ABSTRACT

We present results on the bases and concentrations of methane ice, ammonia ice, ammonium hydrosulfide-solid, water ice, and aqueous-ammonia solution (“droplet”) clouds of Neptune and Uranus, based on an equilibrium cloud condensation model. Due to their similar p-T structures, the model results for Neptune and Uranus are similar. Assuming 30–50× solar enhancement for the condensibles species, as expected from formation models, we find that the base of the droplet cloud is at the 370 bars for 30× solar, and at 500 bars for 50× solar cases. Despite this, entry probes need to be deployed to only 50–100 bars to obtain all the critical information needed to constrain models of the formation of these planets and their atmospheres.

1. INTRODUCTION

Comparative planetology of deep well-mixed atmospheres of the outer planets is the key to the origin and evolution of the solar system, and by extension, extrasolar systems. Critical factors to constrain the formation models are abundances of heavy elements (heavier than helium) below cloud levels of the giant planets. Much has been written previously about the two gas giants, Jupiter and Saturn (e.g., Atreya et al. [1, 2]). In this paper, we focus on the two icy giants, Neptune and Uranus. Methane ice is the only other condensible species on these two planets, in addition to the clouds of ammonia ice, ammonium hydrosulfide (NH₄SH) solid, water ice, and aqueous-ammonia solution (“droplet”) that form also on the gas giants. To the first order, cloud structure can be calculated using an equilibrium cloud condensation model (ECCM) that employs basic principles of thermodynamics. Based on the measured methane (CH₄) mixing ratio, the C/H is 30–50× solar at Neptune, and 20–30× solar at Uranus. Assuming similar enhancement for the other condensibles, as expected from formation models, we find that the base of the droplet cloud is at 370 bars for 30× solar, and at 500 bars for 50× solar cases. Not only such high pressure levels pose immense technological challenges to entry probe missions, the N/H and O/H ratios deduced at these pressures are not even representative of their well-mixed values. On the other hand, noble gases, methane (CH₄), hydrogen sulfide (H₂S), as well as D/H and ¹⁵N/¹⁴N can be accessed and measured at much shallower levels, and would still permit the retrieval of information critical to the formation of Neptune and Uranus and their atmospheres, especially when combined with the elemental abundance information for the gas giants.

2. THERMOCHEMICAL CLOUD MODEL

ECCM was first developed by Weidenschilling and Lewis [3], and improved by Atreya and Romani [4]. The lifting condensation level (LCL), i.e., the base of the cloud, is calculated by comparing the partial pressure and the saturation vapor pressure of the condensable volatile. The LCL is reached at the altitude where 100% relative humidity is attained. The amount of condensate in the ECCM is determined by the temperature structure at the LCL and vicinity. The release of latent heat of condensation modifies the lapse rate, hence the temperature structure, of the atmosphere. The composition and structure of the clouds depend on the composition of the atmosphere, and in particular the distribution of condensible volatiles. For details of the current model, see Atreya and Wong [5].

Thermochemical equilibrium considerations suggest that CH₄, NH₃, and H₂O are the only species likely to condense in the atmospheres of Neptune and Uranus, if the composition were solar. H₂S does not condense even if it were enriched substantially. In the gas phase, H₂S can combine with NH₃ to form NH₄SH, i.e., \( \text{NH}_3(g) + \text{H}_2\text{S}(g) \rightarrow \text{NH}_4\text{SH} \), or ammonium sulfide ((NH₄)₂S) which is less likely. NH₄SH would condense as a solid in the environmental conditions of Neptune and Uranus. NH₃ could also dissolve in H₂O, resulting in an aqueous solution (droplet) cloud in the atmosphere. The extent of such a cloud depends on the mole fractions of NH₃, and H₂O.
2.1 Model Inputs

The presently known elemental abundance information for Neptune and Uranus along with that for Jupiter is given in Table 1. The heavy element ratios for Uranus and Neptune are taken to be the same as C/H from CH₄ measurements on these planets, i.e., N (from NH₃), S (from H₂S), and O (from H₂O) are enriched 30–50 times relative to solar at Neptune, and 20–30 times at Uranus. The progressively larger enrichment in the heavy elements from Jupiter to Neptune is consistent with predictions of the core accretion model. For purposes of cloud structure modeling, it is reasonable to assume factors of 30 and 50 enrichment over solar for all of Neptune’s condensable species, CH₄, NH₃, H₂S, and H₂O. A 20–30 times solar enrichment is expected at Uranus.

