

## CHEMISTRY OF THE SOLAR NEBULA

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**ABSTRACT.** We review theoretical models of thermochemical processes in the solar nebula which consider the effects of nebular dynamics on the chemistry of the abundant, chemically reactive volatile elements H, O, C, N, and S. Specific, testable predictions of these models are described. We also use the theoretical models to interpret the latest available data on the abundances and molecular speciation of volatiles in comet P/Halley.

### 1. Introduction

The thermochemical interactions between gases and grains in the solar nebula played a central role in establishing the observed volatile element inventories of the planets, their satellites, and the small bodies in the solar system (e.g., the asteroids, comets, and meteorites). For example, the oxidation and sulfurization of Fe metal grains, the synthesis of organic compounds by grain catalyzed chemistry between CO + H<sub>2</sub>, the extent of evaporation and thermal reprocessing of presolar grains are all different types of thermochemical interactions which ultimately influenced the volatile element content of the solid planet-forming materials in the solar nebula.

In this paper we review thermochemical processes in the solar nebula with an emphasis on the chemistry of the abundant, chemically reactive volatiles H, O, C, N, and S. We begin by discussing the elemental abundances in solar composition material and then move on to consider the types of interstellar materials accreted by the solar nebula. Next we examine the isotopic evidence for inefficient thermal processing in the nebula. After reviewing the results of thermochemical equilibrium models, which are the foundation for any discussion of nebular chemistry, we describe the basis of thermochemical kinetic models of nebular chemistry which attempt to consider the effects of nebular mixing and dynamics on the chemical processes taking place. We begin reviewing the results of these models with detailed descriptions of the gas phase and grain catalyzed chemistry of carbon and nitrogen, then move on to the sulfurization and oxidation of Fe metal, and the mechanisms for water retention in solid grains. The effects of this high temperature chemistry on the composition of low temperature condensates are then reviewed. At this point we present current observational data on the abundances of volatiles in comet Halley and interpret these data in terms of the nebular chemistry models discussed earlier.

### 2. Elemental Abundances in the Solar Nebula

A knowledge of the elemental abundances in the solar nebula (i.e., in solar composition material) is essential for any discussion of nebular chemistry. An understanding of how the solar abundances of the chemical elements have been determined is also useful for anyone interested in cosmochemical modelling of the solar nebula because the chondritic meteorites, which provide much of the abundance data, originally formed in the solar nebula and their elemental compositions have been little altered since that time.

The first attempts to determine the abundances of the elements probably date back to Clarke (1889) who attempted to find periodicities in the relative abundances of the elements in the Earth's crust. However, as we now know, the relative elemental abundances in the terrestrial crust have been modified by planetary differentiation and weathering processes and generally are not representative of the abundances of the elements in solar composition material. Thus, Clarke's attempts were doomed to failure.

Instead, it is necessary to analyze samples of material which formed in the solar nebula and have retained their elemental composition without alteration since that time. Obviously, spectroscopic determination of the elemental abundances in the Sun can provide the necessary information with the exception of deuterium and a few light elements such as Li, B, and Be which have been partially or totally consumed by thermonuclear fusion reactions. In fact this approach has been taken and is very useful provided that the relevant inputs for the data analysis are well known. For example, it is necessary to know the oscillator strengths for the spectral lines of interest and it is also necessary to realistically model physical conditions in the solar photosphere where the lines are formed. Any possible elemental fractionation processes which affect the elemental abundances in the solar photosphere must also be understood. The topic of solar photospheric abundances is reviewed by Grevesse (1984).

Another highly successful approach has been to determine elemental abundances in the chondritic meteorites (so named because they contain small, rounded glass beads known as chondrules), which were also formed in the solar nebula. In the modern era, chemical analyses of the elemental abundances in chondrites was first done by Goldschmidt, the Noddacks, and their colleagues in the 1920s and 1930s. This work was critically assessed by Goldschmidt (1937, 1954) who compiled the first table of elemental abundances in meteorites. This tabulation showed that to first approximation, the abundances of the non-volatile elements in meteorites and in the Sun were similar. It also served as a stimulus for the seminal work of Suess (1947a,b) who postulated that the abundances of the nuclides, and especially the odd mass number nuclides, are a smooth function of mass number.

Suess (1947a,b) used this postulate to adjust the elemental abundances to produce a smooth variation of abundance with mass number. In some cases, such as Re, adjustments of up to a factor of 100 were made and shown to be correct by subsequent chemical analyses of meteorites. Many of the details of this curve are reviewed by Woolum (1988).

A later paper by Suess and Urey (1956) carried this approach even further and produced an influential table of solar elemental abundances. One outcome of their table was the pioneering studies of stellar nucleosynthesis mechanisms by Burbidge et al (1957). Another outcome was an increasing number of high quality analytical studies of elemental abundances in chondritic meteorites. Much of this work is summarized in the compilation edited by Mason (1971). Much of the later work since that compilation was assembled is reviewed by Mason (1979) and in the papers by Anders and Ebihara (1982) and Anders and Grevesse (1989). It is safe to say that in the intervening 35 years since the publication of Suess and Urey (1956), the improvements in chemical analyses of meteorites, in the understanding of stellar nucleosynthesis mechanisms, and in astronomical observations of elemental abundances in the Sun and other stars have led to vast improvements in our knowledge of the solar abundances of the elements.

The result of all these efforts is displayed in Table 1, based on Anders and Grevesse (1989), which summarizes present knowledge of the solar abundances of the elements. It shows the atomic abundances of the elements in CI chondrites (normalized to  $10^6$  atoms of Si), in the solar photosphere (normalized to  $10^{12}$  atoms of H), and elemental abundances by mass in the Orgueil CI chondrite. The CI chondrites are chosen as an abundance standard because their ele-

mental composition matches that of the Sun more closely than that of any other meteorite class. The Orgueil meteorite is the most widely distributed and frequently analyzed CI chondrite.

Perhaps the single most important point illustrated by the data in Table 1 is that the chemistry of solar composition material and of the solar nebula is overwhelmingly dominated by hydrogen. The third most abundant element overall and the second most abundant chemically reactive element, oxygen, has only about 0.1% of the H atomic abundance in solar matter. Excluding He, the atomic abundances of all other elements combined sum up to about 70% of the oxygen elemental abundance. This situation is in stark contrast to the elemental abundances at the surface of the Earth where O is the most abundant element in the crust and H is a trace element contained in a thin oceanic veneer. The contrast is even more severe on Venus where H is depleted by about a factor of  $10^5$  relative to its observed surficial abundance on the Earth. Clearly one of the most important problems facing cosmochemists is how to explain the evolution of the volatile inventories of Venus, Earth, and Mars from the compositionally very different solar nebula. This problem is still unresolved.

A second important point demonstrated by the solar elemental abundances is that the very similar abundances of carbon and oxygen results in an intimate coupling of their chemistry. In the Anders and Grevesse (1989) tabulation of solar elemental abundances the atomic C/O ratio is  $\sim 0.42$ , while in the earlier tabulations of Cameron (1973, 1982) the C/O ratio was 0.57 and 0.60, respectively. The more recent data of Grevesse et al (1991) on the photospheric carbon abundance correspond to a C/O ratio of 0.47. One of the most stable molecules observed in nature is CO. The similarity of the C and O abundances (C/O  $\sim 0.4-0.6$ ) dictates that over a wide range of P,T conditions in the solar nebula CO is the most abundant carbon gas and is also either the first or second most abundant oxygen gas, depending on the degree of dissociation of water vapor. Changes in the gas phase abundance of CO and H<sub>2</sub>O, for example by freezing out the water vapor (Stevenson and Lunine 1988), can then alter the total C/O ratio in the gas phase. In turn, changing this ratio alters the oxygen fugacity of the solar nebula and the major element mineralogy of grains formed from the nebular gas (e.g., Larimer 1975; Larimer and Bartholomay 1979). Alteration of this mineralogy has first order consequences such as the formation of carbide, nitride, and sulfide minerals that are stable at high temperature, thus leading to efficient retention of these important volatile elements in rocky material. There are also important second order consequences such as the condensation of cohenite Fe<sub>3</sub>C instead of Fe metal, which may influence the nature of grain catalyzed chemistry which can proceed.

The similarity of the C/O ratio is also important for determining the amount of water ice in volatile-rich bodies that formed in the outer solar nebula. If all carbon remained as CO at the low temperatures in the outer nebula, then the water ice abundance was decreased below the amount which could condense if CO had already been converted to CH<sub>4</sub>. On the other hand, if CO were efficiently converted to CH<sub>4</sub> and/or other hydrocarbons, then a sizeable fraction of the total O was released from CO and was available for formation of water ice. As we shall see later, the ice/rock mass ratios in "icy" bodies formed in the solar nebula, where CO was the dominant carbon gas are predicted to be lower than the ice/rock ratios in "icy" bodies formed in giant protoplanetary subnebulae, where CH<sub>4</sub> was the dominant carbon gas.

Another significant point shown by the elemental abundance data is that carbon chemistry was an important facet of nebular chemistry. This stems from the fact that C is the third most abundant chemically reactive element. In fact, several questions such as whether or not CO can be converted to CH<sub>4</sub> in any appreciable quantities with decreasing temperature and the extent to which it undergoes grain catalyzed reactions with H<sub>2</sub> to form organic compounds are fundamental in determining the share of volatiles inherited by the Earth and the form in which these volatiles were provided.

TABLE 1. Abundances of the Elements in CI Chondrites and in the Solar Photosphere.

Atomic Number	Element Name & Chemical Symbol	Abundance in CI Chondrites (Si = $10^6$ atoms)	Abundance (by mass) in Orgueil CI chondrite	Abundance in Solar Photosphere (H = $10^{12}$ atoms)
1.	Hydrogen (H)	$2.79 \times 10^{10}$	2.02%	$1.00 \times 10^{12}$
2.	Helium (He)	$2.72 \times 10^9$	56 nL/g	$9.77 \times 10^{10}$
3.	Lithium (Li)	57.1	1.49 $\mu\text{g/g}$	14.45
4.	Beryllium (Be)	0.73	24.9 ng/g	14.13
5.	Boron (B)	21.2	870 ng/g	398
6.	Carbon (C) <sup>a</sup>	$1.01 \times 10^7$	3.45%	$3.98 \times 10^8$
7.	Nitrogen (N) <sup>b</sup>	$3.13 \times 10^6$	3180 $\mu\text{g/g}$	$1.00 \times 10^8$
8.	Oxygen (O)	$2.38 \times 10^7$	46.4%	$8.51 \times 10^8$
9.	Fluorine (F)	843	58.2 $\mu\text{g/g}$	$3.63 \times 10^4$
10.	Neon (Ne)	$3.44 \times 10^6$	203 pL/g	$1.23 \times 10^8$
11.	Sodium (Na)	$5.74 \times 10^4$	4900 $\mu\text{g/g}$	$2.14 \times 10^6$
12.	Magnesium (Mg)	$1.074 \times 10^6$	9.53%	$3.80 \times 10^7$
13.	Aluminum (Al)	$8.49 \times 10^4$	8690 $\mu\text{g/g}$	$2.95 \times 10^6$
14.	Silicon (Si)	$1.00 \times 10^6$	10.67%	$3.55 \times 10^7$
15.	Phosphorus (P)	$1.04 \times 10^4$	1180 $\mu\text{g/g}$	$2.82 \times 10^5$
16.	Sulfur (S)	$5.15 \times 10^5$	5.25%	$1.62 \times 10^7$
17.	Chlorine (Cl)	5,240	698 $\mu\text{g/g}$	$3.16 \times 10^5$
18.	Argon (Ar)	$1.01 \times 10^5$	751 pL/g	$3.63 \times 10^6$
19.	Potassium (K)	3,770	566 $\mu\text{g/g}$	$1.32 \times 10^5$
20.	Calcium (Ca)	$6.11 \times 10^4$	9020 $\mu\text{g/g}$	$2.29 \times 10^6$
21.	Scandium (Sc)	34.2	5.83 $\mu\text{g/g}$	1,259
22.	Titanium (Ti)	2,400	436 $\mu\text{g/g}$	$9.77 \times 10^4$
23.	Vanadium (V)	293	56.2 $\mu\text{g/g}$	$1.0 \times 10^4$
24.	Chromium (Cr)	$1.35 \times 10^4$	2660 $\mu\text{g/g}$	$4.68 \times 10^5$
25.	Manganese (Mn)	9,550	1980 $\mu\text{g/g}$	$2.45 \times 10^5$
26.	Iron (Fe) <sup>c</sup>	$9.00 \times 10^5$	18.51%	$3.24 \times 10^7$
27.	Cobalt (Co)	2,250	507 $\mu\text{g/g}$	$8.32 \times 10^4$
28.	Nickel (Ni)	$4.93 \times 10^4$	1.10%	$1.78 \times 10^6$
29.	Copper (Cu)	522	119 $\mu\text{g/g}$	$1.62 \times 10^4$
30.	Zinc (Zn)	1,260	311 $\mu\text{g/g}$	$3.98 \times 10^4$
31.	Gallium (Ga)	37.8	10.1 $\mu\text{g/g}$	759

Atomic Number	Element Name & Chemical Symbol	Abundance in CI Chondrites (Si = 10 <sup>6</sup> atoms)	Abundance (by mass) in Orgueil CI chondrite	Abundance in Solar Photosphere (H = 10 <sup>12</sup> atoms)
32.	Germanium (Ge)	119	32.6 µg/g	2,570
33.	Arsenic (As)	6.56	1.85 µg/g	-----
34.	Selenium (Se)	62.1	18.2 µg/g	-----
35.	Bromine (Br)	11.8	3.56 µg/g	-----
36.	Krypton (Kr)	45	8.7 pL/g	-----
37.	Rubidium (Rb)	7.09	2.30 µg/g	398
38.	Strontium (Sr)	23.5	7.80 µg/g	794
39.	Yttrium (Y)	4.64	1.53 µg/g	174
40.	Zirconium (Zr)	11.4	3.95 µg/g	398
41.	Niobium (Nb)	0.698	246 ng/g	26.3
42.	Molybdenum (Mo)	2.55	928 ng/g	83.2
44.	Ruthenium (Ru)	1.86	714 ng/g	69.2
45.	Rhodium (Rh)	0.344	134 ng/g	13.2
46.	Palladium (Pd)	1.39	556 ng/g	49
47.	Silver (Ag)	0.486	197 ng/g	8.7
48.	Cadmium (Cd)	1.61	680 ng/g	72.4
49.	Indium (In)	0.184	77.8 ng/g	45.7
50.	Tin (Sn)	3.82	1680 ng/g	100
51.	Antimony (Sb)	0.309	133 ng/g	10
52.	Tellurium (Te)	4.81	2270 ng/g	-----
53.	Iodine (I)	0.9	433 ng/g	-----
54.	Xenon (Xe)	4.7	8.6 pL/g	-----
55.	Cesium (Cs)	0.372	186 ng/g	-----
56.	Barium (Ba)	4.49	2340 ng/g	135
57.	Lanthanum (La)	0.446	236 ng/g	16.6
58.	Cerium (Ce)	1.136	619 ng/g	35.5
59.	Praseodymium (Pr)	0.1669	90 ng/g	5.1
60.	Neodymium (Nd)	0.8279	463 ng/g	31.6
62.	Samarium (Sm)	0.2582	144 ng/g	10
63.	Europium (Eu)	0.0973	54.7 ng/g	3.2
64.	Gadolinium (Gd)	0.33	199 ng/g	13.2
65.	Terbium (Tb)	0.0603	35.3 ng/g	0.8

Atomic Number	Element Name & Chemical Symbol	Abundance in CI Chondrites (Si = 10 <sup>6</sup> atoms)	Abundance (by mass) in Orgueil CI chondrite	Abundance in Solar Photosphere (H = 10 <sup>12</sup> atoms)
66.	Dysprosium (Dy)	0.3942	246 ng/g	12.6
67.	Holmium (Ho)	0.0889	55.2 ng/g	1.8
68.	Erbium (Er)	0.2508	162 ng/g	8.5
69.	Thulium (Tm)	0.0378	22 ng/g	1
70.	Ytterbium (Yb)	0.2479	166 ng/g	12
71.	Lutetium (Lu)	0.0367	24.5 ng/g	5.8
72.	Hafnium (Hf)	0.154	108 ng/g	7.6
73.	Tantalum (Ta)	0.0207	14.0 ng/g	-----
74.	Tungsten (W)	0.133	92.3 ng/g	12.9
75.	Rhenium (Re)	0.0517	37.1 ng/g	-----
76.	Osmium (Os)	0.675	483 ng/g	28.2
77.	Iridium (Ir)	0.661	474 ng/g	22.4
78.	Platinum (Pt)	1.34	973 ng/g	63.1
79.	Gold (Au)	0.187	145 ng/g	10.2
80.	Mercury (Hg)	0.34	258 ng/g	-----
81.	Thallium (Tl)	0.184	143 ng/g	7.9
82.	Lead (Pb)	3.15	2430 ng/g	70.8
83.	Bismuth (Bi)	0.144	111 ng/g	-----
90.	Thorium (Th)	0.0335	28.6 ng/g	1.3
92.	Uranium (U)	0.009	8.1 ng/g	<0.34

Elemental abundance compilations do not list the following radioactive elements which have no stable isotopes and are not found in meteorites: Technetium (43), Promethium (61), Polonium (84), Astatine (85), Radon (86), Francium (87), Radium (88), Actinium (89).

The abbreviations used for abundances in the Orgueil CI chondrite have the following meanings: % = mass %, nL/g = 10<sup>-9</sup> liters/gram, µg/g = 10<sup>-6</sup> grams/gram, pL/g = 10<sup>-12</sup> liters/gram, ng/g = 10<sup>-9</sup> grams/gram

The abundances in Table 1 are generally from Anders and Grevesse (1989) with the following values also being included:

\*The photospheric carbon abundance is from Grevesse et al (1991).

<sup>b</sup>The photospheric nitrogen abundance is from Grevesse et al (1990).

<sup>c</sup>The photospheric iron abundance is from Biéumont et al (1991) and Holweger et al (1990).

Finally, a fourth point illustrated by the abundances in Table 1 is that the chemistry of the solar nebula is essentially the chemistry of 8 elements (H, O, C, N, Mg, Si, Fe, S). To a lesser extent Al, Ca, Na, Ni, Cr, P, and Mn are also important by virtue of their abundances. However, several of the elements in this second list (Ni, Cr, Mn) simply alloy with Fe without engaging in any other chemistry. Thus, to a good first approximation, the elemental abundances dictate that the chemistry of solar material is the chemistry of only a handful of the naturally occurring elements. Therefore the rest of this review will emphasize the chemistry of these 12 elements while discussing chemistry in the solar nebula.

### 3. Composition and Preservation of Presolar Gases and Grains

The abundances in the preceding section tell us how much of each element was present in the solar nebula but do not tell us what form(s) each element was in when it was accreted by the solar nebula accretion disk. As discussed below, this information is potentially important because thermal processing in the solar nebula was not 100% efficient. Thus a knowledge of the initial gas and grain composition is useful for modelling the nebular reactions affecting the accreted interstellar gas and dust.

Qualitatively we expect that the interstellar gas and grains were thermally and chemically reprocessed to varying degrees depending on several factors such as the distance of the accreted material from the proto-Sun, the type of grains (e.g., rocky, organic, icy, etc.), whether the interstellar material was accreted at an early or late stage of nebular evolution, the rate of radial transport in the solar nebula relative to the rate of equilibrating reactions in the gas parcel, and to the rate of accretion of small grains into larger clumps. Obviously some grains in the solar nebula experienced complex histories such as cycles of evaporation, condensation, re-evaporation, and re-condensation. Other grains were presumably totally destroyed while some others were incorporated into meteorite parent bodies essentially unaffected by nebular processes. The work by Cameron and Fegley (1982) on the position of grain evaporation fronts in the solar nebula is a quantitative attempt to model the survivability of different types of rocky and metallic grains as a function of their radial and vertical position in the solar nebula. Related work has also been done by Morfill and colleagues (e.g., Morfill and Volk 1984).

A variety of sources provide information on the probable composition of the gases and grains accreted by the solar nebula. In recent years radio astronomy has detected a diverse suite of molecules in interstellar space and in the circumstellar shells of carbon stars (e.g., Irvine and Knacke 1989; Ormont 1991). At present over 70 molecules ranging in complexity from OH to HC<sub>10</sub>CN have been detected. Tables 2 and 3 schematically summarize a small subset of these data on the composition of interstellar and circumstellar gas and grains, indicate the possible effects of nebular chemistry on the accreted gas and grains, and also list possible preservation sites for the presolar species.

Several important points are indicated by these two tables. Perhaps the most significant is that the identification of presolar material in primitive objects (e.g., comets and some types of asteroids and meteorites) may be ambiguous because several important interstellar molecules are also predicted to form in the solar nebula. This problem may be most severe for CO and N<sub>2</sub>. If complete chemical equilibrium were attained, all interstellar carbon species would be converted to CO in the high temperature regions of the solar nebula and all interstellar nitrogen species would be converted to N<sub>2</sub>. In the absence of a potentially diagnostic isotopic ratio, it is then impossible to distinguish interstellar CO and N<sub>2</sub> from nebular CO and N<sub>2</sub>. Likewise, interstellar H<sub>2</sub>S, unless it is isotopically distinctive in some way, is impossible to distinguish from nebular H<sub>2</sub>S.

TABLE 2. Representative Interstellar Molecules and Their Possible Fates in the Solar Nebula <sup>a</sup>		
Molecule(s)	Comments on Nebular Chemistry	Possible Preservation Site(s)
H <sub>2</sub>	Major gas, o-p ratio reset to high T value	Does not condense in nebula
CO	Also stable high T form of C in nebula, use C & O isotopes to distinguish nebular from interstellar CO?	Trapped in clathrate hydrate or condensed as CO ice in comets or other icy bodies in outermost nebula
N <sub>2</sub>	Also stable high T form of N in nebula, use N isotopes to distinguish nebular from interstellar N <sub>2</sub> ?	Trapped in clathrate hydrate or condensed as N <sub>2</sub> ice in comets or other icy bodies in outermost nebula
HDO	Isotopic exchange will equilibrate D/H with nebular H <sub>2</sub> at sufficiently high temperatures in inner nebula	HDO ice in comets & icy satellites, HDO in hydrated silicates on asteroids?
HCN	Also produced by shock chemistry in solar nebula & Jovian protoplanetary subnebulae, use isotopes to distinguish source?	HCN ice in comets and outer solar nebula bodies?, conversion to organic matter on meteorite parent bodies
H <sub>2</sub> CO	Thermal decomposition and/or photolysis to H <sub>2</sub> + CO, polymerization to POM?	H <sub>2</sub> CO & POM observed in comets
CH <sub>3</sub> C <sub>2</sub> H	Oxidation to CO at high temperatures	Cometary ices?
CH <sub>3</sub> CN	Thermal decomposition	Cometary ices?
SO <sub>2</sub>	Reduction to H <sub>2</sub> S + HS at high temperatures	Cometary ices? (UV spectra give an upper limit of <0.1% of solar S abundance in several comets) <sup>b</sup>
COS	Thermal decomposition and/or photolysis to CO + S, subsequent conversion of S to H <sub>2</sub> S	Cometary ices? (radio data give an upper limit of <10% of solar S abundance in Comet Levy) <sup>c</sup>
H <sub>2</sub> S	Also stable high T form of S in nebula	Probably difficult to preserve & distinguish from nebular H <sub>2</sub> S
H <sub>2</sub> CS	Thermal decomposition to CO + H <sub>2</sub> S at fairly low temperatures in nebula	Cometary ices? (radio data give an upper limit of about 50% of solar S abundance in Comet Levy) <sup>c</sup>

(a) The most abundant gases listed by Irvine and Knacke (1989), excluding radicals and ions. The latter species were probably chemically reprocessed on a rapid timescale.

(b) Kim and A'Hearn 1991

(c) Crovisier et al 1991



TABLE 3. Major Components of Interstellar Dust and Their Fate(s) in the Solar Nebula<sup>a</sup>

Component	Comments on Nebular Chemistry	Possible Preservation Site(s)
Silicates	Amorphous material will be annealed and equilibrated, crystalline material will attempt to equilibrate at sufficiently high temperatures	Low T meteorite matrices, but difficult to distinguish from more abundant nebular constituents unless isotopically anomalous
Graphite	Oxidized at high T to form CO, hydrogenated at low T to form CH <sub>4</sub>	Circumstellar graphite grains observed in primitive meteorites
Polycyclic Aromatic Hydrocarbons (PAHs)	Oxidized at high T for form CO + H <sub>2</sub> , isotopic equilibration with nebular vapor, partial pyrolysis to more C-rich matter	D-rich organics observed in low T meteorite matrices & interplanetary dust particles, not conclusively identified as PAHs
Amorphous Carbon	Oxidized at high T to form CO, hydrogenated at low T to form CH <sub>4</sub>	Low T meteorite matrices
Icy Grain Mantles	Evaporation of ices, chemical & isotopic equilibration with nebular gas, photolysis in outer nebula	Comets & other icy bodies in outer solar nebula?
Organic Refractory Grain Mantles	More resistant to processes which destroy organics	D-rich organics observed in low T meteorite matrices & interplanetary dust particles
SiC	Oxidation (e.g., by O, OH, H <sub>2</sub> O) to silica & eventually silicates	Circumstellar SiC grains observed in primitive meteorites
MgS	Oxidation (e.g., by O, OH, H <sub>2</sub> O) to Mg oxides & silicates	Low T meteorite matrices?, sensitive to water & O <sub>2</sub>

(a) Major components as reviewed by Tielens and Allamandola (1987).

A similar problem exists for distinguishing presolar silicates from those produced by thermal processing (e.g., condensation, evaporation) in the solar nebula. Again, isotopic differences are one way to distinguish exotic material. If this is not possible, for example by virtue of small sample size which prohibits isotopic measurements, then other approaches may prove useful. Recently Bernatowicz et al (1991) discovered small (7-21 nm) crystals of TiC inside isotopically anomalous graphite grains which are clearly of presolar origin. Thus, the included TiC must also be presolar. Analogously, finding a silicate inside another grain, which by virtue of its mineralogy and/or isotopic composition is clearly presolar, may also be used as proof of a presolar origin. However, because the average composition of the gas and grains accreted by the solar nebula has solar chemical and isotopic composition, by definition, then it is clear that not all presolar material has to be isotopically distinctive from nebular materials.

On the other hand, some interstellar molecules are either less likely to be produced by nebular chemistry or less likely to be produced in amounts as large as those observed in the interstellar medium. It is generally believed that deuterium-rich species fall into this category. Table 4 lists the D/H ratios in molecules in interstellar clouds and in different solar system objects. There is a wide range of D/H ratios from the protosolar value of about  $3 \times 10^{-5}$  to values of a few percent in molecules in interstellar clouds. As discussed later, it is difficult to elevate the protosolar D/H ratio to such high values solely by thermochemical isotopic exchange reactions in the solar nebula because these reactions are kinetically inhibited at the low temperatures where the exchange has to occur (Grinspoon and Lewis 1987). However, ion-molecule reactions are facile at such low temperatures and provide a means for enhancing the D/H ratios in various hydrides.

Likewise, some presolar grains have distinctive compositions which are not representative of thermal processing in the solar nebula. The SiC, TiC, diamond, and graphite grains found in primitive meteorites (Amari et al 1990; Bernatowicz et al 1987, 1991; Lewis et al 1987; Tang and Anders 1988; Virag et al 1992; Zinner et al 1987) are probably the best examples of this situation. As discussed by Fegley (1988), SiC, TiC, and diamond are thermodynamically unstable in the solar nebula and would be oxidized to other compounds at the high temperatures in the inner solar nebula. As discussed later, graphite is stable at low pressures and low temperatures in a solar composition gas, but is thermodynamically unstable under all other conditions. But even in these relatively clear cut cases there is still room for some ambiguity. Silicon carbide and graphite are also predicted to be thermodynamically stable under the highly reducing conditions necessary for formation of the enstatite chondrites (Larimer 1975; Larimer and Bartholomay 1979). Diamond is not thermodynamically stable under these conditions but diamonds formed by impacts are also present in the ureilites, carbon-rich achondrites. Even in these cases, the identification of the SiC, graphite, and diamond grains as presolar rests upon their exotic isotopic compositions.

#### **4. Isotopic Evidence for Inefficient Thermal Processing in the Solar Nebula**

The discussion in the preceding section explicitly assumed that thermal processing in the solar nebula was not 100% efficient. What is the evidence that this is the case? Suess (1965) felt compelled to state that "Among the very few assumptions which, in the opinion of the writer, can be considered well justified and firmly established, is the notion that the planetary objects, i.e. planets, their satellites, asteroids, meteorites, and other objects of the solar system, were formed from a well-mixed primordial nebula of chemically and isotopically uniform composition. At some time between the time of formation of the elements and the beginning of condensation of the less volatile material, this nebula must have been in the state of a

TABLE 4. D/H Ratios in Interstellar Space and the Solar System\*

Material	D/H Ratio	Reference(s)
C <sub>3</sub> HD/C <sub>3</sub> H <sub>2</sub>	0.03-0.15	Gerin et al 1987; Bell et al 1988
NH <sub>2</sub> D/NH <sub>3</sub>	0.003 - 0.14	Olberg et al 1985; Walmsley et al 1987
C <sub>2</sub> D/C <sub>2</sub> H	0.01-0.05	Herbst et al 1987
DNC/HNC	0.01 - 0.04	Brown and Rice 1981
DCN/HCN	0.002 - 0.02	Wootten 1987
DC <sub>3</sub> N/HC <sub>3</sub> N	0.02	Schloerb et al 1981; MacLeod et al 1981
DC <sub>3</sub> N/HC <sub>3</sub> N	~0.02	Langer et al 1980; Wootten 1987
HDCO/H <sub>2</sub> CO	~0.01	Guelin et al 1982
HDO/H <sub>2</sub> O on Venus	0.016-0.019	Donahue et al 1982; DeBergh et al 1991
IDPs	(1.2-16) × 10 <sup>-4</sup>	Zinner 1988
Ordinary chondrites	(0.8-10.5) × 10 <sup>-4</sup>	Zinner 1988
HDO/H <sub>2</sub> O on Mars	(7.8±0.3) × 10 <sup>-4</sup>	Bjoraker et al 1989; Owen et al 1988
Carbonaceous chondrites	(0.8-6) × 10 <sup>-4</sup>	Zinner 1988
Comet Halley HDO/H <sub>2</sub> O	(0.6-4.8) × 10 <sup>-4</sup>	Eberhardt et al 1987b
Terrestrial D/H (SMOW)	1.557 × 10 <sup>-4</sup>	Hagemann, Nief and Roth 1970
D/H in Titan's atm.	~15 × 10 <sup>-5</sup>	Coustenis et al 1989; Owen et al 1986
Meteoritic Phyllosilicates	~14 × 10 <sup>-5</sup>	Yang and Epstein 1983
Neptunian atm. D/H	~12 × 10 <sup>-5</sup>	DeBergh et al 1990
Uranian atm. D/H	~9 × 10 <sup>-5</sup>	DeBergh et al 1986
Nebular HD/H <sub>2</sub>	~3 × 10 <sup>-5</sup>	Anders and Grevesse 1989
Jovian atm. D/H	(2.6±1.0) × 10 <sup>-5</sup>	Fegley and Prinn 1988
Saturnian atm. D/H	(1.7±1.0) × 10 <sup>-5</sup>	Fegley and Prinn 1988
Interstellar HD/H <sub>2</sub>	(0.8-2) × 10 <sup>-5</sup>	Boesgaard and Steigman 1985

(a) Modified from Irvine &amp; Knacke (1989) and Zinner (1988)

homogeneous gas mass of a temperature so high that no solids were present. Otherwise, variations in the isotopic composition of many elements would have to be anticipated." Thus, the formation of the solar nebula was believed to have erased the previously existing record of interstellar chemistry, and the chemical fractionations in meteorites and planetary material were subsequently produced largely by chemical equilibrium processes in the monotonically cooling solar nebula (e.g., see Anders 1968; Barshay and Lewis 1976; Grossman 1972; Grossman and Larimer 1974; Larimer 1967; Lewis 1972a; Lewis 1974).

