MERRILLITE, A WHITLOCKITE-GROUP MINERAL IN YAMATO-75 CHONDRITES

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***Abstract*:** Various sizes of merrillite of whitlockite-group minerals (from 20 to 750 μm in length) occur as irregularly-shaped grains in Yamato-75 chondrites. The merrillite in the Yamato-75135,93 chondrite coexists with olivine, pyroxene, plagioclase, chromite and/or metal phases in the matrix. This calcium magnesium phosphate with small amounts of Na and Fe shows compositional variation in grain to grain larger than that in an H6 chondrite, but smaller than that of lunar rocks. Electron microprobe analysis and textural evidence indicate that the merrillite was initially present as molten droplets, interstitial to olivine, and coexisted with orthopyroxene and plagioclase, and/or to chromite clusters at the stage of matrix-formation induced by multiple-impact metamorphic events.

1. Introduction

In a history of the merrillite-whitlockite dilemma, MASON (1971) summarized the chronology of mineralogical nomenclature in merrillite-whitlockite. He also suggested "whitlockite group" containing related minerals of whitlockite and merrillite compositions. KEPPLER (1965), MASON (1971), CALVO and GOPAL (1975) and DOWTY (1977) pointed out that terrestrial whitlockite is hydrous with composition close to $Ca_{18}(Mg, Fe, Mn)_2H_2(PO_4)_{14}$, rather than pure $Ca_3(PO_4)_2$. DOWTY (1977) proposed that the name merrillite for anhydrous calcium phosphates should be used for lunar and meteoritic minerals. However, the general chemical formula of terrestrial and extraterrestrial whitlockite-group minerals can be shown as follows:

$$Ca_{19-x}Y_{2x}X_2(PO_4)_{14}, \quad \text{where X is Mg, Fe, Mn, Zn, etc., Y is H, Na, Y, rare earths; } x=0, 1, 2, 3.$$

The extraterrestrial calcium phosphate "merrillite" can be distinguished from terrestrial whitlockite on the basis of occurrence, crystal structure, and composition. That is, X-ray structural analysis of the extraterrestrial merrillite shows that it has the anhydrous β-$Ca_3(PO_4)_2$ structure, which is significantly different in having phosphate group inverted from its configuration in terrestrial whitlockite (DOWTY, 1977). In this paper, the names whitlockite and merrillite will be used for hydrous and anhydrous magnesium calcium phosphates, respectively, and the name "whitlockite group" will be used to refer for both names.

Merrillite is a significant phase in meteorites for the following reasons:

(1) It is minor in abundance but almost ubiquitous in occurrence in meteorites.

In fact, the percentages from the previous electron microprobe analysis (EPMA) studied on meteoritic whitlockite group minerals (*cf.* FUCHS, 1968; BUSECK and HOLDSWORTH, 1977) are 2.4% in iron meteorites; 31.7% in stony-iron meteorites (*i.e.* 24.4% in pallasites and 7.3% in mesosiderites); 65.9% in stone meteorites (*i.e.* 63.4% in chondrites and 2.5% in achondrites). In chondritic meteorites, merrillite is widespread in all subgroups; that is, 35.7% in L6 class; 25.0% in H5 class; 10.7% in L5 class; 7.0% in LL6 class; 3.6% each in L3, L4, LL3, LL4, C4 and H6 classes. Thus, merrillite is found in most stone meteorites, especially L6 and H5 chondrites.

(2) It has cosmogenetic and petrologic importance because it often contains relatively large amounts of some geochemically important trace elements (rare earths, uranium and thorium, etc.), and of the alkalis (*i.e.* Na and K), which are not accommodated within the major minerals.

Generally, calcium phosphates (*i.e.* apatite and whitlockite groups) have an important role in human bone and bioceram (synthesized bone), and in cosmogenic and petrologic occurrences. In fact, the composition of the whitlockite-group mineral may give some information about the abundance of certain components in the environment of formation.

