

A PRELIMINARY CLASSIFICATION OF YAMATO CHONDRITES WITH REFERENCE TO METAL-SULFIDE EQUILIBRIUM

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Abstract: Silicates, metals and sulfides of the Yamato chondrites from Antarctica were analyzed by means of EPMA, and the chemical-petrologic classification was made with the supplement of textural observation by microprobe technique. On the basis of per cent mean deviation of iron contents in olivines and orthopyroxenes, the following chondrites have been identified; one H type equilibrated chondrite; one H and three L type moderately unequilibrated ones; 5 H(?) unequilibrated ones.

Three-phase assemblages of kamacite, taenite and troilite are found in moderately unequilibrated chondrites. Cobalt concentrates selectively in kamacite but not in troilite. Nickel partition relationships between metals and sulfides in chondrites suggest the formation of the unequilibrated chondrites at relatively higher temperatures than in the equilibrated ones.

1. Introduction

For the purpose of preliminary classification for the catalog of the Yamato meteorites, electron microprobe analyses of 10 small chondrites (one Yamato-69 and nine Yamato-74) have been carried out. Besides, it is significant to clarify the features of a large number of Yamato small meteorites in order to discuss the possibility of meteorite showers in Antarctica. Considering the ideal preservation conditions at low temperature under exceptionally clean circumstances, we selected a method of investigation allowing least contamination. Very small amounts of sample have been chipped from near surface of meteorite.

In order to improve the chemical-petrologic classification by DODD *et al.* (1967) and VAN SCHMUS and WOOD (1967), YANAI *et al.* (1978) proposed a method of classification on the basis of chemical composition of olivines and orthopyroxenes. But we have to admit that this chemical-petrologic classification includes some uncertainties due to lacking observation of textural features of chondrites. YANAI *et al.* (1978) introduced a statistical method using the per

cent mean deviations of atomic iron content for determining equilibration grade in chondrites. This method is followed in this study.

The studies on the metal-sulfide equilibrium in iron and stony-iron meteorites have been performed by many authors, among whom FISHER *et al.* (1978a, b) described the Yamato meteorites, and also NAGAHARA (1979) discussed the equilibrium relations of metal phase in the equilibrated Yamato chondrites. As the study on the equilibria between metals and iron sulfide is rare in the case of unequilibrated chondrites, the present authors intended to clarify the features of the equilibrium relations.

2. Experimental Procedures

Fragments weighing about 0.01–0.5 g were chipped from the original specimens. Thin fusion crusts were carefully eliminated. Except Yamato-694 of proper size for the preparation of thin-section, fragments of all the specimens were coated with epoxy resin and then made into polished section for microprobe analysis.

The experimental conditions in microprobe analysis are shown in Table 1. Ca, Mg and Fe were simultaneously measured in the olivines and pyroxenes. For the rapid calibration of a large number of measurements, we adopted the method which enables us to calculate mole per cent of end-members of olivines and orthopyroxenes directly from relative intensities of elements in the specimen to standard materials without any correction. The experimental error induced by

Table 1. Analytical conditions by electron microprobe of silicates, metals and sulfides in the Yamato meteorites.

Type	JEOL-5 type
Take off angle	40°
Accelerating potential	15 kV
Beam current	0.015 μ A on pure Fe
Standard materials	Silicates natural Fe ₂ O ₃ for Fe synthetic MgO for Mg synthetic CaSiO ₃ for Ca Metal and sulfide metal Fe for Fe metal Co for Co metal Ni for Ni natural CuFeS ₂
Correction methods	Rapid method by YUSA (1975) BENCE and ALBEE method (1968) ZAF correction method by SWEATMAN and LONG (1969)

Table 2. *Electron microprobe analyses of selected olivines and orthopyroxenes of the Yamato chondrites.*

	Yamato-74187		Yamato-74144		
	O1	OPx	O1-1	O1-2	OPx
SiO ₂	39.05	55.91	37.91	37.59	55.14
TiO ₂	0.00	0.16	0.01	0.01	0.19
Al ₂ O ₃	0.00	0.15	0.01	0.00	0.15
FeO	16.91	11.91	22.46	23.31	13.83
MnO	0.45	0.52	0.46	0.46	0.42
MgO	43.35	30.16	38.28	38.03	28.77
CaO	0.00	0.75	0.00	0.00	0.74
Na ₂ O	0.00	0.02	0.02	0.01	0.02
K ₂ O	0.01	0.01	0.02	0.01	0.01
NiO	0.03	0.17	0.31	0.10	0.01
Total	99.80	99.76	99.48	99.52	99.28
mole % of end-members					
	Fa 17.95 Fo 82.05	Fs 17.88 En 80.69 Wo 1.43	Fa 24.77 Fo 75.23	25.59 74.41	Fs 20.94 En 77.64 Wo 1.43
Rapid method after YUSA (1975)					
	Fa 18.0 Fo 82.0	Fs 17.0 En 81.0 Wo 2.0	Fa 24.8 Fo 75.2		Fs 21.0 En 78.0 Wo 1.0

this method is satisfactorily small owing to "Cancel Effect" as discussed by YUSA (1975). In order to check the accuracy of this method, the analytical results of the bulk compositions of some specimens by the ordinary method after the BENCE and ALBEE correction were compared with those after the rapid method by YUSA (1975) in Table 2. The results indicate a satisfactorily good agreement with each other. Thus this rapid method is sufficient for the present purpose.