However, this picture changed dramatically with the discovery by Clayton, Grossman and Mayeda (1973) of oxygen isotopic anomalies in meteorites. This was significant for several reasons: (1) the anomalies in the  $^{16}\text{O}/^{17}\text{O}$  and  $^{16}\text{O}/^{18}\text{O}$  ratios are not due to mass fractionation processes, (2) the anomalies are present in the most abundant element in rocky material, and (3) the anomalies are present in the third most abundant element overall and the second most abundant chemically reactive element in solar composition material.

It is true that prior to this work, there were reports of isotopic anomalies in some noble gases in meteorites, notably the presence of  $^{129}\text{Xe}$  and of Ne-E, essentially pure  $^{22}\text{Ne}$  (Reynolds 1960; Jeffery and Reynolds 1961; Black and Pepin 1969), and of large D/H ratios in some carbonaceous chondrites (Boato 1954; Briggs 1963). However, the significance of the large D/H ratios was not generally appreciated and because the known isotopic anomalies were otherwise restricted to the chemically unreactive noble gases, their existence did not have an important influence on models of nebular chemistry. However, once it became apparent that non-mass fractionated oxygen anomalies existed in meteoritic material, and were substantial effects (at the several % level), then the model of a solar nebula in which all accreted material was totally vaporized had to be modified because this scenario could not explain the preservation of ubiquitous anomalies in the most abundant element in stony meteorites.

Subsequently, the discovery (or rediscovery) of isotopic anomalies in many other elements reinforced the point that physical and chemical processes in the solar nebula did not completely erase the prior record of interstellar chemistry. This evidence essentially falls into four categories: (1) Large deviations of the D/H,  $^{12}\text{C}/^{13}\text{C}$ ,  $^{14}\text{N}/^{15}\text{N}$  ratios from their terrestrial values in some chondrites (e.g., Pillinger 1984; Zinner 1988). As mentioned earlier, these are difficult to explain solely by mass fractionation processes because chemical reactions between neutral species are probably kinetically inhibited at the low temperatures that are required to explain the observed effects by thermochemical isotopic exchange reactions. Instead either inheritance from interstellar chemistry involving ion-molecule reactions proceeding at low temperatures or from circumstellar chemistry in the atmospheres of certain types of stars is apparently required. (2) Non-mass fractionated isotopic anomalies in all elements analyzed (e.g., O, Mg, Si, Cr, Sr, Ba, Nd, Sm) in a small suite of Ca, Al-rich inclusions (CAIs) in carbonaceous chondrites (e.g., Lee 1988). These CAIs are known as FUN CAIs because of the Fractionated and Unknown Nuclear effects observed in them. (3) Non-mass fractionated isotopic anomalies in Ti in CAIs and meteorites (Lee 1988; Niederer, Papanastassiou, and Wasserburg 1981; Niemeier and Lugmair 1984). These anomalies are attributed to the incomplete mixing and homogenization of Ti isotopes from at least four different stellar sources. (4) Anomalies in  $^{26}\text{Mg}$ ,  $^{53}\text{Cr}$ ,  $^{60}\text{Ni}$ ,  $^{109}\text{Ag}$ ,  $^{129}\text{Xe}$ ,  $^{142}\text{Nd}$ , and  $^{244}\text{Pu}$ -fission Xe which indicate the presence of the now extinct radionuclides  $^{26}\text{Al}$ ,  $^{53}\text{Mn}$ ,  $^{60}\text{Ni}$ ,  $^{109}\text{Pd}$ ,  $^{129}\text{I}$ ,  $^{146}\text{Sm}$ , and  $^{244}\text{Pu}$  in the early solar system (Wasserburg 1985; Podosek and Swindle 1988; Shukolyukov and Lugmair 1992). (5) The ubiquitous non-mass fractionated oxygen isotopic anomalies (Thiemens 1988).

Details of the different isotopic anomalies are reviewed in the articles cited above. However, the important point here is that thermal processing was not 100% efficient at homogenizing the interstellar gas and grains accreted by the solar nebula. In some cases, such as

the light elements, large deviations of the isotopic ratios are observed in bulk meteorites or in phases separated from them. In other cases such as the more refractory elements, smaller effects corresponding to deviations of one part in  $10^4$  to one part in  $10^3$  from the terrestrial ratios are observed. The anomalies in oxygen can be at the percent level but may represent chemical processes which operated at some point during nebular history and may not necessarily require inefficient thermal processing of presolar material. However, inefficient homogenization after the production of the anomalies is still required for their preservation.

### 5. Thermochemical Equilibrium Models of Nebular Chemistry

The observational evidence reviewed above indicates that it is desirable to incorporate the influence of both the prevailing P,T conditions and of dynamics on the chemical reactions between gases and grains in the solar nebula. However, most models of nebular chemistry are based solely on thermochemical equilibrium and assume that only the P,T conditions control the nature and abundance of the gases and grains present in a system of solar composition. The inputs to thermochemical equilibrium models are the total pressure, the temperature, and the overall elemental composition. The outputs of the thermochemical equilibrium models are the temperature- and pressure dependent molecular speciation of all elements in the code, the condensation temperatures of condensed phases (pure solids & liquids, and solid & liquid solutions), and the abundances of the condensed phases as a function of temperature and pressure. Depending on the complexity of the particular code used, not all of these outputs may be calculated. The thermodynamic data used in the codes come from standard compilations such as the JANAF (Joint Army-Navy-Air Force) Tables, which contains data for about 1200 species. The P,T conditions assumed in the calculations come from physical models of the solar nebula (e.g., Boss, Morfill and Tscharnuter 1989; Cameron 1978, 1985; Lin and Papaloizou 1985; Ruden and Lin 1986; Wood and Morfill 1988). In general, current nebular models predict pressures and temperatures of about  $10^{-2}$  to  $10^{-4}$  bars and 1000-2000 K in the inner solar nebula dropping to  $10^{-7}$  to  $10^{-9}$  bars and 20-100 K in the outer solar nebula. The exact pressure and temperature vary as a function of radial distance in the solar nebula. Although nebular accretion disk models do not specify adiabatic structure, many of the P,T profiles do resemble adiabats, perhaps with a discontinuity (or several discontinuities) due to opacity changes induced by grain condensation. A representative P,T profile, initially based on the work of Lewis (1974) is shown in Fig. 1. The same profile is used throughout the rest of this paper.

Thermochemical equilibrium models have enjoyed great popularity because they give a first order description of the chemical and mineralogical composition of the chondritic meteorites. However, as we will discuss in more detail later the great appeal of thermochemical equilibrium models is also their Achilles heel because no consideration is given to either the rate at which chemical equilibrium might be approached or to the pathway by which this occurs. This problem is most severe for chemical reactions predicted to occur at low temperatures in the solar nebula and for chemical reactions involving carbon and nitrogen.

For the present, we will keep these limitations in mind while we review the major results of thermochemical models of nebular chemistry. These results are important for several reasons: (1) they provide the foundation upon which the more detailed and sophisticated thermochemical kinetic models of nebular chemistry are built, (2) as stated above they provide a first order description of the chemical and mineralogical composition of the chondritic meteorites, and (3) they provide important information about the types of rocky and metallic grains that are potential catalysts for heterogeneous chemistry involving C and N compounds.

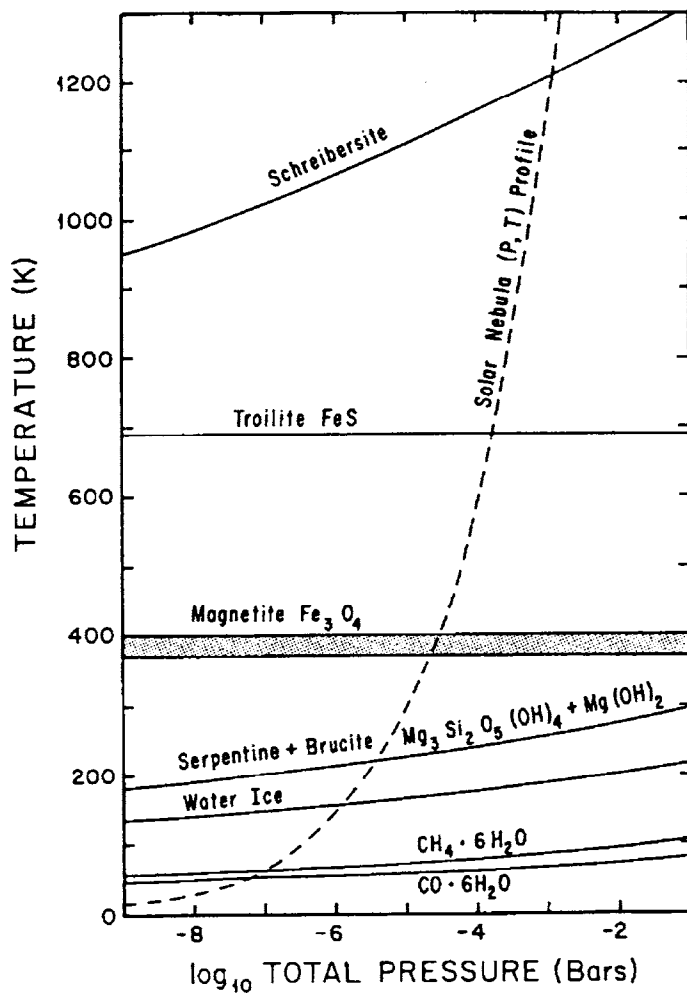


Figure 1. The thermodynamic stability fields for several exemplary gas-grain chemical reactions in the solar nebula. The P,T profile shown is originally based on the work of Lewis (1974), and has also been adopted in several subsequent publications (e.g., Barshay 1981; Fegley 1988; Fegley and Prinn 1989; Prinn and Fegley 1989). The shaded region for magnetite illustrates the range of formation temperatures for the case of all carbon remaining as CO (lower line) and for all carbon being found as CH<sub>4</sub> (upper line). CO clathrate will form if CO remains the major carbon gas in the nebula while CH<sub>4</sub> clathrate will form if CH<sub>4</sub> is present, as in the giant protoplanetary subnebulae. Modified from Fegley (1988).

Table 5 and Figs. 1-3 provide a convenient summary of the major results of thermochemical equilibrium models of nebular chemistry. Table 5 lists the major gases, initial condensates, and condensation temperatures for each of the naturally occurring elements. The data in Table 5 are for an assumed total nebular pressure of  $10^{-4}$  bars. This is because many of the results of condensation calculations in meteoritics and cosmochemistry are done at a constant total pressure, which is generally taken as either  $10^{-4}$  or  $10^{-3}$  bars. Figs. 2-3 illustrate the thermodynamic stability fields and abundances for condensates of the major elements from 150-1800 K in the inner regions of the solar nebula. These results, which are from Barshay (1981), give a detailed picture of the predicted condensate composition as a function of temperature throughout the region where the terrestrial planets and chondrites formed. Although not as comprehensive, a complementary illustration of condensate stability fields is provided by Fig. 1 which shows how the condensation temperatures of selected phases vary as a function of the assumed total pressure in the solar nebula. The important points demonstrated by the results of thermochemical equilibrium models are as follows.

The phases stable at the highest temperatures (either because they are the first condensates or the last phases to evaporate) are Ca-, Al-, Ti-bearing minerals such as hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ), corundum ( $\text{Al}_2\text{O}_3$ ), perovskite ( $\text{CaTiO}_3$ ), spinel ( $\text{MgAl}_2\text{O}_4$ ), gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), and åkermanite  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ . The refractory minerals are predicted to contain the less abundant refractory lithophiles (elements which geochemically prefer to be in a silicate phase) in solid solution. The refractory lithophiles include the REE, Ti, Zr, Hf, V, Nb, Ta, Sc, Y, Sr, Ba, Th, U, and Pu. Also predicted to be stable at these high temperatures are metallic alloys composed of the Pt-group elements (Ru, Os, Rh, Ir, Pt), Mo, W, and Re. Details of the major element condensation calculations, and descriptions of the comparisons of the predicted and observed mineral assemblages are given by Grossman and Larimer (1974), Kornacki and Fegley (1984), Larimer (1988), and Palme and Fegley (1990). The condensation calculations for the refractory trace lithophiles and for the refractory metals (also known as the refractory siderophiles) are discussed by Fegley and Kornacki (1984), Fegley and Palme (1985), Palme and Wlotzka (1976), and Kornacki and Fegley (1986). Descriptions of the mineralogy of CAIs, of the refractory lithophile abundance patterns and of the refractory metal nuggets are given in several references (Bischoff and Palme 1987; Blum et al 1988; El Goresy et al 1978; Fegley and Ireland 1991; Fuchs and Blander 1980; MacPherson et al 1988).

The refractory minerals predicted by the condensation calculations are observed in the CAIs in carbonaceous chondrites and the observed mineral assemblages are more or less similar to the predicted mineral assemblages in the condensation calculations. Likewise, the refractory lithophiles are observed in solid solution in several of these minerals, with abundance patterns which are plausibly explained by the condensation calculations. The predicted refractory metal nuggets are also found in the CAIs and have compositions consistent with those predicted by the chemical equilibrium models. Although many aspects of the formation of CAIs are still controversial, the overall similarity of the predictions and observed phase assemblages and trace element abundance patterns suggests that vapor-solid fractionation processes played an important role in the formation of the CAIs, and by implication were important in at least some regions of the solar nebula at some time (or times).

Another important point for the present discussion is that none of the high temperature phases are considered to be good catalysts for carbon and nitrogen chemistry in the nebular environment. Industrial experience shows that the oxide and silicate minerals found in CAIs are generally not good catalysts for reduction of CO and  $\text{N}_2$  or for organic compound formation. The Pt metal nuggets are of course potentially quite good catalysts, but their availability is limited to high temperature regions where they remain exposed to the nebular gas. However, the

TABLE 5. Equilibrium Condensation Chemistry of the Elements in the Solar Nebula

Atomic Number & Chemical Symbol	Condensation T (K) (P = 10 <sup>-4</sup> bars)	Initial Condensate in Solar Nebula	Major Gases in Solar Nebula	Notes & Sources
1. H	180	H <sub>2</sub> O(s)	H <sub>2</sub>	A, 1.
2. He <sup>a</sup>	<5	He(s)	He	A, 1.
3. Li	1225	Li <sub>2</sub> SiO <sub>3</sub> in MgSiO <sub>3</sub>	LiCl, LiF	MV, 2.
4. Be <sup>b</sup>	1400 (10 <sup>-3</sup> bars)	BeAl <sub>2</sub> O <sub>4</sub> in MgAl <sub>2</sub> O <sub>4</sub>	Be(OH) <sub>2</sub> , BeOH	RL, 3.
5. B <sup>b</sup>	745-759 (10 <sup>-3</sup> bars)	NaBO <sub>2</sub> (s)	NaBO <sub>2</sub> , KBO <sub>2</sub> , HBO <sub>2</sub> , H <sub>3</sub> BO <sub>3</sub>	MV, 3.
6. C <sup>c</sup>	78	CH <sub>4</sub> · 6H <sub>2</sub> O(s)	CO, CH <sub>4</sub>	A, 1.
7. N <sup>d</sup>	120	NH <sub>3</sub> · H <sub>2</sub> O(s)	N <sub>2</sub> , NH <sub>3</sub>	A, 1.
8. O <sup>e</sup>	---	---	CO, H <sub>2</sub> O	A
9. F	736	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	HF	MV, 4.
10. Ne <sup>a</sup>	~5	Ne(s)	Ne	A, 1.
11. Na	970 (50%)	NaAlSi <sub>3</sub> O <sub>8</sub> in feldspar	Na, NaCl	MV, 4.
12. Mg	1340 (50%)	Mg <sub>2</sub> SiO <sub>4</sub> (s)	Mg	ME, 5, 13.
13. Al	1670	Al <sub>2</sub> O <sub>3</sub> (s)	Al, AlOH, Al <sub>2</sub> O, AlS, AlH, AlO, AlF	RL, 6.
14. Si <sup>f</sup>	1529	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub> (s)	SiO, SiS	ME, 6.
15. P	1151 (50%)	Fe <sub>3</sub> P(s)	PO, P, PN, PS	MV, 4, 7.
16. S	684	FeS(s)	H <sub>2</sub> S, HS	MV, 4, 12
17. Cl	863 (50%)	Na <sub>4</sub> [AlSiO <sub>4</sub> ] <sub>3</sub> Cl(s)	HCl, NaCl, KCl	MV, 4.
18. Ar	50	Ar · 6H <sub>2</sub> O(s)	Ar	A, 14.
19. K	1000 (50%)	KAlSi <sub>3</sub> O <sub>8</sub> (s) in feldspar	K, KCl, KOH	MV, 4.
20. Ca	1634	CaAl <sub>12</sub> O <sub>19</sub> (s)	Ca	RL, 6.
21. Sc	1652 (50%)	Sc <sub>2</sub> O <sub>3</sub> (s)	ScO	RL, 8.
22. Ti	1600	CaTiO <sub>3</sub> (s)	TiO, TiO <sub>2</sub>	RL, 6.
23. V	1455 (50%)	diss. in CaTiO <sub>3</sub> (s)	VO <sub>2</sub> , VO	RL, 8.
24. Cr	1301 (50%)	diss. in Fe alloy	Cr	MV, 9.
25. Mn	1190 (50%)	Mn <sub>2</sub> SiO <sub>4</sub> in olivine	Mn	MV, 2.
26. Fe	1337 (50%)	Fe alloy	Fe	ME, 7, 9.
27. Co	1356 (50%)	diss. in Fe alloy	Co	RS, 9.
28. Ni	1354 (50%)	diss. in Fe alloy	Ni	RS, 9.
29. Cu	1170 (50%)	diss. in Fe alloy	Cu	MV, 2.



Atomic Number & Chemical Symbol	Condensation T (K) (P = 10 <sup>-4</sup> bars)	Initial Condensate in Solar Nebula	Major Gases in Solar Nebula	Notes & Sources
30. Zn	684 (50%)	ZnS diss. in FeS	Zn	MV, 2.
31. Ga	918 (50%)	diss. in Fe alloy	GaOH, GaCl, GaBr	MV, 10.
32. Ge	825 (50%)	diss. in Fe alloy	GeS, GeSe	MV, 10.
33. As	1012 (50%)	diss. in Fe alloy	As	MV, 10.
34. Se	684 (50%)	FeSe diss. in FeS	H <sub>2</sub> Se, GeSe	MV, 2.
35. Br <sup>b</sup>	~350	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Br(s)	HBr, NaBr	HV, 4.
36. Kr	54	Kr · 6H <sub>2</sub> O(s)	Kr	A, 14.
37. Rb <sup>b</sup>	~1080	diss. in feldspar	Rb, RbCl	MV, 5, 13.
38. Sr	1217 (50%)	diss. in CaTiO <sub>3</sub> (s)	Sr, SrCl <sub>2</sub> , Sr(OH) <sub>2</sub> , SrOH	RL, 8.
39. Y	1622 (50%)	Y <sub>2</sub> O <sub>3</sub> (s)	YO	RL, 8.
40. Zr	1717 (50%)	ZrO <sub>2</sub> (s)	ZrO <sub>2</sub> , ZrO	RL, 8.
41. Nb	1517 (50%)	diss. in CaTiO <sub>3</sub> (s)	NbO <sub>2</sub> , NbO	RL, 8.
42. Mo	1595 (50%)	refractory metal alloy	MoO, Mo, MoO <sub>2</sub>	RS, 9.
44. Ru	1565 (50%)	refractory metal alloy	Ru	RS, 9.
45. Rh	1392 (50%)	refractory metal alloy	Rh	RS, 9.
46. Pd	1320 (50%)	diss. in Fe alloy	Pd	MV, 9.
47. Ag	993 (50%)	diss. in Fe alloy	Ag	MV, 2.
48. Cd <sup>b</sup>	430 (10 <sup>-5</sup> bars)	CdS in FeS	Cd	HV, 11.
49. In <sup>b</sup>	470 (50%)	InS in FeS	In, InCl, InOH	HV, 11.
50. Sn	720 (50%)	diss. in Fe alloy	SnS, SnSe	MV, 2.
51. Sb	912 (50%)	diss. in Fe alloy	SbS, Sb	MV, 10.
52. Te	680 (50%)	FeTe diss. in FeS	Te, H <sub>2</sub> Te	MV, 2.
53. I	?	?	I, HI	MV/HV?
54. Xe	74	Xe · 6H <sub>2</sub> O(s)	Xe	A, 14.
55. Cs	?	?	CsCl, Cs, CsOH	MV/HV?
56. Ba	1162 (50%)	diss. in CaTiO <sub>3</sub> (s)	Ba(OH) <sub>2</sub> , BaOH, BaS, BaO	RL, 8.
57. La	1544 (50%)	diss. in CaTiO <sub>3</sub> (s)	LaO	RL, 8.
58. Ce	1440 (50%)	diss. in CaTiO <sub>3</sub> (s)	CeO <sub>2</sub> , CeO	RL, 8.
59. Pr	1557 (50%)	diss. in CaTiO <sub>3</sub> (s)	PrO	RL, 8.
60. Nd	1563 (50%)	diss. in CaTiO <sub>3</sub> (s)	NdO	RL, 8.
62. Sm	1560 (50%)	diss. in CaTiO <sub>3</sub> (s)	SmO, Sm	RL, 8.
63. Eu	1338 (50%)	diss. in CaTiO <sub>3</sub> (s)	Eu	RL, 8.

Atomic Number & Chemical Symbol	Condensation T (K) (P = 10 <sup>-4</sup> bars)	Initial Condensate in Solar Nebula	Major Gases in Solar Nebula	Notes & Sources
64. Gd	1597 (50%)	diss. in CaTiO <sub>3</sub> (s)	GdO	RL, 8.
65. Tb	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	TbO	RL, 8.
66. Dy	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	DyO, Dy	RL, 8.
67. Ho	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	HoO, Ho	RL, 8.
68. Er	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	ErO, Er	RL, 8.
69. Tm	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	Tm, TmO	RL, 8.
70. Yb	1493 (50%)	diss. in CaTiO <sub>3</sub> (s)	Yb	RL, 8.
71. Lu	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	LuO	RL, 8.
72. Hf	1690 (50%)	HfO <sub>2</sub> (s)	HfO	RL, 8.
73. Ta	1543 (50%)	diss. in CaTiO <sub>3</sub> (s)	TaO <sub>2</sub> , TaO	RL, 8.
74. W	1794 (50%)	refractory metal alloy	WO, WO <sub>2</sub> , WO <sub>3</sub>	RS, 9.
75. Re	1818 (50%)	refractory metal alloy	Re	RS, 9.
76. Os	1812 (50%)	refractory metal alloy	Os	RS, 9.
77. Ir	1603 (50%)	refractory metal alloy	Ir	RS, 9.
78. Pt	1411 (50%)	refractory metal alloy	Pt	RS, 9.
79. Au	1284 (50%)	Fe alloy	Au	MV, 2.
80. Hg	?	?	Hg	MV/HV?
81. Tl <sup>b</sup>	448 (50%)	diss. in Fe alloy	Tl	HV, 11.
82. Pb <sup>b</sup>	520 (50%)	diss. in Fe alloy	Pb, PbS	HV, 11.
83. Bi	472 (50%)	diss. in Fe alloy	Bi	HV, 11.
90. Th	1598 (50%)	diss. in CaTiO <sub>3</sub> (s)	ThO <sub>2</sub>	RL, 8.
92. U	1580 (50%)	diss. in CaTiO <sub>3</sub> (s)	UO <sub>2</sub>	RL, 8.

### Notes to Table 5

The condensation temperatures either indicate where the condensate first becomes stable or where 50% of the element is condensed and 50% is in the gas. The 50% condensation temperature is generally used when solid solutions are formed.

The major gases vary as a function of temperature and total pressure. The gas chemistry in Table 5 is generally valid at the condensation temperature of each element, and was either taken from the original references below or calculated as part of this work.

Sources cited in Table 5: (1) Lewis 1972; (2) Wai & Wasson 1977; (3) Cameron et al 1973; (4) Fegley & Lewis 1980; (5) Grossman & Larimer 1974; (6) Kornacki & Fegley 1984; (7) Sears 1978; (8) Kornacki & Fegley 1986; (9) Fegley & Palme 1985; (10) Wai & Wasson 1979; (11) Larimer 1973; (12) Larimer 1967, (13) Wasson 1985, (14) Sill & Wilkening 1978.

(a) This temperature is below cosmic background and condensation will not occur.

(b) The condensation temperature and initial condensate are uncertain and need to be re-evaluated.

(c) As discussed in the text, kinetic inhibition of the CO to CH<sub>4</sub> conversion yields either CO·6H<sub>2</sub>O(s) or CO(s) as the initial condensate.

(d) As discussed in the text, kinetic inhibition of the N<sub>2</sub> to NH<sub>3</sub> conversion yields either N<sub>2</sub>·6H<sub>2</sub>O(s) or N<sub>2</sub>(s) as the initial condensate.

(e) Oxygen is the most abundant element in rocky material and a separate condensation temperature is meaningless. The bulk of oxygen condenses as water ice; the remainder is present as CO or in rocky material.

(f) Most Si condenses when the silicates MgSiO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub> form (e.g., 1340 K at 10<sup>-4</sup> bars). See the MgSiO<sub>3</sub> condensation curve in Figure 2.

Key to abbreviations used for cosmochemical classification of the elements: A = atmophile, HV = highly volatile, ME = major element, MV = moderately volatile, RL = refractory lithophile, RS = refractory siderophile

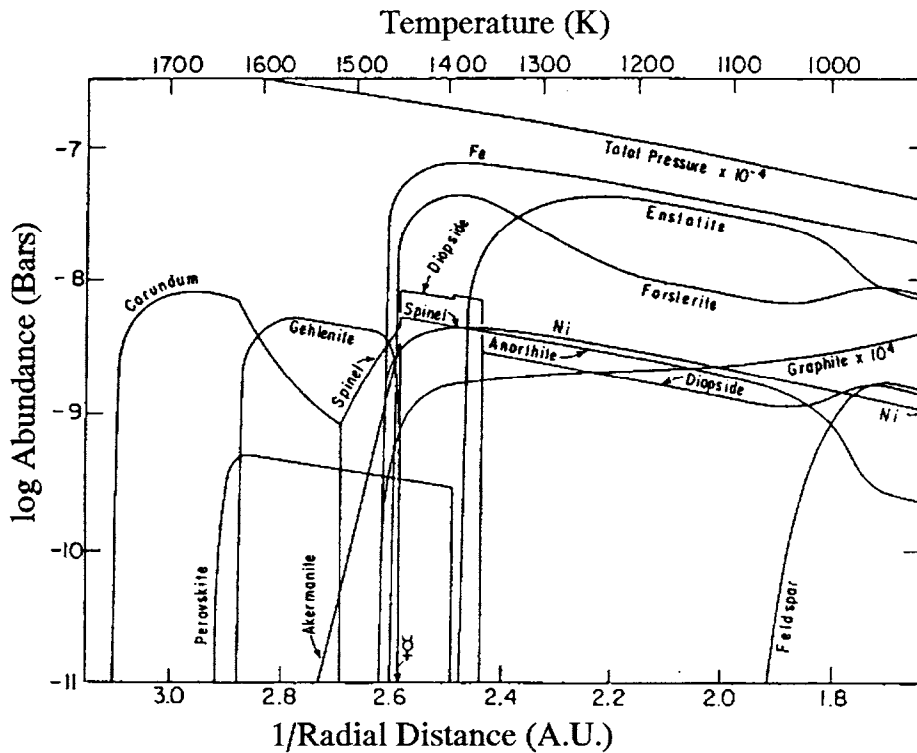


Figure 2. The chemical equilibrium condensation sequence from 900 to 1800 K in the inner regions of the solar nebula. The abundances of the different condensates stable at complete chemical equilibrium are displayed along the P,T profile illustrated in Fig. 1. The condensation of Fe metal at about 1450 K marks the appearance of a potentially important catalyst for reactions involving carbon and nitrogen compounds. The line labelled graphite shows the thermodynamic activity of carbon dissolved in Fe metal under equilibrium conditions. The astrological symbols for Mercury, Venus, Earth, and Mars are shown at the appropriate places on the distance scale which is in inverse astronomical units. Fig. 3 shows the condensate stability fields and abundances at lower temperatures. Modified from Barshay (1981).

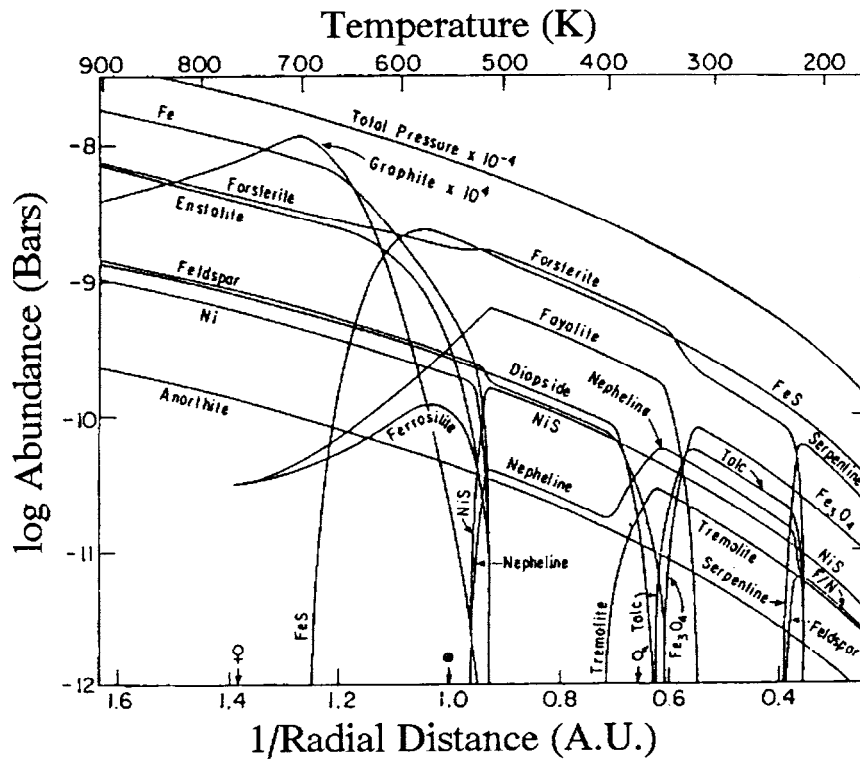


Figure 3. As in Fig. 2 from about 200 to 900 K. The condensate stability fields and abundances are indicated along the nebular P,T profile illustrated in Fig. 1. The astrological symbols for Mercury, Venus, Earth, and Mars are shown at the appropriate places on the distance scale. Note the formation of FeS at 690 K which could potentially deactivate Fe grains as catalysts by coating them with a sulfide layer. The Fe-bearing silicates fayalite  $\text{Fe}_2\text{SiO}_4$  and ferrosilite  $\text{FeSiO}_3$ , which form in solid solution with their magnesian counterparts, first have appreciable abundances at about 800 K. Formation of these two minerals may be kinetically inhibited because of slow solid state diffusion between Fe metal grains and silicates. All Fe metal which has not already been converted to troilite is removed by magnetite formation at about 400 K. Modified from Barshay (1981).

observational evidence shows that the Pt metal nuggets are physically sequestered inside CAIs, and thus are removed from exposure to the nebular gas at fairly high temperatures by condensation of the refractory oxide and silicate minerals. Any remaining Pt metal nuggets which escape this fate will of course be dissolved in the much more abundant Fe metal alloy, once it condenses. Thus, by the time that the nebular temperature has dropped to the point where organic compounds can be formed by processes such as Fischer-Tropsch-type (FTT) reactions, the Pt metal nuggets are no longer available as catalysts.

