REVIEW

Post-hydration thermal metamorphism of carbonaceous chondrites[*]

Tomoki NAKAMURA

Department of Earth and Planetary Sciences, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812-8581, Japan

The presence of abundant phyllosilicates in many carbonaceous chondrites indicates a prevailing activity of low-temperature aqueous alteration in primitive asteroids. However, among the hydrous carbonaceous chondrites known, more than 20 samples show evidence of having been heated at elevated temperatures with corresponding phyllosilicate dehydration. The mineralogical features of dehydration suggest that the heating occurred in situ in meteorites, which demonstrates that there are some hydrated asteroids that have been heated at a certain period after aqueous alteration. Recent studies have uncovered details of heating and dehydration processes in hydrous carbonaceous chondrites: step-by-step changes in mineralogy, trace element chemistry, carbonaceous materials, and reflectance spectra have been clarified. Based on data from synchrotron X-ray diffraction analysis of the matrix, heated hydrous carbonaceous chondrites have been classified as Stages I–IV, with the temperature of heating increasing from I to IV. In spite of recent progress, heat sources are poorly defined, mainly due to a lack of chronological information on the timing of the heating, and therefore more data are needed to fully clarify the thermal metamorphism of hydrous carbonaceous chondrites.

Keywords: Thermal metamorphism, Hydrous carbonaceous chondrites, Serpentine, Dehydration

INTRODUCTION

Carbonaceous chondrites are the most pristine solar-system material in terms of elemental abundance, and therefore they are an important source of information for the processes occurring in the early solar system. Many carbonaceous chondrites are regarded as having been essentially unaffected by post-accretionary, parent-body processes, except for extensive hydration at low temperatures, i.e., aqueous alteration. These alteration reactions replaced anhydrous phases with newly formed phyllosilicates, and the degree of the replacement varies between meteorites (e.g., Zolensky and McSween, 1988; Brearley and Jones, 1998). Phyllosilicates are the dominant mineral in CI- and CM-type carbonaceous chondrites (e.g., Barber, 1981). The presence of a unique hydrous sulfide, tochilinite, (e.g., Tomeoka and Buseck, 1983, 1985; MacKinnon and Zolensky, 1984) in many CM chondrites suggests that aqueous alteration took place in extremely reduced conditions (Eh < 0 V), at low temperatures (< 120 °C), and in variable pH (> 7) and pS^{2-} (< −3) conditions (e.g., Zolen-

sky, 1984; Kozerenko et al., 1996; Browning et al., 1996). The radiogenic ^{53}Cr concentration in some hydrous carbonaceous chondrites indicates that alteration occurred very early until 20 Ma after the formation of Ca- and Al-rich inclusions (CAIs), which are the oldest materials in the solar system (e.g., Hutcheon et al. 1999).

In the early 1980s, three unusual Antarctic carbonaceous chondrites were found: Yamato (Y-) 82162, Y-86720, and Belgica (B-) 7904. They show mineralogies similar to both CM- and/or CI-type carbonaceous chondrites, but all three meteorites had been heated and dehydrated. A research consortium was organized, and many groups in the fields of mineralogy, petrology, inorganic and organic chemistry, and noble gases carried out intensive work for five years, and the results are summarized in Ikeda (1992). In addition to the three meteorites, another thermally metamorphosed CM-type chondrite, Y-793321, has been found (Akai, 1988). The mineralogy and the petrology of these four meteorites indicate that they had been heated in their parent bodies after aqueous alteration (Akai, 1988; Tomeoka et al., 1989a, 1989b; Tomeoka et al. 1990a, 1990b; Akai 1990; Bischoff and Metzler, 1991; Ikeda, 1991). These findings changed the view that hydrous carbonaceous chondrites had not experienced extensive thermal metamorphism. This work pres-

ents a summary of the progress in studies on heated hydrous carbonaceous chondrites, with the main focus being on recent findings occurring after work of the above consortium over the period 1987-1992.

SAMPLES AND EXPERIMENTS

For this review, some CM carbonaceous chondrites, which had already been characterized as heated specimens in previous studies, were investigated using synchrotron X-ray diffraction and scanning electron microscopy. Textural details were characterized using a scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS JEOL 5800), operating at an electron-accelerating voltage of 20 keV and an electron-beam current of 0.5 nA. Based on the textural and compositional characterization obtained from optical and electron microscopy, several small particles, approximately 100 μm in size, were separated from the matrix of each CM chondrite sample, using an edged tool, for X-ray diffraction measurements. The individual small particles were mounted on a thin 5 μm diameter glass fiber, and exposed to synchrotron X-rays in a Gandolfi camera that allowed powder diffraction patterns to be obtained from a single particle. Synchrotron radiation X-rays from Beam line 3A of the Photon Factory at the Institute of Materials Science, High Energy Accelerator Research Organization (Tsukuba, Japan) were utilized in this study. The X-rays were monochromated to 2.161 ± 0.001 Å. The ultrahigh intensity and well-monochromated synchrotron X-rays allowed clear X-ray powder diffraction patterns from each small particle to be collected, with a short exposure time of approximately 30 min (Nakamura et al., 2001, 2003).

CLASSIFICATION OF HEATING OF STAGES I-IV BASED ON MATRIX MINERALOGY

Table 1 lists 21 chondrite samples that were identified as being heated hydrous carbonaceous chondrites from their constituent minerals, volatile element concentrations, and reflectance spectra. The intensity of heating varied between the samples: some meteorites had been heated strongly and showed complete dehydration, while others had been heated weakly and only showed traces of devolatilization. Mineralogically, phase changes due to heating are most easily recognized in the matrix, because the matrix is an assemblage of heat-sensitive hydrous phases, and thus provides critical evidence of any temperature rises. Based on the matrix mineralogy (Table 1), the heated hydrous carbonaceous chondrites were classified into: Stage I (very weakly heated), Stage II (weakly

heated), Stage III (moderately heated), and Stage IV (strongly heated). This classification was mainly based on the characteristics of the X-ray diffraction patterns of the matrix, and therefore, classification of the samples that had no diffraction data, such as Y-82162, was less certain. Among the heated hydrous carbonaceous chondrites, the CM-type was the most dominant, and this was present in all the heating stages from Stages I to IV, whereas other groups, such as CI and CR, were rare. Thus, the CM matrix mineralogy was used as a reference to define the scheme of the heating stages.

Stage I

Samples classified as Stage I were those that showed no heat-induced mineralogical changes in their X-ray diffraction patterns, because they were heated at very low temperatures. The effect of heating was only identified using other characterization methods, such as reflectance spectroscopy and transmission electron microscopy. Figure 1 shows synchrotron X-ray diffraction patterns of unheated (Fig. 1a, b), and very weakly heated (Fig. 1c, d) matrices of CM carbonaceous chondrites. The latter two samples were classified as Stage I (Table 1). The matrices of all four samples in Figure 1 contained serpentine as the dominant phase, which was verified by the presence of a strong basal 001 reflection at 7.1-7.2 Å ($2\theta = 18°$ in Fig. 1), an 002 reflection at 3.6 Å ($2\theta = 35°$ in Fig. 1), and prism reflections occurring above $2\theta = 27°$. Prism reflections are peculiar to phyllosilicates with heavy stacking disorder along their c-axis. The major polytype of the serpentine in all the matrices was probably lizardite, which was identified by the presence of strong 11*l* reflections: 111 at 2.51 Å ($2\theta = 51°$ in Fig. 1), 112 at 2.15 Å ($2\theta = 60°$ in Fig. 1), 113 at 1.79 Å, and 114 at 1.50 Å (Wicks and O'Hanley, 1991). The small 001 spacing of lizardite (< 7.2 Å) suggested that some Si^{4+} in the tetrahedral sites had been substituted by Fe^{3+} to form a lizardite-cronstedtite solid solution (Nakamura and Nakamuta, 1996). Lizardite and cronstedtite have similar structures, and thus form a solid solution, where Fe^{3+} occupies both the tetrahedral and octahedral sites in cronstedtite (Wicks and O'Hanley, 1991).

