

Polycyclic aromatic hydrocarbons in asteroid 2008 TC₃: Dispersion of organic compounds inside asteroids

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Abstract—Among the predominantly polymict ureilite meteorites collected from the impact of asteroid 2008 TC₃ on October 7, 2008 the first time an asteroid was spotted in space and subsequently recovered in the form of meteorites, were many fresh-looking chondrites. Four were classified as EH6 (#16), H5 (sample #25), EL6 (#41), and L4 (#A100) chondrites. All are called “Almahata Sitta,” named after the nearby inhabited outpost of Station 6. Six hundred meteorites were collected, which show a wide range of densities, textures, reflection properties, and elemental compositions. Ureilites are carbon-bearing ultramafic rocks characterized by partial melt depletion and a violent disruption that created graphitic carbon and diamonds. In this study, we employ laser desorption laser ionization mass spectrometry to analyze the polycyclic aromatic hydrocarbon (PAH) contents of six meteorites from 2008 TC₃ that are ureilites (sample #1, #4, #7, #15, #27, and #47) and three anomalous fragments (sample #25, #16, and #41). Numerous organic compounds were detected with a PAH signature that has not been observed in the carbonaceous chondrites previously studied by our experimental apparatus. Specifically, the Almahata Sitta spectra lack the diversity of alkylation series of parent PAHs commonly observed in Murchison, and other carbonaceous chondrites. Spatial mappings of aromatic species across the surface of a fragment of sample #4 are presented including detection of what appears to be the aromatic amino acid tyrosine. Potential sources of terrestrial organic contamination are discussed and ruled out as a source of our observations. Meteorites #25 and #16 are found to have the same distribution of PAHs as the Almahata Sitta meteorites. Other chondrites have much different organic fingerprints. We conclude that both an H5 and E chondrite were included in asteroid 2008 TC₃ as foreign clasts and that organic compounds contained in ureilites can spread into other parts of an asteroid. These clasts may provide a clue as to the identity of the impactor that fragmented the ureilite parent body.

INTRODUCTION

Meteorites almost always arrive on Earth as “dead letters,” that is, with no return addresses. It is through great detective work that only in a few cases we can suspect where they come from. One example is the howardites, eucrites, and diogenites (HED) meteorites that are thought to originate from the Vesta asteroid

family. A rare exception occurred on October 7, 2008 when asteroid 2008 TC₃ entered the Earth’s atmosphere above the Nubian Desert in Northern Sudan. More than 600 meteorites survived on the ground, now called “Almahata Sitta,” and were recovered 2 months later by a team of students and staff of the University of Khartoum (Jenniskens et al. 2009). The asteroid was detected before impact by the Catalina Sky Survey

Telescope on October 6, 2008. The collected meteorites were found to have oxygen isotopes and rare earth elemental abundances that classified this meteorite as a ureilite. The meteorites contained aggregates of carbonaceous material as large as 0.5 mm in diameter, mostly in highly graphitized form, making this meteorite a candidate for organic analysis (Jenniskens et al. 2009).

These freshly fallen samples are of special interest because other known ureilites are contaminated by terrestrial organic matter. This has complicated the interpretation of the chemical and physical processes that resulted in these unique meteorites. All ureilites are thought to originate from one (now broken) ureilite parent body, hiding somewhere in the asteroid belt as an asteroid family. Because of its volatility, the carbonaceous matter may leave a unique fingerprint on all diverse parts of these asteroids, providing clues to the origin and evolution of the protoplanet (for a review see Goodrich 1992; Mittlefehldt et al. 1998; Jenniskens et al. this issue).

Until now, much of the investigation into organic species in meteorites has focused on carbonaceous chondrites (Sephton 2002; Plows et al. 2003; Elsilá et al. 2005). Laser desorption laser ionization mass spectrometry (L^2MS) (Zenobi et al. 1989; Kovalenko et al. 1990; Clemett and Zare 1997) has found a wealth of organic compounds in the Murchison and Allende meteorites, consisting predominantly of polycyclic aromatic hydrocarbons (PAHs) with numerous alkyl side groups.

Some 600 meteorites were collected from the debris of asteroid 2008 TC₃, spread over a length of 29 km along the asteroid's ground trajectory. Over such a large surface area in a pristine desert, several meteorites would have fallen in the past, unrelated to Almahata Sitta. Indeed, several weathered meteorites were readily identified as having been there prior to the fall. Many anomalous samples (#25, #16, and #41), however, were **1** surprisingly fresh-looking and Shaddad et al. (2010) estimate the nonureilites to be 20–30% in mass.

