Origin and Evolution of Outer Solar System Atmospheres

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The atmospheres of bodies in the outer solar system are distinct in composition from those of the inner planets and provide a complementary set of clues to the origin of the solar system. This article reviews current understanding of the origin and evolution of these atmospheres on the basis of abundances of key molecular species. The systematic enrichment of methane and deuterated species from Jupiter to Neptune is consistent with formation models in which significant infall of icy and rocky planetesimals accompanies the formation of giant planets. The atmosphere of the Saturnian satellite Titan has been strongly modified by photochemistry and interaction with the surface over 4.5 billion years; the combined knowledge of this moon's bulk density and estimates of the composition of the surface and atmosphere provide some constraints on this body's formation. Neptune's satellite Triton is a poorly known object for which it is hoped that substantial information will be gleaned from the Voyager 2 encounter in August 1989. The mean density of the Pluto-Charon system is well known and suggests an origin in the rather water-poor solar nebula. The recent occultation of a star by Pluto provides evidence that carbon monoxide, in addition to methane, may be present in its atmosphere.

HE WELL-STUDIED ATMOSPHERES OF THE TERRESTRIAL planets, distinct in their composition and structure, are the products of a diverse set of chemical and physical processes that operated over 4.5 billion years on a common inventory of gases. Most striking is Earth, on which biological metabolic processes have converted an atmosphere that originally may have been rich in carbon dioxide (CO_2) to one dominated by nitrogen (N_2) and oxygen (O_2) . The atmospheres in the outer solar system were long thought to preserve more closely the "original mix" of gases from which the sun and planets formed. Fifteen years of exploration of the outer solar system, along with critically important ground-based studies, have painted a more complex picture. The cold envelopes of gas surrounding the four major planets, Jupiter, Saturn, Uranus, and Neptune, and three minor bodies, Titan, Triton, and Pluto-Charon, in the outer solar system contain key indicators of the processes of planetary formation and evolution, but the interpretations are as yet incomplete.

The Giant Planets

The atmospheres of the giant planets, more than the atmospheres of any other solar system objects, most nearly resemble the composition of the sun. Table 1 lists the abundances of elements (relative to the solar abundances) in the observable atmospheres of the four major planets, taken largely from a review by Gautier and Owen (1, 2). The increasing abundance of methane (CH₄) and certain other species from Jupiter to Neptune is consistent with current understanding of the interiors of the giant planets, derived from gravitational moment data provided by Pioneer and Voyager flybys (3). The interiors are characterized by so-called heavy-element cores, composed of material denser than hydrogen and helium, surrounded by largely hydrogen-helium envelopes with a possibly depthdependent enhancement of heavier elements (4). The cores are, to within a factor of a few, the same mass; hence, the envelopes are progressively a smaller fraction of the planet's mass as one moves from Jupiter out to Uranus and Neptune. The total enrichment relative to the solar value of species heavier than helium is an increasing function of decreasing envelope mass. The notable exceptions to this, such as water in all four planets and CH₄ in Uranus, can generally be accounted for by condensation (cloud-forming) processes and associated atmospheric dynamics (5).

During the past two decades attention has focused on two distinct models of formation of the giant planets. The "giant gaseous protoplanet" model posits gas instabilities in the gaseous disk (or "solar nebula") surrounding the sun, which induce rapid collapse to form spheres of gas whose composition resembles that of the sun. The "nucleated instability" model holds that giant planet formation began with the accretion of condensed rocky and icy material to form a core, which induced rapid collapse of gas to form one or many protogiant planets, which then accreted or added additional gas (or both) to make the objects we see today (6). The gas instability model has been criticized as being unable to explain the present-day cores of the giant planets, because late addition of planetesimals would result in dissolution and release of molecules in rock-ice planetesimals into the well-mixed envelopes (7). In fact, Earth- or Mars-sized bodies could survive to the center of giant planets, and such bodies may be required to explain the tilt of Uranus (8). It seems unlikely, however, that a stochastic, postformation addition of Mars-sized bodies could account for the similar core sizes in the present planets. The first model may also suffer on dynamical grounds. It requires a rather more massive solar nebula than is favored in current models, in which collapse of interstellar material onto the nebula is a gradual process that is occurring contemporaneously with viscous redistribution of mass (9). The core instability model, on the other hand, provides a natural explanation for the presence of cores, but the threshold sizes of the

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cores for envelope collapse are controversial. Although some models predict envelope collapse at close to the present-day core sizes of the giant planets, other calculations that allow for high molecular weight material in the envelopes predict much smaller core sizes (10).

What do the atmospheric abundances tell us about the formation of the giant planets? It is convenient to divide the discussion into three topics: molecular species, helium-to-hydrogen ratio, and deuterium abundance. This grouping allows meaningful comparisons between the giant planets to be described in a short amount of space. It also isolates particular physical processes important in the evolution of these atmospheres.

