CHEMICAL AND PHYSICAL PROCESSING OF PRESOLAR MATERIALS IN THE SOLAR NEBULA AND THE IMPLICATIONS FOR PRESERVATION OF PRESOLAR MATERIALS IN COMETS

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Abstract. Chemical and physical processes in the outer solar nebula are reviewed. It is argued that the outer nebula was a chemically active environment with UV photochemistry and ion-molecule chemistry in its low density regions and grain-catalyzed chemistry in Jovian protoplanetary subnebulae. Presolar material was altered to greater or lesser extent by these spatially and temporally variable processes, which mimic many features of interstellar chemistry. Experiments, models, and observations are recommended to address the questions of presolar versus nebular dominance in the outer solar nebula and of how to distinguish interstellar and nebular sources of cometary volatiles.

1. Introduction

Before being accreted into comets, presolar materials (e.g. grains and molecules formed in cool stellar outflows, in supernova ejecta, and molecules formed in interstellar molecular clouds) were altered to varying extents by chemical and physical processes in the solar nebula. These processes probably included, but were not necessarily limited to, heating and thermochemical reactions, UV photochemistry, ion-molecule reactions, and physical mixing with and dilution by other nebular materials. These processes occurred in the accretion shock, the solar nebula, and the Jovian protoplanetary subnebulae embedded in the outer nebula.

The extent of this reprocessing probably varied spatially and temporally resulting in different proportions of presolar and nebular materials accreted by comets formed at different radial distances in the nebula. The varying efficiencies of nebular processes combined with the different properties (e.g., vapor pressure, chemical reactivity) of presolar materials (gases, ices, organics, rocky grains) plausibly determined the extent of processing.

Three models can be considered for the origin of cometary materials: (1) the pristine interstellar grain model in which no chemical alteration, physical mixing, or dilution happens to accreted presolar material, (2) the complete chemical equilibrium model in which presolar material is altered and chemically equilibrated at the prevailing pressure and temperature conditions in the outer solar nebula, and (3) an intermediate model in which nebular reprocessing of presolar materials, and

physical mixing with and dilution by nebular materials varies in efficiency. I adopt the third model as probably being the most reasonable one.

In this paper, I review observations of the chemical and isotopic composition of cometary volatiles and chemical and physical processes in the outer solar nebula. This leads to two broad questions: What was the balance between presolar and nebular chemistry in the outer solar nebula? How can we distinguish interstellar from nebular chemistry if the same processes occur in both environments? I conclude by recommending laboratory experiments, theoretical models, and astronomical observations that can help to address these questions.

2. Chemical and Isotopic Composition of Cometary Volatiles

Figure 1, based on Eberhardt (1998) and Irvine *et al.* (1999), shows abundances of cometary volatiles relative to water. This figure emphasizes volatiles for which the most data are available; more comprehensive discussion is given in the two papers cited and elsewhere in this volume.

Water. This is the most abundant volatile in all comets where it has been measured, e.g., 80 mol % in Halley (Eberhardt, 1998). The dominance of water is broadly consistent with solar abundances because oxygen is the third most abundant element (after H and He) and is about twice as abundant as carbon in solar material. Because water is the dominant volatile and perhaps also a host phase for less abundant volatiles which may be enclathrated in it and/or absorbed on it, the physical state (discussed in other chapters), isotopic composition, and ortho-para ratio of cometary water is very important for understanding the origin of cometary volatiles. The HDO/H_2O ratios in Hale-Bopp, Halley,and Hyakutake correspond to D/H $\sim 31 \times 10^{-5}$, similar to D/H values for water in hot cores of molecular clouds (Irvine *et al.*, 1999), and about twice the D/H of 15.6×10^{-5} in terrestrial standard mean ocean water (SMOW). The $^{18}O/^{16}O$ in Halley water is $(2.03 \pm 0.15) \times 10^{-3}$, the same within error as in SMOW (Eberhardt, 1998). The ortho-para ratios and deduced spin temperatures are 2.5 ± 0.1 (29 K) in Halley,3.2 ± 0.2 (> 50 K) in Wilson, 2.45 ± 0.10 (25 K) in Hale-Bopp, and 2.7 ± 0.1 (35 K) in Hartley 2 (Irvine *et al.*, 1999). The interpretation of the ortho-para ratio in water is unclear. The D/H ratio has been used to argue for an interstellar origin, but as discussed later, comet-like HDO/H_2O ratios may also be produced by UV photochemistry in the outer nebula. Furthermore, high D/H ratios only indicate low temperature isotopic exchange. Ion-molecule reactions have low activation energies $\sim kT$(where k is Boltzmann's constant) and yield high D/H ratios for hydrides in interstellar molecular clouds and hot cores. But, the same chemistry may also occur in cold, low density regions of protoplanetary disks (Aikawa *et al.*, 1998).

