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Evidence for the extraterrestrial origin of polycyclic aromatic hydrocarbons in the Martian meteorite ALH84001

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Possible sources of terrestrial contamination are considered for the observation of polycyclic aromatic hydrocarbons (PAHs) in the Martian meteorite ALH84001. Contamination is concluded to be negligible.

1 Introduction

In the summer of 1977 the NASA Viking I and II landers successfully touched down on the surface of Mars and began experiments to determine the nature and composition of the Martian topsoil. These experiments showed that Martian surface soils do not contain any organic matter within detection limits, which were generally better than 1 ppb.[1] This result is believed not to indicate Mars is devoid of organic matter, but rather that efficient photochemical degradation processes are operational on the Martian surface.[2] As such, the Viking results do not preclude the presence of organic matter deeper within the Martian crust. Such a sampling of material is now available for study in the form of the 12 Martian meteorites† which are believed to have been ejected from deep in the Martian crust by bolide impacts. Studies of one such Martian meteorite, EETA79001, have shown the presence of carbonaceous material which has been interpreted as being organic in nature.[3] Although it has subsequently been suggested that this material may be terrestrial contamination,[4] no evidence exists to substantiate this conclusion.[5]

More recently, another Antarctic Martian meteorite, ALH84001, has become the subject of considerable interest and controversy after it was claimed to show possible evidence for relic biogenic activity on early Mars.[6] Central to this hypothesis is the observation of indigenous organic material in the form of PAHs concentrated in and about carbonates globules on interior fracture surfaces of the meteorite.[7] Although the observation considered alone neither supports nor refutes the argument for relic biogenic activity, the failure to observe trace amounts of indigenous organic matter would seriously weaken any argument for Martian biogenic activity. Moreover, whether abiotic or biotic products, the detection of such organic material is significant because it represents the first direct observation of specific organic molecules formed on Mars.

We reconsider here the evidence for a Martian origin of the PAHs observed in ALH84001, particularly in the light of claims made by Becker *et al.*[8] that the observed PAHs may be largely the result of terrestrial contamination by Antarctic ice melt water and that a minor extraterrestrial PAH component, if present, is likely the result of exogenous delivery by carbonaceous meteorites to the surface of Mars, a view previously expounded by Bell.[9]

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† The 12 Martian meteorites in collections are: ALHA77005, ALH84001, Chassigny, EETA79001, Governador Valadares, Lafayette, LEW88516, Nakhla, QUE94201, Shergotty, Yamato 793605 and Zagami.

1.1 Evidence for terrestrial contamination

ALH84001 was collected from the Allan Hills blue icesheet in Antarctica during the summer of 1993 and was subsequently identified as Martian by Middlefehldt in 1994.[10] The meteorite is mainly composed of orthopyroxenite interspersed with Fe–Mg-rich carbonates. The petrography of the carbonates[10] supports an extraterrestrial origin as do the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ isotope ratios.[11a] However, as noted by Jull *et al.*,[11a,b] the carbonates in ALH84001 contain too much ^{14}C to be consistent with the meteorite's terrestrial residence time, which has been variously estimated to be 11 000 ± 1000 years,[12] 6500 ± 1300 years[13,14] and most recently *ca.* 13 000 years.[15] Jull *et al.*[11b] have recently demonstrated that the isotopic composition of the C fraction released in the low-temperature stepped combustion (20–450 °C) of ALH84001 may account for the higher than expected ^{14}C levels in the meteorite. This fraction, which is loosely interpreted as 'organic,' has a ^{14}C abundance 40–60% that of modern C and a $*^{13}C$ of between $-22‰$ and $-33‰$. From this they argue that as much as 80% of the organic C in ALH84001 may be terrestrial in origin. Indeed, measurements of water-labile amino acids by Bada *et al.*[16] in ALH84001 argue for these species at least to be terrestrial contaminants. Neither of these results, however, directly address the indigeneity of PAHs which represent a hydrophobic, more refractory organic phase, constituting less than 1% of the total organic content of ALH84001. Intriguingly Jull *et al.*[11b] note that ALH84001 does, however, contain a small extraterrestrial C component which, based on ^{14}C abundance, represents either an unidentified acid-insoluble carbonate phase or refractory organic material, such as PAHs.

In other work, Becker *et al.*[8] claim evidence of the terrestrial contamination of ALH84001 based on the results of two key experiments they performed that appear to demonstrate that: (1) calcium carbonate can selectively sequester PAHs from an aqueous solution of the PAH standard AccuStandard (AccuStandard, 25 Science Park, New Haven, CT 06511, USA); and (2) calcium carbonate is able to scavenge PAHs from meltwater obtained from the Allan Hills blue icesheet. Under their scenario the presence of PAHs in ALH84001 is primarily a consequence of their selective sequestration from Antarctic ice melt water by the Fe–Mg-rich carbonates in ALH84001 during its residence time in Antarctica. They also argue that any minor, indigenous PAHs in ALH84001 are most likely the product of exogenous delivery onto the surface of Mars by meteorite and micrometeorite accretion at an early epoch in the evolution of the Solar System. Anders[17] has suggested that such processes may have played an important role in the prebiotic evolution of early Earth and it is reasonable to assume that this behaviour might also be the case for Mars. In this scenario, accretion of carbonaceous extraterrestrial material on the surface of early Mars would have provided a reservoir of PAHs that could then have been transported by hydrothermal activity into the crust where they could be sequestered by the carbonates in ALH84001. To test this hypothesis Becker *et al.* analysed two Antarctic CM-type carbonaceous chondrites (ALH85006, EET83355) for PAHs using a one-step UV (355 nm) laser ablation–ionization mass spectrometer and both meteorites showed the presence of PAHs that were argued to be similar to those observed by McKay *et al.*[6] in ALH84001.

1.2 Evidence against terrestrial contamination

Subsequent to the report by McKay *et al.*[6] of PAHs in ALH84001, three other groups have independently reported measurements of organic material in ALH84001, and each have argued for an indigenous origin. Bishop *et al.*[18] have made detailed spectroscopic measurements of multiple chip surfaces of ALH84001, focusing particularly on diffuse reflectance IR spectra covering the 2.5–5 μm region. Weak spectral features in the 3.3–3.5 μm region characteristic of C—H stretch vibrations were observed. Although they were unable to rule out laboratory contamination unambiguously, measurements of numerous other non-carbonaceous meteorites and lunar samples failed to show the same features. Furthermore, the spectral variations across the surface of carbonate rich chips suggest a heterogeneous organic component uncharacteristic of terrestrial contamination.

Wright *et al.*[19] have made high-resolution stepped combustion, stable C isotope measurements of carbonates in ALH84001. They observed unusually large $\delta^{13}C$ fractionations of *ca.* 65‰ for the C fraction released below 450 °C. These temperatures are below the decomposition temperature of the carbonates (450–525 °C) and of magmatic C ($>$700 °C) so the signal is considered to be organic in nature. This result is in stark contrast to the $\delta^{13}C$ fractionation of the carbonates themselves, which average +40.1‰. Such large ^{13}C depletion of the organic component is below that expected for terrestrial contamination (typically -20 to -30‰) and beyond the range of fractionation that purely inorganic processes are capable of producing within a planetary setting. Wright *et al.*, however, are cautious in interpreting their results, and note that Teflon contamination during the course of measurement could produce the observed anomalies. This possibility would, however, require that *ca.* 45% of the sample be Teflon, which seems to be unrealistic.

Flynn *et al.*[20] have made C X-ray adsorption near-edge spectroscopy (XANES) analysis of ALH84001 and show that the carbonate globules of ALH84001 contain at least two distinct carbon-bearing phases: (1) carbonate, which is distributed relatively homogeneously and (2) a carbon-bearing phase consistent with PAHs, graphite or other C—C, C=C, and C—H bonded carbonaceous material which is distributed heterogeneously at the sub-micrometre scale.[21] Because XANES is not a surface-sensitive technique, terrestrial contamination issues are considerably alleviated.

2 Methods

To address the issue of the origin of PAHs on ALH84001 we have undertaken a series of experiments designed to answer five specific questions: (1) can carbonates act as a PAH scavenger? (2) Do other meteoritic samples collected from Antarctica and not expected to contain indigenous organic matter show evidence for PAH contamination? (3) Do meteoritic samples that have suffered extensive Antarctic weathering show evidence for a common PAH contaminant? (4) does Allan Hills meltwater contain measurable concentrations of solubilized PAHs? (5) Does the spatial distribution of PAHs in ALH84001 constrain their source?

