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Planetary Materials and Geochemistry Program

for

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entitled
Non-equilibrium Chemistry of the Early Solar System

Period: May 1, 1985–April 30, 1994

from

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1. Introduction

The results of the research carried out under NASA Grant NAG9-108 in the time period May 1, 1985–April 30, 1994 have been published in refereed papers (Section 2), and presented at scientific conferences with published abstracts (Section 3). Also, a large number of invited lectures without published abstracts were given. They are listed in the previous individual annual reports for this grant and a listing is not repeated here.

The very significant record of publications provides direct evidence of the productivity and accomplishments of the research program conducted under this grant.

A copy of the 1993 paper by R. Prinn is appended to this final report since it has not previously been sent to NASA.

2. Publications Supported in Whole or Part by NAG9-108

1985: B. Fegley, Jr. and J.E. Post, A refractory inclusion in the Kaba CV3 chondrite: Some implications for the origin of spinel-rich objeccts in chondrites. *Earth Planet. Sci. Lett.*, **75**, 297-310.

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3. Invited Papers with Abstracts Supported in Whole or Part by NAG9-108

1985: R. Prinn, Impacts, acid rain, and biospheric traumas. *Trans. Amer. Geophys. Union*, **66**, 813.

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PROTOSTARS
AND
PLANETS III

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CHEMISTRY AND EVOLUTION OF GASEOUS CIRCUMSTELLAR DISKS

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The chemical and physical processes which determine the composition and evolution of gas-rich circumstellar disks are discussed. The composition of accreted interstellar material is an important determinant of subsequent chemical evolution. Elemental composition (e.g., C and O abundances) and molecular composition (e.g., N_2 vs NH_3 and hydrous vs anhydrous silicates) are both significant in this respect. Major disk chemical processes are thermochemistry (not necessarily equilibrium) and shock chemistry (during accretion and by lightning). Strong mixing in a thermoclinic environment like an accretion disk leads to thermochemical disequilibration due to "kinetic inhibition" induced by chemical time constants becoming longer than outward mixing (or equivalently cooling) time constants. In this case, species thermodynamically stable at high temperatures but not at low temperatures (e.g., CO, N_2) dominate at all temperatures in the disk. Nonaxisymmetric accretion of material at hypersonic speeds is a major forcing mechanism for mixing in the disk and can produce eddy speeds of 1% of the sound speed. Typical resulting mixing times for trace species are about 10^{10} s compared to a typical disk lifetime of 10^{13} s. Nonlinear processes yield much longer mixing times for momentum than for trace species. Kinetic inhibition in the carbon, nitrogen and anhydrous/hydrous silicate families has major implications for the compositions of the terrestrial planets, giant planets, ice-rich satellites, Pluto, comets, meteorites and asteroids which are discussed. Ice-rich bodies in the outer solar system have rock-to-ice ratios which can be explained by formation in either the CO- and hydrocarbon-rich circumsolar disk or a CH_4- and CO-rich circumJovian planetary disk with some post-formation ice loss being required in some cases. The CO, CH_4, NH_3 and H_2O abundances in comet Halley can be explained by its formation in the circumsolar disk. Observations of key species like CO, CH_4, NH_3 and H_2O in gaseous circumstellar disks could provide important information about these disks (and thus about the original circumsolar gaseous disk).

I. INTRODUCTION

The advancement of our understanding of the chemistry of the gaseous and dusty circumsolar nebular disk in which the planets formed has been guided traditionally by a combination of observations of the composition of the planets, planetary satellites, meteorites and comets together with development of *a priori* models of the circumsolar disk. More recently, astronomical observations of circumstellar disks have begun to provide an important new source of information on disk structure and constraints on both circumsolar and other circumstellar disk models.

In view of the interdisciplinary goals of this book, this chapter will focus more on the general principles determining the composition and chemistry of gas-rich circumstellar disks. A more specific (and very detailed) discussion of the chemistry of the circumsolar nebula already exists (Prinn and Fegley 1989) and these details will not be repeated here. However, the conclusions in the latter paper will be updated where necessary, based on more recent results.

As a preface to the chapter it is useful to paraphrase the principal conclusions from Prinn and Fegley (1989):

1. The starting materials for forming the circumsolar disk were gases and grains in interstellar clouds.
2. As the circumsolar gaseous disk formed and evolved, these gases and grains were at least partially reprocessed with the greatest reprocessing occurring near the proto-Sun.
3. Thermochemical reactions (using thermal energy and shock heating) constitute the major chemical processing mechanism.
4. The gas-rich and later dust-rich circumsolar disk was highly opaque limiting severely the influence of ultraviolet radiation from the proto-Sun in chemically processing the body of the disk.
5. The reduction of N_2 and CO to NH_3 and CH_4 was kinetically inhibited in the circumsolar disk but not in higher pressure disks like circumJovian planetary disks. Thus the circumsolar disk was rich in N_2 and CO (and organics formed from it) while the circumJovian planetary disks were rich in NH_3 and CH_4.
6. Vapor-phase hydration of silicates is kinetically inhibited in the circumsolar disk but not in circumJovian planetary disks.
7. Regular satellites can form in circumJovian planetary disks with distinctly different compositions than bodies formed in the circumsolar disk.
8. Thus certain volatile ratios (e.g., CO/CH_4, N_2/NH_3, H_2O ice/silicate) in ice-rich bodies are diagnostic of their origin.
9. After dissipation of the gaseous circumsolar disk, collisions between objects formed in the circumsolar disk and those formed in circumJovian planetary disks imbedded within it are inevitable and can lead to hybrid heterogeneous objects.

This chapter attempts to generalize the above ideas about the circumsolar nebula disk to other circumstellar nebula disks by addressing the underlying chemical and physical processes. There are five sections devoted respectively to: chemical theories; chemical-dynamical theories (kinetic inhibition); comparison between theory and planetary, satellite observations; comparison between theory and observations of comets, meteorites and asteroids; and finally key new astrophysical observations to test and extend current theories.

II. CHEMICAL PROCESSES

A. Initial Composition and Its Relevance

The *elemental* composition of a circumstellar disk (or equivalently its precursor interstellar cloud) is obviously important in determining the chemical state of the disk. Observations of the gaseous component of dense interstellar clouds show a complex mixture of hydrogen-, oxygen-, carbon-, nitrogen-, and sulfur-containing compounds while observations of the dust component suggest the presence of various silicates, magnetite, carbon-containing compounds (including graphite), and water ice. As reviewed by Irvine and Knacke (1989), hydrogen and helium are generally dominant in interstellar clouds with oxygen, carbon, neon and nitrogen being of the order of 10^{-4} to 10^{-5} by number of the H abundance and silicon, magnesium, sulfur and iron being of the order of 10^{-6} of the H abundance. Two estimates of the elemental abundances in a solar composition medium are given in Table I. In this chapter we will denote the number density of an element or compound *i* by [*i*].

TABLE I[a]

Ratios Relative to H_2 of the Ten Most Abundant Elements in Solar Composition Material

	Anders and Grevesse	Cameron
H_2	1.0	1.0
He	0.195	0.135
O	1.17×10^{-3}	1.38×10^{-3}
C	7.24×10^{-4}	8.35×10^{-4}
Ne	2.47×10^{-4}	1.95×10^{-4}
N	2.24×10^{-4}	1.74×10^{-4}
Mg	7.70×10^{-5}	7.97×10^{-5}
Si	7.17×10^{-5}	7.52×10^{-5}
Fe	6.45×10^{-5}	6.77×10^{-5}
S	3.69×10^{-5}	3.76×10^{-5}

[a] Table uses the abundance estimates of Anders and Grevesse (1989) and Cameron (1982).

Certain elemental ratios are extremely important in defining the disk chemistry. In particular, if carbon equals or exceeds oxygen, the majority of the oxygen can end up as CO leading to: relatively very low H_2O (vapor or ice) abundances (Lewis and Prinn 1980); an excess of carbon leading to abundant graphite and hydrocarbons; and very reducing conditions leading to formation in thermochemical equilibrium of CaS, Fe_3C, MgS, SiC and TiN (Larimer 1975). Conversely, if oxygen significantly exceeds carbon (as it did on the average for the circumsolar nebula), H_2O (vapor or ice) is abundant even if essentially all the carbon is in CO (Lewis and Prinn 1980) and the oxidation state of the nebula is much higher making minerals such as SiC thermochemically unstable if [O] exceeds [C] by more than 10% (Larimer 1975).

