

The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe

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Saturn's largest moon, Titan, remains an enigma, explored only by remote sensing from Earth, and by the Voyager and Cassini spacecraft. The most puzzling aspects include the origin of the molecular nitrogen and methane in its atmosphere, and the mechanism(s) by which methane is maintained in the face of rapid destruction by photolysis. The Huygens probe, launched from the Cassini spacecraft, has made the first direct observations of the satellite's surface and lower atmosphere. Here we report direct atmospheric measurements from the Gas Chromatograph Mass Spectrometer (GCMS), including altitude profiles of the constituents, isotopic ratios and trace species (including organic compounds). The primary constituents were confirmed to be nitrogen and methane. Noble gases other than argon were not detected. The argon includes primordial ³⁶Ar, and the radiogenic isotope ⁴⁰Ar, providing an important constraint on the outgassing history of Titan. Trace organic species, including cyanogen and ethane, were found in surface measurements.

Determining the composition of the atmosphere of Titan and the nature of the aerosols making up the surface-hiding haze layers are two of the primary objectives of the Cassini-Huygens mission. Whereas nitrogen (N₂) and methane (CH₄) were well established as the major atmospheric constituents after the Voyager I encounter¹, the vertical distribution of methane, the isotopic ratio of N in N₂ and the abundances and isotope ratios of noble gases, including radiogenic ⁴⁰Ar, were not measured by the Voyager remote-sensing observations. Similarly, photochemically produced trace gases in the upper atmosphere had been identified by the Voyager Infrared Radiometer and Spectrometer (IRIS)², but the fate of these constituents remained obscure. To what extent did they form more complex molecules, for example, before condensing and precipitating on the surface?

The Gas Chromatograph Mass Spectrometer (GCMS)³ on the Huygens probe was designed to help answer these and other questions concerning the atmosphere of Titan, to measure isotope abundances, and to attempt to analyse condensed phases (including isotope ratios) on the surface.

The GCMS composition and isotopic measurements provide important constraints on models of the formation of Titan and its atmosphere in particular, and on theories of the protosolar nebula and the origin and evolution of planetary systems and atmospheres in general. It is thought that planetary atmospheres are generated in two principal ways: by accretion of a portion of the solar nebula, or by impact of gas-rich planetesimals. A variation on the theme of solar nebula accretion is a subnebula in the region surrounding a giant planet such as Saturn. The giant planets seem to be an example of a

blend of solar nebula accretion and degassing from planetesimals, because Jupiter has a proportional endowment of heavy noble gases and other heavy elements (relative to hydrogen) that is greater than existed in the solar nebula. The rarity of noble gases in the atmosphere of Earth has long been viewed as strong support for a planetesimal influx, and the near absence of noble gases from Titan, as we will discuss later, provides more support for this hypothesis. Except for ³⁶Ar, heavy primordial noble gases were not detected by the GCMS instrument, yielding an upper limit for ³⁸Ar, krypton and xenon below mole fractions of 10⁻⁸. The mole fraction of ³⁶Ar is $(2.8 \pm 0.3) \times 10^{-7}$. This value will become more precise with further work.

The photochemistry of nitrogen and methane leads to the formation of complex hydrocarbons and nitriles. Methane is also key to the maintenance of the thick nitrogen atmosphere. The nitrogen atmosphere would gradually condense in the absence of warming resulting from the hydrocarbon haze and the H₂-N₂ and CH₄-N₂ collision-induced opacity in the infrared⁴. The height dependence of the methane abundance in the well-mixed atmosphere could not be determined until the Huygens probe measurements were carried out. Results of the data analysis show that the mole fraction of methane is 1.41×10^{-2} in the stratosphere, increasing below the tropopause, levelling off at 4.9×10^{-2} near the surface. The uncertainty in these methane measurements is $\pm 5\%$. Rapid increase of the methane signal after landing suggests that liquid methane exists on the surface, together with several species of higher molecular weight. GCMS isotopic measurements of carbon, nitrogen, hydrogen and argon further help to constrain atmospheric evolution and composition

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models. The isotopic ratio of $^{12}\text{C}/^{13}\text{C}$ is 82.3 ± 1 , of $^{14}\text{N}/^{15}\text{N}$ is 183 ± 5 , and of D/H is $(2.3 \pm 0.5) \times 10^{-4}$. Radiogenic ^{40}Ar was detected at a mole fraction of $(4.32 \pm 0.1) \times 10^{-5}$.

