

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

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### ABSTRACT

Thermochemical equilibrium and kinetic calculations for the trace gases CO, PH<sub>3</sub>, and SiH<sub>4</sub> give three independent constraints on the water and total oxygen abundances of Saturn's deep atmosphere. A lower limit to the water abundance of  $\text{H}_2\text{O}/\text{H}_2 \geq (1.7^{+0.7}_{-0.4}) \times 10^{-3}$  is given by CO chemistry, whereas an upper limit of  $\text{H}_2\text{O}/\text{H}_2 \leq (5.5^{+0.8}_{-2.5}) \times 10^{-3}$  is given by PH<sub>3</sub> chemistry. A combination of the CO and PH<sub>3</sub> constraints indicates a water enrichment on Saturn of 1.9–6.1 times the solar system abundance ( $\text{H}_2\text{O}/\text{H}_2 = 8.96 \times 10^{-4}$ ). The total oxygen abundance must be at least 1.7 times the solar system abundance ( $\text{O}/\text{H}_2 = 1.16 \times 10^{-3}$ ) in order for SiH<sub>4</sub> to remain below the detection limit of  $\text{SiH}_4/\text{H}_2 < 2 \times 10^{-10}$ . A combination of the CO, PH<sub>3</sub>, and SiH<sub>4</sub> constraints suggests that the total oxygen abundance on Saturn is 3.2–6.4 times the solar system abundance. Our results indicate that oxygen on Saturn is less enriched than other heavy elements (such as C and P) relative to the solar system composition.

*Subject heading:* planets and satellites: individual (Saturn)

### 1. INTRODUCTION

Spectroscopic observations of water in the upper atmosphere of Saturn indicate an  $\text{H}_2\text{O}/\text{H}_2$  mixing ratio ( $q_{\text{H}_2\text{O}}$ ) of  $\sim(2\text{--}200) \times 10^{-9}$  (Larson et al. 1980; Winkelstein et al. 1983; Chen et al. 1991; de Graauw et al. 1997; Feuchtgruber et al. 1997), well below the solar system (i.e., protosolar)  $\text{H}_2\text{O}/\text{H}_2$  ratio of  $\sim 9 \times 10^{-4}$ . Measurements of  $\text{H}_2\text{O}$  in the  $5 \mu\text{m}$  window probe the  $\sim 3$  bar level in Saturn's troposphere (Larson et al. 1980; de Graauw et al. 1997). However,  $\text{H}_2\text{O}$  cloud condensation occurs deeper, near the 13 bar level, so the water abundance below the clouds and therefore the planetary inventory of water remains unknown. Observations of Saturn's atmosphere show that  $\text{CH}_4/\text{H}_2$ ,  $\text{PH}_3/\text{H}_2$ , and  $\text{AsH}_3/\text{H}_2$  ratios are enhanced over protosolar values, suggesting that a similar enrichment may exist for water. The total oxygen abundance of Saturn's interior is expected to consist primarily of  $\text{H}_2\text{O}$  and O bound in rock. Since oxygen is the third most abundant element in the solar system, water vapor is expected to be an important gas below the clouds of Saturn.

Here we consider the effects of water and oxygen on tropospheric chemistry to determine the water and total oxygen abundances of Saturn's deep atmosphere. We specifically focus on the disequilibrium trace gases CO, PH<sub>3</sub>, and SiH<sub>4</sub> because their chemistry is sensitive to the water and oxygen content of the troposphere. Using a similar approach as Fegley & Prinn (1988), we show that the observed abundance of CO and the upper limit for SiH<sub>4</sub> are incompatible with significant planetary depletions in water and oxygen, while the PH<sub>3</sub> abundance is incompatible with large enrichments. Taken together, our results indicate that water and total oxygen on Saturn are less enriched than heavy elements such as C and P relative to solar system composition. We begin with an overview of the observed composition of Saturn's atmosphere (§ 2) and a brief description (§ 3) of our computational method. In § 4, we present an overview of Saturn's atmospheric chemistry and our results for the CO, PH<sub>3</sub>, and SiH<sub>4</sub> chemical constraints, followed by discussion (§ 5) of their implications for the water and oxygen abundances of Saturn's interior. A summary is given in § 6.

### 2. ATMOSPHERIC COMPOSITION OF SATURN

The observed mixing ratios for several compounds in Saturn's atmosphere are listed in Table 1, along with computed enrichments over solar system abundances. Methane, PH<sub>3</sub>, and AsH<sub>3</sub> are the major C-, P-, and As-bearing gases in Saturn's atmosphere (Lodders & Fegley 1998, p. 213). It is generally assumed that the CH<sub>4</sub>, PH<sub>3</sub>, and AsH<sub>3</sub> abundances represent the total elemental abundances of C, P, and As, respectively, in Saturn's observable atmosphere (e.g., Courtin et al. 1984; Noll et al. 1989; Noll & Larson 1991; Bézard et al. 1989; Fegley & Lodders 1994; Hersant et al. 2004), and the same approach is taken here. Saturn's atmospheric composition below the clouds is generally considered to be uniform because of convective mixing. However, the distribution of elements between different gases (e.g.,  $\text{H}_2\text{O}$ , CO, OH) and (in some cases) between gases and condensates (e.g.,  $\text{H}_2\text{O}$ , rock) is temperature and pressure dependent. Although similar within observational uncertainties, the enrichment factor for As is apparently less than that for C and P, possibly because of the formation of other As-bearing gases such as AsF<sub>3</sub> (see Fegley & Lodders 1994). Ammonia is almost certainly the major N-bearing gas in Saturn's atmosphere. However, the NH<sub>3</sub> abundance is affected by cloud condensation and photolysis and cannot be used as a constraint on the nitrogen enrichment relative to protosolar composition. Likewise, the observed abundances of other gases such as  $\text{H}_2\text{S}$  and GeH<sub>4</sub> cannot be used as constraints because they are affected by condensation (e.g., solid NH<sub>4</sub>SH, Ge, GeTe), photolysis (e.g.,  $\text{H}_2\text{S}$ ), and formation of other gases (e.g., GeS, GeSe, GeTe) (Fegley & Lodders 1994). Briggs & Sackett (1989) inferred an  $\text{H}_2\text{S}$  abundance on Saturn of  $\sim 10$  times the protosolar value. However, because it is difficult to distinguish the microwave opacity of  $\text{H}_2\text{S}$  from other sources, this  $\text{H}_2\text{S}$  abundance is an indirect estimate based on the brightness temperature spectrum for an assumed NH<sub>4</sub>SH cloud (Hersant et al. 2004). Thus, at present we only use the observed enrichments in C and P to constrain the average enrichment of heavy elements on Saturn relative to the solar system composition.