Molecular species and elemental abundance. The elemental abundances listed in Table 1 are based on measurements of certain molecular species that dominate in the highly reducing atmospheres of the giant planets. These species are chemically active deep in the atmosphere, at temperatures above 1000 K; below such temperatures (that is, in the observable atmosphere), reaction rates are much slower than mixing rates and the abundances of the molecular species are fixed (11). The situation changes high up in the atmosphere, above the cold trap, where photochemistry modifies the molecular abundances.

Of the major elements carbon, nitrogen, and oxygen, only the carbon-bearing molecule CH_4 has been measured in all four atmospheres. Both water and ammonia (NH₃) have vertical profiles that are strongly modified by condensation processes in the troposphere (the observable region of the atmosphere below the cold trap or minimum temperature point). Methane is enhanced over solar values by a factor of 2 to 6 in Jupiter and Saturn and roughly 20 to 50 in Uranus and Neptune. (Although the latter numbers are uncertain because of CH_4 condensation in the outer two giant planets, the enhancement in Uranus and Neptune is clearly larger than for Jupiter and Saturn.) The progression of the CH_4 enhancement, if we regard it as reflective of a general enhancement of heavy elements progressing outward from Jupiter to Neptune, seems to track the ratio of core mass to total mass in the giant planets.

It is tempting to argue that the heavy-element enhancement reflects mixing processes that have brought carbon, nitrogen, and oxygen upward from the core to contaminate the envelope. However, the most recent models of giant planet interiors (4) tentatively suggest heavy-element abundances that decrease upward from the core to the adjacent gaseous envelope. Mixing against such a density gradient would be highly inefficient (12). This is particularly a problem for Uranus and Neptune, which on the basis of their energy balance (see Table 1) should have very different rates of mixing but which have similar CH₄ abundances. Heavy-element material may

have been mixed upward during the early history of these planets (2), but the dynamics of such a model have not been quantified.

The progression of CH_4 abundances from Jupiter to Neptune has been reproduced in a model in which the heavy elements observed in the envelope never find their way into the core but rather are contained in planetesimals that ablate, break up, and partially dissolve in the primordial hydrogen-helium envelopes (13). If we assume a fixed abundance of solar nebula carbon in the condensed phase (that is, trapped in rocky or icy planetesimals) and a fixed fraction of the planetesimal mass dissolved in each of the giant planet envelopes, the observed enhancement of carbon over solar values can be reproduced. The effect is due mostly to the decreasing envelope mass from Jupiter to Neptune; the similarity of core sizes becomes a secondary issue.

Is it possible to infer the composition of the planetesimals that were dissolved in the atmospheres of the giant planets? To some extent, the answer may be yes, but the difficulty with inferring oxygen and nitrogen abundances in the giant planet atmospheres makes such an exercise impossible at present. Measurement, in 1995 by the Galileo descent probe, of noble gases should make such an assessment possible for Jupiter. An example of the information that could be gained is shown in Fig. 1. If it is assumed that the planetesimals entering the atmosphere of primordial Jupiter were largely icy and contained gases trapped in clathrate hydrate voids or "cages," definitive compositional predictions can be made. The figure is based on a model (14) that computes the composition of the gas trapped in the clathrate cages, including noble gases, for two cases. In the first, the dominant species trapped in the ice is assumed to be carbon monoxide (CO); in the second, the dominant molecule is CH₄. Because noble gases have differing polarizabilities, the composition of the noble gases trapped in the ice will not be the solar composition, and the deviations from the solar composition bear a definite relation to the abundance of the carbon-bearing species (that is, CH₄) in the Jupiter atmosphere. The noble gas enhancements can be measured by the Galileo probe. The calculation has not been done for the case in which the carbon in Jupiter's atmosphere is largely due to heavy organic material (as in the meteorites); qualitatively, however, the trapping of noble gases would differ from the ice clathrate case and yield a different set of curves from those shown in Fig. 1.

Helium-to-hydrogen ratio. Table 1 lists the ratio of helium to hydrogen in the giant planets, excepting Neptune for which it has not yet been measured. Because helium is a noncondensable gas in the outer, molecular envelope of the giant planets, it should remain uniformly mixed there. However, thermodynamic calculations predict that in the deeper, metallic hydrogen regions in Jupiter and

Table 1. Key elemental and isotopic abundances in the giant planets. Abundances are ratios of a given element relative to atomic hydrogen divided by the solar value, except for deuterium. The molecular species observed is given in parentheses; each species is thought to represent the bulk of a given element in the observable atmosphere. The elemental abundances obtain throughout the envelopes of each planet so long as convective mixing occurs. Data are from (2) except for arsenic, the data for which are from (45). Error bars are explained in (2, 45). A question mark indicates that the species was not detected or that the interpretation of data is highly unclear.

