# SOLAR NEBULA CHEMISTRY: IMPLICATIONS FOR VOLATILES IN THE SOLAR SYSTEM

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**Abstract.** Theoretical models of solar nebula chemistry which take into account the interplay between chemistry and dynamics are presented for the abundant chemically reactive volatile elements hydrogen, carbon, nitrogen, oxygen, and sulfur. The implications of these theoretical models for the volatile inventories of Solar System bodies are also discussed. The principal conclusions of this work are the following: (1) CO and $N_2$ were the dominant carbon and nitrogen gases in the solar nebula while $CH_4$ and $NH_3$ were the dominant carbon and nitrogen gases in giant planet subnebulae, (2) Fe metal grains in the solar nebula catalyzed the formation of organic compounds from $CO + H_2$ in the solar nebula via Fischer-Tropsch-type (FTT) reactions, (3) vapor phase hydration of silicates was kinetically inhibited in the solar nebula but was kinetically favorable in giant planet subnebulae, (4) bulk FeS formation was kinetically favorable in the solar nebula, (5) FeO incorporation into silicates and *bulk* $Fe_3O_4$ formation was kinetically inhibited in the solar nebula, (6) clathrate formation was kinetically inhibited in the solar nebula but was kinetically favorable in giant planet subnebulae, (7) the $CO/CH_4$ and $N_2/NH_3$ ratios in comet P/Halley require that at least some of the material in this comet originated in subnebulae around the giant planets, (8) ice/rock, $CO/CH_4$, and $N_2/NH_3$ ratios in ice-rich bodies are diagnostic of their origin, and (9) the hydrated silicates observed in chondritic meteorites are parent-body products.

## 1. INTRODUCTION

Thermochemical interactions between gases and grains in the solar nebula played a seminal role in establishing the observed volatile element inventories of the planets, their satellites, and the other bodies in the Solar System. These interactions undoubtedly took several forms. For example, the extent of evaporation and thermal reprocessing of interstellar grains accreted by the solar nebula was a primary influence on the abundance and distribution of chemically and/or isotopically anomalous materials incorporated into meteorites, comets, and (possibly) asteroids during their formation. The incorporation of chemically reactive volatiles into planet-forming materials was influenced by the extent to which gas-grain reactions, exemplified by the sulfurization and

oxidation of Fe-alloy grains, the hydration of reactive silicates, and the enclathration of carbon- and nitrogen-bearing gases into water ice, could proceed over the lifetime of the solar nebula. Finally, the synthesis of organic molecules from nebular $H_2$ and CO via Fischer-Tropsch-type reactions was dependent on the availability and catalytic activity of the appropriate grain surfaces (e.g., Fe-alloy grains.)

A comprehensive understanding of these various types of gas-grain chemical interactions and of the resulting implications for the volatile inventories of Solar System bodies requires theoretical models which acknowledge the influence of nebular dynamics on nebular chemistry. However, until recently, much of the published theoretical work in this area (e.g., see Barshay and Lewis 1976) has neglected the influence of nebular dynamics. This chapter therefore concentrates on the interplay between nebular chemistry and dynamics. The abundant, chemically reactive volatiles H, O, C, N, and S are emphasized and the implications of the chemical models for the volatile endowments of some specific objects (e.g., icy satellites of the outer planets and comet P/Halley) are described.

## 2. THEORETICAL MODELS OF SOLAR NEBULA CHEMISTRY

Chemical interactions between gases and grains in the solar nebula took place in a dynamic environment. As the interstellar gas and dust were accreted onto the growing, rapidly rotating accretion disk, they were thermally and chemically processed to varying degrees. The accreted gases from the original interstellar cloud may have been only partially equilibrated (or not at all) as they were warmed and compressed. The extent to which this may have taken place depended sensitively on the distance of the gas parcel from the proto-Sun, on whether the gas parcel was accreted at an early or a late stage of accretion disk evolution, and on the rate of radial transport in the solar nebula relative to the rate of equilibrating reactions in the gas parcel.

Recent work by several groups (e.g., Cameron and Fegley 1982; Morfill 1983) suggests that similar considerations applied to the accreted interstellar dust grains. In particular, the accreting dust grains may have evaporated only partially or not at all depending on the type of grain (e.g., rocky, icy, organic, etc.), the time at which the grain was accreted, the strength of radial mixing in the nebula, and on the distance from the proto-Sun. Furthermore, some dust grains may have experienced complex histories (e.g., evaporation, condensation, re-evaporation, and recondensation) as implied by isotopic data for some of the Ca, Al-rich inclusions in the Allende meteorite (Niederer and Papanastassiou 1984). Such observations and theoretical models suggest that evaporation and recondensation leading to thermal and chemical reprocessing were very probable in the inner regions of the solar nebula.

At the same time, other observations of meteorites imply the preservation of interstellar material (or at least the preservation of its chemical and physical signature). These observations include large isotopic anomalies in several light elements in the volatile-rich carbonaceous chondrites (e.g., see Pillinger 1984), and the observations of SiC and diamonds associated with isotopically anomalous Si, C, N, and noble gases in some primitive carbonaceous chondrites (Bernatowicz et al. 1987; Lewis et al. 1987; Zinner, Ming, and Anders 1987). However, the amounts of (apparently) interstellar material observed in primitive meteorites are generally small (e.g., the SiC found in the Murray carbonaceous chondrite by Bernatowicz et al. (1987) and Zinner, Ming, and Anders (1987) is ~ 20 ppm of the total Si in the meteorite). Thus, as noted by Prinn and Fegley (1988), extensive chemical, isotopic, and petrographic evidence from the

chondritic meteorites, and inferences that asteroids are meteorite parent bodies, suggest that the solar nebula accretion disk was extensively mixed and reprocessed (but not necessarily chemically and isotopically homogenized) out to at least four astronomical units from the proto-Sun.

Theoretical models of solar nebula chemistry which attempt to quantify these qualitative considerations must recognize the influence of both the prevailing $(P, T)$ conditions and of dynamics on the gas-grain interactions taking place in the solar nebula and in the subnebulae around the giant planets. At thermochemical equilibrium, the $(P, T)$ conditions control the nature and abundance of both gases and grains (*e.g.*, see Urey 1952; Grossman and Larimer 1974; Barshay and Lewis 1976). Such models of solar nebula chemistry, which consider only thermodynamic effects, have enjoyed great popularity in large part because the models are easily constructed (specification of the overall elemental composition, which is usually taken as solar composition, and assumption of some set of $(P, T)$ conditions is all that is required in addition to accurate thermodynamic data for species of interest). However, the seductive appeal of these models, which is their explicit assumption of thermodynamic equilibrium, is also their underlying weakness because no consideration is given to the rate at which equilibrium might be approached or to the path by which equilibrium might be approached.

Interestingly, this central problem was perhaps first recognized by Urey who pioneered thermodynamic models of solar nebula chemistry. While discussing the applications of chemical thermodynamic methods and data to solar nebula models, he noted (Urey 1953) that "Our data in this field give much information relative to possible reactions, and at higher temperatures they certainly give us practically assured knowledge of the chemical situations due to the high velocities of reactions, at least in homogeneous systems, providing the data are adequate, which is unfortunately not always the case. At lower temperatures thermodynamic equilibrium may not be reached even in periods of time that are long compared to the age of the universe, and at these temperatures the kinetics of thermal reactions or of photochemical reactions become important."

However, Urey's early recognition that the kinetics of reactions must also be considered in models of solar nebula chemistry was not acted on for nearly 30 years (*e.g.*, Lewis and Prinn 1980; Prinn and Fegley 1981). At present it is generally acknowledged that thermochemistry in the solar nebula and in giant planet subnebulae is profoundly influenced by nebular dynamics (*e.g.*, because the rate of nebular mixing determines the amount of time available for a chemical reaction to proceed) although the exact extent and nature of this influence is currently a matter of great debate. For example, Stevenson (1987, 1988a,b,c), who adopted the prescription for a standard accretion disk model (*e.g.*, see Morfill, Tscharnuter, and Volk 1985), has opined that both the solar nebula and giant planet subnebulae were poorly mixed because the outward diffusive mixing of chemically reprocessed material from the inner regions of the solar nebula (and of giant planet subnebulae) was opposed by the advective inward flow. However, as pointed out by Prinn and Fegley (1987a, 1988), Stevenson's assertion is apparently at odds with the observational evidence for extensive inner nebula processing and mixing found in chondritic meteorites. Furthermore as argued by Prinn (1988), both the solar nebula and giant planet subnebulae were probably very well mixed because (expected) non-linear processes can easily maintain the shear in an accretion disk in which diffusive mixing (and the viscosity) are large enough to overcome the negative effect of the mean inward flow on outward mixing of chemically reprocessed material. Thus, the inclusion of these non-linear processes in the standard accretion disk model (Prinn 1988) leads to the important result that outward mixing of chemically reprocessed material in the

solar nebula and in giant planet subnebulae is an efficient process, which facilitates the predicted extensive thermochemical reprocessing of the solar nebula (Lewis and Prinn 1980) and of giant planet subnebulae (Prinn and Fegley 1981). We explicitly assume that this is indeed the case and will now proceed to examine the effects of nebular dynamics on the chemistry of the abundant, chemically reactive volatile elements H, O, C, N, and S.

## 2.1. Gas Phase Chemistry of Carbon and Nitrogen

The gas phase chemistry of carbon in a $H_2$-rich gas with solar elemental ratios of H:O:C = 1446:1:0.6 (Cameron 1982) is dominated by CO, $CH_4$, and $CO_2$. The net reactions which interconvert these species are

$$CO + 3H_2 = CH_4 + H_2O \tag{1}$$
$$CO + H_2O = CO_2 + H_2. \tag{2}$$
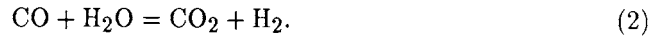
Likewise the gas phase chemistry of nitrogen in a $H_2$-rich gas with solar elemental ratios of H:N = 11,515:1 (Cameron 1982) is dominated by $N_2$ and $NH_3$ which are related via the net reaction

$$N_2 + 3H_2 = 2NH_3 \tag{3}$$

All three net reactions proceed to the right with decreasing temperature at constant pressure. Thus, if chemical equilibrium can be maintained, the $CO/CH_4$, $CO/CO_2$, and $N_2/NH_3$ ratios in the gas phase will all decrease as temperature decreases. This behavior is illustrated in Figure 1 where these ratios are plotted as a function of inverse temperature along the solar nebula $(P, T)$ profile adopted by Prinn and Fegley (1988).

However, the extent to which these three homogeneous gas-phase reactions approach quantitative conversions of CO to $CH_4$, CO to $CO_2$, and $N_2$ to $NH_3$ with decreasing temperature is severely limited by the rates at which the relevant elementary reactions occur relative to the rates of nebular mixing and overall cooling. In particular, the rates of the homogeneous gas phase CO → $CH_4$ and $N_2$ → $NH_3$ conversions are notoriously slow (*e.g.*, see Prinn and Barshay 1977; Prinn and Olaguer 1981).

The kinetic inhibition of the CO → $CH_4$, CO → $CO_2$, and $N_2$ → $NH_3$ conversions can be calculated by comparing the chemical time constants ($t_{chem}$ values) for the conversions with the nebular mixing (or overall cooling) time constant ($t_{mix}$). At sufficiently high temperatures where chemical reaction rates are sufficiently rapid, the inequality $t_{chem} < t_{mix}$ is valid and the equilibrium ratios of $CO/CH_4$, $CO/CO_2$, and $N_2/NH_3$ are obtained. However, at lower temperatures where chemical reaction rates are significantly slower, the inequality $t_{chem} > t_{mix}$ holds and chemical equilibrium cannot be maintained. Instead, the $CO/CH_4$, $CO/CO_2$, and $N_2/NH_3$ ratios in the gas phase are equivalent to the ratios which were quenched, or frozen in, at a higher temperature $T_Q$ where the equality $t_{chem} = t_{mix}$ holds.

