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$^{12}C/^{13}C$ Ratio in Ethane on Titan and Implications for Methane's Replenishment[†]

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The $^{12}C/^{13}C$ abundance ratio in ethane in the atmosphere of Titan has been measured at 822 cm^{-1} from high spectral resolution ground-based observations. The value, 89(8), coincides with the telluric standard and also agrees with the ratio seen in the outer planets. It is almost identical to the result for ethane on Titan found by the composite infrared spectrometer (CIRS) on *Cassini*. The $^{12}C/^{13}C$ ratio for ethane is higher than the ratio measured in atmospheric methane by *Cassini*/*Huygens* GCMS, 82.3(1), representing an enrichment of ^{12}C in the ethane that might be explained by a kinetic isotope effect of approximately 1.1 in the formation of methyl radicals. If methane is being continuously resupplied to balance photochemical destruction, then we expect the isotopic composition in the ethane product to equilibrate at close to the same $^{12}C/^{13}C$ ratio as that in the supply. The telluric value of the ratio in ethane then implies that the methane reservoir is primordial.

1. Introduction

Relative abundances of isotopic variants in planetary atmospheres provide information about the processes of solar system formation. In particular, the present $^{12}C/^{13}C$ isotopic ratio seen on Titan is an end result of the origin and evolution of the atmosphere. The observed carbon isotopic ratio, together with those of nitrogen, oxygen, hydrogen, and argon, offer clues about the material from which Titan accreted and help trace the subsequent relationship among the interior, surface, and atmosphere. Ethane has the important role of being the primary destination of carbon lost in the destruction of atmospheric methane. Ethane is therefore closely related to methane in both the atmosphere and the reservoir from which it is replenished.

Cassini/*Huygens* has recently measured the $^{12}C/^{13}C$ ratio for several species on Titan using both remote infrared spectroscopy and in situ mass spectroscopy (Table 1). Most of these indicate an enrichment in ^{13}C compared with telluric. The observations made by the composite infrared spectrometer (CIRS) on *Cassini*[8] show that among the hydrocarbons ethane exhibits the smallest ^{13}C enrichment, acetylene is intermediate, and methane has the largest enrichment.[1] This led Nixon et al. to suggest that there may be a systematic variation of ^{13}C enrichment with mass in the hydrocarbons. In the present article, we suggest further that the difference in enrichment between ethane and methane is due to kinetic isotope effects (KIEs) in the chemical destruction of methane and, furthermore, that the near-telluric value for $^{12}C/^{13}C$ in ethane indicates that the methane reservoir is also close to telluric.

Ground-based observations provide a means for determining $^{12}C/^{13}C$ on Titan that compliments *Cassini*. CIRS measures the entire 12 μm band at a resolution of 0.5 cm^{-1}, whereas ground-based spectrometers observe groups of features within the band with spectral resolution better than 0.1 cm^{-1}. The ^{12}C- and ^{13}C-ethane $^{R}Q_0$ emission features at 822.30 and 821.53 cm^{-1}, when

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TABLE 1: $^{12}C/^{13}C$ on Titan: This Work Compared with *Cassini/Huygens*

species	ν (cm^{-1})	$^{12}C/^{13}C$	$\delta^{13}C$ (‰)[a]	instrument	reference
C_2H_6	822	89(8)[b]	+5(93)	Celeste	this work
C_2H_6	822	89.8(8.3)[c]	−4(93)	CIRS	1
C_2H_6	822	89.4(5.8)	+0.6(66)	average of Celeste and CIRS	
CH_4	1300	76.6(2.7)[c]	+168(41)	CIRS	1
CH_4		82.3(1.0)[d]	+87(13)	GCMS	2
CH_4		95.6(0.1)[e]	−64(1)	INMS	3
CH_3D	1148	82.0(22.5)	+91(324)	CIRS	4
C_2H_2	729	84.8(3.2)[c]	+55(40)	CIRS	1
HCN	706	75(12)[c]	+193(196)	CIRS	5
HC_3N	660	79(17)[c]	+132(256)	CIRS	6
CO_2	655	84(17)[c]	+65(225)	CIRS	7

[a] Carbon-13 enrichment from telluric: $\delta^{13}C = [89.4/(^{12}C/^{13}C) - 1] \times 1000$ in units of "per mil", or ‰. [b] Uncertainties are listed in parentheses. When plus and minus values are different, they have been averaged. [c] Averaged over latitudes in the reference. [d] At 18.2 to 6.14 km altitude. [e] At 1200 km altitude.

