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Fe-Mg HETEROGENEITY IN THE LOW-Ca PYROXENES DURING METAMORPHISM OF THE ORDINARY CHONDRITES

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Abstract: Pyroxenes in nine ordinary chondrites, ALH-764 (LL3), ALH-77214 (L3.4), ALH-77015 (L3.5), Yamato-74191 (L3.6), Hedjaz (L3.7), ALH-77304 (LL 3.8), ALH-78084 (H3.9), Yamato-75097 (L4) and ALH-77230 (L4), were examined by an optical microscope, a scanning electron microscope with a back-scattered electron image technique, and an X-ray microprobe analyzer. Characteristic textures due to alternating lamellae of Fe-rich and Fe-poor compositions have been found in the low-Ca pyroxenes in the chondrites irrespective of their chemical groups, H, L and LL. As far as the author knows, this is the first observation of such lamellae textures in the pyroxenes. These textures are common and remarkable in the higher subtypes of type 3 chondrites (L3.6, L3.7, LL3.8 and H3.9), while they are rare in lower subtypes (<3.5) and type 4 chondrites. These textures are considered to have been formed in the Fe-Mg homogenization process of the ordinary chondrites during metamorphism.

1. Introduction

Variation in the Fe-Mg ratios of olivines and pyroxenes decreases in the ordinary chondrites with increase of their petrologic types. To examine the petrologic types of the ordinary chondrites, VAN SCHMUS and WOOD (1967) used the percent mean deviation of olivine and pyroxene composition and the texture of matrix. DODD *et al.* (1967) reported for the ordinary chondrites that compositional variations in olivine and low-Ca pyroxenes decrease with increasing degree of recrystallization and that homogenization proceeded in pyroxene more slowly than in olivine. To explain the origin of the petrologic variety of the ordinary chondrites, two models of metamorphism have been proposed. One is progressive metamorphism during which the temperature of chondrite rose to the values corresponding to their petrologic types (*e.g.* DODD, 1969). The other model is autometamorphism during which the temperature decreased monotonically and the petrologic type represents the cooling history of the chondrites (*e.g.* HEYSE, 1978; ASHWORTH, 1980; WATANABE *et al.*, 1985).

In order to elucidate the homogenization process in olivine and pyroxene, nine ordinary chondrites, of different chemical groups, of type 3 and type 4 have been examined. Special attention has been paid to pyroxene because the diffusivities of elements are slower in pyroxene than in olivine (*e.g.* TSUCHIYAMA, 1985). The back-scattered electron image (BEI) technique was used with an electron probe microanalyzer (EPMA) to investigate the compositional heterogeneities, such as Fe-Mg heterogeneity in pyroxene.

2. Experimental

The following nine unequilibrated ordinary chondrites were used in this study: ALH-764 (LL3), ALH-77214 (L3.4) (SEARS *et al.*, 1982), ALH-77015 (L3.5) (SEARS *et al.*, 1982), Yamato-74191 (L3.6) (SEARS *et al.*, 1982), Hedjaz (L3.7) (SEARS *et al.*, 1980), ALH-77304 (LL3.8) (SEARS and WEEKS, 1983), ALH-78084 (H3.9) (SEARS *et al.*, 1982), Yamato-75097 (L4) and ALH-77230 (L4). Twelve polished thin sections were prepared from them.

These samples were examined by an optical microscope, and a HITACHI-S530 scanning electron microscope (SEM) with back-scattered electron image (BEI) technique. The chemical composition of minerals was determined by the EPMA with a HORIBA EMAX-2200 EDX system with a focused beam. The acceleration voltage was 20 kV and the beam current 1.5 nA. X-ray intensities were corrected by the ZAF method.

3. Results

3.1. Fe-Mg heterogeneity in low-Ca pyroxenes and their variation with petrologic types

In the lower subtype 3 chondrites (ALH-764 (LL3), ALH-77214 (L3.4), ALH-77015 (L3.5)), pyroxene crystals usually show the normal Fe-Mg zoning (Fe becomes richer towards the rim) and a characteristic heterogeneity described below is absent or faint (Figs. 1a, 1b, 1c and 1d). With increasing subtypes of the chondrites, the heterogeneity in pyroxenes becomes distinctive as in Y-74191 (L3.6), Hedjaz (L3.7), ALH-77304 (LL3.8) and ALH-78084 (H3.9) (Figs. 1e, 1f, 1g and 1h). The heterogeneity becomes faint again in ALH-77230 (L4) (Fig. 1i), and finally disappears in a typical type 4 chondrite such as Y-75097 (L4) (Fig. 1j). Olivine crystals in the chondrules, fragments and matrices in the lower subtype 3 chondrites have different Fe-Mg compositions with the normal Fe-Mg zoning (Fig. 1a). Olivine grains become homogeneous and have the almost same composition in the chondrites where the heterogeneity in pyroxene is distinctive.

