

# The Physics and Chemistry of Nebular Evolution

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Primitive materials in the solar system, found in both chondritic meteorites and comets, record distinct chemical environments that existed within the solar nebula. These environments would have been shaped by the dynamic evolution of the solar nebula, which would have affected the local pressure, temperature, radiation flux, and available abundances of chemical reactants. In this chapter we summarize the major physical processes that would have affected the chemistry of the solar nebula and how the effects of these processes are observed in the meteoritic record. We also discuss nebular chemistry in the broader context of recent observations and chemical models of astronomical disks. We review recent disk chemistry models and discuss their applicability to the solar nebula, as well as their direct and potential relevance to meteoritic studies.

## 1. INTRODUCTION

Condensation calculations have been used as the basic guides for understanding solar nebula chemistry over the last few decades. As reviewed by *Ebel (2006)*, condensation calculations provide information about the direction of chemical evolution, telling us what the end products would be in a system given a constant chemical inventory, infinite time, and ready access of all chemical species to one another. These studies have been applied to infer the conditions present at the location in the solar nebula where and when a given meteorite, or its components, formed.

While condensation calculations act as a guide for the chemical evolution of the solar nebula, laboratory studies of meteorites and astronomical observations of comets demonstrate that the actual evolution was much more complicated. Protoplanetary disks are known to evolve by transferring mass inward where it is accreted by the central stars, resulting in the disks cooling and becoming less dense over time. Superimposed on this evolution is the transport of chemical species, which will lead to time-varying concentrations of those species at different locations in the disk. In addition, dynamic, transient heating events are known to have occurred within the solar nebula, altering the physical environment over a period of hours to days. All these processes will disrupt or alter the path toward chemical equilibrium. Thus, solar nebula chemistry cannot be studied independently of the physical evolution of the protoplanetary disk.

In this chapter we demonstrate the ways in which the physical processes in the solar nebula affected the chemical reactions that took place within it. This is not a straightforward task, as there is still much uncertainty about what specific processes did occur within the disk as well as the nature of these processes. Despite these uncertainties, we can provide overviews as to what the end result of differ-

ent facets of disk evolution may have been and discuss what effects this evolution may have had on nebular chemistry. (For example, we will discuss the effect of mass transport through the solar nebula even though the driving mechanism for this transport remains an area of ongoing research.) It should be the goal of future studies and future generations of meteoriticists, astronomers, and astrophysicists to improve upon the overviews provided here and make greater strides toward developing a coherent, unified model for the evolution of protoplanetary disks. In the remainder of this introduction, we describe the record of chemical evolution provided by meteorite studies and astronomical observations. We then describe the processes that would shape the different chemical environments in a protoplanetary disk in section 2. In doing so, we deal mainly with physical and chemical processes intrinsic to the solar nebula and astronomical disks — we do not explicitly consider the chemical effects of the external environment on nebular evolution through, for example, the influence of nearby massive stars (e.g., *Hester et al., 2004*). In section 3, we discuss how these different processes would play a role in determining the chemical evolution of primitive materials in the nebula, and focus on explaining the meteoritic and astronomical records identified below. In the last section, we summarize the important points from the chapter and discuss future developments that may help us to further our understanding of chemistry in protoplanetary disks.

### 1.1. The Meteoritic Record

The surviving products of chemical reactions in our solar nebula were eventually incorporated into the asteroids, comets, and planets currently in orbit around our Sun. Once accreted, much of this material was further processed due to heating and differentiation in the bodies they resided in. The unequilibrated chondritic meteorites are the only samples

that we have of materials that escaped significant processing. Many of these objects experienced some thermal and aqueous alteration on their parent bodies, although many still preserve the signatures of their formation and processing within the solar nebula. We focus on these primitive meteorites in discussing the chemical evolution of the solar nebula.

Chondritic meteorites have relative elemental abundances that closely mirror those observed in the Sun. The exceptions to this are the most volatile elements (C, N, and the noble gases), which would not be incorporated into solids until very low temperatures were reached. The bulk elemental compositions of these bodies are taken as evidence that they formed directly in the solar nebula. While their bulk compositions reflect this, there are mineralogical and chemical differences that allow these meteorites to be separated into 3 distinct classes (the enstatite, ordinary, and carbonaceous chondrites), and these classes are further divided into 13 chondritic types. The reasons for these differences are unknown.

While differences exist between the chondrite types, the general makeup of the meteorites are fairly similar. A major component of chondritic meteorites are chondrules, which can make up as much as 80% of the volume of a given meteorite. Chondrules are roughly millimeter-sized, igneous, ferromagnesian silicates that are considered to be evidence for transient heating events in the early solar system (Connolly *et al.*, 2006). In addition to chondrules, refractory objects called calcium-aluminum-rich inclusions (CAIs) are found in various (small, <10%) proportions in the chondritic meteorites. Calcium-aluminum-rich inclusions are the oldest objects in the solar system, consisting of the elements that would be the first to condense from a solar composition gas. Interstitial to these different components is matrix material, consisting of chondrule fragments, metal and troilite grains, and fine-grained silicates. It is the sum of all these objects that determine the chemical compositions of the meteorites. While the different components of the meteorites may have unique compositions, the fact that the whole meteorite has a near-solar composition lends support to the idea of chondrule-matrix complementarity, meaning that what is depleted in one meteoritic component is often equally enhanced in another (Wood, 1996).

In looking at the bulk properties of chondritic meteorites, they can be divided into groups based on a number of properties. The oxidation history of these meteorites is one example, as the chondritic meteorites record a wide range of nebular oxygen fugacities. This is often looked at in terms of how Fe is distributed in the meteorites, as carbonaceous meteorites often contain Fe in the form of oxides with metal nearly absent, whereas most of the Fe (>75%) in enstatite chondrites is in the form of metal grains. In addition to the oxygen fugacity, each type of chondritic meteorite falls in a diagnostic region on the oxygen three-isotope plot (Clayton, 2003). These differences imply that the chondritic meteorites formed in distinct environments. In addition to their chemical makeup, chondritic meteorites also

differ in their physical properties: Each group has different mean chondrule sizes and different volume fractions of chondrules. No clear link has been made to explain these physical properties in chemical models, proving that chondritic meteorite study is as much an astrophysical endeavor as it is a cosmochemical one.

Other properties of chondritic meteorites are likely the results of both physical and chemical processes. For example, water was incorporated into some chondrites, but not all, suggesting some chondrites formed in environments where water ice was present while others did not. Also, while chondritic meteorites are dominated by materials that were isotopically homogenized (except for O) in the solar nebula, unaltered presolar grains are found mixed into these same objects. These grains were formed prior to the formation of the solar nebula, and understanding how they avoided being processed will constrain the extent of various physical events within the solar nebula. Finally, while chondritic meteorites generally have elemental abundances that closely mirror that of the Sun, the relative abundances of elements that condense in the range ~500–1300 K decrease with condensation temperatures in many carbonaceous and ordinary chondrites. This moderately volatile-element depletion provides clues as to how chemical environments evolved in the solar nebula. It is issues such as these that require investigations of how the physical evolution of the solar nebula affected the chemistry that would take place within it.

## 1.2. The Astronomical Record

While the main focus of this chapter is on the processes that affected the chemistry of meteorites, astronomical observations help to constrain the chemical and physical natures of the outer solar nebula as well as disks around other stars. Comets are believed to contain the least-altered primitive materials in the solar system. In principle, they can provide us with information about the chemical and physical processes that operated at large heliocentric distances, as well as the relative contribution of pristine interstellar material to their composition. The molecular ice inventory is very similar to that identified in interstellar ices, with an admixture of trace species known to be present in molecular cloud gas (Ehrenfreund *et al.*, 2004). Cometary molecules, as well as some interplanetary dust particles, exhibit enhanced D/H and  $^{15}\text{N}/^{14}\text{N}$  isotopic ratios, indicative of chemistry at low temperatures (Arpigny *et al.*, 2003; Aléon *et al.*, 2003). However, relative to water, the abundances of some molecules (e.g., methanol) is generally much lower than found in interstellar ices. A more striking difference lies in the presence of crystalline silicate dust in comets (e.g., Wooden *et al.*, 2004). This is in marked contrast to interstellar silicates, which are almost entirely amorphous in nature, but similar to the silicates found in circumstellar debris disks (Wooden, 2002). This suggests that, for the refractory dust component at least, some cometary material experienced high-temperature conditions, similar to those found in the inner nebula, and hence that outward mixing from this region was impor-

tant. Thus, a major aim of nebular models is to understand the spatiotemporal chemical evolution in the comet-forming region of the nebula (5–40 AU).

Protoplanetary disks around young stars serve as analogs for our own solar nebula. Understanding their chemical structure will help us to unravel the chemical structure and evolution of the solar nebula. While huge strides are expected in the coming years with the launch of advanced telescopic facilities, we are already making observations that demonstrate that the chemistry in protoplanetary disks deviates from what is predicted under chemical equilibrium. Observations of SVS 13, a young stellar object, show that H<sub>2</sub>O is depleted by a factor of 10 relative to CO compared to what chemical equilibrium models predict in the inner disk (Carr *et al.*, 2004). Identifying where other deviations from equilibrium occur in other protoplanetary disks will help us understand how our own solar nebula evolved over time.

## 2. PHYSICAL EVOLUTION OF THE NEBULA

### 2.1. Epochs and Timescales

The formation and evolution of the solar nebula can be described as a progression through different stages. While such a description is used by most who study the formation of the solar system, it should be remembered that the boundaries of these stages are not crisp, but instead overlap such that the different stages blur into one another — some of the processes described may have operated during more than just the stages that they are ascribed to below. Here we follow Cameron (1995) in defining four main stages of evolution:

*Stage 1: Formation of the nebula.* This is the period of large-mass infall from the parent molecular cloud from which the solar nebula formed. Due to the angular momentum of the original cloud, most of the material collapses into a disk that orbits the center of mass, with much of it subsequently migrating inward to form the protostar. This phase lasts on the order of 10<sup>5</sup> yr.

*Stage 2: High-mass accretion rate through the nebula.* During this stage, mass from the molecular cloud continues to rain down onto the nebula, but at a diminished rate. The mass accretion rate through the nebula is large ( $\dot{M} > 10^{-7} M_{\odot}/\text{yr}$ ). The accretion rate through the disk may not be steady, and it is during this phase that large episodic increases in the accretion rate may occur, causing FU Orionis (Fuor) or EX Lupi (Exor) events, which are observed to result in increased luminosity for a period of a few decades (Calvet *et al.*, 2000; Bell *et al.*, 2000; Connolly *et al.*, 2006). This stage also lasts on the order of 10<sup>5</sup> yr.

*Stage 3: Low-mass accretion rate through the nebula.* The mass accretion rate through the disk and onto the central star will decrease over time, falling below  $10^{-7} M_{\odot}/\text{yr}$ , and the protoplanetary disk enters the third stage of evolution. During this stage, the infall of material from the molecular cloud has decreased severely. It is during this stage that the star is thought to be in the T Tauri epoch, which is

the phase prior to which it becomes a main sequence star. Observed T Tauri stars are characterized by a median mass accretion rate of  $\sim 10^{-8} M_{\odot}/\text{yr}$  at an age of  $\sim 10^6$  yr, decreasing with time, and a physical extent of up to a few hundred AU (Hartmann *et al.*, 1998; Mundy *et al.*, 2000; Calvet *et al.*, 2000; Bell *et al.*, 2000). This stage likely lasted a few million years.

*Stage 4: Quiescent nebula.* This is the final stage of evolution for the solar nebula, and the period during which different processes (solar wind interactions, photoevaporation) operate to erode it. Mass transport through the disk has become minor, and the nebula is relatively cool. This phase can last up to  $\sim 10$  m.y., depending on the conditions of the nebula and its proximity to other stars (Hollenbach *et al.*, 2000; Matsuyama *et al.*, 2003).

The above stages roughly correspond with the different protostellar classifications identified in the scheme developed by Lada and Shu (1990). These classes are identified based on their different radiative properties. In the Class 0 phase, the young protostar and its attendant disk grow by accreting material from the dense core envelope, and typically emit in the microwave regime. The Class I phase is where the natal envelope is being cleared away, most of the protostellar mass has been accreted, and a lower mass disk is present; the central object grows more massive, the circumstellar environment becomes less dusty, and the radiation is dominated by infrared photons. In the Class II phase, only a disk is present around the protostar and it is here, in the protoplanetary disk, that planets can begin to form, and the star can be observed with optical telescopes. Weak-line T Tauri stars with very tenuous disks represent the final Class III phase, and their observed radiation can be fit by a simple blackbody curve, as there is no significant extra mass to add to the emissions. Most of the material accreted during the Class 0–I phases went into forming the protostar, whereas that surviving the Class II–III evolutionary phases is now present in primitive solar system matter.

As the solar nebula evolved through these stages, a wide variety of chemical environments were produced due to the different processes associated with evolutionary stages outlined above. In Table 1, we list the various physical processes that are associated with each stage and the effects that they would have on primitive materials. We now describe these processes in more detail, so that we can understand the specific effects that they would have on solar nebula chemistry as described in section 3.

### 2.2. Formation of the Solar Nebula

Low-mass stars like the Sun are formed, either singly or as binaries, through the collapse of the dense molecular cores widely observed in molecular clouds such as Taurus, Ophiuchus, and Perseus (Evans, 1999). Thus, the formation of the protosolar nebula leads naturally to interstellar chemistry, particularly that of dense “prestellar cores” (e.g., Caselli *et al.*, 2003), as being responsible for setting the initial chemical composition of protosolar matter (e.g., Sandford,

TABLE 1. Evolutionary processes associated with each stage of protoplanetary disk evolution.

Physical Process	Effect on Primitive Materials/Environments
Stage 1: Infall (rapid) from molecular cloud Formation of the solar nebula	Processing (vaporization) of interstellar grains Define initial pressure, temperature structure Accretion of most material onto Sun
Stage 2: Diminished infall Variable $\dot{M}$ ( $>10^{-7} M_{\odot}/\text{yr}$ ) Protostellar outflows	Processing (vaporization) of ISM grains Rapid P, T evolution Large-scale radial mixing
Stage 3: Decreasing $\dot{M}$ ( $<10^{-7} M_{\odot}/\text{yr}$ ) Turbulence(?) Transient heating events Grain growth/planetesimal formation Giant planet formation	Slow P, T evolution (decreasing values) Extensive radial mixing Chondrule formation Meteorite parent body formation
Stage 4: Negligible $\dot{M}$ Removal of nebular gas Accretion of protoplanets and planetary embryos	Parent-body alteration

1996). This chemistry, as described by *Nuth et al.* (2006), proceeds at around 10 K and is comprised of a gaseous phase dominated by  $\text{H}_2$  and CO with admixtures of other heavy molecules (e.g., HCN,  $\text{NH}_3$ , OH,  $\text{HC}_3\text{N}$ , SO, CS). Refractory silicate and carbonaceous dust grains are also present. These become layered with ice mantles predominantly of water but also containing various polar and non-polar molecules (e.g., CO,  $\text{CO}_2$ , and  $\text{CH}_3\text{OH}$ ).

The initial chemical inventory available to the protosolar cloud is sensitive to the details of its dynamical evolution prior to the final collapse phase when the protosun and nebula formed. If magnetic fields dominated this evolution, then the final rapid gravitation collapse cannot occur until the sustaining magnetic support against gravity has been lost through ion-neutral drift [i.e., ambipolar diffusion (*Shu et al.*, 1987)]. For typical molecular cloud ionization fractions ( $\sim 10^{-8}$ – $10^{-7}$ ) this ambipolar diffusion timescale is several million years. Chemically, this timescale is comparable to that needed for a cosmic-ray-driven chemistry to attain a steady state, but much longer than the timescale ( $\sim 10^5$  yr) to freeze out atoms and molecules containing heavy elements through sticking collisions with cold dust grains (*Nuth et al.*, 2006).