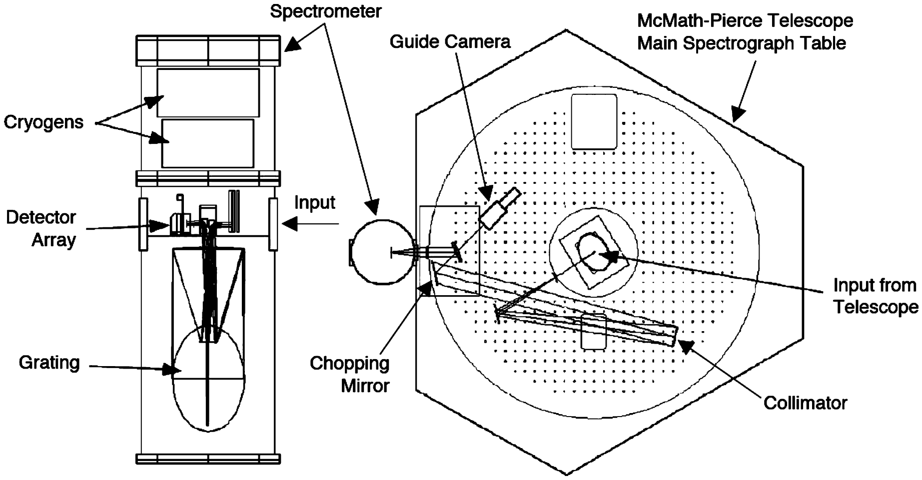

Figure 1. Optical arrangement of Celeste at the McMath−Pierce Telescope. On the right is the view from above the main spectrograph table showing the layout of the optics. The beam from the telescope enters from above the table, passes through collimating, chopping, and guide optics, and is focused into the spectrometer. The spectrometer is housed in a liquid helium dewar that is mounted on the side of the table. The drawing at the left is a side view of the spectrometer showing internal components.

fully resolved in ground-based spectra, provide a direct comparison of the radiances from the two isotopologues. High resolution improves the separation of line emission from thermal continuum and reduces the dependence on modeled line structure. Ground-based observations can be comparable in sensitivity to those of CIRS, but they typically do not resolve Titan spatially and therefore represent global averages. Because they will have been performed before, during and after *Cassini*, ground-based measurements will continue to be used to refine isotopic ratios on Titan. Previous observations of Saturn, Jupiter, and Neptune were performed with the same or similar instruments and permit direct comparisons.[9,10] We note that the first measurement of the $^{12}C/^{13}C$ on Titan was made by Orton[11] from the ground in the 12 μm band of ethane.