Characteristic textures of the Fe-Mg heterogeneity were observed in clinoenstatite and orthoenstatite. The typical textures are shown in Figs. 1e, 1f, 1g and 1h. Details of the textures are as follows:

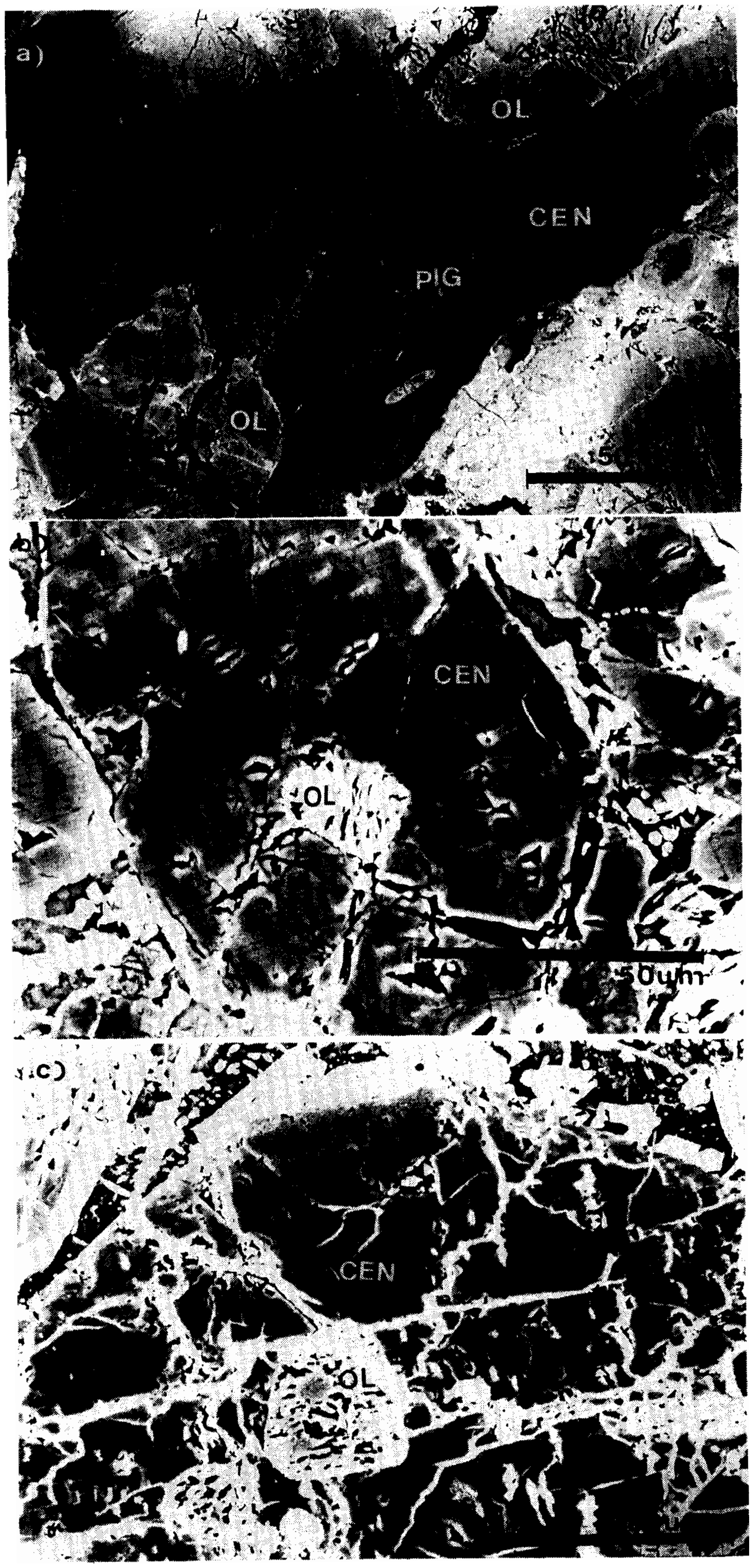
(1) The Mg-rich parts in pyroxenes are always surrounded by the Fe-rich parts except for one Fe-rich pyroxene grain (ALH-77230, L4). Some of the pyroxenes have rims of the Ca-rich pyroxenes, pigeonite and/or augite.

(2) The Fe/Mg ratios of the Fe-richest parts are constant among different pyroxene crystals in each chondrite even if the size, the compositions of the Mg-richest parts, and the occurrence of the pyroxenes are different.

(3) The compositional change in clinoenstatite at the boundaries between the Mg-rich and Fe-rich parts is gradual in the direction parallel to the *c* axis while it is abrupt in the direction normal to the *c* axis (Fig. 1f). The scale of the heterogeneity normal to the *c* axis is about a few to 10 μm. In orthopyroxenes, the boundaries between the Mg-rich and Fe-rich parts are irregular (Fig. 1g).

(4) Small chromite inclusions are present only in the Fe-rich parts.

The textures described above are observed in all the pyroxenes in chondrules and fragments throughout the chondrite specimens as long as the heterogeneity is distinctive.