The [C]/[O] ratio also potentially affects the density of ice-rich condensates in circumstellar disks through its control of the H_2O to silicate ratio. For the circumsolar nebula disk the precise [C]/[O] ratio is controversial with Anders and Grevesse (1989) and Stone (1989) reporting the solar [C]/[O] ratio ≈ 0.42 and Cameron (1982) recommending $[C]/[O] \approx 0.60$. If CO is the dominant C compound ($[CO]/[C] \approx 1$) and if we model anhydrous rock as SiO_2, MgO, FeO and FeS, then the ratio of the oxygen abundances in CO, H_2O and anhydrous silicates (i.e. $[CO]:[H_2O]:2[Si] + [Mg] + [Fe] - [S]$) is 3.2:1.1:1.0 for [C]/[O] = 0.60 and 2.9:3.0:1.0 for [C]/[O] = 0.42. Thus there is 3.0/1.1 = 2.7 times more water available for forming ice-rich bodies when [C]/[O] = 0.42 than when [C]/[O] = 0.60. Water availability is also sensitive to the oxidation state of carbon because if $[CO]/[C] \approx 0$ (i.e., CH_4 and/or organics are the major forms of carbon), then $[CO]:[H_2O]:2[Si] + [Mg] + [Fe] - [S]$ is 0.0:4.3:1.0 for [C]/[O] = 0.60 and 0.0:5.9:1.0 for C/O = 0.42. Thus there is 4.3/1.1 = 3.9 ($[C]/[O] \doteq 0.6$) or 5.9/3.0 = 2.0 ([C]/[O] = 0.42) times more water available for forming ice in a CH_4-rich or organic-rich region than in a CO-rich region.

The *molecular* composition and *physical state* of interstellar material collapsing onto the disk are also important in determining the susceptibility of this material to chemical processing during accretion and later processing within the disk. Highly refractory solid material (e.g., Al_2O_3, $CaTiO_3$, $Ca_2MgSi_2O_7$, Fe-Ni alloy, Mg_2SiO_4) is more likely to survive than less refractory solid material (e.g., graphite, hydrated silicates, polycyclic aromatic compounds, FeS) and both are much more likely to survive than volatile solids (H_2O ice, $NH_3{\cdot}H_2O$, $CH_4{\cdot}7H_2O$, $CO{\cdot}6H_2O$). Survival of solids will also depend on grain size, and on whether compounds are in crystalline or amorphous states. In the gas phase, strongly bound molecules like N_2 are more likely to survive processing than more weakly bound species like NH_3. Some of the organic material in some meteorites may be unaltered interstellar material and one certainly expects a greater probability for survival of such unaltered material in bodies in the least explored outermost regions of the solar system, particularly comets.

B. Energy for Chemical Reactions

Potential sources of energy to drive chemical reactions include the internal thermal energy of the disk, shock heating due to impact of hypersonic interstellar material accreting onto the disk, lightning discharges and thundershocks associated with convection in the disk, ultraviolet photons from the central protostar and the surrounding proximal stars, and very high energy photons and particles from decay of radioactive elements (especially ^{26}Al) in the disk. As discussed by Prinn and Fegley (1989), it is useful to compare the usable energy fluxes ϕ available from the various sources to drive chemical reactions to the net outward flux $\phi_T = sT_e^4$ in the disk where s is Stefan's constant and

$T_e(R)$ is the effective temperature of the disk at radius R. For conditions at $R = 1$ AU in the circumsolar nebula disk they compute

$$\phi(\text{thermal})/\phi_T \approx \exp(-E/NkT) = 4 \times 10^{-5} \tag{1}$$

$$\phi(\text{thundershock})/\phi_T \approx 4 \times 10^{-6} \tag{2}$$

$$\phi(\text{solar photons})/\phi_T \approx 10^4 \times F\exp(-\tau)/\phi_T \approx 0 \tag{3}$$

$$\phi(\text{stellar photons})/\phi_T \approx 10^{-9} \tag{4}$$

$$\phi(\text{radioactivity})/\phi_T \approx 3 \times 10^{-12} \quad . \tag{5}$$

where $E = 5 \times 10^4$ J/mole is a typical activation energy of a chemical reaction quenching at $R = 1$ AU, k is Boltzmann's constant, N is Avogadro's number, τ is the optical depth for solar ultraviolet photons between the proto-Sun and radius R, and F is the present-day solar ultraviolet energy flux at $R = 1$ AU. Evidently for these five energy sources, thermal energy dominates at 1 AU except for reactions with very large E (for which thundershocks could be significant). Solar photons (due to the very large τ value resulting from abundant H_2O, dust, etc., in the disk) and radioactivity (due to the low abundance of ^{26}Al) are neglible at 1 AU. As we approach the proto-Sun ($R << 1$ AU) thermal energy dominates even more while thundershocks become relatively more important further from the proto-Sun ($R >> 1$ AU). Stellar photons are unimportant for $R \leq 1$ AU but could be relatively significant for $R \geq 10$ AU. Very close to the protoSun ($\tau \approx 0$, $R \approx 0$), protosolar ultraviolet photon fluxes will be very large but due to the large opacity, the photons are absorbed wholly in the very hot (temperature >>2500 K) relatively dense innermost part of the gaseous disk. Here, large thermochemical reaction rates involving abundant thermally produced atoms, free radicals, electrons and ions will generally overwhelm the dissociative and ionizing effects of the ultraviolet photons. For this purpose, efficient thermal ionization requires temperatures about 1000 K greater than thermal dissociation. We note parenthetically that protosolar photons emitted in directions other than into the disk (e.g., in polar directions) may suffer little or no absorption and therefore be remotely observable. Thus observations of ultraviolet emissions from T Tauri stars do not provide evidence for photochemistry driven by photons from the central star occurring other than in the innermost regions of a protosolar-type gaseous disk.

The sixth energy source mentioned above, namely shock heating during accretion onto the disk, was not considered quantitatively by Prinn and Fegley (1989). To obtain a measure of the intensity of the shock heating which can occur, we use here the Hugoniot shock relation in an ideal polytropic gas (see Courant and Friedrichs 1976) to obtain the temperature T_s of the shocked disk gas relative to the temperature T_o of the pre-shocked gas

$$\begin{aligned} T_s &\approx T_o[\mu^2(1 - M^{-2}) + 1][\mu^2(M^2 - 1) + 1] \\ &\approx 1031\ \mathrm{K}(\mu^2 = 0.18, T_o = 60\ \mathrm{K}, R = 10AU) \\ &\approx 1847\ \mathrm{K}(\mu^2 = 0.17, T_o = 120\ \mathrm{K}, R = 5AU) \\ &\approx 8224\ \mathrm{K}(\mu^2 = 0.16, T_o = 600\ \mathrm{K}, R = 1AU) \end{aligned} \tag{6}$$

where μ^2 is the average over the interval between T_o and T_s of the gas constant divided by the sum of the heat capacities at constant volume and constant pressure, $M \approx 22$ is the Mach number of the shock front which we equate to the Mach number of the free falling impacting interstellar material, and T_o is a representative solar nebula temperature profile allowing ice condensation in the Jovian formation region. Note that because the free fall speed varies as $R^{-0.5}$, the sound speed varies as $T_o^{0.5}$ and T_o varies approximately as R^{-1}, then the latter Mach number is independent approximately of distance R. Evidently, the disk gas (and to a lesser extent the lower-temperature-impacting interstellar gas) is intensely shock heated for $R \leq 1$ AU but only mildly shock heated for $R \geq 10$ AU. Thus, quite apart from any subsequent processing within the disk, the disk accretion process itself probably led to significant thermochemical reprocessing of disk (and to a lesser extent impacting interstellar) material inside $R = 10$ AU. Depending on the relative magnitudes of the mass per unit area (in the direction of impact) for the accreting gas mass and the nebula disk, the accreting material will be decelerated and force strong mixing near the surface of the disk or throughout its thickness. Chemical reprocessing will occur in both the region of deceleration and beyond this region through propagating shock waves.

