OPAQUE MINERALS IN THE YAMATO-74191 CHONDRULES

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***Abstract*:** Opaque minerals occur often as phenocrysts in porphyritic chondrules. Troilite is common in comparison with metallic iron in chondrules, and is often distributed separately from metallic iron in a chondrule. Since some opaque minerals are included in silicate minerals, opaque minerals had crystallized in a chondrule before the crystallization of silicate minerals. Rare chromites are always in contact with troilites. These chromites, including some other meteoritic chromites, have cation deficiency in the B site. This cation deficiency may be interpreted by a substitution of $3Fe^{2+} = 2Cr^{3+} + \text{Vacancy}$. Chromites and olivines in chondrule crystallized in disequilibrium to each other.

1. Introduction

Opaque minerals occupy 10–30% of L and H chondrites (*e.g.*, KIMURA *et al.*, 1978) and therefore these are important constituents of chondritic meteorites. The significance of opaque minerals as a clue to understand the formation mechanism of chondrule from the primitive solar nebula and its thermal history have been discussed by many workers (*e.g.*, LARIMER and ANDERS, 1970; BLANDER, 1971).

We are also convinced that the origin of chondrules must be discussed on the basis of the study on opaque minerals in chondrules as well as silicate minerals. Thus, in this paper we present the data for the opaque minerals observed in the Yamato-74191 chondrules. The petrological studies of this meteorite, especially chondrules in it, have been carried out by IKEDA and TAKEDA (1979) and KIMURA and YAGI (1980).

2. Sample and Experimental Methods

We deal with the Yamato-74191 which belongs to the L3 group (YABUKI *et al.*, 1978; YANAI *et al.*, 1978). This meteorite is therefore regarded to preserve the original features when it formed in the primitive solar nebula. However, we must be still careful with generalization of the results obtained here to the cases of all unequilibrated chondrites.

All opaque minerals were identified by microscopic observation. We examined 143 chondrules in the Yamato-74191.

Chromites were analyzed with a JEOL JAX–50A electron probe microanalyzer. The acceleration voltage was 15 kV and the electron beam was about 2 μm in diameter. Correction was made after the method of BENCE and ALBEE (1968).

3. Opaque Minerals in Chondrules

We found only three kinds of opaque minerals in the Yamato-74191 as reported by YABUKI *et al.* (1978), *i. e.*, metallic iron, troilite, and chromite. They are common minerals in ordinary chondrites. Opaque minerals occupy 2.7 vol.% of chondrules in the Yamato-74191 (YABUKI *et al.*, 1978) and about 40% chondrules include some opaque minerals (Table 1). Dark-zoned chondrules originated secondarily (DODD and VAN SCHMUS, 1971) are excluded in Table 1. Troilite is more common than metallic iron in chondrules. We can not notice the relation between the type of condrules and the abundance of opaque minerals in chondrules in the Yamato-74191. Chondrule consisting of only opaque minerals is absent.

Table 1. Relative amount of opaque-bearing and -free chondrules.

Type of chondrule*	Opaque-free	Opaque-bearing			Total
		Fe	FeS	Fe+FeS	
Ol-Porphyritic	20(58.8)**	2(5.9)	5(14.7)	7(20.6)	34
Px-Porphyritic	45(60.8)	4(5.4)	15(20.3)	10(13.5)	74
Barred	3(33.3)	0(0)	2(22.2)	4(44.4)	9
Radiating	5(83.3)	0(0)	0(0)	1(16.7)	6
Cryptocrystalline	3(60.0)	0(0)	1(20.0)	1(20.0)	5
Total	76(59.4)	6(4.7)	23(18.0)	23(18.0)	128

* After KIMURA and YAGI (1980).
** Number in parenthesis is percent.

Troilite: This minerals is brown with anisotropism in the reflected light, and shows round to irregular shape, up to 0.2 mm in size (Figs. 1 and 2). Troilite occurs as the aggregate of randomly oriented fine grains stuck with each other, in contrast with the troilites in matrix which usually occurs as loose aggregate of fine grains (YABUKI *et al.*, 1978).

Metallic iron: It is light gray with isotropism in the reflected light. Spherical grains, up to 0.2 mm in size, are common in chondrules (Fig. 2). We do not find the distinct intergrowth between kamacite and taenite as observed by KIMURA *et al.* (1978) and NAGAHARA (1979) in equilibrated chondrites. When metallic iron and troilite are present in a chondrule, they are distributed separately from each other in general (Figs. 1 and 2). Their eutectic intergrowth as found in the Apollo 11 lunar rocks (SKINNER, 1971) is not common in chondrules.

Table 2. Analyses of chromite in A13 chondrule with that of average L3.

