The Starting Materials

In: Meteorites and the Early Solar System II

S. Messenger
Johnson Space Center

S. Sandford
Ames Research Center

D. Brownlee
University of Washington

Combined information from observations of interstellar clouds and star forming regions and studies of primitive solar system materials give a first order picture of the starting materials for the solar system's construction. At the earliest stages, the presolar dust cloud was comprised of stardust, refractory organic matter, ices, and simple gas phase molecules. The nature of the starting materials changed dramatically together with the evolving solar system. Increasing temperatures and densities in the disk drove molecular evolution to increasingly complex organic matter. High temperature processes in the inner nebula erased most traces of presolar materials, and some fraction of this material is likely to have been transported to the outermost, quiescent portions of the disk. Interplanetary dust particles thought to be samples of Kuiper Belt objects probably contain the least altered materials, but also contain significant amounts of solar system materials processed at high temperatures. These processed materials may have been transported from the inner, warmer portions of the disk early in the active accretion phase.

1. Introduction

A principal constraint on the formation of the Solar System was the population of starting materials available for its construction. Information on what these starting materials may have been is largely derived from two approaches, namely (i) the examination of other nascent stellar systems and the dense cloud environments in which they form, and (ii) the study of minimally altered examples of these starting materials that have survived in ancient Solar System materials.

These approaches are complementary to each other and suffer from different limitations. The study of other forming stellar systems is limited by our inability to study the formation process of a single system over the entire formation interval. In addition, since these are distant systems, it is not possible to examine all the processes that are occurring with high spatial resolution. Finally, star formation is observed to occur under a range of environments and one must make educated guesses as to the extent to which observations apply to the specific case of our Solar System. Similarly, the search for presolar materials in Solar System materials is complicated by overprinting of protostellar nebular and parent body processes and dilution within a large amount of materials whose original composition has been erased or severely modified.

Despite these limitations, astronomical and meteoritic studies provide insight into the nature of the starting materials from which the Solar System formed and we review these constraints here. A central theme of this review is that the nature of the starting materials evolved prior to and together with the nascent solar system and varied with location in the Solar System. For instance, terrestrial planets were likely assembled from components that had already undergone substantial cycling through evaporation, condensation, chemical evolution and fractionation. In contrast, Kuiper-belt objects (the sources of short-period comets) are thought to contain abundant interstellar materials because they formed in the relatively cold and quiescent outer (>40 AU) regions of the solar nebula.

In the chapter that follows, we address what we know about the nature of Solar System starting materials on the basis of several different approaches. First, we consider constraints derived from observations of dense molecular clouds and star formation areas within them. We then consider what we can learn about Solar System starting materials on the basis of examination of 'primitive' materials found within the Solar System. In this context, 'primitive' refers to those materials that have been largely unaltered, or only slightly altered from their interstellar forms by nebular or parent body processing. An emphasis is placed on the properties of interplanetary dust particles (IDPs) that may represent relatively pristine samples of these starting materials. Finally, we consider those fractions of meteoritic materials that clearly have a presolar heritage on the basis of preserved isotopic anomalies. These materials are clearly of presolar origin and provide insights into a variety of stellar nucleosynthetic and interstellar chemical processes that imprinted the materials from which our Solar System formed.

2. Dense Molecular Cloud Materials

The population of materials from which new stellar and planetary systems form contains materials with wildly disparate histories (Sandford, 1996). Materials are injected into the interstellar medium by a diversity of stellar sources (supernovae, novae, AGB stars, etc.) (Dorschner and Henning, 1995; Tielens, 1995) whose outflows differ significantly in their elemental compositions, thermal environments, densities, and lifetimes. These materials are then processed to varying degrees by interstellar shocks, sputtering, irradiation, etc. (see the chapter by Nuth et al. in this book for discussion of some of these processes) over timescales of 10^7 years. Despite their varied histories, all these materials share a similar experience in passing through a dense molecular cloud prior to becoming incorporated into a new stellar system.

Other potentially important sources of material in star forming regions are the outflows of newly formed stars themselves. It is likely that the majority of stars (70-90%) form in large clusters (see, Lada and Lada (2003) for a recent review). Most young protostars likely return an enormous amount of processed matter back into the surrounding dust cloud in bipolar outflows. It is important to appreciate that our own solar system may have been seeded with significant quantities of this 'protostellar' dust, and that it ought to have been largely isotopically identical to the solar system. High mass stars, such as those in OB associations, have dramatic effects on surrounding regions as much as parsecs in size through high energy radiation that may ablate materials from nearby protostellar cores and disks (e.g., Smith *et al*., 2003). The most massive stars have such short lifetimes (~10 Ma) that they may die in a supernova explosion while other stellar systems are still forming (*e.g*., Cameron, 1985). In such clusters, the nature of the materials in a forming protonebular disk will depend, in a stochastic fashion, on the timing of the disk's formation and who its neighbors are. Late forming stellar systems are thus more likely to be polluted with material originating from young stars and supernovae. The recent demonstration that there was abundant, live ^{60}Fe in the early solar system is best explained by the polluting of the protostellar nebula by the debris of a nearby supernova or AGB star (Tachibana and Huss, 2003; Busso *et al*., 2003). While either source is possible, the timing of an AGB star passing near the Sun would have been fortuitous, whereas there is growing evidence for a supernova source in particular (Mostefaoui *et al*. 2005).

Dense clouds consist of concentrations of dust, gas, and ice that are sufficiently optically thick that they screen out the majority of the interstellar radiation field. In these relatively protected environments, molecules can form and survive for appreciable times without being photo-disrupted. As a result, these clouds are commonly called dense molecular clouds. By far the most abundant molecular species in these clouds is H_2, formed by the reaction of atomic hydrogen on dust grains, but a host of other molecular species are present as well (see below).

Dense molecular clouds are not uniform entities, but instead show structure in their density, temperature, turbulence, etc. on a variety of size scales (Evans, 1999). On their largest size scales, dense clouds typically show densities of about 10^2-10^3 H atoms/cm^3. Within this general cloud medium are found clumps of various sizes and densities, with typical clumps being a few light years across and having densities of 10^3-10^5 H atoms/cm^3 and temperatures of $10 \text{ K} < T < 30 \text{ K}$ (Goldsmith and Langer, 1978; Goldsmith, 1987). The highest densities occur in small 'cores' that are less than a light year across. Such cores typically have densities of 10^6-10^8 H atoms/cm^3 and warmer temperatures ($50 \text{ K} < T < 300 \text{ K}$) and are often referred to as 'hot molecular cores' (van Dishoeck and Blake, 1998). Under conditions in which further gravitation collapse can occur, these cores can become the sites of new star formation (Mannings *et al.*, 2000). Subsequent formation of the protostar is driven by core collapse and the formation and evolution of an accretion disk, during which pressure and temperature conditions may vary over very large ranges depending on time and location (Cassen and Boss, 1988; Boss 1998).

Careful examination of dense cloud materials, particularly those in dense cores, provides important insights into the population of materials available for the formation of new stellar and planetary systems (Sandford, 1996). However, dense cloud environments span large ranges in densities and temperatures that increase dramatically as star formation proceeds. Consequently, the nature of the starting materials may differ somewhat depending on what one defines as the 'start.' For example, the temperatures in the general dense cloud medium are quite low ($10 \text{ K} < T < 30 \text{ K}$) and under these conditions most molecular species other than H, H_2, He, and Ne are expected to be largely condensed out of the gas phase as ice mantles on refractory grains (Sandford and Allamandola, 1993; Bergin *et al.*, 2002; Walmsley *et al.*, 2004). However, warming of these materials during the in-fall process releases volatiles into the gas phase where they participate in gas phase and gas-grain chemical reactions that are inhibited by the low temperatures of the general cloud medium. Thus, the nature of the population of the 'starting materials' evolves as the collapse proceeds.

2.1 Source materials of dense clouds

Dense molecular clouds are initially formed from materials swept together from the diffuse interstellar medium by interstellar shock waves (Mac Low and Klessen, 2004), and they are thus mixtures of materials with a variety of origins that have been altered to various degrees while in the diffuse ISM. For a more detailed discussion of many of these sources and processes, see the chapter by Nuth *et al*. in this book.

As with the rest of the universe, the majority of the matter in dense clouds is in the form of gas phase atomic and molecular hydrogen and helium. Solid materials, in the form of small (< 1 µm diameter) dust grains are also present. Included within the population of solid materials are silicate grains. These are identified by their infrared absorption features seen near 10 and 20 µm due to O-Si-O stretching and bending mode vibrations, respectively (*e.g.*, Tielens, 1990; Jäger *et al*., 1994). These features are seen in absorption along lines of sight through both the diffuse ISM and dense clouds. The lack of spectral structure in the silicate features suggests that the majority of these silicates are amorphous in nature (see the chapter by Nuth *et al*. for a detailed discussion on the nature of the silicates).

Refractory carbonaceous grains are also expected to be present in dense clouds. Carbonaceous materials are observed along a number of lines of sight through the diffuse interstellar medium, primarily by the detection of absorption bands due to aromatic and aliphatic C-H stretching bands near 3.3 and 3.4 µm, respectively (Butchart *et al*., 1986; Sandford *et al*., 1991; Pendleton *et al*., 1994). The exact nature of this material is not well understood, but it is unlikely to be due to small, free molecular gas phase molecules as these would be rapidly destroyed in the diffuse ISM. Currently available spectral data is consistent with this material residing in grains which may bear some chemical resemblance to the macromolecular 'kerogen' seen in meteorites, i.e., it may consist of aromatic chemical domains that are interlinked by short aliphatic chains (Pendleton and Allamandola, 2002). The spatial distributions of the silicate and carbonaceous materials in the diffuse ISM are very similar (Sandford *et al.*, 1995), although it is not clear how significant this is. The two components could show similar distributions because they are in intimate association (for example, carbonaceous coatings on silicate cores), or they may exist as separate particle populations that show similar distributions because of elemental abundance constraints. Strangely, the relatively strong 3.4 μm absorption feature that marks the presence of these organic materials in the diffuse ISM is not clearly seen in dense clouds. The suppression of this feature may be due to evolution of hydrogen coverage on the material (Mennella *et al.*, 2002).

One of the most ubiquitous components of the ISM is the class of gas phase molecules known at polycyclic aromatic hydrocarbons (PAHs). These materials consist largely of fused hexagon rings of carbon with peripheral bonds ending in hydrogen atoms, although heteroatoms, like N, in their skeletal structures and chemical functional groups attached to their perimeters are possible in some environments. In most space environments, the PAHs are detected through their characteristic infrared emission features (Allamandola *et al.*, 1989). The emission is driven by the electronic absorption of visible and ultraviolet photons by PAHs, which subsequently convert the absorbed energy into vibrational energy. The molecules then cool through the emission of a cascade of infrared photons whose energies are associated with their vibrational modes (Allamandola *et al.*, 1989). The emission features of PAHs are seen in a vast range of astrophysical environments, including stellar outflows, the diffuse ISM, reflection nebulae, and emission nebula. It is estimated that this class of molecules carries more than 5% of the cosmic carbon in many of those environments (*e.g.*, Allamandola *et al.*, 1989; Tielens, 1995). These molecules should be abundant in dense clouds, but are difficult to detect in these environments because the clouds are opaque to the interstellar radiation field that excites these molecules to emit in the infrared. As a result, PAHs in dense clouds can not be seen in *emission*, but instead must be detected in *absorption*. This restricts searching for them along lines of sight towards suitable background sources. Absorption features assigned to PAHs have been observed in a limited number of cases (*e.g.*, Brooke *et al.*, 1999; Chiar *et al.*, 2000; Bregman *et al.*, 2000). Laboratory analog experiments suggest that the concentrations of PAHs in these cases fall between 1-5% that of H_2O along the same lines of sight (Sandford *et al.*, 2004; Bernstein *et al.*, 2005), which would make them a significant carrier of the carbon in dense clouds. However, it is not yet clear whether these molecules reside in the gas phase (as they do when seen in emission in other environments), are clustered together in aggregate grains, or are incorporated into icy grain mantles on refractory grains. These possibilities can be distinguished if sufficiently good infrared spectra are obtained (Sandford *et al*., 2004). Given the very low temperatures found in these clouds, however, it is likely that most of the PAHs in these environments reside in the solid state.

2.2 Probing the Composition of Dense Molecular Clouds

Spectroscopy provides the principal means by which the compositions of dense molecular clouds are studied. At sub-millimeter and radio wavelength, spectroscopy can be used to detect the rotational transitions of gas phase molecules. Such observations have the advantage that they can rigorously identify molecular species with good rotational dipole moments and can be used to derive the temperature of the molecular population. In addition, they can make measurements in a wide range of dense cloud locations. They suffer, however, from an inability to detect solid state materials, materials that make up the vast majority of non-H_2 mass of most dense cloud environments. Complementary measurements can be made at infrared wavelengths, where materials can be detected through their inter-atomic vibrational transitions. Given sufficient spectral resolution, these measurements can also provide identifications and temperatures of specific molecular species, although there is a higher degree of band overlap that makes identifications more difficult. Infrared spectroscopy is also limited in dense clouds to measuring absorption bands produced by materials along the line of sight to a suitable infrared background source. Infrared spectroscopy enjoys the significant advantage, however, that it can detect solid materials, which constitute the major non-H_2 fraction of the cloud (see, for example, van Dishoeck, 2004).

2.3 Chemical Processes in Dense Clouds

Most molecular species are unstable to photo-disruption in the radiation field found in the diffuse ISM (PAHs being one of the notable exceptions). Dense clouds effectively screen out interstellar radiation, providing a safe haven in their interiors for gas phase molecules. Furthermore, the greater densities of these clouds provides for increased atomic and molecular interactions that can lead to the formation of new molecules.

Chemistry in dense clouds does not proceed along the same lines we are familiar with in most environments on Earth. At the very low temperatures characteristic of dense clouds (10 K < T < 50 K) most neutral molecular species are not reactive because there is insufficient energy available to overcome activation barriers. As a result, much of the gas phase chemistry in dense clouds occurs via ion-molecule reactions. For more detail on this chemical process see Herbst (1987), Langer and Graedel (1989) and the chapter by Nuth et al. in this book. Many of the gas phase species so far detected in dense clouds (See Table 1 of Nuth *et al*., this book) were probably created in this manner.

At the low temperatures characteristic of dense clouds, most molecular species rapidly condense out onto any dust grains present (Sandford and Allamandola, 1993; Bergin *et al.*, 2002; Walmsley *et al.*, 2004). As a result, grains in dense clouds are expected to be coated by an icy mantle (Fig. 1). Studies of scattered light indicate that the average grain size in dense clouds is greater than that in the diffuse ISM (Pendleton *et al*., 1990). This growth could be due to grain agglomeration and/or the accretion of icy mantles. Modeling of the scattering in conjunction with observations of the profile of the 3.08 μm H_2O ice band in the reflection nebula surrounding OMC-2/IRS1 suggest ice mantle growth is a significant process (Pendleton *et al*., 1990).

Ice mantles facilitate the production of new kinds of molecules by acting as catalytic surfaces (Brown and Charnley, 1990; Charnley *et al*., 1992; Ehrenfreund and Charnley, 2000). These surficial reactions involve simple atom addition to previously condensed species. One of the most important of these gas-grain reactions is the production of molecular H_2 from atomic H (Hollenbach and Salpeter, 1971). In environments where atomic H dominates the gas phase ($H/H_2 > 1$), gas-grain atom addition reactions act to hydrogenate species, turning atomic O into H_2O, atomic C into CH_4, molecular CO in CH_3OH, and so on. In environments where molecular H_2 dominates ($H/H_2 < 1$), other atom addition reactions can dominate, resulting in the formation of species like CO_2, N_2, and O_2 (Tielens and Hagen 1982, Tielens and Allamandola 1987). The compositions of interstellar ice mantles thus range from highly polar materials to non-polar materials, depending on the local environment and history of the material. Both of these basic ice types have been observed by infrared spectroscopy (Sandford *et al*. 1988; Tielens *et al*., 1991). The primary components of these ices are simple molecules like H_2O, CO, CO_2, HCO, H_2CO, CH_3OH, NH_3, and CH_4 (Tielens *et al*., 1991; Lacy *et al*., 1991; Lacy *et al*., 1998; Allamandola *et al*., 1992; Boogert *et al*., 1996; de Graauw *et al*., 1996; Whittet *et al*., 1996). Molecules like N_2 and O_2 may also be present, but these have no permanent dipole and are difficult to detect spectroscopically.

