ORIGIN OF THE MAJOR PLANET ATMOSPHERES: CLUES FROM TRACE SPECIES

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According to the generally accepted planetesimal accretion hypothesis, the present atmospheres on the major planets, Jupiter, Saturn, Uranus and Neptune, resulted from two sources: outgassing from planetary interiors during the accretionary heating phase the planetesimals making up the core were composed of grains, ices and possibly clathrates - and direct capture of gases from the solar nebula. It is not apparent, however, whether the present atmospheres of these planets are representative of the composition of the dense interstellar cloud from whose collapse the solar nebula initially formed, or whether the interstellar material was further processed in the solar nebula before being accreted into the major planets. Although present observations cannot fully constrain the models of the origin of atmospheres, clues to the physical and chemical nature of the solar nebula and subsequent origin and evolution of the major planet atmospheres are beginning to emerge from studies of the elemental isotopic ratios (such as D/H) and the mole fractions of such trace species as He, CH₄, NH₃, CO and HCN. Since much has been written on D/H, He / H₂ and CH₄ / H₂ [1], this paper focuses on what one can learn about the origin of the major planet atmospheres from the detected presence of CO and HCN in Neptune's atmosphere. On the basis of our calculations, we conclude that the interior of Neptune should contain CO and N_2 , with the N_2 mole fraction close to the value for the cosmic C/N ratio. The presence of these interstellar molecules in the interior of Uranus is suggested also.

CO and HCN have been detected at ppm and ppb levels, respectively, in the stratosphere of Neptune [2,3] and their tentative implications for atmospheric chemistry have been discussed [2,4,5,6,7]. Extraplanetary sources of water vapor (e.g. from ablating meteoroids or comets) and nitrogen (e.g. from Triton) could, in principle, produce CO and HCN following their reactions with the photolysis products of CH₄; they are, however, inadequate for producing the observed mole fractions of CO and HCN [2,4,5,6,7]. The alternative is an intrinsic source in the form of CO and N_2 . This is attractive from many different points of view: (a) it does not require a unique origin for Neptune's atmosphere relative to Uranus' - a planet that is similar to Neptune in "bulk" composition - since the lack of detection of CO and HCN on Uranus can be attributed to the lack or virtual lack of convection in Uranus' interior which would prevent detectable abundances of CO and N₂ from being transported to the stratosphere (presence of CH₄ there could create a potential problem, but it probably has another explanation, as discussed later); (b) it reduces the value of the helium mole fraction on Neptune to 15% [8], which is consistent with the protosolar and the Uranian values, provided that the N_2 mole fraction is 0.3% (N_2 of 0.3% is what one would expect for

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solar C/N ratio with C/H = 30x solar); (c) it explains the observed depletion of NH₃ on Neptune (and Uranus, if $C/N \ge solar$) since most of the nitrogen would be in the form of N_2 . The proposed presence of CO and N_2 in the interiors of Uranus and Neptune implies that these species were incorporated directly from the solar nebula, and that the N₂ and CO of the interstellar cloud were not reduced to NH₃ and CH₄, respectively, in the less than 30 Myr lifetime of the solar nebula before its gas was blown away. Indeed, it seems that equilibrium may not have reached anywhere in the solar nebula despite the possibility of Fischer-Tropsch-type catalytic reactions, since the pressures and temperatures in the solar nebula were inadequate for such reactions. The fact that both Jupiter and Saturn have solar or super-solar NH₃ and CH₄ in their atmospheres appears to imply that once incorporated as N₂ and CO from the solar nebula these gases must have been reduced to NH₃ and CH₄, respectively, by Haber-type processes in the deep, dense, hot interiors of these planets. Such reduction requires presence of an iron catalyst which is expected to be present in their cores. Although the cores of Uranus and Neptune are also expected to have iron, the gases could be separated from the iron by layering in the interior. Since the CO to CH₄ catalysis proceeds somewhat differently than N₂ to NH₃, there is the possibility that some CO hydrogenation occurred in the solar nebula, but most of the CO was reduced to CH₄ in the interiors of Uranus and Neptune as well, leaving some CO behind. It is this CO that is detected in the atmosphere of Neptune, as well as on Jupiter and Saturn. The detection of N₂ and CO on Pluto and Triton lends support to this hypothesis, since the Haber-type reactions cannot occur on these tiny solid bodies, so that they are expected to retain to a large extent the original gases incorporated during their accretion.

Regarding the large CH_4 abundance on the major planets, there is yet another likelihood for the formation of methane on these planets. Since most of the carbon in the interstellar cloud is in the form of grains, perhaps carbon delivered as grains was responsible for the formation of methane.

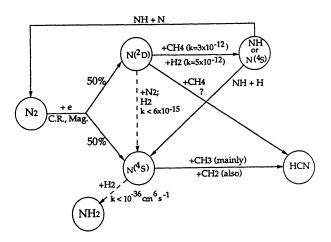


Figure 1. Nitrogen chemistry leading to the formation of HCN.

