



A nuclear microprobe study of the distribution and concentration of carbon and nitrogen in Murchison and Tagish Lake meteorites, Antarctic micrometeorites, and IDPs: Implications for astrobiology

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Abstract—Using a nuclear microprobe, we measured the carbon and nitrogen concentrations and distributions in several interplanetary dust particles (IDPs) and Antarctic micrometeorites (MMs), and compared them to 2 carbonaceous chondrites: Tagish Lake and Murchison. We observed that IDPs are richest in both elements. All the MMs studied contain carbon, and all but the coarse-grained and 1 melted MM contained nitrogen. We also observed a correlation in the distribution of carbon and nitrogen, suggesting that they may be held in an organic material. The implications for astrobiology of these results are discussed, as small extraterrestrial particles could have contributed to the origin of life on Earth by delivering important quantities of these 2 bio-elements to the Earth's surface and their gas counterparts, CO₂ and N₂, to the early atmosphere.

INTRODUCTION

About 30,000 ± 20,000 tons/yr of cosmic dust <2 mm in size is captured by the Earth (Taylor et al. 1998; based on Love and Brownlee [1993 and personal communication]). About 10% of this survives atmospheric entry as micrometeorites and IDPs. The remaining 90% is vaporized in the atmosphere (Taylor et al. 1998). Micrometeorites range from unmelted and partially melted particles that retain much of their original mineralogy to totally melted cosmic spherules that may have lost a significant fraction of their mass by vaporization. In this work, MMs will be considered those particles ranging in mass from 10⁻⁶–10⁻¹ g (40 μm–2 mm). IDPs are extraterrestrial particles collected in the Earth's stratosphere, usually measuring less than 40 μm in size and ranging in mass from 10⁻¹²–10⁻⁶ g.

Micrometeorites about 200 μm in diameter represent the major peak in the mass flux of extraterrestrial matter arriving to the present day Earth (Love and Brownlee 1993). Although IDPs contribute a much smaller proportion of the mass being delivered, they have been found to be rich in carbon and nitrogen (Keller et al. 1993, 1995). Furthermore, Anders (1989) and Chyba and Sagan (1992) proposed that IDPs and MMs, as the particles that best survive atmospheric entry

heating, should carry intact organic matter to Earth. In this context, the contribution of MMs and IDPs to the origin of life may have been of major importance, particularly, the delivery to the early Earth of biogenic elements such as carbon and nitrogen, and their organic counterparts. To evaluate this contribution, we measured the carbon and nitrogen concentrations in MMs and IDPs and in 2 meteorites, Murchison and Tagish Lake. These meteorites are carbonaceous chondrites, which, because of their carbon-rich matrices, are considered the most important group for delivering organics to the Earth's surface (Cronin et al. 1988).

The carbon and nitrogen content of Murchison (Table 1) has been studied using a variety of techniques (Gibson et al. 1971; Kvenvolden et al. 1971; Fuchs et al. 1973; Hayatsu and Anders 1981; Robert and Epstein 1982; Kerridge 1985). These studies give consistent results: an average of 2–2.5 wt% for carbon and 0.09–0.16 wt% for nitrogen. The carbon and nitrogen content in Tagish Lake have been measured using stepped combustion mass spectrometry, and the concentrations found were 5.81 wt% and 0.12 wt%, respectively (Grady et al. 2002).

Both unmelted MMs and IDPs contain carbonaceous matrices (Bradley et al. 1988; Maurette et al. 1995) and organics such as polycyclic aromatic hydrocarbons (PAHs)

Table 1. Carbon and nitrogen concentrations of Murchison and Tagish Lake: Comparison of the nuclear microprobe results to other techniques.^a

Instrument	C weight%	N weight%	Reference
Murchison			
Nuclear microprobe	2.7–2.8	0.14	This study
Gas chromatography	2	0.16	Kvenvolden et al. 1970
Gas chromatography	2.2	0.15	Gibson et al. 1971
Stepwise pyrolysis	1.76	Not determined	Robert and Epstein 1982
Stepwise combustion	1.56–2.15	0.03–0.085	Kerridge 1985
Stepped combustion	1.2	0.07	Halbout et al. 1986
Stepped combustion	0.83	0.02	Alexander et al. 1998
Stepped combustion	2.22	0.097	Grady et al. 2002
Tagish Lake			
Nuclear microprobe	5.5–6.15	0.15–0.22	This study
Stepped combustion	5.81	0.12	Grady et al. 2002

^aTwo values are available for Murchison and Tagish Lake, owing to the heterogeneity of the fragments studied.

(Clemett et al. 1993, 1998) and aliphatics (Alexander et al. 1992; Flynn et al. 1998a, b; Matrajt et al. 2001). For the unmelted micrometeorites, Engrand and Maurette (1997) determined a carbon concentration of ~7 wt% using electron energy loss spectroscopy (EELS); Wright et al. (1997) determined a concentration of <0.2 wt% using stepped combustion; Maurette et al. (2000) determined a concentration of ~2.5 wt% using secondary ion mass spectrometry (SIMS). For nitrogen, Marty et al. (2002) determined a range of concentrations varying from 53 (0.0053%) to 165 (0.0165%) ppm using static mass spectrometry.

For several IDPs, Bradley et al. (1993) determined their carbon concentrations using an analytical transmission electron microscope (TEM). Other authors (Keller et al. 1993; Thomas et al. 1993, 1995), using a scanning electron microscope (SEM) equipped with an X-ray energy dispersive spectrometer, measured carbon concentrations ranging from 1 to 47 wt%. Keller et al. (1995) determined nitrogen/carbon ratios of ~0.1 in several IDPs using EELS. Aléon et al. (2003) determined nitrogen concentrations of 10–20 wt% and carbon and nitrogen distributions on 2 IDPs using SIMS. Feser et al. (2003) have reported “percent-level” nitrogen in 2 carbon-rich IDPs using X-ray adsorption near edge structure (XANES) spectroscopy. Clearly, a wide range of carbon concentrations exists in both IDPs and MMs. Unfortunately, the analyses were not performed with the same technique, making comparisons in concentrations of these different materials difficult.

To compare carbon and nitrogen concentrations among these different samples, we analyzed MMs, IDPs, and pieces of Murchison and Tagish Lake using a nuclear microprobe. The microprobe also allowed us to map the distribution of carbon and nitrogen in the samples. The nuclear microprobe has been used to study the carbon content of olivines in meteorites (Varela et al. 2000; Varela and Metrich 2000) and has been shown to give accurate results. However, because this instrument has not been used to analyze fine-grained materials such as IDPs and MMs, we checked our method by

analyzing a piece of Murchison and Tagish Lake and comparing our results with those obtained using other techniques (Table 1).

In this paper, we present carbon and nitrogen concentrations made on 11 MMs, 3 IDPs, and pieces of Murchison and Tagish Lake. We also map the location of carbon and nitrogen in the particles. Our measurements of carbon and nitrogen concentrations in different types of MMs and IDPs, together with the present day flux of these materials, allowed us to estimate the present day flux of carbon and nitrogen to Earth. We then extrapolated the present day flux back in time to the period of major bombardment (4.5–3.5 Ga) to estimate the delivery, by cosmic dust, of carbon and nitrogen to the early Earth. This flux of carbon and nitrogen has implications for astrobiology, which we discuss in this paper.

MATERIALS AND METHODS

Sample Types and Sample Preparation

Micrometeorites have been collected in Antarctica by several groups (Maurette et al. 1991; Taylor et al. 1998; Yada and Kojima 2000). We had access to micrometeorites (MMs) from the Cap-Prud’homme (CP) (Maurette et al. 1991) and from the South Pole water well (SPWW) (Taylor et al. 1998) and analyzed micrometeorites from both collections. We analyzed:

- Eight MMs from the 1994 Cap-Prud’homme collection (Engrand and Maurette 1998; Maurette 1998), including 3 fine-grained (99-11-21; 99-11-72; 99-12-72), 2 scoriaceous (99-11-73; 99-12-11), 1 coarse-grained particle (99-11-61) and 2 cosmic spherules (N2; N3). The 99-11 particles and the cosmic spherules come from the 100–400 μm size fraction. The 99-12 particles come from the 50–100 μm size fraction.
- Three South Pole MMs from the 2000 collection, including 2 fine-grained particles (K2B; K4C) and 1

scoriaceous particle (K4D). All the particles come from the <75 μm size fraction.

- Three chondritic IDPs (U2-20-GCPA; RB-12A-12; U2-20-GCPD) from the W7154 collector of about 10 μm size (longest axis).
- A fragment each of Murchison and Tagish Lake (100 μm longest axis).

