Assessment of the interstellar processes leading to deuterium enrichment in meteoritic organics

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Abstract–The presence of isotopic anomalies is the most unequivocal demonstration that meteoritic material contains circumstellar or interstellar components. In the case of organic compounds in meteorites and interplanetary dust particles (IDPs), the most useful isotopic tracer has been deuterium (D). We discuss four processes that are expected to lead to D enrichment in interstellar materials and describe how their unique characteristics can be used to assess their relative importance for the organics in meteorites. These enrichment processes are low-temperature gas phase ion-molecule reactions, low-temperature gas-grain reactions, gas phase unimolecular photodissociation, and ultraviolet photolysis in D-enriched ice mantles. Each of these processes is expected to be associated with distinct regiochemical signatures (D placement on the product molecules, correlation with specific chemical functionalities, *etc.*), especially in the molecular population of polycyclic aromatic hydrocarbons (PAHs). We describe these differences and discuss how they may be used to delineate the various interstellar processes that may have contributed to meteoritic D enrichments. We also briefly discuss how these processes may affect the isotopic distributions in C, O, and N in the same compounds.

INTRODUCTION

Isotopic measurements provide definitive evidence for presolar materials within meteoritic samples, including those from both *circumstellar* and *interstellar* environments. The presence of *circumstellar* materials in meteorites is demonstrated by isotopic anomalies measured in a variety of different types of presolar materials (*e.g.*, nanodiamonds, Al_2O_3, graphite, SiC, *etc.*) (cf., Zinner, 1988, 1997). The carriers of these isotopic anomalies are generally believed to have formed in circumstellar ejecta and the anomalies are thought to be of nucleosynthetic origin (Bernatowicz and Zinner, 1997). Indeed, the measurement of isotopic ratios and their correlations in multiple elements is advancing our understanding the details of nucleosynthesis in a number of different stellar environments (cf., Gallino *et al.*, 1997).

The existence of *interstellar* materials in meteoritic samples is also indicated by isotopic evidence, although its nature is significantly different. In this case, the isotopic anomalies are primarily in the form of deuterium (D) enrichments (Robert and Epstein, 1982; Yang and Epstein, 1983; Kerridge and Chang, 1985; Kerridge *et al.*, 1987), although smaller effects have also been seen in nitrogen (Robert and Epstein, 1982; Franchi *et al.*, 1986; Sugiura and Zashu, 1995). In some cases

these enrichments are seen in bulk meteoritic materials (Zinner, 1988), but D enrichments have also been observed in meteoritic subfractions and even within specific classes of molecular species, such as amino and carboxylic acids (Epstein *et al.*, 1987; Pizzarello *et al.*, 1991; Krishnamurthy *et al.*, 1992). These anomalies are not thought to be the result of nucleosynthetic processes, but are instead ascribed to chemical processes occurring in the interstellar medium.

The traditional explanation of these D excesses has been to invoke the presence of materials made in the interstellar medium by low-temperature gas phase ion-molecule reactions (Geiss and Reeves, 1981; Dalgarno and Lepp, 1984). The D/H ratios seen in the simple interstellar molecules amenable to measurement using radio spectral techniques are generally considerably higher than the values seen in enriched solar system materials (Robert *et al.*, 2000). However, the true difference in D/H ratios is obscured by several effects. First, current observations of D enrichment in the interstellar medium have been made of only a few simple molecules and these molecules are not the main carriers of D in solar system materials. Second, some of the interstellar D enrichment is likely to reside on labile moieties that will have exchanged to some degree with more isotopically normal material during incorporation into the warm protosolar nebula, parent body

processing, delivery, recovery, and analysis. Third, ion-molecule reactions represent only one of several processes that can produce strong D-H fractionation in the interstellar medium.

We will discuss four chemical mechanisms that are expected to generate D-H fractionation in the interstellar medium: (1) low-temperature gas phase ion-molecule reactions, (2) low-temperature gas-grain reactions, (3) gas phase unimolecular photodissociation, and (4) ultraviolet photolysis in D-enriched ice mantles. Each process is discussed in two parts: first, we describe the basic chemical process and how it leads to "generic" molecular D fractionation, and second, we describe how the fractionation process manifests itself in the specific case of polycyclic aromatic hydrocarbons (PAHs). In addition, we will describe the relative exchangeability of the D on different chemical species since the more labile portions of the D signature can be modified or erased by exchange after enrichment but prior to conclusion of analysis.

We chose to highlight PAHs for four reasons. First, PAHs are probably the most abundant and widespread class of organic compounds in the universe (Puget and Leger, 1989; Allamandola *et al.*, 1989, 1999). They are observed in the gas phase in a wide variety of interstellar environments, including proto-planetary and planetary nebulae, reflection nebulae, H II regions, the diffuse interstellar medium, ices in dense molecular clouds, and in carbonaceous grains in the diffuse interstellar medium (Allamandola *et al.*, 1989, 1999; Sandford *et al.*, 1991; Sellgren *et al.*, 1995; Brooke *et al.*, 1996, 1999; Onaka *et al.*, 1996; Roelfsema *et al.*, 1996; Chiar *et al.*, 2000; Bregman *et al.*, 2000; Ehrenfreund and Charnley, 2000). Second, PAHs are extremely stable molecules and represent one of the few classes of materials that can exist and survive in all the interstellar environments associated with the four chemical processes listed above. Third, PAHs and related aromatic materials are common in carbonaceous chondrites (Cronin *et al.*, 1988; Hahn *et al.*, 1988; Cronin and Chang, 1993; Gardinier *et al.*, 2000; Cody *et al.*, 2001, and references therein) and interplanetary dust particles (IDPs) (Allamandola *et al.*, 1987; Clemett *et al.*, 1993), and have been reported in the comae of comet P/Halley (Moreels *et al.*, 1994). Fourth, the aromatic fractions of meteorites are known to be significant carriers of D (Kerridge and Chang, 1985). Thus, aromatic molecules represent a known link between the interstellar medium and solar system samples and could potentially serve as probes of the chemical processes associated with interstellar D fractionation.

INTERSTELLAR CHEMICAL PROCESSES AND DEUTERIUM ENRICHMENT

We will consider the processes by which interstellar molecules, including PAHs, can become D-enriched, including gas phase ion-molecule reactions at low temperatures (Dalgarno and Lepp, 1984; Tielens, 1997), gas-grain reactions (Tielens, 1983, 1992, 1997), unimolecular photodissociation (Allamandola *et al.*, 1987, 1989), and UV photolysis in D-enriched ice grains

(Sandford *et al.*, 2000). Each of these processes is expected to leave a distinct signature in the distribution of D enrichment in the PAH population.

Low-Temperature Gas Phase Ion-Molecule Reactions

The Chemical Process–Deuterium fractionation by ion-molecule reactions is perhaps the longest and best known process for the enrichment of interstellar species, and it is not surprising that it is often invoked to account for the D enrichments seen in meteoritic materials (cf., Geiss and Reeves, 1981). It is generally assumed that the fractionation occurred in the interstellar medium rather than in the solar nebula, because this effect falls off rapidly with increasing temperature. The temperatures and timescales associated with inner protosolar disks are not expected to allow significant fractionation to occur, although fractionation could potentially occur in their outer regions (Aikawa and Herbst, 1999).

Chemical reactions between *neutral* gas phase species that are endothermic or possess significant activation barriers will not proceed at any appreciable rate at the low temperatures characteristic of dense clouds ($T < 50$ K). However, exothermic ion-molecule reactions can proceed even at very low temperatures (cf., Herbst, 1987; Tielens, 1997). Thus, most of the *gas phase* chemistry occurring in dense clouds is the result of ion-molecule reactions and exoergic reactions involving radicals.

Such reactions are expected to produce mass fractionation at low temperatures due to the different zero-point energies of H and D, deuterium having a lower energy and hence the potential to form slightly stronger chemical bonds (Dalgarno and Lepp, 1984; Tielens, 1997; Millar *et al.*, 2000). This results in the two having exchange rates that differ by a factor of $\exp(-\Delta E/T)$, where ΔE is the energy difference and T is the temperature. At higher temperatures the difference in energies is proportionally less important and fractionation is a minor effect, but as the gas temperature drops below ~70 K, fractionation becomes increasingly more significant (*e.g.*, Millar *et al.*, 1989).

There is good observational evidence that such fractionation occurs in the interstellar medium. Radio telescopic observations of the rotational lines of several simple molecules and their deuterated counterparts in dense clouds demonstrate that these species are often highly D-enriched; enrichments exceeding a factor of 5000 above the cosmic value of HD/H$_2 \approx 3 \times 10^{-5}$ have been reported (Jefferts *et al.*, 1973; Hollis *et al.*, 1976; Mauersberger *et al.*, 1988). However, this process only operates on molecules in the gas phase, and the majority of species are condensed onto grains at the low temperatures where fractionation is significant. Thus, while ion-molecule reactions clearly contribute to D fractionation in the interstellar medium, they may not be the main contributor to the bulk fractionation of D in dense clouds.

