Bulk mineralogical changes of hydrous micrometeorites during heating in the upper atmosphere at temperatures below 1000 °C

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Abstract—Small particles 200 μm in diameter from the hydrous carbonaceous chondrites Orgueil CI, Murchison CM2, and Tagish Lake were experimentally heated for short durations at subsolidus temperatures under controlled ambient pressures in order to examine the bulk mineralogical changes of hydrous micrometeorites during atmospheric entry. The three primitive meteorites consist mainly of various phyllosilicates and carbonates that are subject to decomposition at low temperatures, and thus the brief heating up to 1000 °C drastically changed the mineralogy. Changes included shrinkage of interlayer spacing of saponite due to loss of molecular water at 400–600 °C, serpentine and saponite decomposition to amorphous phases at 600 and 700 °C, respectively, decomposition of Mg-Fe carbonate at 600 °C, recrystallization of secondary olivine and Fe oxide or metal at 700–800 °C, and recrystallization of secondary low-Ca pyroxene at 800 °C. The ambient atmospheric pressures controlled species of secondary Fe phase: taenite at pressures lower than 10−2 torr, magnesiowüstite from 10−3 to 10−1 torr, and magnetite from 10−2 to 1 torr. The abundance of secondary low-Ca pyroxene increases in the order of Murchison, Orgueil, and Tagish Lake, and the order corresponds to saponite abundance in samples prior to heating. Mineralogy of the three unmelted micrometeorites F96CI024, kw740052, and kw740054 were investigated in detail in order to estimate heating conditions. The results showed that they might have come from different parental objects, carbonate-rich Tagish Lake type, carbonate-poor Tagish Lake or CI type, and CM type, respectively, and experienced different peak temperatures, 600, 700, and 800–900 °C, respectively, at 60–80 km altitude upon atmospheric entry.

INTRODUCTION

Micrometeorites are extraterrestrial material accreting to the Earth with sizes typically ranging from 50 to 100 μm, but occasionally up to several hundred micrometers. During accretion and with few exceptions, they are heated by deceleration in the atmosphere. Considering the difference in micrometeorite accretion rates between at upper atmosphere (Love and Brownlee 1993) and at Antarctic ice fields (e.g., Taylor et al. 1998; Yada et al. 2004), most micrometeorites are evaporated during heating in the atmosphere; only ~10% survive to reach the Earth’s surface. Among the accreted micrometeorites, approximately half are totally melted spherules that have completely lost their preheating mineralogical signatures. The remaining samples are also heated to some extent, but escaped high-temperature heating and form irregularly shaped unmelted or partially melted micrometeorites (e.g., Love and Brownlee 1991, 1994; Maurette et al. 1991). Based on the mineralogy of such weakly heated micrometeorites, we can elucidate the types of parental objects and the formation history of these objects.

Major dust suppliers in the solar system are asteroids and comets, although the ratio of dust from the two sources is under debate (i.e., Kortenkamp and Dermott 1998; Ishimoto 2000). Some unmelted micrometeorites and interplanetary dust particles (IDPs) consist mainly of phyllosilicates and the phyllosilicate mineralogy is basically similar to that of hydrous carbonaceous chondrites such as CI, CM, and Tagish Lake type (e.g., for IDPs, see Bradley and Brownlee 1991 and Rietmeijer 1996; for micrometeorites, see Klöck and Stadermann 1994; Kurat et al. 1994; Nakamura et al. 2001; Noguchi et al. 2002; Nakamura and Noguchi 2004). This suggests that hydrous asteroids are one of parental objects that supply micrometeorites. However, there is no evidence to suggest that hydration in active comets is impossible. In fact, there are observations that a sizeable fraction of CI-like
meteors enter the Earth’s atmosphere on cometary orbits and with cometary velocities (Ceplecha et al. 1998; Rietmeijer 2000). Therefore, the dust-supply contribution from hydrous asteroids to the total micrometeorite accretion is far from known. In addition, phyllosilicates in hydrous particles are decomposed and dehydrated even by heating at low temperature during atmospheric entry. In the present study, a small particle of a hydrous meteorite was heated step-by-step up to 900 or 1000 °C in 100 °C intervals at variable atmospheric pressures. The heating duration at each temperature was 120 s. At each temperature step, the heated particle was investigated by synchrotron X-ray diffraction method in order to demonstrate the changes of bulk mineralogy of hydrous particles during heating at subsolidus temperature. In addition to stepped heating, one-time 10 s heating was also performed to see effects of short-duration heating.

Bulk mineralogy is an effective measure for characterization of micrometeorites because they are composed of numerous fine mineral particles, mostly submicron in size (e.g., Klöck and Stadermann 1994; Kurat et al. 1994; Engrand and Maurette 1998). Any process such as hydration and heating, and any condition of the process such as oxygen fugacity and temperature, are reflected in bulk mineralogy. Therefore, bulk mineralogy can be used to establish a link between micrometeorites and micrometeorites (Nakamura and Noguchi 2004) and also to clarify the heating conditions of micrometeorites upon atmospheric entry. Some experimental simulations of the atmospheric entry of micrometeorites were already reported to investigate changes of properties other than bulk mineralogy: microtextures and abundances of mobile trace elements (Fraundorf et al. 1982; Klöck and Stadermann 1994; Greshake et al. 1998), IR spectroscopic signatures (Sandford and Bradley 1989), and textures and mineral compositions of spinels in particular (Toppani et al. 2001; Toppani and Libourel 2003). By flash-heating a particle of Murchison CM and Orgueil CI chondrite at controlled ambient pressures, Toppani et al. (2001) reproduced textures very similar to partially or totally melted micrometeorites. Most of the heating runs in Toppani et al. (2001) were conducted at temperatures higher than 1000 °C, while in this study, heating was performed at temperatures lower than 1000 °C. Therefore, the temperature regime in this work is complementary to that in Toppani et al. (2001). We have succeeded in reproducing the bulk mineralogy of unmelted micrometeorites by heating hydrous-chondrite particles at subsolidus temperatures. Mineralogical comparison between experimental products and natural micrometeorites allows us to estimate temperatures and ambient pressures during atmospheric heating of the micrometeorites.