YAGI *et al.* (1978) briefly described and figured whitlockite (corresponding to merrillite in our definition) in the Yamato-7304 L5 chondrite. As a contribution to the knowledge of this merrillite in Yamato-75 chondrites, as well as to the knowledge of the formation process of the meteorite itself, the EPMA analysis of magnesium calcium phosphates from Yamato-75135,93 chondrite (classified as L5 ~ 4 (*i.e.* L5 (67%)), MIÚRA and MATSUMOTO, 1981, 1982a) has been carried out.

2. Experimental

Optically, it is very difficult to confirm the presence of phosphates (esp. merrillite), because the phosphates commonly occur together with olivines, orthopyroxenes and/or plagioclases. By using the electron microprobe it is immediately possible to check for the existence of this phase (Figs. 1–5).

The compositions of several grains of merrillite on the carbon-coated, polished thin section have been determined by using JXA-50A electron microprobe at the Department of Mineralogical Sciences, Yamaguchi University by senior author. The

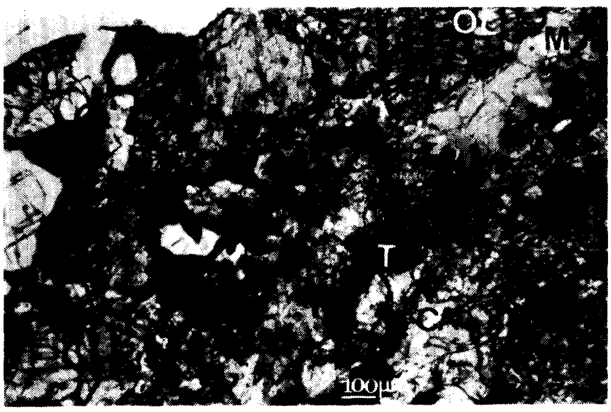

Fig. 1. Photograph with crossed nicols of merrillite (M), coexisting with barred-olivine chondrule (OL), chloraptite (CA) and troilite (T) in Yamato-75135,93 chondrite. No. 10 merrillite.

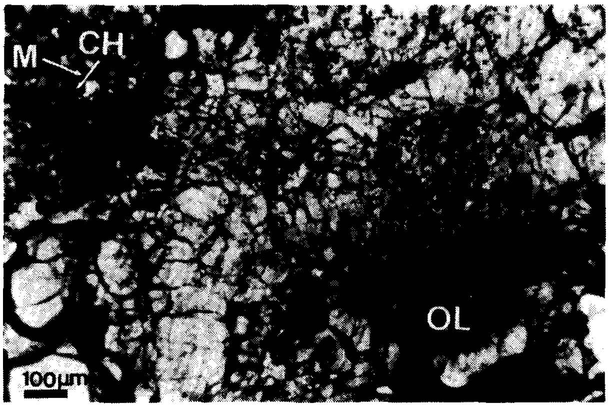

Fig. 2. Photograph with crossed nicols of merrillite (M), coexisting with chromite (CH) and olivine (OL), etc. in Yamato 75135,93 chondrite. No. 12 merrillite.

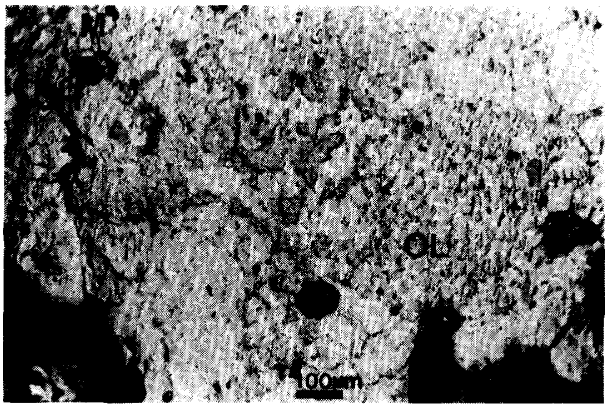

Fig. 3. Reflected-light photograph of the same area in Fig. 2. Yamato-75135,93 chondrite. No. 12 merrillite.

