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CHEMICAL CONSTRAINTS ON THE WATER AND TOTAL OXYGEN ABUNDANCES IN THE DEEP ATMOSPHERE OF JUPITER

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ABSTRACT

The recently reported work by Bjoraker, Larson, and Kunde indicates that the global average H_2O mixing ratio in the Jovian troposphere increases with depth to a value of $qH_2O \approx 3 \times 10^{-5}$ at the 6 bar level. This maximum value is 40 times lower than the H_2O/H_2 ratio ($\sim 1.2 \times 10^{-3}$), which is expected below the predicted H_2O cloud base at the 270 K, 5 bar level in a solar composition Jovian atmosphere. These observations have been interpreted as indicating a possible global depletion of water and of total oxygen in Jupiter's interior. We discuss the resulting implications for the abundances of important nonequilibrium trace gases that are mixed upward from Jupiter's interior. Our calculations show that the observations of CO at mixing ratios $\sim 10^{-9}$ and the stringent upper limit on the SiH_4 mixing ratio of $(2–4) \times 10^{-9}$ are, in fact, incompatible with significant global water and total oxygen depletions in Jupiter's interior. Hence the observed low water vapor abundances must result from unexpected local condensation effects in the cloud-forming region rather than from planetary depletions in water and total oxygen.

Subject headings: planets: abundances — planets: atmospheres — planets: Jupiter

I. INTRODUCTION

After hydrogen and helium, oxygen is the third most abundant element in the Sun and early solar system. Thermochemical calculations for Jupiter indicate that H_2O ($\sim$85%) and silicates ($\sim$15%) are the major oxygen-bearing species and that water vapor is therefore expected to be the third most abundant gas below the clouds of Jupiter. Spectroscopic observations indicating that the Jovian CH_4/H_2 and NH_3/H_2 ratios are enhanced above the solar-composition values (Bjoraker, Larson, and Kunde 1986*a*, and references therein), and interior structure models implying CH_4 and NH_3 enrichments (Hubbard and Horedt 1983) both suggest that the Jovian H_2O/H_2 ratio is also expected to be enhanced above the solar-composition value of $\sim 1.2 \times 10^{-3}$ (specifically by a factor of $\sim$2–5).

However, despite these considerations, the observed H_2O/H_2 ratio on Jupiter is considerably lower than the solar-composition value (Larson *et al.* 1975; Kunde *et al.* 1982). In fact, the recent detailed analysis of Earth-based and *Voyager* spectroscopic observations in Jupiter's 5 μm atmospheric transmission window by Bjoraker, Larson, and Kunde (1986*b*), shows that the H_2O/H_2 ratio at levels between 2 and 6 bars is 3×10^{-5} or less and as shown by them does not follow the calculated profile for water condensation in a solar composition atmosphere (which has a H_2O cloud base at $T = 270$ K, $P = 5$ bars). Instead the H_2O/H_2 ratio at 6 bars ($\sim 3 \times 10^{-5}$) is $\sim$40 times lower than the solar-composition H_2O/H_2 value. The low observed water vapor mixing ratios have been interpreted as indicating a possible global depletion of water and of total oxygen in Jupiter's interior. In this paper we show that the observed abundances of important nonequilibrium trace gases (such as CO), which are mixed upward from Jupiter's interior, are, in fact, incompatible with significant global water and total oxygen depletions. Such constraints in concert with other independent lines of reasoning, require that the low observed H_2O mixing ratios result from condensation effects in Jupiter's cloud-forming region rather than from planetary depletions in water and total oxygen.

