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ORIGIN OF OPAQUE MINERALS IN AN UNEQUILIBRATED ENSTATITE CHONDRITE, YAMATO-691

Makoto KIMURA

Department of Earth Sciences, Faculty of Science, Ibaraki University, 1–1, Bunkyo 2-chome, Mito 310

Abstract: This paper describes the petrographic and chemical features of opaque minerals in an unequilibrated enstatite chondrite, Yamato-691, and discusses the genetic relations among opaque minerals. Most of them occur in and/or around Fe-Ni metal. Opaque minerals formed from the primary metal alloy through various reactions such as exsolution and reaction with surrounding sulfur gas. The sequence of the formation is graphite, schreibersite, troilite with perryite and sphalerite in metal alloy. Niningerite and oldhamite formed independently and attached to the metal alloy at the high temperatures. The primary metal alloy had condensed in the nebula under a very low oxygen fugacity condition, and included P, Si, Cr, Mn and Ti, in addition to Fe, Ni and Co. The condensation sequences of minerals calculated previously under the oxygen depletion condition agree with the results obtained here in general. Fe-Ni metal frequently contains silicate inclusions which are mostly silica minerals. They formed later through the oxidization process of Fe-Ni metal under slightly more oxidizing conditions than the primary stage.

1. Introduction

Enstatite chondrites show several unique features which distinguish them from ordinary and carbonaceous chondrites. These indicate that enstatite chondrites formed under an extraordinarily reduced condition. The opaque minerals in particular have unique compositions and characterize the unique condition of the origin of these chondrites.

At present a few unequilibrated enstatite chondrites, such as Qingzhen and Yamato-691 (Y-691 hereafter), are known. OKADA (1975), NAGAHARA (1985) and others have already studied Antarctic Y-691 chondrite petrologically. They clarified various features and the formation condition of the constituent units in it. In addition to such results, this paper describes especially opaque minerals in it in detail, and discusses the genetic relations among opaque minerals and their formation condition.

2. Petrography of Y-691

Y-691 chondrite, as well as Qingzhen, is classified as E3 (PRINZ *et al.*, 1984). It contains sharply defined chondrules (OKADA, 1975), and does not show evidence for severe shock metamorphism and weathering. All these features show that Y-691 relates its primitive nature.

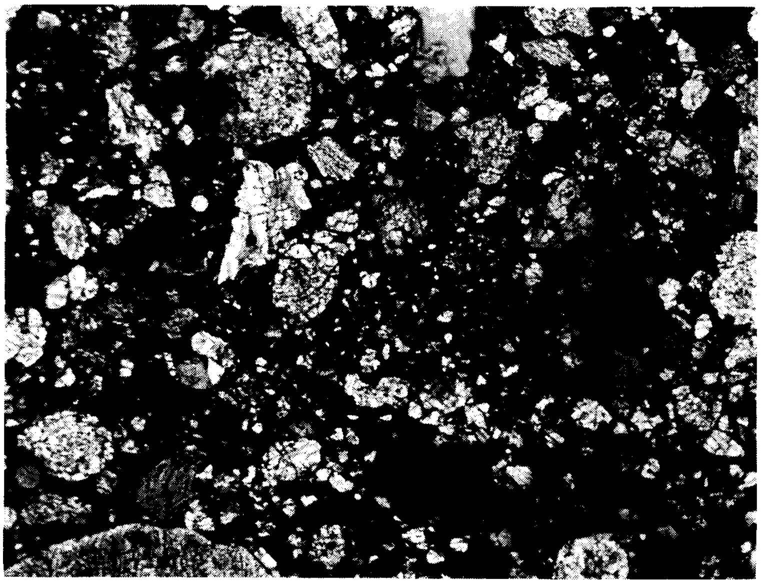

Fig. 1. Thin section of Y-691. Sharply defined chondrules and fragments are abundant. Long dimension of photograph, 2.5 mm.

Y-691 chondrite consists of chondrules, silicate and opaque mineral fragments and matrix (Fig. 1). Such a classification of chondrite units is after KIMURA (1983). Opaque minerals in Y-691 studied here are Fe-Ni metal, graphite, perryite, schreibersite, troilite, niningerite, oldhamite, sphalerite, daubreelite, djerfisherite and alkali-Cr-sulfide. Silicate phases are pyroxene, olivine, plagioclase, glass, silica mineral and roedderite.

Chondrules in Y-691 show mainly irregular to ellipsoidal shapes. Pyroxene-porphyritic chondrules are most common in chondrules. Silicate mineral fragments (SMF's hereafter) are subhedral to anhedral pyroxene, olivine, plagioclase and silica mineral. They fill the interstices among chondrules and coarse opaque mineral fragments. Chondrules and SMF's frequently contain opaque minerals. The kind and mode of occurrence of them are similar to those in opaque mineral fragments.

Opaque minerals in Y-691 are assembled in fragments whose size and shape vary widely. However, the size, shape and constituent minerals change gradually from coarse to fine fragments. Therefore, all these assemblages are called opaque mineral fragments (OMF's hereafter) in this paper. Some coarse prominent OMF's are called "nodules" by NAGAHARA (1985). The matrix of this chondrite consists of fine-grained silicate and opaque minerals filling the interstices among fragments and chondrules.

