#### Proc. NIPR Symp. Antarct. Meteorites, 1, 145-172, 1988

# ON THE PAIRING OF ANTARCTIC UREILITES WITH REFERENCE TO THEIR PARENT BODY

#### Hiroshi TAKEDA, Hiroshi MORI and Hiromi OGATA

Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo 7-chome, Bunkyo-ku, Tokyo 113

*Abstract:* In spite of their apparent igneous textures, ureilites preserve significant records of primitive nature including oxygen isotope anomaly and high planetary-type noble gas contents in the carbonaceous matrices. Mineralogical studies of new Antarctic ureilites revealed that pairing of the small ureilite specimens may be only minor (two out of twenty-two) in comparison with the polymict eucrites. However, we noticed two groupings, which are almost paired but are distinct in pyroxene assemblages and reduction textures. The magnesian and calcic groups have been recognized only in the Antarctic collections. The individual specimens within the group may have evolved in the vicinity within a parent body. A model in conformity with this evolution has been proposed in the context of the ureilite-carbonaceous chondrite connection. However, the carbon-containing chondrite-like materials do not imply the actual chemistry of the known chondrites, because the preferential sedimentation of mafic silicates in the solar nebula may produce source materials much closer to ureilites.

### 1. Introduction

Ureilites are ultramafic achondrites consisting of olivine and pyroxene embedded in a carbonaceous matrix. Ureilites are rare in the non-Antarctic population, but 22 specimens (Table 1) have been recovered from Antarctica and many more are being described. Some of them differ chemically or petrologically (YANAI, 1987; MASON, 1985) from non-Antarctic ones. The significance of differences that exist between Antarctic and non-Antarctic meteorites is beginning to be recognized (DENNISON *et al.*, 1986; TAKEDA *et al.*, 1983). We pointed out that the Antarctic population relative to non-Antarctic falls is overabundant in polymict eucrites, among other HED (howardites, eucrites and diogenites) achondrites, although many specimens of these achondrites may have been derived from the same fall (TAKEDA *et al.*, 1983). Therefore, pairing is an important problem which must be sorted out before Antarctic-non-Antarctic differences can be discussed. In this study, we compared Yamato-82100 with LEW85328 and Y-74123, MET-78008 with Y-74130, and Y-791538 with Y-74659 and LEW85440 mineralogically and discuss the problem of pairing of the Antarctic ureilites by reviewing the literature data on these ureilites.

Although extensive studies of the newly recovered Antarctic ureilites have advanced our understanding on the genesis of ureilites (BERKLEY and JONES, 1982; TAKEDA, 1982, 1987a; BERKLEY, 1986; GOODRICH *et al.*, 1987a), there still remains controversy on three major proposed models on the formation of ureilites. Main problems are

Sample	Weight (g)	Size (cm)	%Fa	%Fs	%Wo	Pairing
Y-74123	69.9	4.5×3.0	20.7	17.9	6.5	
<b>Y-74130</b>	17.9	$3.0 \times 2.7$	22.9	13.0	32.5	
				18.0, 18.7	14.2, 4.4	
Y-74154	2.8	$1.7 \times 1.3 \times 0.7$	2-16	6-13.1		
Y-74659	18.9	$4.2 \times 2.7$	8.1	8.0	7.2, 4.5	
Y-790981	213.0	$6.3 \times 5.5 \times 4.0$	15	18	8	
Y-791538	419.0	8.0×5.3×4.8	8.2	8.1	8.8, 4.8	
Y-791839	5.8	$2.8 \times 2.2 \times 1.2$	24	10-16	4-21	
<b>Y-82100</b>	12.3	$2.6 \times 2.5 \times 1.2$	19	15	9	
Y-84048	53.3	4.8×3.7×1.8				
ALHA77257	1995.7	16×11×9.5	12.9	12.4	6.7	
MET78008	125.5	6×4.5×3.5	22	13	32	
ALHA78019	30.3	$3.0 \times 3.0 \times 2.5$	23.2	18.8	9.6	Α
ALHA78262	26.2	$4.0 \times 2.5 \times 2.0$	22	19		A'
ALHA81101	119.2	$7.2 \times 4.5 \times 3$	10-22	17-25	3-10	
ALH82106	35.1	$4.5 \times 2.5 \times 2.5$	3	4.6	9.6	В
ALH82130	44.6	"	3	4		В
ALH83014	44.6	$1 \times 0.5 \times 0.5$	18	15		
PCA82506	5316.0	22×16×9	21	18	6	
LEW85328	106.8	$5 \times 4 \times 2$	20	17	9	
LEW85440	43.8	$4.5 \times 2.5 \times 2$	9	8	5	
EET83309(p)	60.8	$4.0 \times 4.0 \times 2.5$	15-23	18-6	5-39	
EET83225	44.0	$5 \times 2.5 \times 2.5$				

Table 1. Lists of Antarctic ureilites\*.

\* Data from Berkley (1986), KOJIMA and YANAI (1984), MASON (1985), YANAI (1987), YANAI and KOJIMA (1986), TAKEDA (1987a) and others.

Modal abundances are not known for many ureilites. p: polymict ureilite.

concerned with how high temperature ultramafic rocks are mixed with carbonaceous matrix rich in noble gases. (1) Partial melt residue model requires late-stage injection with carbon (BOYNTON *et al.*, 1976; WASSON *et al.*, 1976). (2) Igneous cumulates formed from a carbon-rich magma may release noble gases during the high temperature episode (BERKLEY *et al.*, 1980; GOODRICH *et al.*, 1987b; SPITZ and GOODRICH, 1987) and the homogeneous mixing of carbonaceous materials at every grain boundary may be difficult. (3) High temperature recrystallization of nebula condensates by planetesimal-scale collision requires removals of Ca-Al-rich residual liquids and Fe-Ni-S eutectic melts (TAKEDA, 1987a). GOODRICH *et al.* (1987b) interpreted this model as a variation of the partial melt residue model, but an important process of this model is that mafic crystals grow from partial melts and the residual liquids are removed. We will discuss these points in this paper on the basis of the pairing of Antarctic ureilites and the new findings after our previous paper (TAKEDA, 1987a). At present, only our model of the previously proposed ones can account for the recently observed oxygen isotopic compositions of ureilites (CLAYTON *et al.*, 1987) without much modification.

The origin of diamonds in the carbonaceous matrices of ureilites is another controversial problem in meteoritics (LIPSCHUTZ, 1964). The occurrence of diamond and lonsdalite in the carbonaceous matrix, mostly graphite, has been understood as an

#### Antarctic Ureilites

evidence that most ureilites have experienced moderate to severe shock. However, mosaicism of olivine in some ureilites is not as extensive as we expect from the formation of diamond. Vapor growth diamond has been known for some time (*e.g.*, DERJAGUIN *et al.*, 1968). When the vapor growth synthesis of diamond was reported by SPITSYN *et al.* (1981), one of us examined the possibility that diamond in ureilites might have formed in such a process (TAKEDA, 1982). The conclusion was that the presence or absence of diamond is not essential in the formation of ureilites. Because similar proposal has been raised recently on the basis of synthesis of diamond rich in noble gases by a process much closer to the ureilite cases (FUKUNAGA *et al.*, 1987), we will discuss this problem in this paper also.

## 2. Samples and Experimental Techniques

Because only small amounts of some specimens of the Yamato ureilites are left at National Institute of Polar Research (NIPR), we will describe in some detail the specimens used. A brief description of the Yamato ureilites was given in TAKEDA (1987a). Additional information on the previously studied samples is given together with description of the new Yamato and Victoria Land ureilites.

Regular polished thin sections (PTS) of Y-82100,51–3, Y-791538,71–2, ALH82106, MET-78008,61–1, LEW85328 and LEW85440 were used for microscopic examination and microprobe analyses. Single crystals were selected from the small fragments from ALH82106 and Y-791538 and were mounted on a glass fiber for X-ray examination. The h0l and 0kl nets were photographed by a precession camera with Zr-filtered Mo radiation.

Selected single crystals of pyroxenes and olivines were examined after the X-ray examination with a Hitachi H-600 analytical transmission electron microscope (AEM), equipped with Kevex Super 8000 system. The method is the same as that used for diogenites (TAKEDA and MORI, 1985). The oriented crystal mounted in resin was sliced and polished to about 10 microns thickness. The sample glued to a 3mm molybdenum AEM grid for support was thinned in a GATAN ion-milling machine until perforation occurred. Examination of microtextures of the sample was carried out by the AEM. Carbonaceous matrices of ALH-78262 have been studied by the AEM method.

The Y-74659 meteorite was collected by K. YANAI and his party of the 15th Japanese Antarctic Research Expedition (JARE) on December 29th, 1974, near the Yamato Mountains in Antarctica (YANAI, 1979). This meteorite originally weighed 18.9 g, but a significant portion (a few grams) has been used for an indefinite purpose before the first identification of it as ureilite (TAKEDA *et al.*, 1978). The piece, when it was found, had a fractured surface on one side, measuring  $4.2 \times 2.7$  cm. It is blackish with a blue tint. The stone is not as brittle as was reported for Haverö, but is not as hard as Kenna, either. The Y-74659 meteorite was first brought to curator's attention at NIPR, because of its unusual appearance. Chemical analysis of small amounts of crushed samples which remained with the large mass by H. HARAMURA (Geol. Inst., Univ. of Tokyo) indicated that its composition matches that of weathered ureilites. On the basis of the chemical composition of olivine and pigeonite and the texture of a small thin section, this meteorite has been identified as the ninth ureilite at that time (TAKEDA *et al.*, 1978). This was the first Mg-rich ureilite.