Carbon compounds. Carbon is the fourth most abundant element in solar material and oxidized carbon compounds (CO, CH_3OH, CO_2, H_2CO) are the next most abundant volatiles (after water) observed in comets. As Figure 1 shows the
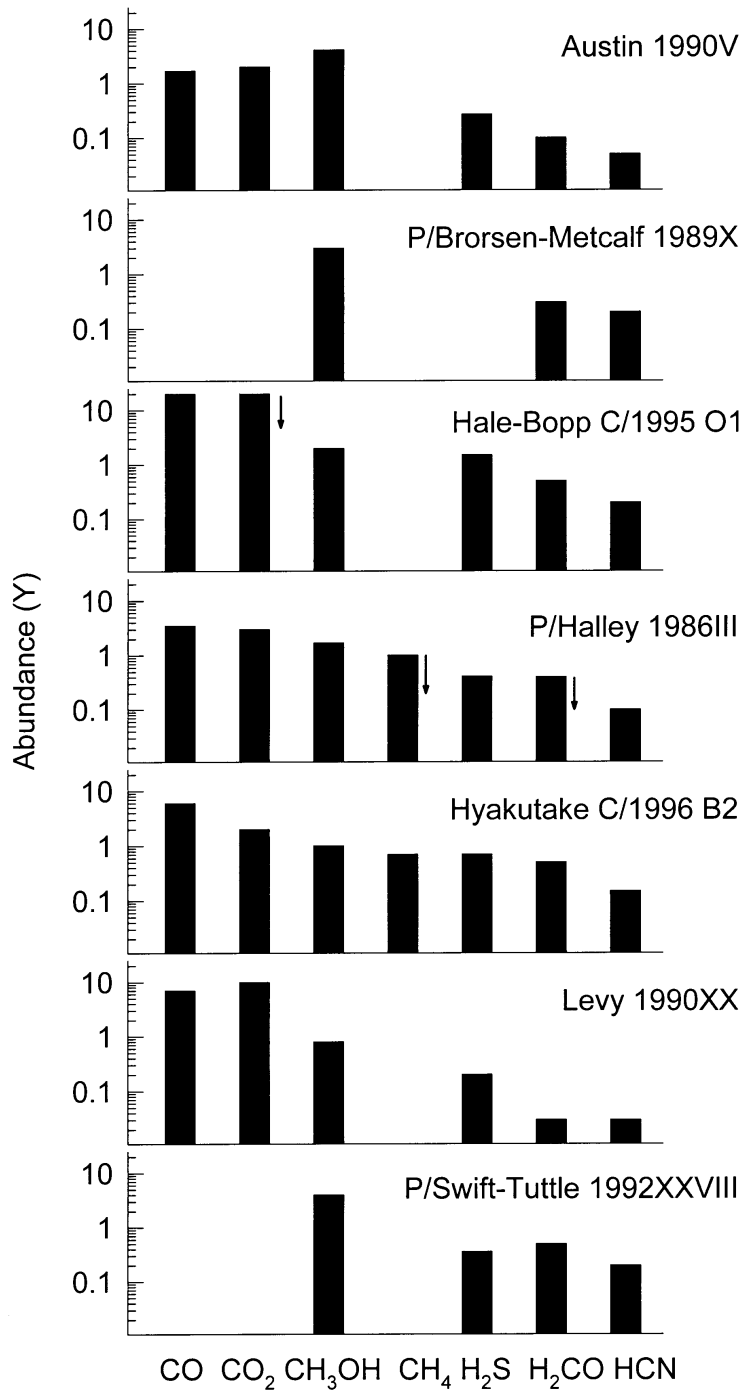
Figure 1. The abundances of different volatiles relative to water in several comets. The data are taken from Eberhardt (1998) and Irvine *et al.* (1999); see these two reviews for additional data on volatiles observed in only one or two comets. Arrows indicate that the value shown is an upper limit.

abundances of oxidized carbon compounds vary somewhat from comet to comet. Some species such as CO and H_2CO are partitioned between nuclear and extended sources (Eberhardt, 1998). Hydrocarbons (CH_4, C_2H_2, C_2H_6) were definitively observed in Hale-Bopp and Hyakutake (Irvine *et al.*, 1999); carbonaceous grains were observed in Halley (Schulze *et al.*, 1997) and presumably exist in other comets as well. The ratio of reduced/oxidized carbon volatiles is $<$ 1 in all comets where both families of compounds are observed, and is intermediate between the ratio of reduced/oxidized carbon compounds due to thermochemistry in the solar nebula and in Jovian protoplanetary subnebulae (Prinn and Fegley, 1989). The cometary CH_3OH/H_2O ratios are similar to CH_3OH/H_2O ratios in hot cores (typically a few to several percent). But CH_3OH/H_2O ratios of about 40% and 5-22% are observed in two sources (Dartois *et al.*, 1999). The upper limit on D/H for CH_3OH in Halley is lower than D/H for CH_3OH in hot cores (Irvine *et al.*, 1999).