3. Petrography and Mineralogy of OMF

Sixteen hundred OMF's whose sizes are above 50 microns, were observed in order to describe the phase assemblages and mode of occurrence. Although they vary in size and shape, most of OMF's are fine-grained and irregular-shaped, some OMF's (so-called nodules) are coarse, up to 0.6 mm in size, and round or ellipsoidal in shape. Many fragments consist of Fe-Ni metal and troilite with minor amounts of other opaque minerals. Coarse fragments tend to contain many kinds of minerals. The most representative assemblage of OMF's is Fe-Ni metal, troilite, perryite and schreibersite. OMF's often include fine-grained silicate minerals (silicate inclusions).

3.1. Opaque minerals in OMF's

Figure 2 shows the petrographic relations between opaque minerals in OMF's. Fe-Ni metal, chiefly kamacite, is the most common opaque mineral in OMF's. This is usually accompanied by other opaque minerals which occur around Fe-Ni metal and as inclusions within it. Table 1 shows the average chemical compositions of opaque minerals in Y-691. The chemical compositions of minerals vary somewhat from OMF to OMF, although minerals within a given OMF are homogeneous in composition and hardly show chemical zoning. The compositions of opaque minerals, up to several microns in size, are not different from those of OMF's in matrix.

Fe-Ni metals in Y-691 contain Si as in the other enstatite chondrites. Their P-contents are lower than those in equilibrated enstatite chondrites (KEIL, 1968).

Perryite is common accessory mineral in OMF's and it is necessarily included and/or

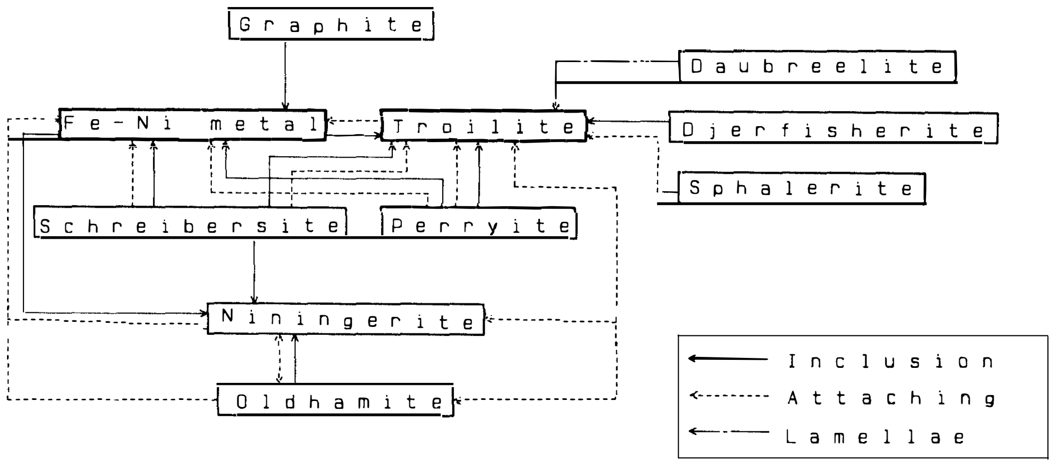

Fig. 2. Summary of the petrographic relations between opaque minerals in OMF's.

Table 1. Chemical compositions of opaque minerals in OMF's (wt%).

	Data	Mg	Si	P	S	Ca	Ti	Cr	Mn	Fe	Co	Ni	Zn	Total
Fe-Ni metal	203		2.07	0.03						94.50	0.35	2.82		99.77
			0.22	0.05						1.20	0.14	0.63		
Troilite	85				36.08		0.22	1.30	0.03	61.43				99.06
					0.65		0.09	0.74	0.04	1.05				
Perryite	58		11.45	2.79						9.06	0.01	75.71		99.02
			0.36	0.59						1.66	0.04	1.73		
Schreibersite	43		0.15	14.53						70.25	0.13	14.87		99.93
			0.05	0.48						1.48	0.12	1.45		
Niningerite	16	30.53			49.06	0.36		0.17	5.64	13.26				99.02
		1.21			1.27	0.06		0.06	0.44	1.20				
Oldhamite	9	0.40			43.78	52.96			0.07	0.54				97.75
		0.08			0.48	0.62			0.04	0.24				
Sphalerite	7	0.79			34.27				1.74	27.58		0.36	33.71	98.45
		0.14			0.28				0.65	1.05		0.35	0.79	

Upper: wt%. Lower: standard deviation.

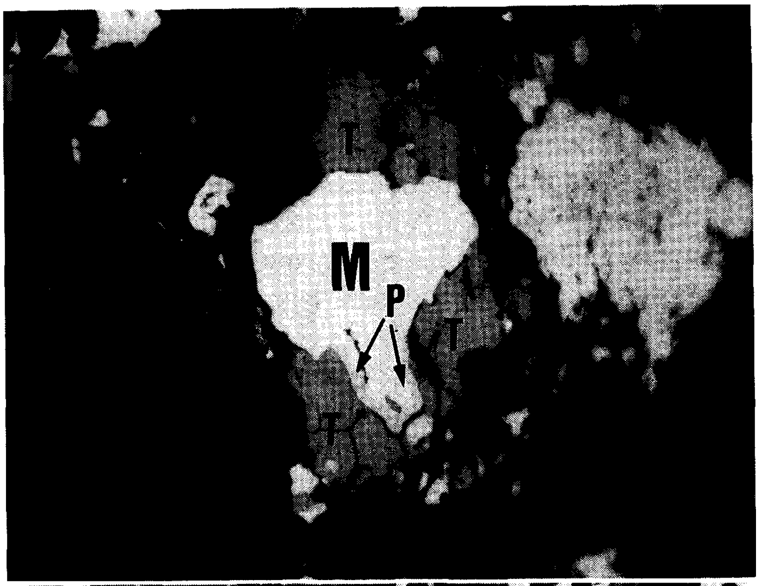

Fig. 3. An OMF consisting of Fe-Ni metal (M), troilite (T) and perryite (P). Perryite occurs as thin band along the boundary between Fe-Ni metal and troilite. Reflected light. Long dimension of photograph, 0.25 mm.

