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Ice sample collection during the 2003/04 ANSMET field season.

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Polycyclic aromatic hydrocarbons and amino acids in meteorites and ice samples from LaPaz Icefield, Antarctica

Oliver BOTTA^{1, 2, 3†*}, Zita MARTINS^{4‡}, Christian EMMENEGGER^{5○}, Jason P. DWORKIN¹, Daniel P. GLAVIN¹, Ralph P. HARVEY⁶, Renato ZENOBI⁵, Jeffrey L. BADA⁷, and Pascale EHRENFREUND⁴

¹NASA Goddard Space Flight Center, Code 699, Greenbelt, Maryland 20771, USA

²Goddard Earth Sciences and Technology Center, University of Maryland, 5523 Research Park Dr., Baltimore, Maryland 21228, USA

³International Space Science Institute, Hallerstrasse 6, 3012 Bern, Switzerland

⁴Astrobiology Laboratory, Leiden Institute of Chemistry, University of Leiden, Einsteinweg 55, 2300 RA Leiden, The Netherlands

⁵Department of Chemistry and Applied Biosciences, Eidgenössische Technische Hochschule Zürich Hönggerberg, Wolfgang-Paulistrasse 10, 8093 Zürich, Switzerland

⁶Department of Geology, Case Western Reserve University, Cleveland, Ohio 44106, USA

⁷Scripps Institution of Oceanography, University of California at San Diego, 9500 Gilman Drive, La Jolla, California 92093–0212, USA

[†]Present address: Swiss Space Office, State Secretariat for Education and Research, Hallwylstrasse 4, 3003 Bern, Switzerland

[‡]Present address: Department of Earth Science and Engineering, South Kensington Campus, Imperial College London, SW7 2AZ London, UK

[○]Present address: Metrohm Ltd., Oberdorfstrasse 68, 9100 Herisau, Switzerland

*Corresponding author. E-mail: botta@issibern.ch

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Abstract—We have analyzed ice samples and meteorites from the LaPaz region of Antarctica to investigate the composition of polycyclic aromatic hydrocarbons (PAHs) and amino acids with the goal to understand whether or not there is a compositional relationship between the two reservoirs. Four LL5 ordinary chondrites (OCs) and one CK carbonaceous chondrite were collected as part of the 2003/2004 ANSMET season. Ice samples collected from directly underneath the meteorites were extracted. In addition, exhaust particles from the snowmobiles used during the expedition were collected to investigate possible contributions from this source. The meteorite samples, the particulate matter and solid-state extracts of the ice samples and the exhaust filters were subjected to two-step laser mass spectrometry (L2MS) to investigate the PAH composition. For amino acids analysis, the meteorites were extracted with water and acid hydrolyzed, and the extracts were analyzed with offline OPA/NAC derivatization combined with liquid chromatography with UV fluorescence detection and time of flight mass spectrometry (LC-FD/ToF-MS). PAHs in the particulate matter of the ice were found to be qualitatively similar to the meteorite samples, indicating that micron-sized grains of the meteorite may be embedded in the ice samples. The concentration levels of dissolved PAHs in all the ice samples were found to be below the detection limit of the L2MS. The PAH composition of the snowmobile exhaust is significantly different to the one in particulate matter, making it an unlikely source of contamination for Antarctic meteorites. The amino acids glycine, β -alanine and γ -amino-*n*-butyric acid that were detected at concentrations of 3 to 19 parts per billion (ppb) are probably indigenous to the Antarctic meteorites. Some of the LaPaz ice samples were also found to contain amino acids at concentration levels of 1 to 33 parts per trillion (ppt), in particular α -aminoisobutyric acid (AIB), an abundant non-protein amino acid of extraterrestrial origin found in some carbonaceous chondrites. We hypothesize that this amino acid could have been extracted from Antarctic micrometeorites and the particulate matter of the meteorites during the concentration procedure of the ice samples.

INTRODUCTION

Carbonaceous chondrites, a rare class of stony meteorites, contain up to 3 wt% of organic carbon, most of which is locked in an insoluble macromolecular material.

Most information about meteoritic organic compounds was obtained from the analysis of the Murchison meteorite, a carbonaceous chondrite that fell in Australia in 1969. Several classes of soluble organic compounds have been isolated at abundances of up to 300 parts per million (ppm) (for reviews

see Botta and Bada 2002a; Sephton 2002; Pizzarello 2006). A suite of more than 80 protein and non-protein amino acids were detected in the water- and acid-soluble components of CM-type carbonaceous chondrites in total abundances of 60 ppm. Over the last 30 years, more than 45,000 meteorite specimens have been recovered from Antarctica by international search expeditions like the US Antarctic Search for Meteorite (ANSMET) program (Harvey 2003), the Japanese Antarctic Research Expedition (JARE) program (Iwata and Imae 2001), the Chinese Antarctic Research Expedition (CHINARE) program (Lin et al. 2006), and the European EUROMET and PNRA (Folco et al. 1995; Folco and Mellini 2000). Several Antarctic meteorites, in particular carbonaceous chondrites, have been analyzed for their organic content. The CM2 meteorites Allan Hills (ALH) 77306 (Cronin et al. 1979; Kotra et al. 1979), Yamato (Y-) 74662 (Shimoyama et al. 1979; Kotra et al. 1981), and Lewis Cliffs (LEW) 90500 (Botta and Bada 2002b; Glavin et al. 2006) have been shown to contain amino acid abundances and distributions similar to the non-Antarctic CM2, such as Murchison and Murray, while the CM2 Y-791198 yielded indigenous amino acids in higher abundances than any CM2 studied to date (Shimoyama et al. 1985; Shimoyama and Ogasawara 2002). Several other carbonaceous chondrites from Antarctica, including ALH 83100 (Glavin et al. 2006), Y-793321 and Belgica (B-) 7904 (Shimoyama and Harada 1984), are highly depleted in amino acids compared to other CM meteorites. Antarctic CM1 chondrites were analyzed for the first time for amino acids by Botta et al. (2007). These CM1s (ALH 88045, Meteorite Hills (MET) 01070, and LaPaz Icefield (LAP) 02277) showed a total amino acid concentration much lower than the average of the CM2s. Recently, the highest amino acid abundances ever measured have been reported in two Antarctic CR2 chondrites (Elephant Moraine (EET) 92042 (approx. 180 ppm) and Graves Nunataks (GRA) 95229 (approx. 250 ppm), while the CR1 chondrite Grosvenor Mountains (GRO) 95577 was depleted in amino acids (Martins et al. 2007a). Besides amino acids, other organic compounds were detected in Antarctic carbonaceous chondrites, including carboxylic acids, hydrocarbons, and purines. Among the Antarctic carbonaceous meteorites, the organic content of Y-791198 has been the most extensively studied. Carboxylic (Shimoyama et al. 1986) and dicarboxylic acids (Shimoyama and Shigematsu 1994) were present in Y-791198 in concentrations and distributions similar to the CM2 Murchison. Y-791198 also yielded aromatic and aliphatic hydrocarbons (Naraoka et al. 1988). This Antarctic CM2 was analyzed for dipeptides and diketopiperazines, but only gly-gly and cyclo(gly-gly) were detected (Shimoyama and Ogasawara 2002). Y-791198, together with other three Antarctic chondrites were analyzed for nucleic acid bases. Purines were identified in the Y-791198 and Y-74662 meteorites, while no purine or pyrimidines were present in the Y-793321 and B-7904

meteorites (Shimoyama et al. 1990). Y-74662 also yielded carboxylic acid and hydrocarbons in concentrations similar to those reported in Y-791198. On the other hand, Y-793321 had no detectable carboxylic acids or hydrocarbons. Finally, three Asuka carbonaceous meteorites, A-881280, A-881334, and A-881458 were also studied for their carboxylic acid content (Naraoka et al. 1999). While more than 30 carboxylic acids were identified in A-881458, including aliphatic and aromatic acids with several structural isomers, A-881280 and A-881334 were depleted in carboxylic acids. A-881458 also contained more than 70 polycyclic aromatic hydrocarbons (PAHs), with fluoranthene and pyrene as the most abundant ones (Naraoka et al. 2000).

Although organic contamination from the long residence time in the ice was believed to be a problem, the abundances of indigenous organic compounds such as amino acids and PAHs in Antarctic carbonaceous meteorites are generally high, which means that the terrestrial contribution is not recognized in the analysis.

Terrestrial contamination starts to become a problem for meteorites with only very low organic content, including, for example, SNC meteorites, which originated on Mars. The presence of PAHs was one of the pieces of evidence for the presence of traces of potentially biological material in the Antarctic Martian meteorite ALH 84001 (McKay et al. 1996). This publication ignited a large number of follow-up investigations, some of which focused on the presence of biogenic organic molecules such as amino acids in the meteorite, and the potential of terrestrial contamination from the Antarctic ice in which the meteorite resided for probably about 13,000 years (Jull et al. 1995).

