NEW PETROGRAPHIC AND TRACE ELEMENT DATA ON THERMALLY METAMORPHOSED CARBONACEOUS CHONDRITES

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Abstract: Mineral grains and matrix of heated chondrites Yamato (Y)-82162, Belgica (B)-7904, Y-86720, and Asuka (A)-881655 were examined for major elements and, where appropriate, phyllosilicate and matrix samples were characterized by TEM. CM chondrites A-881655 and B-7904 were only partially aqueously altered before thermal metamorphism initiated dehydration and recrystallization. Tochilinite is absent in both A-881655 and B-7904 probably due to mild thermal metamorphism. Phyllosilicates in B-7904 are dehydrated but not completely recrystallized to olivine and pyroxene. Y-86720 experienced a history very different from other CM chondrites: its chondrules and other coarse-grained components were completely altered by aqueous fluids. Fine-grained olivine was subsequently replaced during an episode of thermal metamorphism producing compositions near Fo70 and complete destruction of serpentine occurred. Y-82162 comes from a CI parent and is characterized by complete destruction of preexisting anhydrous silicates during aqueous alteration. Subsequent heating at $600-700^{\circ}$ C resulted in dehydration of phyllosilicates. The matrix contains abundant fine-grained olivine which would not likely survive the original aqueous alteration and therefore must have been formed by phyllosilicate metamorphism.

Alternating episodes of oxidation and sulfidization following aqueous alteration are evident in all but Y-86720. Either Y-86720 escaped an oxidizing event or effects of such an event were obliterated by later sulfidization. Based on RNAA data for thermally mobile trace elements in them and in Murchison CM2 samples heated for one week at 500°, 600°, and 700°C under conditions reasonable for interiors of primitive parent bodies, the four thermally metamorphosed carbonaceous chondrites can be ordered by the severity of open-system heating as $500^\circ \le A-881655 < B-7904$ $< Y-82162 < Y-86720 \le 700^\circ C$. Petrographic studies of these meteorites indicate that each bears the signature of a unique sequence of oxidation/reduction/hydration episodes followed by a late stage thermal metamorphic event which occurred in an asteroidal setting, on at least two separate asteroids (the CM and CI parent bodies).

Thermal alterations in these meteorites can be used to identify other carbonaceous chondrites that experienced thermal metamorphism in their parent bodies. Interestingly, all thermally metamorphosed carbonaceous chondrites identified to date were found in Antarctica, mainly in Queen Maud Land, and none are observed falls. Apparently, carbonaceous chondrite parent sources sampled in near-Earth space in the past, differ from those being sampled by the Earth today.

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1. Introduction

To properly understand the early evolution of protoplanetary bodies, and map physical and chemical variations across the Solar System, we must understand the nature of all important geologic processes and where in the Solar System such processing occurred. The current model of the Solar System includes the notion that there was (and is) a "snow-line" (located within the asteroid belt) at a critical heliocentric distance, beyond which liquid water was not generally present, except in the case of tidally-heated moons of the gas giant planets. We wish to determine the location in the primitive Solar System where the geochemical front of aqueous alteration occurred, and the mineralogical variation of reaction products with heliocentric distance. This position was critical in determining the geochemical and biogenic path taken by evolving bodies.

Until about a decade ago, carbonaceous chondrites were regarded as essentially unaffected (except perhaps by hydration) by post-accretionary, parent body processes on this side of the "snow-line". This view changed in 1987, when the unusual nature of three carbonaceous chondrites from Queen Maud Land, Antarctica—Belgica (B)-7904, Yamato (Y)-82162 and Y-86720—was recognized. A consortium, led by Prof. Y. IKEDA, was approved by the Antarctic Research Committee of the Japanese National Institute of Polar Research (NIPR) to study the CI-like Y-82162 and the other two, CM-like chondrites.

Mineralogic-petrologic properties of these three carbonaceous chondrites indicated that they had been thermally metamorphosed in their parent bodies (TOMEOKA *et al.*, 1989a,b; TOMEOKA, 1990a; AKAI, 1990a,b; IKEDA, 1992; *cf.* KOJIMA *et al.*, 1994). Petrographic study of other meteorites recently demonstrated that some asteroids experienced at least two cycles of aqueous alteration, with a metamorphic heating event in between (KROT *et al.*, 1997). The most reasonable view is that some heating events included both pro- and retrograde aqueous alteration. When the second alteration event was non-pervasive, abundant evidence of prior alteration and heating events survives. Thus the modern view of these "primitive" asteroids is that they have actually had a very complex history.

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 B-7904, Y-82162, Y-86720 (and, subsequently, other carbonaceous chondrites), but that these episodes were of the open-system variety. When compared with RNAA data for U, Co, Au, Sb, Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, and Cd (ordered by increasing mobility at 600-700°C) in Murchison CM2 chondrite heated for 1 week in a low-pressure (initially 10^{-5} atm H₂) environment (MATZA and LIPSCHUTZ, 1977), the extent of loss for the 3-5 most mobile elements in the three unusual Antarctic carbonaceous chondrites duplicated trends evident in 500-700°C Murchison samples. Subsequent spectral reflectance data in the UV, visible and near IR for these three Antarctic meteorites and heated Murchison samples proved to resemble those of surfaces on a number of C-, G-, B- and F-asteroids. Thus, HIROI *et al.* (1993, 1994, 1996) suggested that the surfaces of a number of these asteroids consist of carbonaceous chondrite-like

material metamorphosed at a variety of temperatures in their parent bodies' interiors, then excavated by impacts and redeposited on their exteriors.

In the light of this evidence that asteroids previously believed to be physically primitive have, in fact, been considerably altered, we revisited the mineralogy of the first three recognized naturally-heated C chondrites and have made the first characterization of the heated and brecciated CM chondrite Asuka (A)-881655. In this paper, we combine the mineralogical parageneses of these asteroidal samples with data on labile trace elements to arrive at a new understanding of the complexity of what were once regarded as relatively primitive (and simple) asteroids. We consider this task to be high priority, offering the best opportunity to determine the surface mineralogy of the C-type and related primitive asteroids and outer Solar System moons.

2. Experimental

For this study, we examined thin sections provided by the National Institute Polar Research (NIPR) in Tokyo, and their Meteorite Working Group. We examined most of the existing sections of the heated chondrites: two sections of Y-82162, three of B-7904, eight of Y-86720 and four of A-881655. We analyzed mineral grains and matrix in all samples for major elements using CAMECA CAMEBAX and CAMECA SX100 microprobes operated at 15kV and 30nA. We used a focused beam for mineral analyses, employing natural mineral standards: corrections were applied using the CAMECA on-line PAP program. These probe analyses are accurate to within $\pm 0.5\%$, relative. Backscattered electron (BSE) images of clasts were made at the NASA Johnson Space Center (JSC) using a JEOL 35C SEM and at the Mineralogical Institute, University of Tokyo, using an Hitachi S-4500 field emission gun SEM. We operated both SEM at 15 kV, a potential that offers optimum values of resolution vs. electron penetration (and excitation) of the samples. Where appropriate, we also prepared carefully selected phyllosilicate and matrix samples for more detailed characterization All TEM imaging was performed using ultramicrotomed sections of grains by TEM. in EMBED-812 low-viscosity epoxy. We studied the microtomed sections using JEOL 100CX and JEOL 2000FX STEMS equipped, respectively, with Kevex and LINK EDX analysis systems, operated at 100 and 200 kV, respectively. We used natural mineral standards, and in-house determined k-factors for reduction of compositional data, which are considered to be accurate only to within $\pm 6\%$, relative. We used a Cliff-Lorimer thin-film correction procedure (GOLDSTEIN, 1979). Phyllosilicate mineral identifications were made on the basis of both composition and electron diffraction data whenever possible.