Another hydrous phase present was tochilinite, which was detected in Y-791198 (Fig. 1a), Murchison (Fig. 1b), and A-881458 (Fig. 1d). Tochilinite consists of a 1:1 stacking of brucite $(Mg,Fe)(OH)_2$ and mackinawite FeS layers. The strong 002 reflection at 5.4 Å relative to the 001 reflection at 10.8 Å indicated a dominant occupancy of Fe^{2+} in the brucite layer (Nakamura and Nakamuta, 1996). A mixed layer mineral of tochilinite (interlayer spacing = 10.8 Å) and serpentine (interlayer spacing

Meteorites	Heating stage[*]	Reflectance[$] spectra	Trace elements	Oxygen	Carbonaceous material	Noble gas	Petrography	Microtextures
CI-like								
Y-82162	III (or II)		○	○			○	○
Y-86029	III		○	○			○	○
CM-like								
Y-793321	II	○	○	○	○	○	○	○
Y-793595	I	○		○				○
Y-82054	III			○	○			
Y-82098	III (or IV)			○				
Y-86695	II (or III)			○	○			
Y-86720	IV		○	○			○	
Y-86789	IV		○	○	○	○	○	
A-881334	II	○		○	○	○		
A-881458	I	○			○	○		
A-881655	III		○				○	
B-7904	IV	○	○	○	○	○	○	○
WIS-91600	II	○						○
CR-like								
Y-793495	I	○	○					
Ungrouped C2								
EET-83355	I	○	○					
EET-87522	I	○	○	○				
LEW-85332	I		○				○	
MAC-87300	I	○	○	○				
MAC-88107	I	○	○	○				
PCA-91008	III		○					

[*] Heating stage represents the degree of heating in the order: I < II < III < IV. Stages of samples whose X-ray diffraction is not avail-

[$] ○ in columns from reflectance spectra to microtextures means that analysis data are available.

[#] Abbreviation of synchrotron X-ray diffraction. Abundance of minerals is expressed as: X, not detected; △, very minor phase; ○,

[+] References: 1, Ikeda (1992); 2, Tonui et al. (2002); 3, Tonui et al. (2003); 4, Tonui et al. (unpublished data); 5. Akai (1988); 6. Wang Tari (1997); 12, Hiroi et al. (1997); 13, Matsuoka et al. (1996); 14, Xiao et al. (1992); 15, Lipschultz et al. (1999); 16, Akai (1994);

= 7.2 Å), which was identified by the presence of a 001 reflection at 18.0 Å and a 003 reflection at 6.0 Å, was also detected in Y-791198 (Fig. 1a), Y-793595 (Fig. 1c), and A-881458 (Fig. 1d). Several anhydrous minerals also occur in combination with hydrous phases: magnetite, calcite, olivine, and low-Ca pyroxene. The latter two minerals were present in the matrix as isolated small mineral fragments within the phyllosilicate-rich lithology.

Because Y-793595 and A-881458 contained tochilinite, whose breakdown temperature is 245 °C (Fuchs et al. 1972), reflectance spectroscopy (Hiroi et al., 1997) and transmission electron microscopy (Akai and Tari, 1997) studies suggested that these two samples had been heated at low temperatures below 250 °C. The X-ray diffraction patterns of the matrices of these two meteorites were similar to those of Y-791198 and Murchison, which are known to have not been subject to heating, confirming that the effect of heating was minor. The survival of tochilinite in A-881458 (Fig. 1d) and the mixed layer tochilinite-serpentine mineral in Y-793495 (Fig. 1c) confirmed that the samples had been subjected to heating < 250 °C.

Stage II

Stage II samples showed no serpentine reflections and no secondary olivine reflections that would have formed during heating at the expense of serpentine. Therefore, the major phases of the Stage II samples were amorphous materials. The decomposed amorphous serpentine contained some hydroxyl content, and thus it was not completely dehydrated. Samples Y-793321 (Fig. 2a) and A-881334 (Fig. 2b) were classified as Stage II. No basal reflections from serpentine and tochilinite were observed in either matrix; they had decomposed and did not exhibit well-ordered crystal structures (Fig. 2a, b). Both matrices exhibited reflections from olivine and low-Ca pyroxenes. These two minerals were not secondary products, but primary phases that were already present before the sample was subjected to heating; this could be deduced because the two were crystalline and exhibited very sharp reflections that would not be expected for secondary olivine and low-Ca pyroxene, as discussed in the following sections. Low crystalline magnetite and troilite were present

carbonaceous chondrites

Matrix mineralogy based on SR-XRD[#]				References[+]
Hydrous phases	Secondary olivine	Secondary pyroxene	Secondary FeNi metals	
×	○	×	×	Summarized in 1 and references therein 2, 3, 4
×	×	×	×	5, 6, 7, 8, 9, 10
◎	×	×	×	7, 11, 12
×	◎	×	○	7, 9, 11
				7, 11
				7, 9, 11, 12
				Summarized in 1 and references therein
×	◎	○	◎	6, 7, 8, 9, 13
×	◎	○	◎	7, 9, 11, 12
◎	×	×	×	9, 10, 11, 12
				6, 12, 14, 15
×	◎	○	◎	Summarized in 1 also see; 9, 16, 17
△	×	×	×	4
				6, 12
				12, 14
				7, 12, 14
◎	×	×	×	2, 12, 14
				7, 12, 14
×	○	×	×	4, 6

able are estimated from other properties.

minor phase; ◎, major phase.
et al. (1998); 7. Clayton and Mayeda (1999); 8. Nakamura et al. (2000); 9, Kitajima et al. (2002); 10, Nakamura (2003); 11, Akai and
17, Nagao et al. (1984).

in both Y-793321 and A-881334, and they are probably decomposition products of Fe-rich serpentine and tochilinite, respectively.
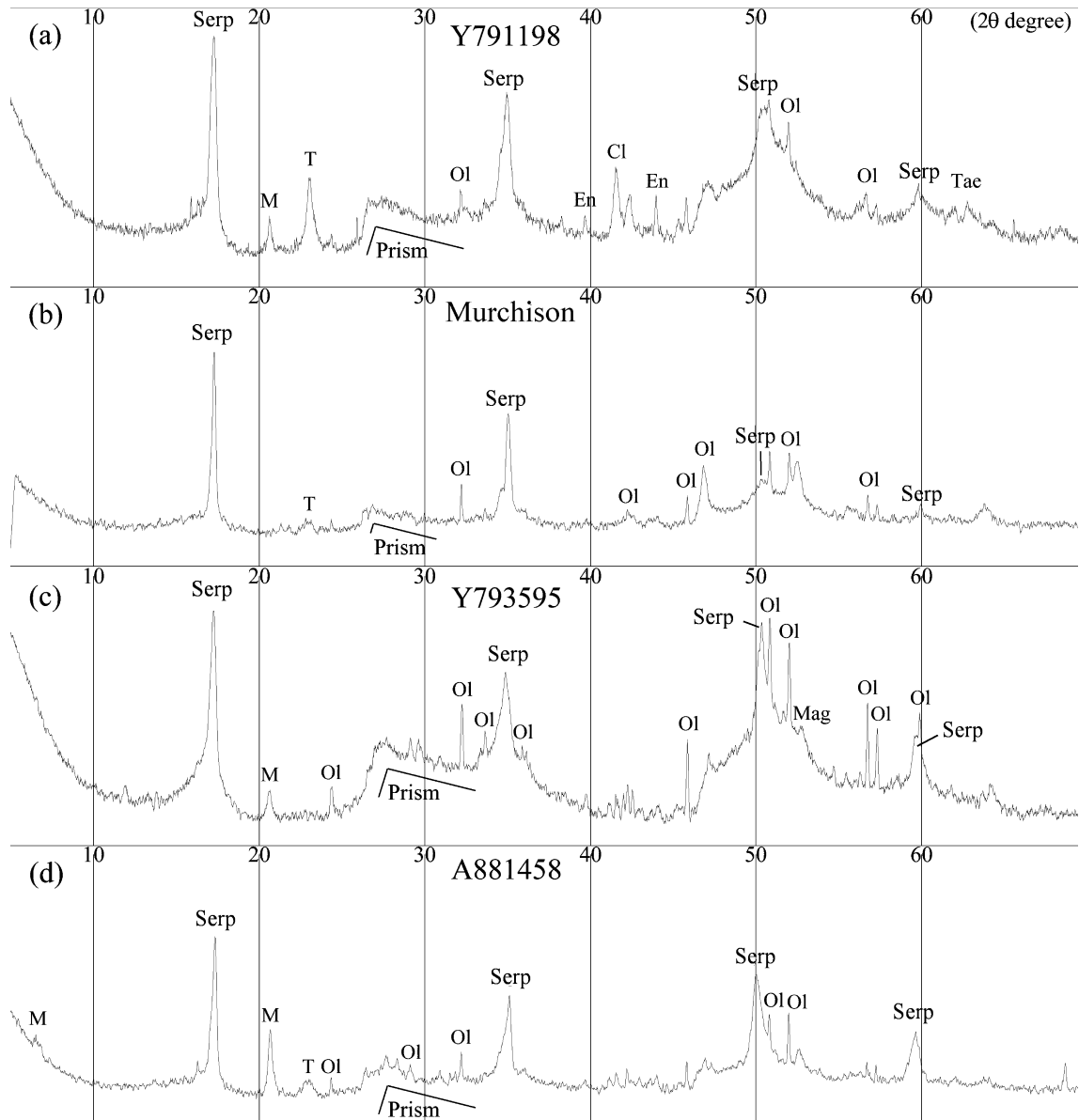
Stage III