Nitrogen compounds. The nitrogen volatiles observed in comets include NH_3, HCN, HNC, CH_3CN, HC_3N, HNCO, and NH_2CO. Molecular N_2 has not been detected directly but its abundance in Halley ($N_2/H_2O \sim 0.02\%$) was inferred from observations of N_2^+. The NH_3/H_2O ratio in Halley is $\sim 1\%$ (Eberhardt, 1998). The derived NH_3/N_2 ratio is ~ 50, intermediate between the values in the solar nebula (~ 0.01) and Jovian protoplanetary subnebula (~ 200) (Fegley, 1993). In the comets where nitrogen compounds are observed, the ratio of reduced/oxidized volatiles is $>$ 1. The $^{14}N/^{15}N$, $^{12}C/^{13}C$, and D/H ratios for HCN in Hale-Bopp have been measured. The D/H ratio is $(230 \pm 40) \times 10^{-5}$ and is consistent with DCN/HCN ratios in hot cores of interstellar clouds. The $^{12}C/^{13}C$ ratio (111 ± 12) and the $^{14}N/^{15}N$ ratio (323 ± 46) are terrestrial within the large uncertainties (Irvine *et al.*, 1999). It is important to measure D/H ratios for NH_3 and HCN in other comets, and for other nitrogen volatiles. Some minor species such as HNCO, may be wholly or partially produced in the coma, as is the case for HNC in Hale-Bopp and Hyakutake (Irvine *et al.*, 1999), and may not be primordial.

Sulfur compounds. The database for sulfur volatiles in comets is limited. Reduced (H_2S, OCS, H_2CS, CS, S_2, S) and oxidized (SO, SO_2) volatiles have been observed; CS_2 is the inferred (but as yet unseen) parent of CS (Eberhardt, 1998; Irvine *et al.*, 1999). The solar S/O ratio is 2.1%. Depending on the oxidation state of carbon and the amount of oxygen tied up in rock, H_2O could have only one third of the solar oxygen abundance giving a (total S)/H_2O ratio slightly over 6%. The observed H_2S/H_2O ratios range from $0.2 - 1.6\%$, and H_2S seems to be a major, but perhaps not always the dominant, sulfur volatile in comets. Carbonyl sulfide is observed in Hale-Bopp and Hyakutake at ~ 0.3-0.5% and most OCS in Hale-Bopp is from an extended source. Sulfur monoxide and SO_2 are observed in Hale-Bopp at $\sim 0.5\%$ and $\sim 0.1\%$, respectively, and at least part of the SO is derived from SO_2 photolysis in the coma (Irvine *et al.*, 1999). Thioformaldehyde (H_2CS) was observed in Hale-Bopp at $\sim 0.02\%$, and S_2 was observed in IRAS-Araki-Alcock and Hyakutake; the origin of these species is unclear (Irvine *et al.*, 1999).

3. Solar Nebula Evolution and Thermal Structure

Before discussing the nebular chemistry of cometary volatiles, we need a model of the physical conditions in the solar nebula and of how these conditions changed with time. Any such model is necessarily imperfect, but astronomical observations of protoplanetary disks and young stars, geochemical analyses and geochronological dating of meteorites, and theoretical modeling of accretion disks can be combined to provide a consistent (and hopefully correct) picture. Here I adopt the recent model of Cameron (1995), which divides the evolution of our solar nebula into four stages, which can be summarized as follows.

Stage 1: Molecular cloud collapse. During this stage the nebular disk is assembled of infalling material from the collapsing molecular cloud core. This stage lasts for a few times 10^5 years. The disk mass is greater than the initial protosolar mass, but most (if not all) of the matter in the disk ultimately goes into the proto-Sun and is not preserved in meteorites or comets.

Stage 2: Disk dissipation. The Sun forms during this stage, which lasts for about 50,000 years (i.e., the Sun accretes at a rate of about 2×10^{-5} solar masses per year). The disk mass is less than the mass of the proto-Sun. Most matter falling onto the accretion disk is transported through the disk into the proto-Sun. Thus, there is a general mass transport inward. There is also an angular momentum transport outward in the (geometrically thin) disk. The major dissipation (i.e., transport) mechanisms include spiral density waves, disk-driven bipolar outflows, and the Balbus-Hawley magnetic instability. Cameron (1995) discusses why turbulent viscosity driven by thermal convection is less important than these other dissipative mechanisms, but other modelers (e.g., Willacy *et al.*, 1998) rely on turbulent viscosity as the main dissipative mechanism. The amount of outward mass transport, that would tend to "contaminate" the outer nebula with products from thermochemical processing in the innermost few AU of the nebula, is controversial and uncertain. Near the end of stage 2, some disk material survived and is preserved in meteorites (e.g., ^{26}Al-bearing minerals). Some materials in comets may date from this stage as well.