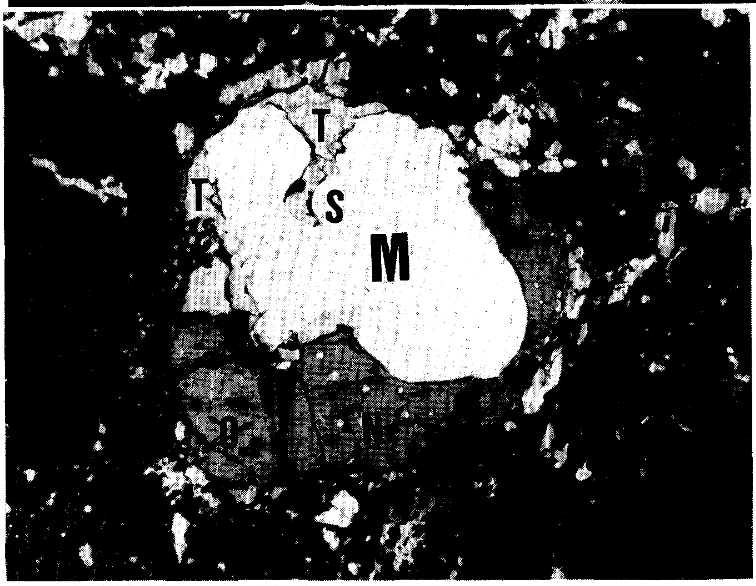

Fig. 4. Intergrowth of Fe-Ni metal (M), troilite (T), schreibersite (S), niningerite (N) and oldhamite (O) in an OMF. Niningerite and oldhamite attach to Fe-Ni metal. Niningerite includes fine spherules, whereas oldhamite does not include them. Troilite surrounds metal and schreibersite. Reflected light. Long dimension of photograph, 0.5 mm.

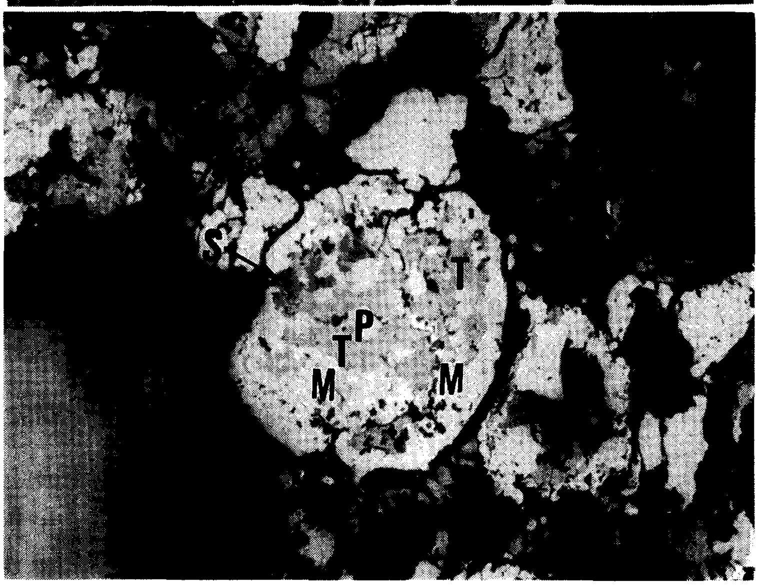

Fig. 5. Intergrowth of troilite (T) and sphalerite (S) in Fe-Ni metal (M) in an OMF. Troilite coexists with perryite (P), too. Reflected light. Long dimension of photograph, 0.4 mm.

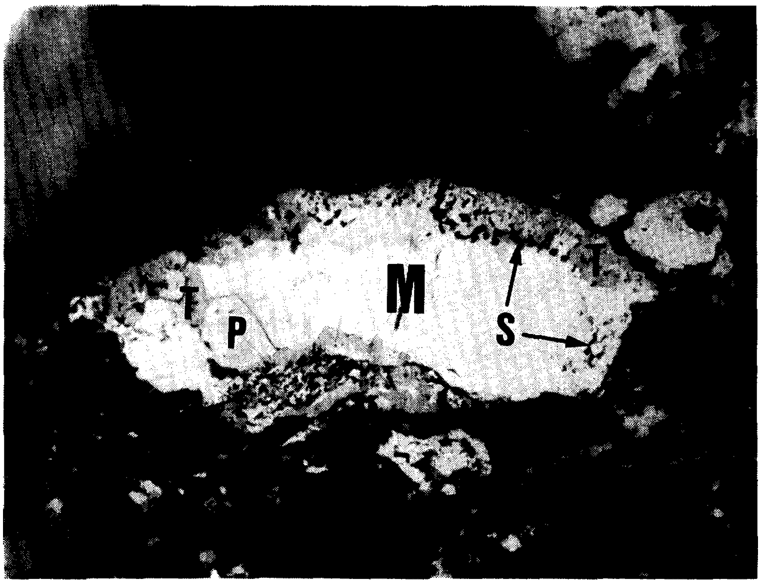

Fig. 6. An OMF consisting of Fe-Ni metal (M), troilite (T) and perryite (P). Metal contains fine-grained silica mineral inclusions (S), distributed in the peripheral part of Fe-Ni metal. Reflected light. Long dimension of photograph, 0.5 mm.

