Can Dust Explain Variations in the D/H Ratio?

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Abstract. The D/H ratio in interstellar gas varies on scales of a few hundred pc in the local Milky Way, with D/H values ranging from ~7 ppm to ~22 ppm. The reduction in D/H relative to the primordial value of D/H ≈ 26 ppm is usually attributed to “astration” – conversion of D into other elements by nuclear fusion in stars. However, it is shown here that astration has difficulty accounting for the observations because the expected associated variations in O/H are not seen. The lower D/H values are instead likely due to “depletion” of the D onto dust grains. Polycyclic aromatic hydrocarbons (PAHs) are a possible repository for the missing D, and it appears possible for gas-grain reactions to achieve extreme deuteration of carbonaceous grain material. Grain destruction will release D from the grains; the gas phase abundance of D should therefore be positively correlated with the gas phase abundances of other elements that exhibit strong depletions, such as Mg, Si, Ti, and Fe, which also will be returned to the gas by grain destruction.

1. Introduction

In recent years it has become clear that the gas-phase D/H ratio varies significantly from one sightline to another within a few hundred pc of the Sun (see, e.g., Moos et al. 2002; Steigman 2003; Wood et al. 2004; Hébrard 2005). This has often been taken to result from regional variations in the extent to which nucleosynthesis in stars, followed by return of matter to the interstellar medium via stellar winds and ejecta, has lowered the interstellar D/H ratio from the primordial value established by nucleosynthesis in the Big Bang.

I argue here that the observed local variations in the gas-phase D/H ratio are not due to variable astration. The low values of \((D/H)_{\text{gas}}\) seen on some sightlines are instead attributed to incorporation of D into dust grains. I discuss processes acting to add D to dust grains, and show that these can strongly deuterate PAH material in the interstellar medium. This hypothesis predicts a positive correlation of \((D/H)_{\text{gas}}\) with gas-phase abundances of strongly-depleted metals, and deuteration of carbonaceous interstellar grains captured by the Stardust mission.

2. D/H Variations in the ISM

Using high resolution spectroscopy with IMAPS, Jenkins et al. (1999) measured \(D/H=7.4^{+1.2}_{-0.9}\) ppm toward δ Ori \((d = 281 \pm 65 \text{ pc})\), and Sonneborn et al. (2000) found \(D/H=21.8^{+2.2}_{-1.9}\) ppm toward γ² Vel \((d = 258\pm35 \text{ pc})\). These two high preci-
sion measurements firmly established the reality of substantial variations in the gas-phase D/H ratio within a few hundred pc of the Sun. Including observations with Copernicus, IMAPS, HST, and FUSE (see the summary by Wood et al. 2004) we now have measurements of D/H on \( \sim 40 \) interstellar sightlines, with D/H values ranging from 5.0 \( \pm \) 1.6 ppm toward \( \theta \) Car (Allen, Jenkins, & Snow 1992) to 21.8 \( \pm \) 2.2 ppm toward \( \gamma^2 \) Vel – a factor of \( \sim 4 \) variation in D/H.

2.1. Problems with Astration

The gas returned to the ISM from stars is expected to be nearly devoid of D, as the D is converted to \(^3\)He during the pre-main-sequence evolution of \( M < 5M_\odot \) stars (Mazzitelli & Moretti 1980). As a result, the D/H ratio in the ISM is an indicator of the fraction of the baryons now in the ISM that have passed through a star. If the primordial value of D/H is 26.2 \( \pm \) 1.8 ppm (Spergel et al. 2003) then a D/H ratio of 5.0 \( \pm \) 1.6 ppm would require that 81 \( \pm \) 6\% of the baryons in the interstellar gas toward \( \theta \) Car have been cycled through a star at least once, whereas on the sightline toward \( \gamma^2 \) Vel, this fraction would be only 17 \( \pm \) 11\%.

