Ni-Fe METALS IN THE TYPE 3 ORDINARY CHONDRITES

Hiroko Nagahara

Geological Institute, University of Tokyo, 3-1, Hongo 7-chome, Bunkyo-ku, Tokyo 113

Abstract: Metals in four type 3 ordinary chondrites (ALH-77015, -77278, -77299 and -77304) are classified into four types based on their occurrence; those within chondrules, those on the surface of chondrules, those in the matrix and those forming chondrules. Metals within chondrules have higher Co contents than those on the surface or in the matrix, indicating that they would have cystallized from the liquid at higher temperatures. Modal ratios of discrete kamacite, discrete taenite and coexisting grains are different from those in the chondrites of higher petrologic types, and they are considered not to have been heated above about 500°C. Most metals in the type 3 ordinary chondrites show compositional zoning due to decreasing temperature; however, zoning in kamacite is more conspicuous than in the chondrites of higher petrologic types. According to diffusion coefficients of Ni in kamacite and taenite, metals in the type 3 ordinary chondrites should have cooled 2 orders of magnitude more rapidly below 500°C than those in the chondrites of higher petrologic types. This difference would be a constraint for the estimation of the parental body of the ordinary chondrites.

1. Introduction

Ni-Fe metals in meteorites are important to estimate the cooling rates at low temperatures and the size of the parental bodies. Wood (1964) analyzed the zoning patterns of Ni in iron meteorites and estimated their cooling rates at 500°C as 10^{-1} to 10^{-2} °/Ma. Wood (1967) further estimated the cooling rates of the chondrites on the basis of the relations between Ni content and grain size and of the cooling rate calculated for the iron meteorites. Recalculation of diffusion equation and use of more precise diffusion coefficients (*i.e.* Goldstein and Ogilvie, 1965; Goldstein and Short, 1967; Taylor and Heymann, 1971; Randich and Goldstein, 1978; Wood, 1980) did not grately change the results of Wood's calculation; the change of cooling rate was within an order of magnitude.

In spite of many petrological and chemical studies on the ordinary chondrites, Ni-Fe metals in them have not been well studied. After Wood's work (1967), only Taylor and Heyman (1971) and Affiatalab and Wasson (1980) studied the metal in the ordinary chondrites. More detailed studies of metal, especially in the type 3 ordinary chondrites, would provide important information on their cooling history, which has not been so well understood as the chondrites of higher types.

In this paper, the occurrence and chemistry of metals in several type 3 chondrties have been studied and compared to those in the chondrites of higher petrologic types, and their cooling history will be discussed. Samples studied are ALH-77015 (L3), -77278 (LL3), -77299 (H3) and -77304 chondrites. The last one, ALH-77304, was

once classified as an LL3 chondrite (MASON, 1979), but the detailed study of chondrules and other silicate minerals revealed that it is an L4 or the most metamorphosed L3 chondrite.

2. Mode of Occurrence

The mode of occurrence of metals in the type 3 ordinary chondrites is classified into four groups on the basis of position, shape and coexisting phases; those in the interior of chondrules, those on the surface of chondrules, those in the matrix and those forming chondrules. The results are listed in Table 1.

Table 1. Occurrence of Ni-Fe metals in the unequilibrated ordinary chondrites.

Position	Shape	Occurrence
Chondrule interior	Small globule	Kamacite ≫ Taenite
		Discrete grains
		Low Co content in kamacite
Chondrule surface	Angular	Kamacite ≥ Taenite
	�	Coexisting with troilite
	Subangular	High Co content in kamacite
Matrix	Large, small	Kamacite > Taenite
	Angular	Discrete grains
	⸣	Coexisting with troilite
	Subangular	High Co content in kamacite
Opaque chondrule	Subangular	Kamacite > Taenite
		Coexisting with troilite

Ni-Fe metals in the interior of chondrules are usually round and occur in the glass of groundmass or in the cracks of crystals (Fig. 1a). They are similar to the metal blebs experimentally crystallized from a liquid under the reducing conditions, indicating that they might have crystallized from the liquid at the time of chondrule formation. Both kamacite and taenite are present in these metals, though kamacite is much more abundant than taenite. The grains are usually so small (less than 10 μm) that compositional zoning is hardly observed. These metals occur as discrete grains and do not coexist with troilite. Irregular metal grains are rarely present in the interior of chondrules, and do not necessarily exist in the glass but in the crystals and/or glass, and which sometimes continue to the outside of the chondrule. They are considered to have formed after crystallization of the chondrules. It is, however, not known whether they were formed before or after the accretion of chondrules into chondrites.