TABLE 1  
GAS ABUNDANCES IN SATURN'S ATMOSPHERE

| Gas                    | Observed Mixing Ratio <sup>a</sup> | Enrichment Factor <sup>b</sup>      |
|------------------------|------------------------------------|-------------------------------------|
| H <sub>2</sub> .....   | ≡1                                 | ≡1                                  |
| He.....                | 0.135 ± 0.025                      | 0.700 ± 0.129                       |
| CH <sub>4</sub> .....  | (4.3 ± 1.3) × 10 <sup>-3</sup>     | 7.4 ± 2.3                           |
| SiH <sub>4</sub> ..... | <(0.2–1.2) × 10 <sup>-9</sup>      | <10 <sup>-5</sup> –10 <sup>-6</sup> |
| GeH <sub>4</sub> ..... | (4.0 ± 4.0) × 10 <sup>-10</sup>    | 0.04 ± 0.04                         |
| NH <sub>3</sub> .....  | (1.8 ± 1.3) × 10 <sup>-4</sup>     | 1.1 ± 0.8                           |
| PH <sub>3</sub> .....  | (5.1 ± 1.6) × 10 <sup>-6</sup>     | 7.4 ± 2.3                           |
| AsH <sub>3</sub> ..... | (2.4 ± 1.5) × 10 <sup>-9</sup>     | 4.8 ± 3.0                           |
| H <sub>2</sub> O.....  | (2–200) × 10 <sup>-9</sup>         | 10 <sup>-4</sup> –10 <sup>-6</sup>  |
| H <sub>2</sub> S.....  | <0.4 × 10 <sup>-6</sup>            | <0.01                               |
| CO.....                | (1.6 ± 0.8) × 10 <sup>-9</sup>     | ...                                 |

NOTES.—Saturn abundance data from Lodders & Fegley (1998), Davis et al. (1996), de Graauw et al. (1997), Feuchtgruber et al. (1997), Conrath & Gautier (2000), and Lellouch et al. (2001). Solar abundance data from Lodders (2003).

<sup>a</sup> Mixing ratios for a gas M ( $qM$ ) are defined as  $M/H_2$ .

<sup>b</sup> Enrichment factor ( $E_M$ ) for a gas M is defined as  $(qM)_{\text{Sat}}/(qM)_{\text{ps}}$ , where the subscripts “Sat” and “ps” refer to Saturnian and protosolar values, respectively.

Elemental abundances for the solar nebula (i.e., protosolar abundances) were taken from Lodders (2003). These are slightly different from photospheric abundances because of heavy element settling in the Sun (Lodders 2003). The protosolar elemental abundances represent the *bulk* elemental composition of the Sun and the solar nebula. Water vapor is expected to be the dominant O-bearing gas in the circum-Saturnian nebula and in Saturn's deep atmosphere (e.g., see § 4.1; Fegley & Prinn 1985, 1989), and the CO/H<sub>2</sub>O ratio in both environments is much less than unity. The protosolar H<sub>2</sub>O/H<sub>2</sub> ratio is defined by taking the total oxygen abundance ( $O/H_2 = 1.16 \times 10^{-3}$ ) and subtracting the portion that forms rock (see Lodders 2004). This is expressed as

$$O_{H_2O} = \Sigma O - O_{\text{rock}}, \quad (1)$$

where the amount of oxygen bound in rock ( $\text{MgO} + \text{SiO}_2 + \text{CaO} + \text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{TiO}_2$ ) is given by

$$O_{\text{rock}} = (\text{Mg} + 2\text{Si} + \text{Ca} + 1.5\text{Al} + 0.5\text{Na} + 0.5\text{K} + 2\text{Ti}). \quad (2)$$

In a gas with protosolar elemental abundances, the formation of rock effectively removes ~23% of the total oxygen. Throughout the following, enrichments in water over the protosolar composition refer to a solar system H<sub>2</sub>O/H<sub>2</sub> ratio of  $8.96 \times 10^{-4}$ .

### 3. METHOD

Thermochemical equilibrium calculations were performed using a Gibbs free energy minimization code and an adiabatic temperature-pressure profile for Saturn's troposphere calculated as described by Fegley & Prinn (1985) using  $T = 134.8$  K at  $P = 1$  bar (Lindal et al. 1985) and a total He/H<sub>2</sub> ratio of 0.135. This value is the mean of the volume-mixing ratio He/H<sub>2</sub> = 0.11–0.16 determined by Conrath & Gautier (2000), considerably greater than the previously accepted value of  $0.034 \pm 0.024$  (Conrath et al. 1984). The corresponding mole fraction of hydrogen ( $X_{H_2}$ ) is 0.881. We adopted a nominal enrichment factor of 7.4 times the protosolar element-to-H<sub>2</sub> ratios for elements heavier than He on the basis of the observed enrichments of CH<sub>4</sub> and PH<sub>3</sub> on Saturn, as described in § 2 and shown in Table 1. We also varied the elemental abundances of C, P, Si,

and O in order to study the resulting effects on Saturn's tropospheric chemistry.

