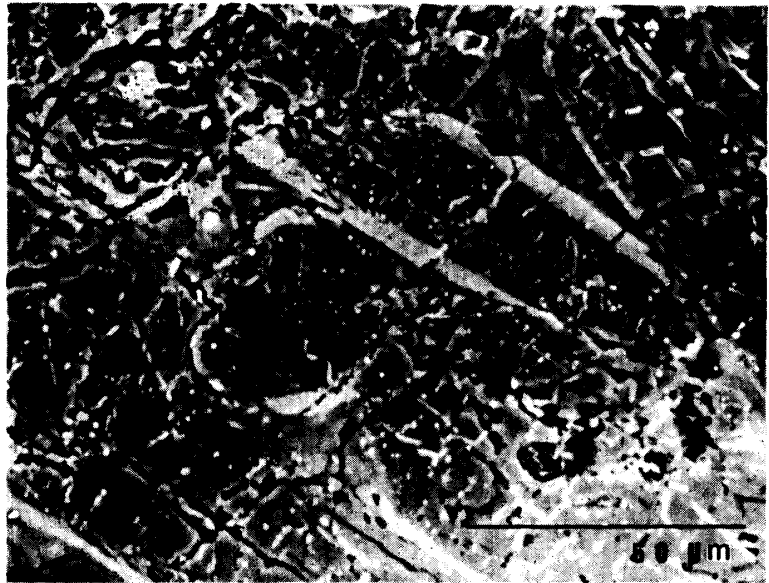
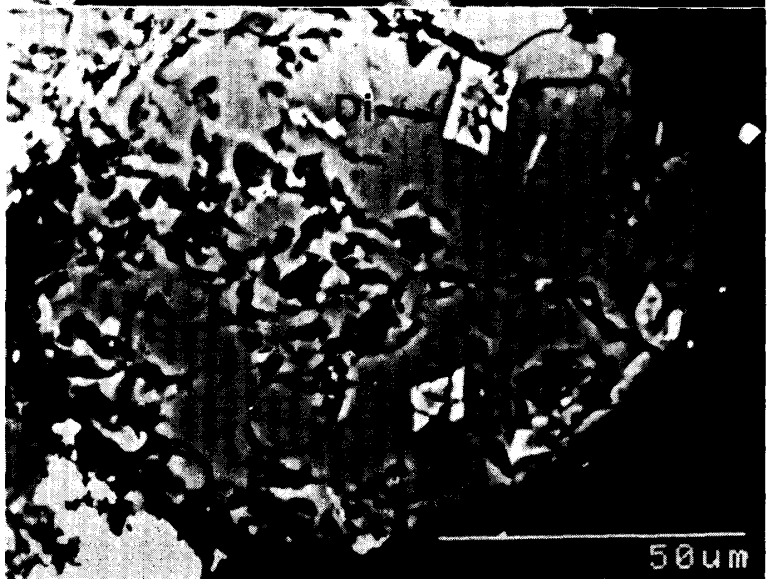


Fig. 2a. Euhedral enstatite (En) partly rimmed by diopside, single grains of diopside (Di), and metal grains are embedded in glass.



Fig. 2b. Small grains of pyroxene with compositional zoning from core of pigeonite to rim of diopside (Di) are in the predominant amount of glass. One grain of forsterite (Fo) also exists.



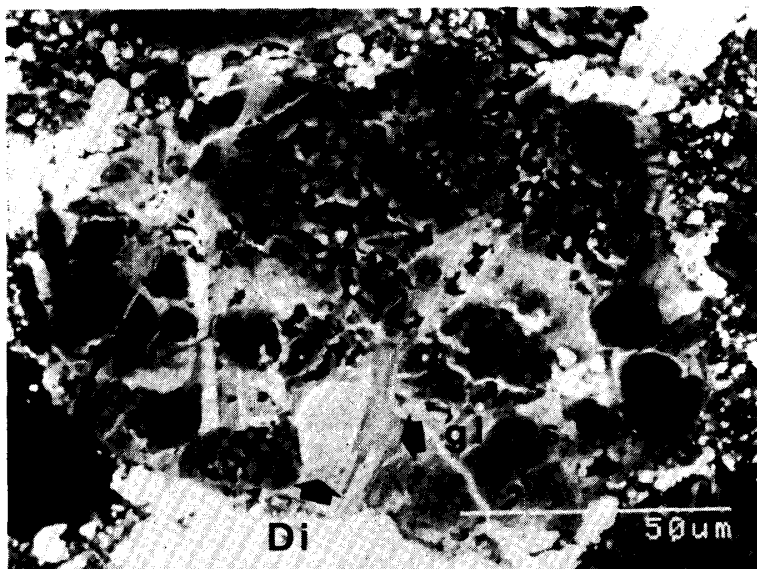


Fig. 2c. A chondrule consists of phenocrysts of forsterite (Fo), diopside (Di) and enstatite (En), and mesostasis of glass.