II. CALCULATIONS

We compute the effects of variable H_2O mixing ratios and variable total oxygen abundances on the abundances of several nonequilibrium trace gases, focusing in particular on two gases (CO and SiH_4) which are extremely sensitive to the assumed H_2O and total oxygen abundances, respectively. Our calculations utilize a Jupiter model atmosphere which is consistent with recent observational constraints on atmospheric composition and thermal structure. Specifically, we assume an adiabatic gradient below the tropopause with $T = 165$ K at $P = 1$ bar (Lindal *et al.* 1981), H_2 and He volume mixing ratios of 0.90 and 0.10 (Conrath *et al.* 1984; Gautier *et al.* 1981), and CH_4 mixing ratios ranging from 2.3 (Gautier and Owen 1983) to 5 times solar (the upper limit on CH_4/H_2 is 4.8 times solar given by Bjoraker, Larson, and Kunde 1986*a*). The enrichment factors of all elements heavier than He correspond to the assumed CH_4 enrichment; variable H_2O/H_2 ratios and variable total oxygen abundances were considered. A comprehensive description of our chemical modelling techniques is given elsewhere and need not be repeated here (Fegley and Prinn 1985; Prinn and Barshay 1977).

a) Carbon Monoxide

We first consider CO which is observed in Jupiter's troposphere at a volume mixing ratio of $\sim(0.7–2.0) \times 10^{-9}$ (Bjoraker, Larson, and Kunde 1986*a*; Larson, Fink, and Treffers 1978; Noll *et al.* 1988). Prinn and Barshay (1977) first showed that the observed CO, which is present at orders-of-magnitude greater abundance than expected for thermochemical equilibrium in Jupiter's cool, visible atmosphere, can be supplied by sufficiently rapid vertical mixing of gas from Jupiter's hot interior where its abundance is much greater. In particular, CO destruction via the net reaction

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

must be quenched at the 1065 K level where the CO mixing ratio is $\sim 10^{-9}$. The required strength of vertical mixing ($K_{eddy} \approx 2 \times 10^8$ cm^2 s^{-1}) is well within the allowable limits ($K_{eddy} \approx 10^7$–10^9 cm^2 s^{-1}) deduced from Jupiter's internal heat flux (Flasar and Gierasch 1977; Stone 1976).

Rearrangement of the equilibrium constant expression for reaction (1) shows that the CO mixing ratio qCO is given by

$$qCO = (qCH_4\, qH_2O)/(K_1\, q_{H_2}^3\, P_T^2)\,, \quad (2)$$

where P_T is the total pressure along the adiabatic profile and K_1 is the equilibrium constant for reaction (1). Inspection of equation (2) shows that $q\text{CO} \propto q\text{H}_2\text{O}$, and thus in the absence of compensating effects, a water depletion in the deep atmosphere of Jupiter will lead linearly to decreased CO mixing ratios in the visible Jovian atmosphere.

The magnitude of this effect is illustrated in Figure 1, where CO mixing ratios at the quench temperature (T_Q) for reaction (1) are plotted as a function of the vertical eddy diffusion coefficient K_{eddy}. Following Prinn and Barshay (1977), T_Q is defined as the level at which $t_{chem} \approx t_{conv} \approx H^2/K_{eddy}$, where H is the atmospheric pressure scale height, t_{conv} is the time constant for vertical mixing, and t_{chem} is the e-folding time for CO destruction calculated as described by Prinn and Barshay (1977).

It is immediately apparent from Figure 1 that the observed $q\text{CO} \approx 10^{-9}$ is incompatible with a global water depletion of a factor of 40 (i.e., $q\text{H}_2\text{O} \sim 3 \times 10^{-5}$) unless $K_{eddy} \approx 6 \times 10^{11}$ cm^2 s^{-1}. However, a K_{eddy} value this large is implausible given our current understanding of convective heat transport in Jupiter's interior. Thus, the intersection of the CO profile for $H_2O/H_2 \approx 4.6 \times 10^{-4}$ with the box defining the range of observed qCO and estimated K_{eddy} values gives the maximum allowable water depletion in Jupiter's deep atmosphere. This depletion is a factor of 3 relative to the solar O/H_2 ratio, or a factor of ~ 2.5 relative to the solar-composition H_2O/H_2 ratio (the latter factor is slightly smaller because $\sim 15\%$ of total