Alternatively, molecular clouds may form, collapse to form protostars, and dissipate on much shorter timescales, on the order of the gravitational free-fall time ( $\sim 10^5$ – $10^6$  yr). This scenario (e.g., *Elmegreen*, 2000; *Hartmann et al.*, 2001; *MacLow and Klessen*, 2004) appears to be more in accord with the apparent chemical youth of molecular clouds, as well as with the estimated dynamical lifetimes of protostellar cores and molecular clouds. A third, intermediate possibility is that the dynamical evolution of the protosolar cloud was influenced by either the ejecta of a nearby supernova, or

by the wind of a late-type AGB star (*Cameron and Truran*, 1977; *Vanhala and Cameron*, 1998). In either case the SNe or AGB wind could initiate collapse of the natal protosolar core at some arbitrary point in its evolution, irrespective of the timescale on which its chemistry would otherwise evolve. This scenario also allows for the injection of fresh nucleosynthetic products into the protosolar nebula, an appealing aspect from the point of view of explaining the presence of live radionuclides in meteorites (e.g., *Boss and Foster*, 1998; *Vanhala and Boss*, 2002).

### 2.3. Disk Structure and Evolution

*2.3.1. Density and temperature structure.* Neglecting the effect of radiation from the forming protostar, to a first approximation the gross physical evolution of the nebula/disk determines its chemical structure. In the gravitational collapse of a rotating core, parcels of infalling gas and dust are spatially redistributed according to their angular momentum. Material with low angular momentum falls toward the center, whereas that with higher angular momentum settles into larger orbits, forming the protostellar disk (e.g., *Cassen and Moosman*, 1981). A molecular disk in differential rotation, where the inner regions rotate more rapidly than the outer ones, forms around the young protostar. The protostar grows both by direct accretion of infalling interstellar matter, and also by the episodic accretion of material from the surrounding disk (e.g., *Hartmann*, 2000).

Differential rotation of the gaseous disk around the star induces shearing motions that provide frictional forces that, in turn, act to drive radial motion. The source of these viscous, dissipative forces could be associated with either gravitational instabilities, magnetic torques, or large-scale con-

vection (Balbus and Hawley, 1991; Ruden and Pollack, 1991; Adams and Lin, 1993). These different mechanisms require different physical conditions in the disk to operate (i.e., mass concentrations, ionization fractions, thermal gradients) and they may operate at different locations or times throughout the lifetime of a disk (Stone *et al.*, 2000). The net result is an evolving disk density structure where most material in the disk loses angular momentum and there is a net radial movement of mass toward the protosun; the remaining disk angular momentum, possessed by a small fraction of the material, is transported outward.

Viscous dissipation will also heat the gas and the thermal structure of the disk is set by how quickly thermal energy is produced by this dissipation and the rate at which the disk can radiate it away (e.g., Boss, 1998). The greatest amount of heat is generated at the interior of the disk due to the greater amount of material present and shearing that takes place. These locations also have the largest optical depths (due to the higher density of material present), making it more difficult for radiation to escape from the disk. This creates a thermal structure with high temperatures close to the star and low ones at larger heliocentric distances. As the mass of the disk decreases, the amount of viscous dissipation that occurs and the optical depth of the disk also decrease, allowing the disk to cool over time.

The density and temperature of a given location of the disk will determine what chemical reactions can take place. There will generally be some location of the disk inside of which a chemical species will not be allowed to form, but outside of which the temperature is low enough that the species is thermodynamically stable. The location where this transition takes place is generally called the *condensation front* for that species, as outside that location the species will begin to condense (if it is a solid). An example of such a condensation front is the *snowline*, which represents the radial location outside of which water was found as solid ice. Because the disk cools over time, the condensation front for different species will move inward over time (Cassen, 1994). (Note that this is a simplification of the real situation, as the location where a chemical species will condense may depend on pressure in addition to temperature.) This implies that the allowed chemistry at a given location would evolve with time.

**2.3.2. Spatial mixing and transport.** Over the course of the lifetime of the solar nebula, different processes would have led to radial movement of the gas and solids within it. These transport processes would bring chemical species into regions of the nebula where they would undergo alteration of some sort or remain intact although they would not have formed in the new environment in which they are found. Here we briefly summarize the different transport processes and refer the reader to Cuzzi and Weidenschilling (2006) for more details.

**2.3.2.1. Large-scale flows:** Regardless of the driving mechanism(s) for protoplanetary disk evolution, the net result is that a large fraction of the gas flows inward and is eventually accreted onto the star, while some is carried outward to transport angular momentum. These flows can carry

gaseous material and small dust grains with them, leading to the radial transport of different species. The particulars of the flow likely vary with the driving mechanism. In the case of turbulent viscosity, Takeuchi and Lin (2002) and Keller and Gail (2004) have demonstrated that the direction of the flow may vary with height above the disk midplane: The upper layers of the disk flow inward, while the midplane material moves outward.

**2.3.2.2. Diffusion:** Diffusion transports things along concentration gradients, from areas of high concentrations to areas of low ones. In the solar nebula, gas molecules would be subject to such transport as would solids, although the mobility of solids due to diffusion would decrease as their masses increased. Thus, dust particles would be those solids most affected by this process. The rate of diffusion would depend on the structure and viscosity (turbulence) of the nebula, and would evolve with time.

**2.3.2.3. Gas-drag migration:** As the nebular gas rotated around the Sun, it was supported radially by a pressure gradient (hot, dense gas near the Sun and cool, sparse gas further away). Solids in orbit around the Sun did not feel this pressure, and thus the central force experienced by solids (gravity) and gas (gravity minus pressure support) differed, causing the gas to revolve at a slower rate. This difference in orbital velocities led to solids experiencing a headwind in their orbits, causing them to migrate inward with time. The rate of this migration depended on the size of the solids being considered, with meter-sized particles experiencing the most rapid migration ( $\sim 0.01$  AU/yr) (Weidenschilling, 1977). In the case of a nonuniform nebula, localized pressure maxima may develop, leading to the outward migration of solids (Haghighipour and Boss, 2003). Bodies larger than a kilometer in size, which likely includes all meteorite parent bodies, were essentially immobile due to their large inertia. Therefore, once bodies that large formed, they likely did not migrate due to this effect.

**2.3.2.4. Outflows:** A feature commonly observed around young stellar objects, and therefore presumably present at some point during the evolution of the solar nebula, are energetic outflows originating from the inner parts of the disk. These outflows are believed to be linked to the accretion of material from the disk onto the star. As material was ejected from near the Sun by outflows, it has been proposed that a fraction of the material may not have reached escape velocity or would travel on trajectories that intersected the nebula. If that was the case, that material would have fallen back and reentered the solar nebula at a radial distance depending on the velocity it was launched at, its trajectory, and the shape of the nebula. Such a process has been proposed as a way of thermally processing chondrules (Shu *et al.*, 1996, 1997; Liffman and Toscano, 2000).

## 2.4. Irradiation

While the rates of gas phase bimolecular and termolecular reactions, and gas-grain processes, depend strongly on disk physics (the local temperature and density), many sources of ionization were also present throughout the neb-

TABLE 2. Molecules detected in protoplanetary disks  
(adapted from *Markwick and Charnley, 2004*).

Object	Detections	Upper Limits	References
DM Tau	$^{12}\text{CO}$ , $^{13}\text{CO}$ , $\text{H}_2\text{D}^+$ , $\text{C}^{18}\text{O}$ HCN, HNC, CN, CS $\text{C}^{34}\text{S}$ , $\text{H}_2\text{CO}$ , $\text{HCO}^+$ , $\text{C}_2\text{H}$	$\text{H}^{13}\text{CO}^+$ , $\text{N}_2\text{H}^+$ , SiO SiS, $\text{H}_2\text{S}$ , $\text{C}_3\text{H}_2$ , HCO $\text{HC}_3\text{N}$ , $\text{CH}_3\text{OH}$ , $\text{CO}^+$ SO, $\text{SO}_2$ , $\text{SiC}_2$ , HNCS $\text{HCOOCH}_3$	1, 2, 3
GG Tau	$^{12}\text{CO}$ , $^{13}\text{CO}$ , $\text{C}^{18}\text{O}$ , HCN CN, CS, $\text{H}_2\text{CO}$ , $\text{HCO}^+$	HNC, $\text{C}^{34}\text{S}$ , $\text{H}^{13}\text{CO}^+$ $\text{C}_2\text{H}$ , $\text{N}_2\text{H}^+$	3
L1157	$\text{CH}_3\text{OH}$		4
LkCa15	$\text{CO}$ , $^{13}\text{CO}$ , $\text{H}_2\text{CO}$ , HCN, CN $\text{HCO}^+$ , $\text{N}_2\text{H}^+$ , CS	$\text{DCO}^+$ , $\text{H}_2\text{D}^+$ , $\text{H}^{13}\text{CO}^+$ , OCS HNC, $\text{CH}_3\text{OH}$ , HDO, DCN	5, 6, 10
TW Hya	$\text{CO}$ , CN, HCN, $\text{DCO}^+$ , $\text{H}_2\text{D}^+$ $\text{HCO}^+$ , $\text{H}^{13}\text{CO}^+$	HNC, DCN, $\text{H}^{13}\text{CN}$ , $\text{CH}_3\text{OH}$ SO, $\text{N}_2\text{H}^+$	6, 7, 8, 9

References: [1] *Dutrey et al. (1997)*; [2] *Dutrey et al. (2000)*; [3] *Ceccarelli et al. (2004)*; [4] *Goldsmith et al. (1999)*; [5] *Qi (2001)*; [6] *Thi et al. (2004)*; [7] *Kastner et al. (1997)*; [8] *van Dishoeck et al. (2003)*; [9] *van Zadelhoff et al. (2001)*; [10] *Aikawa et al. (2003)*.

ula. These processes acted to alter the chemical composition by driving nonequilibrium chemistries, especially close to the protosun, at the disk surface, and deeper in the outer disk. Although the focus here is primarily on chemistry, it should be noted that sources of disk ionization can also strongly influence the global magnetohydrodynamical evolution of a disk (*Hayashi, 1981*; *Balbus and Hawley, 1991*; *Gammie, 1996*) and hence the physics of mass accretion and angular momentum transport.

**2.4.1. Ultraviolet radiation.** There are two possible sources of UV radiation: interstellar and solar. Ultraviolet photons from the external interstellar radiation field can photodissociate and photoionize a thin surface layer of disk material. The disk is radially and vertically optically thick for stellar UV and optical photons. However, in a flared disk structure (*Chiang and Goldreich, 1997*) stellar UV photons can irradiate the disk surface and produce a hot surface layer, out to large radii ( $\sim 10^2$  AU). In this case the stellar UV contribution at the surface can be  $\sim 10^4$  times that of the interstellar field (*Willacy and Langer, 2000*). It is now understood that most of the radicals and ions detected thus far in protoplanetary disks (see Table 2) reside in these surface layers (e.g., *Aikawa and Herbst, 1999b*; *Aikawa et al., 2002*). It should be noted that, if the protosolar nebula formed in the vicinity of massive O and B stars (*Hester et al., 2004*), these objects may have provided a much higher flux of UV radiation to the surfaces of the disk. Published nebular chemistry models have not explored this possibility in detail. An additional, low-level source of UV photons may also exist deeper in the disk, including the midplane, where cosmic-ray particles can penetrate. Electrons produced by cosmic-ray ionization of molecular hydrogen can

excite other  $\text{H}_2$  molecules and UV photons are produced through their subsequent radiative deexcitation (*Prasad and Tarafdar, 1983*).

**2.4.2. X-rays.** Observational surveys of young Sun-like stars show them to be copious producers of X-ray emission early in their evolution (*Montmerle et al., 1983*). Studies of regions with ongoing star formation [e.g., with ROSAT (*Feigelson et al., 1993*)] suggest that X-ray activity continues from the early protostellar phase until around  $\sim 10^8$  yr, with an almost temporally constant hard X-ray component underlying that associated with flaring. Observations of stellar clusters show a range of X-ray brightnesses with luminosities in the range  $L \sim 10^{28}$ – $10^{30}$  erg  $\text{s}^{-1}$ , and that the constant component probably has a luminosity in excess of  $\sim 10^{29}$  erg  $\text{s}^{-1}$ . The origin of these X-rays lies in stellar coronal activity, probably associated with the heating from magnetic reconnection and stellar flaring, and this leads to a hot sphere of X-ray-emitting plasma surrounding the central protostar (e.g., *Glassgold et al., 1997*). Soft X-rays ( $E_X < 1$  keV) can be strongly attenuated by the several magnitudes of extinction supplied by the wind. Harder X-rays ( $E_X \sim 2$ – $5$  keV) can penetrate into the disk and are the main source of ionization within about 10 AU, especially if the (magnetohydrodynamic) wind from the protostar also shields the inner disk from galactic cosmic rays.

X-rays irradiate the disk obliquely and are efficiently attenuated by the high material column densities of the disk. This leads to the upper layers of the disk being ionized and heated most effectively by X-rays (*Glassgold et al., 1997*). Dust grain settling lowers the attenuation and allows the higher-energy X-rays to penetrate further into the material of the upper disk layers and to be the dominant source of

ionization at disk radii of  $\sim 0.1$ – $10$  AU. This provides a much higher X-ray ionization rate ( $\zeta_X$ ) in the upper layers of the disk than in the midplane, where a combination of thermal ionization, cosmic rays, and extinct radioactivities provide most of the ionization.

For example, simple disk chemistry models show that between about 200–400 AU above the disk midplane,  $\zeta_X \sim 10^{-16}$ – $10^{-15} \text{ s}^{-1}$  for  $L \sim 10^{31} \text{ erg s}^{-1}$ , and  $\zeta_X \sim 3 \times 10^{-17} \text{ s}^{-1}$  at 400 AU if  $L \sim 10^{29} \text{ erg s}^{-1}$  (Aikawa and Herbst, 1999b). Apart from ionizing disk material, X-rays can also be an efficient heat source. Heating of the upper layers by X-rays may dominate that from mechanical heating in some cases and lead to extremely hot atomic surface layers ( $\sim 5000$  K) (Glassgold *et al.*, 2004).

**2.4.3. Cosmic rays.** Unless a powerful protostellar wind is present, protoplanetary disks will experience the same cosmic-ray particle flux as their natal molecular cloud cores. However, the much higher disk surface density leads to their strong attenuation, at the surface of the inner disk region, by ionization and elastic and inelastic scattering (Umebayashi and Nakano, 1981). Cosmic rays may be prevented from penetrating deep into the disk by scattering off fluctuations in a disk magnetic field (Dolginov and Stepinski, 1994), or from a magnetohydrodynamic wind, if present. If any magnetic attenuation is neglected, then the lower surface density of the outer disk can allow greater penetration, and so cosmic rays could be a significant source of ionization at the midplane. Cosmic-ray ionization of young disks rich in  $\text{H}_2$  can in principle initiate a chemistry in the same manner as in the interstellar medium, i.e., by production of  $\text{H}_3^+$  and  $\text{He}^+$  (Nuth *et al.*, 2006). This has served as the motivation behind recent models of protoplanetary disk chemistry based on interstellar processes.