attached in Fe-Ni metal or troilite. Three modes of occurrence of perryite are found. The most common occurrence is as a complex intergrowth with troilite, as observed by REED (1968). The second occurrence is as fine-grained perryites which are independently included in Fe-Ni metal. Rare perryites occur as thin bands along the boundary between Fe-Ni metal and troilite in a few OMF's (Fig. 3). Such occurrences were also observed in Qingzhen (RAMBALDI *et al.*, 1986a).

Schreibersite, as well as perryite, does not occur independently and is mainly included and/or attached in Fe-Ni metal. The mode of intergrowth with troilite is different from perryite. Although both troilite and schreibersite often occur in a given OMF, intimate intergrowths between them are rarely found. Schreibersite is occasionally surrounded by troilite in some OMF's (Fig. 4). Schreibersites and perryites are homogeneous in general within a given OMF, although they show compositional variability (Fe/Ni ratio) on the whole in Y-691.

Fine-grained graphite is always included in Fe-Ni metal and is irregular to ellipsoidal in shape. Graphite occurs in various OMF's, in spite of their size and mineral assemblage.

Troilites are abundant next to Fe-Ni metal in opaque minerals in Y-691. They occur around Fe-Ni metal in OMF's and are present in metal with intimate intergrowth with perryite and sphalerite. Some irregular-shaped OMF's comprise mostly troilite with perryite and so on. Troilites contain small amounts of Ti and Cr.

Niningerite is the next most common sulfide mineral after troilite as shown by KEIL (1968), and is typically attached to Fe-Ni metal and troilite (Fig. 4). In a few OMF's it occurs along the boundary between Fe-Ni metal and troilite. Occasionally niningerites are surrounded by troilite. Fine spherical inclusions, up to several microns, are often found in some niningerites, as already found by OKADA (1975). They are Fe-Ni metal and schreibersite, whose chemical compositions are not different from the other ones in OMF's. The Fe-contents in niningerites in Y-691 are lower than those in EH4 chondrites (KEIL, 1968).

The mode of occurrence of oldhamite is similar to that of niningerite, although oldhamite is less common. Oldhamite often attaches to OMF's with niningerite (Fig. 4). Rarely niningerite surrounds oldhamite. Inclusions of the other minerals is not yet found in oldhamite, in contrast with niningerite.

Although sphalerite is not a common mineral, irregular-shaped sphalerites, up to 10 microns in size, are often included in OMF's, where they occur intimately with troilite and perryite (Fig. 5). Sphalerites contain small amounts of Mg and Mn. Qualitative analysis shows that these sphalerites contain very little Ga, different from some sphalerites in Qingzhen (RAMBALDI *et al.*, 1986a).

The abundance of daubreelite is low, and it occurs in troilite as thin exsolution lamella. Such an occurrence is different from that in equilibrated enstatite chondrites, such as Y-74370 (EH4) (KIMURA, unpublished data), in which coarse-grained daubreelites are often intergrown with troilite.

Rare djerfisherites, irregular in shape, are always included in troilite. Their chemical compositions are 0.9–1.1 wt% Na, 6.9–7.3 K, 45–46 Fe, 0.9–1.0 Ni, 3.7–4.8 Cu, and 33.8–34.4 S, which agrees roughly with those in St. Marks (FUCHS, 1966) and Qingzhen (EL GORESY *et al.*, 1983).

Fine-grained alkali-Cr-sulfide occurs as inclusion with troilite, Fe-Ni metal and perryite in a few OMF's . The compositions are 0.8–1.3 wt% Na, 1.6–1.9 K, 1.7–3.1 Cu, 34.0–36.5 Cr, 0.5–1.0 Fe and 42.1–43.8 S. This composition does not correspond to Na-Cr-sulfides in Qingzhen (EL GORESY *et al.*, 1983). In addition, these minerals contain about 13 wt% oxygen, which was determined by semi-qualitative analysis. However, fluorine, nitrogen and chlorine are not detected. Their contents of Cr, S and O are similar to those of dark gray phase in the Norton County enstatite achondrite which was interpreted as a terrestrial weathering product from caswellsilverite (OKADA and KEIL, 1982). OKADA *et al.* (1985) called this mineral schöllhornite.

The above-mentioned minerals in Y-691 are mostly observed in Qingzhen (EH3). The chemical compositions and occurrence of opaque minerals are also similar to those in Qingzhen of RAMBALDI *et al.* (1983) and EL GORESY *et al.* (1983), especially such as the Cr content in troilite, P in Fe-Ni metal and Fe in niningerite except for Mn in niningerite, and clearly different from those in equilibrated enstatite chondrites (KEIL, 1968).

