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### ABSTRACT

We have re-evaluated the *Cassini* Ion Neutral Mass Spectrometer (INMS)  ${}^{12}C/{}^{13}C$  ratios in the upper atmosphere of Titan based on new calibration sensitivities and an improved model for the NH<sub>3</sub> background in the  ${}^{13}CH_4$  mass channel. The INMS measurements extrapolated to the surface give a  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> of 88.5 ± 1.4. We compare the results to a revised ratio of 91.1 ± 1.4 provided by the *Huygens* Gas Chromatograph Mass Spectrometer and 86.5 ± 7.9 provided by the *Cassini* Infrared Spectrometer and determine implications of the revised ratios for the evolution of methane in Titan's atmosphere. Because the measured  ${}^{12}C/{}^{13}C$  is within the probable range of primordial values, we can only determine an upper boundary for the length of time since methane began outgassing from the interior, assuming that outgassing of methane (e.g., cryovolcanic activity) has been continuous ever since. We find that three factors play a crucial role in this timescale: (1) the escape rate of methane, (2) the difference between the current and initial ratios and the rate of methane, and (3) production or resupply due to cryovolcanic activity. We estimate an upper limit for the outgassing timescale of 470 Myr. This duration can be extended to 940 Myr if production rates are large enough to counteract the fractionation due to escape and photochemistry. There is no lower limit to the timescale because the current ratios are within the range of possible primordial values.

Key words: planets and satellites: general - planets and satellites: individual (Titan)

### 1. INTRODUCTION

Stable isotope ratios of atmospheric constituents are a useful tracer for the evolution of an atmosphere. The D/H in the water of Venus's atmosphere has been used to estimate the initial inventory of water that Venus could have had on the surface and in the atmosphere (Donahue et al. 1997). The formation and evolution of Titan's atmosphere may have left important clues in the current isotopic ratios of  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> and  ${}^{12}C/{}^{13}C$ in  $CH_4$ . In Mandt et al. (2009), we evaluated the evolution of  $^{12}\mathrm{C}/^{13}\mathrm{C}$  and D/H in CH<sub>4</sub> over geologic timescales and found that the methane presently in Titan's atmosphere could not have been present for more than 180 million years (Myr). This conclusion was based on fractionation of the  ${}^{12}C/{}^{13}C$  ratio in CH<sub>4</sub> from a primordial value of  $89.01^{+3.19}_{-4.24}$  (Alexander et al. 2007; Martins et al. 2008) to the measured current  ${}^{12}C/{}^{13}C$ ratio of 82.3  $\pm$  1.0 in CH<sub>4</sub> according to the *Huygens* Gas Chromatograph Mass Spectrometer (GCMS; Niemann et al. 2005) and 76.6  $\pm$  2.7 according to the *Cassini* Composite Infrared Spectrometer (CIRS; Nixon et al. 2008). Fractionation of the isotopes over time due to escape was constrained by altitude profiles of the isotope ratios measured by the Cassini Ion Neutral Mass Spectrometer (INMS).

Niemann et al. (2010) re-evaluated the GCMS data and published a revised  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> of 91.1 ± 1.4. This measurement extends from the surface to 140 km altitude at the *Huygens* landing site (approximately 10°S latitude and 190°W longitude). Re-analysis of the CIRS data (Nixon et al. 2012) provides a ratio of 86.5 ± 7.9 in the altitude range

of 250–350 km. These revised ratios are very different from the values previously used to model the evolution of Titan's atmospheric methane. It is also necessary to re-evaluate the INMS sensitivity used for <sup>13</sup>CH<sub>4</sub> in Mandt et al. (2009), which is different from the sensitivity for <sup>12</sup>CH<sub>4</sub>. Electron ionization cross sections are insensitive to isotope effects, so the sensitivity for the two isotopologues should be equal (Tarnovsky et al. 1996; Märk et al. 1977; Märk & Egger 1977). After re-analysis of the INMS carbon ratios, we compare the revised INMS ratios to these new GCMS and CIRS results, and revisit the evolution of Titan's atmosphere based on the new ratios.

INMS measures the altitude profiles of  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> and  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> above 950 km. The  ${}^{12}C/{}^{13}C$  INMS altitude profiles published in Mandt et al. (2009) were determined using the sensitivities and methodologies described in Magee et al. (2009). These ratios were extrapolated to the surface using the Titan Global Ionosphere Thermosphere Model (T-GITM; Bell et al. 2010) to give a ratio close to 80. An evaluation of the methane sensitivity shows that the sensitivity values used for  $^{12}$ CH<sub>4</sub> and  $^{13}$ CH<sub>4</sub> should be equal and the sensitivity for  $^{13}$ CH<sub>4</sub> has been corrected (Tarnovsky et al. 1996; Märk et al. 1977; Märk & Egger 1977). The revised sensitivity for <sup>13</sup>CH<sub>4</sub> increases the ratio measurements by a factor of 1.07. Furthermore, in Mandt et al. (2009) subtraction of NH<sub>3</sub> contamination from the mass 17 channel (where <sup>13</sup>CH<sub>4</sub> is measured) was conducted based on fitting a power-law model to the ammonia as it desorbed from the antechamber wall after a Titan flyby (Magee et al. 2009). Since this time, an improved method for modeling the adsorption and desorption of components such as ammonia and water that are known to stick to the INMS antechamber has been developed based on modeling the mechanical structure of the INMS antechamber and ionization source and the adsorption efficiency of these components (Teolis et al. 2010). This model was developed to evaluate the mass 18 signal at Enceladus, which is primarily water. Because application of the desorption model to a mass channel containing two constituents, <sup>13</sup>CH<sub>4</sub> and NH<sub>3</sub>, is nontrivial we do not determine the complete time evolution of the NH<sub>4</sub> contribution to the mass 17 signal. However, the model demonstrates the existence of a time range (<5 s) relative to closest approach where ammonia contamination of the <sup>13</sup>CH<sub>4</sub> measurements is negligible. We therefore use data in this range to estimate the  ${}^{12}C/{}^{13}C$  ratio down to an altitude of approximately 1000 km. Given the corrected sensitivity for <sup>13</sup>CH<sub>4</sub> and an improved understanding of the NH<sub>3</sub> background, we re-evaluated the INMS  ${}^{12}C/{}^{13}C$ isotope ratios and compare INMS measurements with GCMS and CIRS using a basic model for the upper atmosphere and a slightly more complex diffusion model for the full atmosphere.

Atmospheric models are needed to understand the  ${}^{14}N/{}^{15}N$ and  ${}^{12}C/{}^{13}C$  isotope ratio profiles between 350 and 950 km because there are no Cassini or Huygens measurements of the ratios in this region. Bell et al. (2011) showed with T-GITM that a methane homopause altitude of  $\sim 1000$  km was required to obtain simultaneous agreement between the GCMS  $^{14}N/^{15}N$  $(167.7 \pm 0.7)$  measurements near the surface and the INMS altitude profile of <sup>14</sup>N/<sup>15</sup>N above 1150 km. In Section 2, we explain the data analysis and outline a multi-step approach to determine four important parameters for understanding the isotope ratio profile between the altitudes where measurements are made: (1) the homopause altitude; (2) the altitude at which NH<sub>3</sub> contamination influences the INMS  ${}^{12}C/{}^{13}C$ ; (3) the  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> at the homopause for each INMS Titan flyby; and (4) the change in the  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> and  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> between the surface and the homopause based on assumptions about the eddy diffusion and temperature profiles. The results of this modeling approach are presented in Section 3. The revised  ${}^{12}C/{}^{13}C$  ratios from INMS, GCMS, and CIRS

The revised  ${}^{12}C/{}^{13}C$  ratios from INMS, GCMS, and CIRS are well within the range of possible primordial values, so the evolution of Titan's atmospheric methane must be re-evaluated. In Section 4, we outline the approach for modeling the evolution of Titan's methane over geologic timescales. The primary goal of this modeling is to determine an upper boundary for the timescale during which methane could have been present in the atmosphere. We present the results in Section 5 and discuss any mechanisms that could extend the timescale and evaluate the effectiveness of these mechanisms.