The chemical time constants for the CO → $CH_4$, CO → $CO_2$, and $N_2$ → $NH_3$ conversions are calculated from the appropriate kinetic data as described by Prinn and Fegley (1981). A lower limit to $t_{mix}$ has generally been estimated as $t_{mix} \sim 3H/V_s \sim 10^8$ sec, where $H$ is the radial density scale length and $V_s$ is the sound speed in the solar nebula (*e.g.*, see Prinn and Fegley 1981, 1988). An upper limit to $t_{mix}$ has generally been equated to the lifetime of the solar nebula. This lifetime is approximately $10^{13}$ sec
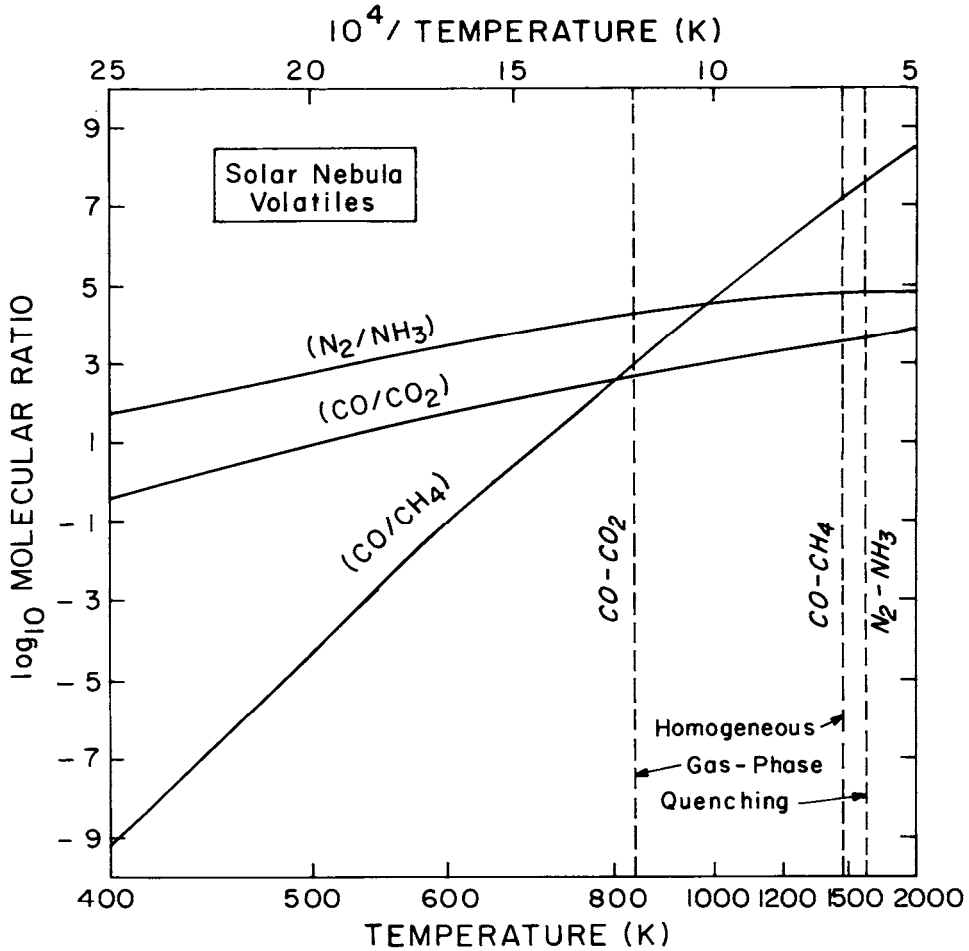
Figure I. Calculated molecular ratios of $(CO/CH_4)$, $(N_2/NH_3)$, and $(CO/CO_2)$ at equilibrium in a solar composition gas. The molecular ratios are for the solar nebula (P, T) profile illustrated in Figures 2-4. The vertical dashed lines illustrate the minimum quench temperatures for homogeneous gas-phase conversions of $CO \rightarrow CH_4$, $N_2 \rightarrow NH_3$ and $CO \rightarrow CO_2$ and correspond to the intersection of the $T_Q^{min}$ lines with the solar nebula (P, T) profile in Figures 2-4.
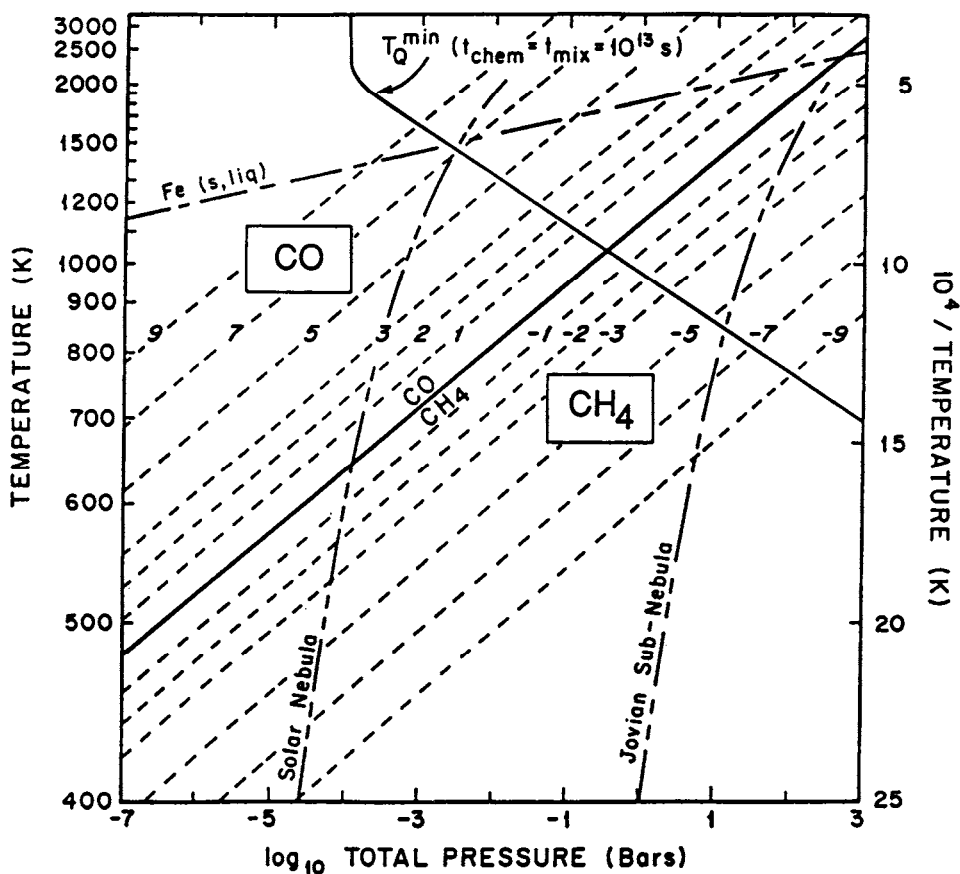
Figure 2    Calculated thermochemical equilibrium ratios of $(CO/CH_4)$ in solar composition gas. The two carbon gases have equimolar abundances along the solid line labelled $CO - CH_4$; $CO$ is more abundant to the left and $CH_4$ is more abundant to the right. Constant $\log_{10}(CO/CH_4)$ contours are shown by the dotted lines labelled $9, 7, 5, \ldots, -5, -7, -9$. The $Fe$(s, liq) evaporation line is also shown; $Fe(g)$ is stable above this line. The other three lines on this graph are representative $(P, T)$ profiles for the solar nebula and the Jovian subnebula, and the minimum quench temperature curve for the homogeneous gas-phase $CO \rightarrow CH_4$ conversion. The $T_Q^{min}$ line is discussed in more detail in the text.
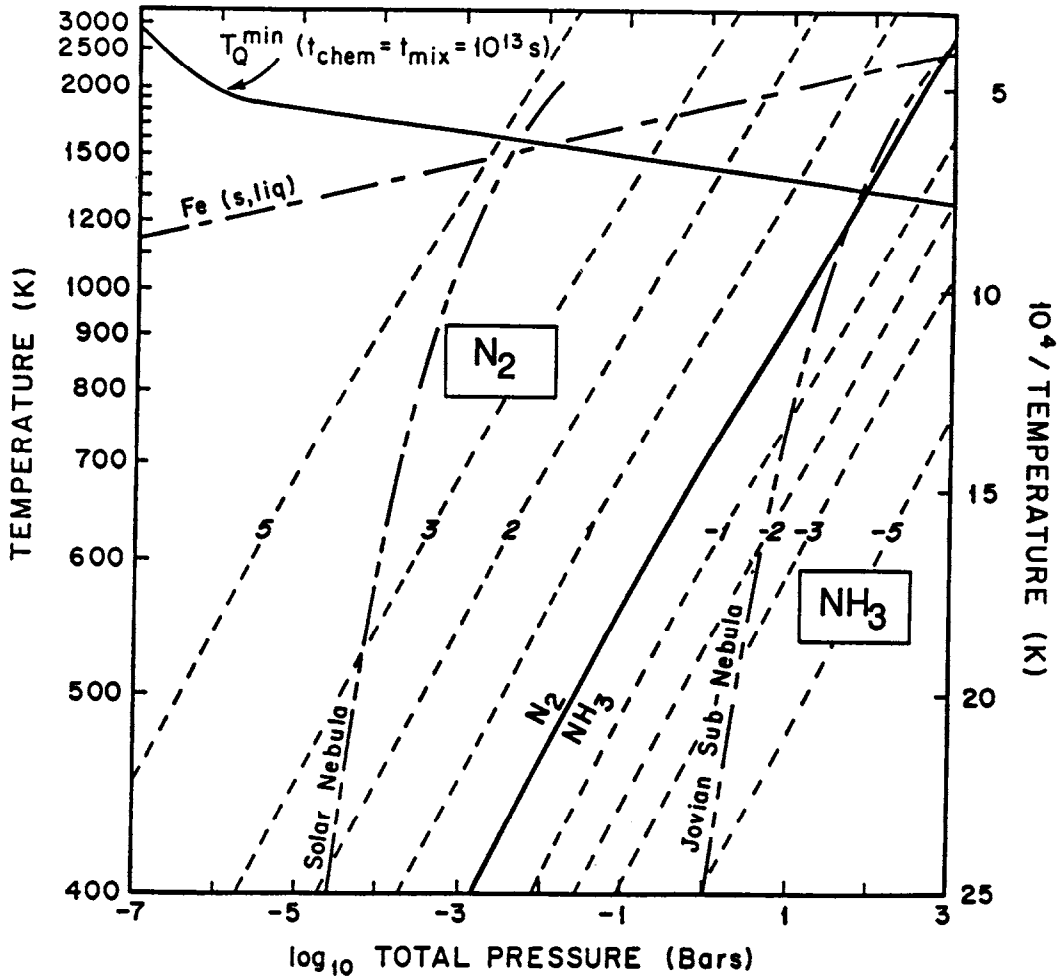
**Figure 3**   As in Figure 2 but for calculated thermochemical equilibrium ratios of $(N_2/NH_3)$ in solar composition gas. In this case the $T_Q^{min}$ curve is for the homogeneous gas-phase $N_2 \rightarrow NH_3$ conversion.
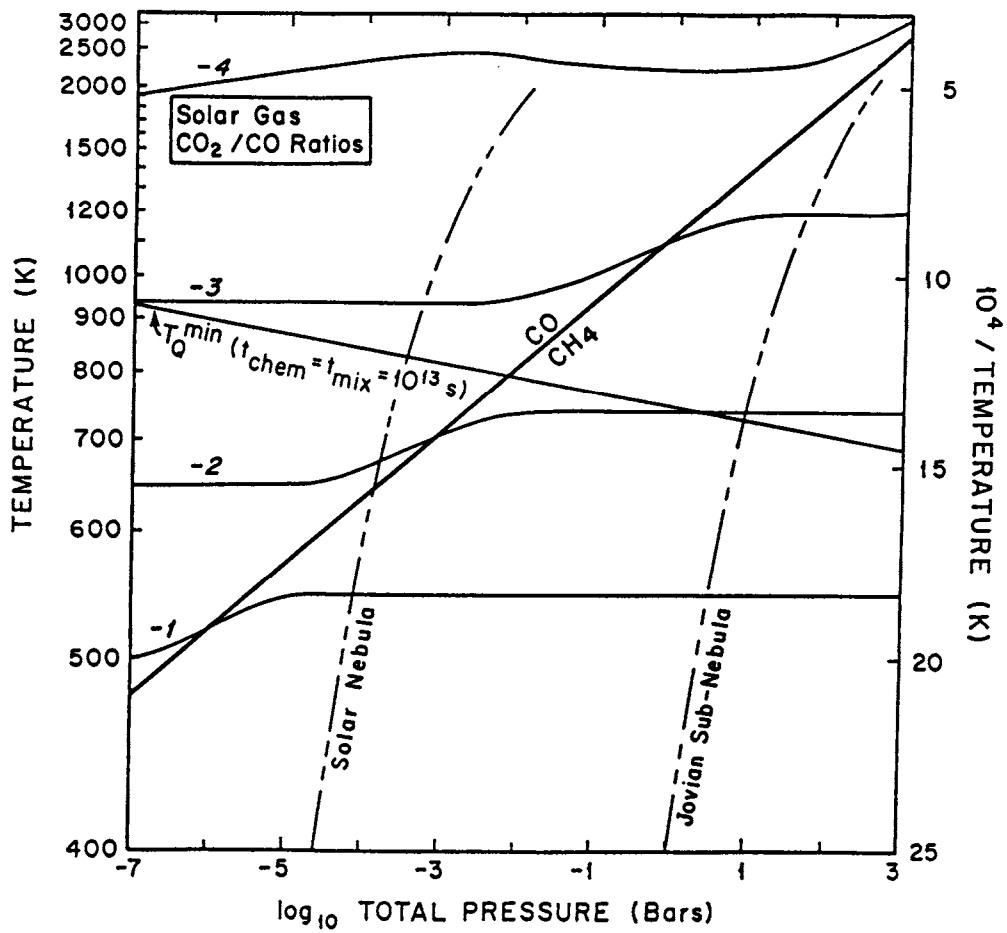
Figure 4   As in Figure 2 but for calculated thermochemical equilibrium ratios of $(CO_2/CO)$ in solar composition gas. Changes in the $H_2O$ abundance from the $CO-$ to $CH_4$-dominated regions cause the inflections in the constant $\log_{10}(CO_2/CO)$ contours. In this case the $T_Q^{min}$ curve is for the homogeneous gas-phase $CO \rightarrow CO_2$ conversion.

in currently accepted nebular models (*e.g.*, see Cameron 1985; Lin and Paploizou 1985; Morfill, Tscharnuter, and Volk 1985). Thus, homogeneous gas phase reactions with a chemical time constant $t_{chem} > 10^8$ sec may be quenched in a turbulent, rapidly mixed region of the nebula but these interactions will certainly be quenched (irrespective of nebular mixing rates) if $t_{chem} > 10^{13}$ sec, the lifetime of the solar nebula.

Because the $t_{chem}$ values *increase* rapidly with decreasing temperature, the maximum $t_{mix}$ value of $10^{13}$ sec therefore corresponds to a minimum quench temperature $T_Q$. These minimum quench temperatures, which have been calculated by Prinn and Fegley (1988), are shown in Figures 1–4. For the representative solar nebula $(P, T)$ profile shown in these figures, the CO $\rightarrow$ CH$_4$ and N$_2$ $\rightarrow$ NH$_3$ conversions quench at 1470 K and 1600 K, respectively, where (CO/CH$_4$) $\sim 10^7$ and (N$_2$/NH$_3$) $\sim 10^5$. As noted by Prinn and Fegley (1988), decreasing pressure leads to increases in these quench temperatures and to increases in the corresponding (CO/CH$_4$) and (N$_2$/NH$_3$) ratios at quench. We note that recent nebular models, such as those of Boss (1988), which lie to the left of the nebula $(P, T)$ profile shown in Figures 2–4, yield higher quench temperatures and thus larger (CO/CH$_4$) and (N$_2$/NH$_3$) ratios.

Finally, we also note that the $CO \rightarrow CO_2$ conversion is relatively facile in comparison to the CO $\rightarrow$ CH$_4$ and N$_2$ $\rightarrow$ NH$_3$ conversions. This situation, which is a consequence of the relatively rapid interconversions among oxidized carbon species such as CO – CO$_2$ – H$_2$ CO (*e.g.*, see Warnatz 1984), leads to a minimum quench temperature of $\sim$ 830 K and a (CO$_2$/CO) ratio $\sim 2 \times 10^{-3}$ for the solar nebula $(P, T)$ profile shown in the figures. Again, as noted above decreasing pressure leads to increasing quench temperatures. However, as Figure 4 shows, the low $T_Q$ values for the CO $\rightarrow$ CO$_2$ conversion suggest that equilibria between these species will be maintained down to relatively low nebular pressures ($\sim 10^{-7}$ bars). Another consequence of this situation is the possible dominance of CO$_2$ ice and CO$_2$-bearing condensates (*e.g.*, NH$_4$HCO$_3$, NH$_4$ COONH$_2$, CO$_2 \cdot$ 6H$_2$O) over CH$_4$ ice and clathrate (CH$_4 \cdot$ 6H$_2$O) in low temperature nebular condensates (Lewis and Prinn 1980).

To summarize, kinetic considerations demonstrate that in the low pressure environment of the solar nebula the CO $\rightarrow$ CH$_4$ and N$_2$ $\rightarrow$ NH$_3$ conversions are quenched at high temperatures where (CO/CH$_4$) $\gg$ 1 and (N$_2$/NH$_3$) $\gg$ 1. However, as first proposed and quantified by Prinn and Fegley (1981), and later discussed by Prinn and Fegley (1987a, 1988), the situation is quite different in the higher pressure environments of subnebulae around the giant protoplanets (*e.g.*, proto-Jupiter, proto-Saturn, etc.)

The reasons for these differences are aptly illustrated by Figures 2–4. The quench temperatures for all three conversions (CO $\rightarrow$ CH$_4$, N$_2$ $\rightarrow$ NH$_3$, and CO $\rightarrow$ CO$_2$) all shift to lower temperatures with increasing pressure. At the same time, the boundaries in $(P, T)$ space where $P_{CO} = P_{CH_4}$ and where $P_{N_2} = P_{NH_3}$ shift to higher temperatures with increasing pressure. Thus, the lower quench temperatures for the CO $\rightarrow$ CH$_4$ and N$_2$ $\rightarrow$ NH$_3$ conversions lead to *smaller* (CO/CH$_4$) and (N$_2$/NH$_3$) ratios. Prinn and Fegley (1988) have noted that for sufficiently high pressures of $\sim$ 0.3 bars for the CO $\rightarrow$ CH$_4$ conversion and of $\sim$ 80 bars for the N$_2$ $\rightarrow$ NH$_3$ conversion, quenching will produce equimolar (CO/CH$_4$) and (N$_2$/NH$_3$) ratios. Likewise, examination of Figure 4 shows that the lower quench temperatures for the CO $\rightarrow$ CO$_2$ conversion lead to slightly larger (CO$_2$/CO) ratios at higher pressures. However, this is a small effect.

Thus, the higher pressure environments hypothesized for subnebulae around the giant planets favor reduced carbon (CH$_4$) and nitrogen (NH$_3$) gases. Specifically, for the Jovian sub-nebula model of Prinn and Fegley (1981) illustrated in the figures, quenching of the CO $\rightarrow$ CH$_4$ conversion occurs at 840 K and (CO/CH$_4$) $\sim 10^{-6}$, quenching of

the $N_2 \rightarrow NH_3$ conversion occurs at 1370 K and $(N_2/NH_3) \sim 1$, and quenching of the $CO \rightarrow CO_2$ conversion occurs at 740 K and $(CO_2/CO) \sim 10^{-2}$ (Prinn and Fegley 1988). Note that the sub-nebular $(CO/CH_4)$ ratio is $\sim 10^{13}$ times smaller than the solar nebula ratio and that the sub-nebular $(N_2/NH_3)$ ratio is $\sim 10^5$ times smaller than the solar nebula ratio. The hypothesized subnebulae around the giant planets are thus very efficient "thermochemical processing plants" for the production of reduced carbon and nitrogen gases. We will return to this point later when we discuss the implications of these chemical models for the origin of volatiles in comet P/Halley and in Saturn's satellite Titan.

## 2.2. Gas-Grain Chemistry of Carbon and Nitrogen

The results described above are applicable to homogeneous gas phase chemistry. However, if catalytically active grains are present in the solar nebula and are well mixed with the nebular gas, they may alter these results by accelerating the rates of the $CO \rightarrow CH_4$, $N_2 \rightarrow NH_3$, and $CO \rightarrow CO_2$ conversions and by converting a substantial portion of the nebular CO to organic compounds via Fischer-Tropsch-type reactions. Theoretical modelling of these possible grain catalyzed conversions is guided by industrial experience with the synthesis of $NH_3$ and the production of synthetic fuels (*e.g.,* Bond 1962; Dry 1981), which indicates that the most active and abundant catalyst present in the solar nebula was Fe metal grains.

In this case, the Fe grain-catalyzed conversions may occur throughout the temperature range where Fe metal grains are thermodynamically stable. At high temperatures the presence of Fe metal grains is limited by their evaporation to Fe gas (see the Fe (s,liq) curve in Figures 2–3) and at low temperatures their presence is limited by "rusting" to form magnetite ($Fe_3O_4$) surface coatings at (the pressure independent) temperatures of $\sim 370$–400 K. However, as emphasized by Fegley (1988) and by Prinn and Fegley (1988), the effective temperature range for Fe metal grain catalysis may be further limited by the formation of FeS coatings at the (pressure independent) temperature of $\sim 687$ K, or by the failure of the metal grains to remain well mixed with the nebular gas.

We can now use Figure 3 to discuss the Fe grain catalyzed $N_2 \rightarrow NH_3$ conversion. An absolute *lower* limit to the nebular $(N_2/NH_3)$ ratio, and thus an absolute *upper* limit to the $NH_3$ abundance in the solar nebula, can be set by making the generous assumption that Fe metal grains are well mixed with the nebular gas and remain catalytically active down to $\sim 370$–400 K where they will be deactivated by $Fe_3O_4$ coatings. Or in other words, the magnetite formation temperature is taken as the quench temperature $T_Q$ for the Fe grain catalyzed $N_2 \rightarrow NH_3$ conversion. In this case we see that the resulting $(N_2/NH_3)$ ratio is $\sim 10^2$ for the solar nebula $(P, T)$ profile illustrated in Figure 3. It is also important to note that the $(N_2/NH_3)$ ratio will be $\gg 1$ for all currently accepted nebular $(P, T)$ profiles, which generally lie to the left of the profile shown in Figure 3. We emphasize that this prediction of nebular $(N_2/NH_3)$ ratios $\gg 1$ is a robust conclusion which is *independent* of the kinetics of the heterogeneously catalyzed $N_2 \rightarrow NH_3$ conversion and of the assumed Fe grain size. For reference, we note that the appropriate kinetic data for the Fe grain catalyzed conversion (see Prinn and Olaguer 1981) and the reasonable assumption of $100\mu m$ radius Fe grains (which is based on the Fe grain size in chondritic meteorites) yields a similar quench temperature $T_Q \sim 530$ K and a $(N_2/NH_3)$ ratio of $\sim 170$ given the nebular lifetime of $10^{13}$ sec to do the conversion (Lewis and Prinn 1980). Thus, the possibility of Fe grain catalysis does *not* alter our

earlier conclusion that the dominant nitrogen-bearing gas in the solar nebula is $N_2$ and that the $(N_2/NH_3)$ ratio is $\gg 1$.

Now we can consider the effects of Fe grain catalysis on the $(N_2/NH_3)$ ratio in the subnebulae around the giant planets. Taking the $Fe_3O_4$ formation temperature of $\sim$ 370–400 K as the $T_Q$ value for the grain catalyzed $N_2 \rightarrow NH_3$ conversion leads to the prediction of $(N_2/NH_3)$ ratios $\ll 1$ in the higher pressure environments of the giant planet subnebulae. Specifically, for the Jovian subnebula $(P, T)$ profile shown in Figure 3, a $T_Q$ value of 400 K corresponds to $(N_2/NH_3) \sim 10^{-5}$. Again, we emphasize that this prediction of subnebular $(N_2/NH_3)$ ratios $\ll 1$ is a robust conclusion which is completely *independent* of any assumptions about the kinetics or Fe grain sizes. However, a similar quench temperature ($\sim$ 495 K) and a similar $(N_2/NH_3)$ ratio $\sim 5 \times 10^{-4}$ were obtained in the (model-dependent) calculations of Prinn and Fegley (1981). Thus, we once again find that the possibility of Fe grain catalysis does *not* alter our earlier conclusions, namely that the dominant nitrogen-bearing gas in the giant planet subnebulae is $NH_3$ and that the $(N_2/NH_3)$ ratio is $\ll 1$.

