

## **Petrography, mineralogy and trace element chemistry of Yamato-86029, Yamato-793321 and Lewis Cliff 85332: Aqueous alteration and heating events**

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**Abstract:** We have examined mineral grains and matrix of new Antarctic carbonaceous chondrites Yamato (Y)-86029, Lewis Cliff (LEW) 85332 and Yamato (Y)-793321 for evidence of parent body aqueous alteration and heating events. Y-86029 and LEW 85332 are unique carbonaceous chondrites with unusual textures. Y-86029 is the second thermally metamorphosed CI chondrite recovered from Antarctica. It is characterized by destruction of preexisting anhydrous silicates during aqueous alteration accompanied by formation of carbonates, which together with the phyllosilicates were subsequently heated at metamorphic temperatures of at least 500–600°C. The carbonates are now present as Fe-rich drusy aggregates and giant periclase clasts and globules that have rarely been encountered in carbonaceous chondrites. LEW 85332 is an unequilibrated and highly brecciated type-3.0–3.1 chondrite that shows no clear evidence of alteration of chondrules or matrix silicate grains. However, matrix phyllosilicates underwent extensive aqueous alteration and subsequent dehydration by moderate thermal metamorphism (at least 500–600°C). This suggests that the formation of hydrous phases and subsequent heating occurred prior to final accretion in the parent body. Y-793321 is a CM2 chondrite that contains a variety of clasts exhibiting varying degrees of aqueous alteration. Petrographic evidence of thermal metamorphism in Y-793321 is only limited to a few phyllosilicate clasts in the matrix. The presence of tochilinite, carbonates and partially dehydrated phyllosilicates suggests that it experienced very mild thermal metamorphism.

RNAA data based on 15 thermally mobile trace elements confirm the severity of open-system heating as  $Y-793321 < 500^\circ\text{C} < LEW\ 85332 < Y-86029 \leq 700^\circ\text{C}$ . It is conceivable that Y-793321 experienced retrograde aqueous alteration after thermal metamorphism but no unambiguous evidence for this is present.

### **1. Introduction**

Significant work and progress has been made in the last decade towards understanding secondary post-accretionary parent body processes in carbonaceous chondrite parent bodies. As a result, the age-old notion that carbonaceous chondrites were simple, pristine samples of solar nebula condensates with no significant record of asteroidal processes has been dispelled. The most dominant post accretionary processes include aqueous alteration, thermal and shock metamorphism, oxidation, sulfidization and volatilization.

The discovery of three unusual Antarctic carbonaceous chondrites—Belgica (B)-7904,

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Yamato (Y)-82162 and Y-86720 in 1987, led to a series of studies aimed at disentangling their thermal histories based on their mineralogical-petrological characteristics (*e.g.* Tomeoka *et al.*, 1989a,b; Zolensky *et al.*, 1989a,b; Tomeoka, 1990; Ikeda 1991; Lipschutz *et al.*, 1999). Based on radiochemical neutron activation analysis (or RNAA) determinations of 15 thermally mobile (*i.e.* easily vaporized and lost) trace elements, Paul and Lipschutz (1989, 1990) concluded that, not only had thermal metamorphism affected these and subsequently other meteorites, but that these episodes were of the open system variety. When compared with RNAA data for Co, Au, Sb, Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, and Cd (ordered by increasing mobility at 600–700°C) in the Murchison CM2 chondrite heated for 1 week in a low pressure (initially  $10^{-5}$  atm H<sub>2</sub>) environment (Matza and Lipschutz, 1977), the extent of loss for the 3–5 most mobile elements in the three meteorites duplicated trends evident in the 500–700°C Murchison samples (Lipschutz *et al.*, 1999).

The significance of petrological, chemical and isotopic differences between non-Antarctic and Antarctic meteorites has long been emphasized (*e.g.*, Takeda *et al.*, 1983) suggesting differences in meteoroid flux between contemporary falls and substantially older Antarctic meteorites, implying distinct genetic histories. Mineralogical-petrological studies of these heated meteorites reveal that they underwent episodes of oxidation/hydration/reduction and late stage thermal metamorphism, which occurred in different asteroids. Spectral reflectance data in the UV, visible and near IR for these meteorites resemble those of surfaces on a number of C-, G-, B- and F-asteroids. Thus, Hiroi *et al.* (1993) suggested that the surfaces of a number of these asteroids consist of carbonaceous chondrite-like material metamorphosed at a variety of temperatures in the parent bodies' interiors, then excavated by impacts and redeposited on their surfaces.

In this paper, we have combined petrographic observations and labile trace element data on the newly recognized thermally metamorphosed Antarctic carbonaceous chondrites Y-86029, LEW-85332 and Y-793321 to gain insights into their aqueous alteration and heating histories. We are also currently examining a host of additional new carbonaceous chondrites in order to better understand these post accretionary processes in primitive asteroids.

## 2. Samples and analytical techniques

We have examined thin sections of Y-86029, LEW 85332 and Y-793321 provided by the National Institute of Polar Research (NIPR) in Tokyo. We analyzed mineral grains and matrix in all samples for major elements using a CAMECA CAMEBAX microprobe operated at 15 kV and 20 nA. We used a focused beam (2  $\mu$ m) for analysis of anhydrous mineral grains and a defocused beam (10  $\mu$ m) for phyllosilicates. Natural mineral standards were utilized, and corrections were applied for absorption, fluorescence, and atomic number effects using the CAMECA on-line PAP program. These probe analyses are accurate to within  $\pm 0.5\%$ , relative. Backscattered electron (BSE) images were obtained using a JEOL JSM field emission SEM operating at 15 kV, a potential that offers optimum values of resolution *vs.* electron penetration (and excitation) of the samples.

Approximately 50 mg of sample for RNAA analysis was sealed in quartz and irradiated with suitable monitors for two days at a flux of  $8 \times 10^{13}$  n cm<sup>-2</sup>s<sup>-1</sup> at the

University of Missouri Research Reactor (UMRR). Irradiation conditions, monitor preparation, chemical processing, and counting conditions were similar to those described by Wang and Lipschutz (1990). Chemical yields were satisfactory, ranging up to 92%, and exceeded 40% for all samples. Chemical yields for monitors exceeded 50% in all cases. Replicate portions of Murchison Meteorite Reference Sample had previously been analyzed to assure the quality of the data.

### 3. Results

#### 3.1. Y-86029

Y-86029 is highly brecciated and consists of fine-grained brownish to yellowish brown millimeter to submillimeter clasts in near-translucent matrix. Y-86029 contains no chondrules and abundant secondary minerals including coarse- and fine-grained phyllosilicates, Fe-Ni sulfides, carbonates and magnetite. No sulfates have been detected. These characteristics are typical of all CI chondrites. A more comprehensive description of this unique meteorite is presented in a separate publication (Tonui *et al.*, 2002).

##### 3.1.1. Anhydrous silicates

Olivine is sparse in Y-86029 and is present within two isolated aggregates ranging in size from 50 to 200  $\mu\text{m}$ . They have a compositional range of Fo<sub>85.5</sub> and Fo<sub>77.1</sub> (Table 1). These aggregates have unique textures. One aggregate (Fo<sub>77.1</sub>) is traversed by a vein ((Mg/Mg+Fe)  $\times$  100=45.5) that is rich in CaO (2.09–4.29 wt%) and Al<sub>2</sub>O<sub>3</sub> (2.19–5.37 wt%) and sprinkled with minute grains (<5  $\mu\text{m}$ ) of pentlandite and pyrrhotite (Fig. 1). The other aggregate (Fo<sub>85.5</sub>) contains a mosaic of zoned subhedral to equigranular grains of olivine (Fig. 2) together with some pyrrhotite, minute grains of pentlandite and opaque inclusions (<10  $\mu\text{m}$ ). These textures are indicative of shock metamorphism (Bauer, 1979; Ashworth, 1985; Scott *et al.*, 1992).

##### 3.1.2. Carbonates

Most of the carbonates in Y-86029 are present as individual euhedral to subhedral crystals (rarely exceeding 25  $\mu\text{m}$ ) or as globular aggregates (10–15  $\mu\text{m}$ ) with high Fe and Mn contents (Table 1). The individual crystals have compositions ranging from magnesite to dolomite (Table 1). Both are associated with pyrrhotite, which often occurs as rims on individual crystals. The carbonate globules (Figs. 3 and 4) have cores of magnetite with traces of S, while the rims are Ca-Fe rich (ankerite compositions). Interstices between the globules are Mg-rich (dolomite composition).