## 2. DATA ANALYSIS AND ATMOSPHERIC MODELING

Data from the *Cassini-Huygens* mission is needed to determine two parameters for modeling the evolution of the methane isotopes: the current  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> and the fractionation due to escape. We first outline the reanalysis of the INMS data, including the updated sensitivity for  ${}^{13}CH_4$ , and the results of the adsorption/desorption model from Teolis et al. (2010). We then describe two atmospheric models used to derive the parameters needed for modeling the evolution of the isotopes. The first model determines the basic diffusion of the isotopes between the homopause and the "escobase," or the point at which particles are escaping from the atmosphere (Hunten 1982), assumed to be the exobase. The second model determines how the isotopes diffuse between the surface and the upper atmosphere.

### 2.1. Data Analysis

INMS measures the ambient neutrals in Titan's upper atmosphere. Isotope ratios of  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> and  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> have been measured for 30 Titan flybys representing a diverse coverage of altitude, latitude, and west longitude. Figure 1 illustrates the geographic coverage of the 30 flybys analyzed for this work. The label for each flyby is located at the ingress point of the path.

The methodology for calculating neutral densities used to determine the isotope ratios is outlined in Magee et al. (2009). Isotope ratios for  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> are limited to the altitude range above 1150 km because of saturation of the mass 29 measurements of <sup>15</sup>N<sup>14</sup>N. The sensitivities for <sup>13</sup>CH<sub>4</sub> reported in Magee et al. (2009) were different from the sensitivity for  $^{12}$ CH<sub>4</sub> and have been corrected. The  $^{14}N_2$  and  $^{15}N^{14}N$  sensitivities were the same and do not need correction so the  ${}^{14}N/{}^{15}N$ measurements are not revised. Because the <sup>13</sup>CH<sub>4</sub> sensitivity has been revised, the value of the  ${}^{12}C/{}^{13}C$  has increased by a factor of  $\sim$ 1.07. Figure 2(a) illustrates the INMS measurements <sup>14</sup>N/<sup>15</sup>N (black circles) and the ingress measurements of  $^{12}C/^{13}C$  (gray circles) using the sensitivities reported in Magee et al. (2009). The blue and purple circles at the lowest altitudes are the recent GCMS  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> and  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>, respectively, including error bars. The cyan points are the CIRS measurements of  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>. The blue and purple lines are a diffusion model (described in Section 2.2.2) for the isotope ratios assuming a homopause altitude of 1000 km and the eddy diffusion and temperature profiles from Model 8 of Bell et al. (2010). The  ${}^{14}N/{}^{15}N$  altitude profiles show good agreement between GCMS and INMS, but the INMS  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> is clearly heavier than would be expected from the GCMS lower boundary condition. Figure 2(b) illustrates the isotope ratios determined using the same sensitivities for both isotopologues (Märk et al. 1977; Märk & Egger 1977; Tarnovsky et al. 1996) with the same comparison to GCMS and CIRS. The INMS  $^{14}N/^{15}N$  shows no change, but the  $^{12}C/^{13}C$  is shifted to a higher value and is in good agreement with GCMS and CIRS.

Figure 2 illustrates only the ingress measurements of  ${}^{12}C/{}^{13}C$ because egress data are contaminated by NH<sub>3</sub> from the thrusters (Sackheim and Zafran, 1999) in the mass 17 channel, where <sup>13</sup>CH<sub>4</sub> is also measured. Ammonia molecules adsorb easily to the INMS antechamber and this adsorption causes a delay between when the molecules enter the instrument and when they are detected, as shown in Figure 3(a), where the T16 count rate of mass 17 as a function of time from the closest approach develops a tail of ammonia desorbing from the instrument well past closest approach where thruster firings (and thus the flux of ammonia into the instrument) are most significant. The green circles are the estimated atmospheric contribution of ammonia to the signal as a function of time based on the photochemical models of Vuitton et al. (2006, 2007) and Yelle et al. (2010). Contamination from the thrusters appears to be the most significant source of ammonia because the atmospheric contribution is clearly too low to explain the measurements. The T16  ${}^{12}C/{}^{13}C$  ratios as a function of time from closest approach without any  $NH_3$  subtraction are illustrated in Figure 3(b). It can be seen in this figure that the NH3 contamination produces a heavier ratio over time.

In Magee et al. (2009), we used a theoretical model of  $NH_3$  desorption to subtract this contamination from mass 17. In the current work, we instead use a model of the propagation of adsorbed gas through the antechamber to the ionizer (described in detail Teolis et al. 2010) to determine the



Figure 1. Latitude and west longitude coverage of the 30 Titan flybys for which INMS data is analyzed. The flyby number (T##) is located at the ingress point of the flyby.



**Figure 2.** INMS (black and gray), GCMS (blue and purple), and CIRS (cyan) measurements of the  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> (black and blue) and  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> (gray, purple, and cyan). The blue line is the inferred altitude profile of  ${}^{14}N/{}^{15}N$  in N<sub>2</sub> based on a diffusion model (Model 2) with the homopause set at 1000 km (Bell et al. 2011) and the temperature in the thermosphere assumed to be 153 K (Westlake et al. 2011). The purple line is the inferred altitude profile of  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>. (a) INMS ratios based on sensitivities reported in Magee et al. (2009) and (b) equal sensitivities for both isotopologues.

point in the flyby at which the contamination will influence the  ${}^{12}C/{}^{13}C$  measurements. The model treats the antechamber and antechamber–ionizer transfer tube as a surface mesh consisting of 1293 elements, and the molecule accumulation rate on each element consists of two contributions that are weighted by the cosine of the arrival incidence angle: (1) the ram flux entering the antechamber from space and (2) the desorbing flux from other elements times their contribution (given by the solid angle) to the field of view. Since ram speeds at Titan are roughly an order of magnitude greater than the average molecule thermal velocity, the ram flux is approximated as a collimated beam, which scatters (and thermalizes) from the back antechamber surface (i.e., a circular patch facing the entrance orifice) to other surface elements within view. We consider the NH<sub>3</sub> ram flux to be proportional (by a factor C < 1) to the H<sub>2</sub> signal spikes at 2 m/z resulting from thruster activity (Magee et al. 2009). The accumulating molecules are assumed to stick for an average time  $\tau$  given by a power law as typically observed for metal surfaces in vacuum systems (Dylla et al. 1993):  $\tau = b\sigma^n$ , where  $\sigma$  is the surface coverage, and b and n are empirical parameters. The signal detected by INMS is considered to be proportional to the flux exiting the transfer tube into the ionizer. We also account for



**Figure 3.** Evidence for ammonia contamination of the INMS  ${}^{12}C/{}^{13}C$  altitude profiles. (a) Count rate in mass channel 17 as a function of time from closest approach (s) for Titan flyby T16. (b)  ${}^{12}C/{}^{13}C$  measured by INMS (circles) as a function of time from closest approach (s) for Titan flyby T16. The modeled isotope ratio (line) is shown for reference. (c) Antechamber simulation results for Titan flyby T16. The count rate in mass channel 17 (black) is again shown as a function of time from closest approach (s). This is compared with the estimated ammonia input flux from the thrusters (red) based on the thruster output of H<sub>2</sub> measured by INMS and to the estimated count rate of ammonia detected by INMS (gray) as a function of time from closest approach.

a 97% probability of immediate return of this flux back into the transfer tube due to the negligible adsorption (since the ionizer is hot) and relative contribution of alternative escape paths out of the ionizer (Teolis et al. 2010).

The model is underconstrained, with a family of viable fits to the mass 17 tail that extends over a volume of threedimensional b, n, C parameter space. There are three reasons: (1) the presence of two components,  ${}^{13}CH_4$  and  $NH_3$  in the data, (2) a lack of laboratory measurements of the sticking parameters b and n for  $NH_3$  on titanium, and (3) uncertainty in C due a lack of knowledge of the relative  $H_2/NH_3$  abundance in the thruster exhaust, and their possibly different expansion and backscattering rates around the spacecraft. However, all model solutions agree on one point: the sticking times required to fit the NH<sub>3</sub> tail also delay transmission of the earliest arriving NH<sub>3</sub> molecules from the antechamber to the ionizer. We find everywhere in the parameter space that the NH<sub>3</sub> contribution to the signal is negligible until a few seconds (no earlier than approximately -5 s) before closest approach, as illustrated in Figure 3(c). We therefore conclude that the mass 17 inbound signal up to -5 s consists approximately of pure <sup>13</sup>CH<sub>4</sub> and use these data to determine the  ${}^{12}C/{}^{13}C$  ratio.