A brief description of the GCMS instrument can be found below in the Methods section. A complete description of the instrument can be found in ref. 3. Data were collected for two hours and 27 min from an altitude of 146 km to the surface. The Huygens probe and the instrument survived the surface impact, allowing data collection of gases evaporated from the surface for an additional 69 min. Here we focus on data obtained from the direct atmospheric measurements of ion source 1, which includes some results from the rare-gas cell.

Origin

The heavy primordial noble gases— $^{36,38}\text{Ar}$, Kr and Xe—have been detected and measured in meteorites, in the atmospheres of Venus and Mars, and in an over-solar abundance in Jupiter with respect to H_2 . Differing patterns of relative abundances and isotopic ratios of the gases provide insights into the origin and evolution of these objects. Hence, their measurements in the atmosphere of Titan were eagerly anticipated. Detection of these elements on Jupiter in amounts relative to C and N, essentially identical to ‘solar’ ratios⁵, confirmed conventional wisdom that the gases must have been present throughout the solar nebula, and should therefore have been incorporated in both Saturn and Titan. Thus, the following results based on the direct atmospheric data and the analysis of the rare-gas cell data were unexpected: the mole fraction of ^{36}Ar is $(2.8 \pm 0.3) \times 10^{-7}$ (Table 1), and no traces of ^{38}Ar , Kr or Xe were detected, with preliminary upper limits on the mole fraction of 10^{-8} . So even $^{36}\text{Ar}/^{14}\text{N}$ is about six orders of magnitude less than the solar ratio of 23. A sample mass spectrum from the stratosphere, averaged from altitudes of 130 to 120 km (~ 4.2 – 5.6 hPa ambient pressure), is shown in Fig. 1a. Major peaks at m/z of 28, 14 and 16, 15, 13, 12 show the presence of N_2 and CH_4 respectively. Figure 1b shows a spectrum from the rare-gas cell analysis, where the primordial noble gases other than a trace of ^{36}Ar and other heavy molecules are absent.

This result is especially interesting because of the huge, nitrogen-dominated atmosphere and because approximately 50% of the mass of Titan is in the form of water ice, known to be a potentially efficient carrier of noble gases^{6,7}. The low upper limits for noble gases may have implications for the origin of nitrogen on Titan, an issue that was one of the specific objectives of the exploration⁸ of Titan. Did the nitrogen arrive in planetesimals as N_2 or as a mixture of nitrogen compounds, presumably dominated by NH_3 ?

Considering the formation of the icy planetesimals that built Titan in the Saturn subnebula, we note that direct condensation of gases, trapping in amorphous ice, or formation of clathrate hydrates would all have the effect of capturing noble gases together with N_2 (refs 7, 9–12). Thus the low abundance of primordial noble gases implies that the nitrogen was captured as NH_3 and in other non- N_2 -bearing compounds. Subsequent photolysis¹³ in a hot proto-

atmosphere generated by the accreting Titan¹⁴ or possibly impact-driven chemistry¹⁵ of NH_3 led to the nitrogen atmosphere we have on Titan today.

The formation of clathrate hydrates in the feeding zones of the giant planets depends upon the efficiency of the trapping of volatiles by microscopic icy grains. It has been suggested that, based on the non-uniform enrichment in C, N and S in Saturn, the solar nebula at 10 AU provided conditions such that only CH_4 and Xe formed clathrates and were trapped in the planetesimals that formed Titan¹¹. The discovery of a small amount of ^{36}Ar in the atmosphere of Titan will allow this model to be refined. An alternative scenario suggests that icy planetesimals formed at temperatures sufficiently warm ($T > 75$ K) that noble gases and CH_4 simply were not captured, whereas NH_3 and CO_2 were. The presence of some CO_2 in the outer solar nebula is suggested by its detection in comets¹⁶.