##### 3.1.3. Periclase

In thin section, periclase appears as large brownish clasts, which can be easily confused with coarse phyllosilicates. We have identified two large grains (300–500  $\mu\text{m}$ ) and a few other smaller (<100  $\mu\text{m}$ ) grains of periclase (Fig. 5) within the matrix of Y-86029. These grains have high Mn contents (3–6 wt%) and average compositions of Mg<sub>0.62</sub> Fe<sub>0.37</sub> Mn<sub>0.01</sub> O (Table 1). They also contain minute grains of a fracture-filling, Fe-S phase, most probably pyrrhotite. Periclase appears to be a product of heating of Mg-rich carbonate. Some CaO (~0.05%) is present (Table 1) suggesting that these Mg-rich carbonates contained traces of calcite.

Table 1. Compositions of selected minerals in Y-86029.

Species	Olivine		Carbonates			Phyllosilicates		Periclase
	Melt vein-1	Melt vein-2	Magnesite	Ankerite	Dolomite	Coarse	Matrix	
SiO <sub>2</sub>	39.85	36.67	1.73	1.78	0.88	46.65	27.32	0.28
TiO <sub>2</sub>	0	0.08	0	0	0	0	0.03	0.03
Al <sub>2</sub> O <sub>3</sub>	0.03	0.80	0.04	0.20	0.05	5.07	2.37	0
FeO <sup>‡</sup>	39.48	29.52	14.33	35.89	12.41	12.40	24.48	40.27
MnO	0.33	0.28	2.20	3.16	3.00	0.68	0.28	1.49
Cr <sub>2</sub> O <sub>3</sub>	0.30	0.35	0.01	0	0.03	1.46	0.47	0.02
MgO	23.42	24.60	37.61	10.50	21.46	26.93	21.49	51.51
CaO	1.11	3.84	4.09	20.49	21.36	0.02	0.27	0.05
Na <sub>2</sub> O	0	0.34	0.08	0.07	0.12	2.52	0.44	0.04
K <sub>2</sub> O	0	0.11	0.03	0.01	0.05	0.19	0.17	0
P <sub>2</sub> O <sub>5</sub>	0.03	1.96	0.05	0.12	0.15	0.03	0.04	0.02
S	0	0.33	0.31	1.17	0.74	0.02	3.93	0.58
NiO	0.15	0.11	0.56	0.07	0.02	0.03	1.28	0.05
Total	99.80	99.91	100.00 <sup>#</sup>	100.00 <sup>#</sup>	100.00 <sup>#</sup>	95.98	92.45	95.32

<sup>‡</sup> All Fe reported as FeO

<sup>#</sup> Totals calculated assuming all Mg, Fe, Ca and Mn as carbonate (all others as oxides)

### 3.1.4. Sulfides and magnetite

Y-86029 shows a high abundance of sulfides, mostly pyrrhotite, and a few grains of pentlandite. Pyrrhotite occurs as large (10–60  $\mu\text{m}$ ) euhedral, anhedral and lath-like grains and also as small grains (sub-micron scale) widely dispersed in the matrix. Pentlandite grains are rare and relatively small (<5  $\mu\text{m}$ ) and occur mainly within the anhydrous mineral grains.

Magnetite is abundant within Y-86029 in different sizes and essentially all morphologies (framboidal aggregates, spherulites, plaquettes and euhedral crystals) either individually or intergrown. These magnetite morphologies are characteristic of CI chondrites (Kerridge *et al.*, 1979) as well as all other types of carbonaceous chondrites. They occur together with coarse phyllosilicates (Fig. 6) and apatite and rarely with the sulfides suggesting simultaneous formation during aqueous alteration. Some magnetite grains contain traces of Fe-S phases (most probably pyrrhotite) implying that some of the grains were produced from heating or oxidation of the sulfides.

### 3.1.5. 'Coarse' and matrix phyllosilicates

Coarse phyllosilicates are distinct from matrix phyllosilicates in that they occur as coarsely crystallized isolated clusters that range in size from about 30–300  $\mu\text{m}$ . They are similar to the phyllosilicates described in the heated CI chondrite Y-82162 (Tomeoka *et al.*, 1989b; Ikeda, 1991). They are quite abundant and often occur together with magnetite, pyrrhotite and apatite (*e.g.* Fig. 6). Microprobe analyses plotted in terms of Fe, Si and Mg (Fig. 7) with selected analyses in Table 1 suggest they are mixtures of serpentine and saponite (this requires verification by TEM). The analyses plot much closer to the trioctahedral smectite ideal solid solution lines as compared with the matrix phyllosilicates.

Microprobe analyses of matrix phyllosilicates suggest that they are mixtures of serpentine and smectite (Fig. 7). Both coarse and matrix phyllosilicates have high analytical totals (86.7–98.3 wt%), which we ascribe to dehydration during thermal metamorphism. This is consistent with petrographic observations from other thermally metamorphosed carbonaceous chondrites (Tomeoka *et al.*, 1989a,b, 1990; Zolensky *et al.*

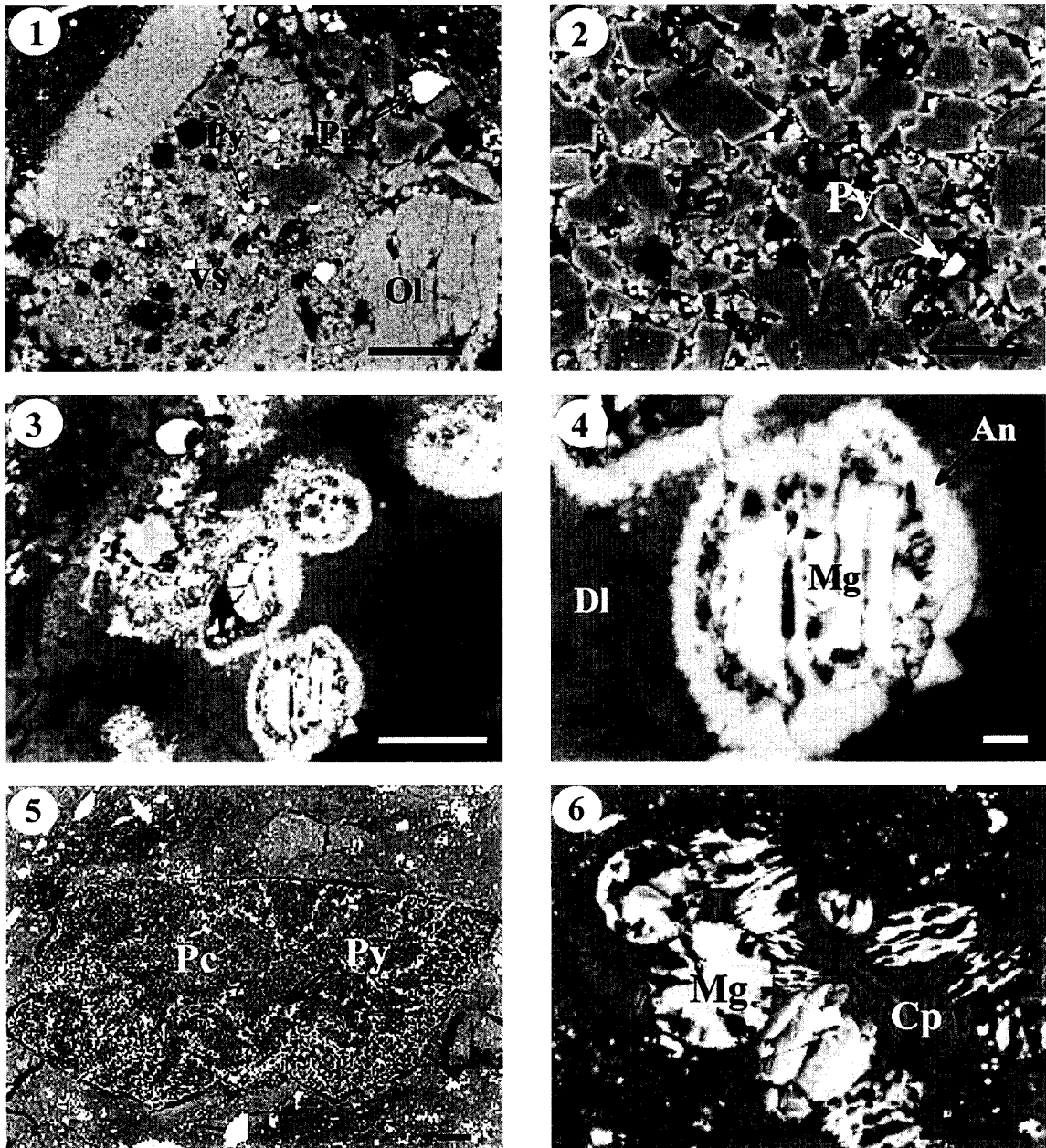


Fig. 1. Shock induced melt vein (Vs) within olivine (Ol) with minute grains of pyrrhotite (Py) and pentlandite (Pn) [Scale bar=10  $\mu\text{m}$ ].