## 2.5. Extinct Radionuclides

The decay of extinct radionuclides over the age of the solar system (i.e., with half-lives  $\sim 10^5$ – $10^8$  yr) also provided a source of ionization. In this case, abundant nuclei with the shortest half-lives, and that produce high-energy particles or  $\gamma$ -rays, can ionize material throughout the disk. The most effective of these are  $^{26}\text{Al}$ ,  $^{60}\text{Fe}$ , and  $^{40}\text{K}$  (e.g., Finocchi and Gail, 1997). The ionization rate due to both cosmic rays and radioactive decay can thus be parameterized (e.g., Umebayashi and Nakano, 1988)

$$\zeta_{\text{CRP}}(r) = \zeta_{\text{ISM}} \exp\left[-\frac{\sigma(r)}{196 \text{ g cm}^{-2}}\right] + \zeta_{\text{RA}}$$

where  $\sigma(r)$  is the mass surface density ( $\text{g cm}^{-2}$ ). The interstellar cosmic-ray ionization rate,  $\zeta_{\text{ISM}}$ , is in the range  $\approx (1-5) \times 10^{-17} \text{ s}^{-1}$  and  $\zeta_{\text{RA}}$ , the ionization rate associated with the decay of radioactive nucleotides, can be expressed as  $8 \times 10^{-23} f_d \text{ s}^{-1}$ , where an elemental depletion factor,  $f_d$ , has to be accounted for since Al and Fe nuclei are expected to be largely incorporated into refractory dust particles. The relative contribution of these two processes to the midplane

disk ionization is such that, early in nebular evolution,  $^{26}\text{Al}$  and  $^{60}\text{Fe}$  are the major sources of ionization within about 10 AU, outside of which cosmic ray ionization dominates. Later, decay products from the longer-lived  $^{40}\text{K}$  decay provide a much weaker ( $\sim \text{few} \times 10^3$  times less) ionization rate that only dominates the cosmic-ray contribution within  $\approx 2$ – $3$  AU.

## 2.6. Transient Heating

As described by Connolly *et al.* (2006), transient heating events are known to have occurred in the solar nebula. Observations of protoplanetary disks have found that FUor and Exor events, which are episodic increases in the mass accretion rate onto the central star, are common, resulting in luminosity fluctuations on timescales that are short compared to the evolutionary time of protoplanetary disks. While these events significantly increase the luminosity of the protoplanetary system, it is doubtful that they affect material embedded in the disk due to the large optical depth to the disk midplane (Bell *et al.*, 2000).

Primitive meteorites also contain evidence of localized transient heating events in the form of igneous (melted) CAIs and chondrules. The location, timing, and manner of these events are uncertain, and a wide variety of mechanisms have been proposed for generating them. Examples of proposed heating mechanisms include shocks from dynamical instabilities in the nebula, bow shocks around supersonic planetesimals, lightning discharges, migration of objects into outflows, and energetic collisions between planetesimals. Any of these events may have occurred in the nebula, although they may not all have been responsible for the formation of chondrules. The effects that they would have on other primitive materials must still be determined.

## 3. MODELS OF NEBULAR CHEMISTRY

While the various processes described above operated in the solar nebula, various chemical environments would have formed defined by their pressures, temperatures, and elemental abundances. In this section, we describe what kinds of chemical environments may have been created by the different modes of protoplanetary disk evolution and discuss how the meteoritic and astronomical records preserve signatures of these environments.

### 3.1. Chemistry of Nebular Formation

The high-energy, dynamical environment encountered by cold interstellar gas and ice-mantled dust grains as they collapsed into the nebular disk presented the first opportunities for their chemical modification. Interstellar matter first experienced direct radiative heating by the central protosun (e.g., Simonelli *et al.*, 1997; Chick and Cassen, 1997), as well as by gas-grain drag heating (Lunine *et al.*, 1991). The gas and dust were also dynamically compressed and heated at the accretion shock and subjected to additional heating,

photoprocessing, and ionization by UV and X-rays from the shock itself (Neufeld and Hollenbach, 1994; Ruzmaikina and Ip, 1994). Chick and Cassen (1997) calculated the survivability of various materials, based on vaporization temperatures, in model nebulae. They found that, generally, the most refractory compounds could survive entry into the nebula up to almost within 1 AU. However, they found that subsequent survival depended upon the disk accretion rate and optical depth. For low disk accretion rates, and consequent lower disk luminosities, silicates and refractory organic material could survive up to within the terrestrial planet region but water ices would be vaporized within about 5 AU. At higher disk accretion rates, silicates could be destroyed out to a few AU, whereas more volatile organics (such as methanol and formaldehyde) and water ices could only survive outward of 20 AU and 30 AU, respectively.

Subtle chemical kinetic effects, as opposed to thermochemistry arguments based on vaporization temperatures, are probably important for determining change in the gaseous molecules. Except at large heliocentric distances, by the time a parcel of gas and dust has reached the nebular surface, the icy grain mantles will have been deposited into the gas — either by thermal desorption as the grains are heated, or by sputtering at the shock. This gaseous mixture of volatile mantle material is heated and compressed and a postshock chemistry occurs as it cools and selectively recondenses onto dust grains (except for H<sub>2</sub> molecules and He atoms).

At the high number densities ( $>10^{12}$  cm<sup>-3</sup>) and temperatures of the accretion shock (~2000–4000 K), collisional dissociation of H<sub>2</sub> can occur and the key parameter for the chemistry is the H/H<sub>2</sub> ratio in the postshock gas. This can increase by many orders of magnitude from its value in quiescent dense gas and the resulting population of highly reactive hydrogen atoms acts to destroy many other molecules (Hollenbach and McKee, 1979; Neufeld and Hollenbach, 1994).

For a given mass accretion rate, the highest shock speeds occur closer to the protosun and here the accretion shock can be fully dissociative, i.e., molecules are atomized. The slow (nondissociative) shock speeds and low preshock densities in the outer nebula would favor the survival of interstellar molecules. For example, Aikawa and Herbst (1999a) estimated that at 100 AU interstellar material would be accreted in pristine form with its D/H ratios intact. At intermediate disk radii, the shock is only partially-dissociative and the chemistry is sensitive to the actual H/H<sub>2</sub> ratio in the postshock gas. Under these conditions, CO and H<sub>2</sub>O can survive the accretion shock and in fact increase from their preshock abundances: Chemical erosion of H<sub>2</sub>O to OH and O by H atom abstraction reactions is overwhelmed by hydrogenation reactions with H<sub>2</sub>. The abundances of some mantle molecules, like CH<sub>4</sub> and CO<sub>2</sub> are partially reduced. However, other molecules, such as CH<sub>3</sub>OH, OCS, and H<sub>2</sub>CO, are completely destroyed since they do not have formation pathways with H<sub>2</sub> in the hot gas (S. B. Charnley and S. D. Rodgers,

personal communication, 2005). Thus, once the disk was formed, an interstellar chemical signature could have been retained over much of the protosolar disk, apart from within about 1 AU. Subsequent processing of this material was then responsible for spatial and temporal chemical alteration of it throughout the nebula.

### 3.2. Chemical Models of Nebular Chemistry

Once the disk has formed, chemical reactions will proceed within it, altering the solids that survived the infall from the molecular cloud and creating new ones out of the vapor of those that were destroyed. Not only will the chemical reactions that take place in the disk depend on the chemical environment that is present at a given location in the disk, but the modes of the chemical reactions will as well. This forces us to develop different models for determining what chemistry will take place under the variety of environments that will exist.

*3.2.1. Equilibrium chemistry.* A basic starting point for looking at the chemical evolution of the nebula is to look at what chemical species are thermodynamically stable under those temperatures, pressures, and elemental abundances that are expected in the nebula, as is done in condensation calculations. Standard condensation sequences present the chemical species expected to be present in a gas of solar composition at constant pressure at different (decreasing) temperatures. This sequence is determined by calculating the distribution of elements among different species using experimentally determined equilibrium coefficients while simultaneously solving the equations of mass balance. The details of calculating a whole condensation sequence are beyond the scope of this chapter, but are discussed and used by a number of authors (Lewis 1972; Grossman, 1972; Saxena and Eriksson, 1986; Wood and Hashimoto, 1993; Ebel and Grossman, 2000; Lodders, 2003; Ebel, 2006). Here we review the general results of such calculations, particularly following the recent results of Lodders (2003).

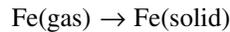
Imagine a parcel of solar composition gas at a pressure of 10<sup>-4</sup> bar, and a temperature high enough such that the only species present are in the gaseous state (while the molecular composition of the gas will change during the following discussion, we focus on the solids that form as they are more relevant to the formation of meteorites). This initial condition may have been appropriate for the inner solar nebula, as it has been speculated that material, out at least to where the current asteroid belt is located, was initially in the vapor phase during the earliest stages of nebular evolution (Cassen, 1996). Such a state may be needed to explain the moderately volatile element depletions described below.

As the gas cools (maintaining the constant pressure), the first solids to form are Ca-, Al-, and Ti-oxides such as corundum, hibonite, grossite, gehlenite, perovskite, and titanates. These refractory minerals begin to form at temperatures near 1700 K, with some not appearing until temperatures reach 1500 K. These minerals are commonly found

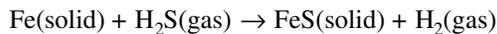
in primitive meteorites as CAIs, and thus support the conclusion that these inclusions are composed of the first condensates in the solar nebula.

As the gas continues to cool, Mg-bearing silicates begin to condense, with the most abundant being forsterite and enstatite. These minerals form over a small temperature range, between 1310 and 1360 K, with metallic Fe appearing at the same time. Magnesium, Si, and Fe are the most abundant rock-forming elements, and make up the bulk of the material found within primitive meteorites, including both chondrules and the surrounding matrix.

After the major rock-forming elements condense at a temperature of ~1300 K, less-abundant elements will continue to be incorporated into solids, adding little to the bulk mass of condensed species. Those elements that condense between this temperature and the condensation temperature of sulfur (~650 K) are called “moderately” volatile elements. As the system cools below the sulfur condensation temperature, leftover Fe is predicted to react with O in gaseous water molecules to form iron oxides, such as magnetite. Significant mass is not added to the solid component until temperatures are low enough for water ice to condense at a temperature of ~160 K. It should be pointed out that the condensation processes may differ from element to element. In the case of Fe, an Fe atom in the gas may condense to become part of an Fe grain



However, under canonical conditions, S condenses when hydrogen sulfide gas reacts with existing Fe grains to form troilite (FeS)



This reaction could only take place if there was solid Fe available to react with the nebular gas. Thus, these condensation calculations assume that the condensed solids remain in contact with the gas and can react with it to form whichever species are thermodynamically stable. In reality, this may not be the case, as accretion of solids would lead to some material being shielded from contact with the gas (*Petaev and Wood, 1998*). This illustrates the importance of considering various timescales in considering the chemical evolution of the solar nebula.

*3.2.2. Kinetic models.* As described above, a drawback to calculations such as these is that they only predict what species would exist under the idealized case of thermodynamic equilibrium. However, for a variety of reasons, equilibrium may not have been reached in the solar nebula. As described above, if solids were removed from contact with the nebular gas, predicted chemical reactions may not be able to take place. While diffusion of atoms inside of solids may allow these reactions to occur by transferring reactants from the gas to the solid interiors, if the solids are large or the temperature is low, then diffusion may not be rapid

enough for the equilibrium products to form. This has led to the consideration of chemical kinetics along with chemical models of the solar nebula.

As described previously, the solar nebula was in place around the Sun for a finite time ( $10^{6-7}$  yr). In chemical reactions, the formation of a product takes an amount of time dependent on the concentration of the reactants as well as their temperature or mobility — it is not instantaneous. If the amount of time needed for a given reaction to take place was long compared to the lifetime of the solar nebula, then, despite being thermodynamically stable, that reaction product would not form in the nebula.

This idea was extensively developed by *Fegley (1988)* and *Fegley and Prinn (1989)* in looking at the kinetics of gas-solid reactions in the solar nebula in trying to understand the origin of different meteoritic components. To do so, these authors developed what is known as the simple collision theory (SCT), which can be used to calculate the collision rate of gas molecules with the solids that they are to react with. Using the kinetic theory of gases, the fraction of collisions that take place with an energy greater than the activation energy of the reaction can also be calculated. When a collision takes place with an energy greater than the activation energy, the reaction of interest is assumed to take place. Using this idea, the time needed for enough collisions to occur for a reaction to proceed to completion can be calculated. In general, those reactions that require higher activation energies, occur on large grains (small surface area to volume ratios), or occur in low-pressure environments take longer to reach completion. As an example of how this work was applied, it was shown that while predicted to be present in the solar nebula by equilibrium condensation calculations, serpentine (as well as other phyllosilicates) could not form via gas-solid reactions in the canonical solar nebula. In addition to the limitations due to gas-solid collision rates and energetics described above, solid-state diffusion as well as gas-gas collisions may not occur rapidly enough in the solar nebula to reflect the equilibrium predictions of condensation calculations (*Lewis and Prinn, 1980; Fegley and Prinn, 1989*).

Kinetic inhibition explains why some equilibrium products are not observed in meteorites. In addition, it also demonstrates that there are other considerations that must be made when looking at the chemical evolution of the solar nebula. For example, all the Fe in some carbonaceous chondrites (CM, CI) is locked up as FeO. As described, as silicates condense, they are expected to be Mg-rich with Fe condensing to form metallic grains. At lower temperatures (<550 K), Fe is predicted to react with water in the gas to form FeO, which will then diffuse into the existing forsterite grains, replacing MgO, to form the observed mineralogy. However, as summarized by *Ebel and Grossman (2000)*, this requires equilibrium to be achieved, which is unlikely at these low temperatures due to the slow diffusion rate through olivine. Despite the expected kinetic inhibition of these species, they are still observed in carbonaceous chon-

TABLE 3. Representative gas phase chemical reactions in the nebula.

Reaction Type	Generic	Example	Rate Coefficient at 10 K*
1. Radiative association of neutrals	$A + B \rightarrow AB + \nu$	$CO + S \rightarrow OCS + \nu$	$\sim 10^{-10} - 10^{-17} \text{ cm}^3 \text{ s}^{-1}$
2. Ion-neutral radiative association	$A^+ + B \rightarrow AB^+ + \nu$	$C^+ + H_2 \rightarrow CH_2^+ + \nu$	$\sim 10^{-10} - 10^{-17} \text{ cm}^3 \text{ s}^{-1}$
3. Neutral-neutral	$A + B \rightarrow C + D$	$CN + C_2H_2 \rightarrow HC_3N + H$	$\leq 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
4. Ion-neutral	$A^+ + B \rightarrow C^+ + D$	$H_3^+ + CO \rightarrow HCO^+ + H_2$	$\sim 10^{-7} - 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
5. Charge transfer	$A^+ + B \rightarrow B^+ + A$	$S^+ + Mg \rightarrow Mg^+ + S$	$\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
6. Radiative recombination	$A^+ + e^- \rightarrow A + \nu$	$H^+ + e^- \rightarrow H + \nu$	$\sim 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
7. Dissociative recombination	$AB^+ + e^- \rightarrow A + B$	$H_3O^+ + e^- \rightarrow OH + 2H$	$\sim 10^{-6} - 10^{-7} \text{ cm}^3 \text{ s}^{-1}$
8. Photoionization <sup>†</sup>	$A + \nu \rightarrow A^+ + e^-$	$S + \nu \rightarrow S^+ + e^-$	$\sim (10^{-9} - 10^{-10})e^{-2\tau} \text{ s}^{-1}$
9. Photodissociation of neutrals <sup>†</sup>	$AB + \nu \rightarrow A + B$	$CO_2 + \nu \rightarrow CO + O$	$\sim (10^{-9} - 10^{-10})e^{-2\tau} \text{ s}^{-1}$
10. Photodissociation of ions <sup>‡</sup>	$AB^+ + \nu \rightarrow A^+ + B$	$CH_2^+ + \nu \rightarrow CH^+ + H$	$\sim (10^{-9} - 10^{-10})e^{-2\tau} \text{ s}^{-1}$

\*Many reactions, particularly neutral-neutral processes, are either endothermic or possess significant activation-energy barriers. These reactions become important at higher temperatures and their temperature-dependent rate coefficients can generally be expressed in the form  $\gamma T^\alpha \exp(-\beta/T) \text{ cm}^3 \text{ s}^{-1}$ , where  $\gamma$ ,  $\alpha$ , and  $\beta$  are constants fitted from experiment.

<sup>†</sup>Photorates typically contain an exponential factor involving the UV optical depth,  $\tau$ , to account for the attenuation of dissociating or ionizing photons in the relevant frequency range.

drites. As discussed below, if the products of a reaction thought to be kinetically inhibited are observed in meteorites or protoplanetary disks, they likely are due to parent-body processes or formation in noncanonical nebular conditions.