The isotope ratios illustrated in Figure 3(b) clearly show the effects of ammonia contamination because over time the ratio becomes heavier. However, the ratio will not be constant as a function of altitude because diffusion in the atmosphere above the homopause causes the ratio to become lighter with increasing altitude. Therefore, the ratios illustrated in Figure 3(b) decrease between -300 and 0 s for two reasons: (1) diffusion in the atmosphere and (2) contamination of the ratios by ammonia. Diffusion is in effect over the entire time period, but as the model of the antechamber showed the contamination from ammonia will appear at some unknown time prior to closest approach. The exact time when ammonia contamination is observed in the ratios is difficult to constrain from the information provided in Figure 3(b). A comparison with atmospheric model predictions for the ratio as a function of altitude is required to isolate this point where ammonia contamination appears in the INMS  ${}^{12}C/{}^{13}C$  measurements.

### 2.2. Atmospheric Modeling

Two atmospheric models were developed for this study. We start with modeling the fractionation of the isotopes above the homopause due to basic mass-dependent molecular diffusion, hereafter referred to as Model 1. Hunten (1982) first developed this methodology to determine the fractionation of isotopes in planetary atmospheres due to diffusion and escape. A more complex diffusion model, referred to as Model 2, was developed to determine the fractionation of the isotopes between the surface and the upper atmosphere because Model 1 is only valid above the homopause. We use Model 2 to extrapolate INMS measurements to the surface and to confirm the results of Model 1 above the homopause. Model 2 requires assumptions about the temperature and eddy diffusion altitude profiles. To constrain the sensitivity of the isotope ratio altitude profiles to assumptions made about temperature and eddy diffusion, two published inputs for eddy diffusion and temperature profiles (Yelle et al. 2008; Bell et al. 2010) are applied to Model 2. We fit Models 1 and 2 to each of the 30 flybys to determine the homopause altitude and the  ${}^{12}C/{}^{13}C$  ratio at the homopause for Model 1 and surface for Model 2 based on the INMS  $^{14}N/^{15}N$  and  $^{12}C/^{13}C$  altitude profiles and the GCMS  $^{14}N/^{15}N$ surface measurements of  $167.7 \pm 1.4$  (Niemann et al. 2010). The objective is to constrain the level of agreement between the three *Cassini-Huygens* measurements of  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub> and to obtain the parameters needed to model the evolution of Titan's methane.

### 2.2.1. Model 1: Diffusion of the Isotopes above the Homopause

Hunten (1982) derived an equation for the isotopic ratio as a function of altitude between the homopause and the "escobase," or the point at which particles escape from the atmosphere. We assume that the "escobase" is the exobase for this study and derive this equation below in order to determine the appropriate way to account for the variation of gravity as a function of altitude. This approach is necessary because Titan's atmosphere extends far enough from the surface for the gravity to vary significantly with altitude.

The density of an atmospheric constituent as a function of altitude in the upper atmosphere, assuming diffusive equilibrium and an isothermal temperature profile, is (Banks & Kockarts 1973)

$$n_i(r) = n_i(r_0) \exp\left(-\int_{r_0}^r \frac{dr'}{H_i}\right),\tag{1}$$

where  $n_i$  is the density of the constituent, r is the distance from the center of the planet or moon,  $r_0$  is the distance between the homopause and the center of the planet or moon, and  $H_i$  is the species-specific scale height

$$H_i = \frac{kT}{m_i g},\tag{2}$$

where k is Boltzmann's constant, T is the temperature in the thermosphere,  $m_i$  is the mass of the constituent, and g is the acceleration due to gravity.

Dividing the density of the heavier (subscript 2) isotope by the density of the lighter isotope (subscript 1) and integrating between the radius, r, and the homopause,  $r_0$ , gives the following equation for the isotopic ratio as a function of altitude in the thermosphere

$$R(r) = R(r_0) \exp\left[\frac{(m_1 - m_2)MG}{kT} \left(\frac{1}{r} - \frac{1}{r_0}\right)\right].$$
 (3)

We fit Equation (3) by a least-squares method to the  ${}^{14}N/{}^{15}N$  and  ${}^{12}C/{}^{13}C$  altitude profiles of all 30 flybys. We first use as fixed parameters an  ${}^{14}N/{}^{15}N$  at the homopause of 167.7,  $R(r_0)$ , and a

temperature, *T*, determined from the N<sub>2</sub> scale heights (Westlake et al. 2011). With these inputs we fit Model 1 to the  ${}^{14}N/{}^{15}N$  altitude profiles to determine the homopause altitude,  $r_0$ . The next step was to fit Equation (3) to the  ${}^{12}C/{}^{13}C$  altitude profiles, with the homopause from the  ${}^{14}N/{}^{15}N$  altitude profile as a fixed value, and to determine the carbon ratio at the homopause,  $R(r_0)$ .

In order to check how well the fit reflects the  ${}^{12}C/{}^{13}C$  altitude profile and to look for systematic trends, the expected enrichment for each INMS data point was calculated based on the fit results from the model. The expected enrichment is the increase in the light isotope relative to the heavy isotope due to mass-dependent diffusive separation of the isotopologues. This enrichment was then used to determine the expected  ${}^{12}C/{}^{13}C$  at the homopause for each data point in the altitude profile. This process gave altitude profiles of the lower boundary ratios that, for an ideal fit of the model to the data, would be constant with altitude. All of the  ${}^{12}C/{}^{13}C$  lower boundary ratios for the 30 flybys were binned in 10 km altitude bins with the goal of identifying a minimum altitude on the ingress of the flyby at which ammonia contamination is not evident in the measurements.

The entire fitting procedure was repeated using  ${}^{14}N/{}^{15}N$  values at the homopause ranging between 150 and 180 to perform a sensitivity study of the homopause and carbon lower boundary ratio fit results to the assumed  ${}^{14}N/{}^{15}N$  lower boundary.

#### 2.2.2. Model 2: Diffusion of the Isotopes from the Surface

Altitude profiles of the densities of neutral species are commonly characterized by diffusion equations in atmospheric models. Banks & Kockarts (1973) developed a formulation of the diffusion equation that is valid for both major and minor neutral species

$$w_s = -D_s \left[ \frac{1}{n_s} \frac{dn_s}{dr} + \frac{1}{H_s} + (1 + \alpha_T) \frac{1}{T} \frac{dT}{dr} \right] - K \left[ \frac{1}{n_s} \frac{dn_s}{dr} + \frac{1}{H_a} + \frac{1}{T} \frac{dT}{dr} \right],$$
(4)

where the subscript *s* refers to the atmospheric constituent of interest and the subscript *a* refers to the bulk atmosphere, *w* is the vertical diffusion velocity, *n* is the density, *K* is the eddy diffusion coefficient,  $D_s$  is the estimated molecular diffusion coefficient for a multi-component atmosphere, and  $\alpha_T$  is the thermal diffusion coefficient. The thermal diffusion coefficient is assumed to be zero. The estimated molecular diffusion coefficient starts with the standard binary molecular diffusion coefficient (Banks & Kockarts 1973)

$$D_{is} = \frac{AT^s}{n_a} \tag{5}$$

where  $D_{is}$  is the diffusion coefficient for species *s* in gas *i*, and *A* and *s* are constants either measured or calculated analytically. The values used in our model are taken from Massman (1998) and Wilson (2002).

Assuming that the vertical diffusion velocity is zero (i.e., diffusive equilibrium) and dividing Equation (4) for the heavy species by the same equation for the light species gives Model 2 outlined in Equation (6) below. This equation is also valid if the vertical velocities of the two isotopologues are equal or very nearly equal

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$$R(r) = R(r_0) \exp\left\{\int_{r_0}^r \left(\frac{MG}{kTr'^2}\right) \left[\frac{D_1m_1 + Km_a}{D_1 + K} - \frac{D_2m_2 + Km_a}{D_2 + K}\right] dr'\right\}.$$
(6)

Fitting Model 2 to the data is more complex than Model 1. An altitude profile for the temperature and a formulation for the eddy diffusion profile must be assumed. Cassini measurements of the temperature below 500 km are available from the Huygens probe, CIRS, and RSS occultations. The most detailed temperature measurements from the Huygens probe were taken during descent from 150 km the surface (Fulchignoni et al. 2005). CIRS measurements have been made during several Titan flybys and show that temperatures vary by as much as 20 K in the stratosphere over latitude and seasonally. The temperature in the thermosphere can be derived from the scale height of the neutral densities measured by INMS within  $\pm 0.5$  K. Between 500 and 1000 km limited results from Cassini instruments are currently available (e.g., Koskinen et al. 2011 temperatures for T41 and T53 and only T41 is part of this analysis). Assumptions, therefore, must be made regarding the thermal structure in this altitude region.