The hypothesis that the observed variations in D/H on different sightlines are due to variations in astration therefore requires that (1) regions separated by only a few hundred pc have had extremely different star formation histories, and (2) turbulent diffusion has not homogenized the elemental abundances in the gas. It is difficult to see how these two conditions can be true: we do not see other evidence of such variations in star formation activity, and turbulent mixing is expected to be effective at mixing gas over length scales of hundreds of pc on 10\(^9\) yr time scales.

The gas returned to the ISM from stars will, on average, be enriched in the products of stellar nucleosynthesis, such as oxygen. Models for evolution of interstellar abundances due to stellar nucleosynthesis and infall predict the joint variation of D/H and O/H. Outside of dark clouds, \( \text{H}_2\text{O} \) is absent, and the O in grains is thought to be mostly in the form of amorphous olivine \( \text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4 \) (see Draine 2003). On typical sightlines 70–99\% of the Si is in grains (Jenkins 2004); thus \( \text{O} \) in dust/\( \text{O} \) in total \( \approx 4 \times (0.85 \pm 0.15) / (\text{Si} / \text{O}) \) in total \( \approx 4 \times (0.85 \pm 0.15) / (\text{Si} / \text{O}) \) in total \( \approx 0.24 \pm 0.04 \): the silicate grains contain 24 \( \pm \) 4\% of the oxygen (for (Si/H) \( \odot \) = 32 ppm from Asplund 2000, and (O/H) \( \odot \) = 457 ppm from Asplund et al. 2004). The gas phase oxygen abundance tracks the total oxygen abundance: \( (\text{O} / \text{H})_{\text{gas}} \approx 0.76 \pm 0.04) (\text{O} / \text{H})_{\text{total}} \).

Figure 1 shows tracks of D/H vs. \( \text{O} / \text{H} \) for two chemical evolution models (Chiappini, Renda, & Matteucci 2002), where the degree of astration is a decreasing function of galactocentric radius. These models, which include infall, have \( \text{O} / \text{H} \) varying from 300 to 600 ppm as D/H declines by only \( \sim 25\% \). It is difficult to envision astration scenarios where D/H varies by a factor of 4 without associated very large variations in \( \text{O} / \text{H} \).

However, unlike the D/H ratio, the \( \text{O} / \text{H} \) ratio does not show large variations. Figure 1 shows measured values of (D/H) \( \text{gas} \) and (O/H) \( \text{gas} \) for 14 sightlines where \( N(\text{HI}), N(\text{DI}), \) and \( N(\text{OI}) \) are all reported with 1-\( \sigma \) uncertainties not exceeding 0.10 dex. For this sample, the median (O/H) \( \text{gas} \) is 430 ppm and the median (D/H) \( \text{gas} \) is 13.2 ppm. There is no indication of a significant anticorrelation between (O/H) \( \text{gas} \) and (D/H) \( \text{gas} \):
Can Dust Explain Variations in D/H?

Figure 1. (D/H)_{gas} vs. (O/H)_{gas} with 1-σ errors (see text). The data do not show anticorrelation of D/H with O/H, as would result from variable astration, such as models C-I and C-IV from Chiappini et al. (2002). Note that the full range of D/H is seen for sightlines with (O/H)_{gas} between 300 and 400 ppm. The observed variations in (D/H)_{gas} must be due to depletion of D into interstellar dust.

Sightlines: WD 1634-573 (Wood et al. 2002); GD 246 (Oliveira et al. 2002); BD+284211 (Sonbein et al. 2002; Spitzer et al. 1974); Feige 110 (Friedman et al. 2002); γ Cas (Ferlet et al. 1980; Meyer et al. 1998; Meyer 2001); δ OriA (Jenkins et al. 1999; Meyer et al. 1998; Meyer 2001); ι Ori (Laurent et al. 1979; Meyer et al. 1998; Meyer 2001); HD 195965 and HD 191877 (Hoopes et al. 2003); HD 90087 (Hébrard et al. 2005); HZ 43A (Kruk et al. 2002); G 191-B2B (Lemoine et al. 2002); LS 1274 (Wood et al. 2004); LSE 234 (Lecavelier des Etangs, Hébrard, & Williger 2005).