Measurement was carried out on about 100 points of different chondrules, grains or crystals of olivine and pyroxene, though in some chondrites the points were not enough in number because of poorly polished surface. The compositional homogeneity in equilibrated chondrite was checked by quantitative and line analyses on the selected single crystals. In the course of this rapid method, we can also detect clinopyroxene and plagioclase in addition to olivine and orthopyroxene. In these measurements, only the relative intensity data within the error of ± 1 molecular % end-members were used for determining the compositions.



Fig. 1. Back-scattered electron photograph of equilibrated chondrite (Yamato-74187). Scale is 100 μ . Ol: olivine, OPx: orthopyroxene, M: Fe-Ni metal, S: iron sulfide (troilite).

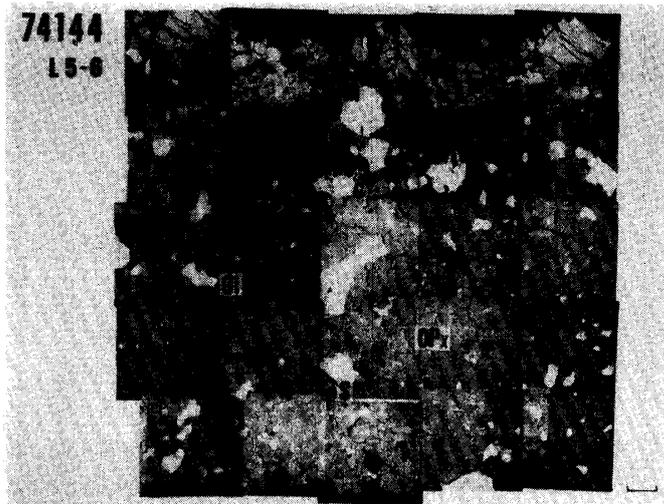


Fig. 2. Back-scattered electron photographs of moderately unequibrated chondrites (Yamato-74144 and -74364). Scale is 100 μ . Abbreviations are the same as in Fig. 1.