Another magnesian ureilite, Y-791538 (Fa<sub>8.2</sub>, Table 1) weighes 419.0 g and has been identified by B. MASON (private communication, 1982) as a ureilite with olivine composition similar to Y-74659. One PTS and a chip were used for the preliminary identification (TAKEDA and ISHII, 1987), and abundant orthopyroxene was found. LEW 85440 (Fa<sub>9</sub>) described recently by MASON (1987) contains pyroxenes similar to this orthopyroxene. Small chips of the more magnesian ureilites, ALH82106 and 82130, have been used for the X-ray examination.

A preliminary inspection of a hand specimen of Y-74123 (FREDRIKSSON, personal report to NIPR, 1977) and the Fe content of one olivine fragment (YANAI *et al.*, 1978) available for the preliminary identification revealed a similarity to an unequilibrated H chondrite. The rare gas pattern of the meteorite (HINTENBERGER *et al.*, 1978) suggested, however, that it might be a ureilite. Our mineralogical examination of a larger sample confirms that Y-74123 is the most olivine-rich ureilite with Fa<sub>20.7</sub> (TAKEDA *et al.*, 1978). The second PTS (Y-74123,92) supplied from NIPR does not contain pigeonite, but the third one (Y-74123,92–1) contained one pigeonite crystal.

Y-790981 weights 213 g and is a fragment  $(6.3 \times 5.5 \times 4.0 \text{ cm})$  bounded by three intersecting flat fracture faces and one round face with partly weathered black fusion crust, which shows polygonal fractures characteristic of ureilites. Round dark crystals, relatively coarse-grained, can be seen on the fracture surfaces, with some spaces between the crystals. White needle-like crystals are found in cavities on the surface. Y-790981 was identified as a ureilite (Fa<sub>15</sub>) by the Preliminary Examination Team (PET) at NIPR (TAKEDA and YANAI, 1982). Y-790981 was studied by TAKEDA and YANAI (1982), TAKEDA (1987a), BERKLEY (1986), and GOODRICH *et al.* (1987a).

Y-82100 (Fa<sub>19</sub>) is a very small stone (12.36 g) and the thin section available for our study is also small. LEW85328 (Fa<sub>20</sub>) is reported to be similar to this meteorite (MASON, 1987).

Y-74130 is a 17.9-g fragment found in the Yamato Mountains, Antarctica by the JARE party in 1974. A very small thin section from a chip supplied for identification, shows all the characteristics of the ureilite textures, but it consisted of olivine  $(Fa_{22.9})$  and augite (TAKEDA *et al.*, 1979). A large mass (1.010g) used for chemical analysis by H. HARAMURA and for larger thin sections is composed mainly of a large single crystal of low-Ca pyroxene with a cleavage plane and a portion similar to the first chip (TAKEDA, 1987a). The PTS supplied from NIPR (Y-74130,63–1) contained two portions of different pyroxene assemblages and carbon-rich veins. Y-74130 has later been described briefly by GOODRICH (1986) on the PTS assigned to BERKLEY.

ALH-77257 collected by YANAI and SHIRAISHI of the joint U.S.-Japan team near the Allan Hills, Antarctica was identified as a ureilite by the Meteorite Working Group and us (TAKEDA *et al.*, 1980). A thin section used by the PET and a chip were used in the previous study. This is the second Mg-rich ureilite (Fa<sub>12.9</sub>) at this time. The pyroxene composition is distinct from the Y-74659 group and is located between the magnesian and intermediate groups. ALHA77257 has been described by several workers, including BERKLEY and JONES (1982), TAKEDA (1987a) and GOODRICH *et al.* (1987a).

ALH-78019 is another ureilite found by the joint U.S.-Japan team for Antarctic

#### Antarctic Ureilites

Meteorite Search (TAKEDA *et al.*, 1980). A polished thin section made at NASA/JSC for PET by SHIRAISHI and small rock fragments were used in the previous study (TAKEDA *et al.*, 1980). We found that this meteorite is one of the most Fe-rich (Fa<sub>23.2</sub>) and the least shocked ureilites (TAKEDA *et al.*, 1980). BERKLEY and JONES (1982) later confirmed this finding. ALHA78262 was identified by the PET as similar to ALHA78019, but only a small chip was available. We investigated microstructures of these samples by the AEM.

### 3. Results

### 3.1. Ordinary group; Y-82100, -74123, -790981 and LEW 85328

The Y-82100 PTS preserves the original outer oval shape of the complete specimen. The minerals in Y-82100 are finely fractured and pigeonite shows coarse twin bands (Figs. 1a, 1b), indicating intermediate-level shock effects. The modal abundance of olivine and pigeonite is approximately 80:20. The Fa content of olivine ranges from 19 to 16 with reduced rims, and the pigeonite composition of Y-82100 is Ca<sub>9</sub>Mg<sub>76</sub>Fe<sub>15</sub> (Fig. 2a and Tables 2 and 3). The interstitial pyroxene-like materials are less abundant than in Y-74123. Ca-rich rim material similar in composition to that in Y-74123 was found at a pyroxene-pyroxene boundary (OGATA *et al.*, 1987). Y-790981 includes such interstitial materials at the grain boundaries, but similar glassy materials produced by a shock event are also present within the pyroxene crystals. The detailed textures and compositions of these phases will be published elsewhere shortly.

LEW85328 shows textures different from common ureilites. The so-called carbonaceous veins are not pronounced and some dark materials reveal a lath-shape with fine opaques scattered around the lath (Fig. 1c). This texture has been previously described by BERKLEY (1986). The pyroxene composition (Fig. 2b) is close to that of Y-82100.

### 3.2. Magnesian group; Y-791538, LEW 85440, Y-74659 and ALH 82106

The PTS of Y-791538 shows an equigranular aggregate of olivine and pyroxene, as rounded to subhedral grains up to 2 mm (Fig. 3a). The grain boundaries are filled with black carbonaceous matrix. The thickness of carbonaceous veins is thinner than those of the Y-74659 ureilite, and along some grain boundaries the matrix appears to be missing. The olivine crystals show well-developed subgrain boundaries with undulatory extinction. They have suffered secondary reduction and dusty metal particles are found at the rims and around the fractures (Fig. 3a). The fine metal particles are deposited along the dislocations and decorate linear tilt boundaries. This feature is different from Y-74659, although microprobe analyses show olivine of uniform core composition, Fa<sub>8.2</sub> (Table 3), almost identical to Fa<sub>8.1</sub> of Y-74659 (TAKEDA, 1987a).

Y-791538 is unusual among ureilites because it contains significant amounts of orthopyroxene (opx) in addition to olivine and pigeonite (pig). The modal abundances of minerals are approximately oliv 55, pig 27 and opx 18. Microprobe analyses show two pyroxenes of uniform compositions: pig,  $Ca_{8.8}Mg_{83.1}Fe_{8.1}$ ; opx,  $Ca_{4.8}Mg_{88.1}Fe_{7.1}$  (Fig. 2b, Table 2). The opx composition is almost identical to the Y-74659 opx but pig is more Ca-rich than the Y-74659 pig ( $Ca_{7.2}Mg_{84.8}Fe_{8.0}$ ). Single crystal X-ray diffraction patterns of an opx crystal indicate that the majority is structurally opx. The opx crystals show



a. Y-82100. Open. Width is 3.3 mm.

b. Y-82100. The same view with cross polarized light. Note parallel slabs of twin bands in pigeonite. Width is 3.3 mm.

c. LEW85328. Width is 3.3 mm.

Fig. 1. Photomicrographs of overall textures of ureilites in the ordinary group.



Fig. 2b. Enlarged portion of py. roxene quadrilateral for Antarctic (solid circles) and non-Antarctic (open circles) ureilites. Only last three digits of sample numbers in Table 1 are given. The other data after TAKEDA (1987a).



Ca

Fig. 2c. Pyroxene quadrilaterals of Ca-rich ureilites, Y-74130 and MET-78008. Compositions of small interstitial grains of pigeonite and augite in LEW 85440 are given (triangle) for comparison.

fine linear lamellae-like features along (100) (Fig. 3b) but the intensity of the X-ray reflection of augite is weak to be detected. The lamellae may be twinned clinoenstatite produced by shock. The pigeonite crystals are characterized by thick twin bands (Fig. 3b).

