Studies of Chemical Abundances in the Outer Solar System

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Ground-based observations and the Pioneer 10 mission have led to new discoveries and revisions of previous ideas about the outer solar system. Among these are the discovery of atmospheres on Io and Ganymede, emission from sodium and hydrogen in a cloud around Io, and the presence of acetylene, ethane, and phosphine in the atmosphere of Jupiter. Titan, the largest satellite of Saturn, continues to be an extremely interesting and baffling object, clearly very different in composition from the bodies we are familiar with in the inner solar system; this is also true of Ganymede and Callisto. New data on the abundances of methane and hydrogen in the atmospheres of Uranus and Neptune suggest that the values of C/H in these atmospheres may be much lower than had been previously thought. This result reinforces the apparent compositional differences between these two planets and Jupiter and Saturn, whose atmospheres exhibit a near-solar value for this ratio.

The exploration of the outer planets and their satellites by means of space probes has only just begun. Pioneer 10 flew past Jupiter on 3 December 1973, on its way to solar system escape. It will be followed by Pioneer 11 approximately 1 yr later, with the next outer planet mission planned by the U.S. to be launched in 1977. But we have been able to acquire a large amount of information about these distant bodies by means of ground-based observations, and such studies are becoming increasingly productive as ever more sophisticated instrumentation becomes available.

An excellent summary of current knowledge about the outer solar system, prior to Pioneer 10 has been published by Newburn and Gulkis (ref. 1). That survey has been updated with a special emphasis on applications to exobiology (ref. 2). A compendium of information about all the satellites has just appeared in print (ref. 3). The present review will therefore emphasize the most recent results and attempt to indicate problems on which substantial progress may be expected in the next few years.

The Satellites

It has been suspected for many years that the Galilean satellites of Jupiter show a systematic decrease in mean density with increasing distance from the planet. As our detailed knowledge about these objects has increased, this density gradient has proven to be less extreme than was thought, but still appears real. It is intriguingly similar to the density gradient observed in the solar system itself and leads to a mean density for the outermost member, Callisto, that requires this object to be radically different in composition from the rocky inner solar system bodies with which we are familiar. These general characteristics should be kept in mind when discussing the origin of the Earth-Moon system to provide some perspective for the interpretation of peculiarities observed in de-

Table 1.—*The Galilean Satellites of Jupiter*

Name	Radius (km)	Mass (10^{23}g)	Density (g/cm^3)
Io (J I)	1820 ± 10	900 ± 60	3.5
Europa (J II)	1550 ± 150	480 ± 10	3.1
Ganymede (J III)	2635 ± 25	1540 ± 2	2.0
Callisto (J IV)	2500 ± 150	910 ± 80	1.4

NOTE: Data from Morrison and Cruikshank (ref. 3), except Io mass revised by Anderson, et al. (ref. 4).

tail in that one case. A summary for the current bulk characteristics of the Galilean satellites is given in table 1.

Searches have repeatedly been made without definite success for evidence of atmospheres about these bodies. Just last year, Brown (ref. 5) reported the unexpected result that the spectrum of Io exhibits the D lines of sodium in emission. These observations have been confirmed and extended, and it now appears that the satellite is surrounded by a cloud of sodium atoms, whose exact shape, origin, and mode of excitation remain to be defined (refs. 6, 7, and 8). This promises to be an exciting subject for future research.

The occultation experiment on Pioneer 10 was successful in detecting the presence of a very tenuous atmosphere on this satellite (refs. 9 and 10). The mean surface pressure deduced was in the range 10^{-8} to 10^{-10} bars. Lyman alpha emission was observed in a torus around Jupiter and from Io itself, suggesting that hydrogen is at least a component of the satellite's atmosphere (ref. 11). Tentative proof for an atmosphere on Ganymede was adduced from a stellar occultation ob- (refs. 9 and 10). The mean surface pressure served by Carlson et al. (ref. 12). The observations in this case were found to correspond to a surface pressure between 10^{-3} and 10^{-6} bars, but it would appear that additional observations are desirable to verify this finding. What is the composition of these atmospheres? How are they produced and maintained? What is their connection (if any) with the post-eclipse brightening of J I and J II discovered by Binder and Cruikshank (ref. 13) ? These and other questions remain to be answered.

Saturn's largest satellite, Titan, has been known for many years to have an atmosphere containing methane (ref. 14). More recently, hydrogen absorptions were detected in the spectrum by Trafton (ref. 15), and the thermal radiation emitted at 12 μ was found to be anomalously high (ref. 16), confirming an earlier observation by Low (ref. 17). These new results spawned a series of interpretive papers attempting to understand the high temperature in terms of the relatively small amount of information about the satellite that was available. A comprehensive summary of the observations and their interpretations may be found in the proceedings of a conference on the atmosphere of Titan, edited by Hunten (ref. 18).