PAH distributions and concentrations were determined by either microprobe two-step laser desorption–laser ionization mass spectrometry (μL^2MS) and/or capillary zone electrophoresis (CE). μL^2MS is a powerful analytical method capable of detecting minute quantities of organic molecules with microscopic spatial resolution. In this technique a pulsed IR desorption laser is focused onto the substrate and volatilizes intact neutral molecules. After an appropriate time delay, the desorbed molecules are selectively ionized with a pulsed UV laser using a (1 + 1) resonance enhanced multiphoton ionization (REMPI) scheme. Only molecules that absorb the UV light and have an ionization potential below the combined energy of two photons are ionized. The ions produced by the UV laser are extracted from the source and injected into a reflectron time-of-flight (RTOF) mass spectrometer. By separating the volatilization and ionization steps, each can be optimized, resulting in greatly enhanced sensitivity and selectivity. A detailed description of the Stanford μL^2MS instrument is given by Clemett and Zare.[22]

CE is a microanalytical technique developed for the analysis of small volumes of solutes containing complex mixtures requiring minimal sample handling. It is the product of recent advances in electrophoresis[23–25] that overcome the problems of analyte volatility, thermal stability, and sample preconcentration. The technique is conceptually simple, the sample in the form of a liquid is injected, either hydrodynamically

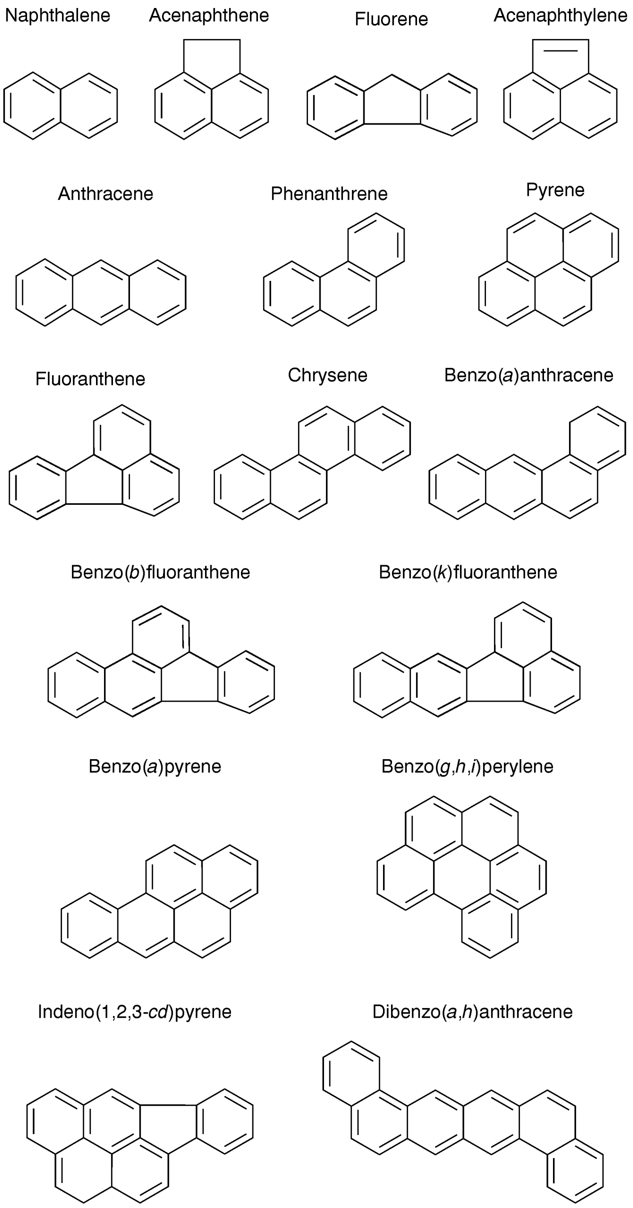

Fig. 1 Structures of the 16 PAHs that constitute the PAH standard, AccuStandard (AccuStandard, 25 Science Park, Newhaven, CT06511, USA)

or electrokinetically, into a silica capillary with id 10–100 μm. An electric field (*ca.* 100–500 V cm^{-1}) is applied across the length of the capillary, and the resulting gradient causes the bulk solution in the capillary to flow by virtue of electro-osmosis. This electro-osmotic flow acts as an essentially noise-free pump, injecting all analytes in the sample, irrespective of charge, into the column and, ultimately, to exit the capillary structure. Differently charged analytes move in the solution, and hence through the column, at different velocities, as a consequence of their differing electrophoretic mobilities (*i.e.* the migration tendency of the analyte in the presence of an applied electric

Table 1 Solubilities of the sixteen PAHs in AccuStandard used in the carbonate affinity experiment of Becker *et al.*[8]

molecular species (AccuStandard)[a]	formula	mass/u	solubility at 25 °C/ mg kg^{-1} [b]	concentration[c]	precipitation mg kg^{-1} [d]
naphthalene	$C_{10}H_8$	128	31.69 ± 0.23	0.063	-none-
acenaphthene	$C_{12}H_{10}$	154	0.453	0.063	-none-
fluorene	$C_{13}H_{10}$	166	1.685 ± 0.005	0.063	-none-
acenaphthylene	$C_{13}H_{12}$	168	16.1	0.063	-none-
anthracene	$C_{14}H_{10}$	178	0.0446 ± 0.0002	0.063	0.0184 (29.2%)
phenanthrene	$C_{14}H_{10}$	178	1.002 ± 0.011	0.063	-none-
pyrene	$C_{16}H_{10}$	202	0.132 ± 0.001	0.063	-none-
fluoranthene	$C_{16}H_{10}$	202	0.206 ± 0.002	0.063	-none-
chrysene	$C_{18}H_{12}$	228	0.0018 ± 0.0001	0.063	0.0612 (97.1%)
benzo(*a*)anthracene	$C_{18}H_{12}$	228	0.0094	0.063	0.0536 (85.1%)
benzo(*b*)fluoranthene	$C_{20}H_{12}$	252	0.0020	0.063	0.0610 (96.8%)
benzo(*k*)fluoanthene	$C_{20}H_{12}$	252	0.0038	0.063	0.0592 (89.2%)
benzo(*a*)pyrene	$C_{20}H_{12}$	252	0.0038 ± 0.00031	0.063	0.0627 (99.5%)
benzo(*g*,*h*,*i*)perylene	$C_{22}H_{12}$	279	0.0003	0.063	0.0627 (99.5%)
indeno(1,2,3-*cd*)pyrene	$C_{22}H_{12}$	276	$\leqslant$0.01	0.063	0.053 (>84.1%)
dibenzo(*a*,*h*)anthracene	$C_{22}H_{14}$	276	$\leqslant$0.01	0.063	0.053 (>84.1%)

[a] PAH Standard 'AccuStandard' (AccuStandard, 25 Science Park, New Haven, CT 06511). This was the PAH standard used by Becker *et al.*[8]. PAH species in bold were observed in ALH84001 (D. S. McKay, E. K. Gibson Jr., K. L. Thomas-Keptra, H. Vali, C. S. Romanek, S. J. Clemett, X. D. F. Chillier, C. R. Maechling and R. N. Zare, *Science*, 1986, **273**, 924).

[b] Experimentally measured solubility of PAHs: D. S. MacKay and W. Y. Shiu, *J. Chem. Eng. Data*, 1977, **22**, 399; F. P. Schwarz, *J. Chem. Eng. Data*, 1977, **22**, 273; W. E. May, J. M. Brown, S. N. Chesler, F. Guenther, L. R. Hilpert, M. S. Hertz and S. A. Wise, in *Polynuclear Aromatic Hydrocarbons*, ed. P. W. Jones and P. Leber, Ann Arbor Science, Ann Arbor, Michigan, 1979, p. 411; W. E. May, S. P. Wasik and D. M. Freeman, *Anal. Chem.*, 1978, **50**, 997; W. R. Walters and R. G. Luthy, *Environ. Sci. Technol.*, 1984, **18**, 395.

[c] Concentration of each PAH stated to have been dissolved in a solution of doubly distilled water in ref. 8.

[d] Quantity of each PAH that could not have been dissolved and thus precipitated out, and its percentage relative to the total quantity of PAH added. In all cases the experimentally measured solubility of each PAH assumes that it is the only aromatic species present, furthermore it is assumed that the PAH is given sufficient time to solubilize.

field), which allows separation of the sample components. These components can then be identified, provided that a suitable detector is placed between the inlet and outlet of the capillary, and the migration times of appropriate standards have been established.