The opx-like grains in Y-74659 and ALH-77257 have been found only as a small inclusion in olivine (TAKEDA, 1987a). In Y-791538, the opx crystals are large discrete grains up to 1 mm in diameter. Some crystals are in contact with the pig crystal with distinctly higher Ca content with a sharp compositional boundary. A few opx crystals

	LEW85440		Y-791538	<b>Y-82100</b>	<b>Y-7</b> 4123	LEW85328	MET-78008	
	Opx	Aug	Орх	Pig	Int.	Pig	Aug	Opx
SiO <sub>2</sub>	56.7	54.9	57.0	55.6	52.1	54.5	52.2	53.5
TiO <sub>2</sub>	0.12	0.21	0.12	0.06	0.21	0.10	0.22	0.11
$Al_2O_3$	0.82	1.31	0.79	0.41	1.81	1.37	3.17	2.24
$Cr_2O_3$	0.76	0.81	0.95	1.11	1.41	1.20	1.76	1.22
FeO	5.21	3.23	4.73	9.85	6.38	10.96	7.76	12.16
MnO	0.43	0.32	0.45	0.44	0.35	0.34	0.36	0.43
MgO	33.1	21.5	33.0	27.6	22.2	26.1	18.36	27.2
CaO	2.71	18.17	2.60	4.42	13.97	4.93	14.84	2.29
Na₂O	0.03	0.21	0.03	0.03	0.17	0.20	0.72	0.12
Total	99.88	100.66	99.67	99.52	98.60	<b>99.7</b> 0	99.39	99.27
Ca*	5.1	35.9	5.0	8.8	28.0	9.9	32.0	4.6
Mg	87.2	59.1	87.9	76.0	62.0	72.9	55.0	76.3
Fe	7.7	5.0	7.1	15.2	10.0	17.2	13.0	19.1

Table 2. Chemical compositions (wt%, individual analyses) of pyroxenes in selected ureilites.

\* Atomic percent.

Table 3. Chemical compositions (wt%, individual analyses) of olivines in selected ureilites.

	LEW85440	Y-791538	<b>Y-82100</b>	<b>Y-7</b> 4123	LEW85328	MET-78008
SiO <sub>2</sub>	40. 3	40.5	38.9	39.3	38.4	38.2
TiO <sub>2</sub>		0.01				
$Al_2O_3$	0.03	0.05	0.03	0.06	0.04	0.05
$Cr_2O_3$	0.45	0.56	0.88	0.40	0.50	0.45
FeO	8.28	8.09	16.68	13.04	19.36	20.8
MnO	0.43	0.46	0.45	0.41	0.40	0.38
MgO	50.0	49.5	42.3	45.7	41.3	39.8
CaO	0.31	0.30	0.39	0.27	0.29	0.23
Na₂O		0.01		0.01	0.02	
Total	99.80	99.48	99.63	99.19	100.31	99.91
Mg*	91.5	91.8	81.8	86.2	79.2	77.3
Fe	8.5	8.2	18.2	13.8	20.8	22.7

\* Atomic percent.

poikilitically enclose round olivine, and olivine encloses pig. The observation indicates that they form an equilibrium coexisting pair and are compatible with the phase diagram of LONGHI and BOUDREAU (1980). The detailed mineralogical study will be given elsewhere.

LEW85440 has olivine and pyroxene compositions almost idential to those of Y-791538 except for the Ca content of the pyroxene. The low-Ca pyroxene shows planar texture similar to opx in Y-791538 (Fig. 3c) and has almost idential composition to the Y-791538 opx (Figs. 2b, 2c and Table 2). The fine metal particle distribution at the olivine crystal rims is also similar to Y-791538.

The ALH82106 ureilite contains more Mg-rich pyroxenes and olivines than Y-74659, -791538 and LEW85440, and may not belong to this group. The olivine crystals con-



a. Y-791538. Open. Width is 3.3 mm. Note dusty olivine (upper middle).

b. Y-791538. Cross-polarized light. The crystal with fine lamellae (upper right) is orthopyroxene, and one with coarse twin bands is pigeonite (left).

c. LEW 85440. Cross-polarized light. The opx crystal shows linear features the same as in Y-791538. Width is 3.3 mm.

Fig. 3. Photomicrographs of overall textures of magnesian ureilite group.



a. Olivine crystals with numerous inclusions of fine metal particles. Open.

b. Primary augite showing twin lamellae. Cross polarized light (upper right).

c. Ropy augite inclusions in pigeonite. Cross polarized light.

Fig. 4. Photomicrographs of the ALH 82106 thin sections. Width is 1.3 mm.



Fig. 5. Electron photomicrographs of pyroxene and graphite in ureilites.

a. Augite blebs in the ALH-82106 pigeonite showing spinodal decomposition. Width is 2.5 µm.

b. TEM micrograph showing heterogeneously nucleated exsolution lamellae in the blebby augite in ALH 82106. Width is 0.73 µm.

c. TEM photograph of graphite crystals from the ALH-78262 ureilite. Width is 1.57 µm.



a. Augite crystals in olivineaugite portion of MET-78008. Open.

b. Ellipsoidal augite and olivine in a low-Ca pyroxene (in extinction position) in MET-78008. Cross polarized light.

c. Ellipsoidal pigeonites (upper middle) in the MET-78008 augite to be compared with Y-74130 (TAKEDA, 1987a). Cross polarized light.

Fig. 6. Photomicrographs of MET-78008 and Y-74130. Width 3.3 mm.

Antarctic Ureilites

- Fig. 7. Transmission electron micrographs of dislocations in olivines and a diamond in the ALH-78019 and -78262 ureilites.
- a. Dislocation substructure in olivine from the ALH-78019 ureilite. Dark field. Note very few dislocations.

b. (001) subboundaries in olivine from the ALH-78262 ureilite. Dark field.

c. Dislocation substructure in diamond from the ALH-78262 ureilite. Bright field.



tain numerous inclusions of small metal particles (Fig. 4a). Small amount of primary augite grains with twin bands are observed (Fig. 4b). The augite inclusions reported (BERKLEY *et al.*, 1985) as representing exsolution show complex wavy tangled, ropy textures and no straight planar (001) exsolution lamella was observed in the ALH82106 pigeonite by an optical microscope (Fig. 4c). The composition image and Ca X-ray image of SEM revealed also a complex texture similar to that observed in some low-Ca inverted pigeonite, but the shapes are more irregular bleb-like ones connected by thinner wavy sheets of augite.

The X-ray diffraction spots of pyroxene are broadened, indicating intense shock events. The h0l precession photo shows that the pigeonite is intimately twinned on (100) and weak diffuse streaks were detected along the a\* direction similar to that of the Y-74130 low-Ca pyroxene. The reflections of augite observed in the thin section were not easily detected on this reciprocal net, because the orientation of the augite may not have a definite geometrical relationship with the pigeonite. The AEM observation showed that pigeonite hosts have extensive lamellar twinning and the augite blebs reveal very fine tweed-like exsolution lamellae produced by spinodal decomposition (Fig. 5a), and heterogeneous neucleation and growth of low-Ca pyroxene (Fig. 5b).

## 3.3. Calcic group; MET-78008 and Y-74130

MET-78008 has been described as an olivine-augite-bearing ureilite (MASON, 1985). The PTS we examined includes two chips of the specimen. One chip consists of olivine and augite (Fig. 6a), but the other chip with fusion crust includes a small portion of what is similar to the large low-Ca pyroxene crystal in Y-74130. Ellipsoidal grains of augite and olivine are poikilitically included in this crystal (Fig. 6b). One augite crystal includes two ellipsoidal crystals of pigeonite as we observed for Y-74130 (Fig. 6c). The chemical compositions of pyroxenes in MET-78008 (Ca<sub>32</sub>Mg<sub>55</sub>Fe<sub>13</sub>) and Y-74130 (Ca<sub>32</sub>Mg<sub>55</sub>Fe<sub>13</sub>) are identical (Table 2 and Fig. 2c) and compositions of olivines are given in Table 3. It is to be pointed out that these two ureilites have similar mg numbers,  $100 \times Mg/(Mg+Fe) = 78-77$ , of olivines.

### 3.4. Microtextures of unshocked ureilites

Two ureilites with Fe-rich pigeonites (e.g., ALH-78019 and -78262) comparable to that in the calcic group show less shocked texture than other ureilites (SCORE et al., 1982). We compared microtextures of their minerals by the AEM. Diamonds in the graphite matrix (Fig. 5c) in ALH-78262 have been studied also by the AEM. The texture that shows euhedral diamonds grown in the graphite matrix is difficult to observe. A diamond includes metal particles which might have been originally in graphite. There are areas of platy graphite devoid of diamonds (Fig. 5c). Y-790981 shows only graphite by our AEM study. In spite of an apparent unshocked texture of olivine, two meteorites, ALH-78019 and ALH-78262 show different dislocations of olivine (Fig. 7a, 7b). The ALH-78262 diamond shows dislocation texture (Fig. 7c).

