

ARE THE POLYCYCLIC AROMATIC HYDROCARBONS IN ALH84001 OF EXTRATERRESTRIAL ORIGIN?: A REEVALUATION. S. J. Clemett,¹ M. T. Dulay,¹ S. Gillette,¹ X. D. F. Chillier,² T. B. Mahajan¹ and R. N. Zare¹,
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Preliminary investigation of organic matter in the Antarctic Martian meteorite ALH84001 by microprobe two-step laser mass spectrometry ($\mu\text{L}^2\text{MS}$), reported at LPSC XXVI (1), demonstrated the presence of trace amounts of polycyclic aromatic hydrocarbons (PAHs) within carbonate-rich regions of the meteorite. More recently, ALH84001 has become the subject of considerable interest and controversy after evidence suggesting it may show signs of relic biogenic activity on early Mars was reported (2). We reevaluate here the evidence for the extraterrestrial origin of PAHs in ALH84001 in light of recent claims suggesting that PAHs may actually be terrestrial contaminants (3-5).

ALH84001 was recovered from the Allan Hills region of Antarctica; it is composed mainly of orthopyroxenite interspersed with Fe-Mg-rich carbonates. The petrography of the carbonates supports an extraterrestrial origin (6), as do the $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ isotope ratios (3, 7). The total C content of ALH84001 is ~ 600 ppm based on stepped-combustion experiments (8), of which 257 ppm is considered "organic" based on its combustion at low temperatures (20-450°C). Recent carbon isotopic measurements by Jull et al., (3) have shown the C isotopic composition of this fraction to have ^{14}C abundance 40-60% of modern terrestrial C and a $\delta^{13}\text{C}$ of between -22 and -33‰. Therefore it appears likely that this fraction is primarily terrestrial contamination. This result is not surprising in light of the work of Swart, Grady & Pillinger (9) who have suggested that in C abundance and isotopic composition measurements of extraterrestrial samples by stepped combustion, all measurements $< 425 \pm 25^\circ\text{C}$ be considered tainted by terrestrial contamination. Indeed measurement of water-labile amino acids by Bada et al. (5) 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 $< 1\%$ of the total organic content of ALH84001 (2). Intriguingly Jull et al. (3) note that ALH84001 contains a small preterrestrial C component, based on ^{14}C abundance, which they conclude as being either an acid-insoluble carbonate or a refractory organic phase. If this phase is organic, it may well contain PAHs and be related to the heterogeneously distributed sub-micron carbonaceous material observed by Flynn et al. (10) within ALH84001 carbonates using x-ray adsorption near edge spectroscopy (XANES).

More directly relevant to the PAH question, Becker, Galvin & Bada (4) have suggested that the PAHs in ALH84001 are primarily terrestrial, arising from interaction of the meteorite with polar melt water during its 13ka residence in Antarctica. Two key experiments were performed to support this argument and appeared to show that: [1] calcium carbonate can sequester PAHs from an aqueous solution of the PAH standard AccuStandard; and [2] calcium carbonate is able to scavenge PAHs from meltwater ob-

tained from the Allan Hills blue ice sheet. We have attempted to repeat these experiments and extend upon them to address five specific issues:

1. Can carbonate act as a PAH scavenger?
2. Do Antarctic meteorites with no indigenous organic matter show evidence for PAH contamination?
3. Do severely weathered Antarctic meteorites show evidence for PAH contamination?
4. Does Allan Hills meltwater contain measurable concentrations of solubilized PAHs?
5. Does the spatial distribution of PAHs in ALH84001 constrain their source?

In our experiments PAH distributions and concentrations were determined by either $\mu\text{L}^2\text{MS}$ (11) and/or capillary zone electrophoresis (12).

To address the first point, we attempted to duplicate the work of Becker et al. (4), but we discovered a serious inconsistency in their carbonate extraction experiments – they took no consideration of the solubilities of PAHs. Although they report preparing a 1 ppm aqueous solution of AccuStandard, we argue this is physically impossible. The solubilities of most of the 16 PAHs in AccuStandard have been reported in the literature to be two to three orders of magnitude below that necessary to create a 1 ppm solution (13-16). Figure 1 illustrates the error in the interpretation of the results. To correctly evaluate whether it is possible for carbonate to act as a PAH sequestration agent we choose two experiments not subject to the same solubility issues. In the first experiment five PAHs of varying sizes were dissolved in diethyl ether and deposited on six mixed sand/carbonate substrates (CaCO_3 :sand = 0:100, 5:95, 10:90, 20:80, 50:50, and 100:0). The sand/carbonate mixtures were then flushed with water and the affinity of PAHs to the carbonate determined by measuring the residual PAH concentration on the carbonate. We found no evidence to support a specific interaction of PAHs with carbonate. In the second experiment, an aqueous saturated solution of naphthalene was prepared and calcium carbonate added. The affinity of the carbonate for naphthalene was measured by removing small aliquots of water over time and measuring the concentration of naphthalene in solution. No decrease in naphthalene concentration over time was observed which indicates that the carbonate did not interact with the naphthalene. These two experiments indicate that carbonates do not preferentially adsorb PAHs and that in general PAHs interact only weakly and nonspecifically with mineral surfaces (17).