3.2. *Silicate minerals in OMF's*

OMF's often contain several silicate inclusions, up to about 10 microns in size (Fig. 6). Silicate inclusions are present in Fe-Ni metal, and they usually form less than about 1 vol% in OMF's. Whether the inclusion is present or not does not depend on the opaque mineral assemblage; coarse OMF's frequently contain silicate inclusions. These silicate minerals, irregular to ellipsoidal in shape, comprise mostly a silica mineral and pyroxene, with minor amounts of albitic plagioclase and roedderite. All inclusions, above about a few microns in size, were analyzed in order to obtain not only the chemical compositions but also the abundance of minerals. Figure 7 shows the relative abundance of them, which probably reflects the modal composition of silicate inclusions in OMF's. Silica mineral is more abundant, in comparison with pyroxene, and olivine and glass are not found in OMF's, which is different from the modal composition of

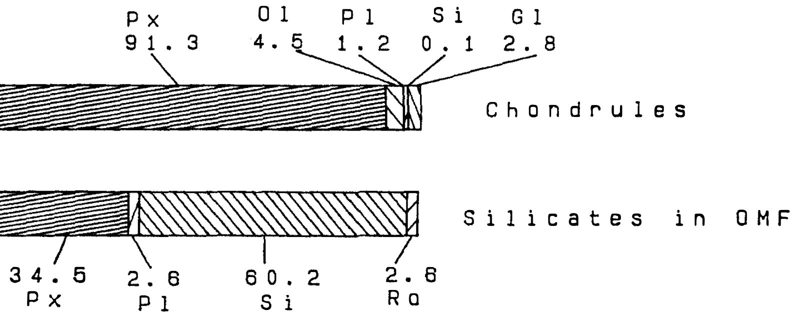

Fig. 7. The diagram for the abundance of silicate minerals in OMF's and chondrules (vol%, after OKADA, *1975). Figures in OMF's show percentages of grains. Total number of grains in OMF's is 113. Px: pyroxene, Ol: olivine, Pl: plagioclase, Sl: silica minerals, Gl: glass, Ro: roedderite.*

Table 2. Chemical compositions of silicate minerals in OMF's (wt%).

	Data	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
Pyroxene	14	57.15	0.07	1.11	0.18	3.61	0.11	36.20	0.78	0.20		99.41
		2.01	0.05	1.18	0.17	2.04	0.07	2.93	0.88	0.19		
Plagioclase	2	67.92		18.40		0.88	0.02	0.06	0.08	11.52	0.11	98.99
		2.60		0.95		0.08	0.03	0.01	0.06	0.75	0.04	
Roedderite	6	69.06		0.94		2.47		20.23	0.08	3.28	3.77	99.83
		1.10		0.24		0.56		0.89	0.07	0.15	0.23	

Upper: wt%. Lower: standard deviation.

chondrules (OKADA, 1975). Roedderite is present as only silicate inclusions in OMF's.

The chemical compositions of pyroxene, roedderite and plagioclase are shown in Table 2. The composition of pyroxenes (En_{86-98}) is consistent with those in chondrules and SMF's (En_{79-99}). Plagioclase is almost pure albite. Roedderite has a lower average atomic Na/(Na+K) ratio (0.56) than that (0.65) of FUCHS *et al.* (1966), but similar to that in Qingzhen (RAMBALDI *et al.*, 1986b). RAMBALDI *et al.* found roedderite within metal or sulfide in Qingzhen which is connected by oxide and silicate veins to the surrounding matrix. However, roedderites in Y-691 are completely included within Fe-Ni metal.

3.3. Modal and bulk compositions of OMF's

The modal compositions of some representative OMF's are estimated from the areas of minerals in each OMF (Table 3). These OMF's (nodule) are coarse in size, and spherical or ellipsoidal in shape, and consist of common opaque minerals as mentioned above. Fe-Ni metals are dominant in every OMF, and the other minerals vary widely in amount. Table 3 shows the bulk compositions of some OMF's obtained from the modal and average mineral compositions. These bulk compositions exclude the compositions of very small amounts of silicate inclusions. The bulk compositions are not related to whether or not OMF's contain silicate inclusions and graphite.

Table 3. Modal and chemical compositions of OMF's (wt%).

OMF	51	85	104	105	178	182	242	249	279	285	319	407
[Mode]												
Fe-Ni metal	93.63	92.09	92.03	95.12	59.76	88.14	89.36	89.91	74.82	93.93	88.36	92.46
Troilite	2.19	0.00	0.79	0.30	22.78	2.82	10.32	4.54	0.00	2.36	4.44	1.74
Perryite	0.37	3.73	1.53	3.54	16.14	2.78	0.31	4.10	7.65	1.81	7.20	5.81
Schreibersite	3.81	0.92	4.31	1.04	0.00	5.54	0.00	1.44	17.53	1.43	0.00	0.00
Sphalerite	0.00	1.49	0.00	0.00	1.32	0.00	0.00	0.00	0.00	0.47	0.00	0.00
Graphite	0.00	1.77	1.35	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00
[Bulk]												
Si	1.93	2.22	2.11	2.55	3.11	2.00	1.91	2.34	2.35	2.18	2.65	2.62
P	0.55	0.26	0.66	0.24	0.35	0.88	0.01	0.12	2.70	0.27	0.23	0.16
Ti	0.00	0.00	0.00	0.00	0.05	0.01	0.02	0.01	0.00	0.01	0.01	0.01
Cr	0.02	0.00	0.01	0.00	0.24	0.03	0.14	0.05	0.00	0.02	0.04	0.03
Fe	91.96	87.49	91.55	90.53	71.98	88.72	91.25	88.60	84.68	91.56	87.31	89.04
Co	0.40	0.34	0.19	0.41	0.22	0.31	0.31	0.41	0.31	0.36	0.22	0.32
Ni	4.08	5.66	3.78	5.46	14.05	5.53	2.43	5.58	10.50	4.44	7.49	7.75
S	0.81	0.51	0.29	0.11	8.69	1.04	3.69	1.65	0.00	1.01	1.60	0.62
Zn	0.00	0.51	0.00	0.00	0.44	0.00	0.00	0.00	0.00	0.16	0.00	0.00
C	0.00	1.77	1.35	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.76	98.76	99.95	99.30	99.13	99.26	99.76	98.76	100.53	100.00	99.55	100.53