#### 4. Discussion

#### 4.1. Comparison of possible paired specimens

As we previously pointed out, no systematic differentiation trend has been reconstructed from the pyroxene quadrilaterals (Fig. 2b) of the ureilites (TAKEDA, 1987a). However, a careful examination of the figure may reveal three groups with somewhat constant mg number, if we exclude ALH82106, ALHA77257 and shock-modified ureilites (Y-790981). The Mg-rich group includes LEW85440, Y-74659 and -791538 pyroxenes with increasing Ca contents. The intermediate ordinary group includes EET83309, PCA82506, Y-74123, -790981, LEW85328, Y-82100 and ALHA78019 with increasing Ca contents, but they are not as tightly grouped as the magnesian one. The Ca-rich group consists of MET-78008 and Y-74130, whose mg numbers are close to the Fe-rich end of the ordinary group. The origin of nearly constant mg trends may be of importance if they were ever established with regard to the grouping of isotopic anomaly of oxygen (CLAYTON *et al.*, 1987) carbon and nitrogen when the complete data are available (GRADY and PILLINGER, 1987). The magnesian group has similar oxygen isotopic compositions (R. N. CLAYTON, personal communication, 1988). We discuss each possible group below.

4.1.1. Ordinary group; Y-82100 with Y-74123, LEW85328 and PCA82506

The chemical compositions of these four pigeonites cluster around an intermediate region among the ureilite pyroxenes (Fig. 2b). The olivine is more abundant in Y-74123 than Y-82100, and the Y-82100 composition is slightly less Fa-rich than Y-74123. The Y-82100 pyroxene composition is also slightly less Fe-rich and Ca-rich than Y-74123 and is intermediate between Dyalpur (D in Fig. 2b) and Y-790981. LEW85328 has an identical Ca content with Y-82100 but is more Fe-rich, and the texture is different. The pyroxene compositions of Y-74123 and PCA82506 are very close but the modal abundance of pyroxene is greatly different. Y-790981 is characterized by the cloudy appearance of pigeonite and its variable composition. The Y-82100 interstitial materials are less abundant than in Y-74123. A Ca-rich rim material similar in composition to Y-74123 was found at a pyroxene-pyroxene boundary. In summary, Y-82100 is closest to LEW85328 in the pyroxene quatrilateral but they are not paired on the basis of texture. The grouping is not as pronounced as the other groups. Y-74154 and ALHA81101 are heavily shocked and their olivines show granoblastic texture, but no other data exist to support the pairing.

4.1.2. Magnesian group; Y-74659 with Y-791538 and LEW85440

Y-74659 was the Fe-poorest ureilite among the Yamato ureilites (TAKEDA, 1987a). A preliminary study of Y-791538 (B. MASON, K. YANAI and H. KOJIMA, private communication, 1982) indicates that the Fa content of Y-791538 is almost identical to that of Y-74659 and the possibility of the pairing has been suggested (YANAI, 1987). Our mineralogical study of Y-791538 (TAKEDA and ISHII, 1987; TAKEDA, 1987b) confirmed their similarity but they differ in texture and pyroxene assemblage. The Y-74659 olivine crystal is less shocked and clear. The Y-791538 olivine is characterized by dusty metal inclusions, and undulatory extinction. The thickness of the carbonaceous veins that reduced the olivine of Y-791538 is thinner than Y-74659.

In the Y-74659 pyroxenes, almost all the grains are pigeonite except for a small

round grain of low-Ca pyroxene poikilitically enclosed in olivine. This grain has distinctly low-Ca content comparable to that of orthopyroxene (TAKEDA, 1987a). In Y-791538, almost exactly the same composition of opx,  $Ca_5Mg_{88}Fe_7$ , has been identified, and this pyroxene has been confirmed to be orthopyroxene by the single crystal X-ray diffraction study (TAKEDA and ISHII, 1987).

The Y-791538 ureilite appears to be unique in having crystallized from a material with moderately low normative Wo content and is distinct from Y-74659. The almost identical opx and olivine compositions and the MnO/FeO ratios of Y-74659 and -791538 suggest that two ureilites formed in the vicinity with a similar redox state. The higher Ca content of Y-791538 pig and the phase diagram (LONGHI and BOUDREAU, 1980) suggest that Y-791538 crystallized at lower temperature than Y-74659 with the same Fe/(Fe+Mg) ratio. Such condition is difficult to reconcile with a magmatic process, but may be easily explained by a working hypothesis proposed by TAKEDA (1987a). GOODRICH *et al.* (1987a) have proposed a model in which Fe/(Fe+Mg) ratios of ureilite parent magma are determined by reduction during the magmatic process and are independent of the Ca content of the magmas. The opx+aug assemblage of LEW85440 suggests that the temperature difference is an important factor.

These Mg-rich ureilites may be related to LEW85440 (MASON, 1987) which contains opx-like pyroxene with  $Ca_5Mg_{87}Fe_8$ . In LEW85440, the majority of the pyroxene crystals are an orthopyroxene-like phase, and augite is present only as small interstitial grains. The fact that the pigeonite compositions were observed as small spots in the interstitial grains suggests that this pigeonite may represent an interstitial material (Fig. 2c).

The mineralogical evidence of Y-74659, -791538 and LEW85440 suggests that they are very closely related on their parent body, but they are distinct as meteorite specimens, namely, they are not paired. The higher Ca content of the Y-791538 pig than the Y-74659 pig has been interpreted as an evidence of higher temperature formation of Y-74659 than -791538 assuming the same bulk compositions. The coexistence of opx and aug in LEW85440 may indicate even lower temperature than Y-791538. The dusty rims of the Y-791538 olivine suggest that the reduction after the breakup of the parent body is different from Y-74659.

## 4.1.3. ALHA82106 and 82130

Among other Antarctic ureilites, the pairing of ALH82106 and 82130 has been well accepted (MASON, 1985). Because they are the most reduced ureilites among the Antarctic ureilites (BERKLEY *et al.*, 1985; TAKEDA, 1987a) and because they include augite precipitates in pigeonites produced by complex thermal histories and the primary augite coexisting with them, we have no reason to doubt their pairing.

The presence of the primary augite grains coexisting with pigeonite in ALH82106 implies that they were on the stable solvus when it was crystallized. BERKLEY *et al.* (1985) dispute that these grains are primary, but it is difficult to produce such large grains by the result of granular exsolution. The blebby texture of the augite inclusions in pigeonites is somewhat similar to that of the decomposed pigeonite of the Kintokisan or Binda type (TAKEDA and MORI, 1985). These decomposed pigeonites are proposed to be formed by the pearlite transformation on or a little below the pigeonite eutectoide reaction (PER) line (ISHII and TAKEDA, 1974). Because the bulk composition of the

ALH82106 pigeonite is difficult to estimate by the broad beam microprobe analysis, we cannot definitly state that the ALH82106 pigeonite is on the PER line. If this pigeonite has a bulk composition on the PER line and if the primary augite is a coexisting pair, the decomposition must have taken place on the PER line, right after the crystallization at the same temperature-composition point. This case is likely only when the host pyroxene is originally orthopyroxene rather than pigeonite as we observe now, and the twinned pigeonite sequences were produced by a shock event. Even in this case the texture was produced by the pearlite transformation of decomposition and not by the exsolution.

If we accept a shock event, which reconverted the orthopyroxene produced by decomposition to twinned pigeonite, it is also possible to speculate that this augite might have been produced by regrowth from a Ca-rich partial melt inclusions produced by shock melting. In any case, the presence of augite alone may not be an indicative of slow cooling of exsolution. BERKLEY *et al.* (1985) argued that the exsolution is a result of the high mg number of the pyroxene, but we have to consider more complex thermal histories as discussed above. The existence of spinodal decomposition (Fig. 5a) in augite blebs indicates rapid cooling at the final stage. In summary, the complex histories of the two meteorites suggest strongly the pairing.

4.1.4. ALH-78019 and -78262

The pairing of ALH-78019 and -78262 has been proposed on the basis of their unshocked textures and Fe-rich olivine compositions (SCORE *et al.*, 1982). ALH-78019 has been proposed to preserve a primary igneous feature (BERKLEY and JONES, 1982), but the deformation microtexture of the ALH-78262 olivine observed by MORI (MORI and TAKEDA, 1983) is different from ALH-78019 (Figs. 7a, 7b). The minor element analyses show that they are not paired (GOODRICH *et al.*, 1987a). Further studies are required to ascertain their pairing.

Mineralogical studies of ALH-78019 and -78262 (TAKEDA *et al.*, 1980) indicated that their olivine compositions are quite similar, although the ALH-78019 olivine is slightly more Fe-rich (Table 1). Pyroxene in both meteorites has a similar composition but ALH-78019 is more Fe-rich consistent with olivine results (BERKLEY and JONES, 1982). The Ca/(Ca + Fe + Mg) ratio is higher in ALH-78019 than in ALH-78262 (9.5 vs. 7.7%). BERKLEY and JONES (1982) suggested that these meteorites represent separate falls in spite of ostensibly similar mineral compositions.

