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ANTARCTIC PRIMITIVE ACHONDRITES, YAMATO-74025, -75300, AND -75305: THEIR MINERALOGY, THERMAL HISTORY, AND THE RELEVANCE TO WINONAITE

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Abstract: Three Antarctic primitive achondrites, Yamato(Y)-74025, -75300, and -75305 were mineralogically and chemically studied. They consist of anhedral to subhedral silicate and opaque minerals. The major constituent minerals are typical of equilibrated ordinary chondrites. However, they do not have any relic of chondrule, and the presence of various accessory minerals, such as K-feldspar, schreibersite, daubreelite, phosphate, Nb-bearing rutile, and magnesiochromite, characterizes these meteorites. Y-75305 has a composite grain containing Cu, Mn, and S, probably consisting of alabandite, an unknown Mn-bearing Cu-sulfide, and digenite. Y-74025 has a REE pattern typical of chondrite. Siderophile elements in Y-74025 are depleted relative to Cl chondrites, which is consistent with poor abundance of Fe-Ni metal in Y-74025. Holocrystalline texture, homogeneous mineral compositions, and high equilibration temperatures for pyroxenes, suggest that these primitive achondrites experienced high-temperature metamorphism. Mineralogical and chemical characteristics suggest that they resemble Winonalike meteorites (winonaites). The compositions of pyroxene and olivine, and accessory minerals suggest that winonaites formed under an intermediate redox condition between E-chondrites and Acapulco-like primitive achondrites. The abundance of troilite and Fe-Ni metal varies widely. The metal-sulfide fractions of winonaites probably melted and fractionated, although silicate fractions of winonaites do not have any evidence for melting.

1. Introduction

Some anomalous meteorites such as Acapulco, Winona, and Pontlyfni, have olivines of intermediate composition between those of H and E-chondrites, and these anomalous meteorites seem to fill the missing gap between H and E-chondrite. The taxonomy of these meteorites is a controversial problem. GRAHAM *et al.* (1977) called Winona, Mount Morris, and Pontlyfni forsterite-chondrites. PRINZ *et al.* (1980) proposed to denote as winonaites, Winona, Acapulco, Mount Morris, Pontlyfni, ALH-77081, and Tierra Blanca. Later KALLEMEYN and WASSON (1985) proposed

the term IAB-chondrite, instead of the terms forsterite chondrite and winonaite. All these meteorites resemble achondrites in texture. Thus, they are also called primitive achondrites (PRINZ *et al.*, 1980), although they are similar in mineralogy and bulk chemistry to chondrites.

Acapulco was mineralogically and chemically studied by PALME *et al.* (1981). Acapulco-like meteorites were also found from Antarctica; Allan Hills (ALH)-77081 (TAKEDA *et al.*, 1980; SCHULTZ *et al.*, 1982), and Yamato (Y)-74063 (KIMURA, 1987; YANAI and KOJIMA, 1991). In addition, Y-74357, -75274, -8002, and ALH-78230 are also similar to Acapulco or lodranite (NAGAHARA *et al.*, 1990; HIROI and TAKEDA, 1991). Here we tentatively call these Acapulco-like meteorites acapulcoite.

On the other hand, Winona-like meteorites, Mt. Morris, Pontlyfni, Tierra Blanca, and Winona, have been studied by BILD (1977), GRAHAM *et al.* (1977), DAVIS *et al.* (1977), PRINZ *et al.* (1980, 1983), and KING *et al.* (1981). Udei Station also appears to belong to this group (KALLEMEYN and WASSON, 1985). We shall tentatively call these meteorites winonaites. All these meteorites have holocrystalline texture and homogeneous mineral chemistry, suggesting thermal meta-morphism at high-temperatures. BILD (1977) pointed out that silicate inclusions in IAB iron meteorites are similar in mineralogy and chemistry to winonaites.

Three winonaites were found in Yamato meteorite collection, *i.e.*, Y-74025, -75300, and -75305. Y-74025 was preliminarily studied by KIMURA (1987) in petrology, and by FUKUOKA and KIMURA (1988) in chemistry. YAMAMOTO *et al.* (1990, 1991) reported the chemistry and Rb-Sr age of Y-75300. The bulk oxygen isotope measurement showed that Y-75305 is similar to the howardite-eucrite-diogenite clan (MAYEDA and CLAYTON, 1989). On the other hand, Y-74025 and -75300 belong to the winonaite group (MAYEDA *et al.*, 1987; MAYEDA and CLAYTON, 1989). This paper presents the results of mineralogical and chemical study of Y-74025, -75300, and -75305, as part of the consortium study on Antarctic anomalous meteorites. The thermal history and classification of these meteorites will be discussed.

2. Samples and Experimental Methods

Thin sections of Y-74025 (52-2), Y-75300 (51-2), and Y-75305 (52-2) were studied. We also studied Y-74063 (52-4) and ALH-77081 (51-2), in order to compare the petrological and mineralogical features of winonaites with those of acapulcoites.

A detailed SEM survey was carried out with a Cambridge 180 scanning electron microscope with a Si(Li) detector and a Tracor northern 5500 system. Quantitative analyses of minerals were performed with SEMQ and JEOL 733 type wave-dispersive electron-probe microanalyzers. The accelerating voltage and beam current were 15kV and 3 to 10 nA, respectively. The Bence-Albee correction method was used for the analysis of silicates and oxides, and the ZAF method was used for phosphates, sulfides, and metals. A special deconvolution program were applied to correct for X-ray overlaps of K_{β} on K_{α} lines of some successive elements such as Ti-V, Cr-Mn, and Fe-Co. The modal composition was measured after the method of KIMURA et al. (1991).

X-ray diffraction patterns for a Cu-Mn-sulfide was measured with a Rigaku PSPC microdiffractometer. Measurement conditions were as follows; fine focus Cr target X-ray tube, 40 kV, 30 mA, V K_{β} filter, 30 μ m diameter collimator, ω axis = 23°, χ axis oscillation = 60°, ϕ axis = rotation, counting times = 26000 s, and 2 θ = 0–150°.