Stage III samples contained low-crystalline secondary olivine. No X-ray diffraction patterns of this stage are given in this work, but the pattern of a Stage III sample, Y-86029 (Table 1), is provided in Tonui et al. (2003). Although this meteorite was defined as CI (Tonui et al., 2002, 2003), CI phyllosilicates had decomposed and had been dehydrated by heating, similarly to CM phyllosilicates (Greshake et al., 1998). The matrix of this meteorite exhibited weak, broad reflections from olivine. The broadness of the peaks indicated a small grain size and low crystallinity of the olivine, and this feature is distinct from that of primary olivine. TEM observations of Stage III samples indicated that amorphous silicates and even poorly crystalline phyllosilicates still remained in the matrix (Tomeoka et al., 1989a and Tomeoka, 1990b for Y-

82162; Tonui et al., 2003 for Y-82029). The X-ray diffraction patterns show that, as in Stage II samples, low crystalline troilite and magnetite were also present.

Stage IV

Stage IV samples consisted entirely of anhydrous minerals, and thus, dehydration by heating was nearly complete in these samples. The X-ray diffraction patterns of Stage IV samples, Y-86789 and B-7904 (Fig. 1c, d), show characteristic large, broad reflections from olivine, troilite, taenite, and kamacite. The broadness of the secondary olivine reflections (Fig. 2c, d) is in clear contrast to the sharpness of the primary olivine reflections (Fig. 2b). Small, broad reflections of secondary low-Ca pyroxene were also observed. The textural setting of the troilite in the matrix of B-7904 suggested that, like olivine and low-Ca pyroxene, it was also a secondary phase that was produced by the decomposition of S-bearing hydrous phases, most probably tochilinite. Figure 3a shows the unique petrologic features of troilite in B-7904, with
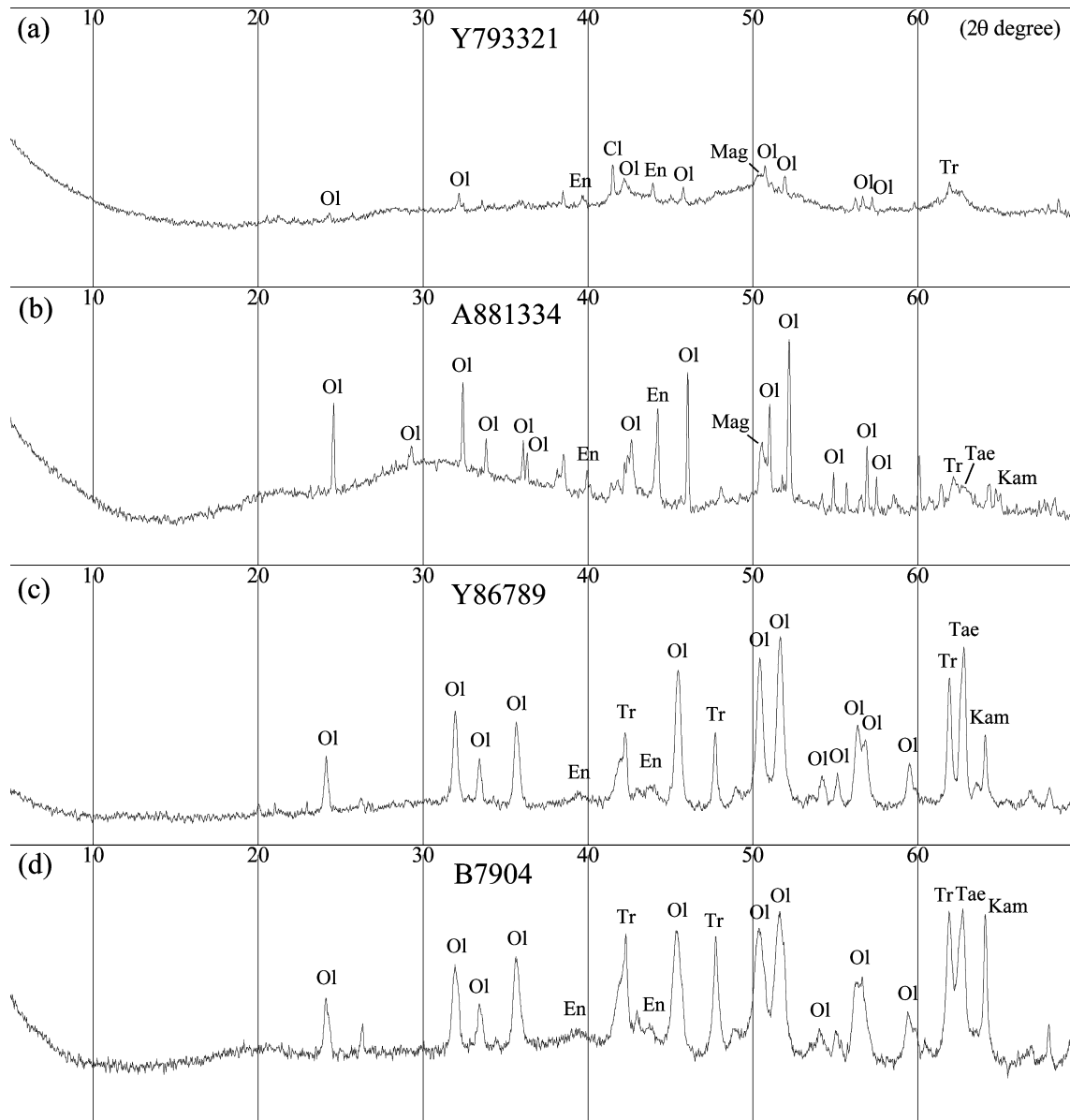
Figure 1. Synchrotron X-ray diffraction patterns of the matrix of CM carbonaceous chondrite samples: (a) unheated Y-791198, (b) unheated Murchison, (c) Stage I Y-793595, and (d) Stage I A-881458. Abbreviations: Serp, serpentine; M, mixed layer serpentine and tochilinite mineral; T, tochilinite; Ol, olivine; En, low-Ca pyroxene; Cl, calcite; Tae, taenite; M, magnetite.

rounded pore spaces present around the troilite in the matrix. This indicates that the preexisting phase was reduced in size during dehydration, and, as a result, a large pore space was generated around the secondary troilite grains (Fig. 3a).