Dissociation of N_2 in the stratosphere, after this gas convects from Neptune's interior, is necessary for producing HCN as detailed in Figure 1 (intermediate product H_2CN is not shown). The dissociating/ionizing flux is most likely provided by the galactic cosmic rays (GCR). The production rate of ion-electron pairs created in gas j by primary GCR [9] can be approximated by (assuming that energy is deposited locally):

$$q_{j}(z) = \frac{1}{\Delta E_{j}} \int_{\Omega} \int_{E_{0}}^{\infty} \Phi(E, z, \Omega) \left[-\frac{dE}{dz} \right]_{j} dE d\Omega$$
(1)

where ΔE_j is the average energy needed to create an ion-electron pair in gas j and is typically 36 eV, $[-dE/dz]_j = n_j\sigma_jE$ is the stopping power, Ω is the solid angle, E is the energy of the cosmic ray, and $\Phi(E,z,\Omega)$ is the differential flux of GCR. The total absorption cross-section for the incident galactic cosmic rays in the atmosphere of Neptune is taken to be $8.5\times10^{-26}\,\mathrm{cm^2}$, and it is based on the work of Schopper [10] and Belletini et al [11]. Secondary electrons, produced in the collision of galactic cosmic rays with the atmospheric constituents, dissociate and ionize N_2 and H_2 in the following manner:

$$\begin{array}{lll} e + N_2 \rightarrow N_2^+ + 2e & q = 0.53 & \sigma = 2.6 \times 10^{-16} \, cm^2 & (2) \\ \rightarrow N(^4S) + N^+ + 2e & = 0.12 & = 6.0 \times 10^{-17} \, cm^2 & (3) \\ \rightarrow N(^4S) + N(^2D) + e & = 0.35 & = 1.8 \times 10^{-16} \, cm^2 & (4) \end{array}$$

and

$$e + H_2 \rightarrow H_2^+ + 2e$$
 $\sigma = 1.0 \times 10^{-16} \text{ cm}^2$ (5)
 $\rightarrow H^+ + H + e$ $= 6.0 \times 10^{-18} \text{ cm}^2$ (6)

where q is the quantum efficiency and σ is the cross section for a given path [12,13]. The previous values of q's for reactions (2), (3) and (4), 0.45, 0.10 and 0.45, respectively, do not alter the results significantly.

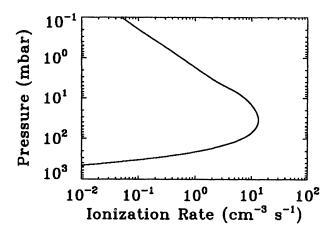


Figure 2: Ion-pair production rate due to penetration of primary galactic cosmic rays into Neptune's atmosphere at a magnetic latitude of 60°.

Using the differential flux of the GCR at Neptune [14], we obtain total ion-pair production rate shown in Figure 2 and a column production rate of ion pairs, $q_T = 6.7 \times 10^7 \, \text{cm}^{-2} \text{s}^{-1}$. The N(⁴S) production rate is 73% of the total nitrogen ion production rate, $q_{N_{\bar{z}}}$; whereas $q_{N_{\bar{z}}} = 3.3 q_{H_{\bar{z}}} f_{N_{\bar{z}}}$, where $q_{H_{\bar{z}}}$ is the total hydrogen ion (H₂⁺ and H⁺) production rate and f_{N_2} is the N₂ mole fraction. Since $q_{H_{\bar{z}}} \approx q_T$, the N(⁴S) production is $1.6 \times 10^8 \, f_{N_2}$. The N(⁴S) required to produce the observed ppb level of HCN is $1.7 \times 10^6 \, \text{cm}^{-2} \text{s}^{-1}$ for $K = 10^5 \, \text{cm}^2 \text{s}^{-1}$ [2] in the production region of HCN (1-2mb) and $1.7 \times 10^5 \, \text{cm}^{-2} \text{s}^{-1}$ if $K = 10^4 \, \text{cm}^2 \text{s}^{-1}$, where K is the eddy diffusion coefficient. Therefore 0.1%-1% mole fraction of N₂ will be needed. The actual required f_{N_2} is probably closer to 0.1% than 1% since $K < 10^5 \, \text{cm}^2 \text{s}^{-1}$, N(²D) could quench and produce 100% more N(⁴S), and the actual cascading process of the

charged particles through the atmosphere than the simplified scenario of local deposition of energy considered here could produce 50-100% more N(4S). Proper treatment of the cascading of charged particles through the atmosphere requires a Monte Carlotype approach where the history of cosmic ray particles and secondary electrons through the atmosphere is followed.

In summary, we propose that the major planets acquired at least a part of their atmospheres from vaporization of ices embedded in the nebula. Whatever the form of C and N compounds in these ices, the material was reprocessed in the planetary interiors. A possible exception to this scenario is provided by laboratory studies of the trapping of gases by ices at low temperature [15]. This work indicates that the relative fractions, as well as abundances of CO and N₂ (as well as other volatiles) trapped in ices, has a strong dependence on temperature. If we believe that these volatiles were delivered to Uranus and to Neptune (and other major planets) by the icy planetesimals, then there is the possibility that far less CO and N₂ were delivered to Uranus than Neptune, which formed in the colder part of the solar nebula [16].

Observational tests as well as improved theoretical models will be needed to confirm and improve upon the hypothesis proposed here. Direct spectroscopic detection of N₂ on the major planets is not possible at this time. However, detection and quantification of nitrogen bearing molecules, such as nitriles, as well as C/H (as in CH₄), P/H (as in PH₃) and the isotopic ratios in the noble gases are relevant and crucial. Thermochemical models for the interior and models of the chemistry initiated by the solar ultraviolet photons and charged particles, including Monte Carlo calculations for determining the N-atom yield are essential. Comparative planetology in this instance has the potential of addressing some of the most fundamental questions of the formation of the planets and their atmospheres.

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