Variation of mineralogy and organic material during the early stages of aqueous activity
recorded in Antarctic micrometeorites

T. Noguchi^{1*}, H. Yabuta², S. Itoh³, N. Sakamoto⁴, T. Mitsunari⁵, A. Okubo⁶, R. Okazaki⁷, T. Nakamura⁸, S. Tachibana⁹, K. Terada², M. Ebihara¹⁰, N. Imae¹¹, M. Kimura⁵, H. Nagahara⁶

¹Faculty of Arts and Science, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

²Department of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka, 560-0043 Japan

³Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University, Kiashirakawa Oiwake-cho Sakyo-ku, Kyoto 606-8052 Japan

⁴Isotope Imaging Laboratory, Creative Research Institution, Hokkaido University, Sapporo, 001-0021 Japan.

⁵College of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan

⁶Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

⁷Department of Earth and Planetary Sciences, Graduate School of Science, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

⁸Department of Earth and Planetary Material Sciences, Faculty of Science, Tohoku University, Aoba Sendai, Miyagi 980-8578 Japan

⁹Department of Natural History Sciences, Hokkaido University, N10W8, Sapporo 060-0810, Japan

¹⁰Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji-shi, Tokyo 192-0397, Japan

¹¹National Institute of Polar Research 10-3, Midori-cho, Tachikawa-shi, Tokyo 190-8518, Japan

*Corresponding author: tnoguchi@artsci.kyushu-u.ac.jp

Revised version

Abstract

Micrometeorites (MMs) recovered from surface snow near the Dome Fuji Station, Antarctica are almost free from terrestrial weathering and contain very primitive materials, and are suitable for investigation of the evolution and interaction of inorganic and organic materials in the early solar system. We carried out a comprehensive study on seven porous and fluffy MMs [four Chondritic porous (CP) MMs and three fluffy fine-grained (Fluffy Fg) MMs] and one fine-grained type 1 (Fg C1) MM for comparison with scanning electron microscope, transmission electron microscope, X-ray absorption near-edge structure analysis, and secondary ion mass spectrometer.

They show a variety of early aqueous activities. Four out of the seven CP MMs contain glass with embedded metal and sulfide (GEMS) and enstatite whiskers/platelets and do not have hydrated minerals. Despite the same mineralogy, organic chemistry of the CP MMs shows diversity. Two of them contain considerable amounts of organic materials with high carboxyl functionality, and one of them contains nitrile ($C\equiv N$) and/or nitrogen heterocyclic groups with D and ^{15}N enrichments, suggesting formation in the molecular cloud or a very low temperature region of the outer solar system. Another two CP MMs are poorer in organic materials than the above-mentioned MMs. Organic material in one of them is richer in aromatic C than the CP MMs mentioned above, being indistinguishable from those of hydrated carbonaceous chondrites. In addition, bulk chemical compositions of GEMS in the latter organic poor CP MMs are more homogeneous and have higher Fe/(Si+Mg+Fe) ratios than those of GEMS in the former organic-rich CP MMs. Functional group of the organic materials and amorphous silicate in GEMS in the organic-poor CP MMs may have transformed in the earliest stage of aqueous alteration, which did not form hydrated minerals.

Three Fluffy Fg MMs contain abundant phyllosilicates, showing a clear evidence of aqueous alteration. Phyllosilicates in these MMs are richer in Fe than those in hydrated IDPs, typical fine-grained hydrated (Fg C1) MMs, and hydrated carbonaceous chondrites. One of the Fluffy Fg MMs contains amorphous silicate, which is richer in Fe than GEMS and contains little or no nanophase Fe metal but contains Fe sulfide. Because the chemical compositions of the amorphous silicate are within the compositional field of GEMS in CP IDPs, the amorphous silicate may be alteration products of GEMS. The entire compositional field of GEMS in the CP MMs and the amorphous silicate in the Fluffy Fg MM matches that of the previously reported total compositional range of GEMS in IDPs.

One Fluffy Fg MM contains Mg-rich phyllosilicate along with Fe-rich phyllosilicate and Mg-Fe carbonate. Mg-rich phyllosilicate and Mg-Fe carbonate may have been formed through the reaction of Fe-rich phyllosilicate, Mg-rich olivine and pyroxene, and water with C-bearing chemical species.

These data indicate that CP MMs and Fluffy Fg MMs recovered from Antarctic surface snow contain materials that throw a light on the earliest stages of aqueous alteration on very primitive solar system bodies. Because mineralogy and isotopic and structural features of organic materials in D10IB009 are comparable with isotopically primitive IDPs, its parent body could be comets or icy asteroids showing mass ejection (active asteroids). By contrast, organic-poor CP MMs may have experienced the earliest stage of aqueous alteration and Fluffy Fg MMs experienced weak aqueous alteration. The precursor materials of the parent bodies of Fluffy Fg MMs probably contained abundant GEMS or GEMS-like

materials like CP IDPs, which is common to fine-grained matrices of very primitive carbonaceous chondrites such as CR3s. However, highly porous nature of organic-poor CP MMs and Fluffy Fg MMs suggests that parent bodies of these MMs must have been much more porous than the parent bodies of primitive carbonaceous chondrites. Given no phyllosilicate among the returned samples of 81P/Wild 2 comet, the MMs may have been derived from porous icy asteroids such as active asteroids as well as P- and D-type asteroids rather than comets.

1. Introduction

Chondritic porous interplanetary dust particles (CP IDPs) have been known so far as the most primitive materials, which are tiny (typically 5-15 μm in diameter) fragile aggregates consisting mainly of submicrometer-sized anhydrous constituents, GEMS (glass with embedded metal and sulfide) and enstatite whisker/platelets (e.g., Bradley, 2014). GEMS grains are typically 200-400 nm-sized spheroidal objects composed of amorphous silicate with nm-sized (up to <50 nm) Fe-Ni metal and Fe-Ni sulfide. Enstatite whiskers/platelets are characterized by their elongation along the a-axis, being composed of a unit cell scale mixture of low-Ca clino- and ortho- pyroxene with abundant stacking disorder (e.g., Bradley, 1983; Bradley, 2014). Due to the high abundance of presolar grains (up to ~ 1 vol.%) (Messenger et al., 2003; Busemann et al., 2009), carbon ($\sim 12\%$) (Thomas et al. 1994) and organic materials with high D/H (up to ~ 30000 ‰ δD) and/or $^{15}\text{N}/^{14}\text{N}$ ratios (up to ~ 3000 ‰ $\delta^{15}\text{N}$) (Floss et al., 2004; Busemann et al., 2009; Matrajt et al., 2013), CP IDPs are thought to be derived from comets (e.g., Ishii et al., 2008; Bradley, 2014) or originated in cold interstellar and protosolar environments.

Although most CP IDPs have anhydrous mineralogy, some of them experienced weak aqueous activities and contain phyllosilicate in addition to GEMS and enstatite whiskers (e.g., Germani et al., 1990; Rietmeijer, 1991; Nakamura et al., 2005), which Nakamura et al. (2005) called hybrid IDPs. Nakamura-Messenger et al. (2011) performed aqueous alteration experiments of CP IDPs and showed that phyllosilicate was easily formed during rapid exposure to liquid water at room temperature in alkaline solution. Their experimental results suggest that aqueous alteration could occur even in cometary nuclei, active asteroids (main belt comets), and water ice-bearing asteroids such as 24 Themis (Campins et al., 2010; Rivkin et al., 2010) if liquid water is transiently formed. These bodies are expected to initially be mixtures of anhydrous materials and water ice, and the anhydrous material may have experienced very weak aqueous alteration.

Micrometeorites (MMs) are extraterrestrial materials that are smaller than 2 mm in diameter (Rubin and Grossman, 2010). Antarctic MMs (AMMs) found in Antarctic ice are kept in a frozen environment with little or no terrestrial alteration (Maurette et al., 1991; Taylor et al., 1998; Duprat et al., 2007). They are collected in a clean condition, which is different from IDPs collected in the stratosphere by using silicone grease. A certain fraction of AMMs are ultracarbonaceous (Nakamura et al., 2005; Duprat et al., 2010; Dobrică et al., 2012; Dartois et al. 2013), which is a new type of primitive solar system material. Noguchi et al. (2015) identified AMMs that are porous aggregates of sub- μm sized constituents containing GEMS and enstatite whisker/platelets and are indistinguishable from CP IDPs, and called them CP MMs after CP IDPs.

In the present study, we will give results of mineralogy, organic chemistry, and isotope analysis of highly primitive AMMs including CP MMs, and discuss the interactions among inorganic, organic and water at very low temperatures that took place in ice-bearing solar system bodies.

2. Experimental techniques

2.1 Micrometeorite samples

Since 2003, the National Institute of Polar Research (NIPR) started to sample surface snow near the Dome Fuji Station at ~3,800 m elevation, Antarctica. In 2010, the 51st JARE team sampled ~300 kg of the snow. It was transferred the snow to Japan and further to Ibaraki University in a frozen state, and stored in a deep freezer in a clean room. The snow was melted and filtered with track etched membrane filters (0.2 μm pore diameter), from which fine-grained particles were collected. They were mounted on Pt sheets for scanning electron microscope (SEM) observation, and almost 400 MMs were found. Their morphology and surface textures were observed with a multibeam focused ion beam-scanning electron microscope (FIB-SEM) JEOL JIB-4501 at Ibaraki University at an acceleration voltage of 15 kV and emission current of 5 nA, and bulk chemical compositions were determined with an energy dispersive spectrometer (EDS) JEOL JED-2300 equipped with the focused ion beam (FIB)-SEM calibrated with the Orgueil CI chondrite as the laboratory standard. In addition, a sample embedded in gold was observed with JSM-7000F field emission SEM (FE-SEM) with Oxford INCA EDS at Hokkaido University.

Micrometeorites were selected based on the SEM-EDS data. We eliminated MMs that suggested the presence of magnetite rim on them. Twelve MMs having a rugged surface and a porous and fluffy interior and a MM with smooth surface morphology were selected. The latter was selected for comparison. These MMs were embedded in annealed Au sheet with a hydraulic press in the clean room and coated with carbon, from which ~100 nm-thick FIB sections were prepared with the FIB-SEM. The FIB sections were processed with a low-voltage argon ion milling machine (Fischione Model 1040 NanoMill) operated at 900 and 500 V to remove the damaged layer of the FIB sections formed by 30 kV gallium ion beam bombardment during FIB sample preparation (Bassim et al., 2012).

After XANES analysis, they were observed by transmission electron microscope (TEM). Five MMs were further eliminated. We eliminated MMs that have so-called magnetite rim consisting of Fe-rich olivine and magnetite and/or aggregates of fine-grained (Mg, Fe) oxide. Magnetite rims are often observed on the surface of partially melted (scoriaceous) AMMs (Maurette et al., 1991), which is thought to be formed by recrystallization of glass at the time of atmospheric entry. We eliminated AMMs containing fine-grained aggregates of (Mg, Fe) oxide, which are observed in slightly heated hydrated MMs (Noguchi et al., 2002). The aggregates are formed by decomposition of (Mg, Fe) carbonate during pulse heating during atmospheric entry. We also excluded AMMs showing preferential destruction of serpentine and shrinkage of basal lattice fringes of saponite down to <1 nm. These features suggest moderate heating (400-600 $^{\circ}\text{C}$) during atmospheric entry (Nozaki et al., 2005). Because such heating probably affected composition and structure of organic materials in these MMs, we did not use these MMs in this study. Finally, seven fine-grained MMs with porous morphology, D10IB009, 356, 064, 004, 178, 163, and 017, and one MM with smooth surface morphology, D10IB087, were used in this study.

Two MMs having a rugged surface and a porous and fluffy interior collected from two ~100 kg snow samples collected by the 41st Japan Antarctic Research Expedition (JARE) team in 2003 and by the 43rd Japan Antarctic Research Expedition (JARE) team in 2005 were also used to show their highly porous internal structures and unique mineralogy. To show their internal structure and unique mineralogy, they were embedded in epoxy and ultramicrotomed into slices ~100 nm thick and observed by TEM.

2.2 X-ray absorption near-edge structure spectroscopy

Carbon (C)-, Nitrogen (N)-, and Oxygen (O)- X-ray absorption near-edge structure (XANES) spectra of the FIB sections were acquired using scanning transmission X-ray microscope (STXM) at the beamline 5.3.2.2, Advanced Light Source, Lawrence Berkeley National Laboratory (Kilcoyne et al. 2003). The beamline employs a bending magnet providing a useful photon range spanning approximately 250–800 eV with a flux of 10^7 photons per second. Energy selection on BL5.3.2 is performed with a low dispersion spherical grating monochromator, affording an energy resolution of 5000. C-XANES transmission spectra were obtained in the stack scan mode, with 0.1 eV resolution across the near edge region, and 0.5 eV resolution below and above the near edge absorption. Energy calibration was conducted by measuring CO₂ and N₂ gas prior to the measurements. The absorption spectra (optical density, OD) were obtained as $OD = -\ln(I/I_0)$, where I is an X-ray intensity transmitted from sample and I_0 is that measured without samples (the energy of the incident X-ray). The absorption peak assignment of the XANES spectra was made based on Leinweber et al. (2007) and Cody et al. (2008).