Microtexture of olivine in the two meteorites is distinct in spite of their essentially unshocked primary textures. The ALH-78019 olivine does not show any evidence of shock in the dislocation texture (Fig. 7a) in agreement with the absence of diamond. However, the ALH-78262 olivine shows microtextures indicating recovery of a dislocation texture in the TEM photograph (Fig. 7b). A diamond in ALH-78262 also shows dislocation texture (Fig. 7c). Although ALH-78262 shows an apparent unshocked texture, the previous shock was annealed during the high temperature episodes. 4.1.5. MET-78008 and Y-74130

As was reported by TAKEDA (1987a), Y-74130 consists of two portions: one, a large clast of low-Ca pyroxene, and the other, an olivine-augite ureilite. The olivine-augitebearing ureilite first reported by TAKEDA *et al.* (1979) was found to be a minor portion of Y-74130 by the later observations on the large thin sections (TAKEDA, 1987a). In MET- 78008, however, the same augite-bearing material with exactly the same compositions constitutes the major portion of MET-78008. One large chip in two chips of the MET-78008,61–1 PTS, is entirely olivine-augite ureilite.

The smaller chip has a small grain of the low-Ca pyroxene, which includes ellipsoidal augite and olivine, and an augite crystal which includes ellipsoidal pigeonites. These two textures and compositions are exactly the same as reported for Y-74130. Considering these evidences, Y-74130 and MET-78008 may be at least related, although their recovery sites are 3000 km apart. More data on the isotopic abundances and terrestrial ages should be determined before we definitely mention the pairing.

In summary, the pairing of the Antarctic ureilites is well established only for one pair out of 22 specimens. This number is small in comparison with the Antarctic polymict eucrites (TAKEDA et al., 1983). A common feature between the two achondrite groups is that they are relatively small-sized specimens and are easily recognized on the bare ice. The fragmentation to produce such small fragments took place during the entry to the earth's atmosphere for polymict eucrites because of the fragile nature of their larger specimens, whereas the small ureilite fragments may have been produced during the breakup of the parent body as we have an evidence of rapid cooling after the fragmentation (TOYODA et al., 1986). The small parental masses of ureilites may lose their surface portions by space weathering before the entry to the earth's atmosphere as indicated by their short cosmic ray exposure ages, but further fragmentation will not take place because of the hardness of their small specimen. Small specimens of the grouped Antarctic ureilites may represent various portions of a parent body, accumulated during a longer period in Antarctica than for the non-Antarctic ureilites. Some of them might have formed very close to each other on the parent body, although they are not paired. Evolution may take place within the proposed groups.

### 4.2. Planetesimal collision model

The magmatic models proposed by BERKLEY *et al.* (1980), GOODRICH *et al.* (1987b) and SPITZ and GOODRICH (1987), which involve crystallization of minerals from a presumably common magma, are hardly compatible with the recent discovery of oxygen isotope anomaly by CLAYTON *et al.* (1987). This is the most severe objection to the magmatic model. By a preferential local melting and recrystallization from the seeds of relict mafic minerals, proposed by TAKEDA (1987a), oxygen anomaly will most likely be preserved. The planetesimal-scale collisions of two or more planetesimals with a radius of about 10 km or larger having different isotopic ratios will also produce additional inhomogeneous oxygen isotope mixing. The oxygen anomaly is somewhat related to Mg/(Mg+Fe) ratios (CLAYTON *et al.*, 1987) and isotopic anomaly of carbon and nitrogen (GRADY and PILLINGER, 1987), but we have to wait until complete data are available for detailed discussion. If it were true, none of the previously proposed models of ureilite formation mentioned above adequately accounts for their oxygen isotopic compositions, except for ours.

The magmatic origin of ureilites proposed by BERKLEY *et al.* (1980) and GOODRICH *et al.* (1987a, b) is based partly on the mineral elongation lineation. They have argued that the fabrics are characteristic of those formed by tabular minerals in a fluid laminar flow regime. However, it is difficult to have a magma chamber on the meteorite parent

body, where a fluid laminar flow may take place. Even on the largest differentiated parent body such as the HED (howardite-eucrite-diogenite) parent body, such preferred orientation has never been observed (DELANEY *et al.*, 1984), and the oxygen isotope anomaly has not been observed. The parent body having a fluid laminar flow should have even more homogeneous oxygen isotope abundance.

If the parent body is highly differentiated and has a large-scale magma, we should find more differentiated products in the brecciated ureilites. However, we only observe very small amounts of differentiated materials such as plagioclase-pyroxene clasts in polymict ureilites (JAQUES and FITZGERALD, 1982). The current magmatic model also requires a complex, multi-stage igneous history (GOODRICH *et al.*, 1987a, b), and any differentiated products after such a complicated magmatic process should be observed in ureilites, but ureilites consist of nearly uniform ultramafic rocks and no such differentiated products have been observed. They claim that these differentiated products need not be observed in ureilites themselves, but they should be observed in polymict ureilites.

TAKEDA (1987a) explained that the preferred orientation of ureilite silicates was produced by planetesimal-scale collision and recrystallization by a process related to the Ostwald ripening (BARONNET, 1982). This process is different from a regular impact or shock compression when a crater was produced by a high-speed impact. The planetesimal-scale collision is very much different from the above process in duration and scale. Arguments that shock-induced fabrics have never been observed in ureilites do not mean the planetesimal-scale collision did not take place. The Leoville carbonaceous chondrite shows beautiful elongation of chondrules cemented by dark matrix materials (Fig. 8). This texture is very similar to the texture of Goalpara, although ureilite textures were produced by different processes. Dingo Pup Donga shows petro-



Fig. 8. Photograph of the Leoville carbonaceous chondrite (British Museum) with elongated chondrules and dark matrix. Width is 15 cm.

fablics more close to carbonaceous chondrites (BERKLEY *et al.*, 1980). The textural affinity of ureilites to the carbonaceous chondrites is consistent with the oxygen isotope anomaly.

It is generally understood that the shock textures are observed in many meteorites and lunar rocks, and correlated with independent indications of degree of shock. Because the planetesimal-scale collision without destruction of the bodies is different from crater-forming impact events in its duration and heat generation, the initial shock textures may be annealed by the heat generated by collision and subsequent crystal growth. Such textures as dislocation creep indicating recovery were observed in ureilites by the TEM (MORI and TAKEDA, 1983). The many shock textures we see now in ureilites are those produced at the last stage, when the diamonds were formed and the parent body was broken up. The large parent body is not consistent with a very rapid cooling of the ureilite pyroxene (TOYODA *et al.*, 1986), because it has less chance to be destructed. The rapid cooling is also explained by the restricted rim reduction after the breakup of a small parent body.

The planetesimal collision model (TAKEDA, 1987a) is not simply one variant of the residue model for ureilite petrogenesis as it was interpreted by GOODRICH et al. (1987b) and SPITZ and GOODRICH (1987). In ureilite problems, it is understood that large mafic silicates grow out of materials known as chondrules, fragments and matrices. Examples of recrystallization of Y-74160 and -790964 are given (TAKEDA, 1987a). The partial melt was produced in the beginning of, or during the process, but during the crystal growth stage large mafic silicates grow at the expense of the small grains by a process related to the Ostwald ripening (BARONNET, 1982) or to the growth of cumulate crystals from a melt, and the residual liquid will be accumulated, extracted and removed to the surface or other places. This process is not isochemical because small crystals in chondrules and matrices are surrounded by glassy materials rich in Al, Ca, etc. The process is rather similar to the zone-refining process because large mafic silicates grow from small impure materials by moving the melt zone. By continuous raise of temperature, a new partial melt which may correspond to a large degree of partial melting will be produced after the extraction of the first stage partial melt and the residual liquid after growth. Such complex processes cannot be represented by a simple partial melt model.

An important point of our model is that the process proposed is not an equilibrium partial melting one, because the growth process is rather similar to the zone-refining process. By inhomogeneous heat generated by compaction of a loosely packed planetesimal by a collision or collisions, low-temperature melting materials in the matrix including Ca-Al-rich materials and Fe-S-Ni-containing materials were preferentially melted, while large mafic silicate crystals existed in the source materials which remained partly in solid state. The removal of such Ca-Al-rich partial melts will reduce Eucontent. In some places melt pockets may be produced, thus facilitating the growth of crystals. Where the heat was accumulated a subsequent melting may take place after the removal of the first melt, producing a mafic-mineral-rich melt. The mafic silicates grow from this melt around the unmelted seeds. This process is in a sense similar to that of the cumulate model with crystals grown from a magma produced by a large degree of partial melting.

### Antarctic Ureilites

The beauty of our model in explaining the anticorrelation of MnO/FeO (TAKEDA, 1987a) is that the small amount of melt is present only in the interface of a growing crystal, while the total amount of melted materials generated throughout the crystal growing stage is large. This process can be envisioned by a picture, where a small scale melted zone as in zone refining is present at the growth front surrounding the growth crystal, and such a zone moves out due to thermal gradient or sometimes removed while the crystal grows large. This process is not certainly the simple partial melting model.

Another important objection to the magmatic cumulate model is the retention of a large amount of noble gases in ureilites as was pointed out by BEGEMANN and OTT (1983). By the melting of carbonaceous chondrites, the major portion of noble gases will be lost. Although a high temperature stage up to 1300°C will be experienced by the planetesimal model, graphite or graphitized diamonds produced by the first stage collision accumulated and grown at the grain boundaries during the crystal growth stage is nearly solid state with some interstitial liquid and the noble gases will be retained. By heating ureilites up to 1300°C, the majority of the noble gases were not released as shown by the Ar-Ar release experiments (N. TAKAOKA, private communication, 1987). With her magmatic model, C. A. GOODRICH (personal communication, 1988) thinks that noble gases may be retained in graphite, which is never melted, but BERKLEY and JONES (1982) mentioned the growth of primary graphite in ALH-78019 from melt. The ability of C to trap noble gases is known, but magma does not contain much noble gases to be trapped.