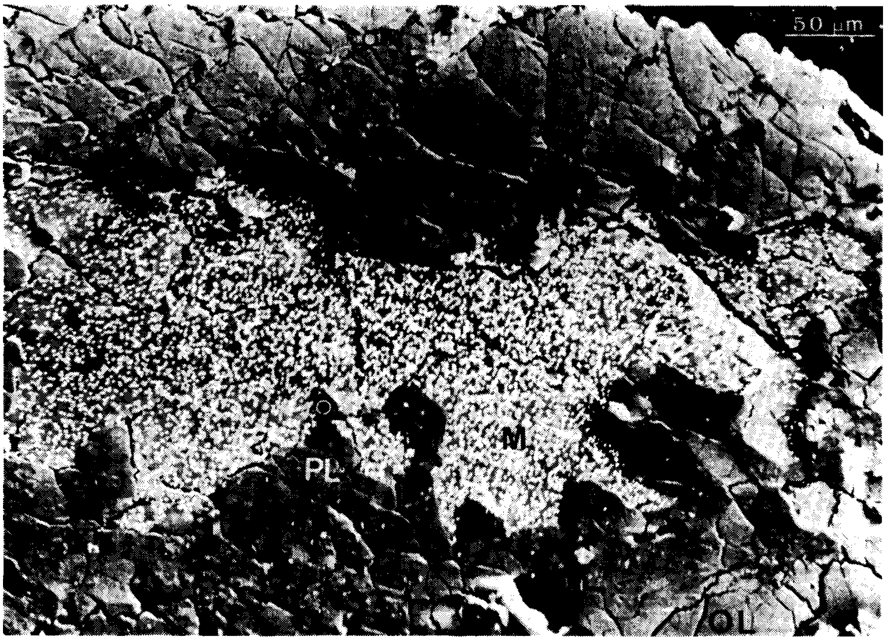

Fig. 4. Scanning P Kα X-ray image mixed with secondary electron image of merrillite (M) of upper part of Fig. 1 in Yamato-75135,93 chondrite. OL, PL and OPX indicate olivine, plagioclase and orthopyroxene, respectively. No. 10 merrillite.

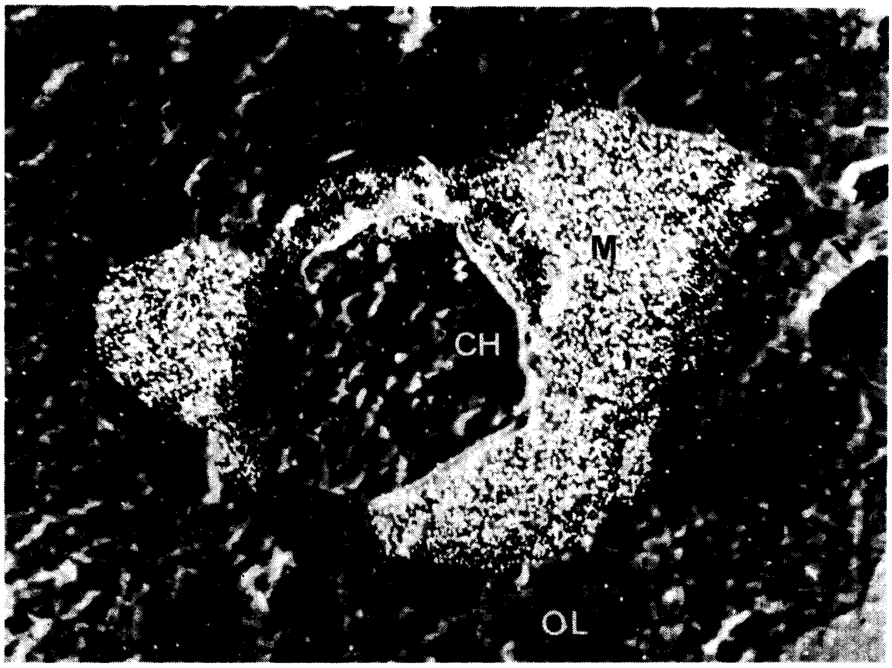

Fig. 5. Scanning P Kα X-ray image mixed with secondary electron image of merrillite (M) of upper left part in Figs. 2 and 3 in Yamato-75135,93 chondrite. Letters CH and OL indicate chromite and olivine, respectively. No. 12 merrillite.

instrument was operated at 15 kV accelerating voltage and 2.0×10^{-8}A specimen current. The quantitative chemical analysis of merrillite was conducted with the same BENCE and ALBEE method (1968) reported by MIÚRA and MATSUMOTO (1981, 1982a).