2.1 Carbonate as a PAH scavenger

PAHs are planar non-polar molecules that with increasing size become virtually insoluble in aqueous solutions. In general, small two- and three-ring PAHs, such as naphthalene and phenanthrene, have solubilities at the few ppm level. Intermediate four- and five-ring PAHs, such as chrysene and benzo(*a*)pyrene, have solubilities at the ppb to parts per trillion level. Finally, large PAH species of six-rings and greater are considered insoluble. Solubilization takes upwards of weeks to several months to achieve equilibrium.[26]

The solubilities of the 16 PAHs contained in the PAH standard AccuStandard are listed in Table 1, and their molecular structures are illustrated in Fig. 1. A logical inconsistency in the carbonate extraction experiment of Becker *et al.*[8] is apparent. In their experiment calcium carbonate and doubly distilled water containing 1 ppm of AccuStandard were mixed together and allowed to interact overnight. The calcium carbonate was then filtered off and toluene extracts were obtained from both the filtered water and the calcium carbonate. When the toluene extracts were analysed for PAHs they observed that nearly all the PAHs were in the carbonate extract and virtually none in the aqueous extract. From this they surmised that the carbonate must be acting as a scavenger for PAHs. However, a 1 ppm aqueous solution of AccuStandard at 25 °C is not physically possible to prepare. From Table 1 final column, it is apparent that virtually none of the PAHs in their experiment could have entered solution at the concentration reported. Hence, their results, although appearing to indicate that calcium carbonate is a PAH scavenger, demonstrate only that PAHs are highly insoluble, as schematically illustrated in Fig. 2.

Therefore, to evaluate whether it is possible for carbonate to act as a selective sequestration agent for PAHs, we chose two experimental approaches that would not be subject to the same solubility issues. In the first experiment, five PAHs of varying sizes were dissolved in diethyl ether and deposited on a mixed sand–carbonate substrate. Sand was chosen for comparison because it provides a manageable, relatively inert substrate that is similar to the chain silicates that compose the majority of ALH84001. The sand–carbonate mixtures were then flushed with water so that the affinity of PAHs to carbonate in an aqueous environment could be examined. In the second experiment an aqueous saturated solution of naphthalene was prepared and calcium carbonate was added. The affinity of the carbonate for naphthalene was then measured by removing small aliquots of water over time and measuring the concentration of naphthalene in each aliquot.

2.1.1 Carbonate–PAH affinity experiment. Beach sand (composed primarily of SiO_2 with some feldspar and other minerals) from a Marin County, CA beach was obtained, crushed to a fine powder (*ca.* 50 μm particles), and cleaned by ultrasonication with doubly distilled water, acetone and, finally, methylene chloride to remove any adsorbed organic material. The sand was then analysed by μL^2MS and found to contain no PAHs. Six mixtures of calcium carbonate (Aldrich, 10 μm) and sand, ranging from 100% sand to 100% calcium carbonate by mass ($CaCO_3$: sand = 0 : 100, 5 : 95, 10 : 90, 20 : 80, 50 : 50, and 100 : 0), were prepared. *Ca.* 1 ml of a 50 ppm solution of phenanthrene, pyrene, perylene, benzo[*g*,*h*,*i*]perylene, and coronene dissolved in diethyl ether was combined with 1 g each of the six $CaCO_3$–sand mixtures, thoroughly stirred and dried. The PAH–$CaCO_3$–sand mixtures were then placed in a chromatography column (8 mm id) and flushed with doubly distilled water for 2 weeks. Samples from each column were removed and analysed by μL^2MS under conditions identical to those used in the

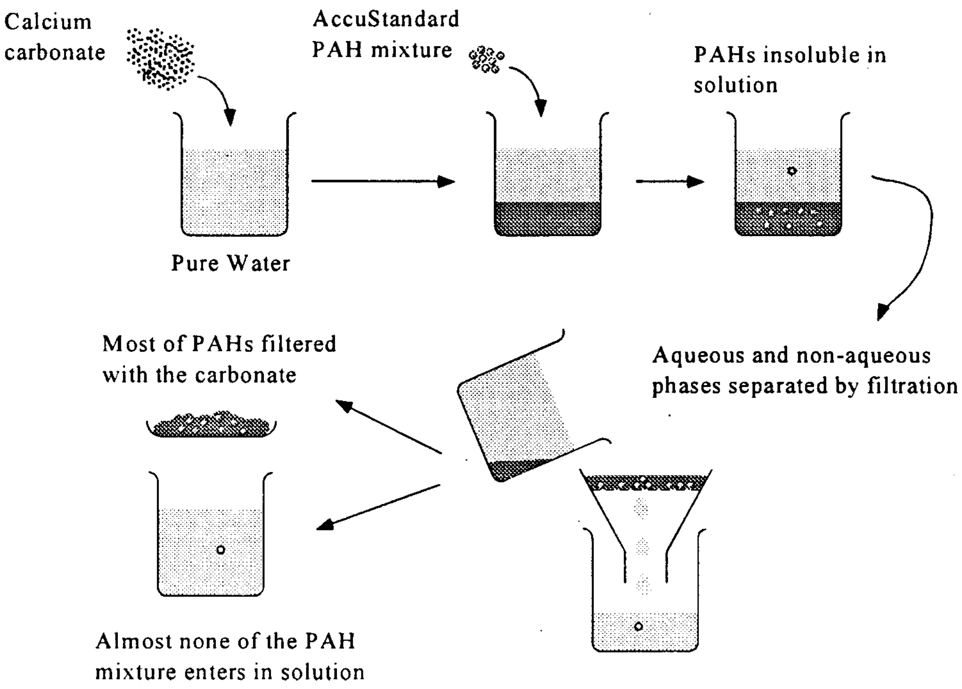

Fig. 2 Schematic of the Becker *et al.*[8] carbonate extraction experiment demonstrating the error in their interpretation of the results. The low solubilities and long equilibration times of PAHs mean that a 1 ppm solution of the PAH standard Accustandard cannot be formed in water at 25 °C. Hence, nearly all the PAHs added to the doubly distilled water would have been filtered out with the carbonate. This would give the impression that the carbonate had sequestered the PAHs but, in reality, they never entered solution.

analysis of ALH84001.

2.1.2 Carbonate–PAH adsorption experiment. A saturated stock solution of naphthalene in nanopure water (31.7 mg l^{-1}) was prepared by vigorously mixing *ca.* 100 μg of finely powdered naphthalene with 500 ml of doubly distilled water in a clean, ground-glass sealed Pyrex volumetric flask for a period of 1 week. Undissolved naphthalene was then allowed to settle out over a 2 day period after which two 100 ml aliquots were transferred to two 250 ml Pyrex conical flasks with Bakelite screw seal tops. To one flask 42 g of calcium carbonate (Aldrich, 10 μm) was added and to the other, 42 g of titanium dioxide (Aldrich, Anatase) was added as a control. Both solutions were periodically shaken to disperse the calcium carbonate–titanium dioxide. At periods of 24, 48, 72, 96 and 130 h, 1 ml aliquots were removed from each conical flask and transferred to 1.5 ml sealed Eppendorf tubes. The naphthalene concentration in the solution from each Eppendorf tube, after centrifuging, was then determined independently by μL^2MS and CE.

For the μL^2MS measurements, 25 μl aliquots were withdrawn from each Eppendorf tube and transferred to 3 × 3 mm^2 cut sections of cellulose nitrate filter paper. The filter paper was immediately mounted and placed into the μL^2MS instrument and the gas-phase background caused by the evaporation of the naphthalene determined. An identical procedure was followed for all measurements. Calibration of the background for a given naphthalene concentration was performed prior to these experiments. For the CE measurements, 20 μl aliquots were withdrawn from each Eppendorf tube and transferred to a 150 μl CE sample tube and analysed in a P/ACE Model 2000 CE instrument (Beckman Instruments, Inc., Fullerton, CA, USA) equipped with a UV absorbance detector at 254 nm. Pressure injection at 85 psi for 1 s was used to introduce the sample into the capillary (150 μm id × 27 cm, fused silica, Polymicro, Inc., Phoenix, Arizona, USA). Analyses were performed at an applied voltage of 5 kV with a running buffer of 10 mM sodium borate (pH 9) and at a temperature of 20 °C.