**3.2.3. Low-temperature/density models.** Over much of the protosolar nebula, chemical equilibrium would not be attained, thus placing a severe limitation on the “classical” chemical models such as those outlined above. Kinetics must be considered as temperatures and gas densities decrease, which continues to large heliocentric distances or high altitudes above the midplane. The chemistry in the outer regions of the disk midplane should be most reminiscent of that in cold molecular clouds (Nuth *et al.*, 2006), whereas the surface layers and the inner disk will experience chemistries similar to that of the diffuse interstellar medium or in regions of massive star formation (Tielens and Hollenbach, 1985; Maloney *et al.*, 1996).

Here we describe how interstellar chemical processes have been incorporated into disk models. Almost all these models include inward radial transport and the chemistry is calculated time-dependently (e.g., Aikawa *et al.*, 1999a). Table 3 shows some of the chemical reactions included in nonequilibrium disk chemistry models [see Le Teuff *et al.* (2000) for more information on astrochemical kinetics]. Isotopic fractionation patterns are crucial discriminants of nebular processes and hence of the origin of presolar material. Recent results on the fractionation chemistry of protoplanetary disks are outlined and discussed primarily in the context of isotopes of H, C, N, and O. Models based on nonequilibrium chemical processes can be regarded as complementary to chemical equilibrium models of the inner nebula (e.g., Fegley, 1999, 2000). The efficacy of nebular mixing processes is critical for the relevance of both treatments to meteoritic studies; results from recent nonequilibrium studies are also described here.

**3.2.3.1. Ionization and gas-grain interaction:** The basic ingredients of modern disk chemistry models can be traced

back to early models of the ionization structure of the solar nebula (Hayashi, 1981; Umebayashi and Nakano, 1988). These steady-state models assumed that cosmic rays would not be shielded and would play an important role in ionizing the outer regions of the nebular midplane. This leads to proton transfer from  $H_3^+$  and  $He^+$  attack on neutral molecules driving ion-neutral and neutral-neutral reactions in the disk midplane. The ionization at these densities is controlled by the gas-grain interaction and so recombination and charge transfer reactions with neutral and charged dust grains also have to be included. However, an unrealistic simplification of these models was that, even at 10 K, this interaction was limited solely to ion-grain, electron-grain, and grain-grain charging processes (e.g., Umebayashi and Nakano, 1981, 1990). In fact, at very low temperatures, neutral molecules collide and stick efficiently to dust grains, as is observed for CO (Dutrey *et al.*, 1994). A simple steady-state model of a Hayashi disk in which realistic molecule depletion and (temperature-controlled) evaporation from dust were also included showed that, while the disk ionization structure was broadly similar to the case when these processes were neglected, the chemical structure beyond about 50 AU was completely different (Charnley, 1995).

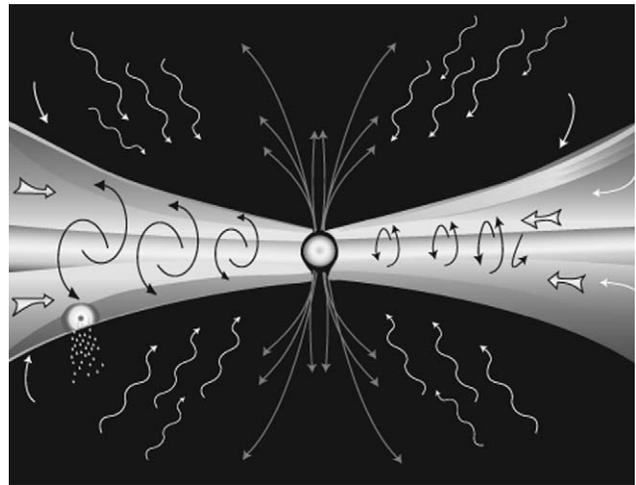
The formation of ice mantles on dust particles, and their exchange with the gas phase, are now seen as fundamental aspects of modern disk models. Aikawa *et al.* (1996, 1997) first constructed models that could account for the observed depletion of CO in disks, and calculated the radial distribution of both the gas- and solid-phase molecular abundances. Willacy *et al.* (1998) showed explicitly that, because of the high removal efficiency of positive ions by neutralization on grains, inclusion of the gas-grain interaction led to the gas-phase chemistry being dominated by neutral-neutral reactions. This result is contrary to the conclusion that ion-molecule reactions dominate the chemistry of the outer regions, as obtained from models that ignored gas-grain charge exchange (Bauer *et al.*, 1997; Finocchi and Gail, 1997). Aikawa *et al.* (1997) showed that the precise nature of the

gas-grain interaction is also important for the chemical structure, specifically whether molecular ions are simply neutralized or are dissociated upon collision with a negatively charged grain. Aikawa *et al.* (1999b) subsequently showed that for HCO<sup>+</sup>-grain collisions, the products were most likely to be CO and H, rather than HCO.

A key issue for the cooler outer disk is the mechanism whereby accreted material can be returned to the gas. In the case where the return of molecules to the gas is by thermal desorption, the rate is most sensitive to the binding energy for physisorption to the grain (e.g., Tielens and Allamandola, 1987), and to the dust temperature. The former dependence means that very volatile species, such as CO and N<sub>2</sub>, will desorb completely above about 25 K, whereas “stickier” species that can form hydrogen bonds (e.g., water, methanol, ammonia) can be retained at much higher temperatures, up to around 100 K in the case of water. The latter dependence means that the chemical structure of the outer disk depends sensitively on the temperature distribution, and hence on the physics of the disk model adopted (see Fig. 1). In regions where the temperature falls to 10 K, thermal desorption rates become vanishingly small and further nonthermal desorption mechanisms have to be considered. Possible mechanisms previously proposed for the interstellar medium (Léger *et al.*, 1985) are spot or whole-grain heating by cosmic rays, photodesorption, or explosion of irradiated mantles (by UV photons or X-rays) triggered by grain-grain collisions (Aikawa *et al.*, 1996). Willacy *et al.* (1998) found that the midplane chemistry was very sensitive to whether pure thermal desorption or mantle explosions were the sole mechanism in operation. The uncertainties in these models and the detection of radicals and ions in protoplanetary disks (Table 2) has led to greater focus on the chemical effects of irradiation from the central protostar.

3.2.3.2. Photochemistry: Protoplanetary disks like the protosolar nebula are irradiated by UV photons from their central star. Due to the high optical depths of the midplane material, the less-opaque upper layers of the disk will be most affected. The surfaces and underlying regions of protoplanetary disks also experience the interstellar radiation field. This means that the physics and chemistry in both the radial and vertical directions of the disk has to be considered.

Aikawa and Herbst (1999b), in the first of these two-dimensional models, solved for the chemistry in a Hayashi (1981) disk, where the vertical structure is isothermal at each radius. They found that they could produce column densities in the outer disk that were broadly similar to those observed by Dutrey *et al.* (1997). However, to overcome the problem that all the heavy gas species are rapidly frozen out as ices, they had to adopt an extremely low sticking efficiency (0.03) for molecule-grain collisions. Willacy and Langer (2000) calculated the two-dimensional chemical structure of a flared accretion disk in which stellar photons create a warm ( $T \sim 120\text{--}35$  K) surface layer in the outer disk (50–100 AU), in contrast to the cooler midplane region ( $T \sim 28\text{--}10$  K). They found that a significant UV flux could penetrate to intermediate depths, and that this could be sufficient to nonthermally detach molecules from the grains by photo-



**Fig. 1.** Schematic representation of the physical structure in a protoplanetary disk. The principal processes that influence the chemical structure are also indicated. Cold material from the *infalling envelope* becomes incorporated into the protostar and its accretion disk. This mixture of gas and dust passes through the *accretion shock* where it is decelerated. The highest postshock temperatures and compressions occur closest to the protostar, where refractory dust, organics, and ice are readily vaporized. Moving farther out in the disk, the increasingly weaker accretion shocks encountered can lead to the survival of even the most volatile interstellar matter. *Interstellar UV photons and cosmic rays* can be important for irradiating the upper disk layers at large radii. The central accreting protostar provides a strong source of *stellar UV photons and X-rays*. These stellar UV photons contribute to heating the uppermost vertical layers of the disk, leading to a hot *UV-illuminated surface* in the outermost regions of a flared disk. In the inner disk, X-rays dominate the heating from the surface to the *disk midplane*. Beyond about a few AU, the midplane region becomes very cold and this allows most of the heavy gas phase molecules to condense onto the (evolving) dust grain population. Between the hot surface and the disk midplane lie the *warm upper layers* where most gaseous molecular emission is currently detected. The physics of disk evolution (see text) allows for the transport and mixing of chemically processed materials from each of these distinct regions. *Inward and outward radial transport* can occur within the disk midplane, whereas vertical diffusion can transfer material between this region and the surface layers.

desorption, for even unit sticking efficiency. Subsequent disk models included a full two-dimensional radiative transfer solution (Nomura, 2002; Aikawa *et al.*, 2002; van Zadelhoff *et al.*, 2003; Millar *et al.*, 2003) and showed the existence of warm molecular layers ( $T \sim 30\text{--}60$  K) between the hotter surface and midplane. The gas-grain interaction in these intermediate layers is thus thermally controlled, and so can retain a gaseous phase without the need for low sticking efficiencies or nonthermal desorption processes. The two-dimensional chemical structures calculated in these two-dimensional models gives good agreement with the molecular emission and column densities observed; it is now generally accepted that most of the chemical species detected thus far reside either in the surface layers or in the warm intermediate layers (e.g., Table 2).

3.2.3.3. X-ray chemistry: Apart from the very innermost regions of the disk midplane, close to the protostar, material in the upper layers experience the most intense illumination by X-rays (Glassgold *et al.*, 1997; Igea and Glassgold, 1999). The ionization and heating of disks by X-rays has been modeled in detail by Gorti and Hollenbach (2004) and by Glassgold *et al.* (2004). These studies contain comprehensive summaries of the relevant physics and chemistry but are focused more on making predictions of the atomic and molecular emission expected from protoplanetary accretion disks. Bergin *et al.* (2001) argued that if the disk has a flared structure then X-rays can also affect the upper layers in the outer disk, and that this could provide an additional nonthermal grain desorption mechanism there. Markwick *et al.* (2002) treated the detailed two-dimensional chemistry within 10 AU of the protostar and showed that X-rays have a profound effect on the ionization structure, even within the first 5 AU of the midplane. At present it is unclear precisely what meteoritic signatures would be expected from the effects of disk X-rays on gaseous molecules. By contrast, an underlying source of hard X-rays, the flux of protostellar “cosmic rays” produced by flares on protostars, has been proposed as a means of producing extinct radionuclides in solid rocky materials similar to those found in meteorites (Lee *et al.*, 1998).

3.2.3.4. Solid-state chemistry: The expectation from the observed CO depletions and gas-grain models is that dust grains in the cold regions of disks should be covered with molecular ice mantles. This has now been directly confirmed by the detection of molecular ices in the disk of CRBR 2422.8–3423 (Pontoppidan *et al.*, 2005). Thus, reactions on the surface of grains is another important means of chemical processing of nebular material. Three chemistries are of interest in the formation and modification of ices in disks.

3.2.3.5. Grain-surface reactions: Ice mantles are laid down in the coolest parts of the disk. As in molecular clouds, below about 15 K highly reactive atoms, primarily H, D, and O, can stick and react on dust grains. Most recent disk chemistry models include an active surface chemistry involving atom addition reactions to other atoms, radicals, and molecules (e.g., Willacy *et al.*, 1998). These schemes tend to lead to mantles showing a mixture of reduced and oxidized states, i.e., H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH, and CO<sub>2</sub>, that depends largely on the local atomic O/H ratio in the gas. It should be emphasized that the mechanisms, reaction rates, and pathways in many of the proposed interstellar schemes are highly uncertain (Herbst, 2000; Charnley, 2001; Nuth *et al.*, 2006). Hence, detailed conclusions derived from disk chemistry models that are strongly dependent on surface chemistry should be regarded with caution.

3.2.3.6. Heavy particle bombardment of ices: Cosmic-ray impacts can occur in the outer midplane of the disk, and can lead to significant chemical changes in the ice structure and composition. Radiation damage of cosmic ice analogs has been extensively studied in the laboratory and has been important over the lifetime of the solar system (e.g., Hudson and Moore, 2001). However, the effects of this process have not yet been evaluated in chemical models.

3.2.3.7. Ultraviolet photolysis of ices: Ultraviolet photolysis also has a long history of study by laboratory astrophysicists (e.g., Allamandola *et al.*, 1988) and was originally proposed as an important means of chemical modification in the cold interstellar medium. Experiments show that, starting from simple ice compositions, consistent with that observed in the ISM, the gross chemical composition of the ices can be altered, and many complex molecules produced, after photolysis and heating (e.g., Bernstein *et al.*, 1995; Allamandola *et al.*, 1997). To date, ice photolysis has also not been considered in disk models. However, this process may in fact be most important for the chemistry in UV-irradiated disks as opposed to interstellar clouds, where ices containing H<sub>2</sub>O and other more refractory molecules (e.g., methanol and ammonia) will persist in the UV-illuminated warm molecular layers found to exist above the midplane (Aikawa *et al.*, 2002).

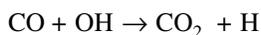
3.2.3.8. Isotopic fractionation: From the meteoritic perspective, perhaps the most interesting aspect of the inclusion of “interstellar” chemical processes in disk models is that this admits many more possibilities for efficient isotopic fractionation throughout the nebula. Isotopic fractionation (in D, <sup>13</sup>C, <sup>15</sup>N, <sup>18</sup>O, and <sup>17</sup>O) of the major molecular volatiles (CO, H<sub>2</sub>O, NH<sub>3</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>), and trace species such as polycyclic aromatic hydrocarbons (PAHs) can occur through ion-molecule reactions in cold gas and on grain surfaces (Nuth *et al.*, 2006).

Deuterium fractionation in the disks has been modeled by Aikawa and Herbst (1999a) and in a two-dimensional model by Aikawa and Herbst (2001). It was found that the D/H ratios in the disk midplane were higher because of the lower temperature. In two-dimensional models containing warm molecular layers above the midplane, computed column density ratios for the LkCa15 and TW Hya disks were found to agree reasonably well with the observed DCN/HCN and DCO<sup>+</sup>/HCO<sup>+</sup> values (Aikawa *et al.*, 2002; Thi *et al.*, 2004). Thermochemical models of a two-dimensional nebula have also been explicitly constructed to explain the apparent reduction of solar system D/H ratios in water and carbonaceous material from the high value seen in the interstellar medium (Drouart *et al.*, 1999; Robert, 2003). However, the importance of ion-molecule chemistry is confirmed by the detection of high abundances of H<sub>2</sub>D<sup>+</sup> in the disks of DM Tau and TW Hya (Ceccarelli *et al.*, 2004). This molecular ion appears to be present in the CO-depleted gas of the disk midplane, and when interstellar deuterium chemistry (Roberts *et al.*, 2003) is included in disk models (Ceccarelli and Dominik, 2005), even higher abundances of D<sub>2</sub>H<sup>+</sup> and D<sub>3</sub><sup>+</sup> are predicted in these sources.

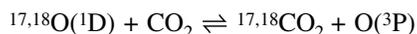
Sandford *et al.* (2001) have reviewed many other interstellar processes that could be responsible for setting the enhanced D/H ratios found in organic meteoritic material. For example, ultraviolet photolysis can also affect the D/H ratios of PAHs. This involves isotope-selective dehydrogenation due to the difference in the C-H and C-D bond energies; simple estimates indicate that about half the peripheral H atoms on a small PAH could be replaced by D (Allamandola *et al.*, 1989). However, apart from ion-molecule reac-

tions and surface reactions (e.g., *Tielens*, 1983), none of these processes (e.g., UV-photolysis of D-rich ices) have thus far been considered in disk models.