Component	Jupiter	Saturn	Uranus ?	Neptune ?	
Oxygen (H ₂ O)	~1*	?			
Carbon (CH_4)	2.32 ± 0.18	2-6	20-30	25-75	
Nitrogen (NH ₃)	~2	2-4	?	?	
Phosphorus (PH ₃)	1.0 ± 0.3	1-8	?	?	
Arsenic (AsH ₃)	$1.5 \begin{array}{c} +1.5 \\ -0.8 \end{array}$	4 +4	?	?	
Helium	0.7 ± 0.1	0.2 ± 0.1	1.0 ± 0.2	?	
Deuterium [†]	2.1 ± 0.6	$1.7 \stackrel{+1.9}{_{-1.0}}$	7^{+8}_{-4}	?	
Energy balance‡	1.67 ± 0.09	1.78 ± 0.09	1.064 ± 0.062	2.52 ± 0.37	

*Water condenses out at pressures above 6 bars on Jupiter. The deep atmospheric abundance is inferred by indirect means (5, 46). †Deuterium abundances are given relative to hydrogen, multiplied by 10⁵. Measurements of deuterated methane only are considered; the rationale for this and a discussion of errors is given in (2). ‡Ratio of internal energy to absorbed sunlight; from (2).

Saturn helium is immiscible in hydrogen below a certain temperature range (15). As a consequence, progressive depletion of helium is expected in the outer envelope if immiscibility is reached in the metallic hydrogen (H⁺) zone. The modest depletion in Jupiter and strong depletion in Saturn are consistent with this model: because Saturn is less massive than Jupiter, it cooled more rapidly and now has a lower temperature profile than Jupiter. Helium rainout was reached first in Saturn, perhaps after 1 billion to 2 billion years (2); rainout in Jupiter began more recently and has not progressed as far. The much higher internal heat source for Saturn is consistent with more extensive precipitation of helium toward the core.

Helium precipitation does not occur in Uranus and Neptune, because pressures do not exceed the predicted molecular-metallic hydrogen transition at 2 to 3 Mbar in the hydrogen-helium zones of those planets (3). Hence, the helium-to-hydrogen ratio should be close to the solar value and it apparently is so for Uranus. Other processes can affect the helium abundance, however. If planetesimals entering the Uranian and Neptunian envelopes during formation contained largely oxidized species such as CO, reequilibration in the envelopes would soak up hydrogen and lead to an apparently enhanced helium abundance. On the other hand, in the very deep interior, any hydrogen-bearing species such as CH4 would be dissociated, contributing hydrogen to the gas and decreasing the helium-to-hydrogen ratio (16). The former effect was quantified in (17): if the solar nebula contained carbon largely in the form of oxidized species, then the predicted helium-to-hydrogen ratio in Uranus would increase by as much as 30% over the solar value. Such an increase is ruled out by the measured Uranus value. The model increase is an upper limit; more detailed studies are required that couple all of the chemical effects on the helium-to-hydrogen ratio to processes that occurred during formation and early evolution.

Deuterium. The abundance of deuterium in the giant planet atmospheres increases outward from Jupiter to Uranus (Table 1). The validity of this assertion hinges on detailed understanding of fractionation effects between deuterated methane and HD. Problems with interpreting HD measurements have forced workers to rely solely on the deuterated methane results. The issue is very complex, but the apparent enrichment over solar values in Uranus and Neptune is consistent with the higher proportion of icy and rocky material in these smaller outer planets. However, it is not clear whether the enrichment pattern in the atmospheres of the giant planets is consistent with the carbon enrichment pattern, when viewed in the context of a quantitative model of planetesimal infall into the forming giant planets; such a model has not yet been applied simultaneously to the data on molecular abundances, helium-to-hydrogen ratio, and deuterium enhancement. The database is sufficiently rich that such an effort should be made. The reader is referred to the review by Gautier and Owen (2).

Smaller Bodies and the Chemistry of the Solar Nebula

Because the giant planets are massive reservoirs of hydrogen, the molecular state of their atmospheres reflects equilibration at high hydrogen pressures and temperatures. Information on the oxidation state of the solar nebula is largely lost. This information is of great interest, because much could be learned about processes occurring in the nebula during planet formation if the molecular composition of the primordial gas could be assessed. The smaller bodies with atmospheres in the outer solar system may provide clues to the molecular composition of the gas out of which they formed, because they never had massive hydrogen envelopes at high temperatures. These clues are, however, hidden by evolutionary processes subsequent to formation, and additional information must be found in the bulk density of these objects. In this section I outline current thinking on the chemical makeup of the solar nebula and so-called giant planet nebulae, disks of gas surrounding the accreting giant planets as a product of the formation process. A more detailed review of nebular chemistry is given elsewhere (17).