Polycyclic Aromatic Hydrocarbon Regiochemistry–Like smaller molecules, gas phase PAHs should become enriched

in D by ion-molecule reactions in dense molecular clouds. The principle reaction path involves a two-step process (Tielens, 1997) (Fig. 1 shows the case for the PAH pyrene). First, a PAH reacts with an H_2D^+ ion to pick up an extra D atom and charge.

$$PAH + H_2D^+ \rightarrow PAH\text{-}D^+ + H_2$$
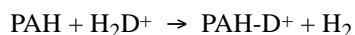
Subsequent reaction with an electron neutralizes the charge and the PAH eliminates an excess H or D atom. The fraction in which an H is lost, as opposed to a D, can be described by a branching ratio, α_H.

$$PAH\text{-}D^+ + e^- \rightarrow \alpha_H(PAH\text{-}D) + H \text{ and } (1 - \alpha_H)PAH + D$$
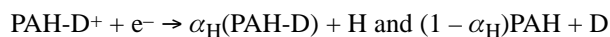
The branching ratio, α_H, is largely determined by statistics (Millar *et al.*, 1989; S. Charnley, pers. comm.) modified by the difference in the H and D zero-point energies. A lower limit to the D-enrichment can be derived easily by ignoring the effect of the zero-point energy difference and simply assuming that every H or D on the molecule has the same chance of being ejected. Thus, this process would be expected to initially preferentially deuterate the *larger* PAHs in dense clouds since they have more H atoms and will lose a higher fraction of H relative to D. Ultimately, all PAHs in the gas phase would be expected to show increasing D/H ratios as they approach steady-state equilibrium with the H in the gas phase. In this manner, over the lifetime of a dense cloud core (~3 × 10^6 years, $n_H = 3 \times 10^4$ cm^-3), individual PAHs have a high probability of acquiring peripheral D atoms. Since PAHs are considerably more stable and more abundant in the interstellar medium than many of the smaller species that show D enrichments (PAH/H_2 ~ 10^-6 compared
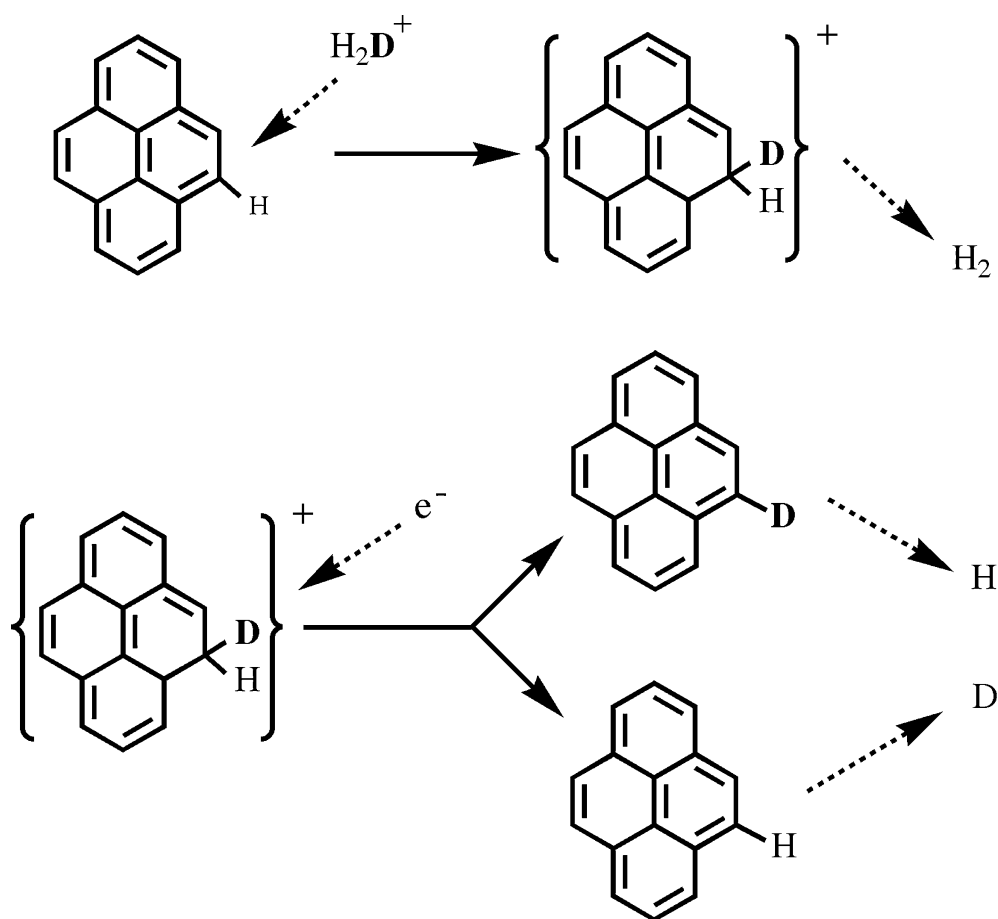

FIG. 1. PAHs become enriched in D *via* gas phase ion-molecule reactions in a two-step process (shown here for the PAH pyrene). First, a PAH reacts with an H_2D^+ ion to pick up an excess D atom and charge. Subsequently, reaction with an electron neutralizes the charge and the PAH eliminates an excess H or D atom. This process should initially preferentially deuterate *larger* PAHs in dense clouds, but ultimately, all PAHs in the gas phase would be expected to become D enriched as they approach steady-state equilibrium with the gas phase.

to $HCN/H_2 \sim 10^{-8}$), PAHs are likely to represent the largest reservoir of materials D-enriched by ion-molecule reactions.

Low-Temperature Gas-Grain Reactions

The Chemical Process–At the temperatures characteristic of dense clouds ($T < 50$ K) most of the volatile species in dense clouds are condensed out of the gas phase into icy grain mantles (Sandford and Allamandola, 1993). Evidence for this condensation is found in the large quantities of mixed-molecular ices (Sandford, 1996) and gas phase depletions (Mauersberger *et al.*, 1992) seen in dense clouds. The composition of the ice mantles does not simply reflect gas phase abundances, however. Instead, additional species are formed when condensing species participate in gas-grain reactions on the grain surfaces, reactions that cannot occur solely in the gas phase (Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985; Brown and Charnley, 1990; Hasegawa *et al.*, 1992). The compositions of these new species are strongly dependent on the local H/H_2 ratio. In environments where H/H_2 is large, surface reactions with H atoms dominate and atoms like C, N, and O are likely to be converted to species like CH_4, NH_3, and H_2O. In contrast, if H/H_2 is less than one, reactive species such as O and N could react with one another to form O_2 and N_2. Thus, two different types of ice mantles can be produced by grain surface reactions: one dominated by polar, H-bonded molecules and the other dominated by less polar, highly unsaturated molecules. Infrared spectral observations of dense clouds confirm this basic dichotomy (Sandford *et al.*, 1988; Tielens *et al.*, 1991; Chiar *et al.*, 1995).

Gas-grain chemistry should produce large D enrichments in the grain mantles as the result of mass fractionation that becomes important at low temperatures (Tielens, 1992, 1997). In this case, except for H-abstraction reactions, the role of the zero-point energy difference between H and D counterparts in creating D fractionation is limited (Tielens, 1983). Instead, D enrichment results primarily from the high atomic D fractionation of the accreting gas. Both the atomic H and D accreted onto grain surfaces are light enough to tunnel through activation barriers on interstellar time scales and thereby hydrogenate species that are not fully reduced. Models indicate that such a process could result in mantle D/H ratios as high as 0.1 for simple molecules like H_2O and CH_3OH (Tielens, 1983, 1992, 1997; Charnley *et al.*, 1997). Values in this range have been reported for HDO/H_2O in interstellar ices (Teixeira *et al.*, 1999). Such values meet or exceed the enrichments produced by ion-molecule reactions in gas phase species like C_3HD/C_3H_2 and DCO^+/HCO^+. Since the grain mantles in dense clouds represent a much larger fraction of the total reservoir of material than does material in the gas phase (H_2 excepted), grain surface processes are likely to be far more important for the total D fractionation in dense clouds than ion-molecule reactions.

Polycyclic Aromatic Hydrocarbon Regiochemistry–D fractionation during gas-grain reactions should only proceed efficiently for molecules that can be hydrogenated. Fully reduced species will not accept additional D in this fashion and simple exchange is unlikely under these low-temperature conditions. Whether PAHs can become D-enriched by this process is unclear. There is currently no laboratory evidence suggesting simple H atom exposure on grain surfaces leads to the excess hydrogenation of PAHs.