2.2 Weathered non-carbonaceous meteoritic samples from antarctica

Seventeen acid-insoluble residues§ from both ordinary and carbonaceous chondrites (CI, CM, H, L, LL classes) were studied by μL^{2}MS. The total integrated PAH concentrations observed from each residue are plotted in Fig. 3. From the figure it is apparent that those chondrites with little to no indigenous PAHs are the ordinary type, petrologic type 5 and 6 chondrites. This finding is consistent with the thermal metamorphism index for such chondrites which, from the mineralogy, suggests they have been heated for

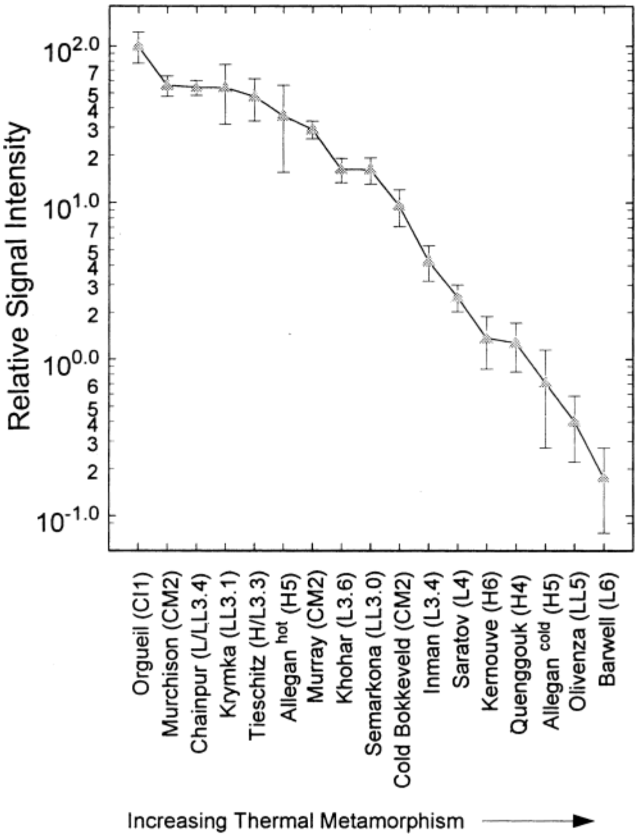

Fig. 3 Log–linear plot demonstrating the correlation between PAH concentration and the petrologic index of thermal metamorphism for the acid-insoluble residues of both ordinary and carbonaceous chondrites. (Allegan contains two visually distinct components, labelled cold (no PAHs) and hot, that show dramatically different PAH concentrations, the explanation for this remains unclear.)

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§ Acid-insoluble residues are the product of the majority silicate phase of a meteorite by a treatment with HF–HCl solutions at elevated temperature over a period of several months. Since PAHs are robust to the acid residue preparation procedure the effect of residue preparation is to increase their concentration in the remaining acid-insoluble residue.

extended periods to temperatures above 700 °C[27] during their time in the early solar system.

Hence, multiple interior and exterior fragments from two Antarctic ordinary chondrites (ALH83013 and ALH83101) of petrographic classes H6 and L6 were studied by μL^{2}MS, see Fig. 4. From the acid residue results and the thermal metamorphism index, we can demonstrate that these two classes of meteorites likely contained no indigenous PAHs at their time of fall. Therefore, observation of any PAHs in such samples can only be a consequence of Antarctic weathering. Additionally, the terrestrial salt deposit (mainly magnesium carbonate) formed on the exterior surface of the heavily weathered H5 chondrite LEW85320[28] was studied for the presence of terrestrial PAHs, Fig. 4. The terrestrial exposure age of LEW85320, estimated to lie between 32 000 and 33 000 years,[29] is *ca.* three times older than ALH84001 and so should provide an upper limit to terrestrial contamination.

2.3 Weathered carbonaceous meteoritic samples from Antarctica

Surface area and composition play an important role in determining contamination susceptibility. Large particles are less effective (50–90% reduction) adsorbers of non-polar molecules than smaller (< 50 μm) particles.[30] Increasing the amounts of organic material increases the adsorption levels of PAHs.[31] A clay-like composition allows more adsorption of hydrophobic molecules than more organized minerals such as chain silicates.[32] Considering these three factors, Antarctic micrometeorites, which are small, and contain a relatively high abundance of organic material and have a more clay-like composition, should be ideal candidates to become contaminated with Antarctic PAHs. To determine the extent and nature of their contamination, if any, we examined a number

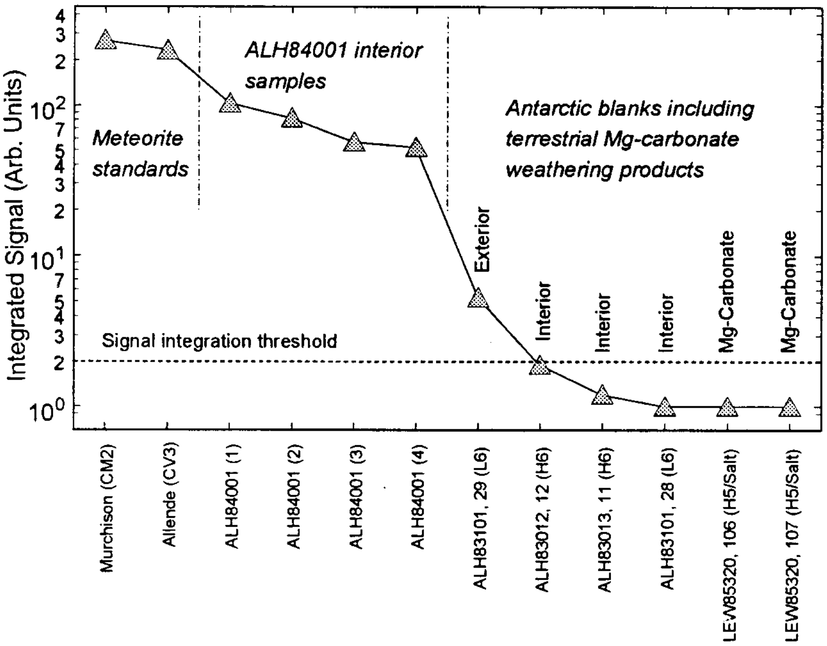

Fig. 4 Comparison of the total integrated PAH signals (masses 100–400 u) for non-carbonaceous Antarctic ordinary chondrites and their evaporated salt deposits, against interior and exterior samples of ALH84001 and the carbonaceous meteorite standards, Murchison (CM2) and Allende (CV3).

of micrometeorites, all collected in a limited area. The differences in their PAH composition indicate that they are not contaminated. Additionally, most are heavily alkylated, unlike the PAHs in ALH84001, and if they were concluded to be contaminated, the PAHs on ALH84001 do not match the contamination pattern.

2.3.1 Giant Antarctic micrometeorites. The study of micrometeorites is considerably more difficult than that of meteorites as a consequence of both their small masses (*ca.* 10^{-7}–10^{-4} g) and the ease with which they can become contaminated, owing to their high surface-to-volume ratio, porosity, and chemical reactivity under prolonged exposure to gases and water. Hence, all steps in micrometeorite studies must be carefully controlled from their collection in the cleanest, most unpolluted spots on the Earth (*e.g.* pre-industrial Antarctic ices) through to their selection and subsequent curation. This process is highly controlled and constantly monitored and is described elsewhere.[33] Five micrometeorites belonging to the dominant family ($>90\%$ of micrometeorites) mineralogically related to the CM-type carbonaceous chondrites, and characterized by a highly unequilibrated assemblage of hydrous and anhydrous subgrains embedded in an abundant carbonaceous component, were chosen for analysis. All five were analysed using the same methods used for ALH84001 and their spectra examined for trends that could give insight into possible contamination.

