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## Invited Review

### Carbonaceous micrometeorites from Antarctica

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(Part of a series of papers dedicated to the memory of Paul Barringer)

**Abstract**—Over 100 000 large interplanetary dust particles in the 50–500  $\mu\text{m}$  size range have been recovered in clean conditions from ~600 tons of Antarctic melt ice water as both unmelted and partially melted/dehydrated micrometeorites and cosmic spherules. Flux measurements in both the Greenland and Antarctica ice sheets indicate that the micrometeorites deliver to the Earth's surface ~2000 $\times$  more extraterrestrial material than brought by meteorites. Mineralogical and chemical studies of Antarctic micrometeorites indicate that they are only related to the relatively rare CM and CR carbonaceous chondrite groups, being mostly chondritic carbonaceous objects composed of highly unequilibrated assemblages of anhydrous and hydrous minerals. However, there are also marked differences between these two families of solar system objects, including higher C/O ratios and a very marked depletion of chondrules in micrometeorite matter; hence, they are "chondrites-without-chondrules." Thus, the parent meteoroids of micrometeorites represent a dominant and new population of solar system objects, probably formed in the outer solar system and delivered to the inner solar system by the most appropriate vehicles, comets. One of the major purposes of this paper is to discuss applications of micrometeorite studies that have been previously presented to exobiologists but deal with the synthesis of prebiotic molecules on the early Earth, and more recently, with the early history of the solar system.

#### INTRODUCTION

"Giant" micrometeorites with sizes of ~100  $\mu\text{m}$  have been collected in large numbers ( $\geq 100\,000$  to date) on the Greenland and Antarctica ice sheets (Maurette *et al.*, 1986, 1987, 1991b). However, the most unbiased and uncontaminated samples were collected in the blue ice fields of Cap-Prudhomme in 1991 and 1994, ~2 km from the margin of the Antarctic ice sheet, by filtering huge amounts of melt ice water (10 to 15 tons daily over ~30 days of good weather every year) through a stack of stainless steel sieves with openings of 25, 50, 100 and 400  $\mu\text{m}$ .

These Antarctic micrometeorites (AMMs) are large interplanetary dust particles that survived their hypervelocity impact with the Earth's atmosphere without being melted into cosmic spherules. Antarctic micrometeorites are mostly fine-grained carbonaceous objects, related to a relatively rare group of meteorites (Kurat *et al.*, 1994c; Engrand, 1995), the so-called carbonaceous chondrites, which represent ~4% of all meteorite falls (Sears and Dodd, 1988). Electron energy loss (EELS) analyses of the AMMs yielded high concentrations of carbonaceous material in the AMMs (average C content ~7% ; Engrand, 1995; Engrand and Maurette, 1997). Complex organic molecules such as amino acids and polycyclic aromatic hydrocarbon (PAHs) have also been identified in AMMs (Brinton *et al.*, 1997; Clemett *et al.*, 1997).

The smaller micrometeorites collected in the stratosphere by Brownlee since 1975 and by NASA since 1981 (interplanetary dust particles or IDPs) will be mentioned only briefly in this paper. For sample collection details and IDP characteristics, see Zolensky *et al.* (1994) and a previous comparison of chemical and mineralogical features of IDPs, AMMs and meteorites can be found in Klöck and Stadermann (1994). Interplanetary dust particles are even more exotic than AMMs, showing, for example, marked H and N isotopic anomalies (Zinner *et al.*, 1983; McKeegan, 1987; McKeegan *et al.*, 1985; Stadermann *et al.*, 1989; Stadermann, 1990; Messenger and Walker, 1997) and unique components such as GEMS ("glass embedded with metals and sulfides," see Bradley, 1994).

The contribution of IDPs to the bulk accretion rate of the Earth is negligible, being ~100 $\times$  smaller than that of the giant micrometeorites (50–500  $\mu\text{m}$  size range, see Love and Brownlee, 1993). Moreover, their smaller sizes prevent both the search for large constituents of the micrometeorite flux (*e.g.*, chondrules) and the formation of observable shooting stars upon atmospheric entry, from which statistical connections with their parent bodies could be obtained (Whipple, 1967, and references therein). However, it should be remembered that they might deliver to the Earth unique particles that are not to be found in the flux of the larger micrometeorites.

In 1991 and 1994, we recovered AMMs with sizes (25–50  $\mu\text{m}$ ) that now overlap the size range of the IDPs; but these small AMMs seem to be related only to the giant micrometeorites and not to IDPs.

A new and important micrometeorite collection was realized in 1996 January by Taylor *et al.* (1996a) from the bottom of the water well of the U.S. South Pole station. It provides the unique opportunity to both sample micrometeorites over time windows of ~300 years (corresponding to the ~10 m ice thickness melted each year) and to estimate the micrometeorite flux reaching the South Pole (Taylor *et al.*, 1996b). This paper does not attempt to make a comparison between the AMMs and this new collection of South Pole micrometeorites, which needs to be more extensively characterized.

The major purpose of this paper is to give an up-to-date summary of the mineralogical, chemical and isotopic characteristics of Antarctic micrometeorites, in comparison with meteorites. These studies have implications for the synthesis of prebiotic molecules on the early Earth and for the evolution of the early solar nebula (see also Engrand, 1995; Maurette, 1997).

#### EXPERIMENTAL PROCEDURES

##### From Clean Antarctic Ices to Sample Preservation

The small size of the micrometeorites, coupled with their dilution by terrestrial dust, greatly complicates their collection and analy-

ses. Moreover, the small sample sizes available often require very highly sensitive analytical instruments.

Micrometeorites can be easily contaminated as a result of their high surface-to-volume ratio, their marked porosity, and their chemical reactivity when exposed to gases and waters. Consequently, all steps in micrometeorite studies must be strictly controlled from their collection in the cleanest terrestrial "sediments" (e.g., Antarctic ices) to their preparation in ultraclean conditions, their microanalysis, and their preservation for future generations.

Micrometeorites were collected in Greenland in 1984 and 1987, and in Antarctica since 1988 by Maurette and collaborators (see Maurette *et al.*, 1994 for a review). The cleanest micrometeorite samples were collected from December 1993 to January 1994 in the blue ice fields of Cap-Prudhomme, Antarctica, 6 km south from the French station of Dumont d'Urville (66°40'S–140°01'E). With a micrometeorite "factory," three pockets of melt ice water were made each day of good weather (~50% of the time). The glacial sand deposited on the bottom of the pockets was pumped to the surface and filtered on a stack of stainless steel sieves, yielding four size fractions (25–50  $\mu\text{m}$ ; 50–100  $\mu\text{m}$ ; 100–400  $\mu\text{m}$ ; >400  $\mu\text{m}$ ; see Maurette *et al.*, 1994, for more details).

During the 1994 operation, all parts of the micrometeorite "factory" exposed to hot water were made of either a grade of stainless steel used in the tubing of French nuclear reactors or Teflon in order to minimize the formation of corrosion and leach products in the melt water, which are potential sources of contamination of the grains. Moreover, heavy snowfalls in 1994 (the heaviest recorded since the opening of the French station Dumont d'Urville in 1950) combined with a strong wind blowing almost constantly from the center to the margin of the ice cap effectively shielded the blue ice fields from manmade contamination. Each daily collection of glacial sand was transferred in the field into two distinct type of vials (made of either glass or Teflon) with a small amount of their original melt ice water and kept since that time in deep frozen conditions at  $-20\text{ }^\circ\text{C}$ .

The sand is very rich in micrometeorites, the 50–100  $\mu\text{m}$  size fraction providing the best yield. In this fraction, up to ~20% of the grains are micrometeorites, and a good day's collection yields typically ~500 melted micrometeorites (cosmic spherules) and 2000 unmelted to partially melted/dehydrated micrometeorites (AMMs). In the larger 100–400  $\mu\text{m}$  size fraction, the concentration of unmelted AMMs is ~10 $\times$  smaller than in the 50–100  $\mu\text{m}$  fraction, and a good day's collection yields ~1000 cosmic spherules and 250 AMMs.

In order to minimize contamination, all samples (including meteorites used as standards) are handled in a clean-room facility. A given grain is first crushed into several fragments in ultraclean conditions. One of these fragments is mounted and polished in an epoxy resin mount for mineralogical and textural characterization.

A second fragment is directly crushed into much smaller grains (sizes up to a few micrometers) onto a Au electron microscope grid held between two glass plates. Then, ~20 of these micrometer-sized grains, partially encrusted into the grid and selected at random, can be analyzed with an analytical transmission electron microscope (ATEM) for C/O measurements.

A third fragment is crushed onto a Au foil for analysis either by microscopic double-laser mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) or by ion microprobe.

Several fragments are kept for additional analyses and/or the future exploitation for the Stardust and Rosetta cometary missions, which will require comparisons between the cometary grains, well-characterized IDPs and AMMs, and primitive meteorites.

For techniques such as high-performance liquid chromatography (HPLC), aliquots of ~35 micrometeorites are prepared and transferred into glass tubes precleaned by combustion at  $400\text{ }^\circ\text{C}$ .

### Chemistry and Mineralogy

The mineralogy of ~800 AMMs and their minor and major element compositions have been investigated over the last six years in collaboration with Gero Kurat and Franz Brandstätter in Vienna (Mineralogische Abteilung, Naturhistorisches Museum), mostly relying on both an analytical scanning electron microscope (SEM) equipped with an EDS system, complemented by accurate electron microprobe measurements. Mireille Christophe Michel-Levy (Laboratoire de Mineralogie, Université Paris VI) also collaborated in these studies. Minor and trace element abundances were determined by instrumental neutron activation analysis (INAA) by the team of Christian Koberl at the University of Vienna, following a procedure described in Kurat *et al.* (1994c).

One of us (C. E.) and Michel Perreau used the 400 kV analytical transmission electron microscope at Laboratoire d'Etudes des Microstructures in Châtillon s/s Bagnoux (CNRS/ONERA), equipped with both an electron energy loss spectrometer (EELS) and an energy dispersive x-ray spectrometer (EDS) to analyze small volumes of material with a size of ~0.1  $\mu\text{m}$ . Fragments of 35 AMMs from three size fractions (25 to 400  $\mu\text{m}$ ) and two carbonaceous chondrites (Orgueil and Murchison used as standards) were analyzed. The EELS has good sensitivity for light elements (C, N, O) and allows the determination of C/O atomic ratios with an accuracy of ~10% relative when the sample is sufficiently thin (*i.e.*,  $\leq 0.1\text{ }\mu\text{m}$  thick) to produce a double-peak structure at the oxygen-K edge. The EDS analyses were used to determine the chemical composition (with an accuracy of ~10% relative) of the major nonvolatile elements in the same volume, which gives clues about the associations between minerals and carbonaceous phases.

