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Isotopes in Titan's atmosphere and the history of methane

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Abstract

We present a re-analysis of the Cassini Ion Neutral Mass Spectrometer (INMS) isotope ratios based on updated sensitivity values [1] and apply a basic atmospheric model to compare the INMS measurements with the revised Huygens Gas Chromatograph Mass Spectrometer (GCMS) isotopic ratios for $^{14}N/^{15}N$ in N_2 and $^{12}C/^{13}C$ in CH_4 [2]. The revised ratios for $^{12}C/^{13}C$ in CH_4 have important implications for modeling of the evolution of methane in Titan's atmosphere [3]. We will present updated results for the evolution of Titan's methane, including: (1) upper limits for the time scale over which methane has been present in the atmosphere; and (2) lower limits for the D/H ratio in the methane in Titan's interior.

1. Introduction

Isotope ratios are a useful tracer for the processes at work in an atmosphere, and of the time history of the atmosphere. Diffusion, escape and chemical processes fractionate the isotopic ratios of N_2 and CH_4 at Titan leading over time to ratios that have evolved from their initial, primordial values. Diffusion followed by escape causes a preferential loss of the lighter isotopes. Photochemistry may cause a loss of the lighter isotopes in CH_4. A model constructed to track the isotopic ratios as a function of time found that the $^{14}N/^{15}N$ in N_2 on Titan could not have evolved from the terrestrial ratio of 272 to its current value as a result of atmospheric escape [3]. Results of the model also showed that the $^{12}C/^{13}C$ measured in CH_4 limited the length of time for methane to have consistently resided in the atmosphere to less than 200 million years.

Recent re-analysis of the Huygens GCMS data from Titan's surface [2] revised the $^{14}N/^{15}N$ in N_2 and $^{12}C/^{13}C$ in CH_4 from previously published values [4] (original and revised values are listed in Table 1). The limitation of the evolution of the nitrogen isotopes due to escape [3] is not impacted by the revised ratios. The revised $^{12}C/^{13}C$ in CH_4, however, has a significant impact on modeling the evolution of methane.

2. Methodology

2.1 Data analysis

Isotope ratios of $^{14}N/^{15}N$ in N_2 and $^{12}C/^{13}C$ in CH_4 measured by INMS were determined from the densities of $^{14}N^{15}N$, $^{14}N_2$, $^{12}CH_4$ and $^{13}CH_4$ using sensitivities that have been updated through a careful reanalysis of the INMS calibration data [1]. The revised sensitivities for $^{12}CH_4$ and $^{13}CH_4$ increase the measured $^{12}C/^{13}C$ by 7% from the measurements used in earlier modelling [3]. We fit the $^{14}N/^{15}N$ altitude profiles to a diffusion model in order to determine a homopause altitude consistent with the ratio measured in the well-mixed region by GCMS. This homopause altitude was used in a fit of the same model to the $^{12}C/^{13}C$ altitude profiles in order to determine the carbon ratio at the surface.

2.2 Evolution

The model for the evolution of Titan's atmospheric methane tracks the isotopic ratio over geologic time scales based on the loss of methane due to photochemistry and escape, the isotopic fractionation associated with these processes, and the outgassing of methane from the interior assumed to be isotopically-isolated from the surface. The above inputs, also listed in Table 1, are used to calculate the time scale required to fractionate the isotopic ratio from an initial value [5,6] to the current measurement. The time scale then provides constraints on the initial D/H in Titan's methane that, we assume, was introduced into the atmosphere from the interior. The measured $^{12}C/^{13}C$ for the previous modeling [4] was enriched in the heavy isotope beyond any possible primordial value [5,6], but the updated $^{12}C/^{13}C$ [2] is well within the primordial range. For this reason, only an upper limit on the time scale and inventory and a lower limit on the initial D/H can be determined.

Table 1: Input parameters for modeling the evolution of Titan's methane for results published in 2009 [3] and for the Current study.

Measurement or Model Parameter	2009	Current
GCMS $^{14}N/^{15}N$	183±5 [4]	167.7±0.6 [2]
GCMS $^{12}C/^{13}C$	82.3±1.0 [4]	91.1±1.4 [2]
INMS $^{12}C/^{13}C$	80 [3]	88.9±1.5
CIRS $^{12}C/^{13}C$	76.6±2.7 [7]	86±8
Initial $^{12}C/^{13}C$ in Titan's CH_4 [5,6]	$89.01^{+3.19}_{-4.24}$	≤ 92.2
Current $^{12}C/^{13}C$ in Titan's CH_4	78.8±4.9	90±3
Photochemical loss rate ($cm^{-2}s^{-1}$)	1.0×10^{10}	
Escape rate ($cm^{-2}s^{-1}$)	2.75×10^9 [8] 2.8×10^7 [9]	

Escape rates in the current literature differ by two orders of magnitude, so two scenarios are evaluated for the evolution of methane: (1) hydrodynamic escape [7] and (2) sputtering [8]. Photochemical loss rates in the literature vary only within a factor of two, and we use a mean value between the two extremes. The rate of outgassing of methane to the atmosphere is unknown, so model outputs are parameterized by ongoing production rates ranging from 0 to a value that matches the total loss rate.

3. Results

The comparison of models with data from GCMS and INMS found that the homopause must be around 950 km and that the $^{12}C/^{13}C$ in CH_4 extrapolated from INMS altitudes to the surface is within the error bars of the GCMS ratio. In the evolution model a value of 90 was used for the current $^{12}C/^{13}C$.

The escape rate of methane plays the greatest role in the evolution of methane. The upper limit for the time scale in the hydrodynamic scenario is less than 50 million years. In the sputtering scenario, the upper limit for the time scale is between 500 and 1500 million years, depending on the production rate. Production of methane, or ongoing resupply of methane from the interior, increases the time scale with increasing production rates. The lower boundary for the initial D/H in methane is 1.2×10^{-4} for the hydrodynamic scenario and $2.5\text{-}5.0 \times 10^{-5}$ in the sputtering scenario.

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