

Formation of Prebiotic Molecules in Interstellar and Cometary Ices

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Abstract. We report here on our lab studies of ice photochemistry of large organic molecules under cometary conditions. We focus on polycyclic aromatic hydrocarbons (PAHs), their photoproducts, and their similarities to molecules seen in living systems today. We note that these kinds of compounds are seen in meteorites and we propose an explanation for both their formation and their observed deuterium enrichments.

1. Introduction

Comets, meteorites, and dust particles fell in profusion on early Earth and these extraterrestrial objects are replete with complex organic molecules, which may have played a role in the origin and evolution of life. Perhaps the most abundant class of complex carbon containing compounds found in extraterrestrial objects are polycyclic aromatic hydrocarbons (PAHs) and, as we shall see, the photoproducts of PAHs are very similar to molecules that are important in living systems today.

PAHs are known to be ubiquitous in the ISM, perhaps accounting for 20% of the cosmic carbon, (Dwek *et al.* 1997; Allamandola *et al.* 1999) because their spectral features are observed emitting from planetary nebulae, reflection nebulae, HII regions, and the diffuse interstellar medium (Allamandola *et al.* 1989; Schutte *et al.* 1998). They have also been observed in absorption toward protostellar objects embedded in dense interstellar molecular clouds (Smith *et al.* 1989; Sellgren *et al.* 1995). The PAHs seen in absorption in dense clouds are presumably frozen into icy grains mantles because at the temperatures characteristic of these clouds (10-50 K) the PAHs should condense (Sandford & Allamandola 1993). Ices in these clouds are processed, in part, by UV photons, even in the densest regions (Prasad & Tarafdar 1983), and our studies of the photoproducts have been the subject of recent papers (Bernstein *et al.* 1999a, 2000).

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In the first paper we showed that the UV photolysis of coronene in low-temperature H₂O ices produces ketones, ethers, alcohols, and partially reduced aromatics known as H_n-PAHs (Fig. 1, Bernstein *et al.* 1999a). More recently we have shown that the H atoms on the PAHs can be replaced by D atoms as a result of irradiation in D₂O-rich ices (Bernstein *et al.* 2000). These results are very interesting because H atoms on PAHs are not considered to be labile, and PAHs represent a major carrier of D excesses in primitive meteorites (Keridge *et al.* 1987). Thus, the photolysis of PAHs in interstellar ices may provide an explanation for the aromatics observed in meteorites and their deuterium enrichment.