This model, requiring *in situ* formation of CH_4 , can be tested by studies of the deuterium to hydrogen ratio D/H, because it implies that the D/H in methane should be the same as that in the water ice that formed Titan, allowing for any fractionation that may have occurred in producing the methane. In principle, the water-ice value could have been measured directly by the GCMS after impact, if the end of the inlet tube had been in direct contact with surface ice. Evidently this was not the case, because the GCMS did not detect any H_2O vaporized from the surface after probe impact. Most of the hydrogen it measured at $m/z = 2$ and 3 must have come from the fragmentation of CH_4 , but some contribution from the interior may

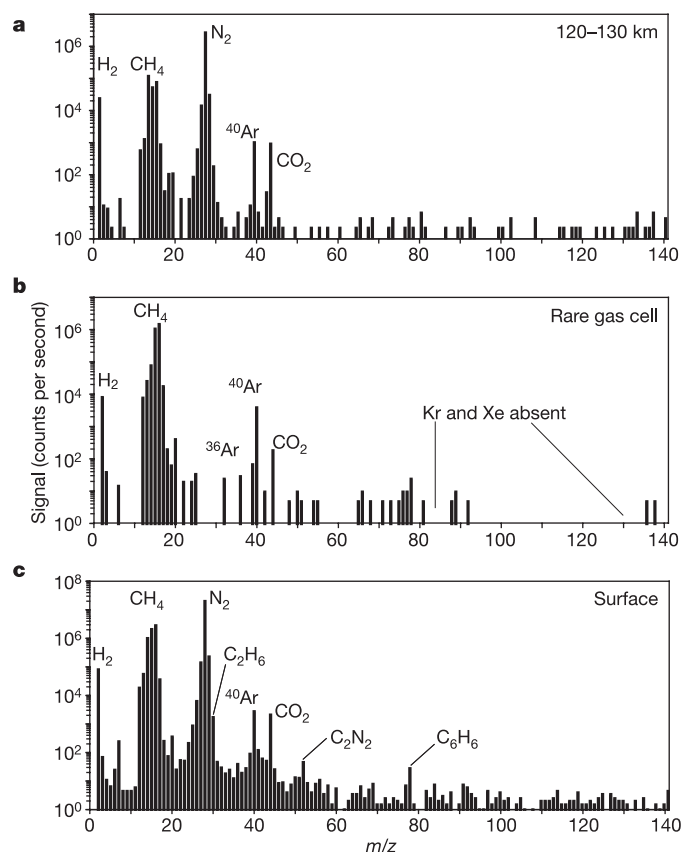


Figure 1 | Sample-averaged mass spectra, showing ion count rates per second versus mass per unit charge (m/z) from direct atmospheric sampling. **a**, An upper atmosphere spectrum from altitudes of approximately 120 to 130 km, averaging 104 mass spectra over 244 s. **b**, The rare-gas cell measurements (about 75–77 km, averaging 43 mass spectra over 81 s), showing the lack of heavy primordial noble gases. **c**, A surface spectrum, averaged over 70 min (432 mass spectra) from surface impact until loss of signal.