The latest observations of this puzzling object suggest that it is very dark at 5 μ, that there is not a large amount of gaseous hydrogen in that part of the atmosphere that is probed at 20 μ (e.g., not enough for a hydrogen greenhouse), that methane and probably ethane are in emission in a high-altitude inversion layer, and that the surface temperature is in the range 135 ± 45 K (refs. 19 through 22). A coherent picture has still not emerged from these observations, but it does appear that some extreme model atmospheres can be ruled out.

The material(s) responsible for the red coloration of Titan pose another interesting problem. The low albedo at 5 μ limits the number of candidates, but the possibility of combining various substances to obtain the red color observed in the visible and the low albedo at 5 μ makes the likelihood of an unequivocal determination very small. Another complication is posed by the need to decide how the materials responsible for the reflection characteristics of the satellite are distributed between the surface of the body and possible clouds or hazes in its atmosphere. Organic polymers are one of several interesting candidates (refs. 23 and 24). One thing that does seem certain is that the material(s) causing the red color on Io are not identical with the chromophores on Titan (ref. 25).

Looking further outward in the solar system, we have examined the spectra of Pluto and Triton to see if they show evidence of the methane absorptions that are so prominent in Titan's spectrum (ref. 2). The results thus far have been negative, which may simply indicate that these bodies have always been too cold to permit substantial vapor pressures of infrared-active gases to exist.

The entire subject of satellites in the solar system will be reviewed at a forthcoming IAU Colloquium (No. 28) to be held at Cornell University; the interested reader is advised to obtain the *Proceedings* volume when it becomes available.

Planets

Until the Pioneer 10 mission, the atmosphere of Jupiter seemed reasonably well understood. However, the occultation experiment on that mission indicated that the upper atmosphere of Jupiter was very much warmer than had been expected, in serious contradiction to the results of ground-based optical spectroscopy and radio observations (refs. 9 and 10). At this writing, no one has been able to devise a model atmosphere that successfully explains both sets of data, and serious questions have consequently been raised about the possibilities of error in the occultation data or their interpretation (refs. 26 and 27). This is a significant confrontation because it affects the interpretation of ground-based data for the atmospheres of all the major planets, not just Jupiter. One may hope that the results to be obtained from the Pioneer 11 mission will prove to be helpful in resolving the present dilemma.

The mixing ratio of hydrogen to helium was also studied by experiments on the Pioneer 10 mission (see Smoluchowski, this conference). A new analysis of the infrared radiometer results by Hogan et al. (ref. 26) suggests that they imply a roughly solar value of $H/He = 10$ instead of the lower values obtained in the preliminary reports (ref. 28). Helium was directly detected for the first time by the Pioneer 10 UV spectrophotometer (ref. 11).

Recent ground-based studies have resulted in the detection of several important trace constituents. The 4–0 P(1) line of HD was discovered by Trauger et al. (ref. 29) who derived a D/H ratio of $(2.1 \pm 0.4) \times 10^{-5}$ for the Jovian atmosphere. This is very similar to the corrected interstellar value of $(1.4 \pm 0.2) \times 10^{-5}$ derived by Rogerson and York (ref. 30) from observations of the Lyman absorption spectrum of interstellar atomic deuterium using the instrumentation on the Orbiting Astronomical Observatory (OAO–C). Taken together, these results imply that the material making up the planet has not undergone nuclear processing, and mass-dependent escape has not occurred from the upper atmosphere since the formation of the solar system.

Other processes have obviously been at work, however, as is evident from the presence of colored regions in the cloud belts (e.g., the Great Red Spot). Support for the hypothesis that these colors might be caused by the presence of complex organic polymers was provided by the recent discovery of small amounts of C_2H_2 and C_2H_6 in the planet's spectrum near 13 μ (refs. 31 and 32). These products will not be present in detectable amounts under conditions of simple thermodynamic equilibrium (ref. 33), but they are expected to be formed as by-products of organic polymer synthesis through the action of ultraviolet light, lightning discharges, etc. Of course their existence does not *require* that these more complex substances be present. In fact, the discovery of a sodium cloud around the satellite Io invites a reinspection of the hypothesis of Wildt (ref. 34) that the colors might result in part from solutions of metallic sodium in ammonia. The discovery that PH_3 is also present in Jupiter's atmosphere (ref. 35) lends further weight to the idea that material contributed from outside the planet (e.g., through meteoritic infall) may play a significant role in the atmospheric chemistry.

