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On the carbon isotope ratio in Titan's atmosphere and interior

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Abstract

To study the evolution of carbon on Titan, $^{12}C/^{13}C$ = 89.7 ± 1.0 in methane should be compared to those in the precipitating haze and sputtering/ion escape. Calculations using the observed $^{12}C/^{13}C$ in the photochemical products, their column rates of condensation and polymerization from the photochemical model, and data on sputtering/ion escape result in $^{12}C/^{13}C$ = 88.5 ± 3.0 for the total loss of carbon. This loss of methane of 7 kg cm^{-2} Byr^{-1} is probably replenished by outgassing/cryovolcanism of methane clathrate hydrate CH_4*5.75H_2O with the above isotope ratio. Here we do not discuss some problems associated with this explanation.

1. Introduction

Carbon has two natural isotopes with $^{12}C/^{13}C$ = 89.4 on the Earth. Methane is the parent carbon species on Titan with mixing ratio decreasing from 5.7% near the surface to 1.5% above the tropopause at 75 km. Averaging a few measurements, the weighted-mean $^{12}C/^{13}C$ = 89.7 ± 1.0 in methane on Titan (Nixon et al. [1]). The methane lifetime is rather short on Titan, ≈30 Myr. Nixon et al. [1] compared $^{12}C/^{13}C$ in methane with that in the outer Solar System and evaluated the isotope fractionation in the loss of methane on Titan. Using data of three photochemical models, they concluded that methane was delivered into Titan's atmosphere 60-1600 Myr ago and its amount exceeded the present value by a factor 4-70. Mandt et al. [2] established an upper limit of 0.5 Byr to the outgassing timescale. Here we will use photochemical products to calculate the carbon isotope fractionation on Titan.

2. Initial data and models

$^{12}C/^{13}C$ in methane on Titan were measured using mass spectrometers at the Huygens probe [3] and the Cassini flybys [2] as well as the CIRS spectra of the CH_4 bands:

Table 1. $^{12}C/^{13}C$ in methane on Titan

$^{12}C/^{13}C$	Instrument	Reference
91.1 ± 1.4	Huygens/GCMS	Niemann et al. [3]
88.5 ± 1.4	Cassini/INMS	Mandt et al. [2]
86.5 ± 8.2	Cassini/CIRS	Nixon et al. [1]
89.7 ± 1.0	Weighted-mean	

From Nixon et al. [1].

$^{12}C/^{13}C$ in the outer Solar System are equal to

Table 2. $^{12}C/^{13}C$ in the outer Solar System

$^{12}C/^{13}C$	Species	Object	Reference
92.6 ± 4.3	CH_4	Jupiter	Niemann et al. [4]
91.8 ± 8.1	CH_4	Saturn	Fletcher et al. [5]
90 ± 4	CN	comets	Hutsemekers et al. [6]
91.3 ± 2.7	all	weighted-mean	
92.4 ± 5.4	CH_4	weighted-mean	

Budget of methane in Titan's atmosphere is given in Table 3 based on our photochemical model [7]:

Table 3. Budget of methane on Titan [7]

Loss by photolysis	2.69+9	k_{12}/k_{13} = 0
Loss by $C_2H + CH_4$	1.62+9	1.019
Other loss	5.29+9	?
Total loss	9.60+9	
Production	1.13+9	?
Flow from surface	8.47+9	
	7.09 kg cm^{-2} Byr^{-1}	
Residence time	32.4 Myr	

2.69 + 9 = 2.69×10^{9} cm^{-2} s^{-1}.

Fractionation of carbon k_{12}/k_{13} was calculated by Nair et al. [8] for photolysis of methane and by Nixon et al. [1] for the reaction $C_2H + CH_4 \rightarrow C_2H_2 + CH_3$. Nixon et al. [1] adopted no fractionation in all other processes. Their calculations are based on comparison of $^{12}C/^{13}C$ on Titan with that in the outer Solar System using the above reaction as the only fractionation process. Mandt et al. [2] analyzed 30 Cassini/INMS flybys and obtained the isotope fractionation factor of methane escape at 0.736 ± 0.045. Using the Cassini/INMS observations, De la Haye et al. [9] evaluated the total loss of carbon from Titan by sputtering and ion escape at $(2.8 \pm 2.1)\times10^{7}$ cm^{-2} s^{-1}.

3. Our model

The basic idea of our approach is to use $^{12}C/^{13}C$ measured in photochemical products of methane (Table 4) as a tool to understand the carbon isotope fractionation.

Table 4. $^{12}C/^{13}C$ in photochemical products on Titan

Species	$^{12}C/^{13}C$	Instrument		C + P[a]
CO	89.9 ± 3.4	ALMA	[10]	-
C_2H_2	84.8 ± 3.2	CIRS	[11]	3.12+8[b]
C_2H_6	89.8 ± 7.3	CIRS	[11]	2.05+9
C_4H_2	90 ± 8	CIRS	[12]	1.98+9
HCN	89.8 ± 2.8	ALMA	[13]	1.47+8
HC_3N	79 ± 17	CIRS	[14]	1.13+9
CO_2	84 ± 17	CIRS	[15]	1.78+6
All	88.3 ± 1.8	weighted-mean (uncertainties)		
All	88.3 ± 3.0	wieghted-mean		

[a] Condensation plus polymerization from table 1 and 4 in [7], in numbers of carbon atoms.
[b] 3.12+8 = 3.12×10^{8} cm^{-2} s^{-1}.

Usually the measured isotope ratios are weighted by their uncertainties, and the weighted-mean $^{12}C/^{13}C$ is 88.3 ± 1.8. However, another important factor is the contribution of each species to production of the haze by condensation and polymerization. These data are taken from the photochemical model [7]. The most significant reactions of polymerization in the model are

$C_4H_2 + C_6H \rightarrow$ polymer; CR = 1.83×10^{8} cm^{-2} s^{-1}
$C_4H_2 + C_3N \rightarrow$ polymer; 2.98×10^{8}
$C_4H + HC_3N \rightarrow$ polymer; 1.49×10^{7}

Here CR is the column rate, and we adopt that $^{12}C/^{13}C$ in C_4H and C_3N are equal to those in C_4H_2 and HC_3N, respectively. The calculated weighted-mean carbon isotope ratio is 88.3 ± 3.0 in the haze on Titan. Comparing with the isotope ratio of methane, the haze is slightly enriched in heavy carbon. This conclusion is opposite to that in [1] and agrees with the recent laboratory simulations of Titan's haze (Sebree et al. [16]).

A minor correction for sputtering and ion escape results is $^{12}C/^{13}C$ = 88.5 ± 3.0 for a source of methane that compensate for its loss. That may be outgassing and/or cryovolcanism of, say, methane clathrate hydrate CH_4*5.75H_2O. However, there are some difficulties associated with this explanation (see for example [1]).

Another scenario with injection of, e.g., ten times the present methane abundance ≈300 Myr ago and its gradual decrease by the photochemistry, results in $^{12}C/^{13}C$ = 87.1 ± 7 for the injected methane. Compared with the permanent outgassing, this scenario is less favorable in both the assumption and the result (the greater difference between the isotope ratio and that in the outer Solar System). Another scenario with a constant outgassing that started some time ago is an intermediate case. Evidently its result is intermediate as well.

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