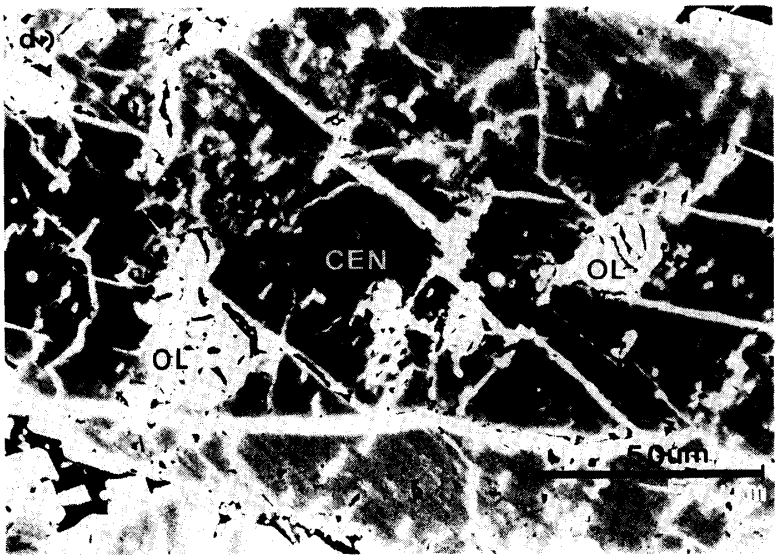


a. Clinoenstatite in a chondrule of ALH-764 showing normal zoning.

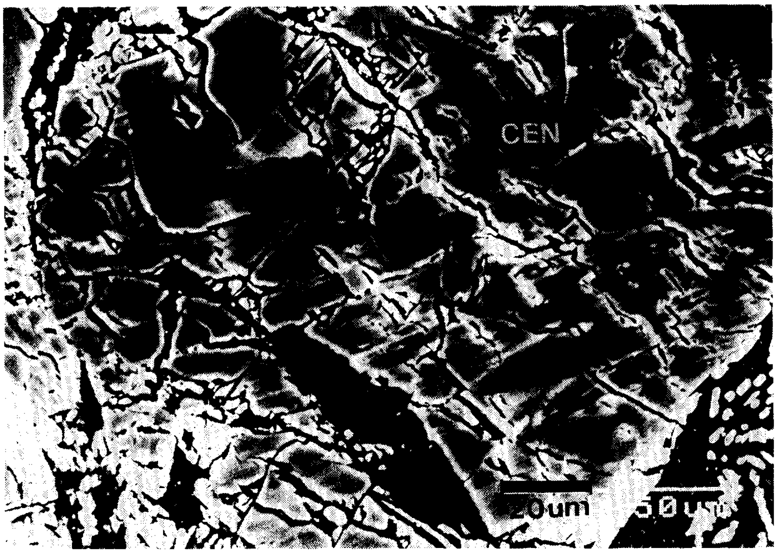
b. Clinoenstatite in a chondrule of ALH-764 showing weak Fe-Mg heterogeneity. Lines crossing the crystal from the upper right to the lower left are scratches of the section.

c. Clinoenstatite in a chondrule of ALH-77214 showing weak Fe-Mg heterogeneity.

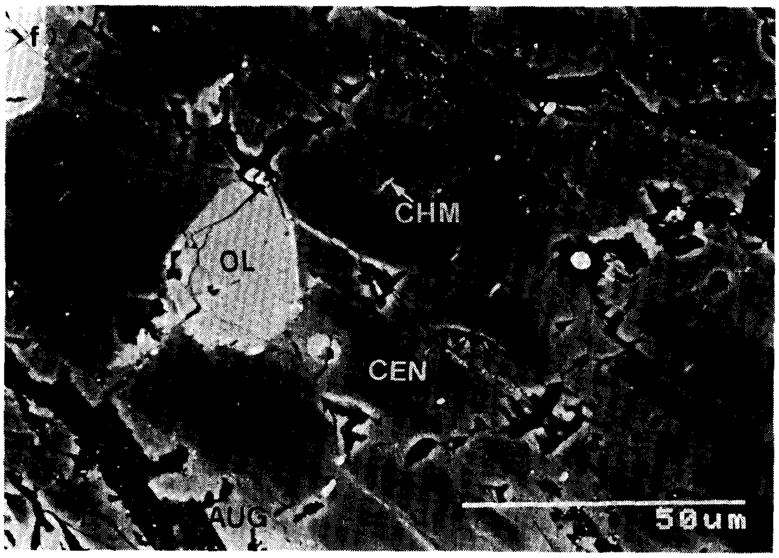
Fig. 1. Photomicrographs of the pyroxene textures under a SEM (BEI's) are arranged in the order of the petrologic types from type 3 to type 4. CEN=clinoenstatite. AUG=augite. PIG =pigeonite. OL=olivine. CHM=chromite. TR=troilite.



d. Clinoenstatite in a chondrule of ALH-77015 showing weak Fe-Mg heterogeneity.