High-energy irradiation can also drive chemical reactions within the ice mantles. In the general cloud, this ionizing radiation is primarily in the form of galactic cosmic rays, UV photons generated locally by cosmic ray interactions, and the attenuated diffuse interstellar radiation field (Norman and Silk, 1980; Prasad and Tarafdar, 1983). In the zones near forming protostars, the radiation density may be greatly augmented by high-energy processes associated with the forming stars. This ionizing radiation breaks chemical bonds in the molecules in the ice and creates chemically reactive ions and radicals. Some of these react immediately with neighboring molecules, others do not react until the mantles are warmed enough to allow some molecular mobility. These processes can produce a wide range of comparatively complex molecules. For example, laboratory studies have shown that the irradiation of interstellar ice analogs results in the production of hundred, if not thousands, of new and more complex and refractory species (e.g., Allamandola *et al*., 1988; Bernstein *et al*., 1995, 2003; Moore *et al*., 1996; Gerakines *et al*., 2000). These include a range of organics, many of which are identical or similar to compounds identified in primitive meteorites (Epstein *et al*., 1987; Engel *et al*., 1990; Krishnamurthy *et al*., 1992; Bernstein *et al*., 2001). Many of these species are also of astrobiological interest, for example, aromatic ketones (quinones), amphiphiles, and amino acids (Bernstein *et al*. 1999b, 2002, Dworkin *et al*. 2001).

The best evidence that radiation-driven chemistry occurs in dense clouds is the presence of an infrared absorption band near 4.62 μm (2165 cm^{-1}) seen in protostellar spectra (Lacy *et al*., 1984; Tegler *et al*., 1993, 1995) that is thought to be due to the OCN^- ion in a molecular complex (Grim and Greenberg, 1987; Park and Woon, 2004). This feature can be well reproduced in the laboratory whenever simple ices containing H, O, C, and N are irradiated (*e.g.*, Lacy *et al*., 1984, Bernstein *et al*. 1995, 2000). Interestingly, this feature appears to be considerably more common and prominent in the spectra of protostars than it is in the spectra of background stars (Pendleton et al. 1999), suggesting that irradiation chemistry may play a more prominent roll in the immediate vicinity of star formation regions.

2.4 Isotopic Fractionation in Dense Cloud Materials

While many of the principal components of dense clouds can be measured remotely, this does not tell us what components of the cloud material actually get incorporated into new stellar systems. In the case of our own Solar System, the principal means of identifying surviving presolar materials is through the detection of isotopic anomalies. Some of these anomalies are nucleosynthetic in origin and have signatures set by their original source stars (see below). However, some of the isotopic anomalies seen in meteoritic materials, particularly those of D and ^{15}N, have their origins in interstellar chemistry, and these can be used as tracers of the survival of incoming interstellar materials.

There are four main interstellar chemical processes that can lead to the production of deuterium-enriched species, three of which are confined to environments associated with dense clouds (Tielens, 1997; Sandford *et al*., 2001). Best known of these are the gas phase ion-molecule reactions mentioned earlier. At the very low temperatures typical of dense clouds, differences in the zero point energies of H and D bonds result in the ion-molecule reaction

$$H_3^+ + HD \rightarrow H_2D^+ + H_2$$

preferentially removing D atoms from HD molecules and redistributing them throughout the gas phase during subsequent reactions (*e.g*., Millar *et al*., 2000). Thus, H-containing species produced by ion molecule reaction are expected to be deuterium enriched. As a second process, the difference in zero point energies may also lead to additional deuterium fractionation during catalytic gas-grain reaction on grain surfaces (Tielens, 1983). Whether these grain surface reactions produce additional fractionation or not, the ices are expected to be highly D-enriched. This is because the same ion-molecule gas phase reactions that fractionate D also enrich the local gas phase atomic D/H ratio by factors of ~100, and grain surface hydrogenation reactions sequester these enrichments in the ice mantles in the form of D-enriched H_2O, CH_3OH, CH_4, NH_3, etc.

Finally, once D-enriched ice mantles form, any radiation processing that occurs will pass these enrichments along to a host of other product molecules (*e.g.*, Bernstein *et al.*, 1995, 2000; Sandford *et al.*, 2000). A fourth process for D enrichment is that of preferential unimolecular photodissociation. This process is restricted to molecular species, like PAHs, that can absorb a high-energy photon without being destroyed, but which will occasionally shed a peripheral H atom if the absorbed energy is large enough. Because of the difference in H and D zero point energies, H atoms should be shed preferentially and repeated loss and capture of peripheral H atoms can lead to D enrichment (Allamandola *et al.*, 1989). All these processes are expected to lead to different distributions of fractionation, both with regards to which molecules the excess D ends up in, and in some cases, where on the molecule it resides (Sandford *et al.*, 2001). Thus, in principle, the placement of D anomalies in meteoritic materials holds clues for assessing the relative roles of the various possible enrichment processes.

Ion-molecule reactions are also expected to yield ^{15}N enrichments in dense clouds (Langer and Graedel, 1989; Terzieva and Herbst, 2000; Charnley and Rodgers, 2002; Rodgers and Charnley, 2004). As with D, fractionations established in the gas phase can then be redistributed into the solid phase through subsequent gas-grain reactions and the irradiation of ^{15}N-enriched ice mantles. Since ion-molecule reactions produce both D and ^{15}N enrichments under similar condition, i.e., in very cold gas, these anomalies would be expected to be correlated, at least qualitatively, in materials made within dense clouds. However, since the extent of the fractionations depend differently on temperature and the specific reaction paths are involved, the relative degrees of fractionation of the two will vary with environmental conditions.

That these various enrichment processes occur for D is amply demonstrated by observation of gas phase D-enriched molecules in dense cloud environments. These include molecules like DCO^+, DCN, HDO, NH_2D, HDCO, CH_3OD, as well as a host of others (Hollis *et al.*, 1976; Walmsley *et al.*, 1987; Mauersberger *et al.*, 1988; Jacq *et al.*, 1990; Turner, 2001; Roberts *et al.*, 2002). Interestingly, recent studies have detected unexpectedly large abundances of multiply deuterated species like D_2CO, ND_2H, D_2S, and CD_3OH (Loinard *et al.*, 2000; Parise *et al.* 2002; Vastel *et al.*, 2003). Deuterium enrichments have also been tentatively reported in PAHs (Peeters et al. 2004). There is currently very little observational evidence constraining the level of D-enrichment in interstellar ices, the sole report being the possible detection of HDO-containing ices in two protostellar spectra with HDO/H_2O ratios of $8x10^{-4}$ and $1x10^{-2}$, respectively (Teixeira *et al*., 1999).

There is currently considerably less evidence for ^{15}N enrichment in interstellar molecules resulting from chemical fractionation. This may be due to the fact that the CN isotopomers are more difficult to resolve spectroscopically and that the predicted isotopic shifts are comparatively much smaller than the case for D/H. Fractionations in ^{13}C and the isotopes of O are also possible in dense clouds. However, in the case of ^{13}C, there are several chemical paths that are expected to fractionate ^{13}C in opposite directions in different species (Langer *et al*., 1984; Langer and Graedel, 1989, Tielens, 1997), so it is difficult to assess what net fractionations might be preserved into meteoritic materials. Similar complications occur for oxygen (Langer *et al*., 1984, Langer and Graedel, 1989). As a result, it is somewhat difficult to separate nucleosynthetic signatures from chemical signatures for these two elements in interstellar molecules.

3. Transition to the solar nebula

As star formation proceeds, the in-fall of material results in increased densities and temperatures. The rising temperatures lead to the sublimation of volatile components of icy grain mantles. The result is relatively high gas phase densities of compounds that did not previously exist together in the gas phase (van Dishoeck and Blake, 1998). These conditions promote a rich gas phase chemistry that can lead to new, more complex species not efficiently produced by gas phase chemistry in the general dense cloud medium (*e.g.*, Charnley *et al*., 1995; Langer *et al*., 2000; Rodgers and Charnley, 2003).

The construction of our planetary system from its natal dust cloud is imagined to have started from smoke-sized (10 – 1,000 nm) ‘starting materials’ that accreted together to form successively larger particles, eventually leading to the formation of large planetesimals and planets. There is some truth to this notion, but the nebula was a messy place and the definition of the starting materials is open to interpretation. Depending on time as well as radial and vertical location in the solar nebula accretion disk, there were actually many types of starting materials. In some cases the building materials that were used to assemble bodies in the solar system were not the original starting materials, but were secondary materials formed within the solar system itself. The nature of the starting materials at each stage of nebular evolution has been obscured by secondary processes and it will always be a challenge to combine information from astronomical observations and laboratory studies of early solar system materials to see through this veil.

A prime example of a "secondary process" is chondrule formation - a process that, in the region of the nebula where ordinary chondrites accreted, efficiently converted most of the nebular solids in into molten spherules. The dramatic chondrule formation process overprinted earlier generations of solids. Other important examples of secondary processes include collisions, gas-grain reactions, parent body heating and aqueous alteration.

The chondrule formation process is one manifestation of the dynamic environment in the inner regions of the solar nebula. It is a sobering fact that, over its <10 Ma lifetime, over a solar mass of material accreted onto the disk and migrated towards its center. The viscous dissipation of the kinetic energy of material spiraling inward is thought to cause disks around very young stars to temporarily outshine the embedded protostar – an enigmatic process known as FU Orionis phenomena (Hartmann and Kenyon, 1996). The temperature distribution of protostellar disks may vary significantly with time (as short as $10^2 – 10^5$ year timescale) and location as the mass accretion rate varies episodically by orders of magnitude. Incredibly, the solar formation process is thought to have ejected as much as one quarter of a solar mass during the accretion process back into the stellar association from which our Sun formed. This processed, 'protostellar material' may have been incorporated into neighboring young stellar systems (and vice versa).

While the inner disk reached temperatures high enough to vaporize silicates, the outer portions of the nebula remained at cryogenic temperatures. It is expected that the grains in the collapsing cloud that formed the nebula were maintained near 10 K during the free-fall phase, assuring that essentially all condensable gas molecules must have condensed on grains. On the basis of astronomical data we would expect this material to be largely composed of submicron grains of amorphous silicates, organic material, and condensed ice and other volatiles with an average elemental composition close to solar abundances for condensable elements. A hallmark of the real starting solid materials of the solar system is that they must have contained ices that condensed at such low temperatures. These low temperatures are not found anywhere in the planetary region of the present solar system and it is unlikely that existed anywhere in the mid-plane of the solar nebula accretion disk except, perhaps, in its outermost regions. The ultra-low temperature condensates present in the starting materials did not fully survive as solids and all currently available primitive solar system materials are at least partially depleted in original volatile compounds.

4. Primitive solar system materials

Today, the starting materials are probably best preserved in comets. These objects derive from two distinct source regions: the Kuiper Belt – a flattened disk ($i < 30°$) of minor planets beyond the orbit of Neptune (30 – 50 AU), and the Oort cloud – a spherically distributed population of bodies residing very far from the Sun (10^3 – 10^4 AU). Comets are rich in volatiles and ices because they formed in the coldest regions of the solar nebula (Boss 1998), marking the endpoint of the radial progression from the volatile-depleted terrestrial planets to gas-giants and ice-rich outer solar system bodies. Whereas Kuiper Belt objects (KBOs) are thought to have formed in place (Luu & Jewitt 2002), the Oort cloud probably originated from the scattering of icy planetessimals that formed in the neighborhood of the giant planets (Oort 1950).

Dynamical arguments point to the Kuiper Belt as the source of most short-period comets (Duncan et al. 1998). Long-period comets originate from the Oort-cloud, and their original orbits are thus nearly hyperbolic. Close planetary encounters, especially with Jupiter, muddle these distinctions in some cases by strongly altering cometary orbits. For instance, most Halley-type comets, with orbital periods between 20 and 200 years, likely originated from the inner portion of the Oort cloud (Levison et al. 2001). The best studied comets (*e.g.* 1P/Halley, C/1995 O1/Hale-Bopp, and C/1996 B2/Hyakutake) probably all originated from the Oort cloud. These comets were well studied for different reasons: Halley was visited by several spacecraft, Hale-Bopp was exceptionally active, and Hyakutake passed close (< 0.1 AU) to the Earth. In the very near future the Stardust spacecraft will return the first direct samples of cometary solids from the short-period comet Wild-2. Undoubtedly, the analysis of this material will revolutionize our understanding of the nature and origin of these enigmatic bodies.

Comets are rich in volatiles because they formed under cryogenic conditions and have remained in cold storage for billions of years since. Certain cometary volatiles provide constraints on their temperature histories. For instance, the common presence of H_2S and CO ice in cometary nuclei is thought to limit the nebular temperature during comet formation to less than 60 K (Mumma *et al*. 1993). Still lower temperature limits are inferred from the nuclear spin states (ortho/para ratio) of cometary water. The value derived from comet Halley (2.5 ± 0.1) corresponds to a 'spin temperature' of only 29 K. An unresolved issue is whether the spin temperature reflects the original formation temperature or subsequent re-equilibration in the cometary nucleus. Short-period comets tend to be more active at great distances from the Sun compared to long-period comets, suggesting that they are richer in low temperature volatiles (Whipple 2000). This is consistent with the idea that many Oort-cloud comets formed in warmer regions of nebula (~100 K, near Jupiter) than Kuiper-belt objects (<30 K). As molecular studies of comets have become more sensitive, significant chemical variability among comets has become evident. For instance, the relative production rates of CO, C_2/CN, and simple organic molecules are observed to vary by factors of several (Mumma et al. 2003, Biver et al. 2002). Such compositional variability may be a reflection of the wide heliocentric range (5 – 50 AU), and the correspondingly diverse environmental conditions, over which comets formed (Dones et al. 2004).

Despite the chemical diversity among comets, the abundances of many simple volatile compounds agree well with those observed in star forming environments such as hot molecular cores (Ehrenfreund & Charnley 2000). Examples include such species as HCOOH, HCNO, NH_2CHO, and methanol – molecules that are produced by single atom additions on grain surfaces, as described above. Other cometary molecules, including C_2H_2, CH_3CN, HC_3N, and HCN, are more likely to have originated in gas-phase chemistry. These comparisons are tempered by the uncertain role of gas-phase reactions in cometary comae that strongly overprint the nuclear chemical compositions. However, the preponderance of the evidence suggests that the volatile component of comets is a mixture of preserved interstellar ices and differing proportions of material processed in the solar nebula.

The isotopic compositions of cometary volatiles also point toward an interstellar heritage. As reviewed in Bockelée-Morvan et al. (2005), several simple molecules have shown anomalous isotopic compositions in one or more comets. The D/H ratio for cometary water is enriched by a factor of 2 relative to the terrestrial value (Eberhardt *et al*. 1995), and a D enrichment of more than an order of magnitude has been reported for HCN in comet Hale-Bopp (Meier *et al*. 1989). A significant (~factor of 2) enrichment in ^{15}N has also been observed in CN molecules from two comets (Arpigny *et al.* 2003). These isotopic measurements represent a small fraction of cometary materials and it is possible that isotopic measurements of additional molecules or on finer spatial scales will reveal a greater isotopic diversity than is apparent so far.

The mineralogy of cometary dust grains provides further insight into their origins. Spectroscopic studies of comets have shown the presence of abundant, fine grained silicates. As with interstellar silicates, the 10 μm feature is generally featureless, indicating the presence of abundant amorphous silicates. However, significant variability in the strength and detailed structure of this band is observed among comets (Hanner et al. 1994). Most importantly, a significant fraction of cometary silicates were found to be crystalline olivine grains, based on a spectral feature at 11.2 μm (Bregman *et al.*, 1987; Campins & Ryan 1989; Hanner *et al.*, 1994). More detailed mineralogical characterization has recently been achieved by far-IR spectroscopy (16 – 45 μm), where features corresponding to forsterite and enstatite were observed (Crovisier *et al*. 2000). The observation that comets contain Mg-rich crystalline silicates is intriguing because although a minor fraction of such grains exist around evolved stars are crystalline (10 – 20 %), they are far rarer in the ISM (~ 0.5 %).

The presence of crystalline silicates in comets suggests that they contain a significant, and variable proportion of solar system materials processed at high temperatures. One possibility is that the crystalline grains were originally amorphous interstellar grains that were annealed by moderate heating. However, it is difficult to envision this process naturally leading to Mg-rich crystalline silicates unless the precursor amorphous grains happened to have had just the right chemical composition. Alternatively, the crystalline grains may be second-generation solids that formed by equilibrium condensation from a high temperature gas. Either scenario is clearly at odds with the evidence that comets to have largely escaped significant thermal processing. A solution to this dilemma is that these materials were processed in the inner portions of the solar nebula, perhaps by shocks (Harker and Desch, 2002), and were transported outward to the comet forming region by turbulence (Cuzzi *et al*., 2003) or as a consequence of early bi-polar outflow of material from the Sun (i.e. the X-wind, Shu *et al*., 2001) or its early stellar neighbors.

Thus, even those bodies that formed in the most quiescent portions of the solar nebula appear to have been partially built from materials that were processed in energetic environments. Other processes that may have been important in altering cometary materials include hypervelocity impacts among icy planetessimals, irradiation by galactic cosmic rays of the upper ~1 meter, and radiogenic heating (for sufficiently large bodies). Disentangling the imprint of these secondary processes from the original primordial compositions can only be achieved by detailed laboratory analysis of primitive materials.