## 4. RESULTS

### 4.1. Overview of Atmospheric Chemistry

The model adiabatic profile for Saturn's atmosphere is shown in Figure 1. This figure also shows the results of thermochemical equilibrium calculations for a gas with protosolar elemental abundances. The lines labeled Fe (s,l), Mg<sub>2</sub>SiO<sub>4</sub> (s,l), and MgSiO<sub>3</sub> (s,l) are the condensation curves for iron, forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), and enstatite (MgSiO<sub>3</sub>), with circles denoting their normal melting points. These three phases constitute most of the “rock” that is expected to condense in Saturn's deep atmosphere. The curves labeled CO/CH<sub>4</sub>, N<sub>2</sub>/NH<sub>3</sub>, and PH<sub>3</sub>/P<sub>4</sub>O<sub>6</sub> show where the partial pressures of these gases are equal, and they are interpreted as follows. Methane (CH<sub>4</sub>) is the major carbon-bearing gas to the right of the CO/CH<sub>4</sub> curve, and carbon monoxide (CO) is the major carbon-bearing gas to the left of the CO/CH<sub>4</sub> curve. However, CH<sub>4</sub> is still present but is less abundant than CO inside the CO field and vice versa. Likewise, ammonia (NH<sub>3</sub>) is the major nitrogen-bearing gas to the right of the N<sub>2</sub>/NH<sub>3</sub> curve, and molecular nitrogen (N<sub>2</sub>) is the major nitrogen-bearing gas to the left of the N<sub>2</sub>/NH<sub>3</sub> curve. Ammonia is still present but is less abundant than N<sub>2</sub> inside the N<sub>2</sub> field and vice versa. A comparison of the model Saturnian adiabat with the CO/CH<sub>4</sub> and N<sub>2</sub>/NH<sub>3</sub> curves shows that methane and ammonia are predicted to be the dominant C-bearing and N-bearing gases throughout Saturn's atmosphere at temperatures below 3000 K.

At pressures characteristic of the deep atmospheres of Saturn and the other gas giant planets, phosphine (PH<sub>3</sub>) is the major phosphorus-bearing gas above the PH<sub>3</sub>/P<sub>4</sub>O<sub>6</sub> curve, and P<sub>4</sub>O<sub>6</sub> gas is the major phosphorus-bearing gas below the PH<sub>3</sub>/P<sub>4</sub>O<sub>6</sub> curve. The partial pressures of the two gases are equal at about the 900 K level in Saturn's atmosphere. This curve is extrapolated

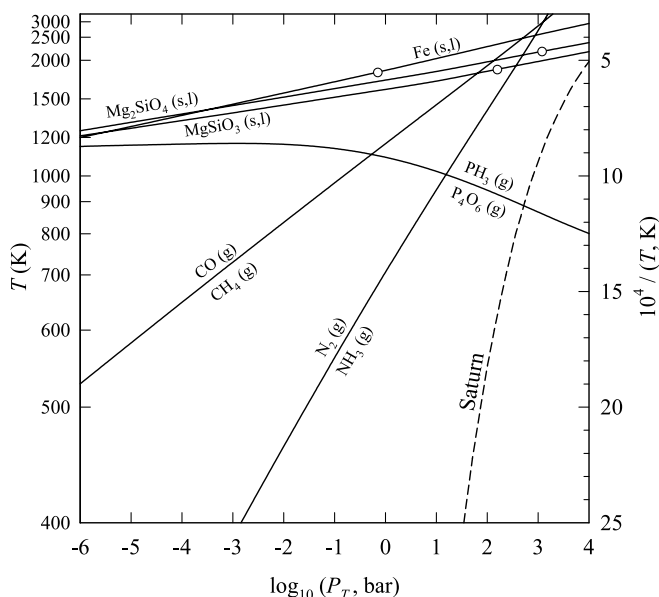
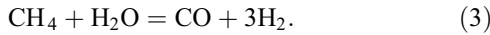


FIG. 1.—Equilibrium chemistry for a protosolar-composition gas as a function of pressure and temperature. The dashed line shows the location of the Saturnian adiabat. The lines labeled CO/CH<sub>4</sub>, N<sub>2</sub>/NH<sub>3</sub>, and PH<sub>3</sub>/P<sub>4</sub>O<sub>6</sub> indicate where the partial pressures of the two gases are equal. The lines labeled Fe (s,l), Mg<sub>2</sub>SiO<sub>4</sub> (s,l), and MgSiO<sub>3</sub> (s,l) show the condensation temperatures of iron, forsterite, and enstatite as a function of pressure, with circles denoting their melting temperatures. Modeled after Fig. 1 in Prinn & Fegley 1981.

to lower pressures, but at these pressures phosphorus chemistry becomes more complex and a number of phosphorus-bearing molecules are found in the gas at high temperatures (e.g., Fegley & Lewis 1980).

#### 4.2. Carbon Monoxide

We first consider carbon monoxide (CO), which is observed in Saturn's atmosphere at a mixing ratio (CO/H<sub>2</sub>) of  $(1.6 \pm 0.8) \times 10^{-9}$  (Noll et al. 1986; Noll & Larson 1991; de Graauw et al. 1997). This is  $\sim 40$  orders of magnitude higher than the CO abundance predicted by thermodynamic equilibrium in Saturn's cool, visible atmosphere (e.g., see Fegley & Prinn 1985; Fegley & Lodders 1994). As discussed by Fegley & Prinn (1985, p. 1076), CO in Saturn's observable atmosphere may result from a combination of internal and external sources. We consider the effects of an additional external source in § 4.2.4. Carbon monoxide in Saturn's deep atmosphere is produced from water via the net thermochemical reaction