Before the nuclear microprobe analysis, the unmelted Cap-Prud'homme samples were characterized using a SEM, to determine their petrographic type. The particles were fragmented, and 1 piece of each was embedded in epoxy, polished, and examined (Fig. 1). A second fragment was used for the nuclear microprobe analyses. These samples, together with a piece of Murchison and a piece of Tagish Lake, were pressed into a gold foil using a clean glass slide. They were coated with gold, since some of them were to be subsequently analyzed with a SIMS.

The cosmic spherules (CS) and the South Pole MMs were pressed into an indium foil. The South Pole samples had previously been embedded in Crystal Bond and examined with the SEM (Fig. 2). They were extracted by dissolving the Crystal Bond with ultra-clean acetone following the methods described by Brownlee et al. (2002a, b). The particles were then pressed into the indium so that the polished surfaces faced upward. Because the gold coating interferes with EDXS analyses, we coated these samples with palladium. The coating was tens of Å thick.

The 3 IDPs (Fig. 3) were also pressed into indium. Since the indium is malleable, the risk of damaging these delicate samples is lower. Both U2-20-GCPA and U2-20-GCPD were "giant cluster particles" composed of anhydrous silicates. RB-12A-12 is a hydrated silicate IDP. To avoid confusion during the analyses, U2-20-GCPA was labeled IDP1, RB-12A-12 was labeled IDP2, and U2-20-GCPD was labeled IDP3.

Standards

Both MMs and IDPs are highly heterogeneous particles formed by a mixture of minerals, including silicates (anhydrous, hydrated), oxides, and sulfides embedded in a carbonaceous matrix (Bradley et al. 1988; Kurat et al. 1994; Genge et al. 1997; Genge and Grady 1998; Engrand and Maurette 1998). Since a standard composed of a mixture of fine-grained (sometimes nm-sized) minerals embedded in a carbonaceous matrix does not exist, most researchers using instruments where matrix effects have to be considered (e.g., ICP-MS, SIMS, nano-SIMS) use single minerals as standards (Engrand et al. 1999; Aléon et al. 2001; Stadermann 2001). In some cases, kerogen and kerogen + olivine standards have been used to determine the aliphaticity and aromaticity of the area studied (Aléon et al. 2003). In our case, we used standard samples of CaCO_3 and TiN to calculate the concentrations of carbon and nitrogen.

Note that we analyzed a glass standard (silicate glass standard CNST2 kindly provided by F. Robert) in which carbon and nitrogen concentrations had been measured. However, 2 problems were found with this standard which precluded its use: 1) it was heterogeneous with respect to carbon; and 2) it was not stable under the nuclear microprobe beam (after a few minutes of analysis, the beam would burn a hole through the sample causing a loss of silicon in the spectrum). Also, we could not use the glass standards prepared for other nuclear microprobe studies (Varela et al. 2000; Varela and Metrich 2000) because: 1) the standards did not match the main phases present in our samples; 2) the matrix effects from other phases in the MMs and IDPs are not the same as those in the standards; and 3) most of the mineral phases in both MMs and IDPs are very tiny, typically 1 micron or less in size. Therefore, even if some of the phases studied in the present work are available as a standard, our $3 \times 3 \mu\text{m}$ spot size is so large compared to the phases present in our samples that it will analyze phases not present in those standards.

Analytical Technique

We made the carbon and nitrogen measurements at the nuclear microprobe facilities of Pierre Süe laboratory (Saclay, France) using a modified version of the procedures described by Varela and coworkers (Varela et al. 2000; Varela and Metrich 2000; Varela et al. 2003). The nuclear microprobe was used in the Nuclear Reaction Analysis mode. We used the $^{12}\text{C}(\text{d}, \text{p}_0)^{13}\text{C}$ (at 1.45 MeV) and $^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$ (at 1.9 MeV) reactions to detect carbon and nitrogen, respectively. Calcite and TiN standards were used to calculate the carbon and nitrogen concentrations. Standard samples of UO_2 , Si, and Mg were used to demarcate in the spectra the main interferences due to (d, p) nuclear reactions of the main constituents of the matrix: O, Si, and Mg. Figure 5 shows the spectra of the 5 standards used in this work.

The samples were irradiated with an incident deuterium beam of 1.45 MeV for the carbon analyses and a deuterium beam of 1.9 MeV for the nitrogen analyses. The protons produced were detected between 2.0 and 3.0 MeV for carbon and between 7.5 and 8.7 MeV for nitrogen. In the region used to detect nitrogen, no interferences from Si, Mg, or O exist. In the region used to detect carbon, interferences from O, Si, and Mg and from surface contamination exist (see Fig. 6 for an example of the distribution of carbon with depth). To avoid measuring the counts produced by the interferences as carbon counts, we used that region of the spectrum (between 2.0 and 2.25 MeV) with no O and Si interference and only a small Mg interference (Fig. 5). To correct for this Mg interference, we subtracted the small Mg contribution found in the Mg standard from the spectrum of our samples. This procedure requires that carbon be abundant so its concentration is not affected significantly by the subtraction. All of our samples had sufficient carbon.

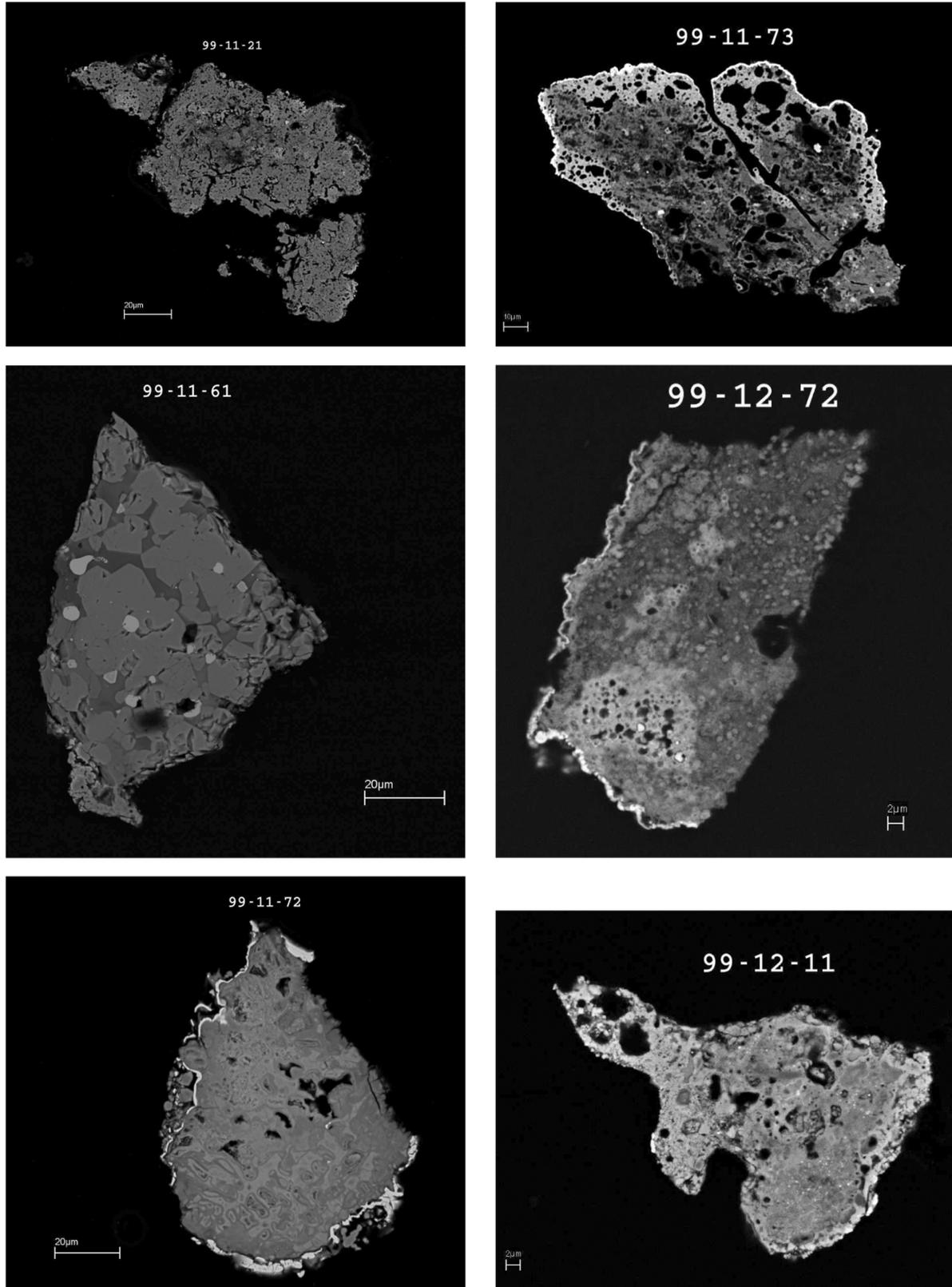


Fig. 1. Backscattered micrographs of the polished sections of the Cap-Prud'homme samples studied.

