CRYSTALLOGRAPHIC AND CHEMICAL STUDIES OF A BRONZITE AND CHROMITE IN THE YAMATO (B) ACHONDRITE

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Abstract : X-ray single crystal diffraction studies, supplemented by electron microprobe analyses, have been made of pyroxene and chromite in the Yamato (b) achondrite. The major phases in the meteorite are homogeneous grains of bronzite ($Ca_2Mg_{74}Fe_{24}$) with no exsolution lamellae of augite, and euhedral to subhedral grains of chromite with high Cr and Mg contents. Troilite and metallic iron are also present. The pyroxene is identical in composition to those of the hypersthene achondrites but the portion of the meteorite examined does not have the very coarse-grained and brecciated texture of most hypersthene achondrites. X-ray diffraction study of an octahedral chromite grain shows that it consists of portions with slightly different orientations. Measurement of the magnetic moment of the chromite shows no abrupt change in magnetization and the absence of a distinct thermal hysteresis between 20 and 400°C, consistent with the magnetic properties of chromite.

Yamato (b) is a unique hypersthene achondrite with a non-brecciated granoblastic texture. We suggest that Yamato (b) may have undergone a reheating event that caused recrystallization of the pyroxene, without change in composition.

1. Introduction

Petrologic investigations of returned lunar samples following the Apollo and Luna missions have revealed the nature of igneous processes active in the early evolution of the moon and contributing to the formation of the primordial crust. Other evidence of extraterrestrial igneous processes, active very early in the history of the solar system, is provided by the achondrite meteorites. This evidence is difficult to interpret in large part because the achondrites are so rare. Thus the discovery of a new achondrite is an important event. The Yamato (b) meteorite is one of the group of meteorites known as hypersthene achondrites, of which only 9 others are known. The sample of Yamato (b) we have studied can readily be identified as a hypersthene achondrite but it shows unique textural features indicative of a thermal history distinctly different from the other members of this group.

The petrology of achondrite meteorites was reported in detail by DUKE and SILVER (1967). MASON (1969) summarized the available data on meteorite pyroxenes and REID and LOVERING (1969) reported compositional data on minerals from a variety of achondrites. Over the last few years we have tried to combine

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crystallographic and chemical data on the major phases in selected achondrites with a view to understanding the processes by which they formed (REID and TAKEDA, 1972). Studies of pyroxene from the hypersthene achondrite, Johnstown (and of bronzite from the stony-iron meteorite, Steinbach) reveal bronzites with exceptionally high Mg-Fe ordering of the M1 and M2 sites, indicative of very slow cooling in the 700–500°C range (MIYAMOTO et al., 1975; REID et al., 1974). Within the bronzites of hypersthene achondrites the presence or absence of exsolution lamellae of augite was interpreted as a function of the original calcium content of the orthopyroxene.

Chromite compositions in achondrites have been studied extensively by BUNCH and KEIL (1971). The crystal structures and cation distributions for lunar chromite were determined by TAKEDA et al. (1974). Chromite is a major opaque phase in the Yamato (b) achondrite. The main magnetic constituents in Yamato (b) are reported by NAGATA et al. (1975) as almost pure metallic iron and an oxidized magnetic spinel.

As part of a general study of pyroxenes and opaque minerals in achondrites, the pyroxenes and a chromite in the Yamato (b) achondrite were studied by the single crystal X-ray diffraction method, combined with microprobe analysis, to search for the presence of other minor exsolved phases in these crystals and to provide information on recrystallization and cooling conditions.

2. Experimental Techniques and Results

A sawn piece of the Yamato (b) meteorite about 8 mm long along the longest edge was supplied by Prof. YAGI, who carried out the petrographic studies of this meteorite (OKADA, 1975; OKADA et al., 1975). The piece was further cut into four slices about 0.5 mm thick, two of which contained the halves of an octahedral grain of chromite, about 1.4 mm in diameter. One such slice was polished for electron probe microanalysis. The chromite grain from the other slice was separated for single crystal diffraction studies. The single crystals of bronzite for the X-ray examination were separated from the slice nearest the interior. Microprobe analyses were performed with an ARL EMX-SM microprobe and the data are corrected for drift, deadtime, background, and matrix effects (FRAZER et al., 1966; BENCE and ALBEE, 1968).

