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The Origin of Carbon Monoxide in Neptune's Atmosphere

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The CO abundance in the observable atmosphere of Neptune can be plausibly explained by rapid vertical mixing from the deeper atmosphere if Neptune has a greater complement of water than Uranus. Thermochemical equilibrium and kinetic calculations reveal that Neptune must and Uranus may have about 10 times more oxygen than carbon, whereas for Jupiter and Saturn equal enrichments of carbon and oxygen are satisfactory to explain the observed CO abundances by deep vertical mixing. Relative to hydrogen and solar composition, the respective enrichment factors for carbon and oxygen are 41, 440 (Neptune); 32, ≤260 (Uranus); 6.6, 6.6 (Saturn); and 2.8, 2.8 (Jupiter). Because water ice is the most refractory ice among the ices assumed to be present in the outer solar nebula, the most massive H_2O enrichment is expected for the outermost planet of this group. Thus, Neptune can indeed be regarded as the "god of the seas." © 1994 Academic Press, Inc.

INTRODUCTION

Recently, Marten *et al.* (1991, 1993a,b) and Rosenqvist *et al.* (1992) detected about 1 ppm of CO in Neptune's atmosphere. Their observations were subsequently confirmed by Guilloteau *et al.* (1993) and Naylor *et al.* (1994). The CO abundance on Neptune is at least a factor of 100 higher than the upper limit for the CO abundance on Uranus. Because both planets are commonly assumed to be similar, the higher abundance of CO on Neptune was unexpected.

The CO abundance in the upper atmosphere of Neptune can be plausibly explained by rapid vertical mixing from the deeper atmosphere, if Neptune has a greater complement of water than Uranus. As is shown below, both planets have large enrichments of heavy elements ($Z \geq 3$), and the enrichment factors over the solar value for carbon or oxygen may not be the same for each planet.

THERMOCHEMICAL MODELING OF OBSERVED CO ABUNDANCES

In all of the jovian planets, CO production in the lower regions of their atmospheres occurs by the net thermochemical reaction:

$$CH_4 + H_2O = CO + 3H_2. \qquad (1)$$

The CO mole fraction, $X(CO)$, is given by

$$X(CO) = K_{(1)}[X(CH_4)X(H_2O)/X(H_2)^3]\Phi(1/P_T^2) \qquad (2)$$

where $K_{(1)}$ is the equilibrium constant for reaction (1), X_i is the mole fraction of compound i, Φ represents the product of fugacity coefficients, and P_T stands for the total pressure. To examine which variables in Eq. (2) determine the CO mole fraction on the jovian planets we compare the ratios of the CO mole fractions for the planet pairs Saturn/Jupiter and Neptune/Uranus:

$$\frac{X(CO)_{Sat}}{X(CO)_{Jup}} = \frac{K_{(1)}[X(CH_4)_{Sat}X(H_2O)_{Sat}/X(H_2)^3_{Sat}]\Phi(1/P_T(Sat)^2)}{K_{(1)}[X(CH_4)_{Jup}X(H_2O)_{Jup}/X(H_2)^3_{Jup}]\Phi(1/P_T(Jup)^2)} \qquad (3a)$$

$$\frac{X(CO)_{Nep}}{X(CO)_{Ura}} = \frac{K_{(1)}[X(CH_4)_{Nep}X(H_2O)_{Nep}/X(H_2)^3_{Nep}]\Phi(1/P_T(Nep)^2)}{K_{(1)}[X(CH_4)_{Ura}X(H_2O)_{Ura}/X(H_2)^3_{Ura}]\Phi(1/P_T(Ura)^2)}. \qquad (3b)$$

The similar pressure–temperature structure on either Jupiter and Saturn or Uranus and Neptune (Fig. 1) means