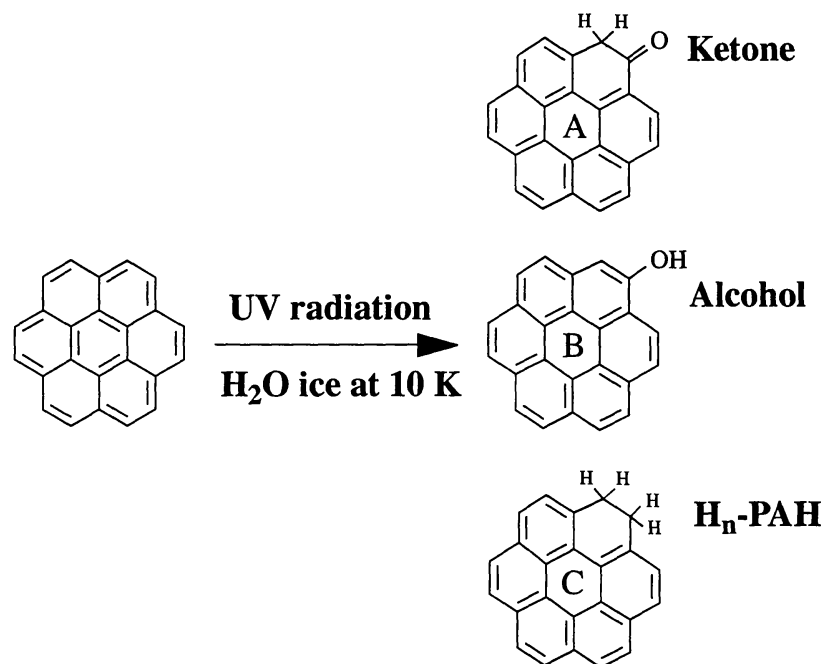


Figure 1. New molecular structures produced by the UV irradiation of coronene-H₂O ice samples. Oxygen atoms add to edge carbons to form ketone and alcohol side groups and the addition of H atoms yield aliphatic edge structures (H_n-PAHs). When bay regions are present, bridging ethers may also form (not shown, see Bernstein *et al.* 1999a). The locations of the functional groups have been selected arbitrarily.

2. Results

2.1. Atom Addition

Figure 2 presents the μ L2MS spectra (a two step laser desorption mass spectrometry technique) of coronene (C₂₄H₁₂), and that of the nonvolatile residues resulting from the 10 minute UV irradiation per layer of C₂₄H₁₂ in H₂O and D₂O ices at \sim 15K. The large peak that appears in all three spectra near 300 amu arises from unreacted coronene. The small peaks near 301 and 302 amu in

the spectrum of the standard (Fig. 2c), are caused by the natural abundance of the ^{13}C isotopes in coronene, which also contribute to these peaks in the other two spectra. The peaks at 316, 332, and 348 amu in the spectra of the UV irradiated coronene- H_2O and coronene- D_2O ices correspond to the addition of one, two, and three oxygen atoms, respectively, to the starting material. In Figure 2b the smaller peaks at 318 and 334 amu correspond to the addition of two H atoms to the mono- and di-oxidized coronenes at 316 and 332 amu, respectively.

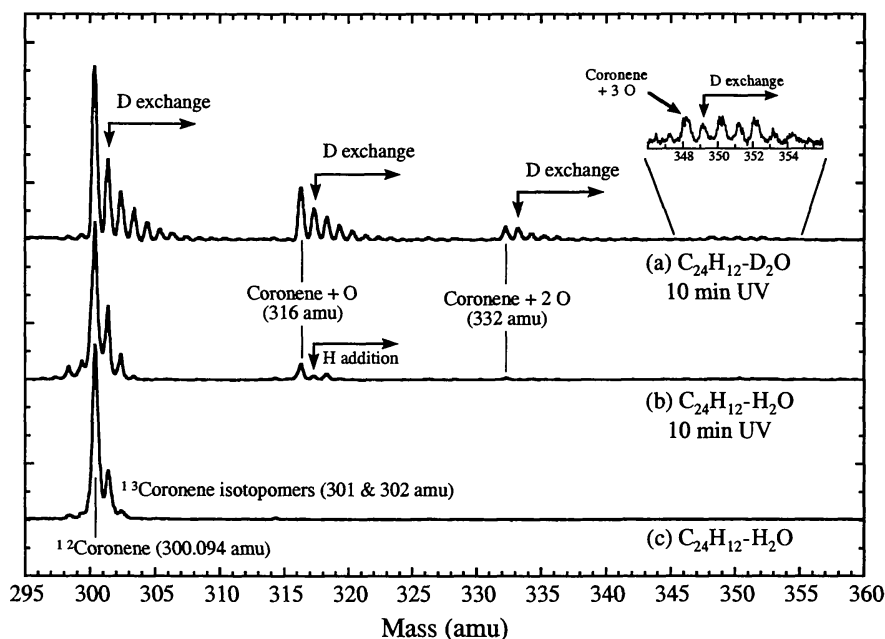


Figure 2. The $\mu\text{L}2\text{MS}$ spectra of (a) a room temperature residue from 10 min per layer UV irradiations of five layers of coronene ($\text{C}_{24}\text{H}_{12}$, 300 amu) in D_2O at $\sim 15\text{K}$, compared with (b) a room temperature residue made using 10 min per layer UV irradiations of five layers of coronene in H_2O at $\sim 15\text{K}$, and (c) a coronene standard deposited into H_2O at $\sim 15\text{K}$, and warmed to room temperature but not photolyzed. Each layer was deposited for ~ 30 minutes. The radiation causes oxidation of the coronene as well as some H-atom addition. The top spectrum also shows that UV photolysis also drives rapid H/D exchange between the water matrix and both coronene and its photoproducts.