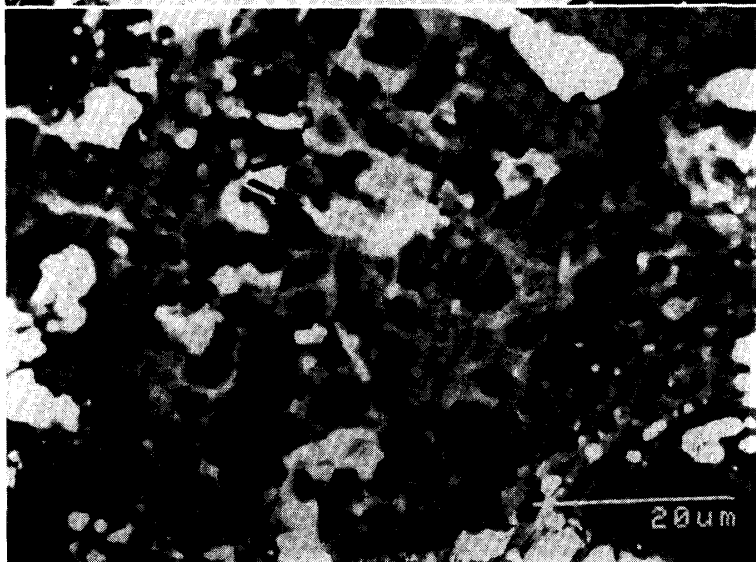


Fig. 2d. Phenocrysts are silica mineral (SM) and diopside (Di).

II. Chondrules including diopside as phenocrysts

II-1: In three chondrules, enstatite and diopside phenocrysts are found in a mesostasis of glass or plagioclase+silica minerals (Fig. 2a). All of them include troilite and two include iron-metal. The enstatite has thicker rims of diopside than type I-1. The crystals of diopside are in a skeletal shape, indicating a rapid growth.

II-2: A chondrule consists of small phenocrysts of one forsterite grain and a few clinopyroxene grains with a zonal structure from pigeonite to diopside. Both minerals are embedded in the predominant glass (Fig. 2b). Small iron-metal and troilite are in bright contrast in the figure. The crystals of diopside are in a skeletal shape, indicating a rapid growth.

II-3: Two chondrules include olivine, diopside and enstatite as phenocrysts. The mesostasis is glass (Fig. 2c). Olivine is predominant. Enstatite grains have no rims detectable by BSE. Both chondrules include troilite and one of them troilite.

II-4: In only one chondrule in the thin section, phenocrysts of SiO_2 minerals and

