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TOF-SIMS analysis of polycyclic aromatic hydrocarbons in Allan Hills 84001

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Abstract–The presence of polycyclic aromatic hydrocarbons (PAHs) in the Martian meteorite Allan Hills 84001 (ALH 84001) was considered to be a major sign of ancient biogenic activity on planet Mars (McKay et al. 1996). An asserted spatial association of PAHs with carbonates, carriers of so-called nanofossils, was crucial for their suggested connection to early life forms. Although both observations can be explained individually without employing living organisms, a lateral correlation of PAHs and carbonates would suggest a genetic link between PAHs and the microstructures, favoring a biogenic explanation. On the other hand, without such a correlation, a biogenic or even a Martian origin of the PAHs cannot be inferred. Here we show that there is no correlation of PAHs and carbonates in ALH 84001. Furthermore, a general trend of high PAH concentrations at locations where terrestrial lead is present obviously suggests a terrestrial origin for PAHs in ALH 84001.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are omnipresent in nature (Allamandola 1996). They are found in fossil fuels, in primitive meteoritic material, in Antarctic ice, and in interstellar molecular clouds. Therefore, the occurrence of PAHs alone cannot be indicative of the presence of life. In the Martian meteorite Allan Hills 84001 (ALH 84001), PAHs were reported to be present on freshly fractured surfaces—the very same surfaces showing carbonate globules (McKay et al. 1996; Thomas et al. 1995). Structures connected to these carbonates were interpreted as fossils of former Martian organisms. One of the major and highly controversial arguments for this conjecture was an asserted spatial association between PAHs and carbonates (McKay et al. 1996), even though the earlier works of the proponents of this interpretation denied a clear correlation (Thomas et al. 1995).

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis of polished thin sections that had revealed no correlation of PAHs with carbonates (Stephan et al. 1998a, b, c) were discredited by assertions that the polishing process might have introduced a PAH contamination or redistributed the existing PAHs (Gibson et al. 2001). Therefore, we focused our present study on freshly broken surfaces to elucidate the true distribution of PAHs in ALH 84001 and their possible connection to indigenous features in this meteorite. TOF-SIMS, with its simultaneous detection of all secondary ions with one polarity, atomic as well as molecular, and its high lateral resolution (0.2–0.4 μm) is ideally suited to search for possible correlations between organic substances and element distributions (Stephan 2001). Although TOF-SIMS is not designed for the analysis of rough surfaces, topographic effects are well understood in principle (Rost, Stephan, and Jessberger 1999) and meaningful results can be acquired, since all secondary ion species show identical behavior.

EXPERIMENTAL METHODS

A TOF-SIMS IV instrument from ION-TOF (Niehuis et al. 1987), equipped with a gallium liquid metal ion source (Niehuis 1997), was used in this study. The energy of the Ga$^+$ ions was 25 keV. No pre-sputtering by Ar, O, or Cs ions was applied to the samples. Pre-sputtering usually increases secondary ion yields for atomic species by more than one order of magnitude. On the other hand, molecular ions like PAHs are typically destroyed during this process. To achieve high sensitivity and high lateral resolution, the Ga source was, in most cases, operated in the so-called "blanked mode" with pulse lengths of ~5 ns, ~50 primary ions per pulse, and a repetition rate of 10 kHz. Although much shorter primary ion pulse lengths and therefore higher mass resolutions can, in principle, be achieved at the expense of ion intensity or lateral resolution, this mode was chosen since the achievable mass resolution ($m/\Delta m_{\mathrm{FWHM}} \approx 800$ at mass 56 amu) was already restricted due to the roughness of the sample. Sample charging due to the primary ion beam was compensated by using low-energy electrons. More details of the TOF-SIMS technique are described in the referenced literature (Stephan 2001).

RESULTS

Fig. 1 shows the lateral distribution of crucial secondary ion species from a fracture surface. The PAH image was obtained from the sum of intensities of characteristic PAH peaks at nominal masses (in amu) 115, 128, 139, 141, 152, 165, 178, 189, 202, 213, 215, 226, 228, 239, 250, 252, 263, 265, 274, 276, 287, 289, and 300. A typical spectrum is given in Fig. 2. The distribution of the major elements is indicative of the major mineral phases found on this surface, which therefore can be easily recognized in the RGB image (Fig. 1). These major phases are orthopyroxene ($^{28}Si^+$), feldspathic glass ($^{27}Al^+$), and carbonate ($^{40}Ca^+$).