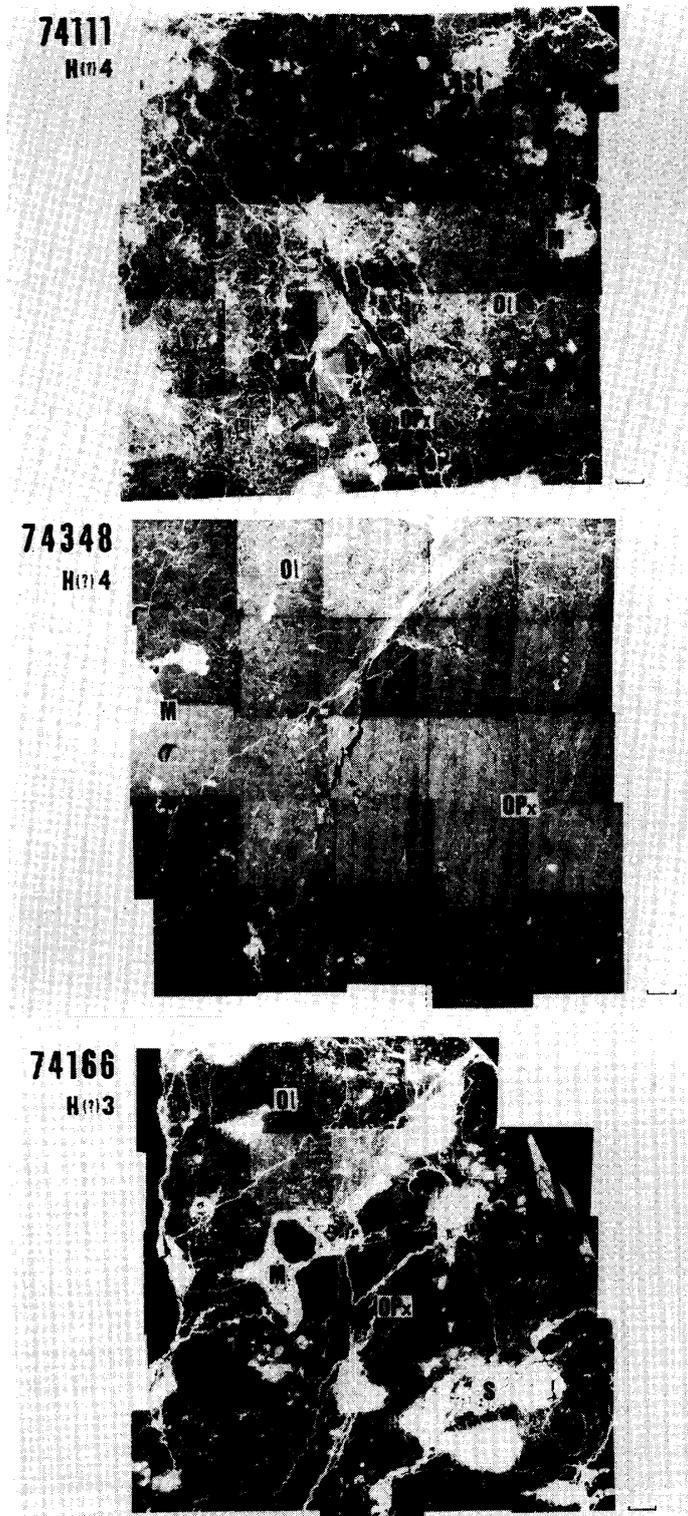


Fig. 3. Back-scattered electron photographs of unequibrated chondrites (Yamato-74111, -74348 and -74166). Large chondrule of orthopyroxene is observed in the right-half of photograph of Yamato-74348. Scale is 100 μ . Abbreviations are the same as in Fig. 1.

From the estimated value of compositions of olivines and orthopyroxenes, we can directly determine the atomic % of Ca, Mg and Fe and construct the histograms of compositional distribution with an interval of 1 atomic %. Mean concentrations of these three elements were calculated for the olivines and pyroxenes in each sample, and the "per cent of mean deviation" has been adopted as an index of heterogeneity in both minerals in chondrites. Then, percentages of measurement were computed by normalizing the total number of measurements to 100%. Petrologic types (VAN SCHMUS and WOOD, 1967) of the chondrites were determined by the supplemental investigation on the back-scattered electron photographs of the specimens (Figs. 1-3).

Contents of Fe, Ni, Co and S in the metals and sulfides were determined by EPMA, using metal iron, nickel, cobalt and natural CuFeS_2 as standard. Correction was made by the ZAF methods (SWEATMAN and LONG, 1969).

3. Results and Discussion

3.1. Classification of chondrites

Histograms of the iron content in olivines and orthopyroxenes of one Yamato-69 and nine Yamato-74 chondrites are shown in Figs. 4-6, which are arranged in the order of the equilibrated grade. The ranges of atomic percentage of iron for the H6, L6 and LL6 type equilibrated chondrites are given at the top of each figure.

The mean compositions and the percentage of mean deviations (% M.D.) of iron concentrations of olivine and orthopyroxene are given in Table 3. The mean deviation of olivines is generally smaller than that of orthopyroxenes as shown in the table. In this study, the equilibration grades are determined chiefly on the basis of the percentage of mean deviations of iron in olivine. YANAI *et al.* (1978) determined the equilibration grade and the petrologic types of chondrites (VAN SCHMUS and WOOD, 1967) by "% M.D.". According to their definition the chondrites with % M.D. less than 2 are grouped as equilibrated chondrite of petrologic type 5 to 6, those with % M.D. of 2 to 5 are moderately unequilibrated ordinary chondrite of type 4, and those with % M.D. greater than 6 unequilibrated chondrite of type 3. In order to determine the petrologic type more exactly, back-scattered electron photographs (Figs. 1-3) are used as supplementary means.

The iron contents of olivine and orthopyroxene in Yamato-74187, an equilibrated H-type chondrite, are shown in Fig. 4, which shows distinct concentration in iron in both minerals. The Ni contents are relatively higher of orthopyroxene than in olivine as shown in Table 2. This equilibrated chondrite shows a well-recrystallized texture, without any distinct chondrule. Iron sulfide and metal occur

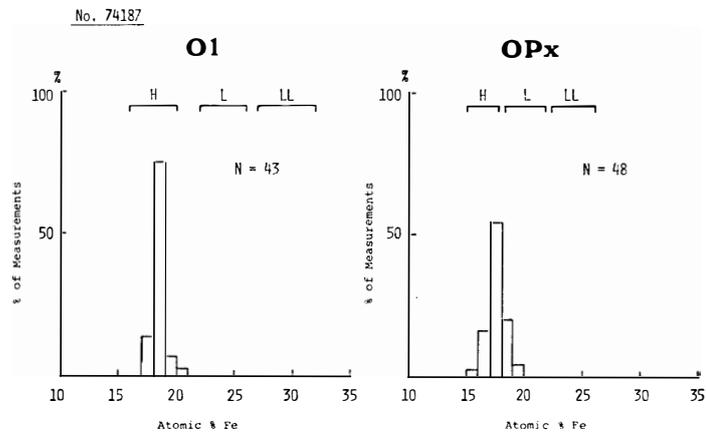


Fig. 4. Iron contents in olivines (O1) and orthopyroxenes (OPx) in an equilibrated chondrite. N gives the total number of measurements.