The phase changes observed in samples of CM chondrites belonging to Stages I to IV can be fully explained based on experimental results from heating CM chondrites and related phyllosilicates (Fuchs et al., 1973; Akai, 1992; Hiroi et al., 1999). Akai (1992) heated Murchison CM chondrite powder to various temperatures in the range 250-1100 °C for periods of 1 to 350 h under a vac-

uum of 10^{-5}-10^{-4} torr, with an aim of constructing the TTT diagram of CM serpentine. Experimentally heated Murchison samples were investigated using transmission electron microscopy (TEM), and the results showed that no phase change occurred below 300 °C. In the range 300-500 °C, serpentine begins to decompose and a transitional structure between serpentine and olivine appears. At 500-750 °C, olivine begins to crystallize, and becomes more crystalline with increasing temperature. At temperatures above 750 °C, low-Ca pyroxene begins to crystallize. This continuous sequence of changes corresponds to the heating stages defined in this paper: Stage I (< 300 °C),

Figure 2. Synchrotron X‑ray diffraction patterns of the matrix of CM carbonaceous chondrite samples: (a) Stage II Y‑793321, (b) Stage II A‑881458, (c) Stage VI Y‑867898, and (d) Stage VI B‑7904. Abbreviations: Ol, olivine; En, low‑Ca pyroxene; Cl, calcite; Tr, troilite; Kam, kamacite; Tae, taenite; M, magnetite.

Stage II (300–500 °C), Stage III (500–750 °C), and Stage IV (> 750 °C). These temperatures decrease by approximately 100 °C with longer heating periods, suggesting that kinetic effects control the transformation of serpentine. Phyllosilicates in CI chondrites decomposed and dehydrated in a similar manner to those in CM chondrites, where saponite and serpentine decomposed to form amorphous phases, with subsequent crystallization of secondary olivine and low‑Ca pyroxene at higher temperatures (Greshake et al., 1998).

In recent studies (Nozaki et al., 2001, 2002; W. Nozaki et al., pers. com.), Nozaki and co‑workers heated a small sample taken from the matrix of Murchison CM chondrite for ~ 2 min at 900 °C, under various pressures of 10^{-4}–10^{0} torr, to determine the variation in secondary Fe‑metal and Fe‑oxides. The results indicated that heating at 10^{-3} and 10^{-4} torr produces metallic iron as the secondary Fe phase, while heating at higher ambient pressures produces magnesiowustite or magnetite. When applying this result to naturally heated CM chondrites, Stage IV samples, enriched in both kamacite and taenite (Fig. 2c, d), were heated at pressures below 10^{-3} torr with an atmospheric composition that corresponded to ~ 10^{-4} torr of oxygen. On the other hand, Stages II and III sam‑
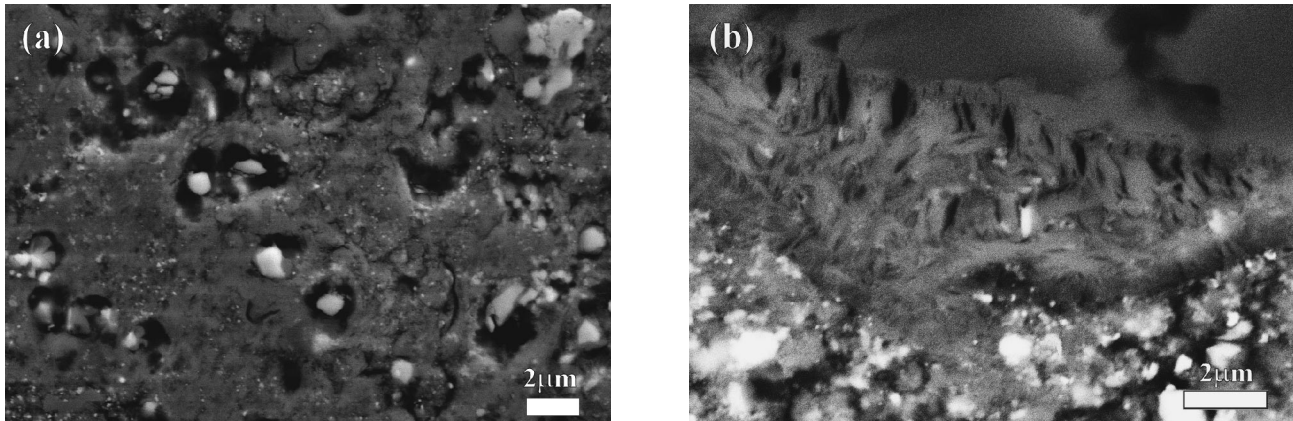
Figure 3. Back-scattered electron images of Stage VI CM chondrite B-7904. (a) Rounded pore spaces are present around the many small bright troilite grains in the matrix. (b) Phyllosilicates have replaced part of the dehydrated chondrules and show a characteristic fibrous texture.

ples contained magnetite as the secondary Fe phase (Fig. 2a, b), suggesting a higher oxygen fugacity at lower heating temperatures. These observations indicated that at low temperatures (Stages II and III), the oxygen fugacity was still high due to the presence of abundant hydroxyl groups, while at elevated temperatures (Stage IV), the oxygen fugacity must have been lower due to the complete dehydration and reduction by carbonaceous materials. Therefore, in the final stage of dehydration, the interior of hydrous asteroids must, at least in part, experience reducing conditions, under which Fe metals are stable, as in anhydrous ordinary-chondrite parent asteroids.

EFFECT OF HEATING ON THE MICROTEXTURE AND REFLECTANCE SPECTRA

Incipient, subtle changes in matrix mineralogy during low-temperature heating can be detected by TEM observation. In the TEM observation of Stage I samples, Y-793495 and A-881458, Akai and Tari (1997) found a 14-Å phyllosilicate phase that they interpreted as a phase that was formed in an initial decomposition stage of 7-Å serpentine. In TEM observations of a Stage II sample, Y-793321, Akai (1988) also found an intermediate phase that was disordered and exhibited a structural defect. Its electron diffraction pattern represented olivine and serpentine, and showed characteristic halo rings. Akai interpreted the latter phase as being an incomplete transformation of a serpentine-type phyllosilicate. In my synchrotron X-ray diffraction analysis (Figs. 1 and 2), neither the 14-Å phase in A-881458 nor the intermediate phase in Y-793321 were detected, which was probably due to the low abundance and/or low crystallinity of these phases. In the Stage III sample, Y-86029, Tonui et al. (2003) found that a phyllosilicate, in this case probably saponite, exhibited a disordered and defective structure, whose electron diffrac-

tion pattern was composed of olivine and weak saponite-type spots. It also exhibited streaks due to stacking disorders. TEM observation of Stage IV samples, Y-86720 and B-7904 (Tomeoka et al., 1989a; Akai, 1990, 1992), showed that they contained aggregates of small secondary olivine particles less than 1,000 Å in diameter. These results are consistent with the X-ray diffraction data (a Stage III pattern is shown in Tonui et al. 2003, and a Stage IV pattern in Fig. 2c, d).

UV, visible, and near IR reflectance spectra are techniques that can measure the extent of dehydration in both hydrous carbonaceous chondrites (Table 1) and hydrous asteroids. Hydroxyl groups and molecular water in phyllosilicates exhibit an absorption peak at wavelengths of 2.7 and 2.9 μm, respectively. Therefore, the intensity of the broad absorption band observed at 3 μm correlates with the amount of phyllosilicate present. Currently, the most reliable evidence for connecting asteroid regoliths and meteorites comes from reflectance spectra (e.g., Gaffey, 1976). Spectroscopic studies suggest that the spectra of C-, G-, B-, and F-type asteroids, having relatively featureless flat patterns except for their UV absorption characteristics, are similar to the three Stage IV-type hydrous carbonaceous chondrites of Y-82162, Y-86720, and B-7904 (Hiroi et al., 1993, 1994, 1996). This demonstrates that these three dehydrated carbonaceous chondrites are mineralogically and compositionally similar to the surface materials of C-, G-, B-, and F-type asteroids. In the further investigations by Hiroi et al. (1997), nine samples were identified as possible candidates for heated hydrous carbonaceous chondrites (Table 1).