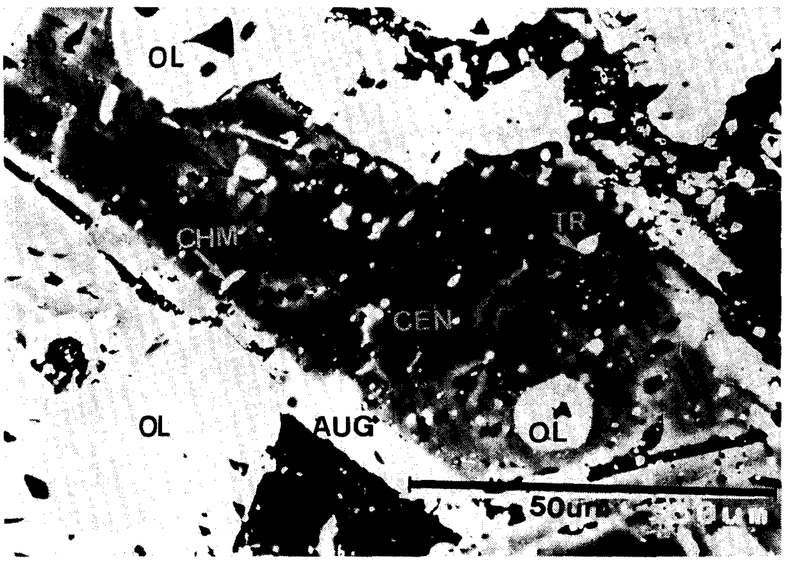
e. Clinoenstatite in a chondrule of Y-74191 showing strong Fe-Mg heterogeneity. Bright parts are Fe-rich and dark parts Mg-rich.



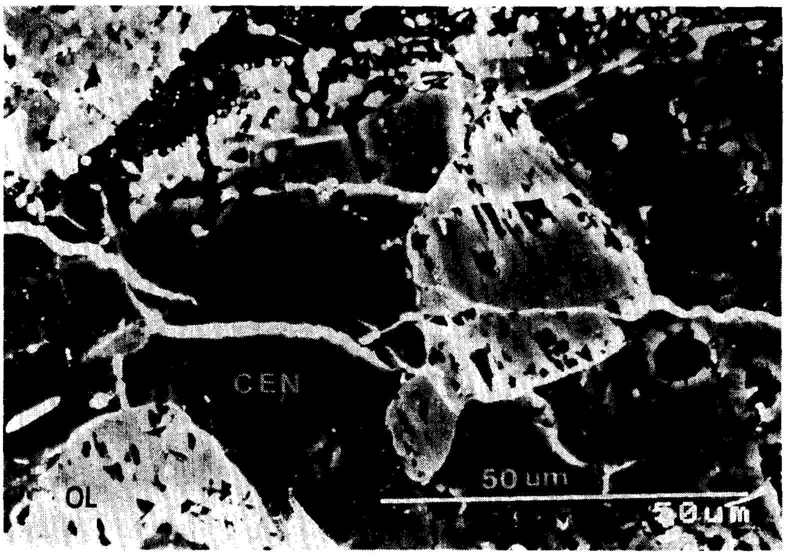
f. Clinoenstatite in a chondrule of ALH-77304 showing strong Fe-Mg heterogeneity.

Fig. 1 (continued).

g. Orthopyroxene in a chondrule of ALH-77304 showing Fe-Mg heterogeneity.



h. Clinoenstatite in a chondrule of ALH-78084 showing strong Fe-Mg heterogeneity.



i. Clinoenstatite in a chondrule of ALH-77230 showing weak Fe-Mg heterogeneity.

Fig. 1 (continued).

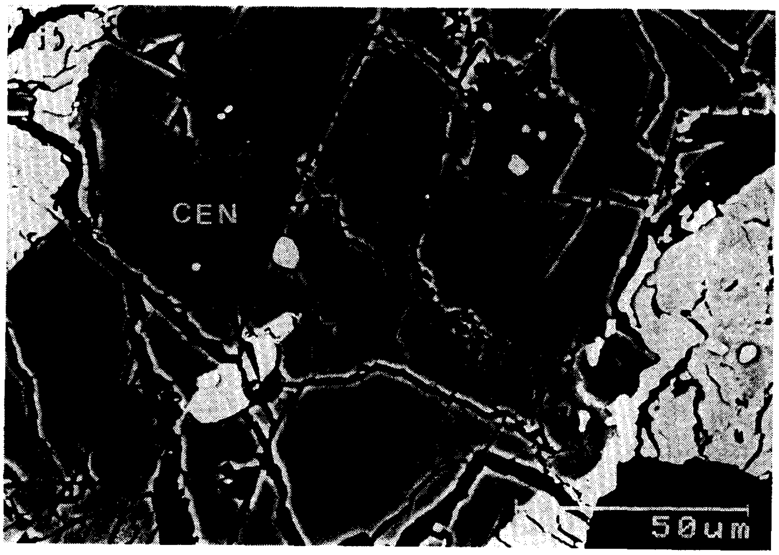


Fig. 1 (continued).

j. Homogeneous clinoenstatite in a chondrule of Y-75097.

As far as the authors know, such textures were observed for the first time in the present paper.

It is known from transmission electron microscopic observations that so-called clinoenstatites with polysynthetic twins found in higher subtype 3 condrite are orthorhombic crystals with residual monoclinic lamellae (ASHWORTH *et al.*, 1984). In the present paper, detailed structures of the pyroxenes were not determined, and the enstatite in which polysynthetic twins are observed under an optical microscope is called "clinoenstatite" for the convenience although some of them might be orthorhombic.