Astronomical observation of star-forming regions such as the Orion molecular cloud, in a variety of wavelength regions, reveals tremendous complexity in physical and chemical properties within clouds (18). The molecular makeup of the solar nebula almost certainly differed from that in surrounding regions of the giant molecular cloud out of which it formed, because gas densities were much higher in the nebula. Models of gas-phase chemistry in the solar nebula predict that, under equilibrium conditions, the outer solar nebula should have been dominated by carbon in the form of CH₄, nitrogen as NH₃, and oxygen entirely as water (minus a small amount locked in highly refractory compounds). However, the reaction rates that interconvert oxidized and reduced species have the usual Arrhenius relationship involving an exponential dependence on reciprocal temperature. Astrophysical constraints on the nebular lifetime center on 1 million to 10 million years; the reactions therefore proceed to equilibrium only above temperatures of 1400 K for carbon and slightly higher for nitrogen (17). The gas-phase composition at these "quench" temperatures consists largely of CO, water, and N₂. The water abundance is depleted by roughly twothirds relative to the total oxygen abundance, because most of the oxygen is in CO. Clearly then, one can distinguish between a CH₄rich and a CO-rich nebula if one could ascertain the water abundance in outer solar system bodies.

In solid bodies, such as icy satellites and Pluto, the bulk density is diagnostic of the primordial nebular water abundance, because ice and rock are the only major condensates. Other material either do not condense out as solids (for example, CO was probably trapped in water ice) or play only a secondary role in affecting the density (NH₃). The density is, of course, size-dependent through the compressibility; for a body the size of Pluto the density is roughly 1.6 g/cm³ if it formed in a highly reduced nebula and 2.1 g/cm³ if it formed in a fully oxidized nebula. (These numbers depend somewhat on the elemental carbon-to-oxygen ratio, assumed here to be 0.6, and on the hydration state of the silicates.)

A fully oxidized solar nebula would have little or no CH4 for incorporation in solid bodies (19), which seems to contradict the observations of CH4 on Titan, Triton, Pluto, and comet Halley. The story must be modified in three ways: (i) heterogeneous catalysis on grains can reduce the quench temperature to as low as 500 to 600 K, at which the abundance of CH₄ becomes comparable to that of CO; (ii) the higher pressures in giant planet nebulae shift the equilibria so that these gaseous regions are dominated by CH₄ and NH₃ at the gas-phase quench temperatures (20); and (iii) CH4 is more efficiently trapped in water ice planetesimals, adsorbed or encaged in the ice structure known as clathrate hydrate, than is CO and hence will appear overrepresented in solid bodies. The efficiency of grain catalysis is controversial, and the numbers cited in (i) must be regarded as a limiting case (21). An additional complication is the efficiency of nebular mixing. Stevenson (22) argues that a solar nebula model in which both angular momentum and trace species are redistributed by viscous processes has an inherent limitation in how much inner solar system material can be mixed outward. According to this hypothesis, only 1 to 10% of the molecular species produced within 1 astronomical unit of the sun can be mixed outward to the region of Pluto and Triton. Prinn (23) has challenged this view, asserting that nonlinear transport processes dominate the mixing of material outward and can ensure a nearly fully homogenized nebula over its lifetime.

For the purposes of our examination of the small body atmospheres, the above discussions can be summarized as follows. The outer solar nebula was rich in CO, with an admixture (up to 10%, but probably much smaller) of CH₄. The dominant nitrogen species was N₂, with the proviso that NH₃ from the surrounding giant molecular cloud may have been preserved. The low water abundance leads to solid bodies with high rock-to-ice ratios, corresponding to densities in excess of 2 g/cm³. In the regions of Jupiter and Saturn, high-pressure gaseous disks were dominated by water, CH₄, and NH₃ (after hydrogen and helium), leading to satellite densities well below 2 g/cm³.

Titan

Several recent reviews have discussed the properties of Titan, the largest satellite of Saturn (24, 25). Titan is remarkably similar in size and mass to the Jovian satellites Ganymede and Callisto and on the basis of density is composed of roughly equal amounts by mass of "rock" (silicates plus iron or nickel) and "ice" (largely water ice but also some NH₃ and more volatile trapped gases). Titan is distinguished from its Jovian cousins by a thick N₂ atmosphere, containing CH₄ as the primary condensable species, with a total gas density at the surface almost five times that at Earth's surface.

The dominant process driving atmospheric evolution is CH_4 photochemistry in the presence of N_2 and consequent atmospheric escape of hydrogen. There are two qualitative differences between the photochemistry of Titan's stratosphere and that of the giant planets: (i) the presence on Titan of nitrogen as the major background gas, leading to a suite of nitriles, and (ii) the predominance of ethane over acetylene as photochemical products in Titan's stratosphere. This last fact complicates the photochemistry but appears to be understood (25a). An outstanding issue is the relative fraction of CH_4 converted to simple hydrocarbons versus that converted to aerosols. Current estimates based on aerosol models suggest that 20% of the CH_4 is converted to complex aerosols, but uncertainties in this number are substantial.

