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Earth and Planetary Science Letters 202 (2002) 229–246

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Mineralogy of phyllosilicate-rich micrometeorites and comparison with Tagish Lake and Sayama meteorites

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Received 27 August 2001; received in revised form 20 March 2002; accepted 6 June 2002

Abstract

Four phyllosilicate-rich micrometeorites (MMs) were investigated by a synchrotron radiation X-ray diffraction technique and transmission electron microscopy. Three are saponite-rich MMs and one is a serpentine-rich one. In the saponite-rich MMs, we could not find serpentine, and vice versa in the serpentine-rich MM. In the saponite-rich MMs, major constituent minerals are saponite, Fe- and Ni-bearing sulfides, and magnetite. Two saponite-rich MMs contain fine-grained magnesiowüstite-rich aggregates. The aggregates consist of <50 nm polygonal magnesiowüstite coexisting with minor Fe sulfide grains. Their texture, chemical composition, and the result of heating experiments on matrix fragments of the Tagish Lake carbonaceous chondrite strongly suggest that these aggregates were formed by the breakdown of Mg- and Fe-rich carbonate grains when the MMs entered the Earth's atmosphere. The estimated major mineral assemblage of the saponite-rich MMs before entering the Earth's atmosphere is very similar to that of the Tagish Lake carbonate-rich lithology, and we suggest that the MMs and the meteorite were derived from similar asteroids. The major mineral assemblage and texture of the matrix of serpentine-rich MM are similar to the matrix of the Sayama CM2 chondrite that experienced heavy aqueous alteration. Chemical compositions of serpentine in the MM suggest that the degree of aqueous alteration of the MM is weaker than that of Sayama. In the MM, cronstedtite does not coexist with tochilinite, which is different from CM2 chondrites that experienced weak to moderate aqueous alteration. However, the possibility that the serpentine-rich MM was derived from the CM chondrite asteroid cannot be ruled out, because tochilinite can be preferentially decomposed during atmospheric entry heating due to its lower decomposition temperature than that of cronstedtite.

Keywords: micrometeorites; Tagish Lake Meteorite; Sayama Meteorite; transmission electron microscopy; sheet silicates

1. Introduction

Micrometeorites (MMs) are small extraterrestrial material (<1 mm in diameter) and occupy most of the mass accreting to the Earth. The MMs have similarities in chemistry and mineralogy to the CI, CM and CR chondrites (e.g. [1]), indicating that they are very primitive materials in the Solar System. But most MMs inevitably experienced atmospheric entry heating that changed primary mineralogy. Synchrotron radiation X-ray diffraction (SR-XRD) of individual MMs showed that most of them are composed of anhy-

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0012-821X/02/$ – see front matter
PII: S0012-821X(02)00777-X

drous minerals [2]. But their mineral assemblages and microstructures strongly suggest that the majority of MMs had contained phyllosilicates before entering the Earth [2]. Because the hydrous particulate is found to be a major component among dust particles that traverse the interplanetary space, mineralogical study of aqueously altered MMs is important to characterize the dust in this Solar System.

Transmission electron microscopy (TEM) studies of phyllosilicate-rich MMs revealed that they are mineralogically different from any known meteorite [3–5], except for one MM including both saponite and serpentine [6] like CI and CR chondrites [7,8]. Except for this MM, all the other MMs contain saponite as the only phyllosilicate [3–5]. The absence of serpentine in the saponite-rich MMs is different from the case of CI chondrites in which serpentine coexists with saponite. Matrices of hydrated CV3 chondrites Kaba and Mokoia and those of some LL3 chondrites Semarkona and Krymka contain only saponite as phyllosilicate [9–11]. However, the chemical compositions of saponite and coexisting minerals are different from those in the MMs [3–5]. Therefore, any meteoritic counterparts for the saponite-rich MMs have not been found among known meteorites.

In this study, we found that the carbonaceous chondrite Tagish Lake, which fell in January 18, 2000 [12], could be a source of the saponite-rich MMs. Also we found similarities in mineralogy between a serpentine-rich MM and matrix of heavily altered CM chondrite, Sayama [13,14]. Based on the mineralogical data of MMs and comparison with meteorites, we will discuss the origin of the phyllosilicate-rich MMs.

2. Samples and experimental procedures

More than 1000 MM candidates were handpicked under a binocular microscope from fine-grained materials in the size range 40–100 μm. Identification of MMs was made by scanning electron microscope (JEOL JSM-5600 SEM) observation and qualitative analysis by energy dispersive spectrometer (EDS; Oxford ISIS 310 EDS). Particles having dominant Mg, Si and Fe Kα lines were considered as MMs. Particles containing considerable amounts of Al, Ca, K and Na as well as these elements were regarded as volcanic particles. MMs having matrices with low analytical totals and phyllosilicate-like chemical compositions as determined by electron microprobe analysis (EMPA) were investigated by SR-XRD analysis using a Gandolfi camera at the Institute of Materials Structure Science, High Energy Accelerator Research Organization. Experimental conditions for the XRD analysis were described elsewhere [2].

To consider the origin of the phyllosilicate-rich MMs, we also investigated fine-grained fragments of matrices of two carbonaceous chondrites, Tagish Lake and Sayama, by the same methods applied for MMs. Because the effect of heating during atmospheric entry is important for the MMs, even those containing abundant saponite, we performed heating experiments of fine-grained fragments of Tagish Lake matrix to compare bulk mineralogy and microstructure of the run products with those of the saponite-rich MMs. Details of the experimental procedures and results will be described separately [15].

Each MM, each fragment of the two carbonaceous chondrites and a run product of the heating experiment were embedded in epoxy resin EMbed-812, and 60–100 nm sections were microtomed by Leitz-Reichert Super Nova ultramicrotome for TEM observation. Microstructure, mineralogy and chemical compositions of minerals of the samples were obtained by JEOL JEM-2000FX II equipped with Philips DX4 EDS. A 100 nm beam was used for the analysis of Fe oxides. The beam diameter was changed from 300 to 500 nm for phyllosilicates to minimize compositional change due to heating during analysis and contamination from the surrounding phases. Semiquantitative analysis was based on the Cliff–Lorimer thin film approximation. Experimental k-factors were obtained from many mineral standards. The k-factors were determined as functions of the thickness of the samples, thereby empirically including the absorption correction. The polished remainders of each embedded MM were observed by scanning electron microscopy (SEM).

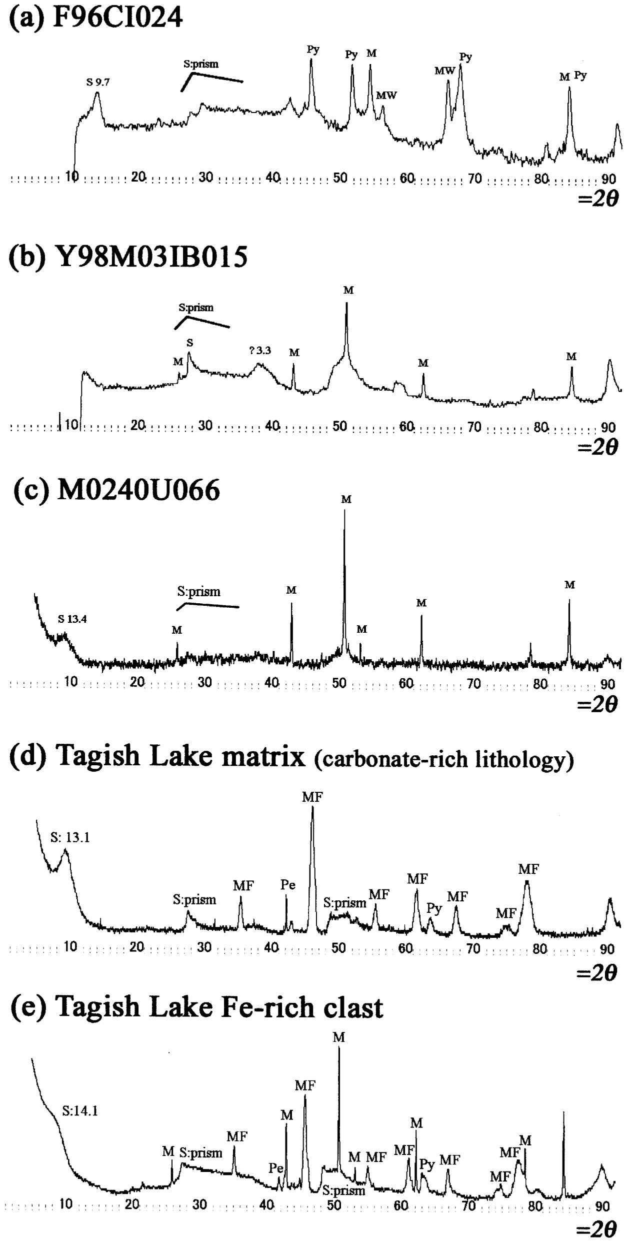

Fig. 1. SR-XRD data of saponite-rich MMs, (a) F96CI024, (b) Y98M03IB015 and (c) M0240U066; and Tagish Lake carbonaceous chondrite, (d) matrix of Tagish Lake carbonate lithology, (e) matrix of a clast. Abbreviations: S: saponite; M: magnetite; Py: pyrrhotite; MW: magnesiowüstite; S: prism: prism reflection of saponite; MF: Mg- and Fe-rich carbonate; Pe: pentlandite. In the X-ray chart of (b), (001) reflection from saponite was shielded by the stopper of the direct X-ray beam. Numerals after S are the interlayer spacing of the (001) plane of saponite (unit: Å).