3.2. Descriptions of individual chondrites

(1) ALH-764 (LL3)

Matrices of this chondrite are opaque and fine-grained (Fig. 2a), and olivines in the matrices are Fe-rich. Olivine crystals in chondrules and fragments have the normal Fe-Mg zoning and different compositions in different grains. The characteristics are of the typical type 3 chondrite. In this specimen some of the low-Ca pyroxenes have a texture due to weak Fe-Mg heterogeneity (Figs. 1b and 3b), while many pyroxenes have the normal Fe-Mg zoning (Figs. 1a and 3a).

(2) ALH-77214 (L3.4) and -77015 (L3.5)

The characteristic textures of the Fe-Mg heterogeneity of the low-Ca pyroxenes were observed in these chondrites although the heterogeneity is weak (Figs. 1c and 1d). Matrices of the two chondrites are also opaque and fine. Olivine crystals have the normal Fe-Mg zoning and different compositions in different grains.

(3) Y-74191 (L3.6) and Hedjaz (L3.7)

Strong Fe-Mg heterogeneity in pyroxenes was observed in Y-74191 (Fig. 1e) and Hedjaz as in ALH-77304 and -78084. Similar textures were also reported by NOGUCHI (1987) in Hedjaz.

(4) ALH-77304 (LL3.8)

This chondrite has partly transparent matrices (Fig. 2b) composed mostly of olivine. The matrix shows that this chondrite is rather metamorphosed in comparison

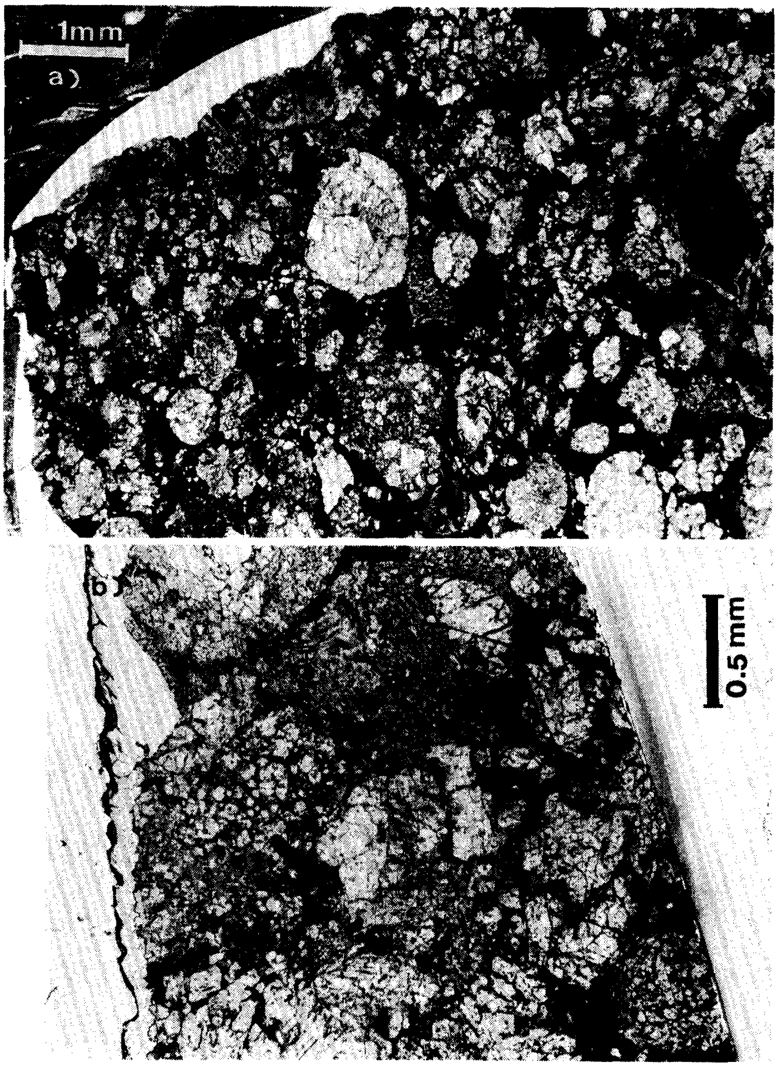


Fig. 2. Photomicrographs of chondrites under an optical microscope (plain polarized light). (a) ALH-764, opaque parts are metals, troilites and fine matrix. (b) ALH-77304 showing partly transparent matrix. Opaque parts are metals and troilites.

with the lower subtype 3 chondrites such as ALH-764. The Fe-Mg heterogeneity is distinctive in pyroxene (Figs. 1f, 1g and 3c). Olivines in the chondrules, fragments and matrices are homogeneous (Fig. 4a) and have the Fe/Mg ratio ($\sim Fo_{75}Fa_{25}$) slightly higher than that of the Fe-rich pyroxenes ($\sim En_{80}Fs_{20}$).

(5) ALH-78084 (H3.9)

Matrices are partly transparent and olivines are homogeneous. Characteristics of pyroxenes (Fig. 1h) are quite similar to those of ALH-77304, except for the chemical compositions (Figs. 3d and 4b).

(6) ALH-77230 (L4)

Not only olivines but also pyroxenes are almost homogeneous (Figs. 1i, 3e and 4c). Only weak heterogeneity was detected in some of the low-Ca pyroxenes. Matrices are transparent. One Fe-rich pyroxene grain was observed in a chondrule of this specimen (Fig. 3e).