2.3 Transmission electron microscopy

Ultrathin sections of two MMs were observed by JEOL JEM-2000FX TEM equipped with EDAX DX4 energy dispersive spectrometer (EDS) at Ibaraki University. After XANES analysis, the FIB sections were examined with JEM-2100 TEM equipped with Oxford INCA EDS at Ibaraki University and FEI Tecnai 20F TEM equipped with EDAX Exact Genesis EDS at Kyushu University. An image of the entire area of each FIB section was obtained to identify structurally intriguing organic materials. High resolution (HR) TEM, selected area electron diffraction (SAED), and high-angle annular dark-field scanning electron diffraction (HAADF) imaging and EDS were used to characterize minerals in the FIB sections. Quantitative analysis of minerals was performed with EDS equipped on JEM-2000FX and JEM-2100 with mineral standards for the k-factors of elements.

2.4 Secondary ion mass spectroscopy

Isotope imaging was performed for the MMs (except for D10IB009) pressed into gold sheet with Cameca ims-1270-E7 secondary ion mass spectrometer (SIMS) equipped with stacked CMOS-type active pixel sensor (SCAPS) at the Hokkaido university (Yurimoto et al. 2003). A ~100 - ~200 pA Cs⁺ primary beam in the aperture illumination mode was used to achieve uniform secondary ion emission from a sample area of $\sim 30 \times 40 \mu\text{m}^2$. A normal incident electron gun was used to compensate the sample charging. The exit slit was narrow enough to eliminate the contribution of interference ions to the isotope images. Images for isotopographs of ¹H⁺, ²H⁺, ¹²C¹⁴N⁺, and ¹²C¹⁵N⁺ were acquired, where a 150- μm contrast aperture (CA) was used for H and D isotopographs, and a 50- μm CA for ¹²C¹⁴N⁺ and ¹²C¹⁵N⁺ isotopographs in order to obtain high lateral spatial resolution. The exposure time was 20 sec for H⁺, and 1,000 sec for D⁺, 50 s for ¹²C¹⁴N⁺ and 400 s for ¹²C¹⁵N⁺. Delta notation is used to express isotopic ratios;

$$\delta D_{SMOW} = \{(D/H)_{sample}/(D/H)_{SMOW} - 1\} \times 1000$$

$$\delta^{15}N_{AIR} = \{(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{AIR} - 1\} \times 1000,$$

where SMOW and Air denotes the standard mean ocean water and the Earth's atmosphere, respectively. The instrumental mass fractionation for the H and N isotopes was estimated by comparing the spot analysis results of the sample and the standard organic matter BBOT (2,5-(Bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene; C₂₆H₂₆N₂O₂S). The isotope-ratio images were obtained by averaging 5 x 5 moving pixels (corresponding to 1.0 x 1.0 μm²) for δD and 3 x 3 pixels (0.6 x 0.6 μm²) for δ¹⁵N in order to reduce the statistical error. Lateral resolutions of the isotopographs are ~1 μm for ¹H⁺ and ²D⁺ and ~0.6 μm for ¹²C⁺, ¹³C⁺, ¹²C¹⁴N⁺, and ¹²C¹⁵N⁺.

3. Results

3.1 Porous micrometeorites collected in 2003 and 2005

Secondary electron (SE) images of two kinds of porous MMs collected in 2003 and 2005 are shown in Fig. 1. They are characterized by the rugged surface, which reflects the presence of abundant <1- to ~2-μm constituents on its surface. First kind of porous MM is CP MM D05IB13 (Figs. 1a to c). It has a highly porous interior with abundant glass with embedded metal and sulfide (GEMS), which is a diagnostic component of CP IDPs (Figs 1a-c). The porosity of an ultrathin section of the MM exceeds ~60% (inset in Fig. 1b).

Another kind of porous MM D03IB34 is a hydrated MM seen in Fig. 1d. The porous hydrated MM does not match micrometeorite classification proposed by a previous study (Genge et al., 2008). Although they reported fine-grained type 3 MMs, the MMs are composed of loosely aggregated magnesian olivine and pyroxene grains with minor phyllosilicate and occasional framboidal magnetite. Fine-grained porous MMs that have a similar morphology with the above MMs were identified among the MMs collected at the Concordia collection and were termed Fluffy fine-grained AMMs (8 % of fine-grained (Fg) MMs in their collection) (Dobrică et al., 2009). Therefore, we use the same term. Because Fluffy Fg MMs are based on their morphology, we add the definition of Fluffy Fg MMs as follows: "Fine-grained porous hydrated MMs. Abundant Si- and Fe-rich phyllosilicate and no isolated magnetite including framboidal aggregates of magnetite. Often contain isolated anhydrous silicates with various sizes." By contrast, typical hydrated MMs are fine-grained and contain abundant saponite often accompanied by framboidal magnetite are called fine-grained type 1 (Fg C1) MMs (Genge et al., 2008). The surface of the Fluffy Fg MM reflects the fine-grained constituents like CP MMs, their grains sizes tend to be larger (1-2 μm) than those in CP MMs (<1 μm) (Figs. 1a and d). An ultrathin section of this MM shows that its porosity reaches ~35% (inset in Fig. 1e). This MM is hydrated and contains abundant phyllosilicate showing >1 nm lattice fringes, suggestive of saponite, pyrrhotite showing superlattice reflections, and hollow organic nanoglobules (Figs. 1f to h). They do not contain isolated magnetite that is common among hydrated MMs. Chemical compositions of phyllosilicate in this MM is Si- and Fe-rich (Fig. 2a), which have not been reported from hydrated IDPs, hydrated MMs, and hydrated carbonaceous chondrites, except for phyllosilicates in refractory inclusions in CM chondrites (Rubin, 2007).

3.2 Morphology of porous MMs collected in 2010

In order to investigate the texture, mineralogy, and chemistry of organic materials of CP MMs and Fluffy Fg MMs, another large MM collection was used in this study. The MMs in the collection were collected in 2010 (Table 1). D10IB0009, 356, 064, and 004 belong to CP MMs. D10IB178, 163, and 017 belong to Fluffy Fg MMs. D10IB087 belongs to Fg C1 MM. SE images of the MMs investigated in this study are shown in Fig. 3. The average size of the MMs is ~33 μm ; the size is most likely to reach the Earth's surface without suffering extensive heating during atmospheric entry (Love and Brownlee, 1996). As shown in an enlarged image of D10IB004 (Fig. 3e), there are abundant fine-grained (<1 μm) constituents on its surface although the size of the fine-grained constituents in D10IB178, 163, and 017 is larger (<2 μm) than those in other MMs. By contrast, the surface of D10IB087 is blocky although some fine-grained materials exist on the surface.

3.3 Petrography of CP MMs and Fluffy Fg MMs

TEM images of ~100-nm-thick FIB sections are shown in Fig. 4. Four MMs, D10IB009, 356, 064, and 004, are mixtures of sub- μm -sized anhydrous materials and coarse-grained (>1 μm across) clasts or inclusions composed of single and/or polycrystalline minerals (Figs. 4a-e, 5) embedded in or connected by organic materials. D10IB004 has a spherical igneous object composed of olivine and aluminosilicate glass with ~1.5 μm in diameter (Fig. 5a). It also contains a clast composed of silica that shows a halo pattern in a selected area electron diffraction pattern, indicative of amorphous nature, roedderite ($\text{Na, K}_2(\text{Mg, Fe}^{2+})_5\text{Si}_{12}\text{O}_{30}$), and low-Ca pyroxene (Fig. 5b-d). Their morphology suggests that roedderite and low-Ca pyroxene crystallized after solidification of amorphous silica. Lattice image and SAED pattern of low-Ca pyroxene show that it is clinopyroxene with orthopyroxene lamellae and stacking disorders, suggestive of rapid cooling from the stability field of protopyroxene. D10IB356 and 064 contain >5- μm -long polycrystalline clasts composed of olivine, low-Ca pyroxene, high-Ca pyroxene, and pyrrhotite. An enlarged image of the largest clast in D10IB064 shows a recrystallization texture of low-Ca pyroxene with a small amount of aluminosilicate glass among the interstices of low-Ca pyroxene (indicated by arrows in Fig. 5e). The low-Ca pyroxene crystals were also clinopyroxene with orthopyroxene lamellae and stacking disorders, suggestive of rapid cooling.

Other three porous MMs, D10IB178, 163, and 017, and one non-porous micrometeorite, D10IB087, are hydrated MMs with various degrees of aqueous alteration (Figs. 4f-i); D10IB178 and 163 contain abundant coarse-grained (>1 μm across) olivine, low-Ca pyroxene, high-Ca pyroxene, and pyrrhotite (Fig. 4f, g) with lesser amounts of hydrated material. In contrast, FIB sections of D10IB017 and 087 have non-porous texture. They were compacted well during the sample preparation using a 2-ton hydraulic press. The MMs contain abundant phyllosilicate and rare tiny (<0.1 μm) olivine, pyroxene, and pyrrhotite (>0.3 μm) are present as anhydrous minerals (Figs. 4h-i).

3.4 Mineralogy of fine-grained components

Anhydrous MMs, D10IB009, 356, 064, and 004, contain sub- μm -sized olivine, low-Ca pyroxene, pyrrhotite, and glass with embedded metal and sulfide (GEMS), all of which are enclosed by organic materials. These minerals are angular to subrounded in shape

and ~0.2 to ~1 μm in size, which often form polycrystalline aggregates. GEMS grains appear in all the FIB sections as 100-400 nm rounded objects containing <20 nm Fe-sulfide and Fe-Ni metal (indicated by white arrows in Fig. 6a-d). Enstatite platelets are much rarer than GEMS grains (Fig. 6e). Low-iron and manganese enriched (LIME) and/or low-iron and chromium enriched (LICE) olivine and low-Ca pyroxene and kosmochlor ($\text{NaCrSi}_2\text{O}_6$) rich high-Ca pyroxene are found in these MMs (Fig. 7). These features indicate that these MMs are CP MMs (Noguchi et al., 2015), which are CP IDPs (e.g., Bradley, 2014; Joswiak et al., 2009).

D10IB178 and 163 are Fluffy Fg MMs containing both anhydrous and hydrated minerals. They contain abundant olivine and low-Ca pyroxene with submicron size. In D10IB178, phyllosilicate exists as units, which are intermixed with amorphous silicate (Fig. 6f) in the interstices of coarse-grained anhydrous minerals such as olivine and pyroxene. The amorphous silicate contains nanometer-sized Fe sulfide but does not contain nanophase Fe metal, which is different from D10IB009, 356, 064, and 004. Phyllosilicate in the phyllosilicate units in D10IB178 shows ~1 nm (Fig. 6g) and rarely ~0.7 nm lattice fringes, suggesting that they are composed mainly of saponite with minor serpentine. In D10IB163, the interstices among coarse-grained minerals are filled by poorly crystalline phyllosilicate (Fig. 6h), which is partly crystalline with ~1 nm lattice fringes (Fig. 6i).

A Fluffy Fg MM D10IB017 and a Fg C1 MM D10IB087 are composed mainly of phyllosilicate with ~1 nm-lattice fringes (Figs. 6j, k), smaller amounts of Mg-Fe carbonate (magnesite-siderite) (Figs. 6l, m), and rare fine-grained (<0.3 μm) olivine and pyroxene, but Fe-Ni-metal is absent. Magnetite, which is expected to be present due to the common occurrence in typical hydrated MMs, is not observed. Because Mg-Fe carbonate decomposes at around ~600 $^{\circ}\text{C}$ (Nozaki et al., 2006), the existence of carbonate constrains the upper limit of heating degree during its atmospheric entry, which is crucial for the preservation of organic material in IDPs and MMs (~550 $^{\circ}\text{C}$) (Matrajt et al., 2006).