OMF	440	461	468	494	512	627	629	669	730	758	774	488
[Mode]												
Fe-Ni metal	79.91	70.39	92.56	84.90	96.64	84.87	87.63	86.83	95.16	75.62	61.42	67.77
Troilite	12.33	20.15	2.51	0.00	0.00	0.00	6.65	5.22	2.39	11.52	34.86	25.63
Perryite	0.63	9.12	3.73	3.55	3.36	8.38	3.84	1.81	0.63	5.06	3.71	0.00
Schreibersite	7.13	0.00	1.20	11.55	0.00	6.75	1.87	5.95	0.48	7.80	0.00	6.60
Sphalerite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00
Graphite	0.00	0.34	0.00	0.00	0.00	0.00	0.00	0.00	1.34	0.00	0.00	0.00
[Bluk]												
Si	1.78	2.51	2.20	2.17	2.66	2.59	2.23	1.75	1.94	2.17	1.77	1.51
P	1.02	0.34	0.31	1.81	0.13	1.30	0.41	0.85	0.02	1.31	0.11	0.96
Ti	0.04	0.05	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.02	0.09	0.09
Cr	0.16	0.25	0.03	0.00	0.00	0.00	0.08	0.09	0.03	0.11	0.35	0.39
Fe	87.42	80.39	91.64	89.13	92.48	86.79	88.91	88.33	92.53	84.59	79.44	84.65
Co	0.23	0.20	0.12	0.30	0.28	0.26	0.32	0.38	0.29	0.20	0.22	0.23
Ni	4.02	8.54	5.54	6.80	4.69	9.24	5.44	3.85	2.85	7.54	4.84	2.68
S	4.34	7.33	0.90	0.00	0.00	0.00	2.42	1.96	0.87	4.20	12.51	9.14
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00
C	0.00	0.34	0.00	0.00	0.00	0.00	0.00	0.00	1.34	0.00	0.00	0.00
Total	98.99	99.94	100.74	100.20	100.24	100.18	99.83	97.29	99.88	100.14	99.33	99.66

Table 3 (continued).

OMF	804	973	1000	1111	1178	1287	1313	1317	1321	1370	1481
[Mode]											
Fe-Ni metal	84.01	59.57	75.49	79.51	97.45	84.30	82.61	75.73	90.28	94.13	95.79
Troilite	13.80	36.71	12.40	10.99	1.01	14.51	9.50	15.58	6.63	2.63	0.45
Perryite	0.53	1.18	1.45	1.30	0.30	0.72	2.05	2.15	0.23	0.65	0.00
Schreibersite	1.42	1.96	10.66	8.21	1.24	0.47	5.85	6.54	2.15	2.59	3.77
Sphalerite	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Graphite	0.00	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.00	0.00
[Bluk]											
Si	2.02	1.21	1.48	1.69	2.07	1.71	1.66	1.70	1.65	2.06	1.87
P	0.23	0.32	1.61	1.23	0.18	0.00	0.84	0.97	0.00	0.39	0.53
Ti	0.06	0.09	0.03	0.04	0.00	0.03	0.02	0.04	0.00	0.00	0.00
Cr	0.16	0.39	0.15	0.15	0.01	0.15	0.10	0.15	0.07	0.03	0.00
Fe	88.81	81.32	87.83	88.28	93.45	88.98	88.28	86.54	90.55	93.31	94.24
Co	0.29	0.19	0.28	0.33	0.25	0.35	0.27	0.18	0.17	0.41	0.25
Ni	2.92	2.41	4.55	3.59	3.43	2.09	3.08	2.70	2.01	3.57	3.22
S	5.07	13.28	4.58	4.06	0.37	5.30	3.37	5.53	2.35	0.95	0.16
Zn	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.72	0.00	0.00
Total	99.64	99.80	100.52	99.37	99.76	98.62	97.63	97.80	97.52	100.73	100.27

4. Phase Relations between OMF Minerals

4.1. Formation of opaque minerals

The origin of opaque minerals in OMF's can be estimated from the above results and the experimental phase equilibria. Since most of the opaque minerals occur in or around Fe-Ni metal, the origin of these minerals must be considered as associated with the formation of Fe-Ni metal.

The common occurrence of graphite is as an inclusion in Fe-Ni metal. It is difficult to estimate from the mode of occurrence whether graphite is the decomposition product of cohenite or not, and whether graphite (cohenite?) was primarily included in metal or a secondary product from C-bearing metal. However, we can understand the phase relations between Fe-Ni metal and graphite in OMF's, using the bulk compositions, and the Fe-C (BRETT, 1967) and Fe-Ni-C systems of ROMIG and GOLDSTEIN (1978). Whether graphite or cohenite is primarily present or not, only C-bearing taenite is present, if the system is held at about 1000–1200°C. Later graphite (cohenite?) is exsolved from taenite at about 900°C. Finally the assemblage of kamacite + graphite forms.