In regard to the second point, multiple interior and exterior fragments from two Antarctic ordinary chondrites (ALH83013 & ALH83101) of petrologic classes H6 and H5 were studied. Meteorites of this type contain little to no indigenous organic matter (18) so that observation of PAHs in such samples must be a consequence of Antarctic contamination. Additionally, the terrestrial salt deposit (mainly

magnesium carbonate) from the extensively weathered H5 chondrite LEW85320 (19) was studied for PAHs (the terrestrial age of LEW85320 is ~32.5ka (20)). In all cases PAH concentrations were significantly below those observed in ALH84001.

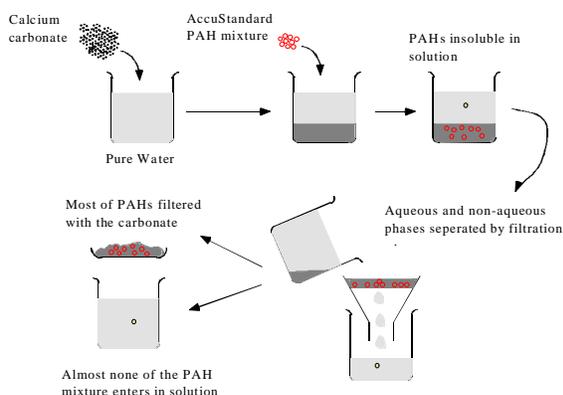


Fig 1: The low solubilities and long equilibration times of PAHs means a 1 ppm solution of AccuStandard cannot be formed in water at 25°C. In the Becker et al. experiment nearly all the PAHs added to the water would have been filtered out with the carbonate. This would give the impression that the carbonate had sequestered PAHs, whereas in reality they never entered solution.

Surface area and composition are important factors in determining susceptibility to contamination, with large particles being less effective absorbers of nonpolar molecules than smaller (< 50 μm) particles (21). Increasing amounts of organic material increases adsorption levels of PAHs (22), and clay-like composition facilitates more adsorption of hydrophobic molecules than more organized minerals such as chain silicates (23). Considering these factors to address the third point, fifteen Antarctic micrometeorites (AMMs), which are small, contain carbonaceous material and have phyllosilicates were chosen to represent ideal candidates for contamination by Antarctic PAHs. PAH intensities between AMMs was observed to vary over two orders of magnitude, all being characterized by extensive PAH alkylation. No two spectra appear identical, which argues against a common contaminant. None of the spectra showed any similarity to the PAH distribution observed in ALH84001.

To address the fourth point, ice melt water from the Allan Hills ice sheet was measured for soluble PAHs. No PAH signal was observed above instrument detection limits, which suggests the soluble PAH concentration of southern polar ice to be at or below the ppb level consistent with the results of northern polar ices (24, 25).

To address the fifth point, spatially resolved studies of four exterior fragments of ALH84001 with intact fusion crust were made to determine the distribution of PAHs perpendicular to the fusion crust surface. In all four samples few PAHs were observed within the fusion crust zone, extending into the meteorite to a depth of ~500 μm . At greater depths the PAH concentration increases. This result can be interpreted to be consistent with volatilization and pyrolysis

of indigenous PAHs during atmospheric entry, and therefore represents a “fossil” thermal overprint of atmospheric entry.

In conclusion, we have examined whether carbonates can act as PAH scavengers, and find no evidence in the literature to support such a hypothesis. The results of multiple independent experiments made by us fail to demonstrate any affinity of PAHs for carbonates compared to other mineral surfaces. 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 the level of terrestrial PAHs in Allan Hills ice is less than 10^{-5} times that found in ALH84001. We have studied both interior and exterior fragments of noncarbonaceous chondrites from the Allan Hills ice sheet and find no evidence of PAHs. We have examined the terrestrial salt deposit formed on a non-carbonaceous meteorite that has a terrestrial residence time in Antarctica three times that of ALH84001 and find no evidence of terrestrial PAHs. We have studied AMMs from Antarctica and can find no evidence of a common terrestrial PAH contaminant. Finally, we have studied the depth profile of PAHs in ALH84001 and find it inconsistent with a terrestrial origin. 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.

From these results we offer two comments: [1] the PAHs observed in ALH84001 by McKay et al. (2) are extraterrestrial; and [2] studies of PAHs in Antarctica meteorites is a worthwhile pursuit.

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