Earth and Planetary Science Letters 410 (2015) 1–11

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Cometary dust in Antarctic ice and snow: Past and present chondritic porous micrometeorites preserved on the Earth's surface

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ARTICLE INFO

Article history:
Received 26 June 2014
Received in revised form 7 November 2014
Accepted 11 November 2014
Available online 26 November 2014
Editor: T. Elliott

Keywords:
Antarctica
micrometeorites
interplanetary dust particles
cometary dust

ABSTRACT

Chondritic porous interplanetary dust particles (CP IDPs) collected in the stratosphere are regarded as possibly being cometary dust, and are therefore the most primitive solar system material that is currently available for analysis in laboratories. In this paper we report the discovery of more than 40 chondritic porous micrometeorites (CP MMs) in the surface snow and blue ice of Antarctica, which are indistinguishable from CP IDPs. The CP MMs are botryoidal aggregates, composed mainly of sub-micrometer-sized constituents. They contain two components that characterize them as CP IDPs: enstatite whiskers and GEMS (glass with embedded metal and sulfides). Enstatite whiskers appear as <2-μm-long acicular objects that are attached on, or protrude from the surface, and when included in the interior of the CP MMs are composed of a unit-cell scale mixture of clino- and ortho-enstatite, and elongated along the [100] direction. GEMS appear as 100–500 nm spheroidal objects containing <50 nm Fe–Ni metal and Fe sulfide. The CP MMs also contain low-iron–manganese-enriched (LIME) and low-iron–chromium-enriched (LICE) ferromagnesian silicates, kosmochlor ($NaCrSi_2O_6$)-rich high-Ca pyroxene, roedderite $(K,Na)_2Mg_5Si_{12}O_{30}$, and carbonaceous nanoglobules. These components have previously been discovered in primitive solar system materials such as the CP IDPs, matrices of primitive chondrites, phyllosilicate-rich MMs, ultracarbonaceous MMs, and cometary particles recovered from the 81P/Wild 2 comet. The most outstanding feature of these CP MMs is the presence of kosmochlor-rich high-Ca pyroxene and roedderite, which suggest that they have building blocks in common with CP IDPs and cometary dust particles and therefore suggest a possible cometary origin of both CP MMs and CP IDPs. It is therefore considered that CP MMs are CP IDPs that have fallen to Earth and have survived the terrestrial environment.

1. Introduction

Very small (typically 5–15 μm in diameter) extraterrestrial materials, known as interplanetary dust particles (IDPs), are collected in the stratosphere. There are two major morphological groups of IDPs with chondritic bulk compositions: chondritic porous (CP) IDPs and chondritic smooth (CS) IDPs (Bradley, 2004). CP IDPs are fragile botryoidal aggregates composed mainly of sub-micrometer-sized constituents (Bradley, 2013). CS IDPs have a relatively smooth surface and are regarded as dust particles that originated from hydrous asteroids (Bradley, 2014), and small extraterrestrial particles similar to CS IDPs have been collected on the ground as micrometeorites (MMs) (Maurette et al., 1991; Taylor et al., 1998; Yada and Kojima, 2000; Noguchi et al., 2002; Duprat et al., 2007; Rochette et al., 2008).

Chondritic porous IDPs are regarded as possibly being cometary dust (Bradley, 2004; Ishii et al., 2008), and this cometary ori-

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http://dx.doi.org/10.1016/j.epsl.2014.11.012

gin is supported by the preservation within abundant (up to ∼1 vol.%) presolar grains formed in circumstellar environments and in supernova outflows (Messenger et al., 2003; Busemann et al., 2009). In addition, they contain abundant organics, thereby showing a high enrichment of D/H (up to ∼ 30 000‰ δD) and/or of $\delta^{15}N$ (up to ∼ 3000‰), which is suggestive of formation in cold (<20 K) molecular clouds (Bradley, 2013; Busemann et al., 2009; Floss et al., 2004; Matrajt et al., 2012). The Stardust mission revealed that comet 81P/Wild 2 is a mixture of materials formed in both the inner hot and the outer cold regions of the protosolar disk (Zolensky et al., 2006; McKeegan et al., 2006; Nakamura et al., 2008b; Matzel et al., 2010). Although the majority of the fine-grained portion of the Wild 2 particles was melted or vaporized during capture in the silica aerogel, some of it remains, including fine-grained with very volatile organics (Sandford et al., 2006). However, it is not necessarily clear to what extent the fine-grained portion of the Wild 2 materials is similar to CP IDPs (Chi et al., 2007; Stodolna et al., 2014).

Recently, ultracarbonaceous Antarctic micrometeorites (UCAMMs) were identified from among MMs recovered from bare ice (Nakamura et al., 2005) and snow (Duprat et al., 2010). These contain organics showing a high enrichment of D/H (up to 2900‰ δD) and constituent minerals which are common to CP IDPs (Duprat et al., 2010; Dobrică et al., 2011, 2012). Their characteristics therefore suggest that UCAMMs are a counterpart of extremely carbon-rich IDPs (Thomas et al., 1994).

