Chemical Processes in the Interstellar Medium: 
Source of the Gas and Dust in the 
Primitive Solar Nebula

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Everything that became part of the primitive solar nebula first passed through the interstellar 
medium and the dense molecular cloud from which the nebula collapsed. We begin with a brief 
discussion of the connection between dense molecular clouds and the formation of solar-type 
stars. We then review processes that occur in these environments in order to constrain the chemi-
cal and physical properties of the matter that might still be preserved in primitive meteorites and 
that was the source material for every asteroid, comet, moon, and planet that exists at the present 
time in our own or in any other planetary system. Much of this history may be completely 
overprinted via processes occurring in the nebula itself or in larger planetary bodies, yet some 
signatures, such as those carried by isotopes of H, O, or N can be much more persistent.

1. INTRODUCTION

Primitive meteorites have a great deal in common with 
metamorphosed sedimentary rocks. The provenance of their 
individual components is somewhat uncertain, as is the pre-
cise time-temperature-pressure history that resulted in their 
formation. Yet these initial materials, no matter how differ-
ent in origin, are found in a single, meter-scale object. We 
examine the likely input to primitive meteorites from the 
interstellar medium (ISM), starting from the source regions 
of the chemical elements and cosmic dust: asymptotic giant 
branch (AGB) stars, novae, and supernovae, and follow the 
likely chemical evolution of this material through regions 
of the interstellar medium and into the nebula. We follow 
the gas and dust from astrophysical sources separately with 
the goal of highlighting the signatures of interstellar pro-
cesses that may be preserved in meteorites. Specifically, we 
describe the processing that dust grains and large molecules 
such as polycyclic aromatic hydrocarbons (PAHs) experi-
ence in the warm, diffuse ISM due to ultraviolet radiation, 
cosmic-ray bombardment, and shock chemistry. We also 
describe the ensuing chemistry when this material is incor-
porated into cold, molecular clouds where dense prestellar 
cores form and in which solar-type stars are born.

We examine these interstellar processes to highlight the 
potential correlations between the isotopic and chemical 
signatures that might be observable in meteorites or inter-
planetary dust particles (IDPs). For example, it has often 
been suggested that circumstellar grains are efficiently de-
stroyed in the ISM. We look into this premise by comparing 
the likely signatures of solids produced in the ISM to those 
produced by circumstellar sources. Similarly, ion-molecule 
reactions in moderate density regions, and reactions in and 
on ice mantles in dense clouds, are suspected of producing 
a number of distinctive isotopic signatures in carbonaceous 
materials. Therefore, we review the gas-phase and solid-
phase fractionation pathways for D, $^{15}$N, and $^{13}$C occurring 
in interstellar molecules and in the meteoritic data. We focus 
on recent detections of “superdeuteration” in specific compo-
unds and on the possible relationship of these compounds’ 
isotopic ratios to those found in meteoritic samples and 
IDPs. Finally, many molecules observed in molecular clouds 
have been proposed as precursors for chemical pathways 
that occurred on the parent bodies of carbonaceous chon-
drites, leading to the rich organic inventory in meteorite 
specimens.

2. INTERSTELLAR MATTER IN 
THE SOLAR SYSTEM

This section gives a brief overview of the connection be-

tween dense molecular clouds and the formation of solar-
type stars. We describe the physical conditions in dense clouds and the processes believed to be involved in star formation, and list some of the measured chemical characteristics of primitive meteorites that can be attributed to interstellar chemistry.

2.1. The Interstellar Medium

The ISM is that region in space between the stars and is composed mainly of H and He gas as well as dust. The ISM ranges from extremely hot (10,000 K) diffuse (1 atom cm$^{-3}$) regions, to cold (10 K) dense (>10$^4$ atoms/molecules cm$^{-3}$) clouds. Gases make up the bulk of the mass of the ISM. The dust is a combination of grains generated in dying stars and modified in the ISM. Although the dust comprises only a small amount of material in the ISM by mass (i.e., 1%), it plays a significantly larger role in interstellar chemistry. While gas is generally transparent to photons from the near-ultraviolet to the far-infrared, dust absorbs and scatters this same energy. This process is referred to as “extinction.” Dust can then serve as a “shield” from ultraviolet energy in denser regions so that more complex reactions might occur in the surrounding gas and on the grains themselves in surface-mediated reactions [see Bakes (1997) for an overview]. In order to learn more about the ISM, numerous spectral observations have been made of the intervening space using a variety of techniques and instruments (e.g., Blitz, 1990). These spectral techniques have revealed a wealth of information and more discoveries are made with each passing year.

The extinction of starlight is caused by the absorbance and scattering of energy by the solid material in the ISM. The degree and wavelength dependence of the interstellar extinction curve is affected by the grain size, composition, and morphology of the dust between the source of the starlight and the observer. As such, the curve has distinct features (see Zubko et al., 2004, and references therein; Mathis, 1990). For example, the cause of the 217.5-nm absorption bump/peak has been under debate for many years and is most certainly due to C in some form. This, and many other dust features, is discussed in more detail in section 5, particularly in section 5.2. However, in the next section we focus on the chemistry that occurs within dense molecular clouds, the diffuse ISM, and in the regions surrounding protostellar cores.

2.2. Dense Molecular Clouds and Star Formation

Dissipation of interstellar turbulence in shock waves leads to the formation of dense molecular clouds from the diffuse interstellar medium (see Mac Low and Klessen, 2004). The high extinction efficiency of dust grains implies that most of the interstellar radiation impinging a cloud does not penetrate to the innermost dense regions. However, cosmic-ray particles can penetrate throughout the cloud to heat the gas, which can cool through emission of radiation in the rotational lines of the CO molecule. These processes lead to typical gas temperatures of around 10 K (Goldsmith and Langer, 1978).

Dense clouds show significant substructure (Evans, 1999). Hydrogen nucleon densities of 10$^3$–10$^5$ cm$^{-3}$ are found in large-scale (~few parsec (pc)) dense clumps, which in turn contained in a more diffuse (~10$^2$–10$^3$ cm$^{-3}$) interclump medium. Much higher densities (>10$^5$ cm$^{-3}$) are found in the small-scale (~0.1 pc) cores that are the future sites of gravitational collapse and low-mass star formation. If molecular clouds are long-lived structures (~10$^7$ yr), then the low galactic star formation rate implied by observations (Zuckerman and Evans, 1974) suggests that their cores must be supported against gravity by magnetic and/or turbulent pressures. There are then three important timescales for the evolution of molecular clouds and star formation. The first is the gravitational free-fall timescale, $\tau_{ff} \sim 4.35 \times 10^7 n_H^{-1/2}$ yr, where $n_H$ is the H nucleon density. In the case where support is due to the combined effects of magnetic field pressure and the turbulent pressure exerted by magnetohydrodynamic (MHD) waves [the “standard model” of low-mass star formation (see Shu et al., 1987)], support is lost by the decline in magnetic flux due to the relative drift between ions and neutrals. It follows that the second timescale is associated with this ambipolar diffusion process, $\tau_{AD}$. For standard assumptions concerning the cosmic-ray ionization rate and depletion of the elements, $\tau_{AD} \sim 7.3 \times 10^3 x_e$ yr$^{-1}$, where the fractional ionization, $x_e$, is ~10$^{-8}$–10$^{-7}$ at molecular cloud densities. As $\tau_{AD} \gg \tau_{ff}$, the loss of magnetic flux leads to a slow quasi-static increase in the central density of the core until gravity dominates, then a protostar forms in a rapid, approximately isothermal, free-fall collapse (Larson, 2003). The third timescale of importance is associated with the dissipation of turbulence ($\tau_{\delta}$) and was found to be comparable to the free-fall time using numerical simulations of MHD turbulence. Clouds and cores cannot be sustained against collapse by turbulent support for much longer than $\tau_{\delta}$ (Mac Low and Klessen, 2004).

This fact and other arguments concerning the observed lack of T Tauri stars in dense clouds recently led to the alternative view that the evolution of molecular clouds and star formation are rapid processes governed by supersonic turbulence (Elmegreen, 2000; Hartmann et al., 2001; Mac Low and Klessen, 2004; Larson, 2003). In this scenario, interstellar clouds spend a significant fraction of their lives in a low-density, mostly atomic state where star formation is inefficient. When diffuse material is compressed to higher densities and molecular H forms, star formation occurs rapidly within only a few free-fall times. In this scenario the molecular clouds themselves are short-lived structures, dissipating soon after star formation has begun (Elmegreen, 2000).

To summarize, the protosolar nebula was likely formed by the nearly free-fall gravitational collapse (~3 × 10$^5$ yr) of a rotating mass of cold gas and dust. This collapsing material was situated near the center of a dense molecular core that itself either formed slowly (several million years) by gradual contraction due to the gradual loss of magnetic sup-
port against gravity (e.g., Shu et al., 1987) or more rapidly (~few free-fall times) by the dissipation of turbulence (e.g., MacLow and Klessen, 2004). An alternative view, discussed in Boss and Goswami (2006), is that a nearby supernova explosion could have triggered the collapse. Irrespective of the uncertainty over the formation timescale and ages of molecular clouds, protostars form by gravitational collapse of a dense molecular core (Evans, 1999). However, it should be pointed out that chemical youth better explains the high CO/O3 ratios commonly found in molecular clouds (Goldsmith et al., 2000), as well as the high abundances of C-chain molecules detected in them (e.g., Suzuki et al., 1992).

Clearly, regions of star formation cannot be characterized in a few sentences: They are complex, time-dependent extremes of hot and cold. Most of the preexisting matter either falls into the central star or is ejected from the system in bipolar outflows. The majority of the tiny fraction of material left orbiting the central star will be found in the form of planets that retain little record of the gas and grains from which they formed. Only comets and the smaller asteroids preserve intact material that might predate the time of star formation, yet these objects also preserve a significant quantity of material produced via the repeated vaporization and recondensation of nebular solids (Boynton, 1985; Clayton et al., 1985).