SAMPLES AND EXPERIMENTS

Stepped heating was performed on particles with diameters of ~200 µm that were separated from Orgueil CI and matrix of Tagish Lake and Murchison CM chondrites. The reason we chose these three meteorites as starting materials is that the bulk mineralogical characteristics of phyllosilicate-rich micrometeorites are basically similar to that of these chondrites (Nakamura and Noguchi 2004). Tagish Lake is composed of two representative lithologies: carbonate-rich and carbonate-poor (Zolensky et al. 2002). The former contains small grains of Mg-Fe carbonate in matrix in high density, while the latter does not. Therefore, we performed heating experiments on particles from both lithologies in the case of Tagish Lake. The experimental configuration is shown in Fig. 1. The experiment was carried out using the following procedure: a particle of carbonaceous chondrite was placed in a sample container and the container was set inside a silicon glass tube that was evacuated to keep pressures constant throughout the heating.

Fig. 1. An experimental set-up for heating hydrous carbonaceous chondrites. A small particle approximately 200 µm in diameter was placed on a small sample container made of Si glass, which can slide in and out from an electric furnace using a hand magnet. A Pt-Rh thermocouple was held 2 mm above the sample container. Both the sample and the thermocouple were put inside of silica tube. The silica tube was evacuated using a rotary pump for pressures of 10^{-2} to 1 torr and using both a turbo molecular pump and the rotary pump for 10^{-3} to 10^{-4} torr. The atmospheric pressure was monitored using a pirani vacuum gauge and controlled using a leak valve to keep pressures constant throughout the heating.
inserted into the furnace. The sample particle was heated by radiation from a hot spot of the furnace. After 120 s, the container with the sample particle was pulled out of the furnace in order to cool the particle rapidly. An example of temperature profiles is shown in Fig. 2. The heating experiments were carried out at variable temperatures and ambient atmospheric pressures, as listed in Table 1. An important aspect of this experiment is that a single particle was heated step by step at intervals of 100 or 300 °C (Table 1), so as to follow continuous mineralogical changes of the single particle with increasing temperature. For instance, a particle from carbonate-rich lithology of Tagish Lake meteorite was heated at 400 °C and for 120 s (hereafter 400 °C/120 s), 500 °C/120 s, 600 °C/120 s, 700 °C/120 s, 800 °C/120 s, and 900 °C/120 s. After heating at each temperature, the sample particle was analyzed by synchrotron X-ray diffraction to characterize bulk mineralogy and then it was heated again to a higher temperature.

The stepped heating and the 120 s duration at each temperature step adopted in our experiments is not relevant to the actual heating of micrometeorites in the atmosphere, because the real heating is one time and much shorter duration. Calculations simulating the atmospheric-entry heating indicated that micrometeorites were heated one time for less than 10 s at peak temperature (e.g., Love and Brownlee 1991; Flynn 2001). In order to understand the differences between mineralogical changes induced by long-duration stepped heating and those by short-duration one-time heating, we conducted a brief heating experiment in which a particle from carbonate-poor lithology of Tagish Lake meteorite was heated once at 900 °C for 10 s. The temperature profile of this experiment is given in Fig. 2. The mineralogy of the particle was compared with that of the particle having been heated step-by-step at 400 °C/120 s, 500 °C/120 s, 600 °C/120 s, 700 °C/120 s, 800 °C/120 s, and 900 °C/120 s.

For characterization of the bulk mineralogy of experimentally heated particles and some natural micrometeorites, we utilized synchrotron radiation X-rays at beam line 3A of the Photon Factory Institute of Material Science, High Energy Accelerator Research Organization, Tsukuba, Japan. A particle sample was mounted on a thin glass fiber 5 μm in diameter and exposed to synchrotron X-rays in a Gandolfi camera that gives a powder diffraction pattern of the particle (Nakamura et al. 2001). The X-rays were monochromated to 0.2161 ± 0.0001 nm and concentrated by mirrors to a position of the Gandolfi camera. The X-ray diffraction pattern was recorded on a high-resolution imaging plate (IP) and the pattern was transformed to an 8-bit TIF image by using an IP reader (Fuji film BAS 2500). The ultra-high intensity and well-monochromated synchrotron X-rays allows us to obtain a clear powder X-ray diffraction pattern of each small particle with short exposure of 15–20 min.