EFFECT OF HEATING ON OXYGEN ISOTOPE SIGNATURES, WATER ABUNDANCE, AND TRACE ELEMENT CHEMISTRY

Clayton and Mayeda (1999) measured the oxygen isotope ratios of 14 heated hydrous carbonaceous chondrites, including the four Stage I samples, EET-87552, MAC-87300, MAC-88107, and Y-793495, the two Stage II samples, A-881334 and Y-793321, the five Stage III samples, Y-82054, A-881655, Y-82098, Y-82162, and Y-86695, and the three Stage IV samples, B-7904, Y-86720, and Y-86789. Tonui et al. (2003) reported on the oxygen composition of a Stage III sample, Y-86029. In total, oxygen data from 15 samples have been reported to date, and a three-isotope plot of all the data is shown in Figure 4. All the data fall on or close to the CM-CO-Tagish Lake line that was defined as the mixing line between water with heavy oxygen and anhydrous minerals with light oxygen (Clayton and Mayeda, 1999, 2001). This suggests that heated hydrous carbonaceous chondrites have a genetic relationship with CM-CO-Tagish Lake-type chondrites. However, consideration of isotope fractionation during dehydration indicates that the oxygen composition of samples prior to heating must differ from that of samples after heating; the preheating samples must have been isotopically lighter than the post-heating samples because of the preferential loss of the light oxygen isotopes during dehydration. Interestingly, all Stage IV samples were located near the intersection between the CM-CO-Tagish Lake line and the terrestrial fractionation line (Fig. 4). Stage IV samples were heavily dehydrated, down to 3 wt% water (Fig. 5), and thus their preheating composition would have been identical to CI chondrites if the fractionation during dehydration was as large as 6-8 permil in $\delta^{18}O$ (Fig. 4). Based on the heating of carbonaceous chondrites in the laboratory, Clayton and Mayeda (1999) pointed out that such a magnitude of fractionation could occur during dehydration. On the other hand, samples from Stages I to III, except for the two Stage III samples, Y-82162 and Y-86029, were located in a region close to the unheated CM chondrites. Since samples from Stages I to III exhibited incomplete dehydration (Fig. 5), they suffered from small oxygen isotope fractionation, and therefore their preheating composition was still close to that of CM chondrites, confirming the genetic relationship (Clayton and Mayeda, 1999).

The concentrations of mobile trace elements: U, Co, Au, Sb, Ga, Rb, Cs, Se, Ag, Te, Zn, In, Bi, Tl, and Cd (in order of increasing ease of vaporization) in many heated hydrous carbonaceous chondrites have been determined by Lipschutz and co-workers using radiochemical neutron activation analysis (Paul and Lipschutz, 1989, 1990;
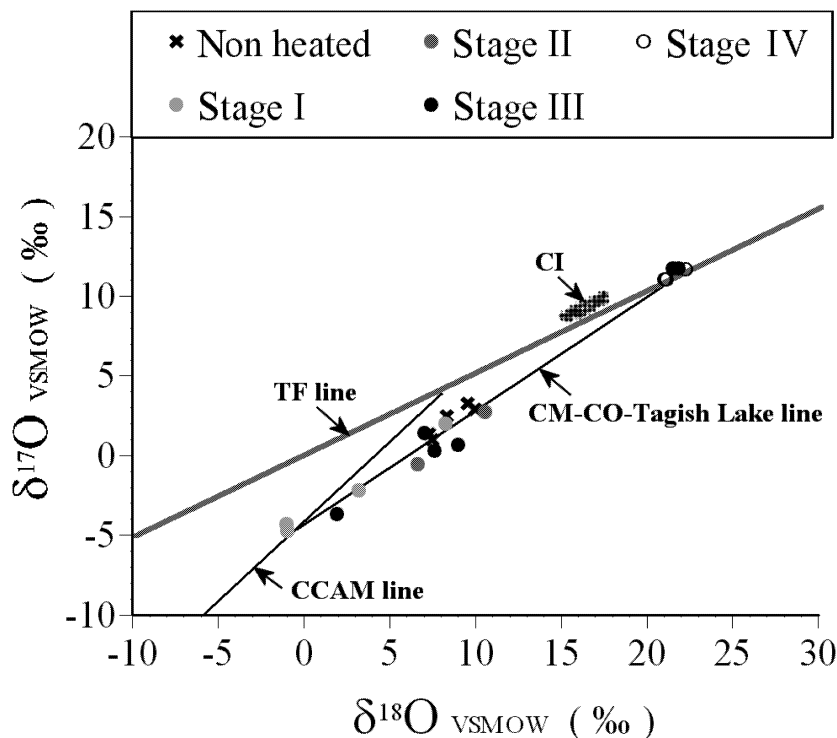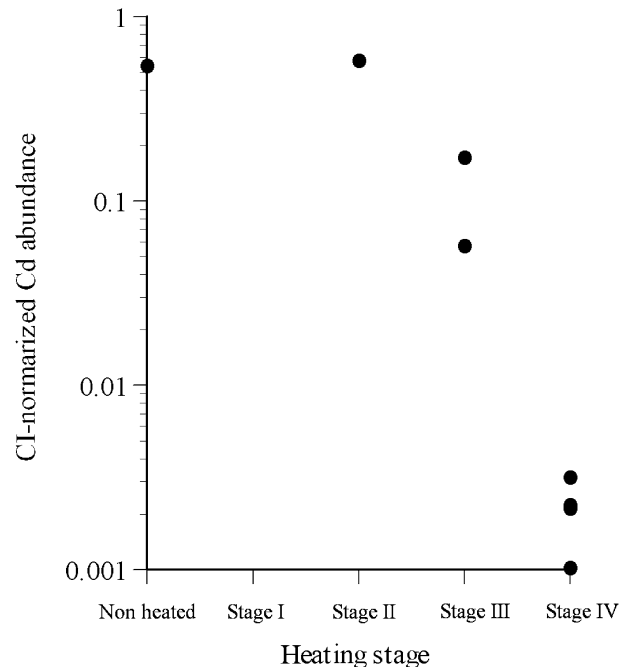

Figure 4. An oxygen three isotope diagram of heated hydrous carbonaceous chondrites. All data fall on or close to a segment of the CM‑CO‑Tagish Lake line connecting the terrestrial fractionation (TF) line and the carbonaceous chondrite anhydrous mineral (CCAM) line. A region of CI oxygen composition is also shown. Data from Clayton and Mayeda (1999) and Tonui et al. (2003).
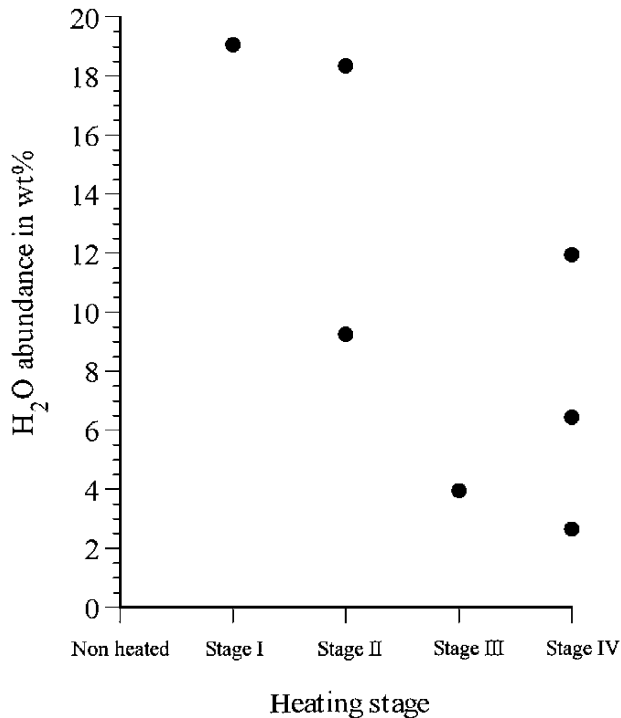
Figure 5. A diagram showing the water content in heated CM carbonaceous chondrites as a function of heating. Data are quoted from Yanai et al. (1995).