The corresponding equilibrium constant expression for reaction (3) is

$$K_3 = [(X_{\text{CO}}X_{\text{H}_2}^3)/(X_{\text{CH}_4}X_{\text{H}_2\text{O}})]P_T^2, \quad (4)$$

where  $K_3$  is the equilibrium constant and  $P_T$  is the total pressure along the adiabatic profile. If we rearrange equation (4) and substitute mixing ratios for mole fractions for CO, CH<sub>4</sub>, and H<sub>2</sub>O (e.g.,  $q\text{CO} = X_{\text{CO}}/X_{\text{H}_2}$ ), the CO mixing ratio is given by

$$q\text{CO} = (q\text{CH}_4q\text{H}_2\text{O}/X_{\text{H}_2}^2)K_3P_T^{-2}. \quad (5)$$

We now rewrite equation (5) to explicitly show the dependence of the CO mixing ratio on the CH<sub>4</sub> and H<sub>2</sub>O enrichments relative to solar system composition. The protosolar mixing ratios for methane ( $5.82 \times 10^{-4}$ ) and water ( $8.96 \times 10^{-4}$ ) and the hydrogen mole fraction of  $X_{\text{H}_2} = 0.881$  are constants, allowing us to write

$$c' = (q\text{CH}_4q\text{H}_2\text{O})_{\text{ps}}/X_{\text{H}_2}^2 = 6.72 \times 10^{-7}. \quad (6)$$

Substitution into equation (5) gives

$$q\text{CO} = c'E_{\text{CH}_4}E_{\text{H}_2\text{O}}K_3P_T^{-2}, \quad (7)$$

where  $E_{\text{CH}_4}$  and  $E_{\text{H}_2\text{O}}$  are enrichment factors over the protosolar composition for the methane (i.e., carbon) and water abundances in Saturn's atmosphere. Examination of equation (7) shows that the CO mixing ratio is proportional to the product  $E_{\text{CH}_4}E_{\text{H}_2\text{O}}$ . Thus, for otherwise constant conditions, the water enrichment required to produce a given CO abundance varies inversely with the methane enrichment. The equilibrium CO mixing ratio as a function of temperature [expressed as  $\xi = 10^4/(T, \text{K})$ ] along the Saturnian adiabat is given by the equation

$$\begin{aligned} \log q\text{CO} = & \log c' - 29.7374 - 1.1770\xi^{-1} - (1.509 \times 10^{-3})\xi^2 \\ & - 34.3300\xi^{1/2} + 0.1619\xi - (1.898 \times 10^{-5})\xi^3 \\ & + 61.5475\xi^{1/3} + \log E_{\text{CH}_4} + \log E_{\text{H}_2\text{O}} \end{aligned} \quad (8)$$

from 300 to 6000 K, where  $\log c' = -6.1726$  from equation (6). Equation (8) has the form of a heat capacity polynomial to

account for the strong temperature dependence of the equilibrium constant  $K_3$ .

##### 4.2.1. Thermodynamic Limit

At constant pressure, reaction (3) proceeds to the right with increasing temperature and yields more CO (Lodders & Fegley 2002). However, at constant temperature, reaction (3) proceeds to the left with increasing pressure and yields less CO. In other words, the equilibrium abundance of CO increases with increasing temperature and with decreasing pressure. Therefore, a maximum occurs in the CO mixing ratio along the Saturnian adiabat, found by differentiating equation (8) and solving for the temperature at which the derivative is zero:

$$\begin{aligned} d(\log q\text{CO})/d\xi = 0 = & 1.1770\xi^{-2} - (3.018 \times 10^{-3})\xi \\ & - 17.1650\xi^{-1/2} + 0.1619 \\ & - (5.694 \times 10^{-5})\xi^2 + 20.5158\xi^{-2/3}, \end{aligned} \quad (9)$$

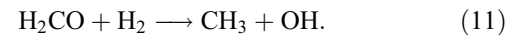
which gives the maximum at 2910 K. The greatest CO abundance is achieved at this temperature over a wide range of water enrichments, and therefore it serves as a thermodynamic lower limit to the total water abundance in Saturn's interior. Using  $T = 2910$  K and the observed mixing ratio  $q\text{CO} = (1.6 \pm 0.8) \times 10^{-9}$  (see Table 1) in equation (8) gives

$$\log E_{\text{CH}_4} + \log E_{\text{H}_2\text{O}} = \log q\text{CO} + 6.476 = -2.320_{-0.301}^{+0.176}. \quad (10)$$

At the nominal carbon enrichment of 7.4 times protosolar, the enrichment factor for water is  $E_{\text{H}_2\text{O}} = (6.5_{-3.3}^{+3.2}) \times 10^{-4}$ . Using the lower bound of this value indicates that  $E_{\text{H}_2\text{O}} \geq 3.2 \times 10^{-4}$  is necessary to produce the observed CO abundance, corresponding to an H<sub>2</sub>O/H<sub>2</sub> mixing ratio of  $2.9 \times 10^{-7}$  in Saturn's troposphere. Thus, water cannot be depleted more than  $3.2 \times 10^{-4}$  times the protosolar value if the observed amount of CO is produced in Saturn's interior. This thermodynamic constraint gives a firm lower limit to the amount of water in Saturn's deep atmosphere. However, it implies mixing of gas from an unrealistic depth (the 2910 K, 46 kbar level) up to the visible atmosphere. In order to better constrain a lower limit to the water abundance, the kinetics of CO destruction must be considered.