- Stepped-heating experiments have provided evidence that most (as much as 80%) of the organic matter in ALH 84001 may be terrestrial in origin (Jull et al. 1998). This number was derived from ^{14}C and $\delta^{13}\text{C}$ measurements to determine the origin of the carbonate mineral and organic carbon components in ALH 84001 and EETA79001, another Martian meteorite found in Antarctica. Applying the same technique, Jull et al. (2000) presented evidence for the presence of extraterrestrial organic material in the Nakhla meteorite, a Martian meteorite recovered in Egypt in 1911 immediately after its fall.
- Data obtained by Becker et al. (1997) suggest that the PAHs observed in both ALH 84001 and EETA79001 are derived from either exogenous delivery of organic compounds to the surface of Mars or terrestrial PAHs present in the Antarctic ice melt water or, more likely, a mixture of these sources. Furthermore, $\delta^{13}\text{C}$ isotope data from ALH 84001 and Antarctic ice suggests that the organic matter associated with the carbonate globules in the meteorite is terrestrial in origin, while the presence of a kerogen-like component, detected by laser desorption/ionization mass spectroscopy (LDMS), with a higher

$\delta^{13}\text{C}$ isotope value appears to be best explained as a pre-terrestrial component (Becker et al. 1999). This latter component is thought to be associated with similar material found in carbonaceous chondrites, thus favoring an abiogenic, exogenous origin.

- Endogenous amino acids were found at levels of 1 part per million (ppm) to 0.4 ppm in samples of EETA79001 (McDonald and Bada 1995). However, the detected amino acids consisted exclusively of the L-enantiomer of the amino acids commonly found in proteins, and were thus considered terrestrial contaminants. In addition, no indication was found of α -aminoisobutyric acid (AIB), one of the most abundant amino acids in carbonaceous chondrites. The relative abundances of amino acids in the druse (carbonate) material resembled those in an Antarctic ice sample from the Allan Hills region, suggesting that the source of these amino acids may be the ice meltwater. Later, ALH 84001 was also investigated with the same techniques (Bada et al. 1998). This meteorite seems to contain even lower amounts of amino acids, and the detected amino acids were found to be uniformly distributed in the carbonate component.
- In contrast to these results, investigations by Clemett et al. (1998) concluded that terrestrial contamination of Antarctic meteorites can be neglected. In one experiment, these authors have analyzed ice from the Allan Hills region and found that the soluble PAH component is below the detection limit of their instrument. However, PAHs were found in the Greenland ice sheet (average concentration of the order of 1500 pg/kg ice; Masclet et al. 1995).

In this paper, we report on our results from a study of cross-contamination between meteorites collected during the 2003/04 ANSMET season and ice samples that were collected at the same time and location as the meteorite. We investigated both amino acids and PAHs in the ice and meteorite samples. In addition, we investigated the PAH composition of the exhaust from the snowmobiles at different performance levels in order to determine a possible PAH contribution from this source.

The most common techniques that have been used for amino acid analyses of carbonaceous meteorites are high performance liquid chromatograph combined with UV fluorescence detection (HPLC-FD) and gas chromatography-mass spectrometry (GC-MS). Although these techniques have been very useful for the characterization of complex organic compounds, including amino acids in meteorites, both of these instruments have limitations. For example, HPLC-FD has a much lower detection limit ($\sim 10^{-15}$ mol) for amino acids than traditional GC-MS ($\sim 10^{-12}$ mol), but relies on the identification of amino acids by retention time only. With traditional GC-MS, amino acids can be identified by both retention time and by their characteristic mass fragmentation

pattern. However, the mass fragments of the parent ions generated by electron impact (EI) ionization can often be difficult to interpret when dealing with unknown compounds. In addition, there is reduced sensitivity in EI ionization GC-MS compared to other soft ionization liquid chromatography-mass spectrometry (LC-MS) techniques such as electrospray (ES) or photoionization. Following on the success of a previous study (Glavin et al. 2006), we have applied a new LC-MS technique coupled with OPA/NAC derivatization, for the analyses of amino acids in meteorite extracts and ice samples. By combining HPLC-FD with ESI time-of-flight mass spectrometry (ToF-MS) detection, amino acids can be identified by retention time and exact mass simultaneously. The LC-ToF-MS instrument is at least a factor of 1000 times more sensitive than traditional GC-MS techniques with demonstrated sub-femtomolar ($\sim 10^{-15}$ to 10^{-16} mol) detection limits for amino acids. We used the highly sensitive LC-FD/ToF-MS instrument at NASA Goddard Space Flight Center (GSFC) to analyze both the ice and the meteorites for amino acids.

The PAHs were investigated in the ice and meteorite samples using the two-step laser mass spectrometry (L2MS) technique to identify and compare the distribution of PAHs in both sample sets. L2MS can be used for the direct chemical analysis of selected compounds in complex mixtures (e.g., Haefliger and Zenobi 1998). In the first step, an infrared laser pulse desorbs neutral molecules from the sample surface. In the second step, a pulse from a ultraviolet laser is used for resonance-enhanced two-photon ionization (1+1 REMPI) of the desorbed species. This soft ionization scheme minimizes fragmentation. Mass analysis is then performed in a reflectron time-of-flight mass spectrometer. The mass spectra are dominated by intact parent ions of aromatic components that strongly absorb the selected ionization laser wavelength (260 nm). Little or no sample preparation is necessary, and the direct measurement of analytes in complex matrices is possible. Furthermore, a measurement is performed within a few minutes. The detection limits are in the picogram range, which is orders of magnitude lower than for most other techniques. The L2MS technique has been used in the past for the analysis PAHs in meteorites (Hahn et al. 1988). PAHs in liquid matrices are a special challenge for L2MS, because the sample has to be in solid form to be analyzed. In this project PAHs were extracted and concentrated from water samples with a solid PVC membrane containing an internal standard (Bucheli et al. 2000; Emmenegger et al. 2003). Limits of detection in the low nanogram per liter (ng/l) range were achieved.

In addition, we also analyzed the exhaust composition of the snowmobiles in order to obtain information about their potential contribution. Similar measurements have already been carried out for cars, diesel trucks, residential heating, cigarette smoke, and wood fire samples collected on filters (Haefliger et al. 2000).

EXPERIMENTAL

Chemicals and Reagents

o-Phthalaldehyde (OPA), *N*-acetyl-L-cysteine (NAC), sodium acetate trihydrate, sodium borate decahydrate, HPLC grade water, dichloromethane (DCM) and all amino acid standards were purchased from Sigma-Aldrich. Ammonium hydroxide (28–30wt%) was purchased from Acros Organics. Methanol (absolute HPLC) was bought from Biosolve Ltd. and Fischer. Sodium hydroxide and hydrochloric acid (37%) were obtained from Boom. AG® 50W-X8 resin was acquired from Bio-Rad. A stock amino acid solution ($\sim 10^{-5}$ M) was prepared by mixing individual standards (97–99% purity) in Millipore (18.2 M Ω) H₂O. The *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC) reagent used for amino acid derivatization was prepared by dissolving 4 mg OPA in 300 μ l methanol and then adding 685 μ l 0.1 M sodium borate buffer (pH 9) and 15 μ l 1 M NAC. A 0.1 M hydrazine (N₂H₄) solution was prepared by double vacuum distillation of concentrated anhydrous hydrazine (98% purity) and subsequent dilution in H₂O. The HCl was doubly distilled, and the ammonium formate buffer used in the LC-ToF-MS analyses was prepared by NH₄OH titration of a 50 mM formic acid solution to pH 8. A 10⁻⁵ M phenolphthalein solution in 99.9% acetonitrile and 0.1% formic acid was used for internal mass calibration of the ToF-MS. Aluminum foil (Al foil) was heated to 500 °C for at least 3 h. before getting in direct contact with solid ice samples. All glassware was wrapped in Al foil and heated to 500 °C for at least 3 h before usage. These procedures have been used in previous studies of organic compounds in meteorites (e.g., Bada et al. 1998; Glavin et al. 2006; Botta et al. 2007; Martins et al. 2007a, 2007b).

Sample Preparation, Extraction, and Purification

Antarctic Ice Samples

During the 2003/2004 ANSMET field season, six ice samples from the LaPaz ice field stranding region were cut out using a pre-cleaned chain saw, which was used only for this purpose during the season (Fig. 1a). The oil used in this chain saw was based on silicon, which should contain only minor amounts of organic carbon. Five of these samples were taken directly underneath a meteorite that was collected at the same time, while the sixth ice sample was collected from a location where there was no meteorite in the immediate neighborhood (“Ice blank”) (Table 1). Sample acquisition time was less than 5 min each, and contact of the ice with any kind of clothing was carefully avoided. The ice samples were wrapped in nylon bags and stored frozen for transport to the US. After arrival at Scripps Institution of Oceanography (SIO), the samples (initial volumes 2250 to 4000 ml) were unwrapped and rinsed with doubly distilled water to remove

≈ 1 cm from each side of the ice blocks. The ice was touched only with the baked-out Al foil, any contact with gloves was avoided. This procedure removed dark material that had resulted from the chain saw cutting. Separate measurements of amino acids and PAHs of this rinsed material from sample #16704 showed neither of these compound classes to be present above the detection limit of the corresponding analytical technique. The pre-cleaned ice blocks were then melted at room temperature inside aluminum foil with the liquid dripping into a 4 l glass beaker. These solutions were concentrated to volumes between 14 and 20 ml using a rotary evaporator at a bath temperature of 50 °C (Table 1). These solutions were transported to ETH (Switzerland) in screw cap bottles with Teflon liners and wrapped in aluminum foil to prevent photoreactions. At ETH the solutions were first filtered through 100 μ m PVDF filters to isolate any particulate material. Filtration was done using a Millipore swinney stainless steel filter holder that was autoclaved and cleaned each time after use with EtOH/H₂O (1:1) in an ultrasonic bath. These filters were not investigated for micrometeorite content, but were analyzed for PAHs that would possibly be present in the particulate matter. Dissolved PAHs were extracted from the resulting filtrates using solid-phase extraction with polyvinyl chloride (PVC) membranes (Emmenegger et al. 2003). The membranes were attached to a stainless steel holder and dipped into the aqueous solutions for 15 h. at room temperature in the darkness. The membrane was removed from the solution and immediately moved to the L2MS apparatus for analysis. The resulting solutions were concentrated under vacuum, and the residues dissolved in 100 μ l high-purity water. 10 μ l aliquots of these solutions were then used for the amino acids analyses (see below). A 1-liter aliquot of doubly distilled water was carried through the same procedure as the ice samples and used as a procedural blank.