Figure 6. A diagram showing the CI‑normalized Cd abundance of heated CM carbonaceous chondrites as a function of heating. Data are quoted from Xiao et al. (1992) and Wang et al. (1998).

Xiao and Lipschutz, 1992; Wang et al., 1998; Lipschutz et al., 1999; Tonui et al., 2002). The most refractory elements, U, Co, Au, and Sb, are similar in abundance to CI chondrites, even in the case of Stage IV samples, while moderately mobile elements, Cs to Tl, are lower in abundance by up to 80% than those in CI chondrites. However, the abundance of the moderately mobile elements cannot be interpreted straightforwardly in terms of the magnitude of the heat experienced. The CI‑normalized average abundance of the moderately mobile elements was 0.53, 0.51, and 0.65 for the unheated sample, Y‑791198, the Stage II sample, Y‑793321, and the Stage IV sample, Y‑86720, respectively (Paul and Lipschutz, 1989, 1990; Wang et al., 1998). In addition, the abundance of these elements in Stage III samples belonging to the CI chondrites, Y‑82162 and Y‑86029, increased to 1.36 and 1.20, respectively (Paul and Lipschutz, 1989, 1990; Tonui et al., 2002). This increase was interpreted as reflecting the heating loss of the more abundant volatiles, such as H_2O and CO_2 (Paul and Lipschutz, 1989, 1990). For example, if H_2O and CO_2, which may constitute ~ 25% of the initial meteorite mass, are lost when no moderately mobile elements are lost during heating, then the CI‑normalized abundance of the moderately mobile elements increases to 1.33. On the other hand, the most mobile element, Cd, appears to reduce in abundance in proportion to the mag-

nitude of the heat experienced (Fig. 6). This suggests that Cd is the best thermal history indicator among the mobile trace elements.

EFFECT OF HEATING ON CARBONACEOUS MATERIALS AND NOBLE GASES

Large amounts of carbonaceous materials are contained in hydrous carbonaceous chondrites, mainly as solvent unextractable macromolecular matter, analogous to terrestrial kerogen or poorly crystalline graphite. During heating, the kerogen‑like amorphous carbonaceous materials lose their labile fractions, and become more and more graphitized. In addition, the kerogen‑like materials are probably a host phase, termed "Phase Q", of heavy primordial noble gases. Therefore, heating of hydrous carbonaceous chondrites results in graphitization of the carbonaceous material, and a loss of any noble gases. Kitajima et al. (2002) analyzed 10 samples using flash pyrolysis‑gas chromatography, and found that graphitization proceeded in heated hydrous carbonaceous chondrites. The small amount and the narrow variety of the pyrolysates, which are weakly bound hydrocarbons extracted during pyrolysis, in a Stage II sample, A‑881334, a Stage II or III sample, Y‑86695, a Stage III sample, Y‑82054, and a Stage IV sample, B‑7904, indicated a higher degree of graphitization had occurred. On the other hand, a Stage I sample, A‑881458, and a Stage II sample, Y‑793321, showed a

low degree of graphitization.

The loss of primordial noble gases accompanied by an increase in graphitization was confirmed by stepped pyrolysis noble‒gas analysis (Nakamura et al., 2000). Primordial ^{36}Ar, ^{84}Kr, and ^{132}Xe concentrations decreased in the following order: the unheated Murchison, the Stage II sample, Y‒793321, and the Stage IV sample, Y‒86789. In Y‒86789, the ^{132}Xe concentration was lower by an order magnitude than the Murchison sample (Nakamura et al., 1999). A low concentration of heavy primordial noble gases in the Stage IV sample, B‒7904, has also been reported in Nagao et al. (1984). The depletion of the heavy noble gases implies a structural change in Phase Q during the course of graphitization of the carbonaceous materials. Carbonaceous materials and noble gases are very sensitive indicators of heating compared to oxygen isotope and mobile trace elements; changes in the signature of Stages I and II samples from heating are difficult to detect using the latter two as references.

POSSIBLE HEAT SOURCES

There is much textural evidence demonstrating that the heating of hydrated asteroids occurred after aqueous alteration. Many heated hydrous chondrites contain chondrules that have been partially, or completely, replaced by phyllosilicates during aqueous alteration, and these phyllosilicates were then dehydrated in situ by heating, as shown in Figure 3b. The isotope chronology indicates that aqueous alteration took place extensively in hydrous asteroids during the early stages of formation of the solar system (e.g., Brearley et al., 2001), but there is no chronological evidence indicating when the post‒hydration heating of hydrous asteroids took place. This is partly because the temperature of heating was below 1000 °C, and also because the duration of the heating stage was too brief to allow crystallization of secondary phases large enough for dating by in‒situ ion‒probe analysis. The timing of the heating provides key information for identifying possible heat sources: if the heating occurred later, then internal heating from short‒lived radionuclides, such as ^{26}Al, is excluded, and other heat sources, such as impacts, are more likely.

Without any chronological information, it is hard to define and refine the conditions experienced during heating. Nevertheless, several mechanisms for heat‒induced dehydration of hydrous asteroids have been proposed. Akai (1988) listed three possible heat sources: (i) thermal metamorphism, (ii) impact metamorphism, and (iii) solar radiation. The thermal metamorphism of carbonaceous chondrite parent bodies by the decay energy of an extinct ^{26}Al nuclide was examined in detail by Grimm and McSween (1989). They found that the heating temperature was lowered by the large latent heat and heat capacity of water, and by an enhanced heat loss under hydrothermal convection. This hydrothermal convection was also responsible for homogenizing the interior temperature of the asteroid. However, Miyamoto (1991) showed based on the internal heating model that the maximum temperature of the interior of a body > 20 km in radius reached 500‒700 °C for a bulk ^{26}Al content with an initial $^{26}Al/^{27}Al = 5 \times 10^{-6}$. Temperatures of ~ 700 °C are high enough for the dehydration of phyllosilicates to occur, as observed in samples from Stages III and IV.

Impact‒induced heating is also a possible mechanism for dehydration. The results of experimental impacts on Murchison CM chondrite indicated that the loss of up to half of the water content occurs in a single 15 GPa impact (Tyburczy et al., 1986), which corresponds to a mutual impact between CM chondrites with a relative velocity of approximately 2 km/s, assuming that the Hugoniot of the CM chondrites is similar to terrestrial serpentine. High velocity impacts can cause instantaneous heating and devolatilization, which result in an ejection of fine mineral particles from the asteroid surface (Tomeoka et al., 2003). However, some of the dehydrated material remains on the asteroid's surface, as demonstrated by reflectance spectra data (e.g., Hiroi et al., 1993). Such surface materials show brecciated textures and phyllosilicate dehydration, and contain implanted solar‒wind noble gases, such as in Y‒793321 (Nakamura, 2005).

Akai and Sekine (1994) conducted shock experiments on Murchison CM chondrite and serpentine lizardite in the pressure range 10‒39.6 GPa, and found that, in samples shocked at pressures > 32 GPa, serpentine changed to an amorphous phase with characteristic void‒like structures similar to those observed in B‒7904 (Akai, 1994). However, they could not verify the formation of secondary olivine grains, which were commonly observed in Stages III and IV samples (Table 1). This implied that shock pressure breaks serpentine crystal structures, but does not generate small secondary silicate phases that are crystallized from the amorphous phase. This lack was probably due to the very high cooling rates of impacted samples in the artificial shock experiments. The shock temperature of the sample rapidly decreased by adiabatic expansion on pressure release, and by high thermal conductivity of the stainless steel used to encapsulate the shocked sample. Crystal growth is a kinetic process that requires high temperature and long crystallization times. Secondary olivine formation from post‒shock residual heat can be reproduced by a brief heating of phyllosilicates. Heating periods of several minutes at 700 °C of phyllosilicates produced secondary olivine (Nozaki et al.,

2001, 2002); therefore, in natural impacts of carbonaceous chondrite parent bodies, secondary olivine would be formed if the post-shock temperature exceeded 700 °C. Kimura and Ikeda (1992) found no evidence for prolonged heating in the Stage IV sample, B-7904, and thus suggested a brief post-shock heating period as the principle cause of the dehydration observed in this meteorite.