Similar considerations apply to the Fe grain catalyzed conversion of $CO \rightarrow CH_4$. Again we can set an absolute *lower* limit to the nebular $(CO/CH_4)$ ratio and thus an *upper* limit to the $CH_4$ abundance in the solar nebula by assuming that Fe grains remain catalytically active and well mixed with the nebular gas down to the magnetite formation temperature of $\sim$ 370–400 K. As Figure 2 shows, this generous assumption leads to $(CO/CH_4) \sim 10^{-9}$ for the solar nebula $(P, T)$ profile shown. Lower density nebular models (*i.e.*, profiles to the left of the one illustrated) lead to larger $(CO/CH_4)$ ratios, but a $T_Q \sim 400$ K leads to $(CO/CH_4) \ll 1$ in all cases.

However, unlike the case of the $N_2 \rightarrow NH_3$ conversion, we have no reasons for supposing that Fe grains can actually catalyze the $CO \rightarrow CH_4$ conversion down to these low temperatures in the solar nebula. This point is illustrated by the model of Prinn and Fegley (1988) who utilized literature data for the rate of the heterogeneously catalyzed $CO \rightarrow CH_4$ conversion on ultra-clean, high purity specially prepared Fe surfaces (*e.g.*, see Vannice 1975, 1982). The rate equation for the $CO \rightarrow CH_4$ conversion on metallic iron particles is

$$\frac{d}{dt}[CH_4] = -\frac{d}{dt}[CO] = [sites]k_{site}P_{H_2} \qquad (4)$$

where [i] is the number density per $cm^3$ of gas $i$, $[sites]$ is the number per $cm^3$ of catalytically active sites on the surfaces of all Fe particles in each $cm^3$ of the solar nebula, $P_{H_2}$ is the hydrogen partial pressure in bars, and $k_{site}$ is the experimental rate constant expressed as the number of $CH_4$ molecules produced per active site per second. The chemical time constant $t_{chem}$ for the Fe grain catalyzed $CO \rightarrow CH_4$ conversion is then given by

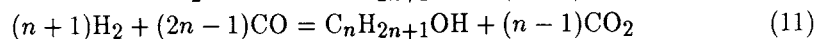$$t_{chem} = -[CO]/\frac{d}{dt}[CO]. \qquad (5)$$

For the shortest feasible mixing times ($\sim 10^8$ sec) implied by transport at 1/3 of sound speed, Prinn and Fegley (1988) found a quench temperature of $\sim$ 900 K and a $(CO/CH_4)$ ratio of $\sim 10^{3.8}$ for this reaction. The longest feasible mixing time of $\sim 10^{13}$ sec, which is equivalent to the nebula being mixed once during its lifetime, gave a lower quench temperature of $\sim$ 520 K and a lower $(CO/CH_4)$ ratio of $\sim 10^{-3.5}$. An analogous treatment of the Fe grain catalyzed $CO \rightarrow CH_4$ conversion by Mendy-bayev *et al.* (1986), who utilized a slightly different rate constant, gives a quench

temperature of $\sim 750$ K where $(CO/CH_4) \sim 10$ in their nebular model which takes $t_{chem} = t_{mix} \sim 10^{9.5}$ sec as appropriate for the inner regions of the solar nebula.

However, we emphasize that both the results of Prinn and Fegley (1988) and the results of Mendybayev *et al.* (1986) are based on rate constants measured for the CO $\rightarrow$ CH$_4$ conversion on ultra-clean, high purity specially prepared Fe surfaces which do not exist in the solar nebula. The inactivation of the Fe surface by rapidly forming carbonaceous coatings (*e.g.*, see Vannice 1982; Krebs, Bonzel, and Gafner 1979), which apparently are similar to the "tar balls" and carbonaceous material commonly observed in interplanetary dust particles (IDPs) (Bradley 1988; Bradley, Brownlee, and Fraundorf 1984; Bradley and Brownlee 1986; Mackinnon and Rietmeijer 1987) was not considered. Thus it is best to view the model results as *upper* limits to the efficiency of the Fe catalyzed CO $\rightarrow$ CH$_4$ conversion and as *lower* limits to the solar nebula (CO/CH$_4$) ratio.

Prinn and Fegley (1988) and Fegley (1988) have emphasized that the more likely course of events is the Fe grain catalyzed synthesis of organic molecules from nebular CO + H$_2$ via Fischer-Tropsch-type (FTT) reactions. This pathway is more likely because (1) carbonaceous material analogous to Fischer-Tropsch-type reaction products is found in primitive chondritic meteorites (*e.g.*, see Hayatsu and Anders 1981; Studier, Hayatsu, and Anders 1968, and references therein), (2) "tar balls" which are associations of carbonaceous matter and Fe-bearing grains (metal or carbide or oxide) are commonly observed in chondritic IDP's (*e.g.*, see Bradley 1988; Bradley, Brownlee, and Fraundorf 1984), and (3) the "tar balls" are similar to carbonaceous deposits found on Fe-based FTT catalysts (*e.g.*, see Vannice 1982; Krebs, Bonzel, and Gafner 1979; Bradley, Brownlee, and Fraundorf 1984).

The Fischer-Tropsch synthesis of alkanes, alkenes, and alcohols are exemplified by net reactions such as

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O \tag{6}$$

$$(n + 1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2 \tag{7}$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \tag{8}$$

$$nH_2 + 2nCO = C_nH_{2n} + nCO_2 \tag{9}$$

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n - 1)H_2O \tag{10}$$

$$(n + 1)H_2 + (2n - 1)CO = C_nH_{2n+1}OH + (n - 1)CO_2 \tag{11}$$
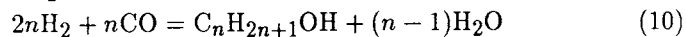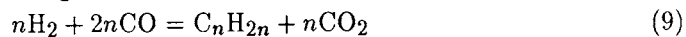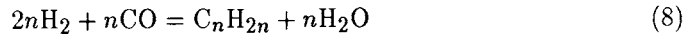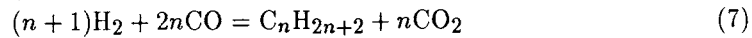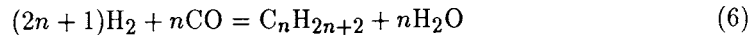
Fegley (1988) estimated the chemical time constants for Fischer-Tropsch-type reactions in the solar nebula by using a simple gas-grain kinetic model. This model hypothesizes that the initial grain catalyzed reaction rate will depend on the collision rate of the reactant gas (CO in this case) with the grain surfaces (Fe metal grains which are assumed to be covered with sufficient sorbed H$_2$). The collision rate $\sigma_i$ of the reactant gas (molecules $cm^{-2}$ sec$^{-1}$) with the Fe grain surfaces is given by

$$\sigma_i = 2.635 \times 10^{25}[P_i/(M_iT)^{1/2}] \tag{12}$$

where $P_i$ is the CO partial pressure in this case, $M_i$ is the CO molecular weight in this case, and $T$ is the temperature. The total number of collisions of the CO molecules with all Fe grains in each cm$^3$ of the nebula is given by

$$\nu_i = \sigma_i A \tag{13}$$

where $A$ is the total surface area of all Fe grains per each $cm^3$ of the nebula. The Fe grains are assumed to be monodisperse, spherical grains that are fully dense and are uniformly distributed at solar abundance in the nebular gas. The grain radii were allowed to vary from $0.1\mu m$ to $100\mu m$ in the model calculations.

Then $t_{coll}$, the collision time constant which is the time for all CO gas molecules to collide with all Fe grains in each $cm^3$ of the nebula, is given by

$$t_{coll} = [CO]/\nu_i \tag{14}$$

where [CO] is the CO molecular number density. If every collision of a CO molecule with an iron grain led to the synthesis of an organic compound, Equation (14) would also be the expression for the chemical time constant $t_{chem}$ for CO destruction. However, only a small fraction of collisions that possess the necessary activation energy $E_a$ lead to chemical reaction. This number of collisions is given by

$$f_i = \nu_i \exp(-E_a/RT) \tag{15}$$

where $R$ is the ideal gas constant. The $t_{chem}$ for CO destruction is then given as

$$t_{chem} = [CO]/f_i = t_{coll}/\exp(-E_a/RT). \tag{16}$$

Taking an activation energy $E_a \sim 90$ kJ mole$^{-1}$ on the basis of $E_a$ values from the literature (*e.g.*, Hayatsu and Anders 1981; Dry 1981), Fegley (1988) found that $100\mu m$ radius Fe grains (which are comparable in size to Fe grains in chondritic meteorites) could convert $\sim 10\%$ of all CO into organics during the nebular lifetime of $\sim 10^{13}$ sec if catalysis of $FTT$ reactions was effective down to $\sim 510$ K. Much smaller $0.1\mu m$ radius Fe grains (which are comparable in size to Fe grains in interplanetary dust particles) were found to continue catalyzing Fischer-Tropsch conversion of this much CO down to $\sim 440$ K. These theoretical considerations, which are probably upper limits because the effects of $H_2O$ sorption on the Fe grain surfaces have been neglected, are consistent with laboratory experiments by Anders and coworkers (*e.g.*, Anders, Hayatsu, and Studier 1973) showing catalysis of $FTT$ reactions down to $\sim 375$ K and with independent theoretical estimates that $\approx 10\%$ of nebular CO was converted to organic material (Simonelli *et al.* 1988).

To summarize the results of this section, a large body of industrial experience with $NH_3$ synthesis (*i.e.*, the $N_2 \rightarrow NH_3$ conversion) and with the production of synthetic fuels (*i.e.*, the CO $\rightarrow$ organics conversion) indicates that the most active and abundant catalyst present in the solar nebula and in the giant planet subnebulae was Fe metal grains. Considerations of the possible effects of these grains on nitrogen and carbon chemistry in these environments lead to three important conclusions. First of all, the possibility of Fe grain catalysis of the $N_2 \rightarrow NH_3$ conversion does *not* alter conclusions based on homogeneous gas phase chemistry that $N_2$ was the dominant nitrogen gas in the solar nebula and that $NH_3$ was the dominant nitrogen gas in giant planet subnebulae. Secondly, the *only* possibility for efficient Fe grain catalysis of the CO $\rightarrow$ $CH_4$ conversion is the presence of ultra-clean, high-purity Fe grains in the solar nebula. However, this situation is inherently unrealistic for three reasons: (1) Fe metal grains will be contaminated by several elements such as phosphorus, sulfur, carbon, hydrogen, nitrogen, and oxygen at $T > 1000$ K in the solar nebula (*e.g.*, see Kozasa and Hasegawa 1988; Fegley and Lewis 1980), (2) as discussed below Fe metal grains will be covered by FeS (which is a catalyst poison) at $T \leq 687$ K in the solar nebula, and (3) laboratory experiments show that ultra-clean, high-purity Fe grains in the presence of
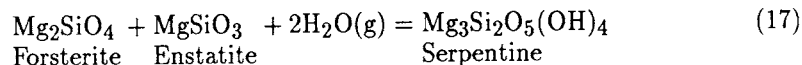
CO + H$_2$ are inactivated by rapidly forming carbonaceous coatings (*e.g.*, see Vannice 1982; Krebs, Bonzel, and Gafner 1979). These considerations lead us to reject the Fe grain catalyzed CO → CH$_4$ conversion as an efficient CH$_4$ production mechanism in the solar nebula. Finally, extensive industrial experience (Dry 1981), laboratory syntheses of Fischer-Tropsch-type reaction products similar to organic compounds in meteorites (*e.g.*, Hayatsu and Anders 1981; Studier, Hayatsu, and Anders 1968), the intimate associations of carbonaceous matter and Fe-bearing grains in IDP's (*e.g.*, see Bradley, Brownlee, and Fraundorf 1984), and kinetic calculations all suggest that the more likely course of events in the solar nebula was the Fe grain catalyzed synthesis of organics from nebular CO + H$_2$ via Fischer-Tropsch-type reactions. Thus, even after considering gas-grain chemistry, we conclude that CO was the dominant carbon gas in the solar nebula, some fraction (on the order of 10%) of this CO was converted to organic compounds, and that CH$_4$ was the dominant carbon gas in giant planet subnebulae.

## 2.3. Water Retention by Solid Grains

The outstanding problem to be solved about water chemistry in the solar nebula is the mechanism for water retention by solid grains. The early suggestions by Latimer (1950) and Urey (1952) that hydrated silicates were responsible for water retention by the terrestrial planets preceded all subsequent work by twenty years. The later, more detailed results, which have been summarized by Prinn and Fegley (1988), illustrate several important points. Thermochemical calculations show that minor H$_2$O-bearing minerals such as tremolite [Ca$_2$ Mg$_5$Si$_8$O$_{22}$(OH)$_2$] become stable in the 460–500 K temperature range in the solar nebula. This has led some investigators (*e.g.*, Lewis 1972) to appeal to tremolite as a source of the Earth's water. However, this approach neglects the fact that tremolite is seldom, if ever, observed in chondritic meteorites. Therefore, the significance of tremolite as the source of the Earth's water is problematic.

On the other hand, major H$_2$O-bearing phases which are observed in chondritic meteorites, exemplified by serpentine [Mg$_3$Si$_2$O$_5$(OH)$_4$], talc [Mg$_3$Si$_4$O$_{10}$(OH)$_2$], and brucite [Mg(OH)$_2$], do not become thermodynamically stable until low temperatures ≤ 400 K. The formation of significant amounts of these hydrous phases at these low temperatures in the solar nebula then *requires* solid-solid (or gas-solid) chemical equilibrium to be reached on a timescale which is at most as long as the solar nebula lifetime of ~ 10$^{13}$ sec, and possibly much shorter than this if the nebula is turbulent. Is this requirement satisfied or is attainment of chemical equilibrium impossible under the $(P, T)$ conditions where the major H$_2$O-bearing minerals are stable?

Prinn and Fegley (1987b, 1988) and Fegley (1988) have emphasized that the formation of hydrated silicates by solid-solid reactions such as:

$$Mg_2SiO_4 + MgSiO_3 + 2H_2O(g) = Mg_3Si_2O_5(OH)_4 \qquad (17)$$
$$\text{Forsterite} \quad \text{Enstatite} \qquad\qquad \text{Serpentine}$$

is likely to be a very sluggish process because it requires the transport and reaction of elements between two minerals at the low temperatures ≤ 400 K where serpentine is thermodynamically stable in the solar nebula. In other words, as anticipated by Urey (1953), the assumption of complete chemical equilibrium breaks down at the low temperatures where the equilibrium models predict H$_2$O-bearing phases are stable.

This failure is easily demonstrated by using the literature data on cation and oxygen diffusion in silicates to model the rate of the possible rate-determining steps involved in

the solid-solid reaction. This was originally done by Prinn and Fegley (1988) and Fegley (1988). In their model both silicate reactants are assumed to be in intimate contact (*e.g.*, in one grain) for long time periods. The (composite) grains are also assumed to be monodisperse, spherical grains with radii of $0.1 \mu m$. This size grain is comparable in size to the very fine-grained matrix found in chondritic meteorites and to the small silicate grains observed in interplanetary dust particles, but is significantly smaller than the majority of silicate grains observed in chondrites.

The characteristic diffusion time for the solid-solid reaction in this small composite grain is then given by the scaling relation $t \sim r^2/D$ where $r$ is the grain radius and $D$ is the diffusion coefficient ($cm^2 \, s^{-1}$) for either cation or oxygen diffusion. In the most favorable case, which was examined by Prinn and Fegley (1988) and Fegley (1988), Mg-Si diffusion is assumed to be the rate-determining step and is assumed to be as rapid as Fe-Mg diffusion in olivine. In this case, the characteristic diffusion time is $\sim 10^{23}$ sec at 400 K and $\sim 10^{55}$ sec at 200 K. In the least favorable case, oxygen diffusion may be rate-determining and then the oxygen self-diffusion data of Reddy *et al.* (1980) lead to a characteristic diffusion time of $\sim 10^{41}$ sec at 400 K and $\sim 10^{89}$ sec at 200 K! It is almost superfluous to note that all of these times are significantly greater than the age of the Solar System ($\sim 10^{17}$ sec), let alone the estimated lifetime of the solar nebula ($\sim 10^{13}$ sec).

Fegley (1988) and Prinn and Fegley (1988) have discussed more realistic (and thus inherently less favorable) assumptions which lead to longer characteristic diffusion times. Instead of reviewing these points we simply note that the solid-solid reactions which have been postulated for hydrated silicate formation in the solar nebula simply do not work because the reactions are orders of magnitude too slow relative to the lifetime of the solar nebula. This leaves the hydration of monomineralic silicate grains as the only possible pathway for hydrated silicate formation in the solar nebula. However, this pathway, which is exemplified by the reactions

$$2Mg_2SiO_4 + 3H_2O(g) = Mg_3Si_2O_5 \, (OH)_4 + Mg(OH)_2 \qquad (18)$$
Forsterite                  Serpentine              Brucite

$$4MgSiO_3 + 2H_2O(g) = Mg_3Si_4O_{10} \, (OH)_2 + Mg(OH)_2 \qquad (19)$$
Enstatite                Talc                 Brucite
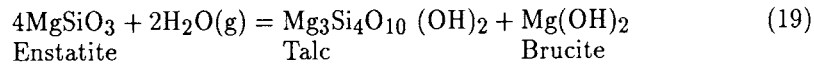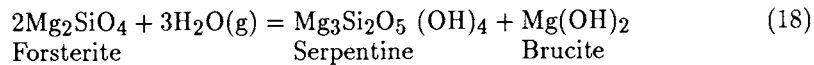
also appears to be too slow to be of any importance. Again, this was first quantitatively demonstrated by Fegley (1988) and Prinn and Fegley (1988), who applied the gas-grain kinetic model described earlier (Equations 12–16) to this problem but with $H_2O$ vapor (instead of CO) and forsterite (instead of Fe) grains. Monodisperse, spherical $0.1 \mu m$ radius silicate grains were assumed to be dispersed at solar abundance in the nebular gas and the chemical time constant for the stoichiometric amount of $H_2O$ vapor ($\sim 20\%$ of available $H_2O$ vapor in a CO-rich nebula) to react with the grains was calculated. This was done by assuming that the experimentally determined activation energy of $\sim 70$ kJ mole$^{-1}$ for the vapor phase hydration of MgO to Mg(OH)$_2$ (Layden and Brindley 1963; Bratton and Brindley 1965) is also the activation energy for reaction (18).