In order to test the sensitivity of the homopause altitude and  $^{12}C/^{13}C$  at the surface to these assumptions when fitting Model 2 to the 30 flybys, two altitude profiles for the temperature were developed based on previously published modeling results. The temperature profile from Yelle et al. (2008, hereafter referred to as Y08) is the solid gray line in Figure 4(a). This profile was determined by the authors based on CIRS measurements below 500 km, calculations from INMS densities above 1000 km, and an interpolation that satisfies the hydrostatic equilibrium constraint. In Y08 the temperature at the surface is 90 K, drops to 70 K around 50 km, and increases to 210 K around 400 km. There is a temperature minimum of 125 K, or about 20% lower than the temperature in the thermosphere, at 750 km and an increase to 150 K above 900 km. Our temperature profile differs from Y08 above 900 km in that we assume that the temperature is isothermal above this altitude, while in Y08 the temperature above 900 km decreased with increasing altitude. In Bell et al. (2010, hereafter referred to as B10), the thermal structure of the atmosphere is calculated self-consistently using T-GITM. The thermal structure from this study that we chose to use for our analysis is based on Model 8 from B10 and is the dashed gray line in Figure 4(a). This thermal structure differs from the Y08 thermal structure with a lower peak temperature of 180 K at 300-400 km and a higher temperature minimum at 900 km of only 145 K, or 3% lower than the temperature in the thermosphere.

Total neutral density is a required input for determining the molecular diffusion coefficient and the eddy diffusion coefficient as a function of altitude. It is calculated in our model using the barometric equation (Equation (1)), each of the two input thermal structures, and a mean mass profile based on the INMS mean mass measurements and a mean mass of 27.7 below the homopause. For each flyby, the total neutral density is compared to the INMS total neutral density that has been corrected by a calibration constant of 3 (e.g., Bell et al. 2010, 2011; Westlake et al. 2011). The temperature between 500 and 1000 km is adjusted so that the modeled neutral density agrees with the INMS density at the lowest altitude of measurement. A flyby-specific isothermal temperature above ~1000 km is used based on the scale height of the total neutral density for each flyby, as determined according to the method outlined in Westlake et al. (2011). The temperature minimum around 750 km in the Y08 temperature profile and at 950 km in the B10 profile is determined based on a reduction of the isothermal temperature above that altitude. Figure 4(a) illustrates the temperature profiles required to fit to the neutral density for Titan flyby T25 based on the approach of Y08 (black solid line) and B10 (black dashed line). The modeled neutral density for these two temperature profiles is illustrated in Figure 4(b) and agrees well with the INMS total neutral density. The temperature at 350 km in the Y08 temperature profile, however, must be nearly 300 K in order to compensate for the influence of the temperature minimum at 750 km. The B10 temperature profile requires the temperature at 350 km to be 195 K, in good agreement with CIRS measurements for this altitude region. The error in the total density for each flyby is calculated as an average percent difference between the INMS total density and the modeled density.

Once the total density profile has been determined, molecular diffusion as a function of altitude is calculated. Then eddy diffusion is determined in one of the two ways. The method used in Y08 is

$$K(r) = \frac{K_0 (n_0 T_0 / nT)^{\gamma} K_{\infty}}{K_0 (n_0 T_0 / nT)^{\gamma} + K_{\infty}},$$
(7)

where the subscript 0 refers to the surface value,  $\gamma$  is 0.9, and the subscript  $\infty$  is a maximum value for the eddy diffusion coefficient that is used to determine the homopause altitude. An alternative method for calculating eddy diffusion, as used in B10 is (Atreya 1986)

$$K(r) = K_0 \sqrt{n_0/n}.$$
(8)

Figure 4(c) illustrates the initial eddy diffusion profiles in gray for Y08 (solid line) and B10 (dashed line) based on the two methods for calculating the eddy diffusion coefficient. The eddy diffusion profile controls the altitude of the homopause and gives different homopause altitudes for N2 and CH4. When we fit Model 2 to the nitrogen isotopes, we adjusted the eddy diffusion profile to place the N<sub>2</sub> homopause at the altitude providing the best fit to the  ${}^{14}N/{}^{15}N$  altitude profile. The adjusted eddy diffusion profile for Titan flyby T25 is illustrated in black (solid line for Y08 and dashed line for B10) in Figure 4(c). We then used this eddy diffusion profile as the input in fitting to the  ${}^{12}C/{}^{13}C$  altitude profile to determine the  ${}^{12}C/{}^{13}C$  at the surface. With this method, the methane homopause is more accurately represented than in Model 1 where it was assumed to be the same as the  $N_2$  homopause. We then determined the  $N_2$  homopause and  ${}^{12}C/{}^{13}C$  at the surface as a function of the assumed  ${}^{14}N/{}^{15}N$ at the surface over a range of values from 150 to 180.

## 3. RESULTS FOR DATA ANALYSIS AND ATMOSPHERIC PARAMETERS

There are two objectives for fitting these models to the INMS altitude profiles. The first is to evaluate the quality of the INMS  ${}^{12}C/{}^{13}C$  measurements regarding the ammonia contamination in mass 17. Any marked departure in the data from the modeled  ${}^{12}C/{}^{13}C$  is a strong indication of contamination of the data. The second objective is to find the most appropriate method for extrapolating the reliable  ${}^{12}C/{}^{13}C$  measurements to the surface. The quality of the profile fit to the INMS measurements, the variance of the fits for the 30 flybys, and the sensitivity of



Figure 4. Input parameters (gray) and fit results (black) for Model 2. (a) Assumed temperature profiles for Model 2 fits to Titan flyby T23 based on the studies of Yelle et al. (2008; solid lines) and Bell et al. (2010; dashed lines). The temperature at 350 km is adjusted as part of the fitting routine to provide the best fit to the INMS total densities. (b) Total neutral density calculated based on the fit result (black solid and dashed lines) temperature profiles illustrated in (a). (c) Eddy diffusion altitude profile based on Yelle et al. (2008; solid line) and Bell et al. (2010; dashed line).

 Table 1

 Summary of the Goodness of Fit for Models 1 and 2

Model	Model 2 Configuration	<sup>14</sup> N/ <sup>15</sup> N Percent Difference	<sup>12</sup> C/ <sup>13</sup> C Percent Difference	Density Percent Difference	Average Homopause (km)	Average <sup>12</sup> C/ <sup>13</sup> C at Lower Boundary
1	n/a	3.2	6.0	n/a	$932 \pm 49$	$89.0 \pm 1.4$
2	1	2.3	4.0	57.3	$938 \pm 49$	$88.4 \pm 1.5$
	2	2.3	4.0	10.9	$948 \pm 50$	$88.5 \pm 1.4$
	3	2.4	3.9	57.3	$962 \pm 53$	$87.8 \pm 1.5$
	4	2.6	3.9	10.9	$984\pm54$	$88.0\pm1.4$

**Notes.** Goodness of fit is measured as the average value of the percent difference |(data-model)/model| for each of the data points compared to the model. There are six configurations for Model 2: (1) temperature and eddy profile from Y08, (2) temperature from B10 and eddy profile from Y08, (3) temperature from Y08 and eddy profile from B10, and (4) temperature and eddy profiles from B10.

the ratio to changes in the temperature profile and method for determining eddy diffusion will be used to determine the error in the INMS inferred surface ratio. This information will be used to determine two parameters for modeling the evolution of methane: the current ratio and the fractionation of the isotopes due to escape.

First, we will compare the goodness of fit for the two models and explore the sensitivity to variations in the assumptions. We will then look for systematic trends in the  ${}^{12}C/{}^{13}C$  results to determine the altitude region where NH<sub>3</sub> contaminates the  ${}^{12}C/{}^{13}C$  measurements. Finally, we report the best fit for the homopause altitude and  ${}^{12}C/{}^{13}C$  lower boundary ratio and the error of the ratio.

### 3.1. Quality of Fit for Models 1 and 2 and Potential Error in Results

The error in the fit for each of the models is determined as the average percent difference between each of the data points in the flyby and the modeled profile for that flyby. Table 1 lists the average of this error for all 30 flybys for both models. Model 1 does not calculate the total neutral density, so no error for the fit to the total neutral density is determined. Model 2 is divided

into four configurations based on the assumed temperature and eddy profile: (1) temperature and eddy profiles from Y08, (2) temperature profile from B10 and eddy profile from Y08, (3) temperature profile from Y08 and eddy profile from B10, and (4) temperature and eddy profiles from B10.