The abundances of 26 major, and trace elements in each of two chips of Y-74025 and -74063 have been determined by instrumental neutron activation analysis (INAA). The chips were activated with thermal neutrons for 1.5 min at 100 kW (1.5×10^{12} n/cm²s) at the Musashi Institute of Technology (MIT), TRIGA II reactor for measurement of short-lived radionuclides. Then, the samples were reactivated with thermal neutrons for 1.5 hrs at 3.5 MW (8.0×10^{13} n/cm²s) in JRR-4 reactor of the Japan Atomic Energy Research Institute for measurement of long-lived radionuclides. The γ -ray spectrometry for the samples was carried out by the MIT and Gakushuin University counting systems. The details of the γ -ray spectrometry were reported by FUKUOKA *et al.* (1987). G.S.J. standard rocks JB-1 and JR-2, and Allende meteorite powder sample were also activated as standard and/or control samples.

3. Petrography of Winonaites

3.1. Overall texture

Y-74025, -75300, and -75305 consist of anhedral to subhedral silicates and opaque minerals. They are similar in texture to equilibrated ordinary (O) chondrites of higher petrologic type, although they do not have any relic of chondrule (Figs. 1a–1c). Y-75300 consists of coarse-grained (usually 100–200 microns in size) and fine-grained (up to 100 microns) parts (Fig. 1b). These meteorites do not show any shock metamorphic features, and experienced moderate terrestrial weathering based on the criteria of YANAI and KOJIMA (1987).

Y-74063 and ALH-77081 (acapulcoites) consist mainly of euhedral to subhedral silicates with opaque minerals (Figs. 1d and e). Y-74063 has coarse-grained anhedral orthopyroxenes, up to 1 mm, among fine-grained subhedral to euhedral orthopyroxene, olivine, diopside, and plagioclase. YANAI and KOJIMA (1991) found a relic of chondrule in Y-74063.

3.2. Modal compositions

Table 1 gives modal compositions of winonaites and acapulcoites. The major constituent minerals of winonaites and acapulcoites are typical of equilibrated O-chondrites such as orthopyroxene, olivine, plagioclase, troilite, and Fe-Ni metal. The abundance ratios of olivine to orthopyroxene in winonaites are much lower than those of acapulcoites. The abundance of diopside varies widely in winonaites, and diopside rarely occurs in Y-75300. Y-74025 and -75300 have higher amounts of troilite than Fe-Ni metal, whereas metal is much more abundant than troilite in Y-75305. At any rate, the total abundances of opaque minerals are higher in winonaites, especially Y-75300 and -75305, than in acapulcoites. The modal com-





Fig. 1b. Winonaite Y-75300, consisting of fine-grained (left side) and coarse-grained parts (right side). Transmitted light, open nicols, and width of 2.5 mm.

Fig. 1c. Winonaite Y-75305. High amount of opaque minerals (mainly Fe-Ni metal) characterizes this meteorite. Transmitted light, open nicols, and width of 2.5 mm. Fig. 1d. Acapulcoite Y-74063, consisting of coarsegrained anhedral orthopyroxenes and fine-grained subhedral to euhedral orthopyroxene, olivine, diopside, and plagioclase. Transmitted light, open nicols, and width of 2.5 mm.



Fig. 1e. Acapulcoite ALH-77081, consisting mainly of euhedral to subhedral orthopyroxene and olivine. Transmitted light, open nicols, and width of 2.5 mm.

positions of coarse- and fine-grained parts in Y-75300 are similar to each other, although opaque minerals are abundant in the coarse-grained part, and diopside seems to be absent in the coarse-grained part.

Chromite and phosphate hardly occur in winonaites, although they are common in acapulcoites. Several accessory minerals characterize winonaites, especially Y-75305 (Table 1); K-rich feldspar, rutile, daubreelite, alabandite, unknown Cu-Mnsulfide, and schreibersite, which are hardly, if ever, encountered in acapulcoites. GRAHAM *et al.* (1977) and PRINZ *et al.* (1980) reported phosphate, schreibersite, alabandite, chromite, and daubreelite in non-Antarctic winonaites. Graphite which has been reported in Winona by PRINZ *et al.* (1980), was not found in the Antarctic winonaites.

	Y-75305 W	Y-74025 W	Y-75300-с W	Y-75300-f W	Y-74063 A	ALH-77081 A
Enstatite	45.0	45.6	41.6	60.7	46.2	43.6
Diopside	1.2	7.2	0.0	+	6.2	3.4
Olivine	7.8	19.9	14.4	18.7	24.3	25.3
Plagioclase	8.3	8.3	11.2	9.3	7.2	13.4
K-feldspar	+	+	+	+		
Apatite	+	+			+	0.8
Whitlockite					+	0.3
Chromite	0.2	+	+		1.0	1.0
Rutile	+					
Fe-Ti oxide	+					
Troilite	9.2	13.5	27.5	10.0	10.6	5.5
Daubreelite	1.0	0.7	1.0	0.4		
Pentlandite	+				+	
Pyrrhotite	+					
Alabandite	+					
Cu-Mn- sulfide	+		+			
Cu-sulfide	+					
FeNi metal	27.0	3.9	3.8	0.7	4.6	6.7
Schreibersite	0.3	0.9	0.4	0.2		+
Graphite						+

Table 1. Modal compositions of winonaites and acapulcoites (vol%).

Y-75300: c=coarse-grained part, f=fine-grained part.

4. Mineralogy of Winonaites

4.1. Pyroxene

Orthopyroxene, up to 500 microns, is predominant in winonaites, and often includes olivine, diopside, plagioclase, Fe-Ni metal, and troilite. Some orthopyroxenes have very thin exsolution lamellae of clinopyroxene in a direction parallel to (100). Diopside, 5 to 150 microns in size, occurs among orthopyroxene and olivine.

Table 2 gives representative compositions of silicate minerals. Orthopyroxene (enstatite) and diopside are homogeneous and similar in composition among these winonaites, respectively; the average compositions of orthopyroxene and diopside are $En_{96,0}Wo_{1,7}$ and $En_{53,0}Wo_{46,1}$ in Y-74025, $En_{96,5}Wo_{1,4}$ and $En_{52,9}Wo_{46,0}$ in Y-75300, and $En_{96,2}Wo_{2,1}$ and $En_{52,8}Wo_{46,2}$ in Y-75305, respectively. Compositional differences of pyroxene and other minerals between coarse-grained and fine-grained parts in Y-75300 are not encountered, *e.g.*, average orthopyroxene compositions are $En_{96,3}Wo_{1,4}$ in the coarse-grained part and $En_{96,6}Wo_{1,4}$ in the fine-grained part, respectively. On the other hand, orthopyroxene and diopside in acapulcoites are enriched in FeO, *i.e.*, $En_{87,4}Wo_{1,5}$ and $En_{50,7}Wo_{44,8}$ in Y-74063, and $En_{88,4}Wo_{1,5}$ and $En_{49,8}Wo_{46,0}$ in ALH-77081, respectively. Orthopyroxene in winonaites has lower MnO and FeO contents than that in acapulcoites, and higher than that in EL-chondrites (Fig. 2). Diopside in winonaites has lower Cr_2O_3 and Na_2O contents than that in acapulcoites (Fig. 3).