2.3. Meteoritic Evidence for Interstellar Signatures

All the materials incorporated into protostellar nebulae — elemental nuclei, PAHs, large macromolecular aromatic-carbon structures, and dust particles — were once in the diffuse ISM. Many astronomical sources contribute to the composition of the refractory dust found in the diffuse ISM: the atmospheres and outflows of late-type stars on the AGB, winds from Wolf-Rayet stars, novae, and supernovae. The gas-phase molecular composition of the diffuse ISM, on the other hand, is largely determined by the local physical conditions (van Dishoeck and Black, 1988). However, it is the active gas phase chemistry occurring in cold molecular clouds that is pivotal in setting the initial chemical inventory of volatile species available to the protosolar nebula. Here, much of the gas is converted to molecular form (H2, CO, N2) and an additional solid phase — the icy grain mantle — is produced through the condensation and reaction of gaseous volatiles. Within the meteoritic record there is clear evidence for chemical processes such as isotopic fractionation, including significant levels of D enrichment that would have been favored in the cold, dense environment of molecular clouds.

The organic inventories of Murchison (a well-studied carbonaceous meteorite), other primitive meteorites, and IDPs display large D enrichments relative to terrestrial values. This constitutes one of the most convincing pieces of evidence that at least some of the original C reservoir was interstellar (e.g., Kerridge and Chang, 1985). Meteoritic organic material also contains a large enrichment in 15N (e.g., Alexander et al., 1998) where the anomalous N is generally associated with carbonaceous material. Many IDPs are also highly enriched in D and 15N (e.g., Messenger and Walker, 1997; Messenger, 2000). In contrast, C isotopes do not show similar anomalies, although there is evidence for variations within specific homologous series (Gilmour and Pilling, 1994). These isotopic anomalies are chemical in origin and distinct from the nucleosynthetic signatures found in circumstellar grains (e.g., Messenger et al., 1998). In cold interstellar clouds, enhanced molecular D/H ratios are observed and can easily be explained by gas phase and grain-surface processes (Tielens, 1983; Millar et al., 1989; Sandford et al., 2001). The 15N anomalies could be due to nucleosynthetic processes; however, such processes also tend to produce anomalous effects in the C isotopes that are more pronounced, and are not evident in the meteoritic data (e.g., Messenger and Walker, 1997). For this reason, the 15N enrichments are also believed to be due to chemical fractionation in interstellar ion-molecule reactions (e.g., Terzieva and Herbst, 2000; Aléon and Robert, 2004).

Interstellar chemistry can explain many of the molecules found in meteoritic extracts. Organic compounds identified in carbonaceous C1 and C2 chondrites include amines and amides; alcohols, aldehydes, and ketones; aliphatic and aromatic hydrocarbons; sulfonic and phosphonic acids; amino, hydroxycarboxylic, and carboxylic acids; purines and pyrimidines; and kerogen-type material (Cronin and Chang, 1993; Botta and Bada, 2002). These molecules show specific enrichments in D, 13C, and 15N (e.g., Cronin and Chang, 1993), indicative of their retention of an interstellar heritage. Some of these simple organics may be of true interstellar origin, whereas the more complex molecules may have had simpler interstellar precursors that subsequently reacted in the solar nebula or meteorite parent body. The initial interstellar inventory determined which reaction pathways would be most likely for secondary processing in the protosolar nebula, for example, as the result of aqueous alteration on meteoritic parent bodies.

Carbonaceous meteoritic material represents a mixture of highly processed interstellar matter and, perhaps, some pristine components. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the ISM (Allamandola et al., 1989; Puget and Léger, 1989), and are also widespread in meteorites (e.g., Basile et al., 1984), as well as in IDPs (Allamandola et al., 1987; Clemett et al., 1998). Most meteoritic carbon is in the form of a kerogen-like material and this may be associated with interstellar PAHs. The PAHs found in meteorites could have originated in the cool envelopes of carbon stars (Frenklach and Feigelson, 1989) although other formation sites are possible, such as in diffuse interstellar gas (Bettens and Herbst, 1996) or by energetic processing of specific ices in dense clouds (Kissel et al., 1997), or by reaction of CO, N2, and H2 on grain surfaces in the solar nebula. The PAH component of meteorites exhibits a D enrichment indicative of a presolar origin (Allamandola et al., 1987). Since D is consumed in stellar burning, the deuteration of astronomical PAHs can occur in the interstellar me-
dium, specifically in the cold environment of dense molecular clouds. In their evolutionary cycle, PAH molecules freeze out onto grains in dense clouds, where they can become fractionated through energetically driven reactions with deuterated water ice. Additionally, several ion-molecule gas phase processes will deuterate PAHs (Sandford et al., 2001) (see section 4.1).

3. INTERSTELLAR CHEMISTRY

From the perspective of providing either the simple molecular precursors or the actual molecules themselves, the pivotal phases of the ISM for meteoritic studies are the dense molecular clouds and the star-forming cores within them. Table 1 presents an inventory of gas-phase astrophysical molecules identified using radio observations. These molecules include those known to be present in the diffuse ISM, dense molecular clouds, and the envelopes of evolved stars. The simpler molecules can be formed by gas-phase chemistry but some of them (e.g., H$_2$O and CO$_2$) can be more efficiently formed on the surfaces of dust grains. It appears that many more complex molecules are formed exclusively by grain catalysis (e.g., CH$_3$OH and C$_2$H$_5$OH). The great majority of these species, particularly the more complex ones, have been detected in cold molecular clouds or in the warmer environs of forming protostars. By no means is this list representative of the bulk of the material in the ISM. For example, no polyaromatic hydrocarbons (PAHs) are listed even though they are likely to be more abundant than almost all the molecules listed in Table 1.

In this section, we describe the principle chemical processes that occur in dense molecular clouds and in star-forming environments. Note that most of these processes also apply to other astrochemically active regions such as the diffuse ISM (Wooden et al., 2004), protoplanetary disks (Markwick and Charnley, 2004; Ciesla and Charnley, 2006), the early universe (Stancil et al., 2002) and in the winds from novae, supernovae, and red giant stars (Rawlings, 1988; Lepp et al., 1990; Glassgold, 1996). These chemical processes are crucial for understanding what is probably the most direct connection between the ISM and the composition of meteorites: isotopic fractionation.

### 3.1. Gas Phase Processes

Interstellar chemistry generally takes place in extreme cold (T < 50 K) and at densities where only bimolecular or unimolecular processes are viable (<10$^{13}$ particles cm$^{-3}$). In dark, starless regions, the chemistry occurs in gas where the H nucleon density, n$_{\text{H}}$, and the gas kinetic temperature, T, fall in the ranges of $\sim$10$^3$–10$^5$ cm$^{-3}$ and $\sim$10–30 K, respectively (e.g., Goldsmith and Langer, 1978). Closer to na-

### Table 1. Identified astrophysical molecules.

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scent protostars, in so-called hot molecular cores, the physical conditions are markedly different: \( n_H \sim 10^6-10^8 \text{ cm}^{-3} \), and \( T \sim 50-300 \text{ K} \) (e.g., van Dishoeck and Blake, 1998). However, it is important to note that densities and temperatures high enough for the gas-phase synthesis of \( \text{H}_2 \) are not achieved even here. Instead, \( \text{H}_2 \) is produced in a three-body reaction where the third body is a dust grain (e.g., Hollenbach and Salpeter, 1971). Surface-mediated reactions on dust grains are discussed in section 3.2. In the following section, we describe the gas-phase chemistry that ensues when almost all the available H has been converted to molecular form.

Galactic cosmic rays ionize \( \text{H}_2 \) molecules to produce electrons, \( \text{H}^+ \) and \( \text{H}_2^+ \). The latter rapidly reacts with \( \text{H}_2 \) to form the \( \text{H}_2^+ \) ion. Since \( \text{H}_2^+ \) readily transfers a proton to most species, it plays a central role in dense molecular cloud chemistry. Thus, the principal gas-phase chemical processes occurring in molecular clouds are ion-neutral reactions, ion-electron dissociative reactions, radiative recombination, and neutral-neutral reactions. Since He atoms are also ionized by cosmic rays, dissociative charge transfer reactions involving \( \text{He}^+ \) play an important role in destroying neutral molecules. External photons from outside the molecular clouds are efficiently extinguished by the dust particles, although a small, weak, residual flux derived from the deexcitation of \( \text{H}_2 \) following the impact of cosmic-ray-produced electrons may have a significant role (Prasad and Tarafdar, 1983) in dark cloud chemistry.

The synthesis of interstellar molecules is initiated by charge transfer between \( \text{H}^+ \) and \( \text{O} \) atoms that leads, via a sequence of ion-molecule reactions with \( \text{H}_2 \), to the production of \( \text{OH} \) and the onset of neutral chemistry. This leads to \( \text{CO} \) and \( \text{N}_2 \) as the most abundant molecules after \( \text{H}_2 \), with \( \text{OH}, \text{NH}_3, \text{and SO} \) also produced in significant abundance. Theoretically, the timescale to attain a chemical steady state for this process is on the order of several million years. In this case almost all the \( \text{C} \) and \( \text{O} \) become incorporated into \( \text{CO} \) and \( \text{O}_2 \). The fact that high atomic \( \text{C} \) and low \( \text{O}_2 \) abundances are observed is evidence either that the lifetimes of molecular clouds are not this long (e.g., Elmegreen, 2000), or that this process is not dominant.

These types of chemical reactions fix the degree of ionization, which in turn controls the magnetic evolution of dense clouds through the rate of loss of magnetic flux by ambipolar diffusion. The dominant ions are \( \text{HCO}^+ \) and \( \text{N}_2\text{H}^+ \) with electron fractions relative to \( \text{H} \) nuclei of \( \sim 10^{-8}-10^{-7} \) (Caselli et al., 1998). It appears that refractory metals (Fe, Mg, Na, Si; i.e., elements heavier than He) are absent from the dense gas, probably by their almost complete incorporation into/onto dust grains. Unsuccessful searches for various related hydrides and oxides provide strong support for this absence (Turner, 1991). If PAH molecules are present in appreciable abundances in cold clouds, they will alter the physics of the plasma, as well as the basic nature of the chemistry (Lepp and Dalgarno, 1988). In this case, PAH anions become the dominant carriers of negative charge and the major ion neutralization pathway becomes mutual neutralization.