The average percent error for fitting both models to the nitrogen and carbon isotope ratio profiles is 6% or less. Model 2 provides a slightly better fit to the isotopes than Model 1, illustrating improvement in the calculation when accounting for diffusive processes. The percent difference between the modeled total neutral density and the data is listed for Model 2 in Table 1. This error is larger than the error in fitting to the isotope ratios. The best fit (average percent error is 10.9%) to the neutral densities is provided by the B10 temperature profile. Configurations 2 and 4 of Model 2 use the B10 temperature profile.

The average homopause altitude is more sensitive to the temperature and eddy diffusion profiles than the  ${}^{12}C/{}^{13}C$  extrapolated to the surface. The  ${}^{12}C/{}^{13}C$  extrapolated to the surface is the most important output of our model fits and varies by  $\sim 0.8\%$  when the eddy diffusion calculation is changed. The surface extrapolated value changes by only  $\sim 0.2\%$  when the temperature profile is changed. The  ${}^{12}C/{}^{13}C$  extrapolated to the surface is, therefore, slightly more sensitive to the eddy diffusion calculation than to the temperature profile. The Y08 temperature profile has steeper gradients than the B10 profile, showing that the value extrapolated to the surface is not very sensitive to thermal gradients below 1000 km. Configurations 2 and 4 of Model 2 determine the  ${}^{12}C/{}^{13}C$  extrapolated to the surface using the B10 temperature profile. In order to test the sensitivity of the extrapolated ratios to the temperature value, we increase the temperature by 5 K and then decreased the temperature by 5 K. In both cases, the average value changed by less than 1%. The extrapolated values should, therefore, be reliable to within 1% when considering reasonable errors in the assumed temperature and eddy diffusion profiles.

The results of Model 2 configurations 2 and 4 are a population of 30 INMS  ${}^{12}C/{}^{13}C$  measurements extrapolated to the surface. These configurations have a 95% and 60% probability of a normal distribution, respectively. Our goal is to determine a global average for the surface value of the methane carbon ratio. Although Figure 1 shows that the INMS sampling of the atmosphere does not provide ideal global coverage of Titan's surface, a population with a normal distribution is more appropriate for statistical analyses that will be used to compare the INMS results to GCMS and CIRS. We therefore adopt configuration 2 of Model 2 for the remainder of the paper because it has the highest probability of a normal population. This population has a mean value and standard deviation of 88.5  $\pm$  1.4 with a range from 85.2 to 91.2. The standard deviation of the mean value is greater than the possible error due to assumptions made in the temperature or eddy diffusion profiles (1.6% compared to less than 1%). The GCMS measurement at the surface is within the range of INMS values but outside of the average and standard deviation.

# 3.2. Trends in the ${}^{12}C/{}^{13}C$ Altitude Profiles

When each model was fit to the data, the lower boundary ratio for each INMS  ${}^{12}C/{}^{13}C$  data point was calculated based on the modeled enrichment of the isotopes between the lower boundary and the altitude of the data point. These results were then binned by altitude to look for potential systematic trends in the fits. Figure 5 illustrates these results for Model 1 (a)

 Table 2

 Summary of Model Fit Results for Each of the 30 Titan Flybys on Which

 INMS Measured Altitude Profiles of the  ${}^{14}N/{}^{15}N$  in  $N_2$  and  ${}^{12}C/{}^{13}C$  in  $CH_4$ 

Flyby	Scale Height	Mode	11	Model 2	
	Temperature (K)	Homopause (km)	<sup>12</sup> C/ <sup>13</sup> C	Homopause (km)	<sup>12</sup> C/ <sup>13</sup> C
Т5	154.8	849	87.8	930	88.1
T16	135.0	973	87.9	970	88.0
T18	133.0	979	90.6	960	89.1
T19	138.3	942	90.5	950	89.9
T21	153.0	961	90.6	960	90.0
T23	144.7	1019	90.3	1000	88.5
T25	167.7	985	91.1	980	89.5
T26	139.1	1008	90.5	1000	89.0
T28	141.9	1006	88.7	1000	86.8
T29	154.0	957	88.5	970	88.9
T30	157.3	917	88.0	920	87.6
T32	131.0	961	89.6	960	89.2
T36	195.4	917	90.2	920	90.1
T39	117.4	1060	91.2	1040	91.2
T40	142.8	1025	91.2	1020	89.4
T41	111.2	983	89.5	990	88.7
T42	152.2	928	87.1	930	86.8
T43	106.6	996	89.1	1020	88.4
T48	156.4	893	85.4	880	85.2
T49	125.7	936	88.7	940	87.5
T50	127.8	980	90.7	960	89.0
T51	140.1	890	87.2	880	86.4
T55	147.0	876	87.8	870	86.6
T56	127.0	911	87.5	930	87.6
T57	141.8	901	89.4	900	88.6
T58	141.5	922	88.9	900	87.5
T59	139.0	950	89.6	960	88.8
T61	109.8	977	93.1	970	91.0
T64	117.6	946	91.6	900	89.3
T65	152.4	877	87.2	830	87.4

and Model 2 (b). The data points are the mean value for the altitude bin and the error bars represent the standard deviation of the points in the error bins. There is a clear systematic trend below 1000 km in Figure 5 that is well outside the error bars. We interpret this systematic trend as the contamination of the  ${}^{12}C/{}^{13}C$  measurements by NH<sub>3</sub>. The contamination appears seconds before closest approach in agreement with the results from the model of the antechamber discussed in Section 2.1 and illustrated in Figure 3(c). For this reason, only inbound  ${}^{12}C/{}^{13}C$  measurements above 1000 km are used for determining the  ${}^{12}C/{}^{13}C$  at the lower boundary.

# 3.3. Homopause and ${}^{12}C/{}^{13}C$ Lower Boundary

The homopause altitudes and  ${}^{12}C/{}^{13}C$  at the lower boundary (homopause for Model 1 and surface for Model 2) are listed in Table 2 for each of the 30 flybys. The average homopause altitude and standard deviation of the mean for Model 1 and Model 2 are  $932 \pm 49$  km and  $948 \pm 50$  km, respectively. This is in good agreement with the results of fitting T-GITM to the globally averaged INMS  ${}^{14}N/{}^{15}N$  altitude profiles (Bell et al. 2011). Error bars in the average homopause altitudes represent the standard deviation of the 30 flybys.

The mean and standard deviation  ${}^{12}C/{}^{13}C$  at the homopause determined in the Model 1 fits is 89.0  $\pm$  1.4. Extrapolating the  ${}^{12}C/{}^{13}C$  ratio to the surface with Model 2 gives an average and standard deviation of 88.5  $\pm$  1.4. The average ratio extrapolated



Figure 5.  ${}^{12}C/{}^{13}C$  extrapolated to the surface in the case of Model 1 (a) or the homopause in the case of Model 2 (b) for each data point measured by INMS and binned in 10 km altitude bins.

to the homopause is  $\sim 0.6\%$  lighter than the ratio extrapolated to the surface.

The INMS  ${}^{12}C/{}^{13}C$  extrapolated to the surface for 30 flybys has a normal distribution with a mean of 88.5 and a standard deviation of 1.4. The GCMS ratio of 91.1 has a  $1\sigma$  error bar of 1.4 and is within the range of the INMS distribution. It is also within  $2\sigma$  of the INMS mean value. Little is understood about how the isotopes of methane fractionate due to condensation and evaporation, but these active processes could lead to variability of the ratios on a global scale. It is possible that the GCMS measurement was made at a location with a lighter ratio than the global average. It is important to note, however, that INMS and GCMS have not been cross-calibrated, which may lead to a small difference in the resulting measurements. Calibration effects would not influence the ratio of the isotopologues, but any subtraction of contaminating species from mass channels (i.e., subtraction of CO from the GCMS mass 28 channel when deriving the  ${}^{14}N/{}^{15}N$  ratio) could cause a systematic difference between the two instrument results. However, the fact that the GCMS measurement is within  $2\sigma$  of the average value determined by extrapolating INMS to the surface suggests that cross-calibration issues between the instruments are not significant.

Updated analysis of CIRS data gives a ratio of  $86.5 \pm 7.9$  (Nixon et al. 2012). Link the GCMS value, the CIRS measured ratio is within  $2\sigma$  of the INMS mean value showing very encouraging consistency between the three instruments.