Fig. 2. A shock melted olivine aggregate consisting of a mosaic of polycrystalline olivine grains with minute grains of pyrrhotite [Scale bar=10  $\mu\text{m}$ ].

Fig. 3. Heated carbonate globules within a void in Y-86029 [Scale bar=10  $\mu\text{m}$ ].

Fig. 4. A close up view of a carbonate globule composed of a magnetite (Mg) rich core, ankerite (An) rim and dolomite (Dl) in interstitial spaces [Scale bar=1  $\mu\text{m}$ ].

Fig. 5. Large periclase grain (Pc) interspersed with minute grains of pyrrhotite within fractures [Scale bar=10  $\mu\text{m}$ ].

Fig. 6. Magnetite crystal (Mg) rimmed by pyrrhotite (Py) and a poorly crystalline Mg-Fe phase (MF) [Scale bar=10  $\mu\text{m}$ ].

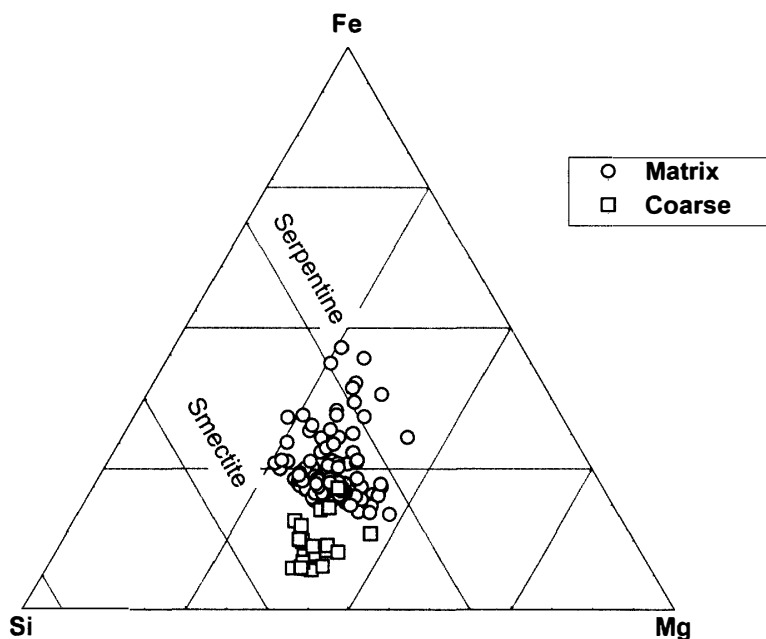


Fig. 7. Ternary plot showing composition of Y-86029 phyllosilicates.

*al.*, 1989a,b; Ikeda, 1991). This level of heating was not sufficiently high for complete transformation of phyllosilicates to olivine or pyroxene. The matrix phyllosilicates also have variable contents of Fe as is commonly observed in most carbonaceous chondrites. The variable compositions between the coarse and matrix phyllosilicates are expressed in their Mg/Fe ratios *i.e.* between 1–2.2 for matrix phyllosilicates and 2.1–4.5 for coarse phyllosilicates. This suggests that the coarse phyllosilicates contain submicron grains of other phases as shown by their high Na<sub>2</sub>O (1.57–4.53 wt%) and Cr<sub>2</sub>O<sub>3</sub> (0.23–3.12 wt%) contents (Table 1) probably Na-rich trioctahedral mica *e.g.* phlogophite (Schreyer *et al.*, 1980) and chromite.

Other minor phases in Y-86029 include minute grains of apatite (up to 5  $\mu$ m), which often occur with magnetite or coarse phyllosilicates. Ilmenite is present but rare.

### 3.2. Y-793321

Based on O-isotopic composition, Y-793321 is a CM2 chondrite (Mayeda *et al.*, 1987) that contains clasts exhibiting varying degrees of aqueous alteration. The major characteristics of this meteorite are described as follows:

#### 3.2.1. Chondrules and anhydrous silicate grains

Most of the chondrules in Y-793321 are olivine-pyroxene porphyritic types although barred and granular types are also present. These chondrules are mainly forsteritic (Fo<sub>96-98.5</sub>; Fig. 8) and are less than 1 mm in diameter. Whereas a few of the chondrules have well preserved fine-grained rims, most have discontinuous phyllosilicate rims probably as a result of abrasion during brecciation. Isolated and zoned olivine inclusions (Fo<sub>72.5</sub>-Fo<sub>80.5</sub>) are quite common in the matrix often associated with sulfides. Like the chondrules, some of the olivine aggregates contain discontinuous phyllosilicate rims. The zoning patterns of these grains is bimodal similar to that observed in most CM2 and some CO3 chondrites (Nagahara and Kushiro, 1982; Akai and Kanno, 1985).

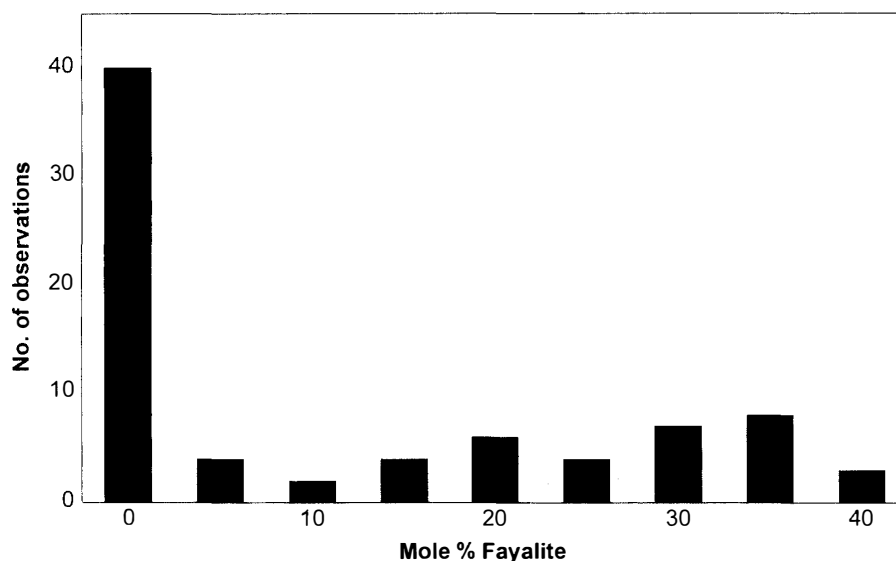


Fig. 8. Histogram showing composition of Y-793321 olivines.

We have observed a barred chondrule with elongated lenses (Fig. 9) of high Ca-pyroxene (diopside). The pyroxenes have preferentially altered along the cleavage planes to Fe-rich phyllosilicates. Fractures and cleavage planes in minerals are solution conduits and energetically favoured sites where dissolution proceeds by preferential attack during aqueous alteration (Berner and Holdren, 1977). The chondrules and isolated olivine grains in Y-793321 exhibit various degrees of aqueous alteration typical of CM 2's ranging from mild to moderate (*e.g.* Zolensky *et al.*, 1997). The mesostasis of the chondrules and Fe-Ni metal grains (kamacite) have altered to Fe-rich phyllosilicates and tochilinite (Table 2). The metal grains also occur as small (<5  $\mu\text{m}$ ) unaltered spherical grains.

### 3.2.2. CAI

The CAI's are present in Y-793321 as spherical concentric objects (Fig. 10) or aggregates within the matrix. The rounded aggregates are composed of slightly altered, near-stoichiometric granular spinel cores, an inner thin fractured rim of Fe-rich phyllosilicate (Table 3) and outer aluminous diopside layer. The CAI's within matrix are highly porous and composed of aluminous diopside and Fe-rich serpentine (Table 2). The Al and TiO<sub>2</sub> contents of diopside ranges from 4 to 8 wt% and <1–3 wt% respectively. These CAI morphologies are typical of CM2 and CR2 chondrites (Weisberg *et al.*, 1993; MacPherson and Davis, 1994).

Curiously, spinel and diopside are the only major phases in these CAI's even in the highly porous altered aggregates. Within the spherical concentric aggregates, spinel has preferentially altered to Fe-rich phyllosilicates whereas diopside is well preserved. The resistance of diopside relative to spinel during chemical alteration has been observed in several carbonaceous chondrites (Hashimoto and Grossman, 1987; MacPherson *et al.*, 1988) and may be due to the high strength of tetrahedral bonding in clinopyroxenes (Nahon and Colin, 1982).