2.4 Allan Hills meltwater

Ca. 150 g of ice from the Allan Hills icesheet (courtesy of Mike Zolensky, NASA Johnson Space Center, Houston, Texas, USA) was allowed to evaporate in a sealed Nalgene disposable filter unit with a cellulose acetate membrane filter (Fischer Scientific, Pittsburgh, Pennsylvania, USA). The meltwater was allowed to stand for several weeks to allow any PAH solubilization to reach equilibrium, after which an aspirator was used to vacuum filtrate the melt water through the 0.25 μm cellulose acetate membrane. From this, a small 25 ml aliquot of the filtered water was mixed with 5 ml of methylene chloride and vortex mixed and allowed to separate out over the course of 1 h. A sterile 10 ml surgical syringe was then used to withdraw *ca.* 3 ml of methylene chloride fraction and transfer it to a small open glass vial. In a fumehood, the methylene chloride was allowed to evaporate down to a few hundred μl and the remaining liquid dipped with a sterile 1 ml surgical syringe on to a warm (*ca.* 45 °C) quartz plate (7 mm diameter) and evaporated to dryness. This quartz plate was then analysed by μL^2MS to determine the presence of any residual PAHs. No PAH signal was observed above the instrument detection limits, suggesting that the soluble PAH concentration of ice in the Allan Hill ice sheet to be significantly below the ppm level.

2.5 Spatial distribution of PAHs in ALH84001

Spatially resolved studies of exterior fragments of ALH84001, with intact fusion crust, were made to determine the distributions of PAHs within the samples perpendicular to the fusion crust exterior surface. Prior to analysis, the meteorite fragments were cleaved with a stainless-steel surgical scalpel to expose a fresh cross-sectional profile of the fusion crust. Analysis was begun within 10 min of cleaving.

3 Results and Discussion

3.1 Carbonate–PAH affinity and adsorption

3.1.1 Affinity. The signal intensities from each $CaCO_3$–sand sample were integrated and totalled. The results were then normalized and a plot of signal intensity *vs.* weight fraction of $CaCO_3$, Fig. 5, was produced and a linear best-fit line with a correlation coefficient (R^2) of 0.91 was calculated. The amount of detected PAHs decreases with increasing amounts of carbonate. Two factors may contribute to this observation: either

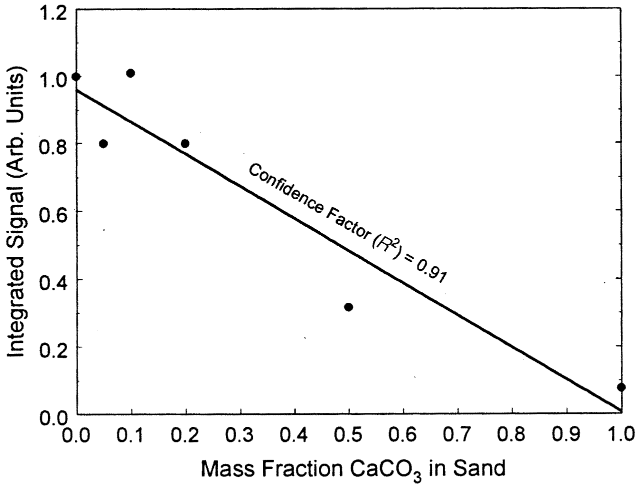

Fig. 5 PAH concentration detected by μL^{2}MS as a function of $CaCO_3$ mass fraction in sand

the carbonate material is a less effective desorbing substrate for the μL^{2}MS instrument than the sand which is primarily SiO_2, or the sand preferentially adsorbs PAHs. Examining the IR absorbances[34] of both $CaCO_3$ and SiO_2, SiO_2 has a greater absorbance at 10.6 μm than $CaCO_3$ and, under ideal conditions, this disparity could account for an increased PAH signal. However, both materials were crushed to <50 μm diameter causing an increased surface area with multiple permutations to diffract and absorb laser radiation. In practice, the $CaCO_3$ does absorb 10.6 μm light and gives similar desorption yields to SiO_2, so matrix effects cannot be the only factor responsible for the downward PAH concentration trend seen. Hydrophobic bonding is generally believed to be the main mechanism for the adsorption of non-polar organic compounds.[35] By this process, the sorbate molecules are attracted to the interfacial zone (the region between the solid phase and the bulk solution where adsorption occurs) by London–van der Waals forces caused by dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions. The adsorption of solutes on mineral surfaces is also affected by competition of solvents for occupancy of free sites. Polar solvents such as water occupy the adsorbing sites on mineral surfaces and non-polar organics such as PAHs are not adsorbed significantly.[32] A possible explanation for the differences seen in the PAH concentrations may lie in the structure of the two minerals. SiO_2 consists of tetrahedra linked into rings resulting in fairly open structures with internal cavities that are able to trap non-polar molecules like PAHs. In contrast $CaCO_3$ is rhombohedral, in which the small Ca cations are octahedrally coordinated to the carbonate ions, providing roughly planar layers with little extra space available for adsorbing PAHs. Consequently, the chain silicate has more places able to hold PAHs but their affinity for PAHs is no different than carbonates. Additional studies were recently conducted that also indicate that PAHs interact weakly and non-specifically with mineral surfaces.[36] Regardless of the specific reasons for PAH signal discrepancies, the results of this experiment and other work indicate that carbonates do not preferentially adsorb PAHs.

3.1.2 Adsorption. The naphthalene concentrations in each time aliquot for both the $CaCO_3$ and TiO_2 were measured and calibrated plots of naphthalene concentration *versus* carbonate exposure time were then produced for both the μL^{2}MS, Fig. 6, and CE, Fig. 7, measurements. In both cases, within experimental uncertainty, no decrease in naphthalene concentration is apparent over the course of the experiments, 120 and 72 h,

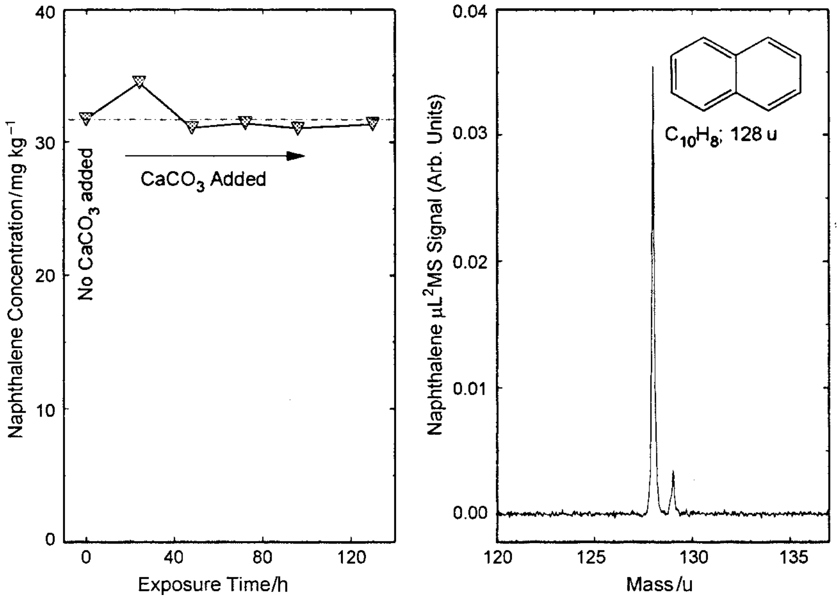

Fig. 6 Left panel: aqueous concentration of naphthalene, as determined by µL^2MS, as a function of time for two 100 ml saturated solutions, one exposed to 42 g $CaCO_3$ and the other 42 g TiO_2 (anatase). Within experimental error, no sequestration of naphthalene from solution is observed for either $CaCO_3$ or TiO_2. Right panel: µL^2MS mass spectrum of naphthalene in aqueous solution after 72 h exposure to $CaCO_3$.

