THE OUTER SOLAR SYSTEM: CHEMICAL CONSTRAINTS AT LOW TEMPERATURES ON PLANET FORMATION

JONATHAN I. LUNINE
CNR-Istituto di Astrofisica Spaziale and University of Arizona

TOBIAS C. OWEN
University of Hawaii

and

ROBERT H. BROWN
University of Arizona

The past decade has seen powerful ground- and space-based techniques applied to the investigation of the composition of outer solar system bodies, including the spectacular measurements of He/H, isotope ratios, and noble gas abundances in the jovian atmosphere by the *Galileo* probe; improved deuterium and trace species measurements in the atmospheres of the giant planets and Titan; and first detection of absorption features on the surface of a Kuiper Belt object. In this chapter we review the new observations and discuss how they constrain the composition of primordial reservoirs supplying material to the giant planets, their moons, and other outer solar system bodies. Planned or anticipated planetary missions in the next decade, along with improved ground-based capability on giant telescopes, will enable models of the early evolution of the outer solar system to be tested and improved, ultimately to provide a picture of how the four giant planets and their moons came to be.

I. INTRODUCTION

The outer solar system is the province of four giant planets, their retinue of more than 60 moons, and an assortment of small bodies that represent leftover planet-forming material scattered by the giant planets. The condensation front of water ice in the later stages of evolution of the protosolar disk (also called the solar nebula) provides a convenient inner boundary for the region. This front existed roughly in the region 4–5 AU from the Sun. There is a corresponding compositional threshold in present-day objects. Inward of the front lie bodies whose composition is largely rock and metal, with water present primarily as water of hydration. The ice that sits on the surfaces of Earth, Mars, and, apparently, the Moon can be considered a volatile veneer rather than a principal planet-building material.

From 5 AU outward, however, the situation is different. Most of the solid bodies beyond 4 AU, with the principal exceptions of rocky inner satellites and rings, have bulk densities or other indicators pointing to water ice as an important or primary constituent. (We do not yet know how much, if any, water ice is contained within the Trojan asteroids or Jupiter's irregular satellites.) The giant planets themselves probably accreted spectacular amounts of water, many tens of Earth masses, though this is an inference from gravitational field data because water is elusive in the jovian atmosphere and buried too deep for quantitative detection in the other giants. Beyond Neptune lie at least two dynamically distinct "junkyards" containing remnants of the rocky and icy planetesimals that fed the voracious appetites of the growing giants; today these regions supply comets to the inner solar system.

The grand scale of the outer solar system, spanning 10 times the linear extent of the inner solar system, and the presence of water as a condensable may well be interrelated. Although still poorly understood, the formation of giant planets probably was aided, if not triggered by, the large amount of condensed material afforded by the presence of water ice (Stevenson and Lunine 1988; Boss 1995). Although giant planets exist at very small orbital distances from other solar-type stars, the consensus is that these bodies formed further out and spiraled inward to their current orbits (Lin et al. 1996; Trilling et al. 1998). As these bodies grew to their present masses, they opened gaps in the surrounding protoplanetary disk, scattered planetesimals gravitationally, and in general made large annular swaths of the nebula unstable for smaller solid bodies. Thus, intrinsically the building of planets tens or hundreds of times more massive than the terrestrial planets involved great distances.

These great distances, in turn, make detailed study of the outer solar system difficult either from Earth or by spacecraft. Therefore, the outer solar system is more poorly understood than the inner, despite the important clues it must hold to planet formation. Understanding the assembly of giant planets has become more imperative as the list of extrasolar giant planets has grown. The discovery of the Kuiper Belt has opened to direct study an important reservoir of planetesimals not ejected or destroyed by the giant planets. The molecular and isotopic compositions of icy phases in the outer solar system provide bridges both to the physical properties in the nascent molecular clouds and to volatile materials that seeded the Earth with water and organics. For these reasons and others, the outer solar system is worthy of increased efforts toward exploration and characterization.

The purpose of this chapter is to summarize some of the highlights of the compositional information derived from observational activities since the publication of *Protostars and Planets III*, and to interpret them in terms of models of solar nebula processes and giant planet formation. Limitations of space demand selectivity in the choice of data to emphasize and models to present. However, the references provided at the end are adequate to open the door to more detailed research by interested readers.

II. DATA

A. *Galileo* Probe and Other Jupiter Measurements

The analysis of the rich harvest of results from the 1995 descent of the *Galileo* Probe through Jupiter's atmosphere is far from complete, and remote sensing data on the jovian atmosphere continue to be returned by the Orbiter. Some basic measurements have been established, however, that tend to support the current paradigm for giant planet formation: Contributions from solid planetesimals are mixed with captured solar nebula gases, and the mixture is subsequently modified by chemistry occurring within the planet itself. The solar nebula should have contributed the overwhelming proportions of hydrogen, helium, and neon, as these gases are not easily retained in planetesimals. Just what the planetesimals carried and in what proportions can in principle be deduced from the composition of the jovian atmosphere today. One can then compare this derived planetesimal composition with that of extant remnants from the early solar system such as comets and meteorites whose volatiles are reasonably well characterized.

1. Hydrogen and Helium. The ratio of helium to hydrogen in Jupiter's atmosphere has been established by both the *Galileo* Probe Mass Spectrometer (GPMS) (Niemann et al. 1996) and the helium abundance detector (HAD) (Von Zahn and Hunten 1996) as $^4He/H_2 = 0.157$. The mass fraction is then $Y/(X + Y) = 0.238 \pm 0.007$, where X and Y are the mass fractions of $H + H_2$ and He, respectively. This is significantly smaller than the protosolar value of $Y/(X + Y) = 0.280$ that would have existed in the solar nebula (Proffitt 1994). The difference may be a result of the formation of helium "raindrops" in the planet's deep interior at a pressure of one to a few megabars. These fall to deeper levels before dissolving, thereby depleting Jupiter's outermost envelope in He (Stevenson and Salpeter 1977). The process is far more evident in Saturn than in Jupiter, because the former's luminosity is much greater than expected after 4.5 Gyr of cooling, but it is at least plausible that the process started (albeit later) in Jupiter as well. Roulsten and Stevenson (1995) predicted that neon would dissolve in the helium drops and would therefore also be deficient. Detecting this gas for the first time, the GPMS indeed found the neon abundance to be only $\frac{1}{10}$ the solar value.

The isotope ratios in these abundant gases should correspond to values that existed in the interstellar cloud from which the solar system formed. Jupiter is too cool for nuclear reactions to occur in its interior, and the helium rainout is not predicted to fractionate the isotopes. The value of D/H measured by the GPMS in jovian hydrogen is D/H $= 2.6 \pm 0.7 \times 10^{-5}$ (Mahaffy et al. 1998). Over the intervening 4.5 Gyr since solar system formation, D/H in interstellar hydrogen should have steadily decreased as a result of the conversion of D to ^{3}He in stars. Its present value in the local interstellar medium (ISM) is D/H $= 1.6 \pm 0.2 \times 10^{-5}$ (Linsky 1996), confirming this expectation.

The jovian value of ^{3}He/^{4}He $= 1.66 \pm 0.05 \times 10^{-4}$ (Mahaffy et al. 1998) agrees closely with the value for primitive helium determined in meteorites: ^{3}He/^{4}He $= 1.5 \pm 0.3 \times 10^{-4}$ (Geiss 1993). This indicates that possible fractionation processes during the trapping of helium in the meteorites or during the helium "rainout" in Jupiter's interior have indeed been negligible. There is not yet a well-determined value for ^{20}Ne/^{22}Ne from the *Galileo* data.

If there are no additional nuclear reactions supplying ^{3}He or depleting D, and no mixing with other parts of the galaxy, we expect (^{3}He + D)/H in the interstellar gas to be time invariant at our distance from the galactic center. Measurements by the *Ulysses* spacecraft yield ^{3}He/H $= 2.48^{+0.85}_{-0.79} \times 10^{-5}$ in the local ISM (Geiss and Gloeckler 1998). Combining this with Linsky's (1996) measurement of D/H, we have the current interstellar ratio (^{3}He + D)/H $= (2.5 + 1.6) \times 10^{-5} = 4.1 \pm 1 \times 10^{-5}$. The jovian values give (^{3}He + D)/H $= 3.9 \pm 0.7 \times 10^{-5}$. Within the uncertainties they indeed agree with each other over 4.5 Gyr, about one-third of the age of the Galaxy.