The resulting chemical time constant for forsterite hydration in the solar nebula is $t_{chem} \sim 10^{18}$ sec, or about $10^5$ times longer than the lifetime of the solar nebula. A similar $t_{chem}$ value is also estimated for other low temperature hydration reactions such as Equation (19). As Fegley (1988) and Prinn and Fegley (1988) have emphasized, this $t_{chem}$ value is really only a *lower* limit to the lifetimes (and thus an *upper* limit to the rates) for silicate hydration reactions in the solar nebula because reactions requiring the migration and diffusion of more than one metal cation will proceed slower than MgO

hydration which involves only one metal cation. Thus, the vapor phase hydration of monomineralic silicate grains in the solar nebula was not responsible for water retention by solid grains because the hydration reactions do not occur over the lifetime of the solar nebula.

However the situation is totally different in the higher pressure environments hypothesized for the giant planet subnebulae. The increased pressure leads to higher formation temperatures for the hydrated silicates (e.g., as shown in Figure 3.11 of Prinn and Fegley (1988) reaction (18) leads to serpentine formation at $\sim$ 325 K at $P \sim 0.6$ bars) and also leads to higher collision rates of $H_2O$ molecules with anhydrous silicate grains. This combination of higher formation temperatures and higher collision rates (and thus shorter collision lifetimes) makes hydrated silicate formation via gas-grain reactions kinetically favorable in the giant planet subnebulae. For example, using the Jovian subnebula model of Prinn and Fegley (1981) and repeating the same types of gas-grain kinetic calculations described above, the time for the stoichiometric amount of $H_2O$ ($\sim$ 4% of total $H_2O$ in the $CH_4$-rich subnebula) to collide with 0.1 $\mu m$ radius forsterite grains is $t_{coll} \sim 6 \times 10^{-3}$ sec. Once again assuming $E_a \sim 70$ kJ mole$^{-1}$ yields $t_{chem} \sim 10^9$ sec, or about $10^{-4}$ of the assumed subnebula lifetime of $10^{13}$ sec. Furthermore, if the hydration rate remains limited by the $H_2O$ collision rate with grains, then silicate grains with radii up to $1000\mu m$ can be hydrated in this subnebula model. Thus, in contrast to the solar nebula, the vapor phase hydration of monomineralic silicate grains was almost certainly a kinetically favorable process in the giant planet subnebulae. Various implications of these results for the solar nebula and giant planet subnebulae will be discussed later in connection with the water inventories and D/H ratios of the terrestrial planets, asteroids, and chondritic meteorites.
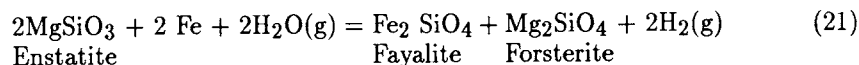
## 2.4. Iron Sulfurization and Oxidation

Two other important gas-grain reactions are the sulfurization of iron (i.e., FeS formation) and iron oxidation (either FeO incorporation into silicates or magnetite $Fe_3O_4$ formation). Troilite formation in the solar nebula is expected to occur via the net reaction:

$$H_2S(g) + Fe = FeS + H_2(g) \qquad (20)$$
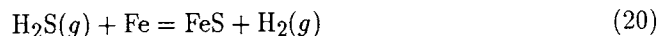
which is thermodynamically favorable at temperatures $\leq$ 687 K in a solar composition gas. The chemical time constant for bulk FeS formation was first estimated by Fegley (1988) who used the gas-grain kinetic model discussed above. Again assuming $0.1\mu m$ radius spherical, monodisperse Fe grains and taking $E_a \sim 105$ kJ mole$^{-1}$ from Worrell and Turkdogan (1968), he derived $t_{chem} \sim 10^{10}$ sec for FeS formation. This $t_{chem}$ value is $\sim 0.1\%$ of the nebular lifetime and suggests that reaction (20) was an important process for sulfur retention by solid grains in the solar nebula. If the $t_{chem}$ for bulk FeS formation remains dependent on the initial collision-determined reaction rate, reaction (20) remains kinetically favorable (i.e., $t_{chem} \leq 10^{13}$ sec) down to $\sim$ 525 K. However, even if cation diffusion becomes rate determining, the relatively fast cation diffusion observed in sulfides (e.g., see Ehlers 1988), suggests that relatively large grains ($r \sim 50\mu m$) can still be completely sulfurized down to low temperatures $\leq$ 600 K. The results of these kinetic calculations are thus in accord with the intuitive expectation that Fe "tarnishing" by $H_2S$ is a rapid process.

On the other hand, kinetic calculations suggest that iron oxidation reactions were relatively slow processes in the solar nebula. The incorporation of FeO into magnesian silicates, which is a solid-solid reaction, will be considered first. The thermochemical calculations of Grossman (1972) and Barshay and Lewis (1976) predict that FeO incorporation into silicates occurs via the net reaction

$$2MgSiO_3 + 2\ Fe + 2H_2O(g) = Fe_2\ SiO_4 + Mg_2SiO_4 + 2H_2(g) \tag{21}$$
$$\text{Enstatite} \qquad\qquad\qquad \text{Fayalite} \quad \text{Forsterite}$$

with lower temperatures leading to higher FeO (and thus higher fayalite $Fe_2SiO_4$) contents in the ferromagnesian silicates. In particular, fayalite contents of $\geq$ 20 mole %, which correspond to the fayalite contents of the ordinary chondrite groups (*e.g.*, see Rubin, Fegley, and Brett 1988), require equilibration at temperatures $\leq$ 500 K.

Fegley (1988) pointed out that if the characteristic diffusion time for homogenizing $0.1\mu m$ radius grains is taken as the nebular lifetime of $\sim 10^{13}$ sec, the required diffusion coefficient is $D \geq 10^{-23}$ cm$^2$ s$^{-1}$. However at the reaction temperatures $\leq$ 500 K required to make the fayalatic olivines observed in the ordinary chondrites, the Fe-Mg interdiffusion coefficient in olivine is $D \leq 10^{-27}$ cm$^2$ s$^{-1}$, or about $10^4$ times too slow. This is a very good argument against the solid-state incorporation of FeO into silicates at low temperatures in the solar nebula. Only the finest-grained matrix in primitive chondritic meteorites is as small as $0.1\mu m$ in size; many grains are substantially larger. The larger silicate grains will be reacted much more slowly because of their much smaller surface to volume ratios. Furthermore, Fe-Mg diffusion in olivine is probably more rapid than Fe-Mg diffusion between enstatite and metal to form olivine at these low temperatures. Thus it is kinetically unrealistic to appeal to reaction (20) for forming FeO-bearing silicates at low temperatures in the solar nebula.

In this case, the unreacted Fe metal grains that remain in contact with the nebular gas may then be "rusted" by reaction with water vapor to form magnetite via the net reaction

$$4H_2O(g) + 3Fe = Fe_3O_4 + 4H_2(g). \tag{22}$$
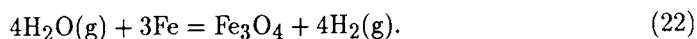
This reaction is thermodynamically favorable below temperatures of $\sim$ 370–400 K. We note parenthetically that although this temperature range is pressure independent it is dependent on the $H_2O$ partial pressure and hence on the carbon distribution between $CH_4$ and CO in the solar nebula. Fegley (1988) estimated the chemical time constant for bulk $Fe_3O_4$ formation from $0.1\mu m$ radius monodisperse, spherical Fe grains by using the gas-grain kinetic model and an activation energy $E_a \sim 80$ kJ mole$^{-1}$ for Fe oxidation to wustite in an $H_2O/H_2$ atmosphere (Turkdogan, McKewan, and Zwell 1965). The derived $t_{chem}$ value, which is $\sim 10^{13}$ sec at 400 K and increases with decreasing temperature, implies at least some kinetic inhibition of reaction (22) and especially so for bulk magnetite formation at $\sim$ 370 K when CO remains the dominant carbon-bearing gas in the solar nebula. Thus, although the formation of $Fe_3O_4$ coatings, which will deactivate the Fe grains as catalysts, is expected to occur, bulk magnetite formation may be kinetically inhibited in the solar nebula. However, because the estimated chemical time constant for $Fe_3O_4$ formation is based on the activation energy for wustite formation, it is premature to make firm conclusions regarding the kinetic favorability of bulk magnetite formation until the $E_a$ for this reaction is measured with the appropriate experiments.

Thus to summarize, application of the gas-grain kinetic model to iron sulfurization (*i.e.*, bulk FeS formation) and to iron oxidation (either FeO incorporation into silicates

or bulk magnetite $Fe_3O_4$ formation) gives two different results. In accord with intuition, FeS formation is predicted to be a rapid process in the solar nebula, even for relatively large $(r \sim 50\mu m)$ grains. In contrast, FeO incorporation into ferromagnesian silicates is predicted to be an impossibly slow process and bulk $Fe_3O_4$ formation (but not the formation of $Fe_3O_4$ coatings which will catalytically deactivate Fe metal grains) is apparently kinetically inhibited in the solar nebula. In this regard it is interesting to note that petrographic studies of magnetites in primitive chondrites suggest a parent body and *not* a nebular origin for the magnetite grains (*e.g.,* Kerridge, Mackay, and Boynton 1979). However, definitive conclusions regarding the kinetic inhibition of "bulk" $Fe_3O_4$ formation in the solar nebula must await experimental measurements of the rate and activation energy of this reaction.

## 2.5. Low Temperature Chemistry

Low temperature chemistry in both the solar nebula and in the giant planet subnebulae is qualitatively different from the high temperature chemistry taking place above the $H_2O$ ice condensation curve. Above this curve, which is illustrated in Figure 1 of Fegley (1988), predominantly "rocky" and metallic grains are condensing from and interacting with the nebular gas while below this curve predominantly "icy" grains are condensing from and interacting with the nebular gas. However, despite this qualitative difference, the same gas-grain kinetic model described earlier can be used to estimate the chemical time constants for low temperature gas-grain interactions such as clathrate formation. Although clathrate formation has long been recognized as a potentially important mechanism for carbon and nitrogen retention by icy bodies (*e.g.,* see Miller (1961) who suggested the importance of methane clathrate $CH_4 \cdot 6H_2O$), very little attention has been paid to the kinetic feasibility of clathrate formation in the low temperature, low pressure environment of the outer solar nebula (Lunine and Stevenson 1985; Fegley 1988).

The most recent study by Fegley (1988) clearly illustrates the inherent difficulties. Thermochemical equilibrium calculations (*e.g.,* see Figure 1 of Fegley 1988) predict that CO clathrate $CO \cdot 6H_2O$ is stable below $T \sim 60$ K in the CO-rich solar nebula. At 60 K Fegley (1988) found that the time for 6% of all CO (which is the maximum amount of CO that can be clathrated before running out of $H_2O$ ice) to collide with $r = 1\mu m$ spherical, monodisperse ice grains is $\sim 4 \times 10^4$ sec for the solar nebula $(P, T)$ profile in Figure 5. In order for the chemical lifetime for $CO \cdot 6H_2O$ formation to be $\leq 10^{13}$ sec, the corresponding activation energy for clathrate formation must be $\leq 8$ kJ mole$^{-1}$. Higher activation energies will lead to longer chemical time constants and thus to the kinetic inhibition of clathrate formation in the solar nebula. Fegley (1988) pointed out that this is a low activation energy even by comparison with a facile process such as $HF$ diffusion through ice, which has an activation energy of $\sim 19$ kJ mole$^{-1}$ (Haltenorth and Klinger 1969). If clathrate formation has a similar activation energy (19 kJ mole$^{-1}$), the corresponding chemical time constant for clathration of $r = 1\mu m$ spherical, monodisperse ice grains would be $\sim 10^{21}$ sec, or about $10^4$ times longer than the age of the Solar System. The formation of $N_2$ clathrate, which becomes thermodynamically feasible at similar temperatures, will require a similarly low $E_a$ value to be kinetically feasible within the solar nebula lifetime of $10^{13}$ sec. Thus unless clathrate formation is essentially a process with *no* $E_a$ barrier, it will probably be kinetically inhibited at the low solar nebula temperatures and pressures where clathrate formation is thermodynamically feasible.

Once again however, the situation is predicted to be different in the higher pressure environments of the giant planet subnebulae. As discussed earlier, $CH_4$ is the dominant carbon gas in these subnebulae and we are therefore concerned with the kinetic feasibility of $CH_4 \cdot 6H_2O$ formation. As Figure 6 illustrates, methane clathrate formation becomes thermodynamically feasible at $T \leq 95$ K and $P \sim 10^{-2}$ bars in giant planet subnebulae. The significantly higher pressures, which are approximately 5 orders of magnitude higher than the corresponding solar nebula pressure at the CO $\cdot 6H_2O$ formation temperature, lead to higher $CH_4$ gas collision rates with $H_2O$ ice grains and thus to shorter collision lifetimes. For example, the time for 22% of all $CH_4$ (which is the maximum that can be clathrated before using up all $H_2O$ ice) to collide with $r = 1\mu m$ spherical, monodisperse ice grains is only $\sim 10^{-1}$ sec. In this case the activation energy for formation of $CH_4$ clathrate can be as large as 25 kJ mole$^{-1}$ to have the process take $\leq 10^{13}$ sec. This higher activation energy, which is slightly larger than the $E_a$ of $\sim 19$ kJ mole$^{-1}$ for $HF$ diffusion through ice, is probably not a severe constraint on clathrate formation in giant planet subnebulae. Therefore, the results of these basic gas-grain kinetic calculations predict (in accord with intuition) that CO and $N_2$ clathrate formation will be kinetically inhibited in the solar nebula but that $CH_4$ clathrate formation will not be kinetically inhibited in giant planet subnebulae.

Another important difference between low temperature chemistry in the solar nebula and in giant planet subnebulae, which has been alluded to above, is the different condensate assemblages produced in these two different environments. This point, which was initially discussed by Prinn and Fegley (1981) and later reiterated by Prinn and Fegley (1987a, 1988), is illustrated in Figures 5 and 6. Figure 5 shows that the major low temperature condensates predicted to form in a CO, $N_2$-rich solar nebula are $H_2O$ ice, CO and $N_2$ clathrates, and finally CO and $N_2$ ices, if low enough temperatures are reached. However, since the formation of CO and $N_2$ clathrates is probably kinetically inhibited in the solar nebula, low temperature condensate assemblages will be poor in carbon and nitrogen unless temperatures drop low enough for CO and $N_2$ ice condensation. Despite this situation, the low temperature condensates will not be totally devoid of carbon and nitrogen because these elements will be retained in small amounts through the condensation of $FTT$-produced organics, clathrates of light hydrocarbons, $CO_2$ ice, and C, N compounds such as $NH_4HCO_3$ and $NH_4CO_2NH_2$ (Prinn and Fegley 1988). The total amounts of such carbon and nitrogen bearing condensates is difficult to quantify but it is not likely to be large because the predicted ($CO_2/CO$) ratio in the solar nebula is small ($\sim 2 \times 10^{-3}$), the predicted ($NH_3/N_2$) ratio in the solar nebula is also small ($\sim 6 \times 10^{-3}$) and the predicted conversion of CO to $FTT$-produced organics is $\approx 10\%$.

Another consequence of the kinetic inhibition of CO and $N_2$ clathrate formation is the maintenance of the $H_2O$ ice/rock mass ratio of $\sim 0.3$ from the $H_2O$ ice condensation point ($\sim 160$ K for the solar nebula model shown in Figure 5) down to the CO and $N_2$ ices condensation point ($\sim 20$ K). However, as Figure 5 shows, even if CO and $N_2$ clathrate formation occurs (which is very unlikely for kinetic reasons), the solar nebula ice/rock mass ratio is still only $\sim 0.4$ at temperatures above 20 K. These low ice/rock mass ratios simply reflect the low $H_2O$ vapor abundance in a CO-rich solar nebula where $\sim 60\%$ of the total oxygen abundance is in the form of CO.