2.2. Deuterium Exchange

In the mass spectrum of the UV-irradiated coronene- D_2O mixture in Fig. 2a, the peaks at 300, 316, 332, and 348 amu (coronene and coronene plus 1, 2, and 3 oxygens, respectively) are each followed by a series of peaks decreasing in intensity with increasing mass over the 301-312, 317-328, 333-344, and 349-354 amu mass ranges. These series provide clear evidence for the UV-mediated exchange of D atoms from the D_2O ice matrix for H atoms on the coronene and its photoproducts. After only 10 minutes of photolysis a majority of the oxidized coronenes have exchanged at least one H atom for a D atom from the

D₂O ice. During this exposure period even the unoxidized coronene starting material has become appreciably deuterated (as is demonstrated by the series of peaks decreasing in intensity with increasing mass over the 301-312 amu range in Fig. 2a). This exchange of H for D, represented schematically in Figure 3a, was somewhat unexpected. Aromatic C-H bonds are normally not labile, even at much higher temperature.

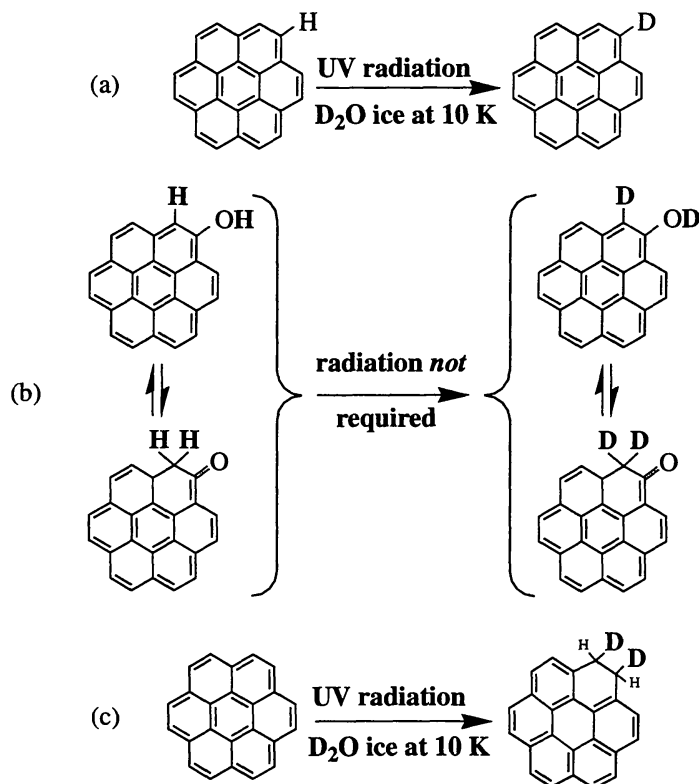


Figure 3. Several coronene photo-reactions that lead to deuterium enrichment. (a) The exchange of fully aromatic C-H bonds requires UV radiation and do not occur in its absence. (b) Hydrogen exchange via keto-enol tautomerism. Only the H atoms on carbon atoms next to a C=O and next to or on a C-OH group are subject to this exchange mechanism. This exchange mechanism can occur even in the absence of UV radiation (such as during aqueous alteration). (c) The UV stimulated addition of D atoms across a double bond to yield an aliphatic ring. This deuterium, once added, is not labile under aqueous alteration.