Limits of detection (LOD) for the PAHs were obtained with calibration curves for membrane measurements. Naphthalene and acenaphthylene were found to be too volatile for L2MS measurements. For fluorene, phenanthrene, pyrene, chrysene, benzo[k]fluoranthene and benzo[ghi]perylene calibrations were achieved after subtracting blank values (with an empty membrane). LODs were determined at 3 times the background signal. LODs for PAHs were found to be in the low ng/l range.

Antarctic Meteorites

The meteorites samples LAP 03624 (LL5), LAP 03573 (LL5), LAP 03637 (LL5), and LAP 03784 (CK5) were obtained from the NASA JSC Antarctic meteorite collection (Table 1). For each specimen, one surface sample and three interior samples representing different distances (depths) from the surface were analyzed (Fig. 1). PAH analysis of the meteorites was carried out directly on the chips without further sample preparation. A serpentine sample, provided by

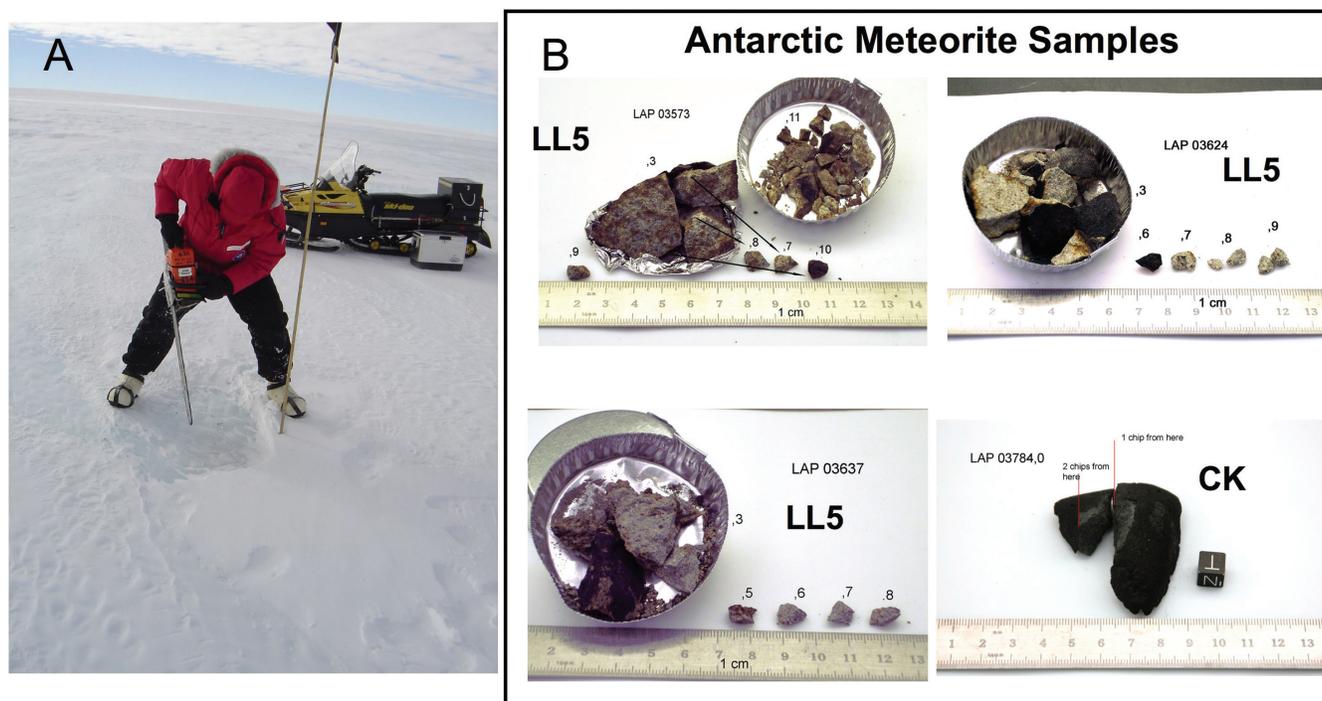


Fig. 1. Sample acquisition. a) Ice sample being cut out with a chain saw after the collection of the meteorite. b) Antarctic meteorite samples after preparation by the Antarctic meteorite curator at NASA Johnson Space Center.

the Museum for Natural History in Bern, Switzerland, was baked out at 500 °C for 3 h and carried through the same extraction and analysis procedures as a blank.

For the amino acid analyses, approximately 100 mg of each powdered meteorite sample was analyzed using the established procedure (Zhao and Bada 1995; Botta and Bada 2002a; Martins et al. 2007b) for extracting and analyzing amino acids in meteorites, which includes each sample being flame sealed in a test tube with 1 ml of HPLC grade water and boiled for 24 h. in a heating block at a temperature of 100 °C. One of two equal parts of the supernatants was then subjected to a 6 N HCl acid vapor hydrolysis for 3 h at 150 °C. The hydrolyzed and the non-hydrolyzed extracts of the meteorites were desalted on a cation exchange resin (Bio-Rad AG® 50W-X8, 100-200 mesh). The amino acids were eluted from the resin with 5 ml of ammonium hydroxide; the resulting elutions were evaporated to dryness under vacuum and the residues dissolved in 100 µl HPLC-grade water. 10 µl aliquots of these solutions (meteorite extract and ice residue) were derivatized with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) for HPLC-FD-ToF-MS analysis (Zhao and Bada 1995).

Snowmobile Exhaust

Three teflon coated quartz fiber filters, PALLFLEX Membrane Filters from PALL Gelmann (Ann Arbor, MI, USA) were used to sample exhaust gas from the snowmobiles (Bombardier Ski-Doo Skandic, equipped with a fan-cooled ROTAX WT 500 F 2-cylinder 2-stroke engine with a displacement of 496.7 cc) directly at the exhaust pipe. The

tests were carried out at LaPaz ice field at a density altitude of approximately 2000 m and the air temperature of −15 °C (with a wind chill of −26 °C). In order to achieve sufficient gas flow through the filters, the filter holder was connected to a rotary vacuum pump. The filter holder is described in detail by Haefliger et al. (2000). The samples were collected under the following different engine performance levels:

1. Warm engine, throttle in idle position (i1), and total collection time: 15 min.
2. Cold start, throttle one-quarter open (q1), total collection time: 10 min.
3. Warm engine, alternating: 1 min full throttle/2 min idle (t1), 5 cycles, total collection time: 15 min.

In addition filter b1 was taken to Antarctica but not exposed to any exhaust, was used as a procedural blank.

Sample Analysis

Two-Step Laser Mass Spectrometry

PAHs were measured using a custom-made two-step laser mass spectrometry (L2MS) system (Haefliger et al. 1998; Emmenegger et al. 2003). A CO₂ laser (Alltec 853 MS) with a wavelength of 10.6 µm and 5 mJ/shot was used for desorption of the molecules from the substrate. Compounds such as PAHs are ionized in a 1 + 1 resonance enhanced multiphoton ionization (REMPI) process, ensuring that the analyte molecules do not fragment. A pyroelectric power detector (ED-100 with EDX-1 amplifier, Gentec) was placed behind the ion source to measure the energy of each laser pulse. The

Table 1. Overview over the ice and meteorite samples investigated in this study.

Ice sample #	Collected on	Original sample volume (l)	Associated meteorite	Type	Sample size (mg) ^a
16186	20 Dec. 2003	2.25	LAP 03784	CK5	270 (,6) 265 (,7) 238 (,8) 162 (,9)
16167	20 Dec. 2003	2.70	LAP 03573	LL5	324 (,7) 339 (,8) 370 (,9) 377 (,10)
16704	20 Dec. 2003	4.00	LAP 03624	LL5	309 (,6) 342 (,7) 317 (,8)
16154	24 Dec. 2003	2.30	LAP 03637	LL5	363 (,9) 425 (,5) 396 (,6) 286 (,7) 285 (,8)
16031	25 Dec. 2003	2.75	LAP 03553	H4	n.o.
Ice blank	24 Dec. 2003	2.70	None		

^aThe number between parenthesis corresponds to the meteorite sample fragment (see Fig. 1b). Increasing number corresponds to increasing sample depth. n.o.: Sample not obtained for analysis.

ions were detected using a reflectron time-of-flight mass spectrometer (R. M. Jordan, Co.).