3. Results

3.1. Mineralogy of previously described naturally-heated carbonaceous chondrites 3.1.1. B-7904

Numerous workers described the mineralogy of B-7904 a decade ago (SKIRIUS et al., 1986; TOMEOKA, 1990a; MAYEDA et al., 1991; IKEDA, 1992; KIMURA and IKEDA, 1992; IKEDA and PRINZ, 1993), but some important characterization work remained undone.

B-7904 is probably best classified as type CM2, with some doubt arising partly from the bulk oxygen isotopic composition, which falls at the juncture of the CM2 mixing and terrestrial fractionation lines, upon which the CI1 meteorites also lie. Furthermore, sufficient mineralogical differences exist between B-7904 and conventional CM2 chondrites, clouding its classification. In fact, TOMEOKA (1990a) recommended a classification of CI2 for B-7904: however, this suggestion has not been adopted by the meteoritic community.

Porphyritic chondrules are abundant in B-7904, with barred chondrules less so: while olivine in these appears undisturbed, all glass and practically all low-Ca pyroxene have been altered to phyllosilicate. Many chondrules have fine-grained rims. B-7904 has only 2.6 wt% H₂O and very low bulk C (~1 wt%) and amino acid contents (0.2% of the amount present in Murchison) for a carbonaceous chondrite (HARAMURA *et al.*, 1983; SHIMOYAMA and HARADA, 1984; GIBSON *et al.*, 1984), which KOJIMA early on suggested might reflect mild thermal metamorphism.

The matrix consists largely of "phyllosilicate" which, though the dominant component in B-7904 meteorite, remains poorly characterized. Only limited TEM observations have been reported of this material, so its characterization depends upon bulk major element composition as determined by EMPA. Bulk compositions for the phyllosilicate generally lie between those for serpentine and saponite, and are generally enriched in Na up to approximately 2 wt% Na₂O. Also, analytical totals for this phyllosilicate are generally too high (between 90 and 96 wt%) for typical phyllosilicates, and considerable Al and Cr can be present. It has been suggested that this material is a dehydrated mixture of saponite and serpentine (AKAI, 1988; TOMEOKA, 1990a), or a dehydrated mixture of Na-Al-talc and serpentine/chlorite (KIMURA and IKEDA, 1992). ZOLENSKY et al. (1989b) suggested that the original phyllosilicates were an assemblage of ferroan serpentine [averaging ($Fe_{1.63}Mg_{1.08}Al_{0.19}Ti_{0.04}Cr_{0.06}Ni_{0.04}$) ($Si_{1.73}Al_{0.27}$) O₅ (OH)₄, with water re-added], serpentine $[(Mg_{1.52}Fe_{0.91}Al_{0.28}Cr_{0.17}Ni_{0.02})$ (Si_{2.08}) O₅ (OH)₄, with water re-added] and clinochlore $[(Mg_{2.84}Fe_{1.54}Cr_{0.01}Ti_{0.01}) Al_{1.24} (Si_{3.51}Al_{0.49})O_{10}(OH)_8,$ with water re-added]. While the exact compositions require verification, it is clear that the bulk serpentine in B-7904 has an Mg: Fe ratio between 0.7 and 1.7. Serpentines (antigorite, cronstedtite, etc.) are the most abundant phases in all CM chondrites, and their compositions are more reliable indicators of the relative extent of aqueous alteration than is modal matrix content (BROWNING et al., 1996). By analogy to the alteration index for CM chondrites of BROWNING et al. (1996), such an Fe-rich serpentine composition indicates that the aqueous alteration responsible for it was incomplete. This "phyllosilicate" is compositionally different in chondrules, matrix and different clasts, as might be expected from the disparate initial mineralogy of these components, but these differences are not of particular importance here. It is likely that some of the heterogeneity arises from minute sulfide, chromite and hercynite inclusions within the dehydrated phyllosilicate, as observed in thermally decomposed phyllosilicates in CV3 dark inclusions (ZOLENSKY and KROT, 1996; KROT et al., 1997).

AKAI (1988) reported that the matrix phyllosilicates in B-7904 are non-crystalline, and contain abundant sub-micron grains of olivine. He concluded that this material formed by mild thermal metamorphism from a mixture of saponite and serpentine. The "phyllosilicate" in the partially-altered chondrules has not been characterized by TEM, but is believed to be similar to that in matrix. The complete absence of phyllosilicate layer structures in B-7904 argue for a significant degree of thermal metamorphism. Laboratory heating experiments conducted by AKAI (1988, 1990a, b) suggest temperatures on the order of 500–700°C, although the actual temperature/ dehydration relationship should also depend upon oxygen fugacity, time, and probably other, even less specific environmental parameters. TOMEOKA (1990a) reported that B-7904 is enriched in Ca relative to CM2 chondrites, 2.22 wt% CaO in B-7904 (HARAMURA *et al.*, 1983), which he ascribed to a lesser degree of aqueous alteration and, consequently, a more limited degree of leaching. TOMEOKA (1990a) also reported narrow veins enriched in Ca, crosscutting B-7904 matrix. Without further characterization, it is impossible to know whether these represent carbonate or sulfate precipitation in veins (as seen in CI1 chondrites), terrestrial contamination, or some other process.

The total S present as sulfides in B-7904 is very high, 4-5 wt% (HARAMURA *et al.*, 1983; GIBSON *et al.*, 1984). Iron sulfides are very abundant in the matrix of B-7904, mainly as micron- and smaller-sized troilite or pyrrhotite (it is unknown which), that apparently fill spaces between matrix grains, and pores in chondrules. Many pyrrhotite grains, especially the larger lath-shaped crystals, have Fe-rich halos, which we believe represent partial sulfide dissolution, followed by reprecipitation of fine-grained sulfides only a short distance away. Some chondrules have sulfide-rich rims, often penetrating into the outer regions of the chondrules themselves: these have clearly been incompletely sulfidized. There are also small veins of pyrrhotite running through some matrix regions. These sulfide textures indicate that sulfidization occurred in the parent asteroid (*in-situ* as opposed to a nebular or pre-asteroidal environment). At some late stage, pyrrhotite briefly became unstable, decomposing to form a solution from which finergrained Fe-sulfides precipitated almost immediately.

Also present are more Ni-rich sulfides, which range in composition between pyrrhotite and pentlandite (TOMEOKA, 1990a; KIMURA and IKEDA, 1992). These strange, intermediate Fe-Ni sulfides are discussed by DI VALENTIN and ZOLENSKY (1998). Briefly, these compositions should only be stable above 300°C, breaking down at lower temperatures to a mixture of pyrrhotite and pentlandite. The reason for the stability of these compositions in some meteorites (most notably UOCs and CM2s) is a mystery. Among all naturally-heated C chondrites, such sulfides have so far been found only in B-7904. The identity of these intermediate sulfides requires verification by TEM, since it is easy to mistakenly analyze a pyrrhotite-pentlandite mixture, if the grain size is smaller than the microprobe spot ($\sim 5\mu$ m). Many pyrrhotite grains have grains of Ni-rich sulfides along their peripheries, apparently representing a late stage overgrowth or replacement.