2.3. Coronene Oxidation Enhances H/D Exchange

The different mass patterns produced by the deuterated species with and without added oxygen (Figs. 2 and 3) indicate that the extent of exchange of H and D between the coronene and the ice matrix is greater for oxidized coronene than it is for unoxidized coronene. This enhanced exchange is not surprising since oxidized PAHs have an additional means of deuterium exchange not available

to unoxidized PAHs. Both unoxidized and oxidized PAHs can directly exchange their aromatic hydrogen/deuterium atoms with the surrounding matrix (§2.2 and Fig. 3a) but aromatic molecules bearing oxygen atoms have an additional way to exchange those H atoms that reside on the same aromatic rings as the oxygen. This involves keto-enol tautomerism, the process that inter-converts the alcohol and ketone forms (Hart 1979, Fig. 3b). Because the two H atoms associated with the oxidized ring are labile, this second mechanism should cause H atoms on oxidized coronenes to exchange with D atoms from the ice far more rapidly than unoxidized coronene, just as is observed.

3. Astrophysical Implications

3.1. Interstellar Deuterium Levels and UV Fluxes

The extent to which interstellar PAHs deuterated in interstellar ices will depend on the concentration of deuterium in the ices and the UV fluences to which they are exposed. Recent measurements of the ratio of HDO to H₂O in interstellar ice grain mantles in three dense molecular clouds yielded D/H ratios ranging from 8×10^{-4} to 1×10^{-2} (Teixeira *et al.* 1999). This is consistent with models of fractionation during gas-grain reactions occurring on the surfaces of the ices (Tielens 1992), thus, both observation and theory suggest that D/H ratios of 10^{-3} – 10^{-2} are likely to be common in interstellar ice mantles. Our results indicate that photolysis of PAHs in interstellar ices leads to the PAHs becoming deuterium-enriched. We have demonstrated that H↔D exchange is rapid under experimental conditions analogous to those in the interstellar medium. Even brief exposures to UV radiation cause PAHs in ices to exchange measurable amounts of hydrogen. Thus, these processes could account for aromatics being deuterium-enriched to the level seen in the Murchison meteorite (D/H $\sim 10^{-4}$, Kerridge *et al.* 1987).

3.2. Relevance to Meteoritic Materials

If the photolysis of PAHs in ices is responsible for a significant fraction of the deuterium enrichments of the aromatics in meteorites, this work predicts that meteoritic aromatics will show characteristic patterns of deuteration that are consistent with our observations and differ from those predicted by other D-enrichment processes for PAHs. For example, whereas unimolecular photodissociation provides largest enrichments for PAHs in the 10-40 Carbon atom size range and diminish with increasing carbon number (Allamandola *et al.* 1989), photolysis of PAHs in ices probably would not. Instead, the degree of deuterium enrichment should correspond to reactivity, and hence molecular structure. If a size effect exists, it will probably favor larger PAHs, inasmuch as larger PAHs tend to ionize more easily or better stabilize ion intermediates.

Furthermore, D enrichment of PAHs by photolysis in ice should put deuterium atoms in locations that correlate with the photo-reactions that have occurred. Specifically, replacement of the H atom on an aromatic C-H with a D atom from the ice (§2.1 and Fig. 3a) results in a partially deuterated PAH, but the structure remains unchanged. Such plain aromatic C-H or C-D bonds will survive subsequent non-radiative processes such as dissolution in liquid water, as

opposed to D atoms that are on an alcohol or are adjacent to either an aromatic alcohol or a ketone (§2.2 and Fig. 3b) that are acquired more rapidly but could be reset during subsequent aqueous alteration, such as is believed to have occurred on the parent bodies of many meteorites, including the CM carbonaceous chondrite Murchison (Zolensky & McSween 1988 for a review). Finally, the rate of D-atom addition to coronene (§2.1 and Fig. 3c) is slower than the exchange processes but results in deuterated (cyclic) aliphatic domains, groups (-CH₂-, -CD₂-) with concomitant loss of aromaticity in that ring. These C-H and C-D bonds are not labile and are chemically distinct from the others.