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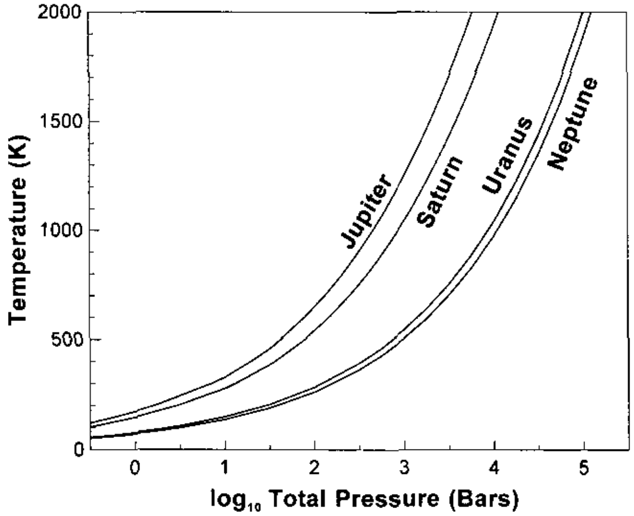

FIG. 1. Temperature–pressure profiles for the deep atmospheres of Jupiter, Saturn, Uranus, and Neptune. The profiles for Jupiter and Saturn were calculated as described by Fegley and Prinn (1988) using H_2 and He mole fractions listed in Table I. Profiles for Uranus and Neptune are obtained from data given by Hubbard and MacFarlane (1980).

that to a first approximation, the quench temperatures and therefore the equilibrium constants and fugacity coefficients are similar too. Thus, these terms drop out of Eqs. (3a) and (3b). The total pressure can be approximated for Jupiter by $P_T(\mathrm{Jup}) = 0.570 \cdot P_T(\mathrm{Sat})$ and for Uranus by $P_T(\mathrm{Ura}) = 0.717 \cdot P_T(\mathrm{Nep})$ for a given temperature (see Fig. 1). Equations (3a) and (3b) then become

$$\frac{X(\mathrm{CO})_{\mathrm{Sat}}}{X(\mathrm{CO})_{\mathrm{Jup}}} = \frac{X(\mathrm{CH_4})_{\mathrm{Sat}} X(\mathrm{H_2O})_{\mathrm{Sat}} X(\mathrm{H_2})^3_{\mathrm{Jup}}}{X(\mathrm{CH_4})_{\mathrm{Jup}} X(\mathrm{H_2O})_{\mathrm{Jup}} X(\mathrm{H_2})^3_{\mathrm{Sat}}}\, 0.325 \tag{4a}$$

$$\frac{X(\mathrm{CO})_{\mathrm{Nep}}}{X(\mathrm{CO})_{\mathrm{Ura}}} = \frac{X(\mathrm{CH_4})_{\mathrm{Nep}} X(\mathrm{H_2O})_{\mathrm{Nep}} X(\mathrm{H_2})^3_{\mathrm{Ura}}}{X(\mathrm{CH_4})_{\mathrm{Ura}} X(\mathrm{H_2O})_{\mathrm{Ura}} X(\mathrm{H_2})^3_{\mathrm{Nep}}}\, 0.542. \tag{4b}$$

For CO and CH_4, we insert the available observations and upper limit from Table I and obtain

$$\frac{X(\mathrm{H_2O})_{\mathrm{Sat}}}{X(\mathrm{H_2O})_{\mathrm{Jup}}} = 1.7 \pm 1.1 \tag{5a}$$

$$\frac{X(\mathrm{H_2O})_{\mathrm{Nep}}}{X(\mathrm{H_2O})_{\mathrm{Ura}}} \geq (90\text{–}170). \tag{5b}$$

TABLE I

Abundance Data in the Solar Photosphere and in the Atmospheres of Jupiter, Saturn, Uranus, and Neptune