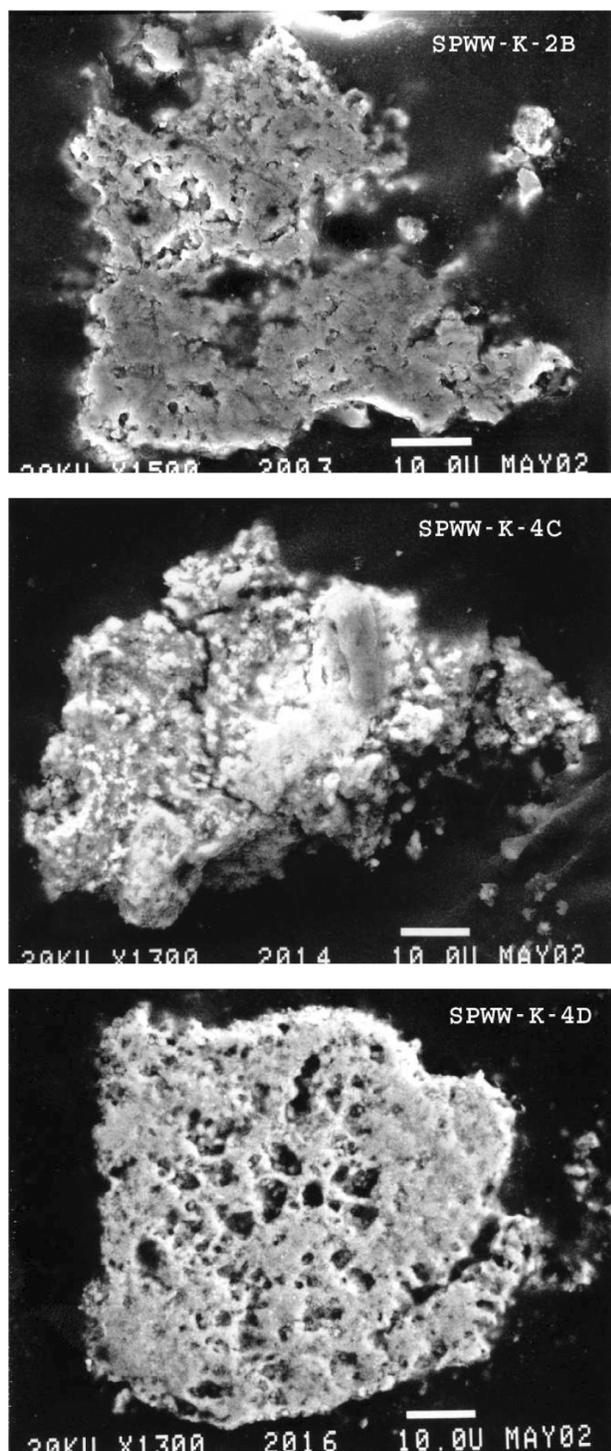


Fig. 2. Backscattered micrographs of the polished sections of the SPWW samples studied.

The carbon and nitrogen counts were measured with an annular Ortec Si detector with a surface barrier of 1500 μm depleted depth. The annular detector is placed at 170° relative to the incident beam, which is perpendicular to the sample. A collimator having a surface of 190 mm^2 is placed in front of



Fig. 3. Micrographs of the IDPs studied (unpolished particles).

the surface barrier detector. This is, in fact, a second detector, the main function of which is to minimize the Mg interferences by slowing down the particles produced by the reaction $^{25}\text{Mg}(d, p)^{26}\text{Mg}$. In this way, the Mg interference is shifted to lower energies and outside the region used to detect

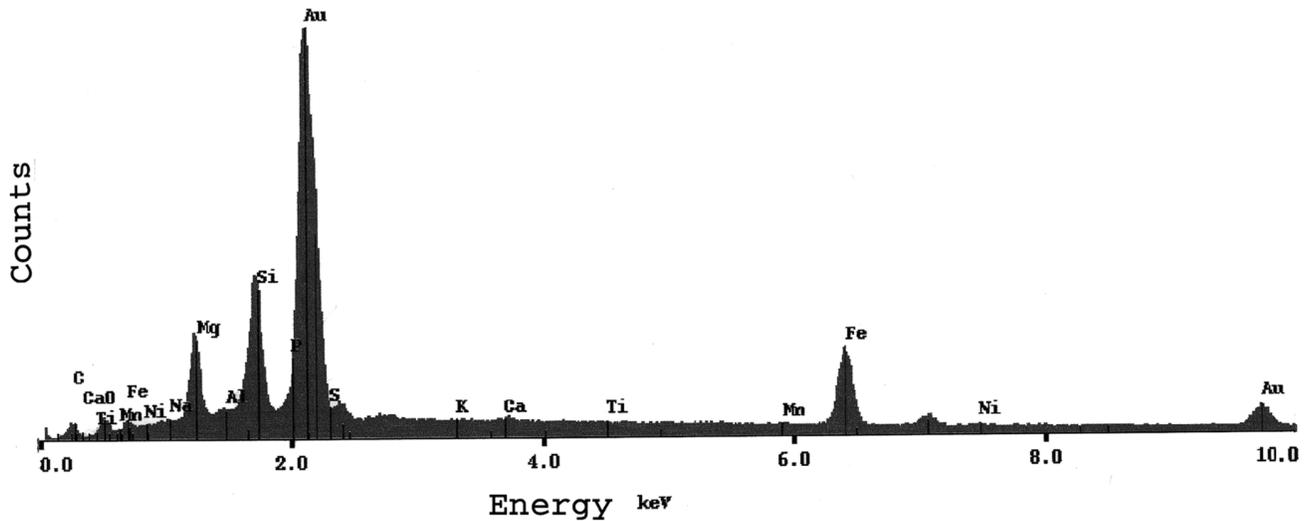


Fig. 4. A representative EDX spectrum of the MMs analyzed. The Au peak is from the gold coating. Mg and Si are the main peaks, followed by Fe. A precise quantification was not possible because of the gold coating. This spectrum is typical of a bulk analysis and also of areas measuring a few μm across, suggesting that several phases are present in the region being analyzed. The raster sizes were chosen according to the size of the region scanned with the nuclear microprobe beam.

carbon. Finally, above this collimator, we placed a mylar screen of 50 μm which has 2 main functions: to suppress all the charged particles produced by deuterium diffusion over the target and to separate the nuclear reaction particles produced by the reaction $^{14}\text{N}(\text{d},\text{p}_0)^{15}\text{N}$ that overlap the particles produced by the nuclear reaction $^{14}\text{N}(\text{d},\alpha_0)^{15}\text{N}$. This minimizes the possible interferences from α_0 particles. Varela et al. (2003) have reported a shift of the Mg interferences to lower energies using this mylar screen, supporting the fact that the use of this screen, together with the second detector, minimizes the Mg interferences.

The analyses were performed with a $5 \times 5 \mu\text{m}^2$ (3×3 for the IDPs analyses) beam size having an intensity of 500–700 pA and an integrated charge between 0.8 to 35 μC . The beam penetration varies with the nature of the analyzed material and with the employed energy. Based on the density of our samples, the penetration depth was estimated to be $\sim 8 \mu\text{m}$ for carbon and $\sim 17 \mu\text{m}$ for nitrogen. The experimental error was $\sim 10\%$. The detection limit depends on the analyzed matrix. Since the matrices of the samples are different from those of the standards, we could not estimate the detection limit for the samples. Therefore, the detection limit used for the samples is the one calculated for the standards ($\sim 0.01\%$). To obtain good counting statistics and, therefore, accurate measurements, we scanned the regions to be analyzed for several hours using 2 pairs of electrostatic deflectors (1 deflecting the deuterium beam horizontally over the target, the other vertically). The data obtained during the acquisitions were processed using the RISMIN software developed at Pierre Süe laboratory. For a more detailed description of the analytical procedure, see Varela et al. (2003).

The concentrations were calculated assuming that the average density of the samples is 2.5 g/cm^3 (Genge and Grady 1998), with a matrix mainly composed of silicates (mostly olivines and pyroxenes). We also assumed that carbon and nitrogen were uniformly distributed in the matrix.