The most detailed information on the processes, conditions, and timescales of the early history of the solar system has come from the study of meteorites. In addition to preserving the earliest nebular condensates, the least altered meteorites contain traces of the starting materials, including interstellar dust grains and molecular cloud material (discussed below). However, even the most primitive meteorites are comprised almost entirely of secondary materials formed within the solar nebula or their parent bodies. Two important selection effects account for the rarity of primitive materials among the meteorite collection: most meteorites are derived from portions of the asteroid belt that lie near orbital resonances with Jupiter, and macroscopic bodies comprised of fragile materials cannot survive the hypervelocity (>12 km/s) passage through the atmosphere.

Interplanetary dust is largely unaffected by the selection effects that limit the diversity of meteorites. First, the Earth accretes dust from *all* dust producing bodies, including comparable proportions of asteroidal and cometary dust. This is due to the fact that all small bodies (<1 cm) in the Solar System have unstable orbits owing to their interaction with solar radiation. While the smallest dust grains (~1 μm) are ejected from the Solar System by radiation pressure, the orbits of most interplanetary dust grains gradually decay toward the Sun because of Poynting-Robertson light drag and solar wind drag (on a 10^4 – 10^5 yr timescale). Some of this dust is captured by the Earth, amounting to ~4 x10^7 kg/year (Love and Brownlee 1993). The second advantage is that fragile materials easily survive atmospheric entry because their relatively large surface areas cause them to decelerate at very high altitude (~ 80 km) where the ram pressure is low.

The smallest particles are the least affected by atmospheric entry, although large size (>100 μm), high velocity (>20 km/s) or steep entry angles can lead to strong heating – even melting – among some particles. The best preserved samples of interplanetary dust are collected in the stratosphere (stratospheric IDPs) by high altitude research aircraft such as the ER-2 and WB-57. Most of these samples are smaller than 20μm in diameter although some of the highly porous "cluster particles" probably exceeded 100μm before they fragmented on the collection surface. Because these particles are collected before they reach the ground, there is minimal potential for chemical weathering. The stratospherically collected IDPs are restricted to small sizes because of the comparative rarity of larger particles.

Unlike primitive meteorites that are widely believed to be samples solely of asteroids, it is nearly certain that stratospheric IDPs include samples of *both* asteroids and comets. Both types of objects are known sources of dust injected into the interplanetary medium (e.g., Sykes & Greenberg, 1986; Sykes *et al*., 1986), and dynamical arguments indicate dust from both sources can be delivered to Earth (e.g., Sandford, 1986; Jackson and Zook 1992). Furthermore, observations of the extent of atmospheric heating (Sandford and Bradley 1989; Nier and Schlutter 1992, 1993) and compositional variations (Bradley *et al.*, 1988) suggest both sources are represented in the IDP collections.

Larger particles, accumulated over time, can be collected in certain localities on the ground, particularly from Greenland and Antarctic ice (Maurette 1994, Duprat *et al*. 2005, Gattacceca *et al*. 2005, Noguchi et al. 2002, Taylor *et al*. 2001). By current convention, these particles collected from surface deposits are called micrometeorites. This terminology differs from Fred Whipple's original definition of micrometeorites as small particles that were not heated to melting temperatures during atmospheric entry, but it is the current convention and it is consistent with the definition of meteorites as samples that actually impact the surface of the Earth. Micrometeorites recovered from Antarctic ice range from 10μm to millimeter-size, but most are much larger than collected stratospheric IDPs. Micrometeorites are valuable samples because they are much more massive than typical IDPs, they can be collected in vast numbers and they include particles near the mass flux peak at ~200μm size that dominates the bulk of cosmic matter accreted by Earth.

Micrometeorites exhibit a diversity of compositions and structures, with the majority being dominated by fine grained anhydrous mineralogy. A large fraction of micrometeorites appear to have originated from CM or (less commonly) CI-like chondrite parent bodies – samples that are much rarer among collected meteorites (Kurat *et al*. 1994). This is likely due to the differing delivery mechanisms between the two types of samples (discussed above). Owing to their larger sizes, the heating effects are more pronounced among micrometeorites with a higher proportion having experienced partial or total melting (Alexander and Love 2001). Some particles up to several hundred microns across do survive entry without being heated above the ~ 1300 °C melting points of chondritic composition materials. The larger unmelted micrometeorites probably survived due to a combination of low entry speed (~ escape velocity) and low entry angle. However, even moderate atmospheric entry heating has apparently dramatically affected the mineralogy of most micrometeorites, decomposing phyllosilicates into complex fine-grained mixtures of olivine, low-Ca pyroxene, magnetite, and amorphous silicates (Nakamura *et al*. 2001).

Unlike IDPs, most micrometeorites have been affected by some degree of weathering, for example particles recovered from solid ice are usually depleted in S, Ni and Ca relative to chondritic proportions due to terrestrial leaching processes (Kurat *et al.* 1994). The best-preserved and probably least biased polar micrometeorites have been recently recovered from Antarctic snow (Duprat et al 2005). The polar micrometeorites are an increasingly important resource of interplanetary particles (Rietmeijer 2002). These samples are strong compliments to conventional meteorites and IDPs as well as primitive solar system samples to be returned by comet and asteroid missions such as Stardust and Hayabusa.

Of the available extraterrestrial materials, Chondritic Porous (CP) interplanetary dust particles (Fig. 2) are the most likely samples of Kuiper Belt Objects and, as such, their properties should most closely resemble the original starting materials. The link between CP IDPs and short period comets is based on a number of independent lines of evidence. First, CP IDPs are structurally similar to cometary materials in being extremely fine grained, porous and fragile (Bradley and Brownlee 1986, Rietmeijer and McKinnon 1987). In fact, CP IDPs are so fragile that these materials are unlikely to survive atmospheric entry as macroscopic bodies, so it is not surprising that similar materials are not represented in the meteorite collections. Second, CP IDPs are highly enriched in

C (2 – 3 x CI, Thomas et al. 1993) and volatile trace elements (Flynn et al. 1993) relative to CI chondrites. Third, as discussed below, detailed chemical, mineralogical, and isotopic studies of these particles show them to have experienced minimal parent-body alteration, and are rich in presolar materials.

The strongest evidence linking CP IDPs to short-period comets comes from their inferred atmospheric entry velocities. Even after thousands of years in space, cometary and asteroidal dust particles, by and large, retain distinct orbital characteristics (Sandford, 1986; Jackson and Zook 1992). Asteroidal particles typically have low eccentricity (*e*) ~0.1 and low inclination (*i*) orbits, while cometary particles usually have eccentricities exceeding ~0.4, and a wider range of inclinations. The higher average *e* and *i* of cometary dust particles result in higher Earth encounter velocities. This difference in Earth-encounter velocities should translate into observable differences in the extent of heating experienced during atmospheric entry (Flynn, 1989; Sandford and Bradley 1989). Peak temperatures experienced by particles during atmospheric entry were most accurately determined by stepwise He release profiles measured in individual IDPs (Nier and Schlutter 1992, 1993). Based on these measurements, Joswiak et al. (2000) showed that the particles with the highest peak temperatures (and therefore the highest inferred entry velocities and orbital eccentricities) were compositionally distinct from those with low peak temperatures. This high-velocity (> 18 km/s) subset is dominated by CP IDPs, and it is likely that many of them have cometary origins. Typical hydrated IDPs have lower (<14 km/s) entry speeds consistent with origin from the asteroid belt. It is much less likely for dust from long-period comets to survive atmospheric entry due to the far higher Earth-encounter velocities (30 – 70 km/s). These high-velocity particles are responsible for the most spectacular meteor showers, such as the Leonids.

The CP particles have near chondritic elemental abundances – an amazing property for samples only a few microns across. They are largely aggregates of subgrains <0.5 μm in diameter, with rare grains larger than several microns. The subgrains are solid non-porous matter containing a mix of submicron GEMS (Glass with Embedded Metal and Sulfides; Bradley *et al*. 1999), organic materials, olivine, pyroxene, pyrrhotite, less well-defined materials, and a number of less abundant phases (Bradley 2004). GEMS grains are sub-μm amorphous Mg-Si-Al-Fe silicate grains that contain numerous 10 to 50 nm-sized FeNi metal and Fe-Ni sulfides, comprising up to 50 wt% of anhydrous IDPs (Figure 3).

One of the most fundamental properties of the CP particles is that they are porous aggregates of submicron grains. Whether CP particles are made of starting materials or not, their porous aggregate structure of micrometer and submicrometer grains is a predictable property of first generation primitive materials that formed by accretion of ice coated submicron grains - the size of interstellar dust. The preservation of a highly porous aggregate structure for billions of years inside a parent body probably required the presence of ice, ice that never melted but was lost by sublimation. Sublimation is a gentle process that does not result in compaction. It is possible, but not proven, that the CP particles or at least some subset of them are freeze dried samples of KBOs. Even if they are comet samples, there is a need of additional information to determine how similar they might be to the original nebular materials. The CP particles have been found to contain presolar grains but what *fraction* of the subgrains are presolar? Even at Kuiper belt distances, it is possible that nebular shocks modified first generation grains and it is also possible that there could have been considerable radial transport outward from the inner, warmer regions of the nebular accretion disk.

The CP particles are dominated by anhydrous phases but they are just one of the types of IDPs collected in the stratosphere. Other IDP types include fine-grained particles composed largely of hydrated silicates and particles dominated by coarse-grained minerals, usually pyrrhotite, forsterite or enstatite. Both the fine-grained hydrous and anhydrous particles are black and have elemental compositions similar to CI chondrite abundances often with enhanced volatile contents and usually higher carbon contents (Flynn et al. 1996). Most of the coarse-grained IDPs have clumps of black fine-grained material with chondritic elemental composition adhering to their surfaces and it is clear that the coarse grained particles were previously embedded in fine-gained matrix material similar to the fine-grained IDP types.

Hydrated IDPs and micrometeorites are likely to have formed by aqueous alteration of materials inside parent bodies that were heated to temperatures high enough to melt ice. This was a common process in primitive asteroids and it is likely that most of the hydrated IDPs and micrometeorites, like carbonaceous chondrites, are from asteroids and are products of the inner regions of the solar nebula. The CP particles, dominated by anhydrous minerals and glass, do not appear to have ever been exposed to liquid water. Their anhydrous nature is consistent with spectral reflectance data from outer solar system primitive bodies that also lack hydrated phases.

The CP particles are believed to be the most primitive type of IDP and it is likely that they are samples of comets or ice-bearing asteroids. They are distinctive in several respects including; their porosity (lack of compaction and their associated fragility), their content of GEMS, their high He abundances with $^{3}He/^{4}He$ that are distinct from solar wind, their high volatile contents, their high abundance of pre-solar grains, and the fact that they do not normally contain hydrated silicates. All of the carbon-rich and volatile-rich meteorite types contain hydrated silicates, presumably formed by secondary processes inside parent bodies. Thus, the CP particles appear to be the best preserved samples of early solar system fine grained materials.

It is possible that the CP particles contain or are even dominated by the initial materials that began the accretion process. This first generation of nebular solids has also been referred to as FAPs or First Accretionary Particles (Brownlee *et al.*, 2004). The CP particles are largely assemblages of relatively equidimensional rounded components about a quarter of a micron in diameter, similar in size to typical interstellar grains. The submicron components of the aggregate particles may be FAPs. Figures 4 and 5 show the results of efforts to mechanically separate the individual components of a CP IDP into components that originally accreted to form the aggregates. The subgrains are typically small solid rocks composed of GEMS, crystalline silicates, sulfides, amorphous silicates, and amorphous organic material. They have wildly varying major element compositions, but groups of a dozen or more of the possible FAPs average close to bulk chondritic compositions. It is interesting that there is a cut-off in size in the potential FAPs particles at about 0.1 µm size. Much smaller components are present, but they are all contained inside the potential FAPs that average about a 0.25 µm diameter across. They are solid particles that seem to be the fundamental building blocks of CP IDPs. Some early, pre-accretional process assembled these particles that into solid femtogram ‘rocks’ that typically range in diameter from 0.1 µm to 0.5 µm.

Although meteorites may be dominated by processed materials such as chondrules, they are also found to contain traces of the original starting materials, including presolar grains. The presolar materials are the only starting materials that can be definitively identified. These presolar components are distinguished by their isotopic compositions, which differ from the well-homogenized solar system materials by degrees that cannot be explained through other local processes such as spallation and isotopic fractionation. Two types of presolar materials are recognized: presolar grains (stardust) and organic matter that likely originated in a cold molecular cloud environment.

4.1 Interstellar dust in the Solar System

The vast majority of the various starting materials that ended up in the Solar System were obliterated by nebular and parent body processes. The Solar System has been homogenized isotopically on scales ranging from micrometers to astronomical units, but strong chemical fractionation processes have obscured the record of the Solar System elemental abundances. Despite being largely comprised of secondary materials, CI chondrite meteorites have bulk abundance patterns (chondritic composition) that closely match that of the Sun and therefore that of the overall Solar System (solar composition) for most non-volatile elements. Determining the elemental abundances of the Sun is challenging because of the difficulty of resolving weak spectral lines, incomplete knowledge of the physical state of the solar photosphere, and insufficiently known atomic transition probabilities. However, only the Sun can yield accurate measures of the relative abundances of volatile elements and all elements heavier than He (metallicity) that are essential parameters for a wide variety cosmochemical studies. On the other hand, the abundances of most non-volatile elements can be much more precisely determined from laboratory studies of CI chondrite meteorites (Anders & Ebihara 1982, Burnett et al. 1989). Since the landmark compilations of Anders & Grevesse (1989) and Anders & Ebihara (1982), the solar abundances of individual elements have been gradually refined. The most recent comprehensive study has shown that the abundances of 31 elements determined from the solar photosphere and CI chondrites agree within 10%, and an additional 5 elements within 15% (Lodders 2003). Further refinements may be possible from analyses of solar wind samples recently returned to Earth by the Genesis spacecraft.

Elemental abundances derived from CI chondrites show smooth functions of mass for odd mass nuclei when broken down into individual isotopic abundances. As first argued by Suess (1947), this smooth abundance curve is unlikely to be the result of fractionation processes that occurred during the chondrite formation process. In fact, the regular variations in solar system elemental and isotopic abundances have retained the imprint of distinct nucleosynthetic processes averaging over many stellar sources. In a seminal paper, Burbidge *et al*. (1957) demonstrated that the average elemental and isotopic abundances of the Solar System could be accounted for by a combination of eight nucleosynthetic reactions occurring in stars. The study of the contributions of particular types of stars and nucleosynthetic processes to these abundances is a field in its own right – galactic chemical evolution, that is treated in the chapter by Nittler and Dauphas.

Because stardust grains sample individual stars and are largely comprised of newly synthesized elements, they are marked by extremely exotic isotopic compositions in both major and trace elements. The isotopic compositions of freshly synthesized elements are functions of the mass, age, and chemical composition of the parent star, leaving an isotopic fingerprint on the stellar ejecta that may differ from solar composition by orders of magnitude. The interpretation of the isotopic compositions of stardust from meteorites in terms of specific stellar sources and nucleosynthesis is reviewed in the chapter by Zinner and Meyer. Here we focus on the nature of these materials.

The types of stardust identified in meteoritic materials to date include nanodiamonds, SiC, graphite, Si_3N_4, TiC, Al_2O_3, TiO_2, hibonite, spinel, forsterite, and amorphous silicates (Zinner, 1998; Table 1). With the exception of nanodiamonds, these grains are large enough (>200 nm) to have their isotopic compositions measured by secondary ion mass spectrometry (Fig. 6). These grains originated from a diversity of stellar sources, including red giant and asymptotic giant branch stars, novae, and supernovae. Their isotopic compositions show that their parent stars had a wide range in mass and chemical composition, requiring contributions from dozens of stars. No single stellar source appears to dominate. Nanodiamonds are by far the most abundant phase (1,000 ppm), but their origins remain uncertain because they are much smaller (~ 2 nm) and their isotopic compositions can only be determined from bulk samples (thousands of nanodiamonds). A minor fraction (10^{-6}) of nanodiamonds is linked to stellar sources by an anomalous Xe component enriched in both heavy and light isotopes (Xe-HL; Lewis *et al*., 1987). However, the average C isotopic composition of nanodiamonds is identical to that of the Solar System, leaving the origins of most nanodiamonds unknown. There is also evidence that some nanodiamonds may have formed in the solar nebula (Russell et al. 1992). In this regard, it is interesting to note that infrared absorption bands characteristic of nanodiamonds have been detected in the dust surrounding several young stars (Guillois *et al.*,1999).

Besides the enigmatic nanodiamonds, the most abundant types of stardust are amorphous and crystalline silicates. Despite their high abundance, these grains were only recently identified because of their small size and the fact that they are a minor component of a silicate-rich matrix of Solar System origin. As it is not feasible to chemically isolate presolar silicates, they have only been identified through systematic searches in primitive meteorite matrix and IDPs by O isotopic imaging with the Cameca NanoSIMS and modified IMS-1270 ion microprobes (Nagashima *et al.*, 2004). Presolar silicates appear to be significantly more abundant in IDPs (450 – 5,500 ppm (bulk); Floss and Stadermann, 2004; Messenger *et al.*, 2003) than in meteorites (<170 ppm matrix normalized; Nguyen & Zinner, 2004; Mostefaoui & Hoppe, 2004), consistent with the suggestion that the population of IDPs contains some of the best preserved samples of early solar system materials.