3. Results

We found four MMs containing abundant phyllosilicates among more than 1000 MMs through the analyses by SEM, EMPA and SR-XRD. Three saponite-rich MMs are: F96CI024, recovered at the Dome Fuji Station, Queen Maud Land in 1996, and Y98M03IB015 and M0240-U066, recovered from bare ice fields, near the Yamato Mountains in 1999 by the 36th and 39th JARE teams, respectively. A serpentine-rich MM is EURO 020, recovered at a bare ice field, near Cap Prudhomme in 1991 by a EUROMET team.

3.1. *Bulk mineralogy and texture of the saponite-rich MMs*

Fig. 1 shows powder X-ray diffraction patterns of saponite-rich MMs. These charts indicate that serpentine and other hydrous phases except for saponite were not identified. Major minerals in F96CI024 are saponite, pyrrhotite, magnetite and magnesiowüstite ((Mg,Fe)O) (Fig. 1a). TEM observation of the MM revealed that it includes a minor amount of pentlandite. Major minerals in Y98M03015 and M0240U066 are saponite and magnetite (Fig. 1b,c). TEM observation of these MMs revealed that Y98M03015 contains minor amounts of pyrrhotite, pentlandite and magnesiowüstite, while M0240U066 contains a trace amount of pyrrhotite and minor poorly crystalline Fe-rich material. Magnesiowüstite was not found in the latter even by using TEM. Anhydrous silicates such as olivine and pyroxene were not found in the three MMs (Fig. 1a–c). Table 1 is a list of constituent minerals of phyllosilicate-rich MMs.

In the cross section of F96CI024, there are some coarse (5–10 μm in diameter) pyrrhotite and pentlandite grains embedded in a compact matrix, although the pentlandite is a minor mineral based on the SR-XRD data (Figs. 1a and 2a). There is also a coarse (15 × 20 μm) aggregate of magnetite plaquette. Coarse Fe sulfides and magnetite were not found in the cross section of Y98M03IB015 (Fig. 2b) although a coarse magnetite grain was observed on the grain's outer surface. Only small amounts of fine-grained (< 1 μm across) magnetite and sulfide were observed within the particle. M0240U066 contains abundant aggregates of magnetite framboids with diameters < 10 μm in a compact matrix (Fig. 2c). Sharp diffraction peaks of magnetite in Fig. 1c correspond to their coarse-grain sizes. No coarse Fe sulfides except for minor small (< 1 μm across) pyrrhotite were found. Therefore, major minerals of the saponite-rich MMs are saponite, Fe oxides and Fe–Ni sulfides, although the relative abundance of each mineral is variable. These bulk mineralogical and textural data show that saponite-

Table 1
Consistuent minerals of phyllosilicate-rich MMs and the matrices of Tagish Lake and Sayama

	Major minerals	Minor minerals
Saperonite-rich MMs		
F96CI024	saponite, pyrrhotite, magnetite, magnesiowüstite	pentlandite
Y98M03IB015	saponite, magnetite	pentlandite, magnesiowüstite, pyrrhotite
M0240U066	saponite, magnetite	pyrrhotite, poorly crystalline fe-rich material
Tagish Lake		
Matrix (carbonate-rich lithology)	saponite, pyrrhotite, magnesian siderite, pentlandite, magnetite	serpentine[a]
Matrix (carbonite-poor lithology)	saponite, magnetite, pyrrhotite, magnesian siderite, pentlandite, calcite	serpentine[a]
Serpentine-rich MM		
EURO 020	cronstedtite, Fe-rich serpentine, magnetite	pyrrhotite
Sayama matrix		
Matrix	serpentine, pentlandite, magnetite	pyrrhotite, chromite

[a] A minor amount of thin (< 10 nm) serpentine layers coexists coherently with saponite.

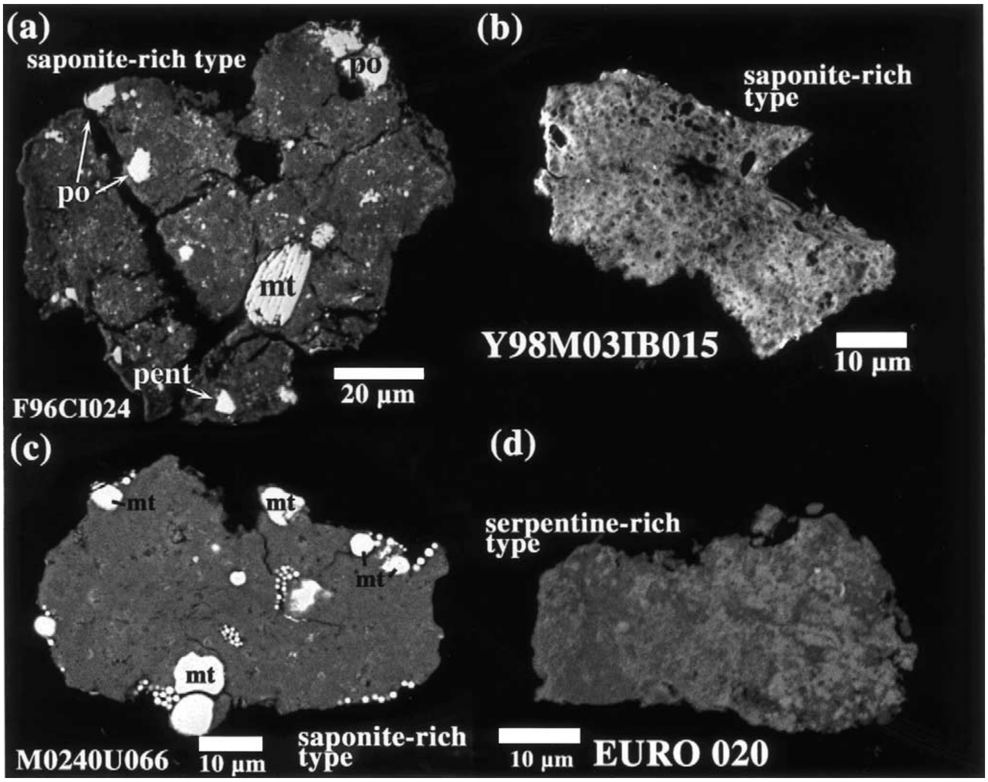

Fig. 2. Backscattered electron images (BEIs) of cross sections of phyllosilicate-rich MMs investigated in this study. (a) F96CI024, (b) Y98M03IB015, (c) M0240U066 and (d) EURO 020. Abbreviations: mt = magnetite; po = pyrrhotite; pent = pentlandite.

rich MMs, in which magnetite framboids and plaquettes are not abundant, contain magnesiowüstite.

The (001) spacing of saponite in F96CI024 determined by SR-XRD is 0.97 nm. This value indicates that the basal spacing of saponite in the MM shrank due to dehydration of interlayer H_2O molecules. The shrinkage probably occurred by atmospheric entry heating because it has already been observed by SR-XRD, which was performed before TEM observation. In the SR-XRD chart of Y98M03IB015, the (001) peak of saponite is not recorded because this MM was measured by a camera incapable of recording peaks from crystal planes with spacing of about 1 nm or larger. But it shows a prism reflection (02*l*), characteristic of phyllosilicates. In the case of M0240U066, saponite (001) spacing is 1.34 nm. This means that interlayer H_2O molecules in saponite in this MM were not severely lost.