The analysis of a single particle for a single element (carbon or nitrogen) requires 6 to 8 hr; thus, each particle required 12 to 16 hr of analysis time. Six to 8 hr is sufficient to determine the bulk carbon and nitrogen content of each particle (obtained by adding all the spot analyses) and to obtain good quality carbon maps on many of the particles that have high carbon contents. The nitrogen maps are of poorer quality because of the lower nitrogen content, but, in some cases, the nitrogen maps allow us to compare the carbon and nitrogen spatial distributions to see if the 2 elements are collocated.

RESULTS

The bulk carbon and nitrogen content were determined by adding all the spot analyses obtained in the scanned region.

Murchison and Tagish Lake

Since this was the first time the nuclear microprobe was used to measure the carbon and nitrogen in such small and heterogeneous particles, we tested the instrument, our method, and our standards by measuring pieces of the Murchison and Tagish Lake meteorites and comparing our results (Table 1) with those obtained with other instruments that do not need matrix corrections: gas chromatography (Kvenvolden et al. 1970; Gibson et al. 1971); stepwise pyrolysis (Robert and

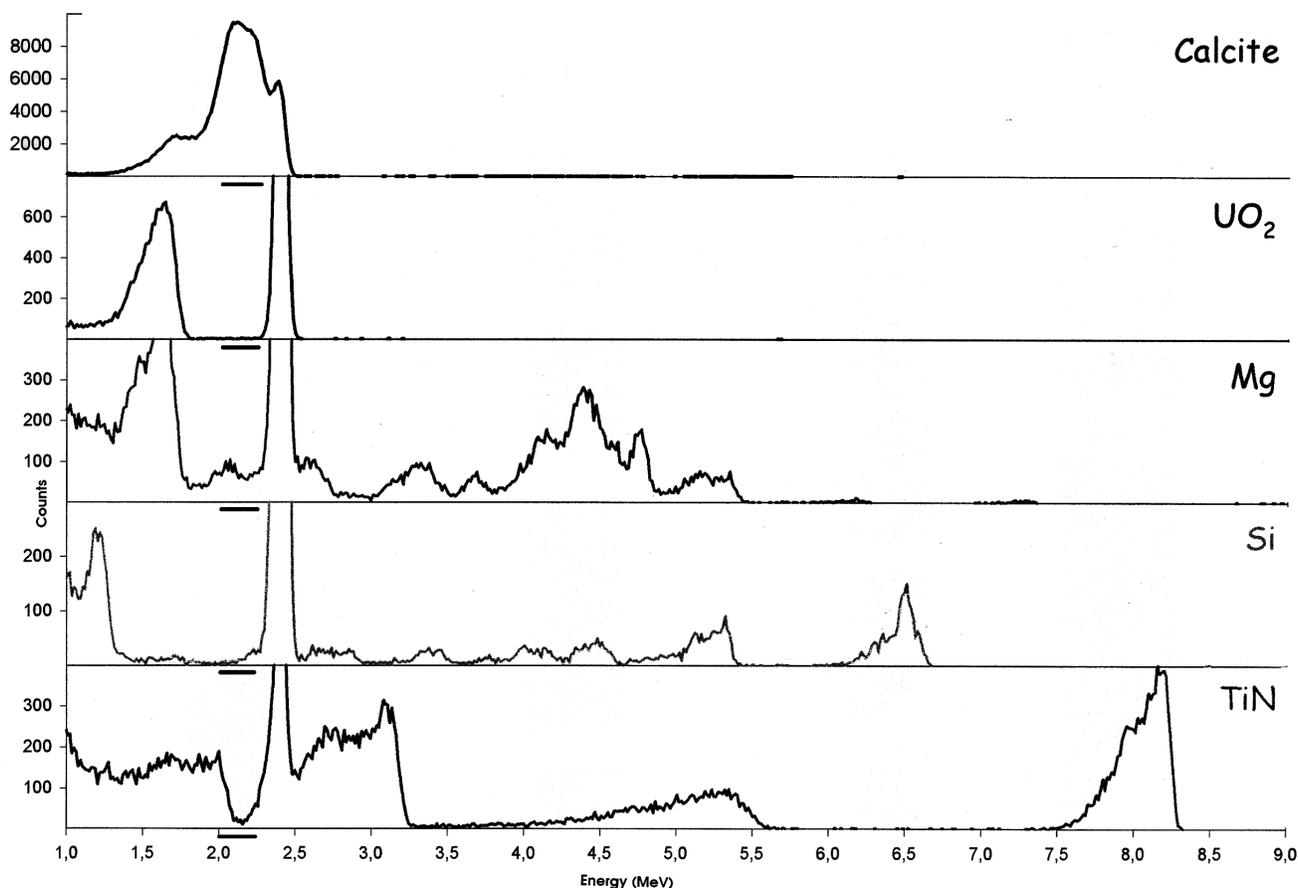


Fig. 5. Spectra of the 5 standards used for this study. For nitrogen, no interference exists in the 7.5 to 8.7 MeV region. For carbon, small interferences (O, Si, and Mg) exist in the 2.25 to 3.03 MeV region used in this study. However, to avoid measuring the counting rates produced by these interferences, only the 2.0 to 2.25 MeV region of the spectrum, which has no interference from O and Si and only a small interference from Mg, was used (shown by a dark line). Using the Mg standard as a reference, we can subtract the small Mg interference found in this region from the spectra of the particles analyzed.

Epstein 1982; Kerridge 1985); static mass spectrometry (Marty et al. 2002); and stepped combustion (Halbout et al. 1986; Alexander et al. 1998; Grady et al. 2002). Both Murchison and Tagish Lake showed variability in the amounts of carbon and nitrogen, with regions of higher and lower concentration (Table 1). For both meteorites, the concentrations measured with the nuclear microprobe are consistent with the concentrations measured by previous studies, supporting the fact that this instrument can accurately measure light element concentrations. The agreement between our results and those obtained previously validate our use of calcite and TiN standards for the present analyses.

MMs and IDPs

Table 2 lists the carbon and nitrogen concentrations measured on the MMs and IDPs. From this table, one can see that the micrometeorites contain carbon in different abundances. The carbon concentrations found in unmelted MMs vary from 0.2 to 2.8 wt%. The 2 melted micrometeorites

still have carbon, but their concentrations are an order of magnitude lower, 0.14 and 1.15 wt%. The 3 scoriaceous particles also have widely varying carbon concentrations, from 0.72 to 2.13 wt%. The unique coarse-grained particle studied (99-11-61) contains a very low concentration of carbon. The 2 fine-grained South Pole micrometeorites K2B and K4C are richer in carbon than the fine-grained Cap-Prud'homme particles. The fine-grained 99-11-72 has a very low carbon concentration compared to the other fine-grained particles. We do not observe a significant difference in the carbon concentration in the particles 99-12 from the 50–100 μm size fraction compared to the 99-11 particles from the 100–400 μm size fraction. Also, we do not observe a significant difference in carbon concentration between the CP and SPWW micrometeorites.

The carbon concentrations found in IDP1 and IDP2 are about twice the carbon concentration found in the richest micrometeorites (K2B), while the third one (IDP3) has a concentration comparable to most of the other micrometeorites.

Table 2. Carbon and nitrogen concentrations.^a

Sample name	Sample type	Sample size (μm)	C weight%	N weight%
99-11-21	CP-MM (fg)	368 \times 356	1.22	0.05
99-11-72	CP-MM (fg)	208 \times 148	0.33	0.01
99-11-61	CP-MM (cg)	96.3 \times 69.2	0.19	<dl
99-11-73	CP-MM (sc)	209 \times 81.4	2.13	0.04
99-12-72	CP-MM (fg)	59.1 \times 57.5	1.98	0.03
99-12-11	CP-MM (sc)	105 \times 56.2	0.72	0.02
N2	CP-MM (cs)	94.1 \times 118	0.14	<dl
N3	CP-MM (cs)	149 \times 127	1.15	0.09
K2B	SPWW-MM (fg)	73.1 \times 51	2.86	0.05
K4C	SPWW-MM (fg)	65.9 \times 45.1	2.12	0.09
K4D	SPWW-MM (sc)	74.5 \times 92.1	1.32	0.03
IDP1: U2-20-GCPA	IDP	14.6 \times 14	4.81	0.12
IDP2: RB-12A-12	IDP	12.8 \times 12.8	4.26	0.24
IDP3: U2-20-GCPD	IDP	9.21 \times 12.9	1.47	0.06

^aMM = Antarctic micrometeorite; SPWW = South Pole water well; CP = Cap-Prud'homme; fg = fine-grained; cg = coarse-grained; sc = scoriaceous; cs = cosmic spherule; <dl = below the detection limit. The length measurements are the 2 longest axes of each particle.