Solar[a]	H_2	He	C	O
Mole fraction ($X_i = n_i/\Sigma(H_2 + He + \cdots)$)	0.835 ± 0.008	0.167 ± 0.008	$(5.91 \pm 0.68) \times 10^{-4}$	$(1.24 \pm 0.20) \times 10^{-3}$
Mixing ratio ($F_i = n_i/H_2$)	1	0.2 ± 0.008	$(7.09 \pm 0.81) \times 10^{-4}$	$(1.48 \pm 0.24) \times 10^{-3}$
Jupiter[b]	H_2	He	CH_4	CO
Mole fraction ($X_i = n_i/\Sigma(H_2 + He + \cdots)$)	0.898 ± 0.02	0.102 ± 0.02	$(1.75 \pm 0.20) \times 10^{-3}$	$(1.3 \pm 0.4) \times 10^{-9}$
Mixing ratio ($F_i = n_i/H_2$)	1	0.114 ± 0.02	$(1.95 \pm 0.22) \times 10^{-3}$	$(1.4 \pm 0.4) \times 10^{-9}$
Enrichment over solar, $E = F_i(\text{planet})/F_i(\text{solar})$	1	0.57 ± 0.10	2.8 ± 0.44	
Saturn[c]	H_2	He	CH_4	CO
Mole fraction ($X_i = n_i/\Sigma(H_2 + He + \cdots)$)	0.963 ± 0.024	0.0325 ± 0.024	$(4.5 \pm 2.2) \times 10^{-3}$	$(1.5 \pm 0.8) \times 10^{-9}$
Mixing ratio ($F_i = n_i/H_2$)	1	0.034 ± 0.024	$(4.7 \pm 2.3) \times 10^{-3}$	$(1.6 \pm 0.8) \times 10^{-9}$
Enrichment over solar, $E = F_i(\text{planet})/F_i(\text{solar})$	1	0.17 ± 0.12	6.6 ± 3.3	
Uranus[d]	H_2	He	CH_4	CO
Mole fraction ($X_i = n_i/\Sigma(H_2 + He + \cdots)$)	0.825 ± 0.033	0.152 ± 0.033	0.019 ± 0.005	$<1 \times 10^{-8}$
Mixing ratio ($F_i = n_i/H_2$)	1	0.184 ± 0.033	0.023 ± 0.006	$<(1\text{–}1.2) \times 10^{-8}$
Enrichment over solar, $E = F_i(\text{planet})/F_i(\text{solar})$	1	0.92 ± 0.17	32 ± 9	
Neptune[e]	H_2	He	CH_4	CO
Mole fraction ($X_i = n_i/\Sigma(H_2 + He + \cdots)$)	0.80 ± 0.032	0.190 ± 0.032	0.023 ± 0.005	$(0.65\text{–}1.2) \times 10^{-6}$
Mixing ratio ($F_i = n_i/H_2$)	1	0.238 ± 0.032	0.029 ± 0.006	$(0.81\text{–}1.5) \times 10^{-6}$
Enrichment over solar, $E = F_i(\text{planet})/F_i(\text{solar})$	1	1.19 ± 0.17	41 ± 10	

[a] Solar abundances from Grevesse and Noels (1993).

[b] Jovian abundances from Bjoraker *et al.* (1986), Gautier *et al.* (1982), Fegley (1994), and Noll *et al.* (1988).

[c] Saturnian abundances from Fegley (1994), Noll and Larson (1990), and Noll *et al.* (1986).

[d] Uranian abundances from Baines *et al.* (1993), Fegley (1994), Guilloteau *et al.* (1993), and Marten *et al.* (1993a,b).

[e] Neptunian abundances from Baines *et al.* (1993), Fegley (1994), Guilloteau *et al.* (1993), Marten *et al.* (1993a,b), and Rosenqvist *et al.* (1992).

The water enrichment on Saturn is about 1.7(±1.1) times higher than on Jupiter; however, within error, this relative enrichment of oxygen is close to the respective carbon ratio of 2.6(±1.3) for Saturn and Jupiter (derived from the CH_4 mole fractions, Table I), indicating that carbon and oxygen are equally enriched over solar on both Jupiter and Saturn.

For the pair Uranus and Neptune, however, this rough estimate shows that Neptune may be more than 90–170 times richer in water (and thus bulk oxygen) than Uranus. Table I also lists the enrichment factors (E) for carbon over the solar value calculated from the element/H_2 abundances. Uranus and Neptune are enriched in carbon by factors of 32 and 41, respectively. By analogy to the pair Jupiter and Saturn we expect that other more refractory elements such as oxygen are at least enriched by the same factors, but a comparison of the calculated water ratio $[X(H_2O)_{Nep}/X(H_2O)_{Ura} \geq (90\text{–}170)]$ with the ratio for $CH_4[X(CH_4)_{Nep}/X(CH_4)_{Ura} = 1.2 \pm 0.4]$ of the two planets implies that heavy elements are not uniformly enriched.