All photolysis products except hydrogen eventually condense out and fall through the cold trap to the troposphere and surface. The escape of hydrogen in atomic form ensures that the photolysis of CH₄ is an irreversible process that, if we assume a constant photolysis rate, has led to the accumulation of photolysis products on Titan's surface to a depth of a kilometer over the age of the solar system, equivalent to of order 100 times the present atmospheric abundance of CH₄. In addition to upward loss of hydrogen, there must also be a downward diffusion of hydrogen into the troposphere where it has a mixing ratio of 0.2 to 0.5%, based on Voyager data (24, 25). Finally, the amount of N₂ that has escaped over the age of the solar system is small, only 10% of the total atmospheric abundance.

The surface of Titan cannot be probed directly except by radio and radar techniques. After the Voyager encounter, debates concerning the nature of the surface revolved around the rapid rate of depletion of CH₄ by way of photolysis and the subsaturation of CH₄ in the lower few kilometers of the troposphere, determined from the Voyager radio occultation profile. The photolysis rate suggested that CH₄ was being supplied from a reservoir more massive than the atmosphere, such as a surface ocean of CH₄. The near-surface subsaturation, on the other hand, ruled out a pure CH₄ ocean. These two views were reconciled by the postulation of a mixed liquid ocean of CH₄, N₂, and CH₄'s photochemical products ethane, propane, and so forth (26). Because the resulting vapor pressure of CH₄ is a function of its mole fraction in the ocean, both the composition and depth of the ocean can be estimated from the

Fig. 1. Predicted noble gas enhancements over solar abundances as a function of the CH4 enhancement in Jupiter's atmosphere. The calculation assumes that gases were brought into the atmosphere in icv planetesimals composed of clathrate hydrate. In (A) CO was the dominant carbon-bearing gas in the clathrate; in (\mathbf{B}) CH₄ was the dominant carbon species. Curves are shown for the thermodynamically preferred clathrate, called "structure I"; the structure II clathrate is not expected to form in the nebula. Adapted from (14).



atmospheric abundance. For the nominal surface temperature of 94 K, ocean CH_4 mole fractions range from roughly 10 to 70% and depths from 0.8 to 2 km.

Much of the uncertainty regarding surface models rests on the issue of the fraction of CH_4 converted to ethane and propane versus acetylenes, polyacetylenes, and nitriles. If a significant fraction (say, at least 10%) ends up as ethane and propane, which condense out at the cold trap and sediment out, then a liquid layer composed at least of these materials must exist at the surface. If only acetylene, polyacetylene, and other polymers are the survivors of CH_4 photolysis, then a solid (though perhaps somewhat sticky) surface cannot be ruled out.

Models of the evolution of Titan's atmosphere and surface identify two epochs, an early one of order 10^8 years in which accretional heating and vigorous outgassing raised an atmosphere composed in large part of primitive gases obtained from the nebula out of which Titan formed and a subsequent period in which photochemical and surface processes led to the present state.

Recent epoch. The driving force that alters Titan's surface and atmosphere is photochemistry, where volcanism and the impact of small bodies are poorly quantified, stochastic, secondary contributors. Photochemistry converts CH₄ to more hydrogen-poor compounds, thereby changing the composition of any surficial hydrocarbon ocean and reducing its volume. The hydrogen released in the course of CH₄ photolysis diffuses upward and downward. The downward component of hydrogen produces a uniform tropospheric mixing ratio and is an important source of thermal infrared opacity. The decreasing CH₄ mole fraction and volume of the ocean with time drives dissolved N2 into the atmosphere, increasing the pressure and infrared opacity. At the same time, the decreasing ocean CH₄ content results in a lower CH₄ mole fraction in the atmosphere at a fixed temperature, decreasing the gas opacity and column density of CH₄-N₂ condensation clouds. These effects of CH₄ photolysis greatly influence the tropospheric thermal structure, and consequent changes in the surface temperature affect the thermodynamic balance between the ocean and atmosphere, altering the composition of both (27).

Formation and early evolution. The outstanding problem in the earliest evolution of Titan is the origin of CH_4 and N_2 . Because CH_4 is characteristic of a highly reducing environment of formation [giant planet nebulae (20)] whereas N_2 is a signature of an oxidizing (solar) nebula, the present chemical composition of Titan's atmosphere cannot be a primordial mix. The most plausible suggestion is that the N_2 is derived from NH_3 by chemical processes (28). The bulk density of Titan provides some constraints on this issue.