On the other hand, Figure 6 presents a very different picture of low temperature condensates in giant planet subnebulae. One important difference is the greater $H_2O$ abundance in the $CH_4$-rich giant planet subnebulae. This leads to a $H_2O$ ice/rock mass ratio of $\sim 1.2$, or about four times larger than expected for low temperature solar nebula

$\log_{10}$ TOTAL PRESSURE (Bars)

-9         -8         -7         -6

ICE / ROCK MASS RATIO

2.0              0.4          0.3

90 —

Solar Nebula
Condensate

(CO, N$_2$)
70 — ICES

MASS %

50 —

ANHYDROUS
"ROCK"

30 —

WATER
ICE

10 —
(CO,N$_2$)·6H$_2$O (s)

10    20         50      100      250
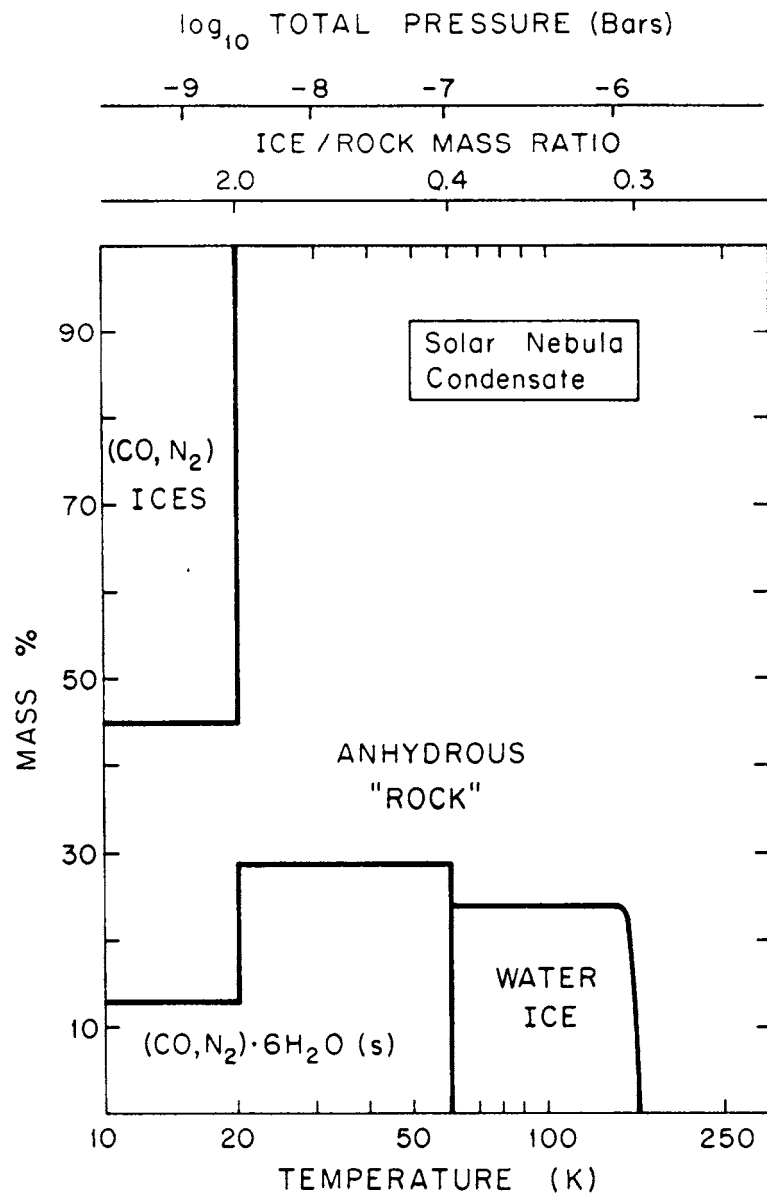
TEMPERATURE  (K)

Figure 5   Composition of low temperature condensate formed in the solar nebula. Theoretical calculations, which are described in the text, predict that the formation of $CH_4$, $NH_3$, and of hydrous "rock" will be kinetically inhibited under $(P, T)$ conditions in the solar nebula. Furthermore, the formation of $CO$ and $N_2$ clathrates may also be kinetically inhibited under certain conditions (Fegley 1988). Note that the condensate composition and ice/rock ratio are very different from that expected in an outer planet sub-nebula.
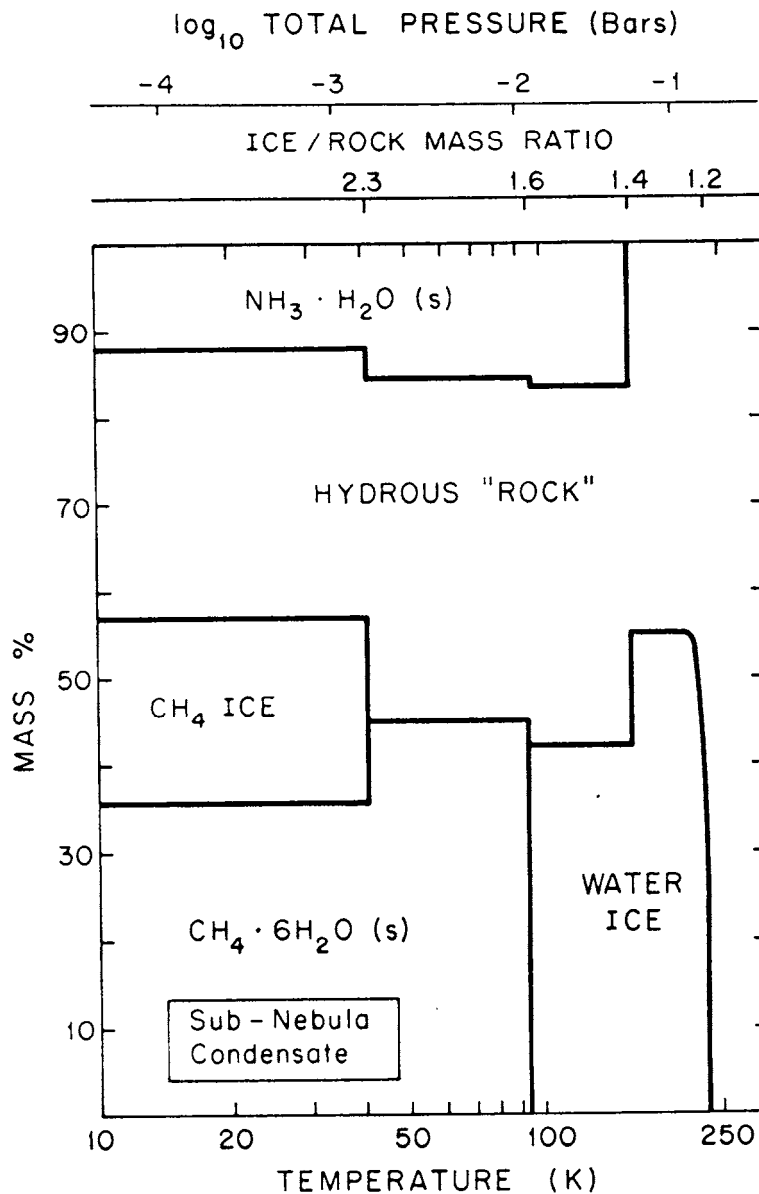
**Figure 6**    Composition of low temperature condensate formed in an outer planet sub-nebula. The formation of hydrous "rock", $NH_3$ hydrate, and $CH_4$ clathrate is assumed to be kinetically favorable within the sub-nebular lifetime under these $(P,T)$ conditions. Minor condensates such as $HCN$ are not illustrated but may play important roles for the production of more complex organic compounds in the atmosphere of an icy satellite such as Titan (Prinn and Fegley 1981). Note that the condensate composition and ice/rock ratio are dramatically different from that expected in the solar nebula.

condensates. One other obvious difference is the presence of condensates containing $NH_3$ and $CH_4$ such as $NH_3 \cdot H_2O$, $CH_4 \cdot 6H_2O$, and (at low enough temperatures) $CH_4$ ice. The formation of these phases, which is expected to be kinetically favorable as discussed above, leads to further increases in the ice/rock mass ratio. Eventually, if the temperature drops low enough, the condensation of $CH_4$ ice leads to an ice/rock mass ratio of $\sim 2.3$, which is $\sim 8$ times greater than expected for solar nebula condensates formed above the CO and $N_2$ ices condensation temperature. Finally, another difference which is not illustrated by Figure 6, but which was first pointed out by Prinn and Fegley (1981), is the condensation of small but nevertheless significant amounts of HCN. For example, in the giant planet subnebula model of Prinn and Fegley (1981), the HCN abundances predicted for low temperature condensates range from $\sim 1$ to 100 ppm by mass depending on the assumed strength of radial mixing in the giant planet subnebula. These authors emphasized that "HCN even at these low predicted abundances could be extremely important as a starting material for the production of more complex organic compounds in the atmosphere of an icy satellite such as Titan."

This brief review of low temperature chemistry in the solar nebula and in the giant planet subnebulae thus shows that the predicted differences in their gaseous chemistry (i.e., CO and $N_2$ in the solar nebula versus $CH_4$ and $NH_3$ in the giant plant subnebulae) also leads to dramatic differences in the nature and abundance of low temperature condensates expected in the two environments. Furthermore, the higher pressures expected in the giant planet subnebulae also lead to kinetically favorable conditions for the formation of $CH_4$ clathrate, while the much lower pressures expected in the solar nebula lead to kinetic inhibition of CO and $N_2$ clathrate formation.

## 3. IMPLICATIONS FOR OBSERVED VOLATILE INVENTORIES OF SOLAR SYSTEM BODIES

### 3.1. Comet P/Halley

The major conclusion derived from the theoretical models of carbon and nitrogen chemistry discussed above is that the dominant carbon and nitrogen gases in the solar nebula were CO and $N_2$ while the dominant carbon and nitrogen gases in the giant plant subnebula were $CH_4$ and $NH_3$. Or in other words, the solar nebula was characterized by having molecular ratios of $(CO/CH_4) \gg 1$ and $(N_2/NH_3) \gg 1$, while the giant planet subnebulae were characterized by the opposite situation where $(CO/CH_4) \ll 1$ and $(N_2/NH_3) \ll 1$. Furthermore, as seen in the discussion of low temperature chemistry, these differences were also reflected in the nature and abundance of low temperature condensates formed in the solar nebula and in the giant planet subnebulae.

It was therefore unexpected when the early analyses of spacecraft observations of volatiles emanating from comet P/Halley indicated intermediate $(CO/CH_4)$ and $(N_2/NH_3)$ ratios (e.g., see Allen et al. 1987, and references therein) which are *not* representative of either the solar nebula or of giant planet subnebulae. (We also note that the observed volatile ratios in comet P/Halley are apparently inconsistent with pristine interstellar material.) Prinn and Fegley (1987a, 1988) first suggested that the inferred $(CO/CH_4)$ and $(N_2/NH_3)$ ratios for comet P/Halley required significant amounts of chemical reprocessing in subnebular environments and specifically proposed a two component mixing model for the origin of volatiles in comet P/Halley. In their model, which is schematically illustrated in Figure 7, an oxidized, CO-, $N_2$-rich component from the solar nebula (and/or from the interstellar medium) is mixed with a smaller amount of

# Two-Component Model for Halley

**Component A**

**Oxidized**

**CO-, N₂- Rich**

**Solar Nebula**

**or**

**Interstellar**

**Material**

**Component B**

**Reduced**

**CH₄-, NH₃- Rich**
**Outer Planet**
**Sub-Nebula**
**Material**

90%

10%

**Mixing**
**Process**

**Halley**
**Mixture of Oxidized**
**and**
**Reduced Materials**

**Intermediate CO/CH₄ Ratio**

**Intermediate N₂/NH₃ Ratio**
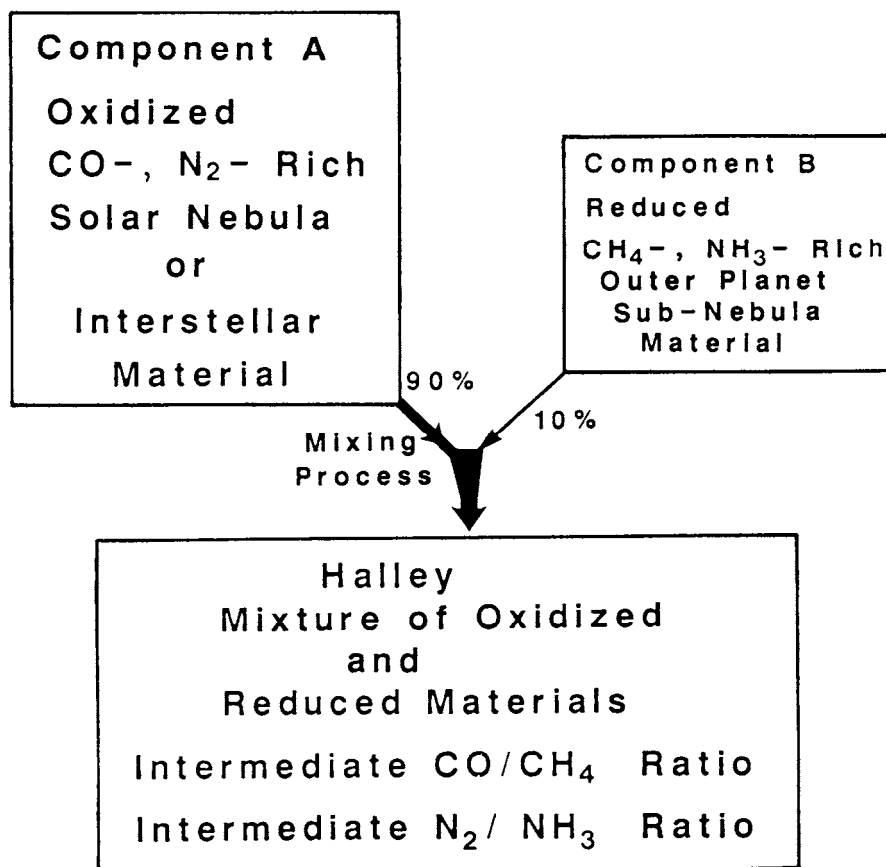
Figure 7    Two component mixing model for the origin of volatiles in comet P/Halley (Prinn and Fegley 1988). The inferred $NH_3/H_2O$ and $CH_4/H_2O$ production rates of Allen et al. (1987) combined with the observations and upper limits on $CO$ and $N_2$ imply that the volatiles in Halley are a mixture of reduced $CH_4, NH_3$—rich materials from outer planet sub-nebulae and of oxidized $CO, N_2$—rich materials either from the solar nebula or the interstellar medium. This model and the relevant observations are explained in more detail in the text.

a reduced, $CH_4$-, $NH_3$-rich component from a giant planet subnebula. The resulting mixture of oxidized and reduced materials has intermediate ($CO/CH_4$) and ($N_2/NH_3$) ratios characteristic of those inferred for comet P/Halley.

Subsequent to their original proposal (Prinn and Fegley 1987a), newer analyses of both spacecraft and Earth-based observations of volatiles in comet P/Halley have appeared, and Lunine (this volume) has suggested an alternative explanation (which does not utilize reduced material from giant planet subnebulae) for the origin of volatiles in comet P/Halley. This section will therefore focus on a reassessment of the Prinn and Fegley model in light of these new observational and theoretical developments. As we will show below, the new observational data lend stronger support to the original proposal by Prinn and Fegley but also pose significant problems for the alternative explanation later advanced by Lunine (this volume). Furthermore, we will show that several aspects of Lunine's model for the origin of volatiles in comet P/Halley are incompatible with the observed chemistry of chondritic meteorites and with theoretical models of solar nebula chemistry.

It is convenient to start by using some recent compilations (*e.g.,* Lunine, this volume; Wyckoff and Theobald 1988; Engel, Tegler, and Wyckoff 1988; Tegler, Engel, and Wyckoff 1988; Wyckoff 1988; Wyckoff *et al.* 1988; Larson *et al.* 1988; Weaver 1989) to review salient facts about volatile abundances in comet P/Halley. Considering carbon gases first, there is a general consensus that the $CO/H_2O$ ratio is in the range of a few percent; the values adopted here are $CO/H_2O \sim 0.02 - 0.07$ (by number) from Weaver (1989). Likewise, the $CH_4/H_2O$ ratio (by number) is also in the range of a few percent. The values adopted here are $CH_4/H_2O \sim 0.01 - 0.05$ (Weaver 1989). These values then lead to a range of values for the $CO/CH_4$ ratio (by number) of $\sim 0.4 - 7.0$, which are not significantly different from the values of $CO/CH_4 \sim 2.5 - 10$ adopted by Prinn and Fegley in their original analysis. Thus, the original conclusion of Prinn and Fegley (1987a, 1988) that the $CO/CH_4$ ratio in comet P/Halley is intermediate between the solar nebula values ($CO/CH_4 \gg 1$) and the giant planet subnebulae values ($CO/CH_4 \ll 1$) is strongly supported by the most recent analyses of the observational data (*e.g.,* Weaver 1989; Lunine, this volume).

The available data on $N_2$ and $NH_3$ in comet P/Halley will now be considered. Allen *et al.* (1987) originally suggested $NH_3/H_2O \sim 0.01 - 0.02$ from their analysis of the Giotto ion mass spectrometer data. A subsequent re-analysis of the same data set by Marconi and Mendis (1988), who unlike Allen *et al.* (1987) assumed a highly elevated UV flux, led to the conclusion that $NH_3/H_2O < 0.01$ and indeed may even be zero. However, total absence of $NH_3$ in comet P/Halley is extremely unlikely given the Earth-based observations of $NH_2$ (Tegler, Engel, and Wyckoff 1988; Wyckoff *et al.* 1988) which is most plausibly produced from $NH_3$. Indeed Wyckoff and colleagues have derived $NH_3/H_2O \sim 0.004 \pm 0.002$ (by number) in comet P/Halley (Tegler, Engel, and Wyckoff 1988). In the absence of any compelling evidence for favoring either the Giotto ion mass spectrometer analysis of Allen *et al.* (1987) or the Earth-based observations of Wyckoff and coworkers, the values adopted here are $NH_3/H_2O \sim 0.004 - 0.02$ (by number). A similar range of values has also been adopted by Lunine (this volume) and by Weaver (1989).

Until recently only upper limits were available for the $N_2/H_2O$ ratio in Halley. However, Wyckoff, and Theobald (1988) observed $N_2^+$ in Halley and calculated a $N_2/CO$ ratio $\sim 2 \times 10^{-3}$. Taking the $CO/H_2O$ ratio as $\sim 0.02 - 0.07$ leads to $N_2/H_2O \sim 4 \times 10^{-5}$ to $1 \times 10^{-4}$ (by number). Wyckoff (1988) and Wyckoff and Theobald (1988) derived a higher ratio of $N_2/H_2O \sim 4 \times 10^{-4}$, but their calculation assumed $CO/H_2O \sim 0.2$.

In any case, our derived range of values for the $N_2/NH_3$ ratio is then $\sim 0.002 - 0.025$. We also note that on the basis of their own observational data, Wyckoff and colleagues obtain $N_2/NH_3 \sim 0.1$. The original analysis by Prinn and Fegley (1987a, 1988), which relied on Giotto upper limits for $N_2$, gave a $N_2/NH_3$ ratio of $< 0.5 - 10$. However, even this constraint on upper limits was sufficient for Prinn and Fegley to conclude that the $N_2/NH_3$ ratio in Halley was not representative of the solar nebula where $N_2/NH_3 \gg 1$ holds. Now, the most recent observational data permit an even stronger conclusion that the $N_2/NH_3$ ratio in Halley, like the $CO/CH_4$ ratio, is intermediate between the solar nebula values ($N_2/NH_3 \gg 1$) and the giant planet subnebulae values ($N_2/NH_3 \ll 1$). Furthermore, unless the $N_2^+$ observations are incorrect by a large factor, the conclusion above is unaffected by the choice of either the Giotto or the Earth-based $NH_3/H_2O$ ratio.

Thus to summarize, the most recent observational data reported in the literature show that $CO/CH_4 \sim 0.4 - 7.0$ and that $N_2/NH_3 \sim 0.002 - 0.025$ in comet P/Halley. The fact that both of these ratios are intermediate between the values expected in the solar nebula (where $CO/CH_4 \gg 1$ and $N_2/NH_3 \gg 1$) and in giant planet subnebulae (where $CO/CH_4 \ll 1$ and $N_2/NH_3 \ll 1$) lends strong support to the two component mixing model for Halley volatiles which was originally proposed by Prinn and Fegley (1987a, 1988). However, the derived $CO/CH_4$ and $N_2/NH_3$ ratios for Halley at the same time pose significant problems for the alternative model of Lunine (this volume). These problems will now be reviewed.