Because of these difficulties, few presolar silicates have been subjected to detailed mineralogical study by transmission electron microscopy (TEM). Of the 6 presolar silicates studies by TEM thus far, 2 are forsterite and 4 are amorphous silicates including GEMS. The observed proportion of amorphous to crystalline presolar silicates (2:1) is at odds with that observed around evolved stars (10:1) and in the diffuse ISM (>100:1) inferred from fitting the 10 μm spectral feature. This is a major unsolved problem that impacts wide ranging fields in astrophysics (Kemper *et al.*, 2004). Two possible resolutions to this discrepancy are that: (1) the abundances of interstellar amorphous and crystalline silicates have been improperly derived from the ~10 μm feature (Bowey and Adamson, 2002), or (2) most of the mass of interstellar silicate grains have been recycled through repetitive sputtering and recondensation in the ISM, rendering them isotopically homogeneous (~solar; Bradley and Dai, 2005). One future test of the interstellar homogenization model will be high precision isotopic measurements of individual GEMS grains, that would be expected to show mixing trends between solar and evolved-stellar isotopic compositions (^{17}O-rich and ^{18}O-depleted).

Whatever their origins, GEMS-like materials (dirty amorphous silicates) were abundant constituents of the protoplanetary disk, and rank among the most important of the starting materials.

The abundances of each type of presolar grain varies considerably among different classes of primitive meteorite, generally following the extent of parent-body metamorphism (Huss *et al*., 1995). In addition, Huss *et al*. (2003) have also argued that nebular heating removed the most volatile and fragile presolar components to varying degrees, generally correlating with the bulk chemical composition (extent of fractionation relative to solar) of the host meteorites. Presolar silicates have also recently been found in Antarctic micrometeorites in abundances (300 ppm; Yada *et al*., 2005) intermediate between those observed in meteorites (<170 ppm; Mostefaoui & Hoppe 2004) and those of IDPs (450 – 5,500 ppm).

The abundance of presolar silicates in primitive extraterrestrial materials is therefore a sensitive probe of the extent of parent body and nebular alteration. The abundance of presolar silicates in the meteorite Acfer 094 are best known (~ 170 ppm) because of the large surface area searched. The abundances in Antarctic micrometeorites and IDPs are not as well known in part because of the smaller amount of material studied. These preliminary studies also suggest that there are substantial variations in the presolar grain abundance between different IDPs and micrometeorites. This may reflect the fact that these particles sample a wider range of parent bodies than are represented in the meteorite collection. Again, the highest abundances have so far been observed in some CP IDPs, suggesting that those materials have undergone less extensive parent body and/or nebular processing.

4.2 Molecular cloud matter in the Solar System

Organic matter in primitive meteorites and IDPs often exhibits large excesses in D and ^{15}N relative to terrestrial values. These anomalies are usually thought to reflect the partial preservation of molecules that formed in a presolar cold molecular cloud by processes that fractionated H and N isotopes as described above (Geiss and Reeves, 1981; Zinner, 1988; Messenger and Walker, 1997; Cronin and Chang, 1993). Elucidating the origin and history of this material is complex, as it has since become altered and diluted with local organic matter to an unknown extent. These molecules may have experienced oxidation, polymerization, and isotopic exchange either in the solar nebula or during parent body hydrothermal alteration. The organic matter in meteorites has been subjected to extensive study, and a detailed discussion of its nature can be found in the chapter by Pizzarello *et al*.

Here we are concerned with the question: What was the original state of the organic matter in the Solar System? Spectroscopic observations of cold molecular clouds and comets, and laboratory simulations of interstellar chemistry provide a useful starting point, but these approaches are of limited value for complex molecules. The value of studying meteorites in this regard is that modern analytical instruments can be brought to bear to reveal the full molecular and isotopic diversity of materials that directly sample remote astrophysical environments. The challenge has been to properly interpret these observations in order to delineate how parent body alteration may have affected the organic matter present.

The nature of organic matter varies among primitive meteorite and micrometeorite classes and even within individual meteorites (Cronin *et al*., 1988; Clemett *et al*., 1993, 1998; Matrajt *et al*., 2004). However the majority (>70 %) of the organic matter in all cases is comprised of an acid insoluble macromolecular material often likened to terrestrial kerogen (Cronin *et al*., 1988; Cody and Alexander, 2005). The insoluble organic fraction is found to be predominantly comprised of small aromatic domains with heteroatomic substitutions crosslinked by alkyl and ether functional groups. The soluble fraction is a complex assemblage of hundreds of identified compounds including amino acids, amines, carboxylic acids, alcohols, ketones, aliphatic hydrocarbons, and aromatic hydrocarbons. Most molecules are found to exhibit full isomeric diversity and chiral molecules are generally racemic, consistent with their formation through abiogenic processes (Epstein *et al*., 1987; Cronin *et al*., 1988).

Considerable variations in the H, N, and C isotopic compositions of the organic matter are observed within and between meteorites. Pyrolysis and combustion experiments have shown that several isotopically distinct components exist within the insoluble organic fraction (Kerridge et al. 1987, Alexander et al. 1998). Several classes of soluble organics have been subjected to compound specific isotopic measurements, including hydroxy, dicarbocylic, and hydroxydicarboxylic acids

(Krishnamurthy *et al*., 1992; Cronin *et al*., 1988), amino acids (Pizzarello and Huang, 2005), and aliphatic, aromatic and polar hydrocarbons (see Cronin *et al*., 1988 for a review). Among these, amino acids exhibit the strongest D enrichments, reaching +3,600 ‰ in 2-amino-2,3-dimethylbutyric acid (Pizzarello and Huang, 2005).

Comparative studies of organic matter in different meteorites suggest that aqueous processing has had a significant impact on both the soluble and insoluble organic compounds. For instance, amino acids have been hypothesized to have formed during aqueous alteration from preexisting aldehydes and ketones in a so-called Strecker synthesis (Cronin *et al*., 1988 and references therein). Alternatively, amino acids could have been synthesized directly in the ISM via grain surface catalysis in hot cloud cores (Kuan *et al.*, 2003) or, as discussed above, via radiation processing of interstellar ices (Bernstein *et al*., 2002). Other evidence for the affect of aqueous alteration is found from the general trend of a sharply decreasing abundance of aliphatic hydrocarbons among meteorites in the order of Tagish Lake < CM2 < CI1 < CR2, inferred to have resulted from low temperature chemical oxidation (Cody and Alexander, 2005).

Future work will benefit from analyzing less altered materials – IDPs and samples taken directly from comets. For instance, it may be possible to distinguish between the two proposed origins of meteoritic amino acids by analyzing cometary materials which are expected to have escaped aqueous processing. Unfortunately, no direct samples of comets are yet available (although the imminent return of the Stardust spacecraft will change that) and the small size of IDPs (~1 ng) precludes standard chemical analysis techniques. However, isotopic studies of IDPs suggest that some particles contain well preserved molecular cloud materials.

Because the magnitude of hydrogen isotopic fractionation is so great in the environment of a cold molecular cloud (factors of 100 – 10,000), D/H measurements provide the most direct means of identifying molecular cloud material. However, recent theoretical studies have suggested that gas phase chemical reactions in the outer portions of the solar nebula may also have resulted in significant D enrichments in regions that were cold enough and were not opaque to interstellar ionizing radiation (Aikawa and Herbst, 2001). In any event, such chemistry would have occurred in conditions that are characteristic of the immediately preceding molecular cloud phase and chemistry in either regime would have isotopically imprinted the starting materials found in the protosolar nebula in a similar manner.

In a simplified view, the most D-rich materials are likely to have experienced the least degree of exchange or dilution. Figure 7 summarizes typical ranges of D/H ratios observed in gas phase molecules in cold molecular clouds with those of meteorites, IDPs, and comets (where only H_2O and HCN have been measured so far). D/H ratios of IDPs reach values (50 x terrestrial) that are significantly higher than those observed so far in meteorites (~8 x terrestrial; Guan *et al*., 1998). However, such extreme values in IDPs are relatively rare, with only ~ 4% of measured cluster IDP fragments exceeding 10 x terrestrial and 8% exceeding 5 x terrestrial (Messenger *et al*., 2002). By comparison, the CR chondrites Renazzo and Al Rais have roughly an order of magnitude lower abundance of these very D-rich materials (Guan *et al*., 1997, 1998; Young *et al*., 2004). The average bulk D/H ratio of cluster IDP fragments (δD = +1,300 ‰; Messenger *et al*., 2002) is higher than that of most chemically untreated meteorite samples studied so far, but is very similar to some CR chondrites including Renazzo (δD ~ +1,000 ‰) and Al Rais (δD ~ +1,280 ‰) (Guan *et al*., 1997, 1998; Young *et al*., 2004; Robert, 2003 and references therein). However, the D/H ratios of cluster IDPs exhibit far greater variability in comparison to similar sized meteorite matrix fragments. Some of this heterogeneity may be due to variable loss of D-rich volatiles during atmospheric entry heating or the loss of soluble D-rich organics during the standard hexane rinse used to clean IDPs of collector (silicone) oil. The similar bulk average D/H ratios of cluster IDPs and CR chondrites suggests that CR chondrites may have accreted organic matter similar to that of CP IDPs that subsequently became isotopically homogenized during parent body hydrothermal processing. While these considerations serve as a useful guide in identifying the least altered material, the great majority (>99%) of the organic matter in cold molecular clouds is condensed onto grains whose isotopic compositions have so far defied spectroscopic measurement. It is possible that some *solid phase* D-rich molecules in meteorites and IDPs are direct samples of interstellar molecules even though their D enrichments (factor of 2 – 4) are much lower than those observed in *gas phase* interstellar molecules.

The most D- and ^{15}N-rich materials in meteorites and IDPs have been located by isotopic imaging by ion microprobe. The first D ‘hotspot’ in an IDP was reported by McKeegan *et al*. (1987) where a small (<2 μm) region was found to reach 10 x terrestrial, and several other similar cases have since been found (Messenger, 2000; Keller *et al*., 2004). These studies were limited to the 1 – 2 μm spatial resolution of the IMS-series ion microprobes and were performed on chemically untreated samples. It is possible that significantly more D-rich materials remain to be found at higher spatial resolution or as minor phases that can only be identified by molecular specific isotopic measurements. Recent studies of IDPs using the NanoSIMS ion microprobe have revealed that this is indeed the case for N, finding that some IDPs contain a mixture of moderately (several hundred per mil) ^{15}N-rich carbonaceous matter and submicrometer inclusions of very ^{15}N-rich material (> +1,200 ‰; Floss *et al*., 2004).

D- and ^{15}N-rich hotspots (Figure 8) are the best candidates for surviving chunks of molecular cloud material. If this is the case, one would expect any mineral grains entrained within these isotopically anomalous materials to also have presolar origins. Recent studies have indicated that stardust abundances are highest within ^{15}N- and D-rich materials (Floss and Stadermann, 2004; Messenger and Keller, 2005). While the first D hotspot investigated so far by NanoSIMS was found to contain one presolar silicate, many isotopically solar crystalline silicates and GEMS grains were also present. It is likely that in such a case, these materials (presolar organic matter, solar system grains, and stardust) accreted in the solar nebula. In another example of this association (Figure 9), a presolar supernova silicate grain in an IDP was found to be coated with ^{15}N-rich organic matter, perhaps the best candidate so far to resemble the classic model of an interstellar grain coated with a refractory organic mantle (Li and Greenberg, 1997; Fig. 1).

Although organic studies of IDPs are still at an early stage, compositional differences are already apparent between anhydrous IDPs and carbonaceous chondrites (see chapter by Pizzarello et al. for further discussion). So far, the only specific organic molecules identified in IDPs are PAHs, determined by two-step resonant ionization mass spectrometry (Clemett *et al*., 1993). The particles studied tended to have more high mass molecules that appeared to be significantly substituted by N-bearing functional groups. A recent FTIR study of IDPs with wide ranging D/H ratios (including the D-rich hotspot in Fig. 8) suggest that the abundance of aliphatic hydrocarbons is higher among D-rich IDPs than D-poor IDPs or meteorites (Keller *et al*., 1995). This observation is in line with the trend of alteration observed in meteoritic organics and suggests that the organic matter in D-rich anhydrous IDPs most closely resembles the original starting composition of solar system organic matter.

5. Overview

We have seen that the nature of the starting materials evolved considerably during the prehistory and early history of the solar system. Nevertheless, these materials share several universal traits that extend to other young stellar systems and therefore provide insight into the nature of other planetary systems. Despite the inherent uncertainties and complex overprinting of secondary processes, we can make the following conclusions:

- The starting materials at all stages were products of long and complex histories beginning with stellar ejection, processing in disparate interstellar environments and in the protonebular collapse.

- The starting materials are generally described as aggregates of submicrometer mineral grains dominated by mixtures of amorphous and crystalline silicates, refractory organic matter that contained a significant aromatic component, and condensed volatile ices.

- The starting materials for planetary construction originated from evolved stars, outflows from young stellar objects, condensation in dense molecular clouds, and variably processed materials in the solar nebula itself.

- The nature of the starting materials is partially obscured by secondary alteration in multiple environments.

- Isotopic anomalies are key indicators for the presence of primitive materials and demonstrate that some starting materials had both stellar and interstellar origins.

- Anhydrous IDPs are the best currently available examples of what the non-volatile portions of the starting materials probably looked like.

- An important constituent of the starting materials are volatiles that have not yet been studied in the laboratory, but are likely present in small outer-Solar System bodies.

The once disparate views of astrophysics and cosmochemistry are beginning to form a unified picture of the complex processes of star formation and the history of the starting materials for their construction. Further advances are anticipated as spatial and spectral resolution of astrophysical observations are improved. Recent advances in cosmochemistry have also been primarily aided by revolutionary advances in analytical instruments. For the future exploration of cosmochemical frontiers, direct samples of comets and asteroids are considered to have overriding importance. The return of cryogenic stored samples from a short-period comet will surely be technically challenging, but such a mission is essential to achieving the clearest view of the starting materials.

REFERENCES

Aikawa Y. and Herbst E. (2001) Two-dimensional distribution and column density of gaseous molecules in protoplanetary discs. *A&A* **371**, 1107-1117.

Alexander C. M. O'D. et al. (1998) The origin of chondritic macromolecular organic matter: a carbon and nitrogen isotopic study. *Met. Planet. Sci*. 33, 603-622.

Alexander C. M. O'D., Love S. (2001) Atmospheric entry heating of micrometeorites revisited: Higher temperatures and potential biases. *Lunar Planet. Sci*. **32**, 1935.

Allamandola, L. J., Sandford, S. A., & Valero, G. (1988) Photochemical and thermal evolution of interstellar/pre-cometary ice analogs. *Icarus* **76**, 225-252.

Allamandola, L. J., Tielens, A. G. G. M., & Barker, J. R. (1989) Interstellar Polycyclic Aromatic Hydrocarbons: the Infrared Emission Bands, the Excitation-Emission Mechanism and the Astrophysical Implications. *Ap. J. Suppl. Ser.* **71**, 733-755.

Allamandola, L. J., Sandford, S. A., Tielens, A. G. G. M., & Herbst, T. M. (1992) Infrared spectroscopy of dense clouds in the C-H stretch region: Methanol and "Diamonds". *Astrophys. J.* **399**, 134-146.

Anders, E., & Ebihara, M. (1982) Solar system abundances of the elements. *Geochim. Cosmochim. Acta* **46**, 2363-2380.

Anders, E., & Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197-214.

Arpigny C. *et al*. (2003) Anomalous nitrogen isotope ratio in comets. *Science* **301**, 1522 -1524.

Bell K. R., Cassen P. M., Klahr H. H. and Henning T. (1997) The structure and appearance of protostellar accretion disks: limits on disk flaring. *Astrophys. J*. **486**, 372.

Bergin, E. A., Alves, J., Huard, T., & Lada, C. J. (2002). N_2H^+ and $C^{18}O$ Depletion in a Cold Dark Cloud. *Astrophys. J.* **570**, L101-L104.

Bernatowicz T. J., Messenger S., Pravdivtseva O., Swan P. and Walker R. M. (2003) Pristine presolar silicon carbide. *Geochim. Cosmochim. Acta* **67**, 4679-4691.

Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Chang, S., & Scharberg, M. A. (1995). Organic Compounds Produced by Photolysis of Realistic Interstellar and Cometary Ice Analogs Containing Methanol. *Astrophys. J.* **454**, 327-344.

Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. (1999a). Life's Far-Flung Raw Materials. *Scientific American* **281**, #1, 42-49.

Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Gillette, J. S., Clemett, S. J., & Zare, R. N. (1999b). Ultraviolet Irradiation of Polycyclic Aromatic Hydrocarbons in Ices: Production of Alcohols, Quinones, and Ethers. *Science* **283**, 1135-1138.

Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. (2000). H, C, N, and O Isotopic Substitution Studies of the 2165 cm^{-1} (4.62 µm) "XCN" Feature Produced by UV Photolysis of Mixed Molecular Ices. *Astrophys. J.* **542**, 894-897.