At lower temperatures, Fe alloy containing other siderophile (metal-loving) elements in solid solution, forsterite ( $\text{Mg}_2\text{SiO}_4$ ), and enstatite ( $\text{MgSiO}_3$ ) are predicted to form. Together, these phases make up the bulk of the condensible rocky material in solar composition gas. The condensation (or evaporation) curve for Fe-Ni alloy is an important phase boundary for carbon and nitrogen chemistry because the metal alloy is potentially the most abundant and most effective catalyst for reactions involving these two elements. At high temperatures some of the Fe alloy can react with P gases to form schreibersite  $\text{Fe}_3\text{P}$ . However, because of the mass balance constraints imposed by solar elemental abundances (see Table 1), this reaction only consumes a minor amount of the total available alloy. Much more of the Fe metal is removed by formation of troilite ( $\text{FeS}$ ), which occurs at the pressure independent temperature of 690 K. This involves the reaction of  $\text{H}_2\text{S}(\text{g})$  with the metal grains to form more Ni-rich metal grains coated by FeS. The reaction is pressure independent because the overall stoichiometry involves consumption of one mole of  $\text{H}_2\text{S}(\text{g})$  and production of one mole of  $\text{H}_2(\text{g})$ . At still lower temperatures of 370–400 K, the remaining metal alloy can be attacked by nebular water vapor to form magnetite ( $\text{Fe}_3\text{O}_4$ ). Again, this reaction is pressure independent because the same number of moles of  $\text{H}_2\text{O}(\text{g})$  and  $\text{H}_2(\text{g})$  are consumed and produced, respectively.

If the Fe-Ni remains well mixed with the nebular gas throughout its stability field, it is a potential catalyst throughout this entire temperature range. However, if the metal grains do not remain well mixed with the nebular gas (e.g., by settling to form much larger metal chunks in the nebular midplane on a time scale that is rapid with respect to nebular cooling) then their catalytic efficiency will be correspondingly diminished. Likewise, if troilite formation at 690 K results in FeS coatings on all metal grains, then no metallic surface will be left exposed to catalyze reactions at lower temperatures. In later sections when we discuss Fe metal grain catalyzed reactions of CO and  $\text{N}_2$  we assume that the metal grains in fact remain well mixed with the nebular gas at the solar Fe/ $\text{H}_2$  abundance ratio, and that the exposed surfaces are not coated by FeS and remain catalytically active down to 370–400 K where magnetite formation occurs.

Two other major events are predicted to occur below 690 K where troilite forms. One is the formation of hydrated silicates by the reaction of nebular water vapor with anhydrous silicates. However, as we discuss later, hydration of anhydrous silicates by nebular water vapor probably did not actually occur. Qualitatively, the process is analogous to hydrating rock in a near vacuum. Quantitatively, as shown later, the time scale for hydrated silicate formation in the solar nebula is orders of magnitude longer than the lifetime of the nebula itself. The other event is the condensation of water ice. Fig. 1 schematically illustrates the pressure-dependent temperatures at which both processes are predicted to occur. Hydrated silicate formation is exemplified by the formation of serpentine [ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ] + brucite [ $\text{Mg}(\text{OH})_2$ ] by the reaction of forsterite and water vapor. The water ice condensation line shown in Fig. 1 simply represents the line along which the partial pressure of water vapor in the solar nebula becomes equal to the water vapor pressure over  $\text{H}_2\text{O}(\text{ice})$ . If nebular pressures ever became high enough, the water ice condensation curve would cross the freezing point (273 K), and liquid water would form. This is unlikely.

**TABLE 6. Summary of Hydrated Silicate Condensation Calculations<sup>a</sup>**

Condensation Temp. (K) <sup>b</sup>	Hydrated Phase(s) and Chemical Formula(s)	Water Content (w/o)	Sources
~500	Tremolite [Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub> ]	2.2	1
<470 <sup>c</sup>	Na phlogopite [NaMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ]	4.5	2
~460 <sup>d</sup>	Hydroxyapatite [Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH]	1.8	3
~400 <sup>e</sup>	Serpentine [Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ]	13	4
~230 <sup>e,f</sup>	Serpentine [Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ]	13	5
<274 <sup>g</sup>	Serpentine [Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ] + Brucite [Mg(OH) <sub>2</sub> ]	16.1	2
~225	Serpentine [Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ] + Brucite [Mg(OH) <sub>2</sub> ]	16.1	6
~400 <sup>e</sup>	Talc [Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ]	4.8	1
~340 <sup>e,f</sup>	Talc [Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ]	4.8	5
~160-280 <sup>h</sup>	Talc [Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ]	4.8	7
~250	Talc [Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ] + Brucite [Mg(OH) <sub>2</sub> ]	8.3	6
~160 <sup>i</sup>	Water Ice [H <sub>2</sub> O]	100	8

(a) Modified from Prinn & Fegley 1989.

(b) The condensation temperature is the highest temperature at which the hydrated phase is stable along the solar nebula P,T profile shown in the figures.

(c) Na phlogopite forms at 470 K at 10<sup>-3</sup> bars and will form at lower temperatures along the solar nebula P,T profile used here.

(d) The water content is calculated on the basis of 1 H<sub>2</sub>O molecule per 2 hydroxyapatites.

(e) This result is predicated on solid-solid chemical equilibrium which is unlikely at these low temperatures (see text).

(f) Barshay's calculations used a feldspar-nepheline buffer for silica at T<600 K.

(g) This assemblage forms at 274 K at 10<sup>-3</sup> bars and will form at lower temperatures along the solar nebula P,T profile used here.

(h) Larimer & Anders 1967 list 2 possible talc formation reactions: 3MgSiO<sub>3</sub>(s) + SiO<sub>2</sub>(s) + H<sub>2</sub>O(g) → Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>(s) and 3Mg<sub>2</sub>SiO<sub>4</sub>(s) + 5SiO<sub>2</sub>(s) + 2H<sub>2</sub>O(g) → 2Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>(s) with condensation temperatures of 160-280 K at total pressures of ~ 10<sup>-6</sup>-10<sup>-3</sup> bars.

(i) The shaded region for water ice condensation in Fig. 10 illustrates the range of condensation temperatures assuming that all carbon is either CH<sub>4</sub> (higher T) or CO (lower T).

Sources: (1) Lewis 1972a; (2) Hashimoto & Grossman 1987; (3) Fegley & Lewis 1980; (4) Lewis 1974; (5) Barshay 1981; (6) Prinn & Fegley 1989; (7) Larimer & Anders 1967; (8) Lewis 1972b

At even lower temperatures below the water ice condensation curve, the highly volatile gases such as CO, N<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, etc. are predicted to condense. This may occur by formation of a distinct hydrate with water ice, as in the case of NH<sub>3</sub>•H<sub>2</sub>O(s) or by trapping the gas in the water ice crystalline lattice as in the case of clathrate hydrate formation. The clathrate hydrates which could have formed involve CO, N<sub>2</sub>, and CH<sub>4</sub>. Their ideal chemical formulas are CO•6H<sub>2</sub>O(s), N<sub>2</sub>•6H<sub>2</sub>O(s), or CH<sub>4</sub>•6H<sub>2</sub>O(s). Finally, at even lower temperatures around 20 K, the pure ices of these gases may have condensed. However, it is very unlikely that nebular temperatures were ever low enough (< 20 K) to condense Ne(s) or H<sub>2</sub>(s).

## 6. Thermochemical Kinetic Models of Nebular Chemistry

The central problem with chemical equilibrium models of nebular chemistry was probably recognized first by Urey, who pioneered the applications of physical chemistry in general and chemical thermodynamics in particular to cosmochemistry. While discussing the applications of chemical thermodynamic methods and data to nebular modelling Urey (1953) noted 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."

It is somewhat ironic that Urey's early recognition of the potential problems with purely chemical equilibrium models of nebular chemistry was not acted on for nearly 30 years (e.g., Lewis and Prinn 1980; Prinn and Fegley 1981). However, one decade later, it is generally acknowledged that thermochemical reactions in the solar nebula were coupled with and influenced by nebular dynamics, although the exact extent and nature of this coupling and influence are currently a matter of great debate. At one extreme there is the view that nebular mixing was very inefficient at transporting thermally reprocessed material outward from the hotter nebular regions inward of a few A.U. to the colder nebular regions at distances of a few to a few tens of A.U. (Stevenson 1990). At the other extreme there is the opposite view that nebular mass transport outward was extremely efficient and that the high temperature speciation formed in the hotter inner regions dominated the chemical composition of the entire solar nebula (Prinn 1990). At present, the efficiency of nebular mass transport for polluting the outer nebula with thermochemical products formed in the inner nebula is still controversial. In the following discussion we adopt the view that nebular thermochemistry played the dominant role in controlling the molecular speciation throughout the entire solar nebula due either to mass transport from the inner nebula, or due to processing in the hot, dense giant protoplanetary sub-nebulae postulated around the gas giant planets during their formation.

## 7. Carbon and Nitrogen Chemistry in the Solar Nebula

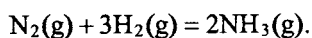
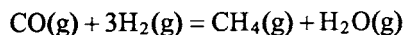
Carbon and nitrogen chemistry in the solar nebula are complex topics which are still incompletely understood. We begin by discussing the gas phase equilibrium chemistry and then consider the effects of kinetic inhibition of the important gas phase thermochemical reactions responsible for interconverting CO & CH<sub>4</sub> and N<sub>2</sub> & NH<sub>3</sub> in the solar nebula. We then review the role of grain catalyzed reactions, such as Fischer-Tropsch-type (FTT) reactions which may



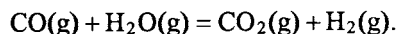
have been important for the production of organic matter found on primitive bodies such as asteroids, comets, interplanetary dust particles, and meteorites.

### 7.1 GAS PHASE CHEMISTRY

To a good first approximation, the gas phase chemistry of carbon in a H<sub>2</sub>-rich gas with solar elemental ratios is dominated by CO, and CH<sub>4</sub>, and to an even better approximation the gas phase chemistry of nitrogen is dominated by N<sub>2</sub> and NH<sub>3</sub>. Neglecting for a moment several complicating factors CO is the dominant carbon gas at high temperatures and low pressures, while CH<sub>4</sub> is the dominant carbon gas at low temperatures and high pressures in solar composition material (Urey 1953; Lewis, Barshay, and Noyes 1979). Likewise N<sub>2</sub> is the dominant nitrogen gas at high temperatures and low pressures, while NH<sub>3</sub> is the dominant nitrogen gas at low temperatures and high pressures (e.g., Fegley 1983). The oxidized (i.e., CO and N<sub>2</sub>) gases are converted into the reduced (i.e., CH<sub>4</sub> and NH<sub>3</sub>) gases by the net thermochemical reactions:



CO is also converted into CO<sub>2</sub> by the net thermochemical reaction



The thermochemical conversions of the oxidized C and N gases to their reduced counterparts proceed to the right with decreasing temperature at constant pressure. The conversion of CO into CO<sub>2</sub> also proceeds to the right with decreasing temperature. Thus, if chemical equilibrium were maintained as the gas cooled, the CO/CH<sub>4</sub>, CO/CO<sub>2</sub>, and N<sub>2</sub>/NH<sub>3</sub> ratios would all decrease as the temperature decreased. This behavior is illustrated in Fig. 4 where these ratios are plotted as function of 1/T along the solar nebula P,T profile shown earlier.

Clearly, the extent to which the homogeneous gas-phase conversions of the oxidized to reduced C and N gases can proceed with decreasing temperature is dependent on the rates of the elementary reactions that make up the reaction pathway relative to the rates of nebular mixing and overall cooling. If the chemical conversion is much faster than the rate at which the gas parcel is mixed outward to cooler nebular regions (or than the rate at which overall cooling of the nebula proceeds) then chemical equilibrium will be closely approached as cooling proceeds. However if the chemical conversion is much slower than the rate at which mixing outward to cooler regions (or overall cooling) occurs, then chemical equilibrium will be frozen in, or quenched at some point, and the gas phase composition in cooler regions will be the same as that established at the quench point. If we denote the chemical lifetime for conversion of the oxidized to the reduced gases by  $t_{\text{chem}}$  and the nebular mixing (or overall cooling) time by  $t_{\text{mix}}$ , the former case is represented by the inequality  $t_{\text{chem}} < t_{\text{mix}}$  and the latter case is represented by the inequality  $t_{\text{chem}} > t_{\text{mix}}$ . The intermediate case which occurs at the quench temperature ( $T_Q$ ) is represented by the equality  $t_{\text{chem}} = t_{\text{mix}}$ . Once expressions for the  $t_{\text{chem}}$  and  $t_{\text{mix}}$  are available, it is then possible to calculate the position of the quench temperature  $T_Q$  in a solar nebula model.

Data from the chemical kinetic and chemical engineering literature can be used to calculate the  $t_{\text{chem}}$  values for the CO → CH<sub>4</sub>, CO → CO<sub>2</sub>, and N<sub>2</sub> → NH<sub>3</sub> conversions (e.g., Lewis and Prinn 1980; Prinn and Fegley 1981, 1989). The  $t_{\text{mix}}$  values can be bounded by considering the

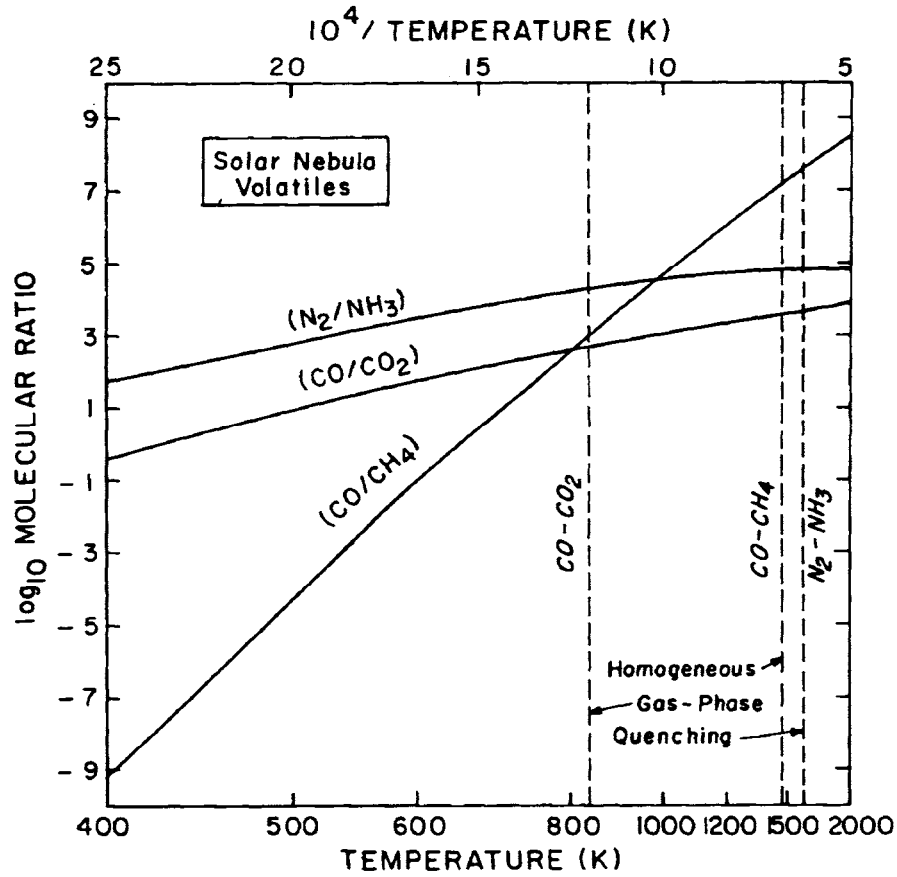


Figure 4. Changes in the equilibrium  $\text{CO}/\text{CH}_4$ ,  $\text{CO}/\text{CO}_2$ , and  $\text{N}_2/\text{NH}_3$  ratios as a function of temperature along the solar nebula P,T profile illustrated in Fig. 1. The vertical dashed lines indicate the temperatures at which the homogeneous gas phase conversions of CO to  $\text{CH}_4$ , CO to  $\text{CO}_2$ , and  $\text{N}_2$  to  $\text{NH}_3$  are quenched in the solar nebula if the conversions can proceed over the entire nebular lifetime of  $10^{13}$  seconds. If mixing of hot gas to cooler regions occurs more rapidly, then the quench temperatures will be higher. Conversely, if the reactions could proceed for longer times, the quench temperatures will be lower. However, the chemical conversions clearly cannot proceed for longer than the nebular lifetime. The effects of Fe metal grains on the rates of these conversions are discussed in the text. Modified from Fegley and Prinn (1989).

fastest and slowest possible nebular mixing times. Following Cameron (1978), the fastest possible mixing time has generally been estimated as  $t_{\text{mix}} \sim 3H/V_s \sim 10^8$  sec, where  $H$  is the radial density scale length and  $V_s$  is the sound speed in the solar nebula. The slowest possible mixing time has generally been equated to the lifetime of the solar nebula. On the basis of astronomical observations of disks around young stellar objects (e.g., Strom, Edwards, and Strom 1989) this lifetime is  $\sim 10^{13}$  sec. The arguments below are unaltered if longer lifetimes of about  $10^{14.5}$  sec (10 million years) consistent with  $^{129}\text{Xe}$  measurements of the time interval between the formation of chondrules and meteorite matrix are used.

The results of comparing the  $t_{\text{chem}}$  and  $t_{\text{mix}}$  values are as follows. Homogeneous gas phase reactions with  $t_{\text{chem}} > 10^8$  sec may be quenched in a turbulent, rapidly mixed region of the solar nebula, but may well proceed down to fairly low temperatures in more sluggishly mixed nebular regions. However, without making any assumptions about nebular mixing rates, it is clear that reactions with  $t_{\text{chem}} \geq 10^{13-14.5}$  sec will certainly be quenched because this time corresponds to the longest possible mixing time, the lifetime of the nebula itself. Longer times are simply not possible (unless either the astrophysical or cosmochemical evidence has greatly underestimated the lifetime of the solar nebula).

In fact, when the  $t_{\text{chem}}$  values are calculated using kinetic data from the literature, we find that the quench temperature for the  $\text{CO} \rightarrow \text{CH}_4$  conversion is about 1470 K. As illustrated in Fig. 5, this temperature is well inside the CO stability field at a point where the  $\text{CO}/\text{CH}_4$  ratio is  $\sim 10^7$ . Likewise the calculated quench temperature for the  $\text{N}_2 \rightarrow \text{NH}_3$  conversion is about 1600 K. As shown in Fig. 6, this temperature is also well inside the  $\text{N}_2$  stability field and corresponds to a  $\text{N}_2/\text{NH}_3$  ratio of  $\sim 10^5$ . The quench temperature for the conversion of CO to  $\text{CO}_2$  is shown in Fig. 7. It is also inside the region where CO is dominant at a temperature of about 830 K and a  $\text{CO}_2/\text{CO}$  ratio of  $10^{-2.7}$ . The  $\text{CO} \rightarrow \text{CO}_2$  conversion is thus more facile than the conversions of the oxidized to reduced species. This is a consequence of the relatively rapid interconversions between oxidized carbon species such as CO,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ , etc.

These quench temperatures are calculated for the representative nebular P,T profile shown earlier. The variation of the quench temperatures  $T_Q$  with the total assumed nebular pressure are also plotted in Figs. 5-7 where it is seen that  $T_Q$  drops with increasing pressure. Lower quench temperatures bring the point where equilibrium is frozen in closer to the boundaries in P,T space where the  $\text{CO}/\text{CH}_4$  and  $\text{N}_2/\text{NH}_3$  ratios are unity. However, total pressures of about 0.3 bars (at 1000-1100 K) are required for  $T_Q$  to intersect the  $\text{CO}/\text{CH}_4$  phase boundary. Somewhat larger pressures of about 80 bars are required to intersect the  $\text{N}_2/\text{NH}_3$  boundary. These pressures are several orders of magnitude higher than those calculated in many currently accepted nebular models. Such high pressures are probably inconsistent with the mineralogy of chondrites because complex multiphase liquids would condense instead of solid minerals under these high pressures (e.g., see Grossman and Larimer 1974), and the trace element abundance patterns in the CAIs in carbonaceous chondrites would also be much different than what is actually seen. Thus, it is very safe to state that the thermochemical kinetic models of homogeneous gas phase chemistry show that CO and  $\text{N}_2$  were the dominant C and N gases throughout the solar nebula.

However, the situation is predicted to have been dramatically different in the higher density environments, known as the giant protoplanetary subnebulae, which existed around the gas giant planets during their formation. A representative P,T profile taken from the work of Prinn and Fegley (1981) on the Jovian subnebula is illustrated in Figs. 5-7. At a given temperature, the expected pressure in the Jovian (or Saturnian, etc.) subnebula is several orders of magnitude higher than that in the surrounding solar nebula. This difference has two important consequences. One is that the Jovian subnebula P,T profile lies within the thermochemical equilibrium stability fields of  $\text{CH}_4$  and  $\text{NH}_3$ . The other is that the kinetics of the  $\text{CO} \rightarrow \text{CH}_4$ ,

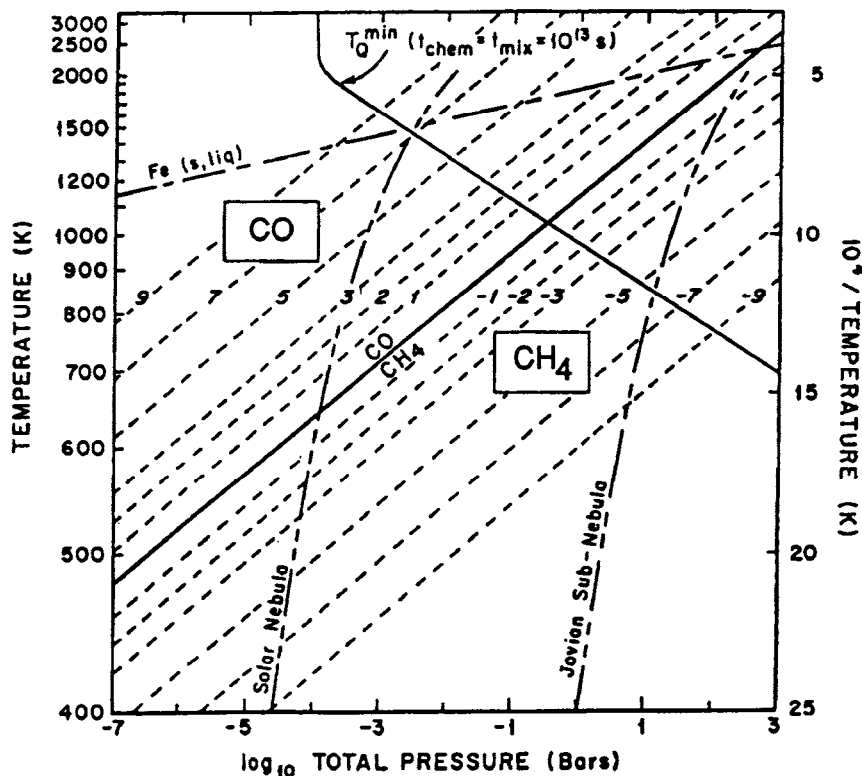


Figure 5. Gas phase equilibrium chemistry of carbon in a solar composition gas. Carbon monoxide is the dominant carbon gas at high temperatures and low pressures and methane is the dominant carbon gas at low temperatures and high pressures. The heavy solid diagonal line is the phase boundary between CO and CH<sub>4</sub>. The two gases have equal abundances along this line. The dashed diagonal lines indicate different CO/CH<sub>4</sub> ratios. For example, the dashed line labelled 1 indicates CO/CH<sub>4</sub> = 10, and the dashed line labelled -2 indicates CO/CH<sub>4</sub> = 0.01. Also shown are the condensation curve for Fe(s, liq), the adopted P,T profiles for the solar nebula and the Jovian protoplanetary subnebula, and the line showing the quench temperature  $T_Q$  for the homogeneous gas phase conversion of CO to CH<sub>4</sub>. This quench temperature is calculated assuming that the time available for the conversion ( $t_{chem}$ ) is the same as the nebular lifetime ( $t_{mix}$ ) of  $10^{13}$  seconds. As mentioned previously, longer conversion times are not physically possible and shorter conversion times, corresponding to more rapid mixing, yield higher quench temperatures. The intersection of the  $T_Q$  line with the nebular and subnebular P,T profiles shows the CO/CH<sub>4</sub> ratio at the quench point. As discussed in the text, quenching yields a CO-rich solar nebula and a CH<sub>4</sub>-rich subnebula. Finally, as first shown by Urey (1953) and later confirmed by Lewis, Barshay and Noyes (1979) there is a graphite stability field off to the lower left of this figure. The maximum temperature for graphite stability is about 470 K and the maximum pressure is about  $10^{-7.6}$  bars. Modified from Fegley and Prinn (1989).

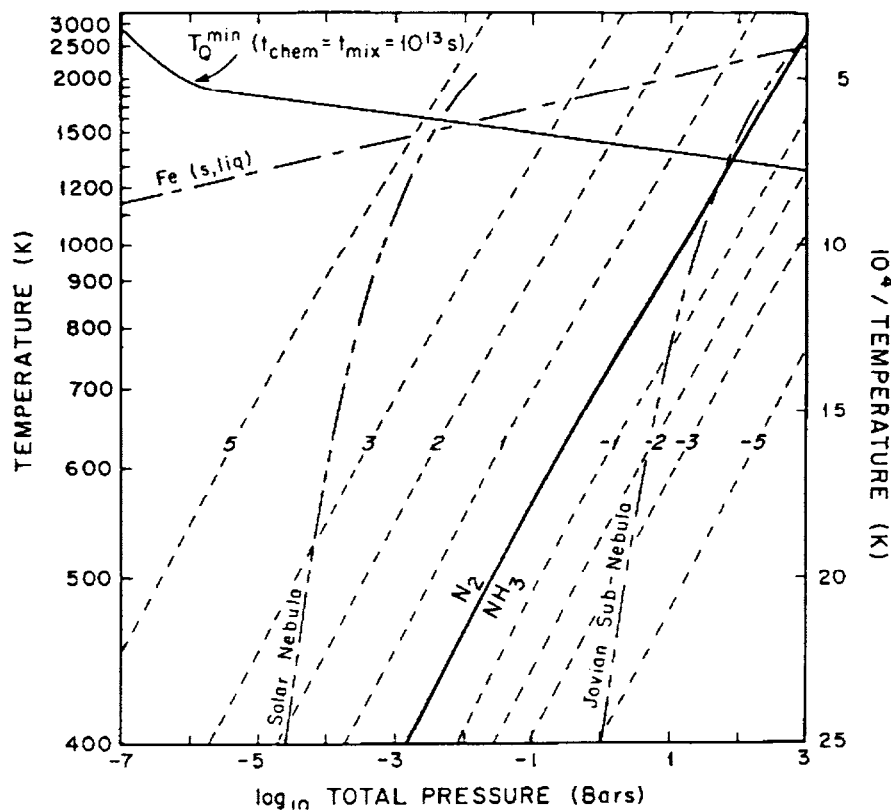


Figure 6. Gas phase equilibrium chemistry of nitrogen in a solar composition gas. Molecular nitrogen is the dominant nitrogen gas at high temperatures and low pressures and ammonia is the dominant nitrogen gas at low temperatures and high pressures. The heavy solid diagonal line is the phase boundary between  $N_2$  and  $NH_3$ . The two gases have equal abundances along this line. The dashed diagonal lines indicate constant ratios of  $N_2/NH_3$ , with a line labelled 2 indicating a ratio of 100 and a line labelled -3 indicating a ratio of 0.001. As in Fig. 5 the adopted P,T profiles for the solar nebula and the Jovian protoplanetary subnebula are also shown along with the quench temperature  $T_Q$  line for  $t_{chem} = t_{mix} = 10^{13}$  seconds. Likewise, the intersection of the  $T_Q$  line with the P,T profiles shows the  $N_2/NH_3$  ratio at the quench points. Quenching yields a  $N_2$ -rich solar nebula and a  $NH_3$ -rich Jovian protoplanetary subnebula. Modified from Prinn and Fegley (1989).

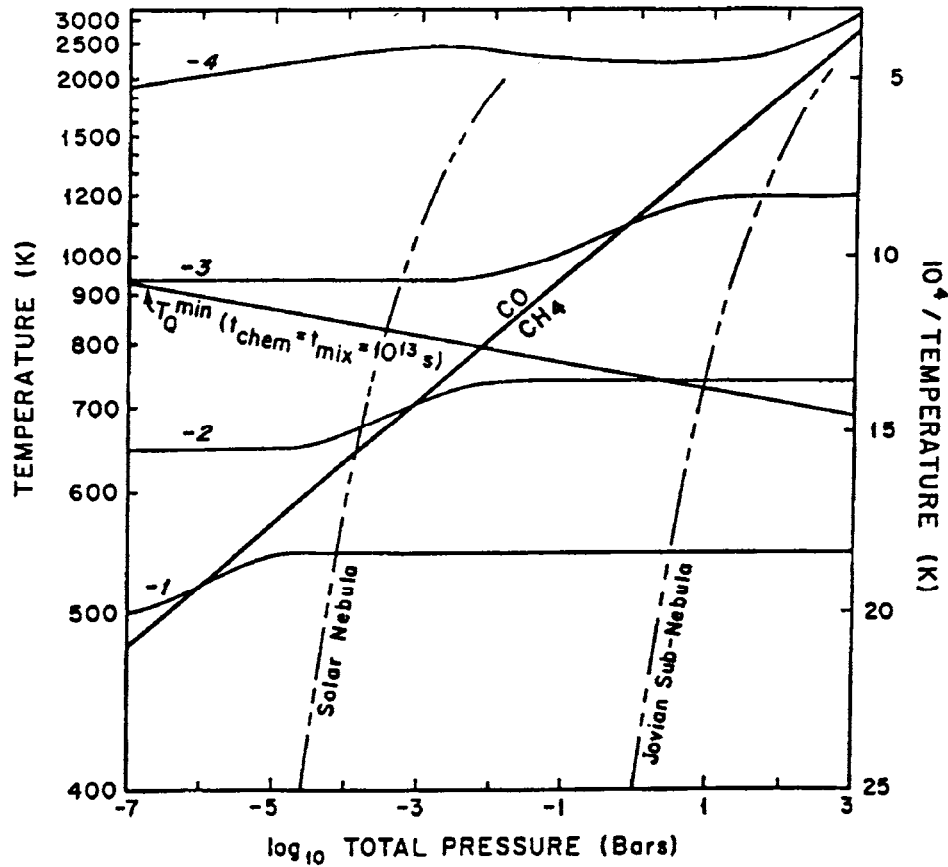


Figure 7. Chemical equilibrium ratios of  $\text{CO}_2/\text{CO}$  in a solar composition gas are plotted as a function of temperature and pressure along with the adopted P,T profiles for the solar nebula and the Jovian protoplanetary subnebula, and the  $T_Q$  line for the CO to  $\text{CO}_2$  homogeneous gas phase conversion. Note that the CO to  $\text{CO}_2$  conversion is relatively facile, leading to lower quench temperatures than for the reduction of CO and  $\text{N}_2$ . The phase boundary between CO and  $\text{CH}_4$  is also shown for reference. The inflections in the contours of  $\text{CO}_2/\text{CO}$  are due to the change in the water abundance at this phase boundary. As shown by Lewis, Barshay, and Noyes (1979) there is a field off to the bottom left of this figure where  $\text{CO}_2$  is the dominant carbon gas. This occurs inside the graphite stability field at temperatures below about 375 K and pressures below about  $10^{-11}$  bars. Modified from Fegley and Prinn (1989).