C. Equilibrium Products of Thermochemical Reactions

The *potential* products of thermochemical reactions are conveniently summarized by addressing the predicted composition in *thermochemical equilibrium*. As discussed later, such equilibrium is possible only if the relevant cooling time (dynamical or radiative) for the gas exceeds the relevant chemical reaction times and it is thus most likely to occur at high temperatures in the disk where reactions are fast (e.g., near the protostar or in a region shock heated by an impact or lightning). Figures 1, 2 and 3 illustrate how three key ratios CO/CH_4, N_2/NH_3 and CO_2/CO vary in thermochemical equilibrium as a function of pressure and temperature in a gas with solar H, O, C and N ratios. Sample disk adiabatic pressure-temperature profiles are shown for the circumsolar nebula disk (Lewis and Prinn 1980) and the circumJovian planetary nebula disk (Prinn and Fegley 1981). Pressure-temperature profiles for any arbitrary near-solar-composition circumstellar disk may also be drawn on these diagrams to illustrate the composition of these disks if thermochemical equilibrium is attained. Similarly, shock heating of the disk gas can be illustrated on these diagrams by imagining a temporary excursion of the shocked gas up an adiabat (as shown) or up a shock-Hugoniot (which would be closer to vertical than the adiabats shown) to higher temperatures and pressures. Evidently, for all these near-adiabatic temperature-pressure profiles the transition to higher temperatures and pressures is accompanied by a shift of the three major equilibria

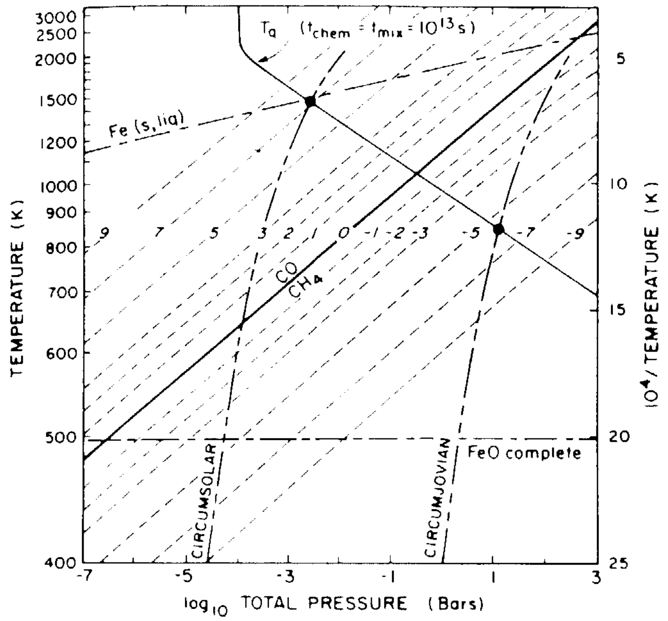

Figure 1. Thermochemical equilibrium $\log_{10}([CO]/[CH_4])$ values in a solar composition medium with $[C]/[O] = 0.6$. Also shown are illustrative temperature-pressure profiles for the circumsolar and circumJovian disks and the quench temperature T_q for homogeneous (gas-phase) conversion of CO to CH_4 assuming an upper limit for $t_{mix} = 10^{13}$ s. Heterogeneous (iron-catalyzed) conversion is possible between the lines designating the iron condensation temperature labeled "Fe(s,liq)" and the temperature where oxidation of Fe to FeO is complete, labeled "FeO complete."

$$CH_4 + H_2O = CO + 3H_2 \tag{7}$$

$$NH_3 + NH_3 = N_2 + 3H_2 \tag{8}$$

$$CO_2 + H_2 = CO + H_2O \tag{9}$$

to the right to yield CO, N_2 and CO_2 until temperatures become high enough ($\geq$3000 K) for atomization and ionization to begin. In addition, the equilibria

$$2CH_4 + N_2 = 2HCN + 3H_2 \tag{10}$$

$$CH_4 + NH_3 = HCN + 3H_2 \tag{11}$$

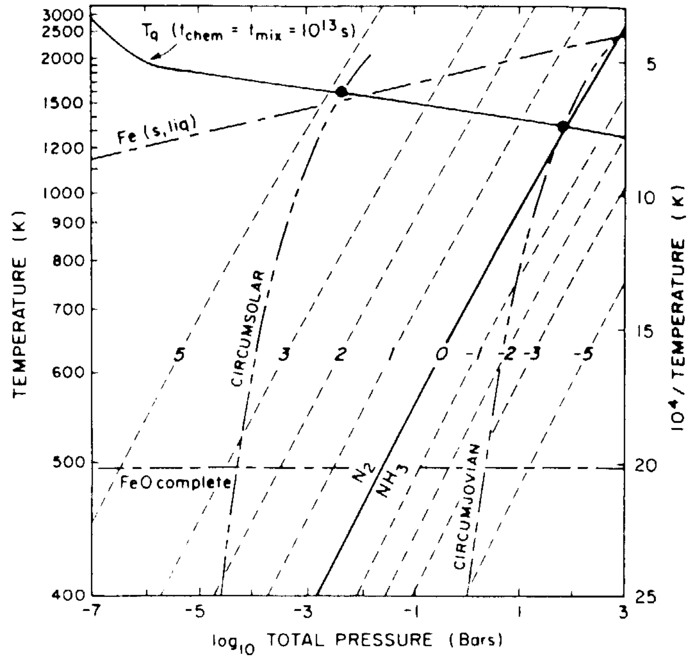

Figure 2. As in Fig. 1 but for the $[N_2]/[NH_3]$ ratio and conversion of N_2 to NH_3.

$$2CO + N_2 + 3H_2 = 2HCN + 2H_2O \tag{12}$$

$$2CH_4 = C_2H_2 + 3H_2 \tag{13}$$

$$2CO + 3H_2 = C_2H_2 + 2H_2O \tag{14}$$

$$2CH_4 = C_2H_6 + H_2 \tag{15}$$

$$2CO + 5H_2 = C_2H_6 + 2H_2O \tag{16}$$

also shift to the right for $T \leq 3000$ K yielding trace amounts of HCN, C_2H_2 and C_2H_6 (see, e.g., Prinn and Fegley 1989, Figs. 5, 6, 9, 10). Figures 1–3 use a [C]/[O] ratio of 0.6 and are quantitatively but not qualitatively altered for [C]/[O] = 0.42.

The equilibrium composition of solid materials under circumstellar disk conditions is also of considerable interest (see Fig. 4). At sufficiently high temperatures, silicates exist in anhydrous forms (olivine $(Fe,Mg)_2SiO_4$; pyroxene $(Fe,Mg)SiO_3$; etc.) and Fe exists as the metal or (as FeO) in olivines and pyroxenes. As the temperature is lowered, Fe oxidation to FeO which is incorporated into olivines and pyroxenes and to FeS which forms troilite depletes this metal, specifically

$$Fe + H_2O = FeO + H_2 \tag{17}$$

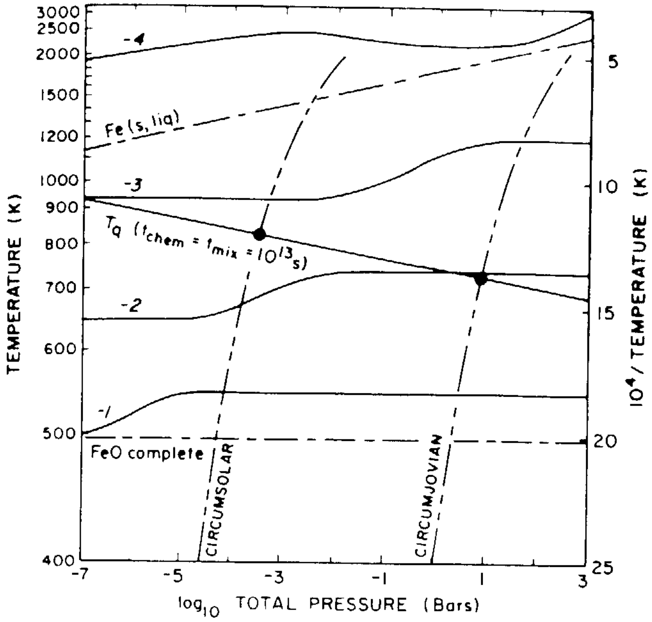

Figure 3. As in Fig. 1 but for the $[CO_2]/[CO]$ ratio and conversion of CO to CO_2.

$$Fe + H_2S = FeS + H_2. \tag{18}$$

Also, as the temperature is lowered further, hydration of olivines and pyroxenes to form hydrated silicates like serpentine and talc and hydroxides like brucite occur. For example,

$$2Mg_2SiO_4 + 3H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \tag{19}$$

$$4MgSiO_3 + 2H_2O = Mg_3Si_4O_{10}(OH)_2 + Mg(OH)_2. \tag{20}$$

Because these latter hydrated silicates and hydroxides are 8 to 16% by weight H_2O they lower the density of the rock material in equilibrium from about 4 g cm^{-3} (anhydrous) to 3 g cm^{-3} (hydrated).