The abundance ratios derived from Eqs. (4a) and (4b) are valid only if the mole fractions of CH_4 and H_2 are the same in the observed regions of the atmosphere and in the deeper regions of the planet where CO originates. While we can assume that the Saturn/Jupiter CH_4 and H_2 mole fraction ratios are approximately constant over a wide depth profile, this assumption may not be valid for Uranus/Neptune, as discussed below.

So far we calculated abundance ratios only for the similar planet pairs. Absolute values for the enrichment factors on the individual outer planets can be calculated considering the equilibrium thermochemistry and kinetic mixing calculations. Details of such calculations are described by Fegley *et al.* (1991) and Fegley and Lodders (1994). The observable CO abundance depends on the CO to CH_4 destruction rate during upward mixing from the deep atmosphere. Prinn and Barshay (1977) proposed the conversion mechanism as

$$CO + H_2 = H_2CO \tag{6}$$

$$H_2CO + H_2 \rightarrow CH_3 + OH \tag{7}$$

$$CH_3 + H = CH_4 \tag{8}$$

where reaction (7) is the rate-determining step. The chemical lifetime of CO is then a function of the CO, H_2CO, and H_2 molecular number densities,

$$t_{chem}(CO) = [CO]/k_7[H_2CO][H_2], \tag{9}$$

where the rate constant $k_7 = 2.3 \cdot 10^{-10} \exp(-36200/T)$ $cm^3\ sec^{-1}$ (Prinn and Barshay 1977).

Results of the kinetic calculations for the outer planets are shown in Fig. 2. Plotted are CO mole fractions as a function of the vertical eddy diffusion coefficient (K_{eddy}). The horizontal dashed lines indicate the observed CO abundance (Jupiter, Saturn, Neptune) or upper limit (Uranus). Table II lists the calculated mole fractions for CO, CH_4, H_2, and H_2O at the quench temperature for Jupiter, Saturn, Uranus, and Neptune. For better comparison all data in the table are shown for the same eddy diffusion coefficient $K_{eddy} = 10^8\ cm^2\ sec^{-1}$. This K_{eddy} value is consistent with literature estimates for all four planets (Prinn and Barshay 1977, Fegley and Prinn 1988, Fegley *et al.* 1991). The last two columns in Table II give

TABLE II
Calculated Mole Fractions and Carbon and Oxygen Enrichment Factors

		Mole fraction, $X_i = n_i/\Sigma(H_2 + He + \cdots)$				Mixing ratios ($F_i = n_i/H_2$) relative to solar	
						C/H_2	O/H_2
	T_{quench} (K)	$X(CO)$	$X(CH_4)$	$X(H_2)$	$X(H_2O)$	Input for calculation[a]	
Saturn	976	1.2e-9	4.6e-3	0.94	10.8e-3	6.6	6.6
Jupiter	1030	2.3e-9	1.8e-3	0.89	4.2e-3	2.8	2.8
Saturn/Jupiter at T_{quench}		0.52	2.6	1.06	2.6	2.4	2.4
Saturn/Jupiter observed		1.15 ± 0.71	2.6 ± 1.3	1.07 ± 0.04	—	2.4	—
Neptune	998	1.1e-6	0.025	0.14	0.60	41	440
Uranus	950	1.1e-8	0.020	0.42	0.37	32	260
Neptune/Uranus at T_{quench}		100	1.25	0.33	1.62	1.3	1.7
Neptune/Uranus observed		>(65–120)	1.21 ± 0.4	0.97 ± 0.06	—	1.3	—

[a] Calculated for $K_{eddy} = 10^8\ cm^2\ sec^{-1}$ and enrichment factors as listed in last two columns. For details see text.