Three particles from the carbonate-rich lithology of Tagish Lake, each of which was heated at 500 °C and 10⁻¹ torr, 700 °C and 10⁻² torr, and 900 °C and 10⁻² torr, and a particle of Murchison heated at 1000 °C and 10⁻² torr were observed by a transmission electron microscope (TEM). The former two Tagish Lake samples and the Murchison sample were prepared only for TEM observation, while the latter Tagish Lake sample was analyzed by X-ray diffraction prior to TEM observation (Table 1). The particle samples were embedded in epoxy resin EMbed-812, and 60 to 100 nm sections were microtomed by Leitz-Reichert Super Nova ultramicrotome for TEM observation. The microstructures, mineralogy, and chemical compositions of minerals in samples were obtained by JEOL JEM-2000FX II equipped with EDAX DX4 energy dispersive spectrometer (EDS). A 100 nm beam was used for the analysis of anhydrous silicates and 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 by using ultramicrotomed mineral standards. Because the remainders after ultramicrotomy of each embedded sample have quite flat surfaces, the surfaces of each remainder were coated by carbon and observed by JEOL JSM-6700F FE-SEM.
RESULTS AND DISCUSSION

Bulk Mineralogical Changes of a Tagish Lake Particle from Carbonate-Rich Lithology

Matrix of natural (unheated) Tagish Lake with carbonate-rich lithology consists mainly of saponite and Mg-Fe carbonate with minor amounts of pyrrhotite (Fig. 3) (detailed description of XRD is given in Nakamura et al. 2003). Average Mg/(Mg + Fe) atomic ratio of coarse saponite is 0.79 ± 0.01 and that of Mg-Fe carbonate is 0.39 ± 0.11 (Nakamura et al. 2003). Heating at 10\(^{-2}\) torr and temperatures from 400 to 900 °C with intervals of 100 °C changed the mineralogy drastically (results are shown in Fig. 3). The first change observed is shrinkage of (001) interlayer spacing of saponite at 400 °C and higher temperatures. The spacing reduced from 1.32 nm to 1.06 nm at 600 °C, which resulted from a loss of water molecules having been present between t-o-t layers of saponite (Fig. 4). This water loss from saponite only causes shrinkage along the c-axis and does not bring about other crystallographic changes. Indeed, TEM observation of a sample heated at 500 °C and 10\(^{-1}\) torr showed that saponite exhibits 1.21 nm (001) lattice fringes that indicate slight shrinkage due to a slight depletion of interlayer water molecules (Fig. 5a). On the other hand, serpentine has no molecular water between t-o layers and thus no loss of the water molecules takes place from serpentine, as shown in later in the results of Murchison heating.

The abundance of Mg-Fe carbonate continuously decreases from 400 to 600 °C (Fig. 3). The decomposition temperature of Fe-rich carbonate is lower than that of Mg-rich carbonate, and thus the gradual depletion of the Mg-Fe carbonate can be interpreted to mean that Fe-rich carbonate starts to decompose at 400 °C and Mg-rich carbonate decomposes almost completely at 600 °C. Magnesiowüstite forms at the expense of Mg-Fe carbonate and its X-ray reflections become narrower with increasing temperature, which is suggestive of coarsening of the crystals. The formation of magnesiowüstite was confirmed by TEM observation of two samples heated at 500 and 10\(^{-1}\) torr and 700 °C and 10\(^{-2}\) torr, respectively: the crystal sizes of magnesiowüstite are larger in the 700 °C sample (50–150 nm across) (Fig. 5b) than in the 500 °C sample (5–30 nm across) (Fig. 5c). Some Mg-Fe carbonate grains are decarbonated to magnetite (Fig. 5d), which depends on the FeCO\(_3\) content of the carbonate grains (Noguchi et al. 2002).

Saponite reflections including 001 at 10°, prism at 28–30°, and 300 at 90°, are weakened at 700 °C (Fig. 3), indicating that saponite decomposes to become amorphous at this temperature. Consequently, magnesiowüstite and

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**Table 1. Temperatures and ambient atmospheric pressure during heating of a particle of hydrous carbonaceous chondrite.**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Temperature (°C)</th>
<th>Ambient Pressure (torr)</th>
<th>Method of characterization</th>
</tr>
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<tr>
<td>Tagish Lake carbonate-rich</td>
<td>200</td>
<td>x</td>
<td>SR-XRD(^a)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>x</td>
<td>SR-XRD</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>x</td>
<td>SR-XRD</td>
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<tr>
<td></td>
<td>500</td>
<td>x</td>
<td>SR-XRD</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>1000</td>
<td>x</td>
<td>SR-XRD</td>
</tr>
<tr>
<td>Tagish Lake carbonate-poor</td>
<td>1.5 \times 10^{-2} torr</td>
<td>x</td>
<td>x</td>
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<tr>
<td></td>
<td>1.5 \times 10^{-2} torr</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Orgueil CI</td>
<td>2.5 \times 10^{-4} torr</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>2.0 \times 10^{-3} torr</td>
<td>x</td>
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<td>1.5 \times 10^{-2} torr</td>
<td>x</td>
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<td>x</td>
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<tr>
<td></td>
<td>0.8 torr</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Murchison CM</td>
<td>2.5 \times 10^{-4} torr</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>2.0 \times 10^{-3} torr</td>
<td>x</td>
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<td></td>
<td>1.0 \times 10^{-1} torr</td>
<td>x</td>
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</tr>
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\(^{a}\)SR-XRD = synchrotron X-ray diffraction.