Therefore, our model is not rejected by the high noble gas abundance of ureilites. During the complex magmatic process (GOODRICH *et al.*, 1987a) in the large magmatic chamber on the large parent body, the noble gases will be lost from the magma and the carbon will not be retained uniformly at the grain boundaries due to the gravity and laminar flow.

### 4.3. Ureilites-carbonaceous chondrites (UCC) connection

The main evidence in favor of the cumulate origin of ureilites was the preferred orientation of minerals in ureilites (BERKLEY *et al.*, 1980). However, such a texture can also be produced by the nebular sedimentation process or by compaction on the parent body (TAKEDA, 1987a). The sedimentation could occur before the formation of the planetesimal by gravitational instability, but more conceivably after planetesimal formation and on its surface by infall of materials. The preferred orientation of elongated minerals can also be produced by compaction of loosely sedimented materials by a static force by planetesimal-scale collision of large scale, or by an impact on the parent body and be enhanced by subsequent crystal growth from the melt during the high temperature episode (TAKEDA, 1987a).

In the Leoville meteorite (CV3) chondrules in the carbonaceous matrix show preferred orientation. It is to be noted that the textures of Dingo Pup Donga and Goalpara are rather similar to that of the Leoville carbonaceous chondrites (Fig. 8). We are not simply pointing out the textural similarity. The lineation texture of ureilites was produced during crystal growth from seeds. In the case of the ureilites, amounts of olivine and pyroxene grains are larger than in carbonaceous chondrites, and the thermal process is extensive. The texture produced by compaction, however, may still have been inherited after the thermal processes to produce recrystallization texture from the seeds or new growth textures will be produced.

Concentration of olivines and pyroxenes in the above two processes has an advantage to solve another important problem in ureilite genesis: whether the carbon veins are indigenous to the olivine-pyroxene assemblage (BERKLEY *et al.*, 1980) or injected into it (WASSON *et al.*, 1976; BOYNTON *et al.*, 1976). We argue that by a process similar to what took place to produce carbonaceous chondrites, the silicates and later-condensed carbon were mixed together. This mixing could also have taken place when the ureilite parent body was formed. Carbon in the matrix will later be concentrated into the grain boundaries during the recrystallization of the mafic silicates. Such a kind of mixing is one way to bring foreign materials together without the need for injection of carbonaceous materials into solidified materials as was proposed previously (WASSON *et al.*, 1976). The presence of carbonaceous chondrites rich in noble gases is a good evidence of this process.

During this mixing process, gases in the solar nebula must be present to supply the very high concentrations of noble gases. Because carbon in the carbonaceous chondrites is not in the form of graphite, it is difficult to claim that gases were trapped in unmelted graphite for a magmatic model. For the magmatic origin of ureilite, therefore, we can only have high concentrations if the gas pressure was high enough during crystallization. However, the temperature of the magma is so high that it may be difficult to keep noble gases in the magma under a pressure expected for a small-sized parent body. The gases may actually have been present absorbed in fine-grained carbonaceous material or trapped in diamonds produced by the first stage shock before high temperature episode. This would be consistent with the fact that the trapped noble gases are closely associated with carbon-rich material as was found by WEBER *et al.* (1976) and GöBEL *et al.* (1978). These authors also reported that Xenon concentrations, *e.g.*, are observed to be 1000 times higher in this matter than in bulk samples from the same meteorite with no significant differences in the isotopic composition (GöBEL *et al.*, 1978).

This process should be similar to what produced matrices of carbonaceous chondrites, since the noble gases of the two meteorite types are of the planetary type and their noble gases abundances and isotopic compositions are similar. Especially, the Xenon isotope abundance pattern of Novo Urei is similar to that of carbonaceous chondrites (Göbel *et al.*, 1978).

As an alternative to pre-existing, noble-gas-bearing carbonaceous matter, the carbon could also have been produced by decomposition of carbon dioxide by reduction at the grain boundaries. In this case, gases containing carbon dioxide and rare gases would have to be present with the carbon trapping the noble gases in this process, but an actual picture of ureilite formation is difficult to visualize. It is difficult to find an appropriate reducing agent such as H and metal and the source of the carbon dioxide.

BEGEMANN and OTT (1983) argued in their critical comment on "The nature and origin of ureilites" by BERKLEY *et al.* (1980), that the inhomogeneous distribution between different mineral phases and the low <sup>40</sup>Ar/<sup>38</sup>Ar ratio in particular can only be satisfied with difficulties. The model reexplained in this paper does not conflict with the constraints imposed by the record of primordial noble gases. The gravitational separation of the olivine and pyroxene grains can explain the low K and <sup>40</sup>Ar abundance in the trapped argon in ureilites. Fixing of Ar in shock-produced diamonds (see below) by impact events at an early stage can accound for the low <sup>40</sup>Ar/<sup>36</sup>Ar ratio.

The presence of many specimens with a close genetic link such as Y-74659, -791538 and LEW85440, and Y-74130 and MET-78008, which look like paired specimens, in addition to other ureilites, is consistent with a parent body with thermally altered carbonaceous chondrite-like materials. Many portions of the parent body or bodies were broken up and distributed with similar orbits, from where the Antarctic ureilites were delivered.

#### 4.4. Origin of diamond in ureilites

Formation of the diamonds in ureilites has been a subject of controversy, but the explanation appears to be generally accepted that the diamonds were produced by conversion of graphite during a shock event (LIPSCHUTZ, 1964). The most intense shock event is expected to take place when the planetesimal was destroyed. However, one recently reported Antarctic ureilite, ALH-78019, shows no evidence of diamonds and the least shock texture (BERKLEY and JONES, 1982). ALH-78262 which was proposed to be similar to ALH-70019, in particular, keeps a record of thermal annealing at high temperature as is evidenced by the preservation of the dislocation recovery texture in the olivines observed by MORI and TAKEDA (1983) with the TEM. ALH-78262 contains diamonds which show defect textures (Fig. 7c). They proposed graphitization of the diamonds in ureilites to have happened during the high temperature event. This would indicate that the high temperature episode lasted long enough to graphitize diamonds in some ureilites. On the other hand, this episode should not be too long, so as not to degas the noble gases. In ALH-78019, the graphite might have grown during the crystal growth stage of the mafic silicates from the melt. We do not require graphite growth in the cumulates as was explained by BERKLEY and JONES (1982).

It has been noted that diamonds probably could not have been produced *in situ* without more damage to the mafic silicates than is apparent. The thermal annealing of the mafic silicates explained above is one explanation for the discrepancy. We have an experiment in growing diamonds with regards to this problem. Crystalline diamond was grown on a substrate by vapor growth from a gaseous mixture of hydrogen and methane under microwave glow discharge conditions, according to the method proposed by KAMO *et al.* (1983) at National Inst. Res. Inorganic Materials and by other methods (*e.g.*, DERJAGUIN *et al.*, 1968; SPITSYN *et al.*, 1981).

Although such experiments existed before this time, the implication of this experiment with reference to the origin of ureilites was pointed out by TAKEDA (1982). He stated that the high pressure either in the interior of a planet or by the shock may not be required to produce diamonds and that the diamonds may be formed on the surface of olivine and pyroxene crystals in the nebula, and they preferentially sediment. This process is in agreement with the above model proposed by us (TAKEDA, 1987a). The C matrix could be graphitized diamonds when it was annealed in the planetesimal.

The experiment by KAMO *et al.* (1983) is not directly applicable to ureilites, but it suggested that there is a way to grow diamonds on the surface of mafic silicates in the nebula during sedimentation. In this process the noble gases may be trapped. Recently, FUKUNAGA *et al.* (1987) performed a chemical vapor deposition experiment, which is much closer to the environment of the ureilite formation. On the basis of this experiment, MIYAMOTO *et al.* (1987) discussed the origin of diamond in ureilite. They observed one FWHM (full width at half maximum) of the Raman line at 1330 cm<sup>-1</sup> from a diamond in the ALH-77257 ureilite. The diamond crystals in ALH-78262 are texturaly different from synthetic diamonds (Fig. 7c). They contain defect textures and sometimes metal particles. The diamonds could grow larger during the high temperature shock episode in the graphite matrix, and may include metal particles contained in the graphite. This condition may approach the static high pressure condition, which may produce the FWHM intermediate between the two cases. Therefore, the agreement of one FWHM does not warrant the validity of the vapor growth origin of the ureilite diamonds.

The vapor-grown diamonds except for those synthesized by ion-assisted deposition (KITABATAKE and WASA, 1987) do not have the lonsdalite-like stacking sequence, which is found in both shock-produced diamonds and ureilite diamonds. The electron diffraction patterns of the ALH-78262 diamond reveal super-lattice reflections with diffuse streaks indicating complex stacking sequences including the lonsdalite-like sequence. In this respect, the ureilite diamonds show one aspect of the shock-produced diamond.