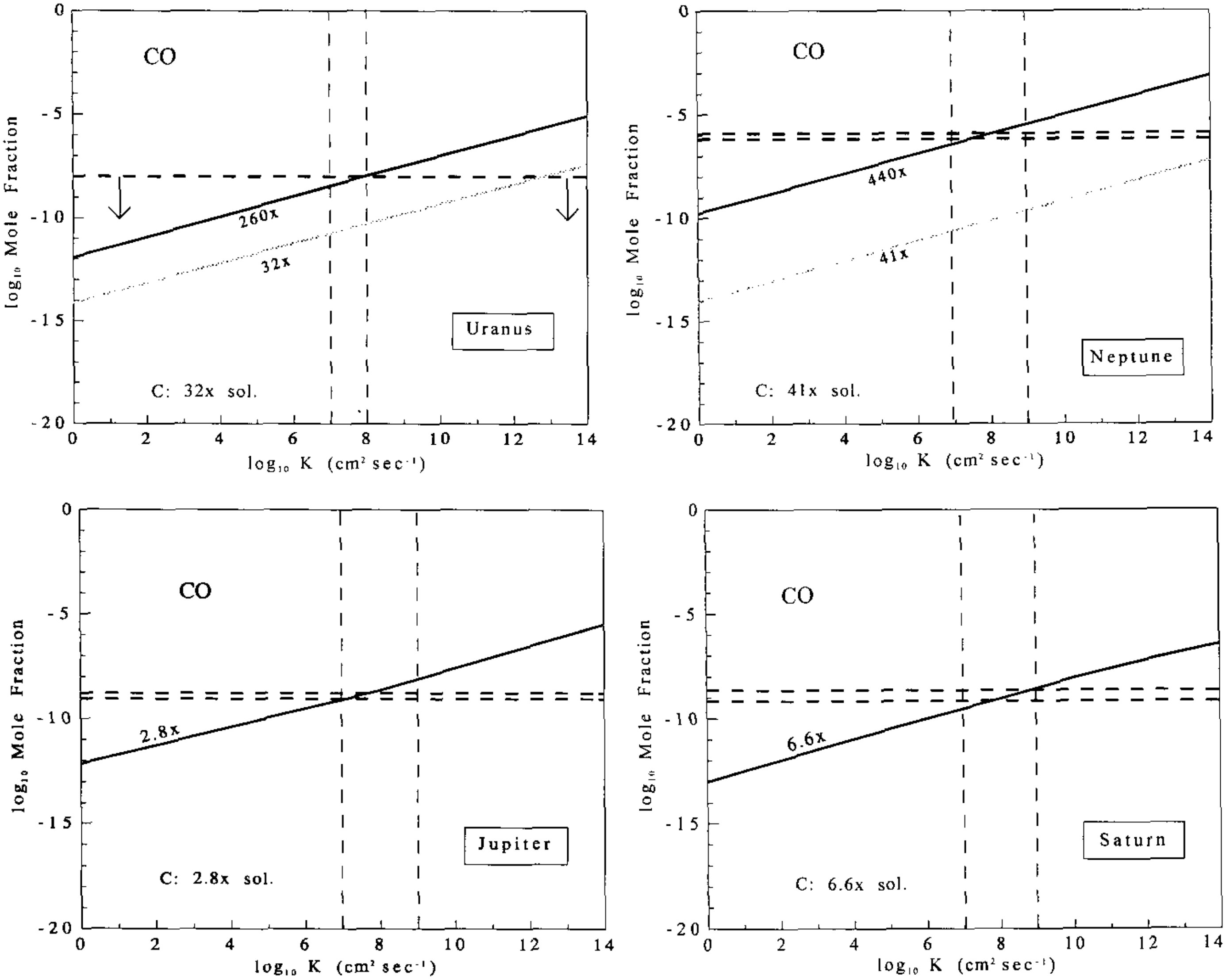

FIG. 2. Predicted CO mole fractions in the visible atmospheres of Uranus, Neptune, Jupiter, and Saturn as a function of the vertical eddy diffusion coefficient (K_{eddy}). The horizontal dashed lines show the observed CO abundances or upper limits on these planets (Bjoraker *et al.* 1986, Guilloteau *et al.* 1993, Marten *et al.* 1993a,b, Noll et al. 1988, Noll and Larson 1990, Rosenqvist et al. 1992). The vertical dashed lines show the range of K_{eddy} values estimated from free convection theory and the observed heat fluxes (Prinn and Barshay 1977, Fegley and Prinn 1988, Fegley et al. 1991). The solid and dotted slanted lines show the calculated CO mole fractions as a function of K_{eddy} for the oxygen enrichments indicated next to each line. For Jupiter and Saturn the observed CO abundances can be matched if oxygen (as H_2O) is as enriched as observed for carbon (as CH_4). For Uranus and Neptune, about ten times more oxygen than carbon is necessary to match the observed CO (Neptune) or the upper limit (Uranus) by deep vertical mixing.

the carbon and oxygen enrichment factors (relative to H_2) over solar, which were inputs in the calculations.