The $CO/CH_4$ ratio in Halley will be considered first. As mentioned earlier, quenching of the homogeneous gas phase $CO \rightarrow CH_4$ conversion will yield a nebular $CO/CH_4$ ratio $\sim 10^7$ if the conversion can proceed for as long as the nebular lifetime of $10^{13}$ sec. A more turbulent nebula would yield more rapid mixing, a higher quench temperature, and an even larger $CO/CH_4$ ratio. How then to produce a $CO/CH_4$ ratio $\sim 0.4 - 7.0$ (as observed in Halley) in the solar nebula? Lunine (this volume) has proposed that $CO/CH_4 \sim 0.1 - 10$ can be produced in the solar nebula "under the restrictive assumptions of efficient heterogeneous surface catalysis and possibly high C/O in the inner nebula." These assumptions are restrictive indeed. As emphasized earlier and also by Fegley (1988) and Prinn and Fegley (1988), the "efficient heterogeneous surface catalysis" required in Lunine's model cannot be justified for the solar nebula. Simply put, the ultra-clean, high purity Fe surfaces which are carefully prepared in the laboratory do not exist in the solar nebula. In fact, almost as soon as Fe grains condense in the solar nebula, they are contaminated by impurities such as carbon, phosphorus, and sulfur (*e.g.*, see Fegley and Lewis 1980; Kozasa and Hasegawa 1988). However, even when Fe surfaces are available it is also important to remember that it is more likely that the Fe grains will catalyze the formation of organic compounds from nebular $CO + H_2$ via Fischer-Tropsch type reactions rather than catalyze the $CO \rightarrow CH_4$ conversion. Thus, we argue that the Fe grain catalyzed $CO \rightarrow CH_4$ conversion is insignificant in the solar nebula at temperatures required to produce $CO/CH_4$ ratios like those observed in Halley.

Lunine's assumption of a high C/O elemental ratio (C/O $\sim 1$) in the inner solar nebula also poses significant problems for his model. In this case, which has been studied in detail by Larimer and coworkers (Larimer 1968, 1975; Larimer and Bartholomay 1979), a C/O ratio $\sim 1$ leads to major changes in the chemistry of chondritic material. These changes include the formation of highly reduced minerals such as CaS (oldhamite), MgS (niningerite), MnS (alabandite), $Si_2N_2O$ (sinoite or silicon oxynitride), TiN (osbornite), and graphite. These and other highly reduced minerals (including

nearly FeO-free enstatite $MgSiO_3$) are indeed found in the rare meteorites known as enstatite chondrites (*e.g.*, see Keil 1968 and Sears 1980 for petrographic descriptions). However, the vast majority of chondritic meteorites, known as ordinary chondrites do *not* contain these highly reduced minerals and in fact could not have been formed from solar nebula gas with a C/O ratio significantly greater than the solar value of $\sim 0.6$. But the *unavoidable* consequence of Lunine's assumption of C/O $\sim 1$ is the production of large amounts of enstatite chondrite-like material and the virtual absence of ordinary chondrite-like material. (We note that although it is not explicitly stated, Lunine's model requires C/O $\sim 1$ during the time when high temperatures $> 500$ K existed in the inner nebula or he would not have any Fe grains available for catalysis.) In other words, instead of comprising $\sim 1\%$ of all chondritic meteorites (Graham, Bevan, and Hutchison 1985), Lunine's model predicts that enstatite chondrites should comprise $\sim 100\%$ of all chondritic meteorites. Thus we argue that the rarity of enstatite chondrites in the world's meteorite collections argues against C/O $\sim 1$ as required by Lunine in widespread regions of the inner solar nebula.

Finally, it is also important to realize that, unlike the original model of Prinn and Fegley (1987a, 1988), Lunine's model for volatiles in Halley *requires* clathrate formation in the low pressure regions of the outer solar nebula. However, as discussed earlier, there are severe (and unavoidable) kinetic barriers to clathrate formation in the solar nebula. These barriers are *not* eliminated by postulating collisions between ice grains (as Lunine suggests) unless sub-micron grains are continually being produced by collisions and no clathrate destruction occurs during the collision process. In contrast, the two component mixing model proposed by Prinn and Fegley (1987a, 1988) does not require CO clathrate formation in the solar nebula (CO ice will do) and although it does require $CH_4$ clathrate formation in giant planet subnebulae, this process has been seen to be kinetically feasible.

Now we can consider the implications of the $N_2/NH_3$ ratio in comet P/Halley. Remember that $N_2/NH_3 \sim 0.002 - 0.025$ (by number) on the basis of observations by Wyckoff and colleagues and using our adopted value for $CO/H_2O \sim 0.02 - 0.07$. In contrast the solar nebula $N_2/NH_3$ ratio is $\geq 170$, which is the minimum value obtained if Fe grain catalysis of the $N_2 \rightarrow NH_3$ conversion can operate throughout the $10^{13}$ sec lifetime of the solar nebula. Also remember that the giant planet subnebulae $N_2/NH_3$ ratios will be $\ll 1$, for example $N_2/NH_3 \sim 5 \times 10^{-4}$ for the Jovian subnebula $(P, T)$ model of Prinn and Fegley (1981) if Fe grain catalysis of the $N_2 \rightarrow NH_3$ conversion is assumed. Thus, the $N_2/NH_3$ ratio in Halley clearly *cannot* be derived from the solar nebula, which Lunine (this volume) acknowledges, and requires a $NH_3$-rich component, such as exists in giant planet subnebulae, for its origin. The Halley $NH_3/H_2O$ ratio of $\sim 0.004 - 0.02$, which is $\sim 2.0 - 10.0$ times larger than the *maximum* possible solar nebula $NH_3/H_2O$ ratio of $\sim 0.002$, also argues against a solar nebula origin for the $NH_3$ in Halley. This point, which was originally made by Prinn and Fegley (1987a, 1988), is in fact a robust conclusion because production of $NH_3/H_2O \sim 0.002$ in the solar nebula requires the extremely generous assumption that Fe metal grains in the solar nebula catalyze the $N_2 \rightarrow NH_3$ conversion down to $\sim 400$ K where $Fe_3O_4$ coatings will deactivate the Fe metal catalysts.

Thus, to summarize this section, both the $CO/CH_4$ and the $N_2/NH_3$ ratios in comet P/Halley are intermediate between the molecular ratios expected in the solar nebula and in giant planet subnebulae. Production of the $CO/CH_4$ and $N_2/NH_3$ ratios observed in Halley can be plausibly explained by a two component mixing model, which was originally suggested by Prinn and Fegley (1987a, 1988), in which a small amount of reduced,

$CH_4$-, $NH_3$-rich material from giant planet subnebulae is mixed with a larger amount of oxidized, CO-, $N_2$-rich material from the solar nebula (and/or from the interstellar medium). Prinn and Fegley (1988) further suggested that this mixing occurred after the dissipation of the solar nebula (and thus of the giant planet subnebulae as well) by collisions between ice-rich Solar System objects and circumplanetary satellite objects around the giant planets. The resulting hybrid collision products would be characterized by a heterogeneous mixture of CO-, $CH_4$-, $N_2$-, and $NH_3$-bearing ices. Two other implications of this mixing model are: (a) the presence of both ices (*e.g.*, CO ice from the solar nebula) and clathrates (*e.g.*, $CH_4$ clathrate from giant planet subnebulae) in comets, and (b) the presence of both anhydrous silicates (from the solar nebula) and hydrous silicates (from giant planet subnebulae) in comets. Although the dynamics of this specific mechanism have not yet been quantitatively modelled, some of the cratering features observed on Voyager images of the icy satellites of Jupiter, Saturn, and Uranus are interpreted in terms of bombardment by Solar System planetesimals during the early evolution of the Solar System (*e.g.*, see Plescia 1987; Morrison *et al.* 1984; Shoemaker and Wolfe 1984). However, the $CO/CH_4$ and $N_2/NH_3$ ratios in Halley also pose significant problems for a model invoking *only* solar nebula chemistry for their origin (Lunine, this volume). In particular, the $N_2/NH_3$ ratio cannot be explained by solar nebula chemistry and the $CO/CH_4$ ratio can only be explained by arbitrarily hypothesizing ultra-clean, high purity Fe grains (such as those prepared in the laboratory) in the solar nebula, and by also assuming $C/O \sim 1$ in widespread regions of the inner nebula. However, this scenario also leads to the production of large amounts of enstatite chondrite-like material and the absence of any ordinary chondrite-like material, which is contradicted by the rarity of enstatite chondrites and the dominance of ordinary chondrites in the world's meteorite collections. These and other problems (such as the kinetic barriers to clathrate formation in the solar nebula) lead us to conclude that a two component mixing model remains the most plausible explanation for the origin of volatiles in comet P/Halley.

## 3.2. Icy Satellites

The major conclusion derived from our review of low temperature chemistry is that the predicted differences in the gaseous chemistry of the CO, $N_2$-rich solar nebula and the $CH_4$-, $NH_3$-rich giant planet subnebulae are reflected in the nature and abundance of the low temperature condensates formed in these two environments. Furthermore, we concluded that clathrate formation was kinetically inhibited in the solar nebula but was kinetically favorable in the giant planet subnebulae. What are the implications of these theoretical results for icy satellites of the giant planets?

Prinn and Fegley (1988) have addressed these issues in some detail and we briefly recapitulate their conclusions here. Considering Titan in particular we note that the high ice/rock ratio inferred from its density requires that $H_2O$ and not CO was the major oxygen reservoir in the gaseous environment (presumably the Saturian subnebula) in which Titan formed. In turn, the requirement that the $H_2O/CO$ ratio was $> 1$ implies $CO/CH_4 < 1$, as indeed first predicted for giant planet subnebulae by Prinn and Fegley (1981). Furthermore, as pointed out earlier in our discussion of carbon and nitrogen chemistry, the same chemical-dynamical conditions that yield $CO/CH_4 < 1$ also yield $N_2/NH_3 < 1$. As seen from Figure 6, the low temperature condensates formed in such an environment are (with decreasing temperature) composed of water ice, $NH_3 \cdot H_2O$, $CH_4 \cdot 6H_2O$, and $CH_4$ ice. Degassing of this condensate assemblage would supply the

$CH_4$ observed in Titan's atmosphere but would also yield $NH_3$ instead of $N_2$. How then to account for the $N_2$ on Titan?

Owen (1982) has proposed that the $N_2$ on Titan was derived from degassing of $N_2$ clathrate. However formation of significant amounts of $N_2 \cdot 6H_2O$ is unlikely in a $CH_4$-, $NH_3$-rich giant planet subnebula for two reasons: (1) $N_2/NH_3 \ll 1$ in the gas phase so that insignificant amounts of $N_2$ are available for incorporation into low temperature condensates, and (2) mass-balance considerations (e.g., see Prinn and Fegley (1981)) show that complete condensation of $NH_3$ and $CH_4$ as $NH_3 \cdot H_2O$ and $CH_4 \cdot 6H_2O$, respectively, would require more than 100% of the available $H_2O$ ice, thus leaving none for formation (at lower temperatures) of the less stable $N_2$ clathrate.

Two more probable scenarios are formation of the $N_2$ from either the photochemical (via solar UV photolysis) or thermochemical (via impact induced high $T$ shock chemistry) destruction of outgassed $NH_3$. The former scenario (Atreya, Donahue, and Kuhn 1978) requires a warm, early Titan atmosphere while the latter scenario (e.g., Anderson and Stevenson 1987; Jones and Lewis 1987; McKay et al. 1988) requires sufficient energy transfer from the impactors to the atmosphere to generate the required high temperatures for $NH_3$ dissociation. The relative merits and demerits of both scenarios have been reviewed by Lunine, Atreya, and Pollack (1988).

Finally, it is interesting to compare ice/rock ratios predicted for solar nebula and giant planet subnebulae condensates with ice/rock ratios derived from satellite densities. From Figure 5 we have the following ice/rock ratios (as a function of temperature) for low temperature condensates in the solar nebula: ice/rock $\sim$ 0.3 (60 K $\leq T \leq$ 160 K), ice/rock $\sim$ 0.4(20 K $\leq T \leq$ 60 K), and ice/rock $\sim$ 2.0($T \leq$ 20 K). From Figure 6 we have the following ice/rock ratios (again as a function of temperature) for low temperature condensates in a giant planet subnebula: ice/rock $\sim$ 1.2(160 K $\leq T \leq$ 230 K), ice/rock $\sim$ 1.4(95 K $\leq T \leq$ 160 K), ice/rock $\sim$ 1.6(40 K $\leq T \leq$ 95 K), and ice/rock $\sim$ 2.3($T \leq$ 40 K). (In both cases these values are slightly different from those given by Prinn and Fegley (1988) because more oxygen was included in anhydrous rock by considering oxides less abundant than FeO.) For comparison, Johnson, Brown, and Pollack (1987) have calculated the following water ice/rock ratios for icy satellites: Ganymede and Callisto (differentiated) $\sim$ 0.8, Saturn satellites (mass average, which is essentially Titan) $\sim$ 0.8, Saturn satellites (object average) $\sim$ 1.6, Uranus satellites (differentiated) $\sim$ 0.7, and finally Uranus satellites (homogeneous) $\sim$ 1.0.

Prinn and Fegley (1988) noted that the icy Galilean satellites, Titan, and the Uranus satellites have ice/rock ratios which are intermediate between those expected for condensates in the solar nebula and condensates in giant planet subnebulae. However, the Saturian satellites other than Titan have ice/rock ratios which are similar to those expected in giant planet subnebulae. Assuming, that the regular satellites of the giant planets formed in subnebulae and that the presence of $CH_4$ on Titan requires $CH_4/CO \gg 1$ in the giant planet subnebula, Prinn and Fegley (1988) preferred to explain the intermediate ice/rock ratios by a scenario in which the $CO \rightarrow CH_4$ conversion was quantitative in the subnebula but then the subnebula (or the circumplanetary disk system left after dissipation of the subnebula) subsequently accreted CO-bearing icy bodies formed in the solar nebula. Alternatively, they noted that larger ice-rich satellites initially formed in a $CH_4$-rich subnebula may have later lost some ice by blow-off induced by post-accretional impacts as reviewed by Lunine, Atreya, and Pollack (1988).

### 3.3. Terrestrial Planets, Chondritic Meteorites, and Asteroids

Implications of theoretical models of solar nebula chemistry for the volatile inventories of the terrestrial planets, chondritic meteorites, and the asteroids have been reviewed in detail by Prinn and Fegley (1987b, 1988). Here we will concentrate on the case of water retention which has been a perennial question and which is now also receiving increased attention because of new theoretical models for the water budget of Venus (Grinspoon 1987), new theoretical models of aqueous alteration processes on chondrite parent bodies (Grimm and McSween 1988), new observations of hydrogen contents and D/H ratios of chondrites (Robert *et al.* 1987a,b), and finally new spectroscopic searches for hydrated silicates on primitive asteroids (Lebofsky *et al.* 1988; Jones 1988).

To begin with it is important to remember that our theoretical treatment of water retention by solid grains showed that the formation of hydrated silicates such as serpentine and talc was kinetically inhibited in the solar nebula but was kinetically favorable in the giant planet subnebulae. This robust conclusion applies both to the solid-solid reactions hypothesized for hydrated silicate formation in strict chemical equilibrium models of solar nebula chemistry (*e.g.*, Barshay and Lewis 1976; Lewis 1972) and to the water vapor hydration of monomineralic grains as exemplified by reactions (18) and (19).

These results have several important implications for water inventories of solid bodies. The first one is that the equilibrium condensation model (Lewis 1972) for water retention by the terrestrial planets and asteroids cannot be correct. In this model, the Earth is predicted to initially have been more water-rich than Venus (which presently has $\sim 10^5$ times less observable water than the Earth) because it accreted significantly more hydrated phases (*e.g.*, serpentine, talc) than did Venus because these minerals only became thermodynamically stable in the cooler nebular region outside of 1 AU. However, if it is kinetically impossible to form these hydrated phases then the predicted trend of increasing water content with decreasing temperature (and thus with increasing radial distance in the solar nebula) cannot materialize. Of course, one can attempt to salvage the equilibrium condensation model by appealing to a minor hydrous phase such as tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$] to supply the terrestrial water inventory (Lewis 1972). However the problem in this case is that tremolite is seldom, if ever, observed in chondritic meteorites. Furthermore, the observed hydrogen contents (equivalent to $\approx 100 - 1000$ ppm $H_2O$ by mass) of the ordinary chondrites (which are generally believed to have bulk composition and chemistry similar to that of the bulk Earth) can easily be accounted for from organic matter without recourse to tremolite (*e.g.*, Yang and Epstein 1983; Robert *et al.* 1987a,b, and references therein).

Of course another long standing problem for the equilibrium condensation model has been the observation by the Pioneer Venus mass spectrometer of $D/H \sim 1.6 \times 10^{-2}$ on Venus (Donahue *et al.* 1982). The observed $D/H$ value, which is $\sim 100$ times larger than the terrestrial value of $1.557 \times 10^{-4}$ (Standard Mean Ocean Water), is consistent with the depletion of an amount of water equivalent to $\sim 0.3\%$ of the terrestrial inventory from Venus over geologic time (McElroy *et al.* 1982; Donahue *et al.* 1982). However as Donahue *et al.* (1982) note, more water may have initially been present since the enhancement of the $D/H$ ratio by hydrodynamic escape will only begin once the $H_2O$ volume mixing ratio drops below $\sim 0.02$; this is equivalent to the 0.3% of the terrestrial inventory mentioned above. Grinspoon (1987) has attempted to resuscitate the equilibrium condensation model by showing that the presently observed $D/H$

value is consistent with a steady state history for water on Venus over the age of the Solar System. However, Grinspoon's model implicitly assumes an initially "dry" Venus which did not accrete its share of hydrated silicates. But since hydrated silicate (*i.e.*, serpentine and talc) formation was kinetically inhibited in the solar nebula and since tremolite is not responsible for the hydrogen contents of the ordinary chondrites, the only ways of supplying water to the Earth (as well as to Venus which has a similar mass and size) are by the late accretion of a volatile-rich veneer (Anders 1968), or by gravitationally scattering ice-rich bodies into the inner Solar System. Both of these physical mechanisms would presumably provide similar initial water inventories on Earth and Venus, instead of leading to an initially "dry" Venus as assumed by Grinspoon (1987).

The (inferred) presence (by IR reflection spectroscopy) of hydrated phases on the asteroid 1 Ceres (Lebofsky 1978) and on other primitive asteroids (Lebofsky *et al.* 1988; Jones 1988) may initially appear to be consistent with predictions of the equilibrium condensation model in which the abundance of hydrated material increases with increasing radial distance (and thus decreasing temperature) in the solar nebula (Lewis 1972). However on closer scrutiny this is seen not to be the case because a detailed IR reflection spectroscopy survey for hydrated phases on asteroids (Jones 1988) reveals a gradual decline in hydrated silicate abundance on asteroids from 2.5 to 3.5 AU and a virtual absence of hydrated objects at greater distance out to $\sim$ 5 AU. Instead as Jones (1988) notes, these observations are consistent with a model in which the original composition of outer belt asteroids is anhydrous rock and organic matter and water ice and a later heating mechanism, such as induction heating, which declined in intensity with increasing radial distance, produced the observed hydrated silicates by aqueous alteration on the parent bodies. We note that the postulated initial composition of anhydrous rock and organic matter and water ice is what is predicted by our theoretical models of carbon and water chemistry, which were described earlier.