<table>
<thead>
<tr>
<th></th>
<th>Sun</th>
<th>Jupiter/Sun</th>
<th>Uranus/Sun</th>
<th>Neptune/Sun</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/H</td>
<td>0.0975</td>
<td>0.807±0.02</td>
<td>0.92–1.0</td>
<td>0.92–1.0</td>
</tr>
<tr>
<td>Ne/H</td>
<td>1.23×10⁻⁴</td>
<td>0.10±0.01</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>Ar/H</td>
<td>3.62×10⁻⁶</td>
<td>2.5±0.5</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>Kr/H</td>
<td>1.61×10⁻⁸</td>
<td>2.7±0.5</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>Xe/H</td>
<td>1.68×10⁻¹⁰</td>
<td>2.6±0.5</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>C/H</td>
<td>3.62×10⁻⁴</td>
<td>2.9±0.5</td>
<td>20–30</td>
<td>30–50</td>
</tr>
<tr>
<td>N/H</td>
<td>1.12×10⁻⁴</td>
<td>3.0±1.1</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>O/H</td>
<td>8.51×10⁻⁴</td>
<td>0.29±0.1</td>
<td>(hotspot)</td>
<td>20–30 (?)</td>
</tr>
<tr>
<td>S/H</td>
<td>1.62×10⁻⁵</td>
<td>2.75±0.66</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
<tr>
<td>P/H</td>
<td>3.73×10⁻⁷</td>
<td>0.82</td>
<td>20–30 (?)</td>
<td>30–50 (?)</td>
</tr>
</tbody>
</table>

Table 1a. Elemental Abundances


The initial temperature profile of Neptune below 1 bar pressure level is calculated with the model using a solar composition for heavy elements but without accounting for heat of condensation or chemical reaction. The temperature at 1 bar is 72 K, consistent with the temperature profile from Voyager [6]. The temperature profile is shown in Fig. 1.

2.2 Van der Waals corrections

The behavior of gas at high pressures departs from that given by the Ideal Gas Law. Under high pressure, hydrogen atoms repel each other and the real pressure is greater than pressure predicted by Ideal Gas Law

\[ p = nRT/V \]

(1)

where \( p \) is the pressure, \( n \) the number of moles, \( R \) the gas constant, \( T \) the temperature, and \( V \) the volume. After the quantities of \( n, T \) and \( V \) are determined from Eq. 1, the modified pressure is calculated using Van der Waals equation

\[ p = \left[ \frac{nRT}{(V-nb)} \right] - a\left(\frac{n}{V}\right)^2 \]

(2)

where for hydrogen, \( a = 0.2453 \text{ bar L}^2\text{ mol}^{-2} \), and \( b = 0.02661 \text{ L mol}^{-1} \). Due to the Van der Waals effects, in the case of 30× solar enrichment of elements, the “ideal gas pressure” of 600 bars increases to 860 bars, 400 bars to 515 bars, and 200 bars to 226 bars.