Oxygen-isotopic ratios in some meteoritic materials/CAIs exhibit mass-independent fractionation patterns ( $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ ) that are highly anomalous (e.g., *Clayton*, 2003). One possibility is that mass-independent effects occurred in the primitive solar nebula through specific gas-phase neutral-neutral reactions (e.g., *Thiemens*, 1999). This could occur through the bimolecular process



or in isotopic exchange reactions involving excited-state oxygen atoms



Alternatively, another interstellar fractionation process — isotope-selective photodestruction (ISP) — may be generally important for nebular/disk chemistry (*Clayton*, 2002a,b, 2003). For molecules that are photodissociated by line photons, such as CO, the main isotopomer is sufficiently abundant that a sufficiently large column of molecules can self-shield against the UV radiation field. Lower-abundance isotopomers that cannot self-shield,  $^{12}\text{C}^{18}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ , are thus preferentially destroyed. Since CO is the major molecular repository of carbon and oxygen in disks, this process could have dramatically altered the fractionation chemistry of the major nebular volatiles as atoms of  $^{18}\text{O}$  and  $^{17}\text{O}$  are selectively released, leading to a  $^{16}\text{O}$ -poor gas.

*Clayton* (2002a) proposed that ISP would probably operate in the inner edge of the disk, close to where the X-wind is formed. Model calculations close to the X-point ( $\sim 0.1$  AU), however, showed that the high temperatures there led to the released oxygen atoms being reincorporated into CO too rapidly for a significant fractionation to occur (*Lyons and Young*, 2003). Using a two-dimensional disk chemistry model, *Young and Lyons* (2003) showed that the lower temperatures of the UV-irradiated diffuse upper layers of the outer disk could produce gas enriched in  $^{17}\text{O}$  and  $^{18}\text{O}$ . Observational support for this picture comes from observations of CO isotopomers in the outer disk of DM Tau. *Dartois et al.* (2003) found that the extent of the outer disk, as traced by  $^{12}\text{C}^{18}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ , is more compact than that inferred from the  $^{12}\text{C}^{16}\text{O}$  data, a result consistent with ongoing isotope-selective photodissociation. Vertical diffusion is then necessary to allow material from the disk midplane to access the photochemical region; calculations indicate that a significant mass-independent fractionation can occur in water at  $R = 30$  AU if this mixing is very efficient (*Lyons and Young*, 2004). *Clayton* (2002c) also proposed that isotope-selective photodissociation could also occur for the  $^{15}\text{N}^{14}\text{N}/^{14}\text{N}_2$  ratio, selectively increasing the  $^{15}\text{N}/^{14}\text{N}$  ratio of the gas. It is unclear whether conditions at the X-point would also limit this process there. As with CO, it may be more favored in the outer nebula, but calculations show that here there are competitive gas-grain processes that could

provide high midplane  $^{15}\text{N}/^{14}\text{N}$  ratios, without the need for vertical mixing (*Charnley and Rodgers*, 2002).

In conclusion, several “interstellar” fractionation processes will occur in different regions of the nebula, with the results depending mainly upon the local temperature and irradiation flux. Mixing of material between different regions will therefore serve to complicate the problem of determining the origin, in space and time, of particular chemical characteristics of meteorites. In the following section we discuss chemical models that address the mixing question.

**3.2.4. Formation of macromolecules.** The carbon in carbonaceous meteorites, such as CI and CM chondrites, is mostly present in complex macromolecular networks, with smaller amounts distributed among relatively volatile aromatic and aliphatic hydrocarbons, as well various small (by the standards of terrestrial biochemistry) organic molecules (e.g., *Cronin and Chang*, 1993; *Botta and Bada*, 2002; *Sephton*, 2002; *Pizzarello*, 2004). The enhanced values of  $\delta\text{D}$  and  $\delta^{15}\text{N}$  found in meteoritic materials (including the amino acids) support the view that they, or their precursor molecules, were formed in a low-temperature environment (*Cronin and Chang*, 1993), such as found in the outer nebula or in the natal molecular cloud core.

Apart from the condensation of refractory elements to form dust, the inner nebula was a region where chemical reactions could also have formed large carbonaceous structures and various hydrocarbons (*Zolotov and Shock*, 2001). In the atmospheres of late-type carbon stars, PAH molecules are believed to form by the polymerization of acetylene, in a chemistry similar to that of sooting flames (*Frenklach and Feigelson*, 1989; *Cherchneff et al.*, 1992). It is possible that the PAHs found in meteorites contain a contribution from these regions, although they must have experienced some degree of chemical modification in their passage through the ISM and into the nebula. At the lower pressures of the protosolar nebula, *Morgan et al.* (1991) found that efficient PAH formation could occur within a well-defined pressure-temperature window, such that the optimal sites for PAH growth in the inner nebula would be above the midplane. If this occurred, and these PAHs found their way into meteorites, then any deuterium enrichments would have to be provided within the nebula and this would first require their transport to the cooler outer regions where the known fractionation mechanisms are more favored (e.g., *Sandford et al.*, 2001).

### 3.3. Chemistry of Disk Evolution

Over the course of the lifetime of the solar nebula, the pressure and temperature structure evolved, causing the allowed chemical reactions throughout the nebula to evolve as well. Thus, understanding how these changes occurred is important to understanding the chemical evolution of the nebula.

*Cassen* (1994) demonstrated how the thinning and cooling of the disk could have affected the chemical environments within the solar nebula. In this work, it was shown

that the evolution of the nebula as described above would cause the condensation fronts of rock and water ice to move inward over the lifetime of the nebula. The rates at which these two fronts would move depend strongly on nebular parameters. The movement of these fronts is important to consider in looking at those meteorites that were exposed to water and those that formed in anhydrous conditions — as the snowline moved into a region where rock had already condensed, water ice would then be available to accrete into larger bodies as well. As this ice was incorporated into large bodies, it would melt and allow the liquid water to react with rock to form hydrated minerals. Anhydrous primitive material would be preserved in those regions of the disk that were not overrun by the snowline or were overrun in the late stages of disk evolution after most of the water was locked away in large planetesimals (*Cuzzi and Zahnle, 2004*).

The change in gas density as the nebula cooled may have also played an important role in determining the bulk compositions of the chondrites. While the elements found in chondrites are near solar in their elemental inventories, a decrease in relative abundance is noticed for the moderately volatile elements that correlates with decreasing condensation temperature (those elements that condense at high temperatures are relatively more abundant than those that condense at lower temperatures). This is thought to have occurred by one of two mechanisms: (1) mixing together of material processed at high temperatures that lost its volatile elements (chondrules or refractory inclusions) with volatile rich material (*Anders, 1975, 1977; Hutchison, 2002*) or (2) removal of gas from a given location as the system cooled such that the reservoir of material available to condense at high temperatures would be greater than that available to condense at lower temperatures (*Wasson and Chou, 1974; Wai and Wasson, 1977; Wasson, 1977*). General consensus, as summarized by *Palme and Boynton (1993)* and *Palme (2000)*, has been that the former mechanism does not work due to the presence of volatiles in chondrules and the inability to produce the observed trends by the vaporization of chondritic material. *Alexander (2005)* has recently argued that if evaporation and recycling of chondrule material occurred, then the two-component mixing model may need to be reinvestigated.

The case of the volatile depletion being caused by gas removal from a cooling nebula was modeled in *Cassen (1996, 2001)*, where it was quantitatively shown that the depletion trend of moderately volatile elements can be reproduced by the dynamical evolution of the solar nebula. The only elements that were depleted were those that condensed at temperatures below the initial temperature at a given location of the nebula. Thus, if an area of the nebula was initially at a temperature of 800 K, then only those elements that condensed at temperatures below 800 K would show any depletion trend. Therefore, in order for all moderately volatile elements to be part of the depletion trend, temperatures must have originally been above the condensation point at which the depletion begins, which with Si is with a condensation temperature of ~1350 K. This would therefore require all

material in the inner nebula to have been completely vaporized to produce the depletion. The level of depletion for the rest of the elements would depend on how quickly the nebula cooled and was depleted of gas, which is determined by the transport of mass and angular momentum as well as the decrease in opacity by the coagulation of dust (*Cassen, 1994*).

### 3.4. Chemical Effects of Dynamical Mixing

Along with changing the physical structure of the nebula, dynamical mixing between different regions would take place. Chondritic meteorites themselves demonstrate this perfectly as they are agglomerates of materials that formed under a variety of conditions: both high and low temperatures as well as reducing and oxidizing environments. Mixing may have occurred from regions at different radial locations or heights above the midplane. Here we discuss how some of the different mixing processes may have affected what products would form in the solar nebula.

An example of how diffusion might operate in the nebula was studied by *Stevenson and Lunine (1988)* and later by *Cyr et al. (1998)* by looking at water vapor. In the inner nebula, temperatures are expected to have been above the condensation temperature of water, and therefore all water would be present as a gas. The outer nebula was cooler, and therefore the water would have been present as water ice. There would therefore be a concentration gradient that would cause the water vapor to diffuse outward. If no sources of water are present to replenish the vapor, all the water could be removed from the inner nebula on very short timescales (~10<sup>5</sup> yr). Because of the importance of water for determining the oxygen fugacity of the nebula, this process would affect the chemistry of the nebula inside the snowline (*Cyr et al., 1999*). For example, removal of water vapor is thought to be needed to explain the mineralogy of the enstatite chondrites, such as larger ratios of enstatite to forsterite than expected under solar conditions as well as the presence of Si-bearing metal (*Hutson and Ruzicka, 2000*). The effect described here can be generalized to conclude that, in the absence of a replenishing source, diffusion may also deplete any given species from the part of the nebula that is inside its condensation front.

The inward migration of meter-sized bodies by gas drag could serve as a way of replenishing the inner nebula with material that diffused outward. In the example outlined above, bodies carrying water ice could migrate inward from the snowline and vaporize, replenishing the inner nebula with water vapor. *Cyr et al. (1998)* showed that the migration of those bodies that formed by the condensation of diffusively redistributed water vapor could slow the dehydration of the inner nebula. This study did not consider the inward migration of material from beyond the snowline, however. *Cuzzi and Zahnle (2004)* showed that if the inward mass flux was high enough, the inward migration and subsequent vaporization of rapidly migrating bodies could lead to enhanced water vapor pressures inside the snowline.

As planetesimals formed in the nebula, increasing the average size of the solids and decreasing the inward mass flux, the vapor would then be diffusively redistributed. Again, if the water vapor increase in the inner nebula was large enough, it could have significantly affected the chemistry that occurred there. As an example, significantly enhanced oxygen fugacities (at least 3 orders of magnitude) are needed to explain why the FeO contents in chondrites are higher than expected for condensation of a gas of solar composition (*Ebel and Grossman, 2000*). Combining the migration and vaporization of icy bodies along with the diffusion of water vapor may explain the evidence for the orders-of-magnitude range of oxidizing conditions inferred for the nebula by chondritic meteorites (*Krot et al., 2000*) or how heavy oxygen isotopes were brought inward from the outer nebula (*Krot et al., 2005*). Kinetics also become important in migration, because material that is chemically altered on long timescales can be delivered to a region of the nebula where it would not normally have formed. *Ciesla and Lauretta (2005)* provided an example of this in looking at the delivery of hydrated minerals from the outer asteroid belt region of the solar nebula to the planetesimals orbiting the Sun where Earth formed.

While radial mixing appears to have been unavoidable in the solar nebula, the chondritic meteorites demonstrate that there were limits to how extensive this mixing was. The observed chondrule-matrix complementarity in meteorites implies that chondrules and matrix are related in some way, perhaps both being processed by the transient heating events that formed chondrules shortly (compared to mixing timescales) before being incorporated meteorite parent bodies. Such a constraint poses problems for the formation of chondrules in protostellar outflows as chondrules and matrix grains would have different aerodynamic properties and would be reaccreted by the solar nebula at different heliocentric distances. There appears to be no reason to expect any chemical relation between chondrules and matrix in such a formation scenario. If chondrules and matrix were chemically processed locally, and then rapidly incorporated into parent bodies, then the chemical relation between the two components can be explained. Unfortunately, the source of these heating events and how meteorite parent bodies are formed are the subjects of ongoing research, and can only provide conceptual constraints rather than detailed quantitative ones.

We conclude this section with a brief review of those recent models that have specifically addressed the chemical effects of radial mixing from distinct regions of a disk. Most of the recent models based on interstellar gas-grain chemistry have included inward radial mixing to some extent. These range from simple implementation of a limiting timescale for solving the time-dependent chemistry at each radius (e.g., *Willacy et al., 1998; Markwick et al., 2002*) to explicit solution of the advection-reaction-diffusion for gas species (*Aikawa et al., 1999a*) and dust (*Gail, 2001; Wehrstedt and Gail, 2002*). Each approach has its advantages and limitations; with the former, for example, allow-

ing for a broader range of chemical reactions to be more easily studied.

Matter at the midplane edge should initially be mostly pristine ISM material and disk gas-grain chemistry will act to modify it as it is transported inward. There should be significant gas-phase depletion at the outer edge with most of the molecules incorporated as ices. As inflowing material encounters higher temperatures, the most volatile ice species are evaporated. These will be CO and N<sub>2</sub> and chemical reactions in the outer disk can act to convert a significant fraction of this carbon and nitrogen to less-volatile species: CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, and HCN (*Aikawa et al., 1999a*). These models can therefore explain the coexistence of oxidized and reduced ices in comets, although pristine interstellar material may provide at least as good an explanation (*Ehrenfreund and Charnley, 2000*). High interstellar D/H ratios should be accreted at the outer disk and *Aikawa and Herbst (1999a, 2001)* have modeled the resulting chemistry as these molecules move inward. However, here it is also difficult to distinguish clear fractionation signatures of the mixing chemistry from that of the pristine ISM. Nevertheless, it does appear that, at least for water and HCN, mixing into the warmer region of giant planet formation tends to reduce molecular D/H ratios to values more in line with those found in comets and meteorites (*Drouart et al., 1999; Hersant et al., 2001; Robert, 2003*).

At the radius where all the volatile (water) ices are desorbed, the gas-grain interaction only sets the charge distribution in the dusty plasma. Inward radial transport to the inner nebula leads to the gas and dust being thermally and chemically modified by the high temperatures there. The nebular chemistry transitions to one close to chemical equilibrium and ultimately the transported dust is destroyed and the release of elements leads to a rich gas-phase chemistry (*Duschl et al., 1996; Bauer et al., 1997*). The composition of the nebular dust thus formed will depend on the overall elemental composition (i.e., metallicity) of the starting materials (*Wehrstedt and Gail, 2003*), as interstellar dust and gas are converted wholesale to nebular materials. For example, interstellar amorphous Mg-Fe-silicate grains will be converted to crystalline Mg-silicate and Fe particles (*Gail, 2004*). The key issue is how much of the chemistry occurring in this hot inner region can be transported radially outward, either by diffusive turbulent transport (*Morfill and Völk, 1984*) or by large-scale radial flow (*Keller and Gail, 2004*). Many detailed studies have previously considered the potential global impact of the distinct chemistries occurring in the inner nebula and the giant planet subnebulae (*Fegley and Prinn, 1989; Fegley, 1999, 2000; Kress and Tielens, 2001; Mousis et al., 2002*). A more recent motivation is the fact that crystalline silicates are found in comets (e.g., *Wooden, 2002*) and this strongly suggests efficient radial mixing out to the 5–30 AU region (*Nuth et al., 2000; Hill et al., 2001*). For example, *Boss (2004)* has considered the transport and mixing of irradiated solid particles containing isotopic anomalies in three-dimensional models of a gravitationally unstable nebula. The grains were presumed

to be deposited in an annulus on the disk surface (at 9 AU), either from the X-wind or a nearby supernova; Boss showed that this initial spatial heterogeneity could be maintained for about 1000 years and this material may have eventually been incorporated into chondrites. Recent modeling by Gail and co-workers have considered the chemical effects of the combustion and oxidation of carbon dust, as well as the annealing of amorphous silicates and the mixing of the products to large heliocentric distances. Combustion of carbonaceous dust occurs above about 1000 K and leads to high abundances of gaseous methane (Gail, 2001; Wehrstedt and Gail, 2002). Amorphous silicates are annealed at about 800 K and are vaporized above 1500 K, leading to the release of metals (Mg, Fe) and oxygen into the hot gas. Oxidation of carbon dust can proceed mainly through attack by reactive hydroxyl radicals and leads to its conversion to CO and hydrocarbons. Mixing models show that chemical compositions broadly compatible with that determined for primitive solar system bodies and materials can be accounted for (Gail, 2001, 2004; Bockelée-Morvan *et al.*, 2002).