The presence of PAHs, oxidized PAHs, and Hn-PAHs in carbonaceous chondrites (Cronin & Chang 1993) is qualitatively consistent with photo-processing of aromatics in ice grains. The further observation that the aromatic materials in these meteorites are enriched in deuterium (Kerridge *et al.* 1987) is compatible with deuteration driven by PAH photolysis in D-enriched ices. We predict that if this process is really responsible for the deuterium enrichments of a significant portion of the aromatic compounds in meteorites, then the abundance of aromatic deuterium should show some dependence on the structure of aromatics and their chemical side groups.

As with the level of deuterium in the ice, the PAH for this study was chosen to be practical as well as germane to astrochemistry. All the C-H bonds of coronene are equivalent, so a reaction occurring on one is equivalent to any other, removing confusion arising from structural isomers for the product molecules (seen in Fig. 3) and thereby making analysis more straightforward. Understanding how deuteration depends on PAH structure will require similar experiments on additional PAHs that sample a range of molecular sizes and structures. Studies using other PAHs are underway.

4. Bio(Astronomical) Implications

These oxidized PAHs that are formed in our experiments are not just meteoritic curiosities, they are also common in living systems and have biochemical activity. For example, Aloe, an anti-inflammatory natural product often added to skin cream, is basically an oxidized anthracene (Fig. 4a). The active ingredient in St. John's Wort (an over the counter anti-depressant), Hypericin, is essentially an oxidized Bisanthene (Fig. 4b). Such a structural similarity between meteoritic and biological molecules would be completely meaningless if it were limited to a few rare contemporary organisms, but there are hints that perhaps there is more to it than this.

Naphthalene, which has been seen in meteorites, produces naphthaquinone (oxidized naphthalenes bearing two ketones) in our ice experiments. Naphthaquinones such as menaquinone (Fig. 4c) play essential roles in the biochemistry of all living things; they form the basis of the K vitamins which even in "primitive" organisms (such as archaea) perform key biochemistry. Menaquinone often augments or replaces ubiquinone or plastoquinone as electron transport and oxidative phosphorylation co-enzymes. For example, *Thermoproteus tenax* use menaquinones to reduce elemental sulfur to H₂S.

Perhaps the similarity between oxidized PAHs in meteorites and our biochemistry is not a coincidence. One could imagine a scenario by which PAHs

would have been incorporated into the biochemistry of the first organisms. PAHs strongly absorb UV radiation so they may have acted as UV shields on early Earth, back before there was an ozone layer, and organisms that incorporated PAHs from the environment may have enjoyed some protection as a result. Once present in the membrane such aromatic quinones, with the capacity to both absorb UV-visible light and having stable radical forms might have then begun to perform some kind of primitive proton pumping or electron transport. Thus aromatics may have been the first molecules that our ancestors used to harness light energy (Bernstein *et al.* 1999b). We hasten to add that we are talking about an organism *before* the last common ancestor, and it is not clear that this conjecture could be tested by examining modern biochemistry. Nevertheless, we note that the structural similarity is not obviously an artifact of modern biochemistry and thus certain extraterrestrial molecules may have been more than a source of reduced carbon to be altered by terrestrial processes but were directly involved in the development of terrestrial biochemistry.