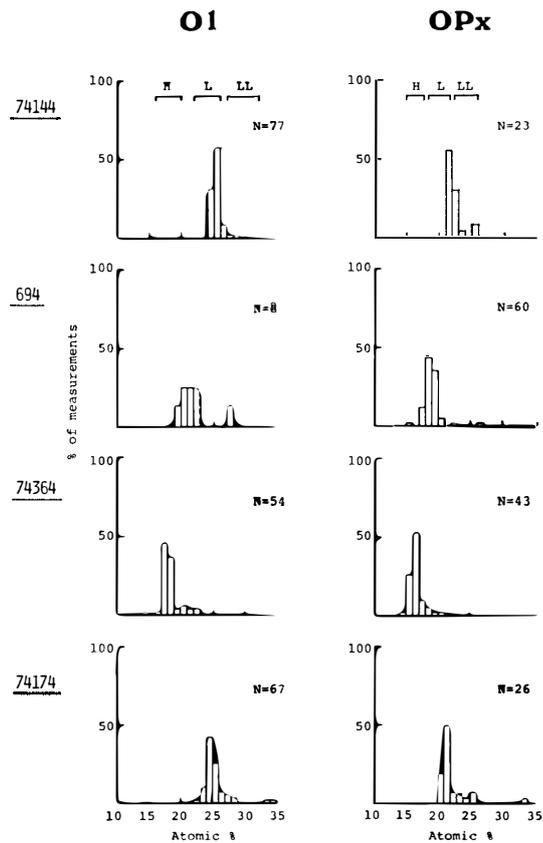


Fig. 5. Iron contents in olivines (O1) and orthopyroxenes (OPx) in moderately unequilibrated chondrites.

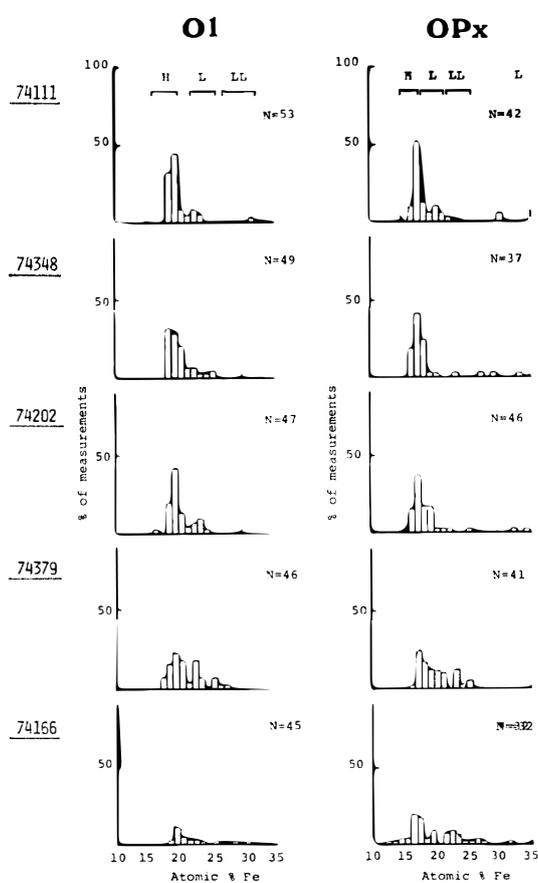


Fig. 6. Iron contents in olivines (Ol) and orthopyroxenes (OPx) in unequilibrated chondrites.

Table 3. Mean compositions and per cent mean deviations of iron concentrations of olivines and orthopyroxenes in the analyzed chondrites.

Sample No.	Original wt.	Sp. wt.	Olivine				Orthopyroxene				Remarks
			Fe*	No.	M.D.	%M.D.	Fe*	No.	M.D.	%M.D.	
Yamato-74187	6.5g	0.022g	18.0	43	0.13	0.72	17.1	48	0.55	3.2	H5-6
-74144	141.4	0.028	24.8	77	0.53	2.1	21.7	23	0.83	3.8	L5-6
-694	62.0	**	21.5	8	0.94	4.4	18.5	60	0.88	4.7	L(?)4-5
-74364	757.8	0.095	17.7	54	0.85	4.8	16.0	43	0.65	4.1	H4
-74174	20.9	0.084	24.9	67	1.25	5.0	21.9	26	1.65	7.6	L4-5
-74111	58.0	0.501	19.4	53	1.28	6.2	18.3	42	1.35	7.4	H(?)4
-74348	20.4	0.112	19.6	49	1.36	6.9	18.4	37	2.22	12.0	H(?)4
-74202	8.1	0.186	20.0	47	1.68	8.4	18.3	46	1.97	10.7	H(?)4
-74379	6.3	0.123	20.5	46	2.09	10.2	19.7	41	2.23	11.3	H(?)3
-74166	1.4	0.010	19.0	45	3.36	17.7	20.8	32	2.14	10.3	H(?)3

M.D.: Mean Deviation, *: Iron content in atomic %, **: Polished thin-section.