Stage 3: Terminal accumulation of the Sun. The final accumulation of the Sun occurs during this stage, which lasts for about $(1 - 2) \times 10^6$ years and the accumulation rate decreases from about 10^{-7} to 10^{-8} solar masses per year. The proto-Sun becomes a classical T Tauri star in this phase. Planetary accretion (almost complete for Jupiter and Saturn, and less advanced for the other planets) also occurs during this stage. Products of thermochemical reactions in the Jovian and Saturnian subnebulae may contaminate the outer nebula and be accreted into comets.

Stage 4: Loss of nebular gas. The Sun becomes a weak line T Tauri star in this stage, which lasts $(3 - 30) \times 10^6$ years, and is no longer accreting material from the disk. The T Tauri wind removes gas in the inner nebula and photoevaporation due mainly to UV radiation from the T Tauri wind removes gas in the outer nebula. UV photochemistry and ion-molecule chemistry may be important disequilibrating

processes in the outer nebula, but depend on the nebular column density, which is poorly constrained and time dependent (Cameron, 1995). Gas-grain chemistry throughout the nebula ceases sometime (although not necessarily at the same time everywhere) during this stage.

In this model of nebular evolution, the accumulation of the Sun consumed essentially all of the material accreted by the nebular disk during the early stages of its history. Comets and all the other bodies in the solar system were then assembled from material accreted after the Sun had formed (i.e., during the time from the end of stage 2 into stage 4). I think the conclusion that most of the material in solar system bodies dates from the latter part of nebular history is robust, whether or not one accepts all details of Cameron's (1995) model or prefers a three stage model as he had proposed earlier. If this conclusion is adopted, the effects of UV radiation and other disequilibrating mechanisms (cosmic rays, X-winds) on nebular chemistry should be considered. The picture of the outer nebula as a cold, chemically inert region is almost certainly over simplified.

The temperature and pressure in the nebula during its latter history were important for chemical and physical reprocessing of presolar material. Three models of temperature and pressure as a function of radial distance in the solar nebula are contrasted in Figure 2. These three models are derived using different assumptions and differ in detail. However, they all predict low temperatures that agree within a factor of two and pressures that agree within an order of magnitude in the outer solar nebula. None of the models extend out as far as 1000 AU, the outer edge of the Kuiper Belt, and background values of temperature ($\sim$10 K) and pressure (10^3 cm^{-3} number density giving $\sim 10^{-18}$ bar at 10 K) are assumed there.

In fact, the radial extent of the solar nebula, the lowest temperatures attained in the outer nebula, and how the nebular disk blended into the surroundings are poorly constrained. The presence of N_2, CO, and CH_4 ices on Triton and Pluto, and of CH_4 ice on the Kuiper Belt Object 1993SC show that temperatures were low enough to condense these ices in the outer solar nebula (i.e., about 25 K for a wide range of plausible pressures). If these bodies formed at or near their present locations then temperatures were $\sim$25 K at 30-40 AU when Triton, Pluto, and 1993SC formed. However, temperatures could not drop below background temperature.