Titan's density falls between that for a rock-ice body formed from a CH₄-rich and CO-rich nebula described above. These two nebulae have very different water abundances because CO can sequester twothirds of the available oxygen. Because it is energetically possible for Titan to lose significant quantities of water by vaporization during accretion, the measured density can be reproduced if Titan formed in a CH₄-rich nebula and lost water during accretion. The CH₄ would occupy most of the available voids in water-ice planetesimals, and very little N₂ could be trapped (14). Titan's atmospheric N₂ would then be derived from primordial NH₃, which readily bonds with water ice.

If instead Titan formed in a nebula with comparable amounts of CH₄ and CO, some N₂ could be incorporated in the water ice, because the propensity of N₂ for incorporation is just slightly less than that of CO. The water ice accreted into Titan would then contain (in order of abundance) CH4, CO, and N2. Because CO and N2 are likely to act similarly in terms of outgassing processes, the resulting atmosphere would be rich in both CO and N2; given the present-day atmospheric N2 abundance of 1.5 bars, anywhere from 1 to 20 bars of CO would need to be destroyed by photochemical processes over the age of the solar system. It is unclear on the basis of current models whether the photochemical conversion of CO to CO_2 is rapid enough to destroy this amount of CO over the age of the solar system. On balance, then, the bulk density of Titan combined with the presence of CH₄ suggests formation in a highly reduced nebula around Saturn. This hypothesis can be tested by measuring the argon-to-nitrogen ratio in the present atmosphere, which could be quite small if the N_2 were derived from NH_3 (29).

The deuterium enrichment in atmospheric CH_4 is as large as that seen for Uranus and Neptune but substantially smaller than values measured in meteorites and the interstellar medium. The enrichment is difficult to produce in processes associated with the formation and evolution of Titan's atmosphere (30). However, the measured enhancement could be produced by dilution of presolar, highly enriched material in the course of formation of Titan in the circum-Saturnian nebula (2). To the limited extent that this can be

Chemical processing in nebula. CO> CH ₄ .	years	Chemical processing in nebula. CO \rightarrow CH ₄ ; N ₂ \rightarrow NH ₃ .		
Condensation and clathrate formation.	10°	Condensation and clathrate formation.		
	1.			
Accretion, incorporation of	1	Accretion, incorporation of		
CO, CH ₄ , N ₂ in core,		CH ₄ in core, formation of		
formation of CO-CH ₄ -N ₂ -H ₂ O		CH ₄ - NH ₃ - H ₂ O atmosphere,		
atmosphere.		NH ₃ - H ₂ O ocean.		
Å. Å				
Escape and cooling of atmosphere,		Escape and cooling of atmosphere,		
loss of CH4, N2, CO;		loss of CH ₄ ; $NH_3 \rightarrow N_2$.		
condensation of H ₂ O	Q, I	Condensation of lower atmosphere		
onto surface.		into NH ₃ -H ₂ O ocean.		
	Ţ			
Formation of solid surface,	1	Formation of solid ice crust,		
outgassing of CH4, N2, CO.	°0	isolating atmosphere from interior.		
Formation of CH ₄ -N ₂ -CO		Outgassing of CH4, formation		
ocean and atmosphere.		of CH ₄ -N ₂ ocean and atmosphere.		
	\ *	d		
Photochemical conversion	T	Conversion of CH_4 to C_2H_6 ,		
of CO to CO ₂ using H_2O ;		consequent coupled evolution		
conversion of CH_4 to C_2H_6 ;		of ocean and atmosphere.		
consequent coupled evolution				
of ocean and atmosphere.				

Fig. 2. Schematic time line of Titan evolution, assuming (left) a CO-rich nebula and (right) a CH₄-rich nebula; C_2H_6 is ethane. In the CO-rich case, it is assumed that a small amount of CH₄ is produced in the nebula. [From Lunine *et al.* (25), with permission of the University of Arizona Press, Tucson]

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quantified, Titan's deuterium budget is consistent with the general picture for the outer solar system.

Two time lines can be drawn for the evolution of Titan (Fig. 2), one assuming formation in a reducing, giant planet nebula, the other assuming formation in an oxidizing solar nebula. The time lines illustrate the extensive chemical processing that bodies in the outer solar system underwent from their formation to the present day.

Triton

Much less is known about Neptune's satellite Triton than about Titan. However, it is expected that the analysis of Voyager 2 flyby data (which is scheduled for August 1989) will yield a bulk density, a radius, and information on atmospheric composition and structure. The presence of CH_4 and N_2 on the surface or in the atmosphere or both was deduced on the basis of near-infrared spectroscopy (31); virtually nothing is known of the radius or mass (and hence density). Triton is intriguing in that two possible origins and hence "analogs" may be identified: formation in a circum-Neptunian nebula, with a resulting chemistry and density resembling those of Titan, or formation in the outer solar nebula followed by capture around Neptune (32), with the resulting satellite resembling Pluto.