- Two of the three sightlines with the lowest values of (D/H)_{gas} (δ Ori and HD 191877) have (O/H)_{gas} below the median.

- The sightline with the highest (D/H)_{gas} in this sample (LSE 234) has the second-highest (O/H)_{gas}.

- The full (factor of ∼3) range of variation of (D/H)_{gas} is seen among the 6 sightlines with (O/H)_{gas} between 300 and 400 ppm (δ Ori, HD 191877, ι Ori, GD 246, HZ 43A, and Feige 110).
It therefore seems very unlikely that the observed variations in $(D/H)_{\text{gas}}$ are due to variations in astration of the interstellar gas. If the $(D/H)_{\text{gas}}$ variations are real, some other process must be responsible.

2.2. Role of Dust: Depletion of D

When we observe variations in the gas-phase abundance of, say, Si or Fe from one local sightline to another, we do not attribute it to variable astration, but instead to variations in the fraction of the Si and Fe “depleted” from the gas by incorporation in solid dust particles. Jura (1982) suggested that even D might perhaps be depleted from the gas phase and sequestered in dust grains. Since 1982 our picture of interstellar grains has evolved to include a substantial population of very small polycyclic aromatic hydrocarbon (PAH) grains (see the review by Draine 2003). Draine (2004) argued that carbonaceous interstellar grains could incorporate enough D atoms to substantially reduce the D abundance in the gas phase. Under sufficiently violent conditions, the “depleted” D atoms could later be released from grains and returned to the gas.

In this interpretation, astration has reduced the D/H abundance from the primordial value to $(D/H)_{\text{total}} \approx 23$ ppm; incorporation of some of the D into dust will then result in $(D/H)_{\text{gas}} < (D/H)_{\text{total}}$. The variations in the gas-phase D/H ratio are attributed to variations from one sightline to another in the fraction of the D sequestered in dust grains.

3. Hydrogen in Dust Grains

3.1. Observations and Grain Models

Measurement of the D/H ratio using ultraviolet spectroscopy is necessarily limited to sightlines through “diffuse” clouds with $A_V \lesssim 2$ mag. Grains in clouds with $A_V \lesssim 3.3$ mag do not have H$_2$O ice mantles (Whittet et al. 1988); the hydrogen present in diffuse cloud grains must be primarily in hydrocarbons. In fact, a broad absorption feature at 3.4µm is observed and is identified as the C-H stretching mode in aliphatic hydrocarbons, although the amount of material necessary to account for the observed feature is uncertain (see, e.g., Pendleton & Allamandola 2002).

In addition to the 3.4µm absorption feature, we also observe emission features at 3.3, 6.2, 7.7, 8.6, and 11.3µm that are attributed to vibrationally-excited polycyclic aromatic hydrocarbon (PAH) molecules. Models that quantitatively reproduce the observed emission require substantial amounts of C in such particles; the model of Li & Draine (2001) has $C/H_{\text{total}} = 45$ ppm in PAH grains containing $\lesssim 2500$ C atoms$^1$. The larger PAH grains are presumed to be clusters of smaller PAH molecules. These might have C:H ratios in the range of 2:1 – 4:1 (e.g., coronene $C_{24}H_{12}$ to dicircumcoronene $C_{96}H_{24}$). If so, the very small PAH grains alone may contain H/$H_{\text{total}} = 10$–20 ppm.

How much C is in all of the grain material? If it is assumed that the total interstellar C abundance is equal to current estimates of the solar abundance ($C/H=246 \pm 23$ ppm; Allende Prieto, Lambert, & Asplund 2002), then

$^1$Here and below, $H_{\text{total}}$ refers to all of the H nucleons, including those in the gas.
the difference between this value and the gas-phase abundances of CI and CII determined from absorption line measurements allow one to estimate that dust contains C/H_{total} = 106 \pm 18 \text{ ppm} (\text{Jenkins 2004}).