\(^{b}\)Short-duration (10 s) heating.
bulk mineralogical changes of hydrous micrometeorites during upper-atmosphere heating

pyrrhotite are major crystalline phases and the hydrous silicates are mostly amorphous at 700 °C (Fig. 3). TEM observation of a sample heated at 700 °C showed that some parts of saponite survive as poorly crystalline with 0.991 nm (001) lattice fringes (the most dehydrated saponite), but most parts become amorphous (Fig. 5e). At 800 °C, secondary olivine and low-Ca pyroxene crystallizes from amorphous silicates (Fig. 3). At 900 °C, olivine and pyroxene reflections become larger and thinner, suggesting that recrystallization proceeds with an increase of temperature. Crystal sizes of the secondary olivine and pyroxene range from 10 to 50 nm (Fig. 5f). The grain size of the recrystallized secondary olivine is consistent with that of the secondary olivine in natural micrometeorites reported by Flynn et al. (1993) and Klöck and Stadermann (1994). Pyrrhotite abundance decreases at 700 °C, but it continues the presence until 900 °C (Fig. 3).

Heating at lower (10^{-4} and 10^{-3} torr) or higher (10^{-1} and 1 torr) ambient pressures resulted in mineralogical changes similar to heating at 10^{-2} torr (Table 1; Fig. 6). Mg-Fe carbonate decomposes at 600 °C, which is consistent with the temperature, as in the case of 10^{-2} torr heating. But a decomposition product of Mg-Fe carbonate being formed at 600 °C differs according to ambient pressures: magnesiowüstite from 10^{-4} to 10^{-2} torr, magnetite and magnesiowüstite at 10^{-1} torr, and magnetite at 1 torr. At 900 °C (Fig. 6), both saponite and carbonate decompose and the resulting secondary Fe phases are taenite, magnesiowüstite, and magnetite. The difference in the....

Fig. 3. Synchrotron X-ray diffraction patterns showing changes of bulk mineralogy during a stepped heating at 10^{-2} torr of a particle from matrix of Tagish Lake with carbonate-rich lithology.
decomposed products reflects differences in oxygen fugacity during heating. Taenite formed at both $10^{-3}$ and $10^{-4}$ torr (Fig. 6) probably through the following two pathways: 1) from magnesiowüstite by further heating to 900 °C, and 2) from saponite together with formation of secondary olivine and low-Ca pyroxene. This suggests that the final decomposition product of Mg-Fe carbonate in the heating at $10^{-3}$ and $10^{-4}$ torr is taenite, but during decomposition, magnesiowüstite formed as a metastable phase because magnesiowüstite can be formed from the carbonate merely by loss of CO$_2$ without any reduction of Fe$^{2+}$. Small amounts of taenite are also detected in a product heated at 900 °C and $10^{-2}$ torr.

It is worth pointing out that Fe metal forms as taenite, not as kamacite (Fig. 6). Taenite gives only three, albeit strong, reflections in the diffraction angle we detected: 0.208 nm at 63°, 0.180 nm at 74°, and 0.127 nm at 116°. All three reflections are clearly observed in the samples heated at low ambient pressures. Since the metal is a decomposition product of Mg-Fe saponite and Mg-Fe carbonate, both of which contain little Ni (e.g., Nakamura et al. 2003), the secondary Fe metal is expected to occur as kamacite. However, the phase diagram of Fe-Ni alloy (Goldstein and Ogilvie 1965) indicates that taenite is the stable phase at temperature higher than 900 °C irrespective of Ni content. Currently it is uncertain why taenite forms instead of kamacite. We suggest that the presence of abundant taenite in the products heated at 900 °C and pressures lower than $10^{-3}$ torr can be interpreted in the following way: 1) during heating at 900 °C, taenite forms through the decomposition of saponite and carbonate, and 2) the taenite retains its crystallographic structure down to room temperature because of a very fast cooling rate after heating (Fig. 2). Therefore, the presence of taenite suggests that the heating occurs at temperature at 900 °C followed by rapid cooling. In fact, heating at 900 °C and lower pressures also results in formation of abundant taenite in samples of both Orgueil and Murchison, as shown later in this paper.

Heating at higher ambient pressures also produces variable silicates. Secondary silicates that formed by the decomposition of saponite are olivine and low-Ca pyroxene in products heated at pressures from $10^{-4}$ to $10^{-1}$ torr and 900 °C, while those formed in a product heated at 1 torr are quartz and probably laihunite (Fig. 6). Laihunite is known to form during subsolidus oxidation of olivine (Tamada et al. 1983; Kondoh et al. 1985). In contrast to previous studies on laihunite that formed by oxidation of olivine, in this study laihunite forms in the course of decomposition of hydrous silicate saponite (Fig. 6). The laihunite in the particle of Tagish Lake heated at 1 torr (Fig. 6) seems to crystallize from amorphous silicates at 800 °C, because at 700 °C no anhydrous silicates are detected and at 800 °C laihunite starts to form. The laihunite contains appreciable amounts of Mg$^{2+}$ as substitution for Fe$^{2+}$ because X-ray reflections from the laihunite (Fig. 6) appear at slightly higher diffraction angles, and thus with slightly smaller interlayer spacings, than laihunite with no Mg$^{2+}$ (Tamada et al. 1983).