In this paper, we report chondritic porous micrometeorites (CP MMs) that are indistinguishable from CP IDPs, and which were collected from both Antarctic blue ice and surface snow. The discovery of the CP MMs suggested the possibility of investigating both past and present cometary dust. The past CP MMs were found to have experienced considerable terrestrial weathering due to their extremely fine-grained and porous nature. The present CP MMs collected within two years after their fall to earth showed very weak terrestrial weathering. Different from the collection of IDPs, they were collected without silicone oil. Therefore, they are suitable for the investigation of GEMS and organic matter (or carbonaceous material), and such materials are extremely important in understanding the origin of solar system materials and their processing in the protosolar disk.

2. Materials and methods

2.1. Collection and identification of micrometeorites (MMs)

In 2000, the Japan Antarctic Research Expedition (JARE) recovered fine-grained particles containing micrometeorites (MMs) near Tottuki Point, located 17 km north of Syowa Station, by melting ice measuring 17.6 m^3 and then filtering the water obtained (Iwata and Imae, 2002). MMs of various size fractions were collected with diameters of >10 μm. More than 3000 particles were identified by using a JEOL JSM-5600LV scanning electron microscope equipped with Oxford ISIS 300 energy dispersive spectrometer (SEM/EDS) at Ibaraki University. However, the exact age of ice at the sampling locality has not yet been determined because ice sheets originating from different areas converge at the Tottuki Point area.

Since 2003, the JARE expedition parties have been collecting surface snow from near Dome Fuji Station. This snow has been transferred to Japan, where it has been melted and filtered in a clean room at Ibaraki University. By using SEM/EDS, approximately 550 MMs were identified from ∼600 kg surface snow collected in the years 2003, 2005, 2007, and 2010. In consideration of the annual accumulation rate of snow fall at the sampling point (∼10 cm/year) (Kameda et al., 2008), surface snow that had fallen within two years was collected in 2003 and 2005, and snow that had fallen within one year was collected in 2007 and 2010. In this paper, MMs collected at Tottuki Point and those collected near the Dome Fuji Station are called "past MMs" and "present MMs", respectively. For characterization of the bulk mineralogy of individual MMs, synchrotron radiation X-ray with a beam line of 3A and 9C was used at the Photon Factory Institute of Material Science, High Energy Accelerator Research Organization, Tsukuba, Japan.

2.2. TEM sample preparation and TEM observation

Ultrathin sections of three CP MMs (To440020, T5BB2066, and D05IB13) and a CP IDP (L2021) were prepared using a Reichert Ultracut N ultramicrotome at Ibaraki University. TT54C394 was ultramicrotomed using a Leica Ultracut UCT ultramicrotome at Westfälische Wilhelms-Universität Münster. A 200-nm section of an enstatite whisker in To440020 was prepared using a Hitachi FB-2000K focused ion beam sample (FIB) preparation machine at the Art, Science, Technology Center for Cooperative Research, Kyushu University. One hundred and fifty-nm FIB electron transparent sections of D10IB004 and D10IB009 were prepared from flattened samples embedded into gold using JEOL JIB-4501 multibeam FIB-SEM at Ibaraki University. For electron energy loss spectroscopy (EELS) analysis and elemental distribution mapping of C, O, and N, fragments of To440020 and Tagish Lake ungrouped carbonaceous chondrite were embedded in elemental sulfur and were ultramicrotomed into ∼100-nm sections using the Reichert Ultracut N ultramicrotome at Ibaraki University.

Ultrathin sections and FIB sections of the CP MMs were observed in the following locations: at Ibaraki University using JEOL JEM-2000FX TEM equipped with an EDAX DX4 energy dispersive spectrometer (EDS) and JEOL JEM-2100 TEM equipped with an Oxford INCA EDS; at the High Voltage Electron Microscope Laboratory, Kyushu University with JEOL JEM-3200FSK energy filter TEM (EF-TEM); and at the Laurence Livermore National Laboratory using 80–300 keV aberration-corrected FEI Titan scanning TEM (STEM). The accelerating voltage of the TEMs was 200 kV for JEM-2000FX and JEM-2100, and 300 kV for JEM-3200 FSK and Titan. Semi-quantitative analysis was performed by EDAX DX4 EDS equipped with JEOL JEM-2000FX. A number of mineral standards were used for the EDS analysis. The procedure used included a counting live time of 100 s for the EDS analysis, and detection limits of elements investigated were ∼0.4 wt.%. To obtain the bulk elemental data of glass with embedded metal and sulfide (GEMS) objects, a defocused beam covering the entire area of each GEMS object was used. EELS analysis and elemental distribution maps of C, O, and N were obtained by JEM-3200FSK using the in-column energy filter.

2.3. TOF-SIMS analysis

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) imaging of an ultrathin section of TT54C394 was performed at the Westfälische Wilhelms-Universität Münster using a high lateral resolution (beam diameter ∼0.3 μm) and high mass resolution (up to $m/\Delta m = 10{,}000$ at full-width half-maximum), which allows an unambiguous identification of most ion peaks. Positive and negative secondary ions were analyzed in two subsequent measurements. Bulk elemental abundance of the MM was then obtained by averaging all data obtained from the ultrathin section of the MM.

2.4. Micro-Raman spectroscopy

Micro-Raman spectroscopy was performed on ∼180 MMs recovered from surface snow to obtain Raman spectra of carbonaceous material, using a JASCO NRS-3100 Raman spectrometer at Ibaraki University. An excitation laser with a wavelength of 785 nm was used to decrease fluorescence from MMs, and laser power was set to considerably below 1 mW to avoid structural change of the