Of course, the interpretation that hydrated silicates on asteroids are the result of parent body (and not nebular) processes is completely in accord with the extensive petrographic evidence summarized by Barber (1985) that implies an origin for hydrated silicates in carbonaceous chondrites by aqueous alteration on the chondrite parent bodies. More recent work by Tomeoka and Buseck (1985) also supports a parent body origin for the hydrated silicates in carbonaceous chondrites. We also note that aqueous activity on the CI1 and CM2 carbonaceous chondrite parent bodies is required to explain the production of sulfate- and carbonate-bearing veins (*e.g.*, see Barber 1985), is consistent with oxygen isotopic compositions of different phases in CI1 and CM2 chondrites (Clayton and Mayeda 1984), is theoretically plausible (Grimm and McSween 1988), and may also explain the observed sulfur isotope compositions of FeS, elemental S, and the sulfate veins via a unidirectional oxidation of FeS (*e.g.*, see Pillinger 1984).

Thus to summarize this section, the kinetic inhibition of hydrated silicate formation in the solar nebula is consistent with interpretations that the hydrated silicates found in chondrites and inferred to be present on primitive asteroids are the result of aqueous alteration on the asteroids and meteorite parent bodies. Furthermore, because hydrated silicate formation was kinetically impossible in the solar nebula, predictions that Venus was initially deficient in water relative to the Earth (*e.g.*, Lewis 1972) because the Earth accreted more hydrated silicates from cooler nebular regions cannot be correct. Instead models in which water (as well as other volatiles) is supplied by the late accretion of a volatile-rich veneer (Anders 1968) or by the gravitational scattering of ice-rich bodies into the early Solar System appear to be required.

## 4. SUMMARY AND RECOMMENDATIONS

Current theoretical models of thermochemical interactions between gases and grains in the solar nebula and in the giant planet subnebulae are still in a developmental stage. Nevertheless, the results of these models tend to reinforce several basic conclusions which are listed below.

1. The dominant carbon and nitrogen gases in the solar nebula were CO and $N_2$. In contrast, the dominant carbon and nitrogen gases in giant planet subnebulae were $CH_4$ and $NH_3$.

2. Fe metal grains in the solar nebula catalyzed the formation of organic compounds from nebular CO + $H_2$ via Fischer-Tropsch-type reactions. On the order of 10% of the total CO inventory was converted into organic compounds in this fashion.

3. Hydrated silicate formation was kinetically inhibited in the solar nebula but was kinetically favorable in the giant planet subnebulae. The hydrated silicates observed in chondritic meteorites and inferred on asteroidal surfaces are therefore parent body products formed by the interaction of anhydrous rock and water (from water ice).

4. Formation of FeS by the sulfurization of Fe metal grains was kinetically favorable in the solar nebula. In contrast, FeO incorporation into silicates and *bulk* $Fe_3O_4$ formation were kinetically inhibited. However, the formation of $Fe_3O_4$ coatings on Fe metal grains at $\sim$ 370–400 K is still kinetically possible and was responsible for the catalytic deactivation of Fe metal grains.

5. Clathrate formation (*e.g.*, CO and $N_2$ clathrates) was kinetically inhibited in the solar nebula but $CH_4$ clathrate formation was kinetically favorable in giant planet subnebulae.

6. The $CO/CH_4$ and $N_2/NH_3$ ratios in comet P/Halley are intermediate between those ratios in the solar nebula ($CO/CH_4 \gg 1$ and $N_2/NH_3 \gg 1$) and in giant planet subnebulae ($CO/CH_4 \ll 1$ and $N_2/NH_3 \ll 1$). These intermediate ratios are most plausibly produced by a two component mixing model in which CO-, $N_2$-rich material from the solar nebula (and/or from the interstellar medium) is mixed with a smaller amount of ($CH_4$-, $NH_3$-rich material from giant planet subnebulae.

7. The $H_2O$ ice/rock, $CO/CH_4$, and $N_2/NH_3$ ratios of icy bodies are diagnostic of their origin in either the solar nebula or in giant planet subnebulae.

Finally it is likely that a combination of experimental, observational, and theoretical studies in some key areas will help to improve our understanding of solar nebula chemistry and of the observed volatile inventories of Solar System bodies. The following studies are worth emphasizing:

1. Quantitative laboratory studies of the kinetics and mechanisms of important gas-grain thermochemical interactions such as volatile retention reactions, grain catalyzed reactions, and presolar grain destruction reactions. Specific examples include the vapor phase hydration of anhydrous silicates, the low temperature and low pressure formation of clathrates, formation of $Fe_3O_4$, Fischer-Tropsch-type synthesis of organic molecules, and oxidation of SiC by water vapor.

2. Theoretical studies of the interplay between dynamics and chemistry in the solar nebula with an emphasis on (a) the quadratically non-linear nature of momentum transport and (b) the kinetic feasibility of various types of gas-grain chemical interactions. Such studies would presumably benefit from the laboratory studies suggested above.

3. Continuation of detailed observational studies of the chemistry, isotopic composition, and mineralogy of primitive, little-metamorphosed meteorites. Especially

interesting investigations include the nature and isotopic composition of organic molecules; the abundance, isotopic composition, and *in situ* characterization of presolar grains; and the chemistry and textural relationships of possible parent-body products (e.g., hydrated silicates and magnetites).

4. Sampling and analyses of primitive, unaltered material from comets, asteroids, and ice-rich satellites.

## REFERENCES

Allen, M. *et al. Astr. Apl.*, **187**, 502.

Anders, E., Hayatsu, R., and Studier, M. H. 1973, *Science*, **182**, 781.

Anders, E. 1968, *Accounts Chem. Res.*, **1**, 289.

Anderson, W. W., and Stevenson, D. J. 1987, in *Origin and Evolution of Planetary and Satellite Atmospheres: An Abstract Book* (Tucson: University of Arizona Press), p. 51.

Atreya, S. K., Donahue, T. M., and Kuhn, W. R. 1978, *Science*, **201**, 611.

Barber, D. J. 1985, *Clay Minerals*, **20**, 415.

Barshay, S. S., and Lewis, J. S. 1976, *Ann. Rev. Astr. Ap.*, **14**, 81.

Bernatowicz, T., Fraundorf, G., Ming, T., Anders, E., Wopenka, B., Zinner, E., and Fraundorf, P. 1987, *Nature*, **330**, 728.

Bond, G. C. 1962, *Catalysis by Metals* (London: Academic Press).

Boss, A. P. 1988, *Science*, **241**, 565.

Bradley, J. P. 1988, *Geochim. Cosmochim. Acta*, **52**, 889.

Bradley, J. P., and Brownlee, D. E. 1986, *Science*, **231**, 1542.

Bradley, J. P., Brownlee, D. E., and Fraundorf, P. 1984, *Science*, **233**, 56.

Bratton, R. J., and Brindley, G. W. 1965, *Trans. Faraday Soc.*, **61**, 1017.

Cameron, A. G. W. 1985, in *Protostars and Planets II*, eds. D. C. Black and M. S. Matthews (Tucson: University of Arizona Press), p. 1073.

Cameron, A. G. W. 1982, in *Essays in Nuclear Astrophysics*, eds. C. Barnes, D. Clayton and D. Schramm (Cambridge: Cambridge University Press), p. 23.

Cameron, A. G. W., and Fegley, B., Jr. 1982, *Icarus*, **52**, 1.

Clayton, R. N., and Mayeda, T. K. 1984, *Earth Planet. Sci. Lett.*, **67**, 151.

Donahue, T. M., Hoffman, J. H., Hodges, R. R., Jr., and Watson, A. J. 1982, *Science*, **216**, 630.

Dry, M. E. 1981, in *Catalysis Science and Technology*, Vol. 1, eds. J. R. Anderson and M. Boudart (Berlin: Springer-Verlag), p. 159.

Ehlers, K. 1988, Ph.D. Thesis, Tech. Univ. Aachen.

Engel, L., Tegler, S., and Wyckoff, S. 1988, *B.A.A.S.*, **20**, 819.

Fegley, B., Jr. 1988, in *Workshop on the Origins of Solar Systems*, eds. J. A. Nuth and P. Sylvester (LPI Tech. Report 88-04), p. 51.

Fegley, B., Jr., and Lewis, J. S. 1980, *Icarus*, **41**, 439.

Graham, A. L., Bevan, A. W. R., and Hutchison, R. 1985, *Catalogue of Meteorites* (Tucson: University of Arizona Press).

Grimm, R. E., and McSween, H. Y. 1988, *Lunar Planet. Sci.*, **XIX**, 427.

Grinspoon, D. H. 1987, *Science*, **238**, 1702.

Grossman, L., and Larimer, J. W. 1974, *Rev. Geophys. Space Phys.*, **12**, 71.

Grossman, L. 1972, *Geochim. Cosmochim. Acta.*, **36**, 597.

Haltenorth, N., and Klinger, J. 1969, in *Physics of Ice*, eds. N. Riehl, B. Bullemer, and H. Engelhardt (New York: Plenum), p. 579.

Hayatsu, R., and Anders, E. 1981, *Topics Curr. Chem.*, **99**, 1.

Johnson, T. V., Brown, R. H., and Pollack, J. B. 1987, *J. Geophys. Res.*, **92**, 14884.

Jones, T. D. 1988, Ph.D. Thesis, University of Arizona.

Jones, T. D., and Lewis, J. S. 1987, *Icarus*, **72**, 381.

Keil, K. 1968, *J. Geophys. Res.*, **73**, 6945.

Kerridge, J. F., MacKay, A. L., and Boynton, W. V. 1979, *Science*, **205**, 395.

Kozasa, T., and Hasegawa, H. 1988, *Icarus*, **73**, 180.

Krebs, H. J., Bonzel, H. P., and Gafner, G. 1979, *Surface Sci.*, **88**, 269.

Larimer, J. W., and Bartholomay, M. 1979, *Geochim. Cosmochim. Acta*, **31**, 1239.

Larimer, J. W. 1975, *Geochim. Cosmochim. Acta.*, **39**, 389.

Larimer, J. W., 1968, *Geochim. Cosmochim. Acta*, **32**, 965.

Larson, H. P., Weaver, H. A., Mumma, M. J., and Drapatz, S. 1988, *Ap. J.*, in press.

Latimer, W. M. 1950, *Science*, **112**, 101.

Layden, G. K., and Brindley, G. W. 1963, *J. Amer. Ceram. Soc.*, **46**, 518.

Lebofsky, L. A., Jones, T. D., and Herbert, F. 1988, in *Origin and Evolution of Planetary Atmospheres*, eds. S. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), in press.

Lebofsky, L. A. 1978, *M.N.R.A.S.*, **182**, 17P.

Lewis, R. S., Ming, T., Wacker, J. F., Anders, E., and Steel, E. 1987, *Nature*, **326**, 160.

Lewis, J. S., and Prinn, R. G. 1980, *Ap. J.*, **238**, 357.

Lewis, J. S. 1972, *Earth Planet. Sci. Lett.*, **15**, 286.

Lin, D. N. C., and Papaloizou, J. 1985, in *Protostars and Planets II*, eds. D. C. Black and M. S. Matthews (Tucson: University of Arizona Press), p. 981.

Lunine, J. I., Atreya, S. K., and Pollack, J. B. 1988, in *Origin and Evolution of Planetary and Satellite Atmospheres*, eds. S. K. Atreya, J. B. Pollack and M. S. Matthews (Tucson: University of Arizona Press), in press.

Lunine, J. I., and Stevenson, D. J. 1985, *Ap. J. Suppl.*, **58**, 493.

Mackinnon, I. D. R., and Rietmeijer, F. J. M. 1987, *Rev. Geophys.*, **25**, 1527.

Marconi, M. L., and Mendis, D. A. 1988, *Ap. J.*, **330**, 513.

McElroy, M. B., Prather, M. J., and Rodriguez, J. 1982, *Science*, **215**, 1614.

McKay, C. P., Scattergood, T. W., Pollack, J. B., Borucki, W. J., and Van Ghyseshem, H. T. 1988, *Nature*, **332**, 520.

Mendybayev, R. A., Makalkin, A. B., Dorofeyera, V. A., Khodakovsky, I. L., and Lavrukhlina, A. K. 1986, *Geochem. Intl.*, **8**, 105.

Miller, S. L. 1961, *Proc. Nat. Acad. Sci.*, **47**, 1798.

Morfill, G. E., Tscharnuter, W., and Volk, H. J. 1985, in *Protostars and Planets II*, eds. D. C. Black and M. S. Matthews (Tucson: University of Arizona Press), p. 493.

Morfill, G. 1983, *Icarus*, **53**, 41.

Morrison, D., Johnson, T. V., Shoemaker, E. M., Soderblom, L. A., Thomas, P., Veverka, J., and Smith, B. A., 1984, in *Saturn*, eds. T. Gehrels and M. S. Matthews (Tucson: University of Arizona Press), p. 609.

Niederer, F. R., and Papanastassiou, D. A. 1984, *Geochim. Cosmochim. Acta*, **48**, 1279.

Owen, T. 1982, *Planet. Space Sci.*, **30**, 833.

Pillinger, C. T. 1984, *Geochim. Cosmochim. Acta*, **48**, 2739.

Plescia, J. B. 1987, *J. Geophys. Res.*, **92**, 14918.

Prinn, R. G. 1988, *Ap. J.*, submitted.

Prinn, R. G., and Fegley, B., Jr. 1988, in *Origin and Evolution of Planetary and Satellite Atmospheres*, eds. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), in press.

Prinn, R. G., and Fegley, B., Jr. 1987a, in *Origin and Evolution of Planetary and Satellite Atmospheres: An Abstract Book* (University of Arizona), p. 14.

Prinn, R. G., and Fegley, B., Jr. 1987b, *Ann. Rev. Earth Planet. Sci.*, **15**, 171.

Prinn, R. G., and Fegley, B., Jr. 1981, *Ap. J.*, **249**, 308.

Prinn, R. G., and Olaguer, E. P. 1981, *J. Geophys. Res.*, **86**, 9895.

Prinn, R. G., and Barshay, S. S. 1977, *Science*, **198**, 1031.

Reddy, K. P. R., Oh, S. M., Major, L. D., Jr., and Cooper, A. R. 1980, *J. Geophys. Res.*, **85**, 322.

Robert, F., Javoy, M., Halbout, J., Dimon, B., and Merlivat, L. 1987, *Geochim. Cosmochim. Acta*, **51**, 1807.

Robert, F., Javoy, M., Halbout, J., Dimon, B., and Merlivat, L. 1987, *Geochim. Cosmochim. Acta*, **51**, 1787.

Rubin, A. E., Fegley, B., Jr., and Brett, R. 1988, in *Meteorites and the Early Solar System*, eds. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), p. 488.

Sears, D. W. 1980, *Icarus*, **43**, 184.

Shoemaker, E. M., and Wolfe, R. F. 1984, *Lunar Planet. Sci.*, **XV**, 780.

Simonelli, D. P., Pollack, J. B., McKay, C. P., Reynolds, R. T., and Summers, A. L. 1988, *Icarus*, submitted.

Stevenson, D. J. 1987, paper presented at the Conference on Origin and Evolution of Planetary and Satellite Atmospheres, Tucson, AZ, March 10–14.

Stevenson, D. J. 1988a, *Lunar Planet. Sci.*, **XIX**, 1123.

Stevenson, D. J. 1988b, paper presented at the Workshop on The Formation and Evolution of Planetary Systems, Baltimore, MD, May 9–11.

Stevenson, D. J. 1988c, *Ap. J.*, submitted.

Studier, M. H., Hayatsu, R., and Anders, E. 1968, *Geochim. Cosmochim. Acta.*, **32**, 151.

Tegler, S., Engel, L., and Wyckoff, S. 1988, *B.A.A.S.*, **20**, 827.

Tomeoka, K., and Buseck, P. R. 1985, *Geochim. Cosmochim. Acta*, **49**, 2149.

Turkdogan, E. T., McKewan, W. M., and Zwell, L. 1965, *J. Phys. Chem.*, **69**, 327.

Urey, H. C. 1953, in XIIIth International Congress Pure and Applied Chemistry and Plenary Lectures (Stockholm: Almquist and Wiksells), p. 188.

Urey, H. C. 1952, *The Planets* (New Haven: Yale University Press).

Vannice, M.A. 1982, in *Catalysis Science and Technology*, Vol. **3**, eds. J. R. Anderson and M. Boudart (Berlin: Springer-Verlag), p. 139.

Vannice, M. A. 1975, *J. Catalysis*, **37**, 449.

Warnatz, J. 1984, in *Combustion Chemistry*, ed. W. C. Gardiner (New York: Springer-Verlag), p. 197.

Weaver, H. A. 1989, *Highlights of Astronomy*, in press.

Worrell, W. L., and Turkdogan, E. T. 1968, *Trans. AIME*, **242**, 1673.

Wyckoff, S. 1988 *B.A.A.S.*, **20**, 841.

Wyckoff, S., Tegler, S., Wehinger, P. A., Spinrad, H., and Beltan, M. J. S. 1988, *Ap. J.*, **325**, 927.

Wyckoff, S., and Theobald, J. 1988, *Adv. Space Res.*, in press.

Yang, J., and Epstein, S. 1983, *Geochim. Cosmochim. Acta*, **47**, 2199.

Zinner, E., Ming, T., and Anders, E. 1987, *Nature*, **330**, 730.

## DISCUSSION

**D. Cruikshank**:   You didn't mention silicon carbide (SiC) which is a substance found in the interstellar medium and also now in some meteorites. Would you care to comment on the formation of that and in what form that might be a catalyst?

**Fegley**:   Yes. Forming it is not difficult. You simply need to have an environment where you get the carbon to oxygen atom ratio above a critical value, which is on the order of 0.8 or a little bit higher. Larimer (1975) and Gilman (1969) were the first people to point this out. By increasing the C/O ratio from $\sim 0.6$ (the solar value) you get an environment which is even more reducing than solar gas and then instead of putting silicon solely into silicates, you also put it into silicon carbide. Depending on the C/O ratio, SiC may be the initial condensate of silicon, or it may form later in the condensation sequence. In both cases, I think if you would follow equilibrium to very low temperatures (<1000 K) you'd get rid of the carbide and make a silicate back out of it.