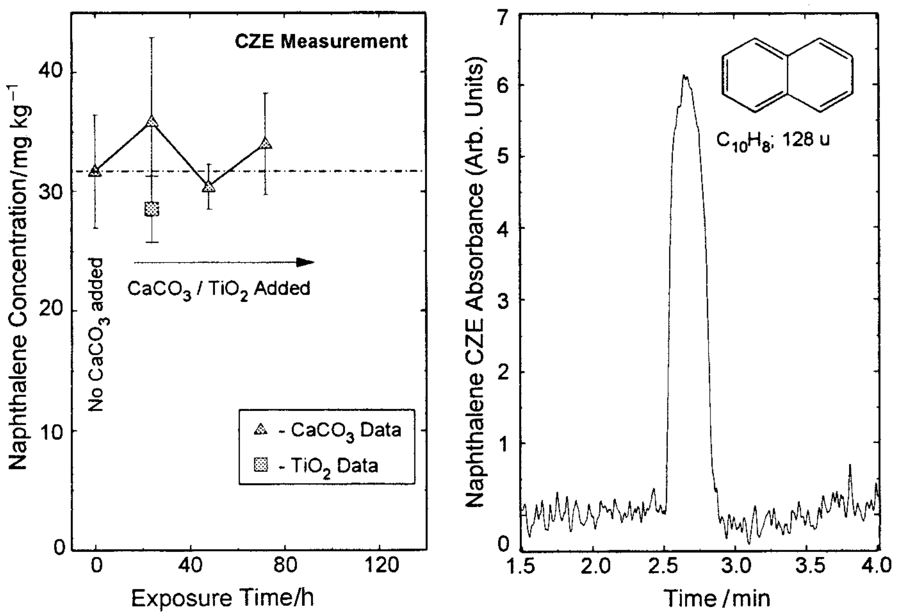

Fig. 7 Left panel: aqueous concentration of naphthalene, as determined by CE as a function of time, for two 100 ml saturated solutions, one exposed to 42 g $CaCO_3$ and the other 42 g TiO_2 (anatase). Each run was repeated five times and error bars are 1 σ, within experimental error, no sequestration of naphthalene from solution is observed for either $CaCO_3$ or TiO_2. Right panel: CE electropherogram of the aqueous naphthalene after 72 h exposure to $CaCO_3$.

respectively. Such behaviour, is in stark contrast to the reports of Becker *et al.*,[8] who reported a ten-fold decrease in concentration with only an eighth the $H_2O : CaCO_3$ ratio of our experiments and less than one tenth the exposure duration. However, as discussed in Section 2.1.2, the results of Becker *et al.* are seriously flawed. Comparison with the blank TiO_2 suggests that there is no specific mineral preference for the physisorption of PAHs, a result consistent with the non-polar character of PAHs. Moreover, there appears to be very little, if any, binding of PAHs to the $CaCO_3$. Fig. 8 shows that no naphthalene signal was observed on $CaCO_3$, even after 170 h exposure to the saturated naphthalene solution (note: the $CaCO_3$ was extracted from the aqueous naphthalene solution by vacuum filtration and washed once with 250 ml of doubly distilled water).

In regard to ALH84001, we note that calcium-rich carbonate minerals are generally rare, with most of the carbonates in ALH84001 being rich in Fe and Mg. We, therefore, expect that the crystalline structure of ALH84001 carbonate globules will be varied and generally different to that of the calcite structure of the $CaCO_3$ used within our experiments and those of Becker *et al.*[8] However, because no evidence exists within the literature (for a general review see Schwarzenbach *et al.*[26] and references therein) to support any argument for an affinity of PAHs to carbonate[37,38] it seems unreasonable to presuppose, without such evidence, that PAHs will be adsorbed differently on different carbonate mineral structures. This conclusion seems especially justified given only the

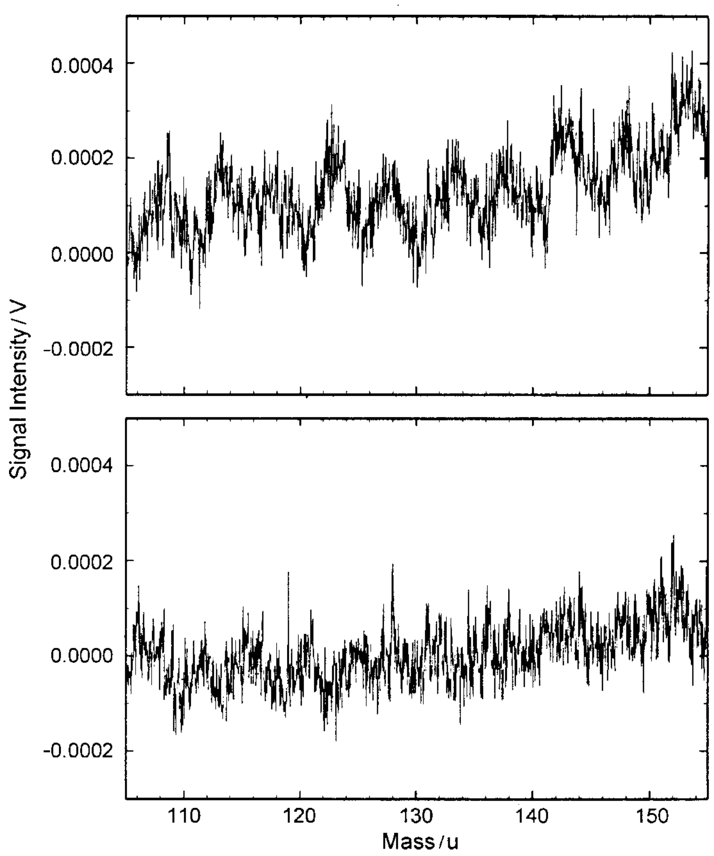

Fig. 8 μL^2MS of blank $CaCO_3$ (top trace) and $CaCO_3$ after exposure to aqueous solution of naphthalene (31.7 mg kg^{-1}) (mass 128 u) for 170 h (bottom trace)

weak structure-independent, dipole–induced-dipole interaction that can exist between these species.

3.2 Weathered non-carbonaceous meteoritic samples from Antarctica

The total integrated signal intensities for both interior (>1 cm in from the fusion-crust exterior) and exterior fragments (<1 cm in from the fusion crust exterior) of the Antarctic chondrites ALH83013 and ALH83101 are plotted in Fig. 4, together with data from four representative spectra of four interior carbonate-rich fragments of ALH84001, and the average spectra from the two meteorite standards, Murchison and Allende. All the spectra were taken within a period of 14 days under identical experimental conditions.

The Murchison meteorite is considered the 'Rosetta Stone', of carbonaceous chondrites and its indigenous organic composition has been more thoroughly studied than any other meteorite (see Cronin *et al.*[39] and references therein). Upwards of 500 indigenous organic compounds have now been measured in Murchison[40] of which PAHs are present at between 15 and 28 ppm. From Fig. 4, the concentration of PAHs in ALH84001 can be estimated to lie between 1 and 10 ppm. In contrast, only one exterior fragment of the non-carbonaceous chondrites, ALH83012, show any evidence for a PAH signal that could arguably be considered above the instrumental background (*ca.* 100 ppb under the experimental conditions). Furthermore, the exterior salt deposit on LEW85320, which is mainly magnesium carbonate[28] and might be expected to show the highest contamination levels, had no measurable PAH signal.

3.3 Weathered carbonaceous meteoritic samples from Antarctica

The spectra of five micrometeorites are presented in Fig. 9 and lead to a couple of conclusions. First, the PAH distribution of each micrometeorite is different from the others. A, C and E all contain relatively large amounts of a 216 u compound, whereas B

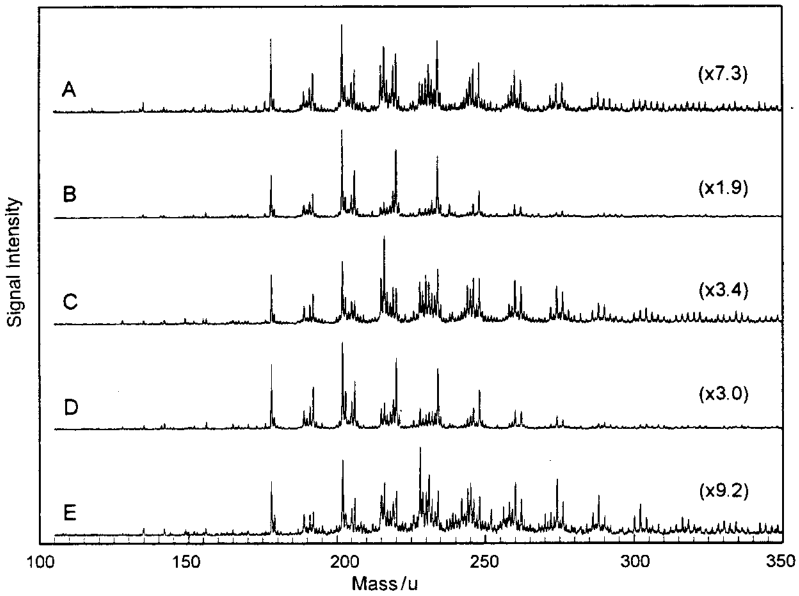

Fig. 9 µL^{2}MS of five Antarctic micrometeorites, all collected from a limited area at the same time. Notable differences in the PAH distributions of each micrometeorite are apparent.

and D do not. Moreover, E differs from A and C in that it contains relatively large amounts of 228 and 252 u compounds, whereas the other two do not. Other discrepancies are also seen. Given the close proximity in which these micrometeorites were found, it would be logical to assume that they have similar terrestrial histories and, if contaminated during their time on Earth, their contamination patterns should be similar. However, this behaviour is not seen, so that the conclusion can be reached that they are uncontaminated. Second, if these PAHs *were* considered to be the result of contamination they appear to have a common signature of extensive alkylation, see Fig. 10. In contrast, the PAHs on ALH84001 show little or no alkylation patterns. From these previous two arguments, it can be surmised that, if micrometeorites, ideal candidates for picking up Antarctic contaminants, are not contaminated, then ALH84001 is not either. And even if the micrometeorites were contaminated, contamination would appear as an alkylation series, something that is not seen in ALH84001.