CO→CO<sub>2</sub>, and N<sub>2</sub>→NH<sub>3</sub> conversions are much more favorable in these environments because of the higher densities at a given temperature. As a result the conversions proceed down to lower temperatures where the reduced gases (or CO<sub>2</sub>) are relatively much more abundant. In particular, for the Jovian subnebula P,T profile illustrated in Figs. 5-7, quenching of the CO→CH<sub>4</sub> conversion is predicted at 840 K and CH<sub>4</sub>/CO ~ 10<sup>5</sup>, quenching of the N<sub>2</sub>→NH<sub>3</sub> conversion is predicted at 1370 K and NH<sub>3</sub>/N<sub>2</sub> ~ 1, and quenching of the CO→CO<sub>2</sub> conversion is predicted at 740 K and CO<sub>2</sub>/CO ~ 0.01 (Prinn and Fegley 1989). The dramatic differences between the predicted chemistry in the Jovian protoplanetary subnebula and the solar nebula are vividly demonstrated by the fact that the subnebular CH<sub>4</sub>/CO ratio is ~ 10<sup>13</sup> times larger than the solar nebula ratio and that the subnebular NH<sub>3</sub>/N<sub>2</sub> ratio is ~ 10<sup>5</sup> times larger than the solar nebula ratio. The giant protoplanetary subnebulae are thus predicted to be very efficient thermochemical processing plants for the production of reduced carbon and nitrogen gases. As we shall see later, this dramatic difference between C and N chemistry in the solar nebula and protoplanetary subnebulae has important implications for the chemistry of volatiles in the coma of comet P/Halley.

## 7.2 GRAIN CATALYZED CHEMISTRY

The results above are specifically for homogeneous gas phase chemistry. However, as mentioned earlier, Fe metal, which is the most abundant transition metal in solar composition material, is predicted to be stable over a wide temperature range in the solar nebula. Industrial experience shows that Fe alloys are catalysts for the production of ammonia from the elements via the Haber process and for the production of synthetic fuels from CO + H<sub>2</sub> (Bond 1962; Dry 1981; Biloen and Sachtler 1981). Thus, the presence of Fe metal grains in the solar nebula may modify the results described above by accelerating the rates of the CO→CH<sub>4</sub>, CO→CO<sub>2</sub>, and N<sub>2</sub>→NH<sub>3</sub> conversions and by converting a substantial portion of nebular CO to organic compounds via Fischer-Tropsch-type (FTT) reactions.

As we can see from Fig. 1, the lowest temperature at which Fe grains are expected to be present in the solar nebula is in the range of 370-400 K where magnetite is predicted to form. The Fe grains may be removed from the gas phase at higher temperatures if they agglomerate together and settle to the nebular midplane at a rate more rapid than that at which the nebula cools. Alternatively the Fe metal grains may remain dispersed, but catalytically inactive in the nebular gas at temperatures below 690 K if they are coated with FeS. In fact, petrographic studies of the unequilibrated ordinary chondrites, which are generally believed to preserve a record of nebular processes, show FeS-rimmed metal grains which may be nebular condensates (Rambaldi and Wasson 1981, 1984). Because neither situation can be predicted with certainty, we adopt the most conservative view possible, namely that Fe metal grains remain dispersed in the nebular gas with an abundance equal to the Fe/H<sub>2</sub> atomic ratio, at temperatures down to 370-400 K where magnetite is predicted to form. However, below this temperature, it is likely that the Fe metal grains will be rendered catalytically inactive by the formation of magnetite coatings, which chemically isolate them from the nebular gas.

By adopting this conservative viewpoint we can set a firm upper limit to the NH<sub>3</sub> abundance and a firm lower limit to the N<sub>2</sub>/NH<sub>3</sub> ratio in the solar nebula because the magnetite formation temperature is taken as the quench temperature for the N<sub>2</sub>→NH<sub>3</sub> conversion. From Fig. 6 we then see that taking T<sub>q</sub> ~ 370-400 K yields N<sub>2</sub>/NH<sub>3</sub> ~ 100 in the solar nebula. Of course, this result is applicable to the P,T profile assumed for our modelling. However, many, if not all of the currently accepted nebular models have P,T profiles which lie to the left of the one adopted here and will thus also yield N<sub>2</sub>/NH<sub>3</sub> >> 1. It is important to note that this treat-

ment of the Fe grain catalyzed  $N_2 \rightarrow NH_3$  conversion is independent of the actual reaction rate and of the assumed Fe grain size. A model dependent estimate of the solar nebula  $N_2/NH_3$  ratio has also been made by (1) making the reasonable assumption that the typical Fe metal grain size (100  $\mu m$  radius) in primitive chondritic meteorites is relevant to the solar nebula and (2) taking kinetic data from the chemical engineering literature for the rate of the Fe catalyzed conversion. This approach yields a slightly higher quench temperature of 530 K and a  $N_2/NH_3$  ratio of about 170 if the  $N_2 \rightarrow NH_3$  conversion is allowed to proceed for the entire nebular lifetime of  $10^{13}$  seconds (Lewis and Prinn 1980). Therefore, the possibility of grain catalyzed  $NH_3$  formation in the solar nebula does not alter the conclusion reached earlier from consideration of the homogeneous gas phase reaction kinetics, namely that  $N_2$  was the dominant nitrogen gas throughout the entire solar nebula.

Of course Fe grain catalyzed  $NH_3$  formation is also possible in the giant protoplanetary subnebulae around Jupiter and the other gas giant planets during their formation. As previously mentioned, the P,T profiles for these higher density environments are expected to lie within the  $NH_3$  stability field. Thus, if catalysis is indeed effective, it will simply lead to the production of even more  $NH_3$  and thus strengthen the conclusions reached earlier. In fact, taking the pressure-independent magnetite formation temperature of 370-400 K as the absolute minimum quench temperature yields  $NH_3/N_2 \sim 10^5$ . The model dependent estimate using the same kinetic data from the literature and the maximum conversion time of  $10^{13}$  sec results in  $T_Q \sim 495$  K and  $NH_3/N_2 \sim 2000$  (Prinn and Fegley 1989). This ratio is applicable to the Jovian subnebula P,T profile shown in the figures. We would expect that the P,T profiles for the Saturnian subnebula and for any subnebulae of the other gas giant planets would lie at slightly lower pressures at a given temperature and thus have slightly lower  $NH_3/N_2$  ratios. However, these ratios are still expected to be  $\gg 1$ .

Now we can consider how the presence of Fe metal grains affects the kinetics of the  $CO \rightarrow CH_4$  conversion. Again, an absolute lower limit can be set by assuming that the Fe metal grains remain catalytically active and well mixed with the nebular gas down to the magnetite formation temperature. In this case, we obtain  $CO/CH_4 \sim 10^{-9}$ , in other words all carbon in the solar nebula is in the form of methane. The lower density P,T profiles found in other nebular models lead to larger  $CO/CH_4$  ratios, but they are all still much less than unity. However, it is important to ask whether or not we actually expect Fe metal grains to catalyze the  $CO \rightarrow CH_4$  conversion down to such low temperatures.

This point has been examined by Prinn and Fegley (1989) who used literature data on the rate of the heterogeneously catalyzed  $CO \rightarrow CH_4$  conversion on ultra-clean, high purity, specially prepared Fe surfaces (Vannice 1975, 1982). The literature rate equation for the  $CO \rightarrow CH_4$  conversion on metallic Fe particles is

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

where  $[i]$  is the gaseous molecular number density per  $cm^3$ ,  $[sites]$  is the number density of all catalytically active sites on the surfaces of all Fe grains in each  $cm^3$  of the solar nebula,  $P_{H_2}$  is the  $H_2$  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 value for  $k_{site}$  was taken as

$$k_{site} \sim 2.2 \times 10^7 \exp(-21,300/RT)$$



for the  $\text{CO} \rightarrow \text{CH}_4$  conversion on clean Fe surfaces. The chemical time constant  $t_{\text{chem}}$  for the Fe grain catalyzed  $\text{CO} \rightarrow \text{CH}_4$  conversion is then given by

$$t_{\text{chem}} = -[\text{CO}] / \frac{d}{dt}[\text{CO}].$$

Taking the shortest feasible mixing times of about  $10^8$  sec based on Cameron's (1978) estimate of transport at 1/3 sound speed, Prinn and Fegley (1989) calculated  $T_Q \sim 900$  K and  $\text{CO}/\text{CH}_4 \sim 10^{3.8}$ . On the other extreme, taking the longest possible mixing time equal to the nebular lifetime of  $10^{13}$  sec gave  $T_Q \sim 520$  K and  $\text{CO}/\text{CH}_4 \sim 10^{3.5}$ . The results of their calculations are displayed in Fig. 8. Mendybayev et al (1986) made an analogous model of Fe grain catalyzed CO reduction in the solar nebula, but used a slightly different rate constant in their calculations. They computed a quench temperature of 750 K and  $\text{CO}/\text{CH}_4 \sim 10$  assuming that  $t_{\text{chem}} = t_{\text{mix}} \sim 10^{9.5}$  seconds.

At this point it is important to emphasize that both the results of Prinn and Fegley (1989) and of Mendybayev et al (1986) are based on the rate constants measured for the  $\text{CO} \rightarrow \text{CH}_4$  conversion on ultra-clean, high purity, specially prepared Fe surfaces, which do not exist in the solar nebula. This is important for two reasons. First, once Fe metal condenses in the nebula it begins acting as a solute, or host phase, for other elements that dissolve in it. Although the other transition metals which can dissolve in the Fe will probably not drastically change its catalytic activity, other predicted solutes such as P, S, C, N, and O (Kozasa and Hasegawa 1988; Fegley and Lewis 1980) will probably have more deleterious effects. Indeed, sulfur is a well known catalyst poison. Second, the laboratory studies of Fe catalyzed CO reduction show that the metal surface is rapidly inactivated by the forming of carbonaceous coatings as the reaction proceeds (e.g., Krebs, Bonzel and Gafner 1979; Vannice 1982). This effect is potentially relevant to the solar nebula because carbonaceous coatings and "tar balls" are commonly observed in interplanetary dust particles or IDPs (e.g., Bradley, Brownlee, and Fraundorf 1984; Bradley and Brownlee 1986). The model results are therefore probably best viewed as upper limits to the efficiency of Fe catalyzed CO reduction and as lower limits to the solar nebula  $\text{CO}/\text{CH}_4$  ratio.

However, another, more likely course of events, is that Fe grains catalyzed organic compound formation from nebular  $\text{CO} + \text{H}_2$  via FTT reactions. As noted previously (Fegley 1988, 1990; Fegley and Prinn 1989; Prinn and Fegley 1989), this pathway is more likely for the following reasons: (1) "tar balls", which are associations of carbonaceous material and Fe-bearing grains such as carbide, metal, or oxide, are commonly observed in chondritic IDPs (Bradley, Brownlee, and Fraundorf 1984; Bradley and Brownlee 1986; Bradley, Sandford, and Walker 1988; Christoffersen and Buseck 1983), (2) the "tar balls" are qualitatively similar to the carbonaceous deposits found on Fe-based FTT catalysts in the laboratory (Vannice 1982; Krebs, Bonzel, and Gafner 1979), (3) graphite is predicted to be stable at low T and P in a solar gas (Lewis, Barshay, and Noyes 1979), but its precipitation may be kinetically inhibited and hydrocarbons may form instead, (4) the low albedos and reflection spectra of many outer solar system objects implies the presence of dark carbonaceous material on the surfaces of these bodies (e.g., Himalia, Elara, Parisphae, Carme, Sinope, Lysithea, Ananke, Leda, Phoebe, the Uranian rings, part of the surface of Iapetus, the nucleus of comet P/Halley, etc.), (5) theoretical estimates of the carbon budget of the outer solar system indicate that about 10% of nebular CO was converted into organic matter (Simonelli et al 1989), and (6) carbonaceous material analogous to FTT reaction products is found in primitive chondritic meteorites (e.g., Hayatsu and Anders 1981; Studier, Hayatsu, and Anders 1968).

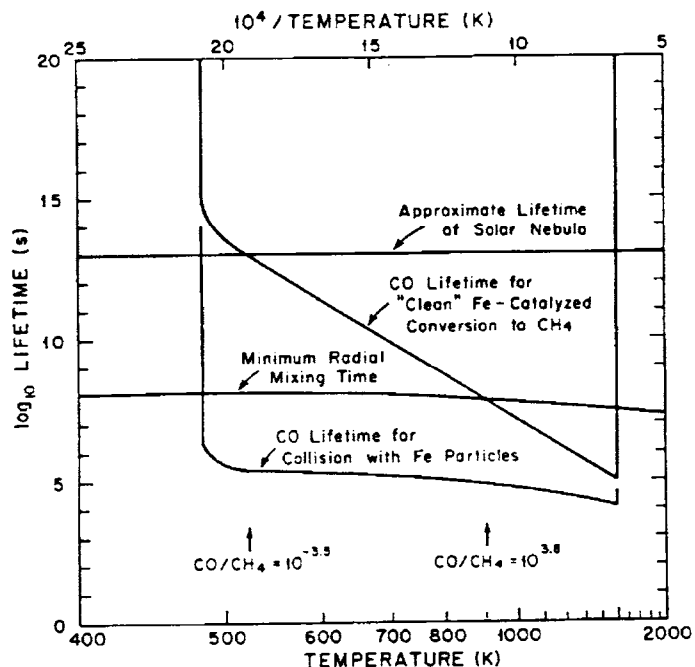
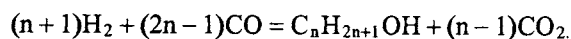
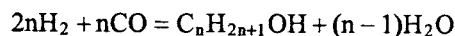
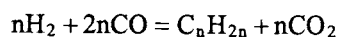
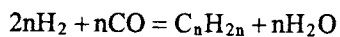
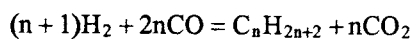
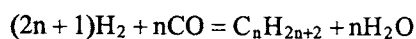


Figure 8. An illustration of the different chemical and physical timescales associated with the Fe grain catalyzed CO to CH<sub>4</sub> conversion in the solar nebula. The two horizontal lines show the estimated lifetime of the solar nebula (which constrains the longest possible time to do chemistry) and the estimated minimum radial mixing time (which fixes the shortest possible time to do chemistry). These two timescales are compared to the collision lifetime for CO to collide with 100  $\mu\text{m}$  radius Fe grains and the chemical lifetime for the Fe grains to catalyze conversion of CO to CH<sub>4</sub>. These times are calculated as described in the text. The results of the calculations show that if the Fe grains in the nebula are as efficient as high purity, specially prepared Fe catalysts in the laboratory, then a substantial fraction of CO may be converted to CH<sub>4</sub>. However, as argued in the text, the more likely outcome of Fe grain catalyzed carbon chemistry is probably the formation of organic compounds via Fischer-Tropsch-type (FTT) reactions. Modified from Prinn and Fegley (1989).

Although some of the evidence presented by Anders and colleagues in favor of a FTT origin for organic compounds in meteorites is currently disputed (e.g., see Cronin's paper in this volume, and Shock and Schulte 1990a,b), these points taken together argue strongly that organic compounds were reasonably abundant in the solar nebula. The most plausible source of this organic matter is Fe grain catalyzed formation from CO, the most abundant carbon feedstock in the solar nebula.

The Fischer-Tropsch syntheses of alkanes, alkenes, and alcohols from nebular CO + H<sub>2</sub> are exemplified by reactions such as



Fegley (1988) estimated the quench temperatures and time constants for FTT reactions in the solar nebula by using the kinetic theory of gases to calculate the rate of the grain catalyzed reactions. This approach is based on the assumption that the initial grain catalyzed reaction rate will depend upon the collision rate of CO (the less abundant reactant gas) with the grain surfaces (Fe metal grains). The grains are further assumed to be covered with sorbed H<sub>2</sub>, which is reasonable since it is by far the most abundant nebular gas. Then, the collision rate ( $\sigma_i$ ) of CO with the grains is given by

$$\sigma_i = 10^{25.4} [P_i / (M_i T)^{\frac{1}{2}}]$$

where  $\sigma_i$  has units of molecules cm<sup>-2</sup> sec<sup>-1</sup>,  $P_i$  is the CO partial pressure in bars,  $M_i$  is the CO molecular weight in g mole<sup>-1</sup>, and T is the temperature in Kelvins. The total number of collisions of the CO molecules with all Fe grains in each cm<sup>3</sup> of the solar nebula is expressed as

$$v_i = \sigma_i A$$

where A is the total surface area of all Fe grains per each cm<sup>3</sup> of the nebula. For the purposes of the calculations, the Fe grains are assumed to be monodisperse, spherical grains that are fully dense and uniformly distributed at solar abundance in the nebular gas. Grain radii from 0.1  $\mu$ m to 100  $\mu$ m were used in the model calculations.

A collision time constant  $t_{coll}$  which is the time required for all CO molecules to collide with all Fe grains in each cm<sup>3</sup> of the solar nebula, can be calculated from the equation

$$t_{coll} = [CO] / v_i.$$

Now, if every collision of a CO molecule with an Fe grain led to organic compound synthesis, then  $t_{\text{coll}}$  would also be the chemical time constant  $t_{\text{chem}}$  for CO destruction. However, only a small fraction of collisions that have the necessary activation energy  $E_a$  lead to a chemical reaction. This fraction of reactive collisions is given by

$$f_i = v_i \exp(-E_a/RT)$$

where  $R$  is the ideal gas constant. Then the chemical time constant for CO destruction is

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

On the basis of  $E_a$  values from the meteoritic and chemical engineering literature (Dry 1981; Hayatsu and Anders 1981), Fegley (1988) took  $E_a = 90 \text{ kJ mole}^{-1}$ . Over the nebular lifetime of  $10^{13}$  sec, iron grains comparable in size to those in chondritic meteorites (100  $\mu\text{m}$  radius) could convert  $\sim 10\%$  of all CO into organic compounds before quenching occurred at about 510 K. On the other hand, much smaller Fe grains comparable in size to those in IDPs (0.1  $\mu\text{m}$  radius) could convert this much CO into organics down to 440 K. However, these theoretical estimates are probably upper limits because  $\text{H}_2\text{O}$  sorption onto the Fe grain surfaces, thus reducing the amount of reactive sorbed  $\text{H}_2$ , was neglected. In any case, the estimated quench temperatures of 440-510 K are consistent with the laboratory results of Anders and colleagues (e.g., Anders, Hayatsu, and Studier 1973) showing that catalysis of FTT reactions was effective down to about 375 K. The estimated conversion of about 10% of CO is also consistent with the independent theoretical estimates of Simonelli et al (1989) that about 10% of the nebular CO was indeed converted into organic matter.

However, many important questions about the importance of FTT reactions in the solar nebula still remain to be answered. Prinn and Fegley (1989) emphasized that no systematic studies were available on the effects of process parameters such as the total pressure, temperature, time,  $\text{CO}/\text{H}_2$  ratios, chemical and physical properties of the Fe metal catalyst, the presence of catalyst poisons such as  $\text{H}_2\text{S}$ , etc. In the absence of such data obtained under conditions relevant to the solar nebula, they used existing studies of FTT reactions under a range of conditions to provide some guidelines about the probable course of events in the solar nebula. Figure 9, taken from their paper, shows the effects of variable  $\text{CO}/\text{H}_2$  ratios on the composition of hydrocarbons formed at a low total conversion of CO to organics. Not surprisingly, as the  $\text{CO}/\text{H}_2$  ratio decreases (i.e., a more  $\text{H}_2$  rich gas), the products in the single pass flow system become more enriched in  $\text{CH}_4$  and  $\text{C}_2$  hydrocarbons. Conversely, the product spectrum from an industrial system used to produce synthetic fuel is  $\text{C}_1$  (2%),  $\text{C}_2$  (2%),  $\text{C}_3$  (5%),  $\text{C}_4$  (5%),  $\text{C}_5$ - $\text{C}_{11}$  (18%),  $\text{C}_{12}$ - $\text{C}_{18}$  (14%),  $\text{C}_{19}$ - $\text{C}_{23}$  (7%),  $\text{C}_{24}$ - $\text{C}_{35}$  (21%), and  $>\text{C}_{35}$  (26%) (Dry 1981). This composition is rich in large molecules because the reactor is run to high total conversion of CO to organics and the outlet gas is recycled through the reactor to promote synthesis of larger molecules (Dry 1981). The FTT synthesis experiments conducted by Studier et al (1968) in static systems also gave larger molecules (as expressed by the maximum number of C atoms per molecule) than experiments run in flow systems under similar conditions. These results apparently indicate that FTT reactions on meteorite parent bodies may have been more important than similar reactions in the nebular environment, but no firm conclusions can be drawn at present.

## 8. Water Retention by Solid Grains

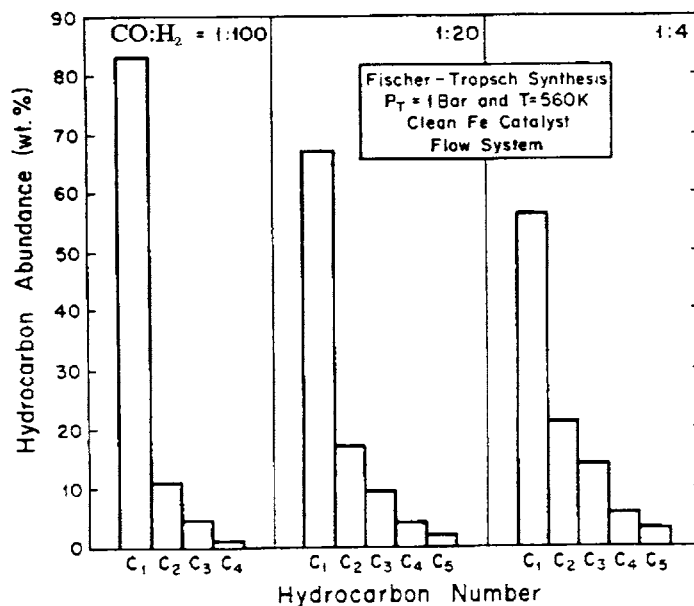
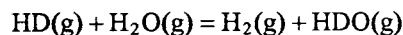


Figure 9. A bar graph showing the hydrocarbons produced by the Fischer-Tropsch synthesis on a Fe catalyst over a range of CO/H<sub>2</sub> ratios from 1:100 to 1:4. The results are for the initial stages of hydrocarbon synthesis (i.e., low total conversion of CO to products) in a flow system (Krebs et al 1979). Note that the lowest CO/H<sub>2</sub> ratio of 1:100 is still about 14 times larger than the solar CO/H<sub>2</sub> ratio from Table 1. Modified from Prinn and Fegley (1989) where the ratios are incorrectly shown as H<sub>2</sub>/CO ratios.

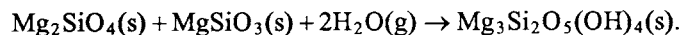
The presence of oceans on the Earth but not on Venus illustrates one of the classic problems of planetary science, namely the mechanism for water retention by solid grains during planetary formation. Latimer (1950) and Urey (1952, 1953) suggested that hydrated silicates were responsible for water retention by the terrestrial planets. Despite the lack of accurate thermodynamic data which prevented them from calculating hydrated silicate stability fields in a solar gas, Urey (1953) was able to calculate the conditions under which water would be retained as brucite  $[\text{Mg}(\text{OH})_2]$ , water ice, and ammonia monohydrate  $\text{NH}_3 \cdot \text{H}_2\text{O}(\text{s})$ . Urey (1953) concluded "that water and ammonia would have condensed in the solar nebula and the existence of the carbonaceous chondrites containing up to 10% of water confirms this conclusion..." Of course, the kinetic inhibition of the  $\text{N}_2 \rightarrow \text{NH}_3$  conversion modifies Urey's original conclusion regarding ammonia hydrate stability.

During the intervening 40 years there have been several studies of hydrated silicate formation in the solar nebula. The results of these are summarized in Table 6, which lists condensation temperatures along the adopted nebular P,T profile, and in Fig. 10 which displays the pressure dependence of the hydrated silicate and water ice condensation curves. Fig. 10 also shows the calculated thermochemical isotopic fractionation for D/H between nebular  $\text{H}_2$  and  $\text{H}_2\text{O}$  as a function of temperature. Several specific predictions result from these calculations. As the temperature decreases the first hydrous minerals to form are relatively water-poor phases such as hydroxyapatite, tremolite, and Na phlogopite. These minerals become stable in the 460-500 K range. However, these phases are seldom, if ever, seen in chondrites, and thus their existence in the solar nebula is problematic. Further decreases in temperature lead to the formation of more water-rich minerals such as brucite, talc, and serpentine, at temperatures of 400 K and below. These minerals are the major hydrous phases which are observed in water-bearing (e.g., CI, CM2, unequilibrated ordinary) chondrites. Decreasing temperature also leads to systematic variation of the D/H ratio in nebular water vapor. The net thermochemical equilibrium



proceeds to the right with decreasing temperature and thus nebular water vapor becomes preferentially enriched in D as the temperature drops. This enrichment is expressed both as a fractionation factor (simply the ratio of D/H in HDO to that in HD) and also as a  $\delta\text{D}$  value relative to Standard Mean Ocean Water (SMOW) in Fig. 10. Assuming that minimal isotopic fractionation occurs between nebular water vapor and the condensed phases, these results can then be used as a guide to the predicted D/H ratio in the hydrated silicates and in water ice. Thus, the hydrous phases formed at higher temperatures would be relatively D-poor and have a D/H ratio about 1-2 times the protosolar value of  $3 \times 10^{-5}$ , while the hydrous phases formed at lower temperatures would be relatively D-rich. In this regard it is interesting to note that the terrestrial D/H ratio of  $1.6 \times 10^{-4}$  (i.e., the D/H of SMOW), is not attained until  $T \sim 200$  K.

The predictions of the thermochemical equilibrium calculations look relatively straightforward, but they are based on the attainment of solid-solid, gas-solid, and gas phase chemical equilibrium at low temperatures in the low density nebular environment. However, there are several good reasons to doubt that complete chemical and isotopic equilibrium are in fact attained under these conditions. We can illustrate some of the potential problems involved by considering serpentine formation via the vapor phase hydration of forsterite and enstatite



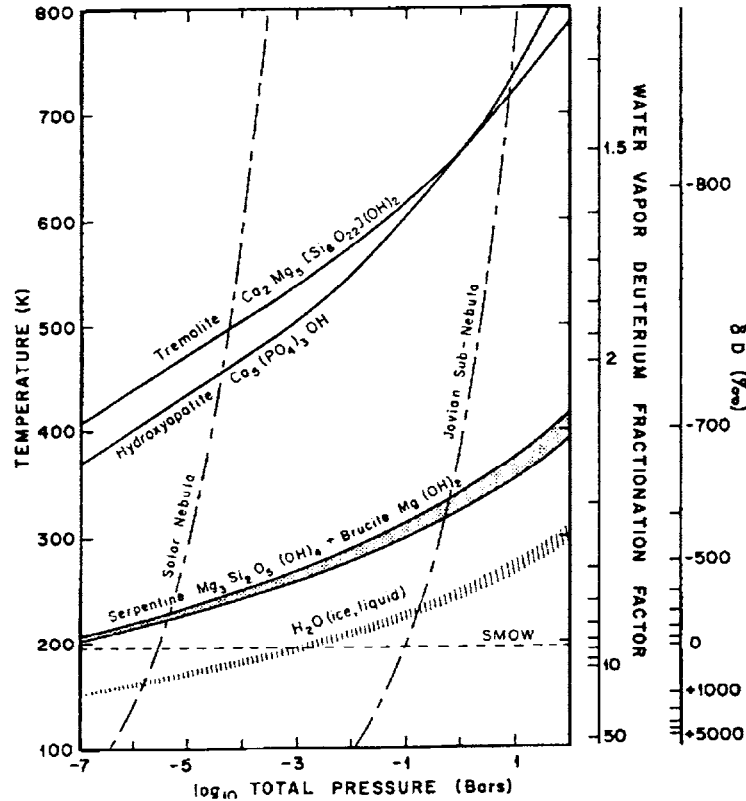


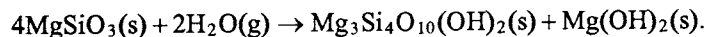
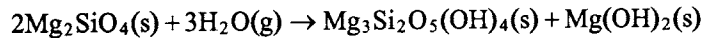
Figure 10. The thermodynamic stability fields of important water-bearing minerals and water ice over a range of temperatures and pressures applicable to the solar nebula and giant protoplanetary subnebulae. From top to bottom the hydrated silicate stability fields are from Lewis (1974) for tremolite, Fegley and Lewis (1980) for hydroxyapatite, and Fegley (1988) for serpentine + brucite and water ice. The shaded regions for serpentine + brucite and water ice illustrate the effects of having either CO (bottom curves) or CH<sub>4</sub> (top curves) as the dominant carbon gases. If CO remains the dominant carbon gas, then the amount of oxygen available for incorporation into water vapor is decreased. The amount of oxygen incorporated into rocky material, modelled as MgO + SiO<sub>2</sub>, was also taken into account in these calculations. The thermochemical equilibrium fractionation factors (Richet, Bottinga, and Javoy 1977) for temperature dependent partitioning of D between HD(g) and H<sub>2</sub>O(g) are also shown. These fractionation factors are independent of the absolute D/H ratio in either phase. However, the  $\delta D$  values, defined as  $\delta D = 10^3[(D/H)_{\text{water}} - (D/H)_{\text{SMOW}}]$ , do depend on the absolute D/H value chosen for H<sub>2</sub> in the solar nebula (taken as  $2 \times 10^{-5}$ ). In this expression SMOW = Standard Mean Ocean Water with a D/H ratio of  $1.557 \times 10^{-4}$  (Pillinger 1984). In the text it is argued that both the gas-solid equilibration of water vapor with anhydrous silicates to form hydrous phases and the isotopic equilibration of HD and H<sub>2</sub>O are kinetically inhibited at low temperatures in the solar nebula, but not in the giant protoplanetary subnebulae. Modified from Prinn and Fegley (1989).

This reaction requires the diffusion of Mg and Si between forsterite and enstatite at temperatures of 200 to 400 K. The literature data on cationic and oxygen diffusion in silicates can be combined with a model of hydrated silicate formation in the solar nebula to estimate the kinetics of this process. This has been done in several papers (Fegley 1988; Fegley and Prinn 1989; Prinn and Fegley 1989). The two silicate reactants, forsterite and enstatite are assumed to be in intimate contact with each other (i.e. in the same grain) for the entire lifetime of the solar nebula. The composite forsterite + enstatite grains are also assumed to be monodisperse spheres with radii of 0.1  $\mu\text{m}$ . This assumed grain size is comparable to that observed in fine-grained matrix in chondritic meteorites and silicate grains in IDPs, but is smaller than that observed for most silicate grains in chondrites.

