Antarct. Meteorites Res., **10**, 217–226, 1997

TEM OBSERVATION OF VOID-LIKE DEFECT STRUCTURES IN MATRIX- AND ISOLATED-OLIVINE GRAINS IN ALLENDE (CV3)

Hidenobu TANAKA[1] and Junji AKAI[2]

[1]*Department of Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-nocho, Niigata 950–21*
[2]*Department of Geological Science, Faculty of Science, Niigata University, 8050, Ikarashi 2-nocho, Niigata 950–21*

Abstract: Olivine grains in the Allende CV3 carbonaceous chondrite matrix were examined mainly by TEM. Compositional data of olivine by EPMA are also given. It was revealed that void-like defects were observed occurring in iron enriched portions of both matrix olivine and rims of isolated olivine grains. Detailed observations of these void-like defects suggest that the void structure was formed during thermal metamorphism and that the thermal metamorphism was also related to some chemical reaction to form fayalitic olivine either in the pre-solar nebula or on a parent body.

1. Introduction

The Allende meteorite is a well known CV3 chondrite. CV3 group was defined by VAN SCHMUS (1969) and plays an important role in meteorite studies. It has been regarded that constituent minerals preserve primitive features. The matrix minerals in CV3 chondrites are generally considered to be condensation products (KORNACKI and WOOD, 1984; MACPHERSON *et al.*, 1985). However, it is also suggested by HOUSLEY and CIRLIN (1983) that some matrix minerals are alteration products of enstatite in chondrules. Recent work by KROT *et al.* (1995) also strongly supports this suggestion.

Many chemical, mineralogical and isotopic studies on matrix, isolated minerals and chondrule mineral grains of Allende (CV3) meteorite have been reported (*e.g.* GROSSMAN, 1980; PECK, 1984; PECK and WOOD, 1987; RUBIN and WASSON, 1987; MACPHERSON *et al.*, 1988; KROT *et al.* 1995). Studies by GROSSMAN (1972) suggested that CAIs are the first condensates from the hot solar nebula. However, subsequent detailed mineralogical and isotopic studies have shown that applications of the equilibrium condensation model are limited. Most chondrite components might have experienced a complex formation history. Later, BUNCH and CHANG (1980), HOUSLEY and CIRLIN (1983) and ARMSTRONG *et al.* (1982) emphasized the significance of parent body processes in the formation of carbonaceous chondrites. However, it is suggested by various data, especially the complex isotopic data, that CAIs and chondrules might have experienced complex cycles of localized thermal history in the solar nebula (WOOD, 1988; WASSON, 1993). CAIs may be condensates according to HUTCHEON and JONES (1995) and SWINDLE *et al.* (1995). Thus, the origins of matrix material still remain obscure; a minor component of matrix may be presolar, and the remainder may be complex mixtures of materials from both nebular and asteroidal processes (HUSS and LEWIS, 1995; BREARLEY, 1995; KROT *et al.*, 1995).

Type 3 chondrites are believed to give important information about solar nebula processes, because type 3 chondrites have experienced least thermal metamorphism and aqueous alteration. MCSWEEN (1977) divided CV3 chondrites into two types: oxidized and reduced subgroups. They have different abundances of metallic Fe, Ni and magnetite. MCSWEEN described that Allende is a member of the oxidized type and has suffered weak metamorphism. In general, H_2O and phyllosilicates are rarely recovered from Allende. Therefore, secondary alteration in Allende may be restricted. It is generally believed that asteroidal alteration effects are very small (KROT *et al.*, 1995).

In general, Allende matrix is composed of isolated mineral grains (mineral fragments) and genuine matrix mineral grains. The isolated minerals are regarded as fragments of chondrules and inclusions. The size of the isolated minerals are usually several μm~100 μm. Large isolated minerals can be observed under the polarizing microscope. However, small isolated minerals which can not be observed by polarizing microscope are also expected to occur as matrix constituent minerals. Therefore, it is often difficult to distinguish isolated minerals from matrix minerals.

There has been little detailed mineralogical examination of Allende matrix minerals using TEM intimately associated with EPMA. If such detailed data on matrix minerals are obtained, they will give information about the formation processes and alteration processes of the Allende matrix. Therefore, the main objective of this paper is to report concisely the first finding of void-like defect structures in olivine grains in the matrix by TEM.