Tochilinite, abundant in CM2 chondrites, is not present in B-7904. TOMEOKA (1990a) cited this as additional evidence for heating, since tochilinite is known to decompose to troilite (or pyrrhotite perhaps) at 245°C (FUCHS *et al.*, 1973). Results for B-7904 by BISCHOFF and METZLER (1991) provide further support, since minor Fe-Ni metal is present along with sulfides in the matrix. Although most is typical kamacite and taenite, Co-rich metal is also present. Similar metal was found in oxidized LL3 chondrites such as Ngawi (KROT *et al.*, 1997). Carbides in B-7904 might be sought, as these are also a feature of the LL3 metal assemblages: however, the low C content of B-

7904 suggests that these might well not be present.

Many chondrules in B-7904 contain unequilibrated mineral assemblages, for example, diopside + enstatite and schreisbersite + phosphate (KIMURA and IKEDA, 1992). Hence, KIMURA and IKEDA (1992) suggested that shock (to a maximum of 45 GPa), not thermal metamorphism, could have been responsible for phosphate dehydration: this appears untenable since no textural evidence for shock is evident in B-7904 olivine.

We agree with TOMEOKA (1990a) that B-7904 is very similar to CM2 chondrites, but apparently suffered less aqueous alteration than they did. We also agree with previous workers who concluded that B-7904 later experienced mild thermal metamorphism for a time too brief to homogenize the entire rock, but sufficient to begin to transform phyllosilicates to olivine, and completely alter tochilinite to troilite (or pyrrhotite). We know of no experiments that have adequately addressed this time factor, so no useful estimate of its duration can be made at this time. Also, the nature of the phyllosilicates in B-7904 requires re-examination in light of recent work on Allende dark inclusions (DI), dehydration which has provided a great deal more information about textures that accompany phyllosilicate dehydration and recrystallization.

PAUL and LIPSCHUTZ (1989, 1990) noted that of the three prototypical thermally

		Pe	trograph	ography ¹ M		obile Trace Elements		
		Thermal	Min.					
Meteorite	Туре	Metam.	Pet.	Ref.	π±σ	Elements (No.)	Cd	
Y-793321	CM2	Yes	х	[5,8]	0.51±0.08	Cs→Cd (9)		
A-881655	CM2	Yes	Х	[13]	0.39±0.17	$Cs \rightarrow Tl(8)$	0.056	
Y-793495	CR2	No	Х	[12]	0.21±0.03	$Cs \rightarrow Tl(8)$	0.0020	
Y-790992	CO3	Yes?	Х	[9,11]	0.24±0.06	$Cs \rightarrow Tl(8)$	0.0026	
ALH 85003	CO3			-	0.23±0.04	$Cs \rightarrow Tl(8)$	0.00440	
LEW 85332	CO3				0.26±0.04	$Cs \rightarrow Tl(8)$	0.0026	
ALH 81003	CV3				0.29±0.09	$Cs \rightarrow Tl(8)$	0.0087	
PCA 91008	C2				0.46±0.13	Cs→Bi (7)	0.0092 [†]	
Y-86789	CM2	Yes	Х	[6]	0.69±0.08	$Cs \rightarrow Te(4)$	0.0031 [‡]	
B-7904	СМ	Yes	Х	[3,7,10,13]	0.57±0.08	$Cs \rightarrow Zn$ (5)	0.0022 °	
Y-82162	CI	Yes	Х	[1,4,7,10,13]	1.36±0.18	$Cs \rightarrow Zn$ (5)	0.0021*	
Y-86720	СМ	Yes	x	[2,4,7,10,13]	0.65±0.16	$Cs \rightarrow Te(4)$	0.0010*	

Table 1. Carbonaceous chondrites presenting petrographic and/or mobile trace element evidence for parent-body thermal metamorphism.

¹Based on mineralogic-petrologic (Min.Pet.) study by the references (Ref.) listed: [1] Tomeoka *et al.* (1989a); [2] Tomeoka *et al.* (1989b); [3] Tomeoka (1990a); [4] Akai (1990a); [5] Akai and Sekine (1994); [6] Matsuoka *et al.* (1996); [7] Bischoff and Metzler (1991); [8] Akai (1994); [9] Shibata (1996); [10] Ikeda *et al.* (1992); [11] Kojima *et al.* (1994); [12] Noguchi (1995); [13] This work.

^{*}Sources for mobile trace element data: Xiao and Lipschutz (1992) - ALH A81003, ALH 85003, LEW 85332; Paul and Lipschutz (1989,1990) - B-7904, Y-82162, Y-86720; all others from Wang and Lipschutz (1998). [†]Also Tl = 0.16.

^tAlso Zn = 0.082; In = 0.12; Bi = 0.080; Tl = 0.033.

^o Also In = 0.36, Bi = 0.13, Tl = 0.032.

* Also In = 0.51, Bi = 0.21, Tl = 0.024.

⁺Also Zn = 0.076, In = 0.16, Bi = 0.028, Tl = 0.038.

metamorphosed carbonaceous chondrites, B-7904 had lost the smallest proportions of highly mobile trace elements (Table 1; *cf.* WANG and LIPSCHUTZ, 1998). The remaining 5 such elements have C1-normalized abundances like those of CM2 chondrites (*cf.* XIAO and LIPSCHUTZ, 1992).

3.1.2. Y-86720

Y-86720 is classified as a CM chondrite, although it lies near B-7904 at the juncture of the CM and terrestrial fractionation lines (MAYEDA *et al.*, 1987). Y-86720 contains scattered remnant chondrules, measuring less than 1.5 mm, lithic clasts (< 1 mm) with fine-grained rims, scattered pyrrhotite crystals, fine-grained Ca-carbonate aggregates, metal (mainly taenite) and fine-grained magnetite crystals set within opaque (*i.e.* unrecrystallized) matrix. The chondrules contain only fine-grained crystals of olivine or pyroxene, and amorphous ferromagnesian materials. This has been widely interpreted as indicating that Y-86720 was thoroughly aqueously altered, and then heated to yield olivine and amorphous ferromagnesian silicate pseudomorphs after the phyllosilicates (TOMEOKA *et al.*, 1989a, b). Large desiccation cracks stretch across the fine-grained rims of chondrules, resembling fine-grained olivine veins in Allende DI (KOJIMA *et al.*, 1994).

Pyrrhotite occurs abundantly as laths and euhedral pseudohexagonal plates measuring up to 0.5 mm in maximum dimension. These sulfides are considerably coarsergrained than in other heated C chondrites described here and they are considerably embayed, due apparently to incipient dissolution. The composition of the pyrrhotite is $Fe_{0.99}S$, *i.e.* very near stoichiometric troilite. In one place, jackstraw pyrrhotite crystals are present within a relict chondrule, suggesting their formation during or after aqueous alteration on the parent asteroid. Some large pyrrhotite crystals have veins projecting from them. As in B-7904, this is evidence that sulfides were briefly unstable, and dissolved only to reprecipitate almost immediately. Tochilinite is not present. Pentlandite often occurs in grains at or near peripheries of large pyrrhotite crystals.

We found that magnetite occurs as scattered aggregates and individual euhedral crystals within chondrules, but only in one thin section. These same chondrules contain small metal grains, and are significantly depleted in sulfides relative to the remainder of the meteorite. TOMEOKA *et al.* (1989a) reported finding no such magnetite, apparently because they never saw this particular section. Ca-carbonate occurs as fine-grained and colloform masses intergrown with fine-grained pyrrhotite. Large individual carbonate crystals are not present.