### Bulk Mineralogical Changes of a Tagish Lake Particle from Carbonate-Poor Lithology and an Orgueil Particle

Bulk mineralogy of Tagish Lake matrix from carbonate-poor lithology is similar to that of Orgueil: both consist of saponite, serpentine, and magnetite with minor amounts of Mg-Ca carbonate and pyrrhotite (Figs. 7 and 8). Detailed mineralogy of both meteorites is given in Tomeoka and Buseck (1988) and Zolensky et al. (2002). Integrated
Fig. 5. TEM photomicrographs of ultramicrotomed sections of the matrix of the experimentally heated Tagish Lake meteorite. From (a) to (f), samples were heated, 500, 700, and 900 °C at $10^{-2}$ torr. a) A high-resolution image of phyllosilicate in the matrix heated at 500 °C. The spacing of (001) of saponite is 1.208 nm, slightly shrunk from unaltered spacing. b) An aggregate of fine-grained (50–150 nm in diameter) magnetite $\text{Fe}_3\text{O}_4$ and magnesiowüstite (Mg, Fe)O that was formed by decarbonation of Mg- and Fe-rich carbonate, heated at 700 °C. c) An aggregate of very fine-grained (5–30 nm in diameter) magnesiowüstite formed by decarbonation of Mg- and Fe-rich carbonate, heated at 500 °C. d) An aggregate of very fine-grained (5–30 nm in diameter) magnetite and magnesiowüstite in the same sample shown in (c). e) High-resolution image of phyllosilicate in the matrix heated at 700 °C. The majority of phyllosilicate has lost their sheet-like structure. Where (001) lattice fringes observed, they are shrunk to 0.991 nm, which indicates that the phyllosilicate completely lost their interlayer $\text{H}_2\text{O}$ molecules. f) When heated to 900 °C, the phyllosilicate predominant matrix recrystallized to the fine-grained (10–50 nm across) aggregates of olivine, low-Ca pyroxene, and magnetite.
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intensities of saponite (001) reflection are roughly similar to those of serpentine 001 reflection (Figs. 7 and 8), suggesting that the abundance of the two phyllosilicates is similar in Orgueil and carbonate-poor lithology of Tagish Lake. A minor difference is that Tagish Lake carbonate-poor lithology tends to have slightly higher abundance of saponite than serpentine. Magnetite reflections are very sharp and large in both meteorites; they probably come from framboidal magnetites that occur in abundance in both meteorites (Tomeoka and Buseck 1988; Zolensky et al. 2002). The results of heating particles from the two meteorites are described together in the following section, since they show similar preheating mineralogy and similar heat-induced mineralogical changes.

As in the case of a Tagish Lake particle from carbonate-rich lithology, 100 °C interval step-by-step heating from 400 to 1000 °C at 10⁻² torr was performed for particles of Tagish Lake with carbonate-poor lithology and Orgueil (Figs. 7 and 8). Bulk mineralogy of particles from both meteorites changes greatly. The 001 spacing of saponite is reduced from the unheated sample (1.38 nm) to the one heated to 600 °C (1.23 nm), while (001) spacing of serpentine remains constant at 0.73–0.74 nm (Figs. 7 and 8). This indicates that interlayer molecular waters are derived from saponite by heating, while they are not derived from serpentine because no molecular water is present in serpentine. At 600 °C, serpentine is decomposed. At 700 °C, saponite is almost decomposed and amorphous silicate seems to be dominant (Figs. 7 and 8). Mg-Ca carbonate dolomite is decomposed at 700 °C. Its decomposed products appear at higher temperatures as magnesiowüstite, but CaO lime cannot be detected by X-ray diffraction. Secondary olivine forms at 800 °C and its reflections become well-defined from 800 to 1000 °C due to an increase of crystallinity (Figs. 7 and 8). Transformation of hydrous phases to anhydrous phases such as olivine is therefore almost complete at 800 °C. The temperature is consistent with that reported by Greshake et al. (1998).

Heating at variable ambient pressures from 10⁻⁴ to 1 torr was performed only for Orgueil (Table 1; Fig. 9), because, again, the bulk mineralogy of Orgueil is similar to that of...
Tagish Lake with carbonate-poor lithology. Heating at low pressures ($10^{-4}$ and $10^{-3}$ torr) results in the formation of taenite and magnesiowüstite as secondary Fe phases, while heating at high pressures ($10^{-2}$ and $10^{-1}$ torr) results in the formation of magnesiowüstite and probably magnetite (Fig. 9). The formation of secondary magnetite is difficult to detect due to the presence of abundant primary magnetite. But secondary magnetite is small and low crystalline, which results in broad reflections as is observed at a diffraction angle of 83° for products heated at pressures higher than $10^{-2}$ torr. Heating at the highest pressure of 1 torr produces magnetite as a secondary Fe phase and olivine, quartz, and probably laihunite as secondary silicates (Fig. 9).