The conclusion that the PAHs in ALH84001 are indigenous is not surprising when work done on other Antarctic meteorites is considered. Several Antarctic meteorites have been examined for the presence of amino acids and a distinction was made as to whether these meteorites were terrestrially contaminated. Compared to PAHs, amino acids are a far more likely contaminant to invade a meteorite. They are more soluble in water and also found in greater quantities in the Antarctic ice. The Antarctic concentration of PAHs is based on levels found in Greenland ice[41] and the assumption that PAHs are deposited in Antarctica in a similar manner. Levels of amino acids are obtained from work done by McDonald and Bada in which 0.4–1 ppm levels were attained after the subtraction of a 30–40 ppm background.[4] The meteorites Allan Hills 77306,[42,43] Allan Hills 77307,[44] Belgica 7904,[45] Yamato 74662,[44] Yamato 791198[46] and Yamato 793321[45] have been studied extensively for indigenous organic matter. Of these six, all but Allan Hills 77307 contained detectable amounts of amino acids. Some of the others

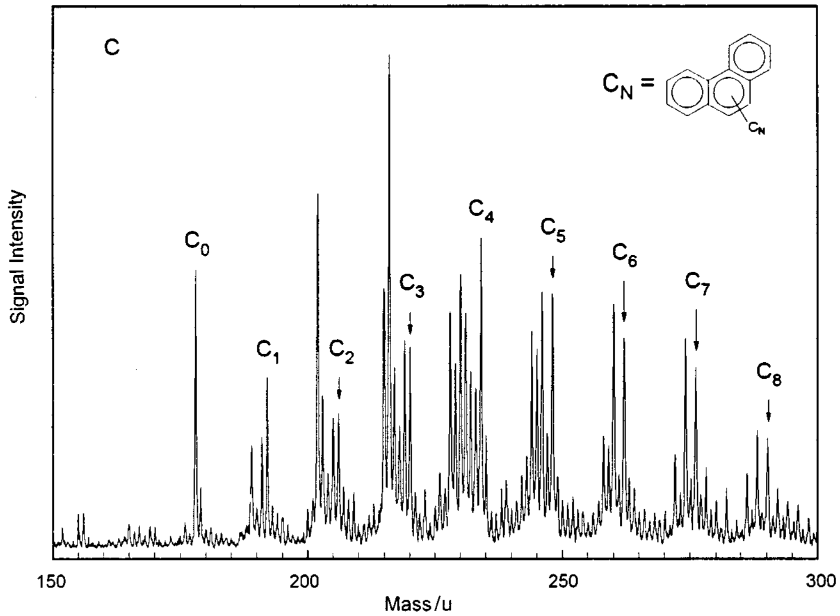

Fig. 10 μL^{2}MS of an Antarctic micrometeorite, emphasizing the extensive alkylation series seen in this and other micrometeorites. The base peak (C_0), identified here as phenanthrene, is associated with additional peaks (C_{1-8}) multiples of 14 u away, which is representative of a series of methyl group additions.

appear to be depleted, but all were concluded to be devoid of terrestrial contamination. These results show that, if anything, meteoritic organics exposed to Antarctic weathering are depleted rather than contaminated.

3.4 Allan Hills meltwater

No experimental evidence could be obtained for an aqueous PAH component in Allan Hills ice at the detection of the μL^2MS instrument. It is possible, however, to infer a reasonable upper limit to the nature and concentration of PAHs beyond the μL^2MS detection sensitivity, using the results from two extensive studies of PAHs in the polar ices of Greenland.[41,47]

Kawamura and Suzuki[41] studied the ice core record of PAHs over the past 400 years from an ice core recovered by the Japanese Arctic Glacialogical Expedition in 1989. The ice core was divided into 26 sections, each representing a period of between 6 months and 4 years. The total concentration of PAHs (*i.e.* soluble and insoluble components) within each section was determined by combined gas chromatography–mass spectrometry (GC–MS). More than 40 PAHs, including both alkylated and non-alkylated species, ranging from naphthalene (128 u) to 2,9-dimethylpicene (306 u) were identified. The total concentration of the major non-alkylated PAHs (dibenzothiophene, phenanthrene, fluoranthene, and pyrene) ranged from 1 part per trillion for ice formed from snow before the industrial revolution (*i.e.* prior to 1800 A.D.) up to 230 parts per trillion for contemporary snow deposition. The ratio of alkylated PAHs to non-alkylated ranged from 3.8 (before 1800 A.D.) to 9.9 (after 1950 A.D.). Finally, PAHs (both soluble and insoluble components) in the Greenland ice sheet constituted only between 0.7 and 5.7 ppm of the total organic C content of the ice.

Jaffrezo *et al.*[47] collected 24 snow samples from the summit of the Greenland ice sheet in the summer of 1991, representing *ca.* 4 years of snow deposition. All PAH concentrations were below experimental detection limits for the soluble fraction (*i.e.* <5 parts per trillion), while the insoluble fraction had an average concentration of 1.3 ppb. The nature of the PAHs, it was argued, suggested their source to be fossil fuel combustion aerosols from industrialized zones and, to a lesser extent, biomass burning of aerosols. Rapid modification and degradation of PAHs after deposition was observed in approximate agreement with the atmospheric reactivity index of the compounds.

Because Greenland is located in the Northern hemisphere, terrestrial PAHs in such ice should represent an upper contamination limit, owing to the significantly higher concentration of industrialized economies in the Northern hemisphere as compared to the Southern hemisphere in which Antarctica is located. Thus we may expect concentrations of PAHs in Antarctic ice to be characterized by the following three properties: (1) a total PAH concentration no greater than 10–100 parts per trillion (similar to that observed in preindustrial times in the Greenland ice sheet); (2) a ratio of alkylated to non-alkylated PAHs $\geqslant 1$ and (3) the major non-alkylated PAHs present are dibenzothiophene, phenanthrene, fluoranthene, and pyrene. None of these properties are observed in the PAH distribution of ALH84001 which seems to argue persuasively against melt water as the source of PAHs in ALH84001.

3.5 Spatial distribution of PAHs in ALH84001

In the four fusion-crust samples studied, few PAHs were observed within the fusion-crust zone, which extended into the meteorite interior to a depth of *ca.* 500 μm. At depths greater than 500 μm the PAH signal was observed to increase significantly levelling off in intensity at a depth of *ca.* 1200 μm from the fusion crust exterior. Fig. 11 shows four comparison spectra at 2 points, 200 and 1500 μm inwards, along analysis

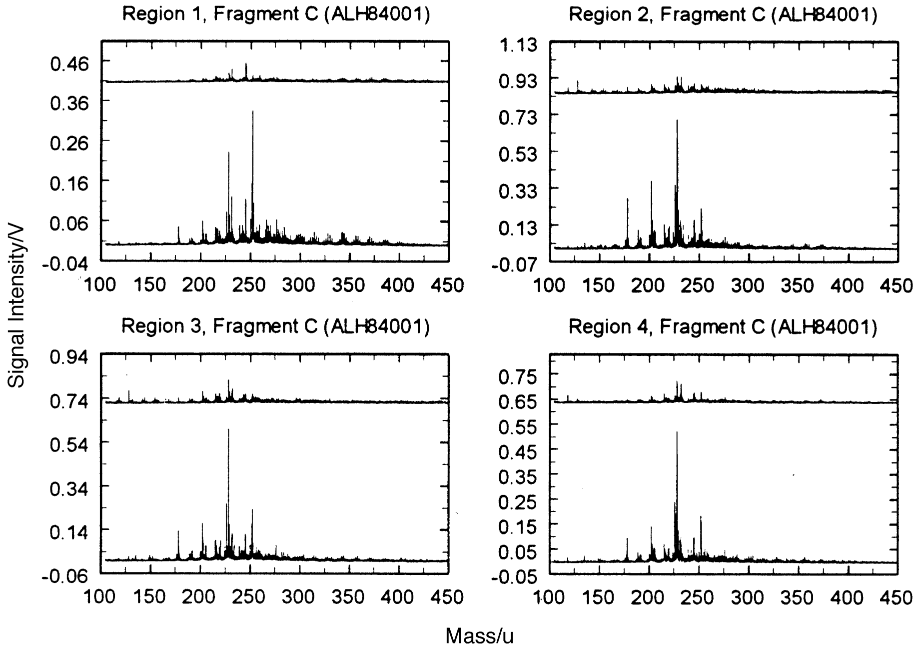

Fig. 11 μL^{2}MS of four separate regions of a 5 mm^3 exterior fragment (Fragment C) of ALH84001 containing an intact fusion crust. Spatially resolved analysis of the PAHs demonstrates a consistent concentration increase from 200 μm in from the fusion-crust exterior, top trace in each plot, to 1500 μm from the fusion-crust exterior, bottom trace in each plot. In all cases the PAH concentrations increase by a factor of *ca.* 10 on moving from the fusion crust to the interior of the meteorite.