Metals on the surface of chondrules occur as irregular grains coexisting with troilite (Fig. 1b). The surface of chondrules is often surrounded by a black opaque rim several tens to a few hundred μm wide, most of which are aggregates of extremely fine-grained iron-rich olivine with irregular troilite and a lesser amount of Ni-Fe metals. Both kamacite and taenite are present, but kamacite is somewhat more than taenite. These metals show compositional heterogeneity; some show a typical zoning of Fe-rich core and Ni-rich rim, and some show nearly uniform composition within individual
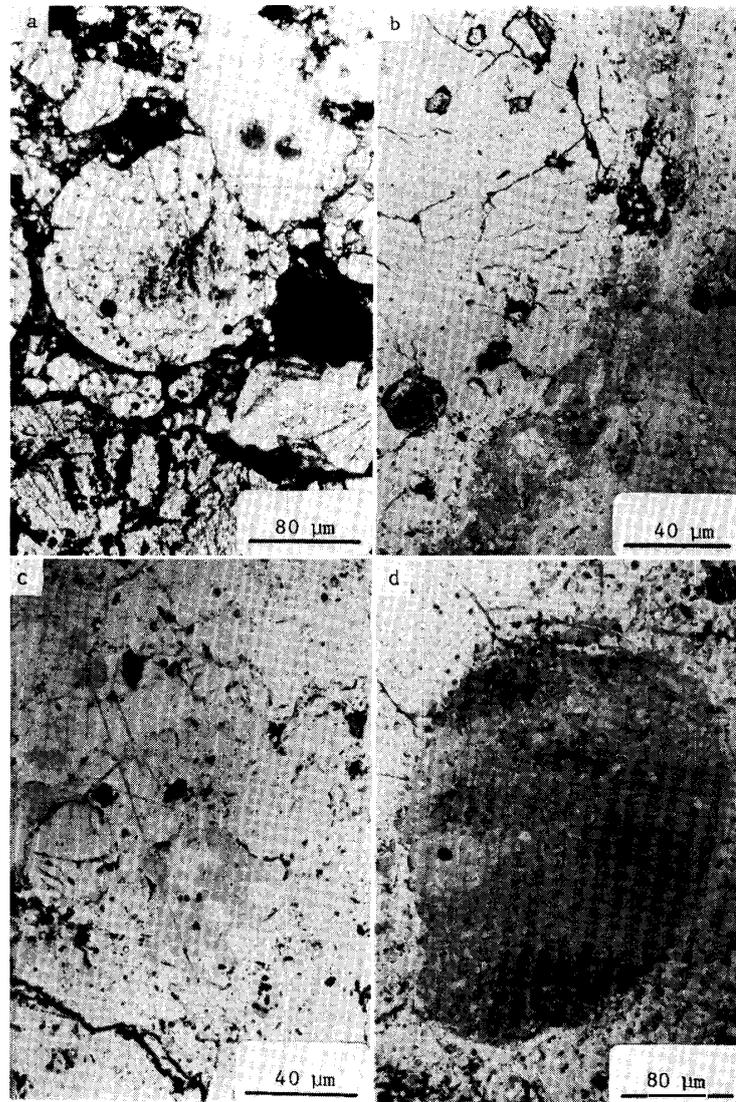
Fig. 1. Photomicrographs of metals in the ALH-77278 (LL3) chondrite.
(a) Blebs of metals within a chondrule.
(b) Irregular kamacite coexisting with troilite on the surface of a chondrule.
(c) Irregular grain composed of kamacite and taenite in the matrix.
(d) Metals forming a chondrule with troilite. Both kamacite and taenite are present.

grains but different compositions among different grains.