The filters (containing the particulate material) and the PVC membranes (containing the soluble PAHs) were directly inserted into the L2MS system. For meteorite measurements the sample holder tip was modified because the aperture of the original cap of the sample holder, was too large to pen in the meteorites. Cover plates where made with various holes smaller than 0.5 cm in diameters slightly off the axis to allow laser desorption. In addition, the samples were supported with a metal plate to avoid contamination. The plates and tweezers used were heat-sterilized prior to each measurement. Each of the filter and membrane sample was analyzed using a total of 72 laser shots, with a rotation of 5 degrees between each of the shots. The meteorites were analyzed using five shots at five different locations (25 spectra in total). All the spectra were averaged.

Liquid Chromatography-Time of Flight-Mass Spectrometry

The fluorescent OPA/NAC amino acid derivatives in the meteorite and blank extracts were analyzed with a Waters 2475 multi- λ fluorescence detector ($\lambda_{\text{ex}} = 340$ nm; $\lambda_{\text{em}} = 450$ nm). Amino acid separation was achieved with a Phenomenex Luna 5 μm reverse phase phenyl-hexyl column (4.6 mm \times 250 mm) and maintained at 30 $^{\circ}\text{C}$; elution was performed using a ternary gradient with water (solvent A), methanol (solvent B) and 50 mM ammonium formate, 8% methanol (pH 8.0) (solvent C) at a flow rate of 1 ml/min. The gradient used was: 0–5 min., 100% C; 5–15 min., 0–83% A and 0–12% B; 15–22 min., 83–75% A and 12–22% B; 22–35 min., 75–35 % A and 20–60% B (Glavin et al. 2006). In

addition to UV fluorescence detection, the exact masses of the amino acid OPA/NAC derivatives that eluted from the column (16% split to MS) were simultaneously detected by ToF-MS using a Waters LCT Premier ToF-MS instrument at GSFC. The LCT Premier mass spectrometer employs an ESI with a mass resolution of 8,000 in the mass range of 100 to 1,000 m/z. The instrument was optimized for maximum sensitivity of OPA/NAC amino acid derivatives in the 300 to 450 m/z range. The ToF-MS was continuously monitoring in ES positive mode to obtain exact masses ($M + 1$) for the parent ion (M) of each OPA/NAC amino acid derivative present in the sample with extremely low fragmentation of the parent ion. The ToF-MS was run in “W mode” to increase mass resolution by employing extra reflections. Continuous mass calibration of the ToF-MS during the runs was achieved with an internal reference compound (phenolphthalein, $M = 318.089$ Da) delivered to the MS via a pump at 5 $\mu\text{l}/\text{min}$ to an independent and alternating electrospray nozzle (the lockspray) via a motorized baffle between the two sprayers. Using the lockspray, the exact mass of OPA/NAC amino acid derivatives can be determined to within ± 0.001 Da (~ 3 ppm). The mono-isotopic mass of the protonated OPA/NAC amino acid derivative ($M + \text{H}^+$) was used for quantification. Mass peak areas were obtained by performing two 4 channel Savitzky-Golay smoothing of the spectrum and then plotting the masses at FWHM (typically 7–9 channels or about ± 0.02 Da around the center of the peak). This was done to exclude interfering background peaks.

A LOD for amino acids using both UV fluorescence and ToF-MS was determined to be $\sim 10^{-15}$ to 10^{-16} mol ($S/N \sim 30$).

RESULTS AND DISCUSSION

The data from this study presented in Figs. 2–4, 7, and 8, and Tables 2 to 5 are based on the analyses using L2MS and LC-ToF-MS techniques described above. The amino acid abundances for the meteorites and ice reported in Tables 2 and 3 are the average of multiple independent analyses of the same extracts. Each peak in the chromatograms was identified by comparison of its UV fluorescence retention time as well as by exact molecular mass with those of authentic reference standards. The amino acid abundances in the meteorite samples were calculated by comparison the integrated peak area, corrected with the abundances in the blank serpentine sample, with the integrated peak area of known amino acid standards.

Antarctic Ice Samples

Amino Acids

The amino acid abundances measured in the Antarctic ice samples using both LC-FD and LC-ToF-MS are shown in Table 2.

The concentration levels of the amino acids in the Antarctic ice samples are found to be close to blank levels. However, we observed some variability between the ice samples with regard to their amino acid composition. Most importantly, the signals corresponding to AIB were found to correspond to concentration levels between <15 and 33 ± 11 ppt in the ice samples (Table 2). A few other amino acids were also detected in the ice samples; however, their distribution is different within samples. For example, samples 16186 and 16167 both contain AIB, alanine and γ -amino-*n*-butyric acid (γ -ABA). On the other hand, sample 16704 contains about 12 ppt AIB, but no other amino acid was detected in this sample. As can be seen from Table 1, ice sample 16186 is associated with a CK chondrite, while all others are associated with ordinary chondrites (OCs). OCs are not known to contain indigenous amino acids, as shown in the H4 OC Forest Vale (Zenobi et al. 1992). This finding and the discovery of amino acids, including AIB, in the blank ice sample, where no meteorite was in the immediate proximity at the time of collection, suggests that the presence of AIB, and consequently of all amino acids, in the ice are not directly associated with the meteorite that was collected with it. Antarctic micrometeorites (AMMs), collected in the South Pole Water Well, have been analyzed for organic compounds, and AIB has been detected in one of the samples (Brinton et al. 1998; Matrajt et al. 2004). It is possible that AMMs were also present in our ice samples, and perhaps at higher concentrations than in other locations such as the high plateau. Since the ice samples were not filtered before they were concentrated in the laboratory at a water bath temperature of 50 °C, it cannot be excluded that these amino acids were extracted from the AMMs during this procedure. Another possibility for the origin of these

amino acids could be leaching from carbonaceous meteorites that were present in this ice earlier and that moved to other locations after being delivered to the ice surface. In this scenario, the amino acids would have been leached from the meteorites during the residence time in the ice.

PAHs

PAHs were measured both in particulate matter and in solid solution. The L2MS of the filtrate of ice sample 16154 is shown in Fig. 2. All L2MS spectra of the filters containing the particulate matter look very similar. The filter of the Ice Blank sample did not show peaks larger than approximately 10% of the corresponding signals in the other ice samples. The spectra are dominated by signals corresponding to phenanthrene/anthracene (m/z 178) as well as its alkylated homologs at m/z 192, 206, 220 and 234, plus a signal at m/z 212. Masses higher than m/z 280 are mostly lacking. In contrast to the filter spectra (particulate matter), the signals in the L2MS spectra of the PVC membranes (solid solution) were at blank level. From the calibration curves obtained with the L2MS instrument (Emmenegger et al. 2003; Emmenegger 2006), the dissolved PAH concentrations in the ice samples were determined to be below 10–80 pg/l (depending on both the concentration factors of the individual samples and the mass signal intensities). These values are in the same range of the upper limit determined for polar ice from Greenland (8 to 460 pg of PAHs/kg ice) (Jaffrezo et al. 1994; Masclet et al. 1995; Clemett et al. 1998).

Becker et al. (1997) found primarily core PAHs (PAHs with no alkyl residues) with masses of up to 300 Da in their analysis of ice from the Allan Hills region. This composition was found to be very similar to the composition of Greenland ice samples and also to the Martian meteorites and EETA79001 and ALH 84001. However, the extraction method applied for these ice analyses included a carbonate extraction, and the actual LDMS analysis was performed on these carbonate extracts, which probably contained primarily the particulate component of the ice (Becker et al. 1997). It is established that high molecular mass PAHs ($m/z > 200$ amu) undergo rapid gas-particle conversion in the atmosphere and can be transported over long distances in particulate form (Masclet et al. 2000 and references therein). The L2MS analysis of the particulate matter in the LaPaz ice samples (Fig. 2) shows a different pattern, including the presence of alkylated PAHs and a lack of molecules with mass higher than m/z 240 amu. This is very similar to the PAH composition detected in the Forest Vale H4 ordinary chondrite (Zenobi et al. 1992). This result indicates that the LaPaz ice samples are depleted in terrestrial PAHs (i.e., very clean), perhaps due to the very remote location on the Antarctic ice sheet. These ice samples may contain material from the meteorite associated with them, although the amounts are at the limit of detection for our methodology.