Bernstein, M. P., Dworkin, J., Sandford, S. A., & Allamandola, L. J. (2001). Ultraviolet Irradiation of Naphthalene in H_2O Ice: Implications for Meteorites and Biogenesis. *Meteoritics and Planetary Science* **36**, 351-358.

Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G. W., & Allamandola, L. J. (2002) The Formation of racemic amino acids by ultraviolet photolysis of interstellar ice analogs. *Nature* **416**, 401-403.

Bernstein, M. P., Moore, M. H., Elsila, J. E., Sandford, S. A., Allamandola, L. J., & Zare, R. N. (2003) Side group Addition to the PAH Coronene by proton irradiation in cosmic ice analogs. *Astrophys. J.* **582**, L25–L29.

Bernstein, M. P., Sandford, S. A., & Allamandola, L. J. (2005) The mid-infrared absorption spectra of neutral PAHs in dense interstellar clouds. *Astrophys. J. Suppl. Ser.*, in press.

Biver N. et al. (2002) Chemical composition diversity among 24 comets observed at radio wavelengths. *Earth Moon Planets* **90**, 323-333.

Bockelée-Morvan D., Crovisier J., Mumma M. J., and H. A. Weaver (2005) The composition of cometary volatiles. In Comets II (eds. M. C. Festou et al.), Univ. Arizona Press., 391 – 423.

Boogert, A. C. A., Schutte, W. A., Tielens, A. G. G. M., Whittet, D. C. B., Helmich, F. P., Ehrenfreund, P., Wesselius, P. R., de Graauw, Th., & Prusti, T. (1996). Solid methane toward deeply embedded prototstars. *Astron. Astrophys.* **315**, L377-L380.

Boss, A. P. (1998) Temperatures in protoplanetary disks. *Ann. Rev. Earth Planet. Sci*. **26**, 53-80.

Bowey J. E. and Adamson A. J. (2002) A mineralogy of interstellar silicate dust from 10-mm spectra. *Mon. Not. R. Astron. Soc*. **334**, 94-106.

Bradley J. P. and Brownlee (1986) Cometary particles: Thin sectioning and electron beam analysis. Science 231, 1542 – 1544.

Bradley J. P. *et al*. (1999) An infrared spectral match between GEMS and interstellar grains. *Science* **285**, 1716-1718.

Bradley, J. P. (2004). Interplanetary Dust Particles, in Treatise of Geochemistry Vol 1 Ed A. Davis Elsiever.

Bradley J. P. and Dai Z. R. (2005). Mechanism of GEMS formation. *Astrophys. J*. **617**, 650-655.

Bradley, J. P., Sandford, S. A., & Walker, R. M. (1988). Interplanetary dust particles. In *Meteorites and the Early Solar System* (Ch. 11), (J.F. Kerridge & M.S. Matthews, eds.), Univ. Arizona Press: Tucson, 861-895.

Bregman, J. D., Campins, H., Witteborn, F. C., Wooden, D. H., Rank, D. M., Allamandola, L. J., Cohen, M., & Tielens, A. G. G. M. (1987). Airborne and ground-based spectrophotometry of comet P/Halley from 5-13 micrometers. *Astron. Astrophys.* **187**, 616-620.

Bregman, J. D., Hayward, T. L., & Sloan, G. C. (2000). Discovery of the 11.2 µm PAH band in absorption toward MonR2 IRS3. *Astrophys. J.* **544**, L75-L78.

Breneman, H. H., & Stone, E. C. (1985). Solar coronal and photospheric abundances from solar energetic particle measurements. *Astrophys. J.* **294**, L57-L62.

Brooke, T. Y., Sellgren, K., & Geballe, T. R. (1999). New 3 micron spectra of young stellar objects with H_2O ice bands. *Astrophys. J.* **517**, 883-900.

Brown, P. D., & Charnley, S. B. (1990). Chemical models of interstellar gas-grain processes - I. Modelling and the effect of accretion on gas abundances and mantle composition in dense clouds. *MNRAS* **244**, 432-443.

Brownlee, D.E. and Joswiak, D.J. (2004) The solar nebula's first accretionary particles (FAPs): Are they preserved in collected interplanetary dust samples? *Lunar Planet. Sci*. **35**, Abstract #1944

Burbidge, E. M., Burbidge, G. R., Fowler, W. A., & Hoyle, F. 1957. Synthesis of the elements in stars. *Rev. Mod. Phys*. **29**, 547-650.

Burnett, D. S., Woolum, D. S., Benjamin, T. M., Rogers, P. S. Z., Duffy, C. J., & Maggiore, C. (1989). A test of the smoothness of the elemental abundances of carbonaceous chondrites. *Geochim. Cosmochim. Acta* **53**, 471-481.

Busso M., Gallino R. and Wasserburg G. J. (2003). Short-lived nuclei in the early Solar System: A low mass stellar source? *PASA* **20**, 356-370.

Cameron, A. G. W. (1985). Formation and evolution of the primitive solar nebula. In *Protostars and Planets II*, (D. C. Black & M.S. Matthews, eds.), Univ. Ariz. Press: Tucson, pp. 1073-1099.

Campins, H., & Ryan, E.V. (1989). The identification of crystalline olivine in cometary silicates. *Astrophys. J.* **341**, 1059-1066.

Cassen, P., and Boss, A. P (1988). Protostellar collapse, dust grains, and Solar System Formation. In *Meteorites and the Early Solar System*, J. F. Derride and M. S. Matthews, eds., (Tucson, Univ. of Arizona Press), pp. 304-328.

Charnley, S. B., Tielens, A. G. G. M., & Millar, T. J. (1992). On the molecular complexity of the hot cores in Orion A: Grain surface chemistry as "the last refuge of a scoundrel". *Astrophys. J.* **399**, L71-L74.

Charnley, S. B., Kress, M. E., Tielens, A. G. G. M., & Millar, T. J. (1995). Interstellar alcohols. *Astrophys. J.* **448**, 232-239.

Charnley, S. B., & Rodgers, S. D. (2002). The end of interstellar chemistry as the origin of nitrogen in comets and meteorites. *Astrophys. J.* **569**, L133-L137.

Chiar, J. E., Tielens, A. G. G. M., Whittet, D. C. B., Schutte, W. A., Boogert, A. C. A., Lutz, D., van Dishoeck, E. F., & Bernstein, M. P. (2000). The Composition and distribution of dust along the line of sight towards the Galactic center. *Astrophys. J.* **537**, 749-762.

Choi B.-G., Wasserburg G. J. and Huss G. R. (1999) Circumstellar hibonite and corundum and nucleosynthesis in asymptotic giant branch stars. *Astrophys. J*. **522**, L133-L136.

Clemett S., Maechling C. R., Zare R. N., Swan P., and Walker R. M. (1993) Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* **262**, 721 – 725.

Clemett, S. J., Chillier, X. D. F., Gillette, S., Zare, R. N., Maurette, M., Engrand, C., & Kurat, G. (1998). Observation of indigenous polycyclic aromatic hydrocarbons in 'Giant' carbonaceous Antarctic micrometeorites. *Origins of Life and Evolution of the Biosphere* **28**, 425-448.

Cody G. D. and Alexander C. M. O'D. (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochim. Cosmochim. Acta* **69**, 1085 – 1097.

Cook, W. R., Stone, E. C.,& Vogt, R. E. (1984). Elemental composition of solar energetic particles. *Astrophys. J.* **279**, 827-838.

Cronin J. R. and Chang S. (1993) Organic matter in meteorites: Molecular and isotopic analysis of the Murchison meteorite. In Chemistry of Life's Origins. (eds. J. M. Greenberg and V. Pirronello), pp. 209 – 258. Kluwer, Dordrecht, The Netherlands.

Cronin J. R., Pizzarello S. and Cruikshank D. (1988) Organic matter in carbonaceous chondrites, planetary satellites, asteroids, and comets. In: Meteorites and the Early Solar System. J.F. Kerridge and M.S. Matthews Eds., pp. 819 – 857. Univ. Arizona Press

Crovisier J. *et al*. (2000)The thermal infrared spectra of comets Hale-Bopp and 103 P/Hartley 2 observed with the Infrared Space Observatory. In Thermal Emission Spectroscopy and Analysis of Dust, Disks, and Regoliths. ASP Conf. Ser. 196 (eds. M. L. Sitko, A. L. Sprague, and D. K. Lynch). Astronomical Society of the Pacific, San Francisco, pp. 109 – 117.

Cuzzi J. N., Davis S. S., and Doubrovolskis A. R. (2003) Blowing in the wind. II. Creation and redistribution of refractory inclusions in a turbulent protoplanetary nebula. *Icarus* **166**, 385-402.

de Graauw, Th. *et al*.,. (1996) SWS observations of solid CO_2 in molecular clouds. *Astron. Astrophys.* **315**, L345-L348.

Dones L., Weissmann P. R., Levison H. F., and Duncan M. J. (2004) Oort cloud formation and dynamics. In Comets II (M. C. Festou et al., eds.) Univ. Arizona Press.

Dorschner, J., & Henning, Th. (1995). Dust metamorphosis in the Galaxy. *Astron. Astrophys. Rev.* **6**, 271-333.

Duncan M., Quinn T., and Tremaine S. (1988). The origin of short-period comets. *Ap. J. Lett*. **328**, 69.

Duprat J., Engrand C., Maurette M., Gounelle M., Kurat G., Leroux H. (2005) Friable micrometeorites from central Antarctica snow. *Lunar Planet. Sci*. **36**, 1678.

Dworkin, J. P., Deamer, D. W., Sandford, S. A., & Allamandola, L. J. (2001). Self-assembling amphiphilic molecules: Synthesis in simulated interstellar/precometary ices. *Proc. Nat. Acad. Sci. USA* **98**, 815-819.

Eberhardt P., Reber M., Krankowsky D., and Hodges R. R. (1995) the D/H and 18O/16O ratios in water from comet P/Halley. *Astron. Astrophys*. **302**, 301 – 316.

Ehrenfreund, P., & Charnley, S. B. (2000). Organic molecules in the interstellar medium, comets, and meteorites: A voyage from dark clouds to the early Earth. *Ann. Rev. Astron. Astrophys.* **38**, 427-483.

Engel, M. H., Macko, S. A., & Silfer, J. A. (1990). Carbon isotope composition of the individual amino acids in the Murchison meteorite. *Nature* **348**, 47-49.

Epstein, S., Krishnamurthy, R. V., Cronin, J. R., Pizzarello, S. & Yuen, G. U. (1987). Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* **326**, 477-479.

Evans, N. 1999. Physical conditions in regions of star formation. *Ann. Rev. Astron. Astrophys.* **37**, 311-362.

Floss C. and Stadermann F. J. (2004). Isotopically primitive interplanetary dust particles of cometary origin: evidence from nitrogen isotopic compositions. *Lunar Planet. Sci*. **35**, Abstract #1281

Floss C., Stadermann F. J., Bradley J. P., Dai Z. R., Bajt S. and Graham G. (2004) Carbon and nitrogen isotopic anomalies in an anhydrous interplanetary dust particle. *Science* **303**, 1355 – 1358.

Flynn G. J. (1989) Atmospheric entry heating: A criterion to distinguish between asteroidal and cometary sources of interplanetary dust. *Icarus* **77**, 287-310.

Flynn G. J. (1993) The volatile content of anhydrous interplanetary dust. Meteoritics 28, 349–350.

Flynn, G.J., Bajt, S., Sutton, S.R., Zolensky, M.E., Thomas, K.L., Keller, L.P. (1996) The abundance pattern of elements having low nebular condensation temperatures in interplanetary dust particles: Evidence for a new chemical type of chondritic material, Astronomical Society of the Pacific Conference Series 104, 291.

Gattacceca J., Rochette P., Folco L., Perchiazzi N. (2005) A new micrometeorite collection from Antarctica and its preliminary characterization by microobservation, microanalysis and magnetic methods. *Lunar Planet. Sci*. 36, 1315.

Geiss, J., & Bochsler, P. (1985). Ion composition in the solar wind in relation to solar abundances. In *Rapports Isotopiques dans le Systeme Solaire*, (Cepadues-Editions: Toulouse), pp. 213-228.

Geiss J. and Reeves H. (1981). Deuterium in the Solar System. *astron. Astrophys.* **93**, 189-199.

Gerakines, P. A., Moore, M. H., & Hudson, R. L. (2000). Energetic processing of laboratory ice analogs: UV photolysis versus ion bombardment. *J. Geophys. Res.* **106**, 3338

Goldsmith, P. F., & Langer, W. D. (1978). Molecular cooling and thermal balance of dense interstellar clouds. *Astrophys. J.* **222**, 881-895.

Goldsmith, P. F. (1987). Molecular clouds - an overview. In *Interstellar Processes*, D. J. Hollenbach & H. A. Thronson, Jr., eds., (D. Reidel: Dordrecht), pp. 51-70.

Grevesse, N., Noels, A., & Sauval, A. J. (1992). Photospheric abundances. In Proc. *1st SOHO Workshop*. ESA SP-348.

Grim, R. J. A., & Greenberg, J. M. (1987). Ions in grain mantles: The 4.62 micron absorption by OCN- in W33A. *Astrophys. J.* **321**, L91-L96.

Guan Y., Messenger S., and Walker R. M. (1997) The spatial distribution of D-enrichments in Renazzo matrix. *Lunar Planet. Sci*. **28**, Abstract #1737.

Guan Y., Hofmeister A., Messenger S. and Walker R. M. (1998) Two types of deuterium-rich carriers in Renazzo matrix. *Lunar Planet. Sci*. **29**, Abstract #1760

Guillois, O., Ledoux, G., & Reynaud, C. (1999). Diamond infrared emission bands in circumstellar media. *Astrophys. J.* **521**, L133-L136.

Hanner M. S., Lynch D. K., and Russell R. W. (1994) The 8 – 13 μm spectra of comets and the composition of silicate grains. *Astrophys. J*. **425**, 274 - 285.

Harker, D.E. and Desch, S.J. (2002) Annealing of pre-cometary silicate grains in solar nebula shocks. *Lunar Planet. Sci*. **33**, Abstract #2002.

Hartmann L. and Kenyon S. J. (1996) The FU Orionis phenomenon. *Ann. Rev. Astron. Astrophys*. **34**, 207-240.

Herbst, E. (1987). Gas phase chemical processes in molecular clouds. In *Interstellar Processes* , eds. D. J. Hollenbach & H. A. Thronson, Jr., (D. Reidel, Dordrecht), p. 611-629.

Hollenbach, D. J., & Salpeter, E. E. (1971). Surface recombination of hydrogen molecules. *Astrophys. J.* **163**, 155-164.

Hollis, J. M., Snyder, L. E., Lovas, F. J., & Buhl, D. (1976). Radio detection of interstellar DCO^+. *Astrophys. J.* **209**, L83-L85.

Huss G. and Lewis R. S. (1995) Presolar diamond, SiC, and graphite in primitive chondrites: abundances as a function of meteorite class and petrologic type. *Geochim. Cosmochim. Acta* **59**, 115-160.

Huss G., Meshik A. P., Smith J. B. and Hohenberg C. M. (2003) Presolar diamond, silicon carbide, and graphite in carbonaceous chondrites: Implications for thermal processing in the nebula. *Geochim. Cosmochim. Act*a **24**, 4823-4848.

Irvine W. M., Schloerb F. P., Crovisier J., Fegley B. Jr. And Mumma M. J. (2000) Comets: A link between interstellar and nebular chemistry. In V. Mannings, A. P. Boss, S. S. Russell (Eds.), Protostars and Planets IV. Univ. Arizona Press, Tucson, pp. 1159 – 1200.

Jackson A. A. and Zook H. A. (1992) Orbital evolution of dust particles from comets and asteroids. *Icarus* **97**, 70 – 84.

Jacq, T., Walmsley, C.M., Henkel, C., Baudry, A., Mauersberger, R., Jewell, P.R. (1990). Deuterated water and ammonia in hot cores. *Astron. Astrophys.* **228**, 447-470.

Jäger, C., Mutschke, H., Begemann, B., Dorschner, J., & Henning, Th. (1994). Steps toward interstellar silicate mineralogy I. Laboratory results of a silicate glass of mean cosmic composition. *Astron. Astrophys.* **292**, 641-655.

Jehin, E., Manfroid, J., Cochran, A. L., Arpigny, C., Zucconi, J.-M., Hutsemékers, D., Cochran, W. D., Endl, M., & Schulz, R. (2004). The anomalous $^{14}N/^{15}N$ ratio in comets 122P/1995 S1 (De Vico) and 153P/2002 C1 (Ikeya-Zhang). *Astrophys. J.* **613**, L161-L164.

Joswiak, D.J., Brownlee, D.E., Pepin, R.O., Schlutter, D.J. (2000) Characteristics of asteroidal and cometary IDPs obtained from stratospheric collectors: Summary of measured He release temperatures, velocities and descriptive mineralogy. *Lunar Planet. Sci*. **31**, Abstract #1500

Keller L. P. *et al*. (2005) The nature of molecular cloud material in interplanetary dust. *Geochim. Cosmochim. Acta* **68**, 2577 – 2589.