2. Carbon and Sulfur. The abundances of the heavier elements in Jupiter's atmosphere are still under review. It is clear that carbon is enriched by a factor of 2.9 ± 0.2 times the solar value (Niemann et al. 1996). This determination was made in methane, which does not condense in Jupiter's atmosphere. The next best-determined abundance is that of sulfur, in the form of H_2S. This gas will combine with NH_3 to form NH_4SH (Wildt 1937), which in turn can condense to make clouds (Lewis 1969). These clouds should occur at 2.2 bar for a solar value of S/H and 2.7 bar for 3 times the solar sulfur abundance (Weidenschilling and Lewis 1973; Atreya and Romani 1995). Below the clouds, one expects H_2S to reach the globally mixed value for the planet, yet the GPMS did not even detect H_2S at altitudes above the 4-bar pressure level, setting an upper limit of 6×10^{-7} (Niemann et al. 1998). This was consistent with the nephelometer showing only traces of clouds, not the expected thick cloud bank (Ragent et al. 1996), and the depletion of NH_3 and H_2O as well (Niemann et al. 1996, 1998; Sromovsky et al. 1996). Evidently the *Galileo* Probe's descent through a 5-micron "hot spot" revealed a local region on Jupiter in which all condensable species were strongly depleted. This would be consistent with a model for these hot spots as massive cells of descending air that have been thoroughly desiccated by ascent to high altitudes (Owen et al. 1997; Atreya et al. 1997). However, the details of this process for the spatial scales and abundances found by *Galileo* remain to be worked out (Showman and Ingersoll 1996).

Further support for the downdraft idea comes from the H_2S abundance found by the GPMS at lower levels: It rises from a value of 0.23 relative to solar at 8.7 bar to about 2.5 times solar at 16 bar. It then remains constant until termination of probe communications at 22 bar (Niemann et al. 1998). The constancy at the end indicates that the probe was then sampling the globally mixed value of H_2S, presumably as a result of entrainment of "normal" air into the downdraft (Owen et al. 1997; Atreya et al. 1997). Unfortunately, it was not possible to measure the ammonia abundance with the GPMS. Also, the water vapor value, while rising by a factor of 10 between 10 and 20 bar pressure, never reached a constant mixing ratio with increasing depth and remained well below solar even at the last received data point. Thus, the GPMS cannot give us the mixing ratios of N and O at this time.

3. Nitrogen and Oxygen. The Net Flux Radiometer derived a value of N from NH_3 of solar to twice solar at 3–6 bar and 20 times less than this at 1 bar (Sromovsky et al. 1996, 1998). At 3–6 bar, the measurement is roughly consistent with the global abundance of $\approx$1.3 times solar derived from Earth-based observations of Jupiter's thermal spectrum at radio wavelengths (0.6 mm–12 cm) (de Pater and Massie 1985). In striking contrast, Folkner et al. (1998) have reported a mixing ratio for NH_3 of 3.6 times solar at 9 bar from an analysis of the attenuation of the Probe's radio transmission. Indeed, even three times the solar abundance of NH_3 will not fit the radio data, so either there is some unexplained error in the probe transmission data, there is an additional source of opacity that becomes important at pressures greater than 5 bar, or ammonia is significantly depleted globally at pressure levels sampled by the ground-based measurements. Steffes (private communication) has just discovered that phosphine has a high opacity at the wavelengths corresponding to the probe's transmission. It thus appears highly probable that this will contribute to the Folkner et al. (1998) result, which must then be seen as an upper limit on the global ammonia abundance. Clearly more work is needed on this important problem.

The NIMS instrument on the *Galileo* Orbiter has demonstrated that the H_2O abundance increases dramatically outside the 5-micron hot spots, but it is not possible to derive quantitative global mixing ratios for H_2O from the results (Roos-Serote et al. 1998). The microwave observations from Earth do not probe sufficiently deeply to contribute an answer to this question. Thus we do not yet have a definitive value for the global oxygen abundance on Jupiter.

B. Recent Bright Comets

Comets provide an opportunity to examine outer solar system bodies at relatively close range to the Earth. However, the points of origin of comets are difficult to ascertain, so the significance of their molecular, elemental, and isotopic compositions remains in dispute. So-called long-period comets appear to originate from a region of space known as the Oort Cloud, ranging in distance from the Sun from 10^4 to 10^5 AU. The consensus view, though not necessarily a unanimous one, is that this is the region to which comets were ejected by gravitational interactions with the giant planets; their birthplace is thought to be within the zone of the giant planets (Weissman 1991). Short-period comets may arrive from two or more reservoirs. Some may be Oort Cloud objects, and others may originate in a so-called inner Oort Cloud ranging from 10^3 to 10^4 AU from the Sun. However, the majority appear to be derived from a region stretching roughly from 30 AU out to 100 AU or so, predicted by Edgeworth and more quantitatively by Kuiper (Jewitt and Luu 1998), and referred to in the current literature as the Kuiper Belt. It is understood now to consist of remnant planetesimals left over from solar system formation, residing (with some important caveats) largely in place since the beginning (Malhotra 1996). In particular, the inner part of the Belt has evolved dynamically under the influence of the giant planets, and a broader swath via collisions among objects, but fresh objects sampled from this zone are certainly less evolved dynamically than Oort Cloud comets (Duncan et al. 1995). Further discussion of the Kuiper Belt in the context of spectroscopic data is provided in the next subsection; a more comprehensive review of the current state of knowledge regarding the region is provided in the chapter by Jewitt and Luu in this volume.

The recent apparitions of Comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp) have permitted detection of many new species and a better determination of abundances of species previously seen in other comets. Both comets are on eccentric, long-period orbits typical of Oort Cloud comets. Of particular interest from the viewpoint of the origin of outer solar system material (and terrestrial water) are the deuterium enrichments measured in H_2O and HCN. The ratio D/H in HCN in Hale-Bopp, using the James Clerk Maxwell Telescope (JCMT) in Hawaii at 362 GHz, is $2.3 \pm 0.4 \times 10^{-3}$ (Meier et al. 1998*a*). The D/H ratio in cometary H_2O is essentially identical in three Oort Cloud comets: In Halley D/H$= 3.08^{+0.38}_{-0.53} \times 10^{-4}$ from the analysis of Balsiger et al. (1995) and $3.16 \pm 0.34 \times 10^{-4}$ from Eberhardt et al. (1995). In Hyakutake D/H $= 2.9 \pm 1.0 \times 10^{-4}$ (Bockelée-Morvan et al. 1998). In Hale-Bopp D/H $= 3.3 \pm 0.8 \times 10^{-4}$ (Meier et al. 1998*b*). The Halley measurements were from the ion neutral mass spectrometer on the *Giotto* spacecraft, the Hyakutake observations were made with the Caltech Submillimeter Observatory (CSO) on Mauna Kea, and those for Hale-Bopp were made with the JCMT at the same site. The close correspondence among the values of D/H for water, from in *situ* and remote measurements on three different comets, suggests that this is a typical value for Oort Cloud comets. A detailed compilation of isotopic abundances in comets is given in the chapter by Irvine et al., this volume.

The D/H values are significant in two respects. First, D/H in HCN is significantly higher than in the H_2O, and the values for both exceed the protosolar value by more than an order of magnitude. The difference in value between HCN and H_2O indicates the absence of significant exchange of hydrogen with a warm solar nebula or giant planet subnebula (Meier et al. 1998*a*). Indeed, the deuterium enrichment is perhaps the most reliable indicator that processing of grains in the outermost solar nebula was limited. The enrichment could be preserved under sublimation and recondensation of molecular cloud grains at low temperatures (Chick and Cassen 1997; Lunine et al. 1991) but not in the face of extensive radial mixing of the solar nebula (Prinn 1993).

On the other hand, the enrichment in HCN is actually less than that generally found for this molecule in molecular clouds (van Dishoeck et al. 1993). Enrichment is most plausibly obtained through ion-molecule reactions in the diffuse cloud regions, where the ion population is significant, and these reactions are strongly temperature dependent. The HCN deuterium abundance in Hale-Bopp implies processing of the material at temperatures of 30 ± 10 K (Meier et al. 1998*a*), warmer than the canonical 10 K in the coldest, most diffuse parts of the cloud but colder than the Neptune-forming zone of the solar nebula itself, which might have been at 50 K or so (Lunine et al. 1991). Dilution of the diffuse cloud value through ion-molecule reactions in the solar nebula itself is unlikely because of the high densities and low ion fractions. Perhaps in the grains of Hale-Bopp we are seeing the results of ion-molecule reactions in somewhat denser, warmer clumps of gas evolving toward collapse and disk formation. Support for this possibility is provided by the recent observations of Hatchell et al. (1998), who found DCN/HCN values in hot molecular cores comparable to that measured in Hale-Bopp.

We do not use this correspondence to argue that cometary species were processed in a hot core region; indeed, such regions, associated as they are with massive stars, are not likely analogs for the site of solar system formation. However, they are an example of the strong environmental variations (temporal and spatial) found in molecular clouds, and one cannot rule out the possibility that molecular cloud environments modestly warmer than the canonical 10 K set the D/H abundance in HCN-bearing grains. Alternatively, the cometary HCN deuterium abundance may reflect the release of that molecule from different populations of grains in Hale-Bopp, some of which formed at 10 K and others formed or modified at 50 K or more. Indeed, the presence of two very different D/H components in the Semarkona and Bishunpur meteorites (Bockelée-Morvan et al. 1998) is a warning that grains from quite distinct source environments or histories may be contained within the same body (see in this regard the chapter by Irvine et al., this volume). Direct sampling of individual volatile-bearing grains on a cometary nucleus, and further measurements of D/H variations within molecular clouds, will eventually resolve these ambiguities. Such sampling of isotopic ratios in species in individual grains could also provide a powerful technique for mapping the history of outer solar system temperatures complementary to meteoritical investigations pertinent to the inner solar system (see the chapters by Wadhwa and Russell and by Bell et al., this volume).