Metals in the matrix, which are most abundant in the chondrite, show angular to subangular shapes. They occur as discrete kamacite grains, discrete taenite grains, composite grains of kamacite and taenite and one of the former three coexisting with troilite (Fig. 1c). As described below, composite grains of kamacite and taenite are less common than those in the chondrites of higher petrologic types and discrete grains are abundant. They have compositional zoning, most of which show normal zoning with iron rich core and nickel-rich rim, but some are nearly homogeneous. Tetrataenite, if present, is observed in the matrix, though its detailed occurrence is not well known because of its scarcity.

Metals rarely occur as chondrules; some chondrules consist of metals and troilite, and some consist of metals and chromian spinel.   The chondrule shown in Fig. 1d is composed of metals and troilite which occur like lamellae.   In this case, kamacite is more abundant than taenite.
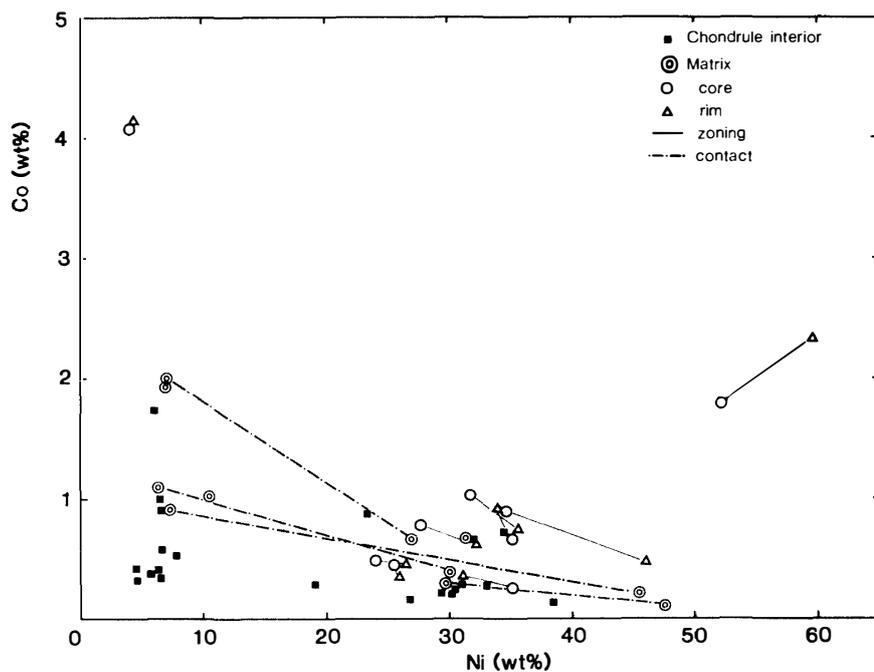
Fig. 2.   Relation between temperature and Co content of metals within chondrules and those in the matrix of ALH-77278 chondrite.
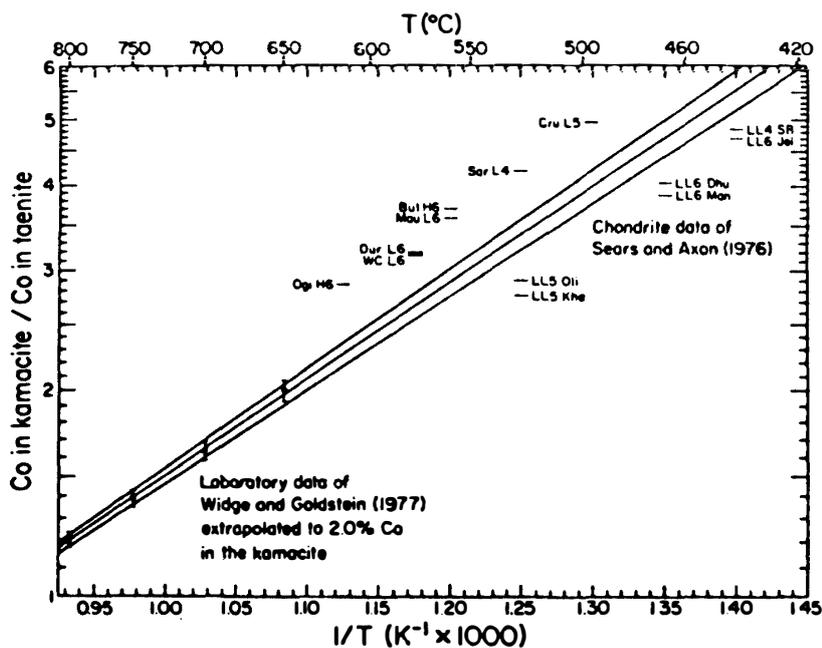
Fig. 3.   Relation between temperature and Co content in coexisting kamacite and taenite.   After AFFIATTALAB and WASSON, 1980.