The rate determining step for hydrated silicate formation is then assumed to be solid-state diffusion in the composite grain. Either cationic (Mg-Si) or oxygen diffusion may be rate determining. Literature data show that anionic diffusion is in fact much slower. The characteristic diffusion time  $t_d$  can be estimated from the scaling relationship  $t_d \sim r^2/D$  where  $r$  is the grain radius and  $D$  is the diffusion coefficient ( $\text{cm}^2\text{sec}^{-1}$ ). Fegley (1988) and Prinn and Fegley (1989) assumed that Mg-Si diffusion was rate determining and in the absence of diffusion constant data for this cationic pair assumed that it could be modelled using the available data on Fe-Mg diffusion in olivine (e.g., from Misener 1974). In this case  $t_d$  is  $\sim 10^{23}$  sec at 400 K and  $\sim 10^{55}$  sec at 200 K. On the other hand, Fegley and Prinn (1989) assumed that the much slower oxygen diffusion in olivine was rate limiting and estimated  $t_d \sim 10^{41}$  sec at 400 K and  $\sim 10^{89}$  sec at 200 K. These times are clearly much longer than the age of the solar system itself  $10^{17}$  sec.

As noted by Fegley (1988), the actual situation in the solar nebula was probably not as favorable as that assumed in the models. Forsterite and enstatite were probably not in intimate contact throughout the entire lifetime of the solar nebula, accretion and coagulation produced grains much larger than 0.1  $\mu\text{m}$  over the nebular lifetime, and solid-state diffusion (bulk and grain boundary) may have been quenched at these low temperatures. Simply put, it appears very probable that solid state chemistry was quenched at the low temperatures where it is needed to produce hydrated silicates.

As a consequence we are left with the vapor phase hydration of monomineralic silicate grains as the only available pathway for making hydrated silicates in the solar nebula. This pathway is exemplified by the two reactions



However, as first noted by Fegley (1988) this pathway is also too slow to have occurred in the solar nebula. This is easily demonstrated by using the gas-grain kinetic model described earlier in connection with Fe grain catalyzed CO reduction. In this case the reactant gas is water vapor instead of CO, the grains are silicates instead of Fe metal, and the activation energy  $E_a$  is taken as  $\sim 70$   $\text{kJ mole}^{-1}$ . This is the activation energy measured by Layden and Brindley (1963) and Bratton and Brindley (1965) for the vapor phase hydration of  $\text{MgO}(\text{s})$  to  $\text{Mg}(\text{OH})_2(\text{s})$ . It is used because no activation energy data are available for the vapor phase hydration of silicates under conditions even close to those expected in the solar nebula. Again taking the most favorable assumptions of monodisperse, fully dense, spherical grains with radii of 0.1  $\mu\text{m}$  we find that the chemical time constant  $t_{\text{chem}}$  for forsterite hydration in the solar nebula is much longer than the nebular lifetime. In fact  $t_{\text{chem}} \sim 10^{18}$  sec is calculated. This calculation is illustrated in Fig. 11 where  $t_{\text{chem}}$  is plotted as a function of temperature along with the collision lifetime  $t_{\text{coll}}$  for colli-



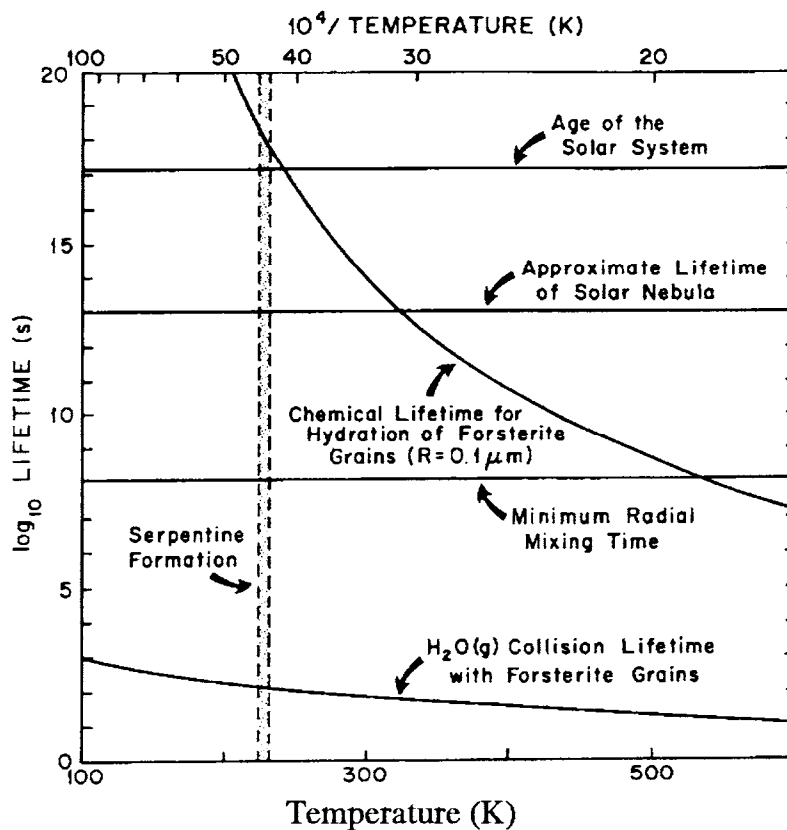


Figure 11. A comparison of the chemical and physical timescales associated with the vapor phase hydration of forsterite to different timescales in the solar nebula. The three horizontal lines represent the age of the solar system, the estimated lifetime of the solar nebula, and the estimated minimum radial mixing time (Cameron 1978) in the solar nebula. The vertical shaded region shows the maximum temperatures at which serpentine is thermodynamically stable in the solar nebula. The upper end of this range corresponds to all carbon being present as  $\text{CH}_4$  and the lower end of this range corresponds to all carbon being present as  $\text{CO}$ . In these calculations, which are described in the text, forsterite is taken as a proxy for the more diverse suite of Mg silicates expected to be present at low temperatures in the solar nebula (e.g., see Fig. 3). Although the collision lifetime for  $\text{H}_2\text{O}$  molecules to collide with small forsterite grains (assumed to be  $0.1 \mu\text{m}$  radius spheres) is short, only a small fraction of the collisions possess the necessary activation energy to hydrate the grains. Thus, the chemical lifetime for hydration of forsterite is much longer than the nebular lifetime at the low temperatures where serpentine first becomes thermodynamically stable. Modified from Prinn and Fegley (1989).

sions of H<sub>2</sub>O molecules with forsterite grains. At the temperatures where serpentine finally becomes thermodynamically stable,  $t_{\text{chem}}$  is 10<sup>5</sup> times longer than the nebular lifetime and is about 10 times longer than the age of the solar system.

Once again however, these large values are probably only a lower limit to the actual times required for vapor phase hydration of silicates in the nebula. The activation energy for MgO hydration to Mg(OH)<sub>2</sub> is almost certainly lower than that required for silicate hydration because more bond breaking and solid-state diffusion is involved in the silicates than in MgO. Also, it is again unlikely that the 0.1 μm grains assumed in the calculation were actually present throughout the entire nebular lifetime. Finally, once the anhydrous silicates became covered by a thin layer of hydrated material, the reaction rate probably decreased due to solid-state diffusion and was not as rapid as that estimated from the water vapor collision frequency with forsterite grains. Thus, the conclusion that silicate hydration was kinetically inhibited in the solar nebula is robust.

On the other hand, similar models indicate that hydrated silicate formation was probably kinetically favorable in the higher density giant protoplanetary subnebulae around the gas giant planets during their formative stages. There are two complementary reasons for this state of affairs. One, which is illustrated by Fig. 10, is that the positive dT/dP for condensation curves leads to hydrated silicate formation at higher temperatures at the higher pressures expected in the giant protoplanetary subnebulae. Thus, for example, serpentine formation becomes thermodynamically favorable at about 325 K in the Jovian subnebula, versus about 225 K in the solar nebula. The higher total pressure in the subnebulae also leads to higher collision frequencies with the silicate grains. The combination of both factors decreases  $t_{\text{chem}}$  for forsterite hydration to 10<sup>9</sup> sec, or about 0.01% of the nebular lifetime for 0.1 μm grains. Much larger grains with radii of 1000 μm could also be hydrated over the nebular lifetime of 10<sup>13</sup> sec if the rate remains controlled by the gas-grain collision frequency instead of solid-state diffusion. These calculations predict that hydrated silicate formation was favorable in the subnebulae around the gas giant planets.

There are several major implications of these calculations. One is that the hydrated silicates found in carbonaceous and unequilibrated ordinary chondrites are parent body, rather than nebular products. This theoretical conclusion is supported by extensive petrographic evidence showing that hydrated silicates in meteorites were produced by aqueous alteration on the meteorite parent bodies (e.g., Barber 1985; Boström and Fredriksson 1966; Bunch and Chang 1980; Tomeoka and Buseck 1985). Aqueous activity on the CI and CM parent bodies is also required to explain the formation of sulfate- and carbonate-bearing veins (e.g., DuFresne and Anders 1962; Fredriksson and Kerridge 1988; Richardson 1978). In addition, unidirectional oxidation of troilite in an aqueous environment provides a plausible explanation for the observed sulfur isotopic composition of FeS, elemental S, and the sulfate veins (Pillinger 1984). Finally, Clayton and Mayeda (1984) have shown that the oxygen isotopic compositions of CM2 chondrites require  $T < 293$  K and liquid water volume fractions >44% to produce the hydrated silicates in them. The oxygen isotopic data for CI chondrites require alteration in an even wetter and warmer environment to produce the hydrated silicates in these meteorites.

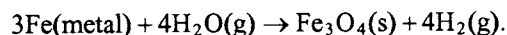
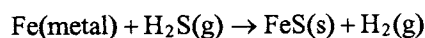
The second implication of the calculations is that the water currently found in hydrated silicates in CI and CM2 chondrites was originally retained on their parent bodies as water ice. The water ice condensation curve in Fig. 10 shows that condensation will take place at about 160 K ( $R \sim 3.4$  A.U.) for this nebular P,T profile which assumes  $T \propto R^{-1}$  and takes  $T \sim 550$  K at 1 A.U. (Lewis 1974). This distance is about at the outer edge of the main asteroid belt. Because of the presence of water ice on the Galilean satellites Europa, Ganymede, and Callisto (Pilcher, Ridgway, and McCord 1972), the water ice front is generally placed at 5 A.U. in

nebular models. However, the position of this front obviously varies with distance during the thermal evolution of the solar nebula (e.g., Ruden and Lin 1986) and first moves outward as the nebula warms up and later moves inward as the nebula cools. Also, the water ice front, like other condensation/evaporation fronts (Cameron and Fegley 1982) is closer to the proto-Sun at higher and lower regions off the midplane of the nebula. The inner boundary will be set by dispersal of the gas phase or by exhaustion of the available water vapor. The vertical structure and the time-dependent behavior of the water ice front are clearly important topics meriting further study, but the results presented here are consistent with water ice retention by the carbonaceous chondrite parent bodies.

Finally, a third implication of the calculations is that the hydrogen isotopic composition of the hydrated silicates in CI and CM2 chondrites should reflect that of the parent water ice, perhaps with some small modification due to the thermochemical isotopic fractionation that may take place during the aqueous alteration process. As noted in Table 4, the inferred D/H ratio in meteoritic hydrated silicates is about  $14 \times 10^{-3}$  ( $\delta D \sim -100$  ‰) (Yang and Epstein 1983). Assuming no modification of the D/H ratio due to aqueous alteration, this corresponds to the D/H ratio of water ice at about 200 K (see Fig. 10). This would be consistent with water ice condensation at a pressure of about  $10^{-3}$  bars. The D/H ratio of the water ice itself may either have been established by thermochemical isotopic exchange or by photochemical enrichment (Yung, et al 1988). However the former process is generally believed to be kinetically inhibited at such low temperatures (but see Lecluse and Robert (1992) for new experimental results that apparently indicate otherwise), while the latter process requires a dust-free nebula to allow penetration of the UV light driving the enrichment process.

### 9. Troilite and Magnetite Formation

Two other important gas-grain reactions are the formation of troilite and magnetite. Both proceed by the reaction of Fe metal grains with nebular vapor:



As stated earlier, both reactions are pressure independent because the total pressure factors out of the equilibrium constant expressions, which depend only on the temperature and on the  $\text{H}_2\text{S}/\text{H}_2$  and  $\text{H}_2\text{O}/\text{H}_2$  mixing ratios. Fegley (1988) applied the same gas-grain kinetic model with the same basic assumptions to these systems as well. In the case of FeS an activation energy of about  $105 \text{ kJ mole}^{-1}$  from the work of Worrell and Turkdogan (1968) on FeS formation from Fe was used. In the case of  $\text{Fe}_3\text{O}_4$ , no activation energy data were available and  $E_a \sim 80 \text{ kJ mole}^{-1}$  from the work of Turkdogan, McKewan, and Zwell (1965) on wüstite formation from water vapor and Fe was used instead.

The results of the kinetic calculations are displayed in Fig. 12. Troilite formation is predicted to be a rapid process with a chemical time constant of  $\sim 10^{10}$  sec (about 0.1% of the nebular lifetime). If the rate of troilite formation stays controlled by gas-grain collisions, it can proceed on a time scale less than the nebular lifetime down to 525 K. On the other hand, solid-state diffusion constraints may take over at some point, but this does not change the basic result that FeS formation at 690 K is rapid. The results of these kinetic calculations are thus in accord with the intuitive expectation that "tarnishing" of Fe grains is a rapid process. The prediction that FeS formation was kinetically favorable in the solar nebula is also in accord with the petro-

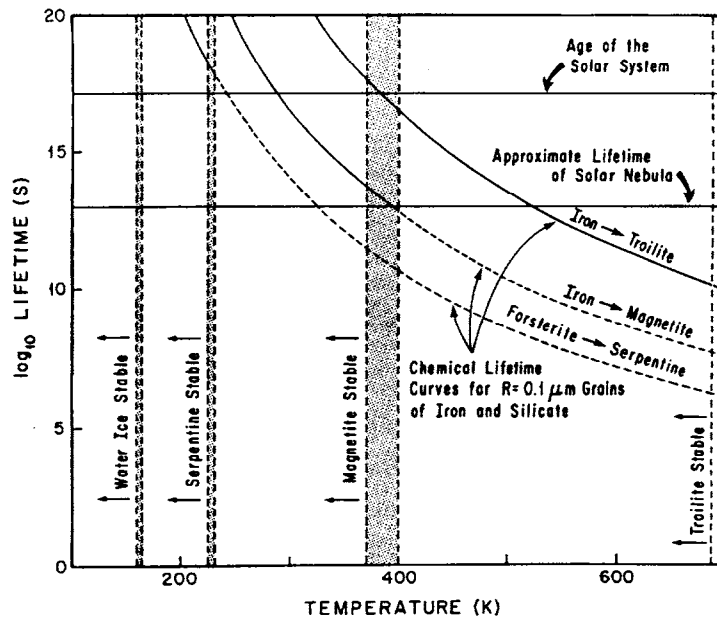


Figure 12. As in Fig. 11 but for troilite, magnetite, and serpentine formation in the solar nebula. The calculations, which are described in the text, show that troilite formation is kinetically favorable in the solar nebula because it proceeds in a short time relative to the nebular lifetime (about 0.1% of the estimated nebular lifetime). Magnetite formation is apparently slower, and may proceed on a timescale comparable to the nebular lifetime. However, intuition suggests that "rusting" of Fe grains by water vapor will be a rapid process and petrographic studies of magnetites in carbonaceous chondrites (Lohn and El Goresy 1992) support a nebular origin. The water ice condensation curve is also shown for comparison. From Fegley (1988).

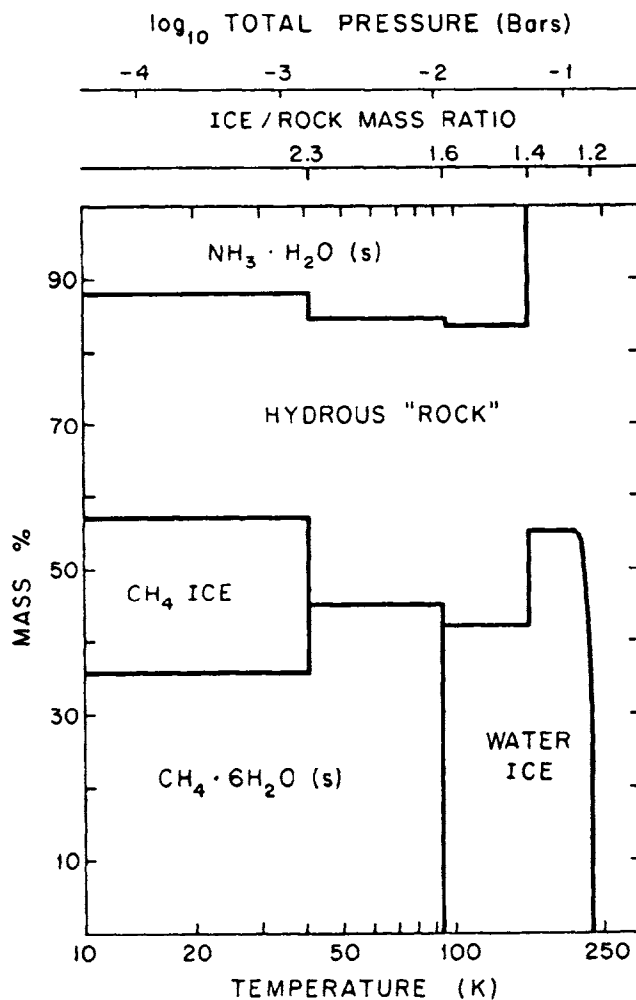


Figure 13. The low temperature condensation sequence in the giant protoplanetary subnebulae. As discussed in the text, the formation of  $\text{CH}_4$ ,  $\text{NH}_3$ , hydrated rock, and clathrate hydrates is predicted to be kinetically and thermodynamically favorable in the giant protoplanetary subnebulae. The pressure scale along the top corresponds to the Jovian protoplanetary subnebula P,T profile adopted throughout this paper. Note that the ice/rock mass ratio is significantly higher than that predicted for the solar nebula (Fig. 14). Minor condensates such as HCN are not shown in this figure, but are nevertheless potentially important for organic compound synthesis in the atmosphere of Titan. Modified from Fegley and Prinn (1989).

graphic evidence of FeS-rimmed metal grains in the unequilibrated ordinary chondrites (Rambaldi and Wasson 1981, 1984). The calculated  $t_{\text{chem}}$  of about  $10^{13}$  sec at 400 K for magnetite formation indicates that bulk magnetite formation may experience some kinetic inhibition, especially if CO remains the dominant carbon gas and magnetite is formed at 370 K. On the other hand, intuition suggests that the "rusting" of Fe metal grains by nebular water vapor is probably a rapid process. Furthermore, recent petrographic work by Lohn and El Goresy (1992) on magnetites in CI and CM2 chondrites suggests that the magnetites are nebular products. However, prior petrographic studies by Kerridge, MacKay, and Boynton (1979) concluded that the magnetites in CI chondrites were parent body products. Because of these petrographic disagreements and because the estimated chemical time constant for magnetite formation is based on the activation energy for wüstite formation, it is premature to draw firm conclusions regarding the kinetic favorability of the  $\text{Fe} \rightarrow \text{Fe}_3\text{O}_4$  conversion in the solar nebula. This must await further experimental measurements and combined petrographic and isotopic studies.

## 10. Low Temperature Chemistry

Low temperature chemistry in these two environments is qualitatively different from the high temperature chemistry taking place above the water ice condensation curve. Above this curve, which is illustrated in Fig. 1, 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 gas.

The nature of the "icy" grains which are formed both in the solar nebula and in the giant protoplanetary subnebulae depends to a large extent on the gas phase and gas-grain chemistry of carbon and nitrogen at higher temperatures. The two extremes are clearly the case of complete chemical equilibrium and the case of complete kinetic inhibition. Each will be examined in turn.

If complete chemical equilibrium is reached, then all carbon is present as  $\text{CH}_4$  and all nitrogen is present as  $\text{NH}_3$  at low temperatures. This case, or more precisely a close approach to it, is relevant to the giant protoplanetary subnebulae. The low temperature condensation sequence (neglecting the noble gases) is  $\text{H}_2\text{O}(\text{ice})$  at 235 K,  $\text{NH}_3 \cdot \text{H}_2\text{O}(\text{s})$  at 160 K,  $\text{CH}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  at 94 K, and  $\text{CH}_4(\text{s})$  at 40 K (Prinn and Fegley 1989). The condensation temperatures given are specific to the Jovian protoplanetary subnebula P,T profile adopted in earlier figures, but the condensation sequence itself is relevant over a wide pressure range. Fig. 13 illustrates the resulting composition of the low temperature condensate as a function of temperature along the Jovian protoplanetary subnebula P,T profile. Initially, the condensate is totally composed of "rocky" material, including hydrous silicates. However, first the condensation of water ice and subsequently the condensation of ammonia hydrate and the other "icy" materials dramatically alter the condensate composition so that the "icy" materials are more abundant than the rock. Obviously, not all of these low temperature condensates will form in all environments because the temperature profile of the protoplanetary subnebula will blend into that of the surrounding solar nebula. In the Jovian subnebula ammonia hydrate is probably the most volatile condensate which will form while in the Saturnian subnebula methane clathrate hydrate  $\text{CH}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  is probably the most volatile condensate formed. Further out, in the Uranian and Neptunian subnebulae (if these existed) it is possible that solid methane ice also condensed.

On the other hand, if CO and  $\text{N}_2$  reduction were both completely inhibited, then all carbon is present as CO and  $\text{CO}_2$  and all nitrogen is present as  $\text{N}_2$ . The low temperature condensation sequence in this case, which may be a good analog to the solar nebula, is  $\text{H}_2\text{O}(\text{ice})$  at 150 K, either  $\text{NH}_4\text{HCO}_3(\text{s})$  at 150 K or  $\text{NH}_4\text{COONH}_2(\text{s})$  at 130 K,  $\text{CO}_2(\text{ice})$  at 70 K, CO clathrate

hydrate, ideally  $\text{CO}\cdot 6\text{H}_2\text{O}(\text{s})$  at 60 K,  $\text{N}_2$  clathrate hydrate, ideally  $\text{N}_2\cdot 6\text{H}_2\text{O}(\text{s})$  at 55 K, and residual CO and  $\text{N}_2$  as the pure ices at 20 K (Prinn and Fegley 1989). Once again the noble gases have been neglected. The condensation temperatures are specifically for the adopted solar nebula P,T profile but the overall sequence remains the same over a wide pressure range. Because only a small fraction of total carbon is expected to be converted to  $\text{CO}_2$ , and because only a small fraction of total nitrogen is expected to be converted to  $\text{NH}_3$ , the masses of condensates containing these species constitute < 1% of total C and N. It is also important to realize that in a CO-rich nebula, the amount of water ice which is available is insufficient to completely enclathrate all CO and  $\text{N}_2$ . At present the thermodynamic data for these two clathrates is also somewhat uncertain. In the case of CO clathrate hydrate, the only available experimental data are the dissociation pressure at the clathrate-liquid water-gas triple point at 273 K (Davidson et al 1987). In the case of  $\text{N}_2$  clathrate hydrate, Miller (1961, 1969) has reported two different vapor pressure equations. Therefore it is difficult to specify exactly how much of each clathrate will form because the volatilities of each are poorly constrained. Fig. 14 displays the composition of low temperature condensate in the solar nebula as a function of temperature. In this instance, the rock is expected to be anhydrous because of the kinetic inhibition of hydrated silicate formation in the solar nebula. Anhydrous rock remains the dominant constituent of the low temperature condensate down to low temperatures where CO and  $\text{N}_2$  ices condense. This is due to the diminished abundance of water ice in the CO-rich solar nebula. If temperatures never were lower than 20 K in the solar nebula, then anhydrous rock remained the major constituent of the low temperature condensate.

A third, intermediate case is somewhat more complex and less well constrained. In this scenario, which is relevant to the solar nebula, some fraction of CO has been converted into hydrocarbons by grain catalyzed FTT reactions. As a result the low temperature condensation sequence in order of decreasing temperature is as follows: anhydrous rock, "refractory" organic compounds analogous to the "tar balls" in IDPs,  $\text{H}_2\text{O}(\text{ice})$ , either  $\text{NH}_4\text{HCO}_3(\text{s})$  or  $\text{NH}_4\text{COONH}_2(\text{s})$ , light hydrocarbons and their clathrate hydrates,  $\text{CO}_2(\text{ice})$ ,  $\text{CO}\cdot 6\text{H}_2\text{O}(\text{s})$ ,  $\text{N}_2\cdot 6\text{H}_2\text{O}(\text{s})$ , and residual CO and  $\text{N}_2$ . The condensation temperatures cannot be specified in this case without first knowing the amount of CO converted into hydrocarbons.

Additional complications are introduced by consideration of the kinetics of clathrate hydrate formation in the two different nebular environments. Briefly, clathrates are cage compounds in which the guest molecule is trapped inside a cage formed by the crystalline lattice of the host species. Clathrate hydrates are simply clathrates in which water ice is the host. Their formation has long been recognized as a potentially important mechanism for retention of carbon and nitrogen in ice-rich objects in the outer solar nebula (e.g., Delsemme and Swings 1952; Miller 1961; Delsemme and Miller 1970; Delsemme and Wenger 1970; Lewis 1972b; Delsemme 1976; Sill and Wilkening 1978; Lewis and Prinn 1980; Lunine 1989; Engel et al 1990). However, until very recently very little attention was paid to the kinetic feasibility of clathrate formation in the low temperature, low pressure environment of the outer solar nebula (e.g., Lewis and Prinn 1980; Lunine and Stevenson 1985; Fegley 1988).

As illustrated in Fig. 1 clathrates only become thermodynamically stable at very low temperatures in the solar nebula. For example,  $\text{CO}\cdot 6\text{H}_2\text{O}(\text{s})$  becomes stable at about 60 K along the solar nebula P,T profile shown in the figure. Now in order for this clathrate to form, CO(g) in the solar nebula must collide with and then diffuse into water ice grains in the nebula. Fegley (1988) modeled this process using the gas-grain kinetic model described earlier. This is equivalent to assuming that the rate at which CO molecules collide with water ice grains is the rate determining step for clathrate formation. If fresh water ice is continually exposed to the nebular gas, for example by low velocity collisions as advocated by Lunine and Stevenson (1985), this

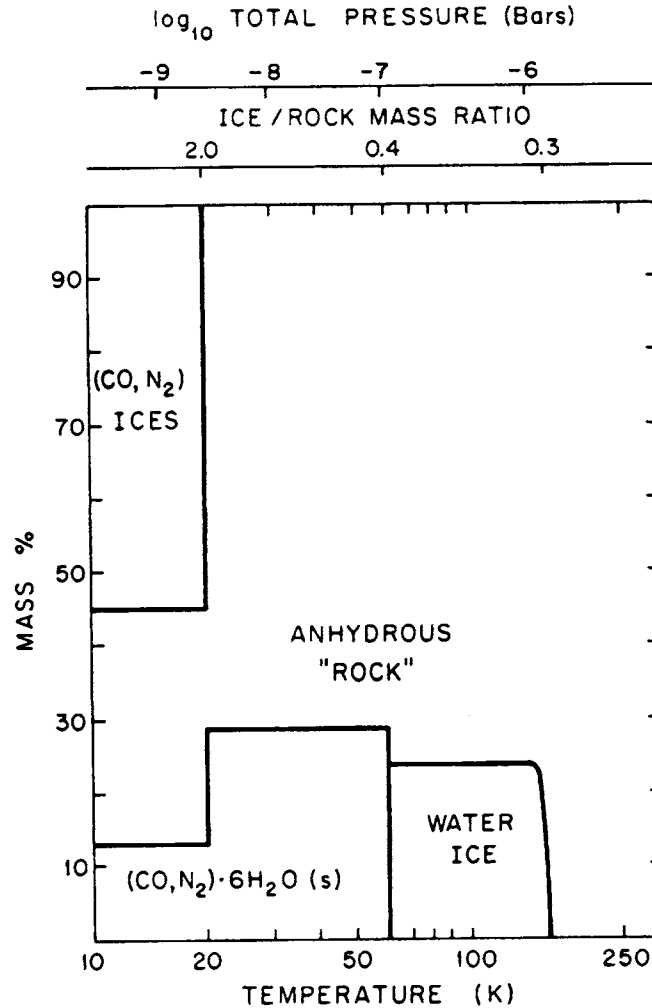


Figure 14. The low temperature condensation sequence in the solar nebula. As discussed in the text, the formation of  $\text{CH}_4$ ,  $\text{NH}_3$ , and hydrated "rock" are predicted to be kinetically inhibited in the solar nebula. The formation of CO and  $\text{N}_2$  clathrate hydrates is also probably kinetically inhibited. The pressure scale along the top corresponds to the nebular P,T profile adopted throughout this paper. Note that the ice/rock mass ratio in the CO-rich solar nebula is significantly lower than that in the  $\text{CH}_4$ -rich giant protoplanetary subnebulae. This difference is potentially diagnostic of the formation conditions of icy bodies in the outer solar system. Modified from Fegley and Prinn (1989).



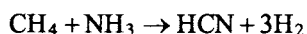
may be the case. However, it is clear that solid-state diffusion may also become rate limiting, which will probably decrease the clathrate formation rate. For now, if we assume that the gas-grain collisions are rate limiting, we can estimate an upper limit to the rate and a lower limit to the time for clathrate formation in the solar nebula and in the giant protoplanetary subnebulae.

In the solar nebula, the time required for 6% of all CO, which is the maximum amount that can be enclathrated before running out of water ice, to collide with 1  $\mu\text{m}$  radius, spherical, monodisperse water grains is about 40,000 seconds for the P,T profile shown in Fig. 1. The fraction of these collisions that have the necessary activation energy will be chemically reactive and lead to  $\text{CO}\cdot 6\text{H}_2\text{O}(\text{s})$  formation. Now in order for CO clathrate formation to take place within the nebular lifetime of  $10^{13}$  sec, this activation energy must be  $\leq 8$   $\text{kJ mole}^{-1}$  (Fegley 1988). Higher activation energies will lead to longer clathrate formation times that exceed the lifetime of the solar nebula. However, 8 kJ is a relatively low activation energy by comparison with the 19  $\text{kJ mole}^{-1}$  required for HF diffusion through ice (Haltenorth and Klinger 1969) or with the 24.7  $\text{kJ mole}^{-1}$  required for  $\text{CO}_2$  clathrate formation (Miller and Smythe 1970). If the activation energy for CO clathrate formation were 19  $\text{kJ mole}^{-1}$  the time required would be about  $10^{21}$  sec, while if about 25  $\text{kJ mole}^{-1}$  is taken by analogy with  $\text{CO}_2$  clathrate, the time required rises to even larger values. Nitrogen clathrate hydrate becomes stable at a similar temperature, and the same arguments apply in this case as well. Thus, it is apparent that clathrate formation will be kinetically inhibited in the low temperature, low pressure environment where it is thermodynamically feasible (but see Lunine et al 1991 for a dissenting viewpoint).