**Comparison Between Long-Duration Stepped Heating and Short-Duration One-Time Heating**

The duration of heating in our experiment, 120 s heating pulses, is much longer than the actual heating pulse experienced by micrometeorites on atmospheric entry. In this section, we will explain why the pulse-heating for more than an order-of-magnitude longer than the actual time produces...
results that are relevant to the actual case of micrometeorite heating. For comparison between long-duration stepped heating and short-duration one-time heating, we conducted a heating experiment on a particle from carbonate-poor lithology of Tagish Lake. The particle was heated to $900 \, ^\circ \text{C}$ at $1.5 \times 10^{-2}$ torr and for only $10$ s (the results are shown in Fig. 10) and compared its mineralogy with the particle heated step-by-step at temperatures from $400$ to $900 \, ^\circ \text{C}$ at $1.5 \times 10^{-2}$ torr and for $120$ s at each temperature step ($400 \, ^\circ \text{C}$/120 s, $500 \, ^\circ \text{C}$/120 s, $600 \, ^\circ \text{C}$/120 s, $700 \, ^\circ \text{C}$/120 s, $800 \, ^\circ \text{C}$/120 s, and $900 \, ^\circ \text{C}$/120 s; the results are shown in Fig. 7). The $10$ s heating at peak temperature is similar to the heating duration obtained by computer simulation of atmospheric entry (Love and Brownlee 1991; Flynn 2001).

The comparison indicates that the mineralogies of the two particles heated in different thermal regimes are very similar: saponite and serpentine are completely decomposed, dolomite is decomposed, secondary olivine and pyroxene...
formed, Fe phases are mixtures of taenite, magnetite, and magnesiowüstite, and pyrrhotite survived (Figs. 7 and 10). This demonstrates that bulk mineralogical changes during heating depend largely on heating temperature rather than heating duration. In addition, the growth of secondary minerals during heating is a kinetically controlled process and thus it is expected that a longer heating duration promotes the growth. But the particle heated at 900 °C/10 s gave reflections of secondary olivine and pyroxene much sharper and stronger than the particle heated stepwisely to 800 °C/120 s, but is more similar to the particle heated to 900 °C/120 s (Figs. 7 and 10). This indicates that 100 °C difference in heating.
temperature is more critical to the growth of secondary minerals than one-order-magnitude difference in heating duration. All these experimental facts verify the application of our stepwise heating experiments to the estimation of peak temperatures experienced by micrometeorites during actual atmospheric entry.

The mineralogical changes observed in our long-duration stepped heating experiments are similar to those observed in short duration (10–60 s) heating experiments of Orgueil CI chondrite done by Greshake et al. (1998). They observed onset of phyllosilicate decomposition at 700 °C/20 s and complete of the decomposition at 800 °C/20 s. The temperatures are exactly the same as those observed in our long-duration stepped heating experiments. This coincidence further supports the validity of our experiments to apply actual micrometeorite heating in the atmosphere. Sandford and Bradley (1989) carried out short-duration (12–15 s) heating experiments of Murchison CM chondrite. They used fourier transform infrared spectroscopy to detect hydration bands at 3 and 6 microns. The results showed that dehydration starts at 395 °C; at 825 °C, small amounts of H2O and OH are left in the Murchison sample, which can be interpreted to mean that at 825 °C, phyllosilicates was decomposed but some H2O and OH still remained in the particle. The results are also essentially consistent with those of our experiments.

**Bulk Mineralogical Changes of a Murchison Particle**

Matrix of the unheated Murchison CM chondrite contains serpentine as a dominant phyllosilicate, which is verified by the presence of strong basal reflection of (001) at 0.71 nm (2θ = 18° in Fig. 11) and (002) at 0.36 nm (35°) and prism reflections rising up from 27°. Prism reflections are peculiar to phyllosilicates with heavy stacking disorder along the c-axis. 001 spacing of serpentine (0.71 nm) (Fig. 11) is smaller than that of normal serpentine (0.72 nm), which suggests that some amounts of Si4+ in tetrahedral sites are substituted by Fe3+ to make crosedtite (Wicks and O’Hanley 1991; Nakamura and Nakamuta 1996). The other hydrous phase present is tochilinite (Fig. 11), which consists of 1:1 stacking of brucite (Mg, Fe)(OH)2 and mackinawite FeS layers (Mackinon and Zolensky 1984; Zolensky 1984). Large reflection of (002) at 0.54 nm relative to (001) at 1.08 nm indicates dominant occupancy of Fe2+ in the brucite layer (Nakamura and Nakamuta 1996). In addition to the hydrous phases, magnetite and very small amounts of olivine and low-Ca pyroxene are present in the unheated Murchison particle (Fig. 11).

Heating of a particle of Murchison matrix was performed at temperatures from 200 to 1000 °C at intervals of 100 °C and ambient pressure of 10−2 torr (Fig. 11). Tochilinite is the first mineral decomposed: its abundance reduces at 300 °C and completely disappears at 400 °C. The decomposition temperature is consistent with that reported in Fuchs et al. (1973). Serpentine starts to decompose at 400 °C and completes the decomposition at 600 °C. At 600 °C, amorphous materials, which were formed by the decomposition of serpentine, are dominant. At 700 °C, secondary olivine and magnetite start to form, but they are still low crystalline. The reflections of secondary olivine and magnetite become narrower and larger with increasing temperature, indicating promoting of recrystallization. At 900 °C, magnesiowüstite forms, probably from magnetite by reduction.