(7) Y-75097 (L4)

Pyroxene crystals are homogeneous (Fig. 1j) and matrices are transparent. Any characteristic textures described above were not observed.

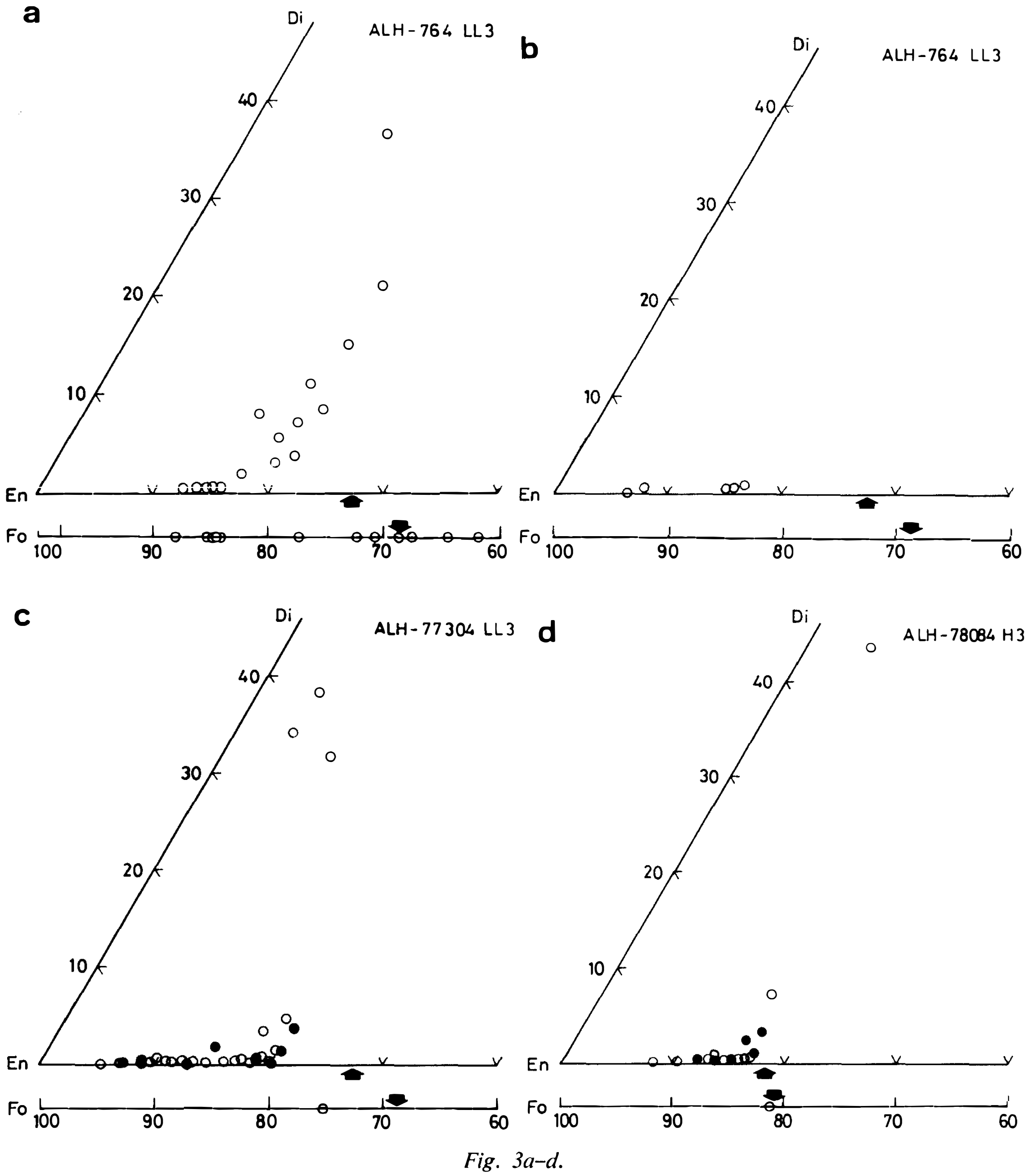


Fig. 3a–d.

4. Discussions

4.1. Possible periods for the formation of the Mg-Fe heterogeneity in pyroxenes

Two different periods can be assumed for the formation of the characteristic heterogeneous texture of pyroxene crystals. They are (1) before chondrite accretion, and (2) during or after accretion but before falling to the earth.

The heterogeneity texture in pyroxenes is common in the whole rocks, fragments and chondrules. If the texture was formed before the accretion, various degrees of heterogeneity should be observed in one chondrite, which is not the case. Thus, the assumption (1) should be excluded and the Fe-Mg heterogeneity in pyroxenes is con-

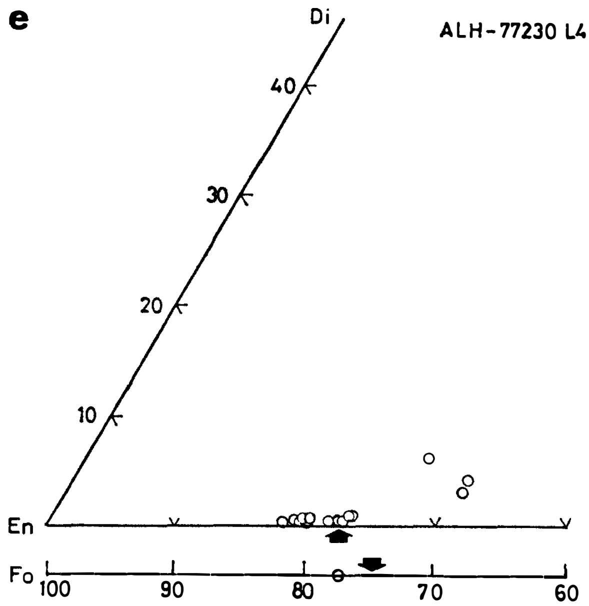


Fig. 3e.