However, as pointed out by Fegley and Prinn (1989), clathrate formation is predicted to be kinetically favorable in the higher pressure environments of giant planet subnebulae. In this case,  $\text{CH}_4$  is the dominant carbon gas and  $\text{CH}_4$  clathrate formation becomes thermodynamically feasible at higher temperatures. As noted above,  $\text{CH}_4\cdot 6\text{H}_2\text{O}(\text{s})$  becomes stable at about 95 K and 0.01 bars for the Jovian protoplanetary subnebula P,T profile. This pressure is approximately 5 orders of magnitude higher than the corresponding solar nebula pressure at the  $\text{CO}\cdot 6\text{H}_2\text{O}(\text{s})$  formation temperature of 60 K and thus leads to higher  $\text{CH}_4$  gas collision rates with water ice grains. For example, the time for 22% of all  $\text{CH}_4$  (which is the maximum amount that can be enclathrated before using up all the available water ice) to collide with  $r = 1$   $\mu\text{m}$  spherical, monodisperse ice grains is only 0.1 seconds. In this case, the activation energy for formation of  $\text{CH}_4\cdot 6\text{H}_2\text{O}(\text{s})$  can be as large as 25  $\text{kJ mole}^{-1}$  to have the process occur during the lifetime of the solar nebula. Therefore, the results of these first order calculations predict (in accord with intuition) that CO and  $\text{N}_2$  clathrate formation will be kinetically inhibited in the solar nebula but that  $\text{CH}_4$  clathrate formation will be kinetically feasible in giant planet subnebulae. However, as previously stressed by Fegley (1988, 1990) and Fegley and Prinn (1989), experimental studies of the kinetics of clathrate formation are required for a comprehensive understanding of the kinetic constraints on clathrate formation in the solar nebula and in giant planet subnebulae. These experiments should focus on  $\text{CH}_4$ , CO, and  $\text{N}_2$  clathrates and should be suitably designed so that the dependence of the rate on gas partial pressures, ice particle sizes, and temperature can be quantitatively measured.

Thus, two qualitatively different low temperature condensation sequences are expected in the solar nebula and in the giant protoplanetary subnebulae as a result of the differences in C and N chemistry at higher temperatures. In the solar nebula condensates of oxidized carbon and nitrogen compounds are important, formation of clathrate hydrates is kinetically inhibited, anhydrous rock is more abundant than water ice, and anhydrous rock remains the dominant constituent of the low temperature condensate down to the point where CO and  $\text{N}_2$  ices condense. In the giant protoplanetary subnebulae condensates of reduced carbon and nitrogen compounds are important, clathrate hydrate formation is thermodynamically and kinetically favorable, hy-

drous rock is less abundant than water ice, and ices are the dominant constituent of the low temperature condensate. Finally, another important difference, first pointed out by Prinn and Fegley (1981), is the condensation of small, but nevertheless significant amounts of HCN in the giant protoplanetary subnebulae. Hydrogen cyanide is an important precursor for the abiotic synthesis of complex organic molecules (Oró and Kimball 1961; Abelson 1966). It is produced by the thermochemical conversion of some of the CH<sub>4</sub> and NH<sub>3</sub> into HCN,



with the exact amount of conversion being kinetically controlled by the chemical reaction and radial mixing rates. For example the HCN abundances predicted by Prinn and Fegley (1981) range from about 1 to 100 µg/g depending on the assumed strength of radial mixing. As noted by these authors, "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."

## 11. Abundances Of C-H-O-N-S Compounds In Comet P/Halley and Other Comets

The preceding discussion has concentrated on theoretical predictions arising from current models of nebular chemistry. At this point it is therefore interesting to compare these predictions with observations in order to determine how useful the models are for understanding the volatile element inventories of solar system bodies. Detailed comparisons of the volatile inventories of the terrestrial planets, the chondritic meteorites and asteroids, the gas giant planets, icy satellites of the gas giant planets, and of Pluto with predictions of nebular chemistry models have already been presented by Prinn and Fegley (1989) and Fegley and Prinn (1989). Instead of repeating these discussions here, we will concentrate instead on a comparison of the model results with the volatile element abundances and molecular speciation in comet P/Halley and other recent comets. This is instructive for several reasons: (1) Earth-based observations and spacecraft flybys have provided a large amount of data on the chemical compositions of Halley and other recent comets, (2) comets are arguably the best preserved samples of nebular material, having presumably undergone less thermal processing subsequent to their formation than any type of chondrite, (3) comets are generally believed to have formed in the outer regions of the solar nebula and thus their compositions should shed light on the relative contributions of interstellar material and of thermally processed nebular material to chemistry in the outer solar nebula, and (4) significant new data have been published since the last such comparison was done by Fegley and Prinn (1989).

### 11.1 WATER VAPOR

As Weaver (1989) has noted, prior to the return of Halley observers had constructed a strong circumstantial case for the dominance of water vapor in the volatiles emitted by comets (e.g., see Delsemme, 1982). However, water vapor was first observed directly in comet P/Halley using the Fourier Transform Infrared Spectrometer (FTIR) on the Kuiper Airborne Observatory (Mumma et al 1986) and was later observed in comet Wilson (1986) with the same apparatus (Larson et al 1989). Subsequent measurements by the Neutral Mass Spectrometer (NMS) on Giotto showed that H<sub>2</sub>O comprised ≥ 80% of the volatiles emitted by Halley (Krankowsky et al 1986) and that the water vapor has a D/H ratio in the range of 0.6 - 4.8 × 10<sup>-4</sup> (Eberhardt et al 1987b). Finally, more recent measurements by Mumma, Weaver, and Larson (1987) and Mum-

ma et al (1988) have provided data on the ortho-to-para ratio of water vapor emitted by Halley and by Wilson(1986l). For Halley, the derived ortho/para ratio is  $2.3 \pm 0.2$  while for Wilson(1986l) the derived ortho/para ratio is  $3.2 \pm 0.2$ . If these data are taken at face value, the Halley ortho/para ratio implies a nuclear spin temperature of 25 K while the Wilson(1986l) ortho/para ratio implies statistical equilibrium ( $T \geq 50$  K). However, Bockelée-Morvan and Crovisier (1990) retrieved different ortho-para ratios from the same data and have recently questioned the analysis of Mumma and colleagues. At present this discrepancy between the two groups is unresolved.

### 11.2 CARBON COMPOUNDS

The second most abundant group of volatiles (after water vapor) emitted from Halley are the oxidized carbon gases CO, CO<sub>2</sub>, H<sub>2</sub>CO, and CH<sub>3</sub>OH. Five different measurements provide information on the abundance and distribution of CO emitted from Halley. The Giotto NMS data for mass 28, which is probably dominated by CO (see the discussion for N<sub>2</sub> below), has been interpreted as indicating a comet nucleus source for CO having CO/H<sub>2</sub>O  $\leq 0.07$  and an extended source in the inner coma for CO having CO/H<sub>2</sub>O  $\leq 0.15$  (Eberhardt et al 1987a). Infrared measurements from the IKS experiment on the Vega space probes yield CO/H<sub>2</sub>O  $\sim 0.05$  for a comet nucleus source (Combes et al 1988). Pioneer Venus Orbiter Ultraviolet Spectrometer (PVOUS) measurements of resonance UV emission from atomic hydrogen, oxygen, and carbon in the coma of Halley yield nominal H:O:C atomic ratios of 1:0.7:0.07, which are consistent with CO/H<sub>2</sub>O  $\sim 0.25$  or with CO<sub>2</sub>/H<sub>2</sub>O  $\sim 0.14$  (Stewart 1987). Rocket-borne ultraviolet spectrometer measurements of resonance UV emission from atomic oxygen and carbon in the coma of Halley also yield similar CO/H<sub>2</sub>O ratios of  $0.20 \pm 0.05$  for the one flight and  $0.17 \pm 0.04$  for a second flight (Woods et al 1986). Finally, measurements from the International Ultraviolet Explorer (IUE) satellite also yield a rough estimate for the CO/H<sub>2</sub>O ratio of 0.1-0.2 for Halley (Festou et al 1986). This set of observations is generally interpreted as indicating a nucleus source for CO having CO/H<sub>2</sub>O  $\sim 0.02 - 0.07$  (by number) and a dispersed source which accounts for the balance of the observed CO (e.g., see Eberhardt et al 1987a; Weaver 1989).

Carbon monoxide has also been detected in comet Austin (1989c1), comet Levy (1990c), comet West (1976 VI) with CO/H<sub>2</sub>O  $\sim 0.3$  and in comet Bradfield (1979 X) with CO/H<sub>2</sub>O  $\sim 0.02$  (Weaver 1989; Mumma et al 1992, and references therein). The CO/H<sub>2</sub>O ratios in Austin and Levy are in the range of 1-7% (Mumma et al 1992). As both Mumma et al (1992) and Weaver (1989) note, the "high" CO abundance in Halley and in comet West (1976 VI), and the "low" CO abundance in comet Bradfield (1979 X), comet Austin (1989c1), and comet Levy (1990c) may be explained as follows. The observations made with large fields of view of comets with large dust production rates (e.g., the rocket UV observations of Halley and West) yield larger apparent CO abundances because CO production from the nucleus and also from evaporating organic grains is being observed, while the observations made with smaller fields of view (e.g., IUE observations of Austin, Halley, and Levy) or observations made of comets with low dust production rates yield smaller apparent CO abundances because only CO production from the nucleus is being observed.

Carbon dioxide was observed with both the NMS experiment on Giotto and the IKS experiment on Vega. The NMS data yield CO<sub>2</sub>/H<sub>2</sub>O  $\sim 0.04$  (Krankowsky et al 1986) while the IKS data yield a ratio of about 0.03 (Combes et al 1988). Both ratios are appropriate for CO<sub>2</sub> emitted from the nucleus and together with the adopted values of  $\sim 0.02 - 0.07$  for CO/H<sub>2</sub>O from the nucleus yield CO/CO<sub>2</sub>  $\sim 0.50 - 2.3$ . In other words, roughly equal amounts of CO and

CO<sub>2</sub> are being emitted from the nucleus of Halley. As discussed below, this rough equality has important implications for the origin of carbon-bearing gases and grains in Halley.

Formaldehyde has also been detected in Halley. The H<sub>2</sub>CO/H<sub>2</sub>O ratio obtained from the IKS measurements is ~ 0.04 (Combes et al 1988; Mumma and Reuter 1989) while a slightly lower value of ~ 0.02 was derived from radio wavelength observations by Snyder et al (1989). The analysis of the Giotto NMS data by Meier et al (1991) gave an upper limit of a few percent for H<sub>2</sub>CO/H<sub>2</sub>O. Both the radio wavelength observations and the Giotto NMS data apparently indicate a distributed source for at least some of the H<sub>2</sub>CO (Krankowsky 1991; Snyder et al 1989). However, the IKS measurements supposedly refer to a nucleus source of H<sub>2</sub>CO and not to formaldehyde released from the decomposition of POM in dust grains (Combes et al 1988). Formaldehyde has also been observed at radio wavelengths in comet Machholz (1988j) with a production rate an order of magnitude larger than that in Halley (dePater et al 1991) and in comet Austin (1989c1) with a H<sub>2</sub>CO/H<sub>2</sub>O ratio of 0.006 (Bockelée-Morvan et al 1991).

The detection of polyoxymethylene or POM (H<sub>2</sub>CO)<sub>n</sub> in comet P/Halley was reported by Huebner (1987), Huebner, Boice and Sharp (1987), and Mitchell et al (1987). These authors interpreted regularly spaced peaks in ion mass spectra from the PICCA instrument (Korth et al 1986) as the cracking pattern of POM released from the dust grains. The POM was suggested to make up 2% (by mass) of the dust emitted from Halley (Mitchell et al 1987). However, Mitchell et al (1989) later proposed that a mixture of complex hydrocarbons containing nitrogen could also explain the observed mass spectra.

Infra-red spectroscopic observations of comets Austin (1989c1), Levy (1990c), Halley, and Wilson (1987 VII) showed the presence of CH<sub>3</sub>OH and gave ratios of ~ 0.01-0.05 relative to water (Hoban et al 1991). Bockelée-Morvan et al (1991) also reported the radio wavelength detection of CH<sub>3</sub>OH in comet Austin (1989c1) at a level corresponding to CH<sub>3</sub>OH/H<sub>2</sub>O ~ 0.01. Geiss et al (1991) interpreted Giotto IMS data as showing a CH<sub>3</sub>OH/H<sub>2</sub>O ratio of 0.003-0.015, and Eberhardt et al (1991) obtained a similar value of ~ 0.01 for the CH<sub>3</sub>OH/H<sub>2</sub>O ratio from the Giotto NMS data.

Carbon suboxide C<sub>3</sub>O<sub>2</sub> has also been claimed in comet Halley at a level of 0.03-0.04 relative to water (Huntress, Allen, and Delitsky 1991). Photolysis of this species yields CO and either atomic C or C<sub>2</sub>O, depending on the wavelength of the UV photons. Thus, it is an alternative to explain the distributed source of CO observed in Halley.

The CH<sub>4</sub>/H<sub>2</sub>O ratio in the volatiles emitted by Halley is currently controversial. Modeling of the Ion Mass Spectrometer data of Balsiger et al (1986) solely in terms of gas phase chemistry by Allen et al (1987) yields a CH<sub>4</sub>/H<sub>2</sub>O ratio of ~ 0.02. However, more recent modeling of the same data by Boice et al (1990) in terms of the decomposition of POM grains gives a lower CH<sub>4</sub>/H<sub>2</sub>O ratio of ≤ 0.005. Infrared observations from the Kuiper Airborne Observatory by Drapatz, Larson, and Davis (1987) gave an upper limit for CH<sub>4</sub>/H<sub>2</sub>O ≤ 0.04 while IR observations at Cerro Tololo by Kawara et al (1988) gave CH<sub>4</sub>/H<sub>2</sub>O ~ 0.002 - 0.01 for assumed rotational temperatures of 50 to 200 K. The value adopted here for the CH<sub>4</sub>/H<sub>2</sub>O ratio is ~ 0.01 - 0.05 from the review by Weaver (1989). This value is adopted despite the more recent work of Boice et al (1990) for 2 reasons: (1) their analysis of the IMS data is based upon estimated rate coefficients for the POM chemistry and the sensitivity of their results to variations in the estimated rate data is not specified, (2) their analysis does not give a good fit to the CH peak at 13 amu without invoking an unidentified grain source for this peak. Together with the adopted CO/H<sub>2</sub>O ratio of ~ 0.02 - 0.07 and the adopted CO<sub>2</sub>/H<sub>2</sub>O ratio of ~ 0.03 - 0.04, the adopted CH<sub>4</sub>/H<sub>2</sub>O ratio leads to CO/CH<sub>4</sub> ~ 0.4 - 7.0 and CO<sub>2</sub>/CH<sub>4</sub> ~ 0.6 - 4.0.

### 11.3 NITROGEN COMPOUNDS

In contrast to the carbon compounds discussed above, neither  $N_2$  nor  $NH_3$  has been observed in Halley. In both cases the inferred abundances of the parent molecules are deduced from observations of daughter molecules presumably produced by photolysis of the parents.

Allen et al (1987) originally derived a  $NH_3/H_2O$  ratio of  $\sim 0.01 - 0.02$  from their analysis of the Giotto IMS data. However, a subsequent reanalysis of the same data by Marconi and Mendis (1988), who unlike Allen et al (1987) assumed a highly elevated solar UV flux at the time of the Halley spacecraft encounters, led to the conclusion that  $NH_3/H_2O < 0.01$  and indeed may even be zero. However, the total absence of  $NH_3$  in Halley is extremely unlikely given the Earth-based observations of  $NH_2$  (Tegler and Wyckoff 1989; Wyckoff et al 1988; Wyckoff, Tegler and Engel 1989, 1991a) which is most plausibly produced by the photodissociation of  $NH_3$ . Tegler and Wyckoff (1989) derived  $NH_3/H_2O = 0.005 \pm 0.002$  in comet P/Halley, which was later lowered to  $NH_3/H_2O = 0.002 \pm 0.0014$  by Wyckoff, Tegler, and Engel (1991a). Ip et al (1990) derived  $NH_3/H_2O \sim 0.005$  from an analysis of Giotto IMS data. The value adopted here for the  $NH_3/H_2O$  ratio is  $\sim 0.005 - 0.02$ . Wyckoff, Tegler, and Engel (1989, 1991a) have also observed  $NH_2$  emission from comet P/Borrelly, comet Hartley-Good, and comet Thiele. The derived  $NH_3/H_2O$  ratios reported in their 1991 paper are  $0.09 \pm 0.06\%$  for Borrelly,  $0.08 \pm 0.06\%$  for Hartley-Good, and  $0.16 \pm 0.11\%$  for Thiele. However, as Weaver et al (1991) note, the only direct observation of  $NH_3$  in a comet is a marginal detection of a radio line in comet IRAS-Araki-Alcock (1983 VII) by Altenhoff et al (1983).

Until recently only upper limits were available for the  $N_2/H_2O$  ratio in Halley. Wyckoff and Theobald (1989) observed  $N_2^+$  in Halley and calculated a  $N_2/CO$  ratio  $\sim 0.002$ . Using the adopted value of  $\sim 0.02 - 0.07$  for the  $CO/H_2O$  ratio leads to  $N_2/H_2O \sim 4 \times 10^{-5}$  to  $1 \times 10^{-4}$ . A higher  $N_2/H_2O$  ratio of  $\sim 2 \times 10^{-4}$  was derived by Wyckoff, Tegler, and Engel (1991b), but the difference is not significant for our arguments. In any case, the low  $N_2/CO$  ratio derived by Wyckoff and Theobald (1989) indicates that most of the mass 28 peak observed in the Giotto NMS is due to CO rather than to  $N_2$ . The adopted values for the  $N_2/H_2O$  and  $NH_3/H_2O$  ratios correspond to  $N_2/NH_3 \sim 0.002 - 0.025$  while the value for  $N_2/NH_3$  calculated by Wyckoff and colleagues on the basis of their own observational data is  $\sim 0.1$ .

Finally, HCN has also been detected at radio wavelengths in comet Kohoutek (Huebner et al 1974), in Halley at  $HCN/H_2O \sim 0.001$  (Schloerb et al 1987; Despois et al. 1986), in comet Austin (1989c1) at  $HCN/H_2O \sim 0.0004$ , and in comet Levy (1990c) (Bockelée-Morvan et al 1991). Ip et al (1991) interpreted the Giotto IMS data as indicating  $HCN/H_2O \leq 0.0002$ . The reasons for the disagreement with the radio wavelength observations are unclear. Wyckoff et al (1989) used high resolution spectra of CN emitted from Halley to derive a  $^{12}C/^{13}C$  ratio of  $65 \pm 9$ , which is significantly lower than the terrestrial value of 89. However, subsequent work by Wyckoff and colleagues (Kleine et al 1991) showed that their initial carbon isotope determination was incorrect and that the  $^{12}C/^{13}C$  ratio in Halley is in fact the same as the terrestrial value within observational error. Prior  $^{12}C/^{13}C$  determinations for comets are  $70 \pm 15$  for Ikeya 1963 I (Stawikowski and Greenstein 1964),  $100 \pm 20$  for Tago-Sato-Kosaka 1969 IX by Owen (1973),  $115(+30, -20)$  and  $135(+65, -45)$  for Kohoutek 1973 XII by Danks et al (1974), and  $100(+20, -30)$  for Kobayashi-Berger-Milon 1975 IX from Vanýsek (1977). All of the other cometary carbon isotopic ratios are derived from observations of  $C_2$ .

#### 11.4 SULFUR COMPOUNDS

The sulfur species CS, S,  $S_2$ , and  $H_2S$  have been spectroscopically observed in comets; however, the only one of these four which is a "parent" molecule is  $H_2S$ . The solar elemental S/O

abundance ratio of 0.021 (Anders and Grevesse 1989) suggests that sulfur species should be fairly abundant in comets, if a sizeable fraction of the total sulfur is in volatile form and not sequestered as FeS or otherwise locked up in the "rocky" component. The CS radical has been observed in many comets with abundances relative to water of about  $10^{-3}$  (Feldman 1991). Although it has not been observed, CS<sub>2</sub> is generally believed to be the parent molecule for CS. Ultraviolet observations of atomic S indicate its presence in several comets, although its abundance relative to water is uncertain because of uncertainties in the atomic S line intensities and oscillator strengths (Crovisier et al 1991). Diatomic sulfur S<sub>2</sub> was observed in comet IRAS-Araki-Alcock (1983 d) by A'Hearn et al (1983). According to the recent analysis of Kim et al (1990) the S<sub>2</sub>/H<sub>2</sub>O abundance ratio is 0.0002 in this comet. Several groups have very recently reported the presence of H<sub>2</sub>S in comets. Crovisier et al (1991) detected H<sub>2</sub>S in comet Austin (1989c1) and comet Levy (1990c) at H<sub>2</sub>S/H<sub>2</sub>O ratios of 0.0027 and 0.0020, respectively. Marconi et al (1990) reported H<sub>2</sub>S<sup>+</sup> in the Giotto Positive Ion Cluster Composition Analyzer (PICCA) data and estimated H<sub>2</sub>S/H<sub>2</sub>O ~ 0.005-0.022. Using newer data for H<sub>2</sub>S photodissociation, Crovisier reanalyzed these data and found H<sub>2</sub>S/H<sub>2</sub>O ~ 0.013. Meier et al (1991) also reported evidence for H<sub>2</sub>S from the Giotto mass spectrometer data and derived H<sub>2</sub>S/H<sub>2</sub>O ~ 0.003. The revised photodissociation lifetimes for H<sub>2</sub>S and the radial ion profile observed in the NMS data are consistent with its production from the nucleus of comet P/Halley, and a dust particle source may not need to be invoked.

## 12. Interpretation of the Observed Molecular Abundances in Comet P/Halley

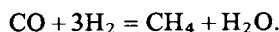
### 12.1 WATER

A fundamental question is whether or not the water in comet P/Halley and other comets is from the solar nebula or from the interstellar medium. If comet P/Halley is an assemblage of interstellar material, as proposed by some, then water, the most abundant volatile, should also have an interstellar origin. On the other hand, if comet P/Halley represents an assemblage of nebular and/or nebular plus interstellar material, then the water could be from the solar nebula. The source of the water has important implications for the source of the other, less abundant volatiles, especially for those which may be trapped in water ice as clathrate hydrates. This point can be illustrated by considering the following scenarios.

In the first scenario, we imagine that the water in comet P/Halley is relict interstellar ice. In this case, the water in Halley was never exposed to nebular temperatures high enough for it to evaporate or to isotopically exchange D and oxygen with nebular H<sub>2</sub> and O-bearing gases. The nuclear spins of the protons may also be representative of the interstellar medium, although this need not necessarily be the case, because spin exchange can occur at fairly low temperatures if the necessary catalysts are present. An important implication of this scenario is that clathrate hydrates would be absent from Halley because it is difficult to imagine how these compounds could have formed in the extremely cold, tenuous interstellar medium. We would then expect that the other volatiles in Halley are all present as pure ices. We would also expect that the chemical and isotopic composition of the volatiles in Halley could have little or no relation to that of average solar system material. In this case, the composition of Halley would be important for understanding the composition of the interstellar medium at the time that the solar system formed, but would provide little or no information about nebular processes.

In the second scenario, we imagine that the water in comet P/Halley is nebular in origin. This water could either be interstellar water that had evaporated and recondensed in the so-

lar nebula, or it could be water that was formed in the solar nebula or in the giant protoplanetary subnebulae from chemical reactions such as:



In this scenario the water in comet P/Halley bears the signature of nebular processes and potentially provides information on these processes. Furthermore, in this case, it is possible that clathrate hydrates would have been formed if the water were chemically produced by CO hydrogenation in the giant protoplanetary subnebulae, where clathrate hydrate formation is kinetically favorable. Other important implications of a nebular origin for the water in Halley are that the isotopic composition could have equilibrated with the D/H ratio of nebular H<sub>2</sub> and O-bearing gases, and that the nuclear spins of the protons were equilibrated at the high temperature value. In this case the molecular composition of Halley provides very little information about interstellar speciation but provides a wealth of information about nebular speciation and nebular chemical processes. Another implication of this scenario is that other species, more volatile than water ice, are unlikely to have an interstellar origin.

The crystalline state (i.e., amorphous vs. crystalline), isotopic composition (D/H, oxygen isotopes), and nuclear spin state (ortho/para ratio) can potentially all shed light on this question. However, no data are available on the crystalline state of water ice in comet P/Halley. Furthermore, the interpretation of the oxygen isotopic data, which show a terrestrial <sup>16</sup>O/<sup>18</sup>O ratio within observational errors, is nonunique given the independent evidence for large oxygen isotopic variations in the chondritic meteorites. Thus, only the D/H ratio and the ortho/para ratio may be potentially diagnostic of the origin of the water in comet P/Halley. We consider the D/H ratio first.

The observed D/H ratio of water in comet P/Halley is  $0.6 - 4.8 \times 10^{-4}$  (Eberhardt et al 1987b). As noted earlier, this is the same as the terrestrial value of about  $1.6 \times 10^{-4}$  within the observational uncertainties. The equilibration temperature corresponding to a given D/H ratio in water can be calculated using the thermochemical isotopic fractionation factors tabulated by Richet, Bottinga, and Javoy (1977). The lower end of the range of D/H values derived for Halley (D/H  $\sim 0.6 \times 10^{-4}$ ) corresponds to a temperature of  $\sim 465$  K, while the upper end of the range of values (D/H  $\sim 4.8 \times 10^{-4}$ ) corresponds to a temperature of  $\sim 148$  K. The classical picture of isotopic exchange envisions increasing deuterium enrichment in hydrides such as H<sub>2</sub>O, CH<sub>4</sub>, etc. with decreasing temperature (Geiss and Reeves 1981). In this picture, the D/H ratio represents the lowest temperature at which nebular water vapor and hydrogen exchanged deuterium. However, there are several reasons for believing that D/H exchange could not occur at low temperatures in the solar nebula. The first reason is that kinetic models of the D/H exchange rate between hydrogen and hydrides such as H<sub>2</sub>O, CH<sub>4</sub>, etc. in the atmospheres of the Jovian planets show that these reactions take longer than the age of the solar system at low temperatures (e.g., Fegley and Prinn 1988). It is therefore unlikely that these reactions will proceed any more rapidly in the much lower density nebular environment. Second, calculations by Grinspoon and Lewis (1987) show that the grain catalyzed D/H exchange rate is also probably too slow for isotopic equilibration to occur at low temperatures. But, as mentioned earlier, the recent experimental work of Lecluse and Robert (1992) apparently shows that D/H exchange between HD and H<sub>2</sub>O will be rapid enough to produce Earth-like D/H ratios in nebular water.

Assume for the moment that the isotopic exchange temperatures are the maximum temperatures at which the water in Halley last exchanged deuterium with nebular H<sub>2</sub>. If this view is taken, then the exchange process is viewed as a back-reaction in which D-rich water is losing deuterium to the surrounding nebular H<sub>2</sub>. This process may occur as a consequence of reactions

driven by thermochemistry (e.g., in the subnebulae surrounding the giant planets) or as a consequence of reactions driven by the interstellar radiation field impinging on the outer layers of the primitive solar nebula. The latter possibility is essentially the reverse of the scheme proposed by Yung et al (1988). Whether or not a purely thermochemical or a photochemical mechanism is envisioned, the temperature range of 148-465 K corresponding to the observed D/H ratio indicates significant amounts of thermal processing within the solar nebula for the water in comet P/Halley. Thus, the observed D/H ratio is compatible with a nebular origin for the water in Halley, or at least with nebular thermal processing at temperatures in the 148-465 K range.

On the other hand, if the ortho/para ratio of  $2.3 \pm 0.2$  deduced by Mumma and colleagues is taken at face value, the situation appears slightly more complicated. This low ratio implies a nuclear spin equilibration temperature of about 25 K, which is below the minimum temperatures predicted in most solar nebula models. An interstellar origin for the water in Halley is clearly implied from this result, unless a way can be found to retain the low temperature ortho/para ratio while isotopically exchanging D up to higher temperatures. As noted previously, Bockelée-Morvan and Crovisier (1990) retrieved different ortho/para ratios from the same data and questioned the analysis of Mumma and colleagues. In the absence of other information we do not use either ortho/para ratio as a constraint. Without compelling evidence in favor of an interstellar origin we regard it as highly probable that the water in comet P/Halley either originated (or was last thermally processed) in the solar nebula.

## 12.2 CARBON COMPOUNDS

The observational data reviewed earlier give the following ratios for the major carbon gases observed in comet Halley:  $\text{CO}/\text{CO}_2 \sim 0.5\text{-}2.3$ ,  $\text{CO}/\text{H}_2\text{CO} \sim 0.5\text{-}1.8$ ,  $\text{CO}/\text{CH}_3\text{OH} \sim 2.0\text{-}7.0$ ,  $\text{CO}/\text{C}_2\text{O}_2 \sim 0.5\text{-}2.3$ ,  $\text{CO}/\text{CH}_4 \sim 0.4\text{-}7.0$ , or in other words roughly equal abundances of all carbon gases within the uncertainties of the data. The elemental mass balance calculations of Delsemme (1988) further indicate that Halley contains the solar complement of carbon with about 25% of the total being found in the gaseous compounds and the remaining 75% being found in the CHON grains. Fegley (1990) pointed out that this carbon mass balance for Halley could be interpreted in two ways. The first approach, which we adopt here, is that the carbon mass balance indicates that both the volatile carbon gases and the more refractory carbon compounds in the CHON grains originated from the same reservoir which was fractionated into two groups of carbon compounds by some suite of chemical processes. The second approach, which was taken by Lunine (1989), is that the carbon mass balance is merely a coincidence and the volatile carbon gases and the refractory carbon in CHON grains have separate and decoupled origins.

Proceeding with the first approach we note that the 3:1 ratio between refractory and volatile carbon in Halley is qualitatively similar to the ratio of  $P_{\text{CO}} \sim P_{\text{CO}_2} \sim P_{\text{CH}_4} \sim (1/3)A_{\text{gr}}$  (the graphite abundance) predicted for the abundance of graphite and carbon gases at low temperatures and pressures ( $T < 470$  K,  $P < 10^{-7.6}$  bars) inside the graphite stability field (Lewis, Barshay, and Noyes 1979). As noted earlier, grain catalyzed chemistry may proceed down to  $\sim 370\text{-}400$  K where magnetite formation will deactivate the Fe grain catalyst. Furthermore, because of the difficulties in precipitating graphite from a solar gas, it is probably best to regard it as a proxy for organic matter. Formaldehyde, methanol, and carbon suboxide were not included in the work of Lewis, Barshay, and Noyes (1979) but the relatively rapid interconversions between oxidized carbon compounds such as  $\text{CO}\text{-}\text{CO}_2\text{-}\text{H}_2\text{CO}\text{-}\text{CH}_3\text{OH}$  (e.g., Warnatz 1984) suggest that all of these species can be formed at fairly low temperatures. We note that Fe catalyzed FTT reactions also produce alcohols, aldehydes, and  $\text{CO}_2$  under laboratory conditions (Bond 1962; Dictor and Bell 1986; Dry et al 1972; Renshaw, Roscoe and Walker 1970). Thus, all of the



volatile carbon species (except  $C_3O_2$ ) can potentially be produced by grain catalyzed reactions. On the basis of calculations by Fegley (1988), Lunine (1989) and Engel et al (1989) also proposed that the abundances of the volatile gases CO,  $CO_2$ , and  $CH_4$  in Halley are the result of grain catalyzed chemistry, but they regarded the involatile CHON grains as having a separate and decoupled origin from the carbon gases and did not discuss its origin in the light of the work by Lewis, Barshay, and Noyes (1979). However, as originally proposed by Fegley (1990) grain catalyzed chemistry may be responsible for both the volatile carbon gases and the refractory organic matter.