##### 4.2.2. Kinetic Limit

As parcels of hot gas rise in Saturn's atmosphere, CO is destroyed by conversion to CH<sub>4</sub>. Therefore, the observable amount of CO depends on both the rate of vertical mixing and the kinetics of conversion (e.g., Fegley & Prinn 1985). In the kinetic scheme proposed by Prinn & Barshay (1977), CO is in equilibrium with formaldehyde, and the rate-limiting step for CO destruction is the breaking of the C=O bond in formaldehyde via



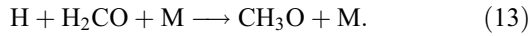
If we assume that the maximum plausible rate of vertical mixing is given by  $K_{\text{eddy}} \sim 10^9 \text{ cm}^2 \text{ s}^{-1}$ , estimated from Saturn's internal heat flux (see Prinn et al. 1984, p. 138), CO destruction is quenched at the 1036 K level on Saturn. Using  $T = 1036$  K in equation (8) along with the observed CO abundance gives

$$\log E_{\text{CH}_4} + \log E_{\text{H}_2\text{O}} = \log q\text{CO} + 10.239 = 1.443_{-0.301}^{+0.176}. \quad (12)$$

Equation (12) defines the lower limit for enrichments in the carbon and water abundances on Saturn. At the nominal carbon enrichment of 7.4 times protosolar, the enrichment factor for water is  $E_{\text{H}_2\text{O}} = 3.7_{-1.8}^{+1.9}$ . The lower bound of this value indicates that  $E_{\text{H}_2\text{O}} \geq 1.9$  is required to produce the observed CO abundance. This corresponds to an  $\text{H}_2\text{O}/\text{H}_2$  mixing ratio of  $q_{\text{H}_2\text{O}} \geq 1.7 \times 10^{-3}$  in Saturn's deep atmosphere.

#### 4.2.3. Alternative Thermochemical Kinetics

An alternative kinetic scheme for CO destruction was proposed by Yung et al. (1988), in which the rate-limiting step involves the conversion of the C=O bond in formaldehyde into a C—O bond via



This alternative kinetic scheme gives significantly less CO at the same vertical mixing rate than the Prinn & Barshay (1977) model because the rate-determining step is significantly faster (e.g., see Yung et al. 1988; Bézard et al. 2002). Vertical mixing that is orders of magnitude more rapid than that implied by observed heat fluxes or mixing lengths significantly smaller than pressure scale heights is required to match observed CO abundances on Jupiter and Saturn using this alternative kinetic scheme. Leaving these problems aside, we compute a quench temperature for reaction (13) of 816 K on Saturn. In this case, using  $T = 816$  K in equation (8) with the observed CO mixing ratio gives

$$\log E_{\text{CH}_4} + \log E_{\text{H}_2\text{O}} = \log q_{\text{CO}} + 12.563 = 3.767_{-0.301}^{+0.176}. \quad (14)$$

The nominal  $E_{\text{CH}_4}$  value of 7.4 times protosolar requires  $E_{\text{H}_2\text{O}} \geq 395$ , or a water abundance of  $q_{\text{H}_2\text{O}} \geq 0.35$  in Saturn's atmosphere. If we employ a mixing length of  $L \sim 0.1H$  in place of the pressure scale height  $H$  (Bézard et al. 2002; Smith 1998), the quench temperature is 922 K, which requires  $E_{\text{H}_2\text{O}} \geq 20.9$  and a water abundance of  $q_{\text{H}_2\text{O}} \geq 1.9 \times 10^{-2}$  in Saturn's atmosphere. However, as we discuss in § 4.3, the observed  $\text{PH}_3$  abundance precludes a water enrichment that is this large. A detailed mechanistic examination of CO quenching kinetics is beyond the scope of this paper. Here we continue our use of the Prinn & Barshay (1977) kinetic scheme for CO destruction kinetics because it accurately reproduces the observed CO abundance on Jupiter, Saturn, and Neptune (Fegley & Lodders 1994; Lodders & Fegley 1994).

#### 4.2.4. External CO Source

As suggested by Fegley & Prinn (1985), Saturn may also have a competing external source of CO. If present, an external CO source would lower the amount of tropospheric water required to produce the observed CO abundance. Possible external sources include direct delivery of CO or photolytic production via stratospheric water from interplanetary dust, cometary impacts, or infalling ring or satellite debris (e.g., Fegley & Prinn 1985; Moses et al. 2000).

Measurements of carbon monoxide on Saturn suggest, but are not diagnostic of, a primarily internal source that produces  $q_{\text{CO}} \sim 10^{-9}$  in the upper troposphere (e.g., see Noll et al. 1986; Noll & Larson 1991; Moses et al. 2000; Ollivier et al. 2000), and most spectroscopic models for the observed CO abundance on Saturn include both an internal and an external source. How-

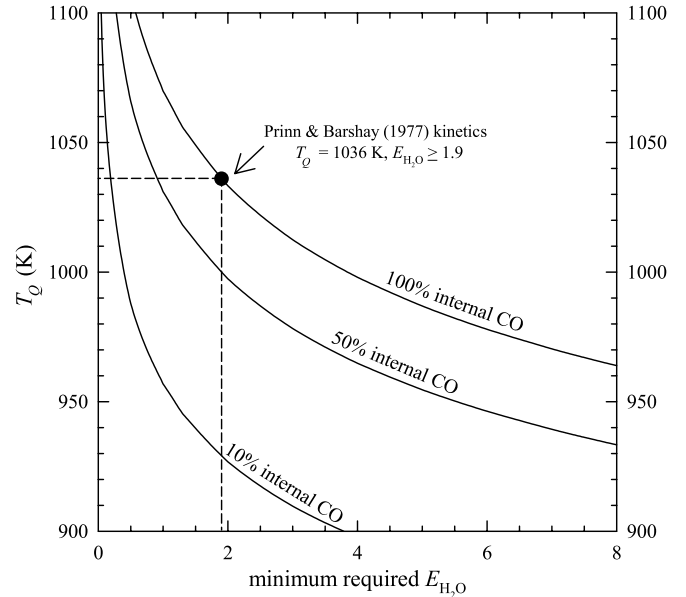


FIG. 2.—Relationship between the amount of CO from an internal deep atmospheric source and the amount of water required to produce the observed CO abundance.