The products of UV or X-ray mediated chemistries in the warm layers and surfaces of the disk require efficient vertical mixing to the midplane to be of relevance to meteoritics. Higher temperatures in the layers above the midplane may also allow specific chemistries to be more viable there, e.g., PAH formation. Vertical chemical mixing has been limited to only a few recent studies. Ilgner *et al.* (2004) studied the effect of mass transport in the inner disk, within a heliocentric distance of 10 AU, by radial advection and vertical diffusion in a 1 + 1-dimensional  $\alpha$ -disk model. They showed that the global chemistry of simple sulfur-bearing molecules (e.g., CS, SO, SO<sub>2</sub>) was strongly influenced by the transport of material between environments with differing temperature and irradiation flux. However, the focus of this work was to make specific predictions for future radio observations of astronomical disks rather than make a connection with nebular chemistry. Lyons and Young (2004) have constructed a simple time-dependent model of the volatile chemistry in the outer nebula (at a heliocentric distance of 30 AU) resulting from the exchange of material between the upper disk layers and the midplane. They showed that vertical diffusion can mix surface material that has experienced the selective photodissociation of the CO isotopomers down into the midplane. Subject to how vigorous the mixing is and the FUV flux at the surface, a mass-independent fractionation in gaseous water molecules can be obtained, consistent with that measured in carbonaceous chondrites.

In summary, the dynamical transport of material could lead to material enhancements or depletions at a given location of the nebula. In addition, if alteration reactions are slow, material can be created in a given location of the nebula and then carried to a region of the nebula where it would not have formed, creating a factory-belt effect for products within the nebula. Because spatial mixing may have been efficient, the diverse chemical products and isotopic abundances seen in chondritic meteorites may reflect temporal changes rather than spatial.

### 3.5. Chemistry of Transient Phenomena

Transient heating events are known to have operated in the nebula, at least affecting the physical nature of chondrules and igneous CAIs. The effects that such events would have on the chemistry of these objects and/or the matrix of chondrites remain to be determined and are the focus of ongoing study. In the case of chondrules, it is still debated whether they behaved as open or closed systems (reacting with the nebular gas or not) during the transient heating events (Sears *et al.*, 1996; Wood, 1996). This issue must be addressed because chondrules can occupy up to 80% of the volume of a given chondrite and understanding the chemical evolution of these components is critical to understanding the chemical evolution of the bodies in which they are located. In the case of matrix material, it is unknown how much of the material was present, if any, during the passage of these events. The presence of presolar grains in these meteorites proves that at least some material escaped significant processing, whereas the chondrule-matrix complementarity of primitive meteorites suggests that a bulk of the material in chondrites was processed in a similar way.

While there has been uncertainty in the chemical behavior of chondrules while they were thermally processed, there is evidence that at least some parts of chondrules did react with the nebular gas during the transient heating event. Lauretta *et al.* (2001) observed layers of fayalite and troilite on metal grains thought to have been expelled from the chondrule melts in the Bishunpur meteorite. These layers likely formed simultaneously, and using equilibrium and kinetic chemical modeling, Lauretta *et al.* (2001) was able to calculate that the corrosion reactions must have taken place at a total pressure of 10<sup>-5</sup>–10<sup>-4</sup> bar, between the temperatures of 1261 and 1173 K, and in an environment where dust was enhanced by a factor of ~300 over the canonical solar value, demonstrating the occurrence of chemical reactions that would not be possible under canonical conditions.

Besides determining chondrule compositions, other chemical effects may have occurred in the nebula, depending on the nature of the transient heating event. If lightning discharges occurred, the increase in short-wavelength photons may have triggered some chemical reactions. If collisions among planetesimals were important, then this could have led to mixing of material depending on the source regions of these objects. Once the details of how these various transient heating events are understood, then the chemistry that would take place as a result can be investigated.

As another example, shock waves have been studied in detail as ways of forming chondrules (Connolly *et al.*, 2006). As gas enters a shock wave, its temperature and density increase, leading to pressure enhancements of factors of 10–100. By creating an environment that would not exist under canonical nebular conditions, shocks may have allowed chemical reactions to take place that would not have otherwise occurred. This is demonstrated by looking at the reaction times given by the simple collision theory. The time for a reaction to take place decreases with increasing partial pressure of the reacting species because collisions are more

common, and if temperatures are increased, more energetic. Increases in the pressure due to shock waves may allow reactions that are kinetically inhibited under canonical conditions to take place in the nebula. *Ciesla et al.* (2003) explored this possibility by calculating the partial pressure of water that would be produced by a shock wave in an icy region of the nebula. It was found that if ice was locally concentrated in the nebula by factors of a few hundred, similar to the dust enhancements required by *Lauretta et al.* (2001), the time for 10–100-nm phyllosilicates to form via gas-solid reactions would be on the order of hours or days as opposed to billions of years under canonical conditions. This could explain the observed textures of fine-grained rims in CM chondrites that have been interpreted to be due to the accretion of both hydrous and anhydrous material by chondrules (*Metzler et al.*, 1992; *Lauretta et al.*, 2000). The enhanced pressures behind a shock wave may also have helped suppress volatile vaporization or isotopic fractionation from chondrules (*Galy et al.*, 2000). Thus, in addition to being able to match the thermal histories of chondrules, shock waves may also be able to explain aspects of chondrite chemistry.

#### 4. SUMMARY AND OUTLOOK

In considering the chemical evolution of the solar nebula, one must also consider its physical evolution. This physical evolution was responsible for determining the conditions within the nebula that directly affected what chemistry could take place. The key quantities to bear in mind in looking at this evolution are the timescales for the various phenomena: the timescale for the chemical reaction to go to completion ( $t_{\text{chem}}$ ), the timescale for the reactants to move out of the region of the nebula where the reaction could take place ( $t_{\text{move}}$ ), and the timescale for the nebular environment to change such that the reaction is no longer favored ( $t_{\text{evolve}}$ ). If either of the latter two timescales are shorter than the former, then the reaction is not going to occur in the area of interest. Thus, those reactions that occurred in the nebula were those that were kinetically fast and could take place over a range of nebular conditions.

In general, the inner nebula had much more energy (higher temperatures) available to facilitate chemical reactions. This energy made chemical reactants more mobile and decreased the amount of time for a chemical reaction to take place. Thus, equilibrium predictions are more closely matched by objects formed in the inner nebula than in the outer nebula. Despite this, local and transient processes occurred that disrupted the path to equilibrium, and evidence for such processes are also observed.

Our best clues of the processes that operated in the inner solar nebula come in the form of the chondritic meteorites. Chondritic meteorites directly sample the chemical products of the solar nebula. The different physical processes that affected the components of these objects and their accretion into the meteorite parent bodies also determined their chemical evolution. The fact that there are differences in chemistry among the chondrites implies their formation

took place in different chemical environments. These environments may have varied with location and/or time. Unraveling the exact cause of these differences remains one of the goals of chemical studies of the solar nebula.

Our understanding of solar nebula chemistry, at finer spatial scales and different evolutionary stages, will benefit greatly in the near future from dynamical-chemical models and observations of astronomical protostellar and protoplanetary disks. Hydrodynamics in three dimensions with a full chemistry is a daunting task, as is even two-dimensional modeling of a realistic, reduced chemistry in a magnetohydrodynamical disk. However, recent approximate methods show that much can be done using simple two-dimensional or 1 + 1-dimensional models (*Bockelée-Morvan et al.*, 2002; *Ilgner et al.*, 2004). Particularly important for meteoritics will be studies of specific fractionation chemistries and the redistribution of enhancements and anomalies, by dynamical mixing, throughout the nebula. Additional gas-grain processes will be included and here input from laboratory astrophysics will be important (e.g., *Gardner et al.*, 2003). Observational diagnostics are beginning to be included into disk models (e.g., *Kamp et al.*, 2003; *Gorti and Hollenbach*, 2004; *Semenov et al.*, 2005), and this approach will allow molecular line emission characteristics (line profiles, etc.) and dust spectral energy distributions to be compared directly with observations.

Spacebased and groundbased telescopes will greatly improve our understanding of disk chemical evolution. Observations with the Spitzer Space Telescope (SST) will now permit “snapshots” to be taken of the evolutionary sequence from molecular cores to protoplanetary disks (*Evans et al.*, 2003). Spectroscopic SST observations of dusty astronomical disks, at different stages of their evolution, will provide important data on their chemical and physical evolution. The Herschel satellite (*Pilbratt*, 2005) will make FIR and submillimeter observations of disks. Here, for example, observations of isotopomers of water, CO, and other molecules will be made that could test currently proposed disk fractionation mechanisms.

Groundbased instruments, operating at millimeter and submillimeter wavelengths, will permit protoplanetary disk chemistry to be studied at high spatial resolution. Observations with the Submillimeter Array (SMA) show that this instrument can be an important tool for studying the chemistry of young disks and their surroundings (*Kuan et al.*, 2004; *Qi et al.*, 2004). At present, apart from CO bandhead from emission from the hot inner disk, molecular emission is only detected from the surfaces and warm intermediate layers of the outer disk (~30–60 AU at 150 pc). The Atacama Large Millimeter Array (ALMA) will allow the chemistry of protoplanetary disks to be studied at spatial resolution of a few AU; ALMA will allow the radial and vertical chemical and physical structures of disks to be measured at scales on the order of a few AU (*Wootten*, 2001). In particular, the chemistry of the disk, within the planet-forming region (~10–30 AU at 150 pc) will also be accessible to ALMA. ALMA will allow many trace species, including isotopomers, to be detected. Astronomical observations will there-

fore constrain the chemical models and hopefully lead to a comprehensive and quantitative understanding of the chemistry in protoplanetary disk analogs of the protosolar nebula.

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## REFERENCES

- Adams F. C. and Lin D. N. C. (1993) Transport processes and the evolution of disks. In *Protostars and Planets III* (E. H. Levy and J. I. Lunine, eds.), pp. 721–748. Univ. of Arizona, Tucson.
- Aikawa Y. and Herbst E. (1999a) Deuterium fractionation in protoplanetary disks. *Astrophys. J.*, *526*, 314–326.
- Aikawa Y. and Herbst E. (1999b) Molecular evolution in protoplanetary disks. Two-dimensional distributions and column densities of gaseous molecules. *Astron. Astrophys.*, *351*, 233–246.
- Aikawa Y. and Herbst E. (2001) Two-dimensional distributions and column densities of gaseous molecules in protoplanetary disks. II Deuterated species and UV shielding by ambient clouds. *Astron. Astrophys.*, *371*, 1107–1117.
- Aikawa Y., Miyama S. M., Nakano T., and Umebayashi T. (1996) Evolution of molecular abundance in gaseous disks around young stars: Depletion of CO molecules. *Astrophys. J.*, *467*, 684–697.
- Aikawa Y., Umebayashi T., Nakano T., and Miyama S. M. (1997) Evolution of molecular abundance in protoplanetary disks. *Astrophys. J. Lett.*, *486*, L51–L54.
- Aikawa Y., Umebayashi T., Nakano T., and Miyama S. (1999a) Evolution of molecular abundances in protoplanetary disks with accretion flow. *Astrophys. J.*, *519*, 705–725.
- Aikawa Y., Herbst E., and Dzegilenko F. N. (1999b) Grain surface recombination of HCO<sup>+</sup>. *Astrophys. J.*, *527*, 262–265.
- Aikawa Y., van Zadelhoff G.-H., van Dishoeck E. F., and Herbst E. (2002) Warm molecular layers in protoplanetary disks. *Astron. Astrophys.*, *386*, 622–632.
- Aikawa Y., Momose M., Thi W.-F., van Zadelhoff G.-H., Qi C., Blake G. A., and van Dishoeck E. F. (2003) Interferometric observations of formaldehyde in the protoplanetary disk around LkCa15. *Publ. Astron. Soc. Japan*, *55*, 11–15.
- Aléon J., Robert F., Chaussidon M., and Marty B. (2003) Nitrogen isotopic composition of macromolecular organic matter in interplanetary dust particles. *Geochim. Cosmochim. Acta*, *67*, 3773–3783.
- Alexander C. M. O'D. (2005) Re-examining the role of chondrules in producing elemental fractionations in chondrites (abstract). In *Lunar and Planetary Science XXXVI*, Abstract #1348. Lunar and Planetary Institute, Houston (CD-ROM).
- Allamandola L. J., Sandford S. A., and Valero G. J. (1988) Photochemical and thermal evolution of interstellar/precometary ice analogs. *Icarus*, *76*, 225–252.
- Allamandola L. J., Tielens G. G. M., and Barker J. R. (1989) Interstellar polycyclic aromatic hydrocarbons — The infrared emission bands, the excitation/emission mechanism, and the astrophysical implications. *Astrophys. J. Suppl. Ser.*, *71*, 733–775.
- Allamandola L. J., Bernstein M. P., and Sandford S. A. (1997) Photochemical evolution of interstellar/precometary organic material. In *Astronomical and Biochemical Origins and the Search for Life in the Universe* (C. B. Cosmovici et al., eds.), pp. 23–47. Editrice Compositori, Bologna.
- Arpigny, C., Jehin, E., Manfroid, J., Hutesmekers, D., Zucconi, J.-M., Schulz, R., and Stuewe J. A. (2003) Anomalous nitrogen isotope ratio in comets. *Science*, *301*, 1522–1524.
- Anders E. (1975) On the depletion of moderately volatile elements in ordinary chondrites. *Meteoritics*, *10*, 283–286.
- Anders E. (1977) Critique of 'Nebular condensation of moderately volatile elements and their abundances in ordinary chondrites' by Chien M. Wai and John T. Wasson. *Earth Planet. Sci. Lett.*, *36*, 14–20.
- Balbus S. A. and Hawley J. F. (1991) A powerful local shear instability in weakly magnetized disks. I — Linear analysis. II — Nonlinear evolution. *Astrophys. J.*, *376*, 214–233.
- Bauer I., Finocchi F., Duschl W. J., Gail H.-P., and Schloeder J. P. (1997) Simulation of chemical reactions and dust destruction in protoplanetary accretion disks. *Astron. Astrophys.*, *317*, 273–289.
- Bell K. R., Cassen P. M., Wasson J. T., and Woolum D. S. (2000) The FU Orionis phenomenon and solar nebula material. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 897–926. Univ. of Arizona, Tucson.
- Bergin E. A., Najita J., and Ullom J. N. (2001) X-ray desorption of molecules from grains in protoplanetary disks. *Astrophys. J.*, *561*, 880–889.
- Bernstein M., Sandford S. A., Allamandola L. J., Chang S., and Scharberg M. A. (1995) Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophys. J.*, *454*, 327–344.
- Bockelée-Morvan D., Gautier D., Hersant F., Hure J.-M., and Robert F. (2002) Turbulent radial mixing in the solar nebula as the source of crystalline silicates in comets. *Astron. Astrophys.*, *384*, 1107–1118.
- Boss A. P. (1998) Temperatures in protoplanetary disks. *Annu. Rev. Earth Planet. Sci.*, *26*, 53–80.
- Boss A. P. (2004) Evolution of the solar nebula. VI. Mixing and transport of isotopic heterogeneity. *Astrophys. J.*, *616*, 1265–1277.
- Boss A. P. and Foster P. N. (1998) Injection of short-lived isotopes into the presolar cloud. *Astrophys. J. Lett.*, *494*, L103–106.
- Botta O. and Bada J. (2002) Extraterrestrial organic compounds in meteorites. *Surv. Geophys.*, *23*, 411–467.
- Calvet N., Hartmann L., and Strom S. E. (2000) Evolution of disk accretion. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 377–399. Univ. of Arizona, Tucson.
- Cameron A. G. W. (1995) The first ten million years in the solar nebula. *Meteoritics*, *30*, 133–161.
- Cameron A. G. W. and Truran J. W. (1977) The supernova trigger for formation of the solar system. *Icarus*, *30*, 447–461.
- Carr J. S., Tokunaga A. T., and Najita J. (2004) Hot H<sub>2</sub>O emission and evidence for turbulence in the disk of a young star. *Astrophys. J.*, *603*, 213–220.
- Caselli P., van der Tak F. F. S., Ceccarelli C., and Bacmann A. (2003) Abundant H<sub>2</sub>D<sup>+</sup> in the pre-stellar core L1544. *Astron. Astrophys.*, *403*, L37–L41.
- Cassen P. (1994) Utilitarian models of the solar nebula. *Icarus*, *112*, 405–429.
- Cassen P. (1996) Models for the fractionation of moderately volatile elements in the solar nebula. *Meteoritics & Planet. Sci.*, *31*, 793–806.