Schreibersite is included in Fe-Ni metal. The bulk compositions of OMF's contain 0.6 wt % P on an average. Accordingly, schreibersites were exsolved from Fe-Ni metal at about 700°C on the basis of the Fe-Ni-P phase diagram (DOAN and GOLDSTEIN, 1970; ROMIG and GOLDSTEIN, 1980).

The occurrence of troilites suggests that they were originated around metal in OMF's. Since troilites surround schreibersite in a few OMF's, it is evident that troilite formed after the formation of schreibersite at about 700°C. Troilites formed through the reaction between Fe-Ni metal and sulfur gas below 700°C.

Since perryites are typically intergrown with troilite, it is probable that most of them formed simultaneously with troilite. Especially, the thin band of perryite along the boundary between troilite and Fe-Ni metal supports this idea. It is probable that Ni and Si from Fe-Ni metal formed perryite with Fe and P when troilite formed around Fe-Ni metal. However, some perryites are independently included in Fe-Ni metal. It is possible that these perryites were directly exsolved from Fe-Ni metal, although the temperature is uncertainty.

Sphalerites in Y-691 accompany troilite in OMF's and the origin of sphalerite seems to be related to that of troilite. When primitive metal alloy reacted with sulfur gas, sphalerite probably formed. From the phase diagram of Fe-Zn-S (BARTON and TOULMIN, 1966), the sequence of the formation of sphalerite and troilite is Zn-bearing metal alloy, through metal+sphalerite, to metal+sphalerite+troilite with increasing sulfurization. The equilibration temperature of sphalerite with Fe-Ni metal and troilite in Y-691 is estimated at about 300–400°C from the method of HUTCHISON and SCOTT (1983), assuming low total pressure. However, this temperature is the final equilibration temperature and does not indicate the formation temperature of sphalerite.

The occurrence of daubreelite shows that it was exsolved from troilite. EL GORESY and KULLERUD (1969) showed the phase equilibria of Fe-Cr-S system at 700 and 600°C. Even at 600°C troilite may contain comparatively high levels of Cr. Therefore, although, the exsolution temperature of daubreelite cannot be determined accurately, it is probable that daubreelite formed at temperatures lower than 600°C.

FUCHS (1966) suggested that djerfisherite with pyroxene, metal and silica mineral formed through the reaction between roedderite and troilite. However, the occurrence of djerfisherite in Y-691 exlcudes such a reaction. Djerfisherite necessarily accompanies troilite, which suggests that it formed through troilite, alkali-bearing phase and Cl-bearing phase.

Niningerite and oldhamite seem to have directly condensed from nebular gas and attached to primitive Fe-Ni metal, judging from their occurrence. The evidences for the other reactions such as between Mg-bearing silicate and S-phase are not observed. Troilite often surrounds niningerite. Troilite and perryite are not found in niningerite as inclusions like Fe-Ni metal and schreibersite. Therefore, niningerite must have formed after the formation of schreibersite at about 700°C, and before the formation of troilite and perryite. The equilibration temperature of niningerite and troilite is below about 400°C from the phase equilibria of (Ca, Mg, Mn, Fe)S of SKINNER and LUCE (1971). This temperature is lower than those of the other EH4–5 chondrite (SKINNER and LUCE, 1971). This is also not a primary formation temperature of niningerite.

Oldhamite is often surrounded by niningerite. This suggests that the former condensed before the latter, which is consistent with the suggestion that oldhamite does not contain inclusions like niningerite. Oldhamite probably formed simultaneously with or before metal formation.

4.2. *Origin of silicate inclusions*

The modal abundance of silicate inclusions in OMF's is evidently different from that of chondrules (Fig. 7). Especially the abundance of the silica mineral in OMF's is too high for OMF's to have been derived from chondrules. Two possibilities on its origin are considered. One is that silica mineral is a primary condensate. However, this is unexpected from condensation theory of LARIMER and BARTHOLOMAY (1979) and SEARS (1980). In the silicate portions of Y-691, evidence for the condensation of silica mineral is not found. Therefore, silica mineral in OMF's may not be condensate. Alternatively, it is possible that the silica mineral formed through the oxidation of Fe-Ni metal. This is consistent with the fact that silica mineral inclusions are found only in Fe-Ni metal. Since the amount of silica mineral present in OMF's is small, the primary Si-content of metal was similar to the present content.

5. Formation of OMF

Figure 8 summarizes the genetic relations among all these opaque minerals in Y-691. Most of opaque minerals originated on Fe-Ni metal. It is, therefore, concluded that the primitive metal alloy had included P, Si, Zn, Cr, Mn and Ti, in addition to Fe, Ni and Co. The condensation of Cr and Mn, and Si into metal alloy at the high temperatures is expected from the calculation of GROSSMAN and OLSEN (1974) and SEARS (1980), respectively. Mg is contained only in sphalerite in OMF's. (Although niningerite attaches to Fe-Ni metal of OMF's, it is not considered to have been derived from metal.) Sphalerite shows the low temperature equilibration. Therefore, it is also possible that Mg was removed from the other phases (niningerite?) to sphalerite at lower temperatures.