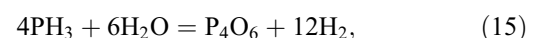
ever, the relative strength of each source is currently unknown. We therefore considered scenarios that include both an internal and an external source of CO.

Results are shown in Figure 2 for internal CO fluxes comprising 100%, 50%, and 10% of the lower bound of the observed CO mixing ratio. At higher quench temperatures ( $T_Q$ ), CO originates deeper in the troposphere, where it is thermodynamically more stable and thus smaller water enrichments are required to produce its observed abundance. At lower quench temperatures, CO originates higher in the troposphere, where it is thermodynamically less stable and therefore requires larger water enrichments to achieve the observed abundance. However, the upper limit on the water enrichment given by  $\text{PH}_3$  chemistry (see § 4.3) indicates that some of the observed CO in Saturn's atmosphere must come from an external source if the CO quench temperature is less than 977 K.

At a constant quench temperature, less tropospheric water is required if some of the observed CO is external in origin. For example, in the model distribution  $S$  of Noll & Larson (1991), the observed CO is mostly stratospheric (external), and  $q_{\text{CO}} = 10^{-10}$  in the troposphere, or about 10% of the nominal CO abundance. At a quench temperature of 1036 K, model  $S$  requires a tropospheric water enrichment of  $E_{\text{H}_2\text{O}} \geq 0.2$ , compared with  $E_{\text{H}_2\text{O}} \geq 1.9$  when all of the observed CO comes from an internal source. For our present discussion, we assume a primarily internal source that produces a mixing ratio of  $q_{\text{CO}} = (1.6 \pm 0.8) \times 10^{-9}$  and thus requires a water abundance of  $\text{H}_2\text{O}/\text{H}_2 \geq 1.7 \times 10^{-3}$  in Saturn's troposphere (see § 4.2.2).

#### 4.3. Phosphine

Phosphine ( $\text{PH}_3$ ) is observed in Saturn's atmosphere at a mixing ratio ( $\text{PH}_3/\text{H}_2$ ) of  $(5.1 \pm 1.6) \times 10^{-6}$  (Table 1). Because it is destroyed by tropospheric water,  $\text{PH}_3$  constrains the upper limit of Saturn's water abundance. The phosphine abundance is governed by the net thermochemical equilibrium

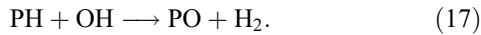


which shows that, according to LeChâtelier's principle, the  $\text{PH}_3$  abundance decreases as the water abundance increases to maintain chemical equilibrium. Rearranging the equilibrium constant expression for reaction (15), the phosphine abundance is given by

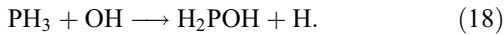
$$X_{\text{PH}_3} = [(X_{\text{P}_4\text{O}_6} X_{\text{H}_2}^{12} P_7^3) / (X_{\text{H}_2\text{O}}^6 K_{15})]^{1/4}. \quad (16)$$

At high temperatures and/or low water abundances, phosphine is the dominant P-bearing gas and  $q\text{PH}_3 \approx q\Sigma\text{P}$ . As parcels of hot gas rise in Saturn's atmosphere,  $\text{PH}_3$  is oxidized to  $\text{P}_4\text{O}_6$ . The observed abundance of  $\text{PH}_3$  is  $\sim 30$  orders of magnitude higher than that predicted by thermodynamic equilibrium, and its presence is evidence of rapid vertical mixing from Saturn's deep atmosphere (Fegley & Prinn 1985). Unlike  $\text{CO}$ , phosphine gives no inherent thermodynamic limit to water enrichment because the  $\text{PH}_3$  abundance generally increases with both temperature and pressure (cf. Fig. 3, Fegley & Prinn 1985). Therefore, we turn directly to  $\text{PH}_3$  quenching kinetics to constrain the upper limit on the water abundance.

The observable amount of phosphine depends on both the rate of vertical mixing and the kinetics of  $\text{PH}_3$  destruction. Prinn et al. (1984) proposed a mechanism for  $\text{PH}_3$  destruction in which the rate-determining step is formation of the P—O bond via



On the basis of work by Twarowski (1995), we take the formation of the P—O bond by direct reaction of  $\text{PH}_3$  with an OH radical as our rate-determining step:



The corresponding chemical lifetime for  $\text{PH}_3$  is

$$t_{\text{chem}}(\text{PH}_3) = 1/(k_{18}[\text{OH}]), \quad (19)$$

where the estimated rate constant  $k_{18}$  is obtained from Twarowski's (1995) kinetic study of phosphine combustion products and is given by

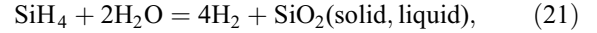
$$k_{18} \approx 5.25 \times 10^{-13} \exp(-6013.6/T) \text{ cm}^3 \text{ s}^{-1}. \quad (20)$$

We again assume that the maximum plausible rate of vertical mixing is given by  $K_{\text{eddy}} \sim 10^9 \text{ cm}^2 \text{ s}^{-1}$  and find that using reaction (18) as the rate-determining step for phosphine destruction gives results similar to reaction (17). Solving equations (16) and (19) at a phosphorus enrichment of  $7.4 \pm 2.3$  times protosolar shows that  $\text{H}_2\text{O}$  in Saturn's deep atmosphere cannot be enriched more than  $6.1_{-2.7}^{+0.9}$  times the solar system abundance because greater water enrichments would reduce the  $\text{PH}_3$  abundance below the observed level. This water enrichment corresponds to an  $\text{H}_2\text{O}/\text{H}_2$  mixing ratio of  $q\text{H}_2\text{O} \leq (5.5_{-2.5}^{+0.8}) \times 10^{-3}$  in Saturn's troposphere.