MIYAMOTO *et al.* (1987) did not consider an important observation on mineralogy of ureilite. Definitely the record of various degrees of the shock is evident. The lack of diamond does not necessary mean the diamond was not formed initially. As TAKEDA (1982) pointed out, the diamond could have been produced when the mafic silicates were floating in the nebula, or when the carbonaceous matrix in the carbonaceous chondrite-like material experienced the first shock event by collision that raised the temperature of the parent body, but subsequent high temperature episodes may graphitize fine-grained diamonds (a few microns in diameter). We have to admit that the initial state of noble gas-carrying carbon may be diamonds produced in either of the above two ways, but the diamonds we see now in ureilites have been produced during the breakup of the parent body (LIPSCHUTZ, 1964).

The existence of a variety of ureilites without much pairing suggests that the sudden breakup of the entire parent body took place to produce small fragments which will not be broken further during the passage in the atmosphere. By this collision some parts of the interior of the parent body reached high pressure before the destruction, to produce diamonds. The importance of the formation of diamond on the mafic silicates in the nebula can be understood only if the ureilites were formed by the preferrential sedimentation of large grown mafic silicates with vapor-grown diamond on the surface towards the mid-plane of the nebula as was proposed by TAKEDA (1982, 1987a). The success of the growth of diamond rich in noble gases from vapor gives us some constraints on the origin of ureilites.

## 4.5. Summary of possible formation processes

A working hypothesis on the history of the ureilite parent body in the preceeding discussion can be summarized and itemized in time and space in the context of the theory of planetesimal formation of the solar system by SEKIYA (1983).

(1) Gravitational sedimentation of early-condensed or vapor-grown olivine and

#### Antarctic Ureilites

pyroxene grains towards the equator in the high temperature region of the solar nebula.

(2) Sedimentation and mixing of fine carbon or growth of diamond on the mafic silicates. Noble gas trapping in the carbonaceous materials and possibly diamonds.

(3) Fragmentation of sediments at the equator by the gravitational instability to produce planetesimals of a size about  $10^8$  g. Mixing of carbon powder and mafic silicate may be facilitated.

(4) Accumulation by sedimentation and compaction by impact or collision of silicate crystals, chondrule and matrix in and on the planetesimals.

(5) A parent body formed consisting of mafic minerals bearing metal, carbon, and matrices.

(6) Planetesimal-scale collisions and compaction to produce possibly diamonds and rise of temperature. Partial melts were produced in multistages.

(7) High temperature annealing for an extended period after crystal growth of mafic silicates with preferred orientation and to knead out the residual liquids during crystal growth. The Ca- and Al-rich residual liquids may produce Angra dos Reis-type clasts in polymict ureilites or augite-bearing ureilites. The metal fractionation may be involved in the oxidation/reduction reaction between silicates, metal and C. Gas in the nebula is still present.

(8) Loss of the gases from the solar nebula, and temperature drop takes place during processes (7) and (8). High temperatures are retained in the interior which is shielded from the surface.

(9) Impacts produce surface polymict breccias.

(10) Destruction of the planetesimal to produce fragments of a size 10 to 100 cm or larger by a collision or a high-speed impact. Diamond formation occurred during this event or as a result of the previous events.

(11) Rapid cooling of the fragments in the gas-poor condition to make reduction rim.

(12) Loss of a surface portion of the fragments during orbit evolution.

(13) Encounter with the Earth.

This planetesimal collision model of the ureilite formation does not encounter any difficulties that are encountered by the existing models as was pointed out above. Gravitational fractionation in the nebula, if at all possible, was considered instead of in the magma. Processes (1) to (4) are the same as those proposed for carbonaceous chondrites. Process (6) is similar to a partial melting model but the growth of mafic silicates (7) is similar to a cumulate residue model. With regard to whether the olivine-pyroxene assemblage is cumulate or the residuum of a partial melt, the present model is, therefore, compatible with both, and is not one variant of residue models.

The REE abundance problem of such a model has been discussed by SPITZ and GOODRICH (1987), but they interpreted the model in their own way. They treated it as a simple partial melt residue model, but crystal growth producing residual liquids is an important process. Our model has an aspect similar to their complex crystallization processes. Since the REE abundance of matrix and rim materials and acid residues are not too well characterized mineralogically at present, it is not possible for any model to satisfy REE constraints quantitatively at present. Partition coefficient at as high temperature as ureilite formation, may be different from the magmatic temperature.

Hiroshi TAKEDA, Hiroshi MORI and Hiromi OGATA

As to another problem in ureilite genesis whether the carbon matrices are indigenous to the olivine-pigeonite assemblage or injected into it, the present model considers that two different materials condensed at different temperature, time and space are mixed together, and that mafic silicates and matrices were never completely equilibrated, thus accounting for the oxygen isotope anomaly. With the presence of a little melt, the olivine and pyroxene crystals were grown and homogenized at high temperature, but the amount of the melt is so small at each stage that the carbon or graphitized diamonds at grain boundaries never floated and mixed with the melt except for some cases where a considerable melting took place after solidification by a local impact event. Our model overcomes many difficulties in the model proposed by BERKLEY *et al.* (1980) as pointed out by BEGEMANN and OTT (1983). More quantitative and experimental approach will be required in the future ureilite studies.

By our model, mafic silicates of ureilites are a kind of highly equilibrated mafic carbonaceous chondrite-like material, but also the mafic silicates may possibly be cumulates produced by a gravitational separation in the solar nebula, or grown from the partial melt produced by the planetesimal-scale collisions. In this respect, ureilites retain the best record of each stage of the evolution of the early solar system according to a theory of planetesimal formation, heating, impact, and breakup of a planetesimal, although the ureilites show igneous textures of differentiated meteorites. Many small specimens of the Antarctic ureilites with a close genetic link can be explained by the above processes. Every C-type asteroid may have an interior of the ureilite-like materials. Ureilite formation is a natural consequence of the planetary evolution. Similar nebula cumulates may be important materials which accreted to the terrestrial planets. Further recovery of large unique Antarctic ureilites is awaited to solve the ureilite paradox.

#### Acknowledgments

We thank Dr. K. YANAI and H. KOJIMA, National Institute of Polar Research (NIPR), and the Working Group on Antarctic Meteorites (U.S.A.) for meteorite samples, Dr. M. PRINZ, J. BERKLEY, M. MIYAMOTO, T. ISHII, M. M. GRADY, A. L. GRAHAM and H. MIZUTANI for discussion and Drs. M. MIYAMOTO and C. A. GOODRICH for critical reading of the manuscript. Part of this study was performed during the stay of one of the authors (H.T.) at British Museum (Natural History) as a JSPS-Royal Society fellow. Microprobe analyses were performed at Geological Institute and Ocean Research Institute, of University of Tokyo. This work was supported in part by the funds from Cooperative Program (No. 84134) provided by Ocean Research Institute, University of Tokyo and by the Grant-in-Aid for Scientific Research on Priority Areas (Origin of the Solar System) of the Japanese Ministry of Education, Science and Culture (No. 62611005).

#### References

170

BARONNET, A. (1982): Ostwald ripening in solution. The case of calcite and mica. Estudio Geol., 38, 185–198.

BEGEMANN, F. and OTT, U. (1983): Comment on "The nature and origin of ureilites" by J. L. Berkley

et al. Geochim. Cosmochim. Acta, 47, 975-977.