It is possible, *with energetic processing*, for PAHs with fully aromatic bonding to accommodate additional peripheral H atoms (Bernstein *et al.*, 1999). The effect of these excess H atoms in these molecules, which are collectively termed H_n-PAHs, is to convert the effected C atoms from aromatic (sp^2) bonding to aliphatic (sp^3) bonding (see Fig. 2). This results in molecules that contain both aromatic and aliphatic rings. In the extreme case when the maximum possible number of H atoms have been added, the result is a polycyclic *aliphatic* hydrocarbon. There is some evidence for the existence of H_n-PAHs in space (Bernstein *et al.*, 1996). In particular, their presence may explain a number of enigmatic weak infrared emission features seen in the outflows of aging stars (protoplanetary and planetary nebulae), but the environmental conditions in these objects are very different from the conditions pertinent for low-temperature gas-grain reactions.

Since there is currently no good theoretical rationale or experimental evidence that suggests PAHs can be hydrogenated to form H_n-PAHs by simple gas-grain interactions, it is likely that PAHs do not accumulate significant H atom excesses, and thus D enrichments, by gas-grain reactions. Thus, while gas-grain reactions may dominate the mass distribution of D in dense clouds, it may leave PAHs largely unaffected. To the extent that this process occurs to PAHs, any D enrichments generated would be expected to correlate with the presence of H_n-PAHs, increasing H/C ratio, or aliphatic structures.

Unimolecular Photodissociation Reactions

In contrast to ion-molecule and gas-grain reaction processes, D enrichment by unimolecular photodissociation does not require low temperatures and is expected to be restricted *solely* to PAHs (Allamandola *et al.*, 1987, 1989; Tielens, 1997). Because of their multiple C bonding and π electrons, PAHs are much more stable against photolytic disruption than most other molecules. This allows PAHs to survive in environments where other species would quickly be reduced to fragments. This is one of the chief reasons why PAHs are one of the most ubiquitously and abundantly distributed classes of molecules in the interstellar medium (cf., Allamandola *et al.*, 1989; Roelfsema *et al.*, 1996).

While PAHs are relatively immune to *complete* photodestruction by interstellar UV photons, individual PAHs may still absorb UV photons that contain more energy than they can accommodate vibrationally. In this case, a bond or bonds will break. The most likely bond to break is that of a peripheral C–H, and because of the zero-point energy difference of the C–D and C–H bonds, the rate of D loss from interstellar
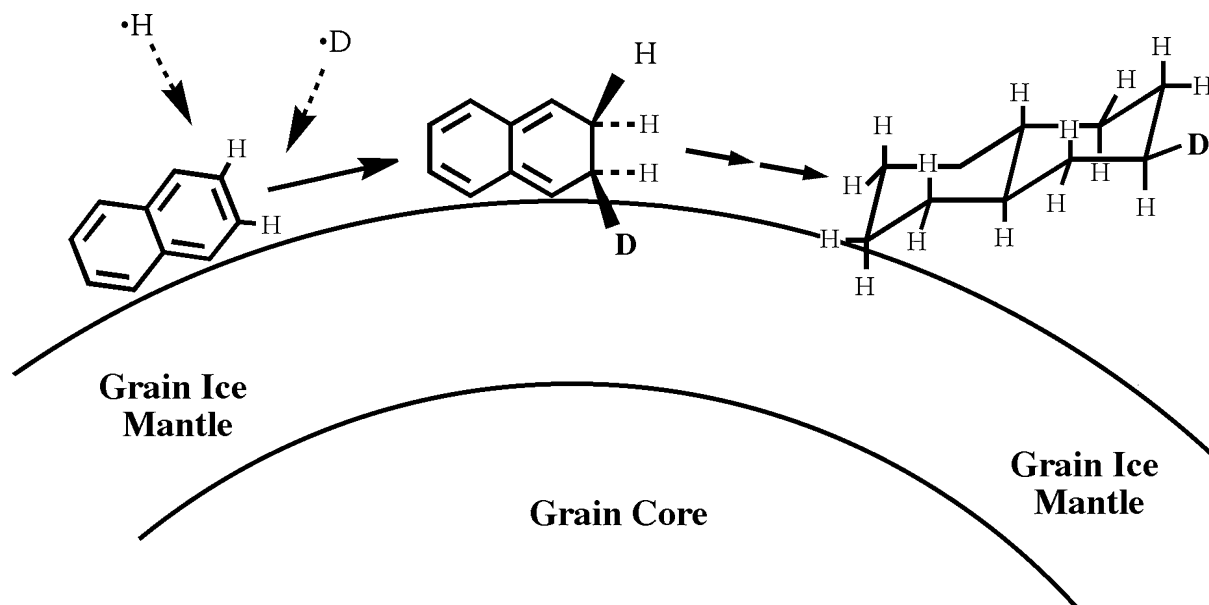
FIG. 2. In dense clouds where H/H_2 is large, gas-grain reactions primarily serve to hydrogenate, and D-enrich, species in the ice. It is not clear if PAHs can be hydrogenated in this manner, but to the extent that this process occurs, any D enrichments generated would be expected to correlate with the presence of H_n-PAHs and cyclic aliphatics.

PAHs should be lower than that of H (Fig. 3). Since *both* H and D will return to this molecular site from the gas phase, repeated processing should gradually enrich interstellar PAHs in D relative to the ambient gas. At steady-state equilibrium, which is expected to be reached in photodissociation regions and, at least for small PAHs, in dense clouds, the fraction of peripheral D relative to H will be 3× the local gas phase ratio of D to H, which can range from 10^{-5} to 10^{-3} (Allamandola *et al.*, 1989; Tielens, 1997). Thus, in these interstellar environments, many PAHs having less than ~25 C atoms should have peripheral D atoms.

This process differs from enrichment by ion-molecule and gas-grain reactions in two ways. First, low ambient temperatures are *not* required to produce fractionations by this process. Second, the extent of the D enrichment depends critically on the size of the PAH. The D photoenrichment of PAHs is expected to be most significant for PAHs in the range of sizes spanned by $C_{10}H_8$ (naphthalene) and $C_{42}H_{18}$ (hexabenzocoronene). Deuterium enrichment is not expected in benzene because this molecule is not stable in the interstellar radiation field. Enrichment in PAHs having more than ~40 C atoms is not expected because these larger PAHs have large numbers of vibrational modes, can accommodate the maximum energy of typical UV photons, and are stable against photolytic bond cleavage (Fig. 3).

Ultraviolet Photolysis Reactions in D-Enriched Ice Mantles

The Chemical Process–Most of the volatile species in dense clouds reside in icy grain mantles. The dominant species

in these ices is usually H_2O, but they also contain CO, CO_2, CH_3OH, NH_3, H_2CO, CH_4, and a number of other simple species in abundances greater than 1% that of the H_2O (see Sandford, 1996). Many of these species should be significantly enriched in D, either by enrichment in the gas phase by ion-molecule reactions followed by condensation onto the grain mantle, or *via* gas-grain reactions occurring on the mantle surface. Once in the ice, these molecules can serve as a D-enriched reservoir from which other enriched species can be made.

One would normally expect few chemical reactions to occur within these ice mantles because of their very low temperatures. However, interstellar ices in dense clouds can be further modified by energetic processing by ambient UV radiation and cosmic rays (Norman and Silk, 1980; Prasad and Tarafdar, 1983). When these ices are irradiated, bonds are broken, molecules are destroyed, and new molecules, radicals, and ions are formed. Most of these new, reactive species remain trapped in the ice matrix. Ultimately their accumulation is interrupted by a thermal event (grain-grain collision, passage of a cosmic ray, exposure to a stellar system, *etc.*) that causes the ice to warm to the point at which molecules can become mobile, react, and form new and often more complex molecules. Thus, a host of species formed by the irradiation and thermal processing of ices made of simpler (D-enriched) molecules is expected to be present in dense interstellar clouds (Moore *et al.*, 1983; Agarwal *et al.*, 1985; Allamandola *et al.*, 1988; Bernstein *et al.*, 1995; Dworkin *et al.*, 2001) and infrared spectra of the ices in dense clouds provide evidence for this process (Tegler *et al.*, 1993; Pendleton *et al.*, 1999; Bernstein *et al.*, 2000).