Major element compositions of olivine, pyroxene, and pyrrhotite in all the MMs are shown in Fig. 8, and Tables 2 and 3. Olivine and pyroxene show compositional variations, and the range of forsterite mol% in olivine and ferrosilite mol% in low-Ca pyroxene in the four anhydrous and hydrated MMs (Figs. 8a, b) are comparable. They are Fe-poor being Fo_{~70} to Fo₁₀₀, although the analysis may contain a considerable degree of uncertainty due to the small size and small number of grains analyzed. S-Fe-Ni ternary diagrams show that most Fe-rich sulfide in both anhydrous and hydrated MMs are pyrrhotite (Figs. 8c, d); those in anhydrous MMs contain <5 at% Ni and <55 at% S in anhydrous MMs, and those in hydrated MMs higher amounts of S, up to 58 at% S. Coarse-grained (>0.1 μm) kamacite, taenite, and pentlandite larger than ~0.1 μm are found in a large olivine polycrystalline aggregate in D10IB356 (Fig. 2b).

3.5 Compositional variation of GEMS, amorphous silicate, and phyllosilicates

Figures 9a and b show the chemical compositions of GEMS in the four CP MMs and amorphous silicate in a Fluffy Fg MM D10IB178 plotted on the [Si+Al]-Mg-Fe and Si-S-Fe ternary diagrams. The chemical composition of GEMS in the four CP MMs are widely distributed in the [Si+Al]-Mg-Fe diagram, which are relatively poor in Fe compared to the solar abundance (Fig. 9a), and shows a compositional range from Si-rich to Fe- (and partly

S)-rich composition in the Si-S-Fe diagram (Fig. 9b). Amorphous silicate in D10IB178 is richer in Fe and often in sulfur than silicate in the four anhydrous GEMS, but the compositions of both the GEMS and the amorphous silicate are within the compositional field of GEMS in CP IDPs (Keller and Messenger, 2011) (Fig. 9a and b).

Phyllosilicate in D10IB178 is more homogeneous than the amorphous silicate and poorer in Mg than the amorphous silicate (Fig. 9c). The compositional range of phyllosilicate in D10IB163 overlaps that in D10IB178 (Fig. 9c). Both of them have overlapping chemical compositions with those in a Fluffy Fg MM D03IB34 (Fig. 2a). It is worth noting that phyllosilicates in these MMs are poorer in S than the amorphous silicate in D10IB178 and even poorer than the GEMS silicates (Fig. 9b and d). D10IB017 is composed mainly of Fe-rich phyllosilicate, which is poor in Fe (Fig. 9e) compared to phyllosilicates in D10IB178 and 163 (Fig. 9c), and a small amount of Mg-rich phyllosilicate of which composition is within the range of those in hydrated IDPs, hybrid IDPs, and hydrated MMs is present (Nakamura-Messenger et al., 2011; Nakamura et al., 2004; Noguchi et al., 2002; Sakamoto et al., 2010) (Figs. 9e). The sulfur abundance of the phyllosilicates in these MMs is as low as those in D10IB178 and 163, but the Si/Fe ratio is higher (Figs. 9d and f). Phyllosilicate in a non-porous hydrated micrometeorite D10IB087 is Mg-rich and its composition completely overlaps those in the IDPs and MMs experienced severe aqueous alteration (Fig. 9g). Sulfur in the phyllosilicate in D10IB087 is much poorer (Fig. 9h) than that in D10IB017.

3.6 Organic material

3.6.1. Distribution of organic carbon

The organic material-enriched areas in the FIB sections of D10IB009, 004, and 163 are shown in Figs. 4a, e, g with yellow closed curves, which were drawn based on the C distribution of X-ray transmission images acquired at 390 eV (blue areas in Fig. 4j). The organic material-rich area is distributed widely including sub- μm -sized GEMS and crystalline phases in D10IB009 and 004 (Figs. 4a and e). Enlarged views in Fig. 5a-d show that carbonaceous material indicated by black arrows and GEMS grains indicated by white arrows are intimately intermixed. The distribution of organic material in Fluffy Fg MM D10IB163 is concentrated in some areas (Fig. 4g). The abundance of organic material in other hydrated MMs is low. Organic nanoglobules are observed in both anhydrous (D10IB009 and 0064) and hydrated (D10IB163) CP MMs (Figs. 10a).

3.6.2. Characteristics of organic material

Figure 10b shows carbon-K α edge-XANES (hereafter C-XANES) average spectra of D10IB004, 356, 009, 163 and 017 as well as acid-insoluble organic matter (IOM) from Murchison meteorite for comparison (data from Cody et al., 2008). All the MMs exhibit three peaks; aromatic/olefinic carbon (C=C) peak A at 285 eV, aromatic ketone (C=C-C=O) peak C at 286.5 eV, and carboxyl carbon (COOH) peak E at 288.4 eV with a shoulder of aliphatic carbon (CH_x) peak D at 287.5 eV. D10IB009 also shows a peak B at 286.0 eV, which is assigned to be nitrile (C $\equiv$ N) and/or nitrogen heterocycles (C-N=C). Most of the MMs have a peak F at 290.5 eV, which can be assigned to both inorganic carbonate and organic carbonic acid or carbonic ester (R-O-(C=O)-O-R').

Relative intensities of these peaks are different between CP MMs (D10IB009, 356, 064, and 004) and Fluffy Fg (D10IB178, 163, and 017) MMs; the intensities of COOH (peak E) are remarkably large in the two CP MMs, D10IB009 and 356, whereas the peak E is weak for CP MM D10IB004. The Fluffy Fg MMs D10IB163 and 017 show more intense aromatic/olefinic C=C peak A than peak E, which is very similar to IOM from Murchison meteorite (Cody et al., 2005).

Nitrogen-K α edge-XANES (hereafter N-XANES) spectra of CP MM D10IB009 show a sharp peak of nitrile (C $\equiv$ N) and/or nitrogen heterocycles (C-N=C) (peak G) at 399.4 eV (Fig. 10c). Of the nitrogen heterocycles, in particular, the peak energy is comparable with that of N-XANES of pyrimidines and purines (e.g., adenine, Leinweber et al. 2007). In contrast, another CP MM (D10IB356) and a Fluffy Fg MM (D10IB163) do not show the peak G.

There is also structural heterogeneity of organic material within a sample. Figure 10d shows C and N STXM distribution maps in D10IB009. Nitrogen-enriched organic material dispersed in some small (<1 μ m in diameter) areas, which are indicated by white arrows. Carbon- and N-XANES spectra of the N-enriched areas indicated by the white arrows have prominent peaks attributed to nitrile (C $\equiv$ N) and/or nitrogen heterocycles (C-N=C) (peaks B and G), aliphatic carbon (CH_x) (peak D), and carboxyl carbon (COOH) (peak E) (Figs. 10e, f). By contrast, these peaks from the organic material without N enrichment are not significantly intense. Although two of the N-enriched areas correspond to organic nanoglobules (indicated by open circles in Fig. 10d), other organic nanoglobules do not show N-enrichment in this MMs. Organic nanoglobules in other MMs do not show N-enrichment, either. An organic nanoglobule in Fluffy Fg MM D10IB163 (Figs. 10a, g) has a C-XANES spectrum (Nanoglobule in Fig. 10h) similar to chondritic IOM (Murchison IOM in Fig. 10b). Organic material coexisting with poorly crystalline phyllosilicate shows variation in C-XANES spectra (Areas 1 and 2 in Fig. 10h), where Area 1 and Area 2 are IOM-like organic material and carboxyl and/or carbonyl group-rich, respectively.

As described above, organic material in D10IB009 is richer in N than that in other MMs and the organic material contains nitrile (C $\equiv$ N) and/or nitrogen heterocycles in its structure. It contains δ D (Fig. 11b) and δ^{15} N (Fig. 11d) hot spots, where δ D value is ~5000 to ~10000‰ and the δ^{15} N ~500 to ~1000‰, however, the δ D and δ^{15} N enrichments are not related to each other.

4. Discussion

4.1 Roedderite-bearing clasts in the primitive solar system materials

CP MM D10IB004 contains a silica-roedderite-low-Ca pyroxene clast (Figs. 5b-d). Roedderite-bearing clasts with similar mineral assemblages were reported from a CP MM and a terminal particle from Stardust Track 56 (a particle derived from 81P/Wild 2 comet) (Noguchi et al., 2015; Zolensky et al., 2006; Joswiak et al., 2009, 2012). Joswiak et al. (2009) suggested that the clast may have been one of precursor of type II chondrules (chondrules containing Fe-rich ferromagnesian silicates, Mg# <90). Considering that the limited numbers of CP MMs (<20, Noguchi et al., 2015 and this study) and Stardust terminal particles (<90,

Joswiak et al., 2012) were investigated, roedderite-bearing clasts may exist rarely but ubiquitously among primitive solar system bodies.

4.2 The earliest stage of aqueous alteration responsible for the compositional variations of GEMS and amorphous silicate

Chemical compositions of GEMS in each CP MM form a cluster rather than distribute a whole range of the compositional field of GEMS in CP IDPs (Figs. 9a, 12). GEMS grains in D10IB009 and 356 are plotted at the Mg-rich area in the compositional field of GEMS. Those in D10IB064 and 004 are plotted center left of the compositional field (Fig. 9a). There are no GEMS grains in these CP MMs plotted lower right (Fe-rich) of the compositional field of GEMS in CP IDPs.

A Fluffy Fg MM D10IB178 contains amorphous silicate units containing nanophase Fe sulfide (Fig. 6f), which has relatively homogeneous chemical compositions plotted lower right of the compositional field of GEMS in CP IDPs (Fig. 9a, first row of Fig. 12). Fe-rich phyllosilicate composed of saponite with minor serpentine in the MM has an overlapping chemical composition with the amorphous silicate but tend to be poorer in Mg than the amorphous silicate (Fig. 9c, second row of Fig. 12). It is expected that the aqueous alteration of the amorphous silicate accompanied by oxidation and disappearance of nanophase Fe metal embedded in the amorphous silicate would have occurred. Although the Fe-rich amorphous silicate is expected to have suffered hydration that did not go far enough to form phyllosilicate, we have not confirmed it yet due to the extremely small size.

Oxidation of Fe metal and incorporation into amorphous silicate in GEMS or GEMS-like amorphous silicate to form Fe-rich amorphous silicate in the Fluffy Fg MM and subsequent formation of Fe-rich phyllosilicate would have been aided by aqueous fluid. Because the Fe-rich phyllosilicate in D10IB163 has overlapping chemical compositions of the Fe-rich phyllosilicate in D10IB178 and because D10IB163 does not contain amorphous silicate, it is plausible that D10IB163 experienced a slightly higher degree of aqueous alteration than D10IB178 did. This interpretation is supported by aqueous alteration experiments of amorphous material with a chemical composition similar to GEMS, which resulted in formation of Fe-rich amorphous hydrated silicate with chemical compositions similar to those of phyllosilicate in D10IB178 and 163 (Le Guillou et al., 2015a).

The expected reaction in the earliest stage of aqueous alteration is summarized as follows:

amorphous silicate in GEMS + nano Fe metal in GEMS + isolated pyrrhotite grains
(only very thin surface was reacted) + aqueous fluid
=> Fe-rich (hydrated) amorphous silicate in GEMS. (1)

Further aqueous alteration formed Fe-rich phyllosilicate is expected as follows:

(Hydrated) amorphous silicate in GEMS + nano Fe-sulfide in GEMS
+ isolated pyrrhotite + aqueous fluid

=> Fe-rich phyllosilicate (Fe-Ph in Fig. 12) + more oxidized isolated pyrrhotite (Fe_{1-x}S with higher x). (2)

Systematic differences of the chemical compositions of GEMS in each CP MM and the amorphous silicate in the Fluffy Fg MM D10IB178 could be interpreted that GEMS grains in CP MMs were changed to be richer in Fe and more homogeneous during the earliest stage of aqueous alteration (Figs. 9a, b) although there is no direct evidence for the incorporation of aqueous fluid in GEMS in some CP MMs at present. Because the entire compositional field of GEMS in CP MMs and the amorphous silicate in the Fluffy Fg MM perfectly matches that of the previously reported total compositional field of GEMS in CP IDPs, the previously reported compositional range of GEMS in CP IDPs includes GEMS that experienced aqueous alteration. If the earliest aqueous alteration had occurred in the parent bodies contain abundant CP MMs-like precursors, aqueous alteration probably ceased in the short period of time due to depletion of aqueous fluid, which may have been caused by evaporation or solidification and subsequent sublimation of aqueous fluid.

4.3 Formation of Mg-rich phyllosilicate and Mg-Fe carbonate during early stages of aqueous alteration

A Fluffy Fg MM D10IB017 experienced a higher degree of aqueous alteration than Fluffy Fg MMs D10IB178 and 163. D10IB178 and 163 contain abundant Mg-rich olivine and low-Ca pyroxene and does not show any evidence of aqueous alteration of these phases. By contrast, mineralogy of D10IB017 is characterized by the appearance of new secondary phases, Mg-rich phyllosilicate and Mg-Fe carbonate, and the disappearance of most olivine and pyroxene.

