

1 **The composition of Titan's lower atmosphere and simple surface**
2 **volatiles as measured by the Cassini-Huygens probe**
3 **gas chromatograph mass spectrometer experiment.**

4 H.B.Niemann¹, S.K.Atreja², J.E.Demick³, D.Gautier⁴,
5 J.A.Haberman¹, D.N.Harpold¹, W.T. Kasprzak¹, J.I.Lunine⁵,
6 T.C.Owen⁶, F.Raulin⁷

7
8 *1. National Aeronautics and Space Administration, Mail Code 699*
9 *Greenbelt, MD 20771, USA*

10 *2. University of Michigan, Ann Arbor, MI 48109-2143, USA*

11 *3.Huntington College, Bellingrath 307A,1500 East Fairview Ave*
12 *Montgomery, AL 36106 USA*

13 *4. LESIA, Observatoire de Paris-Meudon, F-92195 Meudon Cedex, France*

14 *5.The Univesity of Rome Tor Vergata, via della Ricerca Scientifica, 1 Rome Italy 00133*

15 *6. University of Hawaii, Honolulu, HI 96822, USA*

16 *7. LISA, CNRS & Univ. Paris 12 & Paris 7, Ave General de Gaulle,*
17 *94000 Creteil, France*

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21 **Abstract**

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23 The Cassini-Huygens Probe Gas Chromatograph Mass Spectrometer (GCMS)
24 determined the composition of the Titan atmosphere from ~140km altitude to the surface.
25 After landing, it returned composition data of gases evaporated from the surface. Height
26 profiles of molecular nitrogen (N₂), methane (CH₄) and molecular hydrogen (H₂) were
27 determined. Traces were detected on the surface of evaporating methane, ethane (C₂H₆),
28 acetylene (C₂H₂), cyanogen (C₂N₂) and carbon dioxide (CO₂). The methane data showed
29 evidence that methane precipitation occurred recently. The methane mole fraction was $(1.48$
30 $\pm 0.09) \times 10^{-2}$ in the lower stratosphere (139.8 km to 75.5 km) and $(5.65 \pm 0.18) \times 10^{-2}$ near the
31 surface (6.7 km to the surface). The molecular hydrogen mole fraction was
32 $(1.01 \pm 0.16) \times 10^{-3}$ in the atmosphere and $(9.90 \pm 0.17) \times 10^{-4}$ on the surface. Isotope ratios
33 were 167.7 ± 0.6 for ¹⁴N/¹⁵N in molecular nitrogen, 91.1 ± 1.4 for ¹²C/¹³C in methane and
34 $(1.35 \pm 0.30) \times 10^{-4}$ for D/H in molecular hydrogen. The mole fractions of ³⁶Ar and radiogenic
35 ⁴⁰Ar are $(2.1 \pm 0.8) \times 10^{-7}$ and $(3.39 \pm 0.12) \times 10^{-5}$ respectively. ²²Ne has been tentatively
36 identified at a mole fraction of $(2.8 \pm 2.1) \times 10^{-7}$ Krypton and xenon were below the detection
37 threshold of 1×10^{-8} mole fraction. Science data were not retrieved from the gas
38 chromatograph subsystem as the abundance of the organic trace gases in the atmosphere and

39 on the ground did not reach the detection threshold. Results previously published from the
40 GCMS experiment are superseded by this publication.

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44 **1. Introduction**

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46 The GCMS instrument [Niemann et al., 2002] was designed to measure the
47 composition of the ambient atmosphere of Titan during the descent of the Huygens
48 Probe. Atmospheric data were received for 148 minutes beginning at an altitude of 146
49 km down to the surface. Although not designed to survive surface impact, the probe and
50 the instruments did survive the impact undamaged and returned gas composition data for
51 another 72 minutes until contact was lost with the Cassini orbiter. [Lebreton et al., 2005]
52 Preliminary results presented in [Niemann, et al., 2005] have been refined based on
53 further laboratory calibration of the spare flight unit sensor and more detailed analysis of
54 the flight data.