Radiation heating by sunlight is another possible mechanism for heating hydrous carbonaceous chondrites. Small bodies with an orbit passing close to the sun (< 0.1 AU) can be heated to temperatures required for phyllosilicate dehydration. In this case, the surface temperature of the small body rises gradually as the body nears the sun, unlike the sudden heating of shock events. The effect of heat on the mineralogy and chemistry are the same as in the case of internal heating from the decay of radionuclides. However, the timing of heating differs between radiation heating and internal heating. Internal heating occurred very early, while radiation heating has occurred only recently. Radiation heating results in unique noble gas compositions. The heated small-body surface materials can also be irradiated by galactic cosmic rays, which produce spallation-induced noble gases, such as ^3He and ^{21}Ne, but, at the same time, the noble gases produced are lost by radiation heating. This results in a preferential loss of low-retentive cosmogenic ^3He, and a low ratio of $^3He/^{21}Ne$ is observed in some ordinary chondrites (e.g., Eugster et al., 1993). Therefore, to validate the radiation heating model, detailed noble gas analysis of heated hydrous carbonaceous chondrites is required.

SUMMARY

Over the past decade, concentrated work has been carried out to elucidate the thermal effects on the mineralogy, major and minor element abundance, organic chemistry, and oxygen isotope signature of hydrous carbonaceous chondrites. A classification scheme for the thermal history of samples has been proposed based on the latest data derived from studies on thermally metamorphosed carbonaceous chondrites. Previous studies have provided details of how hydrated asteroids were heated and dehydrated, but many issues still need to be clarified, and the major controversies are: (i) When were the asteroids heated?, and (ii) What caused the heating?

ACKNOWLEDGMENTS

REFERENCES

Akai, J. (1988) Incompletely transformed serpentine-type phyllosilicates in the matrix of Antarctic CM chondrites. Geochimca Cosmochimca et Acta, 52, 1593-1599.

Akai, J. (1990) Mineralogical evidence of heating events in carbonaceous chondrites, Y-86720 and Y-82162. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 3, National Institute of Polar Research, Tokyo, Japan, 55-68.

Akai, J. (1992) TTT-diagram of serpentine and saponite, and estimation of metamorphic heating degree of Antarctic carbonaceous chondrites. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 5, National Institute of Polar Research, Tokyo, Japan, 120-135.

Akai, J. (1994) Void structures in olivine grains in thermally metamorphosed Antarctic carbonaceous chondrite B-7904. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 7, National Institute of Polar Research, Tokyo, Japan, 94-100.

Akai, J. and Sekine, T. (1994) Shock effects experiments on serpentine and thermal metamorphic conditions in Antarctic carbonaceous chondrite. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 7, National Institute of Polar Research, Tokyo, Japan, 101-109.

Akai, J. and Tari, S. (1997) Thermally metamorphosed Antarctic CM and CI carbonaceous chondrites in Japanese collections, and transformation processes of phyllosilicates. LPI Technical Report 97-02, Part I, Lunar and Planetary Institute, Houston, USA, 1-2.

Barber, D.J. (1981) Matrix phyllosilicates and associated minerals in C2M carbonaceous chondrites. Geochim. Cosmochim. Acta, 45, 945-970.

Bischoff, A. and Metzler, K. (1991) Mineralogy and petrography of the anomalous carbonaceous chondrites, Yamato-86720, Yamato-82162 and Belgica-7904. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 4, National Institute of Polar Research, Tokyo, Japan, 226-246.

Brearley, A.J. and Jones, R.H. (1998) Chondritic meteorites. In Planetary Materials (Papike, J.J Ed.), Reviews in Mineralogy, 6, Mineralogical Society of America, Washington DC, 234-398.

Bearley, A.J., Hutcheon, I.D. and Browning, L. (2001) Compositional zoning and Mn-Cr systematics in carbonates from the Y791198 CM2 carbonaceous chondrite. Lunar and Planetary Science Conference, 32, 1458pdf.

Browning, L.B. and Bourcier, W.L. (1996) Tochilinite: a sensitive indicator of alteration conditions on the CM asteroidal parent body. Lunar and Planetary Science Conference, 27, 171-172.

Clayton, R.N. and Mayeda, T.K. (1999) Oxygen isotope studies of carbonaceous chondrites. Geochimca Cosmochimca et Acta, 63, 2089-2104.

Clayton, R.N. and Mayeda, T.K. (2001) Oxygen isotopic composition of the Tagish Lake carbonaceous chondrites. Lunar and Planetary Science Conference, 32, 1885 pdf .

Eugster, O., Michel, TH., Niedermann, S., Wang, D. and Yi, W. (1993) The record of cosmogenic, radiogenic, and trapped noble gases in recently recovered Chinese and other chondrites. Geochimca Cosmochimca et Acta, 57, 1115-1142.

Fuchs, L.H., Olsen, E. and Jensen, K.J. (1973) Mineralogy, mineral chemistry, and compositions of the Murchison (C2) meteorite. Smithonian Contribution on Earth Science, 10, 1-39.

Gaffey, M.J. (1976) Spectral reflectance characteristics of the meteorite classes. Journal of Geophysical Research, 81, 905-920.

Greshake, A., Kloeck, K., Arndt, P., Maetz, M., Flynn, G.J., Bajt, S. and Bischoff, A. (1998) Heating experiments simulating atmospheric entry heating of micrometeorites: Clues to their parent body sources. Meteoritics and Planetary Science, 33, 267-290.

Grimm, R.E. and McSween, H.Y. (1989) Water and thermal evolution of carbonaceous chondrite parent bodies. Icarus, 82, 244-280.

Hiroi, T., Peters, C., Zolensky, M.E. and Lipschutz, P. (1993) Evidence of thermal metamorphism of C, G, B, and F asteroid. Science, 261, 1016-1018.

Hiroi, T., Peters, C., Zolensky, M.E. and Lipschutz, P. (1994) Possible thermal metamorphism of the C, G, B, and F asteroids detected from their reflectance spectra in comparison with carbonaceous chondrites. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 7, National Institute of Polar Research, Tokyo, Japan, 230-243.

Hiroi, T., Peters, C., Zolensky, M.E. and Lipschutz, P. (1996) Thermal metamorphism of the C, G, B, and F asteroids seen from the 0.7 μm, 3 μm, and UV absorption strengths in comparison with carbonaceous chondrites. Meteoritics and Planetary Science, 31, 321-327.

Hiroi, T., Zolensky, M.E. and Peters, C. (1997) Characterization of unusual CI/CM/CR meteorite from reflectance spectroscopy. Lunar and Planetary Science Conference, 28, 1463.pdf.

Hiroi, T. and Zolensky, M.E. (1999) UV-VIS-NIR absorption features of heated phyllosilicates as remote-sensing clues of thermal histories of primitive asteroids. Antarctic Meteorite Research, 12, 108-116.

Hutcheon, I.D., Browning, L., Keil, K., Krot, A.N., Phinney, D.L., Prinz, M. and Weisberg, M.K. (1999) Time scale of aqueous activity in the early solar system. Ninth Annual V. M. Goldschmidt Conference, Lunar and Planetary Institute, Houston, USA, 7491pdf.

Ikeda, Y. (1991) Petrology and mineralogy of the Yamato-82162 chondrite (CI). Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 4, National Institute of Polar Research, Tokyo, Japan, 187-225.

Ikeda, Y. (1992) An overview of the research consortium, "Antarctic carbonaceous chondrites with CI affinities, Yamato-86720, Yamato-82162 and Belgica-7904". Proc. NIPR Symp. Antarct. Meteorite, Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 5, National Institute of Polar Research, Tokyo, Japan, 49-73.

Kimura, M. and Ikeda, Y. (1992) Mineralogy and petrology of an unusual Belgica-7904 carbonaceous chondrite: genetic relationships among the components. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 5, National Institute of Polar Research, Tokyo, Japan, 74-119.