If Mg-rich phyllosilicate and Mg-Fe carbonate were formed by further aqueous alteration, the reaction experienced by D10IB017 is as follows:

Fe-rich phyllosilicate (Fe-Ph) + isolated olivine + isolated low-Ca pyroxene + aqueous fluid + CO_2 or C from organic material
=> Mg-rich phyllosilicate (Mg-Ph) + Mg-Fe carbonate. (3)

The coexistence of Mg-phyllosilicate and Mg-Fe carbonate (Figs. 6j, k, l, m) supports the simultaneous formation of these phases. Along with the formation of these phases, obvious oxidation of Fe sulfide occurred, which is supported by the higher S content of pyrrhotite in large isolated grains in D10IB017 than in D10IB178 and 163. Mineralogy of the seven porous MMs investigated could be understood as reaction products of GEMS-rich precursors, which experienced different degrees of aqueous alteration (Fig. 13). Further study is needed to clarify whether there is genetic relationship among these MMs.

4.4 Relationships between Fluffy Fg MMs and Fg C1 MMs and hydrated IDPs

Although chemical compositions of Mg-phyllosilicate in D10IB017 are within the compositional field of phyllosilicates in hydrated IDPs and hydrated MMs (Fg C1 MMs) (Fig. 9e), the majority of phyllosilicate in the MM is rich in Fe. No Fluffy Fg MM containing only

Mg-phylosilicate as hydrated silicates was not identified in this study. By contrast, a Fg C1 MM D10IB087 contain only Mg-rich phyllosilicate as hydrated silicate, which has almost the same mineralogy as Fg C1 MMs investigated in a previous study (Sakamoto et al., 2010) except for the absence of magnetite. Although the MMs investigated by Sakamoto et al. (2010) contain magnetite, bulk X-ray diffraction data of each MM clearly indicate that the abundance of magnetite is low in these MMs because magnetite was identified from only 2 among 6 MMs (Sakamoto et al., 2010). Therefore, it is reasonable that magnetite was not identified from a small single FIB section of D10IB087.

Most hydrated IDPs are non-porous and called as chondritic smooth (CS) IDPs (e.g., Bradley, 2014). CS IDPs contain abundant poorly crystalline saponite as the predominant phyllosilicate (Zolensky and McSween, 1988; Brearley and Jones, 1998; Germani et al., 1990), pyrrhotite as well as pentlandite (Dai and Bradley, 2001), and Mg-Fe carbonate (Germani et al., 1990). Because mineralogy and chemical compositions overlap with those in Fg C1 MMs, it is likely that aqueous alteration conditions experienced by Fg C1 MMs were similar to those experienced by CS IDPs.

It is not necessarily clear whether further aqueous alteration on the parent bodies of Fluffy Fg MMs formed Fg C1 MMs or not. However, from the mineralogical point of view, it could be possible that further reaction in aqueous environments forms Mg-rich saponite, magnetite, pyrrhotite, pentlandite, and Mg-Fe carbonate. Magnetite in Fg C1 MMs occurs as framboidal aggregates, plaquettes, and spherulites, which are common to CI chondrites and other hydrated carbonaceous chondrites (e.g., Brearley and Jones, 1998). Thus, it is expected that pyrrhotite in Fluffy Fg MMs changes to magnetite with the progress of aqueous alteration by the supply of ferric and ferrous ions, which has been pointed out by Zolensky et al. (2002) for Tagish Lake ungrouped C chondrite. Major minerals in the matrix of Tagish Lake are almost the same as those in the Fg C1 MMs. Oxidation of pyrrhotite forms S^{2-} ion, which would form sulfate,

There may be alternative reaction pathway(s) to make the mineralogy shown in CS IDPs and Fg C1 MMs. Porous IDPs containing GEMS and minor (~5vol.%) phyllosilicate with forsterite, low-Ca pyroxene, and pyrrhotite (hybrid IDPs; Nakamura et al., 2005) have been reported, although they are rare (e.g., Germani et al., 1990; Rietmeijer, 1991; Zolensky and Barrett, 1994; Nakamura et al., 2005). The chemical compositions of phyllosilicates in hybrid IDPs overlap the compositional fields of CS IDPs and Fg C1 MMs (Nakamura-Messenger et al., 2011). They contain minor magnetite. Therefore, it is expected that Mg-rich phyllosilicates and magnetite were formed almost simultaneously during aqueous alteration in hybrid IDPs in the earliest stage of aqueous alteration, which might reflect slightly oxidizing conditions during aqueous alteration in their parent bodies than parent bodies of Fluffy Fg MMs. The absence of Mg-Fe carbonate in the hybrid IDPs may be related to the variations in alteration processes such as temperature, composition of aqueous fluid, pH, Eh, and CO_2 partial pressure.

4.5 Comparison with aqueous alteration of the primitive carbonaceous chondrites

At present, there is no meteorite with fine-grained matrices indistinguishable from CP IDPs as well as CP MMs. However, the most pristine chondrites containing a high abundance of presolar grains (<200 ppm in Acfer 094: Nguyen et al., 2007; Vollmer et al., 2009) have fine-grained matrices or chondrule rims that are composed mainly of GEMS-like amorphous silicate containing nanometer-sized Fe sulfide and Fe metal (Brearley, 1993; Greshake, 1997; Chizmadia and Brearley, 2008; Abreu and Brearley, 2010; Keller and Messenger., 2012; Hewins et al., 2014; Le Guillou and Brearley, 2014, 2015b; Leroux et al., 2015).

Although these meteorites are thought to be free from aqueous alteration and thermal metamorphism, Keller and Messenger (2012) showed that Acfer 094 ungrouped C, and QUE 99177 and MET 00426 CR3 chondrites had experienced the earliest stage of aqueous alteration. They found that the amorphous silicates in these three meteorites contain little or no nm-sized Fe metal and are richer in O and Fe and poorer in S relative to GEMS and that their chemical compositions are more homogeneous than those of GEMS. Keller et al. (2011) and Keller and Messenger (2012) concluded that the amorphous silicates in these meteorites were originally GEMS and that Fe metal in GEMS was oxidized and the amorphous silicate in GEMS were hydrated during the earliest stage of aqueous alteration. Hydration of amorphous silicate and oxidation of nano Fe metal to Fe³⁺ in the amorphous silicate in MET 00426 were supported by Le Guillou and Brearley (2014) and Le Guillou et al. (2015a) based on the excess of O than the stoichiometric value expected from the contents of cations, which attributed to the presence of H₂O in the amorphous silicate and high Fe³⁺ contents in the amorphous silicate suggested from the Fe-K α EELS spectroscopy.

Chemical compositions of GEMS-like amorphous silicate in D10IB178 overlap those in the least altered CR chondrites QUE 99177 and MET 00426, those in Acfer 094 (Keller and Messenger, 2012), and those in Paris CM chondrite (Leroux et al., 2015). Not only amorphous silicate, but also phyllosilicates in the CR chondrites and Acfer 094 are enriched in Si and Fe relative to the amorphous silicate (Keller and Messenger, 2012; Greshake, 1997), which is common to the amorphous silicate and phyllosilicate in D10IB178. If the precursor materials of GEMS-like amorphous silicate in these meteorites were almost the same of GEMS in CP MMs (CP MMs in the first row of Fig. 12), the least altered carbonaceous chondrites mentioned above may have experienced a similar aqueous alteration experienced by D10IB173 and 168 (Second row of Fig. 12). Because it is expected that the reaction (1) occurred in the earliest stages of aqueous alteration and because olivine and pyroxene were not participated in the reaction, it is likely that alteration products (both amorphous silicate and Fe-rich phyllosilicate) in Fluffy Fg MMs have chemical compositions similar to those in the least altered CR chondrites and the least altered CM.

Mineralogy of Fg C1 MMs is similar to that of CI chondrites except for the abundance of ferrihydrite in CI chondrite (Tomeoka et al., 1988), which may reflect higher oxidation conditions of CI chondrites than most Fg C1 MMs. In the more hydrated carbonaceous chondrites, magnesian olivine and pyroxene in abundant chondrules came in aqueous alteration reactions. Nonetheless, assemblages and chemical compositions of secondary minerals in altered CR and Tagish Lake are comparable with those in Fg C1 MMs as well as CI chondrites, which was already pointed out by Zolensky et al. (1993) (Fourth and fifth rows in Fig. 12). These schematic diagrams suggest that dolomite seems to control Mg/(Mg+Fe)

ratio of phyllosilicates in heavily hydrated carbonaceous chondrites. The absence of Mg-Fe carbonate, dolomite, and magnetite and abundant Fe-rich serpentine in CM chondrites are obvious (Fig. 12), which may be related to the strongly basic and reducing conditions with a large quantity of H₂ related to CH₄ generation (Rosenberg et al., 2001; Guo and Eiler, 2007).

4.6 Comparison of organic materials in MMs, IDPs, and primitive carbonaceous chondrites

Not only chemical compositions of GEMS but also organic chemistry is different among CP MMs. Organic materials in both D10IB009 and D10IB356 containing Mg-rich GEMS are rich in carboxyl/carbonyl groups (Fig. 10). Especially, organic materials in D10IB009 are macromolecules enriched in carboxyl and/or carbonyl groups with nitrile (C≡N) and/or N-heterocycles (Figs. 10e, f). This tendency is compatible with organic materials in CP IDPs, which contain high carboxyl/carbonyl groups and minor aromatic C (Keller et al., 2004; Wirick et al., 2009). Organic materials enriched in both carboxyl and/or carbonyl groups and nitrile (C≡N) and/or N-heterocycles have not been found in IOMs in primitive chondritic meteorites. The organic materials in D10IB009 accompany D and ¹⁵N enrichments with δD hot spots having +5000 to +10000‰ enrichment and δ¹⁵N hot spots +500 to +1000‰ enrichment (Fig. 6), which are comparable with those in isotopically primitive IDPs with δD up to +11000‰ and δ¹⁵N up to +1300‰ (Keller et al., 2004; Floss et al., 2006) and comet Wild 2 dust particles with δD up to +2200‰ and δ¹⁵N up to +1300‰ (e.g., McKeegan et al. 2006; De Gregorio et al., 2010). It is therefore concluded that the organic macromolecules in D10IB009 were originated from interstellar or outer solar nebula. Since their isotopic range is especially comparable with δD of cometary HCN (~13300‰, Meier et al. 1998) and δ¹⁵N of cometary CN (~600-940‰, Schulz et al. 2008), nitrile or purines (pyrimidines), and carboxyls, major components of the organic macromolecules in D10IB009, may have been formed by photochemistry of HCN- or CN-ice, as well as ¹⁵N-rich nanoglobules.

UCAMMs are another type of very primitive MMs containing GEMS (Duprat et al., 2010; Dobrică et al., 2012; Bardin et al., 2015). In UCAMMs, there are hundreds of μm² areas of the organic material showing large D/H variations (up to +~3000‰) and a moderate ¹⁵N enrichment (δ¹⁵N ~60‰), which are much huger than D and ¹⁵N hot spots (<3-4 μm in diameter, Fig. 11). The organic materials with such large isotopic anomalies are thought to have been originated in very low temperature environments of a molecular cloud or the outer cold region of the protosolar disk. However, quite different sizes and occurrences as well as ¹⁵N isotopic compositions between organic material in CP IDPs (and a CP MM D10IB009) and that in UCAMMs suggest that precursors, formation locations, and formation processes of organic materials were different between these objects, suggestive of different types of parent bodies.

In organic materials in D10IB356, nitrile (C≡N) and/or N-heterocycle groups are less than D10IB009, while other nitrogen-functional groups (e.g., amino, urea) may be constituents based on the featureless, broad N-XANES spectra (Fig. 10c) that indicates complex mixtures of multiple nitrogen species (Cody et al. 2008). There may be due to the molecular heterogeneity of the sample of the same stage. In the similar case, Comet 81P/Wild 2 showed different elemental and isotopic compositions from a particle to a particle (e.g., Cody et al. 2008; De Gregorio et al. 2010).

By contrast, organic materials in a CP MM D10IB004 are poorer than those in D10IB009 (Figs. 4a, e) and depleted in nitrile groups, N-heterocycles, and D and ^{15}N hotspots, and carboxyl and/or carbonyl groups (Figs. 10a, b). The major organic materials in D10IB004 have high aromaticity, which is similar to IOM in Murchison CM2, as well as CI, CR, Tagish Lake, and IDPs (Cody and Alexander 2005; Cody et al. 2008, 2011; De Gregorio et al. 2013; Changera et al., 2015) (Fig. 10a). In a Fluffy Fg MM D10IB163, most organic materials are also aromatic-rich IOM-like one like in D10IB004. However, a small amount of organic material in the MM contains carboxyl and/or carbonyl groups remained (Figs. 10b, c). These data suggest that aqueous activity in the earliest stages may have caused heterogeneous depletion of nitrile groups, N-heterocycles, and D and ^{15}N hotspots, and carboxyl and/or carbonyl groups if the precursor of the organic materials in these MMs would have been similar to those in D10IB009. C-XANES spectrum of organic material in a Fluffy Fg MM D10IB017 that experienced strong aqueous alteration is also very similar to that of Murchison IOM (Fig. 10b), which suggests that Murchison IOM obtained present properties during aqueous alteration.