Due to strong fragmentation of PAHs under primary ion bombardment, identification of the original PAHs in ALH 84001 with TOF-SIMS is difficult. Fragmentation also explains the substantial differences between TOF-SIMS (Fig. 2) and microprobe two-step laser mass spectrometry (μL^2MS) results (McKay et al. 1996). Nevertheless, some general properties of the observed PAHs can be derived from the TOF-SIMS spectra. For example, heterocyclic compounds are not present in the mass spectra. Since their ionization probability in TOF-SIMS is generally higher than for the observed homocyclic PAHs, the presence of significant quantities of heterocyclic compounds is excluded in our ALH 84001 samples. Heterocycles would especially be expected as decomposition products from living organisms. However, a comparison of PAH TOF-SIMS spectra from ALH 84001 with those obtained from the carbonaceous meteorites Murchison and Orgueil and with a spectrum from terrestrial anthracite coal (Fig. 3) reveals no substantial differences, although, especially in the coal sample, larger PAHs seem to be more abundant than in ALH 84001.

To investigate PAH fragmentation during primary ion bombardment, pure pentacene and coronene (Fig. 4) samples were analyzed with TOF-SIMS (Stephan et al. 1998a). Their TOF-SIMS fragmentation pattern (Fig. 3) differs significantly

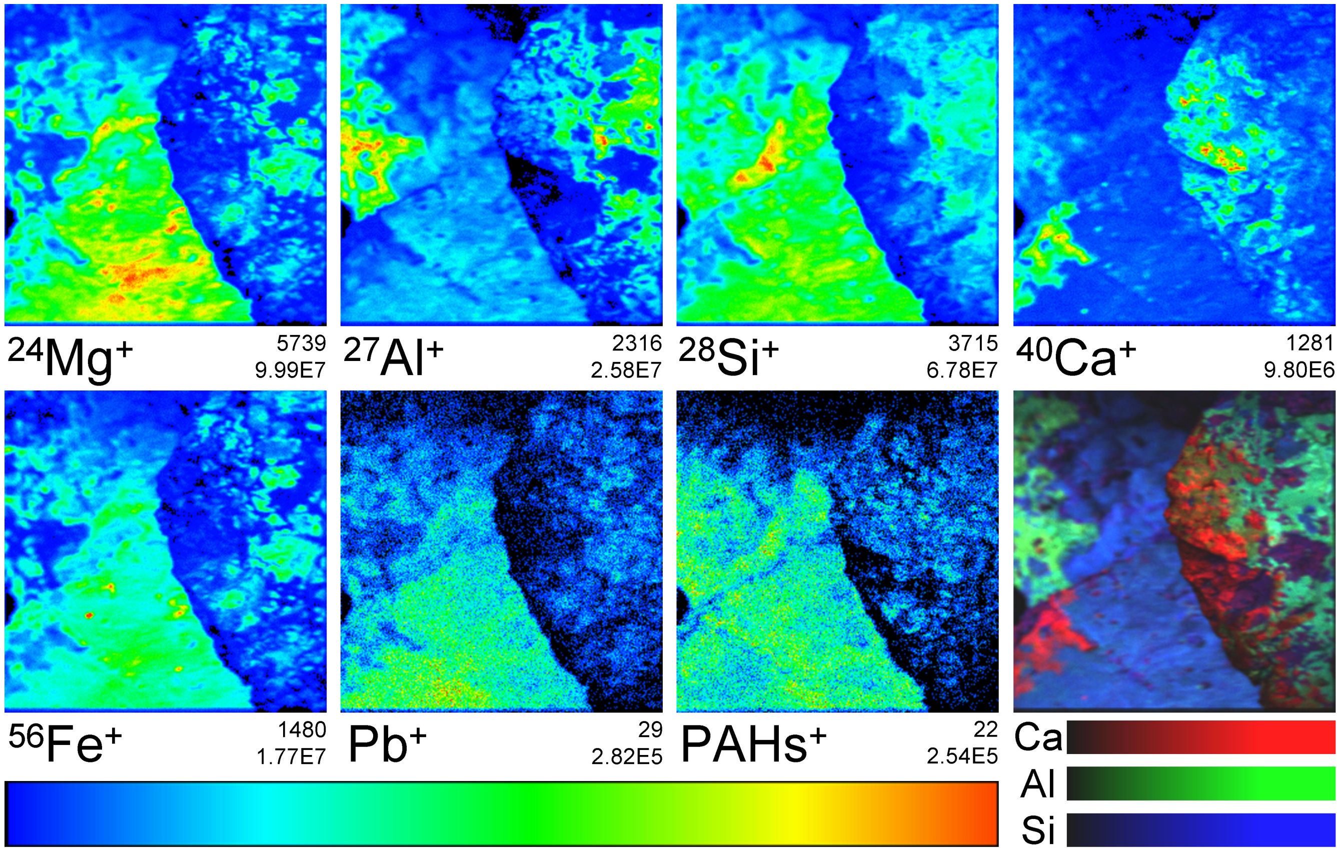