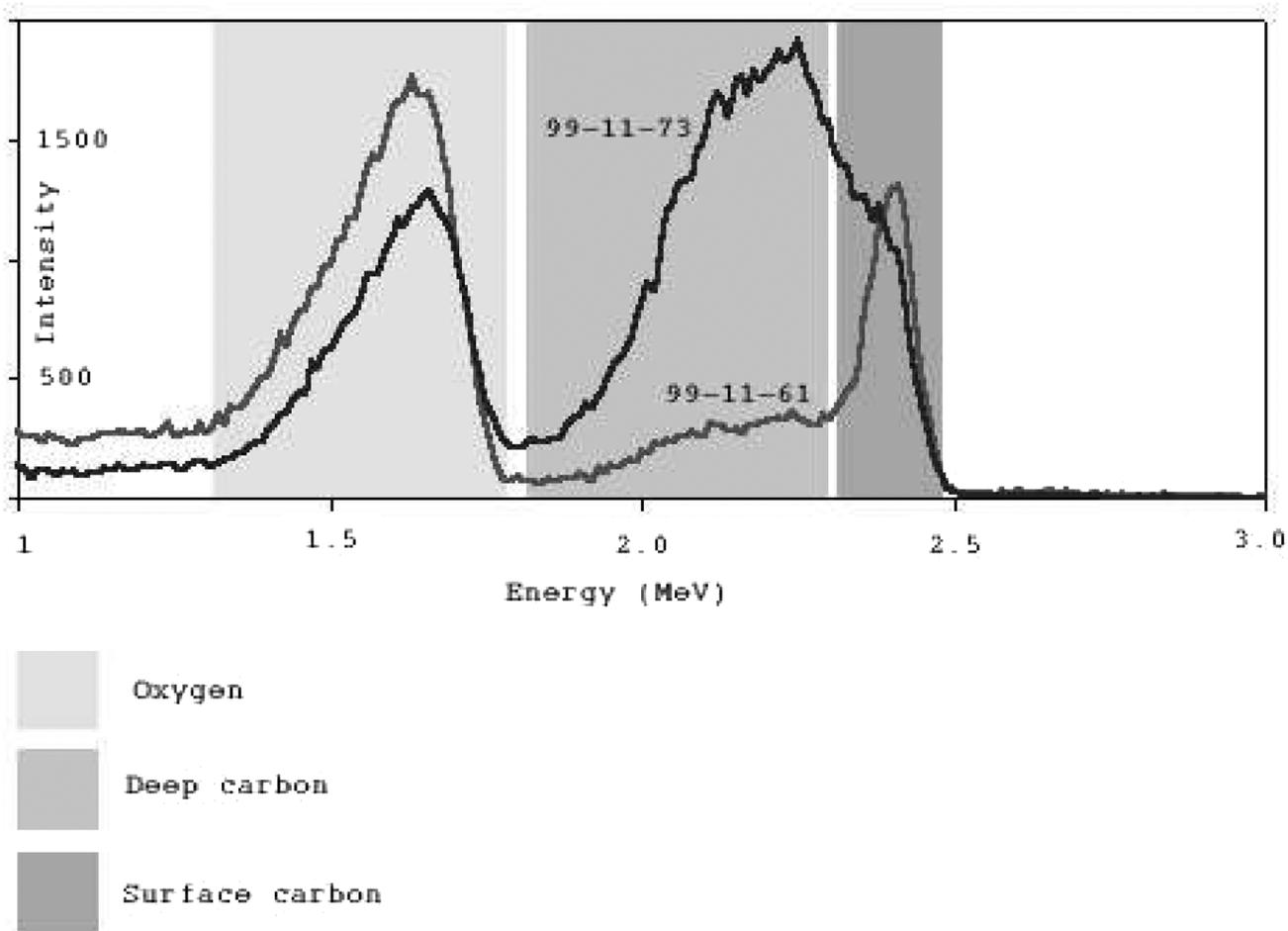


Fig. 6. The carbon spectra of the particles 99-11-73 and 99-11-61. Three regions of the spectra are shown corresponding to low, medium, and high energies. From left to right: the low energy region of the spectrum (light gray) is produced by the nuclear reactions due to the oxygen present in the sample. The middle energy region, from ~ 1.80 to ~ 2.30 MeV (gray), corresponds to the carbon contained in the sample. The highest energy region (dark gray) corresponds to the surface carbon. In fact, the highest energy particles detected are produced during the nuclear reactions with elements found on the surface to a depth of 1500 nm. The counts coming from this region of the spectrum are considered surface contamination and were not taken into account when calculating the carbon concentration.

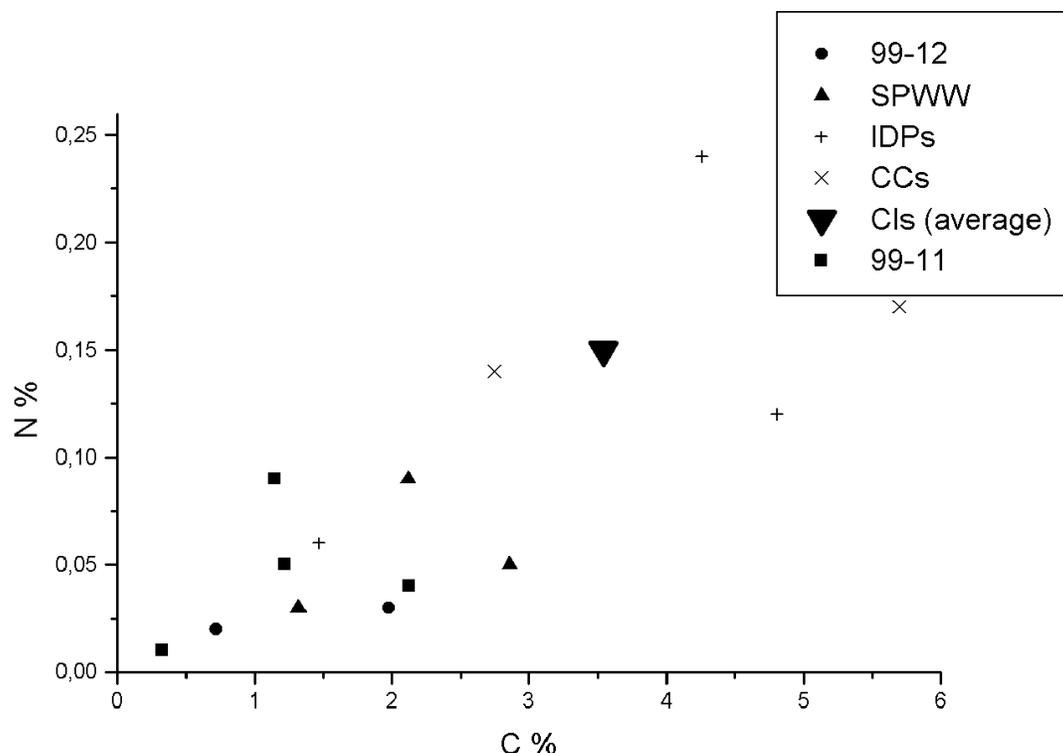


Fig. 7. Relationship between carbon and nitrogen concentrations of all the samples studied. The systematic error (instrumental error) is ~10%. The values of carbon and nitrogen of the CI group are shown for comparison. CCs = carbonaceous chondrites.

All the samples studied contain lower concentrations of nitrogen than carbon. In micrometeorites, these concentrations vary from 0.01 to 0.09 wt%. The 2 fine-grained South Pole micrometeorites K2B and K4C are richer in nitrogen than the fine-grained Cap-Prud'homme particles 99-11-72 and 99-12-72. For the 2 cosmic spherules studied, only N3 had a nitrogen concentration above the detection limit. The 3 scoriaceous particles have nitrogen concentrations between 0.02 and 0.04 wt%. As in the case of carbon, we do not observe a difference in nitrogen concentration between samples from the 2 MM collections or between the 2 different sizes studied. The nitrogen concentrations found in IDP1 and IDP2 are about twice the nitrogen concentration found in the richest micrometeorite K4C. As with carbon, IDP3 has a nitrogen concentration comparable to most of the other micrometeorites.

Distribution of Carbon and Nitrogen

Figures 8 and 9 show carbon and nitrogen distributions in 4 of the MMs studied. For some particles, the elements, especially carbon, are found over the entire surface making it possible to see the particle shape (see for example 99-11-21 and N3). These maps show that the carbon and nitrogen are not homogeneously distributed in the particle. In fact, some high concentration areas of carbon exist, as well as some high concentration areas of nitrogen that frequently overlap (see,

for example, particle 99-11-73 in Fig. 8 and N3 in Fig. 9). The maps of N3 show that carbon and nitrogen are concentrated in bumpy areas on the surface. The distribution of carbon and nitrogen in the IDPs studied are not shown because the images of these small particles are of poor quality. However, the carbon and nitrogen distributions also appear to overlap in the IDPs studied.