Blebs of metals within chondrules are chemically different from those on the surface of chondrules and in the matrix. Figure 2 shows the relation between Ni and Co contents of the metals of different occurrence; metals within chondrules, especially, kamacite, are poorer in Co than those in the matrix. This fact is thought to be due to their different origin; that is, blebs of metals within chondrules were crystallized from the liquid in the course of crystallization of chondrules at higher temperatures, and those on the surface of chondrules and in the matrix were formed at lower temperatures. AFFIATTALAB and WASSON (1980) have pointed out that kamacite coexisting with taenite at higher temperatures contain less Co than that at lower temperatures, on the basis of the experimental results of WIDGE and GOLDSTEIN (1977) (Fig. 3). According to these results, blebs of metals within chondrules were in equilibrium at about 800°C and those in the matrix below 500°C. The former would have crystallized at higher temperatures and then cooled, and the temperature of 800°C would be the lowest temperature for the metal to have equilibrated.

3. Coexistence of Kamacite and Taenite

NAGAHARA (1980) showed that the mode of occurrence of isolated and composite grains of kamacite and taenite in the chondrites of higher petrologic types is different between H and L chondrites, and that this would result from the difference of original chemical composition of metals. In the H chondrites, discrete kamacite and taenite grains are abundant, but composite grains are less abundant. In the L chondrites, composite grains of kamacite and taenite with medium compositions (Ni ~ 15 wt%) are abundant, but discrete grains are less common. According to the phase diagram of the binary join Fe-Ni (GOLDSTEIN and OGILVIE, 1965), the H chondrites with lower Ni and higher Fe contents would have begun to precipitate kamacite at higher temperatures than the L chondrites with higher Ni and lower Fe contents, and the two phases could have been separated coarsely in the H chondrites and finely in the L chondrites, even if the H and L chondrites cooled at the same rate.

The chemical composition of metal grains in the type 3 chondrites determined by a defocussed broad beam of EPMA is shown in Fig. 4. The results are different from those of the chondrites of higher petrologic types. Metals in an H3 chondrite are discrete kamacite, coexisting and discrete taenite grains in the order of decreasing amount, and discrete taenite grains are fewer. Those in an L3 chondrite are discrete kamacite, discrete taenite, and composite grains, in the order of decreasing amount. As already mentioned, if metals in H chondrites, the bulk composition of which contains about 10 wt% Ni in average, was once heated above their liquidus temperatures and then cooled slowly (that is, the case of the chondrites of higher petrologic types), they should have coarsely separated into kamacite and taenite. On the other hand, those in L chondrites should have finely separated into two phases and the amount of composite grains should have become large. Comparing these occurrences with those of the chondrites of higher petrologic types, they are quite different. Those in the type 3 chondrites are considered not to have been heated above the liquidus temperatures and the separation into two phases according to their chemical compositions have not occurred.