The dominant minerals in Y-86720 are "phyllosilicates". These are present as discrete, rounded to irregularly-shaped objects (< 1.5 mm) comprising the bulk of the relict chondrules. A notable feature of this meteorite is the presence of yellow balls of phyllosilicates and submicron sulfides that occur within and decorating relict chondrules, and within matrix and chondrule rims. Identical rounded objects are found within the CR2 chondrite, Al Rais, where they sometimes consist of saponite or a combination of saponite and serpentine, and sometimes solely of ferromagnesian glass (ZOLENSKY *et al.*, 1996b; GUAN and ZOLENSKY, 1997). All relict chondrules and most lithic fragments are composed primarily of phyllosilicates. These materials have high analysis totals, indicating severe dehydration. Because of this and because of the

	Serpentine in EET 83334 [*]		Serpentine in ALH 88045		Kaidun [†]	Y-86720				
Species	F	Range	Ave [‡]	Ra	inge	Ave [¶]	Ave°	HA*	Serpentine ⁺	Clinochlore
SiO ₂	27.39	41.65	34.31	29.81	38.63	33.14	37.86	33.95	43.91	39.34
Ti O ₂	0.13	0.27	0.10	0.06	0.88	0.07	0.03	0.09	nd	nd
Al_2O_3	1.88	19.52	3.42	2.15	8.24	2.64	3.80	21.46	4.20	12.28
FeO [¢]	15.18	41.83	24.31	11.97	43.64	25.09	18.25	16.20	19.00	18.84
MnO	0.16	0.24	0.17	0.16	0.28	0.23	0.24	0.04	nd	nd
Cr_2O_3	0.22	0.72	0.42	0.08	0.48	0.37	0.57	0.29	2.16	0.43
MgO	14.01	32.20	23.04	10.77	32.60	23.45	27.28	23.90	27.00	27.44
CaO	0.05	0.11	0.23	0.07	0.18	0.19	0.29	0.46	nd	nd
Na ₂ O	0.05	0.17	0.12	0.07	0.50	0.26	0.40	1.52	nd	nd
K ₂ O	0.00	0.05	0.04	0.02	0.09	0.05	0.49	0.16	nd	nd
P_2O_5	0.00	0.02	0.11	0.01	0.06	0.04	0.03	1.05	nd	nd
S*	0.19	0.91	0.91	0.07	0.40	0.62	0.21	0.15	nd	nd
NiO	0.23	0.76	0.85	0.02	0.04	0.13	0.09	0.24	0.27	0.00
Total			88.04			86.28	89.54	99.51	96.54	98.34

Table 2. Phyllosilicate compositions in CM1 chondrites.

^{*}From Zolensky *et al.* (1997).

[†]An intergrowth of serpentine and saponite; from Zolensky et al. (1997).

[‡]Average of 49 analyses from matrix and altered chondrules.

[¶]Average of 51 analyses from altered chondrules.

^oAverage of 51 total analyses of sheaths, aggregates and phyllosilicate lumps; from Zolensky et al. (1996a).

*High-aluminum phase; probably a heated mixture of saponite and serpentine; from Tomeoka et al. (1989a).

*This work; EDX analyses from the TEM, so several minor elements are not determined (nd).

⁹All Fe reported as FeO.

*From Fe-Ni sulfide contaminants.

extremely fine-scale intergrowth with matrix phases including apatite and Fe-Ni sulfides, the mineralogy of these phases is difficult to determine. Several workers have reported that their compositions lie between those for saponite, serpentine and clinochlore (TOMEOKA *et al.*, 1989a,b; ZOLENSKY *et al.*, 1989c). The last study concluded that the phyllosilicates were compositionally closest to serpentine [average composition (Mg_{1.88} $Fe_{0.74}Al_{0.22}Cr_{0.08}Ni_{0.01}$) (Si_{2.05}Al_{0.02}) O₅ (OH)₄, with water re-added] and clinochlore [(Mg_{3.62}Fe_{1.39}Cr_{0.03}) Al_{0.81} (Si_{3.48}Al_{0.52}) O₁₀ (OH)₈, with water re-added]. These mineral identifications must be verified by new TEM work. The important point here is that these phyllosilicates are considerably more Mg-rich than those in B-7904, or in any other CM chondrite (Table 2).

As previously described (ZOLENSKY et al., 1989b; TOMEOKA et al., 1989a,b; IKEDA et al., 1992), the matrix of Y-86720 consists largely of olivine (~ Fo_{70}) and low-calcium pyroxene (enstatite) pseudomorphs after phyllosilicate. Compared to those in Y-82162, Y-86720 phyllosilicates are less well-crystallized, suggesting a different initial phyllosilicate, a lower peak metamorphic temperature, or shorter time at peak temperature. Saponite in Y-86720 exhibits few of the characteristic 10–14 Å basal fringes, while serpentine exhibits no fringes at all. The saponite is notably enriched in Na, and exhibits a Mg: Fe ratio of 2 to 3 (compared with < 2 for Y-82162). Serpentine in Y-86720 has an Mg: Fe ratio of approximately 3. By analogy to the alteration index developed for CM chondrites by BROWNING et al. (1996), such a Mg-rich serpentine

composition indicates that the aqueous alteration responsible for it was fairly complete. Clinochlore is present in matrix in small quantity (ZOLENSKY *et al.*, 1989b). Euhedral, 100 nm wide grains of ferrihydrite are abundant in matrix (TOMEOKA *et al.*, 1989a,b). Because euhedral ferrihydrite is very unusual, we suggest that these are pseudomorphs after some other Fe-Ni bearing mineral, probably sulfides or metal. It is interesting that fine-grained sulfides are not abundant in Y-86720, despite the high abundance of coarse-grained sulfides in it.

PAUL and LIPSCHUTZ (1989, 1990) found that the contents of Bi, Tl, In and Cd in Y-86720 are lower than in B-7904 and that Zn is depleted in the former and not in the latter. The C1-normalized abundances of the remaining 4 mobile trace elements (Cs, Se, Ag and Te), in Y-86720, like those of B-7904, are CM2-like (Table 1; *cf.* XIAO and LIPSCHUTZ (1992). Thus, Y-86720 was more severely heated in its parent body than was B-7904. Y-86789 exhibits a trace element pattern virtually identical with that of Y-86720: the two are almost certainly paired (WANG and LIPSCHUTZ, 1998).

3.1.3. Y-82162

From its oxygen isotope composition (MAYEDA et al., 1987), Y-82162 seems to be a CI chondrite, although it lies near the CM chondrite B-7904 along the terrestrial oxygen fractionation line. Y-82162 resembles CI chondrites in that it is a breccia containing no chondrules, and exhibiting abundant partially-filled fractures (veins) and abundant secondary minerals, including Fe-Ni sulfides, carbonates, and magnetite. In contrast to other CI chondrites, Y-82162 contains no sulfates or dolomite but does contain rare awaruite grains. Y-82162 consists mainly of highly variable clasts. The mineralogy of these separate lithologies is well described in previous papers (TOMEOKA et al., 1989a; IKEDA, 1991, 1992), and will not be recapitulated here. Rather, we describe only the most important details of the gross mineralogy, as they relate to the overall geological history of this rock and its bulk composition.

Phyllosilicates are the most abundant phases in Y-82162, and apparently consist of an intimate intergrowth of saponite and serpentine (TOMEOKA *et al.*, 1989b; ZOLENSKY *et al.*, 1989a), sometimes occurring within fracture-filling veins (TOMEOKA, 1990b). IKEDA (1991) concluded that these minerals were actually various combinations of Na-talc and chlorite. The uncertainty in this identification is due to the poor crystallinity, which necessitates using bulk chemistry for characterization. For this discussion, we will use the identifications suggested by TOMEOKA and ZOLENSKY and co-workers, but the reader must recognize that critical uncertainties remain.