### Ion Microprobe for D/H Ratios

In collaboration with Etienne Deloule and Marc Chaussidon (CRPG, Nancy) and François Robert (Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle de Paris), we analyzed 43 micrometeorites, 10 cosmic spherules containing "COPS" nuggets and 7 of these nuggets for their H content and D/H ratio using the Nancy Cameca ims3f ion microprobe (see also Engrand *et al.*, 1996a,b; unpubl. data, 1998). The COPS phase (named after its C, O, P and S content) consists of ferrihydrite enriched in minor elements such as Mg, Al, Si, P, S and Ni (see also Engrand *et al.*, 1993, and see below Host Phases of Complex Organics). The biggest COPS inclusions (up to ~25  $\mu\text{m}$  in diameter) are found as appendages, as well as "nuggets" in cosmic spherules.

A negative primary O beam, with intensity ranging from 4 to 8 nA, is focused to produce a 10  $\mu\text{m}$  diameter beam. The relative precision on water concentrations in hydroxylated minerals is  $\pm 10\%$ . For lower water contents (<1 wt%), the possible systematic error can reach a factor of two. The accuracy of the D/H analyses is  $\pm 3.5\%$ . With this negative O primary beam, the emission of H from phyllosilicates is ~500 $\times$  higher than the emission of H from organic matter (Deloule and Robert, 1995). See Deloule *et al.* (1991), Deloule and Robert (1995), Engrand *et al.* (unpubl. data, 1998) for a more detailed description of the analytical settings used for these analyses.

Hydrogen isotopic compositions are reported both as D/H ratios and as  $\delta\text{D}$  values:  $\delta\text{D}(\text{‰}) = [(D/H)_{\text{sample}}/(D/H)_{\text{SMOW}} - 1] \times 1000$ , with  $(D/H)_{\text{SMOW}} = 155.76 \times 10^{-6}$ .

### Search for Complex Organics

The most sensitive techniques of geochemistry now available to detect complex organic molecules in micrometeorites include microscopic double-laser mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) and high-performance liquid chromatography (HPLC) as presently used in the groups of Richard Zare (Department of Chemistry, Stanford University) and Jeffrey Bada (NSCORT for Exobiology, Scripps Institution of Oceanography, La Jolla), respectively. The major results of these studies are published in Brinton *et al.* (1997) and Clemett *et al.* (1997).

For the  $\mu\text{L}^2\text{MS}$  analyses, small ( $\sim 50\ \mu\text{m}$  size) fragments of micrometeorites as well as chunks of Orgueil, Murchison and Allende are crushed on Au foils. An infrared laser gently desorbs organics from the grains, forming a plume that is irradiated with an ultraviolet laser selectively ionizing the constituent polycyclic aromatic hydrocarbons of the samples. A time-of-flight mass spectrometer yields their mass spectra. Fragments of fifteen AMMs were analyzed by this technique.

The sensitivity of the HPLC technique for amino acids is still not sufficient to analyze individual micrometeorites. Thus, aliquots of  $\sim 30$  to 35 micrometeorites and/or an  $\sim 5\ \text{mg}$  chunk of the fine-grained matrix of the Murchison meteorite have to be run as a "single" grain. Thus far, Brinton *et al.* (1997) have analyzed five aliquots of AMMs corresponding to two distinct daily collections made in 1991 and 1994.

### RESULTS AND DISCUSSION

#### Atmospheric Entry and Textural Classification of Micrometeorites

Micrometeoroids suffer frictional heating during their rapid deceleration in the Earth's upper atmosphere (between 120 km and 80 km of elevation). Observations of polished sections of  $\sim 800$  AMMs selected at random in the glacial sand collected at Cap-Prudhomme with an SEM yields a simple textural classification scheme (Fig. 1) that relates to the degree of atmospheric heating (see Kurat *et al.*, 1994c; Engrand, 1995). Particles are classified according to the relative abundance of vesicles due to the partial loss of the structural water of their constituent hydrous minerals or other volatile species. The "unmelted" micrometeorites are free of vesicles and can be classified into particles constituted mainly of fine-grained matrix ("fine-grained AMMs," see Fig. 1a) or consist of assemblages of coarse-grained crystals ("crystalline AMMs," see Fig. 1b). The "scoriaceous particles" (or scorias) are partially melted/dehydrated (Fig. 1c) and contain various amounts/sizes of vesicles. Being initially fine-grained micrometeorites, the scoriaceous particles were more strongly heated than fine-grained particles but still retain a relatively high amount of water (see below). The "cosmic spherules" (Fig. 1d) are melted micrometeorites.

In the 50–100  $\mu\text{m}$  size fraction of the glacial sand collected at Cap-Prudhomme, the fine-grained and crystalline micrometeorites

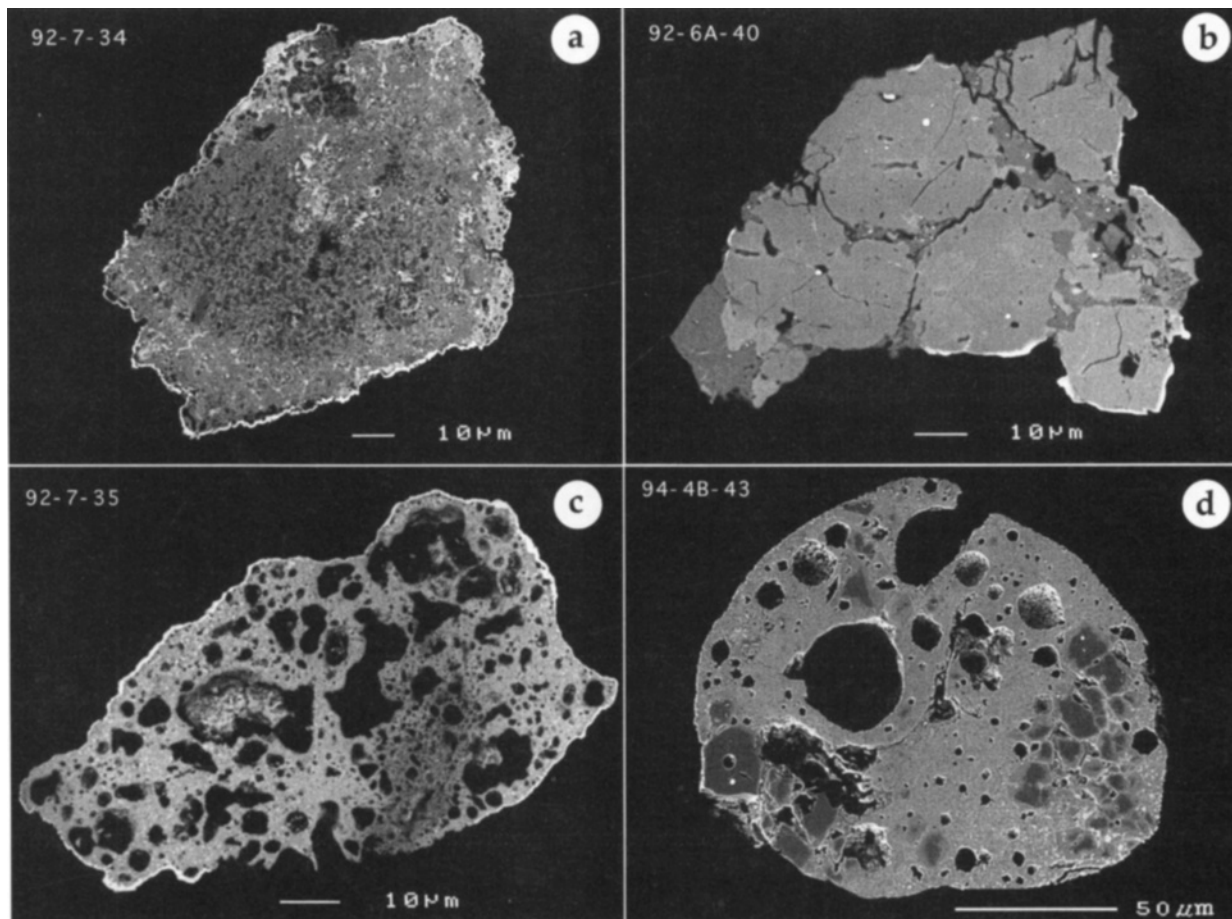


FIG. 1. Textural classification of AMMs (size of  $\sim 100\ \mu\text{m}$ ). This classification is related to their degree of frictional heating upon atmospheric entry: (a) ununmelted fine-grained micrometeorite, (b) ununmelted crystalline micrometeorite, (c) partially dehydrated scoriaceous micrometeorite, and (d) melted cosmic spherule.

represent ~32% and 8% of the chondritic grains, respectively. The scorias and the cosmic spherules account for ~40% and ~20% of the grains, respectively.

The proportion of unmelted micrometeorites decreases with increasing size, as expected due to increased frictional heating in the atmosphere, to reach a low value of ~25% in the 200  $\mu\text{m}$  particles. This value is still higher than the value (<5%) predicted by models of frictional heating (Love and Brownlee, 1991), even considering the uncertainty due to mass loss during atmospheric entry.

The fine-grained micrometeorites and scorias are complex aggregates composed of millions of individual grains embedded in a carbonaceous component. The AMMs have a chondritic composition of nonvolatile major elements, which already suggests a relationship to the ordinary and carbonaceous chondrites, representing ~82% and 4% of the meteorite falls, respectively (Sears and Dodd, 1988). The crystalline micrometeorites are mostly made of a few single crystals of pyroxene and olivine typically containing metallic inclusions of Fe, Ni metal (with usually low-Ni content).

#### Atmospheric Entry and Interactions with the Terrestrial Environment

Some of the primary characteristics of micrometeorites are modified during interactions with the terrestrial environment, from frictional heating in the atmosphere, residence in blue ice for a few tens of thousand years (according to ice flow modelling), and ~8 h exposure in melt ice water at a few degrees Celsius during recovery in Antarctica. We have already described morphological changes occurring to micrometeorites upon atmospheric entry leading to their textural classification. We mostly emphasize below changes in the chemical composition of the important family of unmelted micrometeorites (see also Klöck and Stadermann, 1994).

Backscattered electron micrographs of polished sections of all types of micrometeorites show a bright rim of magnetite that decorates a very thin shell around the grains (see Fig. 1). This shell increases the mechanical strength of micrometeorites and, consequently, their durability in the terrestrial environment. The magnetite shell is not a primary characteristic of micrometeorites; and although its formation is still poorly understood, it is observed also on the IDPs where its development correlates with other independent indicators of heating such as volatile element losses (see Keller *et al.*, 1996). Thus, it seems related to the atmospheric entry frictional heating. However, this shell is observed on both unmelted and scoriaceous AMMs and its thickness (~1  $\mu\text{m}$ ) is independent of the nature of the host AMMs.