3.2. Bulk mineralogy of matrix of Tagish Lake

Fine-grained (about 100 μm across) fragments of the Tagish Lake carbonaceous chondrite were used for comparison with the saponite-rich MMs. This meteorite contains carbonate-rich and carbonate-poor lithologies [16]. We investigated this meteorite and found that the matrix with carbonate (magnesian siderite)-rich lithology contains abundant saponite and is very poor in serpentine [17]. An SR-XRD chart of the matrix indicates that the major minerals are saponite, pyrrhotite, magnesian siderite and pentlandite (Fig. 1d and Table 1). There is another type of fine-grained matrix material that occurs as clasts (< 10–400 μm across). It often contains framboidal aggregates of magnetite as in the case of the carbonate-poor lithology of the meteorite [16]. Major minerals of the clasts are saponite, magnetite, pyrrhotite, magnesian siderite and pentlandite

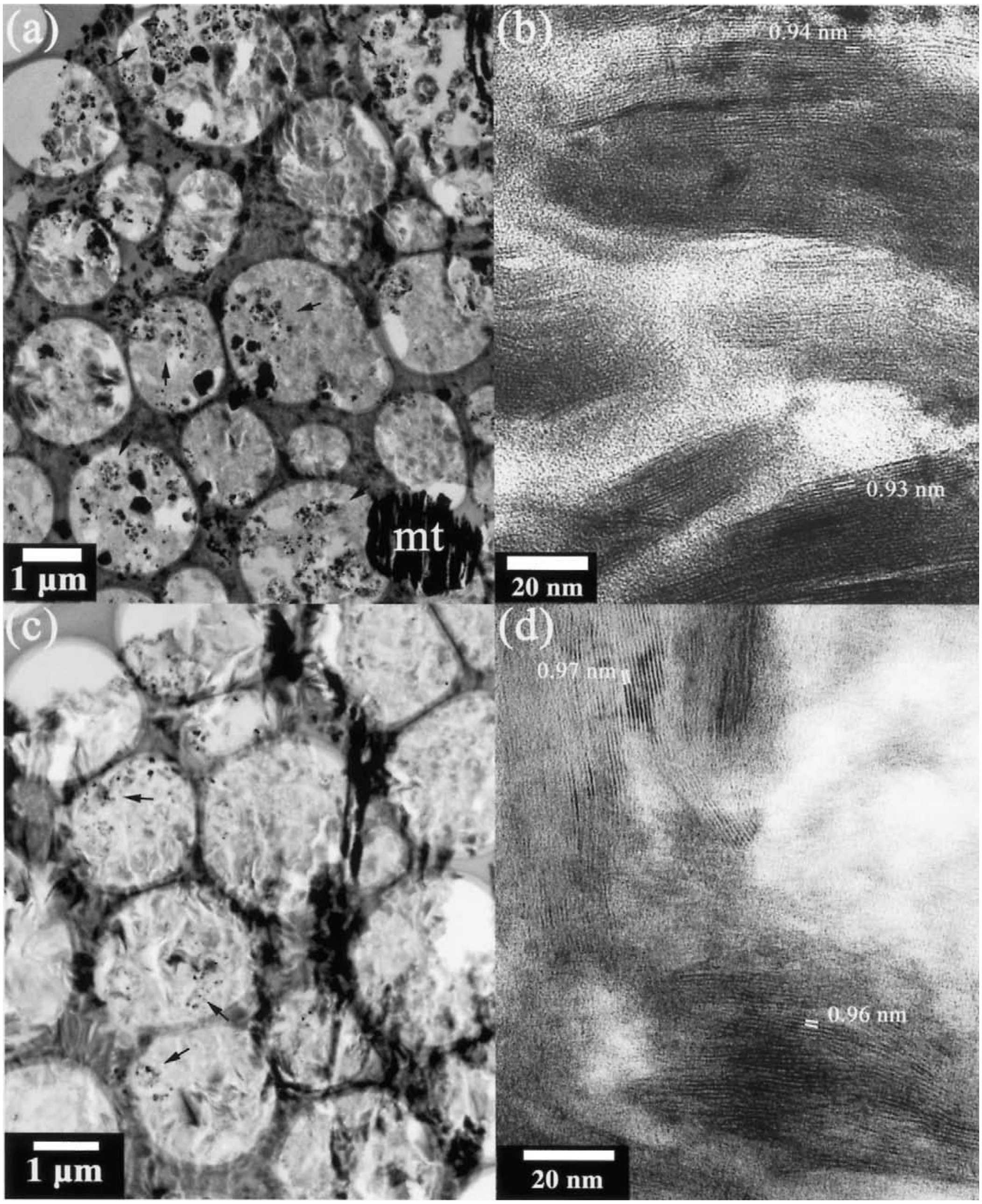

Fig. 3. Low-magnification bright field TEM images of three saponite-rich MMs: (a) F96CI024, (c) Y98M03IB015 and (e) M240U066). (g) Matrix in Tagish Lake carbonate-rich lithology. (b, d, f, h) High-resolution TEM images of phyllosilicates in them, respectively. Arrows in (a) and (c) indicate magnesiowüstite-bearing aggregates. Honeycomb networks in Figs. 3, 7 and 9 are holey plastic films that support ultrathin sections of the samples. Abbreviation: mt = magnetite.

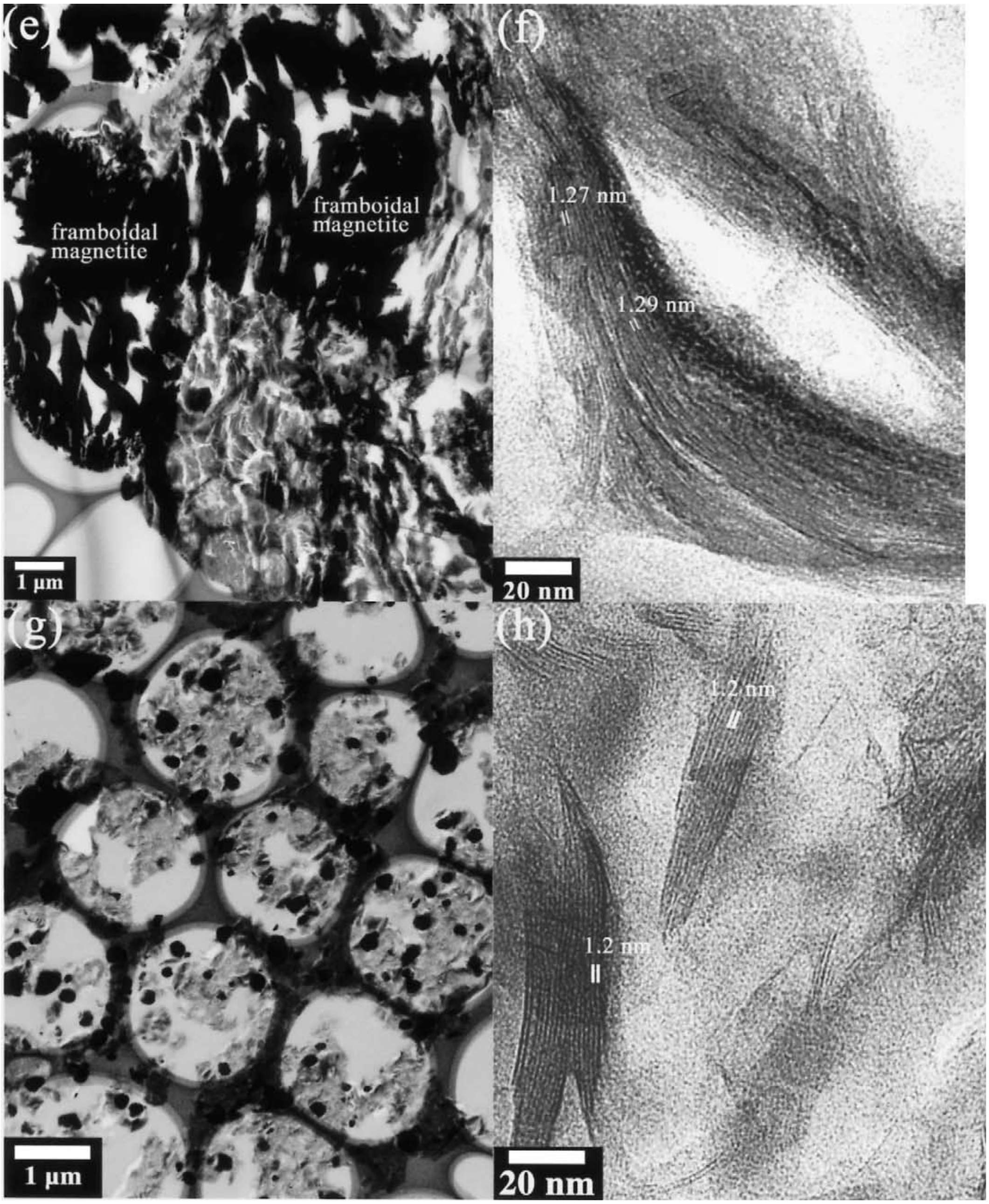

Fig. 3 (*Continued*).

(Fig. 1e). Magnesian siderite is poorer and magnetite is richer in the clasts than the matrix of the carbonate-rich lithology. Serpentine was not found by the SR-XRD technique, although only a small amount of serpentine that is intercalated within saponite was found by TEM observation [17].