### 3.2. Grain-Surface Processes

At gas and dust temperatures near 10 K, efficient adsorption of atoms and molecules from the gas, followed by surface diffusion and reaction of atoms with other surface species, leads to the formation of a “dirty” ice mantle covering the more refractory silicate core (e.g., Sandford and Allamandola, 1993). Infrared observations of dark clouds and subsequent interpretations indicate that ice mantles cover interstellar dust grains and suggest that a rich catalytic chemistry is possible (Ehrenfreund and Charnley, 2000). The Infrared Space Observatory (ISO) observed many massive star-forming regions and these observations have been used to inventory the most abundant ice species in dense clouds (Ehrenfreund and Schutte, 2000; Gibb et al., 2000). The ices are predominately \( \text{H}_2\text{O} \), with \( \text{CO}, \text{CO}_2, \) and \( \text{CH}_3\text{OH} \) as the next most abundant molecules (comprising from \( \sim 5\% \) to \( 40\% \) of the ices). Several other molecules are only present in trace amounts of a few percent or less: \( \text{CH}_3\text{NH}_3, \text{H}_3\text{CO}, \text{HCOOH}, \text{OCS}, \) and possibly \( \text{OCN}^- \) (see Fig. 1). In Fig. 1, \( \text{OCN}^- \) is represented by \( \text{XCN} \) because until recently it was unclear which element X represented. Recent ground-based observations have also identified high abundances of methanol (\( \text{CH}_3\text{OH} \)) ice in regions of low-mass star formation (Pontoppidan et al., 2003).

Cold grain-surface kinetics occurs in two steps following a Langmuir-Hinchelwood catalytic model: First, atoms and molecules stick to the surface, then subsequently diffuse among surface binding sites either by quantum mechanical tunneling, as is the case for H and D atoms, or by thermal hopping. These processes are depicted in Fig. 2. Diffusion of light atoms is many times faster than that of heavier molecules; therefore the chemistry is dominated by exothermic atom-atom reactions, atom-molecular radical reactions, and by reactions involving activation energy barriers where atoms add to molecules with multiple bonds (e.g., Allen and Robinson, 1977; Tielens and Hagen, 1982;...

![Fig. 1](image-url). Molecules detected in interstellar ices surrounding the massive protostar W33A by space-based IR absorption spectroscopy (Gibb et al., 2000).
Charnley, 2001a). On grain surfaces, H2O, NH3, H2S, and CH4 are formed by successive H atom additions to accreted O, N, S and C. Accreted CO molecules can be reduced, oxidized, and deuterated by H, O, and D atoms in additions that possess activation energy barriers (Tielens and Hagen, 1982; Charnley et al., 1997). Extension of the basic kinetic scheme in the CO reduction sequence to additions involving C atoms, with the additional constraint of radical stability, can lead to surface reactions where many known interstellar molecules (e.g., aldehydes, ketones, alcohols, sugars) can be produced (Charnley, 1997a, 2001b).

It appears that many of the most abundant interstellar ice molecules can be accounted for either by direct accretion from the gas (e.g., CO) or by one of the above (cold) atom addition processes. Until recently, this assertion was based solely on theory (e.g., Allen and Robinson, 1977; Tielens and Hagen, 1982), but recent experiments tend to confirm the efficacy of these processes under conditions relevant for interstellar dust. Although the simplest system of H2 production on various surfaces at temperatures around 10 K has been the primary focus of research efforts (Pirronello et al., 1999; Manico et al., 2001), the hydrogenation of CO to HCHO and CH3OH at low temperatures has also been studied extensively (Hiraoka et al., 1994, 1998, 2002; Watanabe and Kouchi, 2002; Watanabe et al., 2003). The reduction of HC3H and the production of CO2 by adding an O atom to CO have also been demonstrated (Hiraoka et al., 2000; Roser et al., 2001).

Once a thick molecular ice mantle has been formed, the bulk ice matrix can itself be subject to further “energetic processing” involving the absorption of UV photons and cosmic-ray impacts. Many experimental studies of these processes have been made (Allamandola et al., 1997; Hudson and Moore, 1999), yet it is still unclear what the relative contributions of photolysis and radiolysis are to the observed interstellar inventory. The carrier of the “XCN” band has been identified as OCN−, and production of this species requires some form of energetic processing in the protostellar environment [see Ehrenfreund et al. (2001) for a recent summary].

Thermal heating, prior to complete desorption of the icy mantle, can be viewed as an energetic process that can lead to molecular rearrangement: This is an important aspect of ISM chemistry. Blake et al. (1991) presented direct structural evidence of such rearrangements, while Ehrenfreund et al. (1998) experimentally showed that the fine structure found by ISO in the 15.2-µm CO2 band is due to the rearrangement of molecules in the matrix to form Lewis base CO2-CH3OH complexes at approximately 70 K.

As ices are formed, there clearly must be retention of the reaction products with a reasonably high (but unknown) efficiency. Nevertheless, some desorption processes do operate and these can be roughly divided into passive and active modes. In passive desorption (e.g., Willacy and Millar, 1998), one considers processes directly connected to the surface or bulk chemistry that act to remove molecules. As heavy atom–hydrogen atom additions are generally exothermic, some of the excess energy may be expended in breaking the weak surface bond. Similarly, absorption of UV photons or cosmic rays can lead to direct ejection of mantle molecules. Such energetic processing will also produce a small population of highly reactive species in the bulk ice, and these can undergo a spontaneous “explosion” resulting in the loss of mantle material (e.g., Schutte and Greenberg, 1991). Ultraviolet processing has also been shown to produce species found in meteorites such as amino acids (Bernstein et al., 2002), amphiphiles (Dworkin et al., 2001), and aromatic ketones (Bernstein et al., 1999, 2001).

Ices are also returned to the gas in the hot cores surrounding young protostars. Evidence for this lies in the high abundances of many molecules known to have been synthesized on grains: H2O, CH4, NH3, OCS, and CH3OH (e.g., Herbst, 2000). In this case, the external physical environment determines the return of grain mantle material and represents active desorption. Protostellar outflows drive shock waves into the surrounding core and cause ice mantles to be lost by nonthermal sputtering (Draine et al., 1983).

Protostars could also affect more distant regions of molecular clouds: The relative streaming of charged and neutral grains in MHD waves may act as an external trigger for the thermal or explosive desorption of ices (Markwick et al., 2000). However, the most elementary mantle loss process is simple thermal evaporation, where the protostellar luminosity heats the infalling icy grains above the evaporation temperatures of the individual mantle molecules (e.g., Rodgers and Charnley, 2003).

Many complex organics detected in protostellar gas (e.g., C2H5OH, HCO2CH3, CH3CHO, HCO2H) may have also formed on dust grains. However, other organics such as (CH3)2O, CH3CO2H, and CH3COCH3 could have been formed, post-evaporation, by chemical reactions in the hot gas (Charnley et al., 1992). These latter molecules were found by radio astronomers at such low abundances that they would currently be undetectable via infrared ice spectroscopy. Ion-molecule reactions based on cation transfer processes among subliming products of grain-surface chemistry could also form many of the large interstellar molecules (Charnley et al., 1995; Charnley, 2001b; Blagojevic
The richness of the organic chemistry found in molecular clouds, particularly in the environments of massive protostars, has long been appreciated (Cronin and Chang, 1993) as a source for many of the precursor molecules that would be needed to start various organic syntheses on meteoritic parent bodies (e.g., the Strecker-cyanohydrin production of amino and hydroxy acids). This connection is greatly strengthened by recent molecular line observations that indicate that the environments of low-mass protostars also contain a rich chemical inventory (Schöier et al., 2002; Cazaux et al., 2003; Kuan et al., 2004; Bottinelli et al., 2004).

4. ISOTOPIC FRACTIONATION IN MOLECULAR CLOUDS

The chemistry outlined above leads to significant isotopic fractionation in cold molecular clouds. Although the key issue is that the zero-point energy difference between isotopomers is not negligible in ion-molecule reactions at 10 K, other, subtler, effects play a role in fractionating interstellar molecules. In this section we present an outline of relevant fractionation processes. The challenge is to understand the fractionation found in IDPs, comets, and meteorites, either as a direct result of interstellar chemistry, or as evidence for the action of these processes in protoplanetary disks (Ciesla and Charnley, 2006).

4.1. Deuterium

The cosmic D/H ratio is close to 3 \times 10^{-5} (Vidal-Madjar, 2002) (D/H_{\text{Earth}} = 1.56 \times 10^{-5}). Radioastronomical observations of many interstellar molecules and their deuterated counterparts (isotopomers) show that they possess substantial enrichments with D/H enhanced by factors of 10–10,000 over the cosmic value [see Ceccarelli (2002) for a recent review]. At low temperatures, such as those found in molecular clouds (~10 K), the ion-molecule reaction

\[ \text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 \]  

breaks D atoms out of HD, allowing D to be redistributed throughout the gas phase (e.g., Millar et al., 2000) and leads to enrichment in the gas phase D/H ratio (~100x). Therefore, a grain-surface chemistry dominated by atom addition reactions (section 3.2) will lead to molecules highly fractionated in D (Tielens, 1983). At higher temperatures (>30 K) the reverse reaction efficiently destroys H$_2$D$^+$ and deuteration is suppressed. Interstellar chemistry based on these fractionation pathways could account for most of the D/H ratios observed prior to 1998 in both massive hot cores and in cold clouds (e.g., Charnley et al., 1997b; Millar et al., 2000).