Triton differs from Titan in a number of important ways. The surface temperature is much lower, 65 K or less (33). Triton is subject to photochemical processing of its atmospheric constituents at a rate roughly 10% of that at Titan and comparable to the rate of processing by cosmic rays (34). Triton's orbit around Neptune is such that the satellite experiences extreme seasonal variations in insolation; as a result, on Triton volatiles are transported to the polar regions (35). The similarities and differences in the composition, atmospheric processes, and bulk density of Triton versus Titan and Pluto provide an important point of agreement for models of the formation of lunar-sized bodies in the outer solar system.

Pluto-Charon

Two special astronomical events have combined to greatly increase our knowledge of this system, namely, a series of mutual eclipses by Pluto and the smaller Charon and a recent stellar occultation by Pluto. Also, a unique set of data on Pluto's thermal emission, provided by the Infrared Astronomical Satellite, suggests that condensed CH₄ is restricted to the polar regions (36). It was known from near-infrared spectroscopy that Pluto has CH₄ in its atmosphere and on its surface (24, 25). The recent data sets make possible a determination of the system density (1.9 to 2.1 g/cm³), radii (Pluto, ~1140 km; Charon, 560 km), and atmospheric structure. The mutual eclipses permitted an assessment of the surface composition of Charon: it is devoid of CH₄ (37). Although the density of Pluto has not been separately determined, the most plausible value is close to the system density.

The curiosity that Pluto presents is that, although the bulk density reflects an object having a rock-to-ice ratio consistent with formation in the water-poor solar nebula (38), its only identified atmospheric gas is CH₄. The models described above would suggest the presence of CO, a gas that is hard to detect in the near-infrared spectral region, where CH₄ bands dominate. An indirect opportunity to infer the presence of gases other than CH₄ was afforded by the stellar occultation of 1988, which detected an atmosphere with a maximum pressure of roughly 10 µbar (39). The occultation yielded a scale height that can be converted into an atmospheric molecular weight, given a temperature profile. A recent model temperature

profile, incorporating heating of the atmosphere due to CH₄ absorption of solar infrared radiation, yields a temperature of 106 K in the 1- to 5-µbar region (40). The corresponding mean molecular weight of roughly 25 is significantly higher than that of CH₄.

If the heavier gas in Pluto's atmosphere is assumed to be CO, then one finds a CO/CH₄ ratio in excess of 0.4, which overlaps with that of the only other outer solar system object for which this ratio has been determined, comet Halley. Unfortunately, the ratio in Pluto's atmosphere may not reflect the bulk composition of the planet's surface and interior. Nonetheless, the density of this planet, coupled with information derived from solar nebula models, strongly suggests that the heavier gas is indeed CO and that the nebula out of which Pluto formed was largely CO-rich and CH4-depleted. Methane is overrepresented in the observations, because it is spectroscopically more active than CO and because it was more readily trapped in icy planetesimals during Pluto's formation. This latter effect has been used to argue that comet Halley was formed in the CO-rich solar nebula as well (17, 41).

Summary and Future Observations

Planetary science is moving toward an understanding of the physical and chemical conditions under which outer solar system objects and their atmospheres formed. The accumulating data on abundances in the four giant planet atmospheres support the notion that these bodies are distinctly nonsolar in composition and in the way in which they formed; the accretion of icy and rocky planetesimals to form a central core has left its signature in the form of an enrichment of heavy elements in all four envelopes. The composition of planetesimals that enriched these envelopes is unknown; models must be matched to a more detailed set of abundances of molecules and noble gases. It is expected that the Galileo entry probe in the mid-1990s will provide that information for a single location in the atmosphere of Jupiter, down below the water clouds (42).

The atmospheres of the smaller bodies, Titan, Triton, and Pluto, test our understanding of the chemistry of the solar nebula and nebulae around the forming giant planets. The preponderance of evidence places Titan's formation in a chemically reducing environment, similar to that predicted for a circum-Saturnian nebula (20). Key ratios of noble gases and other species await the entry of the Cassini probe into Titan's atmosphere in the first decade of the 21st century (43). Also important to models of atmospheric evolution is the nature of Titan's surface, which is to be determined by Cassini but is also potentially accessible to ground-based radar.

It is expected that, in August 1989, Voyager 2 will add enormously to our understanding of the chemical and physical nature of Triton's atmosphere and perhaps surface. Pluto-Charon will not be visited by spacecraft under current plans; the recent eclipses and occultations probably represent the observational watershed for this system. A wealth of information on the chemistry of the outer solar nebula will be gleaned from the analyses of a comet to be performed by the Comet Rendezvous Asteroid Flyby mission, around the year 2000. The in situ examination of a comet nucleus will provide essential information on the gases present in the solar nebula and the processes by which they were trapped in grains that formed the comet.