55 Voyager remote sensing instruments had already identified the major and several
56 minor constituents above Titan's tropopause [Kunde et al., 1981; Hanel et al., 1981;
57 Coustenis et al., 1989; Coustenis et al., 1991]. These measurements were made in the
58 stratosphere. Height profiles, isotope ratios and noble gas concentrations were not
59 retrieved from these data. Thus, the fate of the photochemically produced trace gases in
60 the upper atmosphere remained obscure. Several of the Cassini orbiter instruments, e.g.
61 the Ion and Neutral Mass Spectrometer (INMS), the Composite Infrared Spectrometer
62 (CIRS) and the Ultraviolet Imaging Spectrometer (UVIS) have provided a wealth of
63 information on the composition of organic trace gases in the stratosphere, and the upper
64 atmosphere and ionosphere, i.e. in the regions where they were first formed [Waite et al.,
65 2005, 2007; Cui et al., 2009; Magee, et al., 2009; Flasar et al., 2005; Coustenis et al.,
66 2007; Shemansky et al., 2005]

67 One of the objectives of the Huygens probe experiments was to determine the extent
68 to which the simpler trace gases can form complex molecules, condensates or aerosol
69 particles that ultimately precipitate onto the surface. N₂, CH₄, H₂, and ⁴⁰Ar were
70 measured *in-situ* in the lower atmosphere by the GCMS and altitude profiles were
71 obtained. ²²Ne and ³⁶Ar were detected in a batch sample in a noble gas enrichment cell.
72 Kr and Xe were below the detection limit of the instrument for those species and their
73 abundances are estimated to be less than 1x10⁻⁸ mole fraction.

74 Isotope ratios were determined for hydrogen from H₂ and HD, for nitrogen from
75 ¹⁴N¹⁴N and ¹⁴N¹⁵N, and for carbon from ¹²CH₄ and ¹³CH₄. These GCMS measurements
76 provide important constraints on models for the formation of Titan and its atmosphere.
77 After landing CH₄, C₂H₆, C₂H₂, C₂N₂, and CO₂ were detected as they evaporated from
78 the surface directly below the probe. Benzene (C₆H₆) may also have been evaporating but
79 its abundance was too low to be separated unambiguously from the permanent C₆H₆
80 background in the instrument.

81 The GCMS was also used to analyze the aerosol pyrolysis products from the
82 Cassini-Huygens Aerosol Collector Pyrolyser (ACP) experiment [Israel et a., 2002].
83 Results obtained from that experiment were reported and discussed separately [Israel et
84 al., 2005; Biemann, 2006; Israel et al., 2006].

85 Identification of organic trace constituents with the three-column gas chromatograph
86 subsystem (GC) was not possible because concentrations in the atmosphere were too low
87 to reach the GCMS detection threshold.

88 At the altitude of 74 km, when the probe passed through a region of extensive
89 turbulence, ion source number 5 failed. This ion source was dedicated to obtaining data
90 from a GC column specifically designed for the measurement of carbon monoxide (CO)
91 since the flight mass spectrometer was not designed to separate directly N₂ and CO
92 at m/z = 28.

94 2. Experiment Description

96 The experiment has been described in detail by Niemann et al. (2002)

97 It was designed to measure the chemical composition of the atmosphere of Titan and to
98 determine the isotope ratios of the major gaseous constituents. It was able to also detect
99 gases evaporating from the surface. The GCMS analyzed gas samples from the Aerosol
100 Collector Pyrolyser (ACP). A detailed description of the ACP instrument is given by
101 [Israel et al., 2002].

103 2.1 Instrument

104 A simplified block diagram of the instrument is shown in Figure 1. The instrument
105 [Niemann et al., 2002] consists of a gas inlet and distribution system, a system for
106 pressure reduction, a gas processing system (sample enrichment and chemical scrubber
107 cell), a three column gas chromatograph system (GC 1,2,3) and a quadrupole type mass
108 filter with a secondary electron multiplier ion detector. The interface points of the ACP
109 with the instrument are also indicated in Figure 1 The chemical scrubber cell was used to
110 facilitate interference free noble gas measurements and the sample enrichment cell was
111 intended for enriching high boiling point hydrocarbons.