The composition of the phosphates was checked by monitoring the peak-intensities of thirteen elements (*i.e.* Na, K, Mg, Fe, Si, Mn, Al, Ti, Cr, V, P, F and Cl) with the scanning technique. Grains with total weight percents ($SiO_2+Al_2O_3+FeO+MgO+MnO+Cr_2O_3+CaO+Na_2O+K_2O+P_2O_5+TiO_2$) outside the range between 99 and 101 wt% were ascribed to inaccurate analysis and were rejected.

Minor contents of F and Cl have been detected in this EPMA study. However, discussion of halogens and rare earth elements are withheld pending analysis of the isotopes by using an ion-microprobe mass analyzer.

3. Results and Discussion

When the Yamato-75135,93 chondrite was examined to determine the chemical group and petrologic type, a large grain (250×750 μm) of merrillite optically similar to feldspar was found by the electron microprobe (*cf.* MIÚRA and MATSUMOTO, 1981). Grain sizes are variable; that is 20×40 μm (No. 12 in Table 1), 40×60 μm (in No. 11), 70×100 μm (in No. 01), 160×340 μm (in Nos. 50 and 51) and 250×750 μm (in No. 10). Merrillite of various sizes (from 20 to 750 μm in length) occurs as irregularly-shaped grains and always lacks crystal form, compared with subhedral grains of apatite. Although apatite exists both in the chondrules and the matrix, merrillite is found only in the matrix, coexisting with olivine and plagioclase, orthopyroxene, chromite and/or metal phases. That is, the mineral association of the merrillite is that olivine and

Table 1. Chemical compositions of whitlockite group mineral in Yamato-75135,93 chondrite, compared with those in lunar rock and H6 chondrite.

No. / Oxides	01	50	51	10	11	12	Average [6]**	Lunar rock† [10]	H6 chondrite†† [4]
SiO_2	0.15	0.07	0.07	—	—	—	0.05(5)***	0.66(110)	0.09(2)
TiO_2	—	—	—	—	—	0.01	—	0.03(4)	—
Al_2O_3	0.15	0.05	0.05	0.03	—	0.07	0.06(5)	0.04(8)	—
FeO*	0.42	0.69	0.69	0.35	0.18	0.46	0.47(18)	2.49(171)	0.45(12)
MgO	3.64	3.52	3.70	3.54	3.76	3.81	3.66(11)	2.60(120)	3.35(7)
Cr_2O_3	0.03	0.07	0.07	0.04	0.02	0.05	0.05(2)	—	—
MnO	—	0.02	0.02	0.01	—	—	0.01(1)	0.01(3)	—
Na_2O	2.87	2.89	2.89	3.03	3.30	2.95	2.99(15)	0.38(71)	2.78(2)
CaO	46.08	45.90	46.94	44.15	44.69	44.90	45.44(95)	41.02(334)	46.7 (3)
K_2O	0.05	0.03	0.03	0.03	0.02	0.07	0.04(2)	0.02(3)	—
P_2O_5	47.51	46.73	46.77	48.78	48.82	48.23	47.81(86)	43.42(255)	46.5 (1)
Total	100.90	99.97	101.23	99.96	100.79	100.55	100.58(46)	99.27(103)	99.87

* Total iron oxide as FeO.
** Number of crystals analyzed are shown in square brackets.
*** Numbers in parentheses are standard deviation referring to the last decimal place.
† Statistical analyses of data listed in "Lunar Mineralogy" (FRONDEL, 1975). Total includes Y and rare earth elements.
†† Data reported by ADIB and LIOU (1979).

Table 2. Chemical formulae of whitlockite group minerals.