# 3.4. Sensitivity of the Fit Parameters to the <sup>14</sup>N/<sup>15</sup>N Lower Boundary

In our final stage of fitting, we parameterized the N<sub>2</sub> homopause altitude and  ${}^{12}C/{}^{13}C$  lower boundary ratio according to the assumed  ${}^{14}N/{}^{15}N$  ratio at the homopause (Model 1) or surface (Model 2). We found that the homopause altitude increases linearly with increasing  ${}^{14}N/{}^{15}N$  ratio at the surface, as illustrated in Figure 6(a).

Like the homopause altitude, the  ${}^{12}C/{}^{13}C$  extrapolated to the homopause (Model 1) or to the surface (Model 2) increases linearly with increasing  ${}^{14}N/{}^{15}N$  ratio at the surface, as shown in Figure 6(b). According to Figure 6(b), the INMS measurements, extrapolated to the surface with Model 2 suggest that the global average of the  ${}^{12}C/{}^{13}C$  on the surface is slightly heavier than



**Figure 6.** Model fit results parameterized according to the assumed  ${}^{14}N/{}^{15}N$  at the homopause (Model 1) or surface (Model 2). The GCMS measurements at the surface are shown in purple with the dashed purple lines representing the error bars on the measurements. (a) The homopause altitude derived from fitting two models to the  ${}^{14}N/{}^{15}N$  altitude profiles increases linearly as the  ${}^{14}N/{}^{15}N$  lower boundary increases. (b) The  ${}^{12}C/{}^{13}C$  at the homopause (Model 1) or surface (Model 2) also increases linearly with increasing lower boundary.

what GCMS measured, or that the global average of the  ${}^{14}N/{}^{15}N$  on the surface is slightly lighter than was measured by GCMS. A greater coverage of measurements on the surface would be required to determine the true global average of  ${}^{14}N/{}^{15}N$  and  ${}^{12}C/{}^{13}C$  on the surface.

# 4. MODELING THE EVOLUTION OF TITAN'S ATMOSPHERIC CH<sub>4</sub>

The model for the evolution of Titan's methane isotopes over geologic timescales is outlined in detail in Mandt et al. (2009). In this model, the isotopic ratios are tracked as a function of time from an initial value to the value currently measured by INMS, GCMS, and CIRS. The ratio changes over time as a result of differential-loss processes of the lighter and heavier isotopes and allows the loss processes to vary as a function of time due to solar evolution or changes in methane inventories.

The isotopic ratio of the methane in Titan's interior (or the initial value prior to fractionation) is assumed to be limited to a narrow range of  $89.01^{+3.19}_{-4.24}$  based on the limitations set by measurements made in meteorites for possible primordial carbon ratios in the solar system (Alexander et al. 2007; Martins et al. 2008). The revised  ${}^{12}C/{}^{13}C$  from INMS, GCMS, and CIRS is well within the range suggested for primordial  ${}^{12}C/{}^{13}C$ , requiring one of three scenarios to be true: (1) no fractionating-loss process is taking place in Titan's atmosphere-not even escape at very low rates due to sputtering, (2) methane presence in the atmosphere is very recent, or (3) an unknown production or loss process is balancing the fractionation due to escape by preferentially removing the heavier isotope from the atmosphere. Methane is expected to escape from the atmosphere at least due to sputtering (De la Haye et al. 2007) at a small rate, so option (1) is unlikely. Option (2) is evaluated in this work to determine an upper boundary for the time over which methane has been present in the atmosphere. Option (3) requires further investigation of processes that preferentially deplete the atmosphere of the heavier isotope, some of which will be discussed in Section 6.

Two loss processes are identified in our model for the evolution of the isotopes—photochemistry and escape. Escape depletes the atmosphere of the lighter isotope. Photochemistry was assumed in Mandt et al. (2009) to also deplete the atmospheric  ${}^{12}C/{}^{13}C$  in the lighter isotope, but this fractionation needs to be re-evaluated and is discussed below based on the results of Nixon et al. (2012).

Production of methane due to cryovolcanic activity introducing methane with an isotopic ratio equal to the initial, unfractionated ratio into the atmosphere from the interior is allowed in our model, and is assumed to be constant over the entire time period of fractionation. Time evolution of the production rate requires a better understanding of the evolution of Titan's interior and is left for future work. The model outputs are parameterized by production rates that range between no production and the maximum possible production rate in order to determine upper and lower boundaries for the model outputs based on production rates. The maximum possible production rate represents the rate at which resupply cancels out any fractionation of the isotopes due to the fractionating loss processes.

The outputs of our evolution model are: (1) an upper boundary for the timescale required to fractionate the isotopes, (2) an upper boundary for the inventory of methane that has been introduced to the atmosphere from the interior, (3) a lower boundary for the D/H of the methane in the interior of Titan, and (4) an upper boundary for the production rate over which methane resupply cancels out fractionation. The timescale represents the length of time from the point where methane began outgassing from the interior. The outgassing (or production) is allowed to continue from this initial time up until the current time. According to interior modeling, this time period either began between 350 and 1400 Myr (Tobie et al. 2006) or has been ongoing since the formation of Titan (Fortes et al. 2007).

### 4.1. Modifications to the Model

Photochemical loss rates of methane in Titan's atmosphere are energy limited, meaning that the number of ultraviolet and extreme ultraviolet (UV/EUV) photons available limits the amount of CH<sub>4</sub> that is lost. Stellar evolution models for stars like the Sun show that the UV/EUV flux varies as a function of stellar age according to the following equation (Ribas et al. 2005):

$$\Phi = 29.7\tau^{-1.23},\tag{9}$$

where  $\Phi$  is the solar UV/EUV flux and  $\tau$  is the age of the Sun in Gyr. The UV/EUV flux from the Sun decreases logarithmically over time. In Mandt et al. (2009) we found a timescale for methane outgassing that was limited to less than 200 Mya. During such a limited time period, the UV/EUV flux from the Sun would have decreased by less than 6% and the loss rate would only have changed by that much as well. Since we are now looking for an upper limit for the timescale, we must consider solar evolution. Larger timescales would suggest a greater change to the photochemical loss rate as a function of time is

$$L(t) = L(t_c)(t/t_c)^{-1.23},$$
(10)

where *L* is the photochemical loss rate in cm<sup>-2</sup> s<sup>-1</sup>, *t* is time, and the subscript *c* refers to the current time (4.6 Gyr after formation of the Sun). The column density of  ${}^{12}$ CH<sub>4</sub> in Titan's atmosphere changes as a function of time according to

$$dn_1/dt = P - F_e - L(t),$$
 (11)

where *P* is production,  $F_e$  is the escape flux, and the subscript 1 refers to the lighter isotopes. The column density of <sup>13</sup>CH<sub>4</sub> and CH<sub>3</sub>D varies with time by

$$dn_2/dt = R_0(P - f_e F_e - f_p L(t)),$$
(12)

where  $f_e$  is the fractionation factor for escape and  $f_p$  is the fractionation factor for photochemical loss. These two equations are integrated as a function of time to determine the time evolution of the ratios.

### 4.2. Model Input Parameters

Several input parameters were adjusted from those used in Mandt et al. (2009) in order to evaluate the impact of the revised  $^{12}C/^{13}C$  ratios described in Section 3. Table 3 lists the model inputs and results for the evolution of  ${}^{12}C/{}^{13}C$  and D/H in CH<sub>4</sub> used in Mandt et al. (2009) versus those used in the current analysis. The most significant change between the inputs of the previous study and this evaluation are the current and initial isotopic ratios of  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>. We have found that the INMS ratios extrapolated to the surface are  $88.5 \pm 1.4$ , a value that is outside of error bars of the GCMS ratio of  $91.1 \pm 1.4$  but within the error bars of the CIRS ratio of  $86.5 \pm 7.9$ . For the current ratio we will evaluate both the GCMS and INMS values because evaluating both measurements will test the sensitivity of the model outputs to the value determined for the current ratio. However, we use the INMS ratio to obtain the upper boundary for the timescale because a heavier ratio will provide a longer timescale. Because both of these ratios are well within the range of possible primordial values, we set the initial ratio

Table 3					
Input Parameters and Results for the Evolution of ${}^{12}C/{}^{13}C$ in CH <sub>4</sub> Used in Mandt et al.	(2009, M09) and in the Revised Model				