Therefore, several scenarios have been proposed to explain the formation of the magnetite shell. We previously suggested (Maurette *et al.*, 1993) that it could result from an accretionary process effective near the end of the deceleration range of micrometeorites, in the so-called E-layer of the Earth's atmosphere, which contains a high concentration of Fe ions (Steinweg *et al.*, 1992). The source of these ions is currently attributed to the micrometeorites and meteorites that get the most extensively ablated during atmospheric entry (Kane and Gardner, 1993). The surviving micrometeorites would scavenge these metallic ashes to build up their own magnetite shell. However, from the low column density of Fe presently measured in the E-layer, it seems rather unlikely that the micrometeorites could accrete a 1  $\mu\text{m}$  thick magnetite shell in this manner (see also Flynn, 1994a).

An alternative, more generally accepted scenario could be formation of a magnetite shell through mineral reactions induced by

frictional heating. Indeed, based on petrographic evidence, Keller *et al.* (1996) attribute the formation of the magnetite shell in the IDPs to the oxidation of Fe from host phases such as Fe-Ni sulfide, Fe-Ni metal, olivine, phyllosilicate, and Mg-Fe carbonate. The fact that there is often no relationship between the magnetite shell and the substrate phase (as it is often observed in the case of the AMMs) is attributed to mobility of Fe at the surface of the particle during entry heating. However, atmospheric entry models have failed to predict the formation of such a thin magnetite shell (Bonny, 1990), and laboratory heating experiments have been unable to reproduce it (Greshake *et al.*, 1998).

Another effect of frictional heating is the degree of alkylation of the constituent PAHs of micrometeorites (*e.g.*, the number of substitution on the core PAHs), which clearly increases as a function of thermal metamorphism, as inferred from the density of vesicles, and is indicative of dehydration (see below, and Clemett *et al.*, 1997). Micrometeorites retain high concentrations of PAHs, even in scoriaceous particles almost reaching the stage of melted cosmic spherules. This suggests that frictional heating would not be sufficient to greatly affect the bulk C content of micrometeorites. This observation is also compatible with the high content of solar Ne frequently measured in scoriaceous particles (Olinger *et al.*, 1990).

After their rapid deceleration, micrometeorites gravitationally settle through the various layers of the atmosphere, including the stratosphere. The first evidence for interactions between the micrometeorites and the atmosphere was the observation of thin (<150 Å) S-rich layers at the surface of IDPs (MacKinnon and Mogk, 1985). Subsequently, Jessberger *et al.* (1992) also reported high S contents (2–3 $\times$  chondritic) observed on some of the small IDPs that have the longest settling time, due to their small mass and/or fluffiness. These high S contents probably reflect the scavenging of sulfuric acid aerosols in the stratosphere. Bromine and Zn, two volatile elements, were also found to be enriched in IDPs up to 1000 $\times$  the chondritic values (Jessberger *et al.*, 1992). These enrichments were also interpreted as resulting from the exposure of IDPs to the stratospheric environment.

The AMMs also show Br and Zn enrichments over CI abundances (Flynn *et al.*, 1993; Kurat *et al.*, 1994c), but they are less pronounced than for IDPs. These enrichments in AMMs probably also result from atmospheric interactions, and the lower contamination level of AMMs is likely associated with their faster gravitational settling.

The INAA studies reveal other types of contamination in AMMs, including Pb contents of up to 1000 ppm, which likely originate from the weld joints of the stainless steel sieves used to recover the grains from melt ice water until 1991 (Kurat *et al.*, 1994c, and references therein). Switching subsequently to Sn welding replaced the Pb by an Sn contamination. The sieves to be used during our next Antarctic expeditions have been custom made without welding. Potassium and Rb enrichments in AMMs over CI values probably reflect a contamination of the melt ice water by leach products from morainic debris (see Kurat *et al.*, 1994c).

Antarctic micrometeorites are clearly depleted in S, Ca and Ni (by a factor of 2–5) with respect to chondritic composition (Kurat *et al.*, 1994c; Engrand, 1995). Frictional heating in the atmosphere is probably responsible for partial loss of S, as observed in meteorite fusion crusts (see Genge *et al.*, 1996; Genge and Grady, 1997, and references therein); but the extent of this depletion seems to be independent of the amount of thermal metamorphism suffered by the grains upon atmospheric entry (see Kurat *et al.*, 1994c). Kurat cal-

culated that the depletions in S, Ca and Ni could also be due to the fast dissolution of soluble salts (sulfates and carbonates) during their history in the ice, including an ~8 h exposure to melt ice water (Maurette *et al.*, 1992; Kurat *et al.*, 1994b). In the mass-balance computations supporting this conclusion, the initial contents of these salts in micrometeorites were assumed to be similar to those noted for CM type meteorites since the bulk chemical composition of the AMMs for major and minor elements (except for these three elements) is close to the CM bulk composition (Kurat *et al.*, 1994c; Engrand, 1995).

Soluble salts were probably quickly leached out of AMMs. In carbonaceous chondrites, soluble carbonates can carry up to ~30% of the total C (see Kerridge, 1985; Grady *et al.*, 1988, and references therein). But because carbonates have probably been leached out of AMMs, their bulk C content gives directly that of their carbonaceous matter (see section below).

### Comparison with Meteorites

Mineralogical and chemical studies show that AMMs are mainly related to the CM and CR carbonaceous chondrites (Kurat *et al.*, 1994c) that represent only ~2.5% of the meteorite falls. Indeed, ~80% of the fine-grained AMMs are made of a highly unequilibrated and primitive assemblage of hydrous silicates, anhydrous phases and carbonaceous matter like these chondrites. The crystalline grains are unequilibrated aggregates of a few anhydrous silicates (mostly pyroxenes and olivines), also related in their mineralogical and chemical composition to those observed in CM and CR chondrites. Refractory inclusions in CM meteorites and AMMs are similar with respect to both their excess of  $^{16}\text{O}$  and their mineralogical composition (Kurat *et al.*, 1994a; Hoppe *et al.*, 1995; Greshake *et al.*, 1996; Engrand *et al.*, 1997).

In spite of these similarities, there are also marked differences between micrometeorites and CM chondrites (Maurette *et al.*, 1993, 1996; Kurat *et al.*, 1994c; Engrand, 1995; Maurette, 1997; Brinton *et al.*, 1997): (1) AMMs show higher C/O ratios than Murchison (CM); (2) AMMs are very depleted in chondrules with sizes of 200–300  $\mu\text{m}$  (only one possible chondrule has been identified in a population of ~800 AMMs), while chondrules constitute ~20% of the mass of CM meteorites; (3) AMMs exhibit a ratio of pyroxene to olivine that is ~10 $\times$  larger than in CM chondrites; (4) AMMs lack very refractory olivines poor in Fe and rich in Al and Ca; (5) AMMs have a higher proportion of Ca-poor pyroxene than CM chondrites; (6) AMMs show a higher concentration of the extraterrestrial amino acid  $\alpha$ -amino isobutyric acid (AIB) than CM chondrites, and the proportion of AIB to isovaline is at least 10 $\times$  higher in AMMs than in CM chondrites.

Antarctic micrometeorites could possibly be related to CR chondrites (also composed of unequilibrated assemblages of hydrous and anhydrous minerals) rather than to CM chondrites on the specific basis of the high pyroxene/olivine ratio observed in both the CR chondrites and the AMMs. But important differences also exist between these two populations (see Weisberg *et al.*, 1993; Kallemeyn *et al.*, 1994 for a characterization of CR chondrites): (1) Fe-poor olivines (both Mn-rich and Mn-poor) are rare in AMMs, although they are abundant in CR chondrites; (2) primitive Fe,Ni metal is abundant in CR chondrites (~5 vol%), while metal is only found in AMMs as small inclusions in silicates; (3) CR meteorites contain a high abundance of large chondrules (48 to 69 vol%, mean size ~700  $\mu\text{m}$ ), while AMMs are depleted in chondrules; (4) members of the CR clan (such as Renazzo) show high D enrichment (see

Deloule and Robert, 1995, and references therein) that is not observed in AMMs (Engrand *et al.*, unpubl. data, 1998).

The number of AMMs possibly related to ordinary chondrites is very small. So far, only ~1% of the particles have been identified as showing a potential relationship to ordinary chondrites (Walter *et al.*, 1995). We have not yet found any AMM related to the groups of differentiated meteorites, including iron and stony iron meteorites and the achondrites.

Thus, the micrometeorites that represent the most abundant extraterrestrial matter accreted by the Earth today are not represented in the great diversity of the most abundant meteorites, the ordinary chondrites (~82% of the meteorite falls), and the differentiated meteorites (14% of the meteorite falls). This could be due to an effect of "atmospheric filtering" of the most friable meteorites that would not survive the impact with the Earth's atmosphere and then biasing the collections of meteorites to the detriment of the more friable ones (*i.e.*, the carbonaceous chondrites). If this is the case, the carbonaceous-chondrite-like objects should dominate the meteoroid flux beyond the atmosphere (see Baldwin and Shaeffer, 1971; Zolensky *et al.*, 1996, and references therein).

Micrometeorites show similarities in their mineralogical and chemical compositions only with rare classes of carbonaceous chondrites (CM/CR), but there are also differences between micrometeorites and CM/CR chondrites. Thus, micrometeorites constitute a new population of primitive solar system objects not represented in meteorite collections.

### Carbon Contents of Micrometeorites: The Controversy

Carbon contents have been measured in micrometeorites by two different techniques: C/O ratios have been measured by electron energy loss spectrometry for 35 AMM fragments (Perreau *et al.*, 1993; Engrand and Maurette, 1995; Engrand *et al.*, 1994; Maurette, 1997; Maurette *et al.*, 1995a), and C concentrations have been determined by stepped combustion for seven Greenland and four Antarctic micrometeorites (Wright *et al.* 1997).

Figure 2 gives the average value of the C/O ratios measured by EELS in a random selection of AMMs extracted from three size fractions: 25–50  $\mu\text{m}$  (5 AMMs), 50–100  $\mu\text{m}$  (12 AMMs), and 100–400  $\mu\text{m}$  (18 AMMs). We have also included grains from the fine-grained matrix of two carbonaceous chondrites used as references, Orgueil (CI) and Murchison (CM).

The mean C/O value calculated for the 50–100  $\mu\text{m}$  size fraction is lower than in the two other fractions (25–50  $\mu\text{m}$  and 100–400  $\mu\text{m}$ ). Because there is no plausible reason why the C/O ratios should be depleted in this size range, this probably reflects a bias of our selection in favor of crystalline (hence C-poor) micrometeorites, as 4 of the 12 AMMs from the 50–100  $\mu\text{m}$  fraction are mainly crystalline. This high proportion (one-third) of crystalline particles does not correspond to that estimated from a much larger selection of grains (about one-tenth). A rough correction applied to the observed mean value for the 50–100  $\mu\text{m}$  would put it in a range compatible with both the other size fractions.