Table 1 | GCMS determination of given ratios

Ratio	GCMS	Altitude for GCMS calculations (km)	Titan/Earth
$^{14}\text{N}/^{15}\text{N}$	183 ± 5	40.9–35.9	0.67
$^{12}\text{C}/^{13}\text{C}$	82.3 ± 1	18.2–6.14	0.915
D/H	$(2.3 \pm 0.5) \times 10^{-4}$	124.9–66.8	1.44
$^{36}\text{Ar}/(\text{N}_2 + \text{CH}_4)$	$(2.8 \pm 0.3) \times 10^{-7}$	75–77 (rare-gas cell)	7.0×10^{-3}
$^{40}\text{Ar}/(\text{N}_2 + \text{CH}_4)$	$(4.32 \pm 0.1) \times 10^{-5}$	18 (to surface)	3.61×10^{-3}

For the GCMS values, the errors quoted represent one standard deviation. The altitudes for which the GCMS ratios were calculated were provided by the HASI instrument. The altitude ranges represent periods of least statistical error and best instrument conditions for those data. The Titan values are those measured by the Huygens GCMS (this paper). The $^{12}\text{C}/^{13}\text{C}$ for the Earth is the PDB standard inorganic value of 89.9.

also have been present. The proportions of these two sources will be investigated.

The measured value of $D/H = (2.3 \pm 0.5) \times 10^{-4}$ (Table 1) from HD/H_2 , is well within the uncertainties of the early ground-based $(1.6^{+1.6}_{-0.8}) \times 10^{-4}$ (ref. 17) and Voyager $(1.5^{+1.5}_{-1.0}) \times 10^{-4}$ (ref. 18) results obtained from observations of CH_3D and CH_4 in two different regions of the infrared spectrum of Titan. More recent remote-sensing measurements have led to apparently lower values: $(7.75 \pm 2.25) \times 10^{-5}$ with the Infrared Echelle Spectrometer (IRSHELL)¹⁹ and $(8.7^{+3.2}_{-1.9}) \times 10^{-5}$ with the Infrared Space Observatory/Short Wavelength Spectrometer (ISO/SWS)²⁰. The D/H on Titan is therefore an order of magnitude higher than the value in the solar nebula H_2 , slightly less than the 3.2×10^{-4} found in H_2O from Oort-cloud comets²¹, and very close to the Standard Mean Ocean Water (SMOW) terrestrial value of $D/H = 1.6 \times 10^{-4}$. Using this value of D/H with the new information on nitrogen isotopes and noble gas abundances will enable much-improved models for the origin and evolution of the atmosphere of Titan to be developed.

Evolution and composition

The evolutionary processes that led to the present Titan atmosphere depended greatly on the interaction of N_2 and CH_4 and their byproducts. Establishing an altitude profile of these constituents is critical to understanding these processes. Measurement of the isotopic ratios of the constituents, such as $^{12}C/^{13}C$ and $^{14}N/^{15}N$, is also necessary to understand the chemical processes that have shaped Titan over time. In addition, the measurement of ^{40}Ar assists in deciphering the interaction between interior planetary processes and the atmosphere.

Methane was measured with the GCMS by monitoring the mass peak at $m/z = 16$. Contributions of mass spectral fragments of any heavier molecules to this signal are negligible. The methane mole fraction was then computed from the counting rates at $m/z = 16$ and those at $m/z = 28$, after correcting for counter overflow at high count rates at $m/z = 28$ and accounting for instrument calibration factors. The result is shown as a function of altitude in Fig. 2. Measurement errors are not yet fully evaluated. Systematic deviations resulting from calibration errors are estimated to be less than $\pm 5\%$. Errors due to counting statistics are negligible.

In the stratosphere, methane was found to be uniformly mixed, with a mole fraction of 1.41×10^{-2} (Fig. 2). This finding agrees with the stratospheric CH_4 measurement by the Composite Infrared Spectrometer (CIRS) on the Cassini Orbiter $(1.6 \pm 0.5) \times 10^{-2}$ (ref. 22). At 32 km, the CH_4 mole fraction began to increase gradually, with a more rapid increase observed at approximately 16 km altitude, as indicated by the change in slope in the methane signal relative to the nitrogen signal in the Fig. 2 inset. The CH_4 mole