Fig. 4. Mode of occurrence of metals in four type 3 chondrites. Single grain is represented by one point measurement and the composite grain of two phases by a point with a medium composition.
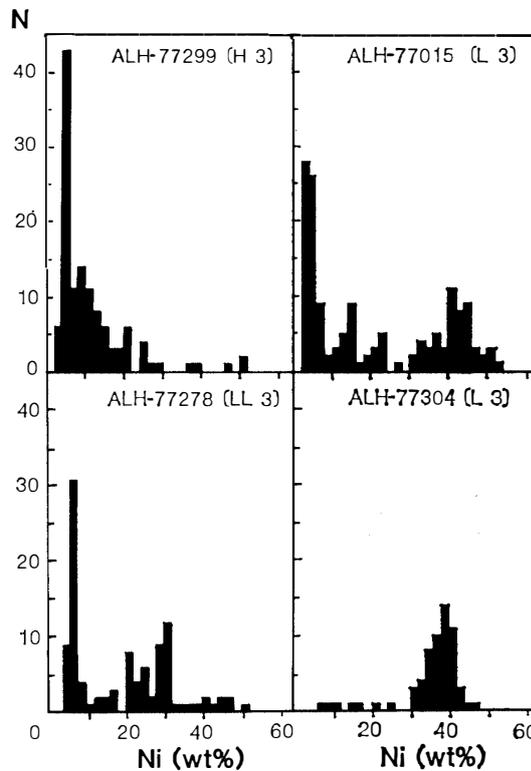
Effective diffusion would have taken place among metals dispersed in the silicate minerals and fine-grained "Huss" matrix at temperatures higher than 450°C, according to the cases of the chondrites of higher petrologic types. The existence of grains with different zonal patterns in an type 3 chondrite (mentioned below) indicates that they have not been heated up to 450°C. The temperature of 450°C is, of course, not a critical temperature, and would depend on the cooling rate, so that the rough estimate of the maximum temperature of heating of the type 3 chondrites is about 500–400°C. Consequently, the mode of occurrence in the type 3 chondrites would represent the original one; both kamacite and taenite would have been originally included in the chondrites but the ratios of taenite/kamacite would have been larger in the L chondrites than in the H chondrites. Hence, primarily different proportion of two phases of metals in the H and L chondrites should be one of the main factors of these chemical groups.

Metals in an LL3 chondrite are similar in mode of occurrence to those in an L3 chondrite (Fig. 4) indicating the genetical similarity, probably in time and/or place of formation, of L and LL chondrites. The occurrence of metals in ALH-77304 is different from those of the L3 or L4–6 chondrites, which may be due to a scarcity of measurements.

4. Zoning Pattern

Compositional zoning of Ni and Fe of taenite in iron meteorites, stony-iron meteorites and chondrites has been studied to evaluate their cooling rate (i.e. WOOD,

1964, 1967); taenite has a remarkably Fe-rich core and a Ni-rich rim, though kamacite coexisting with taenite is almost homogeneous. The zonal patterns of metals in type 3 chondrites are different from this; taenite in the type 3 chondrites generally has a Fe-rich core and a Ni-rich rim, but the compositional difference between them is narrower than that in the chondrites of higher petrologic types. The zonal pattern of a composite grain in an H3 chondrite is shown in Fig. 5. Rarely, "reversely" zoned taenite with Ni-rich core and Fe-rich rim occurs in the same sample, which indicates that such a chondrite has never been heated to temperatures high enough to homogenize the metals. The size of taenite grains in the type 3 chondrites are small and its amount is large; on the contrary, the size is large and the amount is small in the chondrties of higher petrologic types. Fine grains of taenite in the type 3 chondrites might have gathered to become larger by heating. Hence, the original chemical composition of each metal grain in the type 3 chondrites might have scarcely changed and the chemistry and zonal pattern of the metals would preserve the early thermal history of them.
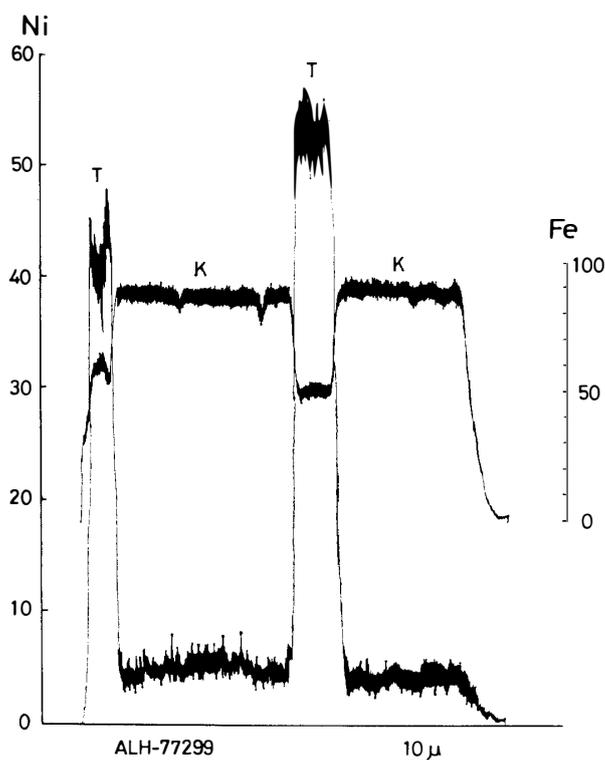
Fig. 5. Zonal patterns of Ni and Fe in a grain composed of kamacite (K) and taenite (T) in ALH-77299 (H3) chondrite. Zoning of Ni in kamacite is conspicuous.