According to ZOLENSKY *et al.* (1989a), serpentine in Y-82162 is very fine-grained ($\ll 1 \mu m$), with the average composition Mg_{1.9}Fe_{1.1} (Si_{1.83}Al_{0.17}) O₅ (OH)₄ (water has been re-added). Saponite is more variable in grain size, with aggregate clusters measuring up to several hundred microns. However, analysis of this saponite is complicated by the ubiquitous presence of submicron-sized grains of an Fe-Ni oxyhydroxide (probably the ferrihydrite so common in CI chondrites). The saponite (including ferrihydrite impurities) analyzed by ZOLENSKY *et al.* (1989a) averages (Mg_{2.45} Fe_{0.59} Cr_{0.02}) (Si_{3.45} Al_{0.55}) (Na_{0.42} Ca_{0.03} K_{0.02}) O₁₀ (OH, Cl)_{2.9}: except for OH, this is a textbook ferrous saponite formula. The low OH content could be due to dehydration during thermal metamorphism or during analysis.

Sulfide grains are ubiquitous within Y-82162: although their distribution varies considerably from clast to clast, they seem more abundant than in other CI chondrites. Sulfides range in size up to 300μ m with the largest crystals being tabular or platy. The most abundant sulfide is pyrrhotite, essentially invariant, between Fe_{0.93}S and Fe_{0.94}Ni_{0.01}S. Small, uncommon crystals of troilite and cubanite are also present. Many pyrrhotite crystals contain small pentlandite grains, as reported by TOMEOKA *et al.* (1989b), with additional small pentlandite grains occasionally found in the matrix. All sulfide crystals are considerably embayed, indicating incipient dissolution.

We found awaruite grains ($Ni_{0.66}Fe_{0.34}$) within one rounded pyrrhotite grain: this composition is at the Ni-poor end of the awaruite compositional range. Metal is not common in CI chondrites, and awaruite is generally found only in oxidized CV3 chondrites like Allende (McSween, 1977). Magnetite is a major component of Y-82162, occurring as framboidal aggregates, spherulites, and plaquettes, as well as aggregates of euhedral crystals (TOMEOKA et al., 1989b; ZOLENSKY et al., 1989a), i.e. in essentially every possible morphology. Magnetite crystal sizes vary considerably: the largest grains are subhedral crystals (up to 12μ m), and spherulites (up to 25μ m). Different magnetite morphologies are frequently encountered intimately mixed within the same aggregates. Though generally pure, some of the subhedral magnetite grains are compositionally $Fe_{2.8}Mn_{0.1}Mg_{0.1}O_4$. Some magnetite aggregates are partially sulfidized along crystal margins to pyrrhotite: however, this is not a widespread phenomenon. Sulfide and magnetite textures indicate that sulfidization occurred in some components of the meteorite before final accretion, but that this process was not sufficiently intense to affect most magnetite grains. At a later stage, sulfides became unstable and began to dissolve.

Merrillite occurs as small ($\langle 8\mu m \rangle$ crystals in some magnetite and carbonate aggregates. It also occurs as vein filling, as first described by WATANABE *et al.* (1988). Periclase is present as both individual grains (generally $\langle 10\mu m \rangle$) and as still finergrained vein filling often intergrowth with carbonates. This brucite has a particularly high Fe-Mn content; its composition varies between Mg_{0.73}Fe_{0.19}Na_{0.05}Mn_{0.02}Ca_{0.01}O and Mg_{0.54}Mn_{0.23}Fe_{0.20}Na_{0.02}Ca_{0.01}O. Calcium carbonates are the most common vein-filling phases in Y-82162 with common impurities being Mg and Fe. The Mg content is not highly variable (up to Ca_{0.94}Mg_{0.06}CO₃), and dolomite is not present as individual crystals. However, Fe content can vary up to Ca_{0.56}Fe_{0.44}CO₃. TOMEOKA *et al.* (1989b) also found Ca-Mn carbonates with up to 21 wt% MnO. Drusy crusts of magnesitebreunnerite are also present within some veins. The Ca-Fe-Mn carbonates are most abundant in Y-82162, rather than calcites (rare here) or dolomite (not present at all), which is the opposite from typical CI chondrites.

The Y-82162 matrix is composed principally of saponite and serpentine [although see IKEDA (1991) for an alternate viewpoint]. Other matrix minerals include olivine (Fo₇₄ average), magnetite, carbonates, merrillite, pyrrhotite, ferrihydrite, and ilmenite. Ilmenite is rare in chondrites: although not previously found in a CI chondrite, Brearley identified it in a C1-like clast of uncertain affiliation in the Nilpena ureilite (BREARLEY and PRINZ, 1992). The bulk major element matrix composition of Y-82162 is similar to that of other CI chondrites (ZOLENSKY *et al.*, 1989b). The presence of abundant olivine within the matrix of Y-82162 suggests that it could be classified as CI2. It is

equally possible that this meteorite represents precursor material to the CI1 chondrites. Alternately, it is possible that Y-82162 has been derived from CI1 chondrites by mild thermal metamorphism, a conclusion supported by the RNAA data of PAUL and LIPSCHUTZ (1989, 1990). The 4 most mobile trace elements (In, Bi, Tl and Cd) are depleted in Y-82162 and contents of the 5 remaining mobile trace elements are well above C1 levels, because this meteorite has been dehydrated preterrestrially (Table 1). It was not subsequently rehydrated even though once on Earth, it lay surrounded by an ocean of (frozen) water. Our saponite analyses include Fe-Ni oxyhydroxide grains as a contaminant (probably ferrihydrite), and should have resulted in higher apparent iron contents for the phyllosilicates. However, these analyses produced perfectly acceptable ferrous saponite compositions. This apparent coincidence, that saponite plus ferrihydrite yields a perfect ferrous saponite composition, can be explained as resulting from ferrous saponite oxidation yielding ferric saponite plus ferrihydrite. This would occur if ferrous saponite formed on the Y-82162 parent asteroid under very reducing, highly alkaline (to give the high Na content) conditions (BAUDAT et al., 1985). Later oxidation conditions would have caused ferrous saponite to break down quickly to ferric saponite, with the ferrihydrite forming from the excluded Fe and Ni (BAUDAT et al., 1985; KODAMA et al., 1988). The ferric saponite has a structure intermediate between tri- and di-octahedral layer silicates. Saponite with a composition almost identical to that in Y-82162 is found in the Orgueil CI1 chondrite, along with the same finelydispersed ferrihydrite. This suggests that Orgueil underwent a similar paragenesis.

3.2. A-881655

3.2.1. Overview

Petrographically, A-881655 resembles a CM2, but its definitive classification is difficult since the meteorite has been severely brecciated into unusually small fragments: constituent clasts have all been heated to varying degrees, and recognizable chondrules are scarce. C1-normalized levels of most trace elements lie below those typical of CM 2 chondrites (Table 1: *cf.* XIAO and LIPSCHUTZ, 1992; WANG and LIPSCHUTZ, 1998). The largest fragment in A-881655 is only about 0.5 mm, with most being only a few tens of μ m. Meteorites with this level of comminution, *i.e.* all CIs, many CM2s and Kaidun (ZOLENSKY *et al.*, 1997), commonly exhibit flow textures (linear deformation) but A-881655 does not.