Small PAHs become D-enriched
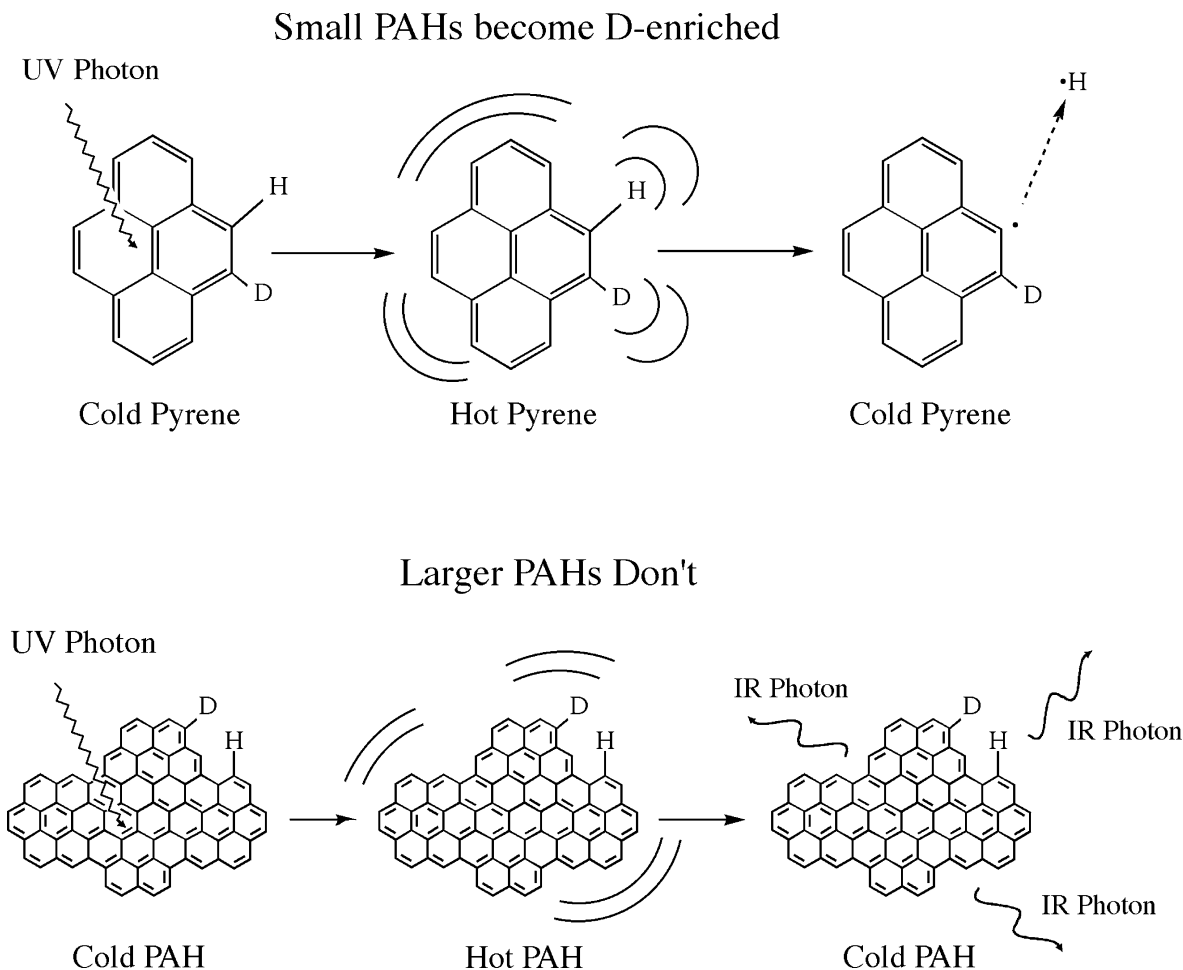

Larger PAHs Don't

FIG. 3. Gas phase PAHs can become enriched in D by repeated unimolecular photodissociation events that favor retention of D over H because of its lower zero-point energy. The extent of the D enrichment depends critically on the size of the PAH. The D photoenrichment of PAHs should be most significant for PAHs in the range of sizes spanned by naphthalene ($C_{10}H_8$) and hexabenzocoronene ($C_{42}H_{18}$). Enrichment in larger PAHs is not expected because they have large numbers of vibrational modes and are stable against photolytic bond rupture. Unlike other D fractionation processes, enrichment by unimolecular photodissociation does not require low ambient temperatures.

Laboratory studies of mixed-molecular ices in which some of the original species are D-enriched have shown that the D ends up in many of the reaction products (Bernstein *et al.*, 1994, 1995, 2000; Sandford *et al.*, 2000). Unlike the processes described above, this process does not *produce* a fractionation of H from D. Instead it *propagates* previous fractionations into new molecular species (*i.e.*, the "global" D/H ratio of the ice mantle remains fixed) but the D/H ratios in individual molecular families may be redistributed into other specific species. Thus, the irradiation of D-enriched interstellar ices produced by other processes will lead to the production of a host of more complex organic species that are also D-enriched.

Polycyclic Aromatic Hydrocarbon Regiochemistry–At the low temperatures of dense molecular clouds, PAHs will condense onto refractory dust grains along with most other gas-phase species. The presence of PAHs in these environments has been demonstrated by detection of their infrared vibrational bands in absorption in the spectra of stars embedded within dense clouds (Sellgren *et al.*, 1995; Brooke *et al.*, 1996, 1999; Chiar *et al.*, 2000; Bregman *et al.*, 2000). Once condensed into interstellar ice mantles, PAHs will be subjected to the same radiation processing as the other ice components. Laboratory irradiation simulations of PAH-bearing interstellar ice analogs have shown that under these conditions PAHs undergo both oxidation and reduction reactions that affect their edge structures (Bernstein *et al.*, 1999, 2001). Oxidation results in the production of aromatic alcohols, ketones, and, in PAHs with "bay" regions in their edge structures, bridging ethers, while reduction leads to the formation of H_n-PAHs (Fig. 4). Many of these aromatic species are very similar to some of those seen in carbonaceous chondrites and IDPs (see Bernstein *et al.*, 1999, 2001).

Laboratory studies of PAHs in D-enriched H_2O ices have shown that UV photolysis results in rapid D enrichment of the
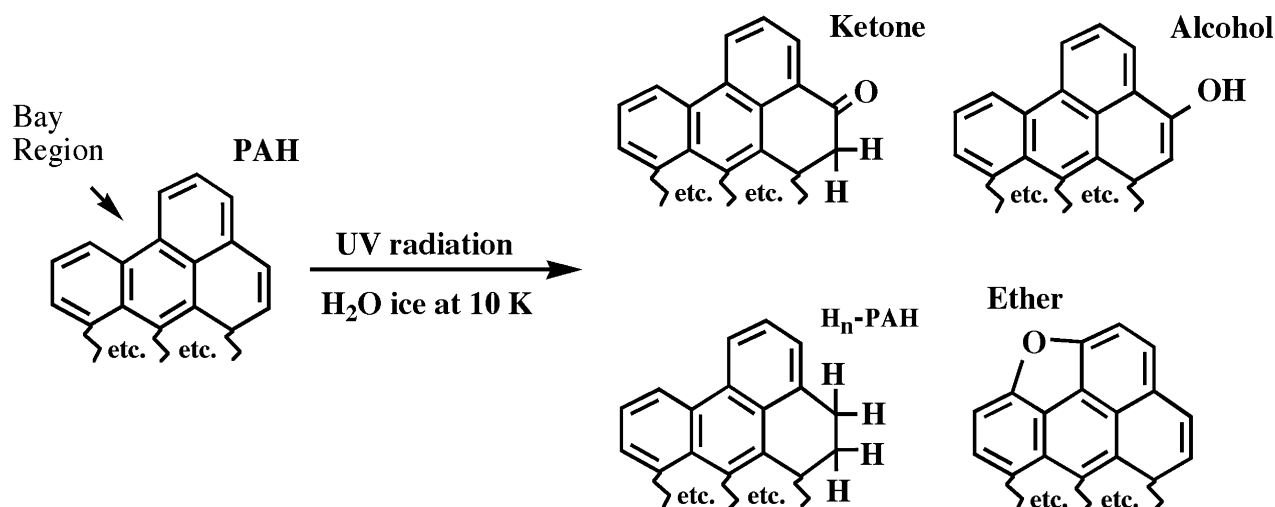
FIG. 4. PAHs undergo both oxidation and reduction reactions that affect their edge structures when they are irradiated in H_2O-rich ices. Oxidation results in the production of aromatic alcohols, ketones, and, in PAHs with "bay" regions in their edge structures, ethers. Reduction leads to the formation of H_n-PAHs, molecules having mixed aromatic and aliphatic rings.

PAHs through aromatic D→H exchange, D atom addition, and exchange through keto-enol tautomerism. Each of these processes produce different compounds with characteristic deuteration patterns and D labilities (Sandford *et al.*, 2000) (Fig. 5). For example, D→H exchange reactions result in D-enriched *PAHs* in which the D resides in relatively non-labile locations (Fig. 5a). D atom addition reactions result in D-enriched *H_n-PAHs* in which the D resides in relatively non-labile aliphatic rings attached to aromatic rings (Fig. 5b). In contrast, enrichment *via* keto-enol tautomeric exchange results in the D being located exclusively on rings that contain oxygen atoms in sites that are relatively labile (Fig. 5c). This latter enrichment would likely not be preserved during aqueous alteration.

Deuterium enrichments produced in aromatic species in this manner are expected to occur largely independent of PAH molecular size, but should show specific regiochemical behaviors. In addition, since this same irradiation process produces both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers) (Bernstein *et al.*, 1999), D enrichments produced by this process would be expected to correlate with the presence of these other species.