Antarctic micrometeorites show C/O ratios that are on average ~2.5 and 3 $\times$  higher than in Orgueil and Murchison, respectively. The C/O ratios are comparable to those measured during the *in situ* analyses of dust grains from comet Halley in 1986 March, ~3 to 10 $\times$  larger than in Murchison (Kissel, 1996, pers. comm.). These analyses, pertaining to masses of cometary dust grains (~10 $^{-14}$  g) that are quite comparable to those analyzed with the ATEM, could reveal a relationship between micrometeorites and cometary dust grains.

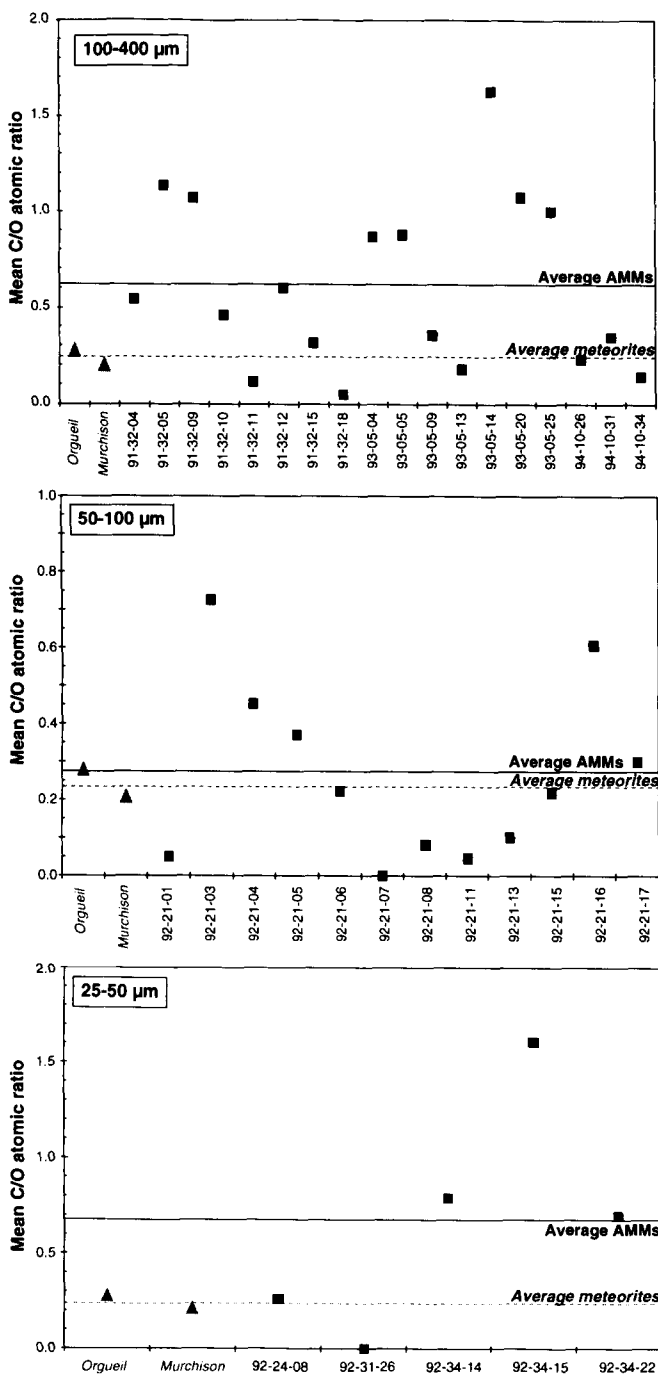


FIG. 2. Mean values of the C/O atomic ratios measured by electron energy loss spectrometry (EELS) for 35 micrometeorites (filled squares) and 2 carbonaceous chondrites, Orgueil (CI) and Murchison (CM) (filled triangles). Each value is the average of individual analyses performed on a random selection of micrometer-sized grains for each micrometeorite (~20 fragments) and meteorite (~60 fragments).

The average C/O value measured for Orgueil divided by the average C/O value for Murchison agrees with the ratio of their respective average bulk C contents determined on much larger volumes of material with the best geochemical techniques (Mason, 1971; Gibson *et al.*, 1971; Kerridge, 1985; Anders and Grevesse, 1989; Jarosewich, 1990) (*i.e.*,  $(C/O)_{\text{Orgueil}}/(C/O)_{\text{Murchison}} \sim C_{\text{Orgueil}}(\text{wt}\%)/C_{\text{Murchison}}(\text{wt}\%)$ ). Thus, we have calculated the C contents of the

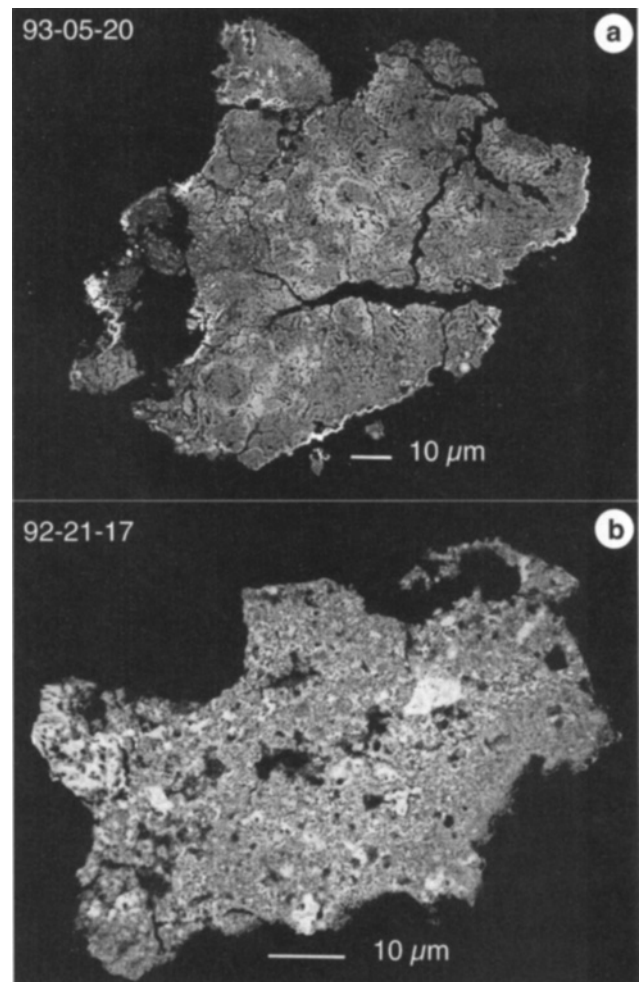


FIG. 3. Scanning electron microscope micrographs of AMMs with different C contents. The two micrographs correspond to micrometeorites belonging to the same mineralogical type (fine-grained chondritic) but that largely differ in their C contents of ~12 wt% (a) and 3 wt% (b).

micrometeorites directly from their C/O values by comparison to those measured in Orgueil and/or Murchison. Based on these C/O measurements, the C contents in Antarctic micrometeorites (~7 wt%) would be ~3× higher on the average than in CM chondrites.

There is no correlation between the C/O ratios and the textural type of the micrometeorite. One could expect that C/O ratios could be higher in unmelted fine-grained particles than in scoriaceous particles. In fact, for each textural type, there is a wide range of average C/O values, and scoriaceous particles might have lower or higher C/O ratios than fine-grained particles. For example, Fig. 3 represents two particles of the same fine-grained textural type that correspond to high (C/O = 1.1, Fig. 3a) and low (C/O = 0.3, Fig. 3b) average C/O ratios.

Wright *et al.* (1997) recently reported studies of the abundance and isotopic composition of C released during the stepped combustion of seven Greenland and four Antarctic micrometeorites with sizes of ~200 μm. The isotopic composition of C is compatible with that observed in carbonaceous meteorites, but the total contents of C inferred from these difficult measurements are much lower (typically <0.2 wt%) than the concentration we deduced from the measurement of C/O ratios (~7 wt%). The selection of micrometeorites analyzed by Wright *et al.* (1997) seems to be inappropriate for C

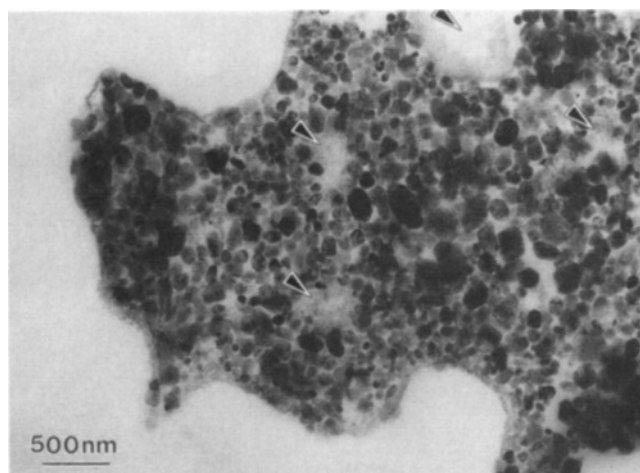


FIG. 4. Transmission electron microscope micrographs of an ultrathin section of a scoriaceous micrometeorite. Note the abundance of carbonaceous matter (arrowed) that is already visible at this low magnification. The carbonaceous phases present a darker contrast than the epoxy used to embed the micrometeorite and a higher C/O ratio.

studies (Engrand and Maurette, 1997). It was dominated by Greenland micrometeorites that were subjected for several hundred years to the biogenic corrosion of siderobacteria that constitute the dark mud (cryoconite) from which micrometeorites have to be extracted by a harsh mechanical treatment, which destroys the most friable micrometeorites in favor of the crystalline particles that are strongly depleted in C. Moreover, from the short description of Antarctic micrometeorite mineralogy given in Wright *et al.* (1997), we infer that they likely belong again to the crystalline type.

Although EELS may overestimate the C contents, we feel that these data are more representative than the data of Wright *et al.* (1997). Additional independent evidence for these high C contents was obtained during the direct observation of ultramicrotomed sections of AMMs with the ATEM. In the field of view shown in Fig. 4, the relative total cross-sectional area of the C-rich grains (as observed by a different contrast, a different electron diffraction pattern, and different C/O ratios than the epoxy resin used to embed the particle) relative to the other grains is at least 10%. Moreover, the small C contents (~0.2 wt%) noted by Wright *et al.* (1997) correspond to the limit of sensitivity of our EELS technique. In this case and contrary to our observations, the C-edge in the EELS spectrum should have been barely detectable in most of the ~ 500 analyses of micrometeorite fragments summarized in Fig. 2. At the present time, more work is needed to understand such discrepancies.

#### Search for Complex Organics

Summarized below are the results obtained during a search for amino acids and PAHs in large Antarctic micrometeorites with a size of 200  $\mu\text{m}$  (for further details see Brinton *et al.*, 1997; Clemett *et al.*, 1997). This size was selected because it corresponds to the bulk of extraterrestrial material accreted by the Earth (Love and Brownlee, 1993), even if the particles have been more strongly heated than micrometeorites from the 50–100  $\mu\text{m}$  size fraction.