2. Observations

Our observations of ethane on Titan were performed with our high-resolution cryogenic grating spectrometer, Celeste,[12] at the McMath−Pierce Telescope of the National Solar Observatory[13] located at Kitt Peak. We have used this 1.5 m aperture telescope in several planetary studies, including our previous observations of isotopic ethane in Jupiter and Saturn.[10] A schematic of our optical arrangement at the telescope is shown in Figure 1. Celeste is mounted on the telescope's main spectrograph table, which moves to compensate for image rotation. Fore-optics form a pupil at a sky chopper, after which the visible portion of the light is diverted to a guide camera, and the infrared is focused through a window onto the slit inside the spectrometer dewar. The spectrometer is liquid-helium cooled. The dispersive element is an aluminum replica echelle grating measuring 18 × 34 cm^2 and ruled with 31.6 grooves per millimeter. It operates in Littrow mode over a 40−66° incident angle. The incoming beam is expanded and collimated by an internal cooled Ritchey−Chrétien telescope, which also forms the image at the focal plane. The detector is a blocked-impurity band (BIB) Si/As array with a 128 × 128 pixel format. Filters mounted in wheels are used to select the grating order to be passed to the detector. For the Titan observations at 822 cm^{-1}, the grating was used in fourth order at an angle of 50.2°. The resolving power of the spectrometer ($R = (1-3) \times 10^4$) is selected with a set of slits of various widths also installed in a wheel. For the Titan observations, a slit width of 4.1 arcsec ($\Delta\nu = 0.07$ cm^{-1}) was chosen to be sure that seeing and guiding errors did not cause signal losses. Titan's disk is about one-third of the telescope diffraction limit. The selected slit width corresponds to 4 pixels of the detector array.

The Titan observations took place on the nights of April 7−10, 2008. Data from the four observing sessions were combined for 10.25 h of total integration. Our observed spectrum is shown in Figure 2. The Celeste bandpass at 822 cm^{-1} is 2.1