112 The mass spectrometer had five electron-impact ion sources with electron energies of
113 70 eV. Lower electron energy of 25 eV was used for short periodic intervals. Three ion
114 sources served as detectors for the GC columns, one was dedicated to direct atmosphere
115 sampling, and one for analyzing the gas samples transferred from the ACP. The multiple
116 ion source approach allowed rapid electronic switching between sample systems and
117 prevented cross contamination from the multiple sample sources.

118 The gas crosstalk between ion sources was less than 1×10^{-6} . The separation was
119 achieved by pumping each ion source and the analyzer/detector regions with separate
120 sets of chemical getters and sputter ion pumps. In addition the ion lenses of the ion
121 sources were especially designed for low the gas conductance between the ionization
122 regions and the common mass analyzer region. The system is described in detail by
123 Niemann et al. (2002)

124 The mass filter produced flat top mass peaks that allowed rapid scanning with 5
125 milliseconds per data sample. Unit step values of mass to charge ratios (m/z) from 2 to
126 141 were used with occasional 0.125 interval sweeps for diagnostics. The nominal
127 detection threshold was at a mole fraction of 10^{-8} . The actual detection threshold for
128 individual species varied depending on interference from other species and chemical
129 noise in the ion sources. The three GC columns were selected to separate C₃ to C₈
130 hydrocarbons and nitriles, C₁ to C₃ hydrocarbons and, nitrogen and carbon monoxide

131 respectively. Micron sized capillary arrays were used to reduce the ambient pressure
132 during the Probe descent, ~3hPa to 150 kPa, to the required ion source pressure as well
133 as to reduce the operating pressure of the GC columns to 180 kPa. Two sets of capillary
134 arrays with different gas conductance were used in sequence for the direct atmosphere
135 ion source in order to cover the wide ambient pressure range traversed during the
136 descent. Gases were removed from the ion sources by conductance limited getter and
137 sputter ion pumps. The maximum ion source operating pressure was 1×10^{-4} hPa. The
138 pressure in the mass filter was always below 1×10^{-6} hPa.

139 The gas inlet was near the apex of the probe fairing and the outlet was at the rear of
140 the probe. The sample inlet and outlet locations on the probe body are shown in Figure 2.
141 Gas flowed through a several millimeter diameter sampling tube, driven by the dynamic
142 pressure. The dynamic pressure is the pressure differential between the stagnation
143 pressure at the tube entrance and the ambient pressure at the tube exit. A small amount of
144 the atmospheric gas was diverted from the flow line through the capillary leaks into the
145 ionization region of the ion source. To minimize surface losses of trace and chemically
146 active constituents, the capillary leaks were located so that the exit flow from the
147 capillaries could enter the ionization region with minimal surface collisions. Upstream
148 from the capillary leaks, the inlet line was heated to prevent condensation and to cause
149 rapid evaporation of condensates that might flow through the sampling line. This also
150 caused a small convective gas flow through the inlet line after landing. The mass flow
151 through the inlet line varied with altitude during the descent from several hPa cm³ per
152 minute to several hundred hPa cm³ per minute. The gas sampling system and mass
153 spectrometer were sealed before launch and maintained under ultra high vacuum until
154 jettison of the probe heat shield when the inlet and outlet seals of the sampling tube were
155 broken and the system was exposed to the ambient atmosphere of Titan.

156 Figure 3 shows the dynamic pressure, ambient pressure and descent velocity versus
157 time from sampling initiation at 147 km. The ambient pressure, mass density and the
158 descent velocity data are from the HASI experiment [Fulchignoni et al., 2005] and the
159 Descent Trajectory Working Group [Kazeminejad et al., 2007]. The dynamic pressure
160 shown in Figure 3, P_d , was not measured directly. It was computed using the familiar
161 relation, $P_d = 1/2 \rho V^2$, where ρ is the in situ mass density of the atmosphere and V is
162 the descent velocity. The abrupt change of the dynamic pressure occurred when the
163 descent velocity increased after jettison of the second parachute.