Fig. 1. Secondary ion images for different ion species measured simultaneously with TOF-SIMS. The field of view is 150 × 150 μm^2. Each image has 256 × 256 pixels and the number of primary ion shots per pixel is 3200. The ion species is mentioned below each image. Each image is normalized to the intensity (in counts) of the most intense pixel (e.g., 5739 for $^{24}Mg^+$), shown in red and given below the image. The color bar represents a linear scale from black (equals zero) to red. The second number represents the integrated intensity of the entire image (e.g. $9.99 \cdot 10^7$ for $^{24}Mg^+$). The Pb$^+$ image is derived from the summed intensities of all lead isotopes. The lower right image is an RGB image that combines the $^{40}Ca^+$, $^{27}Al^+$, and $^{28}Si^+$ ion images.

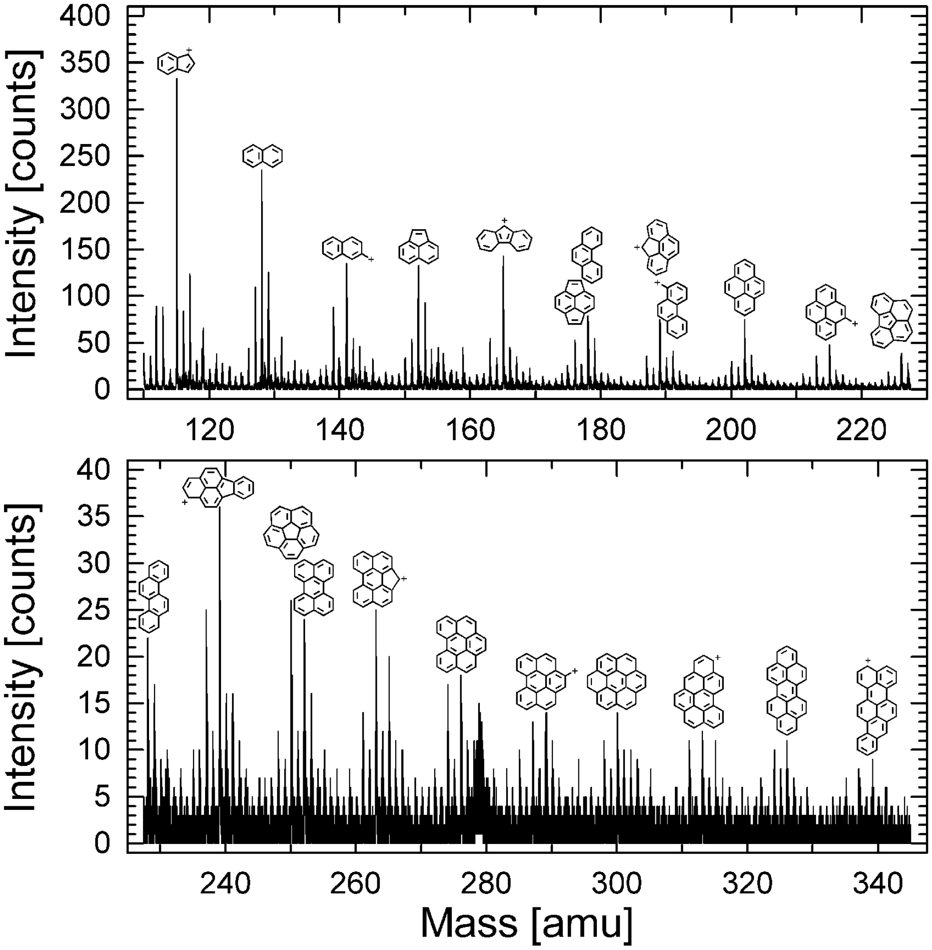

Fig. 2. TOF-SIMS spectrum obtained from a section of ALH 84001. Relative maxima show typical mass differences of 11 or 13 amu. In most cases, several peaks are present separated from each other by a mass difference corresponding to H_2. Since several structural isomers exist for most sum formulae, only examples for major peak identifications are given. The spectrum is shown here in a highly compressed mode. Ion masses in this mass range are determined with an uncertainty of the order of 0.01 amu, generally allowing an unambiguous identification of chemical sum formulae.