2. Experimental

A JEOL 733 microprobe was used for the study. Analyses were carried out at 15 kV and 4 or 8 nA for 20 s counting times. A JEM 200CX TEM, and Phillips CM200 operated at 200 kV were used. Both TEMs were equipped with energy dispersive X-ray detectors for qualitative chemical analyses. Specimens for TEM observations were separated from an epoxy-impregnated petrographic polished thin section by cutting the section. The TEM samples were prepared by ion-thinning. Finely, crushed samples of the Allende specimen were also used for TEM study.

3. Specimens

We used several pieces of Allende meteorite which is a peculiar meteorite in CV3 chondrite. PECK (1983) and MACPHERSON *et al.* (1985) have described matrix minerals in Allende. The following minerals were found in the Allende matrix also in this study: olivine ($Fo_{45\text{-}60}$), high-Ca pyroxene, sodalite, nepheline, Fe-Ni sulfides, magnetite, Ca phosphate, awaruite, chromite, spinel, plagioclase, and andradite. Olivine is the most dominant among the matrix minerals in Allende. Matrix olivine is divided into two types based on their morphology and size: euhedral olivine grains which are prismatic (length about ten μm, width 2~3 μm) (Fig. 1) and irregular olivine grains having chemical zoning (various in size, about 1~100 μm) (Fig. 2). The olivine of the

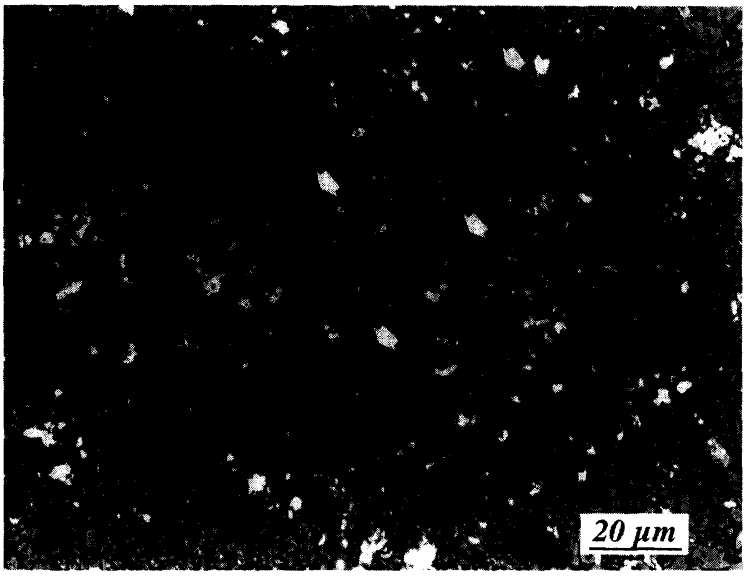


Fig. 1. BSE image of the matrix in Allende. Matrix olivine grains are light-gray and rectangular. Dark-gray grains of irregular shapes (arrows) are pyroxene. White grains are opaque minerals.

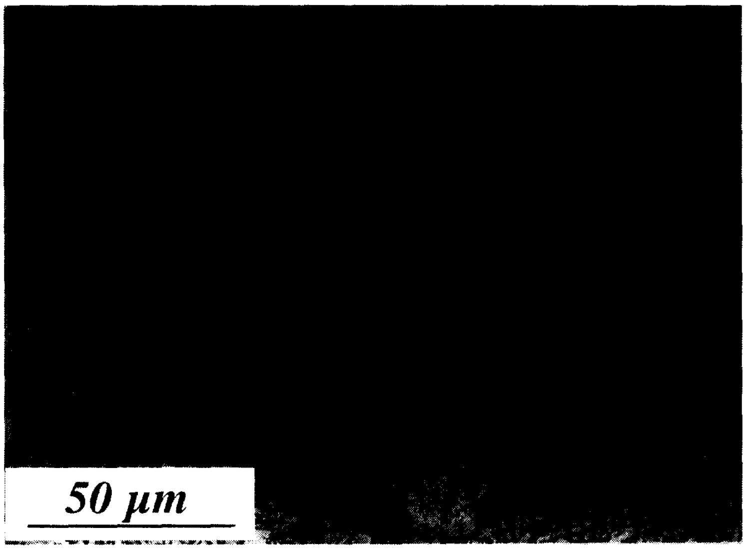


Fig. 2. BSE image of an isolated olivine grain. The shape of olivine grain is spherical.