	A13					L3*
SiO_2	0.13	0.17	0.08	0.31	0.19	—
TiO_2	1.57	1.73	1.34	1.64	1.81	0.41
Al_2O_3	3.45	2.80	3.36	3.28	3.59	3.20
Cr_2O_3	58.06	57.99	60.48	59.78	58.00	61.90
V_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	0.60
FeO	31.10	31.16	30.50	30.10	30.06	30.80
MnO	0.64	0.69	0.62	0.45	0.67	0.58
MgO	1.68	1.73	1.81	1.66	1.79	2.59
CaO	0.01	0.01	0.01	0.01	0.07	—
Total	96.64	96.28	98.20	97.23	96.18	100.08
Cation (O=32)						
Si	0.039	0.051	0.024	0.092	0.057	—
Ti	0.354	0.393	0.297	0.366	0.408	0.090
Al	1.220	0.997	1.167	1.148	1.269	1.099
Cr	13.774	13.854	14.092	14.027	13.754	14.264
V	n.d.	n.d.	n.d.	n.d.	n.d.	0.140
Total	15.387	15.295	15.580	15.633	15.488	15.593
Fe	7.805	7.875	7.518	7.471	7.541	7.508
Mn	0.163	0.177	0.154	0.113	0.170	0.143
Mg	0.751	0.779	0.795	0.734	0.800	1.125
Ca	0.003	0.003	0.003	0.003	0.022	—
Total	8.722	8.834	8.470	8.321	8.533	8.776

* BUNCH *et al.* (1967).

Chromite: It is dark gray in the reflected light. In the Yamato-74191 only three chondrules include euhedral to subhedral fine-grained chromites, up to 0.01 mm in size. They are always in contact with troilites (Fig. 3). PEDERSEN (1979) found such an occurrence of chromites in sulfide blebs in the Disko. The chromites in the chondrule in the Yamato-74191 (A13) show grain-to-grain compositional heterogeneity (Table 2). The compositions of the chromites resemble that of the average chromite in L3 chondrites except for TiO_2 and MgO (BUNCH *et al.*, 1967). Large compositional heterogeneity of chromites is common in unequilibrated chondrites (BUNCH *et al.*, 1967). The cations in 6-fold coordination (B-site) for the chromites in A13 are deficient unless ferric iron is present (Table 2).

Relation between opaque and silicate phases in chondrules: In porphyritic chondrules of KIMURA and YAGI (1980), spherical to irregular shaped metallic iron and troilite are included in silicate minerals, or are distributed in glass (Figs. 1 and 2). Ophitic or intergranular texture of opaque and silicate minerals is rare in chondrules,

Fig. 1. A13 chondrule of pyroxene-porphyritic type consisting of silicate phases (gray), and fine round metallic iron (M) and irregular shaped troilite (T) including chromites. Reflected light. Long dimension of photograph = 0.8 mm.

Fig. 2. Metallic iron (M) and troilite (T) in A32 chondrule of pyroxene-porphyritic type. They are distributed independently in the marginal part of the chondrule. Long dimension of photograph = 1.0 mm. Reflected light.

Fig. 3. Troilite (T) and chromite (C) in A13. The irregular shaped troilite surround olivine grains (gray). Reflected light. Long dimension of photograph = 0.6 mm.

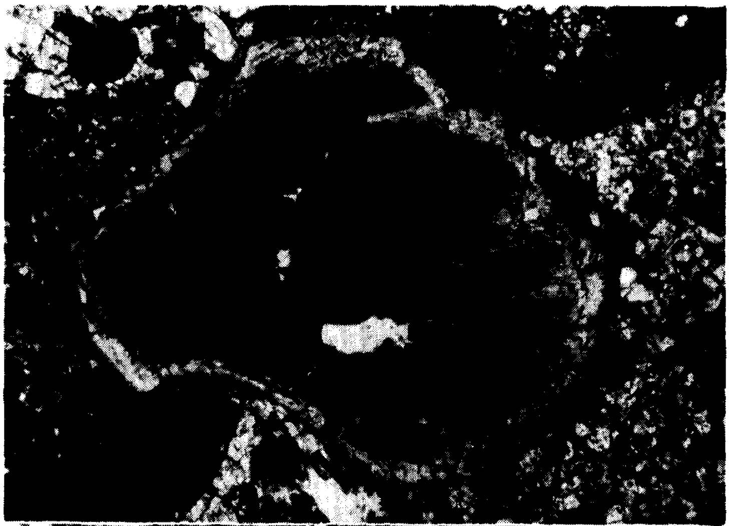

Fig. 4. Troilite (T) in B19 chondrule of cryptocrystalline type. The troilite elongates parallel with very fine laths of pyroxene. Long dimension of photograph = 1.1 mm.

Fig. 5a. A42 chondrule of cryptocrystalline type. Metallic iron (dark) has broken the left portion of this chondrule by collision. Long dimension of photograph = 1.6 mm.