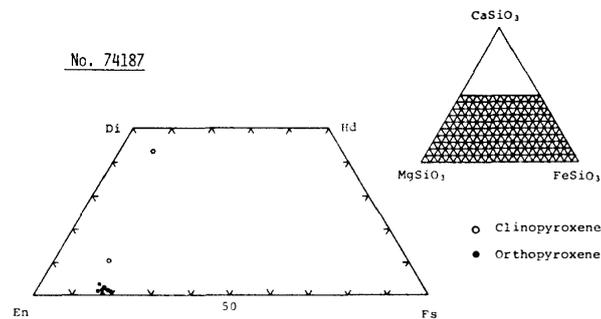


Fig. 7. Chemical compositions of ortho- and clinopyroxenes of equilibrated chondrite. Closed circle: orthopyroxene, Open circle: clinopyroxene.

also as distinctive equigranular grains. Chemical compositions of ortho- and clinopyroxene of this chondrite are plotted in the Di-Hd-En-Fs diagram (Fig. 7). Petrologic type of this chondrite probably corresponds to 5–6.

Yamato-74144(L), -694(L?), -74364(H) and -74174(L) are assigned to moderately unequilibrated chondrites, which belong to petrologic type of 5–6, 4–5, 4 and 4–5, respectively (Fig. 5). The relatively equilibrated 74144 chondrite is characterized by an equigranular texture and a small amount of chondrule, whereas Yamato-74364 of considerably low equilibration lacks an equigranular texture and is characterized by distinct chondrule composed of orthopyroxenes. It is also noted that the range of iron contents of olivines and orthopyroxenes is wider than in the equilibrated chondrite. As shown in Table 2, it is clear that the nickel concentrates selectively into olivine, contrary to the case of the equilibrated chondrites. The ortho- and clinopyroxenes of these chondrites are plotted in the pyroxene diagrams (Fig. 8).

Five chondrites—Yamato-74111, 74348, 74202, 74379 and 74166—are assigned to unequilibrated chondrites. The histograms of iron contents of their olivines and orthopyroxenes are shown in Fig. 6. Yamato-74379 and -74166 belong to a typical unequilibrated type, characterized by a wide range in iron contents of both minerals. Distinct chondrules are found in the poorly crystallized matrix, consisting of irregular grains. As shown in photographs (Fig. 3), metals and iron sulfide occur generally in veinlet and network, though a small amount of them forms single grains. There is a distinct trend that the range of iron content in the histograms generally extends from the peak toward the higher concentration. A similar but less distinct trend is also seen in the moderately unequilibrated ordinary chondrites. Such phenomena might be indicative of the grade of equilibration process in ordinary chondrites. The chemical compositions of ortho- and clinopyroxenes of three chondrites are plotted in Fig. 9.

The nickel contents of granular metals and sulfides of each chondrite are listed

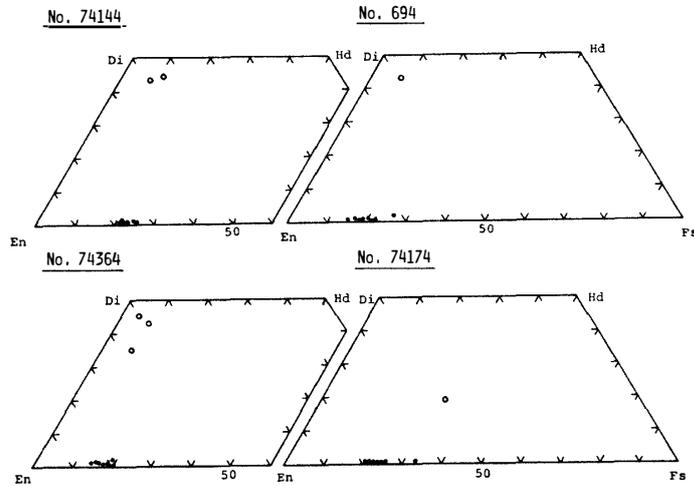


Fig. 8. Chemical compositions of ortho- and clinopyroxenes of moderately unequilibrated chondrites. Symbols are the same as in Fig. 7.