For Jupiter and Saturn we find that the observed CO abundances can be satisfactorily explained by vertical mixing from their deeper atmospheres, if we assume equal carbon and oxygen enrichments above solar of 2.8 (Jupiter) and 6.6 (Saturn). If, however, we assume that carbon and oxygen are equally enriched on Uranus (32 times) and Neptune (41 times), the observed CO abundance on Neptune is not explained by deep vertical mixing. For Neptune a lower CO abundance is predicted than observed (Fig. 2) by using equal enrichment factors.

The only way to increase the CO abundance while having the same carbon and oxygen enrichment factors is to assume faster mixing, i.e., larger eddy diffusion coefficients. However, the estimated K_{eddy} values for the deep atmosphere of Neptune are constrained by the observed heat flux ϕ of 433 erg cm^{-2} sec^{-1} (Pearl and Conrath 1991) via the scaling relationship for free convection in a nonrotating system (Stone 1976):

$$K_{\mathrm{eddy}} \sim H(\phi/(\rho\gamma))^{1/3} \sim 10^7\text{–}10^9\ \mathrm{cm^2\ sec^{-1}}. \qquad (10)$$

Here H is the pressure scale height, ρ the gas density, and $\gamma = C_p/R$. Thus faster mixing of CO from the deep atmosphere of Neptune cannot be the cause for the observed CO mixing ratio.

Therefore we explored the other alternative, higher oxygen than carbon enrichments on Uranus and Neptune, as indicated by the simple calculation above. If we increase the oxygen (and thus the H_2O) abundance on Uranus and Neptune, the observed CO abundance can be matched. The upper limit of about 10 ppb CO on Uranus corresponds to an oxygen enrichment of $\leq$260 times solar in the CO-forming region. For Neptune we need 440 times the solar oxygen abundance to obtain the observed CO mixing ratio of about 0.65–1.2 ppm from deep vertical mixing. This indicates that on Neptune, and possibly Uranus, the oxygen abundance is about 10 times the carbon abundance. The more detailed calculations also reveal that the oxygen enhancement of about 1.7 in Neptune relative to Uranus is not as high as calculated from Eqs. (3b) and (4b), where we obtain a oxygen enhancement of 90–170.

As mentioned above, the calculations with Eqs. (3) and (4) assume that the Neptune/Uranus or Saturn/Jupiter CH_4 and H_2 mole fraction ratios are the same in the upper and lower regions in both planets. However, if massive oxygen enhancements over solar (relative to H_2) are needed to generate the observed CO abundance on Neptune, the mole fraction of molecular H_2 will drop because significant amounts of the total hydrogen are bound in water in the deeper atmosphere. Assuming that all oxygen is present in the form of H_2O we find that in Jupiter and Saturn only 0.5–1% of total hydrogen is bound in water, whereas in Uranus and Neptune oxygen enrichments of 260 and 440 times solar bind 44 or 75% of the total hydrogen in water. From Table II we can see that for Jupiter and Saturn, H_2 is still the major gas at the quench temperatures (and thus deeper in the planet), and a calculation using Eqs. (3) and (4) and the observed abundance data for H_2 agrees with the more exact thermochemical and kinetic results. However, at the quench level for Uranus and Neptune the H_2O mole fractions are 0.60 (Neptune) and $\leq$0.37 (Uranus), and the H_2 mole fractions are 0.14 (Neptune) and $\geq$0.42 (Uranus). Thus the calculations done with Eqs. (3b) and (4b) assuming equal H_2 and CH_4 abundances throughout the atmospheric depth profile on Uranus and Neptune can give only an indication of water enrichment, but not correct values.