Kemper, F., Vriend, W. J., & Tielens, A. G. G. M. (2004). The absence of crystalline silicates in the diffuse interstellar medium. *Astrophys. J.* **609**, 826-837.

Kerridge J. F., Chang S. and Shipp R. (1987). Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* **51**, 2527-2540.

Königl, A., and Pudritz, R. E. (2000). Disk winds and the accretion-outflow connection. In *Protostars and Planets IV*, V. Mannings, A. P. Boss, and S. S. Russell, eds., (Tucson, Univ. of Arizona Press), pp. 867-894.

Krishnamurthy, R., Epstein, S., Cronin, J., Pizzarello, S., & Yuen, G. (1992). Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochim. Cosmochim. Acta* **56**, 4045-4058.

Kuan, Y.-J., Charnley, S. B., Huang, H.-C., Tseng, W.-L., & Kisiel, Z. (2003). Interstellar glycine. *Astrophys. J.* **593**, 848-867

Kurat G., Koeberl C., Presper T., Brandstatter F., and Maurette M. (1994) Petrology and geochemistry of Antarctic micrometeorites. *Geochim. Cosmochim. Acta* **58**, 3879-3904.

Lacy, J. H., Baas, F., Allamandola, L. J., Persson, S. E., McGregor, P. J., Lonsdale, C. J., Geballe, T. R., & van der Bult, C. E. P. (1984). 4.6 micron absorption features due to solid phase CO and cyano group molecules toward compact infrared sources. *Astrophys. J.* **276**, 533-543.

Lacy, J., Carr, J., Evans, N., Baas, F., Achtermann, J., & Arens, J. (1991). Discovery of interstellar methane: observations of gaseous and solid CH_4 absorption toward young stars in molecular clouds. *Astrophys. J.* **376**, 556-560.

Lacy, J. H., Faraji, H., Sandford, S. A., & Allamandola, L. J. (1998). Unraveling the 10 µm 'silicate' feature of protostars: The detection of frozen interstellar ammonia. *Astrophys. J.* **501**, L105-L109.

Lada, C. J., & Lada, E. A. (2003). Embedded clusters in molecular clouds. *Ann. Rev. Astron. Astrophys*. **41**, 57-115.

Langer, W. D., Graedel, T. E., Frerking, M. A., & Armentrout, P. B. (1984). Carbon and oxygen isotope fractionation in dense interstellar clouds. *Astrophys. J.* **277**, 581-604.

Langer, W. D., & Graedel, T. E. (1989). Ion-molecule chemistry of dense interstellar clouds: Nitrogen-, oxygen-, and carbon-bearing molecule abundances and isotopic ratios. *Astrophys. J. Suppl. Ser.* **69**, 241-269.

Langer, W. D., van Dishoeck, E. F.,Bergin, E. A., Blake, G. A., Tielens, A. G. G. M., Velusamy, T., and Whittet, D. C. B. (2000). Chemical evolution of protostellar matter. In *Protostars and Planets IV*, V. Mannings, A. P. Boss, and S. S. Russell, eds., (Tucson, Univ. of Arizona Press), pp. 29-57.

Larimer, J. W., & Wasson, J. T. (1988). Refractory lithophile elements. Siderophile element fractionation. In *Meteorites and the Early Solar System*, J. F. Kerridge & M. S.Matthews, eds., (Univ. Arizona Press: Tucson), pp. 394-435.

Levison H. F., Dones L., and Duncan M. J. (2001) The origin of Halley-type comets: Probing the inner Oort cloud. *Astronom. J*. **121**, 2253-2267.

Lewis R. S., Tang, M., Wacker, J. F., Anders, E., and Steele E. (1987) Interstellar diamonds in meteorites. *Nature* **326**, 160–162.

Li A. and Greenberg J. M. (1997). A unified model of interstellar dust. *Astron. Astrophys*. **323**, 566-584.

Lodders K. (2003) Solar System abundances and condensation temperatures of the elements. *Astrophys. J*. **591**, 1220-1247.

Loinard, L., Castets, A., Ceccarelli, C., Tielens, A. G. G. M., Faure, A., Caux, E., & Duvert, G. (2000). The enormous abundance of D_2CO in IRAS 16293-2422. *Astron. Astrophys.* **359**, 1169-1174.

Love S. G. and Brownlee D. E. (1993) A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science* **262**, 1993.

Luu J. X. and Jewitt D. C. (2002). Kuiper Belt Objects: Relics from the accretion disk of the Sun. *Ann. Rev. Astron. Astrophys*. **40**, 63-101.

Mac Low, M.-M., and Klessen, R. S. (2004). Control of star formation by supersonic turbulence. *Rev. Mod. Phys.* **76**, 125-194.

Mannings, V., Boss, A. P., & Russell, S. S. (eds.) (2000). *Protostars and Planets IV*. (University of Arizona Press: Tucson).

Matrajt, G., Pizzarello, S., Taylor, S., & Brownlee, D. (2004). Concentration and variability of the AIB amino acid in polar micrometeorites: Implications for the exogenous delivery of amino acids to the primitive Earth. *Meteoritics & Planetary Science* **39**, 1849-1858.

Mauersberger, R., Henkel, C., Jacq, T., & Walmsley, C. M. (1988). Deuterated methanol in Orion. *Astron. Astrophys.* **194**, L1-L4.

Maurette, M., Immel, G., Engrand, C., Kurat, G., Pillinger, C.T. (1994) The 1994 EUROMET collection of micrometeorites at Cap-Prudhomme, Antarctica. *Meteoritics* **29**, 499.

Meier R. *et al*. (1998) Deuterium in comet C/1995 O1 (Hale-Bopp): Detection of DCN. *Science* **279**, 1707 – 1710.

Mennella, V., Brucato, J. R., Colangeli, L., & Palumbo, P. (2002). C-H bond formation in carbon grains by exposure to atomic hydrogen: The evolution of the carrier of the interstellar 3.4 micron band. *Astrophys. J.* **569**, 531-540.

Messenger S. (2000) Identification of molecular cloud material in interplanetary dust particles. *Nature* **404**, 968-971.

Messenger S., Keller L. P. and Lauretta, D. S. (2005) Supernova olivine from cometary dust. *Science* **309**, 737-741.

Messenger S. and Keller L. P. (2005) Association of presolar grains with molecular cloud material in IDPs. *Lunar Planet. Sci*. **36**, Abstract #1846.

Messenger S., Keller L. P., Stadermann F. J., Walker R. M. and Zinner E. (2003). Samples of stars beyond the Solar System: Silicate grains in interplanetary dust. *Science* **300**, 105-108.

Messenger S., Stadermann F. J., Floss C., Nittler L. R. and Mukhopadhyay S. (2002) Isotopic signatures of presolar materials in interplanetary dust. *Space Sci. Rev*. **95**, 1 – 10.

Messenger S. and Walker R. M. (1997) Evidence for molecular cloud material in meteorites and interplanetary dust. In *Astrophysical implications of the laboratory study of interstellar materials* (T. J. Bernatowicz and E. K. Zinner, eds.) 545 – 564.

Millar, T. J., Roberts, H., Markwick, A. J., & Charnley, S. B. (2000) The role of H_2D^+ in the deuteration of interstellar molecules. *Phil Trans. R. Soc. Lond. A* **358**, 2535-2547.

Moore, M. H., Ferrante, R. F., & Nuth, J. A. (1996). Infrared spectra of proton irradiated ices containing methanol. *Planet. Spa. Sci.* **44**, 927-935.

Mostefaoui S. and Hoppe P. (2004) Discovery of abundant in situ silicate and spinel grains from red giant stars in a primitive meteorite. *Astrophys. J.* **613**, L149 – L152.

Mostefaoui S., Lugmair G. W., and Hoppe P. (2005) ^{60}Fe: A heat source for planetary differentiation from a nearby supernova explosion. Astrophys. J. 625, 271-277.

Mumma M. J., Weissman P. R., and Stern A. S. (1993) “Comets and the origin of the Solar System: Reading the Rosetta stone.” In Protostars and Planets III, (E.H. Levy, J. I. Lunine eds.) Univ. Arizona Press, 1177 – 1252.

Mumma M. J. et al. (2003) Remote infrared observations of parent volatiles in comets: A window on the early solar system. *Adv. Space Res*. **31**, 2563 – 2575.

Nagashima K., Krot A. N. and Yurimoto H. (2004). Stardust silicates from primitive meteorites. *Nature* **428**, 921-924.)

Nakamura T., Noguchi T., Yada T., Nakamuta Y., and Takaoka N. (2001) Bulk mineralogy of individual micrometeorites determined by X-ray diffraction analysis and transmission electron microscopy. *Geochim. Cosmochim. Acta* **65**, 4385-4397.

Nguyen A. and Zinner E. (2004) Discovery of ancient silicate stardust in a meteorite. *Science* **303**, 1496

Nittler L. R. Hoppe, P., Alexander, C. M. O'D., Amari, S., Eberhardt, P., Gao, X., Lewis, R. S., Strebel, R.,; Walker, R. M., & Zinner, E. (1995). Silicon nitride from supernovae. *Astrophys. J.* **453**, L25-L28.

Noguchi T., Yano H., Terada K., Imae N., Yada T., Nakamura T., Kojima H. (2002) Antarctic micrometeorites collected by the Japanese Antarctic Research Expedition teams during 1996-1999. IAU Colloq. 181: Dust in the Solar System and Other Planetary Systems, 392.

Norman, C., & Silk, J. (1980). Clumpy molecular clouds: A dynamic model self-consistently regulated by T-Tauri star formation. *Astrophys. J.* **238**, 158-174.

Nuth, J. A. III, Charnley, S. B., and Johnson, N. M. (2005). Chemical processes in the interstellar medium: Source of gas and dust in the primitive nebula. THIS BOOK.

Oort J. H. (1950) "The structure of the cloud of comets surrounding the solar system and a hypothesis concerning its origin." *Bull. Astron. Inst. Netherlands* **12**, 91 – 110.

Parise, B., Ceccarelli, C., Tielens, A. G. G. M., Herbst, E., Lefloch, B., Caux, E., Castets, A., Mukhopadhyay, I., Pagani, L., & Loinard, L. (2002). Detection of doubly-deuterated methanol in the solar-type protostar IRAS 16293-2422. *Astron. Astrophys.* **393**, L49-L53.

Park, J.-Y., & Woon, D. E. (2004). Computational confirmation of the carrier for the "XCN" interstellar ice band: OCN^- charge transfer complexes. *Astrophys. J.* **601**, L63-L66.

Peeters, E. Allamandola, L. J., Bauschlicher, Jr., C. W., Hudgins, D. M., Sandford, S. A., & Tielens, A. G. G. M. (2004). Deuterated interstellar polycyclic aromatic hydrocarbons. *Astrophys. J.* **604**, 252-257.

Pendleton, Y., Tielens, A. G. G. M., & Werner, M. W. (1990). Studies of dust grain properties in infrared reflection nebulae *Astrophys. J.* **349**, 107-119.

Pendleton, Y. J., Tielens, A. G. G. M., Tokunaga, A. T., & Bernstein, M. P. (1999). The interstellar 4.62 micron band. *Astrophys. J.* **513**, 294-304.

Pendleton, Y. J., & Allamandola, L. J. (2002). The organic refractory material in the diffuse interstellar medium: Mid-infrared spectroscopic constraints. *Astrophys. J. Suppl. Ser.* **138**, 75-98.

Pizzarello S. and Huang Y. (2005) The deuterium enrichment of individual amino acids in carbonaceous meteorites: A case for the presolar distribution of biomolecule precursors. *Geochim. Cosmochim. Acta* **69**, 599 – 605.

Prasad, S. S., & Tarafdar, S. P. (1983). UV radiation field inside dense clouds: Its possible existence and chemical implications. *Astrophys. J.* **267**, 603-609.

Reames, D. V., Cane, H. V., & von Rosenvinge, T. T. (1990). Energetic particle abundances in solar electron events. *Astrophys. J.* **357**, 259-270.

Richer, J. S., Shepherd, D. S., Cabrit, S., Bachiller, R., and Churchwell, E. (2000). Molecular outflows from young stellar objects. In *Protostars and Planets IV*, V. Mannings, A. P. Boss, and S. S. Russell, eds., (Tucson, Univ. of Arizona Press), pp. 867-894.

Rietmeijer F. J. M. and McKinnon I. D. R. (1987) Cometary evolution: clues from chondritic interplanetary dust particles. In *Symposium on the similarity and diversity of comets*. pp. 363-367.

Rietmeijer, F.J.M. (2002) Collected extraterrestrial materials: Interplanetary dust particles, micrometeorites, meteorites, and meteoric dust. In Meteors in the Earth's Atmosphere. (E. Murad and I.P. Williams. Eds., Cambridge, UK: Cambridge University Press, Cambridge UK,), 215.

Robert F. (2003) The D/H ratio in Chondrites. *Space Sci. Rev*. **106**, 87-101.

Roberts, H., Fuller, G. A., Millar, T. J., Hatchell, J., & Buckle, J. V. (2002). A survey of [HDCO]/[H_2CO] and [DCN]/[HCN] ratios towards low-mass protostellar cores. *Astron. Astrophys.* **381**, 1026-1038.

Rochette P., Gattacceca J., Folco L., Perchiazzi N. (2004) A new micrometeorite collection from Antarctica and its preliminary characterization by magnetic methods. *Met. Planet. Sci*. **39**, Abstract # 5206.

Rodgers, S. D., & Charnley, S. B. (2003). Chemical evolution in protostellar envelopes: Cocoon chemistry. *Astrophys. J.* **585**, 355-371.

Rodgers, S. D., & Charnley, S. B. (2004). Interstellar diazenylium recombination and nitrogen isotopic fractionation. *Mon. Not. Roy. Astron. Soc.* **352**, 600-604.

Roueff, E., Tiné, S., Coudert, L.H., Pineau des Forêts, G., Falgarone, E., & Gerin, M. (2000). Detection of doubly deuterated ammonia in L134N. *Astron. Astrophys.* **354**, L63-L66.

Russell S. S., Pillinger C. T., Arden J. W., Lee M. R., and Ott U. (1992) A new type of meteoritic diamond in the enstatite chondrite Abee, Science 256, 206 – 209.

Sandford, S. A. (1986). Solar flare track densities in interplanetary dust particles: The determination of an asteroidal versus cometary source of the zodiacal dust cloud. *Icarus* **68**, 377-394.

Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., & Valero, G. J. (1988). Laboratory studies of the infrared spectral properties of CO in astrophysical ices. *Astrophys. J.* **329**, 498-510.

Sandford, S. A., & Bradley, J. P. (1989). Interplanetary dust particles collected in the stratosphere: Observations of atmospheric heating and constraints on their interrelationships and sources. *Icarus* **82**, 146-166.

Sandford, S. A., & Allamandola, L. J. (1993). Condensation and vaporization studies of CH_3OH and NH_3 ices: Major implications for astrochemistry. *Astrophys. J.* **417**, 815-825.

Sandford, S. A. (1996). The inventory of interstellar materials available for the formation of the Solar System. *Meteoritics and Planetary Science* **31**, 449-476.

Sandford, S. A., Bernstein, M. P., Allamandola, L. J., Gillette, J. S., & Zare, R. N. (2000). Deuterium enrichment of PAHs by photochemically induced exchange with deuterium-rich cosmic ices. *Astrophys. J.* **538**, 691-697.

Sandford, S. A., Bernstein, M. P., & Dworkin, J. P. (2001). Assessment of the interstellar processes leading to deuterium enrichment in meteoritic organics. *Meteoritics and Planetary Science* **36**, 1117-1133.

Sandford, S. A., Bernstein, M. P., & Allamandola, L. J. (2004). The mid-infrared laboratory spectra of naphthalene ($C_{10}H_8$) in solid H_2O. *Astrophys. J.* **607**, 346-360.

Shu F. H., Shang H., Gounelle M., Glassgold A. E., and Lee T. (2001) The origin of chondrules and refractory inclusions in chondritic meteorites. Astrophys. J. 548, 1029 – 1050.

Smith, N., Bally, J., & Morse, J. A. (2003). Numerous proplyd candidates in the harsh environment of the Carina nebula. *Astrophys.* J. **587**, L105-L108.

Suess, H. (1947). Über kosmische Kernhäufigkeiten I. Mitteilung: Einige Häufigkeitsregeln und ihre Anwendung bei der Abschätzung der Häufigskeitwerte für die mittelsschweren und schweren Elemente. II. Mitteilung: Einzelheiten in der Häufigskeitverteilung der mittelschweren und schweren Kerne. *Z. Naturforsch.* **2a**, 311-321, 604-608.

Sykes, M. V., & Greenberg, R. (1986). The formation and origin of the IRAS zodiacal dust bands as a consequence of single collisions between asteroids. *Icarus* **65**, 51-69.