However, the discovery of enormous fractionation in D$_2$CO and HDCO (D/H ~ 0.1–0.4) in the circumstellar gas of young low-mass protostars, such as the binary system IRAS 16293-2422 (Loinard et al., 2000, 2001), indicated efficient catalytic formation on grains prior to their deproto-

sition. Yet, the discovery of NHD$_2$ in the cold cloud L134N (Roueff et al., 2000), and subsequently ND$_3$ in other regions (van der Tak et al., 2002), can best be explained by gas-phase chemistry in an environment where CO and other heavy molecules were depleted from the gas by condensation on grains (Rodgers and Charnley, 2001). This depletion mechanism acts to enhance fractionation since reaction with CO is the major destruction pathway for H$_2$D$^+$. In such “depletion cores,” the abundances of H$_2$D$^+$ and D atoms rise dramatically, allowing the former to be easily detected (e.g., Caselli et al., 2003). Thus, it appears that most low-mass stars may form from a “starless” core that has undergone a high depletion phase (Bergin et al., 2002). Depletion has also been proposed to account for the high fractionation seen in D$_2$CO and HDCO (Roberts and Millar, 2000), but is not capable of reproducing the highest ratios observed, or the multiple deuteration in methanol (CHD$_2$OH and CD$_2$OH) recently detected by Parise et al. (2002, 2004). The problem with attributing a grain surface origin to the D fractionation seen in HCHO and CH$_3$OH is that the atomic D/H ratios attainable, even in highly depleted gas, are much lower than needed (~0.5). Roberts et al. (2003) have shown that extensions of the ion-molecule deuteration scheme to include D$_2$ and D$_2$H$^+$ become important at the high densities of prestellar cores (>10$^6$ cm$^{-3}$) and can produce the required atomic D/H ratios. D$_2$H$^+$ has recently been detected by Vastel et al. (2004), who found a D$_2$H$^+/H_2D^+$ ratio of unity, as predicted by theory.

4.2. Nitrogen

Apart from D enrichments, the organic matter found in meteorites and IDPs is also known to contain components that exhibit enhancements in $^{15}$N/$^{14}$N ratios (e.g., Messen-ger, 2000; Aleon et al., 2003; Sephton et al., 2003; Aleon and Robert, 2004) and chemical fractionation in ion-molecule reactions at low temperatures appears to be indicated. Terzieva and Herbst (2000) considered several possible processes that could lead to enhanced $^{15}$N/$^{14}$N ratios in interstellar molecules and found that ion-molecule reactions such as those shown in reactions (2) and (3) were the most important.

\[ ^{15}\text{N} + ^{14}\text{N}_2\text{H}^+ \rightarrow ^{14}\text{N} + ^{15}\text{N}^{14}\text{N}\text{H}^+ \]  

\[ ^{15}\text{N} + ^{14}\text{N}_2\text{H}^+ \rightarrow ^{15}\text{N} + ^{14}\text{N}^{15}\text{N}\text{H}^+ \]  

Terzieva and Herbst (2000) calculated the $^{15}$N/$^{14}$N ratios for the chemical evolution of a molecular cloud and found enrichment factors to be much smaller (~0.25) than that needed to explain the component “hot spots” in meteoritic/IPD materials (~0.5). The theoretical prediction (Charnley, 1997b) that there could be dense regions where CO would be selectively depleted into CO ice, relative to both H$_2$ and N$_2$, has been verified by several recent observations (e.g., Bergin et al., 2002). In this situation, N atoms do not convert to N$_2$ but instead participate in very restrictive reactions that involve
the eventual destruction of the gas-phase molecular nitrogen. Charnley and Rodgers (2002) considered such a scenario where all C- and O-bearing species were depleted, except for N\textsubscript{2} and its isotopomers. They showed that reactions (2) and (3) led to more \textsuperscript{15}N nuclei being incorporated into molecular nitrogen, which, after attack by He\textsuperscript{+} ions, then released N\textsuperscript{+} and N atoms into the gas with a correspondingly higher \textsuperscript{15}N/\textsuperscript{14}N ratio. This N\textsuperscript{+} reacts with H\textsubscript{2} to initiate an ion-molecule sequence leading to ammonia, which is then rapidly accreted as ice with the \textsuperscript{15}N/\textsuperscript{14}N ratio in the ammonia enriched by as much as 80\% relative to the starting value.

However, recent experiments by Geppert et al. (2004) indicate that there is a destructive channel that dominates the dissociative electron recombination of N\textsubscript{2}H\textsuperscript{+}. In this case, the NH radicals produced in the recombinations can react with N atoms to reform N\textsubscript{2}. New calculations show that the peak \textsuperscript{15}NH\textsubscript{3}/\textsuperscript{14}NH\textsubscript{3} ratios achievable are substantially reduced (Rodgers and Charnley, 2004), but high \textsuperscript{15}NH\textsubscript{3}/\textsuperscript{14}NH\textsubscript{3} ratios can be recovered if either the fractionation chemistry takes place at densities where N\textsubscript{2}H\textsuperscript{+} recombination occurs primarily on negatively charged macroscopic particles (dust grains or PAHs), or if there is a small barrier to the reaction of N with NH. Recent measurements of \textsuperscript{15}N/\textsuperscript{14}N in anhydrous IDPs by Floss et al. (2004) determined enrichment factors of about 1.3, much higher than reported in the theoretical models. However, solid-state \textsuperscript{15}NH\textsubscript{3}/\textsuperscript{14}NH\textsubscript{3} ratios calculated in these models are the values in the bulk ice mantle; calculations show that, although they are only a fraction of the total number accreted, the late-accreting ammonia molecules exhibit a temporal “spike” in the \textsuperscript{15}NH\textsubscript{3}/\textsuperscript{14}NH\textsubscript{3} ratio, consistent with the high enrichments found by Floss and coworkers (Charnley and Rodgers, 2002; Rodgers and Charnley, 2004). This suggests that the \textsuperscript{15}NH\textsubscript{3}/\textsuperscript{14}NH\textsubscript{3} ratio should vary with depth throughout the mantle, with very high values occurring in the uppermost few monolayers.

Polycyclic aromatic hydrocarbon molecules should also be late-accreting components of these mantles. Due to their relatively slow thermal velocities, PAH molecules will accrete more slowly than lighter atoms and molecules. As the PAH population is depleted, the anion becomes the dominant charge carrier (Lepp and Dalgarno, 1988) and, since about 95\% of the population of larger “classical” grains are negatively charged, Coulomb repulsion will greatly slow the removal of the remaining PAHs. This effect, coupled with the fact that depleted gas will show very high D/H ratios (Roberts et al., 2003), thus offers a means of spatially colocating, in the uppermost monolayers, carbonaceous molecules enriched in D and ammonia molecules enriched in \textsuperscript{15}N. Additional energetic processing of these ices could then incorporate this \textsuperscript{15}N into the carbonaceous matter (Charnley and Rodgers, 2002) with the high enrichments found by Floss and co-workers (Charnley and Rodgers, 2002; Rodgers and Charnley, 2004).

The former result suggests that the cold regions of a protoplanetary disk may be the location of the \textsuperscript{15}N fractionation. A direct nebular connection is also implied by the fact that this model predicts that enhanced \textsuperscript{15}N fractionation and depletion of N\textsubscript{2} should be a basic feature of primitive solar system material. The latter is a well-known, but puzzling, aspect of cometary composition (e.g., Rodgers et al., 2004). Recently, Arpigny et al. (2003) have shown that cometary C\textsuperscript{15}N/C\textsuperscript{14}N ratios are significantly higher than those of its main photochemical parent, HCN, and are comparable to or greater than those found in IDPs. Arpigny et al. (2003) suggested that the secondary source of CN is an unknown organic polymer whose precursor was the isotopically enhanced ammonia predicted by theory. This observation thus strengthens the connection between these fractionation processes and the putative precursors of the organic matter in IDPs.

### 4.3. Carbon and Oxygen

The insoluble carbonaceous matter that dominates the organic inventory of meteorites exhibits isotopically light \textsuperscript{13}C/\textsuperscript{12}C, relative to terrestrial standards. On the other hand, extracts of soluble molecular compounds, such as amino acids and polar hydrocarbons, show enhanced \textsuperscript{13}C/\textsuperscript{12}C ratios, but the enhancements are generally less than those found in D and \textsuperscript{15}N (Cronin and Chang, 1993). The extensive study of \textsuperscript{13}C and \textsuperscript{18}O fractionation by Langer et al. (1984) considered fairly simple and easily detectable interstellar molecules and was important for showing that the fractionation of interstellar \textsuperscript{13}C is controlled by the gas-temperature, density and metallicity. The CO molecule plays a pivotal role, and at low temperatures (~10 K) and densities, the exchange reaction

\[
\textsuperscript{13}C^+ + \textsuperscript{12}CO \rightarrow \textsuperscript{13}CO + \textsuperscript{12}C^+ \tag{4}
\]

significantly enhances \textsuperscript{13}CO. On the other hand, \textsuperscript{12}C becomes enriched in the other gas-phase species (e.g., C\textsubscript{2}H\textsubscript{2} and CH\textsubscript{4}, as well as in atomic C), perhaps by large factors leading to \textsuperscript{12}C/\textsuperscript{13}C ratios in these species of ~100–350. Oxygen-isotopic fractionation can also occur in ion-molecule reactions, as shown below in reaction (5)

\[
\text{H}^{12}\text{C}^{16}\text{O}^+ + \text{H}^{12}\text{C}^{18}\text{O} \rightarrow \text{H}^{12}\text{C}^{18}\text{O}^+ + \text{H}^{12}\text{C}^{16}\text{O} \tag{5}
\]

The results of Langer et al. (1984) indicate that only modest fractionation in \textsuperscript{18}O can be expected. The O-isotopic ratios in interstellar molecules would therefore probably largely reflect nuclear processing in the stellar source. It is unclear whether interstellar chemistry could reproduce the measured O-isotopic ratios in meteoritic matter (see Clayton, 2003). Kinetic processes leading to C- and O-isotopic fractionation on grain surfaces have not been considered. It is probable that, as in the case of D and \textsuperscript{15}N fractionation, the gas-phase-isotope chemistry determines how molecules will be fractionated in \textsuperscript{13}C (Charnley et al., 2004). For example, if multiply bonded molecules such as CO, C\textsubscript{2}H\textsubscript{2}, and HC\textsubscript{3}N act as seeds for hydrogenation reaction sequences, then the molecules formed from them (in-
cluding CH$_2$OH, CH$_3$CH$_3$, and C$_2$H$_5$CN) should have the same $^{12}$C/$^{13}$C ratios as their precursors. Similarly, if C chains grow on 10 K surfaces by single C atom additions, then we may expect these molecules to have $^{13}$C/$^{12}$C ratios reflecting that of the atomic C accreting from the gas. One more fractionation process arises from the CO photochemistry. In dense gas, $^{13}$C$^{18}$O is sufficiently abundant that it can self-shield against photodissociation from line photons, whereas lower-abundance isotopomers $^{13}$C$^{16}$O, $^{12}$C$^{18}$O, and $^{12}$C$^{17}$O cannot. External interstellar UV photons in regions of low extinction near cloud surfaces can lead to the isotopically selective photodestruction of $^{13}$C$^{16}$O and $^{12}$C$^{18}$O with consequent local increases in the number of $^{13}$C and $^{18}$O atoms available for subsequent chemical reactions. Based on the above processes, regions of varying UV flux and temperature gradients should lead to strongly varying $^{12}$C/$^{13}$C fractionation in the ISM. Perhaps the lower-magnitude anomalies in meteoritic $^{13}$C reflect this variation in flux and temperature gradients.