#### 4.4. Silane

Silane ( $\text{SiH}_4$ ) is destroyed by water in the deep atmosphere of Saturn and serves as a constraint on the total oxygen abundance of Saturn's interior. Silicon is about 120, 8300, and 164,000 times more abundant than P, Ge, and As, respectively,

in protosolar composition gas. However, although  $\text{PH}_3$ ,  $\text{GeH}_4$ , and  $\text{AsH}_3$  have each been observed on Saturn (see Table 1),  $\text{SiH}_4$  (predicted to be the dominant Si-bearing gas) remains undetected, with an upper limit of  $q\text{SiH}_4 < (0.2-1.2) \times 10^{-9}$  (Larson et al. 1980; Noll & Larson 1991). This is because silicon is efficiently removed from Saturn's atmosphere by the formation of silicates such as  $\text{MgSiO}_3$  (enstatite) and  $\text{Mg}_2\text{SiO}_4$  (forsterite), exemplified by the net thermochemical reaction (Fegley & Prinn 1988)



which incorporates Si into rock. In order for reaction (21) to remove Si from the atmosphere, it is evident that water vapor must be present to oxidize  $\text{SiH}_4$ . This is only possible if the total oxygen abundance ( $\Sigma\text{O}$ ) is greater than or equal to the oxygen consumed by rock-forming oxides ( $\text{O}_{\text{rock}}$ ). This mass balance constraint can be written as

$$\Sigma\text{O}/\text{O}_{\text{rock}} \geq 1, \quad (22)$$

where the amount of oxygen bound in rock is given by equation (2). Protosolar composition gas (Lodders 2003) has

$$\Sigma\text{O}/\text{O}_{\text{rock}} = 4.4, \quad (23)$$

which clearly satisfies the mass balance criterion. Thus, in order for reaction (21) to destroy all  $\text{SiH}_4$  on Saturn, the oxygen enrichment ( $E_{\text{O}}$ ) in Saturn's deep atmosphere must be

$$E_{\text{O}} \geq E_{\text{rock}}/4.4, \quad (24)$$

where  $E_{\text{rock}} = E_{\text{Mg}} = E_{\text{Si}}$ , etc., that is, all rock-forming elements are assumed to be equally enriched. This assumption is not necessarily correct, because it appears that P and As, both of which are rock-forming elements, may not be equally enriched on Saturn (e.g., Noll et al. 1989; Noll & Larson 1991; see Table 1; § 2). However, we explicitly assume equal enrichment of rock-forming elements and take  $E_{\text{rock}} = 7.4 \pm 2.3$  by comparison with the observed enrichment in phosphorus. Equation (24) then gives a total oxygen enrichment of  $E_{\text{O}} \geq 1.7 \pm 0.5$  times the protosolar oxygen abundance and a mixing ratio of  $\text{O}/\text{H}_2 \geq (2.0 \pm 0.6) \times 10^{-3}$  in Saturn's deep atmosphere. At lower enrichments, there is not enough oxygen available to effectively oxidize silicon, and we would expect to see  $\text{SiH}_4$  abundances well above (up to 5 orders of magnitude) the observational upper limit.

## 5. DISCUSSION

### 5.1. Constraints on Saturn's Oxygen Inventory

The chemical constraints placed on the water and total oxygen abundance on Saturn are summarized in Table 2. The independent constraints given by  $\text{CO}$  and  $\text{PH}_3$  indicate a water abundance of  $q\text{H}_2\text{O} \sim (1.7-5.5) \times 10^{-3}$  in Saturn's deep atmosphere, corresponding to a water enrichment of 1.9–6.1 times the solar system  $\text{H}_2\text{O}/\text{H}_2$  ratio. We therefore expect water vapor to be the third or fourth most abundant gas (after  $\text{H}_2$ , He, and  $\text{CH}_4$ ) below the clouds of Saturn.

The silane mass balance constraint by itself shows that the total oxygen abundance on Saturn must be enhanced by a factor of at least 1.7 times protosolar. However, this constraint neglects

TABLE 2  
CHEMICAL CONSTRAINTS ON SATURN'S WATER AND TOTAL OXYGEN ABUNDANCE

| Constraint                                 | Mixing Ratio                              | Enrichment Factor        |
|--|---|--------------------------|
| Water:                                     |   |                          |
| CO .....                                   | $\geq (1.7^{+0.7}_{-0.4}) \times 10^{-3}$ | $\geq 1.9^{+0.8}_{-0.5}$ |
| PH <sub>3</sub> .....                      | $\leq (5.5^{+0.8}_{-2.5}) \times 10^{-3}$ | $\leq 6.1^{+0.9}_{-2.7}$ |
| Total oxygen:                              |   |                          |
| SiH <sub>4</sub> .....                     | $\geq (2.0 \pm 0.6) \times 10^{-3}$       | $\geq 1.7 \pm 0.5$       |
| SiH <sub>4</sub> and CO .....              | $\geq (3.7^{+0.7}_{-0.5}) \times 10^{-3}$ | $\geq 3.2^{+0.6}_{-0.4}$ |
| SiH <sub>4</sub> and PH <sub>3</sub> ..... | $\leq (7.4^{+0.8}_{-2.4}) \times 10^{-3}$ | $\leq 6.4^{+0.7}_{-2.1}$ |

NOTES.—Constraints on the water abundance are calculated assuming  $E_{\text{CH}_4} \approx E_{\text{PH}_3} \approx 7.4 \pm 2.3$ . Constraints on the total oxygen abundance are calculated assuming a rock enrichment of  $E_{\text{rock}} \approx 7.4 \pm 2.3$ .