3.3. *Microstructure of the matrices of the saponite-rich MMs and Tagish Lake*

Fig. 3a is a bright field image of the matrix of F96CI024. There are abundant fine-grained (< 200 nm across) Fe sulfides and magnetite

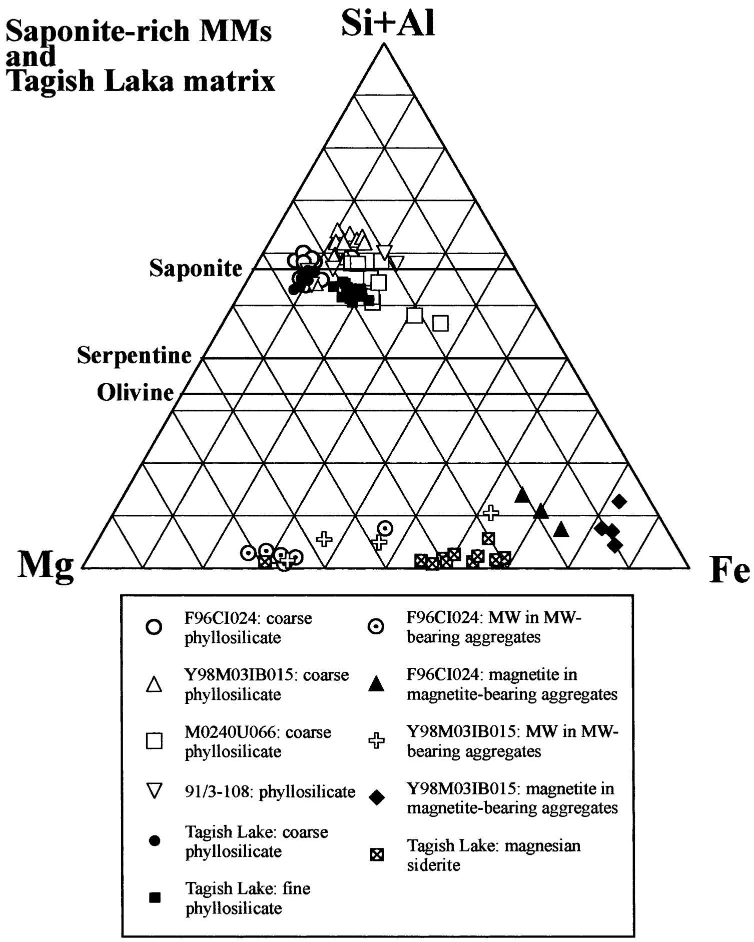

Fig. 4. Chemical compositions of phyllosilicate and Fe oxides in the saponite-rich MMs and those of phyllosilicates and magnesian siderite in the matrix of Tagish Lake carbonate-rich lithology. Due to the small grain sizes, chemical compositions of the Fe oxides are affected by the surrounding minerals, especially phyllosilicates. Chemical compositions of saponite in the MM 91/3-108 are quoted from [11].

grains embedded in the coarse-grained phyllosilicate-dominated matrix. The amounts of fine-grained Fe sulfides and magnetite vary considerably among the three MMs. The amounts in Y98M03IB015 are much lower than those in F96CI024 although the texture of the phyllosilicate-rich matrix in Y98M03IB015 is similar to that of F96CI024 (Fig. 3c). Fine-grained Fe sulfides and magnetite were rarely observed in the matrix of M0240U066 (Fig. 3e).

High-resolution TEM images of saponite in these three MMs show that saponite crystallites have 10–50 nm width perpendicular to their basal planes (about 20 nm is most abundant) (Fig. 3b,d,f). The spacings of basal lattice fringes of the phyllosilicates are 0.93–0.96 nm in F96CI024 and Y98M03IB015, and 1.27–1.29 nm in M0240U066 (Fig. 3b,d,f). The basal spacing obtained by TEM is very consistent with the results obtained by SR-XRD. Basal spacings of 0.7 nm were not observed in these MMs. Therefore, the majority of phyllosilicates in these MMs were saponite (i.e. essentially no serpentine). In F96CI024 and Y98M03IB015, there are also very fine-grained Fe oxide and Fe sulfide grains. They are typically <100 nm in diameter. Magnesiowüstite

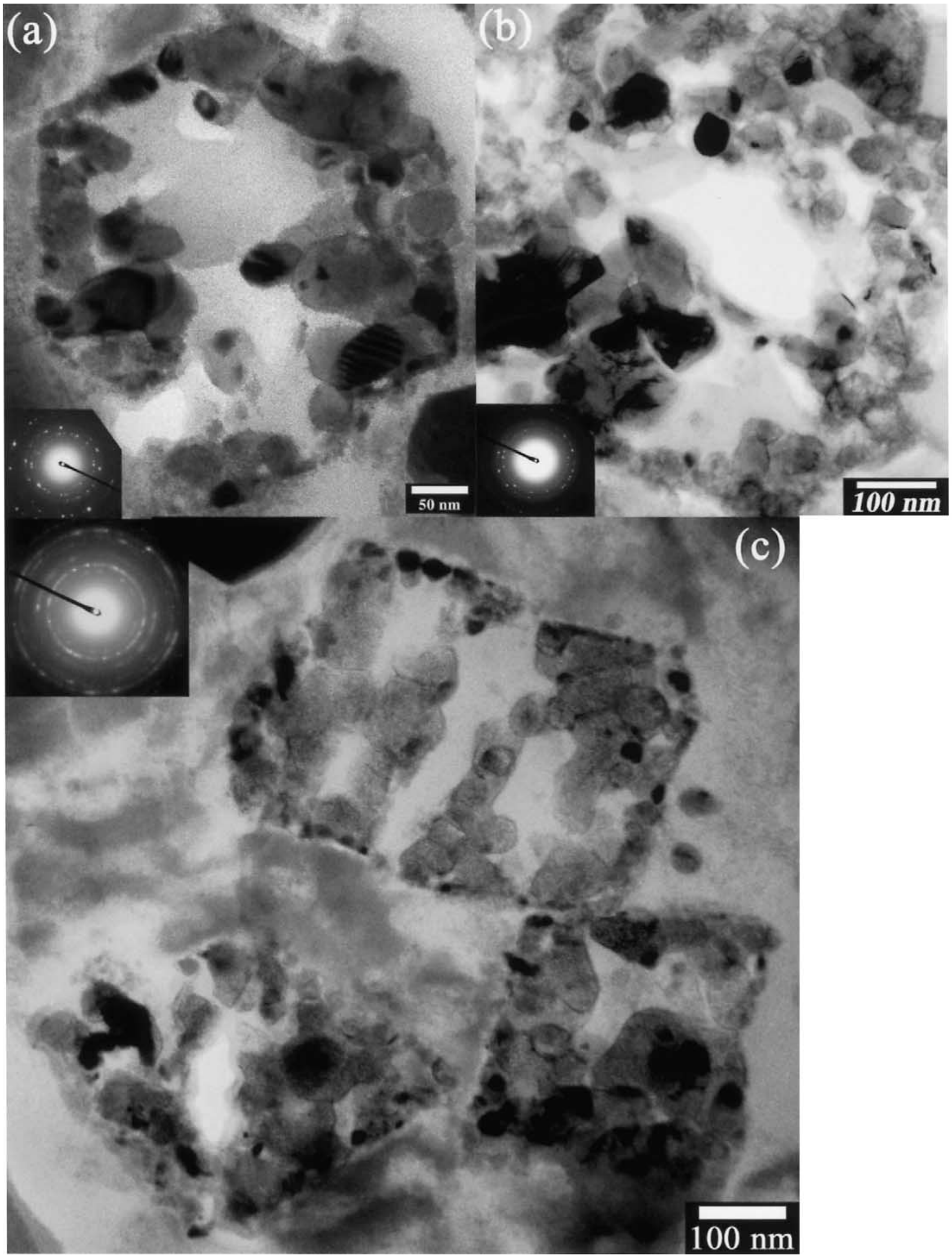

Fig. 5. TEM images of magnesiowüstite-bearing aggregates in (a) F96CI024 and (b) Y98M03IB015, and (c) magnetite-bearing aggregates in F96CI024.

occurs as such fine grains, as will be discussed in Section 3.4.

TEM observation of the Tagish Lake matrix from the carbonate-rich lithology reveals that it has a texture similar to that of the magnesiowüstite-bearing saponite-rich MMs, especially F96CI024. TEM imaging of the Tagish Lake matrix shows that it contains abundant fine-grained (< 300 nm across) pyrrhotite, pentlandite and magnetite embedded in a coarse phyllosilicate matrix (Fig. 3g). The majority of the smallest grains are pyrrhotite, which is consistent with the SR-XRD result. Magnesian siderite occurs as grains of several hundred nm to several μm across. High-resolution TEM imaging shows that the coarse phyllosilicate in the matrix measures 10–20 nm in width normal to their (001) planes and that the vast majority of the phyllosilicate has 1.2–1.3 nm lattice fringes (Fig. 3h). Therefore, saponite is the major phyllosilicate. As shown above, the constituent minerals of the magnesiowüstite-bearing saponite-rich MMs and those of the Tagish Lake matrix from the carbonate-rich lithology are very similar to each other except for magnesiowüstite in the MMs and magnesian siderite in the Tagish Lake matrix.

Analytical electron microscopy (AEM) of the phyllosilicates in the magnesiowüstite-bearing MMs and those of the Tagish Lake matrix shows that the phyllosilicates have similar compositions (Fig. 4). An [Si+Al]–Mg–Fe atomic ratio diagram shows that saponite in the MMs and Tagish Lake overlap one another, although saponite in the MMs shows a wider range of compositions and higher (Si+Al)/(Si+Al+Mg+Fe) ratio than those in the matrix of Tagish Lake. These compositional data also indicate that the phyllosilicates are composed predominantly of saponite.