Now that we have given a general overview of the gas-phase chemistry that takes place in the dense molecular clouds, we move on to the solid matter in the ISM.

5. STELLAR OUTFLOWS AND INTERSTELLAR SOLIDS

Two separate, major populations of grains arise naturally from the circumstellar outflows of C-rich and O-rich stars. These populations are carbonaceous materials, including graphite, diamond and numerous metal carbides, and oxides consisting primarily of amorphous silicates. Until about 1980 the common assumption had always been that interstellar grain populations had their roots in these stellar outflows (Mathis et al., 1977) with only minor modifications arising in special regions of the ISM. Such modifications are attributable to observed phenomena in interstellar environments and include, for example, the growth of a volatile ice mantle or the formation of a carbonaceous residual polymer (Greenberg, 1983; Schutte, 1996; Sandford et al., 1997). Observations of the shock-induced destruction of interstellar grains (Seab and Shull, 1983) have introduced a much more severe modification to this population: the complete destruction of all grains in the ISM on a very rapid timescale ($\sim 10^7$ yr) compared to the rate at which grains are destroyed by incorporation into new stars (Jones et al., 1996). If this rapid destruction really occurs, then the vast majority of grains found in the ISM must also form there.

The models that predict rapid grain destruction in the ISM seldom mention the problems associated with forming refractory grains from hot diffuse vapors and do not present a viable alternative to forming separate populations of C-rich and O-rich grains in appropriate circumstellar environments. This is a huge flaw, as any reasonable scenario for grain formation in the ISM will yield materials whose spectral properties do not match observations (Nuth et al., 1998). We suggest that the mineralogy of the majority of interstellar silicate grains is established in O-rich circumstellar outflows and is only slightly modified by subsequent interstellar processes. This hypothesis is based on a comparison of the IR spectral properties of amorphous Mg silicates observed in the laboratory at various stages of thermal annealing to the infrared spectra of grains in O-rich circumstellar outflows and in the ISM, as detailed in section 6. We should point out that this hypothesis is also consistent with models of the interstellar C distribution: the formation of interstellar diamond grains in supernovae as well as the formation of carbonaceous and graphitic materials in C-rich stellar outflows (Tielens, 1987). However, in the case of C, there is considerable evidence for the growth of grain mantles in cold cloud cores (Pendleton et al., 1990, and references therein; Zinner, 1988). Such processes could therefore be responsible for the production of a significant fraction of the amorphous presolar C found in primitive meteorites as discussed in section 3.2.

5.1. Grain Formation in Stellar Outflows

Dying stars are the best natural laboratories for the study of the grain-formation process, especially the formation of oxide grains. Mass outflows from O-rich AGB and red giant stars are roughly steady-state, homogeneous, dynamic atmospheric escape processes (Kozasa and Hasegawa, 1987; Fleischer et al., 1991, 1992, 1995; Jeong et al., 2003). The stellar atmosphere initially contains only vapor at temperatures well in excess of 2000 K. Gas expansion away from the stellar surface leads to smooth decreases in both the temperature and pressure of the gas. This cooling eventually leads to the nucleation of refractory grains. These grains then serve as condensation nuclei that rapidly deplete the gas of its remaining, less-refractory vapors. Nucleation and grain growth occur on rapid timescales and produce highly amorphous, chemically heterogeneous grains that become more ordered as they are annealed in the outflow (Nuth et al., 2002; Nuth, 1996; Nuth and Hecht, 1990). Experiments to characterize the spectral changes brought about by this annealing are discussed in the following section, although it should be noted that much more work along these lines is needed before all the factors controlling the rate and extent of thermal annealing are fully understood.

Grain formation in C-rich AGB stars is more complex than for O-rich stars due to the greater bonding options for C relative to H (as compared to silicon relative to H in O-rich AGB stars) and to the greater thermal stability of species such as metallic carbides and poorly graphitized C. These factors can lead to the formation and growth of grains in the preexpansion atmospheres of C-rich AGB stars. As an example, Bernatowicz and Cowsik (1997) have shown that the large, presolar graphite grains isolated from meteorites grew under equilibrium conditions for time periods of at least 1 yr around thermodynamically stable nuclei of titanium carbide prior to their expulsion from the star. Growth of the largest grains may have required periods as long as 100,000 yr (Michael et al., 2003). Even though other carbonaceous grains might nucleate homogeneously in these
C-rich outflows, the presence of preexisting condensation nuclei and large graphite and SiC grains that might act to heterogeneously accrete amorphous C vapor make it more difficult to construct a self-consistent model of grain formation in such environments.

Carbonaceous grains might also form in supernovae (Clayton et al., 1999) by a relatively straightforward chemical reaction mechanism that follows the growth of the C-chain molecules in the ejecta. This mechanism relies on the electron-impact-induced destruction of the extremely stable CO molecule to keep C atoms in the active reaction pathway leading to very large C-chain molecules. More work is needed to predict the isotopic signatures that might appear in such materials in order to distinguish them from more common condensates in C-rich stars. A more thorough discussion of these matters is given in Bernatowicz et al. (2006).

5.2. Composition of Interstellar Grains via Spectroscopy

Studies of meteorite matrix and IDPs have shown that, at a minimum, the following materials are present at some level in the interstellar dust: nanodiamonds (Lewis et al., 1989), SiC (Bernatowicz et al., 1987), poorly graphitized C (Amari et al., 1990), amorphous carbonaceous materials that likely formed as grain mantles in cold dark clouds (Zinner, 1988), crystalline and amorphous Al$_2$O$_3$ and MgAl$_2$O$_4$ (Huss et al., 1994; Nittler et al., 1997; Zinner et al., 2003; Stroud et al., 2004), and crystalline and amorphous silicates (Bradley, 1994; Messenger et al., 2003; Nguyen and Zinner, 2004). It is interesting to note that only for amorphous silicates, poorly graphitized C, and amorphous carbonaceous materials is there direct evidence of their existence in the interstellar extinction spectrum though some evidence for the presence of SiC and Al$_2$O$_3$ is seen in stellar outflows (Mutschke et al., 2000; Speck et al., 2000; Hofmeister et al., 2000, Begemann et al., 1997) and in meteorites. It may be that, because the relatively large SiC grains found in meteorites are extremely inefficient extinction agents per unit mass, there may be a significant mass fraction of the available silicon (e.g., 10%) tied up in such grains that can never be detected optically. The other option is that SiC grains have a very low abundance.

The situation is further complicated by the fact that a broad, weak SiC feature could easily be hidden under the wider, stronger silicate band (J. Dorschner, personal communication, 1998). In a similar fashion, nanodiamonds in the ISM will retain some spectroscopic resemblance to amorphous carbonaceous materials due to their relatively large surface-to-volume ratio and the necessity to terminate the sp$^3$ C core of the nanodiamond with sp$^2$ C, as well as with other species such as H, O, and N. Only in the far-UV (Saslow and Gaustad, 1969) or in the far-IR (Hill et al., 1997) might these tiny diamonds have diagnostic spectroscopic signatures due to the diamond bonds themselves. However, the C-H stretch of H atoms bonded to tertiary sp$^2$-bonded C has been detected in the ISM (Allamandola et al., 1992, 1993), and this could very well be due to the H atoms terminating the bonds of the C atoms on the surface of nanodiamonds.

The overall mineralogy of grains in the ISM is highly variable, depending on the particular phase under discussion. The mineralogy of cold, dark molecular cloud cores will certainly differ from that of the hot, diffuse ISM, although refractory phases may be common components of both regions. We have therefore tabulated our estimates of the abundances of individual constituents as a fraction of larger groups (Table 2). The abundances of carbonaceous grains are estimated as a fraction of the total refractory C and not as a fraction of total C, which would include all C-containing compounds, and atomic C as well, in the diffuse ISM. The abundances of oxides are estimated relative to the total refractory oxide grain population while volatiles such as H$_2$O only enter the solid state in cold clouds. Residues of warmed, irradiated ices are counted as amorphous C grains in this tabulation and we assume that molecular species in ice mantles constitute only a small fraction of the total volume.

The ordering of the constituents in Table 2 reflects the degree of certainty in the existence of the individual components in the ISM with a second level of ordering based on abundance. Each of the first seven constituents has been identified in meteorites. Amorphous C-grain coatings have not been isolated from meteorite matrix directly but are inferred from the presence of highly anomalous isotopic abundances of N, C, and D found in the matrix (Zinner, 1988) and in IDPs (e.g., Zinner et al., 1983; Messenger and Walker, 1996), indicative of their possible formation via ion-molecule reactions or surface-mediated processes, for example, in cold cloud cores (sections 3.2 and 4.1). The presence of presolar nanodiamond, graphite (better described as poorly graphitized C), and SiC in meteorite matrix is discussed in more detail in Meyer and Zinner (2006) and Bernatowicz et al. (2005). Note that the primary spectral features listed in Table 2 may not be directly attributable to only one particular component, e.g., the infrared emission bands that have been attributed to PAHs (Leger et al., 1987; Cohen et al., 1986). These PAH-related bands have previously been attributed to various forms of amorphous C such as hydrogenated amorphous C (HAC) (Duley, 1985, and references therein) or quenched carbonaceous composites (QCCs) (Sakata et al., 1983), although such materials might simply be aggregated forms of PAHs linked by aliphatic hydrocarbons. These same IR features may also arise from the amorphous, carbonaceous outer layers on nanodiamonds, although measurements of the IR spectra of chemically processed, meteoritic diamonds do not resemble the aforementioned bands (Mutschke et al., 1995).