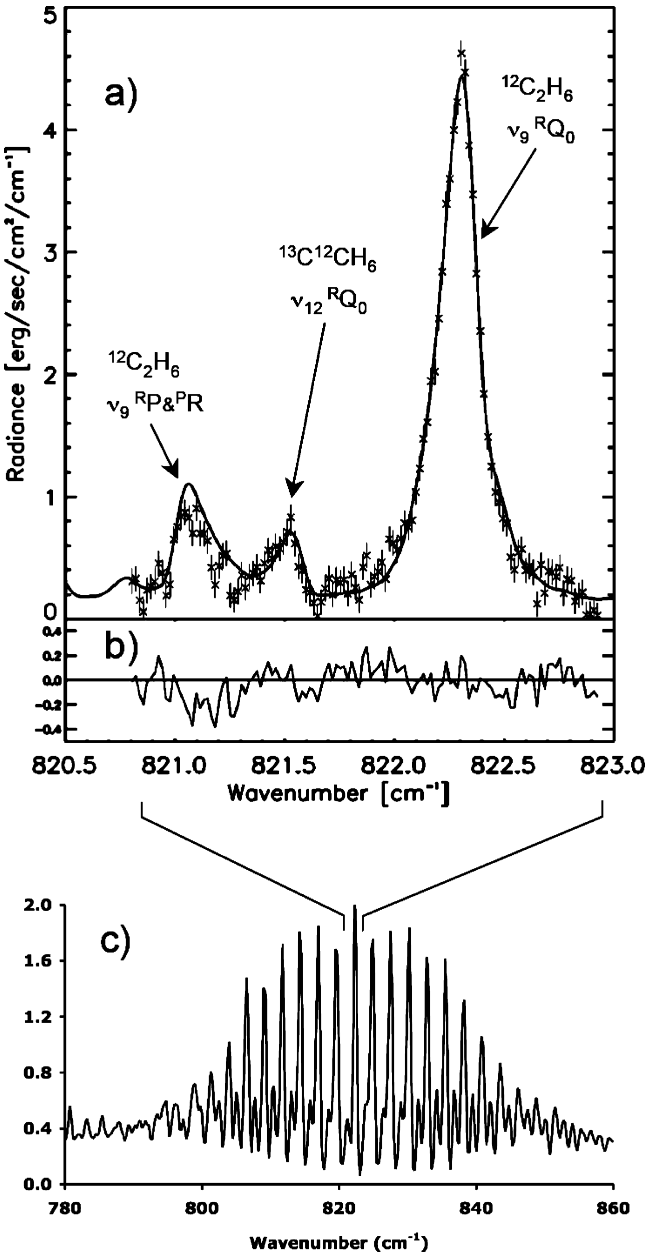

Figure 2. Spectrum of ethane emission from Titan. (a) The bandpass covers two features of $^{12}C_2H_6$ at 821.1 and 822.3 cm^{-1} and one feature of $^{13}C^{12}CH_6$ at 821.5 cm^{-1}. The radiance data are shown as asterisks with error bars (±0.103 erg/sec/cm^2/cm^{-1}), and the best-fit model is shown as a solid line. (b) The difference between the model calculation and the observed data. (c) A spectrum of the entire 12 μm band of ethane recorded by the composite infrared spectrometer (CIRS) on *Cassini* at 0.5 cm^{-1} resolution. The CIR*S* spectrum is an average over 60° S to 40° N latitude. The narrow portion covered by Celeste is indicated near the band center.

cm^{-1}. The ^RQ_o branch of $^{13}C^{12}CH_6$ at 821.5 cm^{-1} is shifted from the much stronger $^{12}C_2H_6$ ^RQ_o branch by -0.8 cm^{-1}, permitting both features to be present in the observed spectrum. In addition, a third group of lines of $^{12}C_2H_6$ corresponding to ^RP and ^PR were detected at 821.1 cm^{-1}. Sky subtraction was accomplished by chopping every 6 s and nodding between the on-source and off-source approximately once a minute. The sub-Earth latitude on Titan was 9.5 S at the time of the observations, and the sub-Earth longitude varied over the range of 69−140 W. Figure 2 also shows a disk-averaged spectrum from *Cassini* CIRS for comparison.

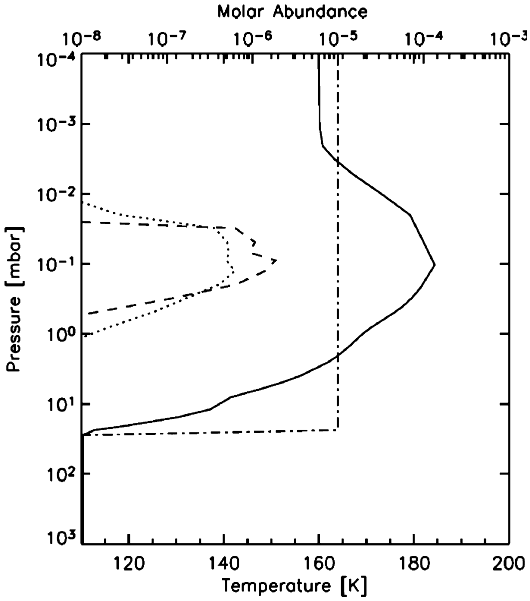

Figure 3. Model profiles for ethane in the atmosphere of Titan used in our analysis. The temperature profile, shown as a solid line, (bottom scale) is a latitude average over results from Achterberg et al.[16] The molar abundance of ethane, shown as a dotted-dashed line (top scale), is taken from Nixon et al.[1] Contribution functions for $^{12}C_2H_6$ and $^{13}C^{12}CH_6$, shown as dashed and dotted lines, respectively, have been normalized relative to each other for comparison.

3. Analysis

Because we are interested only in the relative abundances of $^{12}C_2H_6$ and $^{13}C^{12}CH_6$, we calibrated the radiance in Figure 2a by scaling the stronger $^{12}C_2H_6$ feature at 822.3 cm^{-1} to a Titan model spectrum. Our spectral synthesis modeling program is a version of that developed by Kunde and Maguire.[14] The $^{12}C_2H_6$ line positions and strengths used in the model were taken from the recent results of Vander Auwera et al.[15] The spectrum was calculated using an ethane mole fraction of 10 ppm, as determined by Nixon et al.[1] We applied a stratospheric temperature profile obtained from the results of Achterberg et al.[16] by averaging over latitudes between 40 S and 20 N. This CIRS profile was used above 10 mbar, and the *Huygens*/HASI profile[17] was used at lower altitudes. The adopted mole fraction and temperature profiles are shown in Figure 3 along with the contribution functions for the two ethane isotopologues. After adjusting the radiance scale in the observed spectrum to match the modeled 822.3 cm^{-1} line intensity, the lower stratosphere temperature was adjusted to match the observed continuum.