Clemett *et al.* (1997) inferred the following conclusions from their comparison of the AMM PAH mass spectra with those of three carbonaceous chondrite samples (Orgueil, CI; Murchison, CM; Allende, CV): (1) the meteoritic PAHs show similarities, with simple mass spectra dominated by four peaks corresponding to core PAHs observed at  $m/z$  values of 128, 178, 202, 228; (2) there are very few

fragmentation products observed at mass  $\leq 100$  amu, as well as few PAHs with masses  $\geq 300$  amu; (3) during laboratory pyrolysis experiments, the degree of alkylation (related to the number of substitutions on the core PAHs) reflected in the tails of the high mass peaks increases with temperature; (4) the content of PAHs in meteorites decreases from Allende to Murchison and then Orgueil. It has been suggested that this trend is inversely correlated to a scale of hydrous alteration (on parent bodies) that increases from Allende (which contains few hydrous minerals, although its aqueous alteration history seems to be controversial, see Brearley, 1997) to Murchison (~40% hydrous minerals) and Orgueil (>95% hydrous minerals).

The PAH mass distributions of the giant Antarctic micrometeorites (Clemett *et al.*, 1997) show the following differences when compared to carbonaceous chondrites: (1) a much larger variety of PAH spectra that range from simple spectra rather similar to those of carbonaceous chondrites, to complex spectra with many peaks, extending to higher mass numbers and showing predominant tails around the major peaks; (2) barely detectable peaks at  $m/z = 128$  and  $m/z = 252$ ; (3) yields that vary between the values observed for Allende to a few times those for Orgueil, with most values clustering around the intermediate yield observed for Murchison; (4) a much higher degree of alkylation of the PAHs, which clearly increases with the extent of thermal metamorphism, as inferred from the growth of tiny vesicles in AMMs; (5) vinyl PAHs (*i.e.*, containing a  $\text{CH}_2\text{-CH-}$  group) not observed yet in meteorites and which can be best observed in the mass range 250–290 (see Fig. 5).

The PAHs contamination of meteorites (Becker *et al.*, 1997) and of micrometeorites in the Antarctic ice and during their collection is an issue. Although contamination by terrestrial PAHs cannot be completely ruled out, several observations argue for an extraterrestrial origin of the PAHs found in AMMs (Clemett *et al.*, 1997): (1) the increase in the degree of PAHs alkylation with the extent of vesicle formation in the AMMs shows that the PAH distribution was affected by frictional heating and, thus, already present during atmospheric entry; (2) in a set of AMMs recovered the same day from the same water pocket, each AMM has a unique PAH distribution; (3) rust grains generated in the tubings of the steam genera-

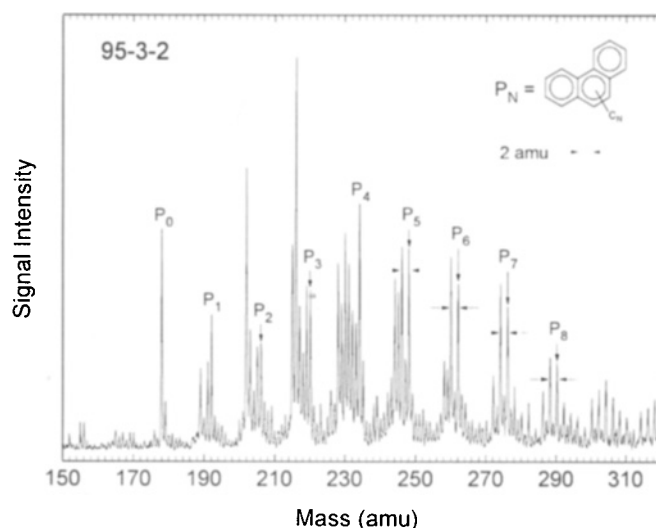


FIG. 5. Polycyclic aromatic hydrocarbon (PAH) mass spectrum of a micrometeorite. This spectrum clearly shows vinyl PAHs, bearing a reactive  $\text{CH}_2\text{-CH-}$  group (courtesy of S. Clemett).



tors and recovered from the same water pocket as the AMMs do not show detectable PAHs signals, besides that corresponding to the background of the analytical chamber; (4) there is no difference between the analyses of the AMMs collected in 1991 (with a dirtier system, and under less favorable climatic conditions) and those collected in much cleaner conditions in 1994.

The major results of Brinton *et al.* (1997) concerning the search for amino acids in the AMMs are summarized in Table 1: (1) the most abundant amino acid is AIB ( $\alpha$ -amino isobutyric acid), a non-proteic amino acid that is considered as a tracer of extraterrestrial origin (Zhao and Bada, 1989, 1995); (2) the ratio of AIB to isovaline is a factor of 10 higher in AMMs than in CM chondrites; (3) the content of AIB is highly variable in these five aliquots, ranging from 280 ppm to the blank level ( $\ll 1$  ppm); (4) the average content of AIB in the five aliquots ( $\sim 180$  AMMs), of  $\sim 80$  ppm, is thus  $\sim 10\times$  higher than the value measured in an  $\sim 5$  mg sample of the Murchison meteorite (5 to 10 ppm) used as a standard during these runs; (5) alanine is the next most abundant extraterrestrial amino acid, with a similar abundance of L- and D- enantiomers; (6) there is a clear contamination of terrestrial amino acids showing a strong dominance of the L enantiomers, which matches the pattern observed for the ice by McDonald and Bada (1995) that was reported to be unique with regard to the small number of amino acids.

#### Extraterrestrial Water in Micrometeorites and Cosmic Spherules

We summarize below the major results of our measurements of the content and isotopic composition of the constituent water of AMMs, which will be discussed in detail by Engrand *et al.* (unpubl. data, 1998). In the same paper, we also describe various tests showing that indigenous water was analyzed and not contamination by Antarctic water, which is characterized by a very low  $\delta D$  value of  $\sim -400\text{‰}$ .

The bulk water contents estimated from the  $H^+$  signal are higher for unmelted micrometeorites (from  $\sim 1$  to  $\sim 4$  wt%) than for scoriaceous particles (between  $\sim 0.4$  and  $\sim 2$  wt%), which is in agreement with our textural classification. The D/H ratios of AMMs show a distribution of values ranging from clearly extraterrestrial ( $\delta D > 0$ ) to terrestrial-like values and resembles that determined for the carbonaceous chondrites (see Engrand *et al.*, unpubl. data, 1998). These values for both carbonaceous chondrites and AMMs are almost totally incompatible with the results obtained on IDPs, which often exhibit much larger positive  $\delta D$  anomalies (McKeegan, 1987; McKeegan *et al.*, 1985, 1987; Messenger and Walker, 1996; Messenger *et al.*, 1996; Zinner *et al.*, 1983).

The amounts of water measured for the cosmic spherules are surprisingly high, typically between  $\sim 0.1$  and  $\sim 1$  wt% (see Table 2).

TABLE 1. Average contents of AIB ( $\alpha$ -amino isobutyric acid) in Antarctic micrometeorites.

Sample	Sample's Mass ( $\mu\text{g}$ )	AIB (ppm)
A91	50	280
I91	175	78
III91	310	22
IV94	166	$<0.1$
V94	259	20

Five aliquots of  $\sim 35$  AMMs with a size of  $200 \mu\text{m}$  were analyzed, except for the first sample (A91) for which we purposely selected the smallest grains ( $\sim 100 \mu\text{m}$ ) of the  $100\text{--}400 \mu\text{m}$  size fraction (courtesy of J. L. Bada).

The unexpectedly high water contents of the cosmic spherules, thought to have been completely melted upon atmospheric entry and hence degassed, highlight the inadequacy of the models of frictional heating and/or the fact that the loss of water is probably not instantaneous and that the kinetics of such processes have not been taken into account in the models thus far.

The water content of the COPS nuggets ranges between  $\sim 1$  and  $\sim 8$  wt% (see Table 2). Three of seven COPS nuggets have high D/H ratios ( $\delta D$  up to  $+200\text{‰}$ , see Fig. 6), which is consistent with an extraterrestrial origin for their constituent water. This suggests that this phase is not the result of hydrous alteration related to cryogenic weathering in Antarctica.

TABLE 2. Water contents and D/H ratios of ten COPS-rich cosmic spherules and water contents and D/H ratios of seven of the cosmic spherules' COPS nuggets (see text).

Sample	$H_2O$ (wt%)		D/H ( $\times 10^6$ )	
	CSs	COPS	CSs	COPS
5M1	0.6		125.4	
	0.1		96.9	
92-23B-77	2.4	2.9	121.9	132.5
		3.4		131.5
93-6C	1.0	3.8	128.4	194.0
	0.6	1.1	120.4	173.4
95-11-1	0.9	5.3	125.8	146.0
	0.5		116.7	
95-11-2	0.8	7.9	124.5	161.9
	0.9		114.7	
95-11-3	0.7	5.0	134.6	157.7
	0.7		129.1	
95-7A	0.1	5.4	111.7	135.4
95-7B	1.2		102.0	
95-7C	0.2		83.4	
95-7D	0.1		65.2	
95-7D	0.2	3.5	95.1	133.4

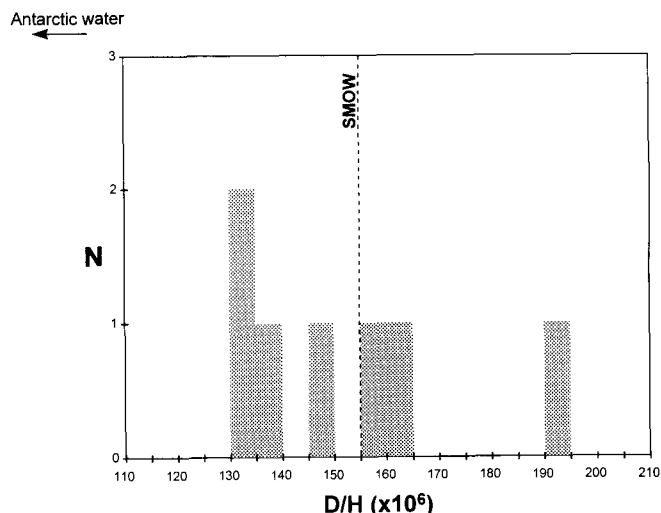


FIG. 6. Distribution of D/H ratios in ferrihydrite COPS nuggets of cosmic spherules. The D/H ratios higher than the SMOW value show that the constituent water of this Fe-rich phase has an extraterrestrial origin. We cannot exclude that the COPS phase might have resulted from the *in situ* hot hydrous alteration of a precursor Fe/Ni-rich phase by the extraterrestrial water being released upon the dehydration of the original hydrous minerals, thus explaining the high-Ni content and high-D/H ratios of this phase.