The 200-nm region of the interstellar extinction curve contains strong absorption features for a wide range of hydrocarbons, and a very broad “featureless” spectrum has often been attributed to carbonaceous solids containing a range of C bond types (see Hecht, 1986; Sorrell, 1990, 1991). For almost three decades the increase in extinction
around 217.5 nm has been primarily attributed to graphite (Stecher, 1969) yet it is possible that only a very small fraction of the C contributing to this feature need be in this form to ensure that the observed characteristics of this peak are produced (Hecht, 1986). Another possibility is that the 217.5-nm peak is due to nanometer-scale particles of hydrogenated amorphous C (Schmainer et al., 1998) or to carbons on the surfaces of nanodiamonds (Sandford, 1996).

Diamond was initially suggested (Saslaw and Gaustad, 1969) as a candidate to explain the steep rise in far-UV extinction at wavelengths shorter than about 150 nm. Unfortunately, this effect is not unique and the far-UV rise has also been modeled as due to small MgO particles (Millar and Daley, 1978), as well as to small olivine and graphite grains (Draine and Lee, 1984). Following the identification of nanodiamonds in meteorites, Allamandola et al. (1992, 1993) observed an infrared feature assigned to the tertiary CH stretch in several astronomical sources that they attributed to terminal hydrogens on the outside of nanodiamonds. Again, this identification is not unique, as some degraded forms of fullerenes will also display tertiary CH stretches. Only features intrinsic to diamond itself might serve to unambiguously identify such material in the ISM, and intrinsic diamond absorption features are very weak (Hill et al., 1997) but may be detectable in some circumstances (see Guilllois et al., 1999). One such feature may be the 22-µm emission band observed around some C-rich protoplanetary nebulae (Hill et al., 1997; Kraus et al., 1997) previously attributed to SiS₃ (Goebel, 1993).

Aluminum oxide grains have occasionally been suggested to explain circumstellar emission peaks near 13 µm around hot stellar sources (Stencel et al., 1990; Begemann et al., 1997; Posch et al., 1999), but these features have never been observed in the ISM. It may be that the population of relatively pure corundum grains in the ISM is quite low due to the fact that aluminum is easily assimilated into silicate grains. Pure corundum grains might only be formed in significant quantity in extremely hot outflows where silicate condensation is inhibited, or in unusual, aluminum-rich environments. Alternatively, Al₂O₃ grains may be one of the metastable eutectics in some Al-rich systems (Nuth et al., 2002). Given the wide range of nucleosynthetic histories of individual corundum grains isolated from meteorites (Nittler et al., 1997), it seems more likely that some very small fraction of relatively pure alumina grains form in all O-rich outflows and that corundum grains in the ISM are only a very small fraction of the oxide grain population. One other such trace Al-bearing constituent is a population of spinel grains, isolated from primitive meteorites, but not seen in the ISM (Zinner et al., 2003). However, the bulk of the cosmic abundance of Al is probably incorporated into amorphous silicate grains.

The chemical compositions of the grains formed in O-rich stellar outflows are predicted to lie at the metastable eutectics in the ternary MgO-FeO-SiO₂ phase diagram (Rietmeijer et al., 1999, 2000; Rietmeijer and Nuth, 2000; Nuth et al., 2002). The individual grains should cluster around the serpentine and talc or greenalite and saponite dehydroxalate compositions, and should also include some MgO, SiO₂, and FeO₂ grains, depending on the overall composition of the stellar outflow. In condensation experiments, individual condensates never contain both Fe and Mg (Nuth et al., 2000), presumably because FeO and MgO are completely miscible with no stable or metastable eutectics to promote condensation and grain growth. If such materials survive transport through the ISM, as we believe they do.

### TABLE 2. Mineralogy of interstellar grains.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction of Solid Phase</th>
<th>Primary Spectral Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous carbon (sp², sp³), PAHs</td>
<td>&gt;80% C</td>
<td>PAH emission bands, ≈200-nm UV absorption, 3.4-µm C-H stretch</td>
</tr>
<tr>
<td>Nanodiamonds (sp³ carbon)</td>
<td>≈10% C</td>
<td>Tertiary C-H stretch (2.9 µm), far-UV absorption, 22-µm peak</td>
</tr>
<tr>
<td>Graphitic carbon (sp²)</td>
<td>≈5% C</td>
<td>217.5-nm peak</td>
</tr>
<tr>
<td>SiC</td>
<td>trace C</td>
<td>Broad 11.2-µm peak</td>
</tr>
<tr>
<td>Amorphous silicate (Fe,Mg)SiO₄</td>
<td>&gt;95% O</td>
<td>9.7- and 18-µm peaks</td>
</tr>
<tr>
<td>Corundum (Al₂O₃)</td>
<td>trace O</td>
<td>12-13-µm peak</td>
</tr>
<tr>
<td>Spinel (Fe,Mg)Al₂O₄</td>
<td>trace O</td>
<td>12-13-µm peak</td>
</tr>
<tr>
<td>Crystalline silicate — rapidly degraded beyond circumstellar environments by cosmic rays</td>
<td>trace O</td>
<td>11.3-µm “olivine” subpeak within the 10-µm silicate feature, far-IR olivine features at 33 and 69 µm</td>
</tr>
<tr>
<td>Water ice — polar (plus organics)</td>
<td>&gt;90% V</td>
<td>3-, 6-, 12-, 45-, 60-µm peaks</td>
</tr>
<tr>
<td>Nonpolar ices (N₂, O₂)</td>
<td>≈5% V</td>
<td>Indirect effects on dissolved species</td>
</tr>
<tr>
<td>Nonpolar ices (CO, CO₂)</td>
<td>≈5% V</td>
<td>4.67- µm (CO), 4.27-µm and 15.2-µm (CO₂) peaks</td>
</tr>
<tr>
<td>Mg₅, CaS, SiS₂ — likely lost by reaction with H₂O in the ISM</td>
<td>Speculation</td>
<td>28-, 40- and 22-µm peaks (respectively) in CS shells</td>
</tr>
</tbody>
</table>

Solid phases: C = solid carbonaceous grains, O = oxide grains, V = volatile ices.
5.3. Infrared Spectra and the Ordering of Amorphous Magnesium Silicates

Amorphous silicates have long been discussed as a significant component of the interstellar dust population (Ney, 1977), but only recently have grains potentially representative of this population become available for detailed laboratory studies (Bradley, 1994; Messenger et al., 2003; Keller and Messenger, 2004). Highly amorphous silicate grains form in the outflows of mass-losing stars, undergo some degree of thermal processing in these shells, and may begin forming more ordered materials. A generalization of this situation was reproduced in the laboratory. Amorphous Mg silicate smokes were prepared in the laboratory by vapor-phase condensation, and then were annealed in vacuum to simulate circumstellar processing. The samples were monitored by IR spectroscopy as a function of annealing time and temperature (1000–1050 K), focusing on the development of the 10- and 20-µm silicate features. The IR spectrum of the initial condensate displayed a broad band at 9.3 µm. As annealing proceeded, the maximum shifted to longer wavelengths and was eventually observed to stabilize at 9.7 µm, the value typically reported for silicates in the interstellar medium and in the circumstellar outflows of O-rich stars (Hallenbeck et al., 1998; Hallenbeck and Nuth, 1998). Further thermal evolution of the amorphous Mg silicate smokes led to the appearance of a dual maximum at 9.8 and 11.2 µm, indicative of “crystalline” olivine. The dual maxima 10-µm feature is a natural consequence of the thermal evolution of the amorphous condensate and is not a mixture of distinct populations of amorphous and “crystalline” materials.

In addition, there is a natural pause or “stall” in the spectral evolution of these samples, midway between the initially chaotic condensate and the more-ordered solid. Recent work indicates that this stall phase may represent the nucleation of microcrystals at the outer edge of the amorphous grains (Kamitsui et al., 2005). Thereafter, individual features sharpen as the sample develops a polycrystalline structure that becomes more ordered with further annealing. For the Mg silicate smoke samples investigated, roughly 11 days of annealing at a grain temperature of 1000 K were required for the peak position of the Si-O stretch to evolve from ~9.3 µm to 9.7 µm. An additional 11 days of thermal annealing (~22 days total) were required before the grains reached the stall, and it is estimated that nearly 300 additional days at 1000 K would be necessary before the infrared spectrum of the annealing Mg silicate progressed beyond the stall. The stall spectrum is therefore a practical endpoint in the spectral evolution of most Mg silicate condensates in circumstellar outflows, although virtually all grains in the outflow should evolve to exhibit the 9.7-µm silicate stretch. Since grain temperatures range from 300 to 600 K in the outer shells of typical stellar outflows (Hron et al., 1997), any Mg silicate grain sufficiently annealed to exhibit the stall spectrum should remain at this stage of evolution for the remainder of its lifetime barring shock-induced destruction or radiation-induced amorphization in the ISM.

The final infrared spectrum of Mg silicate condensates is heavily dependent on the thermal structure and outflow velocity of the circumstellar shell. Due to the exponential dependence of the annealing rate on grain temperature, the final grain spectrum is extraordinarily sensitive to the peak temperature of the newly formed grains. Based on the laboratory results discussed above, grains formed at temperatures in excess of 1067 K anneal from the initial amorphous condensate to a material that displays a spectrum more evolved than the stall on timescales of minutes. At temperatures of 1000 K these transitions require in excess of 300 days. By “choosing” a temperature at which amorphous silicate grains nucleate in a particular circumstellar outflow, and following the progress of the annealing and growth processes as the smokes move down the temperature gradient, away from the star, it should be possible to construct models of the thermal emission spectrum of any O-rich stellar source of known mass loss rate and outflow velocity (Hallenbeck et al., 2000), accounting for the relative fraction of crystalline materials. These same calculations may also be used to predict the infrared spectrum of the final silicate grain population injected into the ISM from such an outflow.