Sykes, M. V., Lebofsky, L. A., Hunten, D. M., & Low, F. (1986). The discovery of dust trails in the orbits of periodic comets. *Science* **232**, 1115-1117.

Tachibana S. and Huss G. R. (2003) The initial abundance of ^{60}Fe in the Solar System. *Astrophys. J*. **588**, L41

Taylor S., Lever J. H., Govoni J. (2001) A second collection of micrometeorites from the South Pole water well. *Lunar Planet. Sci*. **32**, 1914.

Tegler, S. C., Weintraub, D. A., Allamandola, L. J., Sandford, S. A., Rettig, T. W., & Campins, H. (1993). Detection of the 2165 cm^{-1} (4.619 µm) XCN Band in the Spectrum of L1551 IRS 5. *Astrophys. J.* **411**, 260-265.

Tegler, S. C., Weintraub, D. A., Rettig, T. W., Pendleton, Y. J., Whittet, D. C. B., & Kulesa, C. A. (1995). Evidence for chemical processing of precometary icy grains in circumstellar environments of pre-main-sequence stars. *Astrophys. J.* **439**, 279-287.

Teixeira, T. C., Devlin, J. P., Buch, V., & Emerson, J. P. (1999). Discovery of solid HDO in grain mantles. *Astron. Astrophys.* **347**, L19-L22.

Terzieva, R., & Herbst, E. (2000). The possibility of nitrogen isotopic fractionation in interstellar clouds. *Mon. Not. Roy. Astron. Soc.* **317**, 563-568.

Thomas K. L., Klöck W., Keller L. P., Blanford G. E. and McKay D. S. (1993) Analysis of fragments from cluster particles: carbon abundance, bulk chemistry, and mineralogy. *Meteoritics* **28**, 448-449

Tielens, A. G. G. M. and Hagen, W. (1982). Model calculations of the molecular composition of interstellar grain mantles. *Astron. Astrophys.* **114**, 245-260.

Tielens, A. G. G. M. (1983). Surface chemistry of deuterated molecules. *Astron. Astrophys.* **119**, 177-184.

Tielens, A. G. G. M., & Allamandola, L. J. (1987). Evolution of interstellar dust. In *Physical Processes in Interstellar Clouds*, G. E. Morfill & M. Scholer, eds., (D. Reidel: Dordrecht), pp. 333-376.

Tielens, A. G. G. M. (1990). Towards a circumstellar silicate mineralogy. In *From Miras to PN: Which path for stellar evolution?*, eds., M. O. Mennessier & A. Omont, (Editions Frontiere: Gif-sur-Yvette), pp. 186-200.

Tielens, A. G. G. M., Tokunaga, A. T., Geballe, T. R., & Baas, F. (1991). Interstellar solid CO: Polar and nonpolar interstellar ices. *Astrophys. J.* **381**, 181-199.

Tielens, A. G. G. M. (1995). The interstellar medium. In *Airborne Astronomy Symposium on the Galactic Ecosystem: From Gas to Stars to Dust*, ASP Conf. Series, Vol. 73, M. R. Haas, J. A. Davidson, & E. F. Erickson, eds., (ASP; San Francisco), pp. 3-22.

Tielens, A. G. G. M. (1997). Deuterium and interstellar chemical processes. In *Astrophysical Implications of the Laboratory Study of Presolar Materials*, T. J. Bernatowicz & E. K. Zinner, eds., (Amer. Inst. of Physics: Woodbury, NY), pp. 523-544.

Turner, B. E. (2001). Deuterated molecules in translucent and dark clouds. *Astrophys. J. Supplement Series* **136**, 579-629.

van Dishoeck, E. F., & Blake, G. A. (1998). Chemical evolution of star-forming regions. *Annu. Rev. Astron. Astrophys.* **36**, 317-368.

Vastel, C., Phillips, T. G., Ceccarelli, C., & Pearson, J. (2003). First detection of doubly deuterated hydrogen sulfide. *Astrophys. J.* **593**, L97-L100.

Veck, N. J., & Parkinson, J. H. (1981). Solar abundances from X-ray flare observations. *Mon. Not. Roy. Astron. Soc.* **197**, 41-55.

Walmsley, C. M., Hermsen, W., Henkel, C., Mauersberger, R., & Wilson, T. L. (1987). Deuterated ammonia in the Orion hot core. *Astron. Astrophys.* **172**, 311-315.

Walmsley, C. M., Flower, D. R., & Pineau des Forêts, G. (2004). Complete depletion in prestellar cores. *Astron. Astrophys.* **418**, 1035-1043.

Whipple, F.L. (2000) Oort-cloud and Kuiper-Belt comets. *Planet. Space Sci*. **48**, 1011.

Whittet, D. C. B., Schutte, W. A., Tielens, A. G. G. M., Boogert, A. C. A., de Graauw, Th., Ehrenfreund, P., Gerakines, P. A., Helmich, F. P., Prusti, T., & van Dishoeck, E. F. (1996). An ISO SWS view of interstellar ices - First results. *Astron. Astrophys.* **315**, L357-L360.

Yada T. et al. (2005) Discovery of abundant presolar silicates in subgroups of Antarctic micrometeorites. *Lunar Planet. Sci*. **36**, Abstract #1227.

Young A. F., Nittler L. R. and Alexander C. M. O'D. (2004) Microscale distribution of hydrogen isotopes in two carbonaceous chondrites. *Lunar Planet. Sci*. **35**, Abstract #2097.

Zinner E. (1988) Interstellar cloud material in meteorites. In Meteorites and the early solar system (ed. J. F. Kerridge and M. S. Matthews), pp. 956- 983. Univ. Arizona Press.

Zinner E. (1998) Stellar nucleosynthesis and the isotopic composition of presolar grains from primitive meteorites. *Ann. Rev. Earth Planet. Sci*. **26**, 147-188.

Zinner E. *et al*. (2003) Presolar spinel grains from the Murray and Murchison carbonaceous chondrites. *Geochim. Cosmochim. Acta* **24**, 5083-5095.

Grain type	Size	abundance
Nanodiamonds	2 nm	1,000 – 1,400 ppm
amorphous silicates[a-d]	0.2 – 0.5 μm	<20 – 3,600 ppm
Forsterite and enstatite[d]	0.2 – 0.5 μm	<10 – 1,800 ppm
SiC	0.1 – 0.5 μm	14 – 30 ppm
Graphite	1 – 20 μm	7 – 13 ppm
Spinel[e] ($MgAl_2O_4$)	0.1 – 20 μm	1.2 ppm
Corundum (Al_2O_3)[f]	0.2 – 3 μm	100 ppb
Si_3N_4	1 – 5 μm	1 – 20 ppb
TiO_2[g]	n.d.	< 10 ppb
Hibonite[h] ($CaAl_{12}O_{19}$)	1 - 5 μm	20 ppb

Table 1: Identified presolar grain types, their observed size range and abundance in primitive meteorites and IDPs. The meteorite abundances for SiC, graphite and nanodiamond are the observed ranges among CI and CM meteorites according to Huss et al. (2003), matrix normalized and the IDP abundances are bulk values. (a) Total presolar silicate abundances derived for IDPs vary from 450 to 5,500 ppm and for meteorites range from 170 ppm (matrix normalized) to less than 35 ppm. Isotopically anomalous amorphous silicates appear to be twice as abundant as crystalline silicates so far. Further refinements to these numbers are expected. Messenger *et al*. (2003), (b) Floss and Stadermann (2004), (c) Nguyen and Zinner (2004), (d) Mostefaoui and Hoppe (2004), Nagashima, Krot, and Yurimoto (2004) (e) Zinner *et al*. (2003) (f) Nittler *et al*. (1995) (g) rough estimate from Nittler *et al*. (2005) (h) Choi, Wasserburg, and Huss (1999)

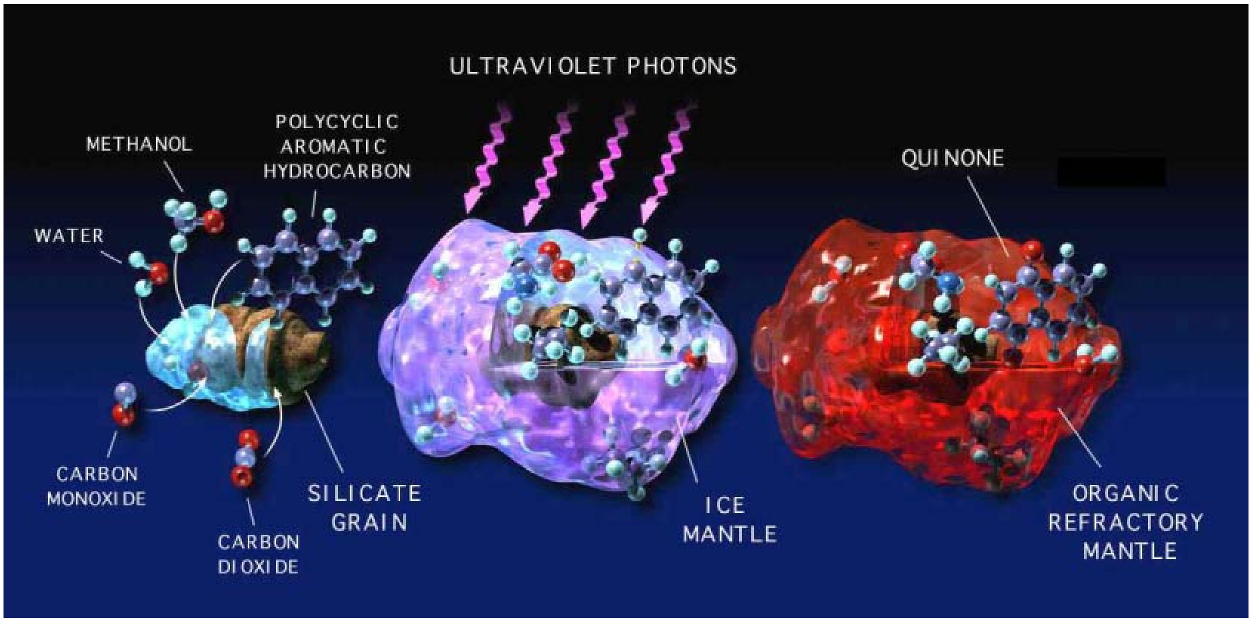

Figure 1 - Dust grains in cold dense clouds will accrete molecules and atoms from the gas phase. Catalytic atom addition reactions can occur on these surfaces and additional chemical reactions may be driven by ionizing radiation in the form of UV photons and cosmic rays. Warming of these grains can drive volatiles from the mantle, resulting in local enrichments of gas phase molecular material and the production of complex refractory organic layers on the grains. (Figure adapted from Bernstein et al. 1999a).

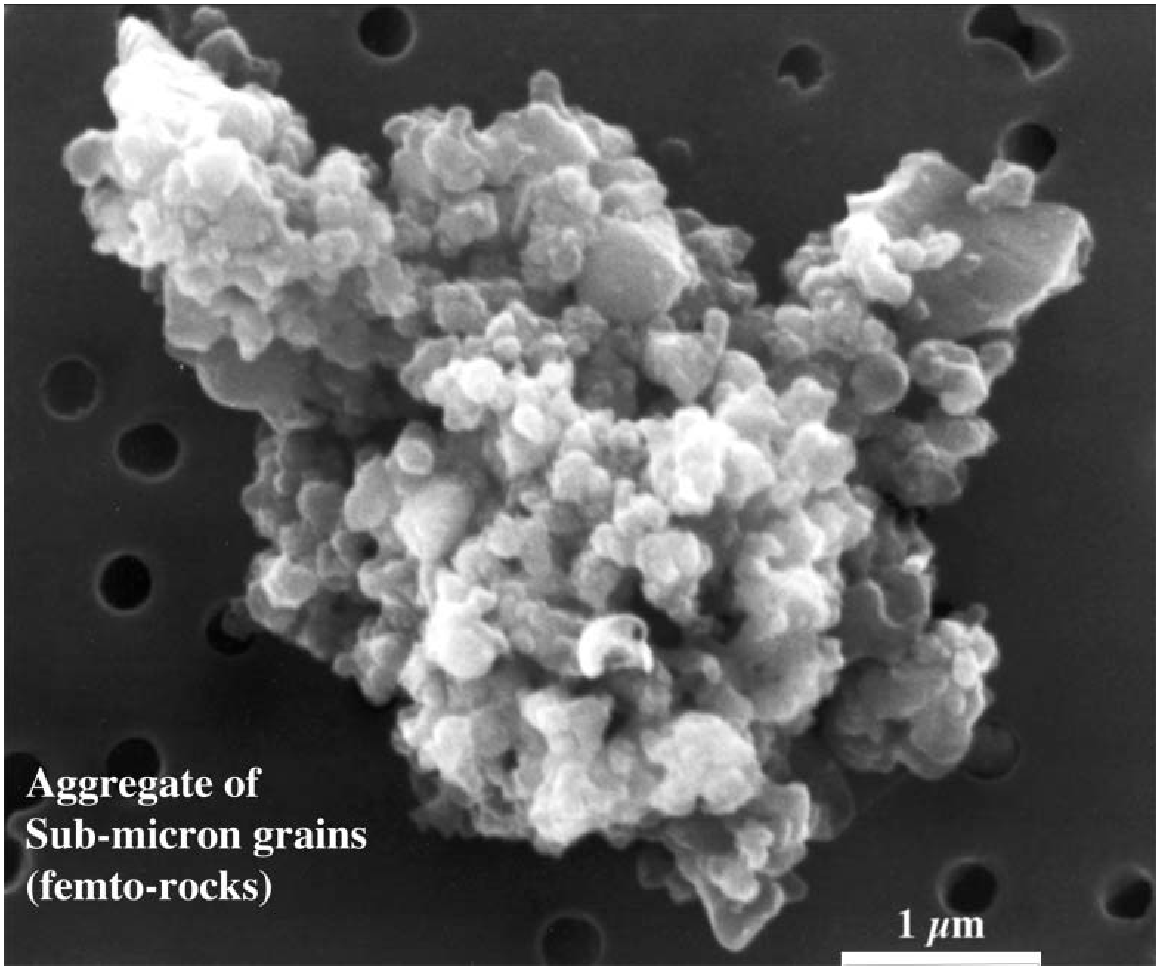

Figure 2: A CP interplanetary dust particle. The nanogram particle is a porous aggregate of large numbers of submicron grains, which individually contain GEMS, glass, crystalline materials and organic components. The fragile particle has not been subject to compaction since its formation in the solar nebula. The individual components in the particle are likely to be the accretionary units that are representative of the time and location in the solar nebula disk where the particle accreted.

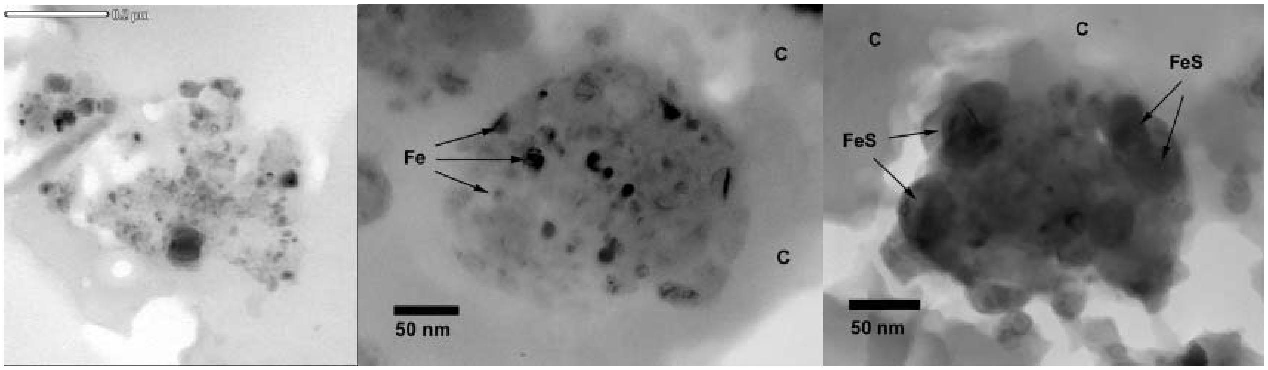

Figure 3: GEMS exhibit a diversity of compositions and morphologies, ranging from A: irregular grains, that may be a composite object (clump) (B): glass-rich GEMS grain (C): sulfide-rich GEMS grain.