Fig. 3. Chemical composition of pyroxene and olivine in chondrites. (a) ALH-764 (LL3), clinoenstatite in a chondrule showing the normal zoning. (b) ALH-764, clinoenstatites showing the Fe-Mg heterogeneity. (c) ALH-77304 (LL3.8). (d) ALH-78084 (H3.9). (e) ALH-77230 (L4). Allows show Fe/Mg ratios of pyroxene and olivine in the equilibrated chondrites (VAN SCHMUS, 1969). Open and solid circles show clinoenstatite and orthoenstatite, respectively.

sidered to have been produced during or after the accretion of chondrites.

4.2. Fe-Mg variation processes of pyroxenes

The normal Fe-Mg zoning of pyroxenes in lower subtype 3 chondrites is a primary texture which was formed during the cooling of chondrules before, or during, accretion. Twinned clinoenstatite was produced from protopyroxene, crystallized from liquids.

During the metamorphism of the chondrites, it is expected that the Fe-Mg homogenization must have taken place by the Fe-enrichment of the mafic minerals in the chondrules and fragments, and the Mg-enrichment of the matrices, since the matrices are generally richer in Fe than the chondrules and fragments in unequilibrated chondrites (HUSS *et al.*, 1981). Because the heterogeneous textures of pyroxenes are distinct only in the slightly metamorphosed type 3 chondrites, the texture is considered to represent an intermediate state in the metamorphic processes between the petrologic types 3 and 4 of the ordinary chondrites of all the chemical groups. Therefore, pyroxenes apparently become heterogeneous in Fe-Mg distribution within each grain during the homogenization of ordinary chondrites. The constant value of the Fe-richest composition of pyroxenes in each chondrite is considered to correspond to an equilibrium value. The Fe content of the Fe-rich pyroxene grain in ALH-77230 must originally have been larger than the equilibrium value.

It is uncertain which process was responsible for the formation of the alternating lamellae of Fe-rich and Mg-rich compositions in clinoenstatite. Fe-Mg diffusion through high diffusivity paths such as cleavages and the (100) polysynthetic twin boundaries in clinoenstatite crystals might cause the lamellar textures. However, it is difficult to explain sharp boundaries of the lamellae in this process. An alternative process for the lamellae formation is related to the phase transition from clinoenstatite to orthoenstatite; for example, the Fe-rich parts would be formed by the transition. A transmission electron microscopic study is required to determine the process.