4.2. Olivine

Anhedral olivine, 10 to 100 microns in size, occurs among orthopyroxenes. Olivine is also homogeneous in composition. Average Fo contents are 98.0 in Y-74025, 98.2 in Y-75305 and 98.3 in Y-75300, whereas olivine in acapulcoites is rich in FeO; $Fo_{88,7}$ in Y-74063 and $Fo_{80.4}$ in ALH-77081. Figure 4 shows the average compositions of olivines in Antarctic and non-Antarctic winonaites and acapulcoites. Olivine composition clearly distinguish winonaites from acapulcoites. Olivine in winonaites is also depleted in MnO, compared with those in acapulcoites (Table 2).

4.3. Feldspars

Plagioclase, 5 to 60 microns in size, occurs among orthopyroxene and often within orthopyroxene and diopside. Average compositions are $Ab_{76.5}An_{21.0}Or_{2.2}$ in Y-74025, $Ab_{79.4}An_{18.1}Or_{2.5}$ in Y-75300, and $Ab_{75.6}An_{22.4}Or_{2.0}$ in Y-75305, respectively. Plagioclase in winonaites is depleted in Na₂O and K₂O, compared with those in acapulcoites ($Ab_{79.9}Or_{4.4}$ in Y-74063 and $Ab_{80.4}Or_{4.1}$ in ALH-77081, respectively) (Fig. 5). The plagioclase composition is heterogeneous in different grains, *i.e.*, $Ab_{80.1-70.3}Or_{4.2-1.0}$ in Y-74025, $Ab_{77.2-73.1}Or_{2.9-0.7}$ in Y-75305, and $Ab_{93.7-73.0}Or_{7.6-0.7}$ in Y-75300. Especially, plagioclase coexisting with K-rich feldspar in Y-75300 is rich in Ab component (above Ab_{82}).

The three winonaites studied here always have K-rich feldspar. This is the first discovery of K-rich feldspar in winonaites, although K-rich feldspar also occurs in IAB silicate inclusion (KRACHER, 1985). Only one K-rich feldspar grain occurs within diopside as a tiny spherule in Y-75305 ($Ab_{78,8}Or_{18,9}$) (Fig. 6a). In Y-74025, a few K-rich feldspar grains occur within a troilite fragment ($Ab_{6,4-9,2}Or_{88,9-92,1}$) (Fig. 6b). K-rich feldspar in Y-75300 occurs as exsolution lamellae from plagioclase (Fig. 6c), and rarely within orthopyroxene. Although K-rich feldspar in Y-75300 shows wide compositional variation, $Ab_{7,0-71,0}Or_{25,3-91,3}$, thick lamellae and a grain within orthopyroxene have higher Or contents (above Or_{80}). Thin lamellae of K-rich feldspars may be due to contamination from surrounding plagioclase during analysis. The abundance of K-rich feldspar in Y-75300 is estimated at about 1% or less of plagioclase, based on modal analysis. No K-rich feldspars in winonaites have any detectable BaO content.

4.4. Chromite

Chromite, 2 to 40 microns in size, occurs abundantly as euhedral grains within Fe-Ni metal (Fig. 7a), and rarely among silicates in Y-75305. Only one chromite grain, 18 microns in size, occurs with schreibersite and troilite in Y-74025 (Fig. 7b). Y-75300 has a few chromites, 3 to 5 microns in size, occurring with orthopyroxene.

Table 3 gives representative compositions of oxide minerals. Since atomic Cr/Al and Mg/Fe ratios of chromites in winonaites are higher than 1, they are strictly called magnesiochromite. Chromite in Y-75305 is heterogeneous, *i.e.*, 0.1–0.6 wt% V_2O_3 , 56.0–74.1% Cr_2O_3 , 0.6–3.1% MnO, 0.1–2.2% TiO₂, 0.8–1.7% ZnO, 2.9–13.6% FeO, 0.2–17.6% Al₂O₃, and 11.2–20.5% MgO, and some

Phase	Name	SiO ₂	TiO ₂	Al_2O_3	Cr ₂ O ₃	FeO	MnO
Enstatite	Y-74025	58.20	0.04	0.33	0.07	1.62	0.26
	Y-75300	58.18	0.09	0.13	0.09	1.33	0.26
	Y-75305	58.67	0.08	0.15	0.06	1.32	0.17
	Y-74063	56.42	0.20	0.46	0.18	7.34	0.66
	ALH-77081	58.27	0.20	0.34	0.25	6.82	0.55
Diopside	Y-74025	54.78	0.75	0.71	0.15	0.51	0.06
	Y-75300	54.98	0.40	0.62	0.24	0.74	0.14
	Y -75305	55.35	0.25	0.48	0.14	0.56	0.12
	Y-74063	53.49	0.65	0.67	1.13	2.85	0.32
	ALH-77081	53.51	0.44	0.86	1.41	2.65	0.32
Olivine	Y-74025	41.49	0.00	0.01	0.02	1.81	0.29
	Y-75300	41.46	0.00	0.02	0.05	1.79	0.17
	Y-75305	42.52	0.00	0.00	0.02	1.75	0.17
	Y-74063	39.36	0.00	0.00	0.03	11.40	0.49
	ALH-77081	40.40	0.00	0.00	0.00	10.25	0.48
Plagioclase	Y-74025	63.13	0.00	23.17	0.00	0.14	0.00
	Y-75300	62.02	0.00	23.41	0.05	0.06	0.09
	Y-75300 ¹⁾	65.87	0.00	21.16	0.02	0.81	0.07
	Y-75305	63.29	0.00	22.48	0.00	0.17	0.00
	Y-74063	64.17	0.10	21.79	0.00	0.13	0.07
	ALH-77081	66.18	0.00	20.75	0.01	0.14	0.00
K-feldspar	Y-74025	64.31	0.00	18.55	0.00	1.39	0.02
	Y-75300	64.66	0.02	17.55	0.00	0.86	0.07
	Y-75305	70.87	0.00	18.98	0.03	0.42	0.00

Table 2. Representative compositions

¹⁾ coexisting with K-rich feldspar.