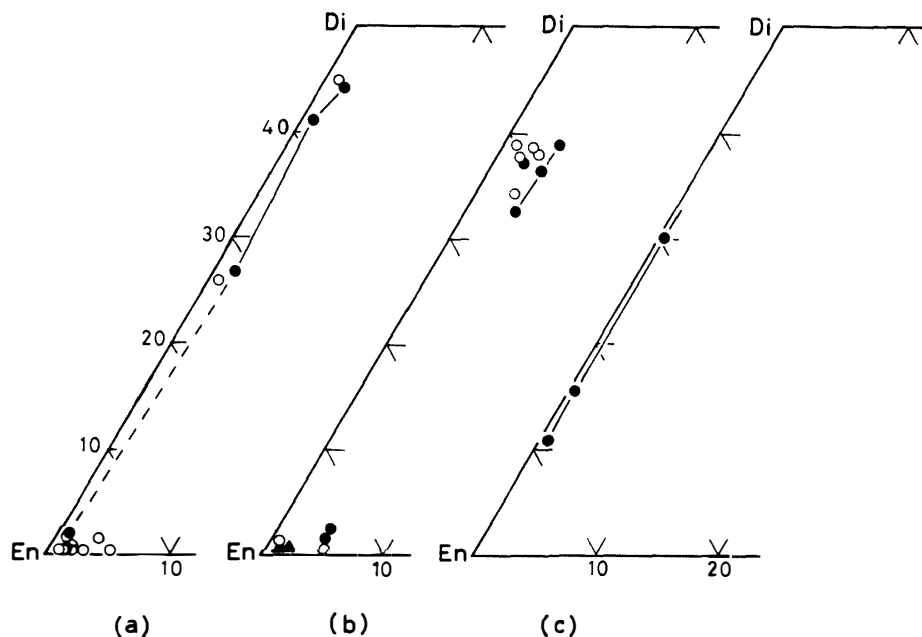


Fig. 3. Chemical compositions of enstatite and diopside plotted in the pyroxene quadrilateral. a: Plot of pyroxene composition of group I chondrules. Open circles are those from several chondrules. Compositions from a grain in Fig. 1 are indicated by solid circles. Broken and solid lines tying the solid circles represent the compositional gap between enstatite and diopside and the continuous zoning within rimming diopside, respectively. b: Plot for the enstatite and diopside phenocrysts. The composition of the rim in some enstatites is neglected in the plot. Open circles are from several chondrules. The pyroxene (enstatite and diopside), and forsterite in the typical chondrule of Fig. 2c are represented by solid circles and solid triangles, respectively. A solid tie line shows the compositional change within a diopside grain. c: Plot for the clinopyroxene grain indicated as Di in Fig. 2b. A solid tie line represents the continuous change in composition from pigeonite to diopside.

diopside in glass mesostasis were encountered (Fig. 2d). Troilite is also observed.

Chemical composition of enstatite and diopside phenocrysts of this group is given in Figs. 3b and 3c.

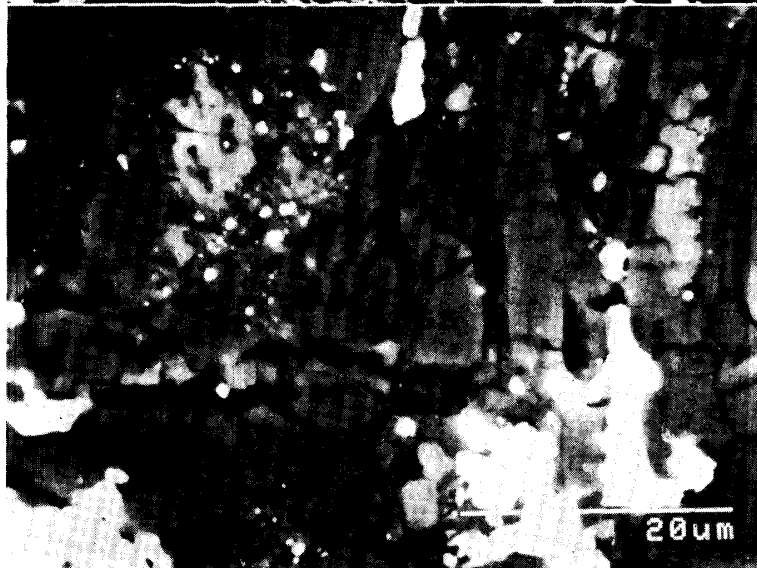
III. Chondrules including diopside enriched in Al

A chondrule ($150 \times 200 \mu\text{m}$ in size) consisting of several curved rods of pyroxene crystals with interstitial iron-metal, troilite, silica mineral and glass (or albite) (Figs. 4a and 4b) was found. Each of pyroxene rods elongated along the *c*-axis shows chemical heterogeneity, and five pyroxenes (three Ca-poor pyroxenes; px 1–3, and two diopside; px 4–5) with distinct but various Al_2O_3 and FeO content were observed. The Ca-Mg-Fe ratios of px 1–5 are plotted in Fig. 5. The Al_2O_3 contents in Ca-poor pyroxenes decrease from px 1 ($\sim 5 \text{ wt}\%$ of Al_2O_3) through px 2 ($\sim 1 \text{ wt}\%$) to px 3 ($\sim 0 \text{ wt}\%$) as the FeO contents decrease. On the other hand, while the Al_2O_3 contents change between px 4 (13–16 wt%) and px 5 (6–7 wt%) and increase with increasing Ca/(Mg+Fe+Ca) ratios in each diopside, the ratios of Fe/(Mg+Fe+Ca) is almost the same and constant in two diopsides.

Occurrence of these five pyroxenes is complex but shows the following general



Fig. 4. A chondrule consists of three Ca-poor pyroxenes different in chemical composition (1-3) and two kinds of diopside (4, 5).
a: Overview of the chondrule.



b: Enlarged photograph of a. Silica mineral (SM) and glass are observed among the pyroxenes.