4.7 Parent bodies of CP MMs and Fluffy Fg MMs

CP MMs and Fluffy Fg MMs have very high porosities (60-35%) (Fig. 1) being similar to CP IDPs, of which porosity is ~40% (Love et al., 1994; Corrigan et al., 1997). In the case of hydrated carbonaceous chondrites, porosity of Orgueil CI chondrite (35%, Macke et al. 2011) and that of Tagish Lake (~30%, Ralchenko et al. 2014) are comparable with the porosity of Fluffy Fg MMs. These meteorites are known as very fragile meteorites. The highly porous structure of the MMs that experienced aqueous alteration suggests suffering of scarce or very weak compaction despite melting of water ice, which would have been possible by the sticky organic materials that covered and connected inorganic phases. It maintained the porous framework structure under very low gravity, and the porous structure may have enabled a “freeze-dry” process; aqueous fluid froze and sublimated near the surface of their parent bodies. The aqueous activity may have occurred at ~0-~60 °C heterogeneously in their highly porous parent bodies.

According to the aqueous alteration experiments on CP IDPs, GEMS was altered to phyllosilicate in 12 hours at 25 °C in pH 12 solution, and it was suggested that alteration would occur in days at 0 °C (Nakamura-Messenger et al., 2011; Miles and Faillace, 2012). Because D10IB178 contains both amorphous silicate and Fe-rich phyllosilicate, its metamorphic conditions may have been comparable with the experiments by Nakamura-Messenger et al. (2011).

Temperatures of aqueous alteration of saponite-rich CI chondrites, GRO 95577 CR chondrite, and Tagish Lake ungrouped C chondrite are estimated to be ~50-~150 °C, ~10-~40 °C, and ~-30-~65 °C, respectively, on the basis of oxygen isotopic compositions of carbonate (e.g., Clayton and Mayeda, 1984; Guo and Eiler, 2007). Because mineral assemblages and chemical compositions of phases in Fg C1 MMs are similar to the matrix mineralogy of hydrated carbonaceous chondrites (Rows 4 and 5 in Fig. 12), temperature of aqueous alteration in Fg C1 MMs may have been comparable with these meteorites. Because aqueous alteration of Fluffy Fg MMs is weaker than that of Fg C1 MMs, temperature of the former seems likely to have been lower than the latter.

Because aqueous alteration in comet nuclei is problematic (e. g. Wooden, 2008 and references therein), icy asteroids (P- and D-type asteroids) may be more plausible parent bodies of the Fluffy Fg MMs as well as some CP MMs like D10IB004. Because Themis family (C-type asteroids) is water ice-bearing (Campins et al., 2010; Rivkin et al., 2010) and because about 15 % of them may have a low level cometary activity (Ferrín et al. 2017), even C-type asteroids may be also one of the plausible parent bodies of the MMs. These asteroids should have microporous structures that is different from parent bodies of hydrated carbonaceous chondrites except for CI and Tagish Lake, which may have compact structure, as suggested low porosities of the most carbonaceous chondrites (15-20%, Macke et al., 2011).

5. Conclusions

We investigated seven porous MMs and one non-porous one preserved in Antarctic snow near the Dome Fuji Station, Antarctica. The MMs, almost free from terrestrial weathering, are suitable for the investigation of evolution of inorganic, organic, and ice materials at low temperature environments.

They show a variety of early aqueous activities. Four MMs are CP MMs containing glass with embedded metal and sulfide (GEMS) and enstatite whiskers/platelets and do not have hydrated minerals. Despite the same mineralogy, organic chemistry showed diversity among these CP MMs. D10IB009 and 356 contain considerable amounts of organic materials with high carboxyl functionality, and D10IB009 also contains nitrile ($C\equiv N$) and/or nitrogen heterocyclic groups with D and ^{15}N enrichments, suggesting formation in the molecular cloud or a very low temperature region of the outer solar system. These MMs probably escaped from aqueous alteration. D10IB064 and 004 are poorer in organic materials than the above-mentioned MMs. Organic material in D10IB004 is richer in aromatic C than the other CP MMs, being indistinguishable from those of hydrated carbonaceous chondrites. In addition, bulk chemical compositions of GEMS in these CP MMs are more homogeneous and have higher $Fe/(Si+Mg+Fe)$ ratios than those of GEMS in the CP MMs above-mentioned. Functional group of the organic materials and amorphous silicate in GEMS in the CP MMs may have transformed in the earliest stage of aqueous alteration, which did not form hydrated minerals.

The other three porous MMs contain abundant phyllosilicates, showing a clear evidence of aqueous alteration. We call them fine-grained porous hydrated (Fluffy Fg) MMs according to the nomenclature scheme of Genge et al. (2008). These Fluffy Fg MMs contain phyllosilicates that are richer in Fe than phyllosilicates in hydrated IDPs and typical non-porous hydrated MMs (Fg C1 MMs according to Genge et al., 2008), and hydrated carbonaceous chondrites. D10IB178 contains amorphous silicate, which is richer in Fe than GEMS and contains little or no nanophase Fe metal but contains Fe sulfide. Because the chemical compositions of the amorphous silicate are within the compositional field of GEMS in CP IDPs, the amorphous silicate may be alteration products of GEMS. The amorphous silicate is chemically similar to that in the least altered carbonaceous chondrites such as CR3 chondrites as well as Acfer 094 ungrouped C chondrite. The entire compositional field of GEMS in CP MMs and the amorphous silicate in the perfectly matches that of the previously

reported total compositional range of GEMS in IDPs. Thus, the previously reported compositional range includes GEMS that experienced slight aqueous alteration. The most pristine CP MMs may be composed of GEMS (amorphous silicate is rich in both Mg and Si), olivine, pyroxene, and Fe-sulfide, which are embedded in organic materials with features for aromatic C bonding, aromatic ketones, and carboxyl functional groups, of which large δD and $\delta^{15}N$ enrichments imply their origin in a very low temperature environment.

D10IB017 Fluffy Fg MM contains Mg-rich phyllosilicate as well as Fe-rich ones with Mg-Fe carbonate. Mg-rich phyllosilicate and Mg-Fe carbonate may have been formed through the reaction of Fe-rich phyllosilicate, Mg-rich olivine and pyroxene, and water with C-bearing chemical species. The Mg-rich phyllosilicate compositions agree with that of hydrated IDPs and Fg C1 MMs, but they differ from phyllosilicates in hydrated carbonaceous chondrites. Further aqueous alteration would form magnetite, which is typical in Fg C1 MMs, where magnetite occurs often as framboidal aggregates and plaquettes.

The Fluffy Fg MMs investigated are as porous as CP IDPs, irrespective of the presence or absence of aqueous alteration. Such high porosity might be obtained by a “freeze-dry” process; freezing of aqueous fluid and subsequent sublimation near the surface of their parent bodies. Icy asteroids (some C-type asteroids such as Themis group as well as P- and D-type asteroids) may be plausible parent bodies of CP MMs like D10IB004 and Fluffy Fg MMs.

Acknowledgements

We would like to especially thank Hideaki Motoyama and Japan Antarctic Research Expedition teams for collecting surface snow near the Dome Fuji Station, Antarctica. We thank Hiroyuki Hanawa at Ibaraki University, and Satoshi Hata, Yoshinori Hata, and Hiroshi Maeno at Kyushu University for supporting to use TEM, Hisayoshi Yurimoto at Hokkaido University to use SIMS, and Hiroshi Naraoka for the standard of BBOT organic matter. The STXM facility at the beamline 5.3.2.2, ALS, is supported by the Department of Energy, Basic Energy Sciences program. We are gratefully indebted to David Kilcoyne for the beamline management. We were supported by a Grant-in-Aid for Scientific Research (S), 22224010, to HN.

References

- Abreu N. M. and Brearley A. J. (2010) Early solar system processes recorded in the matrices of two highly pristine CR3 carbonaceous chondrites, MET00426 and QUE99177. *Geochim. Cosmochim. Acta* **74**, 1146-1171.
- Bardin N., Duprat J., Engrand C., Slodzian G., Baklouti D., Dartois E., Brunetto R., Delauche L., Godard M., Wu T.-D., Guerquin-Kern J.-L. (2015) D/H and $^{15}N/^{14}N$ isotopic ratios in organic matter of ultracarbonaceous Antarctic micrometeorites. 78th Annual Meeting of the Meteoritical Society, Abstract #5275.

- Bassim N. D., De Gregorio B. T., Kilcoyne A. L. D., Scott K., Chou T., Wirick S., Cody G., and Stroud R. M. (2012) Minimizing damage during FIB sample preparation of soft materials. *J. Microscopy* **245**, Pt 3, 288-301.
- Bradley J. P. (1983) Pyroxene whiskers and platelets in interplanetary dust: evidence of vapour phase growth. *Nature* **301**, 473-477.
- Bradley J. P. (2014) Early Solar Nebula Grains - Interplanetary Dust Particles. In *Treatise on Geochemistry* (2nd ed), Vol. 1: Meteorites and Cosmochemical Processes (A. M. Davies, ed.), pp. 287-308. Elsevier, Oxford.
- Brearley A. J. (1993) Matrix and fine-grained rims in the unequilibrated CO3 chondrite, ALH A77307: Origins and evidence for diverse, primitive nebular dust components. *Geochim. Cosmochim. Acta*, **57**, 1521-1550.
- Brearley A. J. and Jones R. H. (1998) Chondritic meteorites. In: *Planetary Materials, Reviews in Mineralogy* (J. J. Papike, ed.) **36**, pp. 3.1-3.398. Mineralogical Society of America, Washington, DC.
- Busemann H., Nguyen A. N., Cody G. D., Hoppe P., Kilcoyne A. L. D., Stroud R. M., Zega T. J. and Nittler L. R. (2009) Ultra-primitive interplanetary dust particles from the comet 26P/Grigg-Skjellerup dust stream collection. *Earth Planet. Sci. Lett.* **288**, 44-57.
- Campins H., Hargrove K., Pinilla-Alonso N., Howell E. S., Kelley M. S., Licandro J., Mothé-Diniz T., Fernández Y. and Ziffer J. (2010) Water ice and organics on the surface of the asteroid 24 Themis. *Nature* **464**, 1320-1321.
- Changela H. G., Le Guillou C., and Brearley A. J. (2015) Analytical constraints on the formation and evolution of organic material by processes on primitive chondrite parent bodies. *Lunar Planet. Sci. Conf.* **46**, 2810.
- Chizmadia L. J. and Brearley A. J. (2008) Mineralogy, aqueous alteration and primitive textural characteristics of fine-grained rims in the Y791198 CM2 carbonaceous chondrite: TEM observations and comparison to ALH81002. *Geochim. Cosmochim. Acta* **7**, 602-625.
- Clayton R. N. and Mayeda T. K. (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67**, 151-161.
- Cody G. D. and Alexander C. M. O'D. (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **69**, 1085-1097.
- Cody G. D., Ade H., Alexander C. M. O'D., Araki T., Butterworth A., Fleckenstein H., Flynn G., Gilles M. K., Jacobsen C., Kilcoyne A. L. D., Messenger K., Sandford S. A., Tyliczszak T., Westphal A. J., Wirick S. and Yabuta H. (2008) Quantitative organic and light-element analysis of comet 81P/Wild 2 particles using C-, N-, and O- XANES. *Meteor. Planet. Sci.* **43**, 353-365.
- Corrigan C. M., Zolensky, M. E., Dahl, J., Long, M., Weir, J., Sapp, C., and Burkett, P. J. (1997) The porosity and permeability of chondritic meteorites and interplanetary dust particles. *Meteoritics* **32**, 509-515.
- Dai Z. R. and Bradley J. P. (2001) Iron-nickel sulfides in anhydrous interplanetary dust particles. *Geochim. Cosmochim. Acta* **65**, 3601-3612.
- Dartois E., Engrand C., Brunetto R., Duprat J., Pino T., Quirico E., Remusat L., Bardin N., Briani G., Mostefaoui S., Morinaud G., Crane B., Szewc N., Delauche L., Jamme F.,