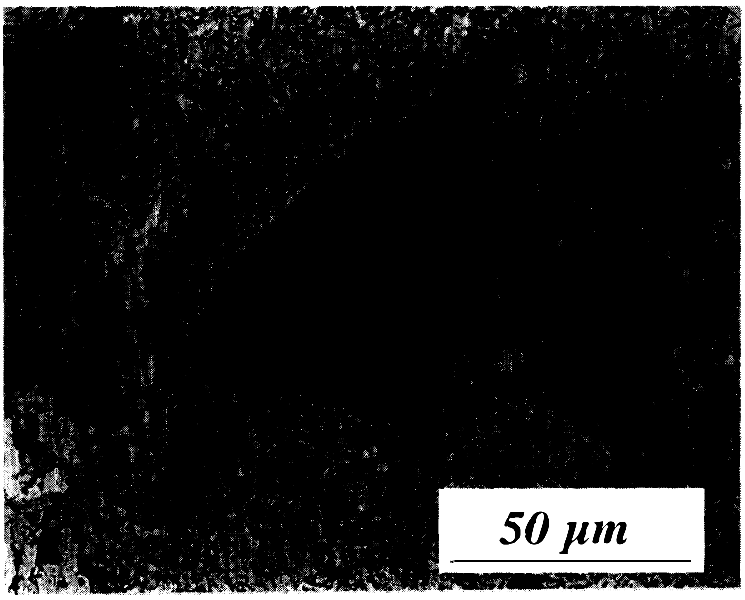


Fig. 3. BSE image of an isolated olivine grain. The shape of olivine grain is fragmental.