5.4. Processing of Interstellar Grains

All fresh condensates in these rapidly changing environments start out as amorphous grains. If the temperature of the outflow at the nucleation point is high enough, then some grains might be annealed to crystallinity, while those that condense at lower temperatures (or materials that require much higher temperatures to anneal) will remain amorphous. As an example, Fe and Mg silicates condense out as separate grain populations; iron silicates require much higher temperatures to anneal than do Mg silicates. Therefore, in high-mass-outflow-rate stars, where the condensation temperatures become higher due to higher concentrations of condensable elements, some Mg silicates can anneal to crystallinity while the Fe silicates remain amorphous. That is why some high-mass-outflow-rate stars are observed to contain pure Mg silicate crystals, and yet no Fe-bearing silicate minerals have ever been seen in any of these sources (Nuth et al., 2000, 2002).

Crystalline silicates present an interesting problem and demonstrate a very significant difference between the properties of grains in the ISM vs. the crystalline silicates observed to form in outflows of evolved stars (Waters et al., 1996). Evidence for crystalline forsterite has also been obtained by ISO in the far-IR, where the emission spectrum of a young main-sequence star, HD 100546 (Waelkens et al., 1996), closely matches laboratory spectra of crystalline olivine (Koike et al., 1993). There are a few stellar sources (Knacke et al., 1993) that have been observed to have an emission feature at 11.3 µm that resembles the mid-IR crystalline olivine peak seen in Comet 1P/Halley (Campins and Ryan, 1989; Hanner et al., 1994). Given this observational
data, there should be some fraction of the interstellar silicate grain population that is crystalline, yet no evidence for crystalline silicates (Dorschner et al., 1995; Henning et al., 1995; Henning and Mutschke, 1997) has yet been found in the general ISM. There is the possibility that as much as 5% of interstellar silicates could be crystalline, but these crystalline features would lie below observational detection limits (Li and Draine, 2001). Based on the structure of the 10-µm silicate feature measured along a single line of sight toward the galactic center, Kemper et al. (2004) calculated an upper limit on the fraction of crystalline silicates along that very long path to be 0.2 ± 0.2%. If interstellar silicates are destroyed on rapid timescales in the ISM then the lack of crystalline silicate grains is perfectly understandable. Since these silicates only form in a small fraction of the O-rich stellar outflows, crystalline grains would be relatively rare to begin with. Rapid grain destruction coupled with no feasible mechanism by which crystalline silicates can form or anneal would predict a dearth of crystalline silicates in the ISM and in the presolar grain population. However, the survival of a host of somewhat delicate carbonaceous materials in the ISM, the new dilemma either becomes explaining the preferential destruction of crystalline interstellar silicates vs. carbonaceous grains or finding an alternative explanation for the observational data. One good alternative is the deterioration of crystalline silicates upon long exposure to cosmic radiation (e.g., Day, 1974; Jäger et al., 2003).

Radiation-induced damage to olivine crystals has been shown to produce spectra consistent with observations of interstellar silicates (Day, 1974). Bradley (1994) has also noted that the amorphous silicates isolated from interplanetary dust grains appear to have been exposed to cosmic rays for a very long time. This damage may in fact be the agent responsible for some aspects of the chemistry of these suspected presolar materials, especially for the chemical gradients of Mg and O observed in the glass with embedded metal and sulfide (GEMS) themselves (Bradley, 1994). If crystalline silicates are only formed in very high mass loss rate stellar outflows, and if such outflows constitute only a minor fraction of the mass flux into the ISM, then this minor grain population would be reduced still further by long exposure to cosmic radiation and one would never expect to see signatures of crystalline silicate minerals in the general ISM. However, since some crystalline silicate grains are observed in meteorites and IDPs that are demonstrably presolar (Messenger et al., 2003; Keller and Messenger, 2004; Nguyen and Zinner, 2004), some small fraction of silicates in the ISM must be crystalline.

6. DUST DESTRUCTION IN THE INTERSTELLAR MEDIUM

Supernovae shock waves destroy refractory grains: This is an observational fact (Seab and Shull, 1983). However, establishing the lifetimes of grains in the ISM requires the use of models that contain assumptions ranging from the efficiency of the individual grain destruction mechanisms, such as chemi-sputtering or grain-grain collisions (Borkowski and Dwelle, 1995; Dwelle et al., 1996), to more difficult questions concerning how much time an individual grain might spend in cold cloud cores vs. the warm ISM. Theoretical astrophysicists have done a great deal of work trying to formulate a comprehensive model to address the efficiency of grain destruction as a function of shock velocity. The general conclusion drawn from such efforts is that an average interstellar grain survives on the order of 10^7–10^8 yr before being destroyed (Jones et al., 1994, 1996).

The timescale for grains, formed in the outflows of dying stars, to be incorporated into new protostellar systems is on the order of 10^9 yr (Dwelle and Scalo, 1980). Given that an average grain injected into the ISM only survives ~10^8 yr before it is destroyed by a supernova shock wave, the inevitable conclusion is that the vast majority of grains now observed in the ISM must have formed in the ISM. A simple corollary to this conclusion is that only a tiny fraction of grains formed in circumstellar outflows can survive intact to be incorporated into protostellar systems. If we assume that 10^8 yr is the equivalent of a “half-life” for grains in the ISM and that each grain must survive at least 10^8 yr before it becomes part of a new stellar system, then only one grain in a thousand survives the passage from a circumstellar environment to be incorporated into a protostellar environment. If 10^8 yr is assumed to be the e-folding time for grain destruction, then only one grain in 10^5 will survive. If the “half-life” for grain destruction is actually 10^7 yr, then only one grain in 10^30 can survive transport from a circumstellar outflow to a newly forming protostar, and finding presolar materials would therefore seem to be a very difficult proposition indeed.

The result of taking these models of grain destruction to their natural conclusion — all grains now present in the ISM must have formed in the ISM — is that it becomes impossible to explain the spectral properties inferred from the interstellar extinction curve (section 2.2). The spectral properties of grain analogs formed in the laboratory under conditions appropriate to the ISM are very different from the actual observations. Alternatively, we are forced to postulate that appropriate amorphous silicate and carbonaceous grains simply reform in the ISM by processes that we do not yet understand and have yet to duplicate in the laboratory.

6.1. Meteoritic Data and Dust Destruction

Presolar diamonds, graphite, and SiC have been isolated from the matrices of primitive (undifferentiated) meteorites (Amari et al., 1994; Anders and Zinner, 1993; Zinner, 1998; Nittler, 2003; Meyer and Zinner, 2005). In addition, several hundred grains of presolar Al2O3 (corundum) and MgAl2O4 have been recovered from these same meteorites (Nittler et al., 1997; Zinner et al., 2003). Given that a large fraction of the material in the meteorite matrix is of nebular origin (Boynton, 1985; Clayton et al., 1985), it is a miracle that any presolar grains survived at all. Considering the generally oxidizing nature of the nebula, it is remarkable that most of the presolar materials isolated to date are carbon-
aceous grains that are easily destroyed via exposure to even moderately high temperatures in the presence of O. Yet in spite of these caveats, one carbonaceous component — nanodiamonds — accounts for approximately 400 ppm by mass of most primitive meteorites. The total C content of such meteorites is less than 10% by mass. If these diamonds are indeed formed in supernovae and injected into the ISM then one would expect, at most, one grain in a thousand (or as few as one in 10^{30}) to survive transport to a protostellar environment and a much smaller fraction of these grains to survive processing in the oxidizing conditions found in the solar nebula. Yet primitive diamonds represent more than four parts in ten thousand of the total mass (or \(\approx 0.04\%\) of the total C content) of the meteorites. This is barely consistent with the most optimistic projection for grain survival in the ISM if only about half the initial fraction of interstellar diamonds that could have been incorporated into the meteorite parent body were actually destroyed by high-temperature processes in the nebula and if the only form of circumstellar carbon was diamond. This large fraction of interstellar diamond in meteorites is inconsistent with high grain destruction rates in the ISM. In addition, a 50% destruction rate is a very low estimate of the fraction of C-bearing grains destroyed via nebular processes (we would estimate the grain destruction efficiency for carbonaceous materials to be well in excess of 90%). The carbonaceous grains that do survive nebular and parent-body processing — such as SiC — show absolutely no signs on their surfaces of pitting (e.g., Bernatowicz et al., 2003) due to chemi-sputtering or to chipping and microcratering due to grain-grain collision processes that should be evident if the interstellar medium were as violent as predicted (e.g., Jones et al., 1996).

6.2. Experiments, Predictions, and Timescales

If refractory atoms and molecules slowly accrete onto the surfaces of surviving grains only after they have reached the comparative safety of a molecular cloud (rather than in the diffuse ISM), then such atoms may have the opportunity to react with additional adsorbed atomic and molecular species before being buried beneath the growing grain surface. The most common of these atomic species is H, while the most common molecular components of astrophysical environments are H\(_2\), CO, and H\(_2\)O. If these reactions occurred, the SiO, Fe, and Mg atoms generated by the annihilation of grains in supernova shocks might never reform the initial silicate compounds observed in the ISM, but might instead form a complex ice (A. G. G. M. Tielens, personal communication, 1984). Experiments made with mixtures of silane (SiH\(_4\)), iron pentacarbonyl (Fe(CO)\(_5\)), and H\(_2\)O ice condensed at very low temperatures (-10 K) have demonstrated that a "silicate" can form from such a mixture, especially if the mixture were irradiated with cosmic-ray energy protons prior to warm-up so as to form chemical radicals in the ice (Nuth and Moore, 1989). However, a major problem with the results of this study is that the IR spectrum of the warmed silicate residue does not resemble typical IR spectra observed for silicates in the ISM. Based on previous laboratory work, Hallenbeck et al. (1998, 2000) showed that the thermal annealing (T \(\geq 1000\) K) of a highly amorphous silicate condensate resulted in more ordered material with an IR spectrum displaying narrower peaks and absorption features that more closely resemble typical ISM silicate spectra. However, no natural process has been identified that would heat grains to temperatures significantly in excess of 1000 K in the ISM for sufficiently long time periods to reproduce the observed silicate spectral profile. Yet this process must occur on a considerably shorter timescale than grain destruction in order to transform all the recondensed refractory material back into the observed amorphous interstellar silicate.