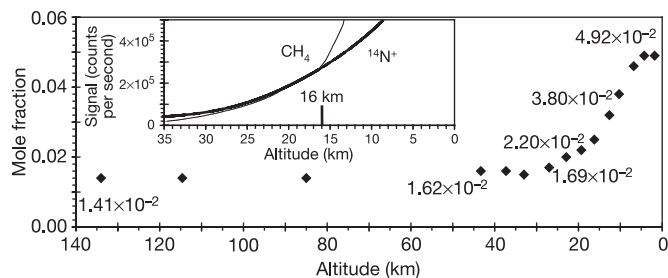


Figure 2 | The mole fraction of methane to nitrogen in the Titan atmosphere is plotted versus altitude. The CH_4 mole fraction is 1.41×10^{-2} in the stratosphere. It begins increasing below 32 km. At about 8 km, it reached a plateau of about 4.9×10^{-2} . The inset shows an increase of methane at 16 m/z , when compared to nitrogen (in this case $^{14}N^+$) at $m/z = 14$, near 16 km. This is probably due to condensates evaporating in the inlet system of the mass spectrometer as the Huygens probe passed through the methane haze.

fraction continued to rise until approximately 8 km, where it reached a value of 4.92×10^{-2} . It then remained relatively constant until the surface impact of the Huygens probe (Fig. 2). Methane was found to be subsaturated at the surface, with a relative humidity of approximately 45%. The observed behaviour of the mixing ratio—uniform up to 8 km and then declining above this altitude—appears to be a classic example in thermodynamics, indicating that methane reached its lifting condensation level, that is, near 100% relative humidity, at approximately 8 km. Indeed, the GCMS-measured CH_4 mole fraction at this level is consistent with the methane saturation values within the range of uncertainty of the Huygens Atmospheric Structure Instrument (HASI)-derived temperatures.

Therefore some haze formation is expected to take place at 8 km. The concentration of haze would probably be low due to eventual fall-out from the atmosphere, and it could escape detection by other means. The methane condensate appears to extend to an altitude of 16 km, as indicated by an increase in the gradient in the CH_4 mole fraction at 16 km. We interpret this increase as being due to the effect of evaporation of methane condensate entering the GCMS heated inlet as the probe descended through the top of the methane haze, which would slightly increase the apparent mole fraction in that region. This contribution is not easily quantitatively assessed. The liquid-binary mixture of CH_4-N_2 could potentially have a lower CH_4 vapour pressure above 'pure liquid methane'^{23,24} than that due to pure CH_4 alone. However, lack of knowledge of many factors, including the extent of pure liquid methane, concentration of N_2 dissolved in this liquid, and the presence of other impurities (many of which have already been detected by the GCMS), makes it difficult to readily ascertain the effect of the $CH_4 - N_2$ mixture on the CH_4 vapour pressure.

The isotopic ratios of $^{12}C/^{13}C$ and $^{14}N/^{15}N$ in the atmosphere were determined by analysing the GCMS measurements of methane ($^{12}CH_4$ and $^{13}CH_4$ at m/z values of 16 and 17) and molecular nitrogen ($^{14}N^{14}N$ and $^{14}N^{15}N$ at m/z values of 28 and 29). In addition, radiogenic ^{40}Ar was detected at $m/z = 40$. The isotopic ratio of $^{12}C/^{13}C$ is 82.3 ± 1 , and of $^{14}N/^{15}N$ is 183 ± 5 . Radiogenic ^{40}Ar was detected at a mole fraction of $(4.32 \pm 0.1) \times 10^{-5}$ (Table 1). The errors listed are derived from signal statistics (one standard deviation), which is the largest source of error. A detailed error analysis including systematic errors is in progress.