- BERKLEY, J. L. (1986): Four Antarctic ureilites; Petrology and observations on ureilite petrogenesis. Meteoritics, 21, 169–189.
- BERKLEY, J.L. and JONES, J.H. (1982): Primary igneous carbon in ureilites; Petrological implications. Proc. Lunar Planet. Sci. Conf., 13th, Pt. 2, A353–A364 (J. Geophys. Res., 87 Suppl.).
- BERKLEY, J.L., TAYLOR, G.J., KEIL, K., HARLOW, G.E. and PRINZ, M. (1980): The nature and origin of ureilites. Geochim. Cosmochim. Acta, 44, 1579–1597.
- BERKLEY, J.L., GOODRICH, C.A. and KEIL, K. (1985): The unique ureilite, ALHA82106-82130; Evidence for progressive reduction during ureilite magmatic differentiation. Meteoritics, 20, 607-608.
- BOYNTON, W.V., STARZYK, P.M. and SCHMITT, R.A. (1976): Chemical evidence for the genesis of the ureilites, the achondrite Chassigny and the nakhlites. Geochim. Cosmochim. Acta, 40, 1439-1447.
- CLAYTON, R. N., MAYEDA, T.K. and YANAI, K. (1987): Oxygen isotopes in ureilites. 50th Meeting of the Meteoritical Society, Newcastle upon Tyne, 44.
- DELANEY, J.S., PRINZ, M. and TAKEDA, H. (1984): The polymict eucrites. Proc. Lunar Planet. Sci. Conf., 15th, Pt. 1, C251-C288 (J. Geophys. Res., 89 Suppl.).
- DENNISON, J.E., LINGER, D.W. and LIPSCHUTZ, M.E. (1986): Antarctic and non-Antarctic meteorites from different populations. Nature, **319**, 390.
- DERJAGUIN, B.V., FEDOSEEV, D.V., LUKYANOVICH, V.M., SPITZIN, B.V., ROYABOV, V.A. and LAVREN-TYEV, A.V. (1968): Filamentary diamond crystals. J. Cryst. Growth, 2, 380–384.
- FUKUNAGA, K., MATSUDA, J., NAGAO, K., MIYAMOTO, M. and ITO, K. (1987): Noble gas enrichment in vapor growth diamonds and the origin of diamonds in meteorites. Nature, **328**, 141–143.
- GÖBEL, R., OTT, U. and BEGEMANN, F. (1978): On trapped noble gases in ureilites. J. Geophys. Res., 83, 855–867.
- GOODRICH, C.A. (1986): Y-74130; A ureilite with cumulus augite. Meteoritics, 21, 373-374.
- GOODRICH, C.A., JONES, J.H. and BERKLEY, J.L. (1987a): Origin and evolution of the ureilite parent magma; Multi-stage igneous activity on a large parent body. Geochim. Cosmochim. Acta, 51, 2255-2273.
- GOODRICH, C.A., JONES, J.H. and SPITZ, A.F. (1987b): Siderophile element tests of ureilite petrogenesis models. 50th Meeting of the Meteoritical Society, Newcastle upon Tyne, 70.
- GRADY, M.M. and PILLINGER, C.T. (1987): The EET 83309 polymict ureilite; Its relationship to other ureilites on the basis of stable isotope measurements. Lunar and Planetary Science XVIII. Houston, Lunar Planet. Inst., 353-354.
- HINTENBERGER, H., JOCHUM, K.P., BRAUN, O., CHRIST, P. and MARTIN, W. (1978): The Antarctic meteorite Yamato-74123—a new ureilite. Earth Planet. Sci. Lett., 40, 187–193.
- ISHII, T. and TAKEDA, H. (1974): Inversion, decomposition and exsolution pheonomena of terrestrial and extraterrestrial pigeonites. Mem. Geol. Soc. Jpn., 11, 151–162.
- JAQUES, A.L. and FITZGERALD, M.J. (1982): The Nilpena ureilite, an unusual polymict breccia; Implications for origin. Geochim. Cosmochim. Acta, 46, 893-900.
- KAMO, M., SATO, Y., MATSUMOTO, S. and SETAKA, N. (1983): Diamond synthesis from gas phase in microwave plasma. J. Cryst. Growth, 62, 642–644.
- KITABATAKE, M. and WASA, K. (1987): Diamond films by ion-assisted deposition at room temperature. Proc. Am. Vacum Soc. 34th Natl. Symp. PF-WeM5 Anaheim.
- KOJIMA, H. and YANAI, K. (1984): Classification of the pebble size meteorites in the Yamato-74 collection. Papers Presented to the Ninth Symposium on Antarctic Meteorites, 22-24 March 1984, Tokyo, Natl Inst. Polar Res., 11-13.
- LIPSCHUTZ, M.E. (1964): Origin of diamonds in the ureilites. Science, 143, 1431-1434.
- LONGHI, J. and BOUDREAU, A.E. (1980): The orthoenstatite liquidus field in the system forsteritediopside-silica at one atmosphere. Am. Mineral., 65, 563-573.
- MASON, B. (1985): Antarctic Meteorite Newsletter, 8 (2), 42.
- MASON, B. (1987): Antarctic Meteorite Newsletter, 10 (1), 17.
- МIYAMOTO, M., MATSUDA, J. and ITO, K. (1987): The origin of diamond in ureilite, Proc. 12th ISAS Lunar Planet. Symp. Tokyo, Inst. Space Astron. Sci., 68–69.
- MORI, H. and TAKEDA, H. (1983): Deformation of olivine in the Antarctic ureilites, Allan Hills 77257 and 78262. Lunar and Planetary Science XIV. Houston, Lunar Planet. Inst., 519–520.

- OGATA, H., TAKEDA, H. and ISHII, T. (1987): Interstitial Ca-rich silicate materials in the Yamato ureilites with reference to their origin. Lunar and Planetary Science XVIII. Houston, Lunar Planet. Inst., 738-739.
- SCORE, R., KING, T.V., SCHWARZ, C.M., REID, A.M. and MASON, B. (1982): Description of stony meteorites. Smithson. Contrib. Earth Sci., 24, 19–48.
- SEKIYA, M. (1983): Gravitational instabilities in a dust-gas layer and formation of planetesimals in the solar nebula. Prog. Theor. Phys., 69, 1116-1130.
- SPITSYN, B.V., BOUILOV, L.L. and DERJAGUIN, B.V. (1981): Vapor growth of diamond on diamond and other surfaces. J. Cryst. Growth, 52, 219–226.
- SPITZ, A.H. and GOODRICH, C.A. (1987): Rare earth element tests of ureilite petrogenesis models. 50th Meeting of the Meteoritical Society, Newcastle upon Tyne, 168.
- TAKEDA, H. (1982): Antarctic ureilites, and some hypotheses for their origin and evolution. Lunar and Planetary Science XIII. Houston, Lunar Planet. Inst., 790–791.
- TAKEDA, H. (1987a): Mineralogy of Antarctic ureilites and a working hypothesis for their origin and evolution. Earth Planet. Sci. Lett., 81, 358-370.
- TAKEDA, H. (1987b): A coexisting orthopyroxene-pigeonite pair in Yamato-791538 and formation condition of ureilites. 50th Meeting of the Annual Meteoritical Society, Newcastle upon Tyne, 172.
- TAKEDA, H. and ISHII, T. (1987): On the low-Ca pyroxene coexisting with magnesian pigeonite. Abstr. Mineral. Soc. Japan, Tokyo, 112.
- TAKEDA, H. and MORI, H. (1985): The diogenite-eucrite links and the crystallization history of a crust of their parent body. Proc. Lunar Planet. Sci. Conf., 15th, Pt. 2, C649–C663 (J. Geophys. Res., 90 Suppl.).
- TAKEDA, H. and YANAI, K. (1982): Mineralogical examination of the Yamato-79 achondrites; Polymict eucrites and ureilites. Mem. Natl Inst. Polar Res., Spec. Issue, 25, 97–123.
- TAKEDA, H., MIYAMOTO, M., DUKE, M.B. and YANAI, K. (1978): The Yamato-74659 ureilite and some new findings on the Yamato achondritic pyroxenes. Meteoritics, 13, 641-645.
- TAKEDA, H., DUKE, M. B., ISHII, T., HANAMURA, H. and YANAI, K. (1979): Some unique meteorites found in Antarctica and their relation to asteroids. Mem. Natl Inst. Polar Res., Spec. Issue, 15, 54–76.
- TAKEDA, H., MORI, H., YANAI, K. and SHIRAISHI, K. (1980): Mineralogical examination of the Allan Hills achondrites and their bearing on the parent bodies. Mem. Natl Inst. Polar Res., Spec. Issue, 17, 119-144.
- TAKEDA, H., WOODEN, J.L., MORI, H., DELANEY, J.S., PRINZ, M. and NYQUIST, L.E. (1983): Comparison of Yamato and Victoria Land polymict eucrites; A view from mineralogical and isotopic studies. Proc. Lunar Planet. Sci. Conf., 14th, Pt. 1, B245–B256 (J. Geophys. Res., 88 Suppl.).
- TOYODA, H., HAGA, N., TACHIKAWA, O., TAKEDA, H. and ISHII, T. (1986): Thermal history of ureilite, Pecora Escarpment 82506 deduced from cation distribution and diffusion profile of minerals. Mem. Natl Inst. Polar Res., Spec. Issue, 41, 206-221.
- WASSON, J.T., CHOU, C.-L., BILD, R.W. and BAEDECKER, P.A. (1976): Classification of and elemental fractionation among ureilites. Geochim. Cosmochim. Acta, 40, 1449–1458.
- WEBER, H.W., BEGEMANN, F. and HINTENBERGER, H. (1976): Primodial gases in graphite-diamondkamacite inclusions from the Haverö ureilite. Earth Planet. Sci. Lett., 29, 81–90.
- YANAI, K., comp. (1979): Catalog of Yamato meteorites. 1st ed. Tokyo, Natl Inst. Polar Res., 188p. with 10 pl.
- YANAI, K. (1987): Ekondoraito (Achondrite). Nankyoku no Kagaku, 6. Nankyoku Inseki (Science in Antarctica, 6. Antarctic Meteorites), ed. by Natl Inst. Polar Res. Tokyo, Kokon Shoin, 51.
- YANAI, K. and KOJIMA, H. (1986): Preliminary studies of the Yamato-791839 ureilite with metportion. Meteoritics, 21, 544-545.
- YANAI, K., MIYAMOTO, M. and TAKEDA, H. (1978): A classification for the Yamato-74 chondrites based on the chemical compositions of their olivines and pyroxenes. Mem. Natl Inst. Polar Res., Spec. Issue, 8, 110-120.

(Received November 24, 1987; Revised manuscript received January 19, 1988)