from the other samples. Coronene in particular showed mainly non-fragmented secondary ions at mass 300 amu, and its fragments are less hydrogen-rich compared to pentacene fragments or PAHs from meteorite and coal samples. Although large PAH fragments also dominate the mass spectrum for pentacene, their H/C pattern (Fig. 3b) more closely resembles those from meteorites and anthracite. Major deviations at carbon numbers C = 22 and C = 26 result from pure pentacene (278 amu) and probably from hexacene ($C_{26}H_{14}^+$, a linear chain of six benzene rings).

The similarities and dissimilarities between PAH mass spectra from widely different samples suggest that in all natural samples, a mixture of low-mass PAHs is present. Linear arrangements of benzene rings, like pentacene, seem to prevail, but two-dimensional structures, like coronene, are certainly underrepresented in the mass spectra due to reduced ionization efficiencies. However, from the mass spectra alone, no unequivocal assignment of PAHs as being either terrestrial or extraterrestrial or as being either biogenic or non-biogenic is possible.

To investigate if the PAH secondary ion signal intensity depends on the substrate, we intentionally contaminated a small piece of ALH 84001 with coronene. In this experiment, coronene was carefully dissolved in benzene. A small droplet of the solution was applied to the sample. After evaporation of the solvent, the surface was analyzed with TOF-SIMS similar to our previous measurements. Although ionization efficiencies in SIMS strongly depend on the chemical neighborhood of an atom or molecule, our results show that these matrix effects are not decisive in the investigation of PAHs in ALH 84001. The contaminated surface showed no differences for orthopyroxene, feldspathic glass, and carbonate—the major constituents of ALH 84001—in their respective PAH signals (Fig. 5). Consequently, it is expected that the imaging TOF-SIMS results of fresh surfaces reflect the proper distribution of PAHs in ALH 84001.