The deuterium enrichment in water is significant as well, beyond the observation that it is identical in three Oort Cloud comets. The cometary value is approximately twice that of Earth's ocean, the so-called standard mean ocean water value (SMOW) of 1.6×10^{-4}. While this difference might not be considered significant if it were measured in just one comet, we have confidence that it is a genuine distinction between SMOW and Oort Cloud comets based on the several objects and different techniques. The higher value in comets rules out the idea that Earth's ocean was supplied exclusively or even principally by comets in unaltered form (Owen and Bar-Nun 1995). One possibility is that dilution of the cometary deuterium abundance occurred after terrestrial impact through exchange of the water with a massive, hot, nebular hydrogen reservoir in contact with the primordial atmosphere. However, such a process would result in loss of water to space and, indeed, might even enhance the terrestrial deuterium abundance through selective retention of deuterium during escape. Thus a more plausible model is one in which Earth's ocean received part of its inventory (tens of percent) from Oort Cloud comets and the rest from a warmer, more processed source of water.

Other sources of water for the Earth remain problematic. We do not know D/H for water ice in Kuiper Belt comets; although we expect this to be similar to or higher than D/H in the Oort Cloud comets (because they formed from grains farther out in the nebula), we cannot rule out a lower value. Meteorite parent bodies containing water of hydration or small amounts of water ice, gravitationally scattered from more distant orbits, are a possibility. Owen (1998) pointed out that new rate coefficients for deuterium exchange between nebular hydrogen and water (Lecluse and Robert 1994) permit a low D/H ratio in water of 8×10^{-5} to be achieved in less than a million years at temperatures above 170 K. The deuterium-poor water, adsorbed on silicate grains, might then be accreted into the Earth and outgassed to dilute the deuterium enrichment supplied by comets. The high value of $^{20}Ne/^{22}Ne$ found in mantle rocks suggests that solar-composition gases in the Earth survived differentiation and formation of the Moon. This, in turn, lends support to the idea that H_2O vapor from the inner nebula was trapped in rocks that formed the Earth. Yet another possibility is water ice condensed in the 3–5 AU region, with a D/H ratio consistent with processing in the inner nebula (Delsemme 1999). We argue later that water vapor transport in the inner nebula might enhance the abundance of such planetesimals.

C. Pluto/Triton/Kuiper Belt Spectra

Optical and near infrared reflectance spectra of Pluto and Triton have been obtained since the late 1970s, but only over the past decade has sufficient spectral resolution been available to make assessment of the inventory of surface ices practical. Additional data come from multiple instruments operating during the 1989 *Voyager* flyby of Triton, ground-based observations of stellar occultations by both Pluto and Triton, mutual events observations of Pluto and its moon Charon, and *Hubble Space Telescope* measurements of the barycentric wobble of the Pluto-Charon system (see the review by Brown and Cruikshank 1997). The first ground-based spectrum of a Kuiper Belt object (KBO) was obtained in 1997 at the Keck I telescope and shows features interpreted to be hydrocarbons (Brown et al. 1997).

Pluto's place in the outer solar system makes a compelling case for its membership as a KBO, one whose size suggests accretion from smaller objects. Many of the directly detected KBOs are in the same 3:2 resonance with Neptune as is Pluto, suggesting a similar early dynamical evolution, and all observed KBOs are large enough to be products of accretion in an early, more populous, primordial Kuiper Belt (Jewitt and Luu, this volume). We present further discussion of such a primordial belt later. Triton may have been a Kuiper Belt body captured by Neptune early in the solar system's history. Despite their evidently very different dynamical histories, Pluto and Triton show surface abundances of key nitrogen- and carbon-bearing species that are remarkably similar to each other (Cruikshank et al. 1993; Owen et al. 1993). These abundances, in turn, appear to differ from the molecular abundances seen in comets to date; in particular, the abundance of N_2 relative to the carbon-bearing volatiles is much larger than that inferred for comets. Perhaps Pluto and Triton reflect a class of objects formed at very low nebular temperatures (30 K) and directly captured N_2. Alternatively, the ratio of nitrogen to methane and carbon monoxide may reflect more efficient photochemical and cosmic ray conversion of these last two species into refractory compounds that are difficult to detect spectroscopically. It is also possible that selective outgassing and escape early in Triton's history led to the current composition of volatile ices. A much more detailed inventory for Pluto and another KBO will be available from the *Pluto/Kuiper Express* mission, but not until 2013 (results to be reviewed in *Protostars and Planets VI*).

It is also instructive to compare the surface compositions of the Centaurs and KBOs. The orbits of the Centaurs (of which seven are known) are dynamically unstable on timescales of about 10^6–10^7 years (Gladman and Duncan 1990; Holman and Wisdom 1993; Dones et al. 1996). This implies a source of bodies to replenish those lost from the Centaur region by collisions or catastrophic gravitational encounters with the jovian planets. The presumed source of the Centaurs is the Kuiper Belt (Gladman and Duncan 1990).

Spectra of three Centaurs have been published: 5145 Pholus (Luu et al. 1994; Cruikshank et al. 1998), 2060 Chiron (Luu et al. 1994), and 1997 CU26 (Brown et al. 1998). Pholus shows a complex spectrum that has been modeled with a mixture of refractory organics, olivine, H_2O ice, CH_3OH ice, and amorphous carbon (Cruikshank et al. 1998). Chiron's spectrum is virtually devoid of color and detectable absorption features in existing data (Luu et al. 1994). CU26 shows evidence in its spectrum of water ice.

From the standpoint of dynamics it is quite compelling that the Kuiper Belt is the source of the Centaurs (Holman and Wisdom 1993); thus, it might be expected that these two groups of objects would show some common compositional patterns. The KBO 1996 TL_{66} (Luu and Jewitt 1998; R.H. Brown, D. P. Cruikshank, Y. J. Pendleton, and G. J. Veeder, unpublished data) shows a relatively flat spectrum that is almost featureless and resembles the spectrum of the Centaur Chiron. The KBO 1993 SC (Brown et al. 1997) shows a number of near infrared spectral features and has no direct spectral analog among the Centaurs, except that it may have light hydrocarbons on its surface, like Pholus. At present, there is no known spectral analog in the Kuiper Belt for the Centaur 1997 CU26.

An explanation for the differences may be that when objects leave the Kuiper Belt and more closely approach the Sun, their surfaces are altered, both chemically and physically. For example, if ices such as methane or methanol are irradiated with photons or charged particles, chemical bonds are broken, and the material proceeds to molecules with increasingly higher carbon abundances (Sagan et al. 1984; Andronico et al. 1987; Thompson et al. 1987; Strazzulla 1997). If the photolytic or radiolytic dose is large enough, in time the color of a high-albedo surface initially composed of light hydrocarbon and water ices can proceed from bluish to very red and eventually back to neutral with a very low albedo 3–5%. Thus the combined photolysis, radiolysis, and thermal escape of volatile material could lead to substantial devolatilization and carbonization of an originally volatile-rich surface (where water ice at the temperatures of interest is considered nonvolatile). In some cases enough dark material may be left behind that absorption bands due to residual water ice in the surface layers would be completely masked.

Centaur spectra might be a result of faster and more complete photochemical alteration and devolatilization of the Centaurs' near-surface layers (because they are closer to the Sun), so that a possible end state is a flat, featureless spectrum similar to that of amorphous carbon (see also Cruikshank et al. 1998). Crucial parameters are the initial inventory of primordial dark material and light hydrocarbons. If those inventories are too low, the final albedo of the surface would be expected to be relatively high (where 3–5% would be considered low), and the water ice absorption bands in the 1–2.5 μm spectral region would never be completely masked. However, we do not fully understand the long-term effects of photolysis, radiolysis, and heating of the surfaces of objects in the outer solar system, nor do we have a complete understanding of the expected initial inventories of amorphous carbon, organics, and light hydrocarbons. Significantly, the Trojan asteroids are very red and yet have spent gigayears well inward of the Centaurs, and the jovian irregular satellites vary in color from red to neutral. Hence, this picture must be considered speculative at present.

D. Titan

Saturn's giant moon Titan possesses a thick atmosphere of molecular nitrogen with secondary amounts of methane, higher hydrocarbons, and hydrogen. The chemical state of the atmosphere and surface have evolved through time as solar ultraviolet radiation photolyzes methane, producing less volatile, heavier compounds and allowing hydrogen to escape (Lunine et al. 1989). Though chemically evolved, the atmosphere retains clues to the environment within which Titan formed. A key question is whether the nitrogen composing Titan's atmosphere today originated as N_2 or in significantly more reduced form, for example as NH_3. If it was the latter, then photochemistry or other chemical processes converted this molecule to molecular nitrogen (Atreya et al. 1978). When the question was originally posed, it was thought that this might distinguish between a cometary origin for Titan's volatiles and a more local, saturnian-processed formation. However, the apparent dominance of ammonia over nitrogen in several comets (Wyckoff et al. 1991*a,b*) suggests that we might expect ammonia to have been the source in either case.