Parameter	Туре	M	M09		Current	
		Hydrodynamic	Sputtering	Hydrodynamic	Sputtering	
Current <sup>12</sup> C/ <sup>13</sup> C in CH <sub>4</sub>	Input	$78.75 \pm 4.85$		88.5 and 91.1		
Initial ${}^{12}C/{}^{13}C$ in CH <sub>4</sub>	Input	$89.01^{+3.19}_{-4.24}$		92.2		
Diffusive fractionation factor	Input	$0.685 \pm 0.044$		0.736		
Photochemical fractionation factor $({}^{12}C/{}^{13}C)$	Input	0.961		0.996		
Photochemical fractionation factor (D/H)	Input	0.84		0.962		
Current photochemical loss rate $(cm^{-2}s^{-1})$	Input	$1.0 \times 10^{10}$		$1.0 \times 10^{10}$		
Escape rate $(cm^{-2}s^{-1})$	Input	$2.75 \times 10^{9}$	$2.8 \times 10^{7}$	$2.75 \times 10^{9}$	$2.8 \times 10^7$	
Time scale (Myr)	Output	$59.5 \pm 4.8$	$183 \pm 15$	≼470		
Total inventory	Output	$3.47\pm0.28$	$4.25\pm0.36$	± 0.36 ≤11		
Initial D/H	Output	$1.05 \times 10^{-4}$	$8.73 \times 10^{-5}$	≥9.53 ×	$10^{-5}$	

to 92.2, which is the lightest possible ratio for insoluble organic matter in meteorites. This will provide an upper boundary for the timescale over which the methane can fractionate.

In Mandt et al. (2009), the evolution of the methane isotopes was evaluated for two possible escape regimes: hydrodynamic escape in which the escape rates were close to the diffusion limited rate (Yelle et al. 2008; Strobel 2008) and sputtering in which the only loss of methane from the top of the atmosphere (i.e., escape) is due to sputtering by particles from the magnetosphere (De la Haye et al. 2007). The escape rates from these publications differ by two orders of magnitude and had a major impact on the time required to fractionate the methane isotopes. In our current study, we repeat the procedure of using two scenarios to test the sensitivity of the timescale to the escape rate, but use the sputtering rate to determine the timescale upper boundary because it will provide a longer timescale than hydrodynamic escape. A lower bound for the initial D/H in CH<sub>4</sub> is also determined by evaluating the evolution of D/H in CH<sub>4</sub> over the timescale determined by the  ${}^{12}C/{}^{13}C$  evolution for both escape scenarios.

In order to evaluate the time evolution of the isotopic ratios, the efficiency with which the two loss processes, escape and photochemistry, fractionate the isotopes must be described with a parameter called a fractionation factor, *f*. Atmospheric escape due to thermal and non-thermal processes results in a preferential loss of the lighter isotope, primarily due to diffusive fractionation of the isotopes in the upper atmosphere. This is represented by a fractionation factor that is less than 1.0. Over time, escape will cause the isotopic ratio for the bulk atmosphere to become heavier than the initial ratio. The fractionation factor for escape is determined based on the analysis of the INMS isotope ratio altitude profiles. The degree of diffusive fractionation is represented by the following fractionation factor (Mandt et al. 2009):

$$f_e = \frac{\text{Rexobase}}{R_{\text{surface}}},$$
 (13)

where  $R_{\text{exobase}}$  is the isotopic ratio (heavy/light) at the exobase and  $R_{\text{surface}}$  is the isotopic ratio at the surface. The average ratio at the surface in the Model 2 fits to the 30 Titan flybys is 88.5  $\pm$  1.4. The INMS counting statistics are too low to determine measured ratios at the exobase, but the average modeled ratio at the exobase for the 30 flybys is 120.2  $\pm$  5.3. This gives a fractionation factor of 0.736  $\pm$  0.045.

Photochemistry is the other loss process considered in the model that can lead to fractionation of the isotopes. Fractionation of the nitrogen isotopes due to photochemistry has been observed through a difference between the  ${}^{14}N/{}^{15}N$  in N<sub>2</sub>, 167.7

 $\pm$  0.6 measured by GCMS (Niemann et al. 2010) and the  ${}^{14}N/{}^{15}N$  in HCN, 56  $\pm$  8 measured by CIRS (Vinatier et al. 2007). This fractionation due to photochemistry has been explained as an isotope-selective shielding during photodissociation that allows the wavelengths that dissociate  ${}^{15}N{}^{14}N$  to penetrate deeper into the atmosphere than the wavelengths that dissociate  ${}^{14}N_2$  (Liang et al. 2007).

Measurements of the  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> by CIRS found that the ratio for the C<sub>2</sub> hydrocarbons was lighter than for CH<sub>4</sub> (Nixon et al. 2008). This difference was taken as evidence of photochemical fractionation of the  ${}^{12}C/{}^{13}C$  and a kinetic isotope effect (KIE) giving a fractionation factor of 0.961 was assumed in Mandt et al. (2009). The CIRS measurement for  ${}^{12}C/{}^{13}C$  in CH<sub>4</sub>, however, has been revised from 76.6 to 86.5 and the evidence for photochemical fractionation of  ${}^{12}C/{}^{13}C$  is no longer as clear as before.

No measurements of a KIE for  ${}^{12}C/{}^{13}C$  during photochemical reactions leading to the loss of methane have been made in the laboratory, so quantum-mechanical models are required to determine an accurate value. Methane is lost in two ways in Titan's atmosphere—photodissociation and bimolecular reactions. The photodissociation cross sections for  ${}^{13}CH_4$  and CH<sub>3</sub>D have been calculated to shift toward blue wavelengths by 0.04 and 0.9 nm, respectively (Nair et al. 2005). The minor shifts allowed no photodissociation fractionation of  ${}^{12}C/{}^{13}C$  and gave a D/H photodissociation fractionation factor of 0.995 at Mars.

The primary bimolecular reaction leading to the loss of CH<sub>4</sub> is

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3. \tag{14}$$

According to Krasnopolsky (2009), ~21% of methane loss is due to this bimolecular reaction, while ~79% of methane loss is due to photodissociation and other bimolecular and ion-molecule chemistry. This reaction was measured in laboratory studies to have a strong KIE for CD<sub>4</sub> versus CH<sub>4</sub> that becomes more effective with decreasing temperature (Opansky & Leone 1996). Nixon et al. (2012) calculated a D/H KIE for this reaction of 0.82 that is in reasonable agreement with the laboratory measurements. Their modeled <sup>12</sup>C/<sup>13</sup>C KIE for this reaction is 0.981. Weighting the fractionation factor by the methane loss percentage gives a photochemical fractionation factor of for 0.996 <sup>12</sup>C/<sup>13</sup>C and 0.958 for D/H.

### 5. RESULTS FOR THE EVOLUTION OF TITAN'S CH4

Three factors combine to control the evolution of the carbon isotope ratios in Titan's atmospheric methane: (1) the loss rate due to escape, (2) the difference between the current and the initial isotopic ratio, and (3) the rate of production or the introduction of methane to the atmosphere from the interior. We will evaluate the sensitivity of the timescale to these parameters and determine the most reasonable upper boundary for the timescale based on this evaluation. We will then discuss the implications of the timescale upper boundary for the methane inventory and the initial D/H. We also consider possible mechanisms that could extend the timescale and evaluate their probable effectiveness.

### 5.1. Sensitivity of the Timescale and Output Parameters to Input Parameters

The published escape rates differ by two orders of magnitude and represent the most significant difference to the model inputs. Decreasing the escape rate increases the timescale over which methane could have been present in the atmosphere by up to a factor of 17. The exact amount by which the timescale decreases depends on the production rate (resupply of methane due to cryovolcanic activity). When methane is assumed to be escaping hydrodynamically, production has no effect on the timescale. Increasing the production of methane in the sputtering scenario, however, will increase the timescale by as much as 25%.

The timescale is also sensitive to the amount by which the heavy isotope is enriched in the current ratio over the initial value. The INMS measurement is more enriched in the heavier isotope than the GCMS measurement, so the timescale using INMS as the current ratio is 3.3 times greater than the timescale using the GCMS ratio. The influences on the timescale described above are illustrated in Figure 7(a) where the timescale is illustrated as a function of relative production (production/total loss) for hydrodynamic (red) and sputtering (blue) escape rates with a current ratio of 91.1 (stars) and 88.5 (circles).