Possible Correlated Effects in Carbon, Nitrogen and Oxygen

Some of the interstellar processes described above can also drive chemistry involving C, N, and O, so in principle they could also result in enrichments in these elements. However, since the zero-point energy differences for the isotopes of C, N, and O are significantly smaller than for H (10–50 K *vs.* a few 100 K), fractionations in these elements should be considerably less pronounced (see Tielens, 1997). Nonetheless,

D enrichments could potentially show some relationship with isotopic fractionations in these other elements.

Gas phase ion-molecule reaction models predict $^{12}C/^{13}C$ fractionations can be produced in organic species from gas phase C^+ generated by isotopic switching reactions with CO. Such fractionations could favor ^{12}C in organic species (*e.g.*, HCN and H_2CO) by as much as a factor of 5, but generally fractionations of a factor of 2 or less are expected (Langer *et al.*, 1984; Langer and Graedel, 1989). Radio observations provide some general support for this scheme (Henkel *et al.*, 1982; Langer and Penzias, 1993). Isotopes of C can also be exchanged in proton transfer reactions involving species like HCO^+, but these effects are expected to be quite small (Langer *et al.*, 1984). Finally, C can be fractionated by isotope-selective photodissociation of CO. In dense cloud regions where $A_v < 6$, UV photodissociation of CO is mediated by excited H_2 and is expected to lead to enhanced atomic $^{13}C/^{12}C$ in the gas phase (*i.e.*, the opposite fractionation expected from ion-molecule reactions) (Tielens, 1997). As a result, the overall C isotope fractionation in the gas phase depends on the relative importance of atomic C and C^+ in the generation of larger molecules, an issue that has yet to be fully understood.

Differences in zero-point energies are relatively unimportant for gas-grain reactions, so carbon-bearing species derived from accreting gas phase CO should not be fractionated differently. Only species that have a direct heritage to gas phase C, for example CH_4, should be fractionated (Tielens, 1997). Thus, as with D, the primary enrichment from this process results from prior fractionation of the accreting gas, which we noted earlier could potentially be either heavy or light.

Oxygen in the gas phase resides primarily in CO, O, and O_2. Theoretical calculations suggest that very little fractionation in the $^{16}O/^{18}O$ ratio should occur in these species or their
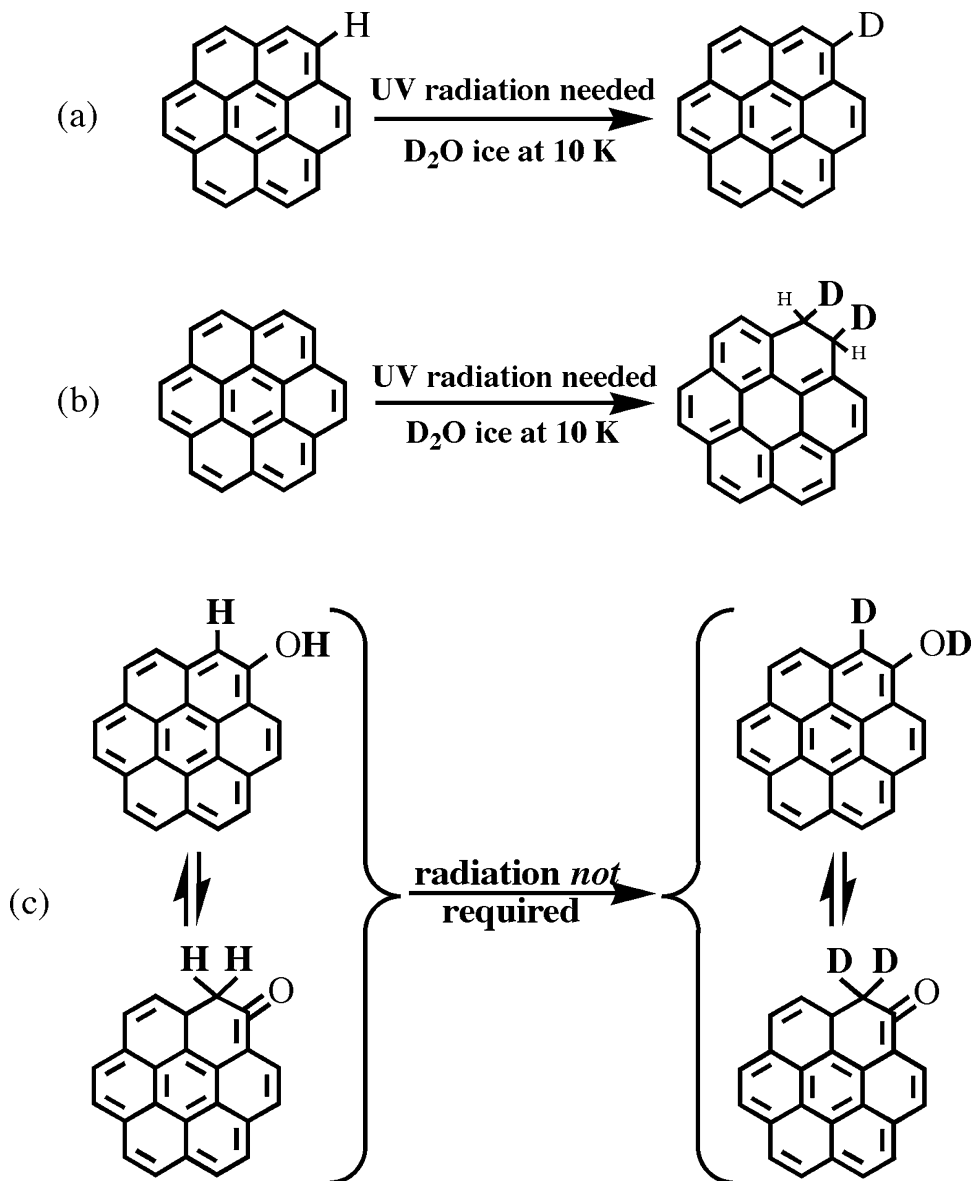
FIG. 5. The UV photolysis of PAHs in D-enriched ices results in rapid D enrichment of the PAHs through (a) aromatic D→H exchange, (b) D atom addition, and (c) exchange through keto-enol tautomerism. Deuterium enrichments produced in this manner are largely independent of PAH molecular size, but should show specific regiochemical patterns and would be expected to correlate with the presence of both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers).

products (Langer *et al.*, 1984). Lacking a significant fractionation in the gas phase, gas-grain reactions are not expected to generate fractionated species either and therefore ice irradiation processes should also not produce new species with fractionated oxygen. Thus, one would not expect D enrichments to correlate with any significant O isotopic fractionation.

The molecular form of most of the N in dense clouds has yet to be determined. Some of it resides in NH_3 (Lacy *et al.*, 1998), but the majority is probably in the form of N_2 (Sandford *et al.*, 2001). Some N fractionation is likely driven by gas phase ion-molecule exchange reactions between N_2H^+ and N_2

(Terzieva and Herbst, 2000). Most of the ^{15}N-enhanced N_2H^+ is simply cycled back to N_2, but some can be propagated through the exchange of both N and H to species like NH, NH_2, HCN, *etc.* The ultimate fractionations expected for such simple hydrides lie between $\delta^{15}N$ values of 10 and 1000‰, depending on the molecule and evolutionary timescale (Terzieva and Herbst, 2000). For the most abundant molecules, such as NH_3, ^{15}N enrichments as high as $\delta^{15}N \approx 250$‰ might be expected. Such values are similar to the enrichments seen in many meteoritic materials, but they cannot explain some of the more extreme values seen in meteorites and IDPs (Messenger, 2000).

However, very recent calculations of ^{15}N gas-grain fractionation suggest that much higher $^{15}N/^{14}N$ ratios might be attained in N_2 and NH_3 at high gas phase densities (Charnley and Rodgers, 2001). Thus, moderate fractionations of N can occur in the gas phase and interstellar ices should be ^{15}N-enriched by both the condensation of enriched gas phase species and *via* gas-grain reactions. Subsequent ice irradiation will propagate this fractionation into new and more complex species.

Currently, no theoretical or experimental work has addressed how gas phase and gas-grain processes involving PAHs might fractionate C, N, or O. However, limited laboratory work has been done on how PAHs are modified when they are UV irradiated in ice mantles containing C, N, and O. Photolysis of PAHs in H_2O ices adds –OH and =O groups and excess hydrogen atoms to PAH edges (Bernstein *et al.*, 1999, 2001). Preliminary experiments involving other interstellar ice species (CO, CO_2, CH_3OH, and NH_3) indicate that the formation of aromatic amino and alkyl moieties is also possible (Elsila *et al.*, 2001). As with D, such photochemistry could result in the addition of peripheral groups containing N, O, and possibly C, that propagate any isotopic fractionations found in the simpler molecules present in the ice. Again, these exchanges should produce fractionations having regiochemistry characteristic of the ice photolysis process.