Host rock	Chemical formula
Terrestrial rock	$Ca_{18}(Mg, Fe)_2H_2(PO_4)_{14}$
Lunar rock††	$Ca_{16}(Y, RE)_2(Mg, Fe)_2(PO_4)_{14}$
Pallastic meteorite†[37]*	$Ca_{18.4(5)}Mg_{2.0(2)}Fe_{0.3(3)}Na_{0.8(8)}P_{14.01(1)}O_{56}$**
Achondritic meteorite††	$Ca_{19}(Mg, Fe)_2(PO_4)_{14}$
Chondritic meteorite	$Ca_{18}(Mg, Fe)_2Na_2(PO_4)_{14}$
In this study	
Yamato-75135,93 chondrite [6]	$Ca_{17.1(4)}Mg_{1.9(1)}Fe_{0.1(1)}Na_{2.1(1)}P_{14.3(2)}O_{56}$

* Numbers of crystals analyzed are shown in square brackets.
** Numbers in parentheses are standard deviation referring to the last decimal place.
† Statistical analyses of data reported by BUSECK and HOLDSWORTH (1977).
†† DOWTY (1977).

plagioclase are the common minerals of the five grains analyzed as in Table 1, and that chromite is found in all the grains except No. 10 grain. Metal phases (plessite and kamacite) are found in the grain of Nos. 50 (in the core) and 51 (in the rim) as adjacent minerals. Orthopyroxene is found in the matrix of the barred-olivine chondrule adjacent to No. 10 merrillite. But apatite-group minerals are found far from merrillite (*cf.* Figs. 1–5).

The following compositional data were obtained in this study:

(1) Merrillite in Yamato-75135,93 has almost the same chemical composition as in other chondritic meteorites. The average composition shows a relatively lower amount of Ca, and higher amounts of Na and P, compared with merrillite of ordinary chondrites as shown in Tables 1 and 2.

(2) Tables 1 and 2 show that slight compositional variation among grains is observed in the merrillite of the Yamato-75135,93 chondrite. Table 1 shows that the compositional variation of each oxide is larger than that in H6 chondrite merrillite reported by ADIB and LIOU (1979), but smaller than that of lunar rock.

(3) Table 1 shows that there is no close relationship between chemical variation and grain size. Nos. 50 and 51 crystals have the largest value of Ca/P ratio with the highest amount of Fe, whereas No. 10 crystal has the smaller value of Ca/P ratio with the lowest amount of Mg.

The reaction-process of phosphate minerals has been discussed by many investigators. Morinite, $Ca_4Na_2Al_4(OH_xF_{5-x})PO_4(5-x)H_2O$ changes into apatite, followed by whitlockite, upon heating in air to successively higher temperatures (FISHER and VOLBORTH, 1960). A whitlockite-group mineral has been identified as one of the product of carious attack on dental hydroxylapatite (JOHNSON *et al.*, 1969). The merrillite which coexists with apatites was not observed in this study. It is found only in the matrix, whereas apatites are found both in the matrix (chlor- and fluorapatites) and the chondrules (only fluorapatite) (*cf.* MIÚRA and MATSUMOTO, 1982b). The crystal forms of these phosphates are slightly different; that is, apatite is subhedral, whereas anhedral crystals with irregular and compressed forms are found both in merrillite and apatites. As the crystal structures of the apatite and whitlockite-group minerals are not closely related, the chemical changes of apatite to merrillite cannot proceed without substantial bond breakage and reformation induced by impact metamorphism. We suggest that X-ray structure determination on single crystals (not by thin-section sample) will be needed to clarify the compositional and structural relationships between these phosphate minerals.

4. Conclusion

Merrillite showing various sizes, compositional variation and irregularly-deformed shapes has been found in a Yamato-75 chondrite. The compositional variation of each oxide is larger than that in H6 chondrite merrillite reported by ADIB and LIOU (1979), but smaller than that of lunar rock, as shown in Table 1.

Electron microprobe data and textural evidence in Figs. 1–5 and Tables 1 and 2 indicate that the merrillite was initially present as molten droplets, interstitial to the olivine, and coexisted with orthopyroxene and plagioclase, and/or to chromite clusters at the stage of matrix-formation induced by multiple-impact metamorphic events.

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