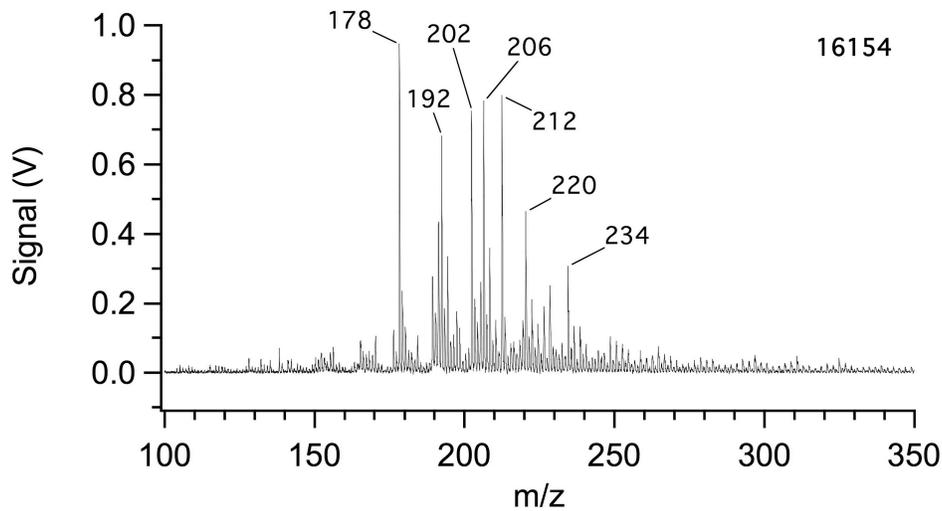


Fig. 2. Average of 25 L2MS spectra of the membrane filter used to extract PAHs from ice sample 16154. X-axis shows m/z ratio, y-axis is the signal intensity in volts (see section 2 for experimental details).

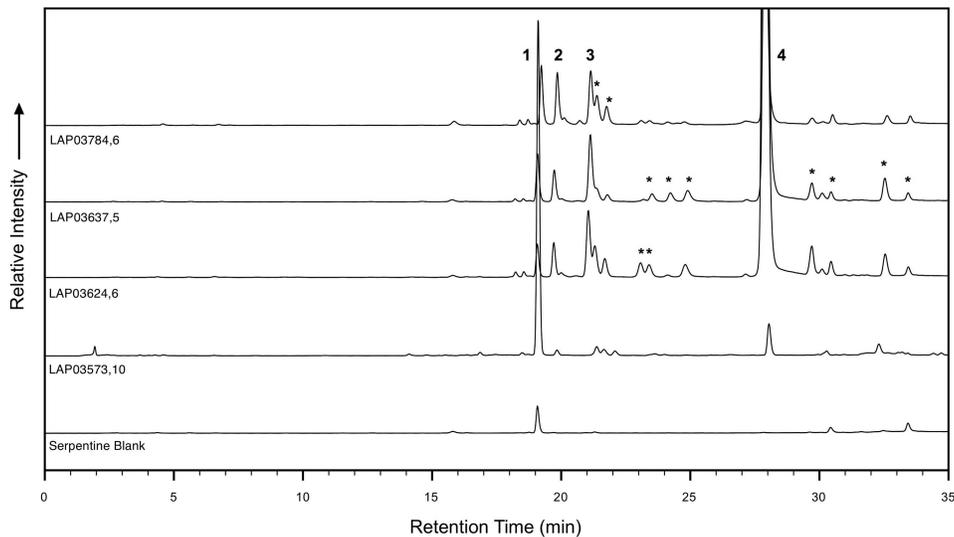


Fig. 3. The 0 to 35 min region of the HPLC-FD chromatograms obtained for the OPA/NAC labeled (1 min derivatization) 6 M HCl acid hydrolyzed extracts of LAP 03784,6, LAP 03637,5, LAP 03624,6, and LAP 03573,10 meteorites and a serpentine blank. Peak identifications are as follows: 1. Glycine; 2. β -alanine; 3. γ -Amino-*n*-butyric acid; 4. ϵ -amino-*n*-caproic acid (EACA). The peaks labeled with asterisk are unknown (see Fig. 4). The conditions for amino acid separations for the mobile phase at 30 °C were as follows: flow rate, 1 ml/min; solvent A (water); solvent B (methanol); solvent C (50 mM ammonium formate, 8% methanol, pH 8.0); gradient 0 to 5 min, 100% C; 5 to 15 min, 0 to 83% A and 0 to 12% B; 15 to 22 min, 83 to 75% A and 12 to 20% B; 22 to 35 min, 75 to 35% A and 20 to 60% B.

Antarctic Meteorites

Amino Acids

The type of meteorite and its association with the ice sample is indicated in Table 1. Figure 3 displays typical LC chromatograms for all four Antarctic meteorites as obtained from meteorite extracts after derivatization with OPA/NAC and fluorescence detection. Figure 4 shows the mass-specific chromatograms for the CK5 LAP 03784,6. Only three amino acids, glycine, β -alanine, and γ -amino-*n*-butyric acid (γ -ABA) could be identified above blank level in these four meteorite samples (Table 3), with slightly higher abundances in LAP

03784 than in the LL5 chondrites (Fig. 5). In contrast, no AIB was detected in any of these meteorites. The abundances of these three amino acids were similar in all four meteorites, indicating no correlation with their weathering grades. All meteorites contained very high levels (130 to 350 ppb) of ϵ -amino-*n*-caproic acid (EACA), the hydrolysis product of Nylon-6 (the bag material in which the meteorites were wrapped during transport) (Glavin et al. 2006). Interestingly, none of this material was found in the ice samples, probably because it was removed during the rinsing of the outermost layers of the ice samples before they were melted.

One possible indication for terrestrial contamination in

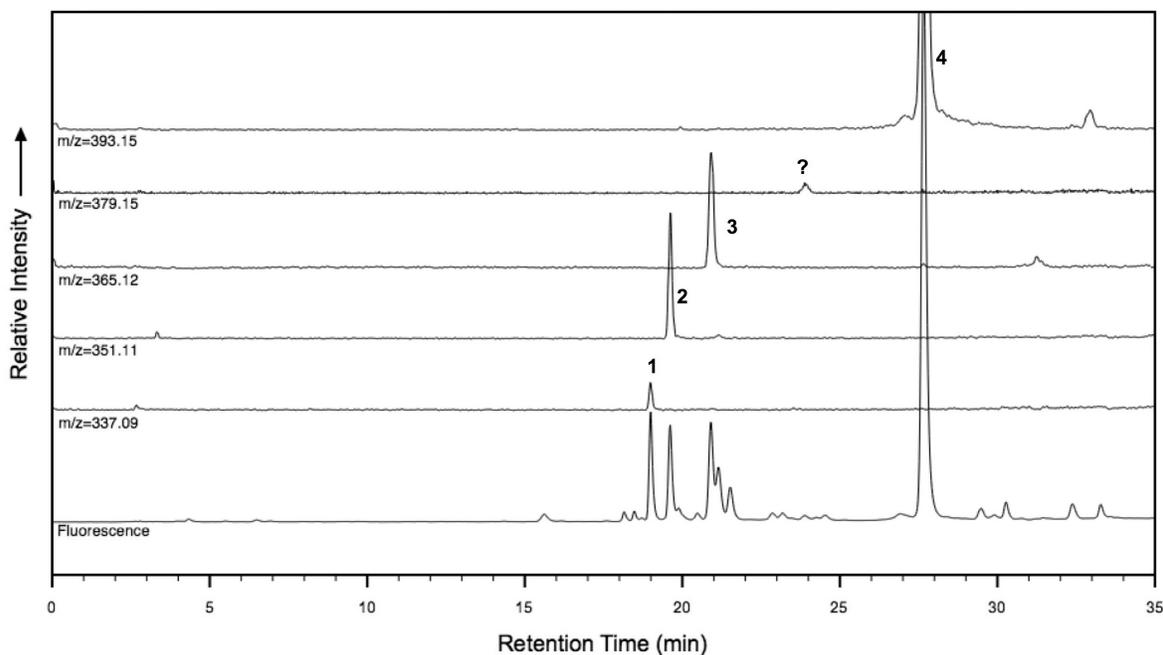


Fig. 4. The 0 to 35 min region of the HPLC-FD and LC-ToF-MS chromatograms obtained for the OPA/NAC labeled (1 min derivatization) 6 M HCl acid hydrolyzed extract of the CK5 meteorite LAP 03784,6. Amino acid peak identifications are given in Table 2. The UV fluorescence trace is shown at the bottom and the exact mass traces were obtained simultaneously in positive electrospray mode for the individual amino acid. See Fig. 3 for the separation conditions.