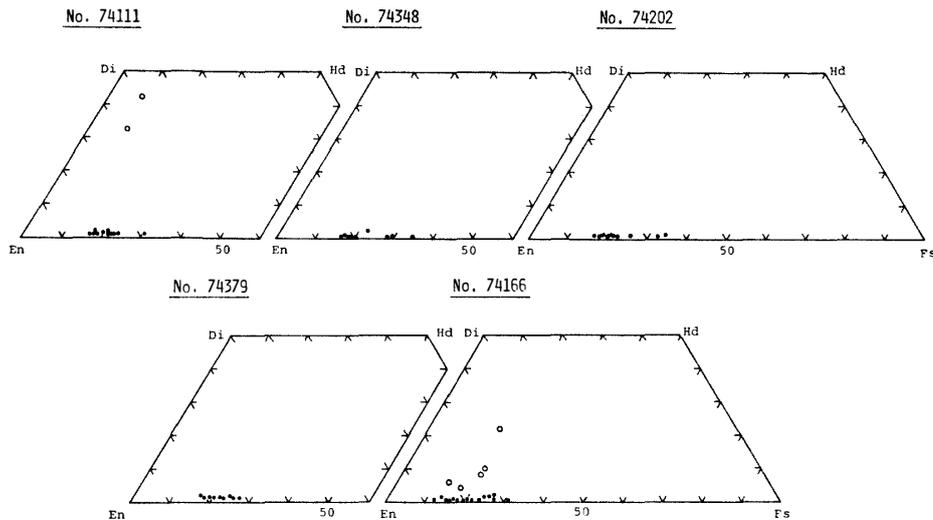


Fig. 9. Chemical compositions of ortho- and clinopyroxenes of unequilibrated chondrites. Symbols are the same as in Fig. 7.

in Table 4. The nickel content of taenite (γ -Fe) is variable, while that of kamacite (α -Fe) is constant. It is noticeable that iron sulfides (troilite) in unequilibrated chondrites contain relatively high Ni contents up to 1.88 wt. % in maximum.

Classification of 10 Yamato chondrites is compiled in Table 5. As mentioned in Introduction, the present method includes some problems with ambiguity about classification. However, it may be a sufficient technique for preliminary study of the classification and the discussion on a possibility that small meteorites might

Table 4. Nickel contents of troilites and Fe-Ni metals in Yamato chondrites.

Sp. No.	Type	Troilite	Kamacite	Taenite
Yamato-74187	H5-6	0.03	6.84	18.61
-74144	L5-6	0.02	5.81	25.41 41.73
-694	L4-5(?)	0.02	5.52	16.40 33.15
-74364	H4	0.01	6.14	50.87
-74174	L4-5	0.05	6.23	12.13 30.79
-74111	H(?)4	0.05	5.20	11.03 18.82
-74348	H(?)4	0.01	6.35	—
-74202	H(?)4	0.04	6.66	29.05
-74379	H(?)3	1.88 0.30	6.62	30.34
-74166	H(?)3	0.72 0.22 1.28	5.82	—

Table 5. Distribution of the analyzed meteorites among the chemical-petrologic types.

Equilibrated ordinary chondrite (Type 5-6)
H: Yamato-74187
Moderately unequilibrated ordinary chondrites (Type 4 or 4-5)
L: Yamato-74144, -74174
L(?): Yamato-694
H: Yamato-74364
Unequilibrated chondrites (Type 3 or 4)
H(?): Yamato-74111, -74348, -74202, -74379, -74166

have been derived from meteorite shower in Antarctica. There may be some requirements to improve the method to obtain higher accuracy in determining the petrologic type. As pointed out by TAKEDA *et al.* (1979), it will be improved more or less through observation on the texture in thin section of even a small fragment. If it is difficult to make thin sections, back-scattered electron photographs will be substituted.

As noticed in unequilibrated and moderately unequilibrated chondrites, there is a distinct trend that the iron contents in the histograms have wide ranges from

peak to higher iron content side. This tendency gives rather low reliability in determining the equilibration grade by means of % M.D. It may be better to use data of low iron content side for calculation of % M.D.

According to our classification, Yamato-74202 belongs to the unequilibrated type (H(?)4), whereas MIYAMOTO *et al.* (1979) classified the different fragment from the same specimen to equilibrated type (H4-5). At present it is not yet clear whether the disagreement between the two is due to the analytical uncertainty of the method mentioned above or the possibility of Yamato-74202's being a monomict breccia.

3.2. Metal-sulfide equilibria

Studies on the equilibrium relation between metal and iron sulfides have been carried out in Yamato iron-meteorite, stony-iron meteorite and even in equilibrated chondrites (FISHER *et al.*, 1978a, b; NAGAHARA, 1979). As discussed in their reports, the Ni partition equilibrium between metal and iron sulfide in each meteorite is maintained at low temperatures. Considering the lack of the investigation on unequilibrated chondrites, we studied the assemblage of metal and iron sulfide in the present chondrites, with special reference to their equilibrium relations.