Microscopic observation and microprobe analysis of the polished thin section indicate that it is a hypersthene achondrite with pyroxenes of bronzite composition. However, the texture of this meteorite is unlike the other hypersthene achondrites. It is not brecciated and texturally the pyroxene seems to have recrystallized to a granoblastic texture (Fig. 1) without stress and without change in mineral composition (Table 1). The composition of the interior and the rims of grains is virtually identical. The single large euhedral opaque grain is chromite (Table 2). Smaller opaque grains are troilite, and metallic iron.

Individual pyroxene crystals were mounted along the c-axis and precession photographs of h0l and 0kl nets were taken using Zr-filtered, MoKα radiation. A diffraction photograph of an average size pyroxene (0.2–0.3 mm in diameter)

(a)   (b)
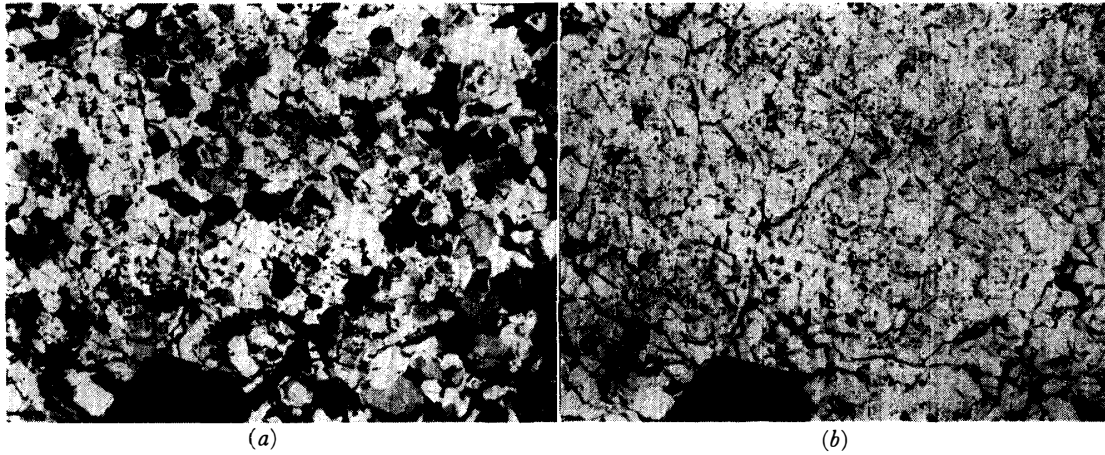
Fig. 1. Photomicrogram of the Yamato (b) hypersthene achondrite. A large opaque mineral is chromite. Note a mosaic texture of bronzite. Field of view is 0.29cm × 0.22cm. (a) cross nicols, (b) open nicols.

Table 1. Chemical data on pyroxenes in Yamato (b), Johnstown, and Mt. Padbury.

Sample	Yamato (b)				Johnstown	Mt. Padbury
Grain	1	2	2 (rim)	Mean*	2	14
SiO_2	55.05	54.99	54.91	54.98	54.74	54.92
TiO_2	.06	.08	.07	.07	.10	.14
Al_2O_3	.45	.76	.66	.60	1.03	.86
Cr_2O_3	.54	.70	.66	.66	.67	.38
FeO	15.36	15.68	15.61	15.50	14.89	15.43
MnO	.54	.54	.52	.54	.48	.52
MgO	27.51	26.97	27.15	27.14	27.60	27.30
CaO	.99	1.21	1.09	1.10	1.38	1.24
Na_2O	—	—	—	—	.02	.02
Total	100.51	100.93	100.67	100.59	100.91	100.81

* Average of 5 grains.

