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# Characterization of the organic matter and hydration state of Antarctic micrometeorites: A reservoir distinct from carbonaceous chondrites

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ABSTRACT

This work presents a multi-analysis on 35 Antarctic micrometeorites (AMMs) (Concordia collection 2006) by coupled Raman and Infrared (IR) spectroscopies, in comparison with samples from type 1 and 2 carbonaceous CM, CR and CI chondrites. We identified the Raman G- and D-bands revealing the presence of polyaromatic carbonaceous material on raw particles in a subset of 16 particles. Thirteen AMMs (10 Fg + 1 Fg-*Sc* + 1 *Sc*) were selected from this first subset, and analyzed by infrared microscopy along with 4 AMMs (2 Fg + 1 Fg-*Sc* + 1 *Sc*) from a previous study by Dobrica et al. (2011). These analyses showed that scoriaceous, fine-grained scoriaceous and part of the fine-grained AMMs are not hydrated, with a weak abundance of carbonaceous matter. According to the Raman criterion defined by Dobrica et al. (2011), hydrous AMMs do not show structural modifications induced by heating through the atmospheric entry. In several hydrous AMMs, the carbonaceous matter abundance is found larger than in Orgueil (CI), Murchison (CM) and QUE 99177 (CR) chondrites and their mineral content exhibit differences reflected by the structure of the silicate 10 µm band. These observations suggest that part of the AMMs originates from one, or several, distinct parent bodies with respect to primitive carbonaceous chondrites. Each hydrous Fg-AMMS displays higher $CH_2/CH_3$ ratio and a smaller carbonyl abundance than chondrites, which point toward a mild processing during atmospheric entry, possibly oxidation, which did not modify the carbon backbone and therefore do not induce differences in Raman spectroscopy.



## 1. Introduction

The majority of small bodies in the Solar System (comets, asteroids and Trans-Neptunian Objects) did not experience melting and differentiation. Some of them only experienced moderate or negligible post-accretional processes. They did not substantially evolve since their formation, about 4.5 Gyr ago, and preserve insightful chemical, chronological and physical information on the material originally present in the protoplanetary disk and on the processes that operated in the early Solar System.

Most of chondrites are fragments of main-belt undifferentiated asteroids. Ordinary chondrites, the most abundant type of meteorites, have been linked to the S-complex asteroids on the basis of their Visible and Near-InfraRed (VNIR) reflectance spectra. This relationship was confirmed by the analysis of Hayabusa-1 particles returned from the asteroid Itokawa (e.g., Nakamura et al., 2011). Carbonaceous chondrites have been linked to the C-complex asteroids (dominant spectral type in the main-belt), but the absence of strong absorption band in VNIR asteroid spectra (De Meo et al., 2009) hinders a connection to be strongly established. Primitive small bodies might be much more diverse than revealed by the few chondrite groups we have in hands . In particular, Vernazza et al. (2015) concluded that the surface compositions of low-density icy asteroids (C-, P-, and D-types) are compatible with those of interplanetary dusts (IDPs).

Extraterrestrial samples available in laboratory not only include meteorites, but also IDPs (dust of asteroidal and cometary origins – see review by Bradley (2014) for their compositions, mineralogy, and geochemical significance and for a discussion on their asteroidal vs. cometary origins), comet Wild-2 grains (samples returned in 2006 by the Stardust mission – e.g., Brownlee et al., 2006; Brownlee, 2014), asteroid Itokawa particles, and micrometeorites. Micrometeorites have been collected in several sites in ocean-floor sediments (e.g., Blanchard et al., 1980; Brownlee, 1985; Parashar et al., 2010), in Greenland (e.g. Maurette et al., 1987), and in Antarctica (e.g. Maurette et al., 1991; Yada and Kojima, 2000; Taylor and Lever, 2001; Duprat et al., 2007; Rochette et al., 2008; van Ginneken et al., 2012).

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Micrometeorites are extraterrestrial dust particles with typical sizes ranging from 20 µm up to 500 µm for the unmelted or partially melted ones. They survived atmospheric entry and possibly sample both asteroids and comets. They are the dominant contribution of the present-day mass flux of extraterrestrial matter accreted by the Earth (Love and Brownlee, 1993; Taylor et al., 1998), about a thousand times more than meteorites (e.g. Halliday et al., 1989; Bland et al., 1996; Engrand and Maurette, 1998; Hutzler et al., 2016).

Based on petrographic, chemical and isotopic investigations, small unmelted micrometeorites (diameter ∼25–250 µm) appear to be mostly related to carbonaceous, possibly cometary parent bodies (CM/CR related) (Kurat et al., 1994; Engrand and Maurette, 1998; Engrand et al., 1999). Owing to the distribution of petrologic types, mineralogy, and minor element compositions, Genge (2008) reported the discovery of micrometeorites related to ordinary chondrites. Ion probe oxygen isotopic analyses, on unmelted micrometeorites and cosmic spherules (Engrand et al., 1999, 2005; Yada et al., 2005, Taylor et al., 2005), revealed that a majority of micrometeorites with sizes smaller than ∼400 µm are related to carbonaceous chondrites with oxygen isotopic ratios below the terrestrial fractionation line. Recent high-precision measurements of the oxygen isotopic compositions of larger (>400 µm) cosmic spherules from the Transantarctic Mountains suggest that there could be a continuity in the composition of the micrometeorites flux. The smaller particles are mostly related to carbonaceous chondrites, while larger spherules (> 800 µm) bear closer relationship to ordinary chondrites (Suavet et al., 2010, 2011; van Ginneken et al., 2017). Levison et al. (2009) suggested that D- and P-type asteroids are the sources of micrometeorites and Vernazza et al. (2015, 2017) included some C-types asteroids as well as the sources of interplanetary dusts. This is in contrast with chondrites having only sampled C- and S-types asteroids. Therefore, micrometeorites offer the opportunity to probe a wider range of small bodies of the Solar System than meteorites.