3.4. Magnesiowüstite aggregates in the saponite-rich MMs

We have already reported that magnesiowüstite is a relatively common mineral among MMs which experienced moderate heating during atmospheric entry [2]. We found magnesiowüstite-bearing aggregates in Y96CI024 and Y98M03IB015, although these MMs experienced weak heating. In

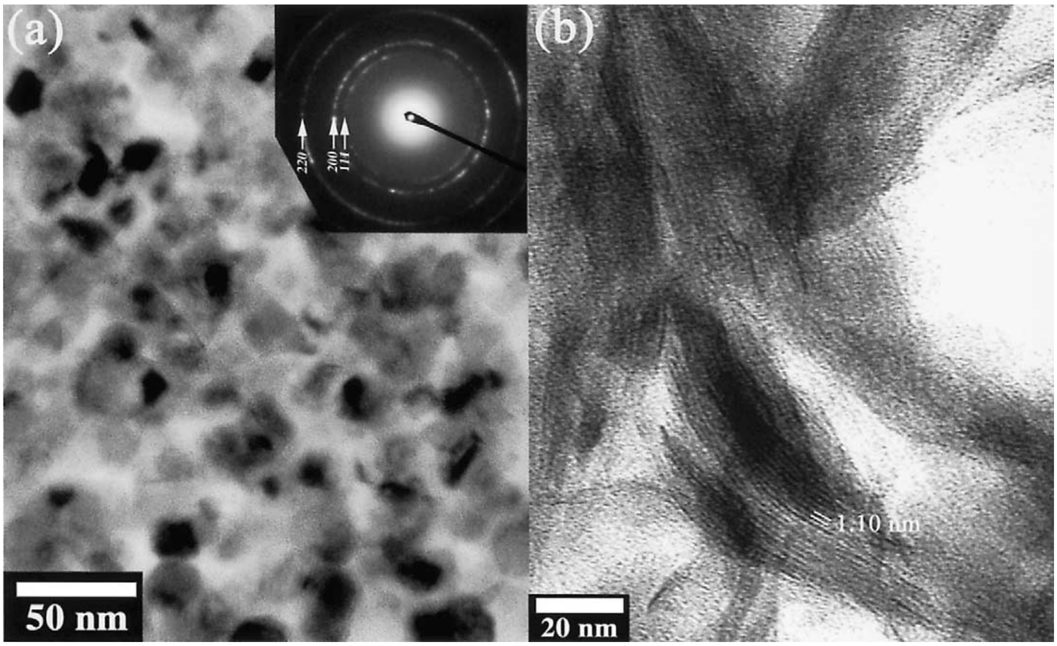

Fig. 6. TEM images of experimentally heated matrix of Tagish Lake carbonate-rich lithology. (a) Magnesian siderite in the matrix is decomposed into aggregates of magnesiowüstite. (b) On the other hand, saponite maintained its layer structure.

F96CI024, the aggregates are more abundant than those in Y98M03IB015. In both MMs, the aggregates have similar size, shape and occurrences. The aggregates range 200–700 μm across and are composed of fine-grained (< 100 nm in diameter), polygonal magnesiowüstite and sometimes contain minor Fe sulfide grains (Fig. 5). Some aggregates show definite hexagonal outlines (Fig. 5a), which indicates that the aggregates are pseudomorphs of minerals with hexagonal prism shape. Selected area electron diffraction (SAED) patterns obtained from such aggregates demonstrate that they consist of randomly oriented magnesiowüstite grains (Fig. 5 and Table 2).

Based on AEM data, the Mg/(Mg+Fe) atomic ratios of magnesiowüstite in F96CI024 and Y98M03IB015 are 0.50–0.73 and 0.31–0.66, respectively. Compositional zoning of Mg, Fe, Mn and Ca was not observed in the aggregates. EDS spectra clearly show that magnesiowüstite grains in F96CI024 and Y98M03IB015 contain MnO because surrounding phyllosilicates do not contain detectable amounts of Mn. MnO contents in all the phyllosilicate analyses in F96CI024 are below the detection limit. Most of the analyses in Y98M03IB015 are also below detection, although a small amount of MnO up to 0.4 wt% was detected in rare cases. On the other hand, the magnesiowüstite grains in F96CI024 and Y98M03IB015 contain up to 1.5 and 3 wt% MnO, respectively. The precursor minerals of the aggregates must contain a small amount of Mn as well as abundant Mg and Fe. The most plausible precursor mineral of the aggregate is Mg- and Fe-rich carbonate. As described in Section 3.3, the Tagish Lake matrix contains magnesian siderite, which often includes a small amount of Mn as well as minor Ca. If the saponite-rich MMs contained Mg- and Fe-rich carbonate before entering the Earth's atmosphere, their major mineral assemblage was similar to that of the Tagish Lake matrix investigated in our study. The estimated mineral assemblage of precursor minerals of the MMs is saponite, Fe–Ni sulfides, magnetite, and Mg- and Fe-rich carbonate.

Magnesiowüstite-bearing saponite-rich MMs also contain another kind of fine-grained Fe oxide aggregates. The size of the aggregates (< 100 nm across) overlaps with that of the magnesiowüstite-

Table 2
Diffraction from magnesiowüstite (MW)-bearing aggregates and that from magnetite-bearing ones, and comparison with MW and magnetite data from JCPDF

F96CI024	Y98M03IB015	Diffraction data from JCPDF		
MW (nm)	MW (nm)		wustite (nm)	periclase (nm)
0.244	0.242	111	0.247	0.24347
0.213	0.208	200	0.214	0.21085
0.149	0.147	220	0.1514	0.14909
n.d.	n.d.	311	0.1293	0.12715[a]
0.122	0.120	222	0.12375	0.12173
magnetite (nm)	magnetite (nm)		magnetite (nm)	
0.492	n.d.	111	0.4852[a]	
0.300	0.299	220	0.2967	
0.255	0.254	311	0.2532	
0.210	0.210	400	0.20993	
0.176	0.176	422	0.17146	
0.163	0.162	333, 511	0.16158	
0.149	0.148	440	0.14845	

n.d.: not detected.
[a] These peaks were not recorded in SAED patterns because of their weak intensity.

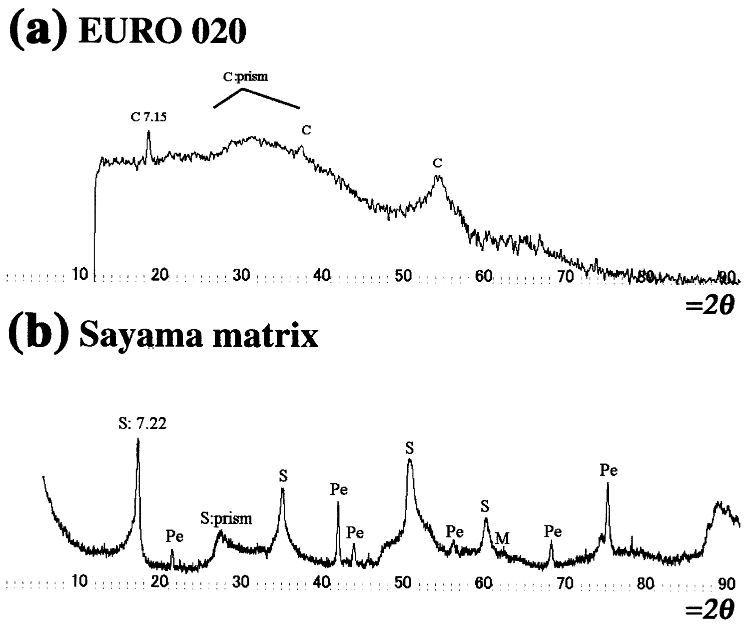

Fig. 7. SR-XRD data of a serpentine-rich MM and Sayama CM chondrite. (a) EURO 020 MM, (b) matrix of Sayama. Abbreviations: C: cronstedtite; S: serpentine. Numerals after C or S mean the spacing (unit: Å) of (001) planes of cronstedtite and serpentine, respectively.

bearing aggregates and also the aggregates often have pseudomorphs of their precursor mineral, probably Fe-rich carbonate (Fig. 5c). These two types of aggregates coexist separately. SAED patterns obtained from these aggregates show they consist of magnetite (Fig. 5c and Table 2). EDS spectra of the aggregates sometimes display small peaks of Mg, Mn, and rarely Ca together with Si from the surrounding phyllosilicates. Mg/(Mg+Fe) atomic ratios of such magnetite inclusions in F96CI024 and Y98M03IB015 are 0.19–0.24 and 0.06–0.11, respectively. Contaminant phases including these minor elements could not be found in the aggregates probably due to very fine-grained sizes of the contaminants. Magnetite aggregates in irregular shape did not contain these elements.