Table 2. Chemical data on chromite in Yamato (b).

Sample	Yamato (b)			Steinbach
Analysis	1	2	Mean*	
SiO_2	—	—	—	.04
TiO_2	.79	.82	.83	.32
Al_2O_3	7.74	8.40	7.97	3.76
Cr_2O_3	60.49	60.00	60.09	66.0
FeO	25.50	25.12	25.47	21.8
MnO	.49	.49	.49	1.39
MgO	5.80	5.91	5.83	6.40
Total	100.81	100.74	100.68	99.7

* Average of 4 analyses.

revealed that it is composed of several much smaller crystals with various orientations. Such crystals were further divided into smaller pieces until true single crystals were obtained. The single crystals thus obtained have a maximum dimension of about 0.1 mm.

The $h0l$ precession photograph of the Yamato (b) bronzite shows no reflection of a calcium-rich pyroxene phase. There are no diffuse streaks along a^*, as was observed in the Johnstown bronzite. The observed intensity distribution and extinction criteria are consistent with space group $Pbca$. An over-exposed photograph (40 kV, 160 mA, 57 hrs.) of the $0kl$ net taken with a Rigaku Rota high intensity X-ray unit, showed no diffraction which violates the b-glide criterion (SMYTH, 1974). However, this does not ensure the real space group is $Pbca$, since the crystal was too small to give satisfactory intensities. Cell dimensions obtained by the precession method agree with the chemical composition determined by microprobe analysis.

For comparison, pyroxenes in other achondrites have been studied by X-ray techniques. Bronzites in Ibbenbüren (spec. #854, Arizona State University), which have high-calcium contents (private comm., GOOLEY, 1972), show reflections of exsolved augite in twinned orientation of (100) with the (100) plane in common with the host orthopyroxene. A large bronzite crystal with CaO content 1.24 wt. percent (the same as that of Yamato (b), Table 1) from the hypersthene achondrite enclaves in the Mt. Padbury mesosiderite (U. S. National Museum, No. 3203), and bronzite of similar composition from the Shalka hypersthene achondrite (GOOLEY, 1972) do not show augite exsolution.

A small fragment about 0.2 mm in diameter of the large octahedral crystal of chromite (Fig. 1) was also investigated by the X-ray precession technique. The crystal was mounted along the [110] zone, and the $hk0$ and hhl nets were recorded. The photographs showed that the grain is composed of several slightly misoriented crystals. The presence of other spinel phases, oriented with their crystallographic axes in common, is not evident. The possible existence of a very minor phase with the nearly identical cell dimensions, can not be ruled out.

The large chromite crystal (3.6 mg) was also used for examination of its magnetic properties. Measurements of magnetic moment of the crystal were conducted between room temperature, 20°C, and 400°C in a magnetic field (H_x) of 10kOe. The unit is the model 155 vibrating sample magnetometer manufuctured by Princeton Applied Research Corporation. In order to avoid oxidation of the sample during heating, the crystal was held in an evacuated holder.

Mass magnetic susceptibility (χ_g), was derived from the observed magnetic moment (M_x). The inverse of magnetic susceptibility ($1/\chi_g$), increases linearly with increasing temperature in the above temperature range. The Neel point estimated from extrapolation of the $1/\chi_g$ values, is about 80° to 85°K, which is consistent with the Neel point of a synthetic chromite $FeCr_2O_4$. The absence of any abrupt change of magnetization and of a distinct thermal hysteresis is consistent with the paramagnetic property of the Yamato (b) chromite between 20° and 400°C.

3. Discussion

The hypersthene achondrites are discussed by MASON (1969) and a detailed study of this group has recently been made by GOOLEY (1972). The major phase is bronzite (hypersthene in the classification used by meteoriticists) with minor amounts of olivine, plagioclase, chromite, nickel-iron and troilite. The bronzite forms large homogeneous irregular fragments in a matrix that itself consists largely of angular fragments of bronzite. However, the texture of Yamato (b) is unlike that of the brecciated hypersthene achondrites. The texture of the Yamato pyroxene (Fig. 1) suggests that the pyroxene has recrystallized.