CAI of a type typical of CM are present, though altered to varying degrees. Also present are highly-altered chondrules, olivine aggregates and lithic clasts. No finegrained rims are apparent around chondrules: they were probably originally present but have been abraded away. Opaques are very abundant in A-881655, consisting mainly of magnetite with subsidiary pentlandite and pyrrhotite. Despite the ubiquitous evidence of aqueous alteration in all clasts studied, there are no phyllosilicate veins as there are in typical CM and CI chondrites (BROWNING *et al.*, 1995). This indicates that aqueous alteration preceded brecciation, or at least was complete before brecciation ceased. Probably, heating also preceded brecciation, although this may be difficult to demonstrate. Earlier Fe-rich serpentine has been replaced by more magnesian phyllosilicates, providing abundant iron for a later generation of iron-rich minerals, mainly magnetite. This generally occurred for CM chondrites (BROWNING *et al.*,



Fig. 1. BSE images of acicular magnetite in A-881655, which is forming as a replacement of pyrrhotite: (a) Small scale image; (b) closeup of the center of (a), with residual pyrrhotite within replacement magnetite being indicated by arrows. Dimensions at lower right.

1996), but not heretofore to the degree exhibited by A-881655. Magnetite with mainly framboidal and acicular morphologies abound in A-881655, with the acicular magnetite always being associated with Fe-Ni sulfide, and in some areas clearly replacing pyrrhotite crystals (Fig. 1). A similar but only incipient, paragenesis was observed in the Kaidun CM1 lithology (ZOLENSKY *et al.*, 1996a). Below, we describe each major mineral in A-881655.

3.2.2. Chondrules

We investigated one porphyritic chondrule of the several evident in the thin section.



Fig. 2. BSE image of a significantly altered CAI in A-881655. In place of the spinel and Fe-rich serpentine, a magnesian-aluminian serpentine with two different compositions (two shades of gray) is present. Most of the magnetite mass (white) is present within or just adjacent to the CAI.

It has a porphyritic texture and contains embayed euhedral olivine crystals set within clinochlore.

3.2.3. CAI

Many rounded CAI are present in A-881655: all appear to be typical of those in CM2 and CR2 chondrites, *i.e.* rounded masses—mainly of granular spinel—containing sparsely distributed perovskite grains, rimmed by a thin layer of Fe-rich serpentine which, in turn, is surrounded by a diopside layer (WEISBERG et al., 1993; MACPHERSON and DAVIS, 1994). Overall, these CAI have an internal sinuous texture, but each has a rounded outward form. While this texture is largely preserved in A-881655, the mineralogy has been significantly altered (Fig. 2). In place of the spinel and Fe-rich serpentine, a magnesian-aluminian serpentine is present. Mass balance calculations suggest that the serpentine present within these altered CAI was produced from dissolution of both Fe-rich serpentine and the spinel it originally enclosed, with much of the iron having been lost. Large masses of magnetite are always present within or just adjacent to the altered CAI, suggesting that these formed from Fe segregated from the later-stage phyllosilicates. In some CAI, the texture is less distinct as replacement of and newly formed magnetite produced a more massive form: the sinuous CAI texture is preserved in only a few regions (Fig. 2). Survival of diopside relative to spinel may seem unusual, but clinopyroxenes are typically observed to be more resistant to aqueous alteration than are other common meteoritic phases like olivine, orthopyroxenes, melilite or glass (Colin et al., 1985; Eggleton, 1986). They must also have been more



Fig. 3. BSE images of andradite clusters (white aggregates in the center) in A-881655. These porous, rounded clusters are only about 10-20 µm across, and are enclosed by clinochlore. They also contain small grains of a Mg-silicate, probably clinochlore, indicating simultaneous formation of these phases.

resistant than spinel in this instance, or alternatively, diopside formed following the aqueous alteration, perhaps during the weak metamorphism responsible for loss of labile Cd (Table 1; *cf.* WANG and LIPSCHUTZ, 1998) and water of hydration. This diopside contains considerable Al and Ti, typical for clinopyroxene in CAI, although it is probable that some or all of these species are actually present as oxide inclusions rather than as an essential component in the clinopyroxene structure.

3.2.4. Andradite clusters

Another feature in A-881655 similar to that in Kaidun CM1 lithology (ZOLENSKY et al., 1996a) is the presence in a few places, of andradite clusters (Fig. 3). These porous, rounded clusters are only about $10-20\mu$ m across, and are enclosed by clinochlore. They also contain small grains of a Mg-silicate, probably clinochlore, indicating simultaneous formation of these phases (Table 3). In the Kaidun CM1 lithology, andradite (melanite, actually) with a similar morphology, though coarser size, is present around relict chondrules. The andradite in A-881655 is lower in Ti, Cr, Al, and higher in Mg than that in Kaidun, and is not melanite. As in Kaidun, their paragenesis in A-881655 is not clear. The inclusions of clinochlore and sulfides suggest that the andradite formed in place on the parent asteroid.

3.2.5. Phyllosilicates

Large grains of saponite, apparently still carrying their full complement of water, are present in A-881655 (Table 4). Fully hydrated saponite can persist to $\sim 700^{\circ}$ C,

Thermally	Metamorphosed	Carbonaceous	Chondrites
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	lithology.	
Species	A-881655 Andradite [§]	Kaidun CM1 Andradite [¶]
Na ₂ O	0.04	0.05
MgO	3.94	0.97
Al_2O_3	0.74	1.31
SiO ₂	34.23	31.75
S*	2.24	0.48
K ₂ O	0.01	0.00
CaO	26.72	32.93
TiO ₂	0.56	2.84
Cr_2O_3	0.65	3.88
MnO	0.48	0.10
$Fe_2O_3^{\dagger}$	27.12	24.78
NiO	2.24	0.50
Total	98.94	99.93

Table 3. Andradite compositions in A-881655 and the Kaidun CM1

[§]Average of 4 analyses. [¶]Average of 19 analyses; from Zolensky *et al.* (1996b).

*From Fe-Ni sulfide contaminants.

[†]All Fe reported as Fe₂O₃.

Table 4. Average clinochlore and saponite compositions in A-881655.

	Clinochlore	Saponite			
Species	Hydrated [*]	Hydrated [†]	Thermally Metamorphosed [‡]		
SiO ₂	36.47	48.23	59.63		
TiO ₂	0.20	0.07	0.02		
Al_2O_3	17.16	3.76	1.64		
FeO [§]	6.65	7.41	1.30		
MnO	0.16	nd	nd		
Cr_2O_3	0.11	0.58	0.15		
MgO	27.70	25.04	31.05		
CaO	2.21	0.34	0.02		
Na ₂ O	0.45	0.12	0.61		
K ₂ O	0.16	0.05	0.06		
S [¶]	0.20	0.09	0.06		
Cr_2O_3	0.16	0.58	0.15		
NiO	1.26	0.22	0.46		
Total	92.69	85.90	94.99		

[†]Average of 5 analyses. [†]Average of 3 analyses. [‡]Average of 4 analyses. [§]All Fe reported as FeO.

[¶]From Fe-Ni sulfide contaminants.

	CM1 Serpentine			Serpe	CM2 Serpentine [†]			
Species	High Mg	High Fe	High Al	High Al, Mg [‡]	High Mg [§]	Desiccated High Al, Mg	High Mg	High Fe [¶]
SiO ₂	41.65	27.39	27.43	37.18	37.96	39.59	36.77	22.11
Ti O ₂	0.20	0.13	0.27	0.09	0.02	0.01	0.00	0.16
Al_2O_3	1.88	2.40	19.52	13.05	6.57	12.38	2.74	3.85
FeO*	15.18	41.83	24.52	4.83	15.61	3.26	18.92	52.62
MnO	0.16	0.24	0.22	nd	nd	nd	0.18	0.17
Cr_2O_3	0.72	0.23	0.22	0.59	0.11	2.36	0.16	0.00
MgO	32.20	14.01	16.51	33.00	29.17	39.42	24.61	7.31
CaO	0.05	0.10	0.11	0.49	1.18	0.01	0.06	0.39
Na ₂ O	0.05	0.16	0.17	0.68	0.39	0.90	0.00	0.05
K ₂ O	0.00	0.01	0.05	0.17	0.07	0.12	0.01	0.03
P_2O_5	0.03	0.02	0.04	nd	nd	nd	0.00	0.01
S ⁺	0.19	0.91	0.23	0.11	0.18	0.01	1.28	0.06
NiO	0.45	0.76	0.23	0.30	0.14	0.09	0.39	0.22
Total	92.78	88.21	89.50	90.50	91.40	98.17	85.09	86.97

Table 5. Serpentine compositions in A-881655, compared to those for a CM1 and a CM2.