3.5. Heating experiment of the matrix of Tagish Lake

We conducted heating experiments with the Tagish Lake matrix to assess the possibility that heating can transform this material into the magnesiowüstite-bearing saponite-rich MMs [25]. When the samples were heated in a vacuum furnace at 600°C for 120 s (duration around 600°C is about 40 s) under 2.0 Pa, SAED patterns of the run products show that magnesian siderite was decarbonated into aggregates of magnesiowüstite (Fig. 6a). On the other hand, XRD [15] and TEM data revealed that saponite keeps its basic structure and chemical composition (Fig. 6b), although the (001) basal spacing of the saponite shrunk to 0.95–1.1 nm due to loss of interlayer H_2O molecules. The heating experiment clearly shows that Mg- and Fe-rich carbonate can be decomposed into oxide aggregates at temperatures where saponite is not significantly decomposed.

3.6. Bulk mineralogy and texture of a serpentine-rich MM and Sayama

We could find only one MM that bears abundant serpentine (Figs. 2d and 7a), EURO 020. XRD reflections of serpentine in this MM are sharp, indicative of well crystallized material. The serpentine has an average basal spacing

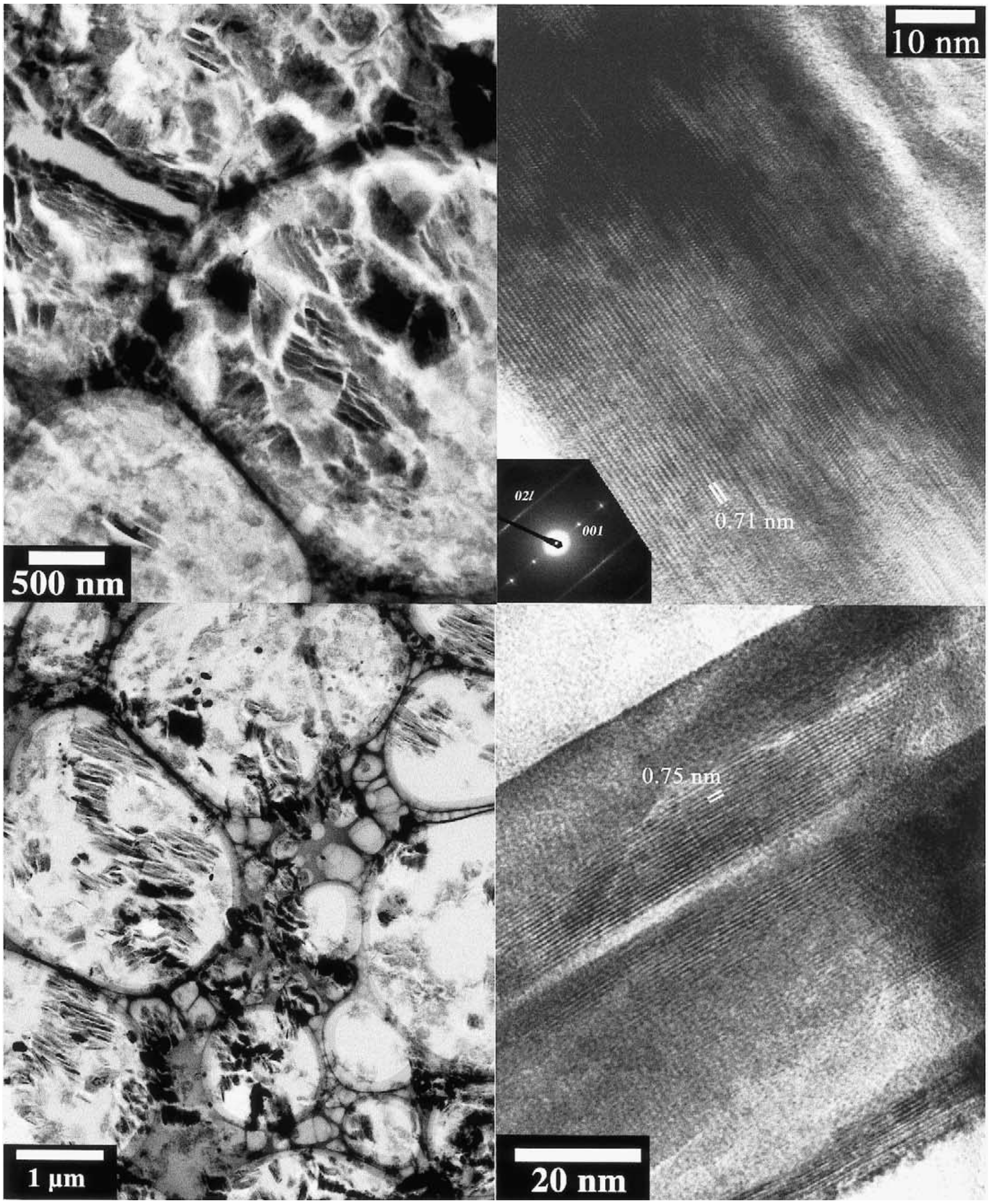

Fig. 8. TEM images of a serpentine-rich MM, EURO 020 and the matrix of Sayama. (a, c) Low-magnification bright field images of EURO 020 and Sayama, respectively. (b, d) High-resolution TEM images of phyllosilicates in them.

(0.715 nm) shorter than that of normal serpentine (0.73 nm), probably due to exchange of some Si^{4+} by Fe^{3+} in the tetrahedral layers. A diffuse (02*l*) prism diffraction due to disordered stacking was also found. This MM is composed mainly of serpentine. Diffraction peaks due to tochilinite were not observed. Relict anhydrous silicates were not found in this MM. Rare magnetite and pyrrhotite

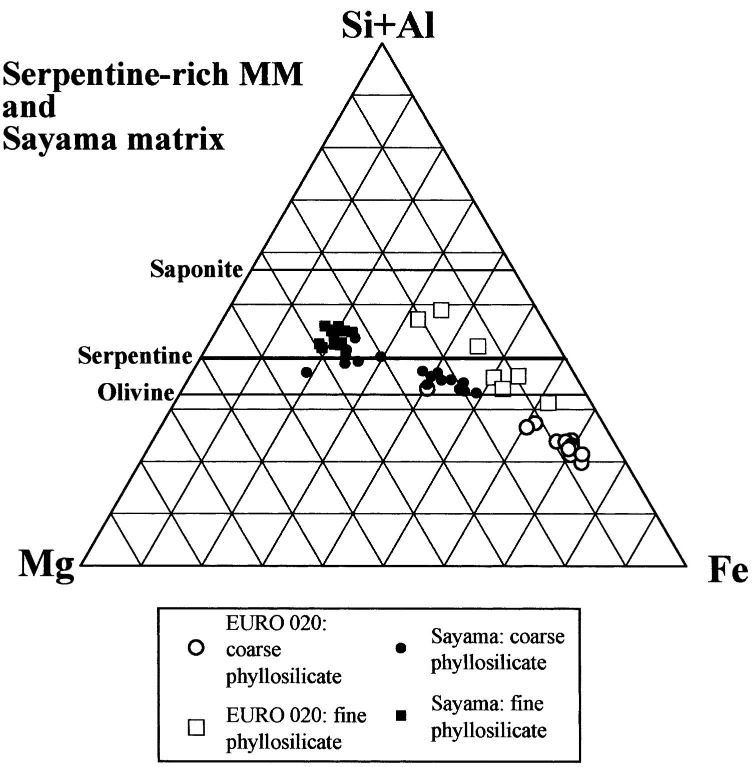

Fig. 9. Chemical compositions of phyllosilicate in the serpentine-rich MM and the matrix of Sayama.

were identified by TEM. Constituent minerals in this MM are displayed in Table 1.

TEM observation of EURO 020 shows that it is composed of coarse-grained (0.1–1 μm across) serpentine crystals that were embedded in very fine-grained serpentine predominant material (Fig. 8a). Magnetite and Fe sulfide grains were rarely encountered during detailed TEM observation of this MM. Fig. 8b displays a typical high-resolution TEM image of the coarse-grained serpentine. EDS analysis of the serpentine indicates that it is cronstedtite. The Mg/(Mg+Fe) atomic ratio of the cronstedtite ranges from 0.08 to 0.18 (Fig. 9). Although its composition is very similar to that in CM chondrites, tochilinite does not coexist with cronstedtite. On the other hand, high-resolution TEM imaging, SAED and EDS analysis show that the very fine-grained serpentine has low crystallinity, is much more heterogeneous in Mg/(Mg+Fe) ratios (0.10–0.39) and contains more Si+Al than the coarse cronstedtite (Fig. 9). Anhydrous silicates such as olivine were not observed by TEM.

We compared the bulk mineralogy of the serpentine-rich MM with that of the matrix in a heavily altered CM chondrite, Sayama [13]. An SR-XRD spectrum of the matrix shows that it contains abundant serpentine and no detectable saponite. Sharp diffraction peaks of serpentine are found as in the serpentine-rich MM. The serpentine in the matrix of Sayama has an average basal spacing (0.722 nm) as large as that of normal serpentine, indicative of more magnesian composition than serpentine in the MM (Fig. 7b). A (02*l*) prism diffraction was also observed. Major minerals identified by SR-XRD are serpentine, pentlandite and magnetite. Diffraction peaks due to tochilinite were not observed. Relict anhydrous silicates were not identified by SR-XRD. Fe sulfide was found only by TEM. The mineralogy of the Sayama matrix is shown in Table 1.