The major element composition of the known hypersthene-achondrite pyroxenes are similar and differ only in detail. These achondritic bronzites contain approximately 25 mol percent ferrosilite and are richer in minor elements such as Ti, Al, Cr, Mn and Ca (Table 1) than the pyroxenes in enstatite achondrites. The Yamato (b) meteorite belongs with the hypersthene achondrites in that the composition $(Ca_2Mg_{74}Fe_{24})$ and abundance of bronzite matches the other hypersthene achondrites and is totally unlike any other meteorite class. No difference of chemical composition was observed between grains or within single grains.

An exceptionally high degree of Mg-Fe ordering of the M1 and M2 sites in the pyroxene structures has been reported for bronzite in Johnstown $(Ca_{2.4}Mg_{75}Fe_{22.6})$, a hypersthene achondrite (MIYAMOTO et al., 1975) and in Steinbach, a stony-iron meteorite (REID et al., 1974). Despite this evidence of very slow cooling, exsolution of augite from bronzite, has been found only for Ibbenbüren and Johnstown, in the hypersthene achondrites. The augite precipitation in the Johnstown bronzite is interpreted as Guinier-Preston zones which may be related to slow cooling at very low temperature where the migration of Ca has almost ceased. The Ca content of the Johnstown bronzite $(CaO=1.38$ wt. percent) is not high enough to produce exsolution at higher temperatures. The Ca contents of the Yamato (b) bronzite and other achondritic bronzites, such as in Mt. Padbury, Shalka and Steinbach, for which no exsolution of augite was found, are lower than for Johnstown. The presence or absence of augite lamellae on (100) in orthopyroxene in the hypersthene achondrites thus appears to be a function of Ca content of the original pyroxene and not solely a function of cooling rate.

An extremely slowly cooled orthopyroxene would have symmetry lower than that of the space group *Pbca*, and some very weak extra reflections violating the extinction rules of *Pbca* have been reported (*e. g.* SMYTH, 1974). SMYTH (1974) suggested *P2₁ca* for a lunar pyroxene, while MATSUMOTO (1974) quoted *Pbc2₁*. After refining the structure of the Steinbach bronzite in these space groups, MIYAMOTO et al. (1975) suggested that a monoclinic space group such as *P2₁/c* should be considered as well as the orthorhombic one. The Yamato (b) bronzite that was studied is too small to draw any definite conclusion about its space group. The effect of recrystallization on the symmetry is an interesting subject for further study.

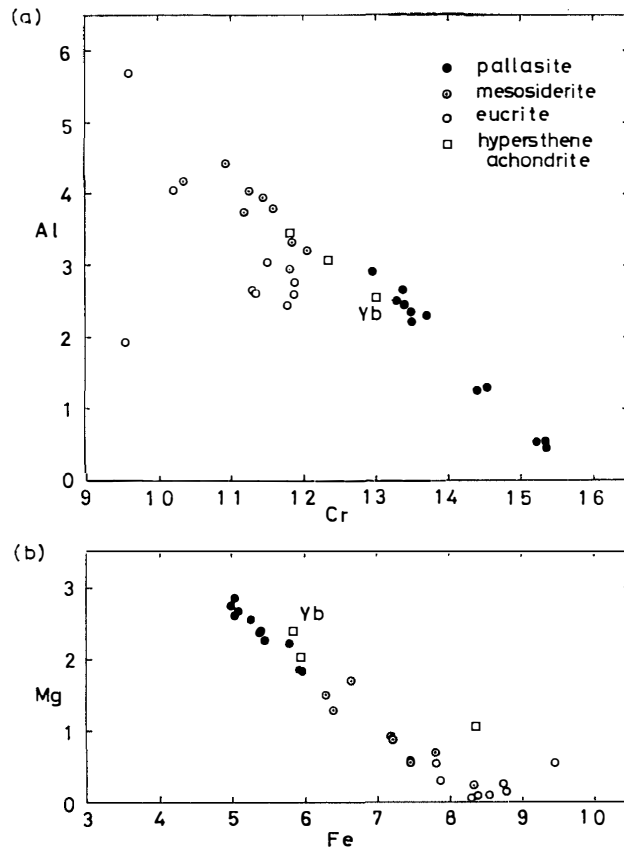The large euhedral chromite grain is very large compared to the grain size