Among the anomalous meteorites, sample #25 was classified as an H5 chondrite by Zolensky of NASA Johnson Space Flight Center and subsequently found to have the expected oxygen isotope composition of an H5 **2** chondrite (Rumble et al. 2010). Similarly, three other samples were identified as an EH6 chondrite (#16), an EL6 chondrite (#41), and an L4 chondrite (#A100) (Herrin et al., this issue). These fragments appeared freshly fallen and of about the same size as nearby meteorites of Almahata Sitta (Shaddad et al. 2010).

Here we report on a study of aromatic compounds found in nine fragments of Almahata Sitta, both ureilites and anomalous meteorites, as determined by

laser desorption laser ionization mass spectrometry (L^2MS). L^2MS couples subfemtomolar sensitivity, high selectivity for PAH detection and 50 μm spatial resolution of PAH composition on complex surfaces. This technique combines focused laser-assisted thermal desorption with resonance-enhanced laser multiphoton ionization to produce the high sensitivity, compound selectivity, and spatial resolution that is beyond the capabilities of many traditional analytical methods.

Microprobe L^2MS has been widely applied in the detection of aromatic organic species in both extraterrestrial and terrestrial samples including interplanetary dust particles (Clemett et al. 1993; Messenger et al. 1995), meteorites and comets (Zenobi et al. 1989; McKay et al. 1996; Spencer and Zare 2007; Hammond and Zare 2008), hydrocarbon-contaminated soils (Dale et al. 1993), and petroleum fractions (Pomerantz et al. 2008, 2009). Microprobe L^2MS is particularly well suited to analysis of samples for which organic contamination is an issue. Application of the technique requires minimal sample processing and handling, thus minimizing the risk of additional sample contamination. This technique has been previously used to assess terrestrial contamination of both meteorites (Plows et al. 2003) and Stardust Mission aerogel capture media (Sandford et al. 2006; Spencer and Zare 2007). Additionally, owing to this technique's low detection limits and surface desorption, the required sample size is very small, and analysis leaves the bulk of the sample unaltered and available for further characterization.

Using L^2MS , we present here analyses that include bulk PAH contents in crushed Almahata Sitta fragments, spatial mapping of the intensity of select PAHs and what appears to be the aromatic amino acid, tyrosine, across the surface of a freshly fractured fragment of sample #4, and an analysis of potential terrestrial organic contamination from laboratory handling and storage. We find that the PAH signature of ureilites is distinctive and that some of the anomalous meteorites contain the same mixture of PAHs.

EXPERIMENTAL TECHNIQUE

Almahata Sitta Meteorite Sample Preparation

Nine meteorite samples were obtained from the University of Khartoum, Khartoum, Sudan. Of these samples, six were confirmed to be part of the asteroid 2008 TC₃ (sample #1, #4, #7, #15, #27, and #47), based on their common dark appearance and fresh fusion crust and their identification as being ureilites (Jenniskens et al. 2009), while three samples (#25, #16, and #41) were of indefinite origin, because of their

1 classification as chondrites. All nine samples were
2 collected in aluminum foil and stored in foil and glass
3 vials to prevent organic contamination through contact
4 with plastics. Additionally, two samples of desert sand
5 were collected during the meteorite recovery to serve as
6 contamination references for possible terrestrial
7 aromatic compounds present in the Almahata Sitta
8 strewn field.

9 All meteorite samples were attached to brass sample
10 platters of 7 mm diameter using double-sided tape
11 which contributes no background signal. For bulk
12 organic component analysis, meteorite samples weighing
13 approximately 3 mg were crushed between aluminum
14 foil layers using a mortar and pestle. For spatial
15 mapping of organic species across a sample surface,
16 fresh fragments of each meteorite sample with diameter
17 ≤ 6 mm were obtained using a chisel. Each analysis was
18 performed on two fragments of each meteorite sample.