Ground-based observations of Titan have revealed a huge fractionation (by a factor of about four) of the nitrogen isotopes in HCN, suggesting the escape of a massive early atmosphere^{25,26}. In contrast, for reasons that are not yet clear, $^{12}C/^{13}C$ in HCN was measured from Earth to lie in the range 70 to 120, embracing the terrestrial ratio²⁷. The GCMS did not measure isotope ratios in HCN on Titan, but it was found from the GCMS measurements that in N_2 the depletion of ^{14}N is much less, leading to a value of $^{14}N/^{15}N$ only 1.5 times less than the terrestrial value. Apparently photochemistry is strongly enriching the heavy isotope of nitrogen in HCN. As the terrestrial value appears to represent the value in nitrogen compounds, especially NH_3 , in the solar nebula²⁸, it seems the right standard to use for comparison with Titan.

With this assumption, calculations using the ground-based HCN-derived $^{14}N/^{15}N$ ratio of four times less than the terrestrial value predicted a primitive atmosphere between 20 and 100 times more massive than today²⁶. Using 1.5 (from the GCMS-measured value in the major nitrogen reservoir, N_2) instead of four leads to an estimate for the mass of the primitive atmosphere of between two and ten times today's value. Therefore, it is estimated that perhaps several times the present mass of the atmosphere was lost over geologic time²⁶. The ratio of $C^{18}O/C^{16}O$ is approximately two times greater than the terrestrial value as inferred from ground-based millimetre measurements²⁹. Modelling has been carried out of the evolution of heavy isotopic isomers of CO (ref. 30), with the constraint to obtain a telluric $^{12}C/^{13}C$ today, and to reproduce the observed $C^{18}O/C^{16}O$ ratio. The conclusion was that the depletion by a factor of 2 ± 0.5 in

$^{18}\text{O}/^{16}\text{O}$ was roughly consistent with a depletion by a factor of 1.5 in $^{15}\text{N}/^{14}\text{N}$, but clearly more work on this problem is needed. In contrast, the GCMS-measured value for $^{12}\text{C}/^{13}\text{C}$ is only slightly smaller than the terrestrial value.

Because photochemistry destroys methane irreversibly on Titan³¹, so that its lifetime in the atmosphere is only 10–100 Myr (refs 32, 33), and because the carbon in CH_4 does not show the same kind of isotopic fractionation as the nitrogen and oxygen isotopes do, methane must be continually or periodically replenished on Titan. Models for atmospheric escape on Titan need to address the cause of the slight depletion of ^{12}C .

The value of $^{12}\text{C}/^{13}\text{C}$ in methane provides no support for suggestions of an active biota on Titan. It takes less energy to form a chemical bond between two ^{12}C atoms than between ^{12}C and ^{13}C , so complex organic molecules associated with biological processes on earth show an enrichment in ^{12}C —the $^{12}\text{C}/^{13}\text{C}$ ratio is greater than the Pee Dee Belemnite (PDB) inorganic standard value of 89.9, and could be as high as 95. Therefore the assumption that such enrichment will occur in carbon-based non-terrestrial biology seems reasonable.

We do not find this enrichment in the methane of Titan. Instead, a geological source for methane, with a possible clathrate reservoir as storage in the interior of Titan is favoured. As occurs on Earth^{34–36}, serpentinization that releases hydrogen from water while oxidizing iron- or magnesium-bearing minerals could produce methane through a Fischer–Tropsch reaction of the H_2 with CO_2 (ref. 37), or reduction of carbon grains in the crustal rocks in the interior.

Alternatively, methane may have been captured from the subnebula in the form of clathrate hydrates^{25,38,39} that now float on a plausible subcrustal ammonia–water ocean (G. Tobie, personal communication)⁹. If the total carbon inventory of Titan exhibits the same ratio to nitrogen of about 20 as is found on Earth, Venus and Halley's comet^{10,40}, and approximately five times the present atmospheric N has been lost, and the total aerosol deposit produced in the last 4.5 billion years is $8\text{--}80\text{ kg cm}^{-2}$ (D. F. Strobel, personal communication), then only 0.8–6% of the total carbon budget has passed through the atmosphere in the last 4.5 billion years, ultimately ending up as solids or liquids on the surface of Titan. Hence, in the clathrate model, we anticipate a layer of several kilometres of methane clathrates still present on top of a plausible subcrustal ocean.