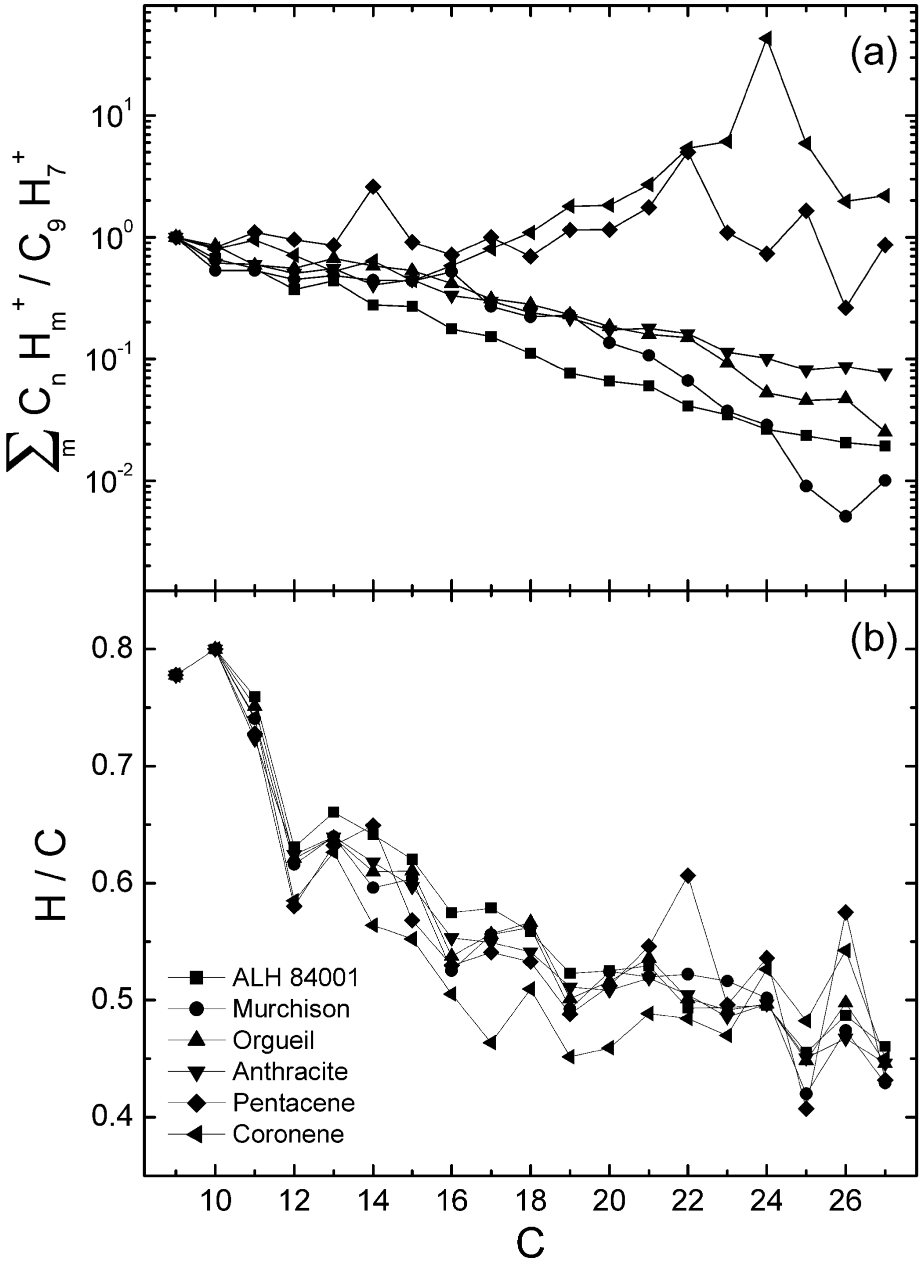

Fig. 3. Comparison of PAH secondary ion signals from different samples. The upper diagram (a) shows the relative abundances of PAHs depending on their number of carbon atoms relative to the abundance of $C_9H_7^+$. In the lower diagram (b), the averaged H/C ratio for PAH ions is given against the number of carbon atoms. The H/C ratio is typically higher for linear arrangements of benzene rings like pentacene than for two-dimensional structures like coronene (Fig. 4).

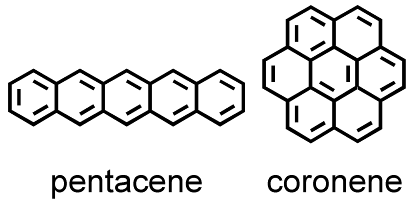

Fig. 4. Structural formulae of pentacene ($C_{22}H_{14}$, 278 amu) and coronene ($C_{24}H_{12}$, 300 amu).

Analyzing the spatial distribution of PAHs in ALH 84001 and possible correlations with elements or molecules indicative of a terrestrial or Martian origin may help to finally resolve the true nature and origin of the PAHs. As mentioned before, no clear correlation of the PAH distribution with any mineral phase was apparent from the analysis of either polished or fractured surfaces. Fig. 6 shows results of a search for correlations of PAHs with key elements on different surfaces. The only trend, which is far from being a clear correlation, seems to be associated with lead. The PAH