At even lower temperatures (Fig. 4), the following transitions occur in order: H_2O condenses as ice; NH_3 (the major form of N in equilibrium) condenses as the hydrate $NH_3 \cdot H_2O$; CH_4 (the major form of C in equilibrium) condenses as the clathrate $CH_4 \cdot 6H_2O$; and finally, excess CH_4 condenses as the pure solid.

For both the gas and condensed phases, we emphasize again that the rates of the above conversions must be fast relative to changes in temperature and pressure for the thermochemical equilibrium products to be relevant. As discussed in the next section, this condition is not always met.

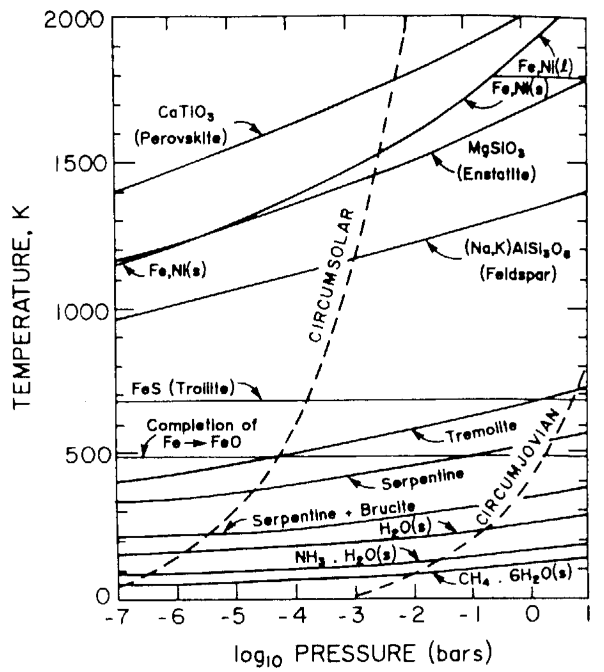

Figure 4. Thermochemical equilibrium stability fields for condensed solid material in a solar composition medium. Also shown are illustrative temperature-pressure profiles for the circumsolar and circumJovian disks.

III. DYNAMICAL-CHEMICAL PROCESSES

Chemistry circumstellar disks is profoundly influenced by sufficiently strong circulation and mixing if it occurs in the disk. Mixing processes in disks are often discussed in the context of a standard model (see, e.g., Pringle 1981; Lin and Papaloizou 1985; Morfill et al. 1985). This model parameterizes the radial angular momentum flux which is fundamentally quadratically nonlinear in velocity solely by a gradient eddy or viscous diffusion expression which is linear in velocity. This simplification (or oversimplification) has enabled conclusions to be reached by simply choosing a viscosity which ensues evolution of the disk on the observed time scale (10^5 to 10^6 yr). A particular difficulty arises when this viscosity is considered applicable also to the transport of trace materials in the disk.

There are arguments (albeit not universally accepted) favoring strong trace material mixing in the circumsolar disk and by analogy probable strong mixing in other circumstellar disks. First, there is considerable observational evidence for extensive inner circumsolar nebular mixing and reprocessing contained in chondritic meteorites. Specifically, these meteorites are an inhomogeneous mixture of materials (chondrules, refractory inclusions, matrix) which formed in distinctly different nebula environments in which they underwent varying degrees of condensation, vaporization and recondensation (see, e.g., review by Wood 1988). Formation of this mixture requires strong mixing of these materials with different histories (although the timing and spatial scale of the mixing is ill defined in part because the separation of these nebula environments is unknown).

Second, the time scale for mixing can be much shorter than the time scale for disk evolution because basic nonlinear acceleration processes enable the shear in an accretion disk to be maintained against viscous dissipation (plus gravitational torques if applicable), so that trace constituents in these disks can be well mixed without momentum being well mixed (Prinn 1990). Stevenson (1990) presents an opposing viewpoint. He concludes that momentum and trace constituents are approximately equally (and in this context both weakly) mixed. These arguments are based on an acceptance of the standard model which as discussed above neglects the nonlinear (in velocity) nature of momentum transport compared to the linear (in velocity) nature of trace material transport. Prinn (1990) argues that the poor trace constituent mixing predicted in accretion disk models which omit nonlinear processes is an artifact of this omission. This is almost certainly true when the system is externally forced by the disk accretion process but the Stevenson (1990) case cannot be ruled out when accretion ceases. An important question to be answered is, therefore, whether the material which formed the present solar system was defined while accretion onto the disk was still proceeding or afterwards.

Third, as we discuss in Sec. III.B, the disk accretion process itself provides an important and perhaps dominant forcing mechanism for strong mixing.

A. Kinetic Inhibition Models

The major effect of strong mixing in the disk is to cause chemical disequilibration. The so-called "kinetic inhibition" theory for thermochemical disequilibration induced by rapid mixing in a thermoclinic environment was first proposed by Prinn and Barshay (1977) to explain the unexpected discovery of CO in the CH_4-rich Jovian atmosphere. It was later applied also to the circumsolar nebula disk (Lewis and Prinn 1980) and to circumplanetary disks around the Jovian planets (Prinn and Fegley 1981). The disequilibration results specifically when the cooling time due to transport in a medium with a temperature gradient becomes shorter than the relevant chemical reaction time for maintaining equilibrium.

In a hot thermoclinic environment like a gaseous circumstellar disk one can define for each chemical species a quench radius (R_q) inside which the temperatures are high enough (and thus thermochemical reactions fast enough) to ensure that the species concentration $[i]$ is essentially equal to that in thermochemical equilibrium (see Fig. 5). To a sufficient approximation R_q is the radius at which the chemical destruction time $t_{\mathrm{chem}} = -[i]/(\mathrm{d}[i]/\mathrm{d}t)$ for the species equals the radial mixing time t_{mix}. Also, since temperature, pressure and hence $[i]/t_{\mathrm{chem}}$ generally decrease with altitude z above the disk plane,

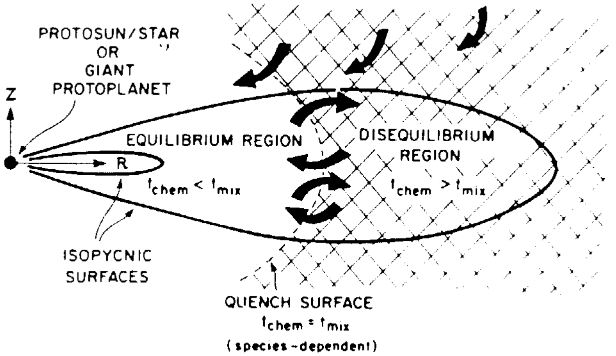

Figure 5. Illustration of the species-dependent quench surface separating thermochemical equilibrium and transport-induced-disequilibrium regions in gaseous circumsolar or circumJovian planetary disks.

the equilibrium region bounded by the quench surface is convex as shown in Fig. 5. We use the mixing ratio form of the species continuity equation in cylindrical coordinates in the region $R > R_q$ with the assumption that the gas is quenched chemically by moving outward a distance $l_{\rm chem}$ from R_q which is much less than the characteristic length L of eddy circulations in the disk. This leads to the solution that the mixing ratio f in the disequilibrium region ($R > R_q$) equals approximately the equilibrium value of f at the quench radius R_q (see Eqs. (13)–(18) of Prinn and Fegley [1989] for details). This latter solution is the one appropriate to reactions with large activation energies such as the conversions of CO to CH_4 and N_2 to NH_3 in the hydrogen-rich circumsolar nebula disk. Referring back to the thermochemical equilibrium calculations in Figs. 1 to 3, the general approach is to compute $t_{\rm chem}$ values for the relevant conversion using equilibrium concentrations and then to compare them to estimates of $t_{\rm mix}$ (see next section). Then we define the quench radius to be where $t_{\rm chem} = t_{\rm mix}$. The temperature at the quench radius is referred to as the quench temperature T_q and it is often more convenient to define the quench position in the disk by T_q rather than R_q. Sample T_q values defined by considering only homogeneous gas-phase conversion reactions to define $t_{\rm chem}$ and equating $t_{\rm mix}$ to the approximate lifetime of the circumsolar disk (10^{13} s) are shown in Figs. 1 to 3. The actual $t_{\rm chem}$ values are shorter (lowering T_q) than the homogeneous ones due to heterogeneous catalysis reactions on Fe particles but this is countered by the $t_{\rm mix}$ values also being less than 10^{13} s (raising T_q). The importance of knowing $t_{\rm mix}$ is clear and in the next section we deduce $t_{\rm mix}$ values for a disk mixed by eddies forced by nonaxisymmetric accretion of interstellar material.