### 3.2.3. Phyllosilicates

Phyllosilicates are abundant in Y-793321 and occur within chondrules, rims and matrix. Ternary plots (Fig. 15) suggest they are serpentines of various compositions (Table

Table 2. Compositions of selected minerals in Y-793321.

Species	Tochilinite		Spinel <sup>§</sup>	CAI's		Phyllosilicate <sup>†</sup>
	Type 1 <sup>†</sup>	Type 2 <sup>†</sup>		Diopside1 <sup>§</sup>	Diopside2 <sup>§</sup>	
SiO <sub>2</sub>	3.95	4.3	0.02	49.06	48.82	24.29
TiO <sub>2</sub>	0.02	0	0.17	1.42	0.95	0.28
Al <sub>2</sub> O <sub>3</sub>	0.57	0.57	69.15	7.84	5.49	12.29
FeO <sup>‡</sup>	55.32	58.82	0.56	0.34	1.49	34.96
MnO	0.05	0.09	0.02	0.12	0.11	0.23
Cr <sub>2</sub> O <sub>3</sub>	2.41	3.83	0.18	0.99	1.18	0.87
MgO	1.85	2.09	27.23	16.95	15.73	13.62
CaO	0.14	0.03	0.02	21.17	24.84	1.48
Na <sub>2</sub> O	0.16	1.37	0	0.05	0.03	0.95
K <sub>2</sub> O	0.37	0.39	0	0	0.01	0.11
P <sub>2</sub> O <sub>5</sub>	0.87	1.67	0.02	0.18	0.22	0.03
S	16.53	7.64	0.02	0	0	0.29
NiO	9.57	6.5	0	0	0.03	0.07
Total	91.81	88.1	97.40	99.01	98.90	89.47

<sup>†</sup> Average of 5 analyses

<sup>§</sup> Average of 6 analyses

<sup>¶</sup> Average of 10 analyses

<sup>‡</sup> All Fe reported as FeO

3). Chondrule and rim phyllosilicates have high FeO compositions (45–65 wt%), low MgO (3–9 wt%) and moderate Al<sub>2</sub>O<sub>3</sub> contents (4–7 wt%). The matrix phyllosilicates contain less FeO (20–30 wt%) and slightly higher MgO (10–20 wt%) and tochilinite (S contents between 2–5 wt%). This is typical of CM 2 serpentines (Table 3).

Discrete Fe-rich coarse phyllosilicate clusters (Fig. 11) occur within the matrix in Y-793321. These phyllosilicates are similar in composition to the chondrule serpentines although they have slightly lower Al<sub>2</sub>O<sub>3</sub> (1–2 wt%) contents (Table 3). They exhibit similar outward morphology (*i.e.* sub-rounded irregular clusters) and often occur together with tochilinite (Fig. 12). Some phyllosilicate clasts (Fig. 13) are also present with slightly high MgO compositions (15–25 wt%; Table 3) and analytical totals (88–92.7%) indicative of mild thermal metamorphism. Phyllosilicate veins such as those in Fig. 11 are abundant within the matrix of Y-793321 suggesting that aqueous alteration occurred after brecciation (Browning *et al.*, 1995).

#### 3.2.4. Tochilinite

Tochilinite is present within chondrules and matrix in Y-793321 (this is based on electron microprobe and SEM data). However, precise morphologies are subject to verification by TEM. Tochilinite within chondrules occur as rounded to sub-rounded inclusions and aggregates ranging in size from 10 to 100  $\mu\text{m}$ . They are a replacement of Fe-Ni (kamacite) grains and have fairly uniform compositions (Table 2). The tochilinite within the matrix occurs as sub-rounded, irregularly shaped clusters ranging in size from 10–150  $\mu\text{m}$ . Together with sulfides, they commonly enclose individual grains of calcium carbonate or occur very close together (Figs. 14 and 16) suggesting simultaneous formation or deposition. Tochilinite is also closely associated with Fe-rich phyllosilicates for probably the same reasons.



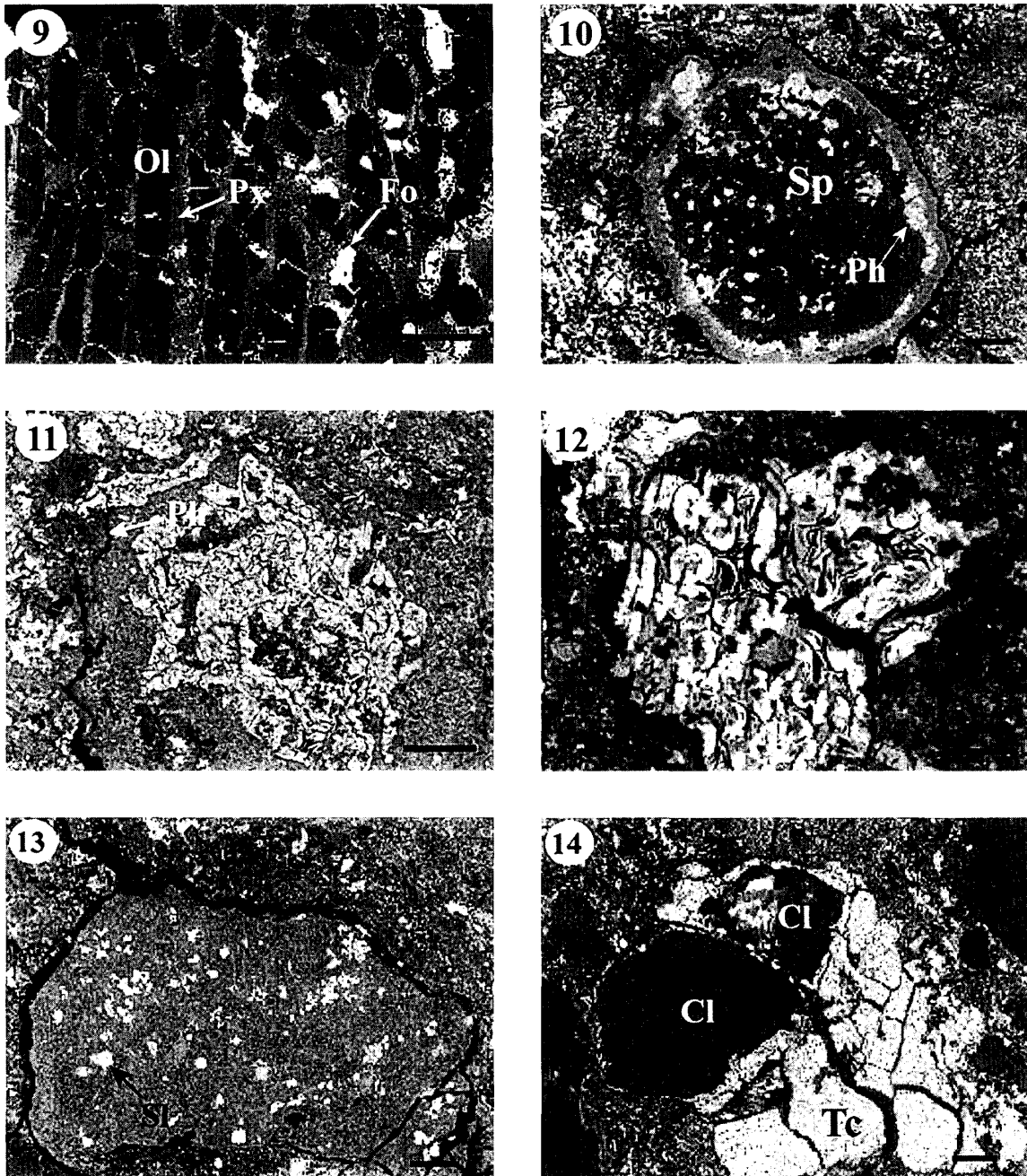


Fig. 9. Elongated lenses of pyroxenes (Px) altered to phyllosilicate and iron oxides (Fo) within cleavage planes of a barred chondrule in Y-793321 [Scale bar=100  $\mu\text{m}$ ].

Fig. 10. Rounded CAI showing an altered granular spinel core (Sp) with an inner thin phyllosilicate (Ph) rim and an outer diopside-rich (Ds) core in Y-793321 [Scale bar=10  $\mu\text{m}$ ].

Fig. 11. Fe-rich phyllosilicate clusters with traces of tochilinite within the matrix of Y-793321. Thin phyllosilicate veins (Ph) are also present within surrounding matrix [Scale bar=10  $\mu\text{m}$ ].