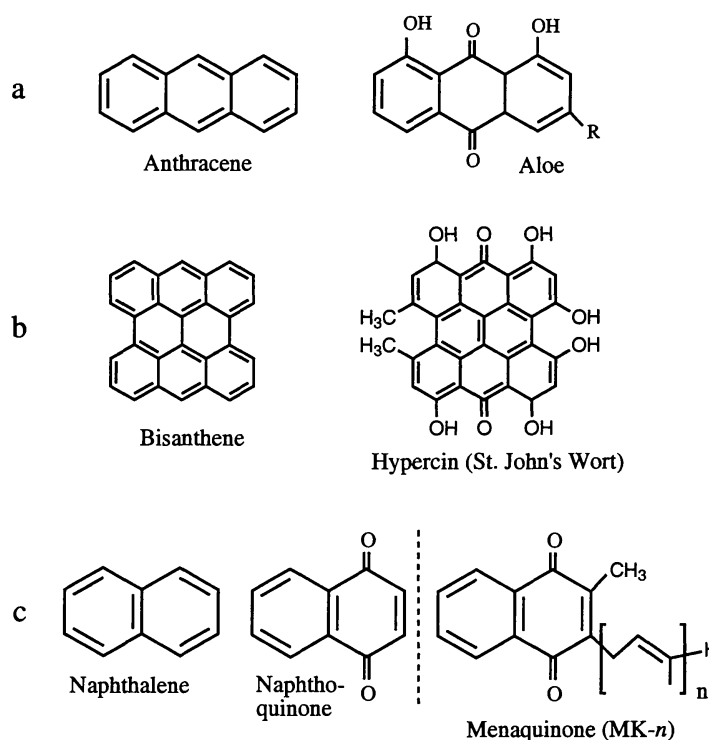


Figure 4. Comparison between several polycyclic aromatic hydrocarbons and natural products that are essentially oxidized versions of the same molecules.

5. Conclusions

PAHs rapidly become oxidized when UV irradiated in water ices under conditions mimicking those in dense interstellar clouds. The molecules that result include aromatic alcohols, ketones, ethers, and Hn-PAHs. We suggest that the source of these molecules (and their deuterium enrichments) in meteorites is in-

terstellar ice photochemistry. Such molecules are also seen in comet and asteroid dust and thus were probably delivered to early Earth in abundance. Given that these kinds of molecules play crucial roles in living systems today, perhaps they were involved in the origin or evolution of life on this planet.

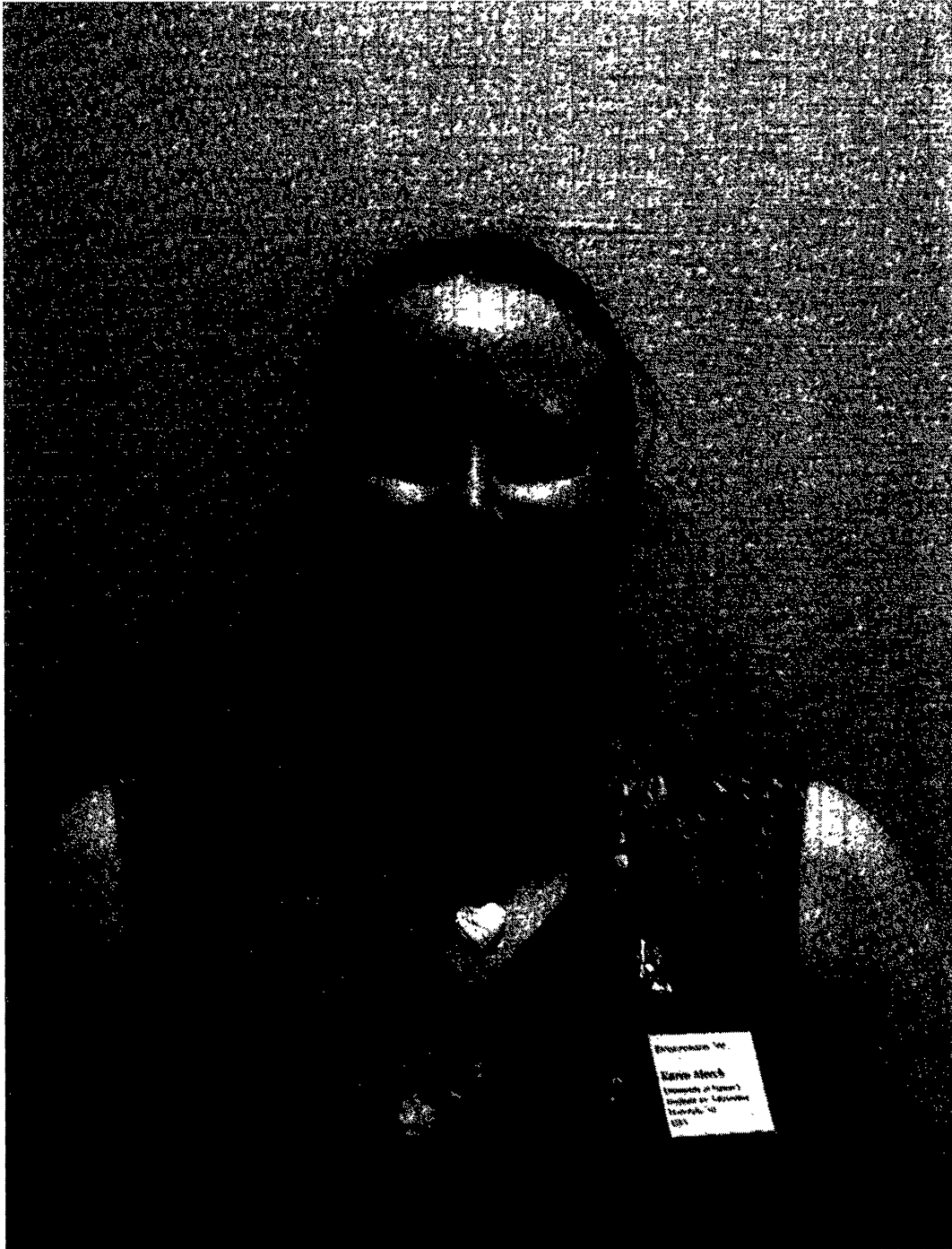
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References