*From EET 83334; Zolensky *et al.* (1997).

[†]From Jodzie CM2 clasts; Zolensky et al. (1996c).

[‡]Average of 7 analyses.

[§]Average of 3 analyses.

[¶]From a CAI.

*All Fe reported as FeO.

⁺From Fe-Ni sulfide contaminants.

⁺MnO and P_2O_5 not determined (nd).

setting an upper bound on the final temperature reached by hydrothermal fluids. These saponite grains appear to be pseudomorphs after olivine, often in what appear to be pseudomorphs of porphyritic chondrules. Some phyllosilicate clasts consist of dehydrated saponite (Table 4) and serpentine (as evidenced by high analytical totals), indicating that they experienced higher temperatures.

The serpentine in A-881655 (Table 5), though dehydrated to varying degrees by asteroidal thermal metamorphism, still can be compared to unheated materials in other CM chondrites (Table 2). The FeO content of A-881655 serpentine varies from 3 to 16 wt%, which is a far smaller range than that seen in typical CM1 or CM2 chondrites. Perhaps heating has preferentially destroyed the more Fe-rich materials, consistent with the petrographic evidence from the CAI. The Al content of the serpentine in A-881655, though also variable, is generally higher than that observed in other CM chondrites. Again, possible explanations include heating or inclusions of hercynitic spinels. The Na and Ca content of these serpentines is also somewhat high, suggestive of other inclusions or perhaps minor inclusion of another layered phase such as a smectite.

Still other clasts consist largely of clinochlore, a common phyllosilicate in other heated carbonaceous chondrites (Table 4, Fig. 4: cf. TOMEOKA et al., 1989a,b; TOMEOKA, 1990a; IKEDA, 1991). Thus, the clasts in A-881655 experienced hydrothermal alteration to varying degrees, under a variety of circumstances. They were then metamorphosed by heating to varying degrees as well. Final accretion of the clasts into the present form displayed by the meteorite occurred following or during the waning stages of the heating. Only the most mobile trace element, Cd, is depleted in A-881655



Fig. 4. BSE images of an A-881655 clast consisting largely of clinochlore (gray) dotted with masses of magnetite (white).

(Table 1; cf. WANG and LIPSCHUTZ, 1998) due to open-system thermal metamorphism under conditions less severe than those that affected B-7904.

3.2.6. Sulfides and magnetite

The opaques in A-881655 are very interesting. Both magnetite and pyrrhotite are very abundant. Sometimes, as in the acicular crystals described above, magnetite is clearly replacing pyrrhotite (Fig. 1). Similarly, some pyrrhotite veins running through matrix and fractured chondrules are partially replaced by magnetite. In other places, pyrrhotite is clearly replacing magnetite. In a few aggregates, this replacement has taken on a rhythmic pattern: pyrrhotite is replacing magnetite which is replacing magnetite. Thus, the components of A-881655 experienced alternating episodes of sulfidization and oxidation. The veining of the earlier pyrrhotite generation demands that these reactions occurred on an asteroid. Another proof of asteroidal origin for the sulfides is provided by the very delicate needles of pyrrhotite growing from sulfide-rich, fine-grained chondrule rims, which project from the rims out into matrix.

4. Discussion

All of the chondrites discussed in this paper are interesting because they experienced heating in an asteroidal setting, on at least two separate asteroids (the CM and CI parent bodies), as the oxygen isotopes require. These meteorites record evidence of other geological processing which makes each unique. Thus, they cannot be part of a single group and, with other thermally altered carbonaceous chondrites (Table 1), can define the full range of parent asteroid evolution. The mineralogy of these chondrites can be used independently to deduce possible formation processes. These can then be checked against the peak heating temperatures suggested by the mobile trace element data. The key minerals here include phyllosilicates, sulfides, carbonates, oxides, oxyhydroxides, and organics.

Based on RNAA data for thermally mobile trace elements (Table 1), we can order the four thermally metamorphosed carbonaceous chondrites by severity of open-system heating as A-881655 < B-7904 < Y-82162 < Y-86720 (PAUL and LIPSCHUTZ, 1989, 1990; WANG and LIPSCHUTZ, 1998). This ordering implicitly assumes that the ease of vaporization and loss of elements from a given carbonaceous chondrite is essentially independent of its classification. [Y-793321 would precede these since it exhibits every other metamorphic indicator except Cd loss.] 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 CV3 chondrites (WANG and LIPSCHUTZ, 1998). The RNAA data for A-881655 and Y-86720 are very similar to data for Murchison heated at 500° and 700°C, respectively, by MATZA and LIPSCHUTZ (1977). As a working hypothesis then, we suggest these as temperature limits for the thermal metamorphic episodes that affected these four prototypical carbonaceous chondrites. Let us see whether the petrographic results are consistent with these temperature estimates.

Both A-881655 and B-7904 were only partially aqueously altered before thermal metamorphism initiated dehydration and recrystallization: as discussed above, the former was heated less severely than the latter. In comparison to other CMs, B-7904 experienced very limited aqueous alteration as evidenced by the extremely Fe-rich phyllosilicates in it, its low content of secondary organic species, such as amino acids (believed to result from aqueous processing), and the excellent preservation of coarsegrained primary silicates such as olivine, pyroxene and glass in chondrules and matrix. B-7904 also experienced a mild oxidation event that produced Co-rich metal, typical of rather oxidized LL3 chondrites, but conditions were not sufficiently oxidizing to permit magnetite to be produced in any significant quantity. Since Fe-Ni sulfides are very abundant in B-7904, often replacing minerals in matrix, chondrule rims, and the peripheries of the chondrules themselves, it appears that sulfidization was a significant alteration process. Furthermore, most sulfides are Ni-poor, whereas in a strongly oxidized assemblage, such minerals should have been transformed to oxides and sulfates. Finally, B-7904 was heated to a maximum of 500-700°C, as evidenced by the phyllosilicates which are dehydrated, but not completely recrystallized to olivine or pyroxene. The lack of tochilinite in B-7904, so prevalent in other CM2s, is also ascribed to this mild thermal metamorphism. While thermal metamorphism clearly followed aqueous alteration, the timing of the sulfidization is not clear.

The CM chondrite Y-86720 experienced a very different history. Its chondrules and other coarse-grained components were completely altered by aqueous fluids (making it a CM1). It was then heated to $600-700^{\circ}$ C as evidenced by the obvious replacement of fine-grained olivine with an equilibrated composition near Fo₇₀ and complete destruction of serpentine. The survival of some saponite crystals indicates that the peak temperature was probably not higher than approximately 700°C. Either Y-87620 escaped an oxidation episode or effects arising from such an event were erased by later sulfidization, because sulfides are especially prevalent in it, and pyrrhotite (near troilite in composition) is the sulfide present, rather than pentlandite.