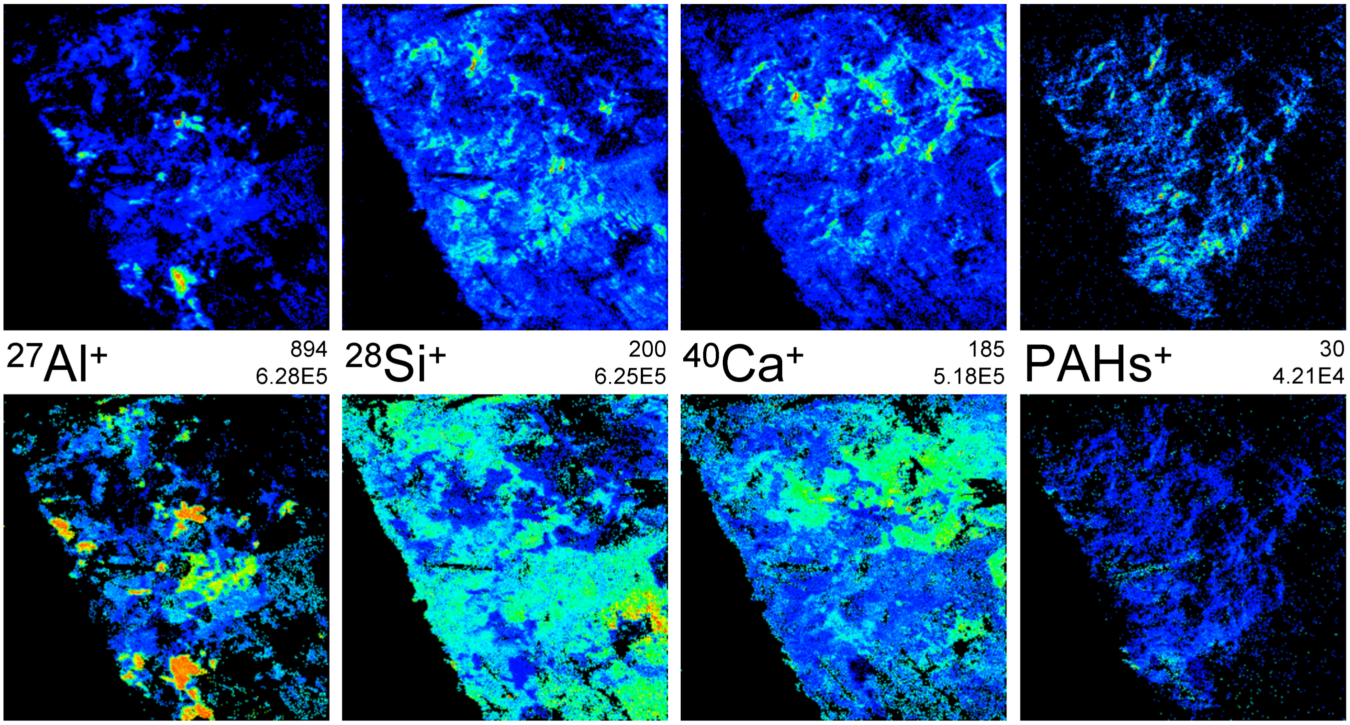

Fig. 5. The TOF-SIMS images from a fracture surface of ALH 84001 intentionally contaminated with coronene show no correlation of the PAH signal with any major mineral phase. In the lower row, all secondary ion images from the upper row are normalized to the sum of ion signals from major elements to suppress topographic effects on the ionization efficiencies. The field of view is 200 × 200 μm^2. Each image has 256 × 256 pixels, and the number of primary ion shots per pixel is 4080.

secondary ion intensity is generally high in areas with high lead concentrations. Isotopic ratios (Fig. 7) for this lead clearly identify it as being terrestrial. The relative intensities of ^{206}Pb, ^{207}Pb, and ^{208}Pb (1:0.84:2.06) show the characteristic isotopic signature of young marine sediments (1:0.83:2.06; Ben Othman, White, and Patchett 1989), which is typical of lead contamination in Antarctic meteorites (Lugmair and Galer 1992). This lead differs significantly from radiogenic lead observed by Borg et al. (1999) in carbonates of ALH 84001 with ^{207}Pb/^{206}Pb = 0.69. In their initial leaching step that did not affect the carbonate, a ^{207}Pb/^{206}Pb ratio of 0.83 was observed and attributed to laboratory or, more plausibly, Antarctic contamination (Borg et al. 1999).