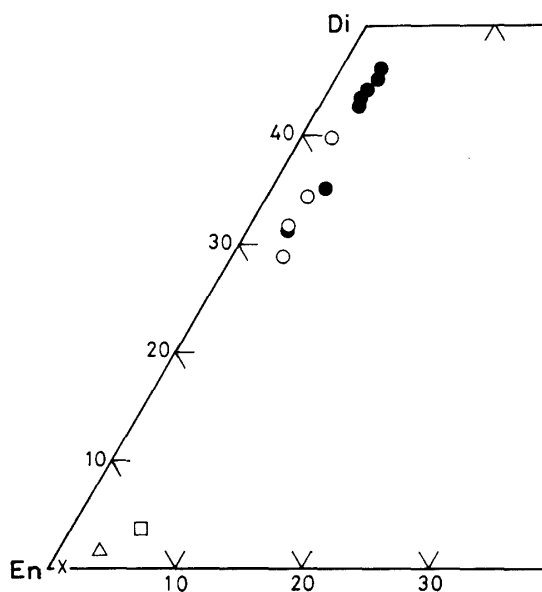


Fig. 5. Plot of chemical composition of pyroxenes in the group III chondrule in Fig. 4. Open square, open triangle and cross represent px1, px2 and px3, respectively. Several analyses in px1, px2 and px3 are represented by one point for each, because of constancy in an analytical error. Solid and open circles represent px4 and px5, respectively. See text for details.

tendency. px 1 (several μm in width and a few tens μm in length) generally appears in the central portion of each rod and is surrounded by px 2 and/or px 3. px 2 (2–10 μm in width and several tens μm in length) is in contact with all the other pyroxenes. px 3, dark in Fig. 4b, ($\sim 10 \mu\text{m}$ in width and several tens μm in length) is parallelly intergrown with px 2. px 4 ($\sim 10 \mu\text{m}$ in diameter) occurs as rather clear crystals with smooth outlines in the interstices among px 2 and px 3. px 5 (several μm in diameter) in an irregular shape also occurs in the interstices, but commonly coexists with iron metal and/or iron sulfide.

IV. Chondrules not including diopside

IV-1: A chondrule was found to consist of phenocrysts of enstatite with inclusions of iron-metal and troilite, and silica minerals with dendritic texture. The mesostasis consists of orthopyroxene and glass. IV-2: A fragment of chondrule includes a silica mineral as phenocryst and the mesostasis consists of enstatite, silica mineral and plagioclase or glass. IV-3: One small chondrule was found to consist entirely of a silica mineral. IV-4: Spherical chondrules with chemical composition nearly of mixtures of forsterite and enstatite. One of them shows fine grains of olivine, pyroxene and iron-metal. The other shows no definitive grains, but a slight variation of the SiO_2 content.

4. Discussion

4.1. Origin of diopside in chondrules

Single crystals of diopside were first found as phenocrysts in some chondrules of Y-691 (Figs. 2a, 2b, 2c and 2d). Since existence of single crystals of diopside was reported for the Qingzhen (E3) chondrite (GROSSMAN *et al.*, 1985), this finding indicates the common existence of diopside single crystals in the E3 chondrites. No single crystals of diopside have, however, been reported in the equilibrated E chondrites, and this has not been fully understood in spite of an explanation by a reaction of diopside with sulfur to form oldhamite (RUBIN, 1984). In the ordinary chondrites, single crystals of diopside in chondrules are common in the EOC's but rare in the UOC's (e.g. VAN SCHMUS and WOOD, 1967; MASON, 1968).

Diopside crystals also occur as the rims of some enstatite grains. Most of the compositional zoning have a discrete change from enstatite to diopside. This zoning is different from that in the UOC's where the continuous zoning from enstatite through pigeonite to augite is common. On the other hand, the zoning in Y-691 resembles that in the EOC's, which display the diopside rims.

Occurrence of the diopside single crystals and the rim diopside in Y-691 resembles that in the EOC's but not in the UOC's. However, the cooling rate of the E3 chondrules is considered to be not much different from that of the UOC's, because glass in mesostasis occurs in the chondrules of the both chondrites but not in the EOC's. Therefore, the bulk chemistry of the individual chondrules is the controlling factor for crystallization of diopside from the silicate melt and not the cooling rate.

The chondrules in Y-691 contain less Fe^{2+} than those in the UOC's (IKEDA, 1983), resulting in less ferrous composition of pyroxenes in Y-691 than in the UOC's. The

decrease of the Fe^{2+} content in Y-691 is expected to result in a higher $\text{Ca}/(\text{Mg}+\text{Fe}^{2+})$ ratio in comparison with the UOC's. However, the bulk chemistries of both chondrules (IKEDA, 1983) show no significant change of the ratio, which may be due to complex reactions of Mg, Fe and Ca with sulfur. Therefore, the $\text{Ca}/(\text{Mg}+\text{Fe}^{2+})$ ratio seems not to affect directly the appearance of diopside single crystals in the E3 chondrite.