The representative modes of occurrences of metals and iron sulfide paragenesis are shown in Figs. 10a and b, together with characteristic X-ray images of Fe, Ni and S. The three phase assemblage (kamacite(α)-taenite(γ)-troilite) as shown in Fig. 10a has not been found in equilibrated chondrites (NAGAHARA, 1979). The chemical compositions of each phase in the figures are shown in Table 6. The Ni content in taenite is variable according to its paragenesis: It is lower when taenite is in contact with kamacite than when taenite is in contact with troilite. This compositional heterogeneity of taenites in the same specimen might be a characteristic feature of unequilibrated chondrites. It is assumed that the isolated grains had been equilibrated independently with each other. Cobalt concentration is generally highest in kamacite and is always low in troilite. FISHER *et al.* (1978a, b) detected a considerable amount of phosphorus in Yamato iron-meteorites which may be due to phosphide such as schreibersite. But phosphorus in metal and sulfide phases is undetectable by EPMA in our study.

BEZMEN *et al.* (1978) suggested an availability of Ni partition between coexisting troilite and metal phases as a geothermometer. Our data are plotted in the Ni partition diagram at 1 atm of BEZMEN *et al.* (1978) (Fig. 11), where the isothermal lines are drawn in centigrade degree scale.

It is noted in the diagram that Yamato-74364 indicates the formation at relatively low temperatures from 500 to 600°C, partly even at 400°C. Attention should be paid to the general tendency that relatively equilibrated chondrites

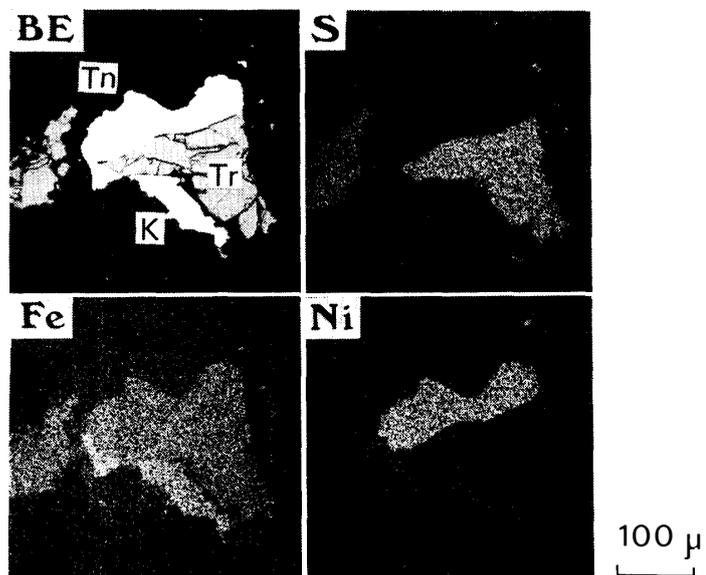
74364-8

Fig. 10a. Back-scattered electron photograph (BE) and characteristic X-ray images for S, Fe and Ni $K\alpha$ lines of coexisting metals and troilite in Yamato-74364.

K: kamacite, Tn: taenite, Tr: troilite.

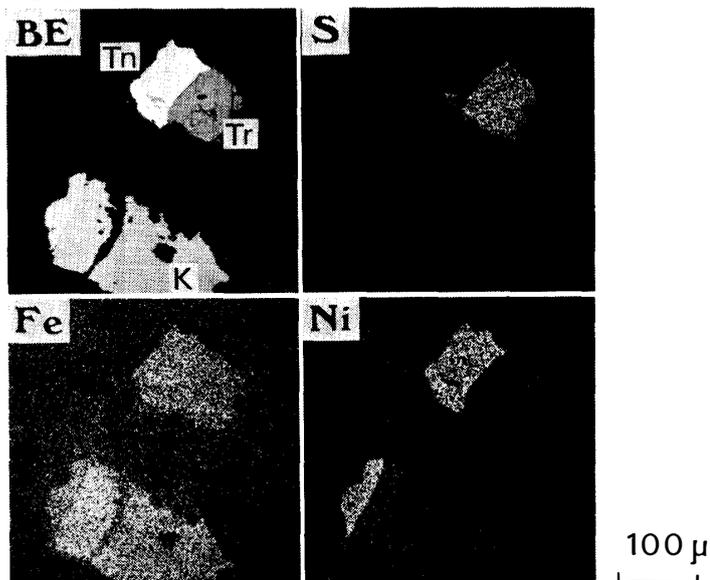
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Fig. 10b. Back-scattered electron photograph (BE) and characteristic X-ray images for S, Fe and Ni $K\alpha$ lines of coexisting metals and troilite in Yamato-74364. Abbreviations are the same as in Fig. 10a.

Table 6. Chemical compositions of troilites and Fe-Ni metals in Yamato-74364 chondrite.