3. MODEL RESULTS

According to the ECCM, the topmost cloud layer at ~1 bar level is made up of CH₄ ice. Voyager radio occultation observations did in fact infer a cloud layer at ~1 bar level. The base of the water-ice cloud for solar O/H is expected to be at ~40 bar level, whereas for the NH₃-H₂O solution clouds it is at approximately twice this pressure. We present cases with 1×, 30×, and 50× solar
enrichment of the condensible volatiles (CH₄, NH₃, H₂S, H₂O) in Fig. 2 for Neptune. The NH₃-H₂O aqueous solution cloud base is calculated to be at 370 bars and 500 bars, respectively for 30× and 50× solar cases. The 30× solar case of Neptune represents very closely the cloud structure at Uranus where the heavy element enrichment is predicted to be 20–30× solar.

Some models (e.g. [7]) predict the presence of an ionic ammonia ocean in the 0.1 megabar region, much deeper than even the solution cloud. Such an ocean is most likely also responsible for the depletion of ammonia in the upper troposphere, which is significantly more severe than can be explained by the loss of this species in the formation of an NH₄SH cloud. Therefore NH₃ (as well as H₂O) will have been depleted well below their predicted LCLs.

**Fig. 2.** ECCM results for Neptune, assuming 1× (dashed lines), and 30× (left panel) or 50× solar enrichment (right panel), of condensible volatiles (CH₄, NH₃, H₂S, H₂O ratioed to H) relative to solar. Cloud bases for 30× and 50× solar cases are marked on the right ordinates. The cloud densities represent upper limits, as cloud microphysical processes (precipitation) would almost certainly reduce the density by factors of 100–1000 or more. The cloud bases will not be affected, however. The structure and locations of the clouds at Uranus are very similar to the 1× and 30× solar (left panel) cases for Neptune due to similar thermal structure (p-T) and 20–30× solar enrichment of condensible volatiles, noble gases and the other heavy elements.

4. **ENTRY PROBES**

Much still remains mysterious about the clouds of the giant planets. It is only by having access to the region well below the main cloud layers that the abundances of key heavy elements can be determined. Comparative study of the gas giants, when combined with a similar study for the icy giants, can provide the most comprehensive constraints for the models of formation of our solar system. Determination of the water abundance on Uranus and Neptune is much more challenging than that on Jupiter and Saturn. The colder atmospheres of the icy giants result in their cloud water
Uranus and Neptune seem insurmountable also in the near future. Survival of the probe structure and scientific payload to kilobar levels (as in Marianas Trench) where temperatures reach 500 K or greater, combined with the difficulty of data transmission from such great depths are only two of a multitude of obstacles. However, even if the entry probes could be designed to survive to only a hundred bar level, critical composition and dynamics information can still be collected. All heavy elements, except O, can be measured. As explained earlier, the O/H and N/H even at the kilobar level are not representative of their well-mixed abundance on Neptune and Uranus. On the other hand, noble gases, He, Ne, Ar, Kr, Xe, as well as C/H, S/H, $^{15}$N/$^{14}$N, and D/H, all of which can be accessed and measured at shallower depths with pressures of 50–100 bars, are fully adequate for constraining models of the formation of the icy giants and their atmospheres, especially when combined with the elemental and isotope abundance measurements, including O/H, at Jupiter and Saturn. Complementary information on disequilibrium species, PH$_3$, GeH$_4$, and AsH$_3$, as well as cloud, wind, and lightning characteristics would greatly enhance the value of the compositional data.

Multiple probes to the giant planets are critical for collecting the data required for understanding the formation of our solar system. Either in a single grand tour or on individual spacecraft missions, 2–3 probes deployed to 50–100 bars at all giant planets is recommended. The deployment of entry probes and proper operation of scientific payloads even to these depths must overcome enormous technological challenges. The transmission of probe radio signal from 100 bars at Neptune is also much more challenging than from 100 bar level at Jupiter. This is due to the 10–20 times greater abundance of the highly microwave absorbing molecules, ammonia and water (and perhaps also phosphine), at Neptune than at Jupiter at corresponding pressure levels (30–50× solar on Neptune, while only approximately 3× solar on Jupiter). Microwave remote sensing from spacecraft in the shorter term can provide a valuable guide to the development of probe missions.

5. REFERENCES