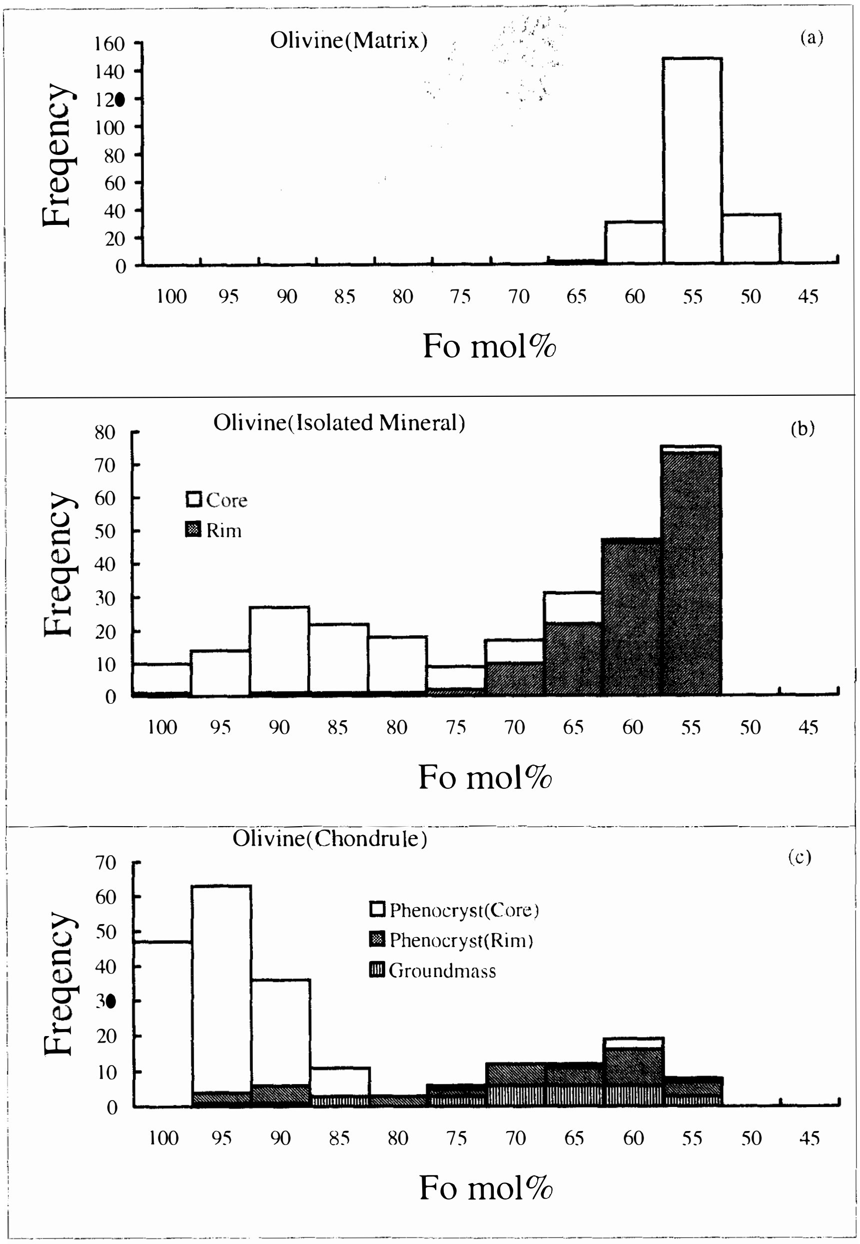


Fig. 4. Histograms of forsterite (Fo) content in olivine grains in a) matrix, b) isolated minerals and c) chondrules.

former type is homogeneous and fayalitic (Fo$_{60-50}$). Olivine in the latter type has forsterite-rich core (Fo$_{100-70}$) and fayalite-rich (Fo$_{70-50}$) rim (Figs. 3 and 4). Olivine of this type grains are called isolated minerals here. These may have been derived from phenocryst grains in chondrules, because large fragments of chondrule which include olivine grains that are similar in composition to those of the latter type are present in the matrix.

4. Results and Discussion

In the TEM observation of the matrix, two types of olivine grains were observed. The first type is smaller and generally have euhedral grains. These olivine grains have a width of a few μm and length of about ten μm (Fig. 5). The second population is larger olivine crystals whose size is more than a few ten μm (Fig. 6). The shapes and sizes of these olivine grains suggest that the former is genuine matrix olivine grains and the latter is isolated mineral grains. Both types of olivine grains are found also in BSE photomicrographs (Figs. 2 and 3). The results of qualitative analyses of both types by AEM were almost consistent with the EPMA results. In the detailed TEM observations, we discovered irregular-shaped void structures in the matrix olivine and the rim of the isolated minerals (Figs. 5 and 6). The sizes of the voids were less than about hundred nm. The shapes were bubble-like or polygon (square or hexagon). It is evident that void structures are found only in iron rich parts of olivine grains. The chemical composition of matrix olivine is homogeneous. Voids are sometimes heterogeneously distributed.