Since none of the processes described above involve changes to the carbon in the PAH skeletal structure, their C isotopic ratios should be primarily defined by the C reservoir from which they were first made. Since interstellar PAHs are probably produced in the outflows of aging stars (Allamandola *et al.*, 1989), their C isotopic ratios should primarily be of nucleosynthetic origin. Any C isotopic fractionation produced by interstellar chemistry at the edges of PAHs would be superimposed on this original nucleosynthetic ratio.

In summary, all the processes described above may produce isotopic fractionations in C and N, but these should be considerably smaller than those seen for D. Fractionation of O is expected to be smaller still. In the case of C, the existence of multiple reaction schemes that can cause fractionation in opposite directions suggests that C isotopes will not correlate in any simple way with D fractionations. Correlations will be further muddled because C, N, and O fractionations are much more sensitive to temperature than D. Nonetheless, it is possible that significant ^{15}N excesses could be produced in the interstellar medium (up to $\delta^{15}N \sim 1000‰$) and these might exhibit some qualitative relationship with D excesses. How these fractionations might manifest themselves in aromatic species is currently poorly understood.

Comparison of the Signatures of the Various Interstellar Deuterium Enrichment Processes

The four different processes described above can all result in the D enrichment of PAHs and related species in the interstellar medium. However, each of these processes produces enrichments that display distinctly different "signatures" within their associated product populations. These differences are summarized in Table 1.

IMPLICATIONS FOR THE AROMATIC FRACTION OF METEORITIC ORGANICS

Aromatic Materials in Meteorites and Interplanetary Dust Particles

The organic fraction of primitive meteorites contains a major aromatic component (Studier *et al.*, 1972; Hayatsu *et al.*, 1977; Cronin *et al.*, 1987; De Vries *et al.*, 1993; Gardinier *et al.*, 2000; Cody *et al.*, 2001), and a host of specific aromatic molecules have been identified (Pering and Ponnamperuma, 1971; Basile *et al.*, 1984; Tingle *et al.*, 1991; Kovalenko *et al.*, 1992; Zenobi *et al.*, 1992; Naraoka *et al.*, 2000). The aromatics in the intractable polymer of meteorites are dominated by domains containing only a few rings (Gardinier *et al.*, 2000; Cody *et al.*, 2001), but measurable quantities of larger domains exist (cf., Becker and Bunch, 1997). Many of the PAHs reported in meteorites have peripheral methyl groups (Basile *et al.*, 1984; Kovalenko *et al.*, 1992; Zenobi *et al.*, 1992), and other functionalities, including ketones, have been reported (Hayatsu *et al.*, 1977; Krishnamurthy *et al.*, 1992). Aromatics have also been detected in IDPs (Allamandola *et al.*, 1987; Clemett *et al.*, 1993).

To date, relatively little attention has been paid to oxidized and reduced aromatics in meteorites. Several groups have used chromatography to detect various three-ringed ketones in aromatic fractions from the Murchison meteorite (Basile *et al.*, 1984; Krishnamurthy *et al.*, 1992). Cronin and Pizzarello (1990) have shown that the principle aliphatic components of the Murchison meteorite appear to be a structurally diverse set of C_{15}–C_{30} branched and alkyl-substituted mono-, di-, and tricyclic alkanes. In addition, infrared spectra of their extracts suggest the presence of carbonyl groups and some double bonds. Similar structures (partially reduced aromatics with peripheral carbonyl groups) are formed when aromatic hydrocarbons are irradiated in H_2O-rich ices (Bernstein *et al.*, 1996, 1999, 2001). Aromatic alcohols have not been reported in meteorites. Whether the lack of detection of aromatic alcohols is due to their absence or whether it is the result of selection effects associated with their extraction from meteorites is not yet clear. Targeted searches for aromatics with –OH edge groups are needed to address this issue.

Fractionations of Deuterium, Carbon, Nitrogen, and Oxygen in the Aromatics in Meteorites and Interplanetary Dust Particles

The aromatic fraction of meteorites is known to contain carriers of excess D. For example, D enrichments exist in both acid-soluble (Yang and Epstein, 1983) and acid-insoluble

TABLE 1. PAH interstellar D-enrichment processes and their signatures.

Process	Low temperatures required?	UV photons directly involved?	Deuterium labile?	Fractionation in other elements?	Signature
Gas phase ion-molecule reactions	Yes	No	No	Yes	Favors PAHs with larger numbers of peripheral H atoms (larger PAHs). Probably independent of regiochemistry.
Unimolecular photodissociation reactions	No	Yes	No	Probably No	Favors smaller PAHs (Number of C atoms $\leq$ 50). Probably independent of regiochemistry.
Gas-grain reactions	Yes	No	No	Yes?	May not occur. If it does, the enrichment will reside on the reduced rings of H_n-PAHs.
Ice-PAH photolysis reactions	Yes	Yes	Variable*	Possibly	Size independent. Enrichment will correlate with oxidation, reduction, and regiochemistry.

*The deuterium associated with oxidized rings on aromatic alcohols and ketones will be labile. Deuterium residing on the reduced rings of H_n-PAHs and on the fully aromatic rings of PAHs will be non-labile.

(Robert and Epstein, 1982) meteoritic hydrocarbon phases with C/H ratios higher than 1. If we assume the fractions with C/H > 1 are dominated by aromatics, these C/H ratios correspond to aromatic moieties containing from 20 to several hundred C atoms.

Using combined C and H isotopic data, Kerridge *et al.* (1987) demonstrated that aromatics were a major carrier of the D. In addition, Krishnamurthy *et al.* (1992) examined meteoritic organics and found δD values that ranged from about +100 to +1000, with aromatics having higher values than aliphatics. Unfortunately, there is currently little information about the distribution of the D within the aromatic fraction, either in terms of its regiochemistry or its distribution among the various aromatic species present.

The C isotopic character of the D-enriched aromatics is also not fully understood. Studies have demonstrated that the larger D enrichments ($\delta D > +1000$‰) in meteorites do not correlate with C isotopic ratios (*e.g.*, Robert and Epstein, 1982; Yang and Epstein, 1983, 1984; Halbout *et al.*, 1990), which tended to be normal ($-40 \leq \delta^{13}C \leq +20$‰). The relative importance of aromatics as carriers in the samples measured in these studies is not well established, although the high C/H ratios of some of the samples imply the presence of large amounts of aromatic materials (Robert and Epstein, 1982; Yang and Epstein, 1983). In a study that specifically targeted the isotopic ratios of C and H in meteoritic aromatics, Kerridge *et al.* (1987) found the aromatics to have $\delta^{13}C$ values of about –20‰ that did not correlate with D

content. Thus, there does not appear to be any clear correlation between D enrichments and C isotopic systematics in meteorites.

Considerably less work has been done in the area of the O isotopic compositions of these materials. Halbout *et al.* (1990) studied the H and O isotopic compositions of kerogen extracted from the Orgueil meteorite by acid demineralization. While they did not focus on the aromatic materials in this sample *per se*, these kerogens are known to be dominated by aromatic structures (cf., Cronin and Chang, 1993). Halbout *et al.* (1990) measured large D excesses in their sample ($\delta D = +1360$‰) but found relatively normal oxygen ($\delta^{17}O = +3.3$‰) and carbon ($\delta^{13}C \leq -48$‰). Thus, there is currently no evidence for anomalous O in these types of materials and, hence, no correlation of D enrichments with O isotopic ratios.

Nitrogen is potentially more interesting. Acid residues from carbonaceous chondrites measured by Robert and Epstein (1982) showed δD values up to +3500‰ that did not correlate with $\delta^{15}N$. In 1986, Franchi *et al.* reported ^{15}N excesses in an acid resistant, presumably carbonaceous, carrier from the Bencubbin meteorite. The carrier yielded $\delta^{15}N$ values as high as +1033‰ but showed normal C with a $\delta^{13}C$ value of about +25‰. Kerridge *et al.* (1987) identified several isotopically distinct reservoirs of N ranging from light ($\delta^{15}N < -6$‰) to heavy ($\delta^{15}N > +60$‰) which they characterized as being associated with aromatics, but they were unable to closely define the reservoirs. Grady and Pillinger (1990) noted that the

primitive chondrite Allan Hills (ALH) 85085 was highly enriched in ^{15}N, a portion of which resides in a carrier that is probably carbonaceous material with C/N = 65–75, $\delta^{15}N \approx$ +860‰, and $\delta^{13}C \approx$ +1‰. In a recent comprehensive study, Alexander *et al.* (1998) examined the C and N isotopic behaviors of the insoluble macromolecular organic matter in 13 primitive chondrites. They found that the range of C isotopic compositions varied by only ~30‰ within their samples, while the N isotopes ranged from $\delta^{15}N$ = –40 to +260‰. They conclude that the most ^{15}N-rich material probably formed in the interstellar medium and that the fraction of organic N in meteorites having an interstellar origin is probably very large. For example, in the Renazzo meteorite, Alexander *et al.* estimate 40–70% of the organic nitrogen may have a direct interstellar heritage. Pearson *et al.* (2000) have examined the highly aromatic, macromolecular kerogen in Murchison using hydrous pyrolysis techniques and demonstrated that it contains a significant portion of organic N that is somewhat isotopically heavy ($\delta^{15}N < +30$‰). Thus, at least a fraction of the aromatics in meteorites appear to be a carrier of isotopically anomalous N, but the nature of the relationship is not understood.