DISCUSSION

From these results an extraterrestrial origin for the observed PAHs in ALH 84001 is unlikely. In fact, it is obvious that this meteorite is contaminated by terrestrial material, namely lead. Furthermore, other studies reveal terrestrial microbial activity in various meteorites including ALH 84001 (Steele et al. 1999, 2000), showing that terrestrial contamination is indeed taking place. Moreover, carbon isotopic studies revealed a terrestrial source for most of the organic material in ALH 84001 (Jull et al. 1998). Although the observed positive trend between terrestrial lead and PAHs in ALH 84001 is not an unambiguous correlation, other correlations are excluded from our data. In particular, a spatial association with carbonate globules is not present. Although this association was not substantiated by the data given in an early paper (Thomas et al. 1995), later publications on this subject used these data as evidence for a genetic link between "nanofossils" and PAHs without presenting any new facts to support this contention (McKay et al. 1996; Clemett et al. 1998). In contrast to TOF-SIMS, the applied technique of μL^{2}MS is lacking in the spatial resolution (~40 μm; Thomas et al. 1995) required to investigate the proposed correlation adequately, considering that typically carbonate globules are 50–100 μm in size. The observation of lower PAH contents in the fusion crust compared to the interior of ALH 84001 (Clemett et al. 1998; Gibson et al. 2001) is also too ambiguous to prove that the PAHS are of Martian origin. The inherently smaller surface area of the fusion crust as well as chemical and mineralogical differences may favor the contamination of the interior, which is accessible to contaminants through cracks. Our lead data clearly support the idea that PAH contamination has taken place on Earth, either in the Antarctic environment or later during handling and storing of the meteorite that was first misclassified as a diogenite and then recognized as a Martian meteorite almost a decade after the find (Mittlefehldt 1994). Another study showing similarities between PAHs in ALH 84001 and various Antarctic meteorites, as well as in polar ice, also supports the idea of contamination in Antarctica (Becker,