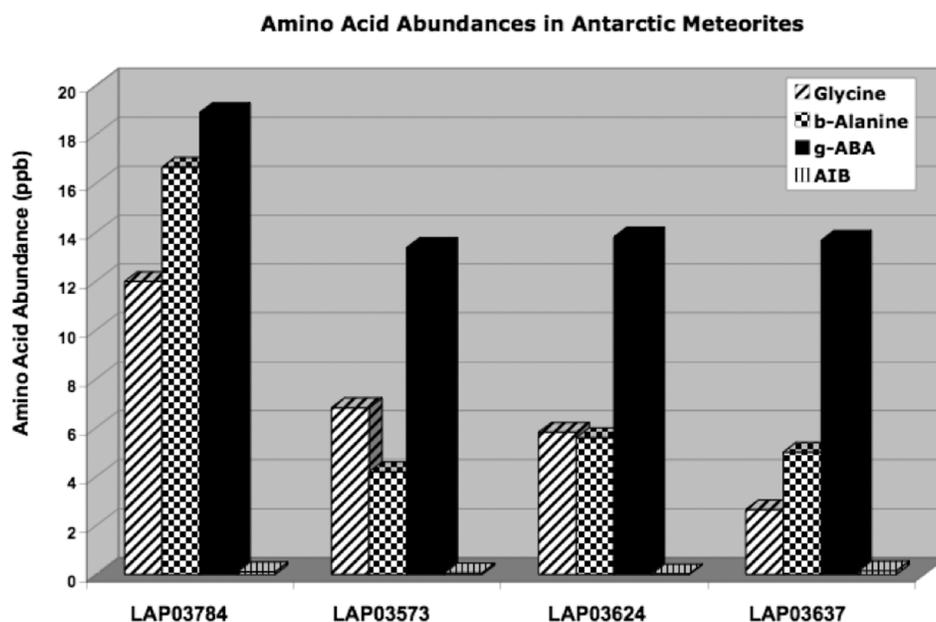


Fig. 5. The distribution of glycine (diagonally striped), β -alanine (b-alanine, checked) γ -amino-*n*-butyric acid (γ -ABA, solid black) and α -aminoisobutyric acid (AIB, vertically striped) in the four meteorites LAP 03784 (CK), LAP 03573 (LL5), LAP 03624 (LL5), and LAP 03637 (LL5). Abundances are given in parts per billion (ppb).

these meteorites would be the presence of a decreasing abundance gradient from the fusion crust of the meteorite towards the interior. Since four fragments of these meteorites were available that represented approximately different depths, we investigated whether or not the three amino acids showed a

concentration gradient in the meteorites. Figure 6 shows the amino acid abundances of different fragments of one of the meteorites, LAP 03573, obtained with the LC-ToF-MS. The concentrations of glycine, β -ala and γ -ABA were found to be very similar in all four fragments. This either means that the

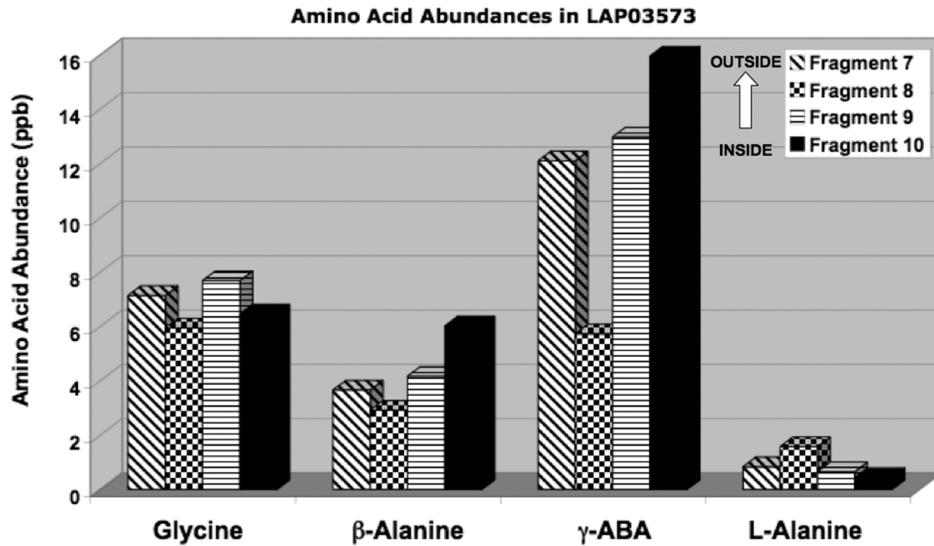


Fig. 6. The distribution of glycine, β -alanine, γ -ABA and L-alanine in fragments 7 (diagonally striped), 8 (checkered), 9 (horizontally striped), and 10 (solid black) of meteorite LAP 03573 (LL5). Abundances are given in ppb.

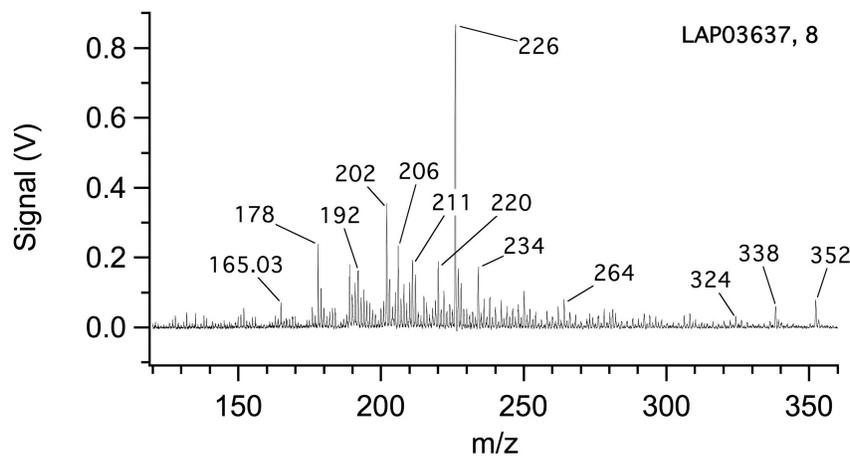


Fig. 7. High-intensity L2MS spectrum obtained for Antarctic meteorite fragment LAP 03637,8. X-axis shows m/z ratio, y-axis is the signal intensity in volts (see section 2 for experimental details).

contamination has penetrated the meteorites over a long period of time so that the initial gradient has been erased, or that these amino acids are indeed indigenous to the meteorite. A comparison with the amino acid composition of the ice (Table 2) shows that these two sample sets are not identical, in particular because of the absence of AIB in any of the meteorite samples and its presence observed in at least three ice samples. If indeed liquid water from the surrounding ice percolated through the meteorite over short periods of time during the residence time in Antarctica, then a signature of AIB should be visible in the meteorites. The absence of this signature points to an indigenous origin of the amino acids glycine, β -alanine and γ -ABA in these meteorites. Compound specific stable isotope measurements will be necessary to confirm if these amino acids are indigenous to these meteorites.

PAHs

The L2MS spectra of the meteorites were generally very low in intensity, with the exception of the interior sample LAP 03637,8 (Fig. 7), which represents the only high intensity spectrum. The most prominent signals were at m/z 226, which can be assigned to a core PAH, and m/z 211, a nitrogen-containing compound. However, these two peaks were also found in the serpentine blank, indicating that these signals may represent compounds that are not indigenous to the meteorites. Furthermore, peaks corresponding to m/z 178 (anthracene/phenanthrene), 192, 206, 220 (C_1 -, C_2 -, and C_3 -alkylanthracenes/phenanthrenes), and 234 were detected, as well as a peak at m/z 202 (pyrene/fluoranthene). Unique for these spectra are the high-mass signals detected at m/z 324, 338 and 352, which are not detected in terrestrial samples.