- Cassen P. (2001) Nebular thermal evolution and the properties of primitive planetary materials. *Meteoritics & Planet. Sci.*, *36*, 671–700.
- Cassen P. and Moosman A. (1981) On the formation of protostellar disks. *Icarus*, *48*, 353–376.
- Ceccarelli C. and Dominik C. (2005) Deuterated H<sub>3</sub><sup>+</sup> in proto-planetary disks. *Astron. Astrophys.*, *440*, 583–593.
- Ceccarelli C., Dominik C., Lefloch B., Caselli P., and Caux E. (2004) Detection of H<sub>2</sub>D<sup>+</sup>: Measuring the midplane degree of ionization in the disks of DM Tauri and TW Hydrae. *Astrophys. J. Lett.*, *607*, L51–L54.
- Charnley S. B. (1995) The interstellar chemistry of protostellar disks. *Astrophys. Space Sci.*, *224*, 441–442.
- Charnley S. B. (2001) Interstellar organic chemistry. In *The Bridge Between the Big Bang and Biology* (F. Giovannelli, ed.), pp. 139–149. Consiglio Nazionale delle Ricerche President Bureau, Rome.
- Charnley S. B. and Rodgers S. D. (2002) The end of interstellar chemistry as the origin of nitrogen in comets and meteorites. *Astrophys. J. Lett.*, *569*, L133–L137.
- Cherchneff I., Tielens A. G. G. M., and Barker J. (1992) Polycyclic aromatic hydrocarbon formation in carbon-rich stellar envelopes. *Astrophys. J.*, *401*, 269–287.
- Chiang E.I. and Goldreich P. (1997) Spectral energy distributions of T Tauri stars with passive circumstellar disks. *Astrophys. J.*, *490*, 368–376.
- Chick K. M. and Cassen P. (1997) Thermal processing of interstellar dust grains in the primitive solar environment. *Astrophys. J.*, *477*, 398–409.
- Ciesla F. J. and Lauretta D. S. (2005) Radial migration of phyllosilicates in the solar nebula. *Earth. Planet. Sci. Lett.*, *231*, 1–8.
- Ciesla F. J., Lauretta D. S., Cohen B. A., and Hood L. L. (2003) A nebular origin for chondritic fine-grained phyllosilicates. *Science*, *299*, 549–552.
- Clayton R. N. (2002a) Self-shielding in the solar nebula. *Nature*, *415*, 860–861.
- Clayton R. N. (2002b) Photochemical self-shielding in the solar nebula (abstract). In *Lunar and Planetary Science XXXIII*, Abstract #1326. Lunar and Planetary Institute, Houston (CD-ROM).
- Clayton R. N. (2002c) Nitrogen isotopic fractionation by photochemical self-shielding (abstract). *Meteoritics & Planet. Sci.*, *37*, A35.
- Clayton R. N. (2003) Oxygen isotopes in the solar system. *Space Sci. Rev.*, *106*, 19–32.
- Connolly H. C. Jr., Desch S. J., Ash R. D., and Jones R. H. (2006) Transient heating events in the protoplanetary nebula. In *Meteorites and the Early Solar System II* (D. S. Lauretta and H. Y. McSween Jr., eds.), this volume. Univ. of Arizona, Tucson.
- Cronin J. R. and Chang S. (1993) Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The Chemistry of Life's Origins* (J. M. Greenberg et al., eds.), pp. 209–258. Kluwer, Dordrecht.
- Cuzzi J. N. and Weidenschilling S. J. (2006) Particle-gas dynamics and primary accretion. In *Meteorites and the Early Solar System II* (D. S. Lauretta and H. Y. McSween Jr., eds.), this volume. Univ. of Arizona, Tucson.
- Cuzzi J. N. and Zahnle K. J. (2004) Material enhancement in protoplanetary nebulae by particle drift through evaporation fronts. *Astrophys. J.*, *614*, 490–496.
- Cyr K. E., Sears W. D., and Lunine J. I. (1998) Distribution and evolution of water ice in the solar nebula: Implications for solar system body formation. *Icarus*, *135*, 537–548.
- Cyr K. E., Sharp C. M., and Lunine J. I. (1999) Effects of the redistribution of water in the solar nebula on nebular chemistry. *J. Geophys. Res.*, *104*, 19003–19014.
- Dartois E., Dutrey A., and Guilloteau S. (2003) Structure of the DM Tau outer disk: Probing the vertical kinetic temperature gradient. *Astron. Astrophys.*, *399*, 773–787.
- Dolginov A. Z. and Stepinski T. F. (1994) Are cosmic rays effective for ionization of protoplanetary disks? *Astrophys. J.*, *427*, 377–383.
- Drouart A., Dubrulle B., Gautier D., and Robert F. (1999) Structure and transport in the solar nebula from constraints on deuterium enrichment and giant planets formation. *Icarus*, *40*, 129–155.
- Duschl W. J., Gail H.-P., and Tscharnuter W. M. (1996) Destruction processes for dust in protoplanetary accretion disks. *Astron. Astrophys.*, *312*, 624–642.
- Dutrey A., Guilloteau S., and Simon M. (1994) Images of the GG Tauri rotating ring. *Astron. Astrophys.*, *286*, 149–159.
- Dutrey A., Guilloteau S., and Guélin M. (1997) Chemistry of protosolar-like nebulae: The molecular content of the DM Tau and GG Tau disks. *Astron. Astrophys.*, *317*, L55–L58.
- Dutrey A., Guilloteau S., and Guélin M. (2000) Observations of the chemistry in circumstellar disks. In *Astrochemistry: From Molecular Clouds to Planetary Systems* (Y. C. Minh et al., eds.), pp. 415–423. Astronomical Society of the Pacific, Sogwipo.
- Ebel D. S. (2006) Condensation of rocky material in astrophysical environments. In *Meteorites and the Early Solar System II* (D. S. Lauretta and H. Y. McSween Jr., eds.), this volume. Univ. of Arizona, Tucson.
- Ebel D. S. and Grossman L. (2000) Condensation in dust-enriched systems. *Geochim. Cosmochim. Acta*, *64*, 339–366.
- Ehrenfreund P. and Charnley S. B. (2000) Organic molecules in the interstellar medium, comets, and meteorites: A voyage from dark clouds to the early Earth. *Annu. Rev. Astron. Astrophys.*, *38*, 427–483.
- Ehrenfreund P., Charnley S. B., and Wooden D. H. (2004) From ISM material to comet particles and molecules. In *Comets II* (M. C. Festou et al., eds.), pp. 115–133. Univ. of Arizona, Tucson.
- Elmegreen B. G. (2000) Star formation in a crossing time. *Astrophys. J.*, *530*, 277–281.
- Evans N. (1999) Physical conditions in regions of star formation. *Annu. Rev. Astron. Astrophys.*, *37*, 311–362.
- Evans N. J. and 17 colleagues (2003) From molecular cores to planet-forming disks: A SIRTf legacy. *Publ. Astron. Soc. Pac.*, *115*, 965–980.
- Fegley B. J. (1988) Cosmochemical trends of volatile elements in the solar system. In *Workshop on the Origins of Solar Systems* (J. A. Nuth and P. Sylvester, eds.), pp. 51–59. Lunar and Planetary Institute, Houston.
- Fegley B. (1999) Chemical and physical processing of presolar materials in the solar nebula and the implications for preservation of presolar materials in comets. *Space Sci. Rev.*, *90*, 239–252.
- Fegley B. (2000) Kinetics of gas-grain reactions in the solar nebula. *Space Sci. Rev.*, *92*, 177–200.
- Fegley B. J. and Prinn R. G. (1989). Solar nebula chemistry — Implications for volatiles in the solar system. In *The Formation and Evolution of Planetary Systems* (H. A. Weaver et al., eds.), pp. 171–205. Univ. of Arizona, Tucson.
- Feigelson E. D., Casanova S., Montmerle T., and Guibert J. (1993) ROSAT X-ray study of the Chamaleon I dark cloud. I. The

- stellar population. *Astrophys. J.*, 416, 623–646.
- Finocchi F. and Gail H.-P. (1997) Chemical reactions in protoplanetary accretion disks. III. The role of ionisation processes. *Astron. Astrophys.*, 327, 825–844.
- Frenklach M. and Feigelson E. D. (1989) Formation of polycyclic aromatic hydrocarbons in circumstellar envelopes. *Astrophys. J.*, 341, 372–384.
- Gail H.-P. (2001) Radial mixing in protoplanetary accretion disks. I. Stationary disc models with annealing and carbon combustion. *Astron. Astrophys.*, 378, 192–213.
- Gail H.-P. (2004) Radial mixing in protoplanetary accretion disks. IV. Metamorphosis of the silicate dust complex. *Astron. Astrophys.*, 413, 571–591.
- Galy A., Young E. D., Ash R. D., and O’Nions R. K. (2000). The formation of chondrules at high gas pressures in the solar nebula. *Science*, 290, 1751–1754.
- Gammie C. F. (1996) Layered accretion in T Tauri disks. *Astrophys. J.*, 457, 355–362.
- Gardner K., Li J., Dworkin J., Cody G. D., Johnson N., and Nuth J. A. III (2003) A first attempt to simulate the natural formation of meteoritic organics (abstract). In *Lunar and Planetary Science XXXIV*, Abstract #1613. Lunar and Planetary Institute, Houston (CD-ROM).
- Glassgold A. E., Najita J., and Igea J. (1997) X-ray ionization of protoplanetary disks. *Astrophys. J.*, 480, 344–350.
- Glassgold A. E., Najita J., and Igea J. (2004) Heating protoplanetary disk atmospheres. *Astrophys. J.*, 615, 972–990.
- Goldsmith P. F., Langer W. D., and Velusamy T. (1999) Detection of methanol in a Class 0 Protostellar disk. *Astrophys. J. Lett.*, 519, L173–L176.
- Gorti U. and Hollenbach D. (2004) Models of chemistry, thermal balance, and infrared spectra from intermediate-aged disks around G and K stars. *Astrophys. J.*, 613, 424–447.
- Grossman L. (1972) Condensation in the primitive solar nebula. *Geochim. Cosmochim. Acta*, 36, 597–619.
- Haghighipour N. and Boss A. (2003) On gas drag-induced rapid migration of solids in a nonuniform solar nebula. *Astrophys. J.*, 598, 1301–1311.
- Hartmann L. (2000) Observational constraints on transport (and mixing) in pre-main sequence disks. *Space Sci. Rev.*, 92, 55–68.
- Hartmann L., Calvet N., Gullbring E., and D’Alessio P. (1998) Accretion and the evolution of T Tauri disks. *Astrophys. J.*, 495, 385–400.
- Hartmann L., Ballesteros-Paredes J., and Bergin E. A. (2001) Rapid formation of molecular clouds and stars in the solar neighborhood. *Astrophys. J.*, 562, 852–868.
- Hayashi C. (1981) Structure of the solar nebula, growth and decay of magnetic fields and effects of magnetic and turbulent viscosities on the nebula. *Prog. Theor. Phys. Suppl.*, 70, 35–53.
- Herbst E. (2000) Models of gas-grain chemistry in star-forming regions. In *Astrochemistry: From Molecular Clouds to Planetary Systems* (Y. C. Minh and E. F. van Dishoeck, eds.), pp. 147–159. Astronomical Society of the Pacific, Sogwipo.
- Hersant F., Gautier D., and Huré J. (2001). A two-dimensional model for the primordial nebula constrained by D/H measurements in the solar system: Implications for the formation of giant planets. *Astrophys. J.*, 554, 391–407.
- Hester J. J., Desch S. J., Healy K. R., and Leshin L. A. (2004) The cradle of the solar system. *Science*, 304, 1116–1117.
- Hill H. G. M., Grady C. A., Nuth J. A. III, Hallenbeck S. L., and Sitko M. L. (2001) Constraints on nebular dynamics and chemistry based on observations of annealed magnesium silicate grains in comets and in disks surrounding Herbig Ae/Be stars. *Proc. Natl. Acad. Sci.*, 98, 2182–2187.
- Hollenbach D. and McKee C. F. (1979) Molecule formation and infrared emission in fast interstellar shocks. I Physical processes. *Astrophys. J. Suppl. Ser.*, 41, 555–592.
- Hollenbach D. J., Yorke H. W., and Johnstone D. (2000) Disk dispersal around young stars. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 401–428. Univ. of Arizona, Tucson.
- Hudson R. L. and Moore M. H. (2001) Radiation chemical alterations in solar system ices: An overview. *J. Geophys. Res.*, 106, 33275–33284.
- Hutchison R. (2002) Major element fractionation in chondrites by distillation in the accretion disk of a T Tauri Sun? *Meteoritics & Planet. Sci.*, 37, 113–124.
- Hutson M. and Ruzicka A. (2000) A multi-step model for the origin of E3 (enstatite) chondrites. *Meteoritics & Planet. Sci.*, 35, 601–608.
- Igea J. and Glassgold A. E. (1999) X-ray ionization of the disks of young stellar objects. *Astrophys. J.*, 518, 848–858.
- Ilgner M., Henning Th., Markwick A. J., and Millar T. J. (2004) The influence of transport processes on the chemical evolution in steady accretion disk flows. *Astron. Astrophys.*, 415, 643–659.
- Kamp I., van Zadelhoff G. J., van Dishoeck E. F., and Stark R. (2003) Line emission from circumstellar disks around A stars. *Astron. Astrophys.*, 397, 1129–1141.
- Kastner J. H., Zuckerman B., Weintraub D. A., and Forveille T. (1997) X-ray and molecular emission from the nearest region of recent star formation. *Science*, 277, 67–71.
- Keller Ch. and Gail H.-P. (2004) Radial mixing in protoplanetary accretion disks. VI. Mixing by large-scale radial flows. *Astron. Astrophys.*, 415, 1177–1185.
- Kress M. E. and Tielens A. G. G. M. (2001) The role of Fischer-Tropsch catalysis in solar nebula chemistry. *Meteoritics & Planet. Sci.*, 36, 75–92.
- Krot A. N., Fegley B., Lodders K., and Palme H. (2000) Meteoritical and astrophysical constraints on the oxidation state of the solar nebula. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 1019–1054. Univ. of Arizona, Tucson.
- Krot A. N., Hutcheon I. D., Yurimoto H., Cuzzi J. N., McKeegan K. D., Scott E. R. D., Libourel G., Chaussidon M., Aléon J., and Petaev M. I. (2005) Evolution of oxygen isotopic composition in the inner solar nebula. *Astrophys. J.*, 622, 1333–1342.
- Kuan Yi-J. and 10 colleagues (2004) Organic molecules in low-mass protostellar hot cores: Submillimeter imaging of IRAS 16293-2422. *Astrophys. J. Lett.*, 616, L27–L30.
- Lada C. J. and Shu F. H. (1990) The formation of sunlike stars. *Science*, 248, 564–572.
- Lauretta D. S., Hua X., and Buseck P. R. (2000) Mineralogy of fine-grained rims in the ALH 81002 CM chondrite. *Geochim. Cosmochim. Acta*, 64, 3263–3273.
- Lauretta D. S., Buseck P. R., and Zega T. J. (2001) Opaque minerals in the matrix of the Bishunpur (LL3.1) chondrite: Constraints on the chondrule formation environment. *Geochim. Cosmochim. Acta*, 65, 1337–1353.
- Lee T., Shu F. H., Shang H., Glassgold A., and Rehm K. E. (1998) Protostellar cosmic rays and extinct radioactivities in meteorites. *Astrophys. J.*, 506, 898–912.
- Léger A., Jura M., and Omont A. (1985) Desorption from interstellar grains. *Astron. Astrophys.*, 144, 147–160.