that after completely oxidizing Si and forming rock, enough oxygen must be left over (as H<sub>2</sub>O) to produce carbon monoxide in Saturn's troposphere. However, if too much oxygen remains, the observed amount of PH<sub>3</sub> cannot form. We therefore combine the CO and SiH<sub>4</sub> constraints and the PH<sub>3</sub> and SiH<sub>4</sub> constraints to estimate the lower and upper limit, respectively, of Saturn's total oxygen abundance (cf. Fegley & Prinn 1988). Rewriting equation (1) using enrichment factors gives

$$E_{\text{H}_2\text{O}}(O_{\text{H}_2\text{O}}) = E_{\text{O}}(\Sigma\text{O}) - E_{\text{rock}}(O_{\text{rock}}), \quad (25)$$

where the terms in parentheses are the protosolar values. If we replace these terms with values from Lodders (2003), equation (25) can be rewritten as

$$E_{\text{H}_2\text{O}} = 1.295E_{\text{O}} - 0.295E_{\text{rock}}, \quad (26)$$

which relates the enrichment factors for water, oxygen, and rock and implicitly contains the silane mass balance constraint given in equation (24) ( $1.295/0.295 \approx 4.4$ ). If we assume  $E_{\text{rock}} \approx 7.4$  in equation (26), the CO water constraint ( $E_{\text{H}_2\text{O}} \geq 1.9$ ) gives an oxygen lower limit of  $E_{\text{O}} \geq 3.2$ , whereas the PH<sub>3</sub> water constraint ( $E_{\text{H}_2\text{O}} \leq 6.1$ ) gives an oxygen upper limit of  $E_{\text{O}} \leq 6.4$ . The upper and lower limits on the total oxygen abundance of Saturn are summarized in Table 2. Taken together, the chemical constraints indicate a total oxygen enrichment in Saturn's interior of 3.2–6.4 times the solar system O/H<sub>2</sub> abundance, similar to that observed for arsenic and less than the observed enrichments in carbon and phosphorus.

From equation (25) it is evident that estimates of the total oxygen enrichment depend on the assumed rock enrichment on Saturn, so smaller or larger rock abundances require, respectively, smaller or larger enrichments in oxygen. However, the observed CO and PH<sub>3</sub> mixing ratios, along with the general mass balance given in equation (25), constrain the *relative* allowed abundances of water, oxygen, and rock over a range of rock enrichments in Saturn's interior.

### 5.2. Oxygen Partitioning into Metallic H-He

The referee asked whether or not our chemical constraints on water and oxygen are valid for Saturn as a whole or apply only to its atmosphere. For example, one could ascribe the relative oxygen depletion in Saturn's atmosphere to internal planetary fractionation processes (e.g., see Fortney & Hubbard 2003, 2004). However, the selective or preferential removal of oxy-

gen (with respect to carbon and other heavy elements) from the molecular envelope into a metallic core is difficult to model with current knowledge about solution properties of C, N, O and other heavy elements in metallic H-He. In fact, the *P-T* curve for the molecular to metallic hydrogen transition is unknown, as is the high pressure phase diagram for the H-He system. The hypothetical partitioning of oxygen into metallic H-He in Saturn's interior is not our preferred model, and we do not consider it further.

Instead, we think that our chemical constraints are valid for Saturn as a whole. In support of this we note that the protosolar H<sub>2</sub>O/CH<sub>4</sub> ratio explains the observed atmospheric chemistry of the brown dwarf Gl 229b (e.g., Saumon et al. 2000). Although Gl 229b apparently has subsolar metallicity (Saumon et al. 2000), there is no evidence from chemical models that the H<sub>2</sub>O/CH<sub>4</sub> ratio itself is significantly smaller than the protosolar value.

### 5.3. The Nebular Snow Line

Our chemical constraints on Saturn's water and total oxygen inventory also have implications for Saturn's formation. Our results indicate that the  $E_{\text{H}_2\text{O}}/E_{\text{CH}_4}$  ratio ranges from 0.26 to 0.82 and the  $E_{\text{O}}/E_{\text{C}}$  ratio ranges from 0.43 to 0.86 on Saturn (see Table 2). On Jupiter, the observed methane abundance is 3.6 times protosolar, whereas the observed water abundance is 0.67 times protosolar, so  $E_{\text{H}_2\text{O}}/E_{\text{CH}_4} \approx 0.19$  and  $E_{\text{O}}/E_{\text{C}} \approx 0.28$  (Lodders 2004). In other words, both Jupiter and Saturn apparently have lower H<sub>2</sub>O/CH<sub>4</sub> and O/C ratios than expected for uniform enrichments of carbon and oxygen (i.e.,  $E_{\text{O}}/E_{\text{C}} \equiv 1$ ). Lodders (2004) proposed that the water depletion and carbon enrichment on Jupiter can be explained by moving the water ice condensation front in the solar nebula (the nebular snow line) beyond Jupiter's formation region. In this scenario, Jupiter never accreted much water ice. Instead, a carbonaceous matter condensation/evaporation front (the nebular tar line) was near Jupiter's formation region and explains the carbon enrichment. This scenario may also explain the subsolar H<sub>2</sub>O/CH<sub>4</sub> and O/C ratios that we have derived for Saturn and account for the large water enrichments derived for Uranus and Neptune by Lodders & Fegley (1994). Further development of these ideas is beyond the scope of this paper and will be pursued elsewhere (K. Lodders & B. Fegley 2005, in preparation).

## 6. SUMMARY

We used CO, PH<sub>3</sub>, and SiH<sub>4</sub> as chemical probes to provide reliable estimates of the water and total oxygen abundances in the deep atmosphere of Saturn. If the observed carbon monoxide mostly forms in the troposphere, water must be enriched at least 1.9 times the solar system abundance. The observed amount of phosphine requires a water enrichment less than 6.1 times the solar system abundance. The total oxygen abundance on Saturn must be enhanced 3.2–6.4 times the protosolar O/H<sub>2</sub> ratio in order to completely oxidize Si and form rock and yet leave an appropriate amount of water to satisfy the CO and PH<sub>3</sub> constraints. Thus, oxygen on Saturn appears to be enriched relative to the solar system composition, but not to the same extent as other heavy elements such as carbon and phosphorus.

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