We then proceeded to vary the relative mole fraction of $^{13}C^{12}CH_6$ in the model to fit the observed spectrum. To model $^{13}C^{12}CH_6$, we used line positions and strengths from Weber et al.[18,19] The $^{12}C_2H_6/^{13}C^{12}CH_6$ relative line strengths were corrected according to Kurtz et al.[20] and Sada et al.[10] We included a 5% uncertainty in the laboratory line strengths, and this was also applied to the ethane results from Nixon et al.[1] We first found a $^{13}C^{12}CH_6$ mole fraction that best matched the 821.5 cm^{-1} feature by minimizing the sum of squares of the differences between the model and the observation. The error bars shown for each data point in Figure 2 were determined from statistics of the fit. We determined the uncertainty in the $^{13}C^{12}CH_6$ mole fraction by increasing and decreasing the abundance until the model coincided with the error bars. Twice the resulting $^{12}C_2H_6/^{13}C^{12}CH_6$ relative mole fraction gave the $^{12}C/^{13}C$ abundance ratio in ethane to be 89(8). The $^{12}C/^{13}C$ ratio is insensitive to small errors in the temperature profile and ethane mole fraction because emissions from both $^{12}C_2H_6$ and $^{13}C^{12}CH_6$ originate at the same altitudes.

4. Results and Discussion

Table 1 compares our $^{12}C/^{13}C$ ratio, derived from ethane, with *Cassini*/*Huygens* measurements of ethane and other molecules on Titan. The table lists the isotopic enrichment $\delta^{13}C$ of each measurement compared with the Vienna Pee Dee Belemnite[21] (VPDB) telluric reference, $[^{12}C/^{13}C]_{\text{ref}} = 89.4$. The enrichment expressed in delta notation

$$\delta^{13}C = [89.4/(^{12}C/^{13}C) - 1]1000 \qquad (1)$$

is the fractional deviation of the measured ratio from the VPDB reference ratio expressed in parts per thousand (‰; for simplicity in what follows, we drop this unit). Our ground-based ethane enrichment is virtually identical to that found for ethane by *Cassini* CIRS.[1] These two measurements (top two rows in the table) can be combined (third row in table) to improve the accuracy of the ethane determination. The combined average value is $\delta^{13}C = 0.6$ (66), where the uncertainty in parentheses is in the same units as the enrichment. The agreement with VPDB is therefore well within the uncertainty. The result is also consistent with the values reported for Saturn: $\delta^{13}C = -26(87)$ from Fletcher et al.[22] and $-97(339)$ from Sada et al.[10] It also agrees with the weighted value for the outer planets: $\delta^{13}C = 16(81)$ from Sada et al. The result is similar to reported cometary enrichments, which tend to be close to solar system values.[23]

However, the zero $\delta^{13}C$ in ethane compared with "primordial" telluric and solar system values should not be taken to mean that the carbon in Titan's ethane has not undergone fractionation. Ethane on Titan derives exclusively from atmospheric methane, and methane shows enrichment in ^{13}C. The *Huygens* gas chromatograph mass spectrometer (GCMS)[2] measured $\delta^{13}C = 87(13)$ for tropospheric CH_4 and CIRS[1] measured $\delta^{13}C = 168(41)$ for CH_4 in the stratosphere. The *Cassini* ion neutral mass spectrometer (INMS)[3] found $\delta^{13}C = -64(1)$ at 1200 km where diffusion causes fractionation, but this constitutes only a small fraction of the total atmospheric methane. Therefore, compared with the methane from which it is formed, ethane is depleted in ^{13}C by about 8%. Because ethane is the predominant product of methane dissociation, it is important to try to understand such a large difference in enrichment between the two species.