Kamacite coexisting with taenite in the type 3 chondrites shows clear compositional zoning (Fig. 5); the core is richer in Ni than the rim. Figure 6 shows the compositional distribution of Ni in a composite grain in ALH-77299 (H3) chondrite; it also shows that kamacite has a remarkable heterogeneity, and in general, the inner portion of kamacite is rich in Ni and Ni decreases toward the outer portion.

According to the binary phase diagram (GOLDSTEIN and OGILVIE, 1965), kamacite coexisting with taenite contains up to a maximum of about 7 wt% Ni at about 450°C and the Ni content decreases as temperature decreases. Consequently, decrease in Ni from core to rim of kamacite grains in the type 3 chondrites represents the cooling
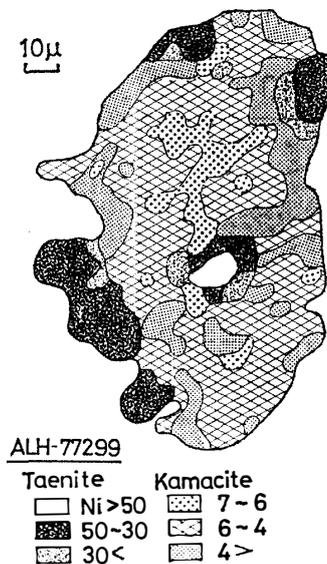
Fig. 6. Distribution of Ni in a composite grain
of kamacite and taenite in ALH-77299
chondrite. Ni in kamacite portion
generally decreases outward, showing
cooling process below 500°C.

process through about 450°C and below it.   Zonal pattern of taenite in the chondrites
of higher petrologic types also represents the cooling process through about 500°C;
though kamacite in the chondrites of higher petrologic types is nearly homogeneous,
taenite shows remarkable zoning.   In general, diffusion coefficient of Ni in kamacite is
2 orders of magnitude larger than that in taenite (MOREN and GOLDSTEIN, 1978), so the
differences of zonal pattern in the type 3 chondrites and the chondrites of higher
petrologic types are considered to be due to the difference of cooling rate; the metals
in the type 3 chondrites would have cooled rapidly to leave compositional zoning in
kamacite, on the contrary those in the chondrites of higher petrologic types would
have cooled slowly to nearly homogenize kamacite and leave compositional zoning in
taenite.