It is interesting to compare Y-86720 with other CM1s recently described by ZOLENSKY et al. (1997). Y-82162 was completely hydrated before the peak metamorphic temperature was attained. Pyrrhotite and pentlandite are common in CM1s, and magnetite (\pm chromite) is more abundant in Y-86720 than in CM2s (ZOLENSKY et al., 1997). Magnetite is often present in CM1s as an overgrowth of pyrrhotite or metal, suggesting extensive secondary (late stage) oxidation. The Kaidun CM1 lithology also contains pentlandite veins and andradite, evidence of high water-rock ratios and a very high aqueous fluid temperature (~450°C). This was true hydrothermal alteration. The evidence for extensive late-stage oxidation in the same meteorites that exhibit the most thorough aqueous alteration suggests that these processes were correlated: hence both occurred on the CM asteroid (s). However, the heated CM1 chondrite Y-86720 has practically no magnetite and pyrrhotite is the commonest opaque phase in it. Conceivably, Y-86720 somehow escaped the late stage oxidation event common to all other CM1s. Alternatively, it is possible that sulfidization accompanying metamorphic heating erased most traces of oxides. The only notable aspect of the sulfides in Y-86720 is the apparently late stage appearance of pentlandite, and minor dissolution textures of pyrrhotite. The sulfur isotopic composition of sulfides in CM1s should be compared to resolve this mystery.

Carbonates in CM2s are typically diminutive and sparse. By comparison, the extensively-altered CMs generally contain a significant amount of coarse-grained carbonates, often intergrown with phyllosilicates and as a major component of relict chondrules. The completely hydrated CM1 chondrite EET 83334, although containing both impure calcite (with Fe and Mg) and dolomite (with Fe and Mn), like other CMs (JOHNSON and PRINZ, 1993), is carbonate-poor compared to the less-extensively aqueously altered meteorites Y-82042 and ALH 83100 (ZOLENSKY et al., 1997). ALH 88045 contains only impure calcite. The Kaidun CM1 lithology contains no carbon-We thus observe that all three CM1s are carbonate-poor relative to typical or ates. extensively-altered CM2s. In Y-86720, a heated CM1, Ca-carbonate occurs as finegrained and colloform masses intergrown with fine-grained pyrrhotite: large individual carbonate crystals are not present. Thus, Y-86720 follows the trend set by other CM 1 chondrites: only small quantities of predominantly Ca-carbonate are present. In Y-86720 and possibly other CM1s, retrograde low water temperatures could have removed carbonates, as previously suggested by ZOLENSKY et al. (1997). The carbonate mineralogy of the CM1s was little changed by any metamorphic heating event.

One way to view the various alteration processes witnessed by the CM chondrites is as a single continuous process. In this case, the CM parent(s) originally accreted as a mixture of anhydrous silicates, ices and other minerals. A heat source, probably ²⁶Al decay, became important when the total asteroid mass reached some critical value, raising the internal temperature to the melting point of ice and initiating aqueous alteration. On some asteroids, or in different regions of a single asteroid, ice was exhausted before complete hydration occurred. In other places, hydration was complete. As the temperature rose, some materials were dehydrated and recrystallized while others did not reach such high metamorphic temperatures. Perhaps they escaped severe heating because they were on bodies too small to support such heating, or were blown into space by fumarolic escape of volatiles at the surface. The peak metamorphic temperature may have been controlled by local geology, the presence of fissures, impact brecciation or some other process(es). It is possible that additional CM chondrites also experienced this metamorphic heating, but that signs of it have been erased by retrograde aqueous alteration.

Y-82162 comes from a CI parent and is characterized by complete destruction of preexisting anhydrous silicates during aqueous alteration. This alteration occurred under alkaline, reducing conditions, as demonstrated by the formation of ferrous saponite. The pervasive nature of this alteration is revealed by the common veins cross-cutting the meteorite. Awaruite and brucite were also formed during this time. Later oxidation transformed this mineral into the ferric saponite + ferrihydrite assemblage. Other evidence of oxidation includes common magnetite but this oxidation was not sufficiently strong to produce sulfates. Minor sulfidization affected some components of this breccia, but not all - indicating that the final meteorite was assembled from materials from different places on the asteroid. Finally, heating at $600-700^{\circ}C$ resulted in dehydration of phyllosilicates. The matrix of Y-82162 contains abundant fine-grained olivine. It appears inconceivable that these could have survived the original aqueous alteration, and so they must have formed by phyllosilicate metamorphism.

Thus, the CI parent asteroid (s) experienced metamorphism similar to that which occurred on the CM parent (s). Here, hydration was apparently complete (or at least it was for the few samples we have to date). However, the end of the story was the same. Some materials were subsequently dehydrated and recrystallized, while others somehow escaped this fate. Ca-Fe-Mn carbonates are most abundant in Y-82162, rather than calcites (rare here) or dolomite (not present at all), the opposite from that in typical CI chondrites (TOMEOKA *et al.*, 1989b). However, as with the less heated CIs, impure calcium carbonate-filled veins are common in Y-82162: unlike the CIs, sulfates are absent. The evidence from the CIs is that the sulfate veins represent the final alteration stage from a late oxidizing event (ZOLENSKY *et al.*, 1989; BOURCIER and ZOLENSKY, 1991). Either Y-82162 somehow missed this final oxidation episode, or heating followed and destroyed sulfates produced by it. Y-82162 witnessed significant oxidation — as evidenced by the ferrous/ferric saponite transition discussed earlier — but it is possible that the fO₂ was not sufficiently high to stabilize sulfates.

As in typical CI chondrites, sulfide grains are ubiquitous within Y-82162: in fact, they appear to be more abundant in Y-82162 than in the others. The most abundant sulfide is pyrrhotite: small, uncommon crystals of troilite, pentlandite and cubanite are also present. Magnetite is a major component of Y-82162, occurring as framboidal aggregates, spherulites, plaquettes, as well as aggregates of euhedral crystals, as in other CIs. Some magnetite aggregates in Y-82162 are partially sulfidized along crystal margins to pyrrhotite: however, this was not a widespread phenomenon. The sulfide and magnetite textures indicate that sulfidization occurred to some components of the meteorite before final accretion, but that this process was not sufficiently intense to affect most magnetite grains. At a later stage, sulfides became unstable and began to dissolve.

5. Conclusions

Detailed petrographic studies of the CM chondrites B-7904 and Y-86720, the CI chondrite Y-82162 and the CM(?) chondrite A-881655 indicates that each bears the signature of a unique sequence of oxidation/reduction/hydration episodes. Late in their evolutionary histories, each experienced a thermal metamorphic episode that must have been of the open-system variety since they have lost some of their complements of thermally mobile trace elements. Similarities in the mobile trace element contents of these four carbonaceous chondrites and those in Murchison CM2 samples heated for one week at 500°, 600° and 700°C under conditions reasonable for interiors of primitive parent bodies indicate that they can be ordered as: $500^{\circ}C \le A-881655 < B-7904 < Y-82162 < Y-86720 \le 700^{\circ}C$. Mineralogic and petrographic properties of these meteorites accord with this sequence. Y-793321 would join this sequence at temperatures $\le 500^{\circ}C$.

Carbonaceous chondrites are not the simple, totally primitive objects that we once thought they were. In fact, there is a complete line of CM chondrites from relatively unaltered Kivesvaara through significantly aqueously altered meteorites like Murchison and Murray, to mostly altered ALH83100, to completely altered CM1 samples like EET 83334 and ALH 88045. Then there is the completely aqueously altered and significantly heated (450°C) Kaidun CM1 lithology. Finally, we have the four meteorites described here that were heated, some to the point of recrystallization, following aqueous alteration. And these are not the end. Trace element data and other properties indicate that > 6 additional carbonaceous chondrites have experienced some degree of late, open-system, thermal metamorphism. Curiously, all are from Antarctica and discovery of even more examples there in the future would not be surprising.

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