TEM imaging shows that the matrix of Sayama also consists of coarse-grained (0.3–4 μm across) serpentine and fine-grained serpentine that fills the interstices with the coarse serpentine (Fig. 8c,d). Fine-grained (< 200 nm across) pentlandite, magnetite, pyrrhotite and chromite were also observed. EDS data of the coarse serpentine in Sayama show that it is Fe-rich (Fig. 9); the Mg/(Mg+Fe) atomic ratio varies from 0.20 to 0.58. Fine serpentine has low crystallinity and is more magnesian within a Mg/(Mg+Fe) ratio varying from 0.55 to 0.72 (Fig. 9). Tochilinite was not found in the matrix. Constituent minerals and texture are very similar between the serpentine-rich MM and the matrix of Sayama although the chemical composition of serpentine is different.

4. Discussion

4.1. Population of phyllosilicate-rich MMs after atmospheric entry

The population of phyllosilicate-rich MMs is about 0.4% in our study. Even if we missed some phyllosilicate-rich MMs during hand picking, the population of such MMs could not greatly exceed 1%. Calculations of the peak temperature during atmospheric entry have been performed before (e.g. [18–20]). Even particles as small as 50 μm (density of 2.0 g/cm^3) entering the Earth's atmosphere at 10 km/s and at a 45° entry angle will be heated to 900°C for a few seconds [19]. Based on our and previous heating experiments [21], it is likely that peak temperatures experienced by the magnesiowüstite-bearing saponite-rich MMs were around 700°C for flush heating. The peak temperature decreases only if such small particles enter at shallower angles [18,22]. Because such particles are thought to be a minority among particles entering the Earth's atmosphere from any direction, the scarcity of phyllosilicate-rich MMs in our study is consistent with these calculations.

4.2. Mineralogy of saponite-rich MMs and comparison to the matrix of Tagish Lake

Our heating experiments strongly suggest that before Earth entry the magnesiowüstite-bearing saponite-rich MMs were composed of saponite, magnetite, magnesite, siderite and pyrrhotite. The estimated mineral assemblage and microstructure of matrices are very similar to that of the matrix of the Tagish Lake carbonate-rich lithology. On the other hand, M240U066 does not contain fine-grained aggregates composed of decarbonation products of Mg- and Fe-carbonate. Rather it contains abundant aggregates of magnetite framboids (Fig. 2c), as in the case of the saponite-rich MM 91/3-103 [3]. The Fe-rich clasts in Tagish Lake investigated in this study also contain abundant magnetite framboids. The clasts are probably fragments of Tagish Lake carbonate-poor lithology based on their mineralogies [16]. The mineralogy of the framboidal magnetite-bearing saponite-rich MMs resembles that in the Tagish Lake carbonate-poor lithology except for magnesian siderite (or its thermally altered equivalent) that often fills the cracks and veins. The MM is more similar to that of the Fe-rich clasts than that of the Semarkona LL3.0 matrix, which does not contain framboidal and plaquette magnetite [3]. These data suggest that both types of saponite-rich MMs were derived from parent bodies that have very similar mineralogy to that of Tagish Lake carbonaceous chondrite.

The reflectance spectra of bulk Tagish Lake are very similar to those of some D-type asteroids [23]. Because D-type asteroids are situated predominantly in the outer asteroid belt, it is reasonable that large fragments of D-type asteroids will rarely fall to the Earth, but that some of the dust derived from D-type asteroids may reach the Earth as fine-grained material by Poynting–Robertson drag instead. The idea that the saponite-rich MMs are fine-grained debris of D-type asteroids must be evaluated by measuring the reflectance spectra of the saponite-rich MMs.

4.3. Decarbonation of Mg- and Fe-carbonates in the saponite-rich MMs, and comparison with IDPs

Some IDPs (both anhydrous and hydrous) also contain siderite and magnesite as in the two saponite-rich MMs in this study. Among them, L2005 Q6 and Calrissian are saponite-rich IDPs [24,25]. Major minerals in L2005 Q6 are saponite, pyrrhotite, magnetite, magnesite and siderite. The mineral assemblage of this IDP is very similar to the estimated mineral assemblage of the MMs before atmospheric entry (see Section 3.4). However, morphologies of magnesite and siderite in this IDP are anhedral [24], different from those in the MMs. On the other hand, breunnerite crystals in Calrissian IDP are similar in size and morphology to pseudomorphic magnesiowüstite and magnetite aggregates (Fig. 5), although this IDP contains rare olivine and pyroxene as well as the minerals found in the MMs and the IDP L2005 Q6 [25]. These data indicate that there are planetary materials including very similar major minerals. However, these planetary materials were probably derived from plural asteroids because there are also differences in relative abundances and textures of major minerals and in accessory minerals.

Transformation to periclase (magnesiowüstite) or to magnetite from Mg- and Fe-carbonate depends on peak temperature, duration of heating, fO_2 (effective fO_2 changes as the speed of the MM changes) and chemical composition of carbonate. The decomposition temperature of the carbonate depends on its chemical composition (about 475°C for siderite and >600°C for magnesite [26]). The experimental data indicate that siderite and magnesite were separately decomposed into magnetite and magnesiowüstite during atmospheric entry heating. This idea is supported by the fact that the SAED patterns show that the major mineral in the pseudomorphic aggregates changes from magnesiowüstite to magnetite at around 0.2 Mg/(Mg+Fe) ratio (Fig. 4).

4.4. Comparison between a serpentine-rich MM and Sayama and the origin of serpentine-rich MMs

The serpentine-rich MM EURO 020 and the matrix of Sayama CM2 chondrite that experienced heavy aqueous alteration have very similar microstructures and major mineral combinations (Figs. 7–9). These similarities support the view that the serpentine-rich MM has an affinity with CM chondrites. Both coarse- and fine-grained serpentines in the MM are more ferroan than those in the matrix of Sayama (Fig. 9). Because carbonaceous chondrites that experienced severer aqueous alteration contain less ferroan phyllosilicates than those that experienced weaker aqueous alteration [27], the degree of aqueous alteration of the MM is weaker than that of Sayama.

Among IDPs, a serpentine-bearing IDP RB12-A44 has a direct link to CM chondrites because it contains tochilinite [28]. Although tochilinite does not coexist with cronstedtite in the MM, the absence may have resulted from heating in the atmosphere. Because tochilinite decomposes at slightly lower temperatures (about 450°C) than cronstedtite by heating [29,30], it cannot be ruled out that tochilinite was preferentially decomposed to Fe sulfide during heating upon atmospheric entry.

Although we discovered three saponite-rich MMs, we found only one serpentine-rich MM. Because the decomposition temperature of serpentine is lower than that of saponite [31], it is plausible that more saponite-rich MMs can survive atmospheric entry heating compared with serpentine-rich MMs if there is no mineralogical bias among these phyllosilicate-rich MMs before entering the Earth.

4.5. MMs as extraterrestrial materials complementary to meteorites

Texture and mineralogy of MMs that preserve pristine mineralogy are basically similar to those of IDPs [2]. This study also supports that MMs have more features in common with IDPs than with meteorites except for a few rare ones. Because MMs as well as IDPs are more unbiased samples of asteroids, abundant cosmic dust comes from asteroids having mineralogy similar to that of saponite-rich MMs (D-type?) and serpentine-rich ones (probably C-type). One the other hand, meteorites come from the asteroids by the Kirkwood gaps, where these types of asteroids are minor. Therefore, MMs as well as IDPs are extraterrestrial materials bringing their unique information on the formation and evolution of their parent asteroids, and are complementary to meteorites. The variation on mineralogy of MMs and IDPs suggests the diversity of their sources in the recent 10^6 yr (lifetime of typical cosmic dust [32]) in the Solar System.

5. Conclusions

We sought phyllosilicate-rich MMs among more than 1000 unmelted MMs, 40–100 μm in size, collected in Antarctica. Only four MMs were found that contained abundant phyllosilicates. The other MMs contain little or no phyllosilicates. The abundance of phyllosilicate-rich MMs in the total MMs investigated must not exceed 1%. The phyllosilicate-rich MMs are three saponite-rich MMs and a serpentine-rich one. Two saponite-rich MMs among the three contain magnesiowüstite-bearing aggregates. Their mineralogy, texture and chemical composition as well as the results of heating experiments on the matrix of the carbonate-rich lithology of Tagish Lake suggest that their precursor mineral is Mg- and Fe-rich carbonate. The mineral assemblage and texture of the matrices of serpentine-rich MM and the Sayama CM chondrite that experienced heavy aqueous alteration are also very similar to each other, although the chemical composition of serpentine in the MM suggests that the degree of aqueous alteration of the MM is lower than that of the Sayama CM chondrite.