### Host Phases of Complex Organics

While EELS spectra yield the C/O ratios of the C-rich grains, their EDS analysis, electron diffraction patterns and textural features reveal clues about their mineralogy. There is no clear correlation between the C/O values and the chemical composition measured in the same volume of material as defined by various element to silicon ratios (see Fig. 7).

Transmission electron microscopic observations reported by Maurette *et al.* (1995b) indicate that the C-rich grains show four major types of carbon distribution: (1) coating of the COPS phase on the external surface of the grain; (2) interstitial COPS particles; (3) ultrathin coatings (<50 nm) on mineral constituents of the micrometeorite; and (4) small vesicles filled with a thin (~100 nm) wall that show only C and O in their EDS and EELS spectra.

All C-rich grains are composed of poorly crystallized phases, which are difficult to identify from electron diffraction patterns. The only one clearly identified is the "COPS phase" (Engrand *et al.*, 1993), which exhibits diffuse rings at 2.41 Å, 2.12 Å and 1.43 Å (typical of ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub>, 9H<sub>2</sub>O)). This phase also contains P, S and Ni, and other minor elements (Si, Mg, Al, *etc.*) and bears a relationship to the variety of ferrihydrite observed in CI chondrites (Tomeoka and Buseck, 1988) and in the unique type-3 Kakangari chondrite (Brearley, 1989). The COPS phase is observed in all types of AMMs (see Fig. 8) and probably represents ~10% of C-rich grains.

With the exception of rare CM2 clasts (Zolensky *et al.*, 1996), which also contain a variety of fibrous ferrihydrite quite similar to

that shown in Fig. 8, the CM chondrites, to which most of the AMMs are related, do not contain ferrihydrite. Rather, they contain other varieties of previously named "poorly characterized phases," which have now been identified as intergrowths of tochilinite and serpentine (Bunch and Chang, 1980; MacKinnon and Zolensky, 1984; Tomeoka and Buseck, 1985). The COPS phase (or ferrihydrite) in AMMs is also different from the varieties reported in carbonaceous chondrites in that it has a higher P content, which is an important element for the chemistry of life (Schidlowski, 1988). All these results indicate that the host phases of complex organics might be quite different in AMMs and CM chondrites, thus adding an important characteristic to their list of major differences.

It has been suggested that ferrihydrite and the poorly characterized phases could be the host phases of complex organics in the hydrated carbonaceous chondrites (Bunch and Chang, 1980; Tomeoka and Buseck, 1988). The same property of the ferrihydrite in the AMMs could explain in turn the high concentrations of terrestrial amino acids naturally "extracted" and concentrated from melt ice water by micrometeorites functioning now as "cosmochromatographs" (see Brinton *et al.*, 1997).

On the Earth, ferrihydrite is frequently associated with clays. It efficiently adsorbs minor and trace elements and, thus, masks the trace chemical compositions of the clays. Clay mineralogists usually wash out this phase in various mixtures of organic and inorganic solvents (Jeanroy, 1983). This procedure could be applied to micrometeorites in order to examine the residual distribution of both PAHs and amino

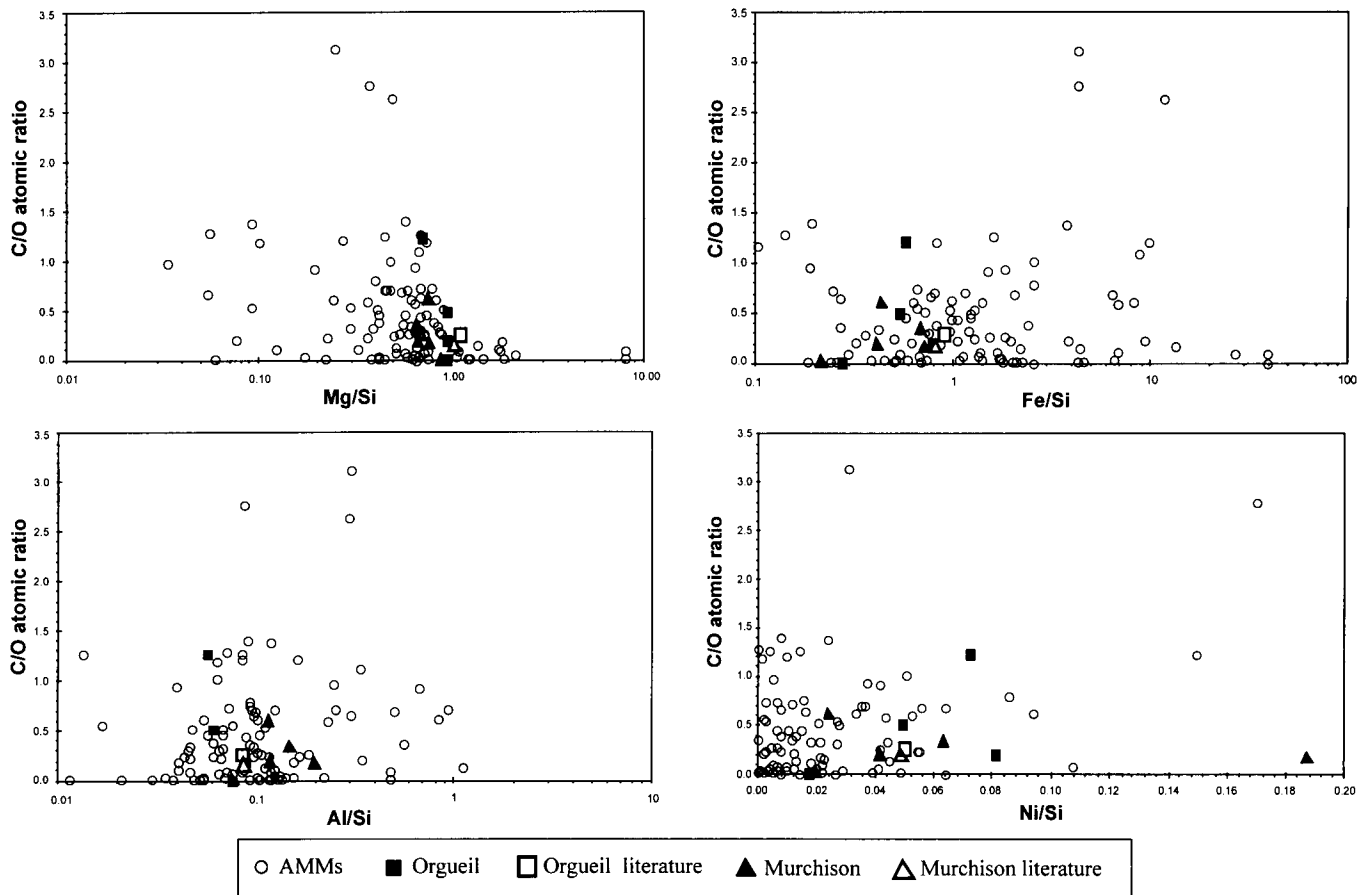


FIG. 7. Search for a correlation between the C/O atomic ratios measured by EELS and the chemical composition of the same zone (~100 nm in diameter) determined by EDS.

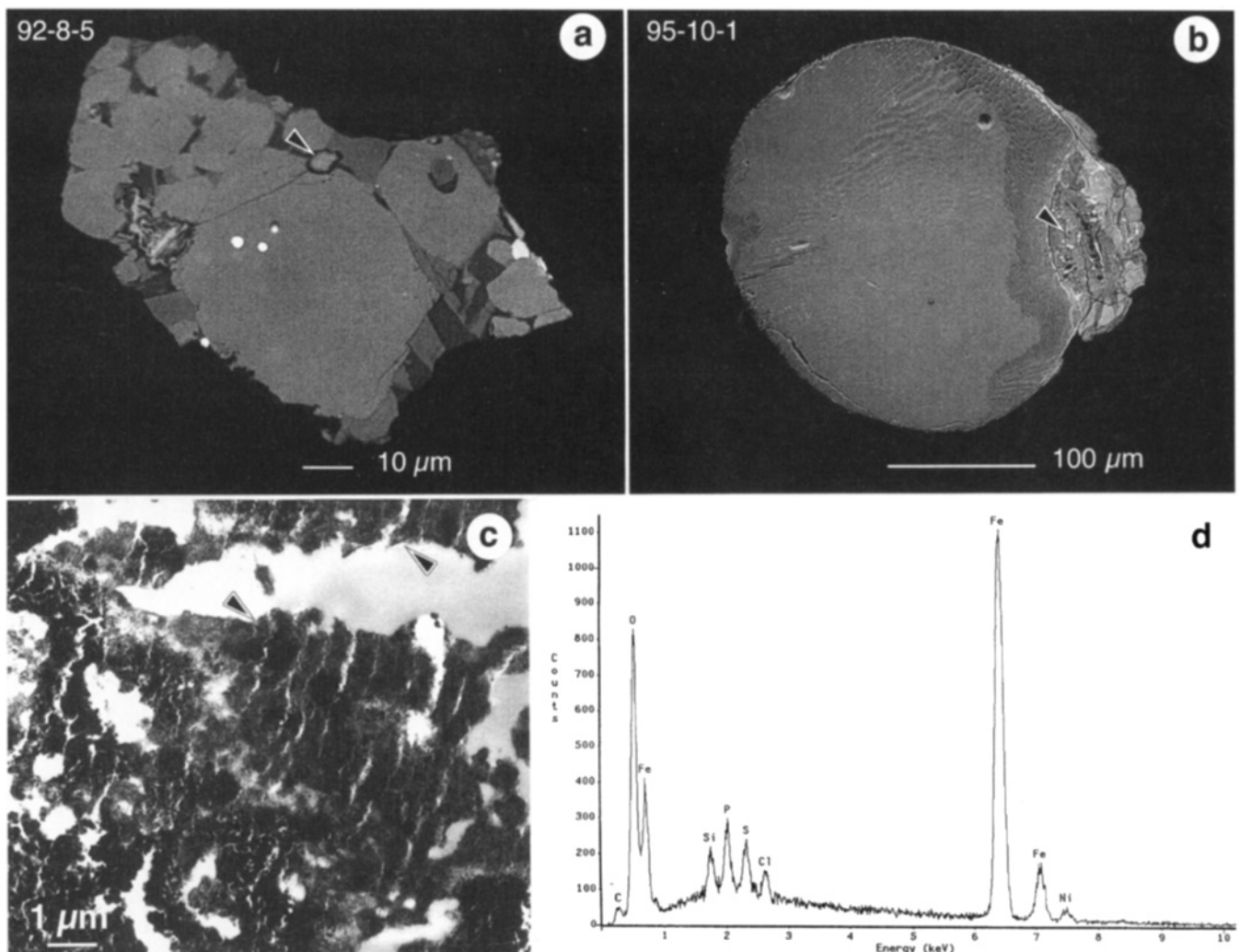


Fig. 8. Electron microscope micrographs of the COPS phase. About 10% of the C-rich grains are made of a poorly crystallized phase of iron hydroxide (ferrihydrite), which is observed as large inclusions on polished sections of micrometeorites (a) and cosmic spherules (b), and on ultramicrotomed sections as a typical fibrous texture (c). The high-Ni content of this phase (see the corresponding EDS spectra, d) supports its extraterrestrial origin.

acids after the washing of ferrihydrite and would then provide a test of whether ferrihydrite is indeed the host phase of complex organics.