Kitajima, F., Nakamura, T., Takaoka, N. and Murae, T. (2002) Evaluating the thermal metamorphism of CM chondrites by using pyrolytic behavior of the carbonaceous macromolecular matter. Geochimca Cosmochimca et Acta, 66, 163-172.

Kozerenko, S.V., Organova, N.J., Fadeev, V.V., Magazina, L.O., Kolpakova, N.N. and Kopneva, L.A. (1996) Tochilinite produced in laboratory. Lunar and Planetary Science Conference, 27, 695-696.

Lipschutz, M.E., Zolensky, M.E. and Bell, S.B. (1999) New petrologic and trace element data on thermally metamorphosed carbonaceous chondrites. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 12, National Institute of Polar Research, Tokyo, Japan, 57-80.

MacKinnon, I.D.R. and Zolensky, M.E. (1984) Proposed structures for poorly characterized phases in C2M carbonaceous chondrite meteorites. Nature, 309, 240-242.

Matsuoka, K., Nakamura, T., Nakamuta, Y. and Takaoka, N. (1996) Yamato-86789: A heated CM-like carbonaceous chondrite, Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 9, National Institute of Polar Research, Tokyo, Japan, 20-36.

Miyamoto, M. (1991) Thermal metamorphism of CI and CM carbonaceous chondrites: An internal heating model. Meteoritics, 26, 111-115.

Miyamoto, M. (1992) Infrared diffuse reflectance spectra of several thermally metamorphosed carbonaceous chondrites. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 5, National Institute of Polar Research, Tokyo, Japan, 155-164.

Nagao, K., Inoue, K. and Ogata, K. (1984) Primordial rare gases in Belgica 7904 (C2) Carbonaceous Chondrite. Memoirs of National Institute of Polar Research Special Issue, National Institute of Polar Research, Tokyo, Japan, 35, 257-266.

Nakamura, T. (2005) Yamato 793321 CM chondrite: Dehydrated regolith material of a hydrous asteroid. Earth and Planetary Science Letters, in press.

Nakamura, T. and Nakamuta, Y. (1996) X-ray study of PCP from the Murchison CM carbonaceous chondrites. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 9, National Institute of Polar Research, Tokyo, Japan, 37-50.

Nakamura, T., Nagao, K., Metzler, K. and Takaoka, N. (1999) Heterogeneous distribution of solar and cosmogenic noble gases in CM chondrites and implications for the formation of CM parent bodies. Geochimca Cosmochimca et Acta, 63, 257-273.

Nakamura, T., Kitajima, F. and Takaoka, N. (2000) Thermal effects on mineralogy, noble-gas composition, and carbonaceous material in CM chondrites. In Workshop on Extraterrestrial Materials from Cold and Hot Deserts (Schults L., Franchi I., Reid A. and Zolensky M.E. Eds.). Lunar and Planetary Institute Contribution Lunar and Planetary Institute, Houston, USA, 997, 61-63.

Nakamura, T., Noguchi, T., Yada, T., Nakamuta, Y. and Takaoka, N. (2001) Bulk mineralogy of individual micrometeorites determined by X-ray diffraction analysis and transmission electron microscopy. Geochimca Cosmochimca et Acta, 65, 4385-4397.

Nakamura, T., Noguchi, T., Zolensky, M. E. and Tanaka, M. (2003)

Noble-gas signatures and mineralogy of the carbonate-rich lithology of the Tagish Lake carbonaceous chondrite: Evidence for an accretionary breccia. Earth and Planetary Science Letters, 207, 83-101.

Nozaki, W., Nakamura, T., Noguchi, T. and Takaoka, N. (2001) D-type asteroids as a possible parental object of micrometeorites: experimental reproduction of micrometeorites from Tagish Lake carbonaceous chondrite. Meteoritics and Planetary Science, 36, A150.

Nozaki, W., Nakamura, T. and Noguchi, T. (2002) Experimental reproduction of micrometeorites by pulse-heating of carbonaceous chondrites. Papers presented to the 27th Symposium on Antarctic Meteorites, National Institute of Polar Research, Tokyo, Japan, 132-133.

Paul, R.L. and Lipschutz, M.E. (1989) Labile trace elements in some Antarctic carbonaceous chondrites: Antarctic and non-Antarctic meteorite comparisons. Zeitschrift für Naturforschung 44a, 979-987.

Paul, R.L. and Lipschutz, M.E. (1990) Consortium study of labile trace elements in some Antarctic carbonaceous chondrites: Antarctic and non-Antarctic meteorite comparisons. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 3, National Institute of Polar Research, Tokyo, Japan, 80-95.

Tomeoka, K. (1990a) Mineralogy and petrology of Belgica-7904: A new kind of carbonaceous chondrite from Antarctica. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 3, National Institute of Polar Research, Tokyo, Japan, 40-54.

Tomeoka, K. (1990b) Phyllosilicate veins in a CI meteorite: evidence for aqueous alteration on the parent body. Nature, 345, 138-140.

Tomeoka, K. and Buseck, P.R. (1983) A new layered mineral from the Mighei CM2 carbonaceous chondrite. Nature, 306, 354-356.

Tomeoka, K. and Buseck, P.R. (1985) Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O and Ni. Geochimca Cosmochimca et Acta, 49, 2143-2163.

Tomeoka, K., Kojima, H. and Yanai, K. (1989a) Yamato-86720: A CM carbonaceous chondrite having experienced extensive aqueous alteration and thermal metamorphism. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 2, National Institute of Polar Research, Tokyo, Japan, 55-74.

Tomeoka, K., Kojima, H. and Yanai, K. (1989b) Yamato-82162: a new kind of CI carbonaceous chondrite from Antarctica. Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites, 2, National Institute of Polar Research, Tokyo, Japan, 36-54.

Tomeoka, K., Kiriyama, K., Nakamura, K., Yamahana, Y. and Sekine, T. (2003) Explosive dispersal of hydrated asteroids by impact as a mechanism to produce interplanetary dust. Nature, 423, 60-62.

Tonui, E.K., Zolensky, M.E. and Lipschutz, M.E. (2002) Petrology, mineralogy and trace element chemistry of Yamato-86029, Yamato-793321 and Lewis Cliff 85332: Aqueous alteration and heating events. Antarctic Meteorite Research, 15, 38-58.

Tonui, E.K, Zolensky, M.E., Lipschutz, M.E., Wang, M. and Nakamura, T. (2003) Yamato 86029: Aqueously altered and thermally metamorphosed CI chondrite with unusual textures. Meteoritics and Planetary Sciences, 38, 269-292.

Tyburczy, J.A., Frisch, B. and Ahrens, T.J. (1986) Shock-induced volatile loss from a carbonaceous chondrite: implications for planetary accretion. Earth and Planetary Science Letters, 80, 201-207.

Wang, M.S. and Lipschutz, M.E. (1998) Thermally metamorphosed carbonaceous chondrites from data for thermally mobile trace elements. Meteoritics and Planetary Science, 33, 1297-1302.

Wicks, F.J. and O'Hanley, D.S. (1991) Serpentine minerals: structures and petrology. In Hydrous phyllosilicates (exclusive of micas) (Bailey, S.W. Ed.). Reviews in Mineralogy, 19, Mineralogical Society of America, Washington DC, 91-168.

Xiao, X. and Lipschutz, M.E. (1992) Labile trace element in carbonaceous chondrites: A survey. Journal of Geophysical Research, 97, 10197-10211.

Yanai, K., Kojima, H. and Haramura, H. (1995) Catalog of the Antarctic Meteorites collected from December 1969 to December 1994, with special reference to those represented in the collections of the National Institute of Polar Research. National Institute of Polar Research, Tokyo, 44-76.

Zolensky, M.E. (1984) Hydrothermal alteration of CM carbonaceous chondrites: implications of the identification of tochilinite as one type of meteoritic PCP. Meteoritics, 19, 346-347.

Zolensky, M.E. and McSween, H.Y. (1988) Aqueous alteration. In Meteoritics and the Early Solar System (Kerridge, J.F. and Matthews, M.S. Eds.). University Arizona Press, Tucson, 114-143.