The above-mentioned features are observed in many type 3 chondrites.   Figure 7
represents the relation between composition and apparent grain size of coexisting taenite
and kamacite shown by WOOD (1967) and revised by ONUMA (1972) for type 3 chondrites
and chondrites of higher petrologic types.   The figure well indicates that both taenite
and kamacite grains are smaller in the type 3 chondrites than in the chondrites of higher
petrologic types, and especially that kamacite in the type 3 chondrites shows large
compositional heterogeneity, while that in the chondrites of higher petrologic types
shows small compositional variation.   The conclusion that the most type 3 chondrites
cooled 2 order of magnitude more rapidly below 500°C than the chondrites of higher
petrologic types is contrary to WOOD's conclusion.   However, WOOD's method is based
on the assumption that the diffusion of Ni in kamacite is rapid enough and kamacite
is homogeneous, so that the cooling rate is given only by the size and Ni content of
taenite grains.   This method can be applied to the meteorite once heated above the
solvus temperatures of bulk chemical composition of metals and can not be applied
to those heated below it.

In general for the internally heated onion-shell model for the parental body of
chondrites (i.e. WOOD, 1980), the cooling rate at 500°C at inner portion should larger
than that at the outer portion.   The larger cooling rate of 2 orders at 500°C of the

Unequilibrated chondrites   Equilibrated chondrites

Distance to edge (µm)
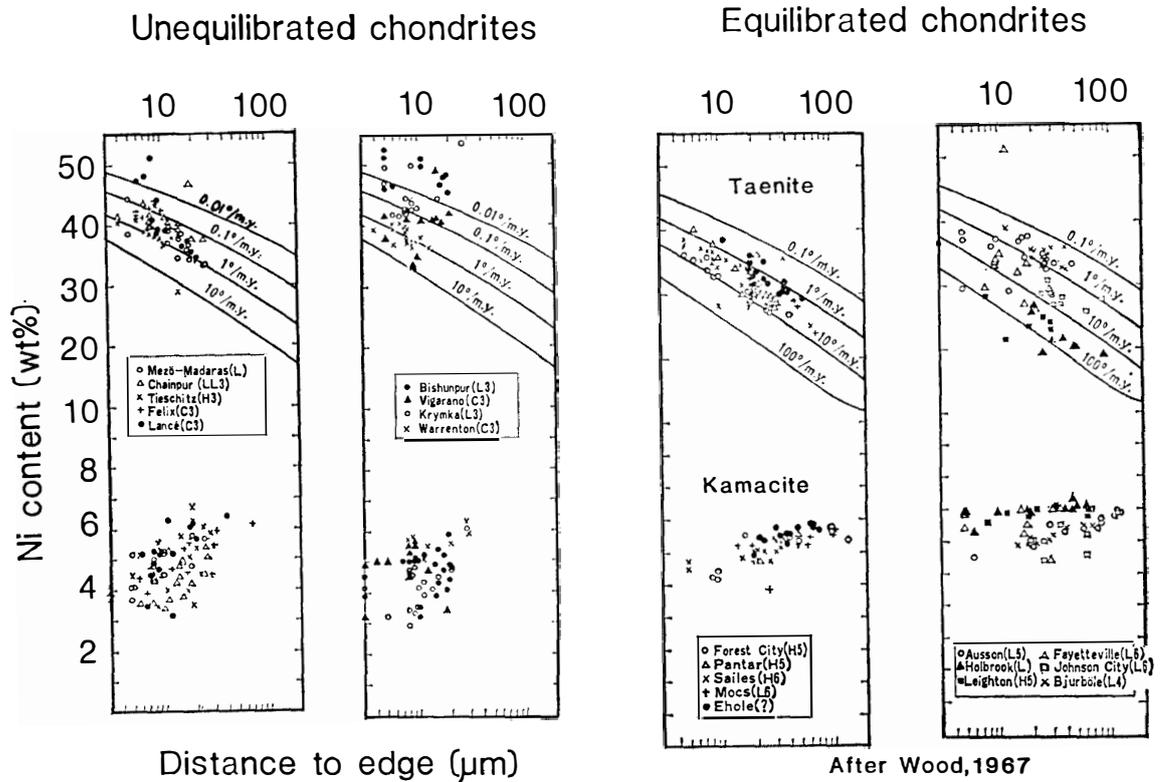
After Wood,1967

Fig. 7.   Composition-dimension plots of metals in the chondrites of type 3 (right) and higher
petrologic types (left).   After WOOD (1967) and ONUMA (1972).