DISCUSSION

Murchison and Tagish Lake

Heterogeneity in the concentration of organic molecules (in pieces of a few mg) in Murchison (Cronin and Chang 1993) and Tagish Lake meteorites (Grady et al. 2002; Pizzarello and Huang 2002) has been observed with other analytical techniques. In our samples, we see regions of high and low concentrations of both carbon and nitrogen. Regions having high concentrations of both elements could be explained if some of the carbon and nitrogen are bound together as organic molecules. For our samples, heterogeneity in concentration occurs at μg or even ng levels.

MMs and IDPs

Carbon was present in micrometeorites in different abundances. The variability in concentration is probably

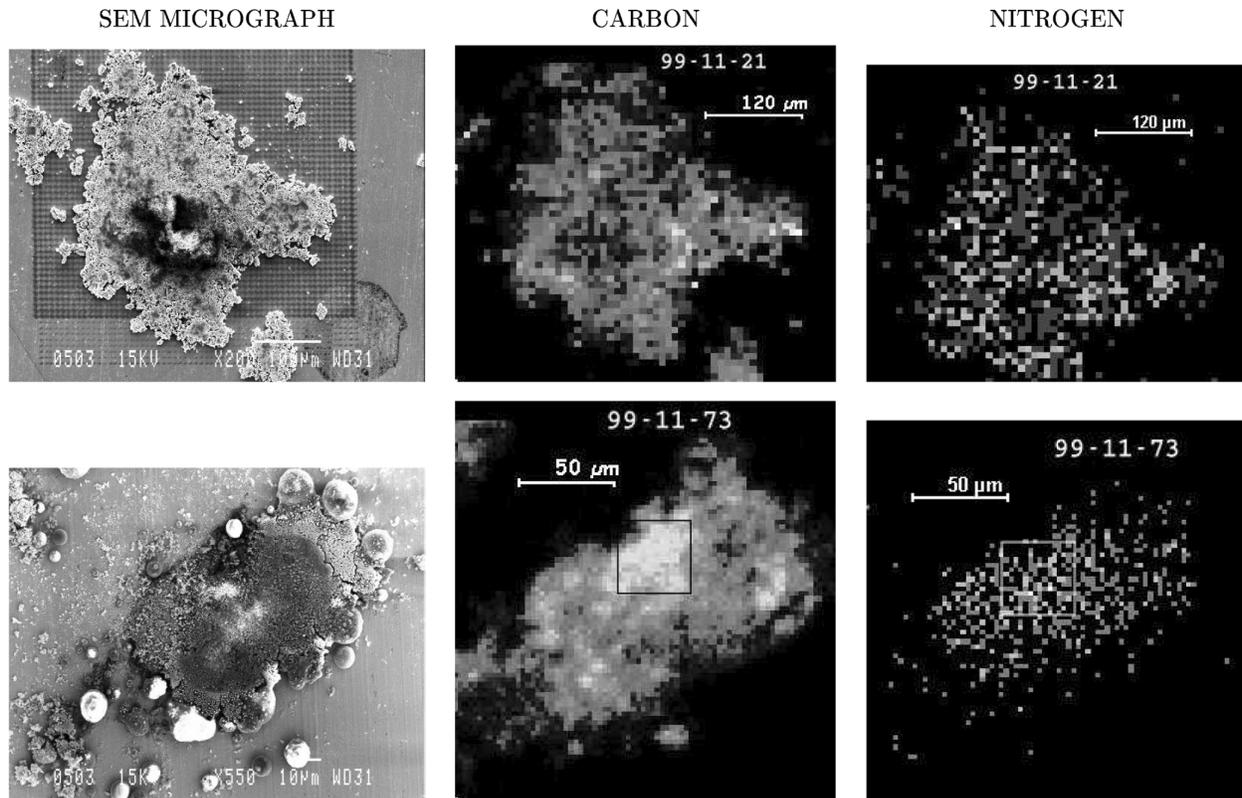


Fig. 8. Images of the particles 99-11-21 and 99-11-73 showing the carbon- and nitrogen-rich regions. A correlation between the distribution of carbon and nitrogen can be observed in some regions of these particles (delimited by a square). The bright areas have the highest concentrations. SEM micrographs of each particle are also shown.

related to the heterogeneous matrix of the micrometeorite but might also be due to loss of carbon and nitrogen during atmospheric entry heating. Generally, we found that the fine-grained Cap-Prud'homme micrometeorites have higher carbon concentrations than the scoriaceous particles. An exception is 99-11-73, a scoriaceous particle that is particularly rich in carbon.

The cosmic spherules still carry some carbon, and, in the case of N3, the concentration of 1.15 wt% is comparable to that found in some of the unmelted micrometeorites. Olinger et al. (1990) reported Ne in some melted MMs, presumably solar wind implanted. Neon, nitrogen, and the carbon associated with a volatile compound are expected to be lost from melted micrometeorites but, as the heating pulse is short, element loss may depend significantly on diffusion rates. Another unexpected observation is that the coarse-grained particle (99-11-61), composed mainly of 5–10 μm -sized crystals of silicates, contains carbon. The carbon may be held in a carbonaceous matrix found between the minerals. We did not observe a significant difference in carbon concentration between the CP and SPWW micrometeorite particles, suggesting that their different terrestrial histories did not affect their carbon composition.

Like carbon, nitrogen is present in micrometeorites in different abundances. Micrometeorites studied by Marty et al.

(2002) also had variable nitrogen concentrations. Our nitrogen results for MMs match the concentrations found with static mass spectrometry (Marty et al. 2002) with 1 exception. The particle in question was divided into 2 fragments, 1 of which was studied with the nuclear microprobe and the other with the static mass spectrometer. Both analyses showed different nitrogen concentrations. We think this difference is due to the heterogeneity of the particle.

As previously reported (Keller et al. 1993; Thomas et al. 1993, 1995), IDPs are very carbon-rich and contain variable carbon concentrations. However, some IDPs have low carbon concentrations, such as the IDP3, which had a carbon concentration comparable to most of the micrometeorites studied. The fact that most IDPs are richer in carbon than micrometeorites could have at least 2 explanations: 1) if most of the carbon measured is organic, we expect that IDPs will be richer in carbon than micrometeorites due to the less severe heating they experience during atmospheric entry; 2) if most of this carbon is contained in a refractory phase, such as a nanodiamond or graphite, then the difference in the carbon content would mean that IDPs are coming from a parent body richer in carbon than the parent body of the micrometeorites.

The nitrogen concentrations in IDPs are higher than in micrometeorites. This could mean that either IDPs are less