However, (1) solar abundances are uncertain, and (2) interstellar abundances may differ from solar abundances. When one seeks to construct a grain model to reproduce the observed extinction per H nucleon as a function of wavelength, one finds that in addition to silicate material, it is necessary to include a substantial amount of carbonaceous material. The dust model of Weingartner & Draine (2001a) assumes C/H_{total} \approx 250 \text{ ppm} in dust (including the small PAH particles). The dust models of Zubko, Dwek & Arendt (2004) use C/H_{total} = 190–275 \text{ ppm}.

Pendleton & Allamandola (2002) estimate that about 85% of the C in dust is aromatic (sp^{2} bonding, e.g., PAHs and graphite), and 15% is aliphatic (“chain hydrocarbons”). They estimate a C:H ratio \sim 2.9:1 for the aromatic material, and \sim 0.46:1 for the aliphatic material. For purposes of discussion, I will assume C/H_{total} = 200 \text{ ppm} and (H+D)/H_{total} = 70 \text{ ppm} in aromatic hydrocarbon material, with an additional C/H_{total} = 40 \text{ ppm} and H/H_{total} = 75 \text{ ppm} in aliphatic material. Because the smallest grains, which contribute most of the surface area, appear to be PAHs, I will focus on deuteration of the aromatic hydrocarbons alone, and neglect possible deuteration of the aliphatic material.

Observed values of (D/H)_{gas} range from \sim 22 \text{ ppm} to \sim 7 \text{ ppm}.^2 For dust to account for the variations in (D/H)_{gas}, the dust grains must be able to hold at least D/H_{total} \approx 15 \text{ ppm}. If the total amount of hydrogen in the aromatic material is H/H_{total} \approx 70 \text{ ppm}, then it must be possible to enrich the deuterium concentration to the point where (D/H)_{dust} \approx 15/55 = 0.27. Given that the overall D/H ratio is of order 2 \times 10^{-5}, processes must act to increase the D/H ratio in the dust by 4 orders of magnitude!

Examples of extreme deuteration are already known. For example, fragments of the hydrocarbon material in one interplanetary dust particle (IDP) analyzed in the laboratory have D/H \approx 0.008 (\text{Messenger 2000}). In some molecular cloud cores, extreme deuteration of small gas-phase molecules is seen, e.g., D_{2}CO/H_{2}CO = 0.01 – 0.1 (\text{Ceccarelli et al. 2001; Bacmann et al. 2003}), NH_{2}D/NH_{3} = 0.07 (\text{Shah & Wooten 2001}), ND_{3}/NH_{3} \approx 0.001 (\text{Lis et al. 2002; van der Tak et al. 2002}), and CH_{2}DOH/CH_{3}OH = 0.9 \pm 0.3 (\text{Parisi et al. 2002}).

Sandford, Bernstein, & Dworkin (2001) discussed 4 processes that could lead to deuterium enrichment in carbonaceous material: low-temperature gas phase ion-molecule reactions; low-temperature gas-grain reactions; UV photon absorption followed by ejection of H; and deuteration of carbon molecules embedded in D-rich ices. I focus here on processes that can deuterate grains in diffuse clouds, and show that D could be removed from the gas on timescales as short as a few Myr.

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^2Some high values: 21.8^{+2.2}_{-1.9} \text{ ppm toward } \gamma^{2}\text{ Vel (Sonneborn et al. 2000)}, 21.4 \pm 4.1 \text{ ppm toward Feige 110 (Friedman et al. 2002), and } 21.9^{+3.7}_{-2.8} \text{ ppm toward LSE 234 (Lecavelier et al. 2005).} Some low values: 5.0 \pm 1.6 \text{ ppm toward } \theta \text{ Car (Allen et al. 1992)}, 7.4^{+1.2}_{-0.5} \text{ ppm toward } \delta \text{ Ori (Jenkins et al. 1999), 7.9 } \pm 1.9 \text{ ppm toward LSE 1274 (Wood et al. 2004).}
3.2. Energetics of Deuteration

While H and D have the same electronic structure, and therefore the same “chemistry”, the C-D bond is stronger than the C-H bond because of the reduced zero-point energy. It is easy to estimate the magnitude of this energy difference. To be specific, let us consider PAH molecules, since we have direct evidence that at least some of the solid carbon is in this form.