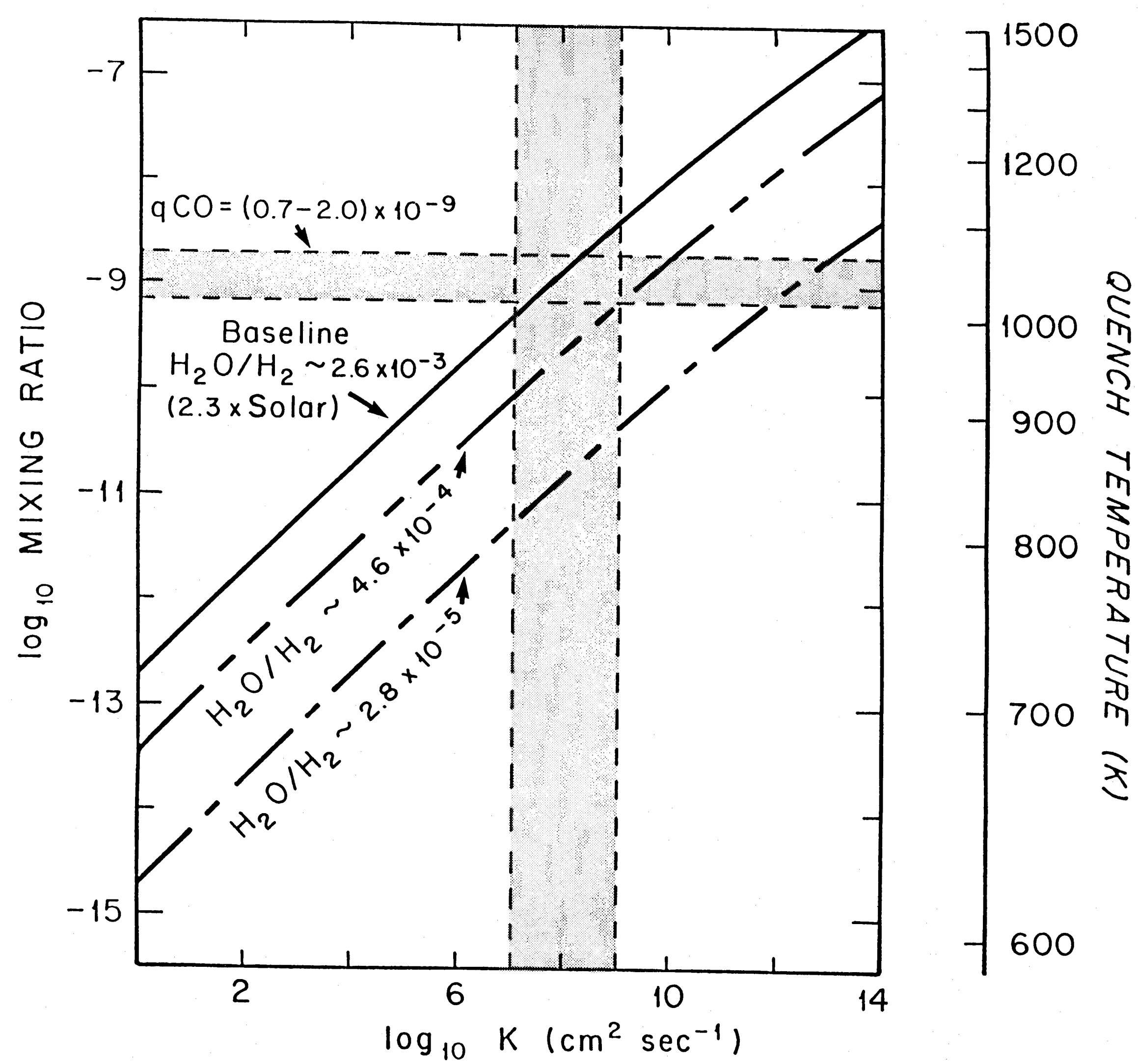

FIG. 1.—Predicted CO mixing ratios in the visible Jovian atmosphere as a function of the vertical eddy diffusion coefficient K for three different assumed H_2O/H_2 ratios. The shaded areas indicate the range of CO mixing ratios reported in the literature (Larson *et al.* 1978; Bjoraker, Larson, and Kunde 1986*a*; Noll *et al.* 1986) and the range of K_{eddy} values (in Jupiter's deep atmosphere) estimated from Jupiter's internal heat flux. Solid line is for a baseline model with all elements heavier than He enriched 2.3 times over solar composition; dashed lines are the same model but with the lower H_2O/H_2 mixing ratios shown.