IDPs are also known to contain D-enriched components, and these components are often distributed heterogeneously within the particles on very small scales (McKeegan *et al.*, 1984, 1985; Messenger, 2000). Ion microprobe studies of the D distribution and correlation with other elements suggest tentative links between the D and a carbonaceous carrier (McKeegan *et al.*, 1985; Messenger *et al.*, 1996; Aléon *et al.*, 2000; Messenger, 2000). IDPs are known to contain abundant aromatics (Allamandola *et al.*, 1987; Clemett *et al.*, 1993), but the relationship between them and D enrichments is not clear. So far, combined ion probe and two-step laser mass spectrometry studies of the same IDP fragments have only detected aromatics in D-rich IDPs, but D enrichments have been seen in IDPs in which aromatics were not clearly detected (Messenger *et al.*, 1995). Aléon *et al.* (2000) reported that δD increases in IDPs with increased C/H, with most enrichments occurring when C/H > 1. They suggested their measurements could be explained by the presence of three phases: (1) a material similar to the kerogen in carbonaceous chondrites with C/H = 1.0–1.5 and a relatively small δD, (2) a component dominated by small molecules with C/H = 1 and larger D enrichments, and (3) a refractory organic material with C/H = 3 and the largest D enrichments. The latter phase was observed to be the major carrier of the D and its C/H ratio well in excess of 1 suggests the carrier is aromatic.

Stadermann *et al.* (1989) used ion microprobe techniques to examine the C and N isotopes in 24 IDPs. They found no ^{13}C enrichments and confirmed earlier observations that $\delta^{13}C$ values showed little variation between different fragments. In contrast, they found that 10 of the 24 IDPs contained heavy N with values of $\delta^{15}N$ up to +442‰ and, as with the D, the ^{15}N showed large spatial variations within an individual particle. The normal ^{13}C ratios and high degree of spatial variability of

D and ^{15}N enhancements within IDPs was confirmed by Messenger (2000), who also noted that the D and ^{15}N appeared to be qualitatively correlated, at least in the broad sense that fragile "cluster" IDPs seem to be more generally D- and ^{15}N-rich than individual IDPs. One of these IDPs, Dragonfly, was found to contain some of the most extreme δD and $\delta^{15}N$ values (δD ~ 50 000‰ and $\delta^{15}N$ ~ 480‰) ever seen in a natural material. Keller *et al.* (2000) used a variety of analytical techniques to show that δD and $\delta^{15}N$ correlate with each other in this particle. Electron energy loss spectroscopic (EELS) measurements indicated that the N was associated with the carbonaceous fraction, although the concentration was too low to specifically identify the N-containing component. The x-ray absorption near-edge specroscopy (XANES) measurements of the carbonaceous material showed prominent C–C, C–H, and C–O absorptions and suggested that the D is carried in C-rich grains that contain aldehydes.

In summary, studies of the D enrichments in meteorites and IDPs suggest that at least a portion of the aromatics in meteoritic material have an interstellar origin. The D enrichments appear to be decoupled from carbon isotopic ratios, while there is a possible relationship between D excesses and excess ^{15}N. The processes by which the D enrichments were created and the true relationships (if any) of the D enrichments to other isotopic systems remain to be clarified.

Placing Constraints on the Interstellar Processes Responsible for Meteoritic Deuterium Enrichments

We now discuss the meteoritic evidence for or against contributions from the various enrichment processes (see Table 1) and point out potential measurements that might help elucidating their relative importance for the creation of meteoritic organics.

Low-Temperature Gas Phase Ion-Molecule Reactions– There are several tests that could constrain the relative importance of ion-molecule reactions for the D fractionation in meteoritic aromatics. First, it would be useful if the presence of PAH-D$^+$ ions could be verified in the gas phase in dense interstellar clouds. In principle, it might be possible to determine PAD/PAH ratios at infrared frequencies using the relative strengths of the aromatic C–H and C–D stretching bands near 3050 and 2270 cm^{-1}, respectively (Hudgins *et al.*, 1994). However, the low expected gas phase abundances of PAHs in such cold environments will make this very difficult. In addition, PAHs are most easily observed in the gas phase when they are excited by UV photons and radiatively cool by emitting a cascade of infrared photons. At the low UV fluxes present in typical dense clouds, this excitation mechanism is strongly curtailed. There may be more hope of measuring the relative strengths of the C–H and C–D aromatic stretching bands in absorption, but in this case the bands would presumably be dominated by PAHs frozen onto grains and it would be difficult to assign any observed fractionation specifically to ion-molecule reactions, as opposed to other processes.

Theoretical models for D enrichments in PAHs by gas phase ion-molecule reactions predict that this process will initially preferentially deuterate the *larger* PAHs in dense clouds, although if sufficient time is available the D/H ratio of all the PAHs in the gas phase should ultimately equilibrate with the gas phase value. Thus, a second, *meteoritic* test for this process would be to examine meteoritic organics for correlations between the D/H ratio and the size of the aromatic moieties of the carriers. In this respect, the report by Aléon *et al.* (2000) that in IDPs the value of δD increases with increased C/H, with most enrichments occurring when C/H > 1 is suggestive; such a distribution is qualitatively consistent with a fractionation of the aromatic *via* ion-molecule reactions. If ion-molecule reactions were the sole source of the observed fractionations seen by Aléon *et al.*, the generally lower δD at lower C/H (smaller aromatics) would then be explained by short interstellar evolutionary times ($<3 \times 10^5$ years).

Low-Temperature Gas-Grain Reactions–Theoretical models and telescopic observations suggest that gas-grain reactions probably result in the single largest reservoir of D fractionated materials in dense clouds (Tielens, 1983; Teixeira *et al.*, 1999). However, the D enrichments produced by gas-grain reactions are expected to reside predominantly in simple hydrogenated species like CH_4, NH_3, and H_2O, not PAHs. These simple, volatile molecules are not significant carriers of the D found in meteorites, implying that interstellar gas-grain reactions did not play a *direct* role in the creation of the D enrichment seen in meteorites.

As mentioned earlier, there are no theoretical or experimental reasons to expect that PAHs can be directly enriched in D by gas-grain reactions. If PAHs condensed in interstellar grain mantles can participate in gas-grain reduction reactions, the resulting products would be partially reduced PAHs (H_n-PAHs). Such structures are seen in meteoritic organics (Cronin and Pizzarello, 1990), but so far no attempt has been made to determine the δD systematics of these materials. A better understanding of the δD values in reduced meteoritic PAHs (H_n-PAHs and cyclic aliphatics) would clearly be of interest.

Independent of its ability to directly produce D-enriched PAHs or H_n-PAHs, this process may still play a key secondary role in the production of D-enriched meteoritic organics. Since gas-grain reactions probably do produce large reservoirs of D-enriched, simple hydrogenated molecules in ices in dense clouds, this process may be largely responsible for providing the feedstock that subsequent chemistry converts into the more complex and refractory species that carry the D in meteorites.

Unimolecular Photodissociation Reactions–Unimolecular photodissociation reactions involving interstellar PAHs are expected to generate a characteristic D-enrichment signature in which the largest D enrichment occur in PAHs smaller than $\sim C_{50}$. This is in contrast to the signature expected from ion-molecule reactions, which should tend to preferentially enrich larger PAHs. There are good theoretical and experimental reasons to expect this process occurs in the interstellar medium,

but there is currently no observational evidence. The challenge is to use the infrared C–D and C–H stretching emission bands near 2270 and 3050 cm^{-1}, respectively, to measure the PAD/PAH ratio in a variety of interstellar environments that sample different UV radiation fields and astrochemical evolutionary histories. If D enrichment by unimolecular photodissociation is occurring, PAD/PAH ratios should be very low in the outflows from carbon stars, where D is largely absent, having been consumed in the star. PAD/PAH ratios should, however, be much larger in diffuse interstellar "cirrus" clouds, H II regions, and reflection nebulae, environments where PAHs have longer UV exposures in environments with higher gas phase D/H ratios.