Fig. 12. Tochilinite intergrown with phyllosilicates within the matrix of Y-793321 [Scale bar=10  $\mu\text{m}$ ].

Fig. 13. A phyllosilicate clast with sulfide inclusions (SI) within the matrix of Y-793321 [Scale bar=10  $\mu\text{m}$ ].

Fig. 14. Calcite grains (Cl) occurring with tochilinite (Tc) within the matrix of Y-793321 [Scale bar=10  $\mu\text{m}$ ].

Table 3. *Phyllosilicate compositions in Y-793321 compared with those for CM2.*

Species	Chondrule related <sup>†</sup>		Matrix related <sup>§</sup>			CM2 Serpentine <sup>¶</sup>	
	Mesostasis	Rim	Matrix	Clusters <sup>*</sup>	Clasts <sup>‡</sup>	High Mg	High Fe
SiO <sub>2</sub>	19.33	21.46	24.10	15.64	36.60	36.77	22.11
TiO <sub>2</sub>	0.04	0.09	0.07	0.05	0.02	0.00	0.16
Al <sub>2</sub> O <sub>3</sub>	4.44	6.89	3.17	1.16	3.95	2.74	3.85
FeO <sup>†</sup>	62.7	45.88	37.78	63.5	21.95	18.92	52.62
Cr <sub>2</sub> O <sub>3</sub>	0.30	0.10	0.10	0.06	0.22	0.16	0.00
MgO	3.52	8.79	15.05	4.94	21.54	24.61	7.31
CaO	0.11	0.36	0.34	0.23	0.65	0.06	0.39
Na <sub>2</sub> O	0.80	0.85	0.81	0.52	0.81	0.00	0.05
K <sub>2</sub> O	0.10	0.02	0.10	0.05	0.03	0.01	0.03
P <sub>2</sub> O <sub>5</sub>	0.03	0.01	0.07	0.01	0.02	0.00	0.01
S	0.42	0.50	4.76	3.60	2.82	1.28	0.06
NiO	0.19	0.03	2.29	0.24	0.74	0.39	0.22
Total	92.2	86.86	88.86	90.14	88.55	85.09	86.97

<sup>†</sup> Average of 10 analyses

<sup>§</sup> Average of 10 analyses

<sup>¶</sup> From Zolensky et al. (1996c); average of 10 analyses

<sup>\*</sup> Fe-rich discrete clusters (Fig. 11)

<sup>‡</sup> Clasts in Fig. 13

<sup>†</sup> All Fe reported as FeO

### 3.2.5. Carbonate

Calcium carbonates are abundant within the matrix of Y-793321 as irregularly shaped, equant or porous grains ranging in size from 10–25  $\mu\text{m}$ . Absence of diffraction data and small sizes preclude determination of actual calcium carbonate phase (*i.e.* calcite or aragonite). As mentioned earlier, it is commonly associated with tochilinite and sulfides suggesting a paragenetic relationship. Apart from calcium carbonate, no other carbonate minerals have been encountered in Y-793321.

### 3.2.6. Sulfides and magnetite

Like calcite, sulfides are abundant within Y-793321 as pyrrhotite and, less commonly, pentlandite and tochilinite. They show no unusual compositions although some matrix sulfides are embayed and occur as replacement of earlier porous minerals suggesting a high level of alteration.

Magnetite is less common and occurs as small (5–10  $\mu\text{m}$ ) spherical equant grains often intergrown with the sulfides. Although some may have formed as low temperature condensates, the association with the sulfides suggests that they formed by secondary replacement during an oxidation event.

## 3.3. LEW 85332

LEW 85332 is a highly unequilibrated type 3.0–3.1 carbonaceous chondrite. It was originally classified as a CO chondrite based on the small size of its chondrules (Mason, 1987). However, it has refractory lithophile and siderophile element abundances that match CI and CR chondrites, although its volatile siderophile abundance ratios differ from both these groups (Rubin and Kallemeyn, 1990; Brearley, 1997). Most of the

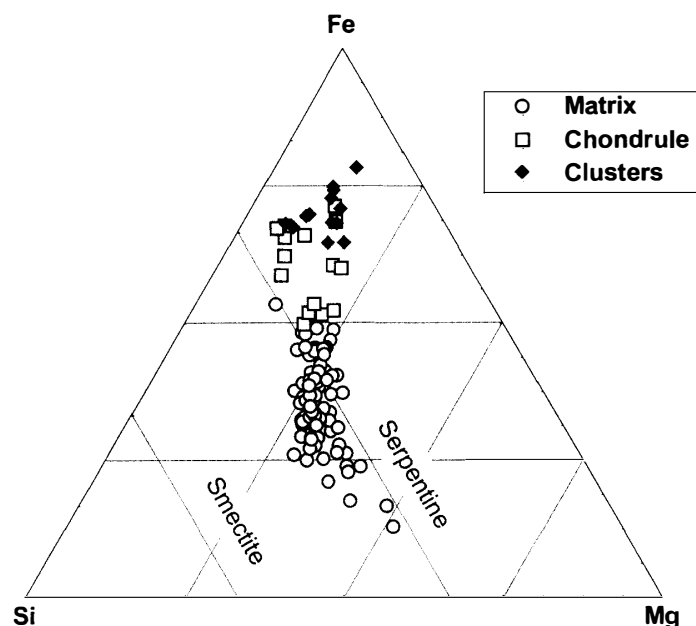


Fig. 15. Ternary plot showing composition of Y-793321 chondrule derived, matrix and Fe-rich (clusters) phyllosilicates.

petrological characteristics of LEW 85332 are similar to those of CO chondrites *i.e.* it mainly consists of chondrules, silicate aggregates, Fe-Ni metal, sulfides and matrix.

Unlike most CO chondrites, LEW 85332 is a breccia based on the presence of carbonaceous chondrite clasts that are similar to CM and CI chondrites. In particular, the matrix is very fine-grained, similar to that observed in CI chondrites. Its O-isotopic composition lies along the CO and CR mixing line, along with another unique CH chondrite ALH 85085 and its N-isotopic composition is intermediate between CR chondrite values and those for ALH 85085 (Prinz *et al.*, 1992). Thus it appears as if this unique meteorite falls within the CO3 chondrite group based on its petrological characteristics and oxygen isotopic compositions.

LEW 85332 exhibits a moderate to high degree of terrestrial weathering. Most of the matrix, chondrules, aggregates and metal grains are stained or coated by iron oxyhydroxides (Figs. 19, 20, 21).

### 3.3.1. Chondrules and anhydrous silicates

Most of the chondrules are olivine-rich ( $\text{Fo}_{94-97}$ ; Fig. 22) porphyritic or granular types, ranging in size from 100 to 350  $\mu\text{m}$ . High Ca-pyroxenes (mainly diopside) are also present. Most of these chondrules are fresh (Fig. 17) and contain unaltered rounded to sub-rounded blebs (5–40  $\mu\text{m}$ ) of kamacite ( $\text{Fe}_{93.35}\text{Ni}_{6.65}$ ). The chondrule mesostasis also shows minimal alteration. Silicate aggregates (10–150  $\mu\text{m}$ ) are olivine-rich ( $\text{Fo}_{75-77}$ ) and range in shape from angular, subhedral to spherical forms. Like the chondrules, some of the aggregates are rimmed by iron oxyhydroxides and kamacite (Fig. 18).

### 3.3.2. Metal and sulfides

Kamacite and rarely taenite occur in LEW 85332 mainly within chondrules and matrix as small spherical inclusions (5–50  $\mu\text{m}$ ). Kamacite grains within chondrules are relatively fresh, while some within matrix show partial weathering to iron oxides (Fig.