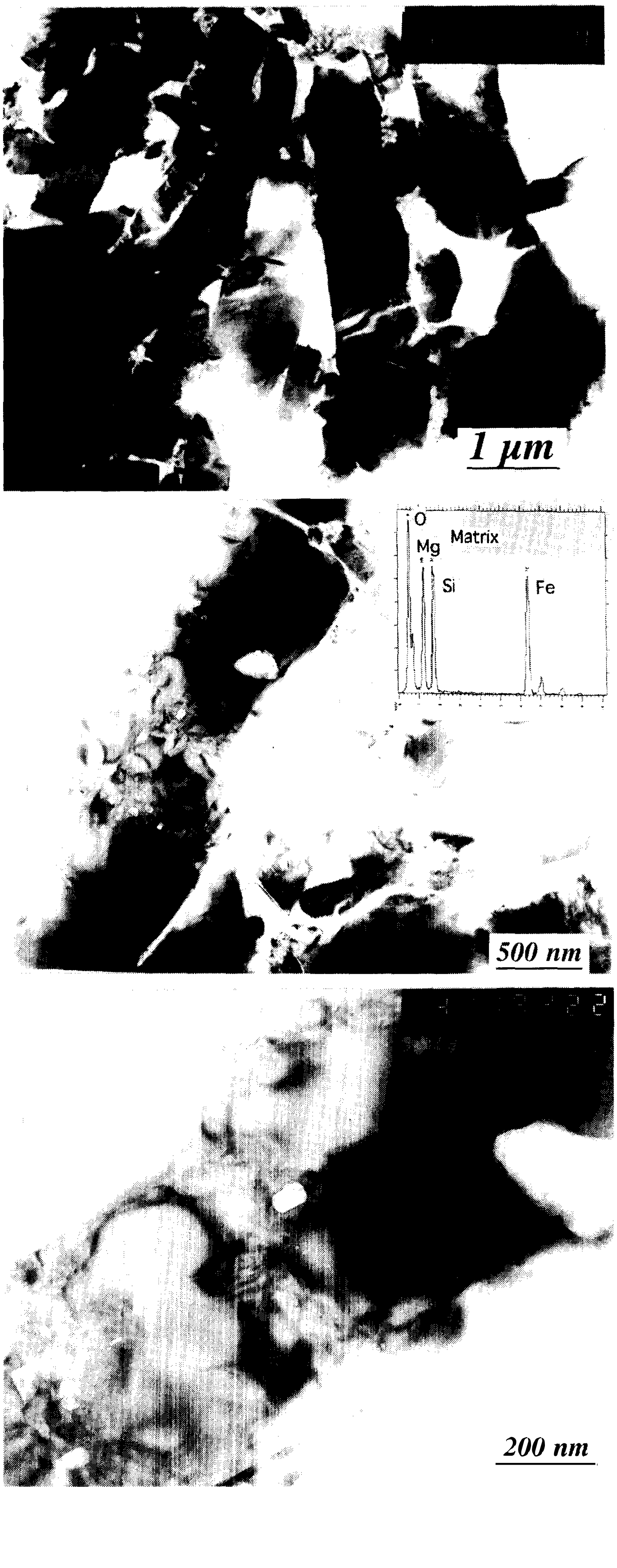
There are many ways to interpret formation processes of fayalitic olivine in both chondrules and matrix in CV3. In one interpretation, it is estimated that the formation process occurred in the primitive solar nebula. It is suggested by PECK and WOOD (1987) that forsterite was exposed to the nebula with vapors to form Cr-, Al-, Ti-enrichments and then condensation of fayalitic olivine occurred. Furthermore, they proposed that matrix olivine had been formed in the oxidized nebular gas. WEINBRUCH *et al.* (1993) suggested that fayalitic rims are condensates from ^{16}O-poor gas, while matrix olivine grains form either by condensation or were originally ^{16}O-rich and equilibrated later with an ^{16}O-depleted nebula.

In the other interpretation, it is estimated that olivine grains were altered in the nebula or an asteroid. HOUSLEY and CIRNIN (1983) suggested that low-Ca pyroxene in Allende altered to fayalitic olivine in the asteroid. The suggested reaction is as follows:

$$\mathrm{Fe(s)+0.5O_2(g)+\underset{enstatite}{MgSiO_3(s)}=\underset{olivine}{(Fe,Mg)_2SiO_4(s)}}. \quad (1)$$

However, IKEDA and KIMURA (1995) argued that the reaction occurred in the nebula. According to them, 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. PALME and FEGLEY (1990) also supports nebular origin and shows the following reactions.

$$\mathrm{MgSiO_3(s)+FeOH(g)=MgFeSiO_4(s)+0.5H_2(g)}, \quad (2)$$



(a)

(b)

(c)

Fig. 5. a) TEM image of matrix olivine grains in the matrix of Allende. Indicate the b) TEM voids with arrows image of matrix olivine grains showing void-like defects. AEM analysis is inserted. c) Enlarged TEM image of Fig. 5b. Distribution of voids is heterogeneous.