The primary metal alloy was formed under very low oxygen fugacity. The silicon was dissolved in the metallic state and a silica mineral was not present before the formation of schreibersite and troilite, because silica minerals are not found in them. Oxygen fugacity at this primary stage is, therefore, calculated to be below about log $PO_2 = -21$ atm at 1500 K for example, on the basis of Si-contents in OMF's and the equation and activity coefficient for Si in metal of LARIMER and BUSECK (1974).

Although the cause of the reducing conditions of formation of the enstatite chondrites is a question under debate, the condensation sequence for several minerals in enstatite chondrites under such reduced conditions has been calculated by some authors

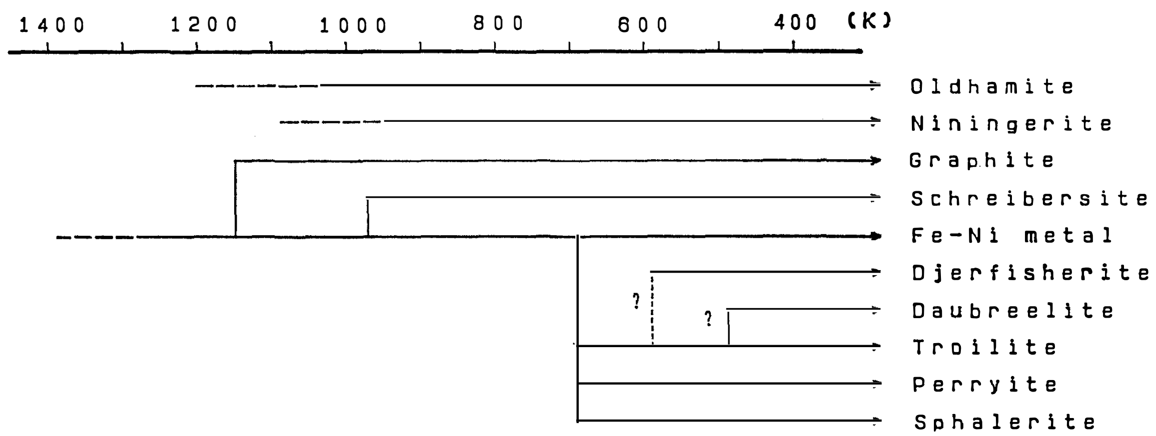

Fig. 8. Schematic diagram for the genetic relations between opaque minerals in OMF's.

as mentioned below. These condensation sequences are tested with the result obtained here. According to LARIMER and BARTHOLOMAY (1979), Ti condenses as TiN under high-C/O ratio, or as perovskite under low-C/O ratio from the nebula. However, these phases are not observed in Y-691. Alternatively, it is probable that Ti partly condenses into metal alloy. FEGLEY and LEWIS (1980) and GROSSMAN and OLSEN (1974) calculated that P condenses as Fe_3P at about 1200 or 1400 K under 10^{-3} atm total pressure. However, their occurrence does not support this idea. Furthermore, even if this condensation takes place, P immediately forms metal alloy at such temperatures and primary schreibersite is lost. Alternatively, P condenses into metal alloy.

SEARS (1980) suggested that the condensation temperature of troilite is about 700 K. This temperature is not inconsistent with the estimated temperature of troilite in OMF's as mentioned before. According to LARIMER and BARTHOLOMAY (1979), the condensation temperatures of oldhamite and graphite depend on the nebular C/O ratio. The condensation sequence agrees with the results here in the case of $C/O > 1.0$, *i.e.*, metal and oldhamite condense in a narrow temperature range. This is consistent with the estimation of the formation of oldhamite as mentioned before. LATTIMER *et al.* (1978) calculated the condensation sequences including niningerite under various gas compositions, and showed that niningerite always condenses later than oldhamite. This agrees with the observation of the mode of occurrence of oldhamite and niningerite.

Thus, the results obtained here in Y-691 are not inconsistent with the calculation under high C/O nebula for the formation of some minerals of OMF's. However, this does not necessarily mean that the enstatite chondrites formed under high C/O in the nebula, because oxygen-depletion is also expected by lithophile element fractionation (SEARS, 1980) or refractory and H_2O fractionation (BAEDECKER and WASSON, 1975). It is not yet explained why oxygen-depletion took place in the region of enstatite chondrite formation.

The formation of a secondary silica mineral in Fe-Ni metal suggests that the oxygen fugacity around OMF's increased later. Thus, the redox state for enstatite chondrite formation changed slightly from the primary condensation stage. Fine-grained OMF's consist of similar minerals and compositions to those of coarse-grained OMF's. Therefore, the fine-grained ones were later derived from coarse-grained ones, by fragmentation.

6. Conclusions

(1) Y-691 is an unequilibrated enstatite chondrite, and was not heated above about 400°C in the parent body.

(2) Primary metal alloy (Fe, Ni and Co) condensed in the nebula and included P, Si, Cr, Mn and Ti. Niningerite and oldhamite condensed and attached to this metal condensate. Such condensation occurred under very low oxygen fugacity.

(3) Opaque minerals in OMF's except for Fe-Ni metal, formed through various reactions such as exsolution and reaction with gas. The order of formation is graphite, schreibersite, troilite with perryite and sphalerite.

(4) Although the cause of oxygen-depletion is not evident, the condensation sequence of minerals calculated previously under oxygen-depletion condition generally agrees with the results obtained here.

(5) A silica mineral formed later through the oxidation of Fe-Ni metal. This reaction occurred under slightly higher oxygen fugacity near the Si-SiO_2 reaction boundary.

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