B. Accretionally Forced Turbulence

The forcing of turbulence in circumstellar accretion disks by the infalling material itself has been recognized by Cameron (1978*a*) and Prinn (1990), but it has not been quantified and indeed has received remarkably little attention. As summarized by Prinn (1990), the thermodynamics of accretion involves the conversion of the initial gravitational potential energy into kinetic energy (mostly orbital but some radial). Next, a large fraction of the kinetic energy is converted into internal (thermal) energy by compression or frictional dissipation as the accreting material collides and merges with the gaseous disk. Some of the latter thermal energy is then lost by radiation to space and some is converted back to kinetic energy by various internal instabilities. Convective instability has received some attention but there are many other instabilities (baroclinic, barotropic, etc.) yet to be considered. However, these internal instabilities cannot reduce the temperature gradient or the absolute temperature to zero and they are capable therefore of converting only a very small fraction of the internal energy back to kinetic energy. Hence the production (through internal instabilities) of disk kinetic energy from disk internal energy is expected to be considerably less than the production of disk kinetic energy (through accretion) from initial gravitational potential energy (Prinn 1990). An approximate estimate of the speed in eddy circulations forced in the disk by accretion is provided here by considering the eddy angular momentum equation in cylindrical polar coordinates for the disk (Prinn 1990, Eq. 4):

$$\frac{1}{R}\frac{\partial}{\partial R}(R^2\sigma\langle V'U'\rangle)+R\sigma\langle V\rangle\frac{1}{R}\frac{\partial}{\partial R}(R\langle U\rangle) = R(\langle U_a\rangle - \langle U\rangle)\left(\frac{d\sigma}{dt}\right)_a \tag{21}$$

where R is the radius, σ is the surface density, $(d\sigma/dt)_a$ is the the rate of change of σ due to accretion, V and U are the radial and azimuthal components of velocity, respectively, U_a is the azimuthal velocity of infalling material, t is time and $\langle i\rangle$ and i' denote, respectively, the azimuthal average and deviation from this azimuthal average of the quantity i. Assuming the radial advective flux is small relative to the radial eddy flux of azimuthal (angular) momentum, equating $\langle U_a\rangle - \langle U\rangle$ to the product of the free-fall velocity $(2GM/R)^{1/2}$ of accreting material and a constant α of order unity, and neglecting any small radial dependence for σ, we have:

$$\frac{2}{R}\langle V'U'\rangle + \frac{\partial}{\partial R}\langle V'U'\rangle = \frac{\alpha}{\tau}\left(\frac{2GM}{R}\right)^{1/2} \tag{22}$$

where $\tau = (d\ln\sigma/dt)^{-1}$ is the evolution time for mass in the disk. Assuming in Eq. (22) the scaling relations $\langle V'U'\rangle \approx v^2$ and $\partial\langle V'U'\rangle/\partial R \approx v^2/L$ where v and L are the characteristic speed and length scale of the eddy circulations, we obtain the following simple expression for the eddy speed

$$\begin{aligned} v &= \left[\frac{GMR\alpha^2}{2\tau^2(1+R/2L)^2}\right]^{1/4} \\ &= 18\left(\frac{M}{M_s}\right)^{1/4}\left(\frac{R}{R_o}\right)^{1/4}\left(\frac{\tau_0}{\tau}\right)^{1/2}\alpha^{1/2}(1+R/2L)^{-1/2} \end{aligned} \tag{23}$$

in m s^{-1} where M_s is the mass of the Sun, $R_o = 1$ AU, and $\tau_o = 10^{13}$ s is the approximate lifetime of the gaseous circumsolar disk. The nominal eddy speed (v_0) of $18/(1+R/2L)^{1/2}$ m s^{-1} is $0.95\%/(1+R/2L)^{1/2}$ of the sound speed in H_2 (1900 m s^{-1} at 600 K). For all L exceeding about $5 \times 10^{-3}R$ this speed equals or exceeds the maximum speed expected from free convection in the disk (Cabot et al. 1987*b*). This v_0 also implies nominal radial eddy mixing times $t_{\rm mix} = R_o/v_o$ of $6 \times 10^9/(1+R/2L)^{1/2}$ s. Thus for all L exceeding about $4 \times 10^{-7}R$, $t_{\rm mix} < \tau_o$ so that the disk is well mixed. Finally, we note parenthetically that the advective velocity $\langle V \rangle$ estimated by equating the right-hand side of Eq. (21) to the second (rather than the first) term on the left-hand side and using the Keplerian velocity for $\langle U \rangle$ is

$$\begin{aligned}\langle V \rangle &= 2^{3/2}\frac{\alpha R}{\tau} \\ &= 0.04\frac{R\tau_0}{R_0\tau}\,\alpha \text{ m s}^{-1}\end{aligned} \qquad (24)$$

which is evidently much less than the eddy speed v.

C. Kinetic Inhibition Results

The quench points for the conditions in Figs. 1 to 3 are located at the intersections of the disk temperature profiles and the quench temperature curves. Remembering that the species mixing ratios at the quench points determine the ratios at all points exterior to them (i.e., at all $T < T_q$ or all $R > R_q$), we conclude from Figs. 1 and 2 that [CO] >> [CH_4] and [N_2] >> [NH_3] for all T in the circumsolar nebula disk. Conversely, [CH_4] >> [CO] and [NH_3] >> [N_2] in the circumJovian planetary nebula disk. From Fig. 3, [CO_2] is 0.2 to 1% of [CO] in both disks but as [CO] is negligible in the circumJovian planetary disk, it is only in the circumsolar disk that CO_2 becomes an important carbon-containing compound. These conclusions from the above simplified approach using Figs. 1 to 3 are qualitatively similar to the conclusions from the more detailed approaches which take into account both homogeneous and heterogeneous (catalyzed) reactions and a wide range of feasible mixing times (Lewis and Prinn 1980; Prinn and Fegley 1981; Prinn and Barshay 1977; Prinn and Olaguer 1981; Prinn and Fegley 1989).

The chemical lifetimes and quench temperatures for formation of hydrated silicates (e.g., serpentine, tremolite in Fig. 4) in the solar nebula have been considered by Prinn and Fegley (1989). They conclude that even the simple hydration (reaction 19) of 0.1 μm radius forsterite (Mg_2SiO_4) grains has $t_{\rm chem} \geq 10^{18}$ s (which certainly exceeds $t_{\rm mix}$ and even exceeds the lifetime of the solar system) at the 225 K temperature at which its hydration to serpentine and brucite becomes thermodynamically possible in the circumsolar nebula disk. Formation of tremolite from hydration of enstatite plus diopside at around 500 K and of serpentine from hydration of enstatite plus forsterite at around 350 K requires solid-solid diffusion leading to even longer $t_{\rm chem}$ times. Tremolite is in any case a minor predicted mineral in the nebula and rare in meteorites. The anhydrous silicates accreted onto the circumsolar disk or produced from thermal reprocessing of accreted interstellar hydrated silicates are expected therefore to be very stable in the disk. In contrast, Fegley and Prinn (1989) conclude that the 100 K higher temperatures (325 K) and 10^5 times greater H_2O concentrations at the serpentine formation point in the circumJovian disk mean that $t_{\rm chem} \approx 10^9$ s which may feasibly be faster than the mixing time due to convection in this disk. Thus unlike in the circumsolar disk, the formation of hydrated silicates may not be kinetically inhibited in the circumJovian disk.

Fegley and Prinn (1989) discussed for the solar nebula the conversion of Fe to FeS (in troilite) and FeO (in olivine and pyroxene) and concluded that FeS formation is not kinetically inhibited at the FeS stability point ($\approx$690 K) whereas the oxidation of Fe and its incorporation into magnesium silicates was almost certainly kinetically inhibited. In this case, the excess Fe not converted to FeS could thermodynamically begin to react with H_2O vapor at about 380 K to form magnetite (Fe_3O_4) but laboratory data are not available to determine if this reaction is not also inhibited.