Fig. 2. (a) *Cr-Al substitution in non-chondritic chromites.*
Substitutional trends are discussed in the text.
Data of chromite in non-chondrititic meteorites are
after Bunch *and* Keil (1971). *Yb: Yamato* (b).
(b) *Mg-Fe substitution in non-chondritic chromites.*
The symbols and the source of data are same as
those used in (a).

of the bronzites. X-ray examination revealed that this crystal is composed of slightly misoriented domains. This misorientation may be the only secondary effect recorded by the chromite, which probably did not recrystallize.

The chemical composition of the Yamato (b) chromite is characterized by higher Cr_2O_3 and MgO contents and lower Al_2O_3, FeO and TiO_2 contents than those of other chromites in the hypersthene achondrites (Fig. 2). It is rather close in composition to the chromites in pallasite (Bunch and Keil, 1971). The TiO_2 content is lower than that of lunar chromites (Haggerty, 1972).

As is evident from Fig. 2, the cation substitution, in chromites from non-chondrites, is between Cr and Al in the B site of the spinel structure and between Fe and Mg in the A site. This mode of substitution is consistent with the observed cation distribution in lunar chromites (Takeda *et al.*, 1974) and accords with the predicted site preferences.

Table 3. Chemical formula of the Yamato (b) chromite.

Cations	Atomic proportions based on 4 oxygen atoms	
Ti	0.021	
Al	0.321	
Cr	1.625	2.000
Fe	0.033	
	0.695	
Mn	0.014	1.007
Mg	0.298	

The presence of more than 8 atoms of iron relative to 32 oxygens (Fig. 2), may indicate the presence of Fe^{3+} in chromites. For microprobe analyses, where the oxidation state of the iron cannot be determined, an excess of cations above stoichiometric proportions indicates analytical error or the presence of Fe^{3+}. The total number of cations per unit cell for balanced chromite is 24.00, and the value for the Yamato (b) chromite of $(2.000+1.007) \times 8$ (Table 3)$=24.06$, is within the analytical error. A portion of the 0.033 Fe per 4 oxygen atoms (Table 3) assigned to the B site may be present as Fe^{3+}. The data are interpreted as indicating that little or no Fe^{3+} is present in this chromite.

The observed magnetic property of the chromite single crystal indicate that it shows paramagnetic property between 20° and 400°C. It is also suggested that neither chemical decomposition nor phase transformation of this chromite may have taken place in the above temperature range. The second ferromagnetic component observed by NAGATA *et al.* (1975) may be an oxidized component other than the chromite.

Summary

The hypersthene achondrites apparently formed by slow near-equilibrium crystallization producing large unzoned homogeneous crystals. The near mono-mineralic hypersthene achondrites may be cumulates of orthopyroxene from a more iron-rich parent liquid. Coexistence of hypersthene achondrite enclaves, which have chemical compositions similar to that of the Yamato (b) bronzite, associated with eucrite enclaves in the Mt. Padbury mesosiderite, emphasizes their close relationship. For most hypersthene achondrites the original crystallization was followed by mechanical brecciation without substantial recrystallization.

The evidence of recrystallization found for the Yamato achondrite indicates its unique nature. The texture is totally unlike that of Tatahouine, which appears to be the only other unbrecciated hypersthene achondrite. It is apparent that some hypersthene achondrites may have a quite complex thermal history involving reheating and, in some cases, almost complete recrystallization.

Acknowldgments

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