164

165 **2.2 Measurement Sequence**

166 The measurement sequence was preprogrammed. The atmosphere was sampled
167 nearly continuously during the entire descent, interrupted only when the contents of the
168 noble gas and the sample enrichment cells were analyzed and when ACP samples were
169 transferred. GC samples were collected in storage volumes in the upper atmosphere for
170 later analysis when the descent slowed and more time was available for analysis. At
171 lower altitudes, close to the surface, GC samples were injected directly from the
172 atmosphere.

173 The measurement sequences are shown in Figure 4. The change of the ambient
174 pressure and temperature are shown in panel a. The ambient pressure and temperature
175 were measured by the HASI experiment [Fulchignoni et al., 2005]. The events in ion
176 source 1 are indicated in panel b and the times when ACP samples were analyzed are

177 shown in panel c. Finally, the GC sample collection and analysis times of the batch
178 samples with ion source 3, 4 and 5 as detectors are plotted in panel d.

179 The mass spectrometer was scanned continuously in unit mass steps over the mass
180 range ($m/z = 2$ to 141) with a dwell time of 4.592 msec per step. Periodic high-resolution
181 spectra, eight steps per unit mass, were taken to verify correct mass tuning. With a small
182 time fraction allowed for settling of transients after each sample step, the period of a full
183 unit mass scan cycle was 937.5 msec. In flight, the time doubled to 1.875 sec between
184 samples because the instrument data stream was split on two quasi-redundant
185 transmission links from the Huygens probe to the Cassini orbiter and one receiver
186 channel was inadvertently not turned on.

187 The preprogrammed measurement sequence was properly executed during the
188 mission. Ion source 5, which served as a detector for the N_2 -CO separation column
189 failed to operate normally at 74 km altitude. This resulted in the loss of the data from
190 this column and the measurement of the CO concentration. A simultaneous sensitivity
191 change of ion source 1 occurred, likely related to the ion source 5 failure. The sensitivity
192 change was mass independent which is consistent with a bias potential change at one or
193 more of the ion focusing lenses. This did not affect the mole fraction and isotope data
194 since absolute ambient partial pressure measurements by the GCMS were not intended.
195 Large atmospheric turbulence affected the probe motion at the same time and it likely
196 triggered the event. The exact cause of that failure in the instrument could not be
197 determined but an examination of the housekeeping data pointed to an electrical
198 malfunction in the ion source supply circuit.

199 As indicated in Figure 4, data were collected from 146 km altitude to the surface for
200 8871 seconds (2 hours and 27 minutes). From 146 km to 65 km, only atmospheric gases
201 were analyzed directly, introduced through leak L1 into ion source 1. Direct atmosphere
202 sampling was interrupted for 6 minutes from 65 km to 56 km to analyze the contents of
203 the noble gas scrubber cell followed by the analysis of the content of the sample
204 enrichment cell. The gas samples for the scrubber and enrichment cell were collected
205 from 77 km to 75 km. Direct atmosphere sampling was resumed at 56 km altitude using
206 the second, lower conductance, leak L2 for ion source 1. The GC analysis was also
207 initiated at this time scanning ion sources 3, 4 and 5. Ion source 2 was operated for two
208 short periods for the analysis of the transferred ACP samples. The Probe and the
209 instrument survived the surface impact although this was not an objective of the mission.
210 Data were collected for an additional 70 minutes from gases evaporating from the
211 surface.

212 The ion arrival rate at the detector during each measurement step constituted the
213 primary measurement. Pulse counting rates per time sample varied from 0 to an
214 equivalent of 10^8 counts per second. Because of pulse pile up and a finite recovery time
215 of the pulse counting system after a pulse was received, a correction needed to be applied
216 to the raw count rates up to 7×10^6 counts per second. The corrected count rate was
217 derived from the expression

$$218 \quad (1) \quad [R] = [n]/(1-[n][T])$$

219 where $[R]$ is the corrected count rate and $[n]$ is the measured count rate. The value of $[T]$
220 was empirically determined as 2.8×10^{-8} sec using cruise checkout data from the
221 background argon present in the sensor at that time.