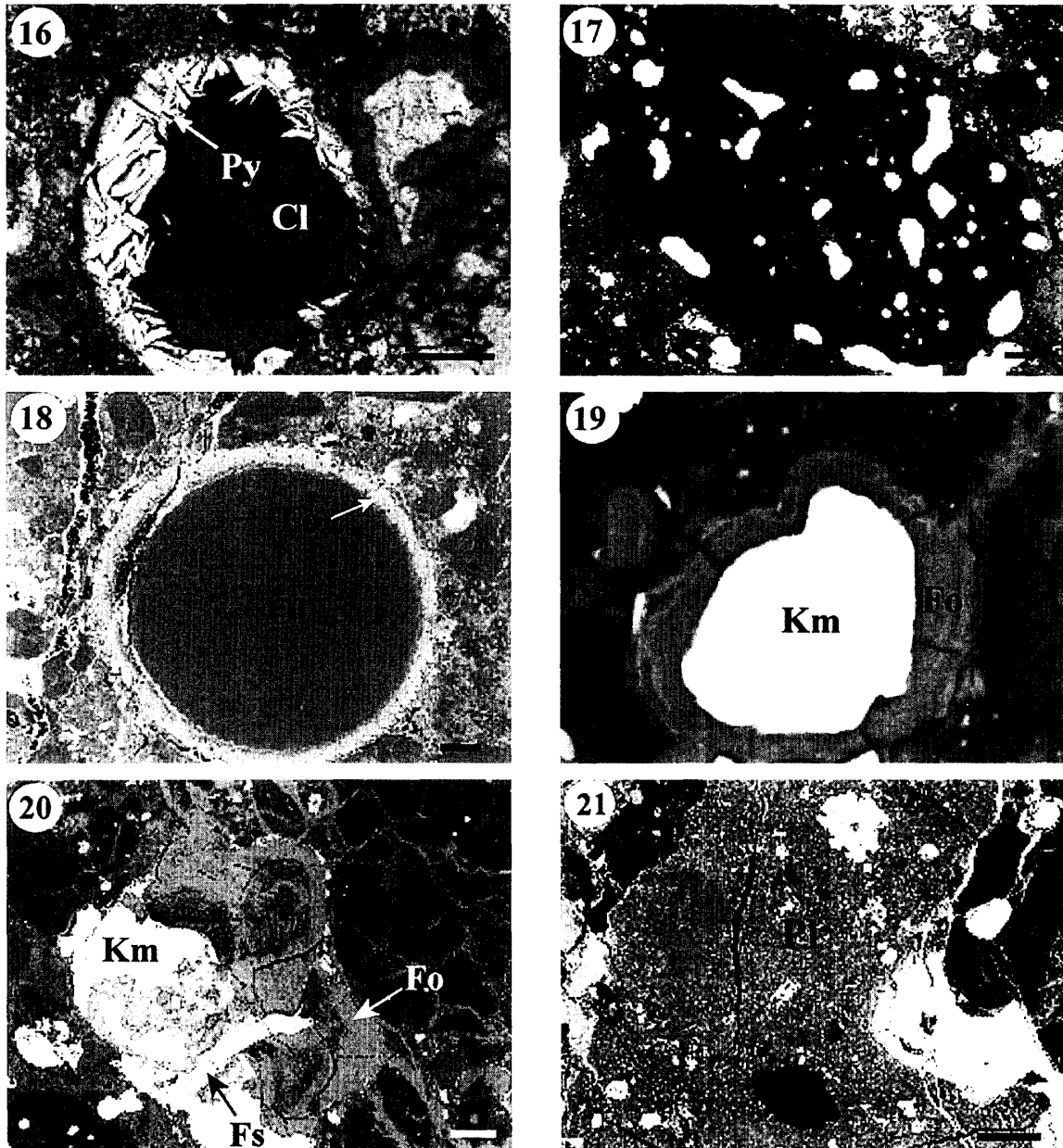


Fig. 16. Calcite grain (Cl) enclosed within acircular crystals of pyrrhotite (Py) in Y-793321 [Scale bar=10  $\mu$ m].

Fig. 17. A fresh porphyritic chondrule with Fe-Ni metal (kamacite) grains within LEW 85332 [Scale bar=10  $\mu$ m].

Fig. 18. A rounded olivine aggregate (Ol) with an inner oxide coating (Fo) and outer discontinuous rim of kamacite in LEW 85332 [Scale bar=10  $\mu$ m].

Fig. 19. Kamacite grain partially weathered to Ni-rich iron oxide in LEW 85332 [Scale bar=10  $\mu$ m].

Fig. 20. Kamacite (Km) and troilite (Tr) grains extensively coated by iron oxides in LEW 85332 [Scale bar=10  $\mu$ m].

Fig. 21. Very fine-grained phyllosilicate matrix exhibiting sharp boundary with anhydrous silicate aggregates in LEW 85332 [Scale bar=10  $\mu$ m].

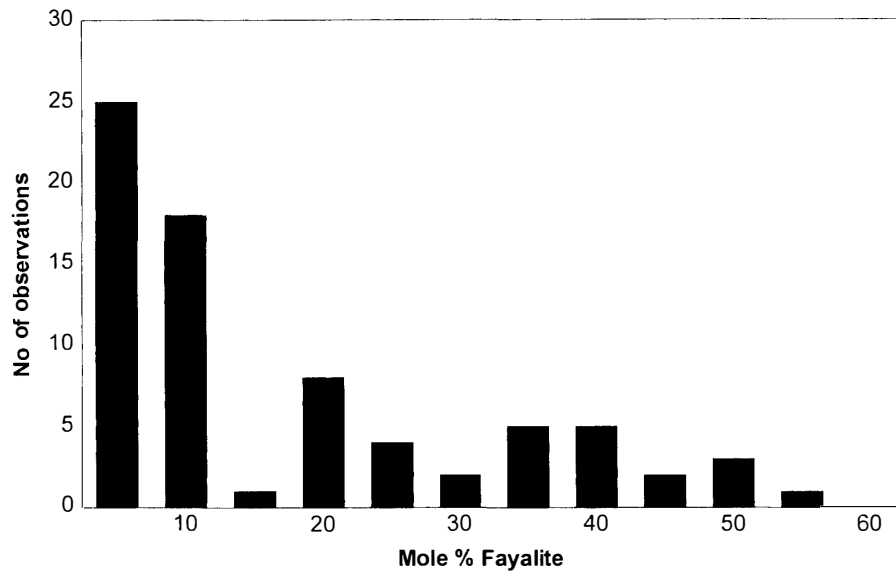


Fig. 22. Histogram showing composition of LEW 85332 olivines.

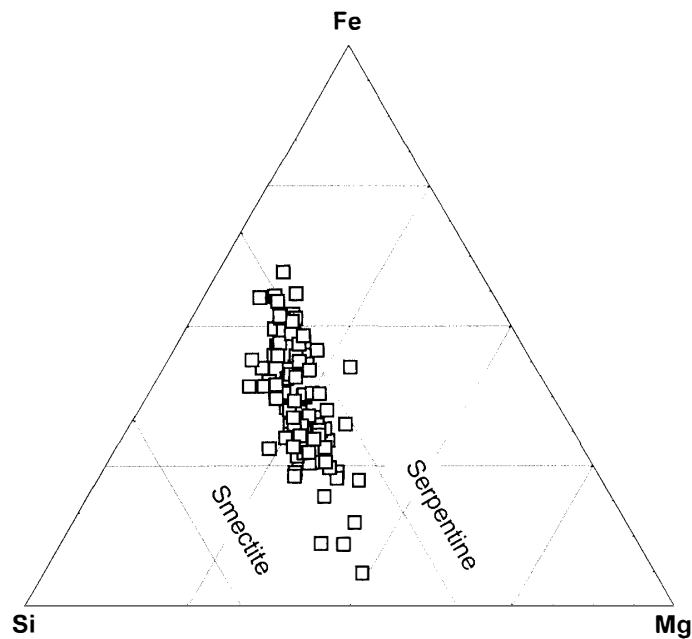


Fig. 23. Ternary plot showing composition of LEW 85332 phyllosilicates.

19). Sulfides are less abundant and occur as small ( $<10 \mu\text{m}$ ) irregular or elongate grains of troilite and rarely pyrrhotite. Apart from the presence of thin oxyhydroxide films the sulfides appear unaltered and often occur close to the Fe-Ni grains (Fig. 20).

### 3.3.3. Phyllosilicates

Phyllosilicates in LEW 85332 occur in clasts and matrix. There is no evidence of alteration of chondrules to phyllosilicates and no clear association with the other phases except iron oxyhydroxides (Fig. 21). Ternary plots suggest that phyllosilicates are mixtures of saponite and serpentine (Fig. 23) with consistently high analytical totals (83.1–94.4 wt%) indicative of mild to moderate thermal metamorphism. It is notable that

the matrix of LEW 85332 is consistently Fe-rich and the data extends towards the Fe apex and intercept the Si-Fe join at an Fe/(Fe+Si) ratio of ~0.8. The variation in Mg/(Mg+Fe) ratios is extremely large and ranges from 0.16 to 0.90 showing that the phyllosilicates are highly heterogeneous. It is also possible that these variable compositions are due to contamination by rust (oxyhydroxides).

Other mineral phases within LEW 85332 include magnetite, which occurs as subhedral grains up to 10  $\mu\text{m}$  in size. The iron oxide products of terrestrial weathering are close to stoichiometric goethite ( $\text{Fe}_{0.9}\text{OOH}$ ).