Ethane is produced from methyl radicals, which are the immediate product of methane destruction. Methyl radicals are produced from methane both by direct UV photodissociation above 700 km altitude and by catalytic dissociation involving acetylene at 200−300 km altitude.[24] At the high altitudes where 20% of the methyl is produced, molecular diffusion causes ^{13}C depletion in the methane. The average ^{13}C depletion in methane above 700 km can be estimated to be 6% with respect to methane at lower altitudes.[25] The 14% depletion measured by INMS[3] at 1200 km represents the upper region of this diffusive fractionation. Assuming that diffusion is the largest factor, the methyl produced by photolysis at these high altitudes will be depleted in ^{13}C compared with methane overall, and the ethane that comes from this methyl will therefore also be ^{13}C-depleted with respect to methane, as we observe. All products, hazes, and compounds formed from methane photolysis at these altitudes should generally exhibit ^{13}C depletion with respect to the bulk methane.

Most of the ethane, however, is created from the 80% of methyl radicals that are produced in catalysis at the altitudes where the methane is evenly mixed and no diffusive fractionation takes place. Here any depletion in ^{13}C in the CH_3 is most likely due to the KIE in the abstraction reaction by the ethynyl radical, $CCH + CH_4 \rightarrow C_2H_2 + CH_3$. The carbon KIE is defined as the ratio of the reaction rates for ^{12}C and ^{13}C, $\text{KIE} = k_{12}/k_{13}$. If this KIE is the most important factor, then the observed ^{13}C depletion in ethane compared with methane requires $\text{KIE} \approx 1.08$. We do not know of any measurements of the carbon KIE for ethynyl reacting with methane. However, the KIE for the abstraction reaction $Cl + CH_4 \rightarrow + CH_3$ can serve as an estimate.[26] Extrapolating the Cl rates to 175 K for Titan's stratosphere gives KIE = 1.08(1). In addition, KIE's have been modeled[27] for $F + CH_4 \rightarrow HF + CH_3$ down to 200 K, and these fall in the range of 1.04 to 1.16. From the large values for the KIEs in these analogous reactions, we believe that it is plausible that the KIE for ethynyl on methane is large enough to generate the observed ^{13}C depletion in ethane with respect to methane. We note that acetylene also appears to be depleted in ^{13}C with respect to methane,[1] although by a smaller amount than ethane (Table 1). Acetylene is formed from the same carbon as ethane, with additional processing, so it would not be surprising to see a similar isotope shift.

Despite the fact that Titan's ethane is not primordial and has been modified in isotopic composition by the formation process, its coincidence with the telluric and outer planet isotopic compositions may not be fortuitous. If we assume that the atmospheric methane is in a steady state, then the total carbon inventory in the material lost from the methane should have the same isotopic ratio as that of the source of methane replenishment. Because ethane comprises the predominant loss constituent, being irreversibly removed (primarily through condensation near the tropopause), the isotope ratio in the ethane should be close to that of the methane reservoir. The carbon isotopic ratios in the components are then related by

$$\left.\frac{^{12}C}{^{13}C}\right|_{\substack{\text{atmosphere}\\ \text{ethane}}} \approx \text{KIE} \cdot \left.\frac{^{12}C}{^{13}C}\right|_{\substack{\text{atmosphere}\\ \text{methane}}} \approx \left.\frac{^{12}C}{^{13}C}\right|_{\substack{\text{reservoir}\\ \text{methane}}} \qquad (2)$$

where KIE is the kinetic isotope effect in converting methane to methyl. Therefore, the observed $\delta^{13}C \approx 0$ in ethane indicates that reservoir also has zero enrichment. This is consistent with the conjecture that the reservoir is primordial; if it is composed of material accumulated during Titan's formation, then its isotopic composition should be close to that of the telluric reference and the outer planets.[28]

There are, of course, certain caveats to this simple picture. The atmospheric methane interacts with the surface through precipitation and evaporation. Some enriched methane from the atmosphere must therefore be deposited on the surface. We assume that the reservoir is very large and that its isotopic ratio is not altered by this exchange with the atmosphere. Lorenz et al. (2008)[29] find that the total liquid in lakes is a small fraction of the quantity of methane in the atmosphere and that a much larger methane reservoir is required to sustain the atmosphere over geologic time if methane photolysis has always occurred at its present rate. In our scenario, it is the $^{12}C/^{13}C$ ratio in the larger reservoir that is primordial, and one implication is that such a larger reservoir exists. The volume of the lakes is small enough that it is likely that they have been enriched to some extent along with the atmosphere.