19 All chemicals used for calibration or sensitivity
20 standards were obtained from Sigma-Aldrich.
21 Investigations into possible sources of contamination
22 were performed on glass microscope slide cover slips
23 (VWR) which were heated under a halogen lamp for
24 72 h while in contact with potential sources of
25 contamination. These potential contamination sources
26 included: nitrile gloves (Fisherbrand), double-sided tape
27 (Scotch 3M), plastic storage bags (Ziploc), aluminum
28 foil (Fisherbrand) and the Almahata Sitta sample
29 storage containers. Furthermore, samples of sand
30 collected from the meteorite-strewn field were analyzed
31 to record the presence of any aromatic organic
32 compounds that may have contaminated the meteorite.

33 **Microprobe Two-Step Laser Desorption/Laser Ionization** 34 **Mass Spectrometry Technique**

35
36
37 The microprobe laser desorption laser ionization
38 mass spectrometer ($\mu\text{L}^2\text{MS}$) has been described in detail
39 elsewhere (Zenobi et al. 1989; Kovalenko et al. 1990;
40 Clemett and Zare 1997). After introduction of each
41 sample platter to the instrument via a vacuum interlock,
42 the platter is positioned 2 mm below the mass
43 spectrometer's ion extraction region, the instrument is
44 evacuated to 2×10^{-7} torr, and the sample is allowed to
45 outgas for 15–30 min to reduce observed background
46 signal. Constituent molecules on the meteorite sample
47 surface are desorbed by rapid heating (Cowin et al.
48 1978) via IR light from a pulsed CO₂ laser (Alltech AL
49 882 APS) focused by a Cassegrainian microscope
50 objective (Ealing Optics, 15x). In order to avoid plasma
51 formation and decomposition while desorbing only
52 neutral species, the IR power used for desorption was
53 approximately 100 mJ per pulse (5×10^6 mJ cm⁻²),
54 which is below the plasma threshold.

After a time delay (10–50 μs) during which the
plume of desorbed neutral molecules forms in the
extraction region, the output of a pulsed Nd:YAG laser
(Spectra Physics DCR11; 4th harmonic, $\lambda = 266$ nm) is
used to selectively ionize organic species containing a
phenyl group moiety via (1 + 1) resonance enhanced
multiphoton ionization (REMPI). Values of UV pulse
energy for ionization are chosen to minimize
fragmentation and maximize parent ion signal and
typically range from 4 to 8 mJ per pulse (130–
260 mJ cm⁻²). The resulting ions are injected into a
reflectron TOF mass spectrometer built using a
modified Wiley-McLaren geometry (Wiley and McLaren
1955) after which the ions are detected using 20 cm²
active area dual microchannel plates arranged in a
chevron configuration. The detector output then passes
through a fast preamplifier (Ortec 9326) and timing
filter (Ortec 474) after which it is displayed on a digital
oscilloscope (LeCroy 9450). The resulting signal is
averaged within the oscilloscope for a series of 7–50
CO₂ laser shots and a computer is used to convert from
time-of-flight to mass-to-charge ratio. This conversion is
performed by use of two internal standards, toluene and
toluene-*d*₈, which are injected as gases into the sample
chamber.

Spectra obtained from powdered meteorite samples
to investigate bulk PAH compositions consist of
averages of 50 mass spectra repeated with varying
desorption (CO₂) and ionization (Nd:YAG) laser
powers as well as varying delay times. Spectra obtained
for spatial mapping of selected PAHs across a meteorite
sample surface consist of averages of seven spectra
acquired using the IR and UV power and delay time
settings producing the most intense spectra in the bulk
analysis of each sample. Species maps were acquired
along two perpendicular transects for each fragment.

RESULTS

Bulk PAH Compositional Analysis

Laser desorption laser ionization mass spectrometry
mass spectra for each of nine obtained meteorite samples
as well as a sample of Murchison meteorite are plotted
in Fig. 1. Several similarities and differences between the
Murchison, a chemically primitive CM2 carbonaceous
chondrite, are immediately obvious. Unlike Almahata
Sitta, Murchison experienced extensive aqueous
alteration of its parent body. All ureilite samples (e.g.,
#4, #27, and #47) showed a distinct pattern of mass over
charge ratio (*m/z*) peaks. Individual samples show small
but significant variations in the relative abundances of
PAHs (see Table 1). Comparison of the Almahata Sitta
spectra to those of the Murchison meteorite shows that