TEM observation of a Murchison sample heated at 1000 °C and 10−2 torr shows that silicates are mostly small, equigranular crystals of olivine less than 200 nm in diameter (Fig. 12a). A low-magnification TEM image of the sample shows that there are abundant small vesicles (less than 200 nm in diameter) that were probably formed during dehydration of hydrous phases (Fig. 12b). There are Fe- and S-bearing object and Fe-, Ni-, and S-bearing object. In the former case, only magnetite is identified by selected area electron diffraction (SAED) (Fig. 12c), although S is detected by EDS analysis as well as abundant Fe. In the latter case, only Ni-rich magnetite is identified by SAED, although S is detected by EDS (Fig. 12d). These data suggest that S-bearing material exists as amorphous material that fills the interstices of magnetite. Magnetite with S-bearing amorphous materials is probably a decomposition product of tochilinite. There are olivine crystals that contain lamellar or breb-like magnetite (Fig. 12e). The SAED pattern of the olivine shows that (100)_{olivine} is parallel to (111)_{magnetite}, which indicates that oxygen packing planes are common to both of the minerals. The olivine with abundant lamellar or breb-like magnetite was originally coarse Fe-rich serpentine that topotactically decomposed into these minerals during heating.

Variations of secondary Fe phases and silicates among Murchison samples heated at different ambient pressures are similar to those of other meteorites. Heating at lower ambient pressures of 10−4 and 10−3 torr produces Fe metal taenite and magnesiowüstite as secondary Fe phases, while heating at elevated ambient pressures produces magnetite and magnesiowüstite for 10−2 torr and magnetite for 10−1 torr (Fig. 13).

Overall results of bulk mineralogical changes in Murchison during heating are consistent with those of Akai (1992), who heated a powder of Murchison CM chondrite at variable temperatures of 250–1100 °C for long durations of 1–350 h under vacuum condition of 10−4 to 10−3 torr, with an aim to construct the T-T-T diagram of CM serpentine. Experimentally heated Murchison samples were investigated by TEM and the results showed that below 300 °C no phase change was observed, at 300–500 °C serpentine starts decomposition and transitional structure between serpentine and olivine appears, and at 500–750 °C olivine starts to crystallize and becomes more crystalline with increasing temperature.
Application to Micrometeorite Bulk Mineralogy

Conditions of heating, temperature, and ambient pressure of hydrous micrometeorites can be estimated based on the results of our experiments. Since our experiments were carried out at relatively low temperatures, the results can apply only to thermal regime of unmelted, nonvesicular micrometeorites that experienced heating at temperatures lower than the melting point. Our results suggest that many primary phases in hydrous micrometeorites such as phyllosilicates and carbonates decompose at relatively low temperatures. Decomposition of hydrous phases occurs at 400 °C for tochilinite, 600 °C for serpentine, and 700 °C for saponite, while that of carbonate takes place at temperatures from 500 to 600 °C for Mg-Fe carbonate and 700 °C for Mg-Ca carbonate. Subsequent to decomposition of the primary phases, many secondary phases such as olivine, pyroxene, and Fe metal or oxides start to form. But it is important to note that at an intermediate temperature between primary-phase decomposition and secondary-phase recrystallization, low-crystalline amorphous materials dominate hydrous meteorites. The temperatures are 600 °C for Murchison and 700 °C for both Orgueil and Tagish Lake. The secondary phases then form at the expense of the amorphous materials. The secondary silicates are mostly olivine and their crystallinity increases with increasing temperatures.
Fig. 12. TEM photomicrographs of ultramicrotomed sections of fine-grained matrix of Murchison meteorite experimentally heated at 1000 °C and 10⁻² Torr. a) A secondary olivine formed by decomposition of serpentine. b) A low-magnification image of the sample. There are many vesicles among the recrystallized matrix. The matrix is composed of coarse (100–300 nm across) olivine and magnetite embedded in glass. Wavy cracks running from lower left to upper right are artifacts during ultramicrotomy. Pore spaces (indicated by arrows) are present prior to the ultramicrotomy, because they are filled with epoxy resin. c) Magnetite probably formed by the decomposition of troilite. Troilite was not found around this crystal, although a small amount of S was detected by EDS. d) Fe-, Ni-, and S-bearing objects where only Ni-rich magnetite is identified by selected area electron diffraction, although S is detected by EDS (inset). e) An olivine single crystal containing elongated magnetite almost parallel to the b-axis. SAED pattern of the olivine and magnetite inclusions shows that (111) planes of all the magnetite inclusions are parallel to the (100) of olivine. It was probably formed by decomposition of tochilinite or Fe-rich serpentine.
Secondary low-Ca pyroxene is detected in abundance in the heated samples of Tagish Lake with carbonate-rich lithology (Fig. 3) that were rich in saponite prior to heating. It is known that the decomposition product of saponite is low-Ca pyroxene (e.g., Akai 1992), while that of serpentine is olivine (e.g., Hiroi and Zolensky 1999). Therefore, the formation of abundant secondary low-Ca pyroxene in Tagish Lake with carbonate-rich lithology is ascribed to the high abundance of saponite prior to heating.

Our experiments produced a variety of secondary Fe phases such as metal, magnesiowüstite, and magnetite, depending on the ambient atmospheric pressures. Taenite is abundantly produced in experimental products heating at $10^{-3}$ and $10^{-4}$ torr (Figs. 6, 9, and 13). On the other hand, magnetite and magnesiowüstite are common Fe phases and metal is minor in micrometeorites (Nakamura et al. 2001), indicating that heating of micrometeorites took place at atmospheric pressures of $10^{-2}$ torr or higher. Heating at 1 torr in our experiments produces laihunite, which has never been detected in micrometeorites. This suggests that atmospheric pressures are lower than 1 torr. Laihunite is therefore a good measure of oxygen fugacity during decomposition of phyllosilicates together with secondary Fe phases. The occurrence of secondary Fe phases and silicates is consistent with the results of our heating experiments at atmospheric pressures from $10^{-2}$ to $10^{-1}$ torr. This pressure range corresponds to 60–80 km altitude and at this altitude most micrometeorites have experienced the highest temperature.