While it will still be difficult to attain the high signal-to-noise emission data required to detect PADs at the expected PAD/PAH ratios of $<10^{-2}$, it should be easier than detecting deuterated PAHs in absorption in dense clouds. First, a larger fraction of the PAH population will be in the gas phase in the warmer environments where most unimolecular photo-dissociation reactions will occur. In addition, the same UV photons driving the unimolecular photodissociation will excite the PAHs and cause them to emit in the infrared, thereby making them easier to detect. The quality of current telescopic infrared spectra is constantly improving and with appropriate spaceborne instrumentation it should be possible to place meaningful constraints on the efficiency of PAH D enrichment by unimolecular photodissociation reactions in a variety interstellar environments.

There is some inconclusive evidence suggesting that unimolecular photodissociation reactions could have played role in the production of the D enrichments seen in meteorites. The D/H ratio of acid-soluble hydrocarbon phases in meteorites increases as C/H increases from 0.2 to 1.5 (Yang and Epstein, 1983), while the D/H ratio in acid insoluble phases drops slightly as the C/H ratio increases from 2.3 to 3.0 (Robert and Epstein, 1982). Allamandola *et al.* (1987) noted that if it is assumed that the soluble and insoluble phases represent different degrees of molecular complexity of related materials (potentially a gross oversimplification, Halbout *et al.*, 1990), then the peak in D enrichment at C/H ~ 2 would imply the dominance of PAHs containing 20–50 C atoms, consistent with unimolecular photodissociation. As is the case for investigating the role of ion-molecule reactions, the most useful tests of meteoritic organics would be to measure the correlation (if any) between D/H ratios and the size of the aromatic moieties of the carriers. While most of the aromatic moieties in meteorites are small (cf., Cody *et al.*, 2001), measurable quantities of larger aromatics are present (Becker and Bunch, 1997) and such comparisons may be possible.

Ultraviolet Photolysis Reactions in Deuterium-Enriched Ice Mantles–The UV irradiation of PAHs in ices in dense molecular clouds should result in the production of a variety of aromatic ketones, alcohols, ethers, and H_n-PAHs (Bernstein *et al.*, 1999, 2001). If the ices are themselves D-enriched, the same irradiation results in the equilibration of D in the ice with

the PAHs (Sandford *et al.*, 2000). Thus, this process may play an important role in "fixing" isotopic fractionations produced by other processes into molecular forms that can survive incorporation into the solar nebula and subsequent parent body accretion and alteration.

In principle, one could examine meteoritic organics for evidence of interstellar UV ice irradiation by searching for isotopic fractionations in putative or probable photolysis products. Such an approach is complicated by several issues, however. For example, the photoproducts will exhibit H, C, N, and O isotopic ratios that reflect the relative mixing, in the ice, of components produced by several other fractionation processes. Also, each of the fractionation processes represented in the ice will produce a different characteristic pattern of fractionation in different molecules which will, in turn, be converted with different efficiencies into different complex organics. Thus, the ultimate isotopic signature of the irradiation products of interstellar ices probably represents a complex convolution of many effects.

Fortunately, aromatics, which carry most of the D in meteorites, also offer the best hope of providing a distinctive signature of ice irradiation. The deuteration of PAHs by photolysis in D-enriched ices proceeds along several different paths: H→D exchange reactions on aromatic rings, D atom addition reactions that convert aromatic rings to aliphatic rings, and keto-enol tautomeric exchange (see Fig. 5). Each of these processes results in the placement of acquired D into characteristic regiochemical sites on the PAHs. Ideally, one would attempt to search for correlations of D enrichments associated with these different kinds of regiochemical sites on meteoritic aromatics found within a single object.

We would note that since these sites have different labilities, they would be expected to suffer differing degrees of exchange with their surroundings during incorporation into the warmer protosolar nebula, parent body processing, delivery, recovery, and analysis. Thus, it would also be useful to see how the D/H ratios vary between the same classes of meteoritic aromatics found in different extraterrestrial materials. For example, meteorites that have experienced hydrous alteration would have exchanged some or all of the labile portion of their aromatic D and could show different systematics than meteorites or anhydrous IDPs that have experienced little or no aqueous alteration. Since the conditions in the protosolar nebula are expected to have promoted isotopic exchange that would have lowered the D/H ratio in water (Drouart *et al.*, 1999), materials that suffered aqueous alteration might be expected to show D/H ratios lowered by their relative proportions of labile and non-labile D-containing moieties. Perhaps this is part of the reason why IDPs are, by and large, more D-rich than meteorites.

It would also be extremely useful to search for correlations of D enrichment with PAH oxidation and reduction state in meteoritic organics. In this regard, the recent report by Keller *et al.* (2000) that the degree of D enrichment in IDPs may correlate with the presence of C–O bonds is of particular interest. Reports that the enrichments of D and ^{15}N may be correlated in IDPs (Keller *et al.*, 2000; Messenger, 2000) is worthy of additional comment. Preliminary photolysis experiments of PAHs in NH_3-containing ices suggest that nitrogen can also be affixed to the edges of PAHs. Since N in NH_3 is expected to become ^{15}N-enriched *via* ion-molecule reactions (Terzieva and Herbst, 2000; Charnley and Rodgers, 2001) and NH_3 is abundant in interstellar ices (Lacy *et al.*, 1998), it would clearly be interesting to see if the observed meteoritic ^{15}N-enrichments correlate in any way with the aromatics, particularly in the form of amine/imine sidegroups.

CONCLUSIONS

There are a number of interstellar processes that can produce significant D fractionation in their products: gas phase ion-molecule reactions, low-temperature gas-grain reactions, gas phase unimolecular photodissociation, and ultraviolet photolysis in D-enriched ice mantles. Some of these processes may also produce isotopic fractionations in the elements C, N, and O, with the fractionations in N most likely to be significant. In the case of PAHs, each of these processes is associated with distinct regiochemical signatures.

Gas phase ion-molecule reactions initially preferentially deuterate the *larger* PAHs in dense clouds, but if sufficient time is available, all PAHs in the gas phase in dense clouds should reach equilibrium with the gas phase. Thus, the characteristic signature of this process would be fully aromatic PAHs whose D/H ratios are uniform across the PAH population or that increase with increasing PAH size. Gas-grain reactions produce D fractionations in dense clouds that are manifested primarily in simple hydrogenated molecules. PAHs probably cannot be enriched in D in this manner, but if they are, D enrichments would be found in H_n-PAHs (*i.e.*, hydrogenated PAHs that contain cyclic aromatic and aliphatic rings). Enrichment *via* gas phase unimolecular photodissociation reactions differs from other processes in that low ambient temperatures are *not* required to produce fractionations. This process should produce a fractionation pattern in which PAHs below the C_{50} size range show the largest enrichments. The principle effect of energetic irradiation of interstellar ices is to transfer preexisting fractionations from simple, volatile compounds to more complex, refractory compounds. This process may preserve the fractionations generated by other mechanisms in forms that can survive incorporation into forming stellar systems. Deuterium enrichments produced in aromatic species by this process will be largely independent of PAH size and should show specific regiochemical behaviors. PAHs enriched in this manner should show correlations between δD and the presence of both reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols, ketones, and ethers).

Our poor understanding of the molecular distribution of the excess D and ^{15}N in meteorites makes it difficult to evaluate the relative contributions of these interstellar processes to the

organic inventory in meteorites. The present data on the relationship of δD with C/H ratio in macromolecular meteoritic organics does not preclude significant contributions from ion-molecule reactions, unimolecular photodissociation reactions, or UV driven exchange in interstellar ices. Reported correlations of D enrichment with the presence of C–O bonds in IDPs is consistent with PAHs enriched by photolysis in ices enriched in D by gas-grain reactions.

The isotopic fractionations in N, and the lack of strong fractionation effects in C and O, are also qualitatively consistent with these processes. The ^{15}N enrichments, and their possible correlation with δD, may be explainable in terms of low-temperature ion-molecule reactions, possibly followed by UV driven exchange reactions in ices. That D and ^{15}N enrichments do not correlate tightly could be due to several effects: (1) the fractionations of these two isotopes have different temperature dependencies; (2) meteoritic organics may contain differing contributions from processes like gas-grain reactions that produce D enrichments without corresponding ^{15}N enrichments; (3) the efficiency with which UV photolysis will "fix" anomalies into more complex species depends on the molecular composition of the ices, which can vary within dense clouds; and (4) differences in the labilities of D and ^{15}N may alter the enrichment ratios during parent body processing of the meteoritic organics. The lack of correlated isotopic effects in O are not surprising since current theory and experimental data suggest that these processes should not produce strong fractionations in O in the interstellar medium. The lack of C isotopic effects is a little more surprising, but C fractionations can proceed along two main paths that fractionate their products in opposite directions and this may moderate the size of any final effect in the interstellar medium.

Thus, there is currently no reason to reject the possibility that all the processes described in this paper may have played a part in the production of the D enrichments seen in meteorites. Determining which processes dominated the overall inventory in meteorites must await additional measurements. Studies that search for the characteristic enrichment patterns expected for these four process (summarized in Table 1) would be particularly useful.

Editorial handling: K. McKeegan

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