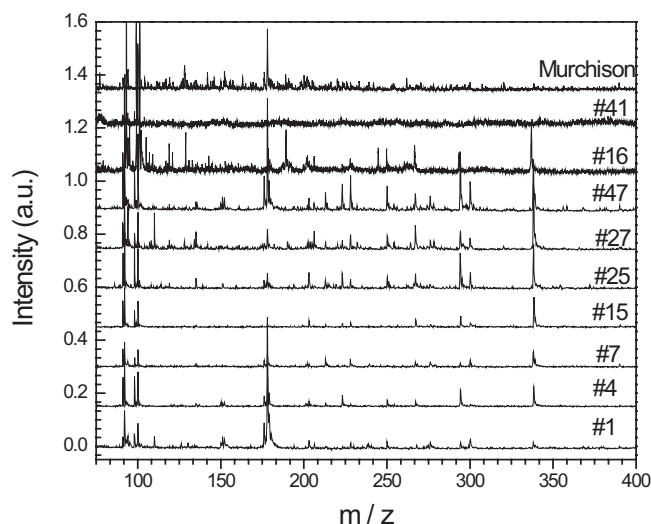


Fig. 1. Laser desorption laser ionization mass spectrometry spectra of all nine samples obtained as well as a sample of the Murchison meteorite. All spectra were recorded using the same instrumental parameters, as described in the Experimental Technique section. A list of m/z values occurring in each sample can be found in Table 1.

Table 1. Detected m/z values for nine meteorite samples. The sign “+” indicates the presence and the “-” one indicates the absence of these peaks.

m/z	Ureilites						Anomalous meteorites		
	#1	#4	#7	#15	#27	#47	#25	#16	#41
110	+	-	-	-	+	+	-	+	-
120	-	-	-	-	+	+	+	+	-
128	-	-	-	-	+	-	-	+	-
135	-	-	-	-	+	+	+	-	-
152	+	+	-	-	-	+	+	-	-
178	+	+	+	+	+	+	+	+	-
192	-	-	-	-	+	-	-	+	-
202	+	+	+	+	+	+	+	+	-
206	+	-	-	-	+	+	-	+	-
212	+	+	+	+	+	+	+	-	-
223	-	+	-	+	+	+	+	+	-
228	+	+	+	+	+	+	+	+	-
234	-	-	-	-	+	-	-	-	-
250	+	+	-	-	+	+	+	+	-
267	-	+	+	+	+	+	+	+	-
276	+	-	+	+	+	+	+	-	-
278	+	-	-	-	+	+	+	-	-
294	+	+	+	+	+	+	+	+	-
300	+	-	+	+	+	+	+	-	-
338	+	+	+	+	+	+	+	+	-

the Almahata Sitta meteorite contains a much sparser array of aromatic organic species than the Murchison meteorite. Specifically, the Almahata Sitta spectra lack

the diversity of alkylation series of parent PAHs commonly observed in Murchison and other carbonaceous chondrites (Elsila et al. 2005).

Within the Almahata Sitta samples analyzed, PAHs seem to be somewhat heterogeneously distributed. Some m/z ratios are commonly observed in samples including m/z 178 (phenanthrene) and 202 (pyrene) among others while others such as m/z 128 (naphthalene) are observed in only one Almahata Sitta sample (Fig. 1 and Table 1).

Surprisingly, as shown in Fig. 1 and Table 1, the spectrum of the nonureilite sample #25 shows a number of PAH peaks in common with the L²MS spectra of other Almahata Sitta samples, especially samples #27 and #47. Additionally, two samples determined to be E chondrites (#16 and #41) (Herrin et al. this issue) were studied. Sample #16 appears to have a PAH envelope very similar to that observed in spectra of ureilite samples (Fig. 1; Table 1). Sample #41, however, exhibits a spectrum free of aromatic compounds (Fig. 1), unlike those of other studied Almahata Sitta samples.

Contamination Experiments

The series of peaks with m/z 135, 223, 267, 294, and 338 (Fig. 1 and Table 1) have previously been observed in this laboratory during its participation in the Stardust Mission organics preliminary examination team (PET) (Spencer and Zare 2007). We investigated whether these peaks might arise from contamination during sample preparation. Glass microscope cover slips were exposed to a variety of materials with which the Almahata Sitta meteorite samples may have come into contact. L²MS spectra of these cover slips revealed only low intensity peaks at m/z 178 and 202 in the case of the plastic storage bag and no signal in the other cases. No peaks at the m/z ratios mentioned above were detected.