Radiogenic argon, ^{40}Ar , was detected by the GCMS below 18 km (Table 1). Above that altitude the measurement was obscured by ^{40}Ar instrument background. Radiogenic ^{40}Ar is a decay product of ^{40}K , which has a half-life of 1.28 billion years. Thus, most of the radiogenic argon on Titan has been produced over the lifetime of the Solar System and is potentially an indicator of the extent to which outgassing of volatile elements has occurred from the deep interior, where the rock (hence the potassium) should reside.

If the rocky component of the interior of Titan has the same composition as that of the Earth and has outgassed to the same extent, ^{40}Ar should be about ten times more abundant than

measured, comprising approximately 0.05% of the atmosphere⁴¹ (corrected for loss of nitrogen). If the interior was warm enough in the past for a liquid water or liquid water–ammonia mantle to have reached all the way to the rocky core, potassium could have leached into the liquid and the radiogenic fraction expressed as ^{40}Ar outgassed to the surface⁴². The ^{40}Ar signature from the GCMS data may thus reflect a complex multi-step process that brought first the parent element, then the argon itself, upward through liquid and solid water layers to the surface. But just the presence of the ^{40}Ar at the levels seen is a strong indication of the geological activity of Titan, and is consistent with the requirement to replace the atmospheric methane episodically as described above. The apparent evidence for cryo- (water or water–ammonia) volcanism seen in the Cassini orbiter radar images⁴³ and the Visual and Infrared Mapping Spectrometer (VIMS) observations⁴⁴ provides one possible process for release of both gases from the interior.

Surface

Although numerous heavy hydrocarbons and nitriles are expected to be produced photochemically above 500 km altitude^{33,45}, and have indeed been detected at infrared wavelengths^{18,22} and in the Cassini Ion and Neutral Mass Spectrometer (INMS) fly-bys⁴⁶, very few avoid condensation at the low temperatures of the lower stratosphere (below ~ 200 km) and the tropopause^{33,47}. Therefore it is not surprising that the GCMS measurements, which were done below 146 km, do not show the presence of many heavy molecules (Fig. 1a). On the other hand, in the measurements at the surface (Fig. 1c), there is a greater likelihood of detecting some of the heavier hydrocarbons that have precipitated out of the atmosphere.

Upon the impact of the Huygens probe, the inlet line heater also heated the areas near the inlet port, including the Titan surface in the near vicinity of the GCMS inlet, either by contact or radiation. The exact nature of the thermal contact of the GCMS inlet port with the surface material is not known, and so nor is the actual contact temperature to which the surface material was heated. The inlet line temperature at the physical position of the heater, which was monitored, stabilized at 80°C . The actual temperature distribution of the inside surfaces along the inlet line was not measured. Prior to the thermal equilibration of the inlet line, the methane count rate increased by 40% while the nitrogen count rate remained constant. This increased value for methane remained nearly constant for about 50 min, and then gradually decreased to about 25% above the pre-impact value at 69 min after impact near the end of the data transmission. The methane and nitrogen signal versus time near impact is shown in Fig. 3. Although the thermal environment at or near the inlet port of the GCMS on the surface cannot be known, we suggest that the behaviour of methane in the surface measurements indicates the presence of liquid methane mixed with the surface material. The slight decrease in CH_4 after 50 min on the surface (not shown in Fig. 3) may be due to the depletion of liquid methane in the immediate vicinity of the GCMS inlet, for example, in a wet, loosely aggregated aerosol deposit. Evaporation of methane previously condensed or trapped inside the sampling system during the descent instead of evaporation from the surface is unlikely because of the high temperature inside the sample line and the long steady rate of evaporation that was observed.

The mass spectra taken on the surface (Fig. 1c) show mass peaks characteristic of more complex molecules. Ethane was firmly identified. Cyanogen (C_2N_2), benzene, and carbon dioxide have been tentatively identified, and work is continuing to identify other constituents. Each of these is much less volatile than methane and hence would be expected to have a smaller signature, regardless of their bulk abundance on the surface.