The kinetic inhibition of the $N_2 \rightarrow NH_3$, $CO \rightarrow CH_4$ and anhydrous → hydrous silicate transitions in the circumsolar disk but not in the circumJovian planetary disks means that low-temperature condensation of ice-rich phases in the two disks are distinctly different (Lewis and Prinn 1980; Prinn and Fegley 1981). In the solar disk, we expect at successively lower temperatures formation of anhydrous rock, H_2O ice, NH_4HCO_3 salt, NH_4COONH_2 salt, CO_2 (dry) ice, $CO{\cdot}6H_2O$ clathrate, $N_2{\cdot}\ 6H_2O$ clathrate, CO solid and N_2 solid. Conversion of some of the CO through Fischer-Tropsch-type reactions to involatile carbonaceous compounds (condensing at higher temperatures than ice) and light hydrocarbons and hydrocarbon clathrates (condensing coincident with or at lower temperatures than ice) is also possible particularly if the metallic Fe catalyst required is not completely oxidized or sulfurized as discussed above or de-activated by organic coatings. If volatilization of interstellar involatile carbonaceous compounds was kinetically inhibited during accretion shock heating and within the circumsolar nebula disk then this would add to the involatile carbon component.

In the circumJovian planetary disks in contrast we have the condensation sequence: hydrous rock, H_2O ice, $NH_3{\cdot}H_2O$ hydrate, $CH_4{\cdot}6H_2O$ clathrate, CO solid and N_2 solid. This looks superficially like the condensation sequence if chemical equilibrium prevailed in the circumsolar nebula but on closer examination it is clearly recognized as different due to the presence of some C and N as CO and N_2. The significant differences between the circumsolar and circumJovian planetary condensation sequences which are summarized in Table II lead to the conclusion that low-temperature condensates in ice-rich bodies may be diagnostic of the type of nebula disk in which they formed (Prinn and Fegley 1981).

Certain caveats concerning the formation of the clathrates in the above sequences are in order. For the Anders and Grevesse [C]/[O] ratio and even more so for the Cameron [C]/[O] ratio, there is insufficient H_2O to enclathrate the majority of the CO let alone the N_2 in the circumsolar disk. Lunine and Stevenson (1985) give theoretical arguments and Davidson et al. (1987) give experimental evidence that $CO{\cdot}6H_2O$ is more stable than $N_2{\cdot}6H_2O$ so the latter clathrate may be very rare indeed. Similar difficulties exist for CO and N_2 clathrates in circumJovian planetary disks where there is insufficient water to enclathrate even the majority of the CH_4. Fegley and Prinn (1989) also point out possible kinetic inhibition of clathrate formation in the circumsolar (but not circumJovian planetary) disk unless the activation energy for diffusion of gas into the ice is very small. Lunine (1989*b*) argues in reply that this activation energy is indeed small. However, if for CO one equates it (arguably) to the recently reported binding energy for CO on H_2O ice (14.5 kJ mole^{-1}; Sandford and Allamandola 1990*b*) this is indeed large enough to cause $CO{\cdot}6H_2O$ formation to be kinetically inhibited in the circumsolar nebula. Specifically, we compute $t_{\rm chem} = 1.6 \times 10^{17}$ s for conversion of ice particles (2 μm dimension) to $CO{\cdot}6H_2O$ at its formation temperature of about 60 K in the circumsolar nebula (Table II). Conversely, this large activation energy would lead to efficient *adsorption* of CO on ice provided the ice is sufficiently *amorphous* to expose a large enough surface area to enable $[CO]/[H_2O]$ stoichiometries like the 1/6 value in the clathrate to be realized. This may be the way in which CO was incorporated into ice to explain its presence in comets. Note also that the salts ammonium bicarbonate (NH_4HCO_3) and ammonium carbamate (NH_4COONH_2) will enable up to 1% of the solar abundances of C and N to be incorporated into ice.

IV. PLANETS AND SATELLITES

The amounts of H, O, C and N in the terrestrial planets, giant planets, satellites of giant planets, Pluto/Charon, and comets provide crucial tests of theories of their origin. This subject is thoroughly discussed by Prinn (1982), Lewis and Prinn (1984), Prinn and Fegley (1987,1989) and Lunine (1989*a*, *c*) so here we present only a brief summary and update (the latter focusing on recent observations of ice-rich satellites and comets).

A. Terrestrial Planets

It has been understood ever since Urey (1952) proposed the idea (based on evidence such as the observed depletion of noble gases like Ne relative to reactive elements like N) that the volatile elements on the terrestrial planets originated not from accretion of disk gas but from accretion of disk solids (before and after disk gas dissipation). Fegley and Prinn (1989) and Prinn and Fegley (1987) review the evidence that the major source of carbon and some hydrogen in the terrestrial planets was accretion of material rich in organic compounds (e.g., of the type produced from CO by Fischer-Tropsch reactions) with thermochemical equilibrium sources like carbon dissolved in Fe-Ni alloy

TABLE II[a]

Condensation Sequences Predicted in the Circumsolar Gas-Dust Disk and CircumJovian Planet Gas/Dust Disk[b]

Circumsolar Disk		CircumJovian Planet disk
CO-Rich	CO + Hydrocarbons	CH_4-Rich
Largely anhydrous rock[c]	Largely anhydrous rock[c] Involatile carbonaceous compounds[(e,f)]	Largely hydrous rock[d]
H_2O (150 K)	H_2O	H_2O (235 K)
NH_4HCO_3/NH_4COONH_2 (150, 130 K)[e]	NH_4HCO_3/NH_4COONH_2[e]	$NH_3{\cdot}H_2O$ (160 K)
	Light hydrocarbons and hydrocarbon clathrates[g]	$CH_4{\cdot}6H_2O$ (94 K)
		CH_4 (40 K)
CO_2 (70 K)[e]	CO_2[e]	CO (20 K)[e]
$CO{\cdot}6H_2O$ (60 K)[h]	$CO{\cdot}6H_2O$[h]	N_2 (20 K)[e]
$N_2{\cdot}6H_2O$ (55 K)[h]	$N_2 \cdot 6H_2O$[h]	
CO (20 K)	CO (20 K)	
N_2 (20 K)	N_2 (20 K)	

[a] Prinn and Fegley 1989.

[b] Condensation temperatures in models (Lewis and Prinn 1980; Prinn and Fegley 1981) are given for each condensate where available. For the circumsolar disk the CO-plus-hydrocarbons sequence is preferred with the condensation temperatures being slightly below those in the CO-rich case (the precise temperatures will depend on the degree of CO to hydrocarbons conversion).

[c] Olivine, pyroxene, troilite, unoxidized Fe, feldspar, etc.

[d] Serpentine, talc, magnetite, troilite, tremolite, etc.

[e] These compounds contain $\leq 10^{-2}$ of the total C or N.

[f] **Exemplified by organic material in chondrites, and formed by nebular Fischer-Tropsch-type reactions and/or of *interstellar* origin.**

[g] **Exemplified by the light (C_1–C_5) hydrocarbons formed as initial products in high H_2:CO environments (see Prinn and Fegley 1989). Precise condensation or enclathration temperature depends on the chain length and hydrocarbon abundances.**

[h] **There is insufficient H_2O to allow the formation of all C and N as CO and N_2** [illegible]

being secondary. This argues in favor of the CO plus hydrocarbons sequence in Table II. The small amount of nitrogen in these planets is easily provided by the same organic compounds. As noted earlier, the kinetic inhibition of hydrous silicate formation in the circumsolar nebula makes the most likely source of H_2O for the terrestrial planets to be accretion of ice-rich material in the post-gas-rich phase of the circumsolar disk (this material could also include hydrous minerals formed in asteroid-sized bodies once these evolved).

B. Giant Planets

It is also well understood that the giant planets are composed of circumsolar disk gases plus additional solid material either contained in a precursor core or accreted later during both the gas-rich and post-gas-rich epochs (see the review by Pollack and Bodenheimer [1989]). Prinn and Fegley (1989) conclude that the solid material must have been 9 to 30% (Jupiter) and 3 to 12% (Saturn) carbon by mass to explain the bulk properties and atmospheric composition of these two planets. This also argues in favor of the CO plus hydrocarbons sequence in Table II because the CO-rich sequence has insufficient carbon at the formation temperatures for Jupiter and Saturn which certainly exceeded 60 K. Similar conclusions for large carbon inputs pertain to Uranus and Neptune with the organic carbon content of the added solid material being at least comparable to the carbon in (solid or clathrate) carbon monoxide (Pollack et al. 1986; Fegley and Prinn 1986; Simonelli et al. 1989).