	Troilite		Kamacite (α)		Taenite (γ)		
	I	II	I	II	I	IIa	IIb
Fe	64.09	63.81	94.29	93.65	51.16	64.31	57.00
Ni	0.11	0.04	5.90	5.91	49.35	35.61	43.03
Co	0.07	0.05	0.56	0.61	0.13	0.19	0.14
S	36.17	36.01	0.01	0.00	0.02	0.00	0.01
Total	100.44	99.91	100.76	100.17	100.66	100.11	100.18
Atomic %							
Fe	50.35	50.39	93.86	93.79	52.07	65.37	58.10
Ni	0.08	0.03	5.59	5.63	47.78	34.44	41.73
Co	0.05	0.04	0.53	0.58	0.13	0.18	0.14
S	49.51	49.54	0.02	0.00	0.03	0.00	0.03
$\frac{100 - X^{Ni}}{1 - X^{Ni}}$	0.08	0.03	5.92	5.97	91.50	52.53	71.60

I: microprobe analyses in Fig. 10a.

II: microprobe analyses in Fig. 10b.

IIa; co-existing with kamacite.

IIb; co-existing with troilite.

are plotted in the lower temperature field, while unequilibrated chondrites are in the relatively higher field from 700 to 900°C. On the other hand, silicate geothermometry of equilibrated chondrites by NAGAHARA (1979), TAKEDA *et al.* (1979), etc., using the paragenesis of olivine-orthopyroxene or orthopyroxene-clinopyroxene shows relatively higher temperatures between 900 and 1100°C, though metal-sulfide geothermometry in this study shows relatively low temperatures around 500°C in equilibrated chondrites. In this respect NAGAHARA (1979) considered that metal-sulfide paragenetic relations were reconstructed at lower temperatures after the formation of chondrites. The heterogeneity in composition of metal-sulfide in unequilibrated chondrite which indicates relatively high temperature suggests high temperature formation of initial chondrites. It is considered that the disagreement between silicate geothermometry and metal-sulfide one may be due to the difference of diffusion rate in both minerals. Generally, it is assumed that the metal-sulfide equilibrium had been maintained to the lower temperatures than silicate mineral in equilibrated chondrites, but in unequilibrated one the equilibrium had been stopped at high temperatures by rapid cooling or by other causes.

The present data on the unequilibrated chondrites will throw a light on the

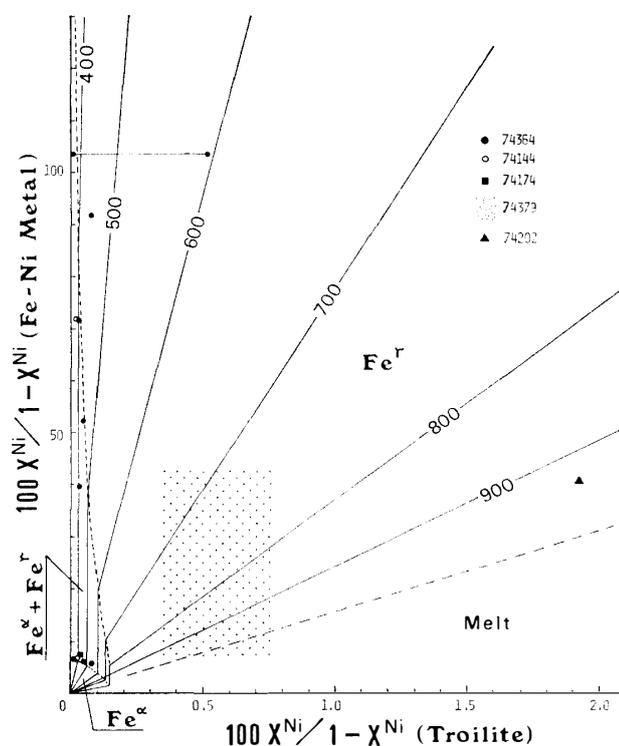


Fig. 11. Ni partition diagram at 1 atm between iron metals (α and γ) and troilite after BEZMEN *et al.* (1978). The isothermal lines are represented in centigrade degree.
 Fe^α : kamacite(α), Fe^γ : taenite(γ).

genetic discussion especially concerning their cooling rate, and further data on metal-sulfide equilibria of unequilibrated chondrites are expected.

4. Conclusions

A preliminary classification of ten Yamato chondrites from Antarctica was tried and the metal-sulfide equilibria in ordinary chondrites was discussed, based on the EPMA data obtained by a rapid method (YUSA, 1975). Chemical-petrologic classification of chondrites was made according to YANAI *et al.* (1978) with some improvement by adopting textural observation of back-scattered electron photographs of polished sections.

The main conclusions are summarized as follows;

1) The ten specimens are classified into:

Equilibrated chondrite;	H	74187
Moderately unequilibrated chondrites;	L	74144, 74174
	L(?)	694
	H	74364

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