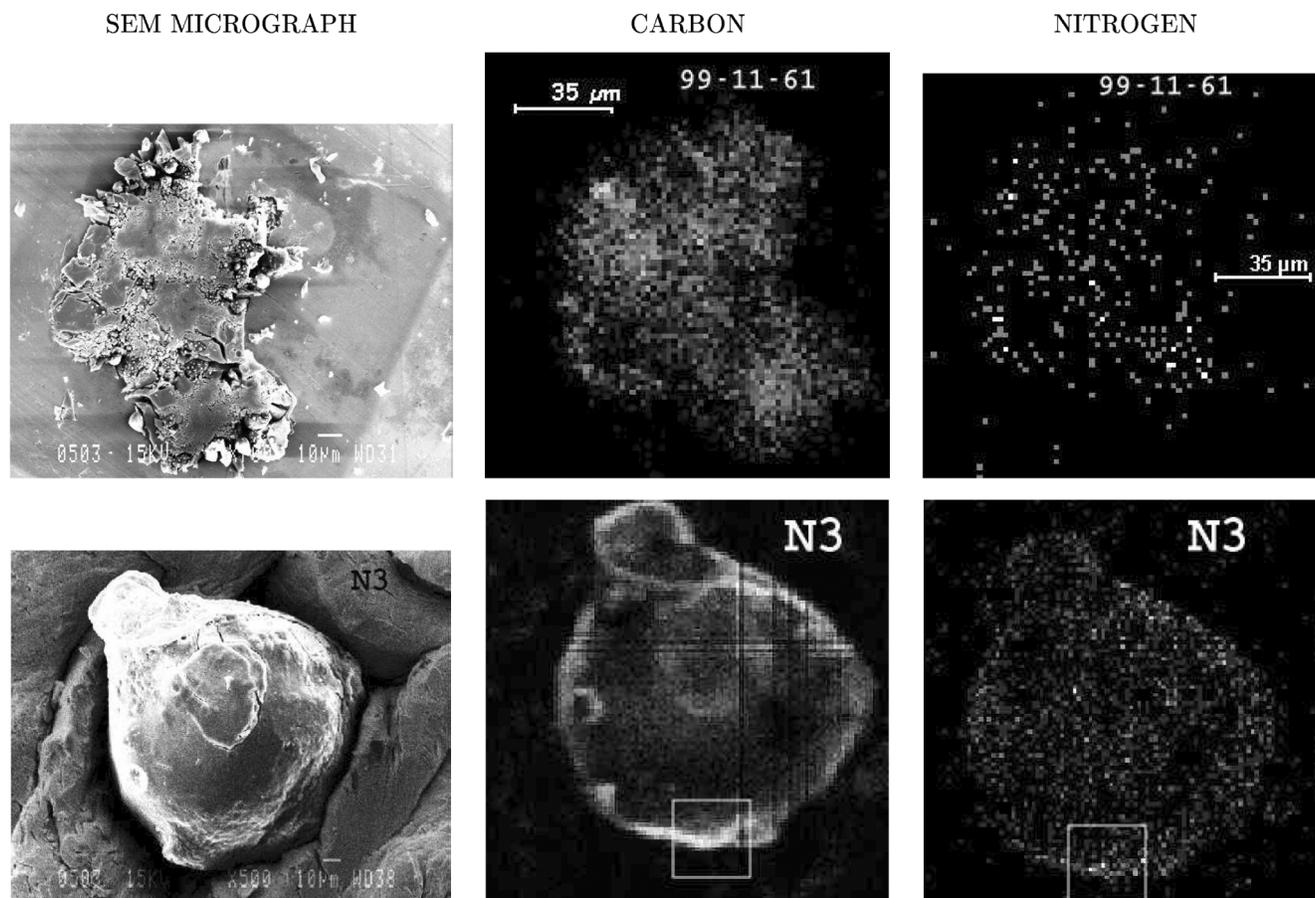


Fig. 9. Images of the particles 99-11-61 and N3 showing the carbon- and nitrogen-rich regions. The bright areas have the highest concentrations. The SEM micrographs of each particle are also shown.

heated than micrometeorites or simply that the parent body of IDPs contained more nitrogen than the micrometeorite's parent body. Nevertheless, the difference in nitrogen concentrations between IDPs and micrometeorites is not as large as that observed for carbon. This implies that nitrogen is not easily removed by heating, probably because it is bound to a more refractory compound. The nitrogen concentrations obtained during this study (0.06–0.24 wt%) are, however, much lower than the nitrogen concentrations (10–20 wt%) reported by Aléon et al. (2003). Because of the small number of IDPs studied, this discrepancy could be explained by the fact that IDPs contain variable nitrogen concentrations, such as was observed for the carbon concentrations.

Our results best match earlier studies using the SEM-EDS (Keller et al. 1993; Thomas et al. 1993, 1995) and the SIMS (Maurette et al. 2000). However, our results for MMs appear to be higher than the values reported by Wright et al. (1997) using the stepped combustion and lower than the values reported by Engrand and Maurette (1997) using the EELS. This could be due not to the techniques but to a significant variability in carbon concentration among the samples studied.

Comparison with Carbonaceous Chondrites

The carbon and nitrogen concentrations of all the samples are plotted in Fig. 7 and compared with CI values of carbon and nitrogen obtained by Kerridge (1985). The carbon and nitrogen concentrations are correlated: particles that have high carbon also show high nitrogen. Given that we have measured carbon and nitrogen concentrations in 3 different types of extraterrestrial material, carbonaceous meteorites, Antarctic MMs, and IDPs, this correlation suggests that the carbon and nitrogen host phases are similar in all 3 types of extraterrestrial material.

The carbonaceous chondrites and IDPs tend to plot at the higher % levels while the MMs plot on the lower % level. Although the number of measurements is small, the difference in carbon and nitrogen concentration suggests that MMs come from a different source than IDPs and carbonaceous chondrites. This would support observations made by Bradley et al. (1988) related to the mineralogy of IDPs and MMs.

For MMs, the nitrogen concentrations are smaller than Murchison and Tagish Lake, often by an order of magnitude

(Tables 1 and 2), while for the carbon concentrations, they are, in some cases, comparable to those found in these carbonaceous chondrites but, often, slightly lower. For IDP1 and IDP2, both carbon and nitrogen concentrations are similar to the Tagish Lake carbonaceous chondrite (see Table 2 and Fig. 7).

Distribution of Carbon and Nitrogen

Figures 8 and 9 show that nitrogen is less abundant than carbon in MMs and IDPs. The correlation in the distribution of carbon and nitrogen in some of the MMs' studied points to specific regions in the matrix where both of these elements are present and suggests that some of the carbon and nitrogen are bound in an organic material. Carbon and nitrogen are also collocated in the IDPs studied, suggesting that here, too, an organic material harbors both elements. A similar correlation between the carbon and nitrogen distributions was also reported by Aléon et al. (2003) for 2 IDPs.

In the cosmic spherules, carbon and nitrogen are concentrated in round-shape regions. SEM observations of these regions revealed that, indeed, these round areas correspond to protuberances on the surface of the sphere. EDS analyses of these protuberances showed that they are mainly composed of silicates, with some spots having iron present as the dominant element. Previous studies of cosmic spherules revealed that these protuberances are often formed of an iron hydroxide, ferrihydrite (Engrand and Maurette 1998). However, the carbon- and nitrogen-rich protuberances of the cosmic spherules analyzed during this work were not ferrihydrite but, rather, an iron-rich silicate.

Unlike the results of Varela et al. (2000, 2003) and Varela and Metrich (2000), who reported that carbon and nitrogen in meteorites are found mainly in glass inclusions of olivines, our results suggest that, for IDPs and MMs, carbon and nitrogen are not carried by individual minerals but are harbored in the carbonaceous matrix of the samples studied.

Astrobiology Implications

The origin of pre-biotic organic matter on the early Earth is not well-understood. Several authors (Oró 1961; Anders 1989; Chyba et al. 1990) have suggested that extraterrestrial materials contributed large amounts of these organic molecules to the early Earth, thus, playing a role in the origin of life. The results obtained during this work show that small extraterrestrial particles, MMs and IDPs, contain carbon and nitrogen in concentrations comparable to the ones found in the carbonaceous chondrites Murchison and Tagish Lake, and, because in some regions these elements are collocated, they might be found in the form of organic molecules. By quantifying the present day carbon and nitrogen mass flux of MMs and IDPs and extrapolating it to the past (4.5 to 3.5 Ga), we hope to estimate the amounts of carbon and nitrogen

delivered to the early Earth by IDPs and MMs, before the appearance of life.

The mass flux of the incoming extraterrestrial material is dominated by particles of a few 100 microns over less than million year time scales and by km-sized objects of masses larger than 10^{15} g over longer time periods (Love and Brownlee 1993; Kyte and Wasson 1986; Chyba and Sagan 1992). Anders (1989) calculated the present mass accretion rate and the carbon accretion rate on Earth for different sized objects: micron (IDP + MM)-sized objects (in the range of 10^{-12} – 10^{-1} g); meteorite-sized objects (in the range of 10^{-1} – 10^8 g); and km-sized objects (in the range of 10^8 – 10^{18} g). Anders' calculations showed that the total mass and the carbon mass accreted from the meteorite-sized objects is negligible compared to the small and km-sized objects. Km-sized object impacts are infrequent (Jenniskens et al. 2000) and the organic carbon is thought to be unable to survive the high temperatures experienced during such impacts (Anders 1989). Therefore, the accretion of organic carbon today is dominated by continuously falling micron-sized objects larger than 10^{-12} g: IDPs and MMs.

The flux of these different sized objects to the Earth has not remained constant, and evidence suggests it was much higher early in Earth's history. In fact, Infrared Space Observatory observations of stars of different ages show that the quantity of dust around young stars (a few million years old) systematically declines with stellar age (Spangler et al. 2001). This observation suggests that intense dust showers affect planets around most stars during their first few hundred million years of existence and supports the assumption that, during this process, the mass flux of objects reaching the planets surfaces is much higher. Moreover, the density of lunar craters clearly shows that the average cratering flux was higher in the period of 4.5–3.8 Ga than today (Hartmann et al. 2000). However, how much higher is unclear, since the lunar data can be interpreted several ways: Hartmann et al. (2000) estimated that the total amount of meteoritic material added to the Moon in the period between 4.4 and 3.8 Ga was roughly 5×10^{21} g, while Morgan et al. (1977) estimated this amount to be 10^{23} g.