Fig. 2. FeO-MnO (wt%) plot for orthopyroxene in winonaites, acapulcoites, H6 chondrites (KIMURA, unpublished data), and EL-chondrites (KEIL, 1968).

MgO	CaO	Na ₂ O	K ₂ O	Total	En	Wo	Fo	Ab	Or
38.69	0.98	0.00	0.00	100.19	96.0	1.7			
38.38	0.82	0.01	0.00	99.29	96.6	1.5			
38.42	0.94	0.00	0.02	99.83	96.4	1.7			
34.07	0.52	0.00	0.00	99.85	88.4	1.0			
32.83	0.80	0.03	0.00	100.09	88.2	1.5			
19.37	23.24	0.42	0.00	99.99	53.3	45.9			
19.06	23.72	0.43	0.03	100.37	52.2	46.7			
18.16	23.43	0.33	0.01	98.83	51.4	47.7			
17.90	22.24	0.62	0.01	99.88	50.4	45.1			
17.28	22.22	0.71	0.00	99.40	49.7	46.0			
56.15	0.00	0.00	0.00	99.77			98.2		
55.40	0.11	0.00	0.06	99.06			98.2		
55.02	0.00	0.00	0.02	99.50			98.2		
48.25	0.02	0.00	0.00	99.55			88.3		
48.75	0.04	0.00	0.00	9 9 .92			89.4		
0.00	4.40	8.69	0.38	99.9 1				7 6.4	2.2
0.00	5.30	8.55	0.31	99.79				73.2	1.7
0.00	1.81	10.13	0.40	100.26				88.9	2.4
0.00	4.46	8.48	0.23	99.11				76.4	1.4
0.00	3.39	8.78	0.74	99.17				78.8	4 .4
0.00	3.30	9.11	0.77	100.26				7 9.6	4.4
0.04	0.29	0.70	15.24	100.55				6.4	92.1
0.00	0.20	1.47	15.52	100.34				12.5	86.6
0.02	0.46	8.82	3.22	102.82				78.8	18.9

of silicate minerals (wt%).



Fig. 3. Cr₂O₃-Na₂O (wt%) plot for diopside in winonaites and acapulcoites.



Fig. 4. Average olivine compositions (forsterite molecules) in winonaites and acapulcoites from Antarctica and non-Antarctica.



Fig. 5. Molar plot of orthoclase (Or)-albite (Ab)-anorthite (An) of plagioclases and K-bearing feldspars in winonaites and acapulcoites.

Primitive Achondrites of Winonaite Subgroup

Fig. 6a. Backscattered electron (BSE) image of a Kbearing feldspar (K-Pl) in a diopside grain (Di) in Y-75305. Olivine (Fo) and orthopyroxene (En) are also included in the diopside. Zircon (Zr) is also included, although it seems to have been introduced during the preparation of thin section from its occurrence. Troilite (Tr) and plagioclase (Pl) coexist with the diopside.



Fig. 6b. BSE image of Kfeldspar (Kf) and enstatite (En) inclusions in a troilite grain (Tr) in Y-74025.

Fig. 6c. BSE image of exsolution lamellae of K-feldspar (Kf) within albite (Ab) in association with enstatite (En) and troilite (Tr) in Y-75300. Width of 40 microns.



Fig. 7a. A euhedral magnesiochromite grain within Fe-Ni metal in Y-75305. Chemical zoning is distinct from Mg-Al-rich core (MgAl) to Fe-Crrich rim (FeCr) in this grain. Very fine olivine grains (Fo) coexist with the chromite. BSE image.

Fig. 7b. BSE image of a magnesiochromite (Mc) with schreibersite (Sch) and troilite (Tr) in Y-74025.

chromites within Fe-Ni metal show distinct zoning from Mg, Al, and Ti-rich core toward Fe, Mn, and Cr-rich rims (Fig. 7a and Table 3). The compositions of chromites in Y-74025 and -75300 are in the compositional range of those in Y-75305, except for lower contents of V_2O_3 (<0.05 and 0.2%) and MnO (0.9 and 0.8–0.9%) in Y-74025 and -75300, respectively. BILD (1977) reported chromites in Winona containing 12.3% FeO, 1.75% ZnO, and 71.3% Cr₂O₃, which are similar in composition to chromites in the Antarctic winonaites. Chromite in acapulcoites has an atomic Mg/Mg + Fe ratio intermediate between those of O-chondrites and winonaites (Fig. 8).

4.5. Rutile

A euhedral rutile grain, 30 microns in size, has intimate intergrowth with troilite in Y-75305 (Fig. 9). This is the first discovery of rutile from winonaites. It

Phase	Name	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	V_2O_3	FeO	MnO	ZnO	MgO	NbO ₂	Ta ₂ O ₅	Total
chromite	Y-74025	0.12	6.41	68.38	0.03	6.60	0.88	1.28	16.16			99.89
	Y-75300	0.18	15.30	56.75	0.17	5.62	0.86	1.50	17.96			98.34
	Y-75300	0.28	19.08	53.53	0.18	5.13	0.79	1.43	20.12			100.54
	Y-75305	0.78	15.12	56.02	0.36	7.39	2.76	1.05	16.35			99.88
	1) Y-75305	0.23	0.56	70.80	0.23	13.62	1.70	1.46	11.58			100.15
	2) Y-75305	0.85	8.74	62.27	0.17	10.46	1.27	1.68	13.77			99.28
	Y-75305	0.36	12.08	59.96	0.38	5.76	0.76	1.43	18.52			100.41
	Y-75305	1.18	9.10	62.20	0.16	10.57	1.25	1.61	13.81			99.95
	Y-74063	1.10	7.96	58.09	0.80	23.49	1.24	0.94	5.78			99 .40
	Y-74063	1.45	7.06	60.17	0.71	21.51	1.10	0.61	7.00			99.61
	ALH-77081	1.02	6.59	59.29	0.58	21.20	1.67	1.26	6.79			98.39
	ALH-77081	1.14	6.69	59.94	0.65	20.97	1.53	1.24	6.86			99 .02
rutile	Y-75305	94.47	0.02	1.44	0.00	0.03	0.03	0.87	0.04	3.76	0.18	100.86

Table 3. Representative compositions of oxide minerals (wt.%)

1) and 2) are rim and core of the same chromite grain, respectively (Fig. 7a).