More than fifteen years ago Owen (1982) proposed a test for the origin of the nitrogen. Because of the similar volatilities of N_2 and Ar, it is expected they would be trapped in the ice to a similar extent, but proportional also to their relative abundances in the gas phase; hence in the atmosphere today Ar/N_2 would be of order 10%. A refinement of this ratio based on trapping of gases in clathrate leads to $Ar/N_2 \approx 1$–10%, although this number needs rework if the ices were amorphous in the protosaturnian nebula (possible) or in the solar nebula (highly probable). Because ammonia, on the other hand, hydrogen-bonds with water, it will be trapped in the water ice to a much greater extent than either N_2 or Ar; hence, if NH_3 is the source of Titan's nitrogen, we expect $Ar/NH_3 \ll 1\%$ at present. The current upper limit to argon is 7% from careful analysis of *Voyager* data (Strobel et al. 1993); it will require the measurements of *Cassini/Huygens* to refine this number and decide between the two cases. In any event we can rule out capture of Titan's atmosphere directly from the nebular gas, because the upper limit on neon is 0.2% (at the surface), far less than solar elemental abundance would yield (Owen 1982). Hidayat and Marten (1998) have detected $HC^{15}N$ in Titan's atmosphere and found $HC^{15}N/HC^{14}N$ to be strongly enhanced relative to the solar value. One way to obtain this enrichment, they argue, is through escape of nitrogen equivalent to many tens of times the current atmosphere. Such an escape process, early in Titan's history, might have involved other species as well and suggests the possibility of a massive early atmosphere on this object (Lunine 1985).

The origin of the methane in Titan's atmosphere is a more difficult issue. The rate of photolysis is such as to deplete the current atmospheric inventory in a time of the order of 1% the age of the solar system. Because of condensation, the atmosphere is in fact not capable of holding more than several times the current inventory without a substantial increase in temperature; hence the idea of "stoking up" the methane early on and storing it in the atmosphere for gigayears is not tenable. The suspicion since the *Voyager 1* encounter is that a large reservoir of methane might exist at Titan's surface, mixed with products of photolysis in a liquid hydrocarbon ocean (Lunine et al. 1983), or just beneath the surface (Stevenson 1992). Remote sensing data do not show evidence for widespread oceans on Titan (for example, Griffith 1993; Smith et al. 1996). Thus, outstanding correlative questions are the following: How much methane has been processed on Titan since its formation, and where is the remainder?

The deuterium abundance on Titan hints at a much larger methane reservoir in the past. The most recently determined ratio of deuterated methane (CH_3D) to normal methane (CH_4) is equivalent to a deuterium enrichment approximately 2–5 times the generally accepted primordial solar value, D/H $= 2.6 \pm 0.7 \times 10^{-5}$ (Gautier 1999). However, it is much lower than that seen in comets (Meier et al. 1998*a*) and suggests that comets could not have been the principle source of the volatile reservoir from which the methane was derived. Much of the deuterated methane enhancement could be the result of photochemical breaking of C–H bonds in preference to C–D bonds, progressively concentrating deuterium in the volatile atmospheric methane molecule while the hydrogen escapes (Pinto et al. 1986). Thus, provided the initial ratio of deuterated to normal methane can be estimated, the photochemical enrichment of D/H provides a means of estimating just how much methane has been photolyzed in the surface-atmosphere system of Titan over geologic time. Other sources of enrichment of CH_3D, such as differential vapor pressure effects of the deuterated species over a surface ocean or near-surface crustal reservoir, have been shown to be very small, changing enhancements by 10–20% at most (Pinto et al. 1986). Using the current D/H value in methane on Titan and assuming less than a factor of 2 enhancement in the original protosaturnian nebula, an original methane reservoir some one to two orders of magnitude larger than the current atmospheric abundance is obtained from a model of photochemical enrichment (Lunine et al. 1999). Because some methane may yet be stored in the crust or on the surface of Titan, the calculation yields a lower limit to the total original methane inventory prior to the start of photolysis.

The conclusion from the foregoing analysis is supported by a simple calculation based on the absolute photolysis rate as inferred from multiple types of *Voyager* data (Yung et al. 1984). The total amount of methane in the atmosphere at present will be irreversibly converted to higher hydrocarbons (with upward loss of hydrogen) in a time approximately 1% the age of the solar system. Thus, if Titan's current state with respect to methane and photochemistry is typical of that over its history, the original reservoir of methane must have been of order 100 times the present atmospheric abundance. It is important to recognize that the ways by which we have derived this number are in large part independent: One depends on knowing the absolute photolysis rate of methane, the other on the ratio of deuterated to normal methane and the relative photolysis rates of the two. The agreement between the two suggests that Titan did not begin with a large enhancement of deuterium in methane and, hence, was composed of planetesimals that were significantly processed relative to the nascent molecular cloud. This is consistent with Titan having been formed within a well-mixed protosaturnian nebula.

III. PROCESSES

In what follows we attempt a selective discussion of nebular processes that may have played a role in altering outer solar system material from molecular cloud composition, in delivering processed water ice to the terrestrial planets, and in seeding giant planet atmospheres. The intention is not to be comprehensive but to be detailed enough to provide a flavor for the kind of modeling required to connect the data described above with the formation of the giant planets and dispersal of planetesimal material throughout the solar system.

A. Grain and Gas Dynamical Heating during Infall

Infall of material from the molecular cloud to the solar nebula, associated with the collapse of the cloud clump from which the solar system was derived, leads to heating and chemical modification of molecular cloud material. This has been modeled extensively beginning with Ziglina and Ruzmaikina (1991) and Hood and Horanyi (1991). Gas dynamical heating is a consequence of the tendency of grains to decouple from the gas as they grow in size or encounter a shock front at the surface of the nebular disk. As the grains partly decouple from the gas and encounter a steepening density gradient associated with passage into the nebula, frictional heating leads to a temperature rise in the grains and possible sublimation of volatile species. The temperature rise and amount of sublimation are rather sensitively dependent on the grain's infrared emissivity or, equivalently, its ability to reradiate the frictional energy. This in turn is a function of the grain size and, secondarily, its composition and fluffiness.

Because typical interstellar grains are so small that they would remain embedded in the gas even through a shock front, growth of grains is essential for gas dynamical heating to be a significant process. Work by Weidenschilling and Ruzmaikina (1994), building on earlier results (Volk and Morfill 1991), show rather convincingly that the collapse of dense cloud clumps leads to significant grain growth during infall to the central protostar or protoplanetary disk. Grains of hundreds of microns or even millimeters in size grow during infall, and these will partly decouple from the gas and more fully decouple at the nebular surface shock front.

Lunine et al. (1991) quantified the heating of crystalline water ice grains and showed that infall to the Jupiter/Saturn region, and possibly even the Uranus/Neptune radial zone, engendered sufficient dynamical heating to permit sublimation of a large fraction of the water ice mass of the grains. Like miniature comets, the sublimating water ice would release volatile gases and entrain silicate dust particles. Lunine et al. (1995) quantified the gas dynamical process for a wider range of particle properties and composition, including amorphous ice, ice composed of species more volatile than water ice, and very fluffy grains. Also potentially important is the effect of solar heating, which is relevant for grains at large distances from the center of the nebula and still high above the midplane. The flared nature of the nebula ensures that both direct and scattered sunlight heat the grains (Simonelli et al. 1997). The most comprehensive study of grain heating and evolution within, and during entry into, the solar nebula is that of Chick and Cassen (1997). All models produce results that are broadly consistent, considering the various assumptions about the nebular environment and grain properties.

The sublimation of much of the grain's icy component suggests that the composition and physical trapping of the volatiles inherited from the molecular cloud is lost for grains that fall inward of 10–20 AU from the center of the nebula. Once in the nebula, cooling of the grain is rapid, and its surface becomes a cold finger on which water ice and other volatiles can condense or be trapped by various means. This natural cold trapping experiment is reproduced by the laboratory work of Bar-Nun and colleagues (Owen and Bar-Nun 1995), which suggests a sensitive temperature dependence to the final compositional state of the ice. Thus, at least in the realm of Jupiter and Saturn, and maybe beyond, much of the nature of solar nebula grains may be determined not by equilibrium condensation, nor by properties derived completely unaltered from the nascent molecular cloud, but by a dynamical two-step process of sublimation during infall followed by recondensation and trapping on the rapidly cooling remnant of the grain.