PAHs show three emission features associated with vibrations of the C-H bond: the C-H stretch at $\lambda_1 \approx 3.3\,\mu m$, in-plane C-H bending at $\lambda_2 \approx 8.6\,\mu m$, and out-of-plane C-H bending at $\lambda_3 \approx 11.3\,\mu m$. The stretching and bending modes can be approximated as harmonic oscillators. If the H is replaced by D, the reduced mass of the C-H oscillator will increase by a factor 13/7, and the frequency will be reduced by a factor $\sim \sqrt{13/7}$. Each of the vibrational modes has zero-point energy $\hbar \omega/2$ associated with it, so (summing over the three modes) the zero-point energy will be lowered by

$$\Delta E(\text{CH} - \text{CD}) \approx \frac{1}{2} \left(1 - \sqrt{\frac{13}{7}}\right) \sum_{j=1}^{3} \frac{\hbar c}{\lambda_j} = 0.083eV = k \times 970K \quad (1)$$

Therefore it is energetically favorable for the H in PAHs to be replaced by D. If atomic H and D in the gas were in thermodynamic equilibrium with deuterated PAH material at temperature $T_d$, we would expect to have

$$\left(\frac{\text{D}}{\text{H}}\right)_{\text{PAH}} < \left(\frac{\text{D}}{\text{H}}\right)_{\text{gas}} e^{\Delta E/kT_d} \quad (2)$$

where the inequality is because we may not reach a steady-state, and there may be other processes acting to return D to the gas.

Now suppose that $(\text{D}/\text{H})_{\text{total}} = 22$ ppm. If the aromatic grains contain $\text{D}/\text{H}_{\text{total}} = 15$ ppm and $\text{H}/\text{H}_{\text{total}} = 55$ ppm, eq. (2) becomes

$$\frac{15}{55} < 7 \times 10^{-6} e^{970K/T_d} \quad (3)$$

or $T_d < 970K/\ln \left[15/(55 \times 7 \times 10^{-6})\right] = 91K$. The ISM is, of course, far from LTE, so thermodynamic arguments are suspect. Nevertheless, since interstellar grain material is generally at temperatures $T_d \lesssim 20K \ll 91K$, we can at least contemplate the possibility that PAH grains exposed to atomic H and D might attain D:H ratios as high as $\sim 0.3$.

It can easily be shown that thermal desorption also cannot be important. At such temperature $T_d \lesssim 91K$, the rate for thermal desorption of chemically-bound H in PAHs is entirely negligible. Therefore it does not appear that the required degree of deuteration can be achieved by the thermal desorption process discussed by Allamandola, Tielens, & Barker (1989).

Because grains can catalyze $\text{H}_2$ formation, it is important to note that the energy difference

$$\Delta E(\text{H}_2 - \text{HD}) \approx \frac{1}{2} \frac{\hbar c}{2.4\,\mu m} \left(1 - \sqrt{\frac{3}{4}}\right) = 0.035eV \quad (4)$$
is 0.048 eV smaller than $\Delta E(\text{CH} - \text{CD})$, so that it is energetically favorable to leave the D attached to C and instead abstract an H to form H$_2$ rather than HD (2.4µm is the wavelength of H$_2$ 1-0 Q branch lines). Thus even if the H$_2$ formation process involves hydrogen abstraction, H$_2$ will be strongly favored over formation of HD, leaving D atoms chemically bound in the hydrocarbon grain. This differs from the prediction by Lipshtat, Biham, & Herbst (2004) of enhanced HD and D$_2$ formation if H and D are only physisorbed on the grain surface.