A-77299 (H 3)   A-77015 (L 3)   A-77033 (LL 3)

A-77304 (L3-4)   A-77278 (LL 3)

Apparent distance to edge (µm·)
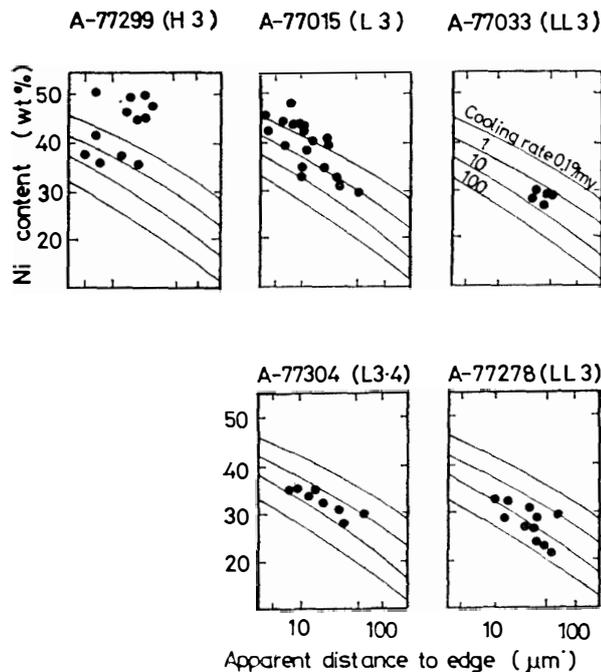
Fig. 8.   Composition-dimension plots of five type 3 chondrites studied.   ALH-77299 and -77015
show widespread points indicating the heating temperature of the chondrites below 500°C.
Data of ALH-77033, -77304 and -77278 are nearly on curves for certain cooling rate.

type 3 chondrites mentioned above is, therefore, contrary to the onion-shell model. Though relaively high temperature of heating for the type 3 chondrites (about 500°C) would enable the cooling rate, and these relative cooling rate of the type 3 chondrites and chondrites of higher petrologic types could define the size and cooling history of them.

Chondrites which are considered not to have been heated above about 500°C do not show any clear relation between grain size and Ni content (WOOD's plot) (Fig. 8). Taenite in ALH-77299 and -77015 shows a wide spread on the figure, those in ALH-77278 are slightly dispersed and those in ALH-77304 and -77033 are nearly on the line of constant cooling rate. These chondrites would represent decreasing degree of metamorphism within type 3 chondrites in this order. The latter three type 3 chondrites might have been heated about 500°C, and original composition and mode of the grains might not be changed. In this sense, type 3 chondrites should be classified into subtypes, which would correspond to the subclassification based on thermoluminescence sensitivity (SEARS et al., 1980).

5. Conclusions

(1) Metals in the type 3 chondrites are classified into four groups on the basis of their occurrence, shape and coexisting relation; (a) small globular grains within chondrules which are mainly discrete kamacite grains, (b) irregular grains on the surface of chondrules which are kamacite and taenite usually coexisting with troilite, (c) large irregular grains in the matrix which are discrete kamacite, taenite, composite grains of both, and one of these three coexists with troilite, and (d) metallic chondrules consisting mainly of metals and troilite.

(2) Modal ratios of discrete kamacite, discrete taenite and composite grains in the type 3 chondrites are different from those in the chondrites of higher petrologic types. This fact indicates that the metals in the type 3 chondrites of lower subclass would not have been heated up to about 500°C and both kamacite and taenite have been originally contained in the chondrite. Some type 3 chondrites (higher subclass) are considered to have been heated above 500°C similar to the chondrites of higher petrologic types.

(3) The zonal pattern of Ni in the coexisting kamacite and taenite in the type 3 chondrites generally shows relatively rapid cooling rate below 500°C, about 2 in order, compared with those in the chondrites of higher petrologic types. The difference of cooling rate below 500°C for the type 3 chondrites and the chondrites of higher petrologic types would be a constraint for the reconstruction of their parental body (or bodies).

Acknowledgments

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