## 4. Discussion

### 4.1. Aqueous alteration and thermal metamorphism

The mineralogy of the three meteorites discussed in this paper is dominated by anhydrous olivines/pyroxenes, phyllosilicates, sulfides, carbonates, oxides and oxyhydroxides. All the three chondrites are interesting because they experienced heating events after aqueous alteration in their asteroidal setting in 3 separate asteroids (*i.e.* CI, CM and CO3 parent asteroids). The petrography/mineralogy of these chondrites reflect their formation histories, which can then be checked against the peak heating temperatures suggested by trace element data.

Based on RNAA data for thermally mobile trace elements (Table 4), we can order these three carbonaceous chondrites by severity of open-system heating as Y-793321 < LEW 85332 < Y-86029. This ordering explicitly assumes that the ease of vaporization and loss of elements from a given carbonaceous chondrite is essentially independent of its classification (Lipschutz *et al.*, 1999). This assumption is supported by similarities of results from open-system heating experiments involving a number of primitive chondrites, including Murchison and Allende (Ikramuddin and Lipschutz, 1975; Matza and Lipschutz, 1977; Bart *et al.*, 1980; Ngo and Lipschutz, 1980) and recent closed system experiments involving them (Wang *et al.*, 1998), and trace element trends in CM2, CR2, CO3 and

Table 4. Mobile trace elements data of Y-86029, LEW 85332 and Y-793321 compared with previously studied thermally metamorphosed carbonaceous chondrites ( $x \pm s$ -mean and standard deviation for elements in next column, unaffected by metamorphism).

Meteorite	Type	$x \pm \sigma$	Mobile trace elements		Ref.†
			Elements (No.)	Elements lost	
Y-793321	CM2	$0.51 \pm 0.08$	Cs→Cd (9)		(2)
LEW 85332	CO3	$0.26 \pm 0.04$	Cs→Tl (8)	Cd	(2)
Y-86029	CI	$1.20 \pm 0.19$	Cs→Zn (5)	In, Bi, Tl, Cd	(4)
A-881655	CM2	$0.39 \pm 0.17$	Cs→Tl (8)	Cd	(3)
Y-82162	CI	$1.36 \pm 0.18$	Cs→Zn (5)	In, Bi, Tl, Cd	(1)
B-7904	CM	$0.57 \pm 0.08$	Cs→Zn (5)	In, Bi, Tl, Cd	(1)
{ Y - 86720	CM	$0.65 \pm 0.16$	Cs→Te (4)	Zn, In, Bi, Tl, Cd	(1)
{ Y - 86789	CM2	$0.69 \pm 0.08$	Cs→Te (4)	Zn, In, Bi, Tl, Cd	(3)

†References: (1) Paul and Lipschutz (1989, 1990); (2) Xiao and Lipschutz (1992); (3) Wang and Lipschutz (1998); (4) Tonui *et al.* (2001)

CV3 chondrites (Wang and Lipschutz, 1998). Some conclusions can be drawn regarding the aqueous alteration processes in these meteorites and heating events as inferred from the trace element data.

Y-793321 exhibits varying degrees of aqueous alteration. This alteration was not complete as evidenced by the presence of Fe-rich phyllosilicates and tochilinite and the well-preserved nature of the coarse-grained anhydrous phases such as olivine and pyroxene. The CAI's also show partial alteration to Fe-rich phyllosilicates. Isolated clusters of Fe-rich phyllosilicates occur in the matrix indicative of mild aqueous alteration. Most of the metal grains are not completely altered and remain as cores surrounded by iron oxide coatings. A few phyllosilicate clasts are present within the matrix that shows evidence of more extensive aqueous alteration and heating.

Carbonates in CM2's are typically diminutive and sparse. By comparison, the extensively altered CM1's generally contain a significant amount of coarse-grained carbonates often intergrown with phyllosilicates. The abundance of calcium carbonates in Y-793321 is typical of more extensively altered CM2's. Since Fe-Ni sulfides are abundant in Y-793321, it appears that sulfidization was a significant alteration process. Intimate association between carbonates, tochilinite and phyllosilicates implies that aqueous alteration and sulfidization were probably concurrent. The presence of phyllosilicate veins suggests that aqueous alteration occurred after brecciation in the parent body.

One of the major petrographic indicators of thermal metamorphism in carbonaceous chondrites is the level of dehydration of matrix phyllosilicates to anhydrous silicates. In drawing this conclusion we look for consistency in degree of heating (apparent in analytical totals) in different clasts or parts of the meteorite as evidence for its pervasiveness. Anhydrous silicates are also usually present as sub-micron sized grains within the matrix in extensively heated meteorites. Petrographic evidence of thermal metamorphism in Y-793321 is only limited to a few phyllosilicate clasts in the matrix, which show appreciably high analytical totals (88–92.7 wt%).

Trace element data shows no evidence for loss even of Cd in Y-793321 (Table 4). In this respect, its abundance pattern resembles that of Murchison heated at 400°C in an open system manner (Matza and Lipschutz, 1977). The presence of tochilinite and absence of magnetite or sulfates show that oxidizing conditions were limited. Interestingly, TEM studies of Y-793321 by Akai (1988) demonstrated the presence of 'intermediate' phase in the transformation of phyllosilicate to olivine, which he ascribed to thermal metamorphism. Infrared reflectance analysis by Miyamoto (1992) also confirmed that Y-793321 contains low H<sub>2</sub>O contents although slightly higher than Y-82162, Y-86720 and B-7904 suggesting partial dehydration of phyllosilicates. We can postulate a number of reasons why this heating is not obvious petrographically.

First it appears that heating in Y-793321 was either not pervasive or was not sufficient enough to result in significant dehydration of phyllosilicates to olivine. Secondly, the various degrees of aqueous alteration exhibited by Y-793321 suggest that aqueous alteration was selective in different parts of the parent asteroid, probably as a result of differences in ambient temperatures. Hence, some materials were dehydrated and recrystallized while others were not. It is also conceivable that the parent body was subjected to two or more episodes of aqueous alteration. Thermal metamorphism could have occurred after the first major aqueous alteration, which might explain the presence of

some heated phyllosilicate clasts in the matrix. While Y-793321 may conceivably have experienced two bouts of aqueous alteration sandwiching mild thermal metamorphism, the case is far from proven. Furthermore, trace element and mineralogic/petrographic data for all other thermally metamorphosed carbonaceous chondrites indicate earlier aqueous alteration, never a subsequent one.

LEW 85332 resembles CI and CR chondrites in its abundance of refractory lithophiles and siderophiles, but differs from these groups in its chemical components. Relative to CI chondrites, LEW 85332 has high abundance ratios of Mn, As, Ga, Sb, Se and Zn and most volatile siderophiles; relative to CR chondrites, LEW 85332 has high abundance of Mn and most volatile siderophiles (Rubin and Kallemeyn, 1990). It is moderate to extensively weathered, corresponding to weathering category B/C for Antarctic meteorites (Score and Lindstrom, 1990). Most of the metal grains are coated by iron oxides, notably goethite. The most dominant type 3 characteristics of this meteorite include sharply defined chondrules with no evident recrystallization, very heterogenous olivine and low-Ca pyroxene compositions and abundant silicate and metal matrix aggregates. The matrix/chondrule abundance ratio and the large proportion of opaque-metal-rich chondrules is also closer to that of CO than CI or CR chondrites. The Fe-Ni metal grains are well preserved and fresh implying a nebular metal component that is normally partially altered in moderately metamorphosed carbonaceous chondrites.

Aqueous alteration in LEW 85332 was limited only to the matrix with no evidence of alteration of chondrules as discussed in the preceding section. The phyllosilicates are very heterogenous in composition and occur as mixtures of serpentine and smectite. Heating was quite pervasive at temperatures of 500–600°C (presumably nearer the former) as shown by Cd loss and partial dehydration of phyllosilicates to olivine (average analytical totals of 91%).

Y-86029 comes from a CI parent body and apart from a few isolated olivine grains is characterized by complete destruction of preexisting anhydrous silicates during aqueous alteration. Like Y-82162, which seem to have been somewhat more heavily metamorphosed (Tonui *et al.*, 2002) the lack of late stage aqueous alteration may also be responsible for the abundance of large clusters of coarse phyllosilicates (Tomeoka *et al.*, 1989b) and Fe-(Ni) sulfides. Extensive oxidation is also evident in Y-86029 as shown by the abundance of magnetite but even then this was not sufficiently strong to produce sulfates. Sulfidization is only evident in a few grains and was not pervasive.