222 At pulse count rates higher than 7×10^6 counts per second the correction could no
223 longer be applied. In that case a proxy mass peak can be used such as the fractionation
224 peak of the parent mass peak, which is at a lower magnitude. This occurred only for
225 molecular nitrogen where the N^+ peak, at $m/z = 14$, with a peak height ratio of 0.0467
226 relative to the parent $m/z = 28$ peak, was used as a proxy for the $m/z = 28$ peak. This ratio
227 was determined from dead time corrected flight data when both pulse count rates were
228 sufficiently low in signal to allow the determination, (from 100 to 1000 seconds descent
229 time). The results were consistent with the laboratory calibration data.

230 Data rate limitations for the link between the Huygens probe and the Cassini orbiter
231 restricted the available data rate for the GCMS to 1770 bits per second for combined
232 science and housekeeping data. To cover the full range of available data from the
233 instrument it was necessary to compress the data. Square root data compression was
234 chosen for this purpose. Maximum resolution for low count rate science data from the
235 detector was maintained, however, by transmitting counts uncompressed from 0 to 127
236 counts per integration period (0 to 27657 counts per second).

237 Figure 5a shows sample mass spectra from the stratosphere averaged from ~ 130 to
238 120 km altitude and ~ 4 to 6 hPa ambient pressure, Figure 5b from the troposphere
239 at ~ 20 to 10 km altitude and ~ 500 to 900 hPa ambient pressure and Figure 5c from the
240 surface at 1500 hPa.

241

242 **2.3 Calibration**

243 The instrument was calibrated on a dynamic flow system where the time, ambient
244 pressure and the ambient temperature profile were simulated as expected during the
245 descent of the Huygens probe. [Niemann et al., 2002] have described details of the
246 calibration facility and the calibration process. The objective of the calibration was to
247 determine the overall system transfer characteristics for molecular species expected to be
248 in the atmosphere of Titan. The transfer function of the instrument is species dependent.
249 The transmission of the gas mixtures through the capillary leaks is pressure dependent
250 and mole fraction dependent. The ionization cross sections and, to a lesser degree the
251 conversion efficiencies of the ion detector, are species dependent. The effective pumping
252 speeds of the vacuum pumps are different for inert and reactive gases. Although the
253 vacuum pumps were conductance limited, i.e. their effective pumping speed was nearly
254 constant for the time of the descent and on the surface, the specific pump properties
255 needed to be determined. While the getters pump reactive gases only, except methane, the
256 sputter ion pumps remove all gases and hence the mole fraction in the ion source was
257 different from that of the ambient atmosphere.

258 Static calibration runs were conducted with hydrocarbon mixtures and noble gas
259 mixtures, introduced at several fixed pressure levels. Dynamic descent simulations
260 verified the system response prior to instrument delivery for flight.

261 The calibration of the flight instrument was not completed before launch. Limitation
262 of the lifetime of the chemical getters and the sputter ion pumps, which needed repeated
263 replacement during the calibration period required more time than was available before
264 launch. After Titan encounter, work continued on the flight spare unit, which was built to
265 be identical to the flight instrument. The effect of unavoidable differences between the
266 two instruments on the measurement accuracies is assumed to be small. The calibration
267 data are expressed as pressure dependent calibration factors. The dead time and

268 background corrected count rates of ions are multiplied by the calibration factors to
269 produce the mole fractions of species in the ambient atmosphere. Calibration factors are
270 pressure dependent because transmission of molecular species through the capillary leaks
271 depends on the molecular properties, mass and viscosity, and on the mole fractions. The
272 diameter and length of the capillaries needed for correct pressure reduction from the
273 ambient pressure to the ion source pressure resulted in the gas flow through the
274 capillaries to be in the transition regime between free molecular and viscous flow.