lines running perpendicular to the fusion-crust exterior. It is apparent that both spectra on the four analysis lines appear qualitatively similar and differ most significantly in terms of overall signal intensity. This result can be interpreted to be a consequence of two factors. First, it can be argued that, since the μL^{2}MS technique is surface sensitive, a substrate with a higher surface area in the analysis spot will, all other things being equal, give a larger signal than a substrate with a smaller surface area. Hence, the smaller observed signal in the fusion-crust zone is perhaps a consequence of the morphological properties of the fusion crust, which has an inherently smaller surface area. Alternatively, the observed concentration profile can be argued to be consistent with volatilization and pyrolysis of indigenous material during atmospheric entry of the meteorite and, therefore, represents a 'fossil' thermal overprint of atmospheric entry. Examination of the results leads us to believe that the latter explanation is the most significant. The temperatures required to volatilize and pyrolyse PAHs (>300 °C for periods of several to tens of seconds) is lower than that required to fuse the bulk orthopyroxenite (typically >1000 °C). Hence the visual appearance of the thickness of the fusion crust, which represents the region in which fusion of the orthopyroxenite has occurred, should not reflect the same thickness as determined by the destruction of PAHs. In all four samples studied the visual thickness of the fusion crust was on the order of 100–300 μm, while the PAH concentration suggests that the depth to which organic material was affected was *ca.* 1500 μm. Thus, the approximate substrate surface area at 200 μm and 1500 μm should be roughly comparable and certainly not enough to account for the 5–10 fold increase in signal observed moving away from the fusion-crust exterior into the meteorite interior.

4 Conclusion

Contamination issues are always serious concerns in any studies of organic matter in extraterrestrial materials and ALH84001 is no different. Ultimately, it may never be possible to rule out terrestrial contamination from Antarctica conclusively as contributing to the PAHs observed by McKay *et al.*[6] We have, however, undertaken the most extensive contamination study of ALH84001 to date, and can find no evidence to support the results of Becker *et al.*[8] who have argued for terrestrial contamination. In regard to extraterrestrial contamination, Fig. 12 shows the average PAH molecular weight for all the meteorite samples examined in our contamination study, note that ALH84001 shows a markedly higher mass distribution than do any of the other samples. While not disproving the suggestion of Becker *et al.*[8] that a minor indigenous

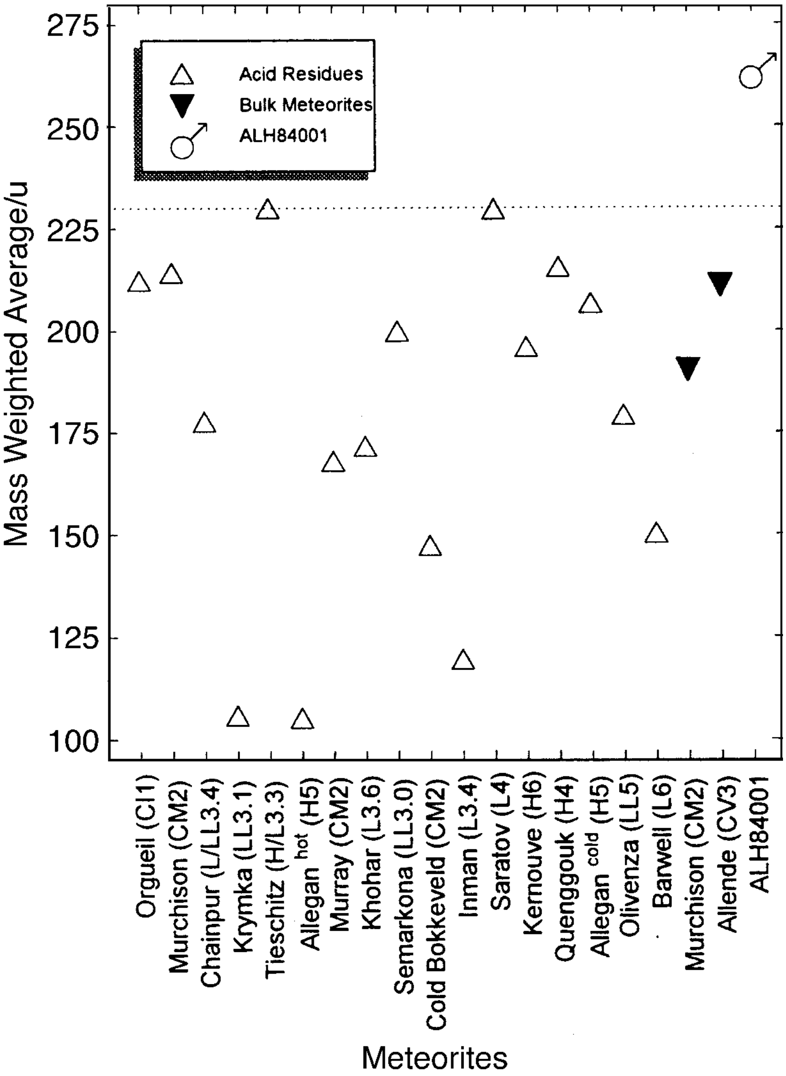

Fig. 12 Comparison of the average mass of the μL^{2}MS measured PAH distributions of 17 meteoric acid residues (△), two carbonaceous chondrite standards (▼) and ALH84001 (♂)

PAH component in ALH84001 could be the consequence of exogenous delivery to Mars, it cautions against making such a conclusion. Even though all the major PAHs observed in ALH84001 can be found in all the other meteoritic samples studied to date (albeit in significantly differing intensities), the same argument can also be made for automobile soot. Clearly, for example, the fact that phenanthrene occurs in both ALH84001 and Murchison provides no evidence either for or against a common origin.

In conclusion, we have examined whether carbonates can act as PAH scavengers, and find no evidence in the literature to support such a hypothesis, nor do the results of multiple independent experiments made by us demonstrate any affinity of PAHs for carbonates. We have studied PAHs in ice recovered from the Allan Hills ice sheet and find it to have a soluble PAH component that is below our detection sensitivity. Evidence in the literature supports this finding and suggests that the level of terrestrial PAHs in Allan Hills ice is less than 10^5 times smaller than in ALH84001. We have studied both interior and exterior fragments of non-carbonaceous chondrites from the Allan Hills ice sheet and find no evidence of terrestrial contamination. We have examined the terrestrial salt deposit formed on a noncarbonaceous meteorite that has a terrestrial residence time in Antarctica three times that of ALH84001 and find no evidence of terrestrial contamination. We have studied carbonaceous micrometeorites from Antarctica and can find no evidence of terrestrial contamination. Finally, we have studied the depth profile of PAHs in ALH84001 and find it inconsistent with a terrestrial origin. From these results we offer three comments: (1) given the rarity of Martian meteorites and that some terrestrial contamination is virtually inevitable, it is not satisfactory to establish that a sample is contaminated. Rather it is important to establish those organic components that represent terrestrial contaminants, so that they may be eliminated from consideration; (2) the PAHs observed in ALH84001 by McKay *et al.*[6] are of extraterrestrial origin and (3) studies of PAHs in meteorites recovered from Antarctica are a worthwhile pursuit because such specimens are unlikely to be seriously contaminated from their Antarctic exposure.

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