Fig. 8. Mg/Mg+Fe vs. Al/Al+Cr (atomic ratio) plot for chromite in winonaites, acapulcoites, and H6 chondrites (average) (after Kimura, unpublished data).

contains 1.4 wt% Cr_2O_3 , 0.9% FeO, 3.8% NbO₂, and 0.2% Ta_2O_5 . Other constituents such as REE, MnO, V_2O_3 , Al_2O_3 , SiO_2 , ZrO_2 , and MgO are not detected. We assume that meteoritic Nb is Nb⁺⁺ following EL GORESY (1971), who reported Nb in rutiles in iron meteorites and mesosiderites (<2.9% NbO₂). Thus, this rutile grain has the highest NbO₂ content among meteoritic rutiles. The Nb/Ta weight ratio is 18.9 which is similar to the cosmic abundance, 17.3 (after ANDERS and GREVESSE, 1989).

4.6. Fe-Ti-oxide

An Fe-Ti-bearing oxide occurs in chromite as a tiny bleb, 2 microns in size,





Fig. 10. A diopside grain (Di) includes apatite (Apa) in Y-75305. A magnesiochromite grain (Mc) has zircon (Zr) and Fe-Ti-oxide grains (FeTi). This zircon may have been introduced during the preparation of the thin section. Troilite (Tr), orthopyroxene (En), and plagioclase (Pl) occur with the diopside and magnesiochromite. BSE image.

in Y-75305 (Fig. 10). Qualitative analysis shows that the Fe content is higher than that of Ti, and the Ti content is much higher than those of host chromite. Therefore, this phase may be ulvöspinel.

Phase	Meteorite	P_2O_5	CaO	FeO	MnO	MgO
Apatite	Y-75305	40.30	55.99	0.23	0.00	0.13
Apatite	Y-74063	41.58	55.03	0.34		0.00
Whitlockite	Y-74063	45.67	45.62	0.75		3.18
Apatite	ALH-77081	42.50	53.68	0.13		0.08
Whitlockite	ALH-77081	47.03	45.82	0.73		0.73

Table 4. Representative comp	ositions
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4.7. Apatite

Rare phosphate always occurs with or within diopside (Fig. 10). These grains are 2–10 microns in size, and only one grain in Y-75305 could be quantitatively analyzed. The phosphate grain in Y-75305 contains handly Na₂O, MgO, FeO, and REE (Table 4). The F content is much higher than Cl, and the atomic Ca/P ratio is about 5/3. Thus, this phosphate is fluorapatite. PRINZ *et al.* (1980) reported a chlorapatite in Mt. Morris and Winona. It is not yet clear whether winonaites have a whitlockite as well as an apatite. The abundance of phosphate in acapulcoites is higher than those in winonaites. Acapulcoites have whitlockite as well as apatite. ALH-77081 has chlorapatite (Table 4).

4.8. Troilite

Troilite has an irregular-shape, and occurs among silicates or with Fe-Ni metals. Table 5 gives representative compositions of sulfide minerals. Troilites in three winonaites contain 0.2-0.6 wt% Cr, and <0.05% Ni, Mn, and Ti. Troilites in Pontlyfni and Mt. Morris have 0.85 and 0.37% Cr, respectively (GRAHAM *et al.*,

Phase	Name	S	Ti	Cr	Mn	Fe	Со	Ni	Cu	Zn	Total
Troilite	Y-74025	36.61	0.00	0.54	0.00	62.65		0.00			99.80
	Y-75300	36.46	0.01	0.37	0.06	62.59				0.00	99.49
	Y-75305	36.53	0.02	0.27	0.00	63.16		0.07		0.16	100.21
	Y-74063	36.21	0.00	0.06	0.05	62.37		0.01			98.7 0
	ALH-77081	36.28	0.01	0.12	0.00	62.74		0.00		0.00	99.16
Daubreelite	Y-74025	44.50	0.00	35.98	1.39	18.97		0.00			100.84
	Y-75300	43.53	0.01	35.64	1.82	17.00				0.00	98.00
	Y-75305	44.73	0.03	36.50	0.21	18.51		0.06		0.14	100.18
Pyrrhotite	Y-75305	36.71	0.04	1.05	0.16	59.39		1.86		0.12	99.33
Pentlandite	Y-74063	33.65	0.00	0.00	0.00	46.49	0.37	18.65			99.16
CuMnS-1	Y-75305	31.46		0.01	34.23	2.91		0.37	29.97	0.00	98.95
	Y-75305	28.23		0.01	18.99	3.38		0.19	48.45	0.07	99.32
CuMnS-2	Y-75305	25.82		0.27	5.27	1.96		0.41	67.27	0.00	101.00
CuMnS-3	Y-75305	21.42		0.15	1.74	1.72		0.32	74.56	0.00	99.91

Table 5. Representative compositions of sulfide minerals (wt%).

MnCuS-1, 2, and 3: areas 1, 2, and 3 of Cu-Mn-sulfide.

of	phosph	iate	mineral	s ('wt%)
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Na ₂ O	Y ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃	F	Cl	O=F, Cl	Total
0.00	0.00	0.04	0.00	3.65	0.49	1.65	99.18
0.21					0.13	0.03	97.26
4.19					0.00		99.41
0.30					3.57	0.80	99.52
2.64					0.00	0.00	99.79

1977). The Cr contents of winonaite troilites are higher than those in acapulcoites (0-0.3%).

4.9. Daubreelite

Daubreelite abundantly occurs in troilite as exsolution lamellae, up to 60 microns in width. Daubreelite in Y-75305 has lower Mn contents (0.1-0.2 wt%) than those in Y-74025 (1.2-1.5%) and -75300 (1.3-2.0%). Daubreelite in these winonaites contains Zn below 0.4%, although PRINZ *et al.* (1980) reported daubreelites containing 4.0-6.1% Zn in Mt. Morris and Winona.