Fig. 5b. A part of Fig. 5a. Metallic iron (white) has collided with A42 (gray). Very fine fused spherules of metallic iron are distributed around the broken side of A42. Reflected light. Long dimension of photograph = 0.8 mm.

although DUKE (1965) found these textures in some basaltic achondrites and interpreted that such a metal formed during magmatic crystallization. Opaque minerals as well as silicate minerals often occur as phenocrysts in the Yamato-74191 chondrules (Fig. 2).

Opaque minerals in barred, radiating, and cryptocrystalline chondrules elongate parallel with the laths of silicate minerals (Fig. 4), or are included in silicate minerals mainly in the marginal parts of chondrules.

Average composition of olivines in A13 chondrule is $Fo_{76.6}$. Since olivines coexist with chromites whose compositions are given in Table 2, we can calculate the average temperature of equilibrium between them. The temperature is surprisingly low, *i. e.*, 738K, using the method of ROEDER *et al.* (1979).

There is one chondrule (A42) which is partly broken by a collision with metallic iron in the Yamato-74191 (Fig. 5a). Very fine metal spherules are present randomly around the broken side of A42 (Fig. 5b).

4. Discussion

4.1. *Metallic iron and troilite*

From only textural evidences as mentioned before, we can not deduce the origin of opaque minerals in chondrules. However, it is evident that opaque minerals had been generally present in molten droplets before silicate minerals began to crystallize, because opaque minerals elongate parallel to the laths of silicate minerals, or are included in olivines and pyroxenes.

However, opaque minerals rarely entered into a solidified chondrules by collision. For A42 chondrule, fine metal spherules are distributed in the chondrule around the broken side by collision with metallic iron.

4.2. *Chromite*

Chromites are present in ordinary chondrites, achondrites, stony irons, and silicate inclusions in iron meteorites (BUNCH *et al.*, 1967; BUNCH and KEIL, 1971). If trivalent cations enter into the B site and divalent cations into the A site, we find cation deficiency in the B site of chromites in A13 chondrule, ordinary chondrites, and some basaltic achondrites (Fig. 6a). We assume that minor Ti forms inverse-type ulvöspinel molecule as Ti^{4+}. However, if Ti enters completely into the B site as Ti^{4+} or Ti^{3+}, the cation deficiency in the B site still remains (Table 2).

BUNCH *et al.* (1967) and TAKEDA *et al.* (1975) supposed that a part of Fe is present in the B site as Fe^{3+} for ordinary chondrites and a diogenite. However, estimated oxygen fugacities of meteorites may not support such an idea. The oxygen fugacity during the genesis of basaltic achondrites was controlled by equilibration of silicate melts with metallic iron (STOLPER *et al.*, 1979). WILLIAMS (1971) pointed out the similarity of oxidation state of the equilibrated ordinary chondrites to the one

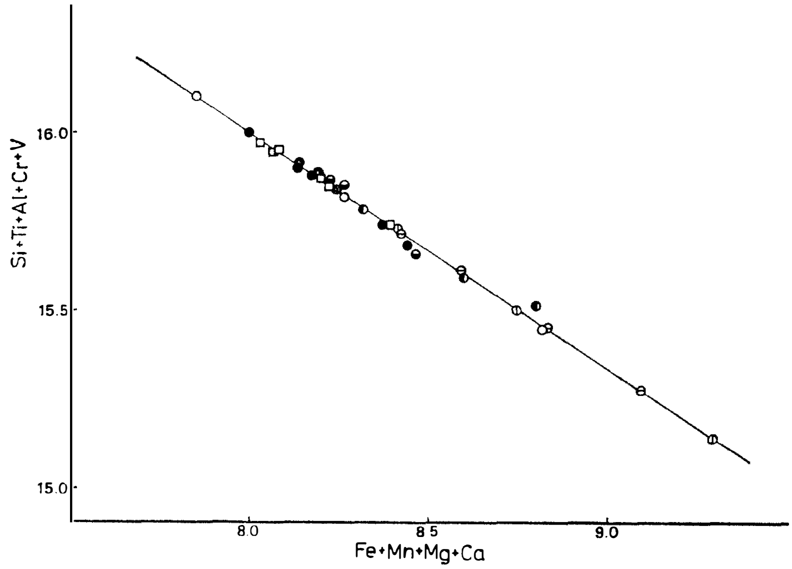

Fig. 6a. Fe+Mn+Mg+Ca versus Si+Ti+Al+Cr+V for meteoritic chromites. Category of meteorites: A13 ; ●, basaltic achondrites ; □ (after BUNCH *and* KEIL, *1971 ;* TAKEDA *et al., 1975, 1978), H3 ; ○, H4–6 ; ◎, L3 ; ⊖, L4–6 ; ◒, LL3 ; ⦶, LL4–6 ; ◐ (*BUNCH *et al., 1967). Average compositions of the chromites in petrologic types 4, 5, and 6 chondrites are plotted. The line corresponds to a substitution of the type 3 $(Mg, Fe)^{2+} = 2(Al, Cr)^{3+}$ + Vacancy, suggested by* PEDERSEN *(1978).*