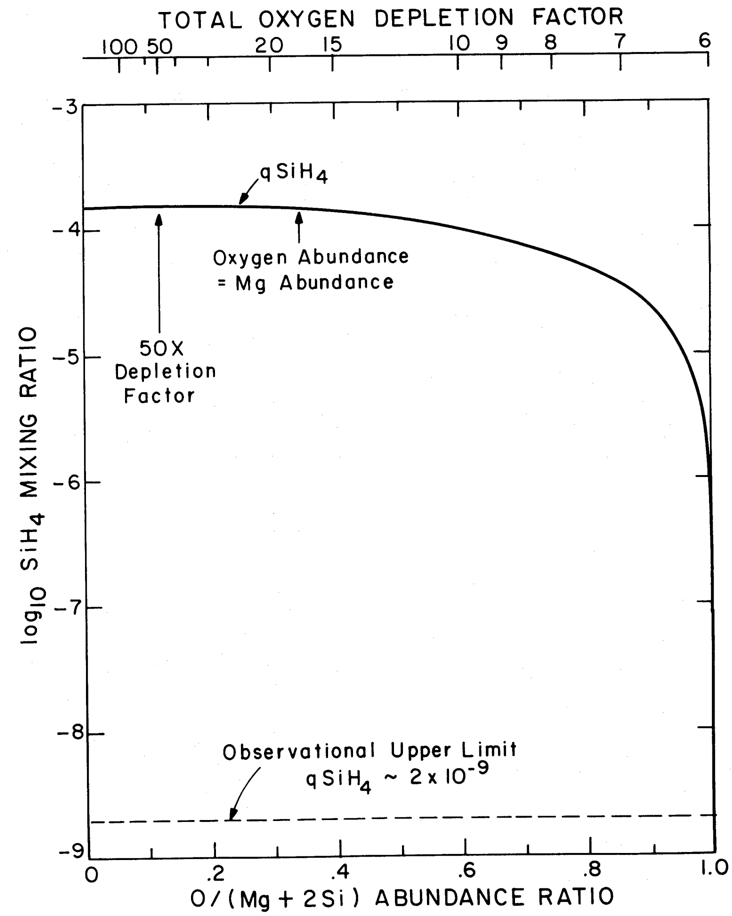

FIG. 2.—Predicted SiH_4 mixing ratios in the visible Jovian atmosphere as a function of the O/(Mg + 2Si) abundance ratio for O/(Mg + 2Si) ≤ 1 (i.e., total oxygen depletion factors ≥ 6, which is the solar abundance ratio). Once the total oxygen abundance is less than the total abundance of Mg + 2Si, there is not enough O to quantitatively remove SiH_4 from the atmosphere. A total oxygen depletion factor of 50 results in $qSiH_4 \approx qSi$(total), which is clearly incompatible with the observational upper limit of $\sim 2 \times 10^{-9}$. A 2.3 times solar baseline model for all elements (except O) is used in this graph.

oxygen on Jupiter is assumed to be present in the rock-forming oxides MgO + SiO_2).

Similar calculations for a 5 times solar enrichment of CH_4 (and of all elements heavier than He), give analogous results despite the fact that CH_4 enhancements offset H_2O depletions (eq. [2]). A global water depletion of a factor of 40 is still inconsistent with the observed qCO values unless $K_{eddy} \geq 8 \times 10^{10}$ cm^2 s^{-1}, which is at least 80 times greater than the value compatible with Jupiter's internal heat flux. The maximum allowable water depletion is now a factor of ~ 6 relative to the solar-composition H_2O/H_2 ratio. We also note that in this case the baseline CO profile (corresponding to $H_2O/H_2 \approx 5.8 \times 10^{-3}$) gives $q\text{CO} \approx 2 \times 10^{-9}$ at $K_{eddy} = 10^7$ cm^2 s^{-1}, which is just barely consistent with the CO observations and K_{eddy} estimates. Thus, the observed $q\text{CO} \approx 10^{-9}$ and the currently accepted CH_4 enrichment factors (~ 2.3 to ~ 5 times solar) are totally incompatible with a global water depletion of a factor of 40 and indeed rule out a global water depletion greater than a factor of ~ 2.5–6 relative to the solar-composition value.