B. Water Transport in the Nebula: From Vapor to Cometary Delivery

Building on initial work by Morfill and Volk (1984) as well as Stevenson and Lunine (1988), several recent modeling efforts have focused on the effects of the transport of water throughout the disk on nebular physical and chemical state, grain evolution, and planet formation. As the principal condensable, water vapor is moved to cold-trapping regions by nebular diffusion and advection, condensed out, and recycled back to the inner nebula through ice grain growth and radial drift of grains (Stepinski and Valageas 1997; Cuzzi et al. 1993). The different dependencies of these processes on various timescales lead to a potentially complex spatial and temporal history of water vapor in the nebula, one that is also sensitive to specific nebular processes. In particular, the existence of the enstatite chondrites, as well as possible water ice in P and D asteroids are consistent with the water diffusion model of Cyr et al. (1998), in which the inner nebula is partly depleted of water vapor and the 3–5 AU region enriched in water ice. The model also predicts a higher abundance of reduced carbon species, such as methane, produced in the inner, chemically active part of the nebula than do standard solar nebula models.

The D/H ratio in water vapor processed in the warm inner nebula and transported outward toward the 3–5 AU region is perhaps half that of the terrestrial ocean value (Lecluse and Robert 1994). This water could serve to dilute the deuterium-rich water coming to early Earth from outer solar system comets. As noted above, such deuterium-poor vapor might be carried to the forming Earth adsorbed on silicate grains. Alternatively, since much of this water vapor ends up condensed as ice in the 3–5 AU region of the nebula (Cyr et al. 1998), gravitational stirring by Jupiter of the orbits of the resulting planetesimals might have delivered some of the water ice to Earth (Delsemme 1999). Indeed, Owen and Bar-Nun (1995) invoke comets formed at the orbit of Jupiter as a way of bringing water to the Earth without altering terrestrial noble gas abundances. Lecluse and Robert (1994) show that the vapor-ice fractionation effect during condensation might lead to a D/H ratio in these planetesimals close to the terrestrial ocean value. Thus they would seem not to be a very effective diluting agent for the high-D/H water brought in by outer solar system comets. Additionally, such Jupiter-region planetesimals might still trap carbon- and nitrogen-bearing species in their grains during formation at 160 K, potentially causing a budget problem in those elements at the Earth. Nonetheless, since large amounts of icy planetesimals are likely to have existed in the 3–5 AU region, it is important to ask how much of this material could have been scattered back to the inner solar system as opposed to being ejected by or accreted into Jupiter. Detailed simulations of the gravitational scattering of such planetesimals during and after the formation of Jupiter must be undertaken to evaluate to what extent these planetesimals contributed to Earth's ocean.

C. Origin of Giant Planet Atmospheres

The currently favored model of the formation of the giant planets invokes nucleation and collapse (Mizuno 1980; Pollack and Bodenheimer 1989; chapter by Wuchterl et al., this volume). According to this model, a core consisting of rock and ice formed first by accretion of planetesimals. When the mass of the core grew sufficiently large, it began to attract gas, eventually leading to the collapse of the surrounding solar nebula. Bombardment by planetesimals would continue even beyond this phase. The atmosphere therefore resulted from three components: volatiles released from the core during accretional heating, those released by infalling planetesimals dissolving in the gaseous envelope, and those contributed directly by the solar nebula. The condensed-phase contribution to the giant planets is largely based on interior models and consideration of nebular dynamics (Hubbard 1989; Pollack and Bodenheimer 1989; Stevenson 1983). This picture implies that those elements whose volatile compounds were initially trapped in the planetesimals that produced the core and dissolved in the envelope should be enhanced in the atmosphere.

To determine expected enhancements requires a model for the composition of the icy planetesimals in the outer solar system. In the interstellar medium, the reservoir of carbon is mostly in the form of grains and refractory organics, rather than volatiles such as CO and CH_4 (see the chapter by Irvine et al., this volume). On the other hand, nitrogen is mostly in the volatile form, that is, N_2 (Irvine and Knacke 1989; van Dishoeck et al. 1993). Most of the comets in the Oort Cloud are thought to have formed at 55 $\pm$15 K in the vicinity of Uranus and Neptune, though some may have been at warmer temperatures in the Jupiter-Saturn part of the nebula.

Temperatures of 30 $\pm$ 10 K are required for ion-molecule reactions to produce the observed ratios of D/H in H_2O and HCN in comet Hale-Bopp (Meier et al. 1998*a,b*). However, most of the grains that went into Jupiter and Saturn were likely exposed to (indeed, may have retrapped volatiles at) higher temperatures, above 40 K. Laboratory experiments have demonstrated that ice at temperatures near 55 K does not trap N_2, CO, or CH_4 well but easily traps refractory organics and NH_3 as well as compounds of other heavy elements (Bar-Nun and Kleinfeld 1989). Unless the temperature is below 25 K, ice does not trap Ne; temperatures below 10 K are required to trap He and significant amounts of H_2, although modest amounts of the latter are trapped at higher temperature (Dissly et al. 1994). The light gases are not readily absorbed in rock, either, so in Jupiter's atmosphere we expect H, He, and Ne to be contributed essentially solely by solar nebula gas and hence to exhibit relative abundances that are solar. Contribution of nitrogen to the atmosphere by the core or by infalling planetesimals is primarily by ammonia, which is present in amounts of order 10^{-3} relative to water in some comets (Wyckoff et al. 1991*a,b*). In this picture, considerable enrichment in the abundances of carbon, sulfur, and oxygen, with much less (or no) enhancement in the nitrogen elemental ratio, should be present in the jovian atmosphere.

These predictions rest on the assumption that most of the icy planetesimals contributing to Jupiter's growth and development were subjected to temperatures above 40 K. This is a reasonable assumption, based on the nebular physics discussed above. However, we cannot rule out *a priori* a population of Kuiper Belt comets that contain ices unaltered from lower molecular cloud temperatures and hence would carry more nitrogen and heavy noble gases, which in turn would lead to some enrichment of even these species over their solar abundances.

The *Galileo* Probe mass spectrometer measured C/H = 2.9 times solar in Jupiter, in accord with ground-based and *Voyager* results. It also measured sulfur, in the form of H_2S, for the first time and found that S/H at the deepest levels probed (20 bar) is 2.5 times solar. The nearly equal enrichment of carbon and sulfur is consistent with the predictions of a model in which icy planetesimals provide the major contribution of heavy elements (Owen and Bar-Nun 1995). Even the carbonaceous chondrites, the most carbon-rich of the meteorites, have C/S = 0.1 times solar. Unless there are rocky bodies unsampled by our collection of meteorites, it appears that only icy planetesimals have the correct composition to enrich these elements equally (Owen et al. 1997). The icy planetesimal model also predicts that oxygen (as H_2O) should be similarly enhanced, perhaps even somewhat more than carbon. Thus we expect water in Jupiter to be significantly greater than solar in abundance, an assertion supported by very recent evolution models of Jupiter (T. Guillot, unpublished manuscript). However, as discussed above, *Galileo* has not provided a quantitative number for the deep water value.

The nitrogen abundance in Jupiter's atmosphere challenges this particular picture of icy planetesimal composition. If the ammonia mixing ratio determined by Folkner et al. (1998) is correct, it suggests that nitrogen is at least as enriched as carbon and sulfur in Jupiter's atmosphere. Although cometary ammonia is a possible source, it is not abundant enough to provide nitrogen abundances comparable to the sulfur and carbon values (Wyckoff et al.1991*a*). Molecular nitrogen is effectively incorporated in ices only at temperatures below about 35 K (Owen and Bar-Nun 1995). Thus, a value of N on Jupiter of approximately 3 times solar would require building up the core and/or dominating the infalling ices with solid material coming directly from the cold regions of the molecular cloud that formed the solar system, without modification by a wealth of possible physical processes (Chick and Cassen 1997).

As we have seen, however (see section II.A.3), there is a fundamental contradiction between the Folkner et al. (1998) mixing ratio and the radio spectrum of the planet; at least a partial solution appears to lie in the existence of an additional absorber. Depending on how strong this additional absorption is, nitrogen may indeed be as deficient as the icy planetesimal model predicts. Another constraint on the problem is provided by the abundances of the heavy noble gases. If N_2 was captured by the icy planetesimals that enriched carbon and sulfur on Jupiter in sufficient amounts to provide a 3-times-solar enhancement of N, the same enrichment should have occurred for argon, krypton, and xenon. Otherwise we would expect these gases to be present in roughly solar proportions, enhanced to a limited extent by any colder material from the outermost disk or molecular cloud. The argon mixing ratio of 1.7 ± 0.6 times solar measured by the *Galileo* mass spectrometer is marginally consistent with this picture, but it must be remembered that some argon may have dissolved along with neon in helium raindrops sinking into the Jovian deep interior.

We must await the determination of mixing ratios for both Kr and Xe to test this point further. However, the present upper limit on Xe from the GPMS yields Xe/Ar $\leq$ 5 times solar in Jupiter, which appears to rule out the carrier phases in comets as being clathrate hydrate, because for clathrate phases Xe/Ar exceeds 9 times solar for C/H greater than 3 times solar in Jupiter (Lunine and Stevenson 1985). The xenon upper limit is thus consistent with the theoretical and laboratory arguments for amorphous water ice as the relevant carrier phase of adsorbed volatiles at the temperatures appropriate to the outer solar nebula. For icy planetesimals composed of amorphous water ice we expect mixing ratios of Xe and Kr in Jupiter's atmosphere to be between solar and twice solar. Again, however, a significant uncertainty in the use of jovian atmospheric noble gas abundances is the poorly determined relative solubilities of these species in the helium raindrops that may be selectively removing elements from the observable atmosphere (Roulston and Stevenson 1995). Indeed, we cannot even be certain that the atmospheric composition is a true reflection of that of the bulk interior, as we do not yet know quantitatively the extent of elemental partitioning at the molecular-metallic phase boundary within Jupiter and Saturn. This uncertainty will fade with time only if experimental and theoretical work enable progress in understanding the phase transition in detail.