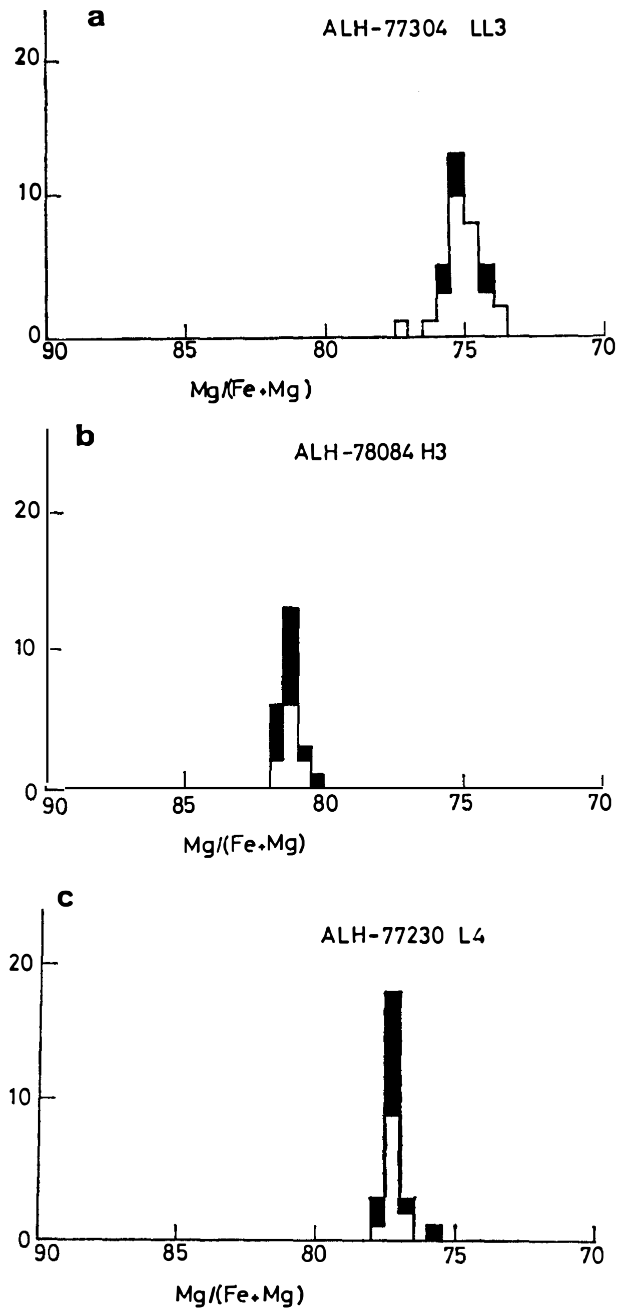


Fig. 4. Chemical composition of olivine in chondrites. (a) ALH-77304 (LL3.8). (b) ALH-78084 (H3.9). (c) ALH-77230 (L4). Open and solid squares show cores and rims of olivines, respectively.

4.3. Implication to metamorphism of chondrites

If the progressive metamorphism is accepted for the chondrites, the pyroxene texture described above should be interpreted as a transitional texture during the metamorphism from the petrologic type 3 to 4 with progressive heating. On the contrary, if the autometamorphism is accepted, the texture should be explained by the cooling histories of chondrites. In this case the texture might be formed only with an intermediate cooling history between the petrologic types 3 and 4. At present it is not possible to conclude which model is more appropriate from the information mentioned above.

5. Conclusion

(1) Characteristic textures of the Fe-Mg heterogeneity were observed in the low-Ca pyroxenes in type 3 and type 4 ordinary chondrites. The textures consists of alternating lamellae of Fe-rich and Mg-rich compositions in clinoenstatite. In orthopyroxene, irregular patches of Mg-rich composition are embedded in Fe-rich parts.

(2) The pyroxenes have maximum degree of the Fe-Mg heterogeneity in the stage of higher subtypes of the type 3 chondrites. These textures are formed in the process of Fe-Mg homogenization of ordinary chondrites during the metamorphism.

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References

ASHWORTH, J.R. (1980): Chondrite thermal histories; Clues from electron microscopy of orthopyroxene. Earth Planet. Sci. Lett., **46**, 167–177.

ASHWORTH, J.R., MALLISON, L.G., HUTCHISON, R. and BIGGAR, G.M. (1984): Chondrite thermal histories constrained by experimental annealing of Quenggouk orthopyroxene. Nature, **308**, 259–260.

DODD, R.T. (1969): Metamorphism of the ordinary chondrites; A review. Geochim. Cosmochim. Acta, **33**, 161–203.

DODD, R.T. (1981): Meteorites; A petrologic-chemical synthesis. Cambridge, Cambridge University Press, 368p.

DODD, R.T., JR., VAN SCHMUS, W.R. and KOFFMAN, D.M. (1967): A survey of unequilibrated ordinary chondrites. Geochim. Cosmochim. Acta, **31**, 921–951.

HEYSE, J.V. (1978): The metamorphic history of LL-group ordinary chondrites. Earth Planet. Sci. Lett., **40**, 365–381.

HUSS, G.R., KEIL, K. and TAYLOR, G.J. (1981): The matrices of unequilibrated chondrites; Implications for the origin and history of chondrites. Geochim. Cosmochim. Acta, **45**, 33–51.

NOGUCHI, T. (1987): Texture and chemical composition of pyroxenes in ordinary chondrites. Papers Presented to the Twelfth Symposium on Antarctic Meteorites, 8–10 June 1987. Tokyo, Natl Inst. Polar. Res., 48–50.

SEARS, D.W. and WEEKS, K.S. (1983): Chemical and physical studies of type 3 chondrites; 2. Thermoluminescence of sixteen type 3 ordinary chondrites and relationships with oxygen isotopes. Proc. Lunar Planet. Sci. Conf., 14th, Pt. 1, **88**, B301–B311 (J. Geophys. Res., **88** Suppl.).

SEARS, D.W., GROSSMAN, J.N., MELCHER, C.L., ROSS, L. M. and MILLS, A.A. (1980): Measuring metamorphic history of unequilibrated ordinary chondrites. Nature, **287**, 791–795.

SEARS, D.W., GROSSMAN, J.N. and MELCHER, C.L. (1982): Chemical and physical studies of type 3 chondrites-I; Metamorphism related studies of Antarctic and other type 3 ordinary chondrites. Geochim. Cosmochim. Acta, **46**, 2471–2481.

TSUCHIYAMA, A. (1985): Partial melting kinetics of plagioclase-diopside pairs. Contrb. Mineral. Petrol., **91**, 12–23.

VAN SCHMUS, W.R. (1969): The mineralogy and petrology of chondritic meteorites. Earth-Sci. Rev., **5**, 145–184.

VAN SCHMUS, W. R. and WOOD, J. A. (1976): A chemical-petrologic classification for the chondritic meteorites. Geochim. Cosmochim. Acta, **31**, 747–765.

WATANABE, S., KITAMURA, M. and MORIMOTO, N. (1985): A transmission electron microscope study of pyroxene chondrules in equilibrated L-group chondrites. Earth Planet. Sci. Lett., **72**, 87–98.

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