- Allamandola, L. J., Tielens, A. G. G. M., & Barker, J. R. 1989, *ApJ Supp. S.*, **71**, 733
- Allamandola, L. J., Hudgins, D. M., & Sandford, S. A. 1999, *ApJ*, **511**, L115
- Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Gillette, J. S., Clemett, S. J., & Zare, R. N. 1999a, *Science*, **283**, 1135
- Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. 1999b, *Scientific American*, **281**, 42
- Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. L. J., Gillette, J. S., Clemett, S. J., & Zare, R. N. 2000, *ApJ*, in press
- Cronin, J. R., & Chang, S. 1993, in *Chemistry of Life's Origins (NATO ASI)*, ed., J. M. Greenberg, V. Pirronello, & C. Mendoza-Gomez, (Kluwer: Dordrecht), p. 209
- Dwek, E. *et al.* 1997, *ApJ*, **475**, 565
- Hart, H. 1979, *Chem. Rev.*, **79**, 515
- Kerridge, J. F., Chang, S., & Shipp, R. 1987, *Geochim. Cosmochim. Acta*, **51**, 2527
- Prasad, S. S., & Tarafdar, S. P. 1983, *ApJ*, **267**, 603
- Sandford, S. A., & Allamandola, L. J. 1993, *ApJ*, **417**, 815
- Schutte, W. A., *et al.* 1998, *Astron. Astrophys.*, **337**, 261
- Sellgren, K., Brooke, T. Y., Smith, R. G., & Geballe, T. R. 1995, *ApJ*, **449**, L69
- Smith, R. G., Sellgren, K., & Tokunaga, A. T. 1989, *ApJ*, **344**, 413
- Teixeira, T. C., Devlin, J. P., Buch, V., & Emerson, J. P. 1999, *Astron. Astrophys.*, **347**, L19
- Tielens, A. G. G. M. 1992, in *Astrochemistry of Cosmic Phenomena*, ed., P. D. Singh, Kluwer: Dordrecht, p. 91
- Zolensky, M., & McSween, H. Y., Jr. 1988, in *Meteorites and the Early Solar System*, ed., J. F. Kerridge & M. S. Matthews, Univ. Ariz. Press: Tucson, p. 114



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