Many of the points mentioned earlier in connection with our discussion of grain catalyzed carbon and nitrogen chemistry argue for this model for the origin of carbon compounds in Halley. Briefly, these include: (1) the high abundance of Fe, the third most abundant cation (after Mg and Si) in rocky material, (2) the known catalytic activity of Fe in industrial processes, (3) the observed association of organic material with Fe phases (Fe alloy, carbides, and oxides) in interplanetary dust particles, and (4) the suspected association of some IDPs and comets. On the other hand, the problems mentioned earlier, such as the possible catalytic deactivation of Fe grains by troilite formation at 690 K, and the lack of laboratory studies under conditions relevant to the solar nebula, also apply here. The promising agreement between the Halley data and the laboratory results on FTT reactions point out the need for further experimental work in this important area.

Alternatively, some researchers have proposed an interstellar origin for the volatile carbon species in Halley because the observed  $CO/CH_4$  ratio of  $\sim 0.4-7.0$  in Halley is similar to the  $CO/CH_4$  ratios in solid grains in different molecular clouds:  $\sim 0.4$  in W33A,  $\sim 0.3$  in 7538 IRS1, and  $\sim 7.5$  in 7538 IRS9 (Lacy et al 1991). The production of  $CH_4$  and other hydrides by laboratory UV irradiation of simulated interstellar ices (e.g., Greenberg 1992) has also been used to argue for an interstellar origin of carbon gases in Halley. However, an interstellar origin for the CO and  $CH_4$  in Halley requires preservation of the pristine interstellar grains. This is apparently contradicted by the arguments above showing that the water in Halley was processed to temperatures in the range of 148-465 K in the solar nebula. The more volatile CO and  $CH_4$  ices would totally evaporate at these temperatures. An important implication of the interstellar model is that high D/H ratios are expected in  $CH_4$ ,  $NH_3$ , and other hydrides formed on grains in molecular clouds (Tielens 1983). In contrast, the D/H ratios expected in  $CH_4$  formed by grain catalyzed chemistry should reflect those of the starting HD, presumably the protosolar value of  $\sim 3 \times 10^{-5}$ . Thus, isotopic analyses of the volatiles emitted by comets will provide an important test of interstellar versus nebular origins.

It is also important to note, as emphasized by Prinn and Fegley (1989) and Fegley and Prinn (1989) that the  $CO/CH_4$  ratio in Halley is compatible with nebular chemistry. Their model, which is schematically illustrated in Fig. 15, is a two component mixing model in which CO-rich nebular material is mixed with a smaller amount of  $CH_4$ -rich giant protoplanetary subnebular material. The mixing process may occur via collisions of icy bodies formed in the two environments after the nebular gas has dissipated, or chemical exchange between the two environments. Prinn and Fegley (1989) and Fegley and Prinn (1989) favored a collisional mixing process but did not model the dynamics of this mechanism. However, photogeologists have interpreted some of the cratering features observed in Voyager images of the icy satellites of Jupiter, Saturn, and Uranus in terms of bombardment by planetesimals during the early evolution of the solar system (e.g., Plescia 1987). Potentially testable implications of the two component mixing model include: (1) low D/H ratios in  $CH_4$  because it originates from CO hydrogenation in the giant protoplanetary subnebulae, (2) a heterogeneous structure for the comet nucleus because it is a physical mixture of materials from two different nebular environments, (3) the

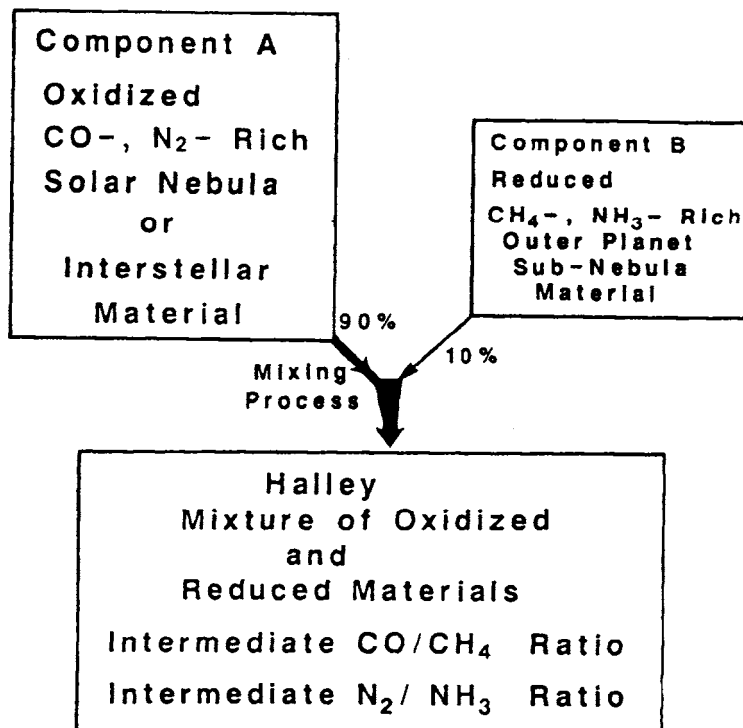


Figure 15. A schematic diagram illustrating the two component mixing model for the origin of volatiles in comet P/Halley (Prinn and Fegley 1989; Fegley and Prinn 1989). The inferred  $\text{CH}_4/\text{CO}$  and  $\text{NH}_3/\text{N}_2$  ratios in the coma of Halley are intermediate between those expected in the solar nebula and in the giant protoplanetary subnebulae. This implies that the volatiles emitted from Halley are a mixture of material from the solar nebula (and/or interstellar medium) and the giant protoplanetary subnebulae. The additional data on abundances of  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{S}$ , and POM, which have become available since this model was originally proposed, also can be interpreted in terms of grain catalyzed chemistry in the solar nebula (Fegley 1990, this paper). As discussed in the text, there is no firm evidence showing that comet P/Halley represents pristine interstellar material. Modified from Fegley and Prinn (1989).

presence of both clathrate hydrates formed in the giant protoplanetary subnebula and of pure ices formed in the solar nebula, and (4) the presence of both anhydrous rock from the solar nebula and hydrated silicates from the giant protoplanetary subnebulae.

### 12.3 NITROGEN COMPOUNDS

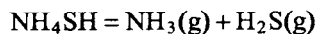
Now we consider the interpretation of the observed abundances of nitrogen compounds in comet Halley. Prinn and Fegley (1989) and Fegley and Prinn (1989) pointed out that the  $\text{NH}_3/\text{H}_2\text{O}$  ratio of  $\sim 0.005\text{--}0.02$  and the  $\text{N}_2/\text{NH}_3$  ratio of  $\sim 0.002\text{--}0.025$  in Halley are incompatible with either a solely solar nebula ( $\text{N}_2/\text{NH}_3 \sim 170$ ) or a solely subnebula source ( $\text{N}_2/\text{NH}_3 \sim 0.0005$ ). However, like the  $\text{CO}/\text{CH}_4$  ratio, the  $\text{N}_2/\text{NH}_3$  ratio can be explained by the mixing of material from these two different environments. On the other hand, the observed  $\text{NH}_3$  abundances in the hot core of the OMC-1 molecular cloud (Blake et al 1987) have led Lunine (1989) and Engel et al (1989) to suggest an interstellar source for the  $\text{NH}_3$  in Halley. Wyckoff, Tegler, and Engel (1991a) have also proposed an interstellar source on the basis of the very similar ammonia abundances they derived for four comets. They argued that a two component mixing process would be unlikely to give similar abundances in four comets with different dynamical characteristics. Again, the two alternatives can probably be tested by measuring the D/H isotopic ratio in the  $\text{NH}_3$ , because the interstellar source should give a substantially higher D/H ratio than the giant protoplanetary subnebula source.

The origin of HCN in Halley is also interesting. Fegley (1990) discussed the possibility that the HCN in Halley originated from lightning induced shock chemistry in nebular environments. This is an intriguing mechanism because nebular lightning has been suggested as a mechanism for chondrule formation (e.g., Cameron 1966; Whipple 1966). However, Prinn and Fegley (1989) noted that nebular lightning may also have distinctive chemical consequences. The high temperatures (several times  $10^3$  K) reached in lightning discharges lead to increasing degrees of molecular dissociation, atomization, and ionization with increasing temperatures. The recombination of these simple fragments during the rapid cooling of the shocked gas leads initially to the production of more complex fragments, then to thermally stable molecules such as HCN. Sufficiently rapid cooling quenches these stable molecules at their high temperature abundances, which are generally enhanced over their equilibrium abundances at much lower temperatures. Lightning is a potentially significant source of disequilibrium products, especially in the outer nebula beyond the water ice condensation front where comets are generally believed to have originated.

Prinn and Fegley (1989) modelled lightning induced shock chemistry in the solar nebula and in the giant protoplanetary subnebulae as adiabatic shock heating and predicted that the maximum HCN concentrations in these two environments occurred near temperatures of 3000–4000 K where  $\sim (0.2\text{--}6) \times 10^{18}$  HCN molecules are formed per mole of shocked gas. This corresponds to maximum conversions of  $\sim 0.3\%$  (in the solar nebula) and  $\sim 6.5\%$  (in the Jovian protoplanetary subnebula) of total nitrogen into HCN. This compares favorably with Halley where the  $\text{NH}_3/\text{H}_2\text{O}$  ratio of  $\sim 0.005\text{--}0.02$  and the  $\text{HCN}/\text{H}_2\text{O}$  ratio of  $\sim 0.001$  correspond to a  $\text{HCN}/\text{NH}_3$  ratio of  $\sim 0.05\text{--}0.2$ . Thus, as proposed by Fegley (1990) the HCN in Halley can be explained on the basis of lightning induced shock chemistry in either nebular environment, but only small dilution factors ( $<20$  times in the solar nebula and  $<70$  times in the Jovian subnebula) of the shocked gas by the unshocked gas are implied. Fegley (1990) noted that the low  $^{12}\text{C}/^{13}\text{C}$  ratio of  $65 \pm 9$  derived for CN emitted by Halley (Wyckoff et al 1989) posed a problem for this model, but with the upward revision of the carbon isotopic ratio to an Earth-like value (Kleine et al 1991) this problem disappears.

## 12.4 SULFUR COMPOUNDS

Here we focus on H<sub>2</sub>S and S<sub>2</sub>. The H<sub>2</sub>S/H<sub>2</sub>O ratio in Halley is in the range of 0.003-0.022, which is similar to the NH<sub>3</sub>/H<sub>2</sub>O ratio of ~ 0.005-0.02. This suggests that the two gases are produced in equimolar amounts by the decomposition of NH<sub>4</sub>SH. Ammonium hydrosulfide is a fairly volatile compound which can be formed in the solar nebula if not all sulfur reacts with Fe metal grains to form troilite. This could occur if accretion were sufficiently rapid to remove the metal from contact with the gas or if large chunks of metal reacted inefficiently with the nebula gas. Fegley and Lewis (1980) calculated that NH<sub>4</sub>SH would form at 134 K if a pure heterogeneous accretion model was adopted. Grains of NH<sub>4</sub>SH emitted from the nucleus of comet Halley will decompose according to the reaction



which has the equilibrium constant (Kelley 1937)

$$\log K = \log(P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}}) = 15.20 - 4823/T$$

Thus, the NH<sub>4</sub>SH source explains the approximately equimolar amounts of NH<sub>3</sub> and H<sub>2</sub>S observed in Halley. It also alleviates the need to postulate an extremely low temperature to preserve H<sub>2</sub>S ice (e.g., Crovisier et al 1991). Ammonium hydrosulfide also provides a nebular source for H<sub>2</sub>S at an abundance level lower than the solar S/H<sub>2</sub>O ratio, because most of the sulfur has already reacted with Fe at higher temperatures to form troilite. The amounts of sulfur left to form NH<sub>4</sub>SH will clearly depend on the efficiency with which troilite formation occurs, but this is not easily quantified. Another attractive feature of NH<sub>4</sub>SH is that it is a potential source of the S<sub>2</sub> observed in comet IRAS-Araki-Alcock (1983d) by A'Hearn et al (1983). Grim and Greenberg (1986) have shown that S<sub>2</sub> can be produced by the UV irradiation of sulfur-bearing simulated interstellar ices. However, the work of Lebofsky and Fegley (1976) on the UV irradiation of NH<sub>4</sub>SH led to the production of more complex sulfur compounds, such as polysulfides. They did not specifically look for S<sub>2</sub>, but it is conceivable that it is also produced by UV irradiation of NH<sub>4</sub>SH at sufficiently low temperatures.

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## References

- Abelson, P.H. 1966. Chemical events on the primitive Earth. *Proc. Natl. Acad. Sci. (USA)* **55**, 1365-1372.
- A'Hearn, M.F., P.D. Feldman, and D.G. Schleicher 1983. The discovery of S<sub>2</sub> in comet IRAS-Araki-Alcock 1983d. *Astrophys. J. Lett.* **274**, L99-L103.
- Allen, M., M. Delitsky, W. Huntress, Y. Yung, W.H. Ip, R. Schwenn, H. Rosenbauer, E. Shelley, H. Balsiger, and J. Geiss 1987. Evidence for methane and ammonia in the coma of comet Halley. *Astron. Astrophys.* **187**, 502-512.
- Altenhoff, W.J., W. Bartla, W.K. Huchtmeier, J. Schmidt, P. Stumpff, and M. Walmsley 1983. Radio observations of comet 1983d. *Astron. Astrophys.* **187**, 502-512.
- Amari, S., E. Anders, A. Virag, and E. Zinner 1990. Interstellar graphite in meteorites. *Nature* **345**, 238-240.
- Anders, E. 1968. Chemical processes in the early solar system, as inferred from meteorites. *Acc. Chem. Res.* **1**, 289-298.
- Anders, E., and M. Ebihara 1982. Solar system abundances of the elements. *Geochim. Cosmochim. Acta* **46**, 2363-2380.
- Anders, E., and N. Grevesse 1989. Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197-214.
- Anders, E., R. Hayatsu, and M.H. Studier 1973. Organic compounds in meteorites. *Science* **182**, 781-790.
- Balsiger, H., K. Altwegg, F. Bühler, J. Geiss, A.G. Ghielmetti, B.E. Goldstein, R. Goldstein, P. Hemmerich, G. Kulzer, A.J. Lazarus, A. Meier, M. Neugebauer, U. Rettenmund, H. Rosenbauer, R. Schwen, E.G. Shelley, E. Ungstrup, and D.T. Young 1986. Ion composition and dynamics at comet Halley. *Nature* **321**, 330-334.
- Barber, D.J. 1985. Phyllosilicates and other layer-structured minerals in stony meteorites. *Clay Minerals* **20**, 415-454.
- Barshay, S.S. 1981. Combined condensation-accretion models of the terrestrial planets. Ph.D. thesis, Massachusetts Institute of Technology. 67pp.
- Barshay, S.S. and J.S. Lewis 1976. Chemistry of primitive solar material. *Ann. Rev. Astron. Astrophys.* **14**, 81-94.
- Bell, M.B., L.A. Avery, H.E. Matthews, P.A. Feldman, J.K.G. Watson, S.C. Madden, and W.M. Irvine 1988. A study of C<sub>3</sub>H<sub>2</sub> in cold interstellar clouds. *Astrophys. J.* **326**, 924-930.
- Bernatowicz, T., G. Fraundorf, T. Ming, E. Anders, B. Wopenka, E. Zinner, and P. Fraundorf 1987. Evidence for interstellar SiC in the Murray carbonaceous chondrite. *Nature* **330**, 728-730.
- Bernatowicz, T., S. Amari, E.K. Zinner, and R.S. Lewis 1991. Interstellar grains within interstellar grains. *Astrophys. J.* **373**, L73-L76.
- Biéumont, E., M. Baudoux, R.L. Kurucz, W. Ansbacher, and E.H. Pinnington 1991. The solar abundance of iron: a "final" word! *Astron. Astrophys.* **249**, 539-544.
- Biloen, P. and W.M.H. Sachtler 1981. Mechanism of hydrocarbon synthesis over Fischer-Tropsch catalysts. in *Advances in Catalysis*, ed. D.D. Eley, H. Pines, and P.B. Weisz, Academic Press, NY, pp. 165-216.
- Bischoff, A. and H. Palme 1987. Composition and mineralogy of refractory-metal-rich assemblages from a Ca,Al-rich inclusion in the Allende meteorite. *Geochim. Cosmochim. Acta* **51**, 2733-2748.

- Bjoraker, G.L., M.J. Mumma, and H.P. Larson 1989. The value of D/H in the Martian atmosphere: Measurements of HDO and H<sub>2</sub>O using the Kuiper Airborne Observatory. in *Abstracts of the Fourth International Conference on Mars*, pp. 69-70.
- Black, D.C. and R.O. Pepin 1969. Trapped neon in meteorites. II. *Earth Planet. Sci. Lett.* **6**, 395-405.
- Blake, G.A., E.C. Sutton, C.R. Masson, and T.G. Phillips 1987. Molecular abundances in OMC-1: The chemical composition of interstellar molecular clouds and the influence of massive star formation. *Astrophys. J.* **315**, 621-645.
- Blum, J.D., G.J. Wasserburg, I.D. Hutcheon, J.R. Beckett, and E.M. Stolper 1988. Origin of opaque assemblages in C3V meteorites: Implications for nebular and planetary processes. *Geochim. Cosmochim. Acta* **53**, 543-556.
- Boato, G. 1954. The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **6**, 209-220.
- Bockelée-Morvan, D. and J. Crovisier 1990. in *Asteroids, Comets, and Meteors III*, ed. C.I. Lagerkvist et al, Uppsala University Press, Uppsala, pp. 263-265.
- Bockelée-Morvan, D., P. Colom, J. Crovisier, D. Despois, and G. Paubert 1991. Microwave detection of hydrogen sulphide and methanol in comet Austin (1989c1). *Nature* **350**, 318-320.
- Boesgaard, A.M. and G. Steigman 1985. Big bang nucleosynthesis: Theories and observations. *Ann. Rev. Astron. Astrophys.* **23**, 319-379.
- Boice, D.C., W.F. Huebner, M.J. Sablik, and I. Konno 1990. Distributed coma sources and the CH<sub>4</sub>/CO ratio in comet Halley. *Geophys. Res. Lett.* **17**, 1813-1816.
- Bond, G.C. 1962. *Catalysis by Metals*, Academic Press, London.
- Boss, A.P., G.E. Morfill, and W.M. Tscharnutter 1989. Models of the formation and evolution of the solar nebula. in *The Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S.K. Atreya, J.B. Pollack, and M.S. Matthews, University of Arizona Press, Tucson, pp. 35-77.
- Boström, K. and K. Fredriksson 1966. Surface conditions of the Orgueil parent meteorite body as indicated by mineral associations. *Smithson. Misc. Coll.* **151**, No. 3, 39pp.
- Bradley, J.P. and D.E. Brownlee 1986. Analytical electron microscopy of thin-sectioned interplanetary dust particles. *Science* **231**, 1542-1544.
- Bradley, J.P., D.E. Brownlee, and P. Fraundorf 1984. Carbon compounds in interplanetary dust: Evidence for formation by heterogeneous catalysis. *Science* **223**, 56-58.
- Bradley, J.P., S.A. Sandford, and R.M. Walker 1988. Interplanetary dust particles. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, AZ, pp. 861-895.
- Bratton, R.J. and G.W. Brindley 1965. Kinetics of vapor phase hydration of magnesium oxide. Part 2. Dependence on temperature and water vapor pressure. *Trans. Faraday Soc.* **61**, 1017-1025.
- Briggs, M.H. 1963. Evidence for an extraterrestrial origin for some organic constituents of meteorites. *Nature* **197**, 1290.
- Brown, R.D. and E. Rice 1981. Interstellar deuterium chemistry. *Phil. Trans. Roy. Soc. London* **A303**, 523-533.
- Bunch T.E. and S. Chang 1980. Carbonaceous chondrites-II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543-1577.

- Burbidge, E.M., G.R. Burbidge, W.A. Fowler, and F. Hoyle 1957. Synthesis of the elements in stars. *Rev. Mod. Phys.* **29**, 547-650.
- Cameron, A.G.W. 1966. The accumulation of chondritic material. *Earth Planet. Sci. Lett.* **1**, 93-96.
- Cameron, A.G.W. 1973. Abundances of the elements in the solar system. *Space Sci. Rev.* **15**, 121-146.
- Cameron, A.G.W. 1978. Physics of the primitive solar accretion disk. *Moon and Planets* **18**, 5-40.
- Cameron, A.G.W. 1982. Elemental and nuclidic abundances in the solar system. in *Essays in Nuclear Astrophysics*, eds., C.A. Barnes, D.D. Clayton, and D.N. Schramm, Cambridge University Press, Cambridge, pp. 23-43.
- Cameron, A.G.W. 1985. Formation and evolution of the primitive solar nebula. in *Protostars and Planets II*, eds., D.C. Black and M.S. Matthews, University of Arizona Press, Tucson, pp. 1073-1099.
- Cameron, A.G.W. and M.B. Fegley 1982. Nucleation and condensation in the primitive solar nebula. *Icarus* **52**, 1-13.
- Cameron, A.G.W., S.A. Colgate, and L. Grossman 1973. Cosmic abundance of boron. *Nature* **243**, 204-207.
- Christoffersen, R. and P.R. Buseck 1983. Epsilon carbide: A low temperature component of interplanetary dust particles. *Science* **222**, 1327-1329.
- Clarke, F.W. 1889. The relative abundances of the chemical elements. *Bull. Phil. Soc. Washington* **11**, 131.
- Clayton, R.N. and T.K. Mayeda 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67**, 151-161.
- Clayton, R.N., L. Grossman, and T.K. Mayeda 1973. A component of primitive nuclear composition in carbonaceous meteorites. *Science* **182**, 485-488.
- Combes, M., V.I. Moroz, J. Crovisier, T. Encrenaz, J.P. Bibiring, A.V. Grigoriev, N.F. Sanko, N. Coron, J.F. Crifo, R. Gispert, D. Bockelée-Morvan, Y.U. Nikolsky, V.A. Krasnopolsky, T. Owen, C. Emerich, J.M. Lamarre, and F. Rocard 1988. The 2.5 - 12  $\mu\text{m}$  spectrum of comet Halley from the IKS-Vega experiment. *Icarus* **76**, 404-436.
- Coustenis, A., B. Bézard, and D. Gautier 1989. Titan's atmosphere from Voyager infrared observations II. The  $\text{CH}_3\text{D}$  abundance and D/H ratio from the 900-1200  $\text{cm}^{-1}$  spectral region. *Icarus* **82**, 67-80.
- Crovisier, J., D. Despois, D. Bockelée-Morvan, P. Colom, and G. Paubert 1991. Microwave observations of hydrogen sulfide and searches for other sulfur compounds in comets Austin (1989c1) and Levy (1990c). *Icarus* **93**, 246-258.
- Danks, A.C., D.L. Lambert, and C. Arpigny 1974. The  $^{12}\text{C}/^{13}\text{C}$  ratio in comet Kohoutek (1973f). *Astrophys. J.* **194**, 745-751.
- Davidson, D.W., M.A. Desando, S.R. Gough, Y.P. Handa, C.I. Ratcliffe, J.A. Ripmeester, and J.S. Tse 1987. A clathrate hydrate of carbon monoxide. *Nature* **328**, 418-419.
- DeBergh, C., B.L. Lutz, T. Owen, J. Brault, and J. Chauville 1986. Monodeuterated methane in the outer solar system. II. Its detection on Uranus at 1.6 microns. *Astrophys. J.* **311**, 501-510.
- DeBergh, C., B.L. Lutz, T. Owen, and J.P. Maillard 1990. Monodeuterated methane in the outer solar system. IV. Its detection and abundance on Neptune. *Astrophys. J.* **355**, 661-666.
- DeBergh, C., B. Bézard, T. Owen, D. Crisp, J.P. Maillard, and B.L. Lutz 1991. Deuterium on Venus: Observations from Earth. *Science* **251**, 547-549.

- Delsemme, A.H. 1976. Chemical nature of the cometary snows. *Mém. Soc. Roy. Sci. Liège IX*, 135-145.
- Delsemme, A.H. 1982. Chemical composition of cometary nuclei. in *Comets*, ed. L.L. Wilkening, University of Arizona Press, Tucson, pp. 85-130.
- Delsemme, A.H. 1988. The chemistry of comets. *Phil. Trans. Roy. Soc. London A325*, 509-523.
- Delsemme, A.H. and D.C. Miller 1970. Physico-chemical phenomena in comets--II. Gas adsorption in the snows of the nucleus. *Planet. Space Sci.* **18**, 717-730.
- Delsemme, A.H. and P. Swings 1952. Hydrates de gaz dans les Noyaux Cométaires et les Grains Interstellaires. *Annales d'Astrophys.* **15**, 1-6.
- Delsemme, A.H. and A. Wenger, Physico-chemical phenomena in comets--I. Experimental study of snows in a cometary environment. *Planet. Space Sci.* **18**, 709-715.
- dePater, I., P. Palmer, and L.E. Snyder 1991. A review of radio interferometric imaging of comets. in *Comets in the Post-Halley Era*, ed. R. Newburn and J. Rahe, Kluwer Academic Publishers, Dordrecht, Netherlands.
- Despois, D., J. Crovisier, D. Bockelée-Morvan, J. Schraml, T. Forveille, and E. Gerard 1986. Observations of hydrogen cyanide in comet Halley. *Astron. Astrophys.* **160**, L11-L12.
- Dictor, R.A. and A.T. Bell 1986. Fischer-Tropsch synthesis over reduced and unreduced iron oxide catalysts. *J. Catalysis* **97**, 121-136.
- Donahue, T.M., J.H. Hoffman, R.R. Hodges, Jr., and A.J. Watson 1982. Venus was wet: A measurement of the ratio of D to H. *Science* **216**, 630-633.
- Drapatz, S., H.P. Larson, and D.S. Davis 1987. Search for methane in comet P/Halley. *Astron. Astrophys.* **187**, 497-501.
- Dry, M.E. 1981. The Fischer-Tropsch synthesis. in *Catalysis Science and Technology*, vol. 1, eds., J.R. Anderson and M. Boudart, Springer-Verlag, Berlin, pp. 159-255.
- Dry, M.E., T. Shingles, and L.J. Boshoff 1972. Rate of the Fischer-Tropsch reaction over iron catalysts. *J. Catalysis* **25**, 99-104.
- DuFresne, E.R. and E. Anders 1962. On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26**, 1085-1114.
- Eberhardt, P., D. Krankowsky, W. Schulte, U. Dolder, P. Lämmerzahl, J.J. Berthelier, J. Woweries, U. Stubbemann, R.R. Hodges, J.H. Hoffman, and J.M. Illiano 1987a. The CO and N<sub>2</sub> abundance in comet P/Halley. *Astron. Astrophys.* **187**, 481-484.
- Eberhardt, P., U. Dolder, W. Schulte, D. Krankowsky, P. Lämmerzahl, J.H. Hoffman, R.R. Hodges, J.J. Berthelier, and J.M. Illiano 1987b. The D/H ratio in water from comet P/Halley. *Astron. Astrophys.* **187**, 435-437.
- Eberhardt, P., R. Meir, D. Krankowsky, and R.R. Hodges 1991. Methanol abundance in comet P/Halley from in-situ measurements. *Bull. Amer. Astron. Soc.* **23**, 1161.
- El Goresy, A., K. Nagel, and P. Ramdohr 1978. Fremdlinge and their noble relatives. *Proc. Lunar Planet. Sci. Conf.* **9**, 1249-1266.
- Engel, S., J.I. Lunine, and J.S. Lewis 1990. Solar nebula origin for volatile gases in Halley's comet. *Icarus* **85**, 380-393.
- Fegley, B., Jr. 1983. Primordial retention of nitrogen by terrestrial planets and meteorites. *Proc. 13th Lunar Planet. Sci. Conf. J. Geophys. Res.* **88**, A853-A868.
- Fegley, B., Jr., 1988. Cosmochemical trends of volatile elements in the solar system. in *Workshop on the Origins of Solar Systems*, ed. J.A. Nuth and P. Sylvester, LPI Technical Report No. 88-04, pp. 51-60.



- Fegley, B., Jr. 1990. Disequilibrium chemistry in the solar nebula and early solar system: Implications for the chemistry of comets. in *Proc. of the Comet Nucleus Sample Return Workshop*, ed. S. Chang, NASA CP, in press.
- Fegley, B., Jr. and T.R. Ireland 1991. Chemistry of the rare earth elements in the solar nebula. *European J. Solid State Inorg. Chem.* **28**, 335-346.
- Fegley, B., Jr., and A.S. Kornacki 1984. The geochemical behavior of refractory noble metals and lithophile trace elements in refractory inclusions in carbonaceous chondrites. *Earth Planet. Sci. Lett.* **68**, 181-197.
- Fegley, B. Jr., and J.S. Lewis 1980. Volatile element chemistry in the solar nebula: Na, K, F, Cl, Br, and P. *Icarus* **41**, 439-455.
- Fegley, B., Jr., and H. Palme 1985. Evidence for oxidizing conditions in the solar nebula from Mo and W depletions in refractory inclusions in carbonaceous chondrites. *Earth Planet Sci. Lett.* **72**, 311-326.
- Fegley, B., Jr. and R.G. Prinn 1988. The predicted abundances of deuterium-bearing gases in the atmospheres of Jupiter and Saturn. *Astrophys. J.* **326**, 490-508.
- Fegley, B., Jr., and R.G. Prinn 1989. Solar nebula chemistry: Implications for volatiles in the solar system. in *The Formation and Evolution of Planetary Systems*, eds. H.A. Weaver and L. Danly, Cambridge University Press, Cambridge, pp. 171-211.
- Feldman, P.D. 1991. Ultraviolet spectroscopy of cometary comae. in *Comets in the Post-Halley Era*, ed. R. Newburn and J. Rahe, Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 139-148.
- Festou, M.C., P.D. Feldman, M.F. A'Hearn, C. Arpigny, C.B. Cosmovici, A.C. Danks, L.A. McFadden, R. Gilmozzi, P. Patriarchi, G.P. Tozzi, M.K. Wallis, and H.A. Weaver 1986. IUE observations of comet Halley during the Vega and Giotto encounters. *Nature* **321**, 361-363.
- Fredriksson, K. and J.F. Kerridge 1988. Carbonates and sulfates in CI chondrites: Formation by aqueous activity on the parent body. *Meteoritics* **23**, 35-44.
- Fuchs, L. and M. Blander 1980. Refractory metal particles in refractory inclusions in the Allende meteorite. *Proc. Lunar Planet. Sci. Conf.* **11**, 929-944.
- Geballe, T.R., F. Bass, J.M. Greenberg, and W. Schutte 1985. New infrared absorption features due to solid phase molecules containing sulfur in W33A. *Astron. Astrophys.* **146**, L6-L8.
- Geiss, J. and H. Reeves 1981. Deuterium in the solar system. *Astron. Astrophys.* **93**, 189-199.
- Geiss, J., K. Altwegg, E. Anders, H. Balsiger, W.H. Ip, A. Meier, M. Neugebauer, H. Rosenbauer, and E.G. Shelley 1991. Interpretation of the ion mass spectra in the mass per charge range 25-35 amu/e<sup>-</sup> obtained in the inner coma of Halley's comet by the HIS-sensor of the Giotto IMS experiment. *Astron. Astrophys.* **247**, 226-234.
- Gerin, M., H.A. Wooten, F. Combes, F. Boulanger, W.L. Peters, T.B.H. Kuiper, P.J. Encrenaz, and M. Bogey 1987. Deuterated C<sub>2</sub>H<sub>2</sub> as a clue to deuterium chemistry. *Astron. Astrophys.* **173**, L1-L4.
- Goldschmidt, V.M. 1937. Geochemische Verteilungsgesetze der Elemente IX. *Skrifter Norske Videnskaps-Akademiend, Oslo I. mat. Natur. Kl.* No. 4.
- Goldschmidt, V.M. 1954. *Geochemistry*, Oxford: Clarendon Press.
- Greenberg, J.M. 1991. Physical, chemical, and optical interactions with interstellar dust. in *Chemistry in Space*, ed. J.M. Greenberg and V. Pirronello, Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 227-261.
- Grevesse, N. 1984. Abundances of the elements in the Sun. in *Frontiers of Astronomy and Astrophysics*, ed. R. Pallavicini, Ital. Astron. Soc., Florence, Italy, pp. 71-82.