b) Silane

An independent observational constraint on the total oxygen abundance in Jupiter's interior is the nondetection of silane (SiH_4) at a mixing ratio of $\sim(2\text{–}4) \times 10^{-9}$ (Treffers *et al.* 1978; Larson *et al.* 1980). Although Si is orders of magnitude more abundant than the two rock-forming elements P and Ge (e.g., Cameron (1982) lists Si = 10^6, P = 6500, and Ge = 117 atoms), SiH_4, unlike PH_3 and GeH_4, has not been observed on Jupiter presumably because SiH_4 is much more efficiently removed from rising gas parcels by reactions exemplified by

$$SiH_4 + 2H_2O = 4H_2 + SiO_2(s, \text{liq}) , \qquad (3)$$

which readily incorporate Si into rocky materials. Rearrangement of the equilibrium constant expression for reaction (3) and substitution of the appropriate thermodynamic data (JANAF 1985) shows that the SiH_4 mixing ratio $qSiH_4$ is given by

$$\log_{10} qSiH_4 = 4 \log_{10} qH_2 + \log_{10} P_T - 2.21 - 22,159/T - 2 \log_{10} qH_2O . \qquad (4)$$

For the 2.3 times solar baseline atmospheric model, $qSiH_4 \approx 2 \times 10^{-9}$ (the observational upper limit) at 1440 K and decreases rapidly with decreasing temperature. Furthermore, the consideration of stable silicates (such as Mg_2SiO_4 and $MgSiO_3$) predicts even lower SiH_4 mixing ratios in the rising gas parcels (e.g., see Figure 11 of Barshay and Lewis 1978).

However, oxidation of SiH_4 by water vapor is an efficient removal mechanism for Si only as long as the total oxygen abundance is larger than or equal to the abundance of oxygen consumed by SiO_2 and other rock-forming oxides. Iron oxides are predicted to be unstable in Jupiter's highly reduced interior (Barshay and Lewis 1978) and only Mg (1.06×10^6 atoms) is as abundant as Si; all other rock-forming elements combined are only $\sim 20\%$ of the Si abundance. Thus in order for SiH_4 to be quantitatively removed by H_2O oxidation mass balance constraints alone require that the inequality $O \geq (Mg + 2Si)$ for the Jovian abundances of O, Mg, and Si must be satisfied. This is clearly the case for solar composition models of Jupiter or for models in which ice- and rock-forming elements are equally enriched relative to solar composition.

However, this inequality is not satisfied if total oxygen is depleted on Jupiter by a factor of 50 relative to solar ($O = 1.84 \times 10^7$ atoms). In this case the opposite inequality $O < (Mg + 2Si)$ is satisfied and there is insufficient oxygen to remove SiH_4 from Jupiter's atmosphere. Because MgO is more refractory than SiO_2, global depletion of total oxygen relative to solar abundance by any factor greater than the solar abundance ratio $O/(Mg + 2Si) \approx 6$ will lead to SiH_4 mixing ratios $qSiH_4 \approx qSi - \frac{1}{2}(qO - qMg)$, which are much greater than the observational upper limit of $qSiH_4 \approx (2\text{–}4) \times 10^{-9}$ (see Fig. 2). In fact, as Figure 2 further illustrates, once $qO \leq qMg$, $qSiH_4 \approx qSi$ ($\sim 2 \times 10^{-4}$ for the 2.3 times solar model shown). We note that no other SiH_4 removal processes considered (e.g., SiH_4 pyrolysis to elemental Si, Si_3N_4 formation) are thermodynamically and kinetically plausible; only oxidation by water vapor is effective. Furthermore, the observation of PH_3 at mixing ratios $\sim(4\text{–}7) \times 10^{-7}$ and of GeH_4 at mixing ratios $\sim 7 \times 10^{-10}$ (Bjoraker, Larson, and Kunde 1986*a*) demonstrates that P and Ge (and by inference) other rock-forming elements are present in Jupiter's deep atmosphere at approximately solar abundance. Thus, the presence of large amounts of SiH_4 in the visible atmosphere of a Jupiter highly depleted in total oxygen appears inescapable.