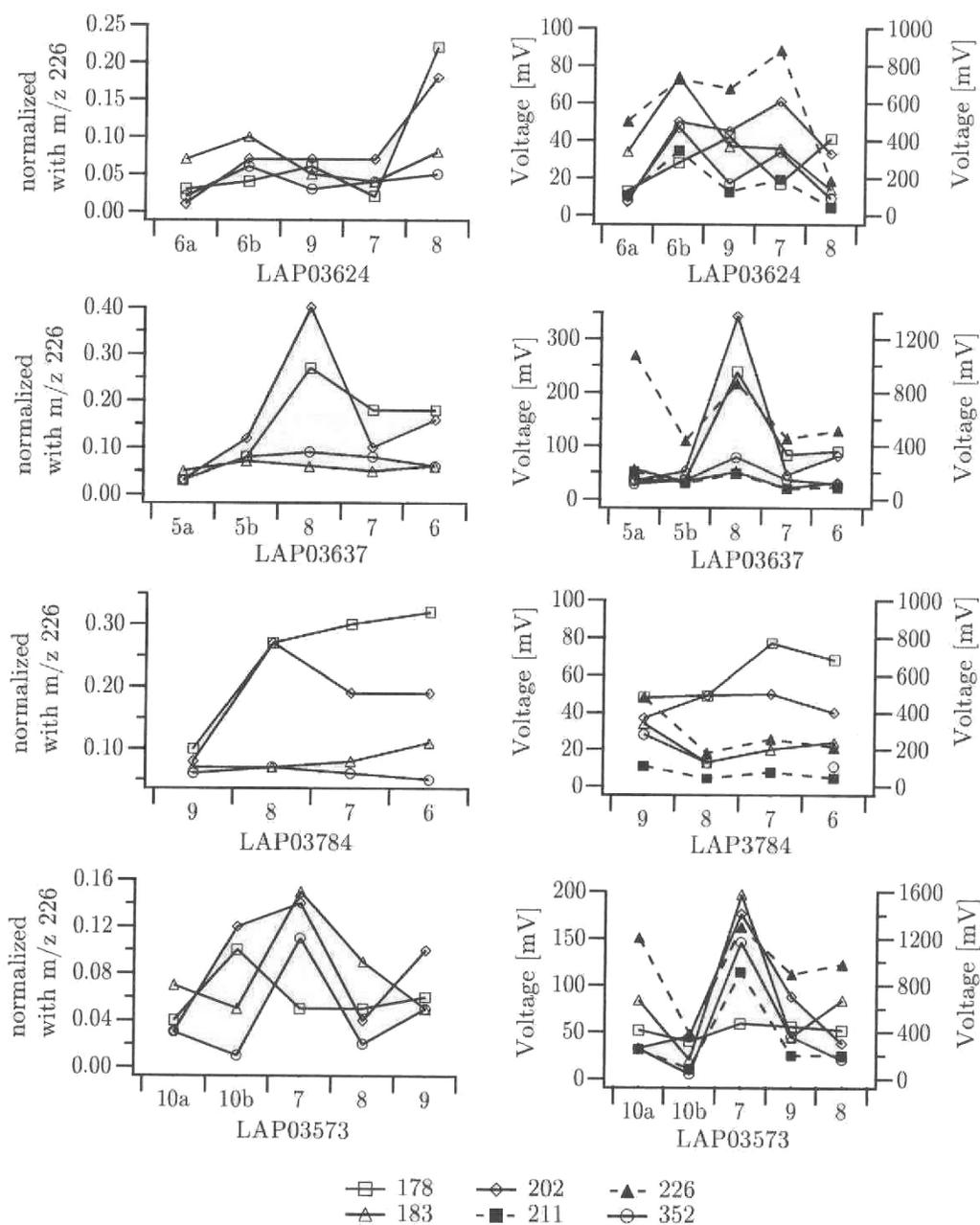


Fig. 8. Normalized PAH compositions of the fragments of the four Antarctic meteorites to illustrate potential concentration gradients from the fusion crust to the interior from left to right. Left: signals corresponding to m/z 178, 183, 202, and 352 normalized with m/z 226. Right: absolute voltages measured for m/z 178, 202, 352 (left ordinate) and m/z 211 and 226 (right ordinate). Labels a and b indicate two independent measurements of the same fragment.

While there are no straightforward PAHs for the masses 324 or 338, there are many 7-ring aromatic compounds with a molecular formula of $C_{28}H_{16}$, corresponding to m/z 352, which is the most distinctive one of these “higher” mass region of the spectra.

Absolute and relative (against the m/z 211 signal) signal measurements for several peaks in the L2MS spectra of the different fragments of each meteorite were plotted together to

visualize any trends in the abundances from the fusion crust inwards (Fig. 8). The spike in the LAP 03637 plots is due to the high-intensity signal for fragment 8. Although these plots look different for each meteorite, there is no trend observable in any of these samples that would indicate a concentration gradient for these PAHs (Emmenegger 2006). The only exception is fragment LAP 03624,6, which clearly shows the lack of PAHs.

Table 2. Summary of the average blank-corrected amino acid concentrations, reported in parts per trillion (ppt), in Antarctic ice samples 16186, 16167, 16704, 16154, and 16031 from the LaPaz ice field. The uncertainties of the values are based on the standard deviation of the average value between four and eight separate measurements. The data are either from fluorescence or mass-specific signals. For upper limits, the lower value of the two measurements is reported.

Amino acid	16186 LAP 03784 ^a	16167 LAP 03573	16704 ^b LAP 03624	16154 LAP 03637	16031 LAP 03553	Ice blank No meteorite
D-aspartic acid	<1.3 ^c	<0.2	<0.5	<1.3	<1.0	<0.8
L-aspartic acid	<1.4	<1.7	<1.2	<0.9	<1.1	<0.8
L-glutamic acid	<1.8	<2.1	<0.02	<4.9	<1.1	<1.1
D-glutamic acid	<0.2	<0.5	<0.02	<1.1	<1.5	<0.7
D-serine	<0.5	<0.1	<0.02	<0.5	<0.4	<0.4
L-serine	1.6 ± 1.1	<8.0	<0.02	<2.7	<1.1	<2.7
Glycine	8.9 ± 2.0	<18.7	<3.9	4.9 ± 2.3	<7.5	7.2 ± 4.8
β-alanine	<0.7	<0.8	<0.1	0.5 ± 0.6	<0.3	<0.6
γ-amino- <i>n</i> -butyric acid (γ-ABA)	1.1 ± 0.3	1.4 ± 0.1	<0.03	<0.6	<0.7	0.2 ± 0.2
D-alanine	2.3 ± 0.8	4.0 ± 0.6	<0.1	0.1 ± 1.1	<1.08	1.5 ± 1.6
L-alanine	4.4 ± 0.8	<8.3	<0.6	2.0 ± 1.0	<0.6	<4.1
α-aminoisobutyric acid (AIB) ^f	14.3 ± 6.7 ^d 27.9 ± 2.6 ^e	4.3 ± 1.0 ^d 1.5 ± 0.3 ^c	11.8 ± 3.01 ^d 11.7 ^e	<0.18	<0.15	20.1 ± 4.5 ^d 33.1 ± 10.6 ^e
D,L-α-amino- <i>n</i> -butyric acid	<0.09	<0.007	<0.03	<0.0005	<0.07	<0.003
D-isovaline	<0.5	<0.4	<0.04	<0.2	<0.2	<0.3
L-isovaline	<1.2	<6.9	<0.05	<0.6	<0.6	<0.5
D-valine	<0.1	<0.2	<0.01	<0.004	<0.1	<0.1
L-valine	<2.5	<6.1	<0.04	<0.6	<0.1	1.5 ± 1.8

^aName of the meteorite collected simultaneously with the ice sample.

^bThe concentration data for this sample is based on three measurements.

^cConcentrations reported with "<" were very similar to blank levels and are considered to be maximum values.

^dFrom fluorescence data.

^eFrom mass data.

^fThese enantiomers could not be separated under the applied chromatographic conditions.

Table 3. Summary of the average blank-corrected amino acid concentrations in the acid-hydrolyzed hot-water extracts of the Antarctic LL5 ordinary chondrites LAP 03573, LAP 03624, LAP 03637, and the CK5 chondrite LAP 03784^a.

Amino acid	LAP 03784 (B) ^b	LAP 03573 (B) ^b	LAP 03624 (A) ^b	LAP 03637 (A/B) ^b
Glycine	12.0 ± 3.6	6.8 ± 1.0	5.8 ± 1.5	2.7 ± 1.1
β-alanine	16.7 ± 2.8	4.2 ± 0.8	5.6 ± 1.3	5.0 ± 0.9
γ-ABA	18.9 ± 1.9	13.4 ± 1.0	13.8 ± 2.8	13.7 ± 2.9
AIB	<0.1 ^c	<0.07 ^c	<0.03 ^c	<0.2 ^c

^aAll values are reported in parts-per-billion (ppb) on a bulk sample basis. Meteorite extracts were analyzed by OPA/NAC derivatization and HPLC separation coupled with UV fluorescence and simultaneous ToF-MS measurements. Quantification of the amino acids included background level correction using a serpentine blank and a comparison of the peak areas with those of an amino acid standard. The uncertainties (δx) are based on the standard deviation of the average value of between three and six separate measurements (N) with a standard error, $\delta x = \sigma_x (N-1)^{1/2}$. For all UV fluorescence data, co-eluting amino acid peaks and/or compounds with interfering peaks were not included in the average.

^bWeathering grade: A: minor; B: moderate.

^cThese values must be considered upper limits.

A summary of literature data on core PAHs detected in Antarctic carbonaceous and Martian meteorites, the Murchison carbonaceous chondrites and the LaPaz LL5 and CK5 chondrites using the L2MS technique is given in Table 4. It should be emphasized here that this technique is suited to account for only a limited number of PAHs, and that other techniques, in particular hydrous pyrolysis and supercritical fluid extraction (SFE) in combination with, for example, GC-MS, have been applied to identify a much wider range of PAHs in the insoluble matter in carbonaceous meteorites (e.g., Sephton et al. 2000; Sephton 2002 and references therein). In our study using L2MS, the abundance

of core PAH in Antarctic meteorites that are neither CM nor Martian meteorites can be reduced to probably two signals, *m/z* 178 and 202, corresponding to anthracene/phenanthrene and pyrene. This is in contrast to the presence of core PAHs at *m/z* 228 (benzanthracene/chrysene), 252 (benzofluoranthene/benzopyrene/peryene) and 300 (coronene) found in the Antarctic carbonaceous chondrites ALH 83355 and ALH 85006 using LDMS (Becker et al. 1997). Interestingly, this distribution is distinct from the distribution found in Murchison using L2MS (Hahn et al. 1988) as well as the Martian meteorites EETA79001 and ALH 84001 (Table 4). In addition to the

Table 4. Core PAHs found in Antarctic shergottites EETA79001 and ALH 84001, the carbonaceous chondrites EETA83355 and ALH 85006, the Murchison meteorite, and the CK and LL5 Antarctic meteorite samples investigated in this study by the L2MS technique in comparison with an Allan Hills ice carbonate extract and the LaPaz ice particulate matter.

m/z	EETA79001 (shergottite) ¹	ALH 84001 (shergottite) ¹	EETA83355 (CC) ¹	ALH 85006 (CC) ¹	Murchison (CM2) ²	LAP CK and LAP LL5 (this work)	Allan Hills ice (carbonate extract) ¹	LaPaz ice (filters) ^a (this work)
128	–	–	–	–	+	–	–	–
166	+	–	+	+	–	–	–	–
178	+	+	–	–	+	+	+	+
202	+	+	–	–	+	+	+	+
228	+	+	+	+	–	–	+	–
252	+	+	+	+	–	–	+	–
276	+	+	–	–	–	–	–	–
278	+	+	–	+	–	–	+	–
300	+	–	+	–	–	–	+	–

^aThe filters contain PAH in particulate matter. Dissolved PAH were found to be below the LOD of 10–80 pg/l.