C. Ice-Rich Satellites and Pluto

The ice-rich satellites of the outer planets and Pluto provide a wealth of significant information on the circumsolar nebula disk. The information refers not only to the outer regions of the nebula disk but also to inner regions as kinetic inhibition of CO → CH_4, N_2 → NH_3, and anhydrous rock → hydrous rock, and catalytic conversion of CO to light or heavy hydrocarbons are inner nebula processes impacting the composition of outer nebula objects (Lewis and Prinn 1980; Prinn and Fegley 1981,1989; Lunine 1989*a*, *c*).

Using observations and models for satellite interiors, Johnson et al. (1987), Johnson (1990), McKinnon and Mueller (1988,1989), and Simonelli et al. (1989) have computed the ratio r = (rock mass)/(rock mass + ice mass) in various ice-rich bodies in the outer solar system and these are shown in Fig. 6. To compare with these "observed" r values, we have computed models for a variety of kinetic inhibition scenarios and for the C and O abundances A_C and A_O (measured relative to $A_{Si} = 10^6$) of both Anders and Grevesse (1989) and Cameron (1982). We model the rock as SiO_2+ MgO + FeO + FeS (i.e., anhydrous) and noting the similarity of the Si, Mg, Fe and S abundances of Anders and Grevesse (1989) and Cameron (1982), we use the average of these two abundance estimates for these latter 4 elements. We consider carbon in three forms: CO (noncondensing), light hydrocarbons including CH_4 (noncondensing), and heavy hydrocarbons (condensing). We model the heavy condensing hydrocarbons as CH_2 and add them to the ice mass in the

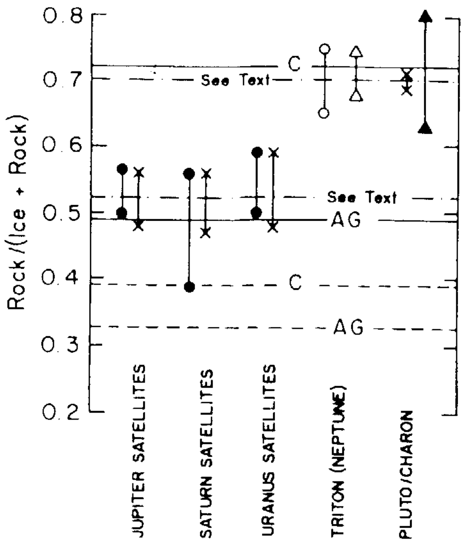

Figure 6. Ranges of r = (rock mass)/(ice plus rock mass) for ice-rich bodies in the solar system deduced from observations by Johnson et al. (1987; filled circles), Johnson (1990; open circles), Simonelli et al. (1989; crosses), McKinnon and Mueller (1988; filled triangles) and McKinnon and Mueller (1989; open triangles). Also shown are predicted r values for condensates in a CO-rich solar-composition environment (solid horizontal lines) and a CH_4-rich solar-composition environment (dashed horizontal lines). Predictions are shown for solar C and O abundances from Cameron (1982; labeled "C") and from Anders and Grevesse (1989; labeled AG). The dot-dashed horizontal lines at r = 0.52 and r = 0.70 are predictions from a variety of models discussed in the text.

definition of r. We define the mole fractions of total carbon in CO, light hydrocarbons, and heavy hydrocarbons as α, $1 - \alpha - \beta$, and β, respectively. Thus the CO-rich nebula of Lewis and Prinn (1980) has $\alpha \approx 1 - \beta$, $1 - \alpha - \beta \approx 0$, and $\beta < \alpha$ (allowing for some conversion of CO to heavy hydrocarbons by Fischer-Tropsch-type reactions). Conversely the CH_4-rich nebula of Prinn and Fegley (1981) has $\alpha \approx 0$, $1 - \alpha - \beta \approx 1$, and $\beta \approx 0$, respectively.

With the above definitions, we obtain

$$r = 9.755 \times 10^6 [A_O - \left(\alpha - \frac{14}{18}\beta\right) A_C + 6.296 \times 10^6]^{-1}. \quad (25)$$

Note that r does not depend on the [C]/[O] ratio A_C/A_O alone but on the *separate values* of A_O and A_C.

In Fig. 6, we see distinctly lower values of r for the satellites of Jupiter, Saturn and Uranus ($r \approx 0.52$) than for Triton, Pluto and Charon ($r \approx 0.7$). For A_C and A_O from Anders and Grevesse (1989), we could approximately explain the Jovian, Saturnian and Uranian satellites as objects formed in a CO-rich ($\alpha = 1$, $\beta = 0$) solar nebula disk but must then rely on *ad hoc* explanations (e.g., massive post-formation water loss) to explain Triton, Pluto and Charon. Conversely for A_C and A_O from Cameron (1982), we could easily explain Triton, Pluto and Charon as objects formed in a CO-rich ($\alpha = 1$, $\beta = 0$) solar nebula disk but must then rely on *ad hoc* explanations (e.g., massive post-accretional water addition) to explain the Jovian, Saturnian and Uranian satellites.

To address this failure of the simplest models to fit the data, we can use Eq. (25) to deduce the values of $\alpha - (14/18)\beta$ which will fit the apparent r values (0.52, 0.7) of the above two classes of objects. We thus obtain for the Anders and Grevesse (1989) abundances

$$\begin{aligned}\alpha - \frac{14}{18}\beta &= 1.104 \text{ (Jovian, Saturnian, Uranian)}\\ &= 1.586 \text{ (Triton, Pluto, Charon)}\end{aligned} \tag{26}$$

and for the Cameron (1982) abundances

$$\begin{aligned}\alpha - \frac{14}{18}\beta &= 0.349 \text{ (Jovian, Saturnian, Uranian)}\\ &= 0.831 \text{ (Triton, Pluto, Charon)}\end{aligned} \tag{27}$$

As $\alpha+\beta\leq 1$, we see that for the Anders and Grevesse (1989) abundances no values of α and β will suffice (consistent with both the Anders and Grevesse values being less than 0.52 in Fig. 6).

The almost ubiquitous presence of some dark presumably carbonaceous material in ice-rich bodies in the outer solar system argues either that $\beta \neq 0$ or that the bodies contained some CH_4 which was photochemically converted to carbonaceous material (i.e., $1 - \alpha - \beta \neq 0$). Also, the presence of CH_4 on Titan, Triton (Spencer et al. 1990; Broadfoot et al. 1989), and Pluto argues either for $1 - \alpha - \beta \neq 0$ or for thermochemical conversion of organic material in object interiors to form CH_4 (i.e., $\beta \neq 0$). Therefore we can fit the observations in Fig. 6 with the Cameron (1982) abundances if we make the following reasonable assumptions: (a) the Jovian, Saturnian and Uranian satellites formed in a CH_4-rich circumplanetary disk with the carbon being 65% CH_4, 35% CO, and only trace amounts of heavy hydrocarbons (i.e., $\alpha = 0.349$, $1-\alpha-\beta = 0.651$, $\beta\approx 0$), and (b) Triton, Pluto and Charon formed in a CO-rich circumsolar disk with the carbon being 90% CO, 9% heavy hydrocarbons and 1% CH_4 (i.e., $\alpha = 0.9$, $\beta\approx 0.0887$, $1-\alpha-\beta = 0.0113$).

Alternatively, we can assume that the C and O abundances are unknowns and ask what values of A_C and A_O in Eq. (25), would allow the Jovian, Saturnian and Uranian satellites to form in very CH_4-rich circumplanetary nebulae ($\alpha = 0$, $\beta = 0$) while Triton, Pluto and Charon formed in the CO-rich environment discussed in the previous paragraph (α=0.9, β=0.0887, $1-\alpha-\beta = 0.0113$). This requires $A_o = 1.25\times 10^7$ and $A_c = 0.59\times 10^7$ which are each significantly less than either the Cameron (1982) or Anders and Grevesse (1989) values. This explanation would therefore require the C and O abundances in the circumsolar disk to be much less than the current solar values due to some unforeseen evolutionary process which seems very unlikely.

Finally, we can model the data by postulating post-formation water loss. Using Anders and Grevesse (1989) abundances, the Jovian, Saturnian and Uranian satellites could have formed in a CH_4-rich (α=0, β=0) environment if they subsequently suffered 56% loss of their original ice content while Triton, Pluto and Charon could be explained as being formed in a CO-rich ($\alpha = 1$, $\beta = 0$) environment if they subsequently lost 59% of their ice content. For the Cameron (1982) abundances, formation of the Jovian, Saturnian and Uranian satellites in the same CH_4-rich environment requires 41% post-formation loss of ice while formation of Triton, Pluto and Charon in the same CO-rich environment requires essentially no post-formation water loss.