Acknowledgements

We thank Drs. H. Kojima, M. Maurrette, M.E. Zolensky, and S. Yoneda for giving us specimens of MMs, Tagish Lake and Sayama. We also thank Dr. M. Tanaka and Mr. T. Mori for technical support during X-ray diffraction analysis at the Institute of Materials Structure Science, High Energy Accelerator Research Organization. We thank Prof. N. Takaoka for his encouragement to investigate MMs. Prof. H. Nagahara is appreciated for her permission to use an electric furnace for preliminary heating experiments of Tagish Lake. Dr. T. Yada, Ms. N. Matsumoto and Messrs. J. Kamata and Y. Uryu are also appreciated for their endeavor to seek phyllosilicate-rich MMs with us. We also thank Dr. M.E. Zolensky and an anonymous reviewer for their constructive comments. This study is partially supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (no. 11440163: principal investigator (PI), H. Kojima; no. 13440158: PI, T. Noguchi, and no. 13740318: PI, T. Nakamura). ***[BOYLE]***

References

[1] G. Kurat, C. Koeberl, T. Piresper, F. Brandstätter, M. Maurette, Petrology and geochemistry of Antarctic micrometeorites, Geochim. Cosmochim. Acta 58 (1994) 3879–3904.

[2] T. Nakamura, T. Noguchi, T. Yada, Y. Nakamuta, N. Takaoka, Bulk mineralogy of individual micrometeorites determined by X-ray diffraction analysis and transmission electron microscopy, Geochim. Cosmochim. Acta 65 (2001) 4385–4397.

[3] W. Klöck, F.J. Stadermann, Mineralogical and chemical relationships of interplanetary dust particles, micrometeorites, and meteorites, in: M.E. Zolensky, T.L. Wilson, F.J.M. Rietmeijer, G.J. Flynn (Eds.), Analysis of Interplanetary Dust, Am. Inst. Phys., New York, 1994, pp. 51–87.

[4] T. Noguchi, T. Nakamura, Mineralogy of Antarctic micrometeorites recovered from the Dome Fuji Station, Antarct. Meteor. Res. 13 (2000) 285–301.

[5] T. Noguchi, T. Nakamura, Mineralogy of phyllosilicate-rich micrometeorites and comparison with Tagish Lake CI and Sayama CM chondrites, Lunar Planet. Sci. Conf. XXXII (2001) 1541–1542.

[6] M.J. Genge, J.P. Bradley, C. Engrand, M. Gounelle, R.P. Harvey, M.M. Grady, The petrology of fine-grained micrometeorites: Evidence for the diversity of primitive asteroids, Lunar Planet. Sci. Conf. XXXII (2001) 1546–1547.

[7] K. Tomeoka, P.R. Buseck, Matrix mineralogy of the Orgueil CI carbonaceous chondrite, Geochim. Cosmochim. Acta 52 (1988) 1627–1640.

[8] A.J. Brearley, Mineralogy of fine-grained matrix in the Ivuna CI carbonaceous chondrite, Lunar Planet. Sci. Conf. XXIII (1992) 153–154.

[9] K. Tomeoka, P.R. Buseck, Phyllosilicates in the Mokoia CV carbonaceous chondrite: Evidence for aqueous alteration in an oxidizing condition, Geochim. Cosmochim. Acta 54 (1990) 1787–1796.

[10] C.M.O'D. Alexander, D.J. Barber, R. Hutchison, The microstructure of Semarkona and Bishunpur, Geochim. Cosmochim. Acta 53 (1989) 3045–3057.

[11] M.K. Weisberg, M.E. Zolensky, M. Prinz, Fayalitic olivine in matrix of the Krymka LL3.1 chondrite: Vapor-solid growth in the solar nebula, Meteorit. Planet. Sci. 32 (1997) 791–801.

[12] P.G. Brown, A.R. Hildebrand, M.E. Zolensky, M. Grady, R.N. Clayton, T.K. Mayeda, E. Tagliaferri, R. Spalding, N.D. MacRae, E.L. Hoffman, D.W. Mittlefehldt, J.F. Wacker, J.A. Bird, M.D. Campbell, R. Carpenter, H. Gingerich, M. Glatiotis, E. Greiner, M.J. Mazur, P.J.A. McCausland, H. Plotkin, T.R. Mazur, The fall, recovery, orbit, and composition of the Tagish Lake Meteorite: A new type of carbonaceous chondrite, Science 290 (2000) 320–324.

[13] S. Yoneda, M. Ebihara, Y. Oura, A. Okada, M. Kusakabe, T. Nakamura, K. Nagao, H. Naraoka, Sayama Meteorite: A new CM chondrite fall in Japan with highly aqueously altered textures, Lunar Planet. Sci. Conf. XXXII (2001) 2034–2035.

[14] N. Takaoka, T. Nakamura, T. Noguchi, E. Tonui, M. Gounelle, M.E. Zolensky, N. Ebisawa, T. Osawa, R. Okazaki, K. Nagao, S. Yoneda, Sayama CM2 chondrite: Fresh but heavily altered, Lunar Planet. Sci. Conf. XXXII (2001) 1645–1646.

[15] W. Nozaki, T. Nakamura, T. Noguchi, N. Takaoka, D-type asteroids as a possible parental object of micrometeorites: Experimental reproduction of micrometeorites from Tagish Lake carbonaceous chondrites, Meteorit. Planet. Sci. 36 (2001) A150–A151.

[16] M. Gounelle, M.E. Zolensky, E. Tonui, T. Mikouchi, Mineralogy of Tagish Lake, a unique type 2 carbonaceous chondrite, Lunar Planet. Sci. Conf. XXXII (2001) 1616.

[17] T. Nakamura, T. Noguchi, M.E. Zolensky, N. Takaoka, Noble gas isotopic signatures and X-ray and electron diffraction characteristics of Tagish Lake carbonaceous chondrite, Lunar Planet. Sci. Conf. XXXII (2001) 1621–1622.

[18] S.G. Love, D.E. Brownlee, Heating and thermal transformation of micrometeoroids entering the Earth's atmosphere, Icarus 89 (1991) 26–43.

[19] S.G. Love, D.E. Brownlee, Peak atmospheric entry temperatures of micrometeorites, Meteoritics 29 (1994) 69–70.

[20] T. Yada, T. Nakamura, M. Sekiya, N. Takaoka, Formation processes of magnetic spherules collected from deep-sea sediments – Observations and numerical simulations of the orbital evolution, Proc. NIPR Symp. Antarct. Meteor. 9 (1996) 218–236.

[21] A. Greshake, W. Klöck, P. Arndt, M. Maetz, G.J. Flynn, S. Bajt, A. Bischoff, Heating experiments simulating atmospheric entry heating of micrometeorites: Clues to their parent body sources, Meteorit. Planet. Sci. 33 (1998) 267–290.

[22] G.J. Flynn, Atmospheric entry heating of micrometeorites, Proc. 19th Lunar Planet. Sci. Conf. (1989) 673–682.

[23] T. Hiroi, M.E. Zolensky, C.M. Pieters, The Tagish Lake meteorite, a possible sample from a D-type asteroid, Science 293 (2001) 234–235.

[24] M.E. Zolensky, D.J. Lindstrom, Mineralogy of 12 large 'chondritic' interplanetary dust particles, Proc. Lunar Planet. Sci. Conf. 22 (1992) 161–169.

[25] K. Tomeoka, P.R. Buseck, A carbonate-rich, hydrated, interplanetary dust particle: Possible residue from protosolar clouds, Science 231 (1986) 1544–1546.

[26] D.C. Golden, D.W. Ming, C.S. Schwandt, H.V. Lauer Jr., R.A. Socki, R.V. Morris, G.E. Lofgren, G.A. McKay, A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteorite ALH84001, Am. Mineral. 86 (2001) 370–375.

[27] M.E. Zolensky, T. Barrett, L. Browning, Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites, Geochim. Cosmochim. Acta 57 (1993) 3123–3148.

[28] J.P. Bradley, D.E. Brownlee, An interplanetary dust particle linked directly to type CM chondrites and an asteroidal origin, Science 251 (1991) 549–552.

[29] S. Caillère, S. Hénin, The chlorite and serpentine minerals, in: The Differential Thermal Investigation of Clays, Chapter VIII, Alden Press, Oxford, 1957, pp. 207–230.

[30] J.L. Gooding, M.E. Zolensky, Thermal stability of tochilinite, Lunar Planet. Sci. Conf. XVIII (1987) 343–344.

[31] J. Akai, TTT-diagram of serpentine and saponite, and estimation of metamorphic heating degree of Antarctic carbonaceous chondrites, Proc. NIPR Symp. Antarct. Meteor. 5 (1992) 120–135.

[32] S.F. Dermott, K. Grogan, D.D. Durda, S. Jayaraman, T.J.J. Kehoe, S.J. Kortenkamp, M.C. Wyatt, Orbital evolution of interplanetary dust, in: E. Grün, B.A.S. Gstafson, S.F. Dermott, H. Fechtig (Eds.), Interplanetary Dust, Springer, Berlin, 2001, pp. 569–639.