- Grevesse, N., D.L. Lambert, A.J. Sauval, E.F. van Dishoeck, C.B. Farmer, and R.H. Norton 1990. Identification of solar vibration-rotation lines of NH and the solar nitrogen abundance. *Astron. Astrophys.* **232**, 225-230.
- Grevesse, N., D.L. Lambert, A.J. Sauval, E.F. van Dishoeck, C.B. Farmer, and R.H. Norton 1991. Vibration-rotation bands of CH in the solar infrared spectrum and the solar carbon abundance. *Astron. Astrophys.* **242**, 488-495.
- Grim, R.J.A. and J.M. Greenberg 1987. Photoprocessing of H<sub>2</sub>S in interstellar grain mantles as an explanation for S<sub>2</sub> in comets. *Astron. Astrophys.* **181**, 155-168.
- Grinspoon, D.H. and J.S. Lewis 1987. Deuterium fractionation in the presolar nebula: Kinetic limitations on surface catalysis. *Icarus* **72**, 430-436.
- Grossman, L. 1972. Condensation in the primitive solar nebula. *Geochim. Cosmochim. Acta* **36**, 597-619.
- Grossman, L. and J.W. Larimer 1974. Early chemical history of the solar system. *Rev. Geophys. Space Phys.* **12**, 71-101.
- Guélin, M., W.D. Langer, and R.W. Wilson 1982. The state of ionization in dense molecular clouds. *Astron. Astrophys.* **107**, 107-127.
- Hagemann, R., G. Nief, and E. Roth 1970. Absolute isotopic scale for deuterium analysis of natural waters. Absolute D/H ratio for SMOW. *Tellus* **22**, 712-715.
- Haltenorth, H. and J. Klinger 1969. Diffusion of hydrogen fluoride in ice. in *Physics of Ice*, ed. N. Riehl, B. Bullemer, and H. Engelhardt, Plenum Press, NY, pp. 579-584.
- Hashimoto, A. and L. Grossman 1987. Alteration of Al-rich inclusions inside amoeboid olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta* **51**, 1685-1704.
- Hayatsu, R. and E. Anders 1981. Organic compounds in meteorites and their origins. *Topics in Current Chemistry* **99**, 1-39.
- Herbst, E., N.G. Adams, D. Smith, and D.J. DeFrees 1987. Ion-molecule calculation of the abundance ratio of CCD to CCH in dense interstellar clouds. *Astrophys. J.* **312**, 351-357.
- Hoban, S., M. Mumma, D.C. Reuter, M. DiSanti, R.R. Joyce, and A. Storrs 1991. A tentative identification of methanol as the progenitor of the 3.52  $\mu$ m emission feature in several comets. *Icarus* **93**, 122-134.
- Holweger, H., C. Heise, and M. Kock 1990. The abundance of iron in the Sun derived from photospheric Fe II lines. *Astron. Astrophys.* **232**, 510-515.
- Huebner, W.F. 1987. First polymer in space identified in comet Halley. *Science* **237**, 628-630.
- Huebner, W.F., D.C. Boice, and C.M. Sharp 1987. Polyoxymethylene in comet Halley. *Astrophys. J.* **320**, L149-L152.
- Huebner, W.F., L.E. Snyder, and D. Buhl 1974. HCN radio emission from comet Kohoutek (1973f). *Icarus* **23**, 580-584.
- Huntress, W.T., M. Allen, and M. Delitsky 1991. Carbon suboxide in comet Halley? *Nature* **352**, 316-318.
- Ip, W.H., H. Balsiger, J. Geiss, B.E. Goldstein, G. Kettman, A.J. Lazarus, A. Meier, H. Rosenbauer, R. Schwenn, and E. Shelley 1990. Giotto IMS measurements of the production rate of hydrogen cyanide in the coma of comet Halley. *Ann. Geophys.* **8**, 319-326.
- Irvine, W.M. and R.F. Knacke 1989. The chemistry of interstellar gas and grains in *The Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S.K. Atreya, J.B. Pollack, and M.S. Matthews, University of Arizona Press, Tucson, pp. 3-34.
- Jeffery, P.M. and J.H. Reynolds 1961. Origin of excess <sup>129</sup>Xe in stone meteorites. *J. Geophys. Res.* **66**, 3582-3583.

- Kawara, K., B. Gregory, T. Yamamoto, and H. Shibai 1988. Infrared spectroscopic observation of methane in comet P/Halley. *Astron. Astrophys.* **207**, 174-181.
- Kelley, K.K. 1937. *Contributions to the Data on Theoretical Metallurgy VII. The Thermodynamic Properties of Sulphur and its Inorganic Compounds*, U.S. Bureau of Mines Bull. No. 406, U.S. GPO, Washington, D.C.
- Kerridge, J.F., A.L. MacKay, and W.V. Boynton 1979. Magnetite in CI carbonaceous meteorites: Origin by aqueous activity on a planetesimal surface. *Science* **205**, 395-397.
- Kim, S.J. and M.F. A'Hearn 1991. Upper limits of SO and SO<sub>2</sub> in comets. *Icarus* **90**, 79-95.
- Kim, S.J., M.F. A'Hearn, and S.M. Larson 1990. Multi-cycle fluorescence: Application to S<sub>2</sub> in Comet IRAS-Araki-Alcock 1983 VII. *Icarus* **87**, 440-451.
- Kleine, M., S. Wyckoff, P.A. Wehinger, and B.A. Peterson 1991. The carbon isotope abundance ratios in comets. *Bull. Amer. Astron. Soc.* **23**, 1166.
- Kornacki, A.S., and B. Fegley, Jr. 1984. Origin of spinel-rich chondrules and inclusions in carbonaceous and ordinary chondrites. *Proc. 14th Lunar Planet. Sci. Conf. J. Geophys. Res.* **89**, B588-B596.
- Kornacki, A.S., and B. Fegley, Jr. 1986. The abundance and relative volatility of refractory trace elements in Allende Ca, Al-rich inclusions: Implications for chemical and physical processes in the solar nebula. *Earth Planet. Sci. Lett.* **75**, 297-310.
- Korth, A., A. K. Richter, A. Loidl, K.A. Anderson, C.W. Carlson, D.W. Curtis, R.P. Lin, H. Réme, J.A. Sauvaud, C. d'Uston, F. Cotin, A. Cros, and D.A. Mendis 1986. Mass spectra of heavy ions near comet Halley. *Nature* **321**, 335-336.
- Kozasa, T. and H. Hasegawa 1988. Formation of iron-bearing materials in a cooling gas of solar composition. *Icarus* **73**, 180-190.
- Krankowsky, D. 1991. The composition of comets. in *Comets in the Post-Halley Era*, ed. R.L. Newburn, J. Rahe, and M. Neugebauer, Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 855-877.
- Krankowsky, D., P. Lämmerzahl, I. Herrwerth, J. Woweries, P. Eberhardt, U. Dolder, U. Herrmann, W. Schulte, J.J. Berthelier, J.M. Iliano, R.R. Hodges, and J.H. Hoffmann 1986. *In situ* gas and ion measurements at comet Halley. *Nature* **321**, 326-330.
- Krebs, H.J., H.P. Bonzel, and G. Gafner 1979. A model study of the hydrogenation of CO over polycrystalline iron. *Surface Sci.* **88**, 269-283.
- Lacy, J.H., J.S. Carr, N.J. Evans II, F. Baas, J.M. Achtermann, and J.F. Arens 1991. Discovery of interstellar methane: observations of gaseous and solid CH<sub>4</sub> absorption toward young stars in molecular clouds. *Astrophys. J.* **376**, 556-590.
- Langer, W.D., F.P. Schloerb, R.L. Snell, and J.S. Young 1980. Detection of deuterated cyanoacetylene in the interstellar cloud TMC-1. *Astrophys. J.* **239**, L125-L128.
- Larimer, J.W. 1967. Chemical fractionations in meteorites--I. Condensation of the elements. *Geochim. Cosmochim. Acta* **31**, 1215-1238.
- Larimer, J.W., 1973. Chemical fractionations in meteorites--VII. Cosmothermometry and cosmobarometry. *Geochim. Cosmochim. Acta* **37**, 1603-1623.
- Larimer, J.W. 1975. The effect of C/O ratio on the condensation of planetary material, *Geochim. Cosmochim. Acta* **39**, 389-392.
- Larimer, J.W. 1988. The cosmochemical classification of the elements. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, pp. 375-389, Tucson: University of Arizona Press.
- Larimer, J.W. and E. Anders 1967. Chemical fractionations in meteorites, 2, Abundance patterns and their interpretation. *Geochim. Cosmochim. Acta* **31**, 1239-1270.

- Larimer, J.W. and M. Bartholomay 1979. The role of carbon and oxygen in cosmic gases: some applications to the chemistry and mineralogy of enstatite chondrites, *Geochim. Cosmochim. Acta* **43**, 1453-1466.
- Larson, H.P., H.A. Weaver, M.J. Mumma, and S. Drapatz 1989. Airborne infrared spectroscopy of comet Wilson (1986I) and comparisons with comet Halley. *Astrophys. J.* **338**, 1106-1114.
- Latimer, W.M. 1950. Astrochemical problems in the formation of the Earth. *Science* **112**, 101-104.
- Layden, G.K. and G.W. Brindley 1963. Kinetics of vapor phase hydration of magnesium oxide. *J. Amer. Ceram. Soc.* **46**, 518-522.
- Lebofsky, L.A. and M.B. Fegley, Jr. 1976. Laboratory reflection spectra for the determination of chemical composition of icy bodies. *Icarus* **28**, 379-387.
- Lecluse, C. and F. Robert 1992. Origin of the deuterium enrichment in the solar system. *Meteoritics* **27**, 248.
- Lee, T. 1988. Implications of isotopic anomalies for nucleosynthesis. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 1063-1089
- Lewis, J.S. 1972a. Metal/silicate fractionation in the solar system. *Earth Planet. Sci. Lett.* **15**, 286-290.
- Lewis, J.S. 1972b. Low temperature condensation from the solar nebula. *Icarus* **16**, 241-252.
- Lewis, J.S. 1974. The temperature gradient in the solar nebula. *Science* **136**, 440-443.
- Lewis, J.S., S.S. Barshay, and B. Noyes 1979. Primordial retention of carbon by the terrestrial planets. *Icarus* **37**, 190-206.
- Lewis, J.S., and R.G. Prinn 1980. Kinetic inhibition of CO and N<sub>2</sub> reduction in the solar nebula. *Astrophys. J.* **238**, 357-364.
- Lewis, R.S., T. Ming, J.F. Wacker, E. Anders, and E. Steel 1987. Interstellar diamonds in meteorites. *Nature* **326**, 160-162.
- Lin, D.N.C. and J. Papaloizou 1985. On the dynamical origin of the solar system in *Protostars and Planets II*, ed. D.C. Black and M.S. Matthews, University of Arizona Press, Tucson, pp. 981-1072.
- Lohn, B. and A. El Goresy 1992. Morphologies and chemical composition of individual magnetite grains in CI and CM chondrites: A potential genetic link to their origin? *Meteoritics* **27**, 252.
- Lunine, J.I., 1989. Primitive bodies: Molecular abundances in comet Halley as probes of cometary formation environments. in *The Formation and Evolution of Planetary Systems*, ed. H.A. Weaver and L. Danly, Cambridge University Press, Cambridge, pp. 213-242.
- Lunine, J.I. and D.S. Stevenson 1985. Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. *Astrophys. J. Suppl.* **58**, 493-531.
- Lunine, J.I., S. Engel, B. Rizk, and M. Horanyi 1991. Sublimation and reformation of icy grains in the primitive solar nebula. *Icarus* **94**, 333-344.
- MacLeod, J.M., J.W. Avery, and N.W. Broten 1981. Detection of deuterated cyanodiacetylene (DC<sub>2</sub>N) in Taurus Molecular Cloud 1. *Astrophys. J.* **251**, L33-L36.
- MacPherson, G.J., D.A. Wark, and J.T. Armstrong 1988. Primitive material surviving in chondrites: Refractory inclusions. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 746-807.
- Marconi, M.L. and D.A. Mendis 1988. On the ammonia abundance in the coma of Halley's comet. *Astrophys. J.* **330**, 513-517.

- Marconi, M.L., D.A. Mendis, A. Korth, R.P. Lin, D.L. Mitchell, and H. Réme 1990. The identification of  $\text{H}_3\text{S}^+$  with the ion of mass per charge (m/q) 35 observed in the coma of comet Halley. *Astrophys. J.* **352**, L17-L20.
- Mason, B. (ed.) 1971. *Handbook of Elemental Abundances in Meteorites*. Gordon & Breach, New York.
- Mason, B. 1979. Cosmochemistry. Part 1. Meteorites. in *Data of Geochemistry, Sixth Edition*, ed. M. Fleischer, Geol. Surv. Prof. Paper 440-B-1, U.S. Govt. Print. Office, Washington, D.C.
- Meier, R., P. Eberhardt, D. Krankowsky, and R.R. Hodges, The spatial distribution of the hydrogen sulfide and formaldehyde sources in comet P/Halley, *Bull. Amer. Astron. Soc.* **23**, 1167, 1991.
- Mendybayev, R.A., A.B. Makalkin, V.A. Dorofeyeva, I.L. Khodakovsky, and A.K. Lavrukina 1986. The role of CO and  $\text{N}_2$  reduction kinetics in the chemical evolution of the protoplanetary cloud. *Geochem. Intl.* **8**, 105-116.
- Miller, S.L. 1961. The occurrence of gas hydrates in the solar system. *Proc. Natl. Acad. Sci. USA* **47**, 1798-1808.
- Miller, S.L. 1969. Clathrate hydrates of air in antarctic ice. *Science* **165**, 489-490.
- Miller, S.L. and W.D. Smythe 1970. Carbon dioxide clathrate in the Martian ice cap. *Science* **170**, 531-533.
- Misener, D.J. 1974. Cationic diffusion in olivine to 1400°C and 35 kbar. in *Geochemical Transport and Kinetics*, edited by A.W. Hofmann, B.J. Gilletti, H.S. Yoder, Jr., and R.A. Yund, Carnegie Institution of Washington, Washington, D.C., pp. 117-129.
- Mitchell, D.L., R.P. Lin, K.A. Anderson, C.W. Carlson, D.W. Curtis, A. Korth, H. Réme, J.A. Sauvaud, C. d'Uston, and D.A. Mendis 1987. Evidence for chain molecules enriched in carbon, hydrogen, and oxygen in comet Halley. *Science* **237**, 626-628.
- Mitchell, D.L., R.P. Lin, K.A. Anderson, C.W. Carlson, D.W. Curtis, A. Korth, H. Réme, J.A. Sauvaud, C. d'Uston, and D.A. Mendis 1989. Complex organic ions in the atmosphere of comet Halley. *Adv. Space Res.* **9**, 35-39.
- Morfill, G.E. and H.J. Volk 1984. Transport of dust and vapor and chemical fractionation in the early protosolar cloud. *Astrophys. J.* **287**, 371-395.
- Mumma, M.J. and D. Reuter 1989. On the identification of formaldehyde in Halley's comet. *Astrophys. J.*, **344**, 940-948.
- Mumma, M.J., W.E. Blass H.A. Weaver and H.P. Larson 1988. Measurements of the ortho-para ratio and nuclear spin temperature of water vapor in comets Halley and Wilson (1986I) and implications for their origin and evolution. in *The Formation and Evolution of Planetary Systems: A Collection of Poster Papers*, ed. H.A. Weaver, F. Paresce, and L. Danly, STScI publication, pp. 157-168.
- Mumma, M.J., S.A. Stern, and P.R. Weissman 1992. Comets and the origin of the solar system: Reading the Rosetta stone. in *Protostars and Planets III*, ed. E.H. Levy, J.I. Lunine, and M.S. Matthews, University of Arizona Press, Tucson, in press.
- Mumma, M.J., H.A. Weaver and H.P. Larson 1987. The ortho-para ratio of water vapor in comet P/Halley. *Astron. Astrophys.* **187**, 419-424.
- Mumma, M.J., H.A. Weaver, H.P. Larson, D.S. Davis, and M. Williams 1986. Detection of water vapor in Halley's comet. *Science* **232**, 1523-1528.
- Niederer, F.R., D.A. Papanastassiou, and G.J. Wasserburg 1980 Endemic isotopic anomalies in titanium. *Astrophys. J.* **240**, L73-L77.

- Niemeyer, S. and G.W. Lugmair 1984. Titanium isotopic anomalies in meteorites. *Geochim. Cosmochim. Acta* **48**, 1401-1416.
- Olberg, M., M. Bester, G. Rau, T. Pauls, G. Winnewisser, L.E.B. Johansson, and Å. Hjalmarsson 1985. A new search for and discovery of deuterated ammonia in three molecular clouds. *Astron. Astrophys.* **142**, L1-L4.
- Ormont, A. 1991. Circumstellar chemistry. in *Chemistry in Space*, ed. J.M. Greenberg and V. Pirronello, Kluwer Academic Publishers, Dordrecht, Netherlands, pp. 171-196.
- Oró, J. and A.P. Kimball 1961. Synthesis of purines under possible primitive Earth conditions. I. Adenine from hydrogen cyanide. *Arch. Biochem. Biophys.* **94**, 217-227.
- Owen, T. 1973. The isotope ratio  $^{12}\text{C}/^{13}\text{C}$  in comet Tago-Sato-Kosaka 1969g. *Astrophys. J.* **184**, 33-43.
- Owen, T., B.L. Lutz, and C. DeBergh 1986. Deuterium in the outer solar system: Evidence for two distinct reservoirs. *Nature* **320**, 244-246.
- Owen, T., J.P. Maillard, C. DeBergh, and B.L. Lutz 1988. Deuterium on Mars: The abundance of HDO and the value of D/H. *Science* **240**, 1767-1770.
- Palme, H., and B. Fegley, Jr. 1990. High-temperature condensation of iron-rich olivine in the solar nebula. *Earth Planet. Sci. Lett.* **101**, 180-195.
- Palme, H., and F. Wlotzka 1976. A metal particle from a Ca, Al-rich inclusion from the meteorite Allende, and the condensation of refractory siderophile elements. *Earth Planet. Sci. Lett.* **33**, 45-60.
- Pilcher, C.B., S.T. Ridgway, and T.B. McCord 1972. Galilean satellites: Identification of water frost. *Science* **178**, 1087-1089.
- Pillinger, C.T. 1984. Light element stable isotopes in meteorites – from grams to picograms. *Geochim. Cosmochim. Acta* **48**, 2739-2766.
- Plescia, J.B. 1987. Cratering history of the Uranian satellites: Umbriel, Titania, and Oberon. *J. Geophys. Res.* **92**, 14918-14932.
- Podosek, F.A. and T.D. Swindle 1988. Extinct radionuclides. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 1093-1113.
- Prinn, R.G. 1990. On neglect of non-linear momentum terms in solar nebula accretion disk models. *Astrophys. J.* **348**, 725-729.
- Prinn, R.G., and M.B. Fegley, Jr. 1981. Kinetic inhibition of CO and N<sub>2</sub> reduction in circumplanetary nebulae: Implications for satellite composition. *Astrophys. J.* **249**, 308-317.
- Prinn, R.G., and B. Fegley, Jr. 1989. Solar nebula chemistry: Origin of planetary, satellite, and cometary volatiles. in *The Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S.K. Atreya, J.B. Pollack, and M.S. Matthews, University of Arizona Press, Tucson, pp. 78-136.
- Rambaldi, E.R. and J.T. Wasson 1981. Metal and associated phases in Bishunpur, a highly unequilibrated ordinary chondrite. *Geochim. Cosmochim. Acta* **45**, 1001-1015.
- Rambaldi, E.R. and J.T. Wasson 1984. Metal and associated phases in Krymka and Chainpur: Nebular formational processes. *Geochim. Cosmochim. Acta* **48**, 1885-1897.
- Renshaw, G.D., C. Roscoe, and P.L. Walker, Jr. 1970. Disproportionation of CO I. Over iron and silicon-iron single crystals. *J. Catalysis* **18**, 164-183.
- Reynolds, J.H. 1960. Determination of the age of the elements. *Phys. Rev. Lett.* **4**, 8.
- Richardson, S.M. 1978. Vein formation in the CI carbonaceous chondrites. *Meteoritics* **13**, 141-159.

- Richet, P., Y. Bottinga, and M. Javoy 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Ann. Rev. Earth Planet. Sci.* **5**, 65-110.
- Ruden, S.P. and D.N.C. Lin 1986. The global evolution of the solar nebula. *Astrophys. J.* **308**, 883-901.
- Schloerb, F.P., R.L. Snell, W.D. Langer, and J.S. Young 1981. Detection of deuteriocyanobutadiyne (DC<sub>3</sub>N) in the interstellar cloud TMC-1. *Astrophys. J.* **251**, L37-L42.
- Schloerb, F.P., W.M. Kinzel, D.A. Swade, and W.M. Irvine 1987. Observations of HCN in comet P/Halley. *Astron. Astrophys.* **187**, 475-480.
- Sears, D.W. 1978. Condensation and the composition of iron meteorites. *Earth Planet. Sci. Lett.* **41**, 128-138.
- Shock, E.L. and M.D. Schulte 1990a. Amino-acid synthesis in carbonaceous meteorites by aqueous alteration of polycyclic aromatic hydrocarbons. *Nature* **343**, 728-731.
- Shock, E.L. and M.D. Schulte 1990b. Summary and implications of reported amino acid concentrations in the Murchison meteorite. *Geochim. Cosmochim. Acta* **54**, 3159-3173.
- Shukolyukov, A. and G.W. Lugmair 1992. First evidence for live <sup>60</sup>Fe in the early solar system. *Lunar Planet. Sci. XXIII*, pp. 1295-1296.
- Sill, G.T., and L.L. Wilkening 1978. Ice clathrate as a possible source of the atmospheres of the terrestrial planets. *Icarus* **33**, 13-22.
- Simonelli, D.P., J.B. Pollack, C.P. McKay, R.T. Reynolds, and A.L. Summers 1989. The carbon budget in the outer solar nebula. *Icarus* **82**, 1-35.
- Snyder, L.E., P. Palmer, and I. dePater 1989. Radio detection of formaldehyde emission from comet Halley. *Astron. J.* **97**, 246-253.
- Stawikowski, A. and J.L. Greenstein 1964. The isotope ratio <sup>12</sup>C/<sup>13</sup>C in a comet. *Astrophys. J.* **140**, 1280-1291.
- Stevenson, D.J. 1990. Chemical heterogeneity and imperfect mixing in the solar nebula. *Astrophys. J.* **348**, 730-737.
- Stevenson, D.J. and J.I. Lunine 1988. Rapid formation of Jupiter by diffusive redistribution of water vapor in the solar nebula. *Icarus* **75**, 146-155.
- Stewart, A.I.F. 1987. Pioneer Venus measurements of H, O, and C production in comet P/Halley near perihelion. *Astron. Astrophys.* **187**, 369-374.
- Strom, S.E., S. Edwards, and K.M. Strom 1989. Constraints on the properties and environment of primitive solar nebulae from the astrophysical record provided by young stellar objects. in *The Formation and Evolution of Planetary Systems*, ed. H.A. Weaver and L. Danly, Cambridge University Press, Cambridge, pp. 91-109.
- Studier, M.H., R. Hayatsu, and E. Anders 1968. Origin of organic matter in early solar system - I. Hydrocarbons. *Geochim. Cosmochim. Acta* **32**, 151-173.
- Suess, H.E. 1947a. Über kosmische Kernhäufigkeiten. I. Mitteilung: Einige Häufigkeitsregeln und ihre Anwendung bei der Abschätzung der Häufigkeitswerte für die mittelschweren und schweren Elemente. *Z. Naturforsch.* **2a**, 311-321.
- Suess, H.E. 1947b. Über kosmische Kernhäufigkeiten. II. Mitteilung: Einzelheiten in der Häufigkeitsverteilung der mittelschweren und schweren Kerne. *Z. Naturforsch.* **2a**, 604-608.
- Suess, H.E. 1965. Chemical evidence bearing on the origin of the solar system. *Ann. Rev. Astron. Astrophys.* **3**, 217-234.
- Suess, H.E., and H.C. Urey 1956. Abundances of the elements. *Rev. Mod. Phys.* **28**, 53-74.

- Tang, M. and E. Anders 1988. Isotopic anomalies of Ne, Xe, and C in meteorites. II. Interstellar diamond and SiC: Carriers of exotic noble gases. *Geochim. Cosmochim. Acta* **52**, 1235-1244.
- Tegler, S. and S. Wyckoff 1989. NH<sub>2</sub> fluorescence efficiencies and the NH<sub>3</sub> abundance in comet Halley. *Astrophys. J.* **343**, 445-449.
- Thiemens, M.H. 1988. Heterogeneity in the nebula: Evidence from stable isotopes. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 899-923.
- Tielens, A.G.G.M. 1983. Surface chemistry of deuterated molecules. *Astron Astrophys.* **119**, 177-184.
- Tielens, A.G.G.M. and L.J. Allamandola 1987. Evolution of interstellar dust. in *Physical Processes in Interstellar Clouds*, ed. G.E. Morfill and M. Scholer, D. Reidel, Netherlands, pp. 333-376.
- Tomeoka, K. and P.R. Buseck 1985. Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* **49**, 2149-2163.
- Turkdogan, E.T., W.M. McKewan, and L. Zwell 1965. Rate of oxidation of iron to wüstite in water-hydrogen gas mixtures. *J. Phys. Chem.* **69**, 327-334.
- Urey, H.C. 1952. *The Planets*, New Haven: Yale University Press.
- Urey, H.C. 1953. Chemical evidence regarding the Earth's origin. in *XIIIth International Congress Pure and Applied Chemistry and Plenary Lecture*, Almqvist & Wiksells, Stockholm, pp. 188-217.
- Vannice, M.A. 1975. The catalytic synthesis of hydrocarbons from H<sub>2</sub>/CO mixtures over the group VIII metals. *J. Catal.* **37**, 449-461.
- Vannice, M.A. 1982. Catalytic activation of carbon monoxide on metal surfaces. in *Catalysis Science and Technology*, vol. 3, eds. J.R. Anderson and M. Boudart, Springer-Verlag, Berlin, pp. 139-198.
- Vanýsek, V. 1977. Carbon isotope ratio in comets and interstellar medium. in *Comets, Asteroids, and Meteorites: Interrelations, Evolution, and Origins*, ed. A.H. Delsemme, University of Toledo Press, Toledo, OH, pp. 499-503.
- Virag, A., B. Wopenka, S. Amari, E. Zinner, E. Anders, and R.S. Lewis 1992. Isotopic, optical, and trace element properties of large single SiC grains from the Murchison meteorite. *Geochim. Cosmochim. Acta* **56**, 1715-1733.
- Wai, C.M., and J.T. Wasson 1977. Nebular condensation of moderately volatile elements and their abundances in ordinary chondrites. *Earth Planet. Sci. Lett.* **36**, 1-13.
- Wai, C.M., and J.T. Wasson 1979. Nebular condensation of Ga, Ge and Sb and the chemical classification of iron meteorites. *Nature* **282**, 790-793.
- Walmsley, C.M., W. Hermsen, C. Henkel, R. Mauersberger, and T.L. Wilson 1987. Deuterated ammonia in the Orion hot core. *Astron. Astrophys.* **172**, 311-315.
- Warnatz, J. 1984. Rate coefficients in the C/H/O system. in *Combustion Chemistry*, ed. W.C. Gardiner, Jr., Springer-Verlag, New York, pp. 197-360.
- Wasserburg, G.J. 1985. Short-lived nuclei in the early solar system. in *Protostars and Planets II*, eds., D.C. Black and M.S. Matthews, University of Arizona Press, Tucson, pp. 703-754.
- Wasson, J.T. 1985. *Meteorites*. New York: W.H. Freeman and Co.
- Weaver, H.A. 1989. The volatile composition of comets. in *Highlights of Astronomy* **8**, 387-393.



- Weaver, H.A., M.J. Mumma, and H.P. Larson 1991. Infrared spectroscopy of cometary parent molecules. in *Comets in the Post-Halley Era*, ed. R. Newburn and J. Rahe, Kluwer Academic Publishers, Dordrecht, Netherlands.
- Whipple, F.L. 1966. Chondrules: Suggestions concerning their origin. *Science* **153**, 54-56.
- Wood, J.A., and G.E. Morfill 1988. A review of solar nebula models. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 329-347.
- Woods, T.N., P.D. Feldman, K.F. Dymond, and D.J. Sahnou 1986. Rocket ultraviolet spectroscopy of comet Halley and abundance of carbon monoxide and carbon. *Nature* **324**, 436-438.
- Woolum, D.S. 1988. Solar-system abundances and processes of nucleosynthesis. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 995-1020.
- Wootten, A. 1987. Deuterated molecules in interstellar clouds. in *Astrochemistry*, eds. M.S. Vardya and S.P. Tarafdar, D. Reidel, Dordrecht, Netherlands, pp. 311-320.
- Worrell, W.L. and E.T. Turkdogan 1968. Iron-sulfur system, Part II: Rate of reaction of hydrogen sulfide with ferrous sulfide. *Trans. AIME* **242**, 1673-1678.
- Wyckoff, S., E. Lindholm, P.A. Wehinger, B.A. Peterson, J.M. Zucconi, and M.C. Festou 1989. The  $^{12}\text{C}/^{13}\text{C}$  abundance ratio in comet Halley. *Astrophys. J.* **339**, 488-500.
- Wyckoff, S. and J. Theobald 1989. Molecular ions in comets. *Adv. Space Res.* **9**(3), 157-161.
- Wyckoff, S., S. Tegler, and L. Engel 1989. Ammonia abundances in comets. *Adv. Space Res.* **9**(3), 169-176.
- Wyckoff, S., S. Tegler, and L. Engel 1991a. Ammonia abundances in four comets. *Astrophys. J.* **368**, 279-286.
- Wyckoff, S., S. Tegler, and L. Engel 1991b. Nitrogen abundance in comet Halley. *Astrophys. J.* **367**, 641-648.
- Wyckoff, S., S. Tegler, P.A. Wehinger, H. Spinrad, and M.J.S. Belton 1988. Abundances in comet Halley at the time of the spacecraft encounters. *Astrophys. J.* **325**, 927-938.
- Yang, J. and S. Epstein 1983. Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta* **47**, 2199-2216.
- Yung, Y.L., R.R. Friedl, J.P. Pinto, K.D. Bayes, and J.S. Wen 1988. Kinetic isotopic fractionation and the origin of HDO and  $\text{CH}_3\text{D}$  in the solar system. *Icarus* **74**, 121-132.
- Zinner, E. 1988. Interstellar cloud material in meteorites. in *Meteorites and the Early Solar System*, ed. J.F. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, pp. 956-983.
- Zinner, E., M. Tang, and E. Anders 1987. Large isotopic anomalies of Si, C, N, and noble gases in interstellar silicon carbide from the Murray meteorite. *Nature* **330**, 730-732.