Studying micrometeorites and IDPs, in addition to meteorites allows to get a better sampling of small bodies and to constrain the origin and the evolution of the organic matter reservoirs in the Solar System. Laboratory studies of elemental, chemical, and isotopic compositions of organics from meteorites, IDPs, and micrometeorites reveal some similarities, and subtle differences. For example, the so-called ultra-carbonaceous micrometeorites (UCAMMs) contain an unusually high nitrogen- and deuterium-rich organic matter as compared to chondrites (Duprat et al., 2010; Dartois et al., 2013).

The link between some micrometeorites and meteorites has been essentially assessed through oxygen isotopes, petrography and mineralogy. We focus here on the organic matter and hydrated mineralogy of a series of Antarctic micrometeorites (AMMs), using combined Raman and IR spectroscopic characterizations. The objective is to better understand the post-accretion history experienced by micrometeorites and to constrain the nature and diversity of their parent bodies.

## 2. Samples and sample preparation

### 2.1. Samples

We worked on 35 AMMs from the Concordia collection (Table 1) collected at Dome C in January 2006 from snow layers ranging from 1950 to 1980. The details on the sampling procedure are provided in Duprat et al. (2007). Thanks to the cleanliness of the snow and the specific sampling procedure, the Concordia collection appears to be among the least contaminated and preserves the most friable particles (Duprat et al., 2007; Dobrica, 2010). The 35 AMMs selected for this work have been fragmented into several pieces in order to perform complementary analyses and to keep a witness sample of each AMM. The sizes of the fragments range between 20 and 98 µm (Table 1).

Although micrometeorites survived atmospheric entry, they nevertheless experienced some heating during their deceleration in the atmosphere as reflected by their texture. This led to a classification into four main groups (Genge et al., 2008; Dobrica et al., 2011). Fine-grained (Fg) AMMs are the best preserved and did not experience extensive heating through the atmospheric entry. They are subdivided into the Fg-compact and Fg-fluffy, the latter being the most friable. Fine-grained-Scoriaceous (Fg-*Sc*) and Scoriaceous (*Sc*) particles are partially melted and covered by a partial or complete magnetite shell. *Sc* particles have a vesicular texture resulting from their degassing during atmospheric entry. Cosmic spherules (CS) are fully melted, and crystalline micrometeorites (Xtal) consist in a single mineral.

Each of the 35 AMMs was assigned a textural group based on their SEM images (Fig. 1). 19 AMMs are Fg, 10 are intermediate Fg-*Sc*, 1 is a *Sc* particle, and 5 are CSs (Table 1). The classification done here relies on SEM images previously acquired by E. Dobrica at CSNSM. Comparative Raman and IR spectra were also acquired on QUE 99,177 (CR2), Murchison (CM2) and Orgueil (CI1) chondrites. We chose type 1 and 2 chondrites that escaped significant thermal metamorphism, similarly to the considered AMMs and in contrast to type 3 chondrites (see Section 4.1).

### 2.2. Sample preparation for spectroscopic investigation

We performed measurements of AMMs on 1) each bulk fragment without specific preparation and 2) series of pressed fragments (Table 1). Bulk fragments of AMMs were stored at IPAG on individual glass slides in a vacuumed desiccator (the initial AMMs had been stored at CSNSM Orsay in purged-air desiccators). Raman measurements of the raw AMMs were performed on their initial glass slide. For IR transmission measurements, each particle was transferred by hand with a tungsten needle on a diamond or on a germanium window. Samples handling was done under an ISO 5 laminar hood located in an ISO 7 clean room.

Infrared spectra collected on micrometer-sized particles may be severely affected by scattering effects. In order to minimize these effects, the samples were pressed between two windows (diamond or germanium) with a dedicated tool designed to get thin and flat samples (Raynal et al., 2000). The infrared spectra of QUE 99177, Murchison, and Orgueil were collected on matrix samples that were separated from the bulk meteorites under a binocular microscope and prepared along the same protocol. Germanium is not as hard as diamond. The quality of the preparation was thus not as good as with diamond windows; we then stopped using the germanium substrates.

## 3. Analytical techniques

Raman micro-spectroscopy was performed at the Laboratoire de Géologie de Lyon Terre, Planètes, Environnement (France) and Infrared micro-spectroscopy at the Institut de Planétologie et d'Astrophysique de Grenoble (France).

### 3.1. Raman spectroscopy

Raman spectroscopy was performed in order to identify the AMMs including polyaromatic carbonaceous matter and to characterize their thermal history (heating through the atmospheric entry and thermal metamorphism) as reflected by the structural order of their polyaromatic carbonaceous matter.