Other processes besides the conversion of methane to methyl and ethane will cause isotope fractionation in methane and ethane. Precipitation and evaporation will deplete the atmospheric methane in ^{13}C, whereas photolysis and escape will enrich the atmospheric methane in ^{13}C. Also, ethane precipitation will deplete ^{13}C in the gaseous ethane. In stating eq 2, we assume that fractionations in these other processes are small compared with the KIE in forming methyl.

Methane has followed a different evolutionary history from that of the bulk of the atmosphere, as evidenced by the dissimilar isotopic enrichments seen in methane and nitrogen. GCMS[2] measured a high $\delta^{15}N = 486(41)$ enrichment in N_2, implying that Titan has lost a factor of 2 to 10 of its original atmosphere. In contrast, the much smaller $\delta^{13}C$ enrichment in methane seen by GCMS supports the proposal that methane, unlike nitrogen, has been replenished over geologic time.[28] In this interpretation, the atmosphere we see today consists of the remaining N_2, which retains the $\delta^{15}N$ enrichment, plus CH_4 that originated in the solar nebula, was trapped in the interior during Titan's accretion phase and has outgassed from the internal reservoir. An alternative suggestion for the source of methane replenishment has been presented by Atreya et al.[30] in which serpentinization produces methane in the interior. Our result could be consistent with this scenario provided that the carbon that becomes incorporated in the methane has a $^{12}C/^{13}C$ ratio close to that of the solar system and if little fractionation occurs in the creation of methane. Our result would not support any theory in which the carbon in the methane reservoir has undergone processing that yields substantial isotope fractionation.

The means by which interior methane is released to the atmosphere is not well understood. The evidence of cryovolcanism[31,32] points to possible episodic methane release, but this may not be the only mechanism. A more gradual release may also be taking place, and gradual release can be mimicked by a series of cryovolcanic releases over the atmospheric replacement time. Our result would be consistent with either case. Conversely, the observed isotopic ratios imply that no recent large episodic event has occurred. If we had seen a $\delta^{13}C$ in the ethane that was significantly lower than telluric, then we might reasonably interpret it as evidence of a recent large release of primordial methane. Such a release would drive down the $\delta^{13}C$ in the atmospheric methane and thus shift the ethane to lower values. As a possible corollary to this, *Cassini* might be able to search for evidence of isolated cryovolcanic activity on Titan by looking for local enhancements in $^{12}C/^{13}C$.

5. Conclusions

We conclude that the $\delta^{13}C$ enrichment in ethane with respect to methane can be explained by diffusion in the upper stratosphere together with the KIE in the formation of methyl radicals at lower altitudes. The $\delta^{13}C \approx 0$ we see in ethane implies that the methane reservoir is close to telluric. This is consistent with the conjecture that the methane reservoir is primordial.

Many details of the chemical and physical processes involved in carbon transport on Titan are not known. Evaporation, condensation, photochemistry, diffusion, and escape of both methane and ethane will all contribute to fractionation to some degree. Our assumption is that methane diffusion (at higher altitudes) and methane−ethynyl reactions (at lower altitudes) dominate other fractionation mechanisms, but this needs further study. Uncertainties in relative laboratory line strengths between ^{12}C- and ^{13}C-ethane are at about the same level as observational errors in the Titan spectroscopy, and both need to be improved. But in the case of ethane, we have reached the point where the combined uncertainties are small enough to test our understanding of the history of carbon on Titan. Carbon isotopic ratios can now constrain models of the methalogical cycle, aid in establishing whether the methane infusion has been steady or episodic, and help determine the origin of methane.

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