Petrographic observations are consistent with Y-86029 having undergone extensive heating at 500–600°C as trace element data would require. This is evidenced by the dehydration of the phyllosilicates to near olivine compositions. It is important to emphasize that this dehydration was not uniform *i.e.* some materials were completely dehydrated while others were partially so. The high level of heating is also apparent in the compositions of the carbonates. Ca-Fe-Mn carbonates are abundant in Y-86029 rather than calcite or dolomite as is the case in most CI chondrites. The most dominant product of heating of carbonate in Y-86029 is periclase, which occurs as large aggregates that have not been described in CI chondrites. The drusy and elongate morphologies of some magnetite crystals are consistent with heating of sulfides.



#### 4.2. Unusual textures of Y-86029 and LEW 85332

Y-86029 and LEW 85332 show unusual textures that have rarely been encountered in carbonaceous chondrites. Two large olivine aggregates in Y-86029 show evidence of shock-induced melt recrystallisation defined by the presence of a vesicular vein in one aggregate and a mosaic of fine-grained polycrystalline aggregates in the other. Both the vein and aggregate have inclusions of minute blebs or crystals of sulfides notably pentlandite and pyrrhotite. One aggregate exhibits Mg-Fe zoning at the edges of grains, while the other does not. It is important to note that shock effects are not discriminative *i.e.* they can occur in both altered/unaltered and zoned/unzoned mineral grains. Also, shock effects are known to be inhomogeneously distributed throughout meteorites; unshocked grains can occur very close to highly shocked material (Fred Horz pers. commun.). The melting of olivine occurred rapidly within regions of the same sample, the resulting eutectic melt mixing instantaneously with coexisting, simultaneously shock-melted sulfide grains. These features are typical of shock-induced intragranular microfractures associated with low to medium pressure ( $\leq 60$  GPa) impacts and thermally activated processes such as annealing, oxidation, recrystallisation and melting (Scott *et al.*, 1992; Bauer, 1979; Dodd and Jarosewich, 1979; Ashworth, 1985).

Y-86029 also contains large periclase clasts (300–500  $\mu\text{m}$ ) that have rarely been encountered in CI chondrites. These clasts are present as heating products of Mg-rich carbonates. Carbonates are abundant in Y-86029 as irregular aggregates within the matrix or as globular aggregates within voids. The presence of distinct concentric chemical zoning or globular morphology of carbonates has rarely been observed in CI chondrites.

The spherical carbonate globules of Y-86029 are small in size (10–15  $\mu\text{m}$ ) and occur in a void within the matrix. They show simple but uniform compositional zoning consisting of cores of magnetite with traces of S and Ca-Fe rich rims (mainly ankerite and some siderite). The absence of carbonate or sulfate veins in Y-86029 suggests that they formed after brecciation within the parent body. The interstitial spaces between the globules are Mg-rich (dolomite composition). Pyrrhotite occurs at the peripheries of these globules. Sulfides are commonly associated with carbonate globules in terrestrial (*e.g.* Laverne, 1993) and extraterrestrial rocks (*e.g.* Golden *et al.*, 2001). The magnetite that forms the core of the globules in Y-86029 could have precipitated directly from solution or resulted from heating of sulfides. It most probably resulted from the latter because the elongated morphology of magnetite is similar to that encountered in this meteorite and other thermally metamorphosed CI chondrite Y-82162 (Tomeoka *et al.*, 1989a,b; Zolensky *et al.*, 1989b; Ikeda, 1991). This suggests that the core of the globules was probably pyrrhotite and siderite before heating and the Ca-Fe rich rims were originally calcite (with traces of Mg).

This inference, however, appears to conflict with the thermal metamorphic temperatures evident in Y-86029 (*i.e.* 500–600°C) and the presence of periclase in the matrix. How is it possible that these carbonate globules did not thermally decompose to the oxides like the matrix carbonates? It is possible that heating was not uniform in different regions of the meteorite or that these carbonate globules formed after the peak heating temperatures. A more plausible explanation lies in the decomposition temperatures ( $T_d$ ) for carbonates of Mg, Ca, and Fe at varying  $\text{CO}_2$  total pressures (Ikornikova and Sheptunov, 1973; D.C. Golden pers. commun.). For most of the

carbonates the order is as follows:

$$\sim 470^{\circ}\text{C } T_{\text{dFeCO}_3} < T_{\text{dMgCO}_3} \ll T_{\text{dankerite}} \ll T_{\text{ddolomite}} \ll T_{\text{dcalcite}} \sim 900^{\circ}\text{C}.$$

The thermal decomposition of magnesite occurs at the temperature range of 500–600°C, while that of ankerite and dolomite occurs at 600–800°C. The decomposition temperature of siderite takes into account pure siderite. The carbonate rims of Y-86029 are mainly ankeritic with minor amounts of siderite. The siderite also contains impurities of CaO (up to 5%), which has the effect of elevating the thermal decomposition temperature suggested above. It is important to note that microenvironment of formation governs the nature of the resultant products and that low-temperature carbonate minerals can form in apparent violation of equilibrium thermodynamics and kinetic processes (Valley *et al.*, 1997). High CO<sub>2</sub> partial pressures in closed conditions can result in thermal decomposition of carbonates at elevated temperatures than that suggested by thermodynamic data (D.C. Golden pers. commun.). We have discussed the mechanisms of formation of these globules in a separate publication (Tonui *et al.*, 2002) and argued that the fine and uniform texture of the spherules, identical zoning and preferential siting in a void suggests crystallization from a fluid circulating in interconnected pore spaces.

The most unusual characteristic of LEW 85332 is the absence of direct evidence for alteration of chondrules. The mesostasis and Fe-Ni metal grains within it are also relatively fresh. These chondrules exhibit a sharp contact with the matrix, which by all accounts is extensively altered although not to the level of CI chondrites as shown by the absence of carbonates, magnetite and high Fe-contents of the phyllosilicates. LEW 85332 also underwent extensive brecciation similar to that in CM and CI chondrites. Brearley (1997) also observed a similar trend of matrix phyllosilicates as in this study, which he characterized as intergrowths of serpentines and saponite from TEM analysis. He also noted the unaltered nature of the chondrules but did not mention the partial dehydration of the phyllosilicates that we have observed in this study.

The absence of clear evidence of alteration of chondrules and silicate aggregates and highly altered nature of the matrix suggests that formation of hydrous phases and subsequent heating occurred prior to final accretion in the parent body. Brearley (1997) suggested that preferential alteration of matrix phases is likely, because of their fine-grained nature and high surface area to volume ratio, such that the rates of mineral dissolution would be accelerated. The formation of hydrous phases in the matrix would effectively act as a sink, absorbing water and thus preventing it from interacting to a large degree with coarser grained chondrule silicates. This model however does not fully account for the absence of alteration within other smaller grains, like silicate aggregates within the matrix, which show similar unaltered characteristics as the chondrules.

The moderate level of heating in LEW 85332 suggested by petrographic and mobile trace element data would have also affected both chondrule and matrix alike if it occurred after the dominant aqueous alteration as is commonly observed in other heated carbonaceous chondrites. It is important to note, however, that this meteorite is lacking in phases like tochilinite and magnetite, which are more sensitive to heating than Fe-Ni metal, especially if they are present as a component of alteration of chondrules. The level of heating was not high enough to have resulted in integration of chondrules and matrix as observed in other heated carbonaceous chondrites *e.g.* B-7904 or Y-86720

(Lipschutz *et al.*, 1999). The partitioning of these components, diverse chemical characteristics and probable effects of terrestrial weathering appear to explain the unique characteristics of LEW 85332.

## 5. Conclusions

Petrographic studies of the CI chondrite Y-86029, CM chondrite Y-793321 and CO3 chondrite LEW 85332 indicate that they were subjected to varying degrees of aqueous alteration and heating events in asteroidal settings. Y-86029 and LEW 85332 have unusual textures that have rarely been encountered in carbonaceous chondrites. These include the first documented presence of spherical carbonate globules, shock related melt veins and aggregates and large periclase clasts in Y-86029 and differences in aqueous alteration histories of chondrules and matrix in LEW 85332. There is also evidence of a possible *late stage* retrograde aqueous alteration episode in Y-793321 that obscured an earlier thermal metamorphic event.

Based on trace element chemistry, the thermal histories of these meteorites compared to those of other heated Antarctic meteorites (Lipschutz *et al.*, 1999) can be ordered as: **Y-793321** < 500°C < A-881655 ≤ **LEW85332** < **Y-86029** < B-7904 = Y-82162 < Y-86720 ≤ 700°C. This sequence is consistent with petrographic properties of these meteorites. The growing number of these heated carbonaceous chondrites is clear evidence of the complex nature of what we once regarded as relatively primitive but simple asteroids. Unusual textures of some of these meteorites provide an important source of information regarding the diversity of materials that formed in the early solar system.

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