- Le Teuff Y.-H., Millar T. J., and Markwick A. J. (2000) The UMIST database for astrochemistry 1999. *Astron. Astrophys. Suppl. Ser.*, 146, 157–168.
- Lewis J. S. (1972) Metal/silicate fractionation in the solar system. *Earth Planet. Sci. Lett.*, 15, 286–290.
- Lewis J. S. and Prinn R. G. (1980) Kinetic inhibition of CO and N<sub>2</sub> reduction in the solar nebula. *Astrophys. J.*, 238, 357–364.
- Liffman K. and Toscano M. (2000) Chondrule fine-grained mantle formation by hypervelocity impact of chondrules with a dusty gas. *Icarus*, 143, 106–125.
- Lodders K. (2003) Solar system abundances and condensation temperatures of the elements. *Astrophys. J.*, 591, 1220–1247.
- Lunine J. I., Engel S., Rizk B., and Horanyi M. (1991) Sublimation and reformation of icy grains in the primitive solar nebula. *Icarus*, 94, 333–344.
- Lyons J. R. and Young E. D. (2003) Towards an evaluation of self-shielding at the X-point as the origin of the oxygen isotope anomaly in CAIs (abstract). In *Lunar and Planetary Science XXXIV*, Abstract #1981. Lunar and Planetary Institute, Houston (CD-ROM).
- Lyons J. R. and Young E. D. (2004) Evolution of oxygen isotopes in the solar nebula (abstract). In *Lunar and Planetary Science XXXV*, Abstract #1970. Lunar and Planetary Institute, Houston (CD-ROM).
- Mac Low M.-M. and Klessen R. S. (2004) Control of star formation by supersonic turbulence. *Rev. Mod. Phys.*, 76, 125–194.
- Maloney P. R., Hollenbach D. J., and Tielens A. G. G. M. (1996) X-Ray irradiated molecular gas. I. Physical processes and general results. *Astrophys. J.*, 466, 561–584.
- Markwick A. J. and Charnley S. B. (2004) Physics and chemistry of protoplanetary disks: Relation to primitive solar system material. In *Astrobiology: Future Perspectives* (P. Ehrenfreund et al., eds.), pp. 32–65. Kluwer, Dordrecht.
- Markwick A. J., Ilgner M., Millar T. J., and Henning Th. (2002) Molecular distributions in the inner regions of protostellar disks. *Astron. Astrophys.*, 385, 632–646.
- Matsuyama I., Johnstone D., and Hartmann L. (2003). Viscous diffusion and photoevaporation of stellar disks. *Astrophys. J.*, 582, 893–904.
- Metzler K., Bischoff A., and Stoeffler D. (1992). Accretionary dust mantles in CM chondrites — Evidence for solar nebula processes. *Geochim. Cosmochim. Acta*, 56, 2873–2897.
- Millar T. J., Nomura H., and Markwick A. J. (2003) Two-dimensional models of protoplanetary disk chemistry. *Astrophys. Space Sci.*, 285, 761–768.
- Montmerle T., Koch-Miramond L., Falgarone E., and Grindlay J. E. (1983) Einstein observations of the Rho Ophiuchi dark cloud — an X-ray Christmas tree. *Astrophys. J.*, 269, 182–201.
- Morfill G. E. and Völk H. J. (1984) Transport of dust and vapor and chemical fractionation in the early protosolar cloud. *Astrophys. J.*, 287, 371–395.
- Morgan W. A. Jr., Feigelson E. D., Wang H., and Frenklach M. (1991) A new mechanism for the formation of meteoritic kero-gen-like material. *Science*, 252, 109–112.
- Mousis O., Gautier D., and Bockelée-Morvan D. (2002) An evolutionary turbulent model of Saturn's subnebula: Implications for the origin of the atmosphere of Titan. *Icarus*, 156, 162–175.
- Mundy L. G., Looney L. W., and Welch W. J. (2000). The structure and evolution of envelopes and disks in young stellar systems. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 355–376. Univ. of Arizona, Tucson.
- Neufeld D. and Hollenbach D. J. (1994) Dense molecular shocks and accretion onto protostellar disks. *Astrophys. J.*, 428, 170–185.
- Nomura H. (2002) Structure and instabilities of an irradiated viscous protoplanetary disk. *Astrophys. J.*, 567, 587–595.
- Nuth J. A., Hill H. G. M., and Kletetschka G. (2000) Determining the ages of comets from the fraction of crystalline dust. *Nature*, 406, 275–276.
- Nuth J. A. III, Charnley S. B., and Johnson N. M. (2006) Chemical processes in the interstellar medium: Source of the gas and dust in the primitive solar nebula. In *Meteorites and the Early Solar System II* (D. S. Lauretta and H. Y. McSween Jr., eds.) this volume, Univ. of Arizona, Tucson.
- Palme H. (2000) Are there chemical gradients in the inner solar system? *Space Sci. Rev.*, 92, 237–262.
- Palme H. and Boynton W. V. (1993) Meteoritic constraints on conditions in the solar nebula. In *Protostars and Planets III* (E. H. Levy and J. I. Lunine, eds.), pp. 979–1004. Univ. of Arizona, Tucson.
- Petaev M. I. and Wood J. A. (1998) The condensation with partial isolation model of condensation in the solar nebula. *Meteoritics & Planet. Sci.*, 33, 1123–1137.
- Pilbratt G. L. (2005) *The Herschel Mission: Overview and Observing Opportunities*. ESA Special Publication SP-577, in press.
- Pizzarello S. (2004) Chemical evolution and meteorites: An update. *Origins Life Evol. Biosph.*, 34, 25–34.
- Pontoppidan K. M., Dullemond C. P., van Dishoeck E. F., Blake G. A., Boogert A. C. A., Evans N. J. II, Kessler-Silacci J. E., and Lahuis F. (2005) Ices in the edge-on disk CRBR 2422.8-3423: Spitzer spectroscopy and Monte Carlo radiative transfer modeling. *Astrophys. J.*, 622, 463–481.
- Prasad S. S. and Tarafdar S. P. (1983) UV radiation field inside dense clouds: Its possible existence and chemical implications. *Astrophys. J.*, 267, 603–609.
- Qi C. (2001) Aperture synthesis studies of the chemical composition of protoplanetary disks and comets. Ph.D. thesis, California Institute of Science and Technology, Pasadena. 141 pp.
- Qi C. and 12 colleagues (2004) Imaging the disk around TW Hydrae with the submillimeter array. *Astrophys. J. Lett.*, 616, L11–L14.
- Robert F. (2003) The D/H ratio in chondrites. *Space Sci. Rev.*, 106, 87–101.
- Roberts H., Herbst E., Millar T. J. (2003) Enhanced deuterium fractionation in dense interstellar cores resulting from multiply deuterated H<sub>3</sub><sup>+</sup>. *Astrophys. J. Lett.*, 591, L41–L44.
- Ruden S. P. and Pollack J. B. (1991). The dynamical evolution of the protosolar nebula. *Astrophys. J.*, 375, 740–760.
- Ruzmaikina T. V. and Ip W. H. (1994) Chondrule formation in radiative shock. *Icarus*, 112, 430–447.
- Sandford S. A. (1996) The inventory of interstellar materials available for the formation of the solar system. *Meteoritics*, 31, 449–476.
- Sandford S. A., Bernstein M. P., and Dworkin J. P. (2001) Assessment of the interstellar processes leading to deuterium enrichment in meteoritic organics. *Meteoritics & Planet. Sci.*, 36, 1117–1133.
- Saxena S. K. and Eriksson G. (1986) Chemistry of the formation of the terrestrial planets. In *Chemistry and Physics of Terrestrial Planets* (S. K. Saxena, ed.), pp. 30–105. Springer, New York.
- Sears D. W. G., Huang S., and Benoit P. H. (1996) Open-system behaviour during chondrule formation. In *Chondrules and the*

- Protoplanetary Disk* (R. H. Hewins et al., eds.), pp. 221–232. Cambridge Univ., Cambridge.
- Semenov D., Pavlyuchenkov Y., Schreyer K., Henning Th., Dullemond C., and Bacmann A. (2005) Millimeter observations and modeling of the AB Aurigae system. *Astrophys. J.*, *621*, 853–874.
- Sephton M. A. (2002) Organic compounds in carbonaceous meteorites. *Natl. Prod. Rep.*, *19*, 292–311.
- Shu F. H., Adams F. C., and Lizano S. (1987) Star formation in molecular clouds: Observation and theory. *Annu. Rev. Astron. Astrophys.*, *25*, 23–81.
- Shu F. H., Shang H., and Lee T. (1996) Toward an astrophysical theory of chondrites. *Science*, *271*, 1545–1552.
- Shu F. H., Shang H., Glassgold A. E., and Lee T. (1997) X-rays and fluctuating X-winds from protostars. *Science*, *277*, 1475–1479.
- Simonelli D. P., Pollack J. B., and McKay C. P. (1997) Radiative heating of interstellar grains falling toward the solar nebula: 1-D diffusion calculations. *Icarus*, *125*, 261–280.
- Stevenson D. J. and Lunine J. I. (1988) Rapid formation of Jupiter by diffuse redistribution of water vapor in the solar nebula. *Icarus*, *75*, 146–155.
- Stone J. M., Gammie C. F., Balbus S. A., and Hawley J. F. (2000). Transport processes in protostellar disks. In *Protostars and Planets IV* (V. Mannings et al., eds.), pp. 589–612. Univ. of Arizona, Tucson.
- Takeuchi T. and Lin D. N. C. (2002) Radial flow of dust particles in accretion disks. *Astrophys. J.*, *581*, 1344–1355.
- Thi W.-F., van Zadelhoff G.-J., and van Dishoeck E. F. (2004) Organic molecules in protoplanetary disks around T Tauri and Herbig Ae stars. *Astron. Astrophys.*, *425*, 955–972.
- Thiemens M. H. (1999) Mass-independent isotope effects in planetary atmospheres and the early solar system. *Science*, *283*, 341–345.
- Tielens A. G. G. M. (1983) Surface chemistry of deuterated molecules. *Astron. Astrophys.*, *119*, 177–184.
- Tielens A. G. G. M. and Allamandola L. J. (1987) Composition, structure, and chemistry of interstellar dust. In *Interstellar Processes* (D. J. Hollenbach, eds.), pp. 397–469. Reidel, Dordrecht.
- Tielens A. G. G. M. and Hollenbach D. J. (1985) Photodissociation regions. I. Basic model. II. A model for the Orion photodissociation region. *Astrophys. J.*, *291*, 722–754.
- Umebayashi T. and Nakano T. (1981) Fluxes of energetic particles and the ionization rate in very dense interstellar clouds. *Publ. Astron. Soc. Japan*, *33*, 617–636.
- Umebayashi T. and Nakano T. (1988) Ionization state and magnetic fields in the solar nebula. *Prog. Theor. Phys. Suppl.*, *96*, 151–160.
- Umebayashi T. and Nakano T. (1990) Magnetic flux loss from interstellar clouds. *Mon. Not. R. Astron. Soc.*, *243*, 103–113.
- van Dishoeck E. F., Thi W.-F., and van Zadelhoff G.-H. (2003) Detection of DCO<sup>+</sup> in a circumstellar disk. *Astron. Astrophys.*, *400*, L1–L4.
- van Zadelhoff G.-J., van Dishoeck E. F., Thi W.-F., and Blake G. A. (2001) Submillimeter lines from circumstellar disks around pre-main sequence stars. *Astron. Astrophys.*, *377*, 566–580.
- van Zadelhoff G.-J., Aikawa Y., Hogerheijde M. R., and van Dishoeck E. F. (2003) Axi-symmetric models of ultraviolet radiative transfer with applications to circumstellar disk chemistry. *Astron. Astrophys.*, *397*, 789–802.
- Vanhala H. A. T. and Boss A. P. (2002) Injection of radioactivities into the forming solar system. *Astrophys. J.*, *575*, 1144–1150.
- Vanhala H. A. T. and Cameron A. G. W. (1998) Numerical simulations of triggered star formation. I. Collapse of dense molecular cloud cores. *Astrophys. J.*, *508*, 291–307.
- Wai C. M. and Wasson J. T. (1977). Nebular condensation of moderately volatile elements and their abundances in ordinary chondrites. *Earth Planet. Sci. Lett.*, *36*, 1–13.
- Wasson J. T. (1977) Reply to Edward Anders: A discussion of alternative models for explaining the distribution of moderately volatile elements in ordinary chondrites. *Earth Planet. Sci. Lett.*, *36*, 21–28.
- Wasson J. T. and Chou C. (1974) Fractionation of moderately volatile elements in ordinary chondrites. *Meteoritics*, *9*, 69–84.
- Wehrstedt M. and Gail H.-P. (2002) Radial mixing in protoplanetary disks. II. Time dependent disk models with annealing and carbon combustion. *Astron. Astrophys.*, *385*, 181–204.
- Wehrstedt M. and Gail H.-P. (2003) Radial mixing in protoplanetary accretion disks. V. Models with different element mixtures. *Astron. Astrophys.*, *410*, 917–935.
- Weidenschilling S. J. (1977) Aerodynamics of solid bodies in the solar nebula. *Mon. Not. R. Astron. Soc.*, *180*, 57–70.
- Willacy K. and Langer W. D. (2000) The importance of photoprocessing in protoplanetary disks. *Astrophys. J.*, *544*, 903–920.
- Willacy K., Klahr H. H., Millar T. J., and Henning Th. (1998) Gas and grain chemistry in a protoplanetary disk. *Astron. Astrophys.*, *338*, 995–1005.
- Wood J. (1996) Major unresolved issues in the formation of chondrules and chondrites. In *Chondrules and the Protoplanetary Disk* (R. H. Hewins et al., eds.), pp. 55–70. Cambridge Univ., Cambridge.
- Wood J. A. and Hashimoto A. (1993) Mineral equilibrium in fractionated nebular systems. *Geochim. Cosmochim. Acta*, *57*, 2377–2388.
- Wooden D. H. (2002) Comet grains: Their IR emission and their relation to ISM grains. *Earth Moon Planets*, *89*, 247–287.
- Wooden D. H., Woodward C. E., and Harker D. E. (2004) Discovery of crystalline silicates in Comet C/2001 Q4 (NEAT). *Astrophys. J. Lett.*, *612*, L77–L80.
- Wootten A., ed. (2001) *Science with the Atacama Large Millimeter Array*. ASP Conference Proceedings 235, Astronomical Society of the Pacific, San Francisco.
- Young E. D. and Lyons J. R. (2003) CO self shielding in the outer solar nebula: An astronomical explanation for the oxygen isotope slope-1 line (abstract). In *Lunar and Planetary Science XXXIV*, Abstract #1923. Lunar and Planetary Institute, Houston (CD-ROM).
- Zolotov M. Y. and Shock E. L. (2001) Stability of condensed hydrocarbons in the solar nebula. *Icarus*, *150*, 323–337.