4.10. Pyrrhotite and Fe-Ni-sulfide

Only one Ni-bearing Fe-sulfide grain, 80 microns in size, occurs in Y-75305 (Fig. 11). This grain contains 1.0-1.9 wt% Cr and 1.9-2.7% Ni, and the atomic (Fe+Ni)/S ratios are 0.94–0.97. This is pyrrhotite, and includes other tiny Ni-rich Fe-sulfide grains, up to 2 microns. Qualitative analysis shows that the tiny blebs have higher Ni and lower S contents than the host pyrrhotite. They may be pentlandites. Pentlandite, below 50 microns, occurs within troilites in Y-74063, containing 17.9–19.1 wt% Ni.





4.11. Cu-Mn-sulfide

Y-75305 has a composite Cu-Mn-sulfide grain, 30 microns in size (Fig. 12), which occurs with troilite and daubreelite. This grain is divided into three compositional areas (Fig. 13). Area 1 is bluish gray in color under reflected light, and does not show internal reflection and anisotropy. This area has variable contents of Mn (15.2–47.1 wt%) and Cu (15.2–52.9%), with low Fe (2.3–3.9%), and is a mixture of dark and bright parts in back-scattered electron (BSE) image. The dark part in BSE image is rich in Mn, and is near alabandite in composition. The bright part is rich in Cu, and has a composition like the area 2 phase. An X-ray diffraction pattern shows that area 1 includes alabandite. Thus, this area is probably

180



Fig. 12. BSE image of a composite Cu-Mn-sulfide grain coexisting with troilite (Tr) and daubreelite (Dau) in Y-75305 (upper right corner). K_{α} images for Mn, Cu, and Fe show that area 1 is rich in Mn, whereas areas 2 and 3 are rich in Cu. Fe contents are low in all areas of this composite grain. Width of 65 microns, respectively.

a very fine-grained mixture of alabandite and area 2 phase. Area 2 is also bluish gray in color, and has no internal reflection and anisotropy. This area is rich in Cu (65.1-69.2%), and poor in Mn (3.6-5.4%) and Fe (2.0-2.3%), hence corresponds to a chemical formula of $Cu_{5,33}(Mn_{0.40}, Fe_{0.19})_{0.59}S_4$ on the average. The phase in this area is probably an unknown Mn-bearing Cu-sulfide. Area 3 is gray in color, and has no anisotropy and internal reflection. It is the most rich in Cu (72.9-74.6%), and poor in Mn (1.4-2.0%) and Fe (1.7-2.2%), and corresponds to a chemical formula of $Cu_{1.77}(Mn_{0.05}, Fe_{0.05})_{0.10}S_1$ on average. Optical and chemical data suggest that the phase of area 3 may be digenite $(Cu_{1.8}S_1)$, although it contains little Mn and Fe.

Y-75300 also has a Cu-Mn-sulfide grain, 5 microns in size, occurring intimately with troilite. This grain is compositionally similar to the Mn-rich part of area 1 in Y-75305 (Fig. 13).

4.12. Fe-Ni metal

Fe-Ni metal consists of abundant kamacite and taenite. Table 6 gives representative compositions of metallic phases. Fe-Ni metal contains <0.05% Si, P, and Cr,



Fig. 13. Atomic S-(Mn+Fe)-Cu plot of compositions of areas 1, 2, and 3 of a composite Cu-Mn-sulfide grain. Analytical data of area 1 are distributed between alabandite and a phase of area 2. A phase of area 3 has composition close to anilite ($Cu_{1,75}S$), digenite ($Cu_{1,8}S$), or chalcocite ($Cu_{2}S$).

and kamacite is almost homogeneous. Taenite shows a distinct chemical zoning of Ni and Fe. Kamacite in acapulcoites also does not contain Si, P, or Cr, and taenite shows zoning.

Phase	Name	Si	P	Cr	Fe	Со	Ni	Total
Fe-Ni metal	Y-74025	0.02	0.02	0.03	93.85	0.30	6.06	100.28
	Y-74025	0.03	0.00	0.00	57.71	0.09	41.64	99.47
	Y-75300	0.03	0.04	0.00	92.67	0.40	6.38	99.52
	Y-75300	0.00	0.00	0.00	69.78	0.21	30.40	100.39
	Y-75305	0.00	0.04	0.00	93.48	0.54	5.82	99.88
	Y-75305	0.00	0.01	0.01	58.50	0.16	40.64	99.32
	Y-74063	0.04	0.00	0.00	92.65	0.44	5.97	99.10
	Y-74063	0.00	0.00	0.00	50.08	0.08	49.22	99.38
	ALH-77081	0.00	0.05		92.93	0.41	6.54	99.93
	ALH-77081	0.01	0.00		63.50	0.14	35.27	98.93
Schreibersite	Y-74025	0.00	15.02	0.00	35.35	0.01	49.91	100.35
	Y-75300	0.04	15.30	0.02	34.21	0.00	49.88	99.45
	Y-75305	0.00	14.78	0.02	33.80	0.01	50.45	99.06
	ALH-77081	0.00	14.76		32.29	0.05	50.30	97.41

Table 6. Representative compositions of metallic minerals (wt%).

4.13. Schreibersite

Schreibersite, 20–60 microns in size, usually occurs within Fe-Ni metal, and rarely with troilite and silicate. Different grains vary compositionally (35.1-51.6 wt%) Ni in Y-74025, 48.9–54.1% in Y-75300, and 48.0–53.8% in Y-75305). Ni-poor schreibersite in Y-74025 occurs within pyroxene. Schreibersite does not occur in Y-74063, and only one grain, containing 50.3% Ni, occurs in ALH-77081.

5. Bulk Chemical Compositions of Y-74025 and -74063

Table 7 shows INAA results together with the results for standard rock JB-1 and a powder sample of the Allende meteorite. Figure 14 shows C1-normalized rare earth elements (REE) and Ss, and Figure 15 shows siderophile, lithophile, and chalcophile element abundances normalized to C1 chondrite.