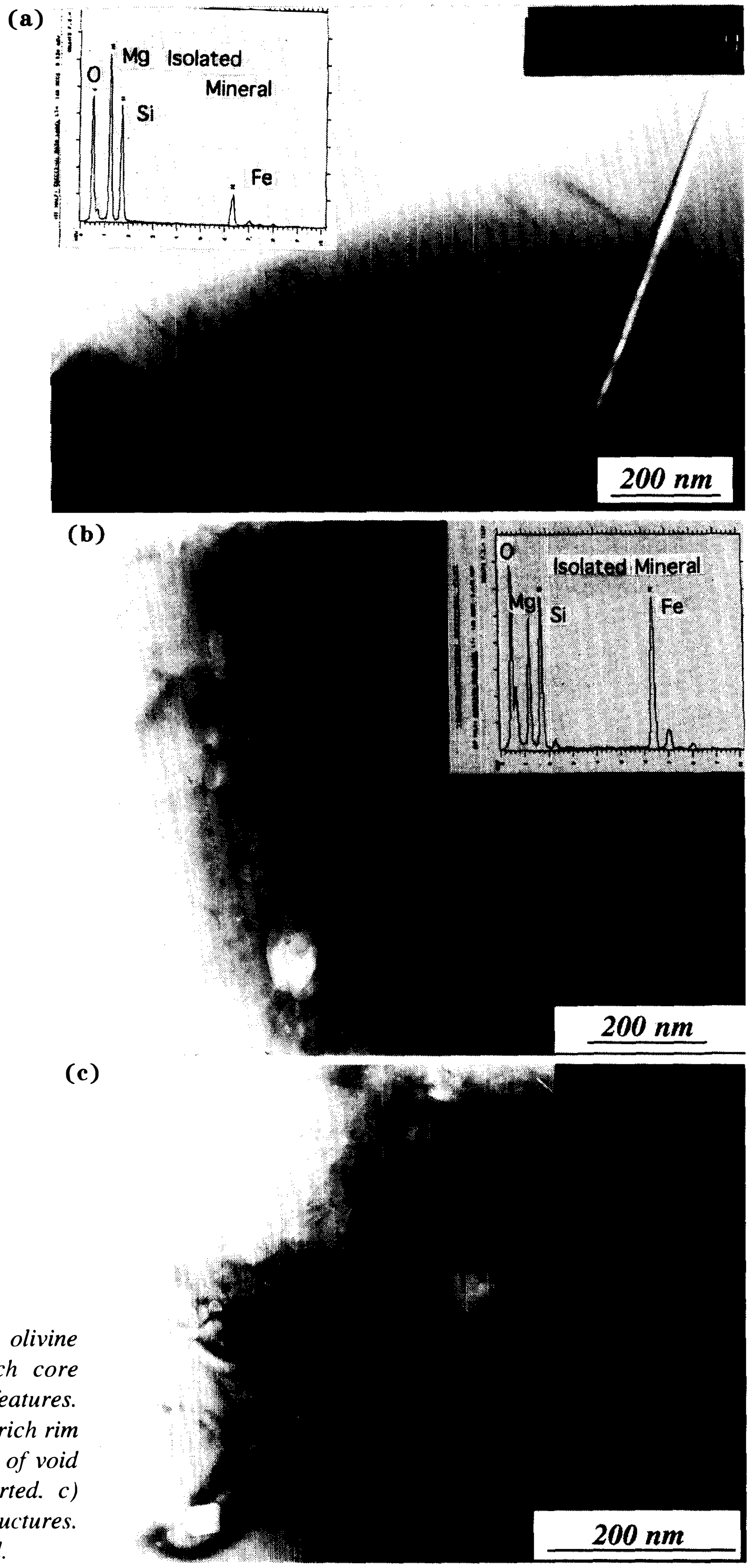


Fig. 6. TEM image of isolated olivine grains, a) the magnesium rich core part has no void or planar features. AEM analysis inserted. b) Iron rich rim has void structures. The shape of void is bubbly. AEM analysis inserted. c) Iron rich rim part has void structures. The shape of void is polygonal.

$$MgSiO_3(s)+Fe(OH)_2(g)=MgFeSiO_4(s)+H_2O(g). \quad (3)$$

Various formation processes of matrix have also been proposed. For example, MACPHAERSON *et al.* (1985) and KORNACKI and WOOD (1984) suggested that matrix minerals are primary minerals and condensation products from the pre-solar nebula. Other interpretation explains that the matrix minerals are secondary products and are alterated minerals on the asteroid or in the pre-solar nebula (*e.g.*, BUNCH *et al.*, 1986; HOUSLEY and CIRLIN, 1983; KROT *et al.*, 1995). In CV3 matrices, nepheline and sodalite are often observed but low-Ca pyroxene is rare. This fact implies that low-Ca pyroxene converted to fayalitic olivine in the nebular (PALME and FEGLEY, 1990) or during aqueous alteration in the parent asteroid (ZOLENSKY *et al.*, 1993). We could not explain the unique formation process of the void structure. However the finding of void structure in this study may not be inconsistent with assumption that fayalitic olivine grains are the secondary products.

The chemical composition of matrix olivine is more fayalitic than olivine grains in the other components (chondrules and CAIs). The chemical composition of matrix olivine grains in Allende is more homogeneous than in the other CV3 chondrites (SCOTT *et al.*, 1988).