The harvest of new results on the other outer planets has been less rich. Phosphine

Table 2.—*Abundances in the Outer Solar System*

Object	H_2 (km atm)	NH_3 (m atm)	CH_4 (m atm)	H/ /C
Jupiter	75 ± 15	12 ± 5	50 ± 15	3000 ± 300
Saturn	75 ± 20	2 ± 1	60 ± 12	2500 ± 400
Uranus	450 ± 100	< 2.5	$>10 \times 10^3$	< 100
Neptune	450 ± 100	—	$>10 \times 10^3$	< 100
Pluto	—	< 10	< 2?	—
Titan	5 ± 2.5	< 2.5	200 to 1600	6 to 50
Triton	—	—	< 2?	—
			Sun	2700 ± 300

and ethane have been suspected in the atmosphere of Saturn, but available spectral resolution is not yet adequate for a definitive identification (ref. 36). Ammonia has been detected in the spectrum at 6450 Å, with an abundance of 2 ± 1 m atm (ref. 37). This result disagrees with an upper limit of < 2 cm atm derived at 1.55 μm (ref. 38). This same discrepancy in abundances determined at these two wavelengths has been found on Jupiter and may represent a change in the opacity with wavelength in the atmospheres of these two planets. The relatively low ammonia abundance derived for Saturn implies a thick ammonia cloud and a model that carries with it a prediction that the ammonia abundance should vary with time, as appears to be the case (refs. 37, 39, and 40).

Recent work on the interpretation of spectra of Uranus and Neptune has indicated that the atmospheric methane abundances derived for these two planets may be seriously low. It has not been possible to observe some of the bands seen in the planetary spectra with laboratory pressure-path lengths as high as 10 km atm, implying vertical column abundances in the range 10 to 50 km atm (refs. 41 and 42). New values for the hydrogen abundances have also been reported, with mean values in the neighborhood of 450 km atm for the atmospheres of both planets (refs. 43 through 46).

A first attempt to identify the 4–0 P(1) line of HD in the spectrum of Uranus led to a crude upper limit of 20 mÅ on the equivalent width of this line, corresponding to a limit of $D/H < 4 \times 10^{-4}$ (ref. 47). It would be useful to lower this limit, since these two planets have apparently experienced some early differentiation, being enriched in heavy elements in comparison with, say, Jupiter and Saturn. Hence, some enrichment of D relative to H may also have occurred. If the methane is enriched as much as the previous discussion implies, it will probably be necessary to consider the distribution of deuterium between methane and hydrogen in order to interpret this result properly. Thus, we are also planning to improve the present detection threshold for CH_3D absorption, which leads to a limit of $D/H < 3 \times 10^{-3}$ (ref. 48).

Summary

The current status of abundance studies for major constituents in the atmospheres of the bodies we have been discussing is given in table 2. This table should not be viewed as definitive, it is simply an attempt to summarize some current estimates for constituent abundances. All of these estimates were made from analyses of photographic and near-infrared planetary spectra. Simple reflecting models have been assumed throughout, so the figures should not be taken seriously as absolute abundances. The upper limits were established with the additional assumption that the absorption bands involved were not saturated. This implies that some other gas (e.g., neon) is present to provide the necessary pressure broadening.

The new discoveries of trace constituents (C_2H_2, C_2H_6, PH_3) are not included in the table since mixing ratios for these gases are still very uncertain. Ridgway's (ref. 31) original estimates of 4×10^{-3} and 8×10^{-5} for C_2H_6 and C_2H_2 seem rather high, since the mixing ratio for CH_4 is roughly 10^{-3} (see table 2). Combes et al. (ref. 32) suggest that these values should be reduced by a factor of 20. The difficulty lies in the fact that these gases are observed in the upper atmosphere where a thermal inversion occurs, and hence the interpretation of the observations is extremely model-dependent (refs. 27 and 49).

The relative abundances on a given planet shown in table 2 should have more significance; the final column giving values for C/H should therefore reflect real differences among the objects being surveyed. The new results for the methane abundances on Uranus and Neptune emphasize the difference between these planets and Jupiter and Saturn. The large depletion of light gases in the atmospheres of the outer two planets must be explained by any comprehensive theory for the origin and evolution of the solar system. In the case of Titan, we are really still in the beginning stages of a proper investigation, while even the gross characteristics of Pluto and Triton are presently only poorly known.

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