#### PRELIMINARY IMPLICATIONS

##### A New "Chondrites-without-Chondrules" Interplanetary Material

Micrometeorites from the 50–500 μm size fraction recovered from the ice correspond to the most abundant matter accreted by the Earth today. Their mass flux (~20 000 tons per year), which was determined independently by counts of chondritic particles on both the Greenland (Hammer and Maurette, 1996) and Antarctic ice sheets (Taylor *et al.*, 1996b), is ~2000× higher than the value of the macroscopic meteorite flux (Bland *et al.*, 1996).

In a previous section (comparison with meteorites), we outlined similarities but also marked differences between micrometeorites and CM and CR chondrites. The differences most likely reflect residences in different parent bodies for ~4.5 Ga, before being released recently in the interplanetary medium.

The possible relationship between micrometeorites and CM and CR chondrites could suggest that CM and CR type chondritic matter

might also dominate the composition of the meteoroid flux in the interplanetary medium, but that it is preferentially destroyed during atmospheric entry due to its friability, thus explaining its rarity in the meteorite collections. This explanation is favored by Sears (1997) who quotes an enhancement factor of ~1000 for such meteorites before atmospheric entry (from Baldwin and Shaeffer, 1971).

If micrometeorites were formed by disaggregation of the abundant and large CM and CR type meteoroids, a fraction of AMMs should show low  $^{26}\text{Al}/^{10}\text{Be}$  ratios due to the short penetration depth of solar cosmic rays (with regard to the size of the meteoroid) as compared to that of galactic cosmic rays in the meteorite parent body. However, this is not observed in ~100 individual cosmic spherules with a size  $\geq 400$  μm. Indeed, high values of the  $^{26}\text{Al}/^{10}\text{Be}$  ratios were measured in these particles, which indicate that these cosmogenic nuclides were accumulated inside small micrometeoroids, with a maximum size of ~1 cm (Nishiizumi *et al.*, 1991; Raisbeck and Yiou, 1987; Raisbeck *et al.*, 1985, 1986).

The identification of the parent bodies of micrometeorites is still a challenge. In favorable cases, the light and/or ion trails delineating meteors in the atmosphere allow the determination of their or-

bits. These studies, which apply to large meteorites in the visible range and to the fastest micrometeorites down to a size of 100  $\mu\text{m}$  in the radar range, indicate that the parent bodies of meteorites are asteroids from the main asteroidal belt; while micrometeorites originate predominantly from comets formed at much larger heliocentric distances (Whipple, 1967).

The optical properties of the zodiacal cloud and the study of the dust bands detected by the IRAS satellite indicate that the zodiacal cloud is made of a mixture of asteroidal and cometary dust, which should both contribute to the flux of interplanetary dust accreted by the Earth (Levasseur-Regourd *et al.*, 1991; Liou *et al.*, 1995, and references therein). Liou *et al.* (1995) proposed that the shape of the zodiacal cloud, as observed by IRAS, can be accounted for by a combination of one-fourth to one-third asteroidal dust and about three-fourths to two-thirds cometary dust.

However, the relative proportions of cosmic dust from both origins collected on Earth should be different from those in the zodiacal cloud. This is due to both the Earth's gravitational focusing and atmospheric entry heating. Flynn (1990) outlines the effect of the Earth gravitational focusing (first described by Öpik, 1951) that strongly increases the effective Earth-capture cross-section for cosmic dust particles having low geocentric velocities (even if they constitute only a few percent of the incoming flux). This effect should greatly favor then the capture of asteroidal dust particles over cometary dust grains since the latter usually have higher geocentric velocities than typical asteroid particles. However, Liou and Zook (1996, 1997) and Liou *et al.* (1996) showed that cometary dust trapped in a mean-motion resonance with planets (in particular with Jupiter) can see a decrease of their eccentricity and inclination and would later approach the Earth with typical asteroidal velocities. On the other hand, some special sets of asteroids can inject dust in the Earth's atmosphere with cometary like trajectories and velocities, although their contribution to the flux is probably small (Flynn, 1994b). Thus Liou and Zook (1996, 1997) and Liou *et al.* (1996) propose that cometary grains constitute a significant fraction of the IDPs collected on Earth.

Our comparison of meteorites and large ( $\geq 100 \mu\text{m}$ ) AMMs independently supports this conclusion. In the case of carbonaceous chondrites, it is frequently stated that an increase in C content or a decrease in the chondrule abundance compared to most ordinary chondrites indicates that their parent bodies formed at larger heliocentric distances (Rubin and Wasson, 1995). We can apply the same reasoning to micrometeorites. As they show both a higher C content ( $\sim 3\times$ ) and a very strong depletion of chondrules (by at least a factor of 20) with regard to CM carbonaceous chondrites, their parent bodies were likely formed at larger heliocentric distances. The lack of differentiated objects in the micrometeorite collection further supports this conclusion, because the outer solar system contains dark and featureless small bodies (Owen *et al.*, 1995), which are indicative of undifferentiated objects.

We now question how this new "chondrite-without-chondrules" matter might help place new constraints on the formation of the solar system, relying on unpublished results of M. Gounelle at C.S.N.M. (Orsay).

#### Micrometeorites and the Early Solar Nebula

We have shown that large (50–500  $\mu\text{m}$ ) AMMs are made of a CM/CR type chondritic matter, showing "normal" refractory inclusions, but both are enriched in carbonaceous matter and strongly depleted in chondrules. Micrometeorites probably sample new types

of carbonaceous asteroids different from the ones that are the source of the meteorites, but it is also probable that at least a fraction of the micrometeorites have a cometary origin (see previous section). Additional evidence for a cometary origin like the very high ratio of AIB to isovaline that suggests a HCN-rich environment for their synthesis (see next section) supports this statement. This conclusion would challenge the widespread belief that cometary dust should be made of frozen interstellar matter considered to be much more primitive than carbonaceous chondrites (Greenberg and Hage, 1990).

These studies might also yield new clues about early processes in the solar nebula. Besides chondrules, carbonaceous chondrites contain refractory inclusions (CAIs). In the chronological interpretation of the  $^{26}\text{Al}$  data of CAIs and chondrules (Russel *et al.*, 1996), the formation of both components were related, with CAIs being the first high-temperature phases to condense during the cooling of a hot solar nebula, and chondrules being formed thereafter ( $\sim 2 \text{ Ma}$ ) during fast cooling of molten droplets (see also Hewins *et al.*, 1996). In the hot nebula models, both processes occurred within the formation zone of the terrestrial planets (including the main asteroidal belt). Further away, beyond the frost line where icy bodies could survive, both processes would be inoperative.

Antarctic micrometeorites change this classical view. In spite of being strongly depleted in chondrules (the upper limit of the chondrule concentration among the  $\sim 200 \mu\text{m}$  size micrometeorites is  $< 1\%$ ), micrometeorites still contain CAIs showing striking similarities with those observed in carbonaceous chondrites (Kurat *et al.*, 1994a; Hoppe *et al.*, 1995; Greshake *et al.*, 1996; Engrand *et al.*, 1997).

In the formation zones of the AMMs, the production of chondrules and CAIs could have been uncoupled, with the formation of chondrules severely impaired, while that of CAIs remaining relatively efficient. An alternative view is that chondrules and CAIs were formed in the same place, but CAIs got preferentially delivered to the presumed formation region of the AMMs in the outer solar system.

Matthieu Gounelle is attempting to model the origin of CAIs and chondrules in the outer solar system, relying on various scenarios proposed for the origin of the solar system. The most appropriate ones seem to derive from the "T-Tauri" model proposed by Shu *et al.* (1996), based on the study of the complex motions of matter observed in the region within a few stellar radii of proto-stars. In this model, both CAIs and chondrules are formed during the emission of the "x-wind" near the young star. Very early in the emission of this wind, where the temperature is sufficiently high, only CAIs can survive and chondrules are evaporated. These CAIs, then, could be delivered easily to the outer solar system. This scenario requires that the small bodies of the outer solar system were formed shortly before asteroids in order to prevent the admixture of chondrules in the micrometeorite matter.

In another model (Boss, 1996), "clouds" of accreting nebular material (*e.g.*, gases containing  $\sim 1 \text{ wt}\%$  dust grains) with masses of  $\sim 10^{22} \text{ g}$  were "raining" over the whole nebular disk at high speed ( $> 100 \text{ km/s}$ ). The constituent dust of these clouds suffered an aerodynamical "drag" during their impact with the gas of the nebular disk. This impact can trigger the whole sublimation and/or the partial evaporation residues of the initial presolar grain aggregates that could generate CAIs either as condensates or "boiling" residues, even in the coldest part of the nebula at large heliocentric distances. However, one has to explain why chondrules were not formed during this process.

McKeegan *et al.* (1998) have recently measured the O isotopic composition of ordinary chondrite CAIs, and their results support the hypothesis that the formation of CAIs and chondrules could have been uncoupled. Furthermore, they infer that the formation of chondrules and CAIs could have happened in different places of the solar nebula, and this will have to be taken into consideration in the models.

### Micrometeorites and Exobiology

If the infall of extraterrestrial material was important in the synthesis of prebiotic molecules on the early Earth, ~4 Ga ago, then micrometeorites could bring enough carbonaceous material to the early Earth; it is, therefore, not necessary to rely on the survival of a minute fraction of a cometary nuclei impacting the Earth or on a delivery of organic molecules by meteorites (Anders, 1989; Chyba and Sagan, 1992; Chyba, 1995). Although direct flux measurements (see above) show that micrometeorites are the dominant source of extraterrestrial materials that reach the Earth's surface today, models of frictional heating during atmospheric entry (see Love and Brownlee, 1991, and references therein) predict that >90% of micrometeorites (in the size range 100–300  $\mu\text{m}$ ) should evaporate, with half of the remaining 10% being melted into cosmic spherules and losing their carbonaceous matter by pyrolysis, and only 5% of the particles remaining unmelted. Thus, one should assess how much of this material survives unmelted to deliver carbonaceous material to the Earth.

From the characteristics of AMMs, including their classification in three major groups (*e.g.*, unmelted, partially melted/dehydrated and melted) and the measurement of the average C content of each group, we estimate that AMMs presently deliver ~500 tons of C to the Earth per year. This is a value ~50 000 $\times$  higher than that expected from carbonaceous chondrites (assuming an average C content for the carbonaceous chondrites of ~2.5 wt%, which is probably a maximum value). This value for the present C flux deduced from our measurements is in rather good agreement with the independent estimation of Anders (1989), based on an extrapolation of the C content of IDPs. Similarly, from the average content of AIB (~80 ppm) and the average yield of PAHs (similar to that of Murchison) in AMMs, the micrometeorite delivery rate of complex organics to the Earth is between ~500 000 (AIB and associated amino acids) and ~50 000 (PAHs) times higher than the corresponding values estimated for carbonaceous chondrites (see Brinton *et al.*, 1997; Clemett *et al.*, 1997).