Two samples of Nubian Desert sand were studied that were handled in the same aluminum foil and containers as the meteorite samples. No aromatic compounds were detected (Fig. 2). This adds to the lack of organic compounds detected in sample #41. Thus, these peaks appear not to be the result of sample handling.

Moreover, L²MS spectra were obtained along a set of perpendicular transects over the surface of a fragment of Almahata Sitta sample #4 with dimensions of approximately 6 mm by 3 mm (Fig. 3). Normalized intensities of coronene and phenanthrene signals are presented, which have been observed at intervals along the two transects. These m/z ratios (178 for phenanthrene and 300 for coronene) were chosen because they were detected in all analyzed Almahata Sitta samples and were considered to be ubiquitously present in the 2008 TC₃ asteroid. Additionally, choosing

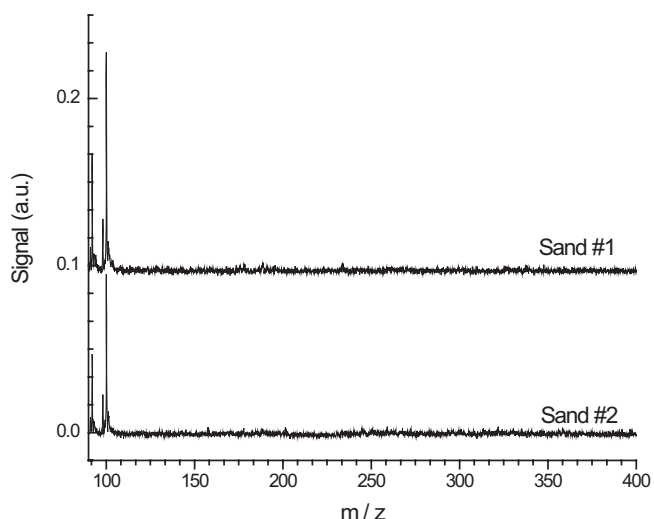


Fig. 2. Laser desorption laser ionization mass spectrometry spectra of sand #1 and sand #2.

m/z ratios with strong intensities in sample #4 was a necessary choice due to the limited number of spectra that can be acquired and averaged for each location on the transect. L²MS is a surface technique and, if many spectra are obtained from one location on the sample surface, the PAHs in that area are quickly depleted, resulting in artificially low signal intensity.

The signals from these two PAHs are distributed randomly across the analyzed sample surface, exhibiting no trend of increasing or decreasing intensity when moving from the sample edge to the center. Similar random distributions are detected when analyzing other species along these transects not presented here, indicating that our measurements of coronene and phenanthrene are representative. A similar study of laboratory contamination was performed by Plows et al. 2003 in which a fragment of a meteorite was exposed to solid coronene in a laboratory setting and subsequently analyzed. This study showed a clear trend of decreasing coronene signal as detection moved to 80 μm from the edge; no trend—increasing or decreasing—was detected in the center of the sample.

In addition to detecting PAHs, a peak at m/z 181 was observed at four locations on the surface of Almahata Sitta sample #4 (Fig. 4). We suggest that this peak corresponds to tyrosine, an aromatic amino acid with mass 181, based on the observation of many amino acids in the chromatographic analysis of Almahata Sitta extracts (Glavin et al. this issue). An experiment to measure the L²MS sensitivity to tyrosine relative to coronene was performed in which equal masses of coronene and tyrosine were deposited on the sample platter and subjected to the same instrumental conditions used to detect m/z 181 in sample #4. This

experiment indicates that the L²MS technique is less sensitive to tyrosine than to PAHs.

DISCUSSION

Laser desorption laser ionization mass spectrometry spectra of the analyzed Almahata Sitta samples show some similarities in their aromatic organic species features to those observed in carbonaceous chondrites including the Murchison meteorite (Fig. 1). The absence of highly alkylated PAHs in the Almahata Sitta samples supports further the assertion that we have insignificant contamination by atmospheric pollutants. These alkylated PAHs are widely considered to be constituents of pollution from incomplete combustion in industrial plants, especially in the Northern Hemisphere (Kawamura et al. 1994; Gingrich and Diamond 2001).