The maximum timescale is 470 Myr and is obtained in the scenario in which methane is escaping at a low rate (sputtering), production is ongoing at a rate that is 20% greater than the total current loss rates, and the current ratio is 88.5. This is in agreement with a surface age of 200 Myr–1 Gyr based on cratering (Lorenz et al. 2007; Neish & Lorenz 2011) and interior models suggesting the onset of outgassing between 350 and 1350 Myr ago (Tobie et al. 2006).

The initial D/H in methane must be greater than  $9.53 \times 10^{-5}$  as illustrated in Figure 7(b). Essentially, the D/H in methane in Titan's interior is between  $9.53 \times 10^{-5}$  and the current D/H in methane of  $1.59 \times 10^{-4}$  measure by CIRS (Nixon et al. 2012). The initial D/H is less than half the value of the D/H in water measured at Enceladus (Waite et al. 2009). It is reasonable to assume that the D/H in water in Titan's interior is the same as that of Enceladus based on formation scenarios for the Saturnian satellites (Mousis et al. 2009). A D/H in methane in Titan's interior rules out the possibility that the methane in Titan's interior rules out the possibility that the methane in Titan's interior formed due to serpentinization processes and instead suggests that the methane in the interior was trapped during the formation of the planetesimals that formed Titan (Mousis et al. 2009).

The upper boundary for the timescale gives an upper boundary for the total inventory of methane released from the interior of 11 times the current atmospheric and lake inventory. This inventory would not have been released as a single event, but as an ongoing process over the entire time period. No more than 2,600,000 GT of carbon would have been converted into aerosols and deposited onto the surface. Figure 7(c) illustrates the total GT carbon deposited to the surface as a function of the relative



Figure 7. Evolution model outputs parameterized either by production rate or timescale. Production is defined as methane introduced to the atmosphere from the interior due to processes such as cryovolcanism. The results are broken down into four scenarios based on variability of two input parameters: escape rate (hydrodynamic: red; sputtering: blue) and current ratio (INMS: stars; GCMS: circles). (a) Upper boundary for the length of time since the methane outgassing from the interior began (timescale) as a function of the relative production rate (total production/total loss). (b) Lower boundary for the initial D/H in methane outgassed from the interior as a function of the relative production rate (total production/total loss). The primordial D/H ratio is the purple line (Mousis et al. 2002) and the D/H measured in water in Enceladus (Waite et al. 2009) is the green line. (c) Upper boundary for the total amount of carbon deposited on the surface (in gigatons, GT, carbon) over the entire timescale as a function of relative production rate. The purple line represents the upper and lower boundaries for the surface inventory of carbon in dunes according to the Cassini RADAR observations (Lorenz et al. 2008).

production rate for the same four scenarios described above. According to an inventory of the dunes on the surface of Titan (Lorenz et al. 2008), the total GT carbon visible on the surface in the form of dunes is between 160,000 and 640,000 (represented by the purple lines in Figure 7(c)). The maximum GT carbon deposited on the surface in the hydrodynamic scenario is less than the minimum GT carbon currently observed on the surface. The upper boundary for the GT carbon deposited on the surface in the sputtering scenario, however, allows for enough carbon to be converted to aerosols and deposited onto the surface to account for the dunes currently observed on the surface and possibly to exceed what has been observed.

### 5.2. Conditions Required to Extend the Timescale

The upper limit for the timescale determined above could be extended under a couple of very strict conditions. Nixon et al. (2012) derived the conditions for a simultaneous steady state of methane supply (production = loss) and isotope ratio. In their derivation, there are strict conditions for the initial ratio of the methane source and the current ratio of the methane inventory in the atmosphere. Evolution of the loss rates over time complicates the steady-state conditions because a steady state is only stable so long as the total fractionation as determined by the fractionation factors and the photochemical and the escape loss rates remains constant. We know that over long timescales that the photochemical loss rate would vary in accordance with the evolution of the solar flux (Ribas et al. 2005), so the steadystate scenario is only stable if the escape rate and the diffusive fractionation for escape change in a manner that keeps the total fractionation constant. The probability for such strict conditions to be met for extended geologic time periods is not very likely, so a limited timescale is more probable than this scenario.

Another situation discussed in Nixon et al. (2012) that could extend the timescale would be a production rate that is large enough to counter the fractionation due to photochemistry and escape. Our model determines the production rate that is necessary to counteract fractionation for each of the scenarios discussed above and can be seen in Figure 7(a). In the sputtering scenario, the case providing the longest timescale, the production rate must be at least 20% greater than the total current loss rate using the INMS ratio as the current  ${}^{12}C/{}^{13}C$ . A production rate that is greater than the loss rates will cause the methane inventory in the atmosphere to increase over time, leading eventually to saturation of the atmosphere and rainout of the methane to form extensive lakes and seas. We do not see extensive seas today; the polar lakes and seas constitute a smaller volume of methane than what is in the atmosphere (Lorenz et al. 2008). Absent other information on the waxing and waning of methane in the atmosphere over time, the observed current inventory of methane in the atmosphere can be used to determine an upper bound for the timescale in a scenario where outgassing cancels out fractionation of the isotopes due to escape and photochemistry. Integrating Equation (11) for the methane abundance as a function of time and requiring that the atmospheric abundance of methane be its measured value at the current time, 4.6 Gyr after solar system formation, gives an upper bound to the start of the current outgassing episode of 940 Myr. This is an interesting timescale, being consistent with that for the age of the surface derived from cratering (Neish & Lorenz 2011) and for the onset for the dehydration of a possible hydrated rocky core (Castillo-Rogez & Lunine 2010), which would release warm water into Titan's mantle and possibly destabilize the crust.

Of the two alternatives discussed for extending the timescale for methane to be present in the atmosphere, one has a reasonable probability for doing so: production large enough to cancel out fractionation. In this case the upper limit for the timescale is extended to no more than 940 Myr.

## 6. ALTERNATIVE FRACTIONATING PROCESSES

GCMS, INMS, and CIRS have measured a  ${}^{12}C/{}^{13}C$  in the methane on Titan's surface that is well within the possible range

for a primordial isotopic ratio. The upper bound of the timescale over which the methane could have been present in the atmosphere has been determined, assuming that the only processes fractionating the isotopes are escape and photochemistry. The possibility exists that other processes are at work that would deplete the atmospheric methane of the lighter isotope, thus countering the effect of escape. We now consider alternative processes and scenarios that are outside the current scope of our model.

Condensation and evaporation preferentially remove the lighter isotope from the gas phase, and may have an influence on both the  ${}^{12}C/{}^{13}C$  and the D/H. On Earth, the  ${}^{16}O/$ <sup>18</sup>O and D/H in atmospheric water vapor fractionate in a temperature-dependent fashion. Cloud formation in Earth's atmosphere causes the isotopic ratios to become lighter with increasing altitude because condensation preferentially removes the heavier isotope. The altitude profiles measured by GCMS  $^{12}C/^{13}C$  show a constant ratio from 140 km to the surface. These measurements pass through the region in which methane clouds form, and show no evidence for fractionation of the carbon isotopes due to condensation, at least not within the error bars of the GCMS measurements. Evaporation preferentially releases the lighter isotope into the atmosphere, but no measurements of the ratios in the lakes of Titan or in the atmosphere directly above the lakes are available to check if evaporative fractionation is occurring.

## 7. SUMMARY

We have found that extrapolation of the INMS  ${}^{12}C/{}^{13}C$  measurements in CH<sub>4</sub> to the surface for 30 flybys provides a population of  ${}^{12}C/{}^{13}C$  surface values that are normally distributed and have a mean value and standard deviation of  $88.5 \pm 1.4$ . Both the CIRS and GCMS measurements are within the range of values measured by INMS and are within  $2\sigma$  of the mean value. Because some disagreement between the three instruments would be expected due to a lack of cross-calibration, this agreement is very encouraging.

All of the measurements are within the range of values expected for the methane that originally entered Titan's atmosphere from the moon's interior so the possible timescale during which methane could have been present in the atmosphere is limited. We determined an upper limit of no more than 470 Myr for the length of time since methane began outgassing from the interior unless the outgassing rate is large enough to counteract the fractionation of the isotopes due to escape and photochemistry. In this case, the upper boundary for the timescale can be extended to no more than 940 Myr. There is no lower limit for the timescale.

The range of possible values for the timescale is in agreement with a surface age of 200 Myr–1 Gyr based on cratering (Lorenz et al. 2007; Neish & Lorenz 2011) and interior models suggesting the onset of outgassing between 350 and 1350 Myr ago (Tobie et al. 2006).

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