In the past decade of research on outer solar system bodies, planetary science has made important connections with astrophysical studies of the chemistry and physics of star-forming regions. The solar nebula out of which the planets formed was the smallest scale gaseous structure in a hierarchy of phenomena in the giant molecular cloud out of which the sun formed. Our current understanding of the composition of outer solar system atmospheres and comets,

and the origin models derived therefrom, challenge our astrophysical colleagues to obtain chemical and physical information on starforming regions at a level of detail well beyond that achieved at present (44). Synergy between the two 20th-century sciences of planetary science and astrophysics is rapidly revealing the profound link between the birth of our planetary system and the process of star formation that is a driving force in the evolution of galaxies.

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Immunologic Tolerance: Collaboration Between Antigen and Lymphokines

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Immunologic tolerance is the process whereby limits are placed on the degree to which lymphocytes respond to an animal's inherent antigens. It is a quantitative rather than an absolute term, as some autoantibody formation is common. Contrary to early hopes, it is not due to some single, simple causative mechanism confined to early developmental stages of the fetal immune system. Rather, self-tolerance results from a variety of complementary mechanisms and feedback loops in the immune system and is thus best seen as part of the general process of immunoregulation.

WO KINDS OF LYMPHOCYTES, T CELLS AND B CELLS, interact in normal immune responses. Each population consists of cells with different recognition potentials; each cell has only one specificity, conferred on the cell by a surface receptor for antigen. The T cell and B cell repertoires are quite different: the former recognizes small linear peptides in association with certain cell surface molecules, and the latter recognizes conformational determinants on proteins and carbohydrates. The activation of T and B cells by antigen involves not only binding antigen, but also collaborative cellular interactions and regulatory signals delivered by many specific cytokines.

Key results from this and other laboratories support the notion that self-tolerance involves two distinct ways of eliminating from the repertoire high-affinity anti-self T and B cells. For the T cell, an elimination of immature anti-self T cells within the thymus seems to be the chief, but not the sole, mechanism. For the B cell, a downregulatory signaling process that does not involve cell killing appears to occur when immature B cells encounter self antigens. Thus, the repertoire is functionally purged by the process of clonal anergy. The anergic state can now be probed by means of refined single-cell culture techniques and the cloning of cytokines to interact with antigen in lymphocyte stimulation.

Background

Burnet and Medawar were awarded the 1960 Nobel Prize for their discovery of immunologic tolerance (1). To understand the capacity of the immune system to distinguish between self and nonself, it is necessary to define three features of immune responses.

First, immune recognition depends on specific cell surface receptors that are generated somatically (2) by gene translocation mechanisms; each lymphocyte bears on its surface just one combining specificity (3). Second, immune responses involve collaboration between two different kinds of lymphocytes: thymus-derived T cells and bone marrow-derived B cells (4). T cells mediate chronic inflammation and regulate immune responses by secreting lymphokine factors. The T cell receptor (TCR) for antigen recognizes cellprocessed peptide fragments of antigen (5) that is noncovalently but firmly associated with an antigen-binding groove on a class I (6) or class II (7) major histocompatibility complex (MHC) molecule. In other words, the T cell is "blind" to antigen unless it is associated with MHC on a cell surface. B cells are responsible for antibody synthesis. They recognize antigen by immunoglobulin M (IgM) and IgD molecules tethered to the cell membrane. The combining sites of these two isotypes of antibody are identical to each other and to those of antibody secreted by that cell and its progeny. Antibodies recognize conformational determinants of proteins and carbohydrates in free solution. The combining site (about 20 by 30Å) is capable of uniting with 16 amino acids of a protein antigen (8). Third, an antigen entering the body must induce lymphocytes specific for that antigen to leave the G₀ state and undergo a series of mitoses. This process, which results in a differentiated clone of immunologic effector cells (2), either activated T cells or antibodyforming B cells, is the process of clonal selection. The immunoproliferative cascade is not induced simply by a union of antigen with receptor, but rather requires the cross-linking of multiple receptors, a flux of cytokine growth and differentiation factors, and perhaps other signals dependent on particular forms of cell-cell contact (9). In view of the complexity of clonal activation, the responsiveness of a cell to signaling events represents a major variable in immunoregulation (10).

The populations of T and B cells of an adult animal represent repertoires of recognition units designed so that most pathogens will elicit both T and B cell responses. Constraints operate on the two recognition systems, however. As regards the T cell system, most typical proteins have only one or two peptides (of a dozen or so amino acids in length) capable of appropriately associating with the MHC molecules of a given animal. The possibility thus exists for nonrecognition of, and therefore genetic nonresponsiveness to, a protein if none of the processed peptides, known as T cell epitopes, fit the particular constellation of MHC gene products of the animal. Clear-cut associations between MHC genotype and susceptibility to

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