We have characterized in detail three unmelted, nonvesicular micrometeorites recovered from Antarctica (Nakamura et al. 1999; Yada and Kojima 2000), by SEM/EDS and synchrotron X-ray diffraction. Nonvesicular micrometeorites are those that are free of gas bubbles because of low-temperature heating upon atmospheric entry (Genge et al. 1997). Therefore, bulk mineralogical and textural features of the three micrometeorites are well explained by comparison to the results of our experiments. F96CI024 (Fig. 14a) is a fine-grained micrometeorite with skeletal crystals of magnetite. It consists of saponite, magnetite, magnesiowüstite, and pyrrhotite (Fig. 14b). Detailed mineralogy of this micrometeorite was already reported in Noguchi et al. (2002). The diffraction pattern (Fig. 14b) is very similar to that of Tagish Lake with carbonate-rich lithology that was heated to 600 °C and

![Fig. 13. Synchrotron X-ray diffraction patterns showing the bulk mineralogy of a particle from Murchison matrix heated to 900 °C and atmospheric pressures of $10^{-4}$, $10^{-3}$, $10^{-2}$, and $10^{-1}$ torr.](image)
at $10^{-2}$ or $10^{-1}$ torr (Fig. 3). At 600 °C, saponite survives but its 001 basal spacing is shrunk, while the large amounts of magnesiowüstite are formed by decomposition of carbonates. Therefore, this micrometeorite is consistent with an origin from a Tagish Lake–type asteroid and heating to 600 °C at 60–80 km altitude upon atmospheric entry. The result confirms the interpretation given in Noguchi et al. (2002).

Kw740052 is also a fine-grained nonvesicular micrometeorite that contains frambooidal magnetite. The occurrence of bundles of fibrous materials in submicron size suggests the presence of abundant phyllosilicates (Fig. 15a). However, the X-ray diffraction pattern (Fig. 15b) indicates that crystalline phases of the micrometeorites are only magnetite and neither phyllosilicates nor secondary anhydrous silicates are detected: amorphous material dominates the micrometeorite. Therefore, the bundles of fibrous materials are apparently decomposed phyllosilicates.

Fig. 14. Antarctic micrometeorite F96CI024. a) A backscattered electron (BSE) image indicating the presence of abundant magnetite in dark gray fine-grained phyllosilicates. b) A synchrotron X-ray diffraction pattern showing that the micrometeorite consists of saponite, pyrrhotite, magnetite, and magnesiowüstite.
The X-ray diffraction pattern of the micrometeorite (Fig. 15b) is very similar to that of Orgueil or Tagish Lake with carbonate-poor lithology heated to 700 °C at 10^{-2} or 10^{-1} torr (Figs. 7 and 8).

The last micrometeorite is kw740054, which is also classified to nonvesicular type (Fig. 16a). Compact fibrous materials occur in an entire region of this micrometeorite, which again indicates the presence of abundant phyllosilicates. X-ray diffraction analysis indicates that olivine and magnetite are major phases and no phyllosilicates are detected (Fig. 16b). The olivine and magnetite are low crystalline because their reflections are broad. This suggests that they are secondary phases recrystallized from decomposed hydrous phases. The lack of sharp reflections of primary magnetite suggests that the micrometeorite is a piece of neither Orgueil nor Tagish Lake with carbonate-poor lithology. The lack of abundant magnesiowüstite suggests that the micrometeorite is not a decomposed product of Tagish Lake with carbonate-rich lithology. The presence of abundant secondary olivine and minor amounts of secondary low-Ca pyroxene suggests that pre-heated mineralogy of this micrometeorite would have been dominated by serpentine. Therefore, the best candidate for the micrometeorite prior to heating is a hydrous particle whose mineralogy is similar to CM carbonaceous chondrites. The X-ray diffraction pattern of this micrometeorite (Fig. 16b) is similar to that of a Murchison particle heated to temperatures of 800 and 900 °C at 10^{-2} or 10^{-1} torr (Figs. 11 and 13).
In summary, on the basis of bulk mineralogical changes observed during experimental brief heating of various hydrous carbonaceous chondrites at variable atmospheric pressures, heating conditions of unmelted, nonvesicular micrometeorites are successively evaluated. Three micrometeorites, F96CI024, kw740052, and kw740054, which now consist of shrunk phyllosilicates, amorphous materials, or low-crystalline anhydrous phases, respectively, are identified as heated hydrous micrometeorites. They might have come from different parental objects, carbonate-rich Tagish Lake type, carbonate-poor Tagish Lake or CI type, and CM type, respectively, and experienced different peak temperatures, 600, 700, and 800–900 °C, respectively, at 60–80 km altitude upon atmospheric entry.

Fig. 16. Antarctic micrometeorite kw740054. a) A whole view of the micrometeorite showing that compact, fibrous phyllosilicates-like materials are dominant. BSE image. b) A synchrotron X-ray diffraction pattern showing that the micrometeorite consists of olivine, magnetite, and low-Ca pyroxene. No phyllosilicates are detected.
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