Because small particles are produced by collisions between larger objects in a power-law size-frequency distribution (Flynn and McKay 1990), for our calculations, we assume that the cosmic dust flux was increased by the same factor (F) estimated for the km-sized object flux that produced the cratering record observed on the Moon. Using the carbon and nitrogen concentrations shown in Table 2, together with the present mass flux of cosmic dust, the total carbon ($[C]_T$) and nitrogen ($[N]_T$) delivered to the early Earth could be calculated by the following equation (in tons/yr):

$$[C]_T = [C] \times 0.01 \times (PMF) \times F$$

where $[C]$ is the carbon concentration measured during this study, PMF is the present mass flux, and F is the factor by

which this mass flux was increased during the heavy bombardment period (its value is, at present, still unknown).

Tables 3 and 4 show the flux of carbon and nitrogen arriving in MMs and IDPs to the Earth's atmosphere and surface, respectively. The estimates were performed using the equation shown above and the present mass flux for both the atmosphere and the surface of the Earth. To estimate the flux of carbon and nitrogen delivered on top of the atmosphere (Table 3), we used the concentration values shown in Table 2 for MMs and IDPs and the concentration values shown in Table 1 for the Murchison and Tagish Lake meteorites, together with the following PMF: $30,000 \pm 20,000$ tons/yr for cosmic dust (Love and Brownlee 1993; Taylor et al. 1998); and 29 tons/yr for carbonaceous chondrites (Anders 1989). To estimate the flux of carbon and nitrogen delivered to the surface (Table 4), we used the same carbon and nitrogen concentrations, together with the following PMF: 2700 ± 1400 tons/yr for MMs, measured at the South Pole by Taylor et al. (1998) for particles ranging in size from 50–700 μm ; 3.2×10^3 for IDPs, calculated by Anders (1989) for the unmelted material surviving atmospheric entry in the size range of 10^{-12} – 10^{-6} g; 1.9×10^{-1} tons/yr for carbonaceous chondrites, calculated by Anders (1989) for the material surviving atmospheric ablation.

The values in Table 4 are smaller than those in Table 3 because incoming cosmic dust is vaporized while entering the atmosphere. These calculations show that the top of the atmosphere accretes 300 to 500 times more carbon and nitrogen from cosmic dust than from carbonaceous chondrites and that, at the surface, this accretion is about 10^4 times higher than for carbonaceous chondrites. The delivery of carbon and nitrogen by MMs and IDPs may be even greater for Mars, where larger particles are decelerated with less severe heating due to the lower scale height of its atmosphere and its lower surface gravity (Flynn 1996).

These surface mass fluxes, however, are valid only for a

1-bar atmosphere, and we do not know the density of the early atmosphere. If the early atmosphere was thicker than the present one, as stipulated by Walker (1985) and Kasting and Ackerman (1986), then the mass flux to the surface would increase due to the extended aerobraking of the particles (Anders 1989; Chyba and Sagan 1992). If the cosmic dust mass flux increases by the same factor as the mass flux of carbonaceous chondrites, cosmic dust would still remain the main contributor of organic molecules. However, in the case of a thick atmosphere, comets may also have contributed $\sim 10^6$ kg of organics per yr to the surface during the heavy bombardment period, between 4.5 and 3.5 Ga (Chyba et al. 1990). In any case, our calculations show that during the period that preceded the origin of life (4.5–3.5 Ga), cosmic dust may have been the main source of carbon and nitrogen to the surface of the Earth.

How the primitive atmosphere formed is still unknown, but several sources are thought to have contributed to its formation (Owen 1998). Volcanoes may have contributed CO_2 (Williams et al. 1992; Whittet 1997). Williams et al. (1992) have calculated the present CO_2 emission of volcanoes to the atmosphere to be 65×10^{12} g/yr. This emission was probably higher ~ 4 Ga ago, when volcanism was more active than today (Rubey 1955; Holland 1984), but no data exists on how much CO_2 was released by volcanoes early in the Earth's history. In addition, extraterrestrial materials may also have contributed to the formation of the primitive atmosphere through a late-accreting veneer of volatile-rich materials delivered by icy planetesimals derived from comets (Chyba 1989; Owen et al. 1992). IDPs and MMs would also have added CO_2 and N_2 to the atmosphere as the particles volatilize during atmospheric entry. Unmelted to partially melted micrometeorites show different degrees of vesiculation, which has been attributed to the loss of volatiles during atmospheric entry (Greshake et al. 1998; Toppani et al. 2001). By comparing the values in Tables 3 and 4, we see that extraterrestrial materials clearly lose mass

Table 3. Carbon and nitrogen flux estimates on top of the atmosphere delivered to the early Earth.^a

Source	Present mass flux (tons/yr)	[C] average (%)	$[\text{C}]_{\text{T}} \div \text{F}$ (tons/yr)	[N] average (%)	$[\text{N}]_{\text{T}} \div \text{F}$ (tons/yr)
MMs + IDPs	$30000 \pm 20000^{\text{b}}$	1.787 ± 1.42	536.1 ± 284	0.061 ± 0.05	18.3 ± 10
CCs	29^{c}	4.48 ± 1.67	1.3 ± 0.48	0.19 ± 0.04	0.06 ± 0.01

^aThe average concentrations used were obtained during this study. CCs = carbonaceous chondrites; F is the factor by which the mass flux was increased during the heavy bombardment period.

^bLove and Brownlee 1993; Taylor et al. 1998.

^cAnders 1989.

Table 4. Carbon and nitrogen flux estimates on the surface delivered to the early Earth.^a

Source	Present mass flux (tons/yr)	[C] average (%)	$[\text{C}]_{\text{T}} \div \text{F}$ (tons/yr)	[N] average (%)	$[\text{N}]_{\text{T}} \div \text{F}$ (tons/yr)
MMs (50–700 μm)	$2700 \pm 1400^{\text{b}}$	1.287 ± 0.86	34.7 ± 12	0.046 ± 0.03	1.24 ± 0.4
IDPs	3.2×10^3	3.51 ± 1.46	112.3 ± 46.7	0.14 ± 0.07	0.45 ± 2.2
CCs	$1.9 \times 10^{-1}^{\text{c}}$	4.48 ± 1.67	$8.5 \times 10^{-3} \pm 0.003$	0.19 ± 0.04	$0.36 \times 10^{-3} \pm 7 \times 10^{-5}$

^aThe average concentrations used were obtained during this study. CCs = carbonaceous chondrites; F is the factor by which the mass flux was increased during the heavy bombardment period.

^bTaylor et al. 1998.

^cAnders 1989.

as they pass through the atmosphere. In the case of cosmic dust, for example, the 30,000 tons/yr entering the top of the atmosphere are reduced to ~3,000 tons/yr landing on the surface. Thus, 90% of the material is lost by pyrolysis and volatilization during atmospheric entry. Most of this material is deposited in the atmosphere's layers, and, in the case of carbon and nitrogen component, the molecules formed after pyrolysis of the organic matter are probably CO₂, N₂, and H₂O. When subjected to electrical discharges in the atmosphere, CO₂, N₂, and H₂O react to form organic molecules (Navarro-Gonzalez et al. 2001). The delivery of gases to the atmosphere by MMs and IDPs, therefore, may be another path to organic synthesis and the origin of life on Earth.

CONCLUSIONS

Among all the types of extraterrestrial objects studied here, the IDPs and Tagish Lake samples have the highest carbon and nitrogen concentrations. These are higher than the concentrations found in Murchison, a representative meteorite of the carbonaceous chondrite group. We found that all types of MMs have carbon, and the unmelted ones contain nitrogen, with the fine-grained particles frequently containing the highest concentrations. Even cosmic spherules still contain carbon and nitrogen, suggesting that carbon and nitrogen do not totally volatilize during the atmospheric heating of some of these particles. In addition, the coarse-grained micrometeorite studied also contained carbon and nitrogen, suggesting that these elements are harbored in an interstitial carbonaceous material. The distributions of carbon and nitrogen often coincide, suggesting that part of the carbon and nitrogen may be bounded together in an organic material.

Since the organic carbon could not survive the impact of big objects (Anders 1989) but was being continuously released by the micron-sized objects, MMs and IDPs may have been the dominant delivery source of organic carbon to the primitive Earth (Chyba and Sagan 1992; Whittet 1997). Moreover, this organic material may have formed by different processes (i.e., solar nebula, circumstellar, and interstellar processes) than those thought to occur on Earth (i.e., Miller-Urey reactions) and probably contained a different mix of organic compounds. Therefore, through the delivery of such organic molecules, the cosmic dust may have contributed to the origin of life on Earth.

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