Now the key question is: can we imagine a kinetic pathway whereby extreme deuteration of grains might come about?

### 3.3. Kinetics of Deuteration

While it is known that PAHs can form in the high-temperature chemistry of flames, the processes responsible for the formation of interstellar PAHs and other carbonaceous material remain unclear. We will assume that at the time of their formation, the carbon solids are minimally deuterated, incorporating H and D approximately in proportion to gas-phase abundances. Given that carbonaceous grains incorporate only $\sim$145 ppm of all of the hydrogen, a negligible fraction of the D would initially be trapped in PAHs.

For grains to become heavily deuterated, it is necessary that

1. D or D$^+$ arriving at a carbonaceous grain must have a significant probability of being incorporated into the grain;

2. D that has been incorporated must not be removed by exchange reactions with arriving H or H$^+$ – if this were to happen with any appreciable probability, the steady-state abundance of D in the grain would be very low.

We consider conditions in cold HI clouds (the “cold neutral medium”, or CNM), with density $n_H \approx 30$ cm$^{-3}$, electron density $n_e \approx 0.03$ cm$^{-3}$, with perhaps 1/3 of the electrons contributed by ionized metals, and 2/3 by ionized hydrogen. Thus the hydrogen ionization fraction $x_H \approx 7 \times 10^{-4}$; because of rapid charge exchange, deuterium will have the same ionization fraction. We take the local average starlight background.

Impinging low-energy D atoms are probably unable to react chemically with an already saturated neutral hydrocarbon – the arriving D will most likely be physisorbed or chemisorbed on the surface of the neutral PAH, from which it can subsequently be removed by reacting with an arriving H to form HD, or by thermal desorption following heating of the PAH by photon absorption.

As discussed by Bauschlicher (1998) for the naphthalene cation C$_{10}$H$_8^+$, a D atom can react with a PAH cation, producing a hydro-PAH cation, with two hydrogens sharing a single carbon (see Figure 2). How rapidly will this occur?

It is not known if thermal D atoms will react with PAHs much larger than naphthalene if they are only singly or doubly charged, so let us consider only PAH cations containing $< 100$ C atoms. Collision cross sections are estimated following Draine & Sutin (1987), the PAH size distribution is from Li & Draine (2001) and Weingartner & Draine (2001a), and the PAH charge distribution is estimated following Weingartner & Draine (2001b). For a neutral D in the
Figure 2. Examples of reaction pathways for deuteration of a generic PAH (see text), by collision of D\(^+\) with a neutral PAH (upper left) or collision of D with a PAH\(^+\) cation (lower left) to create a hydro-PAH cation, with two H atoms bonded to one C. Subsequent reaction with incoming H would remove one of the extra H atoms and form H\(_2\). Other pathways also exist.

CNM, I find the rate to collide and react with PAH cations containing < 100 atoms is 1.3 \times 10^{-14}\text{s}^{-1}; if the probability of reaction is of order unity, and there is no process returning D to the gas phase, then the gas-phase D abundance in the CNM would decline by a factor 1/e in only \sim 2.4\text{Myr}.

Another pathway begins with D\(^+\) colliding with a neutral (or negative) PAH; the D\(^+\) will arrive at the PAH with sufficient kinetic energy that atomic rearrangements can take place among the peripheral hydrogens near the point of impact. The excess energy will be thermalized in the vibrational modes; the collision complex is expected to maximize its binding energy by an exchange reaction that would replace a C-H bond with a C-D bond, thus incorporating the D and creating a hydro-PAH cation just as for the case of a neutral D colliding with a PAH cation. It seems likely that every arriving D\(^+\) ion will be incorporated into the PAH via this pathway, thus deuterating the PAH and removing D from the gas.