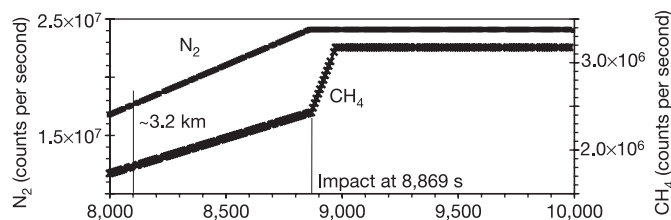


Figure 3 | Pulse count rates of nitrogen and methane are shown versus time. The methane count rate increases 2 min after impact by about 40%. This correlates with the rapid increase in temperature of the GCMS heated inlet, which heated the surface in the vicinity of the inlet port.

Future work

There is a large body of data from the GCMS that remains to be analysed in detail, including the gas chromatograph data, enrichment

cell data, and surface data. For example, heavy hydrocarbons with mole fractions less than 100 p.p.b. may yet be identified in the enrichment cell data. Collaborations with the other probe instruments will continue to provide new and refined models of the Titan atmosphere, and will improve our understanding of the history and present chemistry of both atmospheric and surface processes.

METHODS

The GCMS uses a quadrupole mass filter with a secondary electron multiplier detection system and a gas sampling system providing continuous direct atmospheric composition measurements and batch sampling through three gas chromatographic columns³. The mass spectrometer used five electron impact ion sources with available electron energies of either 70 or 25 eV. Three ion sources served as detectors for the gas chromatographic columns and two were dedicated to direct atmosphere sampling and Aerosol Collector Pyrolyser (ACP)⁴⁸ gas sampling, respectively. The multiple ion source approach allowed rapid switching between sample systems and prevented cross-contamination. The instrument was also equipped with a chemical scrubber cell for noble-gas analysis and a sample-enrichment cell for selective measurement of high-boiling-point carbon-containing constituents. The mass filter produced flat-top mass peaks that allowed rapid scanning in 5-ms steps of unit values of mass to charge (m/z) ratios over a range from 2 to 141. The nominal detection threshold was at a mixing ratio of 10^{-8} .

Pressure reduction from the ambient pressure, ~ 3 to $\sim 1,500$ hPa (~ 1.5 bar), during the probe's descent to the vacuum level of $< 10^{-4}$ hPa was achieved with micrometre-sized glass capillary arrays. A choice of two capillary arrays of different gas conductance was used for the direct atmosphere ion source to cover the wide pressure range during the descent. Gases were removed from the ion sources by conductance limited getter and sputter ion pumps. The maximum ion source operating pressure was 10^{-4} hPa and the mass filter pressure was always kept below 10^{-6} hPa. The ambient atmosphere was sampled from flow through a tube whose inlet was near the apex of the probe fairing and whose outlet was at the rear of the probe. The pressure difference created between the inlet and outlet owing to the motion of the Probe caused the atmospheric gas to flow through the tube during the descent. To prevent condensation and to cause rapid evaporation of condensates that might flow through the gas sampling system, the inlet section, upstream from the sampling area, was heated up to 80 °C, and reached temperatures that depended on gas flow rates through the inlet line.

The measurement sequence was pre-programmed. Direct atmospheric samples were taken nearly continuously during the entire descent, interrupted only when the ACP samples and the contents of the rare-gas and the sample-enrichment cells were analysed.

The sample inlet system and the mass spectrometer were sealed under vacuum until exposed to the ambient atmosphere after jettison of the probe's heat shield. The descent sequence was properly executed during the mission. However, ion source 5, serving as the detector for the N_2 -CO separation column, ceased operation owing to an electrical malfunction early in the descent. This resulted in the loss of all data from this column, and in particular the measurement of the CO height profile. Coincidentally, external perturbations affecting the Huygens probe motion were also experienced at the same time.

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