Finally, it is important to note that all three models are snapshots at one point in time when the snowline, where water ice condenses, was at Jupiter's orbit (5.2 AU). This is also the time when Jupiter started to form because water ice was the glue needed for its runaway accretion (Stevenson and Lunine, 1988). Observations of asteroids with hydrous spectral features (Jones *et al.*, 1990), and time-dependent calculations of nebular thermal structure (e.g., Ruden and Lin, 1986) suggest that later in time the snowline moved inward to the asteroid belt.
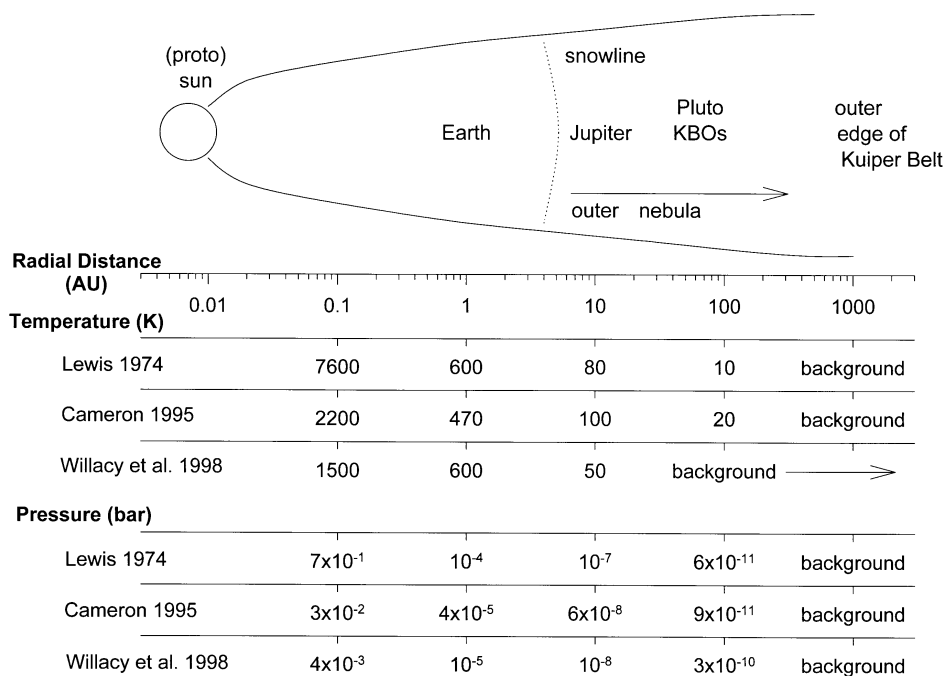
Radial Distance (AU)	0.01	0.1	1	10	100	1000
Temperature (K)						
Lewis 1974		7600	600	80	10	background
Cameron 1995		2200	470	100	20	background
Willacy et al. 1998		1500	600	50	background $\longrightarrow$	
Pressure (bar)						
Lewis 1974		7×10^{-1}	10^{-4}	10^{-7}	6×10^{-11}	background
Cameron 1995		3×10^{-2}	4×10^{-5}	6×10^{-8}	9×10^{-11}	background
Willacy et al. 1998		4×10^{-3}	10^{-5}	10^{-8}	3×10^{-10}	background

Figure 2. A schematic diagram comparing the radial variation of temperature and pressure for three solar nebula models. The distance scale is extended to 1000 AU to include the Kuiper Belt. The background temperature and pressure are about 10 K and $\sim 10^{-18}$ bar (a number density of 10^3 per cm^3). In the cartoon at the top the calculated snowline, where water vapor condenses to water ice, divides the solar nebula into an inner (< 5.2 AU) and an outer (≥ 5.2 AU) region. As discussed in the text, the position of the snowline moves inward as the nebula cools, but it was at or possibly beyond 5.2 AU when water ice provided the glue for the runaway accretion that led to the formation of Jupiter (at its present location or possibly at a greater radial distance).

4. Reprocessing of Presolar Materials in the Outer Solar Nebula

Presolar dust, gas, and ice accreted by the solar nebula were subjected to more or less chemical reprocessing and physical mixing before accretion into comets and other bodies. As schematically illustrated in Figure 3, with the exception of Jovian protoplanetary subnebulae, heating and thermochemical reactions were generally less important in the outer nebula than in the inner nebula. Chemical reaction rates between neutral atoms, radicals, and molecules vary exponentially with temperature, and the temperatures beyond the snowline were less than about 160 K (this is slightly higher or lower depending on the total pressure). Thus chemical reactions with activation energies $\gg kT$ would proceed at insignificant rates in the outer nebula.

However, it is unlikely that the outer nebula was simply an "icebox" that preserved interstellar (and other presolar) matter in a pristine state. Highly volatile
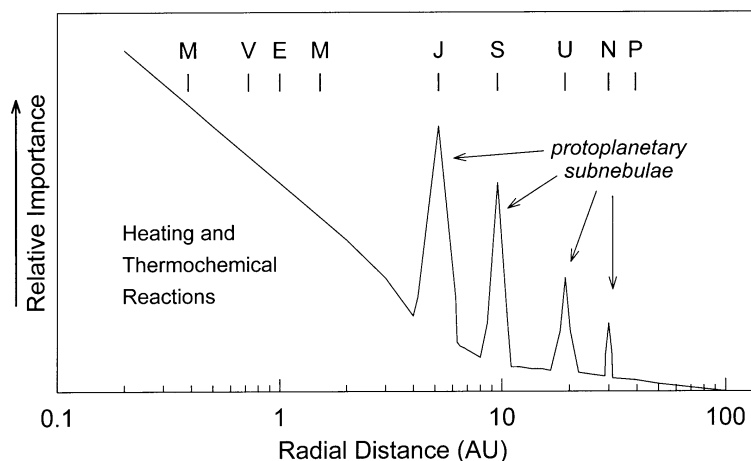
Figure 3. A cartoon illustrating the relative importance of heating and thermochemical reactions as a function of radial distance in the solar nebula. The symbols along the top show the present positions of the planets. The hypothesized Jovian protoplanetary subnebulae are hotter, higher density regions where thermochemical and grain-catalyzed reactions are favored relative to the cooler, lower density outer solar nebula.

ices (e.g., CO, N_2, CH_4, O_2) may have been partially or completely vaporized in the accretion shock or in the outer nebula itself. Other volatile ices may have been partially or completely vaporized depending on the distance at which grains were accreted. Atoms and radicals trapped in interstellar ices could diffuse and react once temperatures were a few tens of K above the background temperature. Volatiles that were vaporized may have reacted and undergone isotope exchange with nebular gas prior to recondensation.