In addition, the organics-free spectra of Nubian Desert sand samples and other laboratory materials support the conclusion that meteorite fragments were not exposed to terrestrial organics contamination. Study of relevant laboratory materials revealed only low intensity peaks at m/z 178 and 202 which are observed at much higher intensity from the meteorite fragments themselves, indicating that, while a small portion may be contamination, the bulk of these signals represent species native to the meteorite. Based on this exclusion of terrestrial contamination as the source of PAHs in the Almahata Sitta and the observation of relatively high PAH signal intensity, we conclude that these species are native to the asteroid at the time of impact.

The fact that samples #25 and 16 have the same PAH signature as other samples of Almahata Sitta, and after excluding a variety of possible terrestrial contamination sources, strongly suggests that samples #25 and #16 belonged to asteroid 2008 TC₃ at the time of atmospheric entry. This result implies that the PAHs in ureilites can spread throughout an asteroid body. The clasts of ureilitic material are found in much smaller units than the approximately 10 m sized fragments which originally were released from the parent body. The ureilites underwent a dramatic reduction in size by numerous violent collisions with other asteroids (Herrin et al. 2010). During the reaccretion of these fragments, foreign chondritic material was mixed in. In subsequent collisions, the asteroids may have been heated to sufficient degree to enable the dispersion of the organic compounds in the ureilite material and thus contaminate the foreign chondritic clasts.

The lack of organic aromatic species in sample #41 invites two speculations as to the origin of this sample. One is that the porosity of #41 prevents the diffusion of PAHs into this sample. The other is that this meteorite originated from an unrelated meteorite fall.