The void structure found in this study is very characteristic. Similar voids structures have already been found in B-7904 by AKAI (1994). In his paper he discussed the origin of the void; 5 possibilities are suggested; 1) thermal metamorphism, 2) irradiation by high energy particles in the solar nebula, 3) impact events, 4) sample preparation artifacts or 5) hydrous alteration. Very similar voids have been discovered in the experiments of ion beam irradiation to metals by HOJOU *et al.* (1992), FURUNO *et al.* (1993) and FURUNO *et al.* (1994). However, the second possibility is low because the voids are found only in the iron-rich part of olivine grains. The possibility of 3 and 4 may also be low by the same reason. Although the last possibility can not be denied completely, hydrous alteration may not be the case because phyllosilicates and H_2O are scarcely found. Thus, the most probable explanation for the formation of the void structure may be as follows; they have formed during thermal metamorphism which is also related to some chemical reaction to form fayalitic olivine either in the nebula or on the asteroid. Detailed mechanism has not been disclosed.

5. Summary

Characteristic void-like defect structures were found in olivine grains in the Allende CV3 carbonaceous chondrite. The areas where the void-like defects occurred were mainly related to either iron enriched portions of matrix olivine or iron-enriched rims of isolated olivine in the matrix. The density of the voids distribution were not homogeneous but heterogeneous even within iron enriched parts.

The formation processes of void-like defects were discussed. It was suggested that the void structure was most likely formed during thermal metamorphism which is also related to some chemical reaction to form fayalitic olivine either in the nebular or asteroidal processes.

Acknowledgments

One of the author (H. TANAKA) is grateful to Dr. M. KIMURA, Prof. Y. IKEDA and Dr. T. NOGUCHI, Ibaraki University for their helpful discussions and advices. He is also grateful to Prof. S. YANAGIDA, Ibaraki University for providing Allende samples. Our special thanks go to Dr. M. E. ZOLENSKY, NASA and Dr. T. NOGUCHI, Ibaraki University for their critical reading of the manuscript and making a number of helpful suggestions. Mr. T. J. CHOI and Mrs. D. GURUG of Niigata University kindly checked the English of the manuscript.

References

AKAI, J. (1994): Void structures in olivine grains in thermally metamorphosed antarctic carbonaceous chondrite B-7904. Proc. NIPR Symp. Antarct. Meteorites, **7**, 94–100.

ARMSTRONG, J. T., MEEKER, G. P., HUNEKE, J. C. and WASSERBURG, G. J. (1982): The Blue Angel: I. The mineralogy and petrogenesis of a hibonite inclusion from the Murchison meteorite. Geochim. Cosmochim. Acta, **46**, 575–595.

BREARLEY, A. J. (1995): Nature of matrix in unequilibrated chondrites and its possible relationship to chondrules. Chondrules and The Protoplanetary Disk, ed. by R. H. HEWINS *et al.* Cambridge, Cambridge Univ. Press.

BUNCH, T. E. and CHANG, S. (1980): Carbonaceous Chondrites-II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. Geochim. Cosmochim. Acta, **44**, 1543–1577.

BUNCH, T. E., CHANG, S., CASSEN, P. and REYNOLDS, R. (1986): Allende: Profile of parent body growth. Lunar and Planetary Science XIIV. Houston, Lunar Planet. Inst., 89–90.

FURUNO, S., HOJOU, K., OTSU, H., IZUI, K., KAMIGAKI, N. ONO, K. and KINO, T. (1993): *In-situ* observation of damage evolution in aluminium irradiated with H and He ions. Microsc. Microanal. Microstruct., **4**, 323–330.

FURUNO, S., HOJOU, K., NISHIDA, T., IZUI, K., ONO, K. and KINO, T. (1994): *In-situ* observation of bubble formation and growth in aluminum during helium ion irradiation at some elevated temperatures. ICEM 13-PARIS, **17-22**, 1153–1154.

GROSSMAN, L. (1972): Condensation in the primitive solar nebula. Geochim. Cosmochim. Acta, **36**, 597–619.

GROSSMAN, L. (1980): Refractory inclusions in the Allende meteorite. Ann. Rev. Earth Planet. Sci., **8**, 559–608.