IV. SOME CONCLUSIONS

1. *The amount and variation of processing of outer solar system grains remain uncertain.* The protoplanetary disk from which the solar system formed was not isolated; it was embedded within a nascent molecular cloud, and there was a continuum of processing of material between the two. Even grains destined for the outermost reaches of the planetary formation zone underwent significant growth in size, as well as heating by direct exposure to the Sun and by frictional effects, during their infall. Some grains may have completely sublimated and recondensed as far out as the Uranus-Neptune zone of the nebula. Thus, the relative and absolute abundances of the adsorbed phases trapped in the water ice may have been altered from molecular cloud values. Because the efficiency of volatile trapping varies from one molecular species to another, the relative abundances of carbon-, sulfur-, oxygen- and nitrogen-bearing compounds trapped in the ice could have changed. A counterindication lies in the jovian nitrogen abundance. Should it prove to be three times solar, then the source of such large amounts of nitrogen must lie in very cold ($\leq$35 K) icy grains preserved from colder regions of the molecular cloud. In any event, the isotopic composition of molecular species was probably not changed by processing of icy grains; this should remain preserved in comets from the

presolar values, unless there was a significant (and, we believe unlikely) exchange of material between the outer disk and the warm, inner nebula.

2. *The water abundance in the nebula varied significantly in time and space*. Advective and diffusive transport of water vapor from the warm inner disk to the water condensation boundary, accompanied by radial drift of icy planetesimals inward through the boundary, created a complex profile of water vapor and ice that changed substantially on timescales short compared to planet formation. In the inner disk the water profile overall was depleted relative to the bulk starting value (usually assumed to be solar), but in selected locations it might have had a substantial peak. There were always water ice planetesimals venturing significantly inward of the condensation boundary because of gas drag drift and gravitational perturbations. Outward of the condensation front, water was mostly in the form of ice because of the very steep falloff of ice vapor pressure with temperature at low temperature. The ice was a time-varying mixture of native condensed water vapor from the inner disk (significant only near Jupiter), ice moved inward from more distant parts of the nebula by drift and gravitational perturbations, and ice falling directly from the surrounding molecular cloud.

3. *Earth's ocean was not principally derived from Oort Cloud comets*. The D/H ratios determined for the three Oort Cloud comets Hyakutake, Hale-Bopp and Halley are inconsistent with the significantly lower value for the Earth's ocean. Thus, unless Earth's water budget exchanged deuterium with a large hydrogen reservoir after delivery (possible but difficult to accomplish without loss of the water to the nebula), the source had to be less deuterium rich than these three comets. Under the assumption that these comets are typical of the Oort Cloud reservoir, we must look elsewhere for the source of terrestrial ocean water. Determination of deuterium abundance in KBOs or Jupiter-family short-period comets (thought to be derived from the Kuiper Belt) is required to assess whether these could be sources. We expect, however, such objects to have high D/H values as well. Eliminating Oort Cloud and Kuiper Belt sources would rule out much or all of the outer solar system as candidate sources, because the Oort Cloud comets formed in the giant planet zone. Potential alternatives include water of hydration or adsorbed nebular water in silicates, and inner solar system water vapor condensed at the water condensation front and brought back inward by drag-induced radial drift and gravitational scattering.

4. *Surface volatile budgets of Triton and Pluto remain unexplained*. Whether by origin, chemical processing, or escape processes, the abundances of volatiles on the surfaces of Triton and Pluto differ significantly from those measured to date in comets. Models must account for the remarkable similarity in volatile composition of the two bodies, despite their different early dynamical histories. Also, the atmospheric compositions of Triton and Pluto are not all that different from what one would achieve

by lowering the temperature on Titan to Triton or Pluto values. Whether this resemblance is carried through to the bulk volatile budget must await *Cassini/Huygens* measurements of Titan and future, more detailed observations of Triton and Pluto.

5. *There were multiple sources of organics in the outer solar nebula*. Organic molecules in molecular clouds are highly enriched in deuterium. Data from Hale-Bopp indicate that this comet, at least, preserved that enrichment in the one organic molecule measured, HCN. The D/H value in methane in Titan's atmosphere, on the other hand, is only modestly enhanced relative to solar. Much of this may be the result of photochemical processing, over gigayears, of methane originally formed in a compact subnebula around Saturn. However, the fact that Titan's deuterium enrichment is essentially the same as that measured on Uranus and Neptune suggests that a solar nebular origin might be considered as well: for example, exchange of deuterium between hydrogen and water, followed by formation of methane during impacts of accreting planetesimals. Deciding between these two possibilities is important because it lies at the heart of the issue of how Titan acquired its prodigious volatile budget. It will require a determination of the deuterium abundance in multiple hydrogen-bearing species, noble gas abundances, and more precise (or de novo) determinations of isotopic ratios in carbon- and nitrogen-bearing species, all in Titan's atmosphere. The *Cassini/Huygens* mission represents a unique opportunity to make these measurements *in situ* and with high precision.

V. FUTURE PROSPECTS

In the coming two decades, seven missions are expected or proposed to return data from outer solar system bodies. These include *Cassini/Huygens* to orbit the Saturn system; *Pluto Kuiper Express* to fly past Pluto and a KBO; *Europa Orbiter Mission*; and *Rosetta, Stardust, Contour,* and *Deep Impact* to explore several comets. *Stardust* will collect coma dust samples, and *Deep Impact* will expose subsurface layers of the nucleus for spectroscopic analysis. Each of these missions has a well-designed Web site, to which the reader is referred in place of descriptive material here, for which space does not allow.

Continued progress in ground-based studies of the outer solar system depends in large part on access to large telescopes and increases in detector performance. The challenge for the Kuiper Belt is to probe deeper in terms of larger distances and smaller sizes. Earth-based spectroscopy will continue to be a principal tool for determining the composition of small bodies. Increasing sensitivity and aperture are essential for determining isotopic ratios and abundances of atoms and molecules that are relatively inactive spectroscopically. The future looks bright for availability of large-aperture systems. Government-funded projects such as Gemini in the United States; the 8-meter Japanese National Telescope, Subaru; and the European Very Large Telescope promise broader access to systems comparable to Keck in capability. The technology of large mirrors and structures has progressed to the point where smaller consortia of universities and research organizations can afford 6-meter apertures and larger. At least four such systems in the 6-to-10-meter class are scheduled to come on line between now and the time of the next *Protostars and Planets* book.

Acknowledgments The authors thank Drs. T. Guillot and S. Russell for helpful reviews. J. L. is most grateful to Dr. A. Coradini and the CNR/Istituto di Astrofisica Spaziale in Rome, Italy, for hosting him during the writing of this chapter. He is also grateful to Dr. G. Valsecchi for unselfishly troubleshooting TEX. Support for the preparation of this chapter came from NASA and CNR.

REFERENCES

Andronico, G., Baratta, G. A., Spinella, F., and Strazzulla, F. 1987. Optical evolution of laboratory-produced organics: Applications to Phoebe, Iapetus, outer belt asteroids and cometary nuclei. *Astron. Astrophys.*184:333–336.

Atreya, S. K., and Romani, P. N., 1995. Photochemistry and clouds of Jupiter, Saturn, and Uranus. In *Recent Advances in Planetary Meteorology*, ed. G. E. Hunt (Cambridge: Cambridge University Press), pp. 17–68.

Atreya, S. K., Donahue, T. M., and Kuhn, W. R. 1978. Evolution of a nitrogen atmosphere on Titan. *Science* 201:611–613.

Atreya, S. K., Wong, M., Owen, T. C., Niemann, H. B., and Mahaffy, P. 1997. Chemistry and clouds of the atmosphere of Jupiter: A Galileo perspective. In *Three Galileos: The Man, the Spacecraft, the Telescope*, ed. C. Barbieri, J. Rahe, T. Johnson, and A. Sohus (Dordrecht: Kluwer), pp. 249–260.

Balsiger, H., Altwegg, K., and Geiss, J. 1995. D/H and $^{18}O/^{16}O$ ratio in the hydronium ion and in neutral water from *in situ* ion measurements in comet P/Halley. *J. Geophys. Res.* 100:5827–5834.

Bar-Nun, A., and Kleinfeld, I. 1989. On the temperature and gas composition in the region of comet formation. *Icarus* 80:243–253.

Bockelée-Morvan, D., Gautier, D., Lis, D. C., Young, K., Keene, J., Phillips, T. G., Owen, T., Crovisier, J., Goldsmith, P. F., Bergin, E. A., Despois, D., and Wooten, A. 1998. Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origin of comets. *Icarus* 133:147–162.