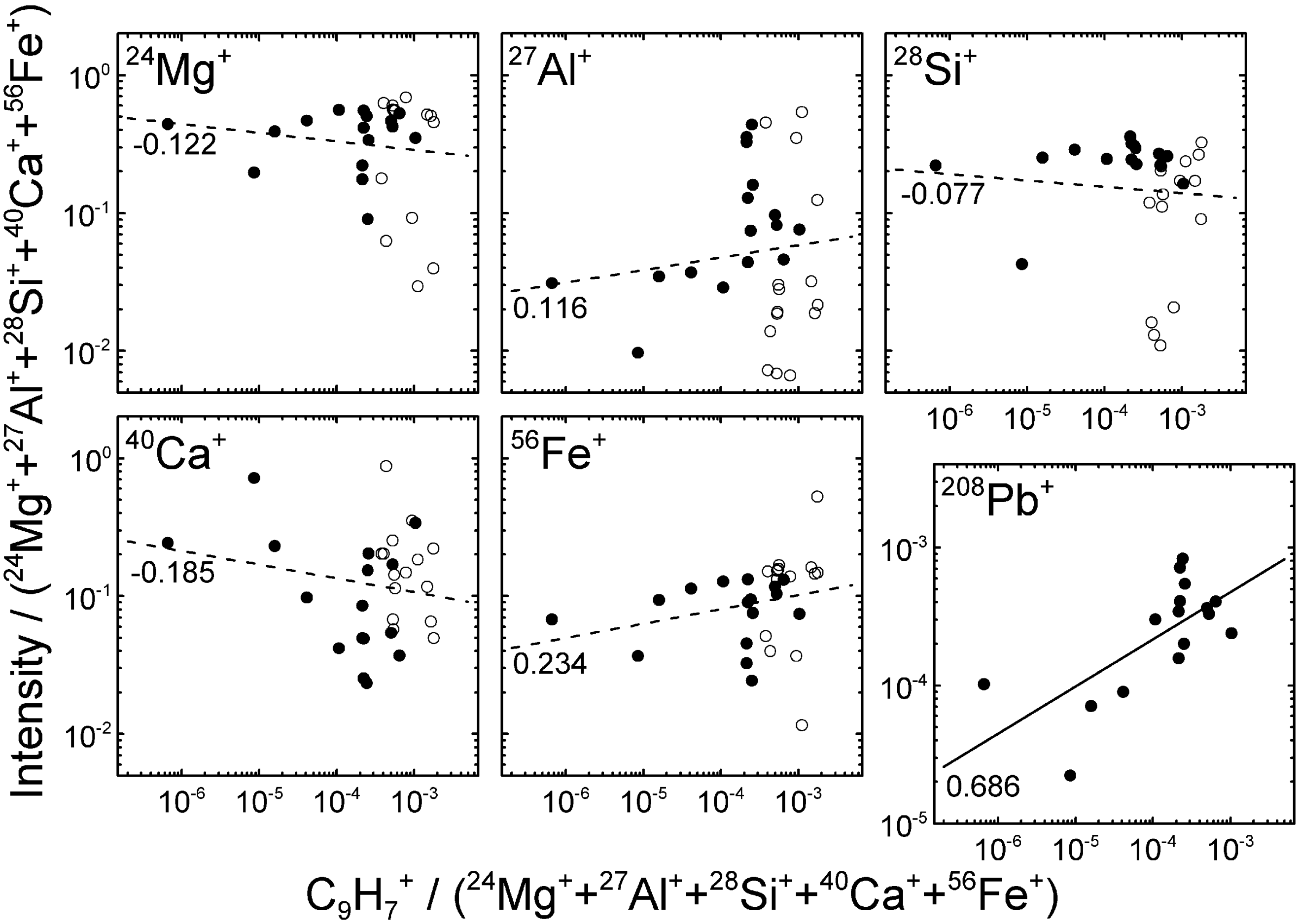

Fig. 6. Intensities of secondary ions from various major elements and lead compared with $C_9H_7^+$ as the major PAH ion show no obvious correlation. However, in these double-logarithmic diagrams, calculated correlation coefficients are given in each image together with a linear least-square fit (straight lines). Although still only a trend, the highest correlation coefficient was found for lead. All ion intensities are normalized to the sum of ion signals from major elements to minimize topographic effects from rough surfaces. Solid symbols represent measurements on fracture surfaces and open data points result from polished thin sections.

Glavin, and Bada 1997).

However, the exogenous delivery of meteoritic or cometary debris to the surface of Mars that has been suggested (Becker et al. 1999) would also be consistent with our results, taking into account the similarities of PAH spectra from ALH 84001 and those from Murchison and Orgueil (Fig. 3), although such a scenario seems to be unlikely. In this case, the similar behavior of PAHs and terrestrial lead in ALH 84001 would be indicative of similar contamination processes on Mars and Earth.

CONCLUSIONS

In any case, a genetic link between microstructures present in carbonates and PAHs is refuted by our TOF-SIMS investigation of ALH 84001. Furthermore, the proposed biogenic origin of these PAHs is not supported by the TOF-SIMS study. On the contrary, the lack of heterocyclic compounds suggests a non-biogenic origin. The similar behavior of PAHs and terrestrial lead points towards terrestrial origin of PAHs in ALH 84001.

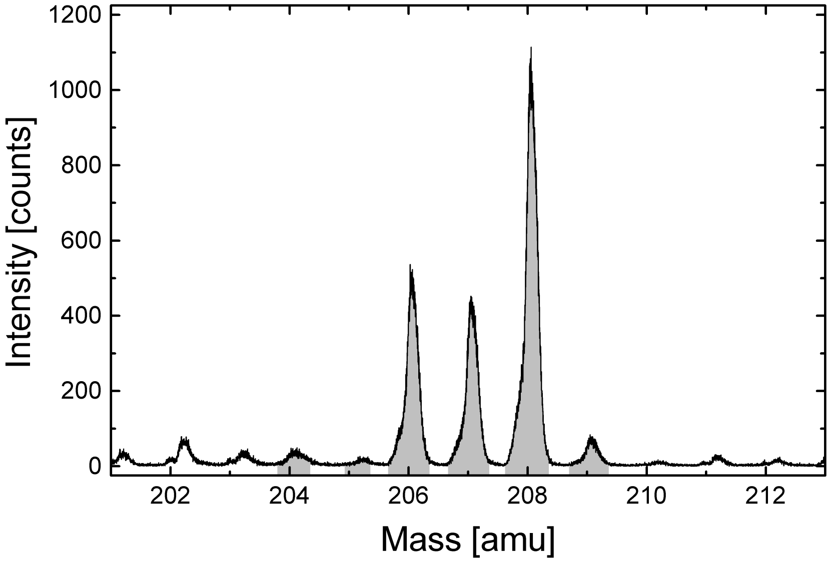

Fig. 7. TOF-SIMS spectrum in the mass range of lead. Lead ion signals are clearly identified at masses 204, 206, 207, and 208 amu. The peaks at 205 and 209 amu are due to hydride ions ^{204}Pb^{1}H^{+} and ^{208}Pb^{1}H^{+}. At 207 and 208 amu, the hydride signals from ^{206}Pb^{1}H^{+} and ^{207}Pb^{1}H^{+} cannot be separated from the elemental peaks, but using the ^{208}Pb^{1}H^{+} signal at 209 amu, their contribution can be calculated. Relative statistical errors are ~5%. The relative intensities of ^{206}Pb, ^{207}Pb, and ^{208}Pb (1:0.84:2.06) correspond to isotopic ratios observed in modern ocean sediments.

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