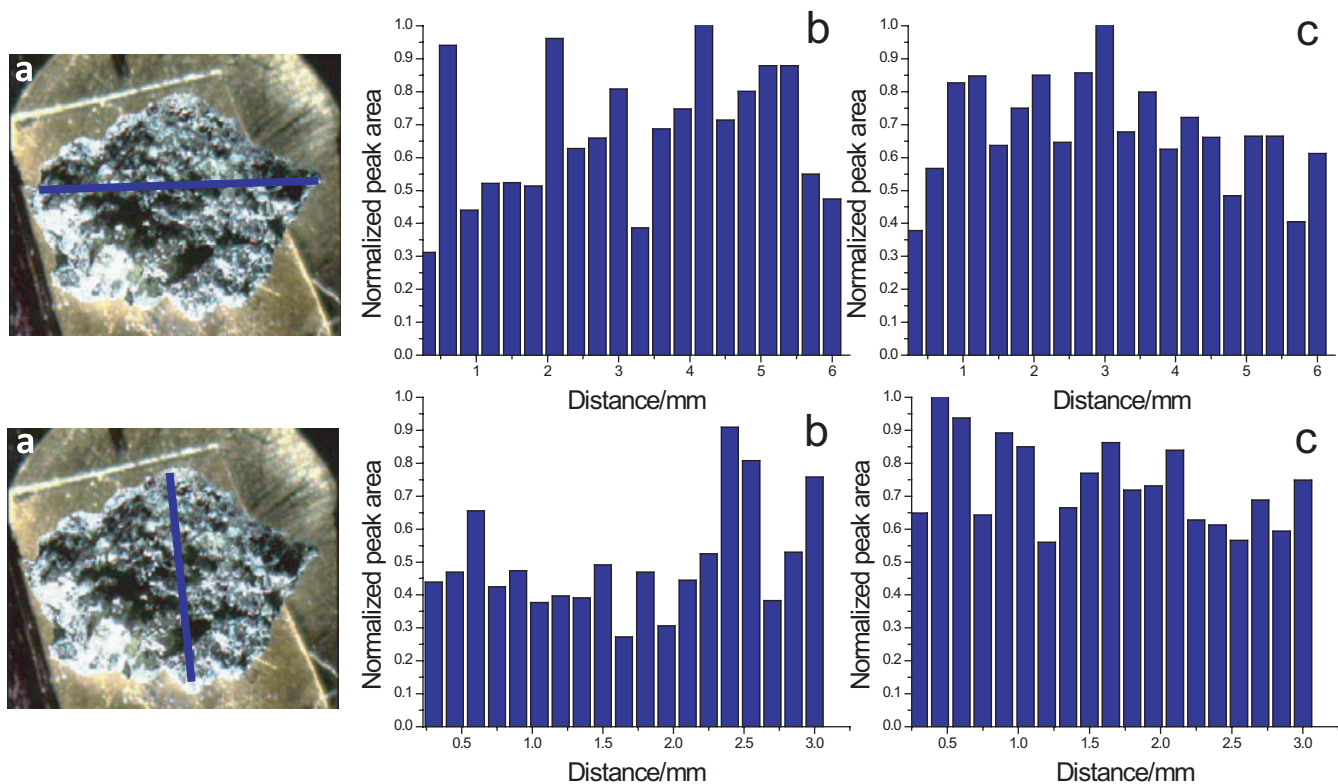


Fig. 3. Spatial map of coronene and phenanthrene across the surface of a fragment of sample #4. a) Transect paths across **II** sample #4 fragment. b) Normalized intensity of coronene signal along transects indicated in (a). c) Normalized intensity of phenanthrene signal along transects indicated in (a).

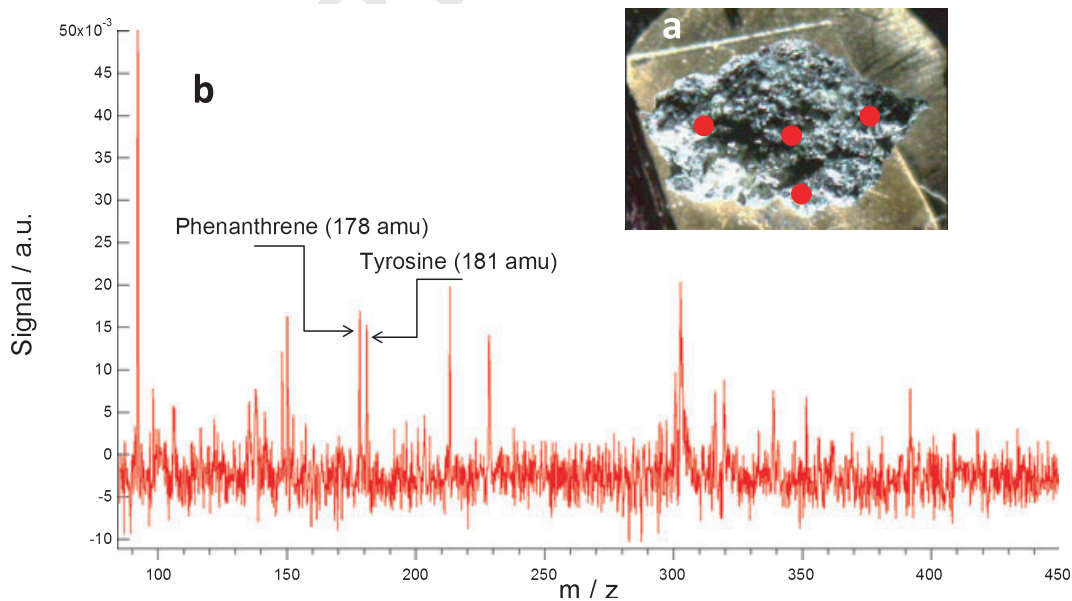


Fig. 4. Detection of m/z 181 (tyrosine) from Almahata Sitta sample #4: a) approximate locations of detection of m/z 181; and b) sample spectrum showing peak at m/z 181, which is tentatively identified as the amino acid tyrosine.

CONCLUSION

Based on the PAH signature, we conclude that ureilites contain a distinctive range of PAHs and other aromatic compounds. For a sensitive L²MS technique—approximately 1 attomole—the freshly fallen Almahata Sitta ureilites are rich in a limited number of PAHs without alkyl side chains. Identification of most of these compounds awaits analysis with a higher *m/z* resolution. Other organic compounds may remain undetected, because the selectivity of (1 + 1) REMPI for PAHs and other aromatic species blinds us to the presence of compounds such as straight-chain alkanes and nonaromatic amino acids.

The ureilite fragments of 2008 TC₃ did not experience heating above PAH destruction temperatures—several hundred degrees Celsius—during atmospheric entry and catastrophic disruption.

The observed PAH compounds were formed prior to atmospheric entry, but presumably after the catastrophic event that disrupted the Ureilite Parent Body, when temperatures increased to well above the PAH destruction temperature. It is likely, that the distinctive set of PAHs were created in subsequent collisions after the pieces of this parent body reassembled into asteroids. Later collisions may have heated the organic matter again, volatilizing the PAHs, and allowing them to spread to any newly aggregated foreign parts, such as samples #25 and #16. The PAH profile identifies both fragments as part of 2008 TC₃ before it impacted the Earth's atmosphere.

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