Boss, A. P. 1995. Proximity of Jupiter-like planets to low-mass stars. *Science* 267:360–362.

Brown, R. H., and Cruikshank, D. P. 1997. Determination of the composition and state of icy surfaces in the outer solar system. *Ann. Rev. Earth Planet. Sci.* 25:243–277.

Brown, R. H., Cruikshank, D. P., Pendleton, Y., and Veeder, G. J. 1997. Surface composition of Kuiper Belt object 1993SC. *Science* 276:937–939.

Brown, R. H., Cruikshank, D. P., Pendleton, Y., and Veeder, G. J. 1998. Identification of water ice on the Centaur 1997 CU26. *Science* 280:1430–1432.
Chick, K. M., and Cassen, P. 1997. Thermal processing of interstellar dust grains in the primitive solar environment. *Astrophys. J.* 477:398–409.
Cruikshank, D. P., Roush, T. L., Owen, T. C., Geballe, T. R., de Bergh, C., Schmitt, B., Brown, R. H., and Bartholomew, M. J. 1993. Ices on the surface of Triton. *Science* 261:742–745.
Cruikshank, D. P., Roush, T. L., Bartholomew, M. J., Geballe, T. R., Pendleton, Y. J., White, S. M., Bell, J. F. I., Daviews, J. K., Owen, T. C., de Bergh, C., Tholen, D. J., Bernstein, M. P., Brown, R. H., Tryka, K. A., and Dalle Ore, C. M. 1998. The composition of Centaur 5145 Pholus. *Icarus* 135:389–407.
Cuzzi, J. N., Dobrovolskis, A. R., and Champney, J. M. 1993. Particle-gas dynamics in the midplane of a protoplanetary nebula. *Icarus* 106:102–134.
Cyr, K. E., Sears, W. D., and Lunine, J. I. 1998. Distribution and evolution of water ice in the solar nebula: Implications for solar system body formation. *Icarus* 135:537–548.
de Pater, I., and Massie, S. T. 1985. Models of the millimeter-centimeter spectra of the giant planets. *Icarus* 62:143–171.
Delsemme, A. H. 1999. The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. *Planet. Space Sci.* 47:125–131.
Dissly, R. W., Allen, M., and Anicich, V. G. 1994. H_2-rich interstellar grain mantles: An equilibrium description. *Astrophys. J.* 435:685–692.
Dones, L., Levison, H. F., and Duncan, M. 1996. On the dynamical lifetimes of planet-crossing objects. In *Completing the Inventory of the Solar System*, ed. T. W. Rettig and J. M. Hahn (San Francisco: Astronomical Society of the Pacific), pp. 233–244.
Duncan, M. J., Levison, H. F., and Budd, S. M. 1995. The dynamical structure of the Kuiper Belt. *Astron. J.* 110:3073–3081.
Eberhardt, P., Reber, M., Krankowsky, D., and Hodges, R. R. 1995. The D/H and $^{18}O/^{16}O$ ratios in water from comet P/Halley. *Astron. Astrophys.* 302:301–316.
Folkner, W. M., Woo, R., and Nandi, S. 1998. Ammonia abundance at the Galileo Probe site derived from absorption of its radio signal. *J. Geophys. Res.* 103:22847–22855.
Gautier, D. 1999. Deuterium in the solar system and cosmogonical implications. In *Planetary Systems: The Long View*, ed. L. Celnikier (Gif-sur-Yvette: Editions Frontières), in press.
Geiss, J. 1993. Primordial abundance of hydrogen and helium isotopes. In *Origin and Evolution of the Elements*, ed. N. Prantzos, L. Vangioni-Flam, and M. Casse (New York: Cambridge University Press), pp. 89–106.
Geiss, J., and Gloeckler, G. 1998. Measurement of the abundance of helium-3 in the local interstellar cloud and the Sun. *Space Sci. Rev.* 84:239–250.
Gladman, B., and Duncan, M. 1990. On the fates of minor bodies in the outer solar system. *Astron. J.* 100:1680–1683.
Griffith, C. A. 1993. Evidence for surface heterogeneity on Titan. *Nature* 364:511–514.
Hatchell, J., Millar, T. J., and Rodgers, S. D. 1998. The DCN/HCN abundance ratio in hot molecular cores. *Astron. Astrophys.* 332:695–702.
Hidayat, T., and Martin, A. 1998. Evidence for a strong $^{15}N/^{14}N$ enrichment in Titan's atmosphere from millimetre observations. *Ann. Geophys.* 16 (suppl. 3) C998.
Holman, M. J., and Wisdom, J. 1993. Dynamical stability in the outer solar system and the delivery of short period comets. *Astron. J.* 105:1987–1999.

Hood, L. L., and Horanyi, M. 1991. Gas dynamic heating of chondrule precursor grains in the solar nebula. *Icarus* 93:259–269.

Hubbard, W. B. 1989. Structure and composition of giant planet interiors. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), pp. 539–563.

Irvine, W. M., and Knacke, R. F. 1989. The chemistry of interstellar gas and grains. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), pp. 3–34.

Lecluse, C., and Robert, F. 1994. Hydrogen isotopic exchange reaction rates: Origin of water in the inner solar system. *Geochim. Cosmochim. Acta* 58:2927–2939.

Lewis, J. S., 1969. Observability of spectroscopically active compounds in the atmosphere of Jupiter. *Icarus* 10:393–409.

Lin, D. N. C., Bodenheimer, P., and Richardson, D. C. 1996. Orbital migration of the planetary companion of 51 Pegasi to its present location. *Nature* 380:606–607.

Linsky, J. L. 1996. GHRS observations of the LISM. *Space Sci. Rev.* 78:157–164.

Lunine, J. I. 1985. Volatiles in the outer solar system. Ph.D. Dissertation, California Institute of Technology.

Lunine, J. I., Yung, Y. K., and Lorenz, R. D. 1999. On the volatile inventory of Titan from isotopic abundances in nitrogen and methane. *Planet. Space Sci.* in press.

Lunine, J. I., and Stevenson, D. J. 1985. Evolution of Titan's coupled ocean-atmosphere system and interaction of ocean with bedrock. In *Proc. of the NATO Workshop on Ices in the Solar System,* ed. J. Klinger, D. Benest, A. Dollfus, and R. Smoluchowski (Dordrecht: D. Reidel), pp. 741–757.

Lunine, J. I., Stevenson, D. J., and Yung, Y. L. 1983. Ethane ocean on Titan. *Science* 222:1229–1230.

Lunine, J. I., Atreya, S. K., and Pollack, J. B. 1989. Evolution of the atmospheres of Titan, Triton and Pluto. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), pp. 605–665.

Lunine, J. I., Engel, S., Rizk, B., and Horanyi, M. 1991. Sublimation and reformation of icy grains in the primitive solar nebula. *Icarus* 94:333–343.

Lunine, J. I., Dai, W., and Ebrahim, F. 1995. Solar system formation and the distribution of volatile species. In *Deep Earth and Planetary Volatiles*, ed. K. Farley (New York: AIP Press), pp. 117–122.

Luu, J. X., and Jewitt, D. C. 1998. Optical and infrared reflectance spectrum of Kuiper Belt object 1996TL66. *Astrophys. J. Lett.* 494:L117.

Luu, J. X., Jewitt, D., and Cloutis, E. 1994. Near-infrared spectroscopy of primitive solar system objects. *Icarus* 109:133–144.

Mahaffy, P. R., Donahue, T. M., Atreya, S. K., Owen, T. C., and Niemann, H. B. 1998. Galileo Probe measurements of D/H and ^{3}He/ ^{4}He in Jupiter's atmosphere. *Space Sci. Rev.* 84:251–263.

Malhotra, R. 1996. The phase space structure near Neptune resonances in the Kuiper Belt. *Astron. J.* 111:504–516.

Meier, R., Owen, T. C., Jewitt, D. C., Matthews, H. E., Senay, M., Biver, N., Bockelée-Morvan, D., Crovisier, J., and Gautier, D. 1998*a*. Deuterium in comet C/1995 O1 (Hale-Bopp): Detection of DCN. *Science* 279:1707–1710.

Meier, R., Owen, T. C., Matthews, H. E., Jewitt, D. C., Bockelée-Morvan, D., Biver, N., Crovisier, J., and Gautier, D. 1998*b*. A determination of the HDO/H_2O ratio in comet C/1995 O1 (Hale-Bopp). *Science* 279:842–844.

Mizuno, H. 1980. Formation of the giant planets. *Prog. Theor. Phys.* 64:544–557.

Morfill, G. E., and Volk, H. J. 1984. Transport of dust and vapor and chemical fractionation in the early protosolar cloud. *Astrophys. J.* 287:371–395.

Niemann, H. B., Atreya, S. K., Carignan, G. R., Donahue, T. M., Haberman, J. A., Harpold, D. N., Hartle, R. E., Hunten, D. M., Kasprzak, W. T., Mahaffy, P. R., Owen, T. C., Spencer, N. W., and Way, S. H. 1996. The Galileo Probe mass spectrometer: Composition of Jupiter's atmosphere. *Science* 272:846–849.