According to the phase relations of the pyroxene quadrilateral, a decrease of the Fe^{2+} content constrains the stability field of pigeonite to higher temperatures. In fact, pigeonite overgrowth on enstatite is more common in the chondrules of the UOC's than in Y-691. In the crystallization process of pyroxenes, consumption of the Ca component takes place by appearance of pigeonite in the UOC's but not in Y-691. This is considered to be the reason why diopside appears in Y-691 instead of pigeonite.

The crystallization temperature of the pyroxenes cannot be obtained rigorously, because compositional trends of enstatite with the diopside rims (Fig. 3a) and of single crystals of diopside in glass (Fig. 3c) indicate the metastable crystallization. However, single crystals of diopside coexisting with enstatite, both of which are phenocrysts, show no large variation in composition (Fig. 3b). The crystallization temperature was roughly estimated to be 1300–1200°C, using the phase relations deduced from the work of LINDSLEY (1983). However, the influence of the kinetics of growth on the composition of the diopside phenocrysts is still unknown.

4.2. *Origin of diopside enriched in Al*

Since the group III chondrule contains too many silicate phases to be explained as resulted from a single stage, the mineral assemblage should have formed by multi-stages. Since the chemical composition of px 3 is in the compositional range of pyroxenes in the typical chondrules of group I, px 3 must have crystallized during the chondrule formation. Since the Ca-poor pyroxenes of px 2 and px 3 surround px 1, px 1 must have crystallized first. Therefore, the sequence of crystallization of Ca-poor pyroxenes is considered to be in the order of px 1, px 2 and px 3.

Since px 5 is commonly surrounded by fine crystals such as iron metal indicating the reduced condition, it must have been formed during the chondrule formation. Therefore, the formation stage of px 5 should be the same as that of px 3. On the other hand, px 4 not coexisting with the fine grains of iron metal should have been formed before the chondrules formation. px 4 must have been formed in a different stage from that of px 1, for the reason that no direct contact of px 4 with px 1 was observed and that the $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios of px 1 and px 4 differ considerably from those expected for the coexisting phases. On the other hand, the texture and the compositions of px 2 and px 4 are not contradictory with coexistence of both phases. Therefore, the crystallization sequence can be simply assumed to be of three stages in the order of px 1, px 2+px 4, and px 3+px 5. A silica mineral which appeared in contact with px 2, not with px 3, suggests its formation in the second stage.

In the initial stage, a mineral with CaO , Na_2O , Al_2O_3 and SiO_2 , such as plagioclase, should be assumed to have existed, because no pyroxenes other than px 1 and no minerals in the interstices were formed. Then, px 1 and the mineral such as plagioclase in the first stage must have reacted to form the mineral assemblage of the second

stage. Since this reaction should result in one of the mineral assemblages observed in the chondrule, it must be the reaction to produce the CaTs's mole and a silica phase. Therefore, the most probable assemblage is that of px 2, a silica mineral and px 4, and this reaction can also well explain the texture. This reaction must occur at high pressure, because the incorporation of the CaTs's mole in the pyroxenes due to metastable crystallization would hardly occur in the silica-saturated system such as the present case with the silica phase coexisting in the chondrule. The CaTs's component in the system $\text{CaO-MgO-Al}_2\text{O}_3$ saturated with silica can be used to estimate the pressure (GASPARIK and LINDSLEY, 1980). The estimated pressure is about 20 kb, neglecting the effect of the En and Fs components. The temperature effect on the estimation is also neglected, because the solubility of the CaTs component around 20 kb does not strongly depend upon temperature. Since the survival of px 1 during the formation of px 2 and px 4 indicates the reaction in a short time, a shock event seems to be the best explanation.

In the third stage, the cluster must have been heated again in the formation of chondrules, resulting in crystallization of px 3 and formation of px 5. Because px 5 is commonly in irregular shapes surrounded by fine crystals, it is considered to be produced from px 4 by its break-down reaction with melt, reserving a possible interpretation by crystallization.

5. Concluding Remarks

(1) Most of the chondrules in Y-691 (EH3) include enstatite single crystals, some of which are rimmed by diopside.

(2) Single crystals of diopside appear in Y-691 as phenocrysts in some chondrules, in contrast with the equilibrated E chondrites and unequilibrated ordinary chondrites. Appearance of them is also considered to be related with the reducing condition. Crystallization temperature of the diopside crystals is roughly estimated to be 1300–1200°C.

(3) Two types of single crystals of diopside different in Al content were observed in a chondrule. The Al content of the pyroxenes implies high pressure episodes by shock process.

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