- Sandt Ch. and Dumas P. (2013) Ultracarbonaceous Antarctic MMs, probing the Solar System beyond the nitrogen snow-line. *Icarus* **224**, 243–252.
- De Gregorio B. T., Stroud R. M., Nittler L. R., Alexander C. M. O'D., Kilcoyne A. L. D. and Zega T. J. (2010) Isotopic anomalies in organic nanoglobules from comet 81P/Wild 2: comparison to Murchison nanoglobules and isotopic anomalies induced in terrestrial organics by electron irradiation. *Geochim. Cosmochim. Acta* **74**, 4454–4470.
- De Gregorio B. T., Stroud R. M., Nittler L. R., Alexander C. M. O'D., Bassim N. D., Cody G. D., Kilcoyne A. L. D., Sandford S. A., Milam S. N., Nuevo M., and Zega T. J. (2013) Isotopic and chemical variation of organic nanoglobules in primitive meteorites. *Meteorit. Planet. Sci.* **48**, 904–928.
- Dobrică E., Engrand C., Duprat J., Gounelle M., Leroux H., Quirico E., and Rouzaud J. N. (2009) Connection between micrometeorites and Wild 2 particles: From Antarctic snow to cometary ices. *Meteorit. Planet. Sci.* **44**, 1643–1661.
- Dobrică E., Engrand C., Leroux H., Rouzaud J. N. and Duprat J. (2012) Transmission electron microscopy of CONCORDIA ultracarbonaceous Antarctic micrometeorites (UCAMMs): mineralogical properties. *Geochim. Cosmochim. Acta* **76**, 68–82.
- Duprat J., Engrand C., Maurette M., Kurat G., Gounelle M., and Hammer C. (2007) Micrometeorites from Central Antarctic snow: The CONCORDIA collection. *Adv. Space Res.* **39**, 605–611.
- Duprat J., Dobrică E., Engrand C., Aléon J., Marrocchi Y., Mostefaoui S., Meibom A., Leroux H., Rouzaud J.-N., Gounelle M. and Robert F. (2010) Extreme Deuterium excesses in ultracarbonaceous micrometeorites from central Antarctic snow. *Science* **328**, 742–745.
- Ferrín I., Pérez M., Rendón J. (2017) Secular light curves of 25 members of the Themis Family of asteroids, suspected of low level cometary activity. *Planet. Space Sci.* <http://dx.doi.org/10.1016/j.pss.2017.01.011>.
- Floss C., Stadermann F. J., Bradley J., Dai Z. R., Bajt S., and Graham G. (2004) Carbon and nitrogen isotopic anomalies in an anhydrous interplanetary dust particle. *Science* **303**, 1355–1358.
- Floss C., Stadermann F. J., Bradley J. P., Dai Z. R., Bajt S., Graham G., and Lea A. S. (2006) Identification of isotopically primitive interplanetary dust particles: A NanoSIMS isotopic imaging study. *Geochim. Cosmochim. Acta* **70**, 2371–2399.
- Frank D. R., Zolensky M. E., Le L. (2014) Olivine in terminal particles of Stardust aerogel tracks and analogous grains in chondrite matrix. *Geochim. Cosmochim. Acta* **142**, 240–259.
- Genge M. J., Engrand C., Gounelle M., and Taylor S. The classification of micrometeorites. *Meteorit. Planet. Sci.* **43**, 497–515.
- Germani M. S., Bradley J. P., Brownlee D. E. (1990) Automated thin-film analyses of hydrated interplanetary dust particles in the analytical electron microscope. *Earth Planet. Sci. Lett.* **101**, 162–179.
- Greshake A. (1997) The primitive matrix components of the unique carbonaceous chondrite Acfer 094: a TEM study. *Geochim. Cosmochim. Acta* **61**, 437–452.

- Guo W. and Eiler, J. M. (2007) Temperatures of aqueous alteration and evidence for methane generation on the parent bodies of the CM chondrites. *Geochim. Cosmochim. Acta* **71**, 5565-5575.
- Hewins R. H., Bourot-Denise M., Zanda B., Leroux H., Barrat J. A., Humayun M., Göpel C., Greenwood R. C., Franchi I. A., Pont S., Lorand J. P., Courne`de C., Gattacceca J., Rochette P., Kuga M., Marrocchi Y. and Marty B. (2014) The Paris meteorite, the least altered CM chondrite so far. *Geochim. Cosmochim. Acta* **124**, 190-222.
- Ishii H. A., Bradley J. P., Dai Z. R., Chi M., Kearsley A. T., Burchell M. J., Browning N. D. and Molster F. (2008) Comparison of comet 81P/Wild 2 dust with interplanetary dust from comets. *Science* **319**, 447-450.
- Joswiak D. J., Brownlee D. E., Matrajt G., Westphal A. J. and Snead C. J. (2009) Kosmochloric Ca-rich pyroxenes and FeO-rich olivines (Kool grains) and associated phases in Stardust tracks and chondritic porous interplanetary dust particles: Possible precursors to FeO-rich type II chondrules in ordinary chondrites. *Meteorit. Planet. Sci.* **44**, 1561-1588.
- Joswiak D. J., Brownlee D. E., Matrajt G., Westphal A. J., Snead C. J., Gainsforth Z. (2012) Comprehensive examination of large mineral and rock fragments in Stardust tracks: Mineralogy, analogous extraterrestrial materials, and source regions. *Meteorit Planet Sci* **47**, 471-524.
- Keller L. P., Messenger S., Flynn G. J., Clemett S., Wirik S. and Jacobsen C. (2004) The nature of molecular cloud material in interplanetary dust. *Geochim. Cosmochim. Acta* **68**, 2577-2589.
- Keller L. P. and Messenger S. (2011) On the origins of GEMS grains. *Geochim. Cosmochim. Acta* **75**, 5336-5365.
- Keller L. P. and Messenger S. (2012) Formation and processing of amorphous silicates in primitive carbonaceous chondrites and cometary dust. *Lunar Planet. Sci. Conf.* **43**, 1880.
- Kilcoyne A. L. D., Tyliszczak T., Steele W. F., Fare S., Hitchcock P., Franck K., Anderson E., Harteneck B., Rightor E. G., Mitchell G. E., Hitchcock A. P., Yang L., Warwick T., and Ade H. (2003) Interferometer-controlled scanning transmission X-ray microscopes at the Advanced Light Source. *J. Synchrotron Rad.* **10**, 125-136.
- Le Guillou C. and Brearley A. E. (2014) Relationships between organics, water and early stages of aqueous alteration in the pristine CR3.0 chondrite MET00426. *Geochim. Cosmochim. Acta* **131**, 344-367.
- Le Guillou C., Dohmen R., Rogella D., Müller T., Vollmer C., and Becker H.-W. (2015a) New experimental approach to study aqueous alteration of amorphous silicates at low temperatures. *Chem. Geol.* **412**, 179-192.
- Le Guillou C., Changela H. G., and Brearley A. J. (2015b) Widespread oxidized and hydrated amorphous silicates in CR chondrites matrices: Implications for alteration conditions and H₂ degassing of asteroids. *Earth Planet. Sc. Lett.* **420**, 162-173.
- Leinweber P., Kruse J., Walley F. L., Gillespie A., Eckardt K.-U., Blyth R., and Regier, T. (2007). Nitrogen K-edge XANES - An overview of reference compounds used to identify 'unknown' organic nitrogen in environmental samples. *J. Synchrotron Rad.* **14**, 500-511.

- Leroux H., Cuvillier P., Zanda B. and Hewins R.H. (2015) GEMS-like material in the matrix of the Paris meteorite and the early stages of alteration of CM chondrites. *Geochim. Cosmochim. Acta* **170**, 247-265.
- Love S. G., Joswiak D. J., and Brownlee D. E. (1994) Densities of stratospheric micrometeorites. *Icarus* **111**, 227-236.
- Love S. G. and Brownlee D. E. (1996) Peak atmospheric entry heating temperatures of micrometeorites, *Meteorit. Planet. Sci.* **31**, 394-402.
- Macke R. J., Consolmagno G. J., and Britt D. T. (2011) Density, porosity, and magnetic susceptibility of carbonaceous chondrites. *Meteorit. Planet. Sci.* **46**, 1842-1862.
- Matrajt G., Brownlee D., Sadilek M., and Kruse L. (2006) Survival of organic phases in porous IDPs during atmospheric entry: A pulse-heating study. *Meteorit. Planet. Sci.* **41**, 903-911.
- Maurette M., Olinger C., Christophe Michel-Levy M., Kurat G., Pourcher M., Brandstatter F., and Bourot-Denise M. (1991) A collection of diverse micrometeorites recovered from 100 tonnes of Antarctic blue ice. *Nature* **351**, 44-47.
- McKeegan K. D., Aléon J., Bradley J., Brownlee D., Busemann H., Butterworth A., Chaussidon M., Fallon S., Floss C., Gilmour J., Gounelle M., Graham G., Guan Y., Heck P. R., Hoppe P., Hutcheon I. D., Huth J., Ishii H., Ito M., Jacobsen S. B., Kearsley A., Leshin L. A., Liu M.-C., Lyon I., Marhas K., Marty B., Matrajt G., Meibom A., Messenger S., Mostefaoui S., Mukhopadhyay S., Nakamura-Messenger K., Nittler L., Palma R., Pepin R. O., Papanastassiou D. A., Robert F., Schlutter D., Snead C. J., Stadermann F. J., Stroud R., Tsou P., Westphal A., Young E. D., Ziegler K., Zimmermann L. and Zinner E. (2006). Isotopic compositions of cometary matter returned by Stardust. *Science* **314**, 1724-1728.
- Meier R., Owen T. C., Jewitt D. C., Matthews H. E., Senay M., Biver N., Bockelée-Morvan D., Crovisier J., and Gautier D. (1998) Deuterium in Comet C/1995 O1 (Hale-Bopp): Detection of DCN. *Science* **279**, 1707-1710.
- Messenger S., Keller L. P., Stadermann F. J., Walker R. M. and Zinner E. (2003) Samples of Stars Beyond the Solar System: Silicate Grains in Interplanetary Dust. *Science* **300**, 105-108.
- Miles R. and Faillace G. A. (2012) On liquid phases in cometary nuclei. *Icarus* **219**, 567-595.
- Nakamura K., Keller L. P., Nakamura T., Noguchi T. and Zolensky M. E. (2004) Mineralogical study of hydrated IDPs: X-ray diffraction and transmission electron microscopy. *Lunar Planet. Sci. Conf.* **35**, 1862.
- Nakamura K., Messenger S., and Keller L. P. 2005. TEM and NanoSIMS study of hydrated/anhydrous phase mixed IDPs: Cometary or asteroidal origin? *Lunar Planet. Sci. Conf.* **36**, 1824.
- Nakamura, T., Noguchi, T., Ozono, Y., Osawa, T. and Nagao, K. (2005) Mineralogy of ultracarbonaceous large micrometeorites (abstract). *Meteorit. Planet. Sci.* **40**, A110.
- Nakamura-Messenger, K., Messenger S., Keller L. P., Clemett S. J., Zolensky M. E. (2006) Organic globules in the Tagish Lake meteorite: remnants of the protosolar disk. *Science* **314**, 1439-1442.