References: 1) Becker et al. 1997; 2) Hahn et al. 1988.

core PAHs anthracene/phenanthrene and pyrene found in our samples, C₁-, C₂-, and C₃-alkyl-derivatives were also detected. The same compounds were detected in a freshly cleaved surface from the interior of the Forest Vale H4 ordinary chondrite (Zenobi et al. 1992). Although the relative abundances are dissimilar, the same signals (m/z 178, 192, 206, 220, 202) were also detected in the particulate matter in the ice samples (Fig. 2), indicating that some of the particulate matter in the ice samples is probably present in the form of micron-sized particles from the meteorites.

Snowmobile Exhaust

L2MS spectra of the filters of exhaust gas collected from the Ski-Doo are shown in Fig. 9. The three exhaust sample filters displayed very strong signal intensities, with t1 being slightly lower in intensity than i1 and q1. No relevant peaks were detected in the spectrum of the blank filter b1. The mass spectra of filters i1 and q1 are dominated by the alkylated homologs of phenanthrene (m/z 178), including m/z 192 (methyl (C₁-), 206 (C₂-), 220 (C₃-), 234 (C₄-phenanthrene). Note that anthracene and alkylanthracene are discriminated against their phenanthrene-based isomers due to a greatly reduced L2MS ionization efficiency (Haefliger et al. 2000). Also, in all cases the alkylated derivatives are more abundant than their corresponding core PAHs. Peaks at m/z 194, 208, and 222 are due to oxygenated PAHs (OPAHs) such as polycyclic aromatic ketones (PAKs) or polycyclic aromatic quinones (PAQs), which have been reported in urban aerosol particles, in particular from diesel engines (Haefliger et al. 2000). While displaying the same peaks, the mass spectrum of filter t1 also includes some higher-mass signals up to m/z 300 that are not apparent in i1 and q1. Also, the largest signals are shifted to higher mass (from m/z 192 to 206), and aromatic compounds are found with core PAHs of m/z 228, 252, 276.

These homologs are also found in measurements of gasoline cars and diesel trucks (Haefliger et al. 2000). Other core PAHs such as pyrene (m/z 202) were also detected in all snowmobile exhaust samples.

It has been discovered previously (Haefliger et al. 2000) that the chemical composition of the exhaust of diesel engines is influenced significantly by the combustion process, at least in the case of diesel engines. A higher load on the engine enhances the survival of PAH cores relative to alkylated derivatives, while a lower load diminishes the formation of PAH cores, but increases the formation of larger amounts of OPAHs. A way to quantify this is to compare the ratios m/z 202/206 (pyrene/C₂-phenanthrene) and m/z 208/206 (phenanthrenequinone/C₂-phenanthrene). Typically, an increase in one ratio should lead to a decrease in the other and vice versa. The same trend can be observed for the Ski-doo exhaust. While in both i1 and q1 (idle and low throttle) the m/z 202/206 is ~0.2 and m/z 208/206 is ~0.5, in t1 (alternating full throttle/idle) m/z 202/206 increased to ~0.6, while 208/206 decreased to ~0.3.

In gasoline engines, only low amounts of OPAHs were observed, and the alkylphenanthrenes are less abundant than phenanthrene itself (Haefliger et al. 2000). Although the dependence of the emission profile on the driving cycle was stronger in gasoline cars than in diesel trucks, the relative intensities did not change such that the alkylated derivatives were more abundant than the corresponding core PAHs.

Both the dominance of the alkylated derivatives over the corresponding core PAH as well as the inverse trends of alkylated PAH versus OPAHs at different engine loads strongly indicate that the Ski-doo engines have an emission pattern that is very similar to that of diesel engines rather than that of gasoline engines although these engines run with gasoline. The environmental conditions under which these tests were carried out, in particular the density altitude of approximately 2000 m and the air temperature of –15 °C

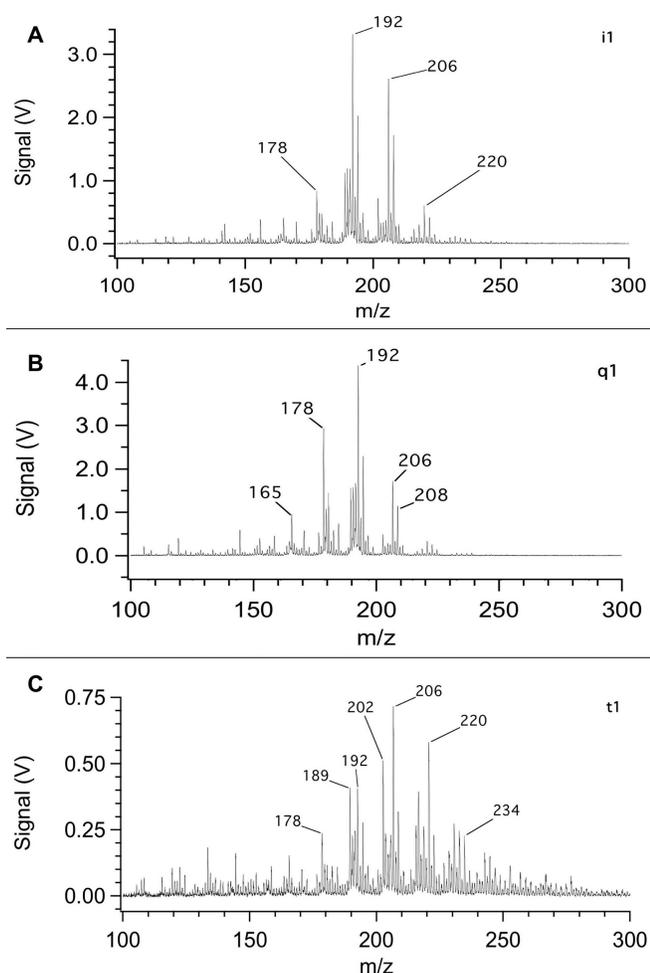


Fig. 9. L2MS spectra of snowmobile exhaust obtained at LaPaz ice field. a) Spectrum for performance level i1: warm engine, throttle in idle position (total collection time: 15 min). b) Spectrum for performance level q1: cold start, throttle one quarter open (total collection time: 10 min). c) Spectrum for performance level t1: warm engine, alternating: 1 min full throttle/2 min idle, 5 cycles (total collection time: 15 min).

(and a wind chill of -26 °C) may have contributed to these combustion behavior as well.

CONCLUSIONS

This study aimed at performing a comparative study of PAHs and amino acids in Antarctic meteorites and ice samples collected underneath them using highly sensitive L2MS and LC-ToF-MS techniques. The results show generally very low levels of terrestrial contamination for both compound classes in both ice and meteorite samples. More specifically, the following conclusions can be drawn:

4. The LaPaz ice samples, as measured with the L2MS instrument, shows no similarity to the ALH ice samples (Becker et al. 1997). A predominance of phenanthrene/anthracene as well as their alkylated homologs indicates that these compounds originated from the ordinary

chondrites and CK chondrites, respectively, with which they were associated.

5. The concentration levels of dissolved PAHs (extracted with membrane extraction) in all the ice samples are below the detection limit of the L2MS of 10–80 pg/l.
6. Most of the amino acid concentrations in the ice samples are below the detection limit of the instrument. However, some of the ices samples contain AIB at concentration levels of 1–33 ppt. The source of AIB is unknown, but we hypothesize that this amino acid could have been extracted from AMM during the concentration procedure of the ice samples in the laboratory.
7. In the five Antarctic meteorite samples, only trace amounts of glycine, β -alanine and γ -amino-*n*-butyric acid were detected. The compositions are very similar despite that there are two different types of meteorites (four ordinary chondrites and one CK chondrite). No AIB was detected in these meteorites, which indicates that these meteorites are not the source of the AIB detected in the ice samples.
8. The five CK and LL5 Antarctic meteorites investigated in this study contain a number of core PAHs (phenanthrene/anthracene and pyrene). The presence of C_1 -, C_2 -, and C_3 -alkyl-derivatives of phenanthrene/anthracene is very similar to the H4 OC Forest Vale, strongly indicating that these compounds are probably indigenous to the meteorite.
9. The composition of the ice samples indicates that the detected compounds were obtained from the meteorites during their residence time (PAHs in the particulate matter) and from micrometeorites embedded in the ice (amino acids). Further investigations are underway to confirm this hypothesis.
10. The PAH composition of the snowmobile exhaust gas looks very similar to that of diesel engines, with a predominance of alkylated derivatives over the corresponding core PAH as well as the inverse trends of alkylated PAH versus OPAHs at different engine loads. This pattern is significantly different than what was found in the ice, which makes snowmobile exhaust an unlikely source of contamination for Antarctic meteorites.

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