Now as far as SiC acting as a catalyst, I don't think it's that good. And the reasons that I say that is that catalysts are generally transition metals with vacant d-orbitals or zeolitic or clay-like materials with pores (or sites) of specific size and/or shape (*e.g.*, Bond 1962). Furthermore, I am unaware of SiC being used as an industrial catalyst for the transformations ($N_2 \rightarrow NH_3$, CO $\rightarrow$ hydrocarbons) I have been talking about. And if it (SiC) is a catalyst for these reactions it is certainly less efficient than iron metal or it would be used industrially instead of the Fe-based catalysts used today. You have about, I think, SiC comprising 20 ppm of total silicon in some chondrites (Murray) that Anders and his colleagues have studied (Bernatowicz *et al.* 1987; Zinner *et al.* 1987). From my perspective an important question is how was the SiC preserved? Because SiC is thermodynamically unstable in nebular gas (C/O $\sim 0.6$) which is not reducing enough to keep it around. Then at high temperatures ($\sim 1500$ K) in the solar nebula you have a net thermochemical reaction with water vapor leading to silica:

$$SiC + 3H_2O = SiO_2 + 3H_2 + CO$$
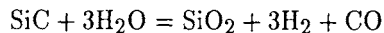
What that does, however, is start forming a silica film around the silicon carbide, then diffusion through that $SiO_2$ coating becomes an inhibitor for further SiC oxidation. However at the same time, silica is evaporating to SiO gas $SiO_2 + H_2 = SiO + H_2O$ and magnesium vapor is reacting with the $SiO_2$ to make forsterite $SiO_2 + 2 Mg + 2 H_2O = Mg_2SiO_4 + 2H_2$. So, depending on the relative rates of these 3 reactions you might preserve the SiC.

**D. Stevenson:**  Because you structured your talk so much around the role of thermo-chemistry, I think there is a danger that the audience will leave here with the impression that thermochemistry has some relevance ... (Laughter) ... to the chemical speciation in the outer solar nebula beyond about 5 AU. I would like to suggest, as indeed you implied yourself when you discussed comets, that there is no evidence whatsoever for the relevance of thermochemistry in most of the solar nebula. The dominance of CO is a statement about the interstellar medium. With respect to the other species, like for example $N_2$ and $NH_3$, we simply don't know what the interstellar medium abundance is and therefore we can't decide. So, I think one of the very important issues that we have to confront in thinking about this question is where does interstellar speciation dominate. And where are we going to find the evidence of solar nebula processes. And I think that we might be able to do it with comets, but we can't do it yet. I want to also mention that there are other processes that may be important. And one of the interesting things that came up yesterday with respect to the UV flux from T Tauri stars is that evidently there is no high UV flux from naked T Tauri stars suggesting that the UV may come from the disk, suggesting that the disk can be processed very effectively by UV and that may be a very important process.

**Fegley:**  Yes. I am aware that you have repeatedly argued (*e.g.*, Stevenson 1987, 1988a, b, c) that materials in the solar nebula and giant protoplanetary subnebulae must have been poorly mixed. However, as recently pointed out by Prinn (1988), this erroneous conclusion is based on a flaw in the standard accretion disk model. This flaw is that the quadratically non-linear (in velocity) radial eddy angular momentum flux is parameterized by a linear (in velocity) viscous diffusion process. Once this flaw is corrected, as Prinn (1988) has shown, *efficient* mixing is predicted for both the solar nebula and giant planetary subnebulae. Furthermore, I would like to say that you have to remember there are cosmo-chemical processing plants (*i.e.*, giant planet subnebulae) imbedded throughout the outer regions of the solar nebula. You have your little plant around Jupiter which has apparently left us a volatility dependent trend in the Galilean satellites around that planet. You have a little heat engine that has been hypothesized to have been operating around Saturn. And one has the possibility of one around Neptune as well. So that all one needs to do, and it is unclear as to the extent one did this, is to take material in the outer nebula, those cool regions, and move it into the inner regions of these little heat engines, these little processing plants, and reprocess it there. And to the extent to which that has happened is unclear, and has not been quantified in the literature. Of course it is generally acknowledged that interstellar signatures will potentially be more abundant in the outer Solar System simply because it is (and was) colder out there, and thus less thermally processed.

Now as to your other assertion, let me start getting into that. If one looks at the various ways of doing processing in the solar nebula (*e.g.*, Prinn and Fegley 1988) by comparing the usable energy fluxes for doing chemistry relative to total thermal flux one sees that in fact thermochemistry dominates in the inner regions of the nebula.

Now as you move further out in the nebula, this situation changes somewhat and one would expect that lightning becomes a little more important. However, the efficient mixing expected in the solar nebula (*e.g.*, Prinn 1988) will still lead to significant "contamination" of thermally processed material in the outer regions of the solar nebula. Now, considering UV in particular, even if I'm getting UV coming out of, say, the exterior regions of the disk, say its boundary, penetrating vertically into the nebula, it is not at all clear that it is going to be very efficient. And this is why. You have a lot of water vapor. If you are in the region of the disk, where you have water vapor in the gas phase, vertically from the midplane to the photosphere, the optical depth is fairly high. And the calculation for this is given by Prinn and Fegley (1988). The result is that you get an optical depth $\tau \sim 2 \times 10^7$ in the vertical. So that if you're emitting UV at the boundary surface and irradiating the nebula (say from the skin), until you move out radially from the region where you have water vapor in the gas ($\approx 5$ AU), you cannot do much photochemical processing. And the amount of $H_2O$ you'd be processing if you look at, say interstellar starlight, or UV light being made at the exterior of the disk, is about 0.07 to 0.7% of the $H_2O$ column density at any point. What happens and what could be relevant in some cases is that once you get beyond the water condensation boundary, that tremendous opacity source disappears, it condenses out. And then you have to worry about CO gas as an opacity source in the far UV and you could conceivably be irradiating ice-rock grains. But the region where, in fact, you can get the UV into the disk is the region where everything is condensed out and it is hard to do much chemistry because you just have solid stuff in grains and then you're irradiating them.

**D. Stevenson:** I will make one comment about this particular issue. You have to remember that as with atmospheres of planets, there is no problem in principle in processing a thin layer and then contaminating the rest of the region by bringing new material out. I accept that the amount of material you are processing at any instant is small, but it is not clear that that is an unimportant process given the fact that thermochemistry is zero. In those regions, the contamination of the thermochemical processes in the outer solar nebula due to what you are doing in the inner solar nebula may also be almost nearly zero.

**Fegley:** However, your assertion (Stevenson 1987, 1988a, b, c) that mixing is inefficient in the solar nebula and in the giant planetary subnebulae is directly contradicted by the recent work of Prinn (1988).

**R. Thompson:** Actually I found that comment interesting in the sense that I would have said exactly the opposite. In a sense it looks to me exactly like a high temperature gas, such as you see in a light star, which is then processed out. In fact we have absolute direct evidence of CO in star formation objects. We see it in emission at a temperature of around 4 or 5 thousand degrees, and at a distance which is few AU out from the object. So, we have that evidence directly, and it would seem that your ratios of CO to $CH_4$ are simply that material that was processed through the nebula and has reached a time when the timescale for further chemical reaction was reached at the point where you have that equilibrium ratio. So it would seem that that would be direct evidence the other way. Since we see it observationally in a very high temperature state before the conditions that you were talking about.

**Fegley**: I'm not sure I get what you're saying. You're seeing the high CO to CH$_4$ at high temperatures already.

**R. Thompson**: You're seeing CO in a high density state at a high temperature in young stellar objects. And this, through the spectroscopy, has to be at distances of just a few AU from the object itself. And at that point in those temperatures, pressures and conditions you would have the thermochemistry you are talking about.

**H. Weaver**: And, so you are saying it should be converted to methane, for example?

**R. Thompson**: No. No. It should have a high CO to CH$_4$ ratio, which is what is said there (the diagram), because the CO/CH$_4$ ratio is greater than one. And if you produce that in the disk and move it, how would you expect it to go? It will stay at a given ratio when it reaches a temperature-pressure point at which the processing time is too slow for the ratio to change.

**P. Cassen**: Everything that you bring into the nebula from the interstellar medium region has to, in some sense, be processed, or survive, or at least encounters the luminosity field of the protostar. And what I was wondering is what kind of processes do you expect to go on during that event. That is, some models of formation of solar mass stars indicate that you could vaporize grains out as far as 1 AU and further just in the infall. And that means that you have, you know, very high temperatures compared to some of the nebula temperatures that you are talking about that extend quite a bit beyond that. The densities are lower and the time available is shorter. But what kind of process would you expect to go on in those regions?

**Fegley**: Well, if you are giving me higher temperatures at greater distances and lower densities, that is not a problem for getting to the stable high temperature molecules at all. For example, if I start out with something like ammonia or methane, then going to N$_2$ or CO is fast (there is no kinetic barrier), or evaporating grains is fast. And if I have lower densities, I'd start atomizing things and get a higher fraction of atoms and radicals. And then when I go back to lower temperatures and start cooling it down, I'd have an easier time setting up equilibrium. It's not inhibiting production of my high temperature species, it is in fact further inhibiting, if I'm at lower densities while I'm cooling, the production of *low* temperature species.

**P. Cassen**: It seems to sort of go along with what Rodger (Thompson) was saying. You can produce stuff elsewhere and have it spread further out into the nebula.

**M. Greenberg**: Yes, a couple of short comments. You discussed the formation of gas only considering the CO and CH4 for some sort of thermal reaction. We know that there is an awful lot of organic materials coming in from the interstellar medium which are relatively non-volatile. The question is have you taken that into consideration, or do you think that they are totally evaporated and pyrolized? That is one. One other comment.

**Fegley**: The fraction of interstellar organics which are totally evaporated and/or thermally reprocessed depends of course on the ambient conditions (T, P, time) in any region of the solar nebula. Destruction of interstellar organics (and other interstellar materials) will obviously be more severe in the inner regions of the solar nebula and

inside outer planet subnebulae. I think that under some conditions it would be hard to get rid of some of the "refractory" organics. However, there is a problem in quantitatively evaluating these destruction processes because there are a couple of ways for getting rid of interstellar organics. I could evaporate the refractory organic grains and then thermally reprocess the vapor. Alternatively, hydrogen atoms could hit the solid and start hydrogenating it or breaking it up. Or I have an OH or O hitting them, which are basically the dominant oxidizers present in the nebula, could collide with the grains and eventually oxidize them. Such destruction processes have not been 100% efficient because there are remnants of interstellar organics in some meteorites. If you look at the primitive chrondrites, the amounts of these interstellar organics that you have are small. But we don't have samples (*e.g.*, comets) where you might expect them to survive in abundance.

**M. Greenberg**:   I have another comment. But instead of that one, I am going to make one other. There is evidence of the isotopic ratios of the heavy noble gases being preserved in the carbonaceous component of meteorites which, at least, somebody has attributed to trapping in interstellar dust and bringing it in. If that were the case then certainly you would not be evaporating a very large fraction of the original organics. That is the comment and whether you have any comment on that, I don't know.

**G. Wasserburg**:   The fraction of carbon represented by these organic grains is a very small fraction of the total carbon, something like $10^{-4}$ or $10^{-5}$.

**M. Greenberg**:   Yes. But that is where you see these pre-solar isotopic abundances. So, OK we will talk about it.

**J. Lunine**:   In their chapter, Fegley and Prinn raise several specific criticisms of my model of solar nebula chemistry and mixing as the source of Halley's volatile composition. My response to these criticisms follows:

   (1) **Low quench temperature for $CH_4$ formation from CO**: The laboratory data required to infer the yield of organics in the solar nebula from Fischer-Tropsch-type reactions is inadequate; experiments in the literature involve hydrogen pressures and gas-phase abundances completely different from solar nebular conditions. Specific laboratory studies under appropriate conditions are required to determine the amount of methane (relative to more complex molecules) produced from gas-grain reactions in the nebula.

   (2) **Low O/C ratio in the nebula**: My justification for invoking a subsolar O/C ratio comes from a model for diffusive redistribution of water vapor in the solar nebula (Stevenson and Lunine 1988). This model predicts a water vapor abundance which varies with time and radial distance over the history of the nebula. Likewise, the oxygen fugacity derived for chondrites has a wide variation both within and between individual meteorite samples, and is dependent both on nebular temperature and water vapor abundance (Rubin, Fegley, and Brett 1988). It has proved difficult to relate the range of meteorite fugacity values to a single, near-solar elemental oxygen abundance in the nebular gas. Finally, the percentage of different chondrite types on earth probably reflects selection effects in the orbital dynamics of bringing meteorite material from the main belt to the earth, rather than the original mass fraction of the different chondrite parent bodies formed in the nebula. It is known that certain orbital semi-major axes

in the belt are much more likely to deliver material to the earth than others (Wetherill and Chapman 1988).

(3) Formation of clathrate: A range of laboratory studies (reviewed in Lunine and Stevenson 1985) indicate that clathrate formation down at least to 70 K is extremely rapid on laboratory timescales when fresh ice is exposed to the gas. This implies a low (or zero) activation energy for conversion of an ice I surface layer to clathrate. Diffusion of HF through ice is probably not an appropriate analogue process for deriving the activation energy. Diffusion of gases through the bulk volume of the ice is slow, however, and quantitative uptake of nebular gases by clathrate requires collisions to expose fresh ice to the gas. Laboratory experiments indicate that such collisions allow further gas uptake; little clathrate is destroyed. Collision timescales in the nebula may have been short enough to expose most of the ice to the gas. Note also that nebular temperature profiles are not favorable for condensation of pure CO; its presence in Halley argues for clathration or physical adsorption on ice. It appears from laboratory evidence that the process of adsorption involves volatile fractionation effects similar to those in clathrate.

(4) Stevenson nebular mixing model: Enhanced nebular mixing beyond that calculated by Stevenson (1989) aids my model in allowing more methane and ammonia from the inner nebular "chemistry" zone to reach the formation region of comet Halley.

**Fegley and Prinn:**   In reply to Lunine's comments we suggest that his model for Comet P/Halley would have the following consequences:

(1) Highly reduced materials (*e.g.*, carbides, nitrides, sulfides) similar to those found in the rare enstatite chondrites will dominate all planet-forming solids condensed in the inner solar nebula. In particular, a subsolar O/C ratio will lead to the formation of a volatile-rich planet Mercury which will contain 12% of the solar carbon abundance, 4% of the solar nitrogen abundance, and 100% of the solar sulfur abundance. This consequence, which had previously been pointed out by Fegley and Cameron (1987) and by Cameron *et al.* (in press), is at odds with generally accepted models of the composition of Mercury.

(2) Extremely FeO-poor silicates (with Fe/(Fe + Mg) ratios of zero) and reduced, anhydrous minerals typical of enstatite chondrites will dominate the inorganic dust component of Comet P/Halley. Although the interpretation of the PUMA spectra is complex and not unambiguous, the available data show that the observed Fe/(Fe + Mg) ratios are not exclusively zero and in fact vary from 0 to 1 (Jessberger, Kissel, and Rahe 1988). This behavior is not typical of highly reduced enstatite chondrite-like materials. Also we note that Soviet analyses of the PUMA spectra (Dikov *et al.* 1988) which attempt to assign mineral compositions to the Halley particles, conclude that C1 chondrites (which are highly oxidized and water-rich) are an appropriate analog to the Halley particles. This is at odds with a highly reduced, anhydrous composition predicted for a nebula with subsolar O/C.

We note that both of these consequences of Lunine's model are potentially testable by further analyses of available data and by appropriately designed spacecraft experiments.

## Additional References

Bernatowicz, T., Fraundorf, G., Ming, T., Anders, E., Wopenka, B., Zinner, E., and Fraundorf, P. 1987, *Nature*, **330**, 728.

Bond, G. C. 1962, *Catalysis by Metals* (London: Academic Press).

Cameron, A. G. W., Fegley, B., Benz, W., and Slattery, W. L. 1989, in *Mercury*, ed. C. Chapman, F. Vilas, and M. S. Matthews (Tucson: University of Arizona Press), in press.

Dikov, Yu. P., Evlanov, E. N., Fomenkova, M. N., Mukhin, L. M., Nazarov, M. A., Prilutsky, O. F., Sagdeev, R. Z., and Zubkov, B. V., 1988, *Adv. Space Res.*, submitted.

Fegley, B., and Cameron, A. G. W., 1987, *Earth Planet. Sci. Lett.*, **82**, 207.

Gilman, R. C. 1969, *Ap. J. (Letters)*, **155**, L185.

Jessberger, E. K., Kissel, J., and Rahe, J. 1988, in *Origin and Evolution of Planetary and Satellite Atmospheres*, eds. S. Atreya, J. Pollack, and M. Matthews (Tucson: University of Arizona Press), in press.

Lunine, J. I., and Stevenson, D. J. 1985, *Ap. J. Suppl.*, **58**, 493.

Larimer, J. W. 1975, *Cosmochim. Acta*, **39**, 389.

Prinn, R. G. 1988, *Ap. J.*, submitted.

Prinn, R. G., and Fegley, B., Jr. 1988, in *Origin and Evolution of Planetary and Satellite Atmospheres*, eds. S. Atreya, J. Pollack, and M. Matthews (Tucson: University of Arizona Press), in press.

Rubin, A. E., Fegley, B., and Brett, R., 1988 in *Meteorites and the Early Solar System*, eds. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), p. 488.

Stevenson, D. J. 1987, Paper presented at the Conference on Origin and Evolution of Planetary and Satellite Atmospheres, Tucson, AZ, March 10-14, 1987.

Stevenson, D. J. 1988a, *Lunar and Planetary Science XIX*, pp. 1123-1124.

Stevenson, D. J. 1988b, Paper presented at the Workshop on The Formation and Evolution of Planetary Systems, Baltimore, MD, May 9-11, 1988.

Stevenson, D. J. 1988c, *Ap. J.*, submitted.

Stevenson, D. J. 1989, *Ap. J.*, submitted.

Stevenson, D. J., and Lunine, J. I. 1988, *Icarus*, **75**, 146.

Wetherill, G. W., and Chapman, C. R., 1988, in *Meteorites and the Early Solar System*, eds. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), p. 35.

Zinner, E., Ming, T., and Anders, E. 1987, *Nature*, **330**, 730.