Niemann, H. B., Atreya, S. K., Carignan, G. R., Donahue, T. M., Haberman, J. A., Harpold, D. N., Hartle, R. E., Hunten, D. M., Kasprzak, W. T., Mahaffy, P. R., Owen, T. C. and Way, S. H. 1998. The composition of the Jovian atmosphere as determined by the Galileo Probe mass spectrometer. *J. Geophys. Res.* 103:22831–22845.

Owen, T. 1998. The Origin of the atmosphere. In *The Molecular Origins of Life*, ed. A. Brack (Cambridge: Cambridge University Press), pp. 13–34.

Owen, T., and Bar-Nun, A. 1995. Comets, impacts and atmospheres. *Icarus* 116:215–226.

Owen, T., and Bar-Nun, A. 1996. Comets, meteorites and atmospheres. *Earth Moon Planets* 72:425–432.

Owen, T., Bar-Nun, A., and Kleinfeld, I. 1991. Noble gases in terrestrial planets: Evidence for cometary impacts. In *Comets in the Post-Halley Era*, Vol. 1, ed. R. L. Newburn, Jr., M. Neugebauer, J. Rahe (Dordrecht: Kluwer), pp. 429–437.

Owen, T. C. 1982. The composition and origin of Titan's atmosphere. *Planet. Space Sci.* 30:833–838.

Owen, T. C., Roush, T. L., Cruikshank, D. P., Elliot, J. L., Young, L. A., de Bergh, C., Schmitt, B., Geballe, T. R., Brown, R. H., and Bartholomew, M. J. 1993. Surface ices and the atmospheric composition of Pluto. *Science* 261:745–748.

Owen, T. C., Atreya, S. K., Mahaffy, P., Niemann, H. B., and Wong, M. H. 1997. On the origin of Jupiter's atmosphere and the volatiles on the Medicean stars. In *Three Galileos: The Man, the Spacecraft, the Telescope*, ed. C. Barbieri, J. Rahe, T. V. Johnson, and A. Sohus (Dordrecht: Kluwer), pp. 289–298.

Pinto, J. P., Lunine, J. I., Kim, S.-J., and Yung, Y. L. 1986. D to H ratio and the origin and evolution of Titan's atmosphere. *Nature* 319:388–390.

Pollack, J. B., and Bodenheimer, P. 1989. Theories of the origin and evolution of the giant planets. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), pp. 564–604.

Prinn, R. G. 1993. Chemistry of the protosolar nebula. In *Protostars and Planets III*, ed. E. H. Levy and J. I. Lunine (Tucson: University of Arizona Press), pp. 1005–1028.

Proffitt, C. R. 1994. Effects of heavy-element settling on solar neutrino fluxes and interior structure. *Astrophys. J.* 425:849–855.

Ragent, B., Colburn, D. S., Avrin, P., and Rages, K. A. 1996. Results of the Galileo Probe nephelometer experiment. *Science* 272:854–855.

Roos-Serote, M., Drossart, P., Encrenaz, T., Lellouch, E., Carlson, R. W., Baines, K. H., Kamp, L., Mehlman, R., Orton, G. S., Calcutt, S., Irwin, P., Taylor, F., and Wier, A. 1998. Analysis of Jupiter north equatorial belt hot spots in the 4–5 micron range from Galileo/near-infrared mapping spectrometer observations: Measurements of cloud opacity, water and ammonia. *J. Geophys. Res.* 103:23023–23041.

Roulston, M. S., and Stevenson, D. J. 1995. Prediction of neon depletion in Jupiter's atmosphere. *EOS* 76:343.

Sagan, C., Khare, B. N., and Lewis, J. S. 1984. Organic matter in the Saturn system. In *Saturn*, ed. T. Gehrels and M. S. Matthews. (Tucson: University of Arizona Press), pp. 788–807.

Showman, A. P., and Ingersoll, A. P. 1996. Deep dry downdraft as an explanation for low Jovian water observations. *Bull. Am. Astron. Soc.* 28:1141.

Simonelli, D. P., Pollack, J. B., and McKay, C. P. 1997. Radiative heating of interstellar grains falling toward the solar nebula: 1-D diffusion calculations. *Icarus* 125:261–280.

Smith, P. H., Lemmon, M. T., Lorenz, R. D., Sromovsky, L. A., Caldwell, J. J., and Allison, M. D. 1996. Titan's surface, revealed by HST imaging. *Icarus* 119:336–339.

Sromovsky, L. A., Best, F. A., Collard, A. D., Fry, P. M., Revercomb, H. E., Freedman, R. S., Orton, G. S., Hayden, J. L., Tomasko, M. G., and Lemmon, M. T. 1996. Solar and thermal radiation in Jupiter's atmosphere: Initial results of the Galileo Probe net flux radiometer. *Science* 272:851–853.

Sromovsky, L. A., Collard, A. D., Fry, P. M., Orton, G. S., Lemmon, M. T., Tomasko, M. G., and Freedman, R. S. 1998. Galileo Probe measurements of thermal and solar radiation fluxes in the Jovian atmosphere. *J. Geophys. Res.* 103:22929–22977.

Stepinski, T. F., and Valageas, P. 1997. Global evolution of solid matter in turbulent protoplanetary disks: II. Development of icy planetesimals. *Astron. Astrophys.* 319:1007–1019.

Stevenson, D. J., 1983. Structure of the giant planets: Evidence for nucleated instabilities and post-formational accretion. *Lunar Planet. Sci.* 14:770–771.

Stevenson, D. J. 1992. The surface of Titan. In *Proceedings of the Symposium on Titan*, ESA SP-338 (Noordwijk, The Netherlands: ESA), pp. 29–33.

Stevenson, D. J., and Lunine, J. I. 1988. Rapid formation of Jupiter by diffusive redistribution of water vapor in the solar nebula. *Icarus* 75:146–155.

Stevenson, D. J., and Salpeter, E. E. 1977. The dynamics and helium distribution in hydrogen-helium planets. *Astrophys. J. Suppl.* 35:239–261.

Strazzulla, G. 1997. Ion bombardment of comets. In *From Stardust to Planetesimals*, ed. Y. J. Pendleton and A. G. G. M. Tielens (San Francisco: Astronomical Society of the Pacific), pp. 423–433.

Stroble, D. F., Hall, D. T., Zhu, X., and Summers, M. E. 1993. Upper limit on Titan's atmospheric argon abundance. *Icarus* 103:333–336.

Thompson, W. R., Murray, B. G. J. P. T., Khare, B. N., and Sagan, C. 1987. Coloration and darkening of methane clathrate and other ices by charged particle irradiation: Applications to the outer solar system. *J. Geophys. Res.* 92:14933–14947.

Trilling, D. E., Benz, W., Guillot, T., Lunine, J. I., Hubbard, W. B., and Burrows, A. 1998. Orbital evolution and migration of giant planets: Modeling extrasolar planets. *Astrophys. J.* 500:428–439.

van Dishoeck, E. F., Blake, G. A., Draine, B. T., and Lunine, J. I. 1993. Chemical evolution of protostellar and protoplanetary matter. In *Protostars and Planets III*, ed. E. H. Levy and J. I. Lunine (Tucson: University of Arizona Press), pp. 163–241.

Volk, H. J., and Morfill, G. E. 1991. Physical processes in the protoplanetary disk. *Space Sci. Rev.* 56:65–73.

Von Zahn, U., and Hunten, D. M. 1996. The helium mass fraction in Jupiter's atmosphere. *Science* 272:849–850.

Weidenschilling, S. J., and Lewis, J. S. 1973. Atmospheric and cloud structures of the Jovian planets. *Icarus* 20:465–476.

Weidenschilling, S. J., and Ruzmaikina, T. V. 1994. Coagulation of grains in static and collapsing protostellar clouds. *Astrophys. J.* 430:713–726.

Weissman, P. R. 1991. Dynamical history of the Oort cloud. In *Comets in the Post-Halley Era*, Vol. 1. ed. R. L. Newburn Jr., M. Neugebauer, and J. Rahe (Dordrecht: Kluwer), pp. 463–486.

Wildt, R. 1937. Photochemistry of planetary atmospheres. *Astrophys. J.* 86:321–336.

Wyckoff, S., Tegler, S. C., and Engel, L. 1991*a*. Ammonia abundances in four comets. *Astrophys. J.* 368:279–286.

Wyckoff, S., Tegler, S. C., and Engel, L. 1991*b*. Nitrogen abundance in comet Halley. *Astrophys. J.* 367:641–648.

Yung, Y. L., Allen, M. A., and Pinto, J. P. 1984. Photochemistry of the atmosphere of Titan: Comparison between model and observations. *Astrophys. J. Suppl.* 55:465–506.

Ziglina, I. N., and Ruzmaikina, T. V. 1991. The influx of interstellar matter onto a protoplanetary disk. *Astron. Vest.* 25:53–60 (in Russian).