6.3. Evidence from the Interstellar Extinction Curve

If we assume for a moment that grain destruction is as ubiquitous as the models predict, what might be the observable consequences? First, we know from measurements of interstellar depletion that \(~99.9\%\) of all refractory materials reside as solids in the ISM (Savage and Sembach, 1996; Sandford, 1996). Therefore, if grains are destroyed in the ISM, they must reform in situ, close to the site of grain destruction. It might be interesting to make measurements of the gas-phase depletion of atomic species at close intervals in the wake of a supernova shock wave to constrain the timescale over which refractory materials are redeposited onto surviving grain surfaces. What spectral properties might characterize such grains?

If a few surviving grains (or grain fragments) serve as substrates onto which refractory atoms are deposited in the low density ISM, then it is relatively easy to predict the spectral properties of the redeposited solids based on measurements of the optical constants of vacuum-deposited refractory materials, models of the size and shape distributions of the grain populations, and the use of Mie theory (Bohren and Huffman, 1983). Simple silicates evaporate to form primarily SiO, Mg atoms, Fe atoms, and O\(_2\) vapors. If we assume that a large fraction of the O\(_2\) might be lost, initially via reaction with carbonaceous grains to form CO, or because it simply did not recondense due to its volatile nature, then the recondensed solids will be chemically reduced compared to the initial grain population. Characteristic IR features of these recondensed silicates would be due primarily to solid SiO and possibly to simple MgO and FeO bands, although both Mg and Fe might exist largely as metallic species. A simple grain model of just such a composition was proposed by Millar and Duley (1978), but the predictions of this model are inconsistent with observations of the positions or overall shapes of either the 10- or 20-\(\mu\)m IR features that dominate the mid-IR region of the interstellar extinction curve. In this model, any C not converted to CO might be deposited onto the metallic grains — potentially forming carbides or an amorphous C film. To our knowledge, no other models of the interstellar grain population based along these lines have ever been published de-
spite the widespread acceptance of the rapid grain destruction hypothesis.

A second argument against rapid, widespread grain destruction in the ISM has been advanced by Mathis (O’Donnell and Mathis, 1997; Mathis, 1996). Studies of the interstellar extinction curve along various lines of sight have shown that both the grain size distributions and the overall composition of the grain populations are far from constant. The simplest models that successfully account for such variations in, for example, the shape or relative strength of the 217.5-nm feature vs. the strength of the far-UV rise (characteristic signatures of interstellar spectra), or the depth of the silicate absorption band, all require separate, independently variable populations of carbonaceous and oxide grains. Grain destruction, followed by rapid accretion of refractory (including C) atoms onto grain surfaces, should quickly result in a homogeneous solid state where an average grain contains both SiO and carbonaceous matter. No mechanism has yet been proposed by those advocating the rapid destruction of grains in the ISM that would maintain separate populations of oxide and carbonaceous grains.

Chiar et al. (1998) observed the 3.4-µm C-H stretch in the outflow around the protoplanetary nebula CRL 618, thus proving that this feature does form in the ejecta from evolved C-rich stars. The 3.4-µm feature also appears along several lines of sight in the diffuse interstellar medium (Butchart et al., 1986; Adamson et al., 1990; Sandford et al., 1991; Pendleton et al., 1994). The 3.4-µm feature is not observed in the spectra of dust in dense molecular clouds, although this could simply mean that it becomes obscured by the deposition of an ice mantle. Because it can be formed via UV processing of organic ice mantles (e.g., Bernstein et al., 2002, 2001, 1999; Dworkin et al., 2001; Greenberg, 1989; Greenberg et al., 1995; Hudson and Moore, 2004), its presence in the ISM is often cited as a measure of the importance of such processes. If subjected to shock, it is easy to imagine that grains could simply dehydrogenate as an effective cooling mechanism. Once the shock passes, grains could react with ambient H to reform C-H bonds on the surfaces of carbonaceous grains. Sorrell (1989, 1990) and Hecht (1991) both suggested an analogous process that could modulate the relative intensity of the 217.5-nm feature against the much broader, underlying carbonaceous absorption in a manner that was consistent with observations. In their scenario, grains entering the diffuse interstellar medium lost most of their H to form graphitic dust, thus increasing the strength of the 217.5-nm feature. Upon entering denser media, these grains reacted with ambient H to break down many of the “new” aromatic, graphitic centers and decrease the strength of the 217.5-nm peak (Sorrell, 1991).

6.4. Summary of Grain Destruction in the Interstellar Medium

As noted above, shock-induced grain destruction is observed to occur in the ISM; observations across a shock front show refractory solids in front of the shock and refractory vapor behind. The problem arises in applying this simple observation to the general grain population in order to predict the probability that an individual grain will experience a destructive shock within a specific time. Astrophysicists have used the average number of supernovae observed per year to calculate the frequency of destructive shocks and the mass of grains that such shocks might destroy per year. They divide the mass of dust in our galaxy by this rate of grain destruction to calculate the time it would take to destroy all the grains in the galaxy. This timescale is then defined as the lifetime of the average grain. Alternatively, these shocks may simply serve to break up the grain aggregates favored by Mathis (1996) without much erosion of their individual components. These components would then reaggregate in the lee of the shock. A deeper understanding of the dynamics of gas and dust in the ISM is required before any shock-destruction timescale is finalized or even before the relative importance of grain destruction in the ISM can be definitively assessed.

In the preceding sections we have approached the problem of grain destruction from three different perspectives. First, we used the meteoritic record to demonstrate that the unaltered grains from many stars survived passage through the ISM (as well as the destructive processes that occurred in the solar nebula) in vastly greater numbers than would be consistent with a high rate of grain destruction in the ISM. Then we demonstrated that the spectral properties of the grains likely to have formed in either dense clouds or in the diffuse ISM are very different from those actually observed in the ISM. Finally, we argued that the rapid destruction of grains in the ISM should lead to a much more homogenized grain population than is observed. If grains are not efficiently destroyed in the ISM then we must look to the grain populations formed in circumstellar outflows (see Bernatowicz et al., 2006; Ebel, 2006) in order to predict the properties of the grains present at the time the solar nebula formed. Indeed, it is quite likely that the mineralogy of interstellar grains is primarily established in the fiery death throes of the stars and only slightly modified in the ISM.

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REFERENCES


Jäger C., Fabian D., Schrempe F., Dorschner J., Henning Th., and


ciety of the Pacific, San Francisco.
Nittler L. R. (2003) Presolar stardust in meteorites: Recent ad-
vances and scientific frontiers. *Earth Planet. Sci. Lett.*, 209,
259–273.
Nittler L. R., Alexander C. M. O’D., Gao X., Walker R. M.,
and Zinner E. (1997) Stellar sapphires: The properties and origins
Cosmic Dust Connection* (J. M. Greenberg, ed.), pp. 205–221.
Kluwer, Dordrecht.
Fe(CO)3H2O ices: Production of refractory silicates and im-
19th, pp. 565–569.
terstellar and interplanetary grains: Recent developments and
new opportunities for experimental chemistry. *Earth Moon
Planets*, 80, 73–112.
ratory studies of silicate smokes: Analog studies of circumstel-
sation processes in astrophysical environments: The composi-
O’Donnell J. Z. and Mathis J. S. (1997) Dust grain size distribu-
tions and the abundance of refractory elements in the diffuse
Parise B., Ceccarelli C., Tielens A. G. G. M., Herbst E., Leflo-
ch B., Caux E., Castets A., Mukhopadhyay I., Pagani L., and
the solar-type protostar IRAS 16293–2422. *Astron. Astrophys.*, 393,
L49–L53.
Parise B., Castets A., Herbst E., Caux E., Ceccarelli C., Mukho-
Studies of dust grain properties in infrared reflection nebulae.
Pendleton Y. J., Sandford S. A., Allamandola L. J., Tielens
spectroscopy of interstellar hydrocarbon grains. *Astrophys. J.*, 437,
683–696.
Pirronello V., Liu C., Roser J. E., and Vidali G. (1999) Measure-
ments of molecular hydrogen formation on carbonaceous
Pontoppidan K. M., Dartois E., van Dishoeck E. F., Thi W. F., and
d’Hendecourt L. (2003) Detection of abundant solid methanol
around young low mass stars. *Astron. Astrophys.*, 404, L17–
L21.
Posch T., Kerschbaum F., Mutschke H., Fabian D., Dorschner J.,
ISO-SWS spectra of oxygen-rich AGB stars. *Astron. Astro-
phys.*, 352, 609–618.
Prasad S. S. and Tarafdar S. P. (1983) UV radiation field inside
dense clouds — Its possible existence and chemical implica-
Puget J. L. and Léger A. (1989) A new component of the inter-
stellar matter — Small grains and large aromatic molecules.
equilibrium brought down to Earth. *Eos Trans. AGU*, 81, 409,
414–415.
stable eutectic condensation in a Mg-Fe-SiO2H2O vapor: Analog
(2000) Metastable eutectic equilibrium in natural environments:
Recent developments and research opportunities. In *Res. Trends
Geochem. *, 1, 30–51.
Roberts H. and Millar T. J. (2000) Gas-phase formation of doubly-
fractionation in dense interstellar cores resulting from multiply
protostellar envelopes — Cocoon chemistry. *Astrophys. J.*, 585,
355–371.
Rodgers S. D., Charnley S. B., Huebner, W. F., and Boice D. C.
(2004) Physical processes and chemical reactions in cometary
Univ. of Arizona, Tucson.
tion of carbon dioxide by surface reactions on ices in the inter-
Roueff E., Tine S., Coudert L. H., Pineau des Forets G., Falgarone
E., and Gerin M. (2000) Detection of doubly deuterated am-
Does a 2.200 Å hump observed in an artificial carbonaceous
composite account for UV interstellar extinction? *Nature*, 301,
493–494.
Sandford S. A. (1996) The inventory of interstellar materials avail-
able for the formation of the solar system. *Meteoritics & Planet.
Sandford S. A. and Allamandola L. J. (1993) Condensation and
vaporization studies of CH3OH and NH3 ices: Major implica-
stretching band near 3.4 microns — Constraints on the composi-
tion of organic material in the diffuse interstellar medium.
composition and ultraviolet and thermal processing of inter-
stellar ices. In *From Stardust to Planetesimals* (Y. J. Pendleton
Sandford S. A., Bernstein M. P., and Dworkin J. P. (2001) Assess-
ment of the interstellar processes leading to deuterium enrich-
ments.