In summary, a variety of explanations can be put forward to explain the r values of ice-rich bodies. To differentiate between them, more knowledge is needed about current A_O and A_C values, the possibility, if any, of evolution of A_O and A_C over time, and mechanisms for post-formation evolution of r.

V. COMETS, METEORITES AND ASTEROIDS

A. Comets

Comets also contain important information on the circumsolar nebula disk. Prinn and Fegley (1989) concluded that the analyses of Halley observations available at that time which indicated the presence of several percent CO, a few percent CH_4, and up to 1% NH_3 relative to H_2O could be explained by this comet being a heterogeneous mixture. Specifically, they proposed a mixture of a small amount of condensate containing CH_4 and NH_3 from a circumJovian planetary disk (Prinn and Fegley 1981) and a large amount of condensate containing CO from either the processed circumsolar disk (Lewis and Prinn 1980) or from unprocessed interstellar material. Engel et al. (1990) proposed an alternative model in which CH_4 was provided by partial conversion of CO to CH_4 in the inner circumsolar disk followed by outward mixing and the NH_3 was of interstellar origin. The Prinn and Fegley (1989) proposal involves ejection of circumJovian planetary disk material out into the solar system through (post-gas-phase) collisions but the process has not been quantified. The Engel et al. (1990) proposal requires catalysis of the CO → CH_4 conversion down to temperatures of 600 to 800 K which is unlikely (Fegley and Prinn 1989), and also survival by interstellar NH_3 condensate of accretional shock heating.

Recent Halley analyses indicate that the two above proposed mechanisms for producing heterogeneous mixtures may not be necessary. Boice et al. (1990) have specifically reanalyzed the Giotto mass spectrometer data for Halley and concluded that abundant CH_4 is not required because the hydromonocarbon ions observed can be explained by the presence of heavier organic compounds (e.g., polymerized formaldehyde) on Halley. Specifically, they conclude that CH_4 is $<0.5\%$ of CO which is consistent with its origin exclusively in the CO-rich circumsolar nebula disk (Lewis and Prinn 1980). As noted earlier, up to 1% of the solar C and N is predicted to condense as NH_4COONH_2 and NH_4HCO_3 in a CO-rich circumsolar disk so that provided there are no kinetic barriers to their formation these species are potential sources of NH_3, CO_2 and HCN. Also Boice et al. (1990) note that organics could also be the sources of the HCN and inferred NH_3 in the Halley coma. Thus sources of NH_3 beyond those expected in circumsolar disk condensates may also not be required.

Finally, on the issue of interstellar material being present in comets Tokunaga and Brooke (1990) have compared infrared spectra of comets and interstellar dust and gas in molecular clouds and found significant differences in both the silicate and organic band profiles and in the relative abundances of some molecules (CH_4, CH_3OH). They conclude that comets did not therefore form from unaltered interstellar grains in agreement with the Boice et al. (1990) conclusion.

B. Chondritic Meteorites

Chondritic meteorites provide the rare luxury of detailed laboratory chemical, physical and isotopic analyses of ancient material in the solar system. A detailed review of current knowledge is provided in a recent Space Science Series book (Kerridge and Matthews, eds. 1988). We focus here only on a few results relevant to the preceding discussion. The reader should be aware, however, that there are many detailed aspects of meteorites not easily explained by current models (e.g., origin of chondrules).

One idea which can be addressed through meteorites is whether the CO-rich nebula predicted by kinetic inhibition theory is conducive to organic synthesis. As reviewed by Hayatsu and Anders (1981), Fischer-Tropsch-type reactions in the circumsolar disk could have led to some of the organic material in these meteorites. For example, CI1 and CM2 chondrites contain organic material light in ^{13}C and carbonates heavy in ^{13}C and this pattern has been reproduced in organics and CO_2 synthesized by Fischer-Tropsch reactions from CO and H_2 (note that this has not yet been done in laboratory environments appropriate to the circumsolar disk). On the other hand, Yang and Epstein (1983) and Pillinger (1984) note that the D/H ratio in chondritic organic matter can be up to 50 times that in solar composition requiring equilibration of organic material with the major D reservoir (HD) at very low temperatures (e.g., <100 K). Such low-temperature equilibration is undoubtedly kinetically inhibited in the circumsolar nebula but may proceed over much longer time scales in (ionized) interstellar clouds. How much of the organic material in meteorites is circumsolar and how much is interstellar remains an open question.

Petrographic evidence (see, e.g., Barber 1985) favors an origin for the hydrous silicates found in CI1 and CM2 meteorites in environments which are expected in "asteroid-like" meteorite parent bodies but not expected in the circumsolar disk. This is in accordance with the prediction discussed earlier that the hydration of silicates in the circumsolar disk is kinetically inhibited. Concerning the origin of the water needed to carry out hydration on the parent bodies, Bunch and Chang (1980*b*) presented water ice as a possibility. Prinn and Fegley (1989) concurred noting that the D/H ratio in the meteoritic hydrated silicates (Yang and Epstein 1983; Pillinger 1984) was consistent with (but did not demand) the source of this water being simply ice condensed at about 200 K.

C. Asteroids

Asteroids have so far been investigated only by remote sensing but these studies have already provided insight into circumsolar nebula processes. Jones et al. (1990) have recently presented results of laboratory and telescopic observations of the low-albedo outer-belt asteroids (the C, P and D asteroids between 2.4 and 5.2 AU). Some 66% of the C asteroids have hydrated silicate surfaces. In contrast, the P and D asteroids appear to have anhydrous silicate surfaces. They conclude that their data is consistent with the initial asteroidal composition being anhydrous silicates, water ice and complex organics (i.e., the expected asteroidal composition in the CO-plus-hydrocarbons sequence of Prinn and Fegley [1989] as summarized in Table II), with subsequent evolution forced by solar wind induction heating leading to selective silicate hydration reactions. The latter reactions would maximize in the nearest C asteroids and minimize in the most distant P and D asteroids thus explaining the observed variations in the degree of surface silicate hydration.

VI. CONCLUSIONS

Observations of solar system objects have already provided much significant information on the gaseous circumsolar disk environment in which they originated. Current observations of many volatile-rich bodies, though impressive in some cases, are still however insufficient to totally constrain current models. The need is great ultimately to sample and analyze unperturbed material from comets, asteroids, and ice-rich satellites as well as to continue work on remote sensing of these bodies and on meteorites. A great deal of information is contained in the trace compounds as well as the dominant compounds in these bodies. Such information may be necessary, for example, to differentiate definitively between pristine interstellar material and reprocessed disk material in these solar system objects.

Future observations of certain key chemical species in circumstellar disks obtained with sufficient sensitivity and spectral and spatial resolution could yield very significant new information about the chemistry and physics of these disks. Answers to the following key questions would be especially revealing:

1. Is the $[CO]/[H_2]$ ratio constant over the disk or does it decrease with radius due to conversion of CO to light (e.g., CH_4) or heavy hydrocarbons?
2. Is NH_3 detectable and if so is the $[NH_3]/[H_2]$ ratio constant over the disk or does it increase with radius due to conversion of N_2 to NH_3?
3. Are silicates in the disk in anhydrous forms (olivines, pyroxenes, feldspar, etc.) as expected in the circumsolar disk or hydrous forms (serpentine, talc, etc.)? Are there changes with radius?
4. Is iron present as the metal, as FeO in olivines and pyroxenes, or as magnetite? Are there changes with radius?
5. Is there evidence for a sudden large drop in the $[H_2O]/[H_2]$ ratio at a particular radius indicating condensation of ice? Is there evidence for the expected increase in the ratio of condensate mass to gas mass at this radius?
6. What is the $[CO]/[H_2O]$ ratio at temperatures above the H_2O condensation point in the disk? If $[CO]/[H_2O] >> 1$ indicating reducing conditions, one would expect to find also abundant graphite and hydrocarbons and exotic minerals like SiC.

Finally, we still lack quantitative laboratory studies of the kinetics and mechanisms of a wide range of homogeneous and heterogeneous reactions (e.g., Fischer-Tropsch-type reactions) under conditions relevant to circumsolar, circumJovian planetary, and circumstellar gas-rich disks. This knowledge is essential to further development toward more realistic models of circumstellar disk chemistry.

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