The rate for species X to collide with a grain can be written \(n_{\text{H}}\alpha_g(X)\), where \(\alpha_g(X)\) depends on the PAH charge distribution. Ions have relatively high rates for collisions with neutral PAHs because of the induced polarization interaction, and even higher rates for negative PAH ions because of Coulomb focussing. Weingartner \& Draine (2001c) estimated \(\alpha_g(\text{H}^+) \approx 6 \times 10^{-14}\text{cm}^3\text{s}^{-1}\).
in the CNM; $\alpha_g(D^+)$ will be smaller by $1/\sqrt{2}$, $\alpha_g(D^+) \approx 4 \times 10^{-14}\text{cm}^3\text{s}^{-1}$. Thus the rate for D nuclei to react with a grain by this pathway is $x_{\text{H}_2}\alpha_g(D^+) \approx 8 \times 10^{-16}\text{s}^{-1}$. This is a factor of 16 slower than the rate for D nuclei to react with PAH cations, and therefore is of only secondary importance. Together, the gas-phase processes appear able to remove D from the gas, and deuterate PAHs, on a time scale of $\sim 2.3\text{ Myr}$.

Evolution of the grain population is not well understood, but it appears that the larger grains move relative to the gas with speeds of $\sim 1\text{ km s}^{-1}$ resulting from MHD turbulence (Yan et al. 2004). This can sweep up the PAHs on $\sim 10^7\text{yr}$ timescales and incorporate them into larger grains; occasional shattering of larger carbonaceous grains when they collide replenishes the PAH population. In this scenario, all of the aromatic grain material eventually becomes enriched with D, not just the fraction that is instantaneously present in small free-flying PAHs.

The proposed extreme deuteration of PAH material imposes strong requirements on branching ratios for reactions of PAH material with impinging H and D atoms and ions, and is therefore subject to laboratory test. In particular, an experiment with low energy D$^+$ impinging on partially-deuterated PAH material should have a high probability of incorporating the D into the solid, while reactions of low energy H$^+$ with the same sample should have a very small probability of abstracting D from the sample.

4. Return of D to the Gas Phase

Grains don’t last forever – sputtering and grain-grain collisions following the passage of $v_s > 100\text{ km s}^{-1}$ shock waves can return atoms – including D – from the solid to the gas phase. When this occurs, $(D/H)_{\text{gas}}$ should increase, along with the gas-phase abundances of other elements, such as Si, Ti, and Fe, that are normally strongly depleted. The hypothesis that dust is responsible for the observed variations in $(D/H)_{\text{gas}}$ therefore predicts that the gas-phase abundances of Si, Ti, Fe and other refractory metals should show a positive correlation with the gas-phase abundance of D.

This prediction appears to be confirmed by a recent study finding a positive correlation between $(D/H)_{\text{gas}}$ and $(Fe/H)_{\text{gas}}$ (Linsky et al. 2005).

5. Can D in Grains be Observed?

5.1. Spectroscopy

The emission features at 3.3, 8.6, and 11.3$\mu$m provide direct spectroscopic evidence for the presence of C-H bonds in vibrationally-excited interstellar PAH material. Can C-D bonds be observed through corresponding emission features? The C-D in-plane bending mode at $\sim 1.36 \times 8.6\mu m = 11.7\mu m$ would be confused with the C-H out-of-plane bending modes at $\sim 11.3\mu m$, and the out-of-plane bending mode at $\sim 1.36 \times 11.3\mu m = 15.4\mu m$ falls in a region where other PAH features (C-C skeleton modes) are present. The best hope appears to be the C-D stretching mode at $\sim 1.36 \times 3.3\mu m \approx 4.5\mu m$. In fact, Peeters et al. (2004) report detection of weak emission features at 4.4$\mu m$ and 4.68$\mu m$ from the Orion
Bar and M17 photodissociation regions. Identification of the features as due to C-D is uncertain, but if the features are indeed due to C-D modes, Peeters et al. estimate \((D/H)_{PAH} = 0.17 \pm 0.03\) in Orion and \(0.36 \pm 0.08\) in M17. These D/H values are just in the range that we have estimated above to be necessary to lower \((D/H)_{gas}\) to the observed values!