- Nguyen A. N., Stadermann F. J., Zinner E., Stroud R. M., Alexander C. M. O'D., and Nittler L. R. (2007) Characterization of presolar silicate and oxide grains in primitive carbonaceous chondrites. *Astrophys. J.* **656**, 1223-1270.
- Noguchi T., Nakamura T., Nozaki W. (2002) Mineralogy of phyllosilicate-rich micrometeorites and comparison with Tagish Lake and Sayama meteorites. *Earth Planet. Sci. Lett.* **202**, 229-246.
- Noguchi T., Ohashi N., Tsujimoto S., Mitsunari T., Bradley J. P., Nakamura T., Toh S., Stephan T., Iwata N. and Imae N. (2015) Cometary dust in Antarctic ice and snow: Past and present chondritic porous micrometeorites preserved on the Earth's surface. *Earth Planet. Sci. Lett.* **410**, 1-11.
- Nozaki W., Nakamura T., and Noguchi T. (2006) Bulk mineralogical changes of hydrated micrometeorites during heating in the upper atmosphere at temperatures below 1000 °C. *Meteorit. Planet. Sci.* **41**, 1095-1114.
- Rietmeijer F. J. M. (1991) Aqueous alteration in five chondritic porous interplanetary dust particles. *Earth. Planet. Sci. Lett.* **102**, 148-157.
- Rivkin A. S. and Emery J. P. (2010) Detection of ice and organics on an asteroidal surface. *Nature* **464**, 1322-1323.
- Ralchenko M., Britt D. T., Samson C., Herd C. D. K., Herd R. K., and McCausland P. J. A. (2014) Bulk physical properties of the Tagish Lake meteorite frozen pristine fragments. *Lunar Planet. Sci. Conf.* **45**, 1021.
- Rosenberg N. A., Browning L., Bourcier W. (2001) Modeling aqueous alteration of CM carbonaceous chondrites. *Meteorit. Planet. Sci.* **36**, 239-244.
- Rubin A. E. (2007) Petrography of refractory inclusions in CM2.6 QUE 97990 and the origin of melilite-free spinel inclusions in CM chondrites. *Meteorit. Planet. Sci.* **42**, 1711-1726.
- Rubin A. E. and Grossman J. N. (2010) Meteorite and meteoroid: New comprehensive definitions. *Meteorit. Planet. Sci.* **45**, 114-122.
- Sakamoto K., Nakamura T., Noguchi T., and Tsuchiyama A. (2010) A new variant of saponite-rich micrometeorites recovered from recent Antarctic snowfall. *Meteorit. Planet. Sci.* **45**, 220-237.
- Schulz R., Jehin E., Manfroid J., Hutsemékers D., Arpigny C., Cochran A., Zucconi J. -M., Stüwe J. A. (2008) Isotopic abundance in the CN coma of comets: Ten years of measurements. *Planet. Space Sci.* **56**, 1713-1718.
- Taylor S., Lever J. H., Harvey R. P. (1998) Accretion rate of cosmic spherules measured at the South Pole. *Nature* **392**, 899-903.
- Thomas K., Keller L.P., Blanford G. E. and McKay D. S. (1994) Quantitative analyses of carbon in anhydrous and hydrated interplanetary dust particles. in: Analysis of interplanetary dust, (M. E. Zolensky, T. L. Wilson, F. J. M. Rietmeijer, G. J. Flynn eds.), 165-172.
- Tomeoka K. and Buseck P. R. (1988) Matrix mineralogy of the Orgueil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta* **52**, 1627-1640.
- Yurimoto H., Nagashima K. and Kunihiro T. (2003) High precision isotope micro-imaging of materials. *Appl. Surf. Sci.* **203-204**, 793-797.

- Vollmer C., Hoppe P., Stadermann F. J., Floss C., and Brenker F. E. (2009) NanoSIMS analysis and Auger electron spectroscopy of silicate and oxide stardust from the carbonaceous chondrite Acfer 094. *Geochim. Cosmochim. Acta* **73**, 7127-7149.
- Wirik S., Flynn G. J., Keller L. P., Nakamura-Messenger K., Peltzer C., Jacobsen C., Sandford S., and Zolensky M. E. (2009) Organic matter from comet 81/Wild 2, IDPs, and carbonaceous chondrites; similarities and differences. *Meteorit. Planet. Sci.* **44**, 1611-1626.
- Wooden D. H. (2008) Cometary refractory grains: interstellar and nebular sources. *Space Sci. Rev.* **138**, 75-108.
- Zolensky M. E. and McSween H. Y. (1988) Aqueous alteration. in: Meteorites and the early solar system, (J. F. Kerridge and M S. Matthews, eds.), 114-143.
- Zolensky M. E., Bourcier W. L., and Gooding J. L. (1989) Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulation. *Icarus* **78**, 411-425.
- Zolensky M. E., Barrett R., and Browning L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 31273-3147.
- Zolensky M.E. and Barrett R.A. (1994) Composition variations of olivines and pyroxenes in chondritic interplanetary dust particles. *Meteoritics* **29**, 616-620.
- Zolensky M. E., Nakamura K., Gounelle M., Mikouchi T., Kasama T., Tachikawa O. and Tonui E. (2002) Mineralogy of Tagish Lake: An ungrouped type 2 carbonaceous chondrite. *Meteorit. Planet. Sci.* **35**, 737-761.
- Zolensky M. E., Zega T. J., Yano H., Wirick S., Westphal A. J., Weisberg M. K., Weber I., Warren J. L., Velbel M. A., Tsuchiyama A., Tsou P., Toppani A., Tomioka N., Tomeoka K., Teslich N., Taheri M., Susini J., Stroud R., Stephan T., Stadermann F. J., Snead C. J., Simon S. B., Simionovici A., See T. H., Robert F., Rietmeijer F. J. M., Rao W., Perronnet M. C., Papanastassiou D. A., Okudaira K., Ohsumi K., Ohnishi I., Nakamura-Messenger K., Nakamura T., Mostefaoui S., Mikouchi T., Meibom A., Matrajt G., Marcus M. A., Leroux H., Lemelle L., Le L., Lanzirotti A., Langenhorst F., Krot A. N., Keller L. P., Kearsley A. T., Joswiak D., Jacob D., Ishii H., Harvey R., Hagiya K., Grossman L., Grossman J. N., Graham G. A., Gounelle M., Gillet Ph., Genge M. J., Flynn G., Ferroir T., Fallon S., Ebel D. S., Dai Z. R., Cordier P., Clark B., Chi M., Butterworth A. L., Brownlee D. E., Bridges J. C., Brennan S., Brearley A., Bradley J. P., Bleuet P., Bland P. A., and Bastien R. (2006) Mineralogy and petrology of comet 81P/Wild 2 nucleus samples. *Science* **314**, 1735-1739.

Figure captions

- Fig. 1 Secondary electron (SE) images, bright field transmission electron microscope (BF TEM) images of two porous MMs collected in 2005. (a) SE image of a chondritic porous micrometeorite (CP MM) D05IB13, (b) BF TEM image of an ultrathin section of D05IB13, (c) an enlarged BF TEM image showing glass with embedded metal and sulfide (GEMS), (d) SE image of a fluffy fine-grained (Fluffy Fg) MM D03IB34, (e) BF TEM image of an ultrathin section of D03IB34, (f) phyllosilicate in this MM showing 1.29-nm lattice fringes, suggestive of saponite, (g) a pyrrhotite grain showing superlattice reflections, (h) a hollow organic nanoglobule.
- Fig. 2 Chemical compositions of phyllosilicate and Fe-bearing sulfide in D03IB34. (a) Si+Al-Mg-Fe plot showing chemical compositions of phyllosilicates. (b) S-Fe-Ni ternary diagram plotting chemical compositions of Fe-Ni sulfides.
- Fig. 3 Secondary electron (SE) images of MMs investigated. (a) D10IB009, (b) D10IB356, (c) D10IB064, (d) D10IB004, (e) an enlarged image of D10IB004, (f) D10IB178, (g) D10IB163, (h) D10IB120, (i) D10IB017, and (j) D10IB087. These images show that the MMs except for D10IB087 are porous and covered by from (a-e) sub- μm to (f-i) $<2\text{-}\mu\text{m}$ sized material.
- Fig. 4 Transmission electron (TEM) images of focused ion beam (FIB) sections of the MMs investigated. Coarse-grained minerals and aggregates of minerals are labeled. (a) D10IB009, (b) D10IB356, (c, d) D10IB064, (e) D10IB004, (f) D10IB178, (g) D10IB163, (h) D10IB120, (i) D10IB017, and (j) D10IB087. Carbon-enriched areas in D10IB009, 004, and 163 are indicated by yellow closed curves, which were drawn based on an X-ray transmission image acquired at 390 eV. Abbreviations: Ol (olivine), LPx (low-Ca pyroxene), HPx (high-Ca pyroxene), Po (pyrrhotite), Pent (Pentlandite), Ka (Kamacite), Ta (Taenite), PO chondrule (porphyritic olivine chondrule), Am (Amorphous), Polycryst (Polycrystalline).
- Fig. 5 Coarse-grained components in (a-d) D10IB004 and (e, f) D10IB064. (a) A tiny ($\sim 1.5\text{ }\mu\text{m}$ across) porphyritic olivine chondrule. An inset shows the selected area electron diffraction (SAED) pattern of an olivine crystal in this chondrule. (b) An object composed mainly of amorphous silica with roedderite (Rd) and low-Ca pyroxene (LPx). The SAED pattern shows the amorphous nature of silica in the object. (c) An enlarged image of (b). The SAED pattern is consistent with that of roedderite. (d) Lattice image and SAED pattern of the LPx indicated by a small box labeled d in (b). SAED and lattice image show that LPx is clinopyroxene with orthopyroxene lamellae and stacking disorders. (e) An enlarged image of a large ($\sim 8\text{ }\mu\text{m}$) polycrystalline LPx aggregate in Fig. 2c. Interstitial aluminosilicate glass are indicated by arrows.
- Fig. 6 TEM images of phases in the MMs investigated. (a) to (d) GEMS (glass with embedded metal and sulfide), enstatite platelets in (a) D10IB009, (b) D10IB356, (c) D10IB064, and (d) D10IB004. GEMS are indicated by white arrows and organic material are indicated by black arrows. (e) Enstatite platelet in D10IB004. (f) Amorphous silicate units containing tiny ($<20\text{ nm}$) Fe-Ni sulfide and phyllosilicate units in D10IB178. (g) Phyllosilicate in a phyllosilicate chunk in D10IB178 showing well developed $\sim 1\text{-nm}$ lattice fringes. (h) Poorly crystalline phyllosilicates with fibrous morphology in the interstitial material. Olivine on the left corner shows

abundant solar flare tracks, which appear as dark lines. BF image. (i) Poorly crystalline phyllosilicate showing vague ~1-nm lattice fringes in D10IB163. (j) Poorly crystalline phyllosilicate in D10IB017 showing vague ~1-nm lattice fringes. (k) Phyllosilicate in D10IB087 showing well developed ~1-nm lattice fringes. (l) high-angle annular diffraction (HAADF)-scanning transmission electron image and C, O, Mg, Si, and Fe elemental distribution images of a magnesite in D10IB017. (m) Magnesite in D10IB087. Abbreviations: Phy (phyllosilicate).

Fig. 7 FeO vs MnO and FeO vs Cr₂O₃ diagrams of ferromagnesian silicates in (a, b) D10IB009, 356, 064, and 004, and (c, d) in D10IB178, 163, 017, and 087. Blue fields in (a, c) are the compositional range of minerals in chondrules. Yellow fields in (a, c) and pink fields in (b, d) are those in matrices of the primitive chondritic meteorites, interplanetary dust particles (IDPs) and Wild2 grains (Klöck et al., 1989; Klöck and Stadermann, 1994; Zolensky et al., 2006; Frank et al., 2014).

Fig. 8 Pyroxene quadrilateral plots of pyroxene, Forsterite (Fo) mol% histograms of olivine, and S-Fe-Ni ternary diagrams plotting chemical compositions of Fe-Ni sulfides and Fe-Ni metals in MMs investigated. Enlarged diagrams of the hatched areas in the quadrilaterals and ternary diagrams are also plotted.

Fig. 9 Chemical compositions of GEMS, amorphous silicate, and phyllosilicate in the MMs investigated. (a) Si-Mg-Fe plot and (b) Si-S-Fe plot showing chemical compositions of GEMS in anhydrous CP MMs and those of amorphous silicate (Am silicate) in a hydrated micrometeorite D10IB178. A compositional field of GEMS in IDPs (Keller and Messenger, 2011) is also indicated. (c) Si+Al-Mg-Fe and (d) Si-S-Fe plot showing chemical compositions of phyllosilicate and amorphous material in D10IB178 and 163. Compositional fields of GEMS in IDPs (Nakamura-Messenger et al., 2011), amorphous materials in IDPs (Nakamura et al., 2004) and MET 00246 CR 3.0 (Le Guillou and Brearley, 20014) are also indicated. (e) Si+Al-Mg-Fe and (f) Si-S-Fe plot showing chemical compositions of phyllosilicate in D10IB120 and 017, (g) and (h) those in D10IB087. Compositional fields of phyllosilicates in hydrated IDPs (Nakamura et al., 2004), hybrid IDPs (Nakamura-Messenger et al., 2011), and hydrated MMs (Noguchi et al., 2002; Sakamoto et al., 2010), and Orgueil CI chondrite (Tomeoka and Buseck, 1988; Murchison CM 2 (Zolensky et al., 1993) are also indicated. Solar ratios among Si+Al, Mg, and Fe, and those among Si, S, and Fe are also plotted as boxes labeled S.