	- <u></u>		Y-7402	5		Y-74063	3	ID 1		Error*
		А	В	Wtd. mean	Α	В	Wtd. mean	JR-I	Allende	(%)
Wt	mg	88.2	108.4		95.5	82.2		93.1	78.1	
Ti	%	0.084	0.060	0.071	0.072	0.11	0.090	0.743		$20-30^{2}$
Al	%	1.50	1.41	1.45	1.22	1.34	1.28	7.62		1–2
Fe ¹⁾	%	14.7	15.0	14.9	20.1	19.0	19.6	=6.30		0.5
Mg	%	16.5	16.9	16.7	15.6	16.0	15.8	4.64		2–5
Ca	%	1.41	1.87	1.66	1.03	1.79	1.38	6.07		4-10
Na	%	0.797	0.737	0.764	0.674	0.740	0.705	=2.07	0.381	0.5-1
Mn	%	0.168	0.167	0.167	0.262	0.265	0.263	0.112		0.5-1
Cr	%	0.196	0.199	0.197	0.292	0.245	0.270	=0.0414	0.314	0.5
Sc	ppm	10.4	12.8	11.7	8.20	11.9	9.91	=28.9	13.0	0.5
V	ppm	36	41	39	94	88	91	208		2–5
La	ppm	0.29	0.33	0.31	0.32	0.39	0.35	=38.8	0.56	5–7
Ce	ppm	0.5	0.5	0.5	1.1	0.6	0.87	=63	0.9	20-40
Sm	ppm	0.146	0.250	0.203	0.188	0.286	0.233	=5.02	0.338	1–2
Eu	ppm	0.078	0.071	0.074	0.088	0.085	0.087	=1.59	0.12	5–6
Dy	ppm	0.44	0.38	0.41	0.57	0.46	0.52	3.94		16–25 ³⁾
Yb	ppm	0.26	0.29	0.28	0.20	0.28	0.24	=2.4	0.30	7–10
Lu	ppm	0.050	0.043	0.046	0.043	0.047	0.045	=0.37	0.083	8–15
Hf	ppm	0.18	0.20	0.19	0.24	0.22	0.23	3.46	0.35	10–174)
Zn	ppm	51	46	48	109	79	95	=83	90	1–2
As	ppm	1.21	1.31	1.27	1.77	1.68	1.73	2.38	2.12	6–14
Se	ppm	36	29	32	24	21	23	6.8	=11	3-4
Со	ppm	323	369	348	470	449	460	=39.1	698	0.5
Ni	%	1.63	1.63	1.63	1.25	1.13	1.19	0.0172	=1.55	0.5 ⁵⁾
Os	ppb	244	162	199	220	150	190		=674	9–14
Ir	ppb	292	201	242	306	236	274	—	=853	1
Au	ppb	126	128	127	184	149	168		=157	2

Table 7. Chemical compositions of bulk Y-74025 and -74063.

* Errors for INAA are due to counting statistics.

¹⁾ Total iron as Fe. ²⁾ Except for JB-1 (4%). ³⁾ Except for JB-1 (3%). ⁴⁾ Except for JB-1 (2%).

⁵⁾ Except for JB-1 (3%).



Fig. 14. C1 chondrite (non-volatile) normalized abundance patterns of rare earth elements (REE) and Sc of (a) Y-74025 and (b) Y-74063.

The mass-weighted mean REE patterns of Y-74025 and -74063 are typically chondritic (Fig. 14). The REE pattern of Y-74063 by YAMAMOTO *et al.* (1990) is also chondritic. On the other hand, heterogeneous distributions of some elements (*e.g.*, Sc, Sm, and Ir) are noticed in 100 mg sized samples of both Y-74025 and -74063 (Table 7 and Fig. 14). Elemental abundances on Y-74025 and -74063 are generally not fractionated relative to C1 chondrite (Fig. 15), in comparison with Lodran and enstatite achondrites (Norton County and Peña Blanca Spring) which are of igneous origin. However, contents of V, Cr, Mn, Zn, and siderophile elements (except for Ni) in Y-74025 are depleted, compared with C1 chondrites. The abundance patterns of elements in Y-74025 and -74063 are similar to each other (Figs. 14 and 15). However, V and Zn are much poorer in Y-74025 and Y-74063.

6. Discussion

6.1. Formation condition of winonaites

Holocrystalline texture and homogeneous mineral compositions suggest that Antarctic winonaites were highly metamorphosed, like non-Antarctic winonaites. The two-pyroxenes geothermometer of LINDSLEY and ANDERSEN (1983) gives equilibration temperatures of about 850°C in Y-74025, 800°C in Y-75300, and 900°C in Y-75305, respectively, for diopsides coexisting with orthopyroxenes (Table 2). An equilibration temperature of a plagioclase (An_{8.7}Or_{2.4}) coexisting with a K-rich feldspar in Y-75300 is about 720°C using the geothermometer of IKEDA *et al.* (1978). These temperatures are consistent with the high metamorphic degree of these meteorites.

Winonaites are characterized by the presence of some minerals typical of Echondrites. Daubreelite as well as chromite occur in winonaites, whereas only chromite occurs in acapulcoites. Schreibersite is common in winonaites, whereas phosphate is common in acapulcoites. Alabandite occurs only in winonaites. On the other hand, Fe-Ni metal in winonaites contains hardly any Si, differing from SAMPLE / C1 CHONDRITES



Fig. 15. Elemental abundance ratios relative to C1 chondrite (non-volatile) for Y-74025 and -74063; (a) siderophile elements, and (b) chalcophile and lithophile elements. Data of Y-691 (FUKUOKA, 1986), Hvittis (HUGHES and SCHMITT, 1985), Peña Blanca Spring (P. Bla. Spr) and Norton County (N. County) (WOLF et al., 1983), Pillistfer (SEARS et al., 1982), Lodran (FUKUOKA et al., 1978), Acapulco (PALME et al., 1981), and Pontlyfni (DAVIS et al., 1977) are also plotted for reference.

Si-bearing metal in E-chondrites (KEIL, 1968). Troilite in winonaites contains hardly any Ti or Mn, which are present in E-chondrite troilites. FeO contents of pyroxene increase as E-chondrites<winonaites<acapulcoites<H-chondrites (Fig. 2). Thus, the redox condition of winonaites is intermediate between E-chondrites and acapulcoites.

6.2. Partial melting process

Acapulcoites may have been derived from a common precursor material by partial melting of various degrees (NAGAHARA *et al.*, 1990). This is supported by the observation of euhedral pyroxene and other silicates in them. However, no silicate grain in winonaites has a euhedral form.