ORIGIN AND IMPLICATIONS OF THE WATER ENRICHMENT ON NEPTUNE AND URANUS

Positioned in the outermost part of the solar system, we can expect that Uranus and Neptune acquired more water ice than Jupiter and Saturn because they are further away from the water condensation front at ~4–5 AU. Equilibrium condensation calculations for water ice, CO, CH_4, and their clathrates in the outer solar nebula are shown in Fig. 3 (Fegley 1988, 1993). Because water ice is the most refractory of these ices, Neptune and Uranus may have incorporated larger amounts of water ice than of carbon-bearing ices. From this perspective it is also plausible that the more distant Neptune incorporated more water ice than Uranus but that both planets collected more water ice than Jupiter and Saturn. This also holds for the incorporation of carbon-bearing ices, as indicated by the higher carbon enrichments on Neptune and Uranus than Jupiter or Saturn (e.g., Gautier and Owen 1985).

The larger amount of water that our model predicts in the atmosphere of Neptune (440 times solar) is within a factor of 2–4 of the 100–200 times solar water enrichment predicted by Podolak and Marley (1991) for the outer regions of Neptune. Hubbard *et al.* (1991) also constructed water-rich models for the interior of Neptune, but their conclusions are somewhat dependent on the amount of differential rotation (i.e., the difference between the slower rotation rate of atmospheric features in

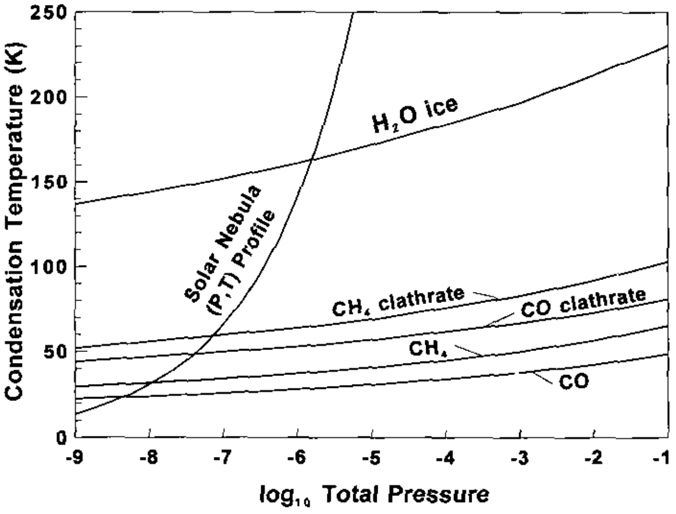

FIG. 3. Condensation temperatures of water, methane, carbon monoxide, and some clathrates in the outer solar nebula (e.g., Fegley 1988, 1993). Condensation temperatures for carbon-bearing ices were calculated assuming all carbon being present as either CO or CH_4 and are therefore upper limits for the respective condensation temperatures. Water ice is the most refractory ice, which condenses about 100 K higher than carbon-bearing ices.

the equatorial regions and the faster magnetic field rotation rate). However, Hubbard *et al.* (1994) note that the observed J_4 for Neptune can be matched by postulating progressively denser envelopes with deeper differential rotation. Although current Neptune interior models do not uniquely constrain the planet's bulk composition, Hubbard *et al.* (1994) emphasize that water probably dominates the interior composition of Neptune.

In the case of Uranus, our models predict a water mole fraction ≤ 0.37, which corresponds to a water mass fraction ≤ 0.78 (for a CO upper limit of 10 ppb). However, Podolak *et al.* (1991) concluded that the low value of J_4 for Uranus constrains the mass fraction of water to be less than about 0.30. Taken at face value, the two numbers are apparently in conflict. Comparing these two limits seems unwise to us. For example, the constraints imposed by the interior models and the atmospheric chemistry models would agree if the CO upper limit (or abundance) were ~ 5 ppb, or about a factor of 2 less than the present upper limit.

As can be seen from Table II, our model predicts that water vapor is the most abundant gas below the aqueous solution clouds in the deep atmospheres of Uranus and Neptune. The H_2O mole fractions in Table II correspond to cloud base temperatures of ~ 480 K on Uranus and ~ 530 K on Neptune. Larger H_2O enrichments will lead to cloud condensation at higher temperatures until the critical point of water (647 K) is reached.

As previously noted by Fegley and Prinn (1986), the latent heat for the vapor-to-liquid phase change goes to zero at the critical point as the distinction between the two phases vanishes. As a result, the wet and dry lapse rates become identical. Other thermodynamic properties (e.g., isothermal compressibility β_T, constant pressure and constant volume heat capacities C_p and C_v, isobaric thermal expansion coefficient α_p, sound speed) and transport properties (e.g., viscosity and thermal conductivity) all show anomalies at the critical point (Sengers and Levelt Sengers 1986).