Heating and thermochemical reactions. The outer solar nebula was possibly contaminated with thermochemical products from the Jovian protoplanetary sub-nebulae (e.g., by cometesimals ejected into the surrounding solar nebula or by gas exchange) and from the inner solar nebula as well. Prinn and Fegley (1989) attributed the small amounts of CH_4 and NH_3 in comets to sub-nebular ices because CO and N_2 are the dominant carbon and nitrogen ices expected in the solar nebula and in the interstellar medium. The importance of contamination of the outer solar nebula by thermochemical products from Jovian protoplanetary subnebulae and/or the inner solar nebula is twofold.

First, the isotopic compositions of presolar gas and grains may have been altered by mixing with nebular materials with normal isotopic compositions before their incorporation into comets. In general, these nebular materials could have been thermochemically processed in Jovian protoplanetary subnebulae or in the inner solar nebula. (In some cases, such as CH_4 and NH_3, species are only produced in the Jovian protoplanetary subnebulae because their production is kinetically inhibited in the solar nebula.) Hydrides from Jovian protoplanetary subnebulae

and the inner nebula would have D/H ratios slightly higher than the D/H ratio of 2×10^{-5} for hydrogen in the solar nebula, because these gases were formed by chemical reactions in a warmer environment. The D/H ratio of 7.5×10^{-5} for CH_4 on Saturn's satellite Titan (Coustenis *et al.*, 1998) agrees with this model.

In contrast, hydrides formed at lower temperatures by ion-molecule chemistry would have significantly higher D/H ratios. A mixture of hydrides formed at higher and lower temperatures would have an intermediate D/H ratio. The D/H ratio of $\sim 31 \times 10^{-5}$ for H_2O in comets Hale-Bopp, Halley, and Hyakutake may indicate mixing of higher and lower D/H water. The upper limit on D/H for CH_3OH in Halley also may indicate mixing of CH_3OH from two sources.

Second, disequilibrium assemblages of oxidized and reduced molecules may have been produced by mixing presolar material with thermochemically processed nebular material. A mixture of CH_4 and NH_3 ices from Jovian protoplanetary sub-nebulae and CO and N_2 ices (presolar or nebular) has been proposed to explain the CO/CH_4 and N_2/NH_3 ratios in comets. These mixtures are disequilibrium assemblages and are probably also heterogeneous. However, the extent of mixing from the inner to outer nebula, and the mechanisms for this mixing are controversial (Prinn, 1990; Stevenson, 1990). The contamination of the outer nebula by thermochemical products from the Jovian protoplanetary subnebulae is also debated (see parts of the discussion following the paper by Fegley and Prinn, 1989).

Grain Catalyzed Chemistry. Industrial Fischer-Tropsch (FT) reactions use a Fe or Co based catalyst to convert a CO/H_2 gas mixture into hydrocarbons such as gasoline. Oxygenated organics such as methanol (CH_3OH) can also be formed in significant amounts depending on the reaction conditions and catalysts. In the late 1960s and early 1970s Anders and colleagues studied FT type reactions using Fe based catalysts and smixtures of CO, H_2, and NH_3 (Anders *et al.*, 1973; Hayatsu and Anders, 1981). They produced a variety of organic compounds and argued that the organic compounds in meteorites were products of nebular FT reactions. This conclusion is now controversial because Anders' results do not match the chemical and isotopic composition of organic compounds in the Murchison CM2 chondrite (e.g., see Cronin and Chang, 1993).

However, recent work shows that Fe and Fe-based catalysts (iron meteorites, ordinary chondrites, magnetite) convert CO to CH_4 in CO-H_2 gas mixtures with the solar C/H ratio at one bar total pressure and temperatures of a few hundred degrees (Fegley, 1998; Fegley and Hong, 1998). Iron-catalyzed NH_3 synthesis occurs at similar temperatures in N_2-H_2 mixtures with 10 times the solar N/H ratio at one bar pressure (Fegley, 1998). The experimental conditions match (P, T, C/H ratio) or come close (N/H ratio of 10 times solar) to those for the Jovian subnebula. The results support the subnebula chemistry models of Prinn and Fegley (1989). Grain-catalyzed chemistry is also thought to produce saturated compounds observed in circumstellar outflows from cool carbon stars (Glassgold, 1996).