The delivery rate of carbonaceous matter to the early Earth (between 4.2 and 3.9 Ga ago) can be inferred from these present-day values as follows. Microcraters produced during micrometeorite impacts on tiny crystals recovered at a depth of 3 m in the lunar regolith indicate that the micrometeorite flux already existed in the interplanetary medium at a similar level at least 3 Ga ago (Morrison and Zinner, 1976; Poupeau *et al.*, 1977). But we need to go further back in time, when the solar system was still heavily "congested" with bodies of all sizes during a period of much enhanced bombardment, known as the accretionary tail. These earlier bodies produced large impact craters on the Moon indicating that the collisions between the small bodies of the solar system and the Earth/Moon system were much more frequent in the distant past (Chyba, 1987; Anders, 1989).

This direct method cannot be applied to the much more abundant smaller meteoroids that generated micrometeorites on the early Earth. Indeed, their small craters overlap many times, producing a saturation concentration of craters that cannot be used to determine the meteoroid flux.

It is likely that the big meteoroids of the accretionary tail were comets and asteroids. They generated meteorites and micrometeorites on the early Earth by the same processes we observe today, including the sublimation of cometary ices, and collisions between asteroids. Consequently, if the flux of these parent bodies was ~1000 $\times$  higher, we can assume that the fluxes of micrometeorites and meteorites were increased by a similar factor.

If we make this conservative hypothesis, the total amount of C delivered to the early Earth by unmelted and partially melted/dehydrated micrometeorites between 4.2 and 3.9 Ga ago was then ~150 $\times$  larger than that trapped in the present-day biosphere. This satisfies a constraint imposed on any prebiotic scenario that is to deliver an amount of total C at least equal to the amount of C engaged in the biomass (~10<sup>18</sup> g) (Brack, 1996).

Other experimental observations suggest that each micrometeorite could have functioned individually as a microscopic "chondritic" chemical reactor to generate complex organics (at least amino acids), as soon as they were in contact with water on the Earth, by some catalyzed hydrolysis of their carbonaceous components (Maurette *et al.*, 1990, 1991a, 1995a; Engrand, 1995; Maurette, 1997). This model is derived from a scenario proposed by organic geochemists ~20 years ago to explain the formation of the numerous organic molecules found in the CM Murchison chondrite (Bunch and Chang, 1980). In this scenario, the catalyzed hydrolysis of a carbonaceous precursor was effective in the early damp regolith of the parent bodies of meteorites (Bunch and Chang, 1980; Shock and Schulte, 1990). A similar catalytic chemistry could occur, in principle, for AMMs that typically consist of millions of grains embedded into abundant carbonaceous material. Even the partially dehydrated scoriaceous AMMs, like the one shown in Fig. 1c, still contain an abundant carbonaceous component.

Some of the minerals in contact with the organics in micrometeorites are presently used to catalyze industrial chemical reactions. They include oxides and sulfides of metals, and clays showing different degrees of dehydration and/or disordering. The thin shell of magnetite that encapsulates all types of micrometeorites might further act as a kind of inorganic vesicle to confine reactants within the small volume of the grains. This would minimize one of the major objections facing all other "primitive soup" scenarios: dealing with the fast dilution of the reactants in water and a concomitant sharp decrease in reaction rates. A dirty variety of ferrihydrite noted as the COPS phase could also be a very effective "cosmochromatograph" to concentrate complex organics including amino acids. The recent detection of AIB and PAHs (see above) gives further support to this scenario, which indicates in particular that the synthesis of amino acids in micrometeorites was already effective in some environment.

A major difference between CM chondrites and micrometeorites is the much higher AIB to isovaline ratio observed in AMMs. This might reflect a distinct process of cyanide synthesis of amino acids involving HCN. A high proportion of comets show CN<sup>-</sup> ions in their plasma tails (Mumma *et al.*, 1993; Wagner and Schleicher, 1997, and references therein). This would provide the right environment for cyanide synthesis, which was possibly triggered by the percolation of water vapor (generated during the sublimation of cometary ice near perihelion) through the dark cometary crust, in which cometary micrometeorites resided temporarily. It would be much more efficient in the "mature" crust of periodic comets that were subjected many times to this reprocessing by water vapor (and other

cometary gases) than in nonperiodic comets with an immature surface, never processed before in the inner solar system.

It has been suggested that a purely terrestrial prebiotic synthesis could occur in hydrothermal sources on the ocean floors (Hennet *et al.*, 1992; Yanagawa and Kobayashi, 1992). This scenario has the great merit to propose a shielding of the chain of processes involved in the origin of life from the sterilization induced on the Earth's surface and/or shallow waters by the cataclysmic impacts during the accretionary tail (Sleep *et al.*, 1989). But the "early micrometeorites" scenario would also share the same advantage, as ~500 000 micrometeorites were deposited over each square meter of the early Earth over the expected lifetime (~10 years today) of a hydrothermal source, including the specific area where the sources were operating. We cannot exclude that some type of synergetic effect between early hydrothermal sources and early micrometeorites was important to the formation of the prebiotic molecules required for the origin of life.

### CONCLUSIONS AND FUTURE PROSPECTS

The flux of micrometeorites reaching the Earth's surface after atmospheric entry has been determined from direct particle counts in the Greenland and Antarctica ice sheets: ~20 000 tons per year, mostly found in the size range 100–200  $\mu\text{m}$ . This value is similar to that inferred before atmospheric entry by Love and Brownlee (1993), ~30 000 tons/year ( $\pm 10 000$  tons), after a downward revision of the initial value of 40 000 tons (Brownlee, 1994, pers. comm.), with a peak in the mass distribution being observed at ~200  $\mu\text{m}$ . Thus, AMMs yield a representative sampling of the micrometeoroids existing in interplanetary medium, and they correspond to the dominant material accreted by the Earth today.

A striking feature of AMMs is their relationship with CM/CR chondritic matter. Indeed, the most abundant meteorites (ordinary chondrites and differentiated meteorites) are not represented in the micrometeorite flux. This supports an origin of the parent bodies of micrometeorites in the outer solar system, also thought to be depleted in differentiated material (Owen *et al.*, 1995). This feature, that we reported frequently over the last six years, now has to be considered with the abundance of CM/CR clasts in various classes of meteorites (Zolensky *et al.*, 1996), which suggests that these clasts' matter were also an abundant material over much of the solar system history.

This CM/CR type matter was possibly the most abundant widespread material to be synthesized in the early solar nebula. Consequently, it might have been the building material of planets and should have played a role in the origin of life on the early Earth.

We have already argued (see for example Maurette, 1997; Maurette *et al.* 1996, 1997) that micrometeorites were synthesized in the outer solar system and delivered to the Earth by comets. This would imply that comets are made of the same "chondrites-without-chondrules" material and not from a dominant interstellar component as defined by Greenberg and Hage (1990). The dust analyzers on the future Stardust and Rosetta cometary missions should be designed to distinguish easily between these two distinct types of cometary models, in case the capture of cometary dust by Stardust fails. As shown by preliminary work of Gounelle (1997, unpublished), the cometary origin hypothesis puts new constraints on scenarios proposed for the origin of the solar system, which still have to be fully explored: understanding how "normal" refractory inclusions could have been selectively produced and/or injected in the outer solar system without being "contaminated" by a much higher flux of chondrules.

Additional work should be conducted to fully understand the interactions of micrometeorites with the terrestrial environment. In

particular, the micrometeorites survive their hypervelocity capture with the Earth's atmosphere much better than predicted by models. Philippe Bonny has reported first several possible explanations for the discrepancy (Bonny, 1990; Bonny and Balageas, 1990; Bonny *et al.*, 1988): (1) the possibility that material (such as organics) that decomposes upon heating through a complex set of endothermic reactions cools down micrometeorites from the inside; (2) the importance of the short duration of the flash heating suffered by micrometeorites; and (3) the poor theoretical description of the gas envelope formed on the leading edge of micrometeorites.

Further evidence of inadequacy of the models of frictional heating comes from the fact that AMMs sometimes exhibit evidences for partial melting (*i.e.*, a temperature gradient inside an individual micrometeorite), with pristine phyllosilicates intermixed with scoriaceous material. Szydlik and Flynn (1992a,b) showed that a model simply based on the thermal diffusivity of the particle cannot explain this kind of temperature gradient, as the time required for equilibration of the temperatures between the surface and the interior of the particle is shorter than the duration of the pulse heating. They invoke local phase transformations (of phyllosilicates for example) to explain this phenomenon. Such transformations could possibly explain the unexpected survival of the micrometeorites upon atmospheric entry heating, as pointed out previously by Bonny (1990), Bonny and Balageas (1990) and Bonny *et al.* (1988).

Another important example of interaction with the terrestrial environment is observed in the distribution of amino acids in AMMs. Clearly, AIB (a nonproteic amino acid very rare on the Earth) has an extraterrestrial origin. But, there is also contamination by terrestrial amino acids that show a unique distribution quite similar to the simple one observed in Antarctic ice, which is still poorly understood (see Bada *et al.*, 1996). An odd feature is their concentration level in AMMs, ~100 000 $\times$  higher than in the ice. Antarctic micrometeorites would function then as very efficient "cosmochromatographs" by highly concentrating amino acids already present in the Antarctic ice. This characteristic, which greatly complicates the study of their primary amino acid distribution, also illustrates one of their important properties that have implications for the interactions of AMMs with gases and waters in planetary environments, such as those of the Earth, Mars and Europa. Further work (in progress) is required to understand whether ferrihydrite is the phase responsible for this property.

Recent experiments of Bada *et al.* (1996) indicate that if a mixture of amino acids sealed in a glass tube is quickly exposed to high temperature (~1 s, as to simulate pulse heating), then a high fraction of this mixture is transported to the coldest area where it recondenses without degradation. These types of experiments have to be pursued in order to examine the mechanisms that protect delicate organics during the pulse heating of micrometeorites at a residual pressure of  $10^{-4}$  bar in the upper layers of the atmosphere. This protection might involve the COPS phase acting as a cold trap for the flux of migrating amino acids.

In spite of complications related to change in characteristics resulting from their complex interactions with the terrestrial environment, it is possible to identify the primary characteristics of the large micrometeorites recovered from clean Antarctic ices. Early studies exploited such characteristics in exobiology. The more recent merging of micrometeorite and meteorite studies, which supports the likely dominance of CM/CR type chondritic matter throughout the history of the solar system (and possibly throughout the whole volume of the solar nebula), will certainly open new frontiers in meteoritics and planetology.

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