Additional spectroscopy of the emission from PDRs in the 4–5\(\mu m\) region to confirm these detections and identifications would be of great value. Unfortunately, the IRS instrument on Spitzer only works longward of 5.2\(\mu m\).

Detection of absorption features produced by deuterated PAH material is unpromising, because absorption by the C-H stretching mode in aromatic hydrocarbons is quite weak – even the 3.3\(\mu m\) aromatic C-H stretch feature has not been seen in absorption. Detection of the 4.5\(\mu m\) C-D stretch in absorption does not appear to be possible. The C-D bending modes will also be too weak to detect, and in any case would be confused with other PAH modes, as discussed above.

5.2. Interstellar Grains in the Laboratory

The local interstellar medium appears to have \((D/H)_{gas} \approx 15\) ppm (see Fig. 6 of Wood et al. 2004). If the total D/H \(\approx 23\) ppm, then the local dust grains would be deuterated. For our above provisional value of \((H+D)_{dust} \approx 145\) ppm (including aliphatic hydrocarbons), we would estimate \((D/H)_{dust} = 8/145 \approx 0.06\). The Stardust mission (Brownlee et al. 1994) should have captured interstellar dust grains in its aerogel dust collectors, to be returned to earth in January 2006. If it has collected grain material that is representative of the interstellar grain population, this would be expected to have D/H \(\approx 0.06\) if dust is responsible for the observed variations in \((D/H)_{gas}\); the aromatic component of such grains, if isolated, might have an even higher D/H ratio. Laboratory measurements of D/H in the returned interstellar grain samples will test this hypothesis.

As noted above (§3.1.), IDPs are sometimes seen to be strongly deuterated. The largest D/H ratio seen thus far is 0.008 (Messenger 2000). If interstellar grains have D/H ratios as large as 0.3, as proposed here, why are these not seen in IDPs that are thought to originate in comets?

First, while the median \((D/H)_{gas} \approx 14\) ppm in Figure 6, two of the 14 sightlines have \((D/H)_{gas} > 20\) ppm. Presumably this material was shocked relatively recently. Perhaps the solar system formed out of such matter 4.5 Gyr ago. Second, while comets are thought to be made of relatively primitive material, it is possible that accretion into the solar nebula might involve a phase with sufficiently high temperatures and densities for significant exchange of H and D with the gas to take place, thereby lowering the D/H ratio in the grains.

The observed D/H ratios in interplanetary dust particles are compatible with the hypothesis that interstellar grains can reach \((D/H)\) values as large as \(\sim 0.3\).

6. Summary

1. The lack of correlation between \((D/H)_{gas}\) and \((O/H)_{gas}\) in Figure 6 argues strongly against variations in astration as the explanation for the observed variation in \((D/H)_{gas}\).
2. It appears possible for dust grains to remove D from the gas phase in amounts sufficient to account for the observed variations in \((D/H)_{\text{gas}}\) from one sightline to another.

3. Collisions of D with PAH cations, and collisions of \(D^+\) with PAHs, are expected to result in incorporation of D into the PAH. The rate of such collisions is sufficient to deplete D from the gas on time scales of \(\sim 2\) Myr in cool H I clouds.

4. Grain destruction should return D to the gas along with other elements found in refractory grains. There should therefore be an observable correlation between \((D/H)_{\text{gas}}\) and the gas-phase abundances of Mg, Si, Ca, Ti, Fe, and other elements that exhibit strong depletions. This prediction appears to be confirmed by a recent study finding a positive correlation between \((D/H)_{\text{gas}}\) and \((Fe/H)_{\text{gas}}\) (Linsky et al. 2005).

5. Carbonaceous interstellar material collected by Stardust, if representative of grains from the local interstellar medium, should be strongly deuterated.

6. Laboratory studies can test whether the proposed deuteration reactions have the required branching ratios.

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