Fegley (1993) suggested that grain-catalyzed chemistry may have produced some of the volatile carbon compounds and refractory organic matter in comets.
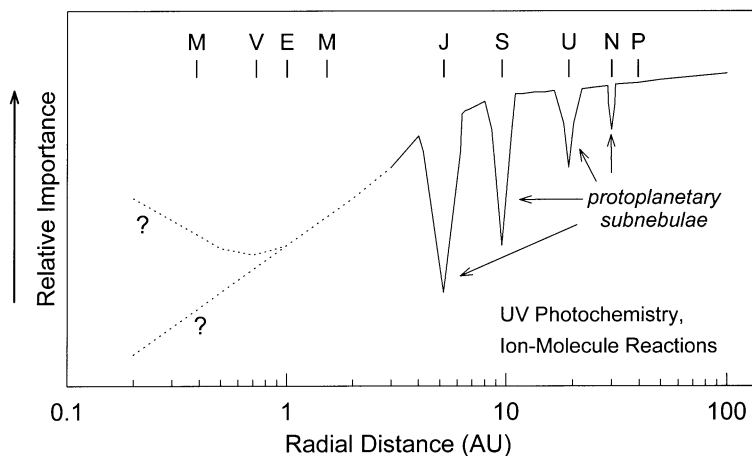
Figure 4. A cartoon showing the relative importance of disequilibrating processes (e.g. UV photochemistry and ion-molecule chemistry) as a function of radial distance in the solar nebula.

Conversion of CO to CH_4 is observed in a solar gas, but more work is needed to test this proposal. For example, no significant amounts of other hydrocarbons or oxygenated organics were produced in the initial experiments studying CO hydrogenation in a solar gas. However, other hydrocarbons, CO_2, methanol, and other oxygenated organics are produced in industrial FT reactions and may also be produced in FT reactions in a solar gas under some conditions. The lowest effective temperatures for the grain catalyzed CO to CH_4 and N_2 to NH_3 conversions are also unknown and need to be measured.

UV Photochemistry. Disequilibrating processes such as UV photochemistry and ion-molecule chemistry are potentially important during the later stages of nebular evolution. The cartoon in Figure 4 indicates that disequilibrating reactions were plausibly more important in the outer nebula than in the inner nebula. (The higher density Jovian protoplanetary subnebulae are the exception.) UV photochemistry can potentially drive isotopic exchange reactions (enrichment or depletion). The UV photon flux and amount of vertical mixing (midplane to nebular photosphere) needed to reach photochemical steady-state throughout the gas depend on the nebular column density. Yung *et al.* (1988) considered photochemistry driven by UV starlight and modeled the net photochemical reactions

$$HD + H_2O \rightarrow HDO + H_2 \tag{1}$$

$$HD + CH_4 \rightarrow CH_3D + H_2 \tag{2}$$

in optically thin regions of the solar nebula. They calculated D/H fractionation factors of 26 and 115 for reactions (1) and (2), respectively, at 150 K. Thus a D/H

ratio of 52×10^{-5}, which is larger than the observed D/H ratio in cometary water, could be produced at photochemical steady-state.

Gladstone (1993) and Gladstone and Fegley (1997) proposed that solar HI Lyα (121.6 nm), He I (58.4 nm), and He II (30.4 nm) UV radiation backscattered by H atoms in the interplanetary medium was an important UV source in the outer solar nebula and did preliminary modeling showing that photodissociation rates of H_2O, CH_4, NH_3, and H_2S could be significant. Photolysis of H_2O is a source of OH radicals, which are important oxidizing agents for driving conversions of reduced carbon, nitrogen, and sulfur to the oxidized forms. Photolysis of H_2O, CH_4, NH_3, and H_2S is also a source of H atoms which may drive conversions of unsaturated to saturated compounds, carbonaceous dust to CH_4, and of oxidized carbon species (e.g., $CO_2 + H \rightarrow CO + OH$). Beyond the snowline, water vapor, the major UV opacity source, condenses out, and grains become the major source of UV opacity. This raises the potential for UV photoprocessing of ices, perhaps analogous to the current conversion of water ice to O_2 and ozone (O_3) observed on the three outermost Galilean satellites and on two Saturnian satellites (Rhea, Dione). Disequilibrium chemistry driven by UV light may proceed in the outer nebula and reprocess presolar gas and grains. Nebular photochemistry may also produce species thought to be diagnostic of interstellar molecular cloud chemistry.

Ion-molecule chemistry. Ion-molecule reactions driven by galactic cosmic rays and/or short-lived nuclides (^{26}Al) may occur in low density regions of the outer solar nebula. These reactions may lead to D/H fractionation in the nebula and produce the same molecules observed in interstellar molecular clouds. Depending on the nebular column density, ion-molecule chemistry may be limited to the nebular skin or occur throughout sufficiently low density regions in the outer nebula. ion-molecule chemistry would probably be less important in Jovian protoplanetary subnebulae than in the lower density solar nebula itself.