Another possible consequence of our model is the increased solubility of many rock-forming minerals in an H_2O-rich supercritical fluid below the aqueous cloud base. Fegley and Prinn (1986) pointed out that under some circumstances the H_2O supercritical fluid is rock-rich. This is known in the H_2O–SiO_2 system where SiO_2 solubility reaches ~ 750 g per 1 kg of fluid at the upper critical endpoint of 1353 K and 9.7 kbar (Kennedy *et al.* 1962). More complex minerals such as ferromagnesian silicates and feldspars also dissolve in supercritical water fluid (e.g., Morey 1957, Holland and Malinin 1979). The miscibility of water and rock in the deep atmosphere of Neptune has also been proposed by Hubbard *et al.* (1994).

A third consequence of our model is that HDO and not HD or another hydride such as CH_3D is the major deuterium reservoir in the deep atmospheres of Uranus and Neptune. Thus, to a first approximation, the atmospheric D/H ratios on Uranus and Neptune should reflect the relative water enrichment on the two planets (e.g., see Gautier *et al.* 1994). The CH_3D/CH_4 observations of deBergh *et al.* (1986, 1990) and the fractionation factors of Fegley *et al.* (1991) lead to D/H ratios on Uranus and Neptune of $(6.9^{+6.9}_{-3.5}) \times 10^{-5}$ on Uranus and $(1.15^{+1.15}_{-0.75}) \times 10^{-4}$ on Neptune. The CH_3D/CH_4 observations of Orton *et al.* (1992) and the fractionation factors of Fegley *et al.* (1991) lead to a D/H ratio of $(6.69 \pm 1.0) \times 10^{-5}$ on Neptune, which agrees with the value of deBergh *et al.* (1986) within the mutual uncertainties. The ratios of the Neptunian and Uranian D/H values calculated from the deBergh *et al.* (1986, 1990) data or from the deBergh *et al.* (1986) Uranus data and the Orton *et al.* (1992) Neptune data are $1.7^{+1.7}_{-1.4}$ and $0.97^{+0.98}_{-0.51}$, respectively, which are the same within the mutual uncertainties. Both calculated Neptune/Uranus D/H ratios are consistent with the ratio of the predicted water enrichment on Neptune (440 times solar) and Uranus (≤ 260 times solar), which is ≥ 1.7. Although this consistency is encouraging, the observed D/H values on Uranus and Neptune probably do not provide unique constraints on our model because other factors such as the original D/H values of the ices that were accreted by the two planets, the amount of D/H exchange during planetary accretion and during the postulated large impact on Uranus (Slattery *et al.* 1992), and the extent of D/H exchange between the planetary interiors and atmospheres of the two planets after their formation are unknown and not necessarily the same for the two planets.

Finally, our model also predicts the production of about as much CO_2 as CO on Uranus and Neptune. Although CO_2 may dissolve in the aqueous solution clouds and will be frozen out of the upper atmosphere of Uranus and Neptune, it may be detectable by deep entry probes to these planets.

CONCLUDING REMARKS

The derived high water enrichments on Uranus and Neptune can explain the observational CO abundance on Neptune and match the CO upper limit on Uranus. Independent ways to test these predictions are improved Earth-based observations capable of detecting 0.05–0.1 ppb CO on Uranus and *in situ* measurements of the vertical profile of CO in Neptune's atmosphere. A detection of CO on Uranus will constrain the water (and oxygen) abundance, while a vertical profile of CO on Neptune would distinguish between a deep atmospheric and extraplanetary source. The recent observations by Guilloteau *et al.* (1993) strengthen the case for a deep atmospheric origin of CO on Neptune. The thermochemical calculations also predict that CO_2 is about as abundant as CO at about 1000 K on Uranus and Neptune. Although vertical mixing of CO_2 could be hindered by its dissolution into aqueous clouds, some CO_2 may be detected by a new generation of deep atmospheric entry probes. Finally, other tests are Earth-based or *in situ* observations of the water abundance below the predicted water clouds in the atmospheres of Uranus and Neptune.

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