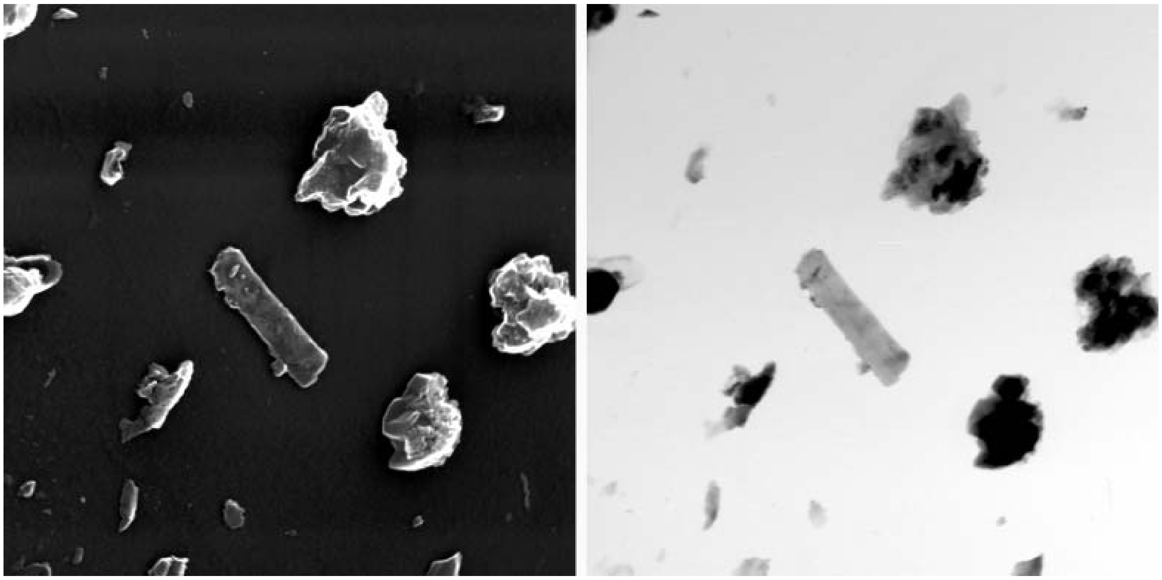

Figure 4: Individual submicron components mechanically separated from a CP interplanetary dust particle. On the left is a SEM image and a transmission image is on the right.

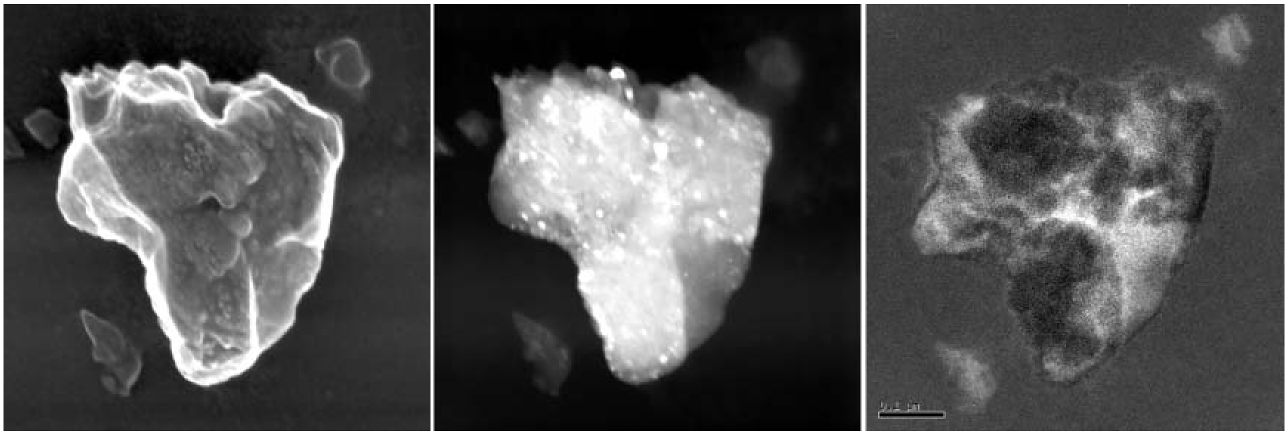

Figure 5: Images of a single submicron grain, a possible First Accretionary Particle or FAPs, shown with an SEM image on the left, a dark field transmission electron microscopy image in the center and a electron energy loss carbon map on the right. The femtogram rock is a solid mix of GEMS, glass, mineral grains and amorphous organic material. Scale bar is 0.1 micrometers.

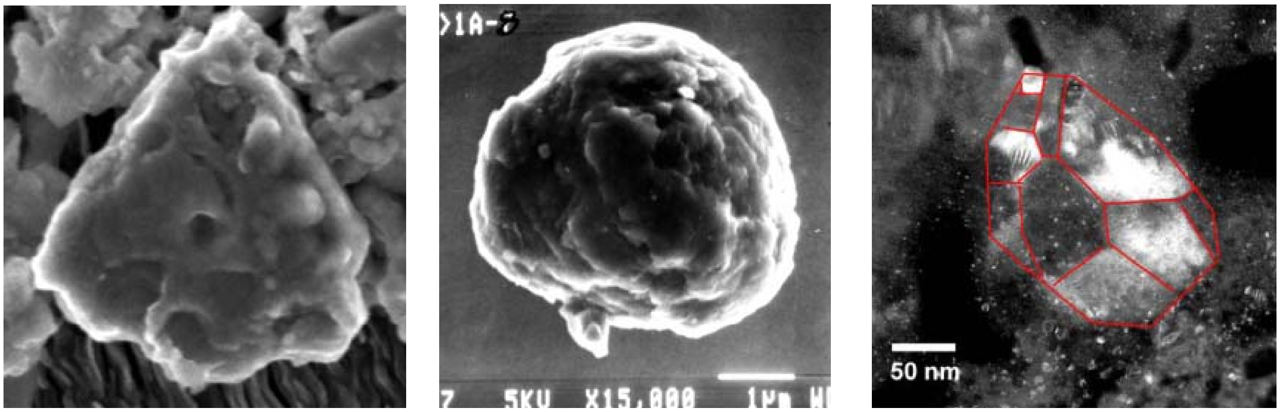

Figure 6: (A) presolar silicon carbide (Bernatowicz et al. 2004) (B) graphite and (C) forsterite grains (Messenger, Keller and Lauretta 2005). The red lines indicate equilibrium grain boundaries between 50-100 nm forsterites that may have experienced moderate thermal annealing.

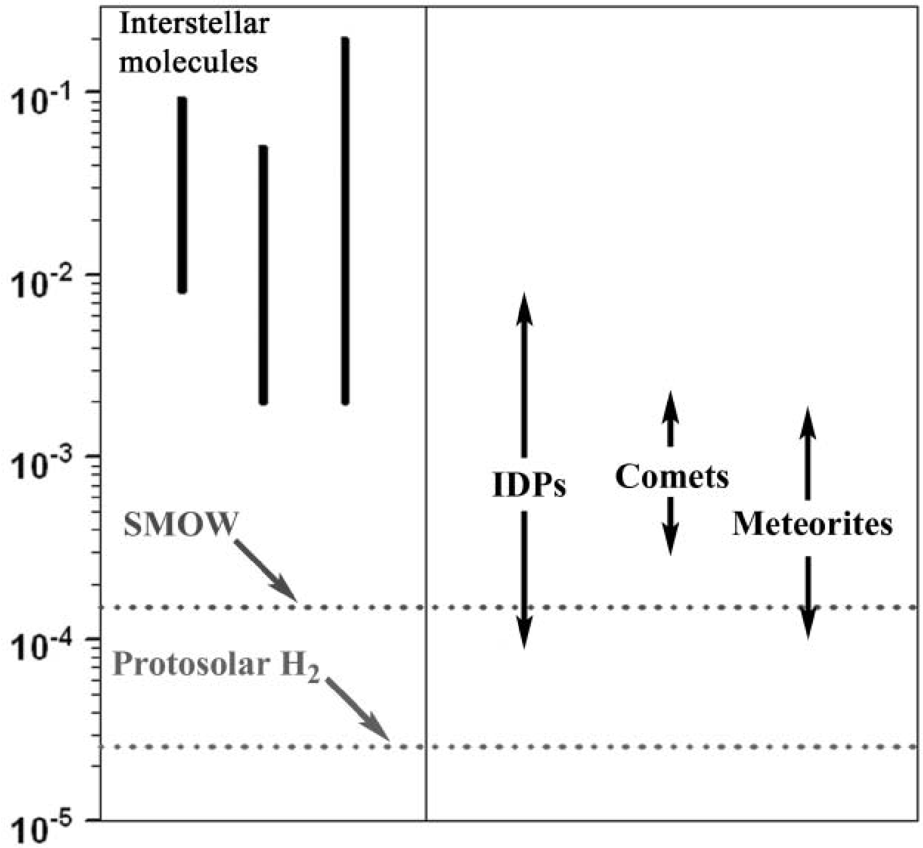

Figure 7: Comparison of the typical range of D/H ratios observed in gas phase molecules in cold interstellar molecular clouds with those of IDPs, comets (H_2O and HCN) and meteorites. D/H ratios of terrestrial standard mean ocean water (SMOW) and protosolar H_2 are shown for reference. Figure adapted from Messenger 2000.

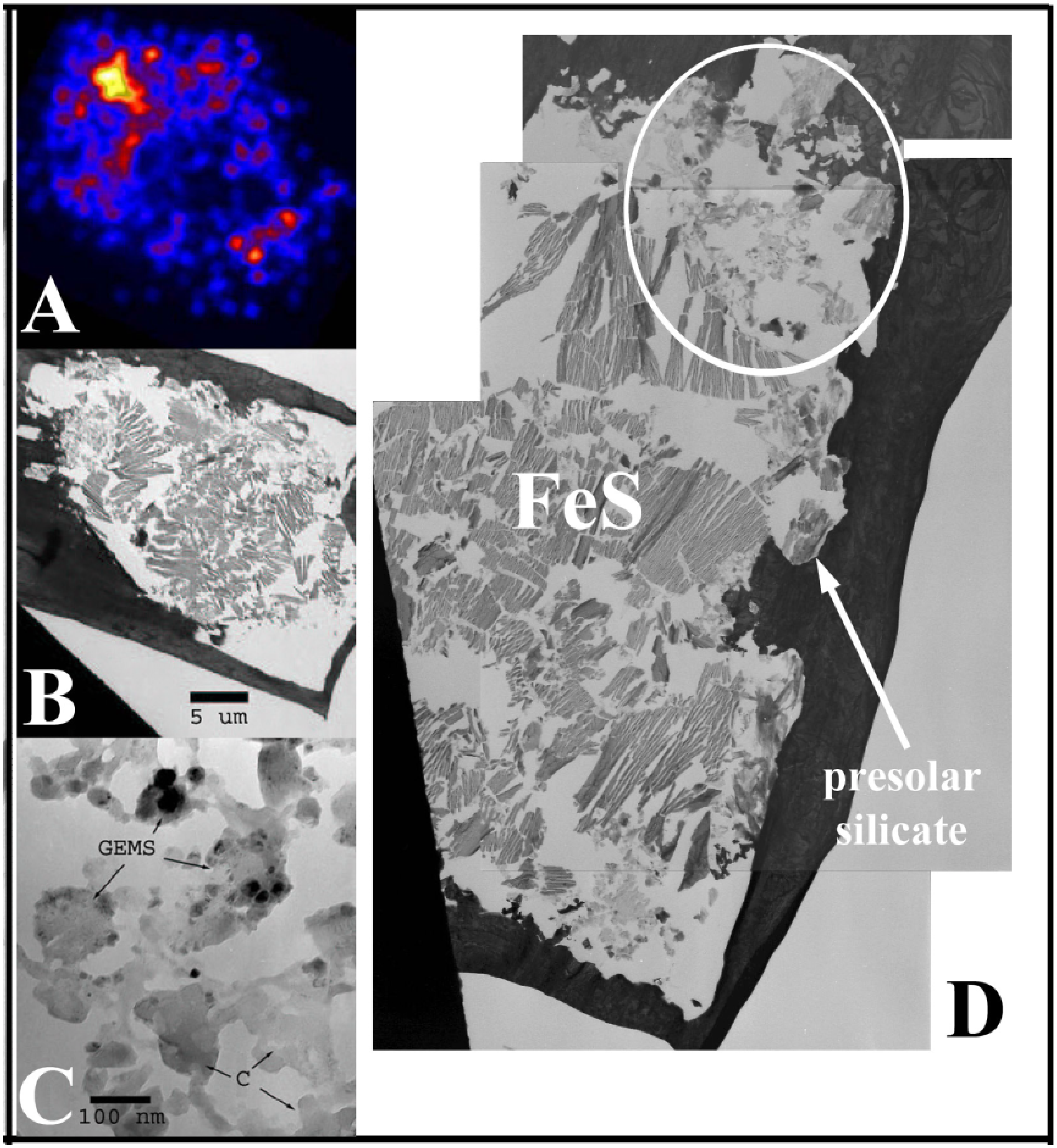

Figure 8: (A) D/H ratio image of IDP L2011 D11. D/H ratios in the image range from 2 to 10 x terrestrial. (B) TEM brightfield image of the IDP after being extracted from the gold substrate, embedded in elemental S and sliced by diamond ultramicrotomy (C) representative TEM view of materials found within the D hotspot, including GEMS grains, forsterite, enstatite, FeS, and carbonaceous matter (D) location of Group 1 presolar silicate grain found by NanoSIMS with location of D hotspot indicated by the ellipse. Messenger & Keller 2005

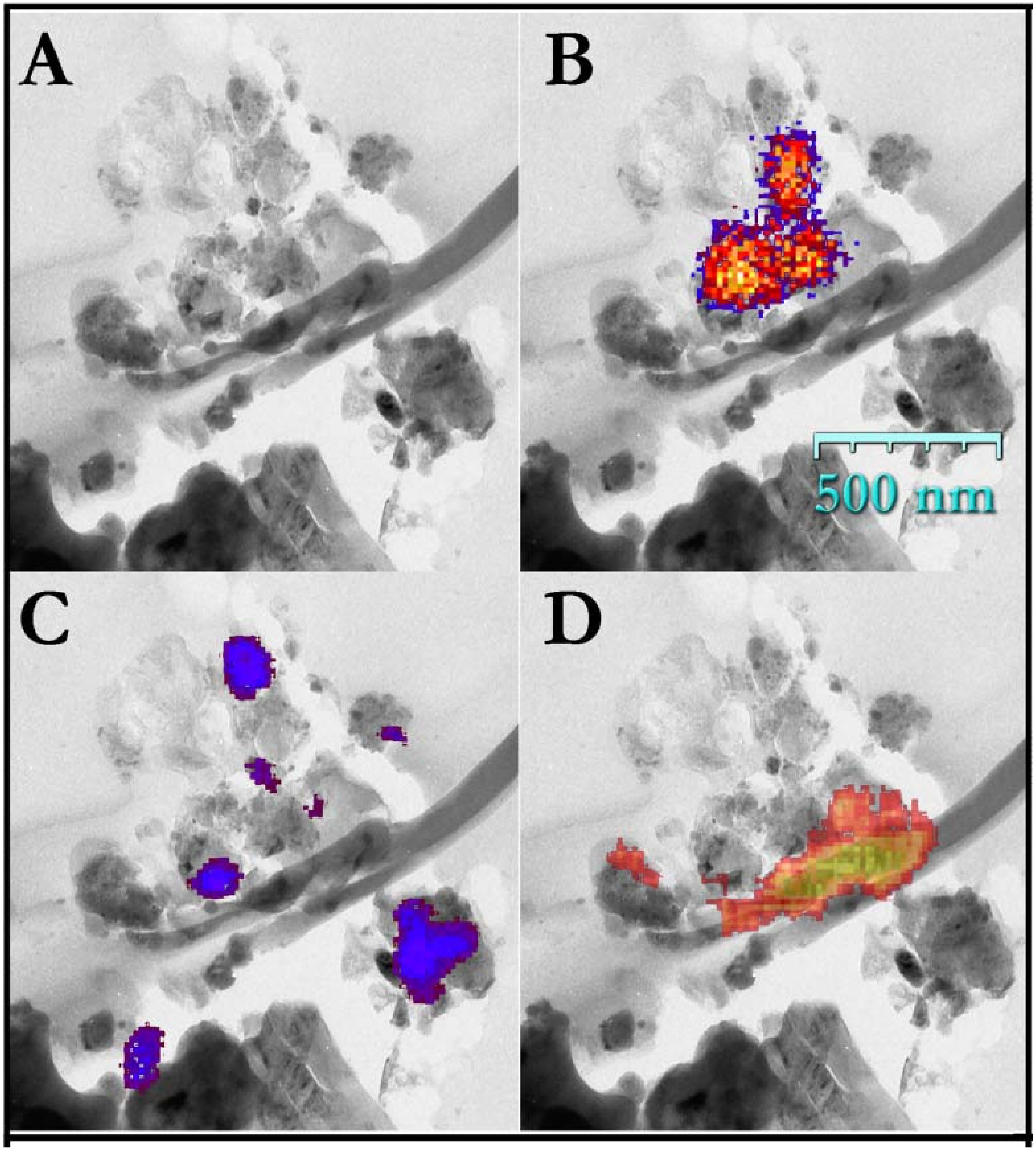

Figure 9: (A) TEM brightfield image of IDP L2011 B10A containing forsterite, enstatite, GEMS grains and carbonaceous matter. (B) Overlay of ^{18}O-rich region identifying a supernova olivine grain. (C) ^{32}S hotspots show the locations of FeS and GEMS grains (D) 15N-rich carbonaceous matter associated with presolar olivine grain. Messenger, Keller and Lauretta, 2005.