K-rich feldspars in Y-74025 and -75305 are completely included in troilite and diopside, respectively. Thus, these feldspars survived from dissolution into plagioclass during the high-temperature metamorphism. It is impossible to explain such a K-rich feldspar (Ab_9Or_{89}) in Y-74025 by partial melting from plagioclase ($Ab_{77}Or_2$), based on a ternary feldspar phase diagram (CARMICHAEL *et al.*, 1974). Accordingly, Y-74025 may have primarily included a K-feldspar. One unusual H-like meteorite (Y-74359) also has primary condensates of K-feldspar (IKEDA *et al.*, 1991). On the other hand, K-feldspars exsolved from some plagioclases in Y-75300. Primordial feldspars bearing K_2O before an exsolution of K-feldspar in Y-75300 and a K-rich feldspar ($Ab_{79}Or_{19}$) in Y-75305 can be explained either by partial melting from plagioclase, or by primary condensation of K-feldspar. KRACHER (1985) suggested that a K-bearing feldspar of unknown composition in IAB inclusion may have originated by *in situ* melting. However, if Y-75300 and -75305 once melted, the degree of melting may be very small, because plagioclase and other silicates in them do not show a crystallization texture from melt.

From fractionated patterns of REE, PRINZ et al. (1980) and DAVIS et al. (1977) suggested that Winona, Mt. Morris, and Pontlyfni experienced igneous activity. YAMAMOTO et al. (1990, 1991) also found a fractionated pattern of REE in Y-75300, and suggested that the fractionation may be related to extensive thermal metamorphism. However, the fractionated REE pattern of Y-75300 may be explained by heterogeneous distribution of feldspar and pyroxene. On the other hand, we found that the mean REE pattern of Y-74025 is chondritic and not fractionated (Fig. 14). However, we found heterogeneous distributions of some elements in 100 mg sized samples of Y-74025. This heterogeneity may be due to primary heterogeneous distribution of minerals such as feldspar and pyroxene, and is not due to partial melting, because silicates in Y-74025 do not show any crystallization texture from melt.

Chromite in Y-75305 has usually a euhedral form within Fe-Ni metal, and shows chemical zoning (Fig. 7a). They should have crystallized from melt. Chromite in Y-74025 occurs in association with troilite. KRACHER (1985) found euhedral chromites in sulfides or metal in IAB silicate inclusions, with the chromites having crystallized under reducing conditions from a sulfide melt containing chalcophile Cr, Mn, and Zn. Chromites in Y-74025 and -75305 may have also crystallized from a sulfide-metal liquid under reducing conditions, suggesting that sulfide-metal

186

fractions of the winonaites once melted. The variable abundances of troilite and Fe-Ni metal in winonaites (Table 1) may be explained by the melting and segregation of sulfide and metal in the parent body. Silicate fraction of winonaites did not melt, in the case that primordial material including silicate, troilite, and Fe-Ni metal was heated at a temperature lower than 1100–1200°C, the solidus temperature of ordinary chondrite at 1 atmosphere (ISOBE, 1990). The depletion of siderophile elements in Y-74025 (Fig. 15) is consistent with the low abundance of Fe-Ni metal in it.

6.3. Classification of winonaite

Antarctic winonaites studied here are similar in mineralogy to non-Antarctic winonaites, as mentioned in Section 4. On the other hand, mineral chemistry and accessory minerals, which reflect the redox condition, in these winonaites are different from those in acapulcoites. Orthopyroxenes (Fig. 2) and olivines in winonaites are more depleted in MnO and FeO than those in acapulcoites. However, troilite contains little Mn, and abundances of alabandite and Mn-bearing daubreelite are low in winonaites. Thus, the low content of MnO in pyroxenes cannot be explained by the presence of chalcophile Mn in winonaites. Diopside in winonaites is depleted in Na_2O and Cr_2O_3 (Fig. 3). Plagioclase in winonaites has lower Na_2O and K_2O contents than those in acapulcoites (Fig. 5). Rare K-feldspar enriched in Na₂O and K₂O cannot explain the depletion of alkalis in plagioclase. Alternatively, all these mineral compositions probably reflect the bulk compositional difference between winonaites and acapulcoites; the bulk contents of Mn, Cr, and Na are 0.26-0.30 and 0.17-0.21, 0.27-0.74 and 0.19-0.21, and 0.62-0.75 and 0.37-0.76% for acapulcoites and winonaites, respectively, after neutron activation analyses (PALME et al., 1981; SCHULTZ et al., 1982; DAVIS et al., 1977; KALLEMEYN and WASSON, 1985; this study).

Winonaites and acapulcoites are primitive achondrites after PRINZ et al. (1980). However, mineralogy and chemistry distinguish winonaites from acapulcoites. Winonaites are reduced primitive achondrites, whereas acapulcoites are oxidized ones. Three terms have been proposed for Winona-like meteorites. The term forsteritechondrite is not proper for them, because olivine is much poorer in amount than pyroxene, and forsterite also occurs in E-chondrites. IAB-chondrite is not proper either. Although silicate inclusions in IAB-iron meteorites resemble winonaites in mineralogy and chemistry (BILD, 1977) and oxygen isotopes (CLAYTON and MAYEDA, 1983), the modes of occurrence are different from each other; IAB inclusions are found in iron meteorites. Although Winona has an olivine which is slightly enriched in FeO than those of the other winonaites (Fig. 4), we do not prefer to propose another term for this subgroup. Thus, we recommend use of the term winonaite after PRINZ et al. (1980). Winonaite previously included ALH-77081 and Acapulco (PRINZ et al., 1980). However, here we propose that winonaite is defined as a subgroup of primitive achondrite, which includes Y-74025, -75300, -75305, Winona, Pontlyfni, Mount Morris, and Tierra Blanca. Winonaite is also defined mineralogically to contain magnesian olivine (Fo₉₄₋₉₉) (Fig. 4), and some characteristic minerals</sub> such as daubreelite, chromite, schreibersite, and phosphate.

7. Conclusions

(1) Although winonaites and acapulcoites are primitive achondrites, they can be clearly distinguished from each other, based on their constituent minerals and mineral chemistry.

(2) Winonaites are characterized by the presence of various accessory minerals such as daubreelite, chromite, schreibersite, phosphate, and K-feldspar. They reflect formation of winonaites under redox conditions intermediate between E-chondrites and acapulcoites.

(3) Holocrystalline texture, homogeneous mineral composition, and high equilibration temperature for pyroxenes suggest that winonaites experienced high-temperature metamorphism.

(4) Silicate fractions of winonaites do not show any textural and mineralogical evidence for melting, which is consistent with a chondritic REE pattern of Y-74025. On the other hand, the metal-sulfide fractions of winonaites probably melted and fractionated.

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