Fig. 10 (a) Bright-field images of organic nanoglobules in D10IB009, 064, and 163, respectively. Arrays of dark spots indicated by black arrows are redeposition during FIB processing. (b) Averaged C K α edge-XANES spectra of D10IB009, 356, 004, 163 and 017. That of Murchison meteorite insoluble organic matter (Cody et al., 2008) is also plotted for comparison. (c) Averaged N K α edge-XANES spectra of D10IB009, 356, and 163. (d) Carbon- and Nitrogen distribution maps of D10IB009, acquired by STXM (optical density images). The N-enriched areas are indicated by white arrows. The circled regions correspond to organic nanoglobules. (e) Carbon- and (f) Nitrogen- K α edge-XANES spectra of a N-enriched area and an area without N enrichment in D10IB009. (g) X-ray transmission image (upper) and carbon elemental maps (optical images, center and lower) of D10IB163. (h) Carbon K α

edge-XANES spectra of the dotted line regions of (a), Area 1 (orange), Area 2 (blue), and organic nanoglobule (yellow). Peak A: $1s-\pi^*$ transition of aromatic/olefinic carbon ($C=C$) at 285 eV; Peak B: $1s-\pi^*$ transition of nitrile ($C\equiv N$) and/or nitrogen heterocycles ($C-N=C$) at 286 eV; Peak C: $1s-\pi^*$ transition of vinyl-keto ($C=C-C=O$) at 286.5 eV; Peak D: $1s-3p/s^*$ transition of aliphatic carbon (CH_x) at 287.5 eV; Peak E: $1s-\pi^*$ transition of carboxyl carbon ($COOH$) at 288.4 eV; Peak F: $1s-\pi^*$ transition of carbonate or carbonic acid ($RO(C=O)OR'$) at 290.6 eV; Peak G: $1s-\pi^*$ transition of nitrile ($C\equiv N$) and/or nitrogen heterocycles ($C-N=C$) at 399.4 eV.

Fig. 11 Isotopographs of D10IB009. White and black circles (S) of each image (a-d) denotes the spot analyses area by SIMS to estimate the IMF. (a) H. (b) δD_{SMOW} . H1 and H2 denotes δD hot spots (H1: $\sim 10000\%$ and H2: $\sim 8000\%$). (c) $^{12}C^{14}N$ and (d) $\delta^{15}N_{air}$. H3 and H4 denotes $\delta^{15}N$ hot spots (H3: ~ 1000 and H4: $\sim 600\%$).

Fig. 12 Comparison of chemical compositions of major phases in MMs [chondritic porous (CP) MMs, fluffy fine-grained (Fluffy Fg) MMs, typical non-porous hydrated (Fg C1) MMs], IDPs [CP IDPs, Hybrid IDPs], primitive carbonaceous chondrites [CI, CM, CR, and Tagish Lake ungrouped C]. Abbreviations: GEMS (glass with embedded metal and sulfide), LPx (low-Ca pyroxene), Ol (olivine), Am sil (amorphous silicate), Ph (phyllosilicate), Met (metallic Fe), Po (pyrrhotite), Mgt (magnetite), Carb (carbonate). Schematic diagrams describing compositions of coexisting major phases in matrices of meteorites. Abbreviations: LPx (low-Ca pyroxene), Se (serpentine), Ol (olivine), Am sil (amorphous silicate), Cr (cronstedtite), Toc (tochilinite), Ph (phyllosilicate), Met (metallic Fe), Po (pyrrhotite), Tr (troilite), Fer (ferrihydrite), Wü (wüstite), Mgt (magnetite), Pen (pentlandite), Dol (dolomite), Carb (carbonate). Data sources: Tomeoka and Buseck (1988), Brearley and Jones (1998), Zolensky et al. (2000), Zega et al. (2006), Keller and Messenger (2011), Lee et al. (2015), Le Guillou et al. (2015a), Le Guillou et al. (2015b), Leroux et al. (2015).

Fig. 13 Schematic diagrams describing aqueous alteration to form Fluffy Fg MMs from CP MMs. Abbreviations: Px (pyroxene), Ol (olivine), Po (pyrrhotite), Am sil (amorphous silicate), Ph (phyllosilicate), Carb (carbonate).

Table 1 Characteristic features of inorganic and organic materials in micrometeorites investigated in this study and comparison with those in typical hydrated MMs.

Aqueous alteration		No	No	No	No	Weak	Weak	Moderate	Moderate	Strong
Sample		D10IB 009	D10IB 356	D10IB 064	D10IB 004	D10IB 178	D10IB 163	D10IB 017	D10IB 087	Typical hydrated MMs*
Classification of MMs		CP	CP	CP	CP	Fg PH	Fluffy Fg	Fluffy Fg	Fluffy Fg	Fg C1
Mineralogy	GEMS or Amorphous silicate	GEMS	GEMS	GEMS	GEMS	Amorphous silicate	Absent	Absent	Absent	Absent
	Metal and/or Sulfide in GEMS or Amorphous silicate	Metal + Sulfide	Metal + Sulfide	Metal + Sulfide	Metal + Sulfide	Sulfide	Absent	Absent	Absent	Absent
	Phyllosilicates	Absent	Absent	Absent	Absent	Fe-rich sap + minor Fe-rich serp	Fe-rich sap + minor Fe-rich serp	Fe-rich sap + minor Mg-rich sap	Mg-rich sap	Mg-rich sap
	Aqueous alteration in Ol and LPx	Absent	Absent	Absent	Absent	Absent	Absent	Remarkable	Remarkable	Remarkable
	Sub-µm ol and LPx	Abundant	Abundant	Abundant	Abundant	Abundant	Abundant	Rare	Rare	Absent
	Fe oxide	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Magnetite
	Carbonates	Absent	Absent	Absent	Absent	Absent	Absent	Magnesite	Magnesite	Mg-siderite, dolomite
Isolated pyrrhotite		Present	Present	Present	Present	Present	Present	Present	Present	Present
Organic material										
N-heterocycles		Present	Absent	-	Absent	-	Absent	Absent	-	-
Carboxyl/carbonyl		Abundant	Abundant	-	Poor	-	Poor	Poor	-	-
Aromatic C		Poor	Poor	-	Abundant	-	Abundant	Abundant	-	-
Globules		Abundant	Absent	Present	Absent	Absent	Present	Absent	Absent	Present
δD (‰)		+5000 to +10000	-	-	0	-	-	-	-	-
δ ¹⁵ N (‰)		+500 to +1000	-	-	+300	-	-	-	-	-

-: not investigated
Abbreviations: Ol, olivine; LPx, low-Ca pyroxene; GEMS, glass with embedded metal and sulfide; sap, saponite; serp, serpentine.
*References: Noguchi et al. (2002), Sakamoto et al. (2010)

CP: Chondritic porous (according to the definition of CP IDP; Noguchi et al., 2015), Fg C1: Fine-grained type C1 (Compact, chemically homogeneous fine-grained MMs. Often contain framboidal magnetite; Genge et al., 2008), Fluffy Fg (Highly porous fine-grained hydrated MMs. Often contain isolated anhydrous silicates. Abundant Si- and Fe-rich phyllosilicate and no isolated magnetite including framboidal aggregates of magnetite; definition of this study)

Table 2 Representative chemical compositions of phases in CP MMs. 100wt% normalized.

Sample	D10IB009				D10IB356			D10IB064				D10IB004						
Mineral	Ol	LPx	Glass	GEMS	Ol	LPx	GEMS	Ol	LPx	HPx	Glass	GEMS	Ol	LPx	HPx	GEMS	Am silica	Rd
SiO ₂	38.70	59.87	71.89	50.74	41.45	58.97	42.56	39.73	54.11	52.92	70.37	45.46	41.06	57.07	55.64	46.74	100	75.44
TiO ₂	b. d.	0.08	b. d.	b. d.	b. d.	0.05	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	0.20	0.75	b. d.	b. d.	0.26
Al ₂ O ₃	b. d.	0.07	17.44	3.79	b. d.	0.64	2.41	b. d.	4.58	4.82	28.06	5.70	b. d.	4.42	0.97	2.28	b. d.	0.73
Cr ₂ O ₃	0.13	0.64	b. d.	0.33	0.74	0.94	0.58	b. d.	1.72	1.38	b. d.	0.95	0.15	0.10	2.04	b. d.	b. d.	b. d.
FeO	19.47	0.26	1.43	13.74	3.64	1.69	13.1	14.27	3.97	6.27	b. d.	29.74	8.76	0.95	4.36	21.53	b. d.	4.41
NiO	b. d.	b. d.	b. d.	0.24	b. d.	b. d.	1.56	b. d.	b. d.	b. d.	b. d.	1.41	b. d.	b. d.	b. d.	0.82	b. d.	b. d.
MnO	1.02	0.39	b. d.	0.35	b. d.	0.44	b. d.	0.59	1.12	0.93	b. d.	b. d.	1.09	0.56	4.62	0.23	b. d.	0.66
MgO	40.53	38.62	8.47	27.53	54.00	36.00	9.40	45.41	33.13	21.07	b. d.	7.46	48.82	35.66	16.94	15.38	b. d.	14.62
CaO	0.14	0.07	0.13	0.33	0.16	1.26	1.17	b. d.	1.38	12.60	1.57	1.14	0.11	1.04	13.23	1.24	b. d.	0.28
Na ₂ O	b. d.	b. d.	0.48	0.93	b. d.	b. d.	1.74	b. d.	b. d.	b. d.	b. d.	1.06	b. d.	b. d.	1.45	0.57	b. d.	2.79
K ₂ O	b. d.	b. d.	0.15	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	0.81
SO ₃	b. d.	b. d.	b. d.	2.01	b. d.	b. d.	27.40	b. d.	b. d.	b. d.	b. d.	7.06	b. d.	b. d.	b. d.	11.22	b. d.	b. d.
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Fo mol%	78.8				96.4			85.0				90.9						
Wo mol%	0.1				2.4			1.7				2.0						
En mol%	99.5				95.1			90.8				96.5						
Fs mol%	0.4				2.5			7.5				1.4						

Abbreviations: Ol, olivine; LPx, low-Ca pyroxene; HPx, high-Ca pyroxene; GEMS, glass with embedded metal and sulfide; Am silica, amorphous silica; Rd, roedderite.

Table 3 Representative chemical compositions of phases in Fluffy Fg MMs and a Fg C1 MM. 100wt% normalized.

Sample	D10IB178				D10IB163				D10IB017			D10IB087			
Mineral	Ol	LPx	HPx	Phy	Amorph. silicate	Ol	LPx	HPx	Phy	HPx	Phy	Ol	LPx	HPx	Phy
SiO ₂	37.83	59.20	41.33	37.25	29.27	38.78	57.30	52.45	38.92	54.53	56.15	43.32	52.66	56.85	58.11
TiO ₂	b. d.	b. d.	4.09	b. d.	b. d.	b. d.	0.70	1.97	b. d.	0.56	b. d.	b. d.	b. d.	b. d.	b. d.
Al ₂ O ₃	b. d.	b. d.	16.55	7.40	2.29	b. d.	1.15	2.46	4.75	1.68	4.65	b. d.	5.35	1.26	5.63
Cr ₂ O ₃	b. d.	b. d.	0.82	b. d.	b. d.	b. d.	0.95	1.47	0.77	3.07	b. d.	b. d.	1.93	1.47	b. d.
FeO	23.37	0.72	0.78	43.51	31.17	18.07	0.94	0.63	47.29	8.25	32.54	1.70	11.26	1.58	18.72
NiO	b. d.	b. d.	b. d.	b. d.	1.07	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.
MnO	0.81	0.78	b. d.	b. d.	b. d.	0.36	1.07	0.67	b. d.	0.77	b. d.	b. d.	0.87	0.94	b. d.
MgO	37.15	39.13	17.33	9.18	7.26	42.78	35.72	20.60	6.12	19.66	6.66	54.98	25.10	27.41	16.51
CaO	0.84	0.17	18.95	b. d.	0.51	b. d.	2.16	19.75	0.21	10.55	b. d.	b. d.	2.18	10.50	b. d.
Na ₂ O	b. d.	b. d.	0.15	2.66	1.76	b. d.	b. d.	b. d.	b. d.	0.93	b. d.	b. d.	0.65	b. d.	1.03
SO ₃	b. d.	b. d.	b. d.	b. d.	26.66	b. d.	b. d.	b. d.	1.94	b. d.	b. d.	b. d.	b. d.	b. d.	b. d.
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Fo mol%	73.9				80.8							98.3			
Wo mol%		0.3	43.4				4.1	32.9		23.8			4.8	21.1	
En mol%		98.7	55.2				94.5	58.6		61.7			76.1	76.5	
Fs mol%		1.0	1.4				1.4	8.5		14.5			19.2	2.5	

Abbreviations: Ol, olivine; LPx, low-Ca pyroxene; HPx, high-Ca pyroxene; Amoprh. silicate, amorphous silicate; Phy, phyllosilicate.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

CP MMs
ex. D10IB009

CP MMs
ex. D10IB004

Fluffy Fg MMs
ex. D10IB178

Fluffy Fg MMs
ex. D10IB163

Fluffy Fg MMs
ex. D10IB017