III. DISCUSSION

The observed CO mixing ratio of $\sim 10^{-9}$ alone rules out global water depletions greater than a factor of $\sim 2.5\text{–}6$ relative to the H_2O/H_2 ratio in a solar-composition atmosphere. The upper limit on the SiH_4 mixing ratio of $\sim(2\text{–}4) \times 10^{-9}$ alone rules out global depletions of total oxygen by any factor greater than $O/(Mg + 2Si) \approx 6$ (for solar composition). Combining these two results (i.e., $0.85/2.5 + \frac{1}{6} \approx \frac{1}{2}$ or $0.85/6 + \frac{1}{6} \approx \frac{1}{3}$) thus rules out total oxygen depletions greater than a factor of $\sim 2\text{–}3$ relative to the solar O/H_2 ratio. This constraint on total oxygen depletion is even more restrictive for Jovian rock/H_2 ratios enhanced over the solar value.

Even smaller allowable total oxygen depletions are predicted from simple cosmogonic arguments. Water-bearing carbonaceous meteorites (Mason 1979) and (presumably similar) water-bearing carbonaceous asteroids in the Main Belt (reviewed in Lewis and Prinn 1984) are obvious candidates for the rocky component of Jupiter. Unless the rocky component incorporated into Jupiter contained no such hydrated material, the oxygen incorporated in rock alone would endow Jupiter with a total O/H_2 ratio of $\sim 6 \times 10^{-4}$ (assuming a solar rock/H_2 ratio) or $\sim 1.3 \times 10^{-3}$ (assuming a rock/H_2 ratio enhanced 2.3 times over solar). Thus these cosmogonically deduced total O/H_2 ratios are incompatible with a global depletion of total oxygen by a factor of 50 relative to solar and in fact O/H_2 is solar for a 2.3 times enhanced rock/H_2 ratio.

These cosmogonic arguments become even firmer by considering the addition of oxygen by accretion of water ice. The observations of H_2O ice on several Galilean satellites (Lewis and Prinn 1984) demonstrate that water ice is and was stable at Jupiter's distance from the Sun. Furthermore, the enhanced CH_4/H_2 and NH_3/H_2 ratios on Jupiter imply incorporation of significant amounts of C- and N-bearing compounds in Jupiter. If these compounds were in the form of N_2 (or (NH_3) and CO (or CH_4) clathrates as predicted by condensation calculations (Lewis and Prinn 1984) it is difficult to envision accretion models which would *not* also incorporate large amounts of the readily available water ice into Jupiter (e.g., see the discussion by Bjoraker, Larson, and Kunde 1986*b*). We also note that if all carbon was originally accreted as CO (or CO_2), then reactions with H_2 in the accreting protoplanet would form correspondingly large amounts of H_2O as the oxidized carbon was reduced to CH_4.

On the other hand, incorporation of large amounts of C- and N-bearing disequilibrium organic matter could in principle enhance these elements in Jupiter without necessarily also enhancing oxygen. However, in this case we note that the reaction of sufficiently large amounts of disequilibrium organic compounds with H_2 (to form CH_4 and NH_3) in the giant planets would decrease the H_2/He ratio below the solar value (Fegley and Prinn 1986).

These cosmogonic considerations in concert with the observational constraints set by the observations of tropospheric CO and the nondetection of SiH_4 lead us to conclude therefore that the low observed H_2O mixing ratios cannot represent massive global water and total oxygen depletions but instead must result from condensation processes in the cloud-forming region of Jupiter's atmosphere (e.g., see Lunine and Hunten 1987 for a possible scenario). Thus the available observations are important clues to dynamical processes in this region of the Jovian troposphere.

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Note added in proof, 1987 September 25.—Noll *et al.* (1988, *Ap. J.*, in press) have independently concluded that the observed CO mixing ratio shows that the global oxygen abundance in Jupiter's gaseous envelope must be near the solar value.

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