The key factor determining whether or not ion-molecule chemistry was important in the outer solar nebula is the fractional degree of ionization. When this is high ion-molecule chemistry is relatively important. In turn, the ionization fraction depends on the balance between the ionization rate and the neutralization rate. These rates are poorly constrained and the fractional degree of ionization in the outer solar nebula is model dependent and controversial.

In the nominal model of Aikawa *et al.* (1998) the ionization rate and the grain size are the same as in interstellar molecular clouds. Significant chemical reprocessing occurs in 10^6 years in this model. Initially, CO, N_2, H_2O, and atomic S are assumed to be the major gases of these elements and they are reprocessed into oxidized and reduced species. For example, CO is converted to CO_2, H_2CO, HCN, CH_4, C_2H_2, C_3H_4; N_2 is converted to NH_3, NO, NO_2, HCN, HC_3N; H_2O is converted to O_2; and S atoms are converted to OCS, SO, SO_2, CS, H_2CS, and H_2S. This mixture of reduced and oxidized species matches some features of the chemistry of cometary volatiles.

In contrast, Willacy *et al.* (1998) calculate that ion-molecule chemistry was relatively unimportant in the outer solar nebula because they compute a lower fractional degree of ionization due to effective neutralization of ions by grains. Their chemistry is dominated by neutral-neutral reactions, although several of the products are the same as those calculated by Aikawa *et al.* (1998).

5. Concluding Remarks and Recommendations

As described above, presolar materials were probably subjected to a variety of chemical and physical processes before being accreted into comets. Several of these processes such as UV photochemistry and ion-molecule chemistry in cold, low density regions of the outer nebula mimic interstellar chemistry and produce the same suite of molecules and isotopic fractionations. Products from thermochemical reactions and grain-catalyzed chemistry in Jovian protoplanetary subnebulae can mix with and alter the isotopic compositions of presolar materials. It is unlikely that nebular processes were efficient enough to completely reprocess all presolar material before accretion into comets. But as Figures 3 and 4 suggest, as thermochemistry becomes insignificant in the cold, low density outer nebula, UV photochemistry and ion-molecule chemistry become significant. What was the balance between presolar and nebular chemistry in the outer solar nebula?

Many of the volatiles in comets are attributed to interstellar chemistry because the same species are also observed in ices in interstellar molecular clouds. In some cases, a high D/H ratio supports this correspondence (e.g., HCN in Hale-Bopp) because similar D/H ratios are also observed in the interstellar molecular clouds. However, how can we distinguish interstellar from nebular chemistry if the same processes occur in both environments? Below I suggest some experiments, models, and observations that can help to address these two questions:

1. The D/H ratio in hydrous minerals on asteroids and in ices on satellites of the Jovian planets, Pluto, Charon, Centaur objects, and Kuiper Belt objects should be measured by remote sensing and/or in situ methods. These data can show if D/H values of hydrous and icy bodies in the solar system exhibit trends with radial distance and/or hypothesized formation location (solar nebula vs. subnebulae).

2. Similar data for the ortho-para ratio of water ice on cold outer solar system bodies (Triton, Charon, Kuiper belt objects) may show a relationship between the ortho-para spin temperature and D/H ratio.

3. Measurements of the D/H ratios in several volatiles from one comet and of the same volatile in a large number of comets, optimally from different dynamical families can assess intra- and inter-comet variability. This dataset would help to distinguish a high temperature origin (low D/H ratio from subnebula or inner nebula chemistry) from a low temperature origin (high D/H ratio from ion-molecule chemistry in an interstellar cloud or low density region of the outer

solar nebula) for H_2O, CH_4, NH_3, H_2S, hydrocarbons, and other H-bearing species.

4. High spatial resolution observations of protoplanetary disks are needed to measure abundances of neutrals, ions, and isotopic ratios (D/H) as a function of radial distance. Resolutions of a few percent of the disk radius are needed. The current angular resolution corresponds to $\sim$100 AU in the Taurus molecular cloud, the nearest star-forming region. This is insufficient to see if ion-molecule reactions and UV photochemistry occur in protoplanetary disks (Aikawa *et al.*, 1998).

5. Theoretical modeling of ion-molecule chemistry and UV photochemistry in the outer nebula is needed to predict steady state abundances of volatile O, C, N, and S species and isotopic ratios for comparison with cometary observations.

6. Laboratory studies of D/H exchange kinetics for cometary volatiles and ortho-para conversion kinetics for water, and of low temperature grain-catalyzed chemistry in a solar gas are needed for nebular chemistry models.

Acknowledgements

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