HOJOU, K., FURUNO, S., KUSHITA, K. M., OTSU, H. and IZUI, K. (1992): *In-situ* observation of damage evolution in SiC crystals during He^+ and H_2^+ dual-ion beam irradiation. J. Nuclear Materials, **191-194**, 583–587.

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.

HUSS, G. R. and LEWIS, R. S. (1995): Presolar diamond, SiC, and graphite in primitive chondrites: Abundances as a function of meteorite class and petrologic type. Geochim. Cosmochim. Acta, **59**, 115–160.

HUTCHEON, I. D. and JONES, R. H. (1995): The ^{26}Al- ^{26}Mg record of chondrules: Clues to nebular chronology. Lunar and Planetary Science XXVI. Houston, Lunar Planet. Inst., 647–648.

IKEDA, Y. and KIMURA, M. (1995): Anhydrous alteration of Allende chondrules in the solar nebula I: Description and alteration of chondrules with known oxygen-isotopic composition. Proc. NIPR Symp. Antarct. Meteorites, **8**, 97–122.

KORNASHI, A. S. and WOOD, J. A. (1984): The mineral chemistry and origin of inclusion matrix and meteorite matrix in the Allende CV3 chondrite. Geochim. Cosmochim. Acta, **48**, 1663–1676.

KROT, A. N., SCOTT, E. R. D. and ZOLENSKY, M. E. (1995): Mineralogical and chemical modification of components in CV3 chondrites: Nebular or asteroidal processing? Meteoritics **30**, 748–775.

MACPHERSON, G. J., HASHIMOTO, A. and GROSSMAN, L. (1985): Accretionary rims on inclusions in the Allende meteorite. Geochim. Cosmochim. Acta, **49**, 2267–2279.

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

MCSWEEN, H. Y., Jr. (1977): Petrographic variations among carbonaceous chondrites of the Vigarano type. Geochim. Cosmochim. Acta, **41**, 1777–1790.

PALME, H. and FEGLEY, B. (1990): High-temperature condensation of iron-rich olivine in the solar nebula. Earth Planet. Sci. Lett., **101**, 180–195.

PECK, J. A. (1983): An SEM petrographic study of C3(V) meteorite matrix. Lunar and Planetary Science XIV. Houston, Lunar Planet Inst., 373–374.

PECK, J. A. (1984): Origin of the variation in properties of CV3 meteorite matrix and matrix clasts. Lunar and Planetary Science XV. Houston, Lunar Planet Inst., 635–636.

PECK, J. A. and WOOD, J. A. (1987): The origin of ferrous zoning in Allende chondrule olivine. Geochim. Cosmochim. Acta, **51**, 1503–1510.

RUBIN, A. E. and WASSON, J. T. (1987): Chondrules, matrix and coarse-grained chondrule rims in the Allende meteorite. Geochim. Cosmochim. Acta, **51**, 1923–1937.

SCOTT, E. R. D., BARBER, D. J., ALEXANDER, C. M. O., HUTCHISON, R. and PECK, J. A. (1988): Primitive material surviving in chondrites: Matrix. Meteorites and the Early Solar System, ed. by J. F. KERRIDGE and M. S. MATTHEWS. Tucson, Univ. Arizona Press, 718–745.

SWINDLE, T. D., DAVIS, A., HOHENBERG, C. M., MACPHERSON, G. J. and NYQUIST, L. E. (1995): Formation times of chondrules and Ca-Al-rich inclusions: Constraints from short-lived radionuclides. Chondrules and The Protoplanetary Disk, ed. by R. H. HEWINS *et al.* Cambridge, Cambrige Univ. Press.

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

WASSON, J. T. (1993): Constraints on chondrule origins. Meteoritics, **28**, 13–28.

WEINBRUCH, S., ZINNER, E. K., EL GORESY, A., STEELE, I. M. and PALME, H. (1993): Oxygen isotopic composition of individual olivine grains from the Allende meteorite. Geochim. Cosmochim. Acta, **57**, 2649–2661.

WOOD, J. A. (1988): Chondritic meteorites and the solar nebula. Ann. Rev. Earth Planet. Sci., **16**, 53–72.

ZOLENSKY, M. E., BARRETT, R. and BROWNING, L. (1993): Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. Geochim. Cosmochim. Acta, **57**, 3123–3148.

(Received July 30, 1996; Revised manuscript accepted May 28, 1997)