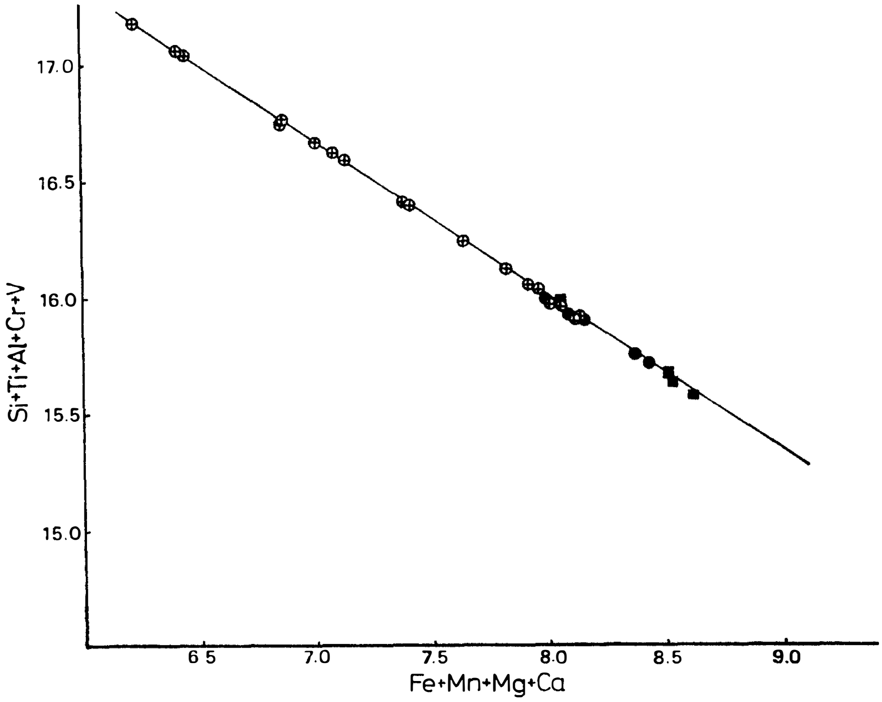

*Fig. 6b. Fe+Mn+Mg+Ca versus Si+Ti+Al+Cr+V for the chromites from A13 (●), and from shale xenoliths (⊕) (*PEDERSEN, *1978) and sulfide blebs (■) (*PEDERSEN, *1979) in the Disko volcanic rocks. The line coincides with that in Fig. 6a.*

atmosphere graphite surface. The presence of metallic irons in chondrules suggests that the oxygen fugacity during the crystallization of chondrules may have been also very low. We may exclude the presence of Fe^{3+} in these chromites.

Instead of the above-mentioned hypothesis on the presence of Fe^{3+} in chromites, a preferred hypothesis on this problem is discussed. PEDERSEN (1978) noticed that spinels in shale xenoliths in the native iron-bearing andesite from Disko show the cation deficiency in the A site, and assumed that the composition of spinels deviates from stoichiometry through a substitution of 3 $(Mg, Fe)^{2+} = 2(Al, Cr)^{3+} + \text{Vacancy}$ (Fig. 6b). Since some meteoritic chromites lie on the extension of the line showing this substitution, their cation deficiency in the B site can be also interpreted by such a type of substitution, although in the opposite direction to that in the A site by PEDERSEN (1978). ALPER *et al.* (1962, 1964) showed in their experiments that the compositions of spinels, $MgAl_2O_3$ and $MgCr_2O_3$, deviate from stoichiometry toward MgO at high temperatures. If such a deviation also occurs in spinels in the system FeO-$FeCr_2O_3$, the non-stoichiometry of the meteoritic chromites may be explained by the substitution as proposed by PEDERSEN (1978). The observation that chromites are always included in troilites in the Yamato-74191 suggests that non-stoichiometric chromites formed in the Fe-rich melt. PEDERSEN (1979) also found non-stoichiometric chromites toward FeO in the sulfide blebs in the Disko basalt (Fig. 6b).

The glass in A13 chondrule does not devitrify in spite of the very low equilibrated temperature between the olivine and chromite as mentioned before. Therefore, the olivines and chromites in A13 crystallized in disequilibrium to each other. However, it is not yet clear whether the chromites also crystallized in the chondrule, or the chromites entered into A13 without remelting.

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