275 Calibration data were obtained for CH₄ and H₂ in N₂ using certified premixed gas
276 mixtures of 2%, 5% and 10% methane and 1% and 3% hydrogen in molecular nitrogen.
277 When normalized, the differences in the calibration results for the different mole
278 fractions were smaller than the calibration errors. Polynomials were fitted to the
279 calibration curves and were applied to the flight data. For gas species not directly
280 calibrated in either the flight unit or flight spare unit, literature ionization cross sections
281 were used relative to N₂.

282 The laboratory calibration data showed an inconsistency between the flight and the
283 flight spare instrument in the system pump down of hydrogen. This was observed during
284 the transition period from the leak L1 to the leak L2 measurement phase when ion source
285 1 was isolated from the atmosphere for 90 seconds for pump down to remove residual
286 gases from the leak L1 operating period. Different from the results for all other gases, the
287 hydrogen remained at a higher background level in the flight unit than what was observed
288 before flight and in the flight spare unit in the laboratory. The discrepancy can be
289 resolved if it is assumed that the getter pumps for ion source 1 in the flight instrument did
290 not pump hydrogen during the descent and only the sputter ion pump was effective for
291 ion source 1. This would be possible if a small hydrogen leak in the isolation valve from
292 the gas chromatograph hydrogen reservoir to the sample inlet system had developed
293 during or shortly after launch. The leak rate would have been too small (less than
294 1×10^{-6} std.cc/sec) to detect after launch, but over a time of 7 years would have gradually
295 saturated the getters of ion source one.

296 Since the gettering process for hydrogen is different from the other gases (going into
297 solution reversibly rather than chemical bonding), the hydrogen present in the getter has
298 only a small effect on the pumping speed of the getters for the other gases. The hydrogen
299 loading on the getters for the other ion sources was only small because they are
300 decoupled and the gas flow from the sample inlet system is six orders of magnitude lower
301 than the flow to the getters in ion source 1. However, the getter in the noble gas and
302 sample enrichment cells was also exposed to a higher gas flow. The possible effect on the
303 enrichment cell data is still being evaluated. The assumption is also consistent with
304 theoretical and experimental data obtained in our laboratory of the getter capacities and
305 equilibrium vapor pressure values for the getter mass and material. With that caveat the
306 hydrogen data are presented with the assumption that the hydrogen in ion source one was
307 pumped by the sputter ion pump only. The ratio of the total pumping speed, with fully
308 activated getters, to that of the sputter ion pump only was determined to be 9.02 in the
309 laboratory calibration for the flight spare instrument. The indicated H₂ mole fraction was
310 corrected by that factor. Since it can not be determined with certainty, based on the flight
311 and laboratory calibration data, that the effective pumping speed for hydrogen of the ion
312 source 1 getter in the flight instrument was exactly zero, the hydrogen mole fraction
313 presented is considered to be a the lower limit.

314 Ambient pressure data from the HASI experiment [Fulchignoni et al.,2005] and the
315 Descent Trajectory Working Group [Kazeminejad et al.,2007] were used to correlate the
316 flight data with the calibration data.

317 Simulation experiments of the interaction of the instrument sample inlet line with
318 the surface are needed for a more thorough understanding of the data obtained on the
319 surface of Titan.

320

321 3. Data

322

323 3.1 Methane

324 As already observed from the ground for methane [Kuiper, 1944] and from
325 Voyager 1 for nitrogen, [Broadfoot et al., 1981; Tyler et al., 1981], molecular nitrogen
326 (N₂) and secondarily methane (CH₄) are the major constituents of the atmosphere of
327 Titan. The GCMS measurements confirmed this and determined the mole fraction of
328 methane from 140 km altitude to the surface during the probe descent.

329 In the mass spectra received during the descent, the contributions to the mass peak
330 intensities at m/z = 28 and 16 were primarily from N₂ and CH₄ respectively.

331 Contributions from other species were negligible because their parent peak intensities
332 were much lower.

333 Calibration data were applied as described in section 2.3. At m/z = 14, the peak
334 intensity needed to be corrected for the contribution from methane fractionation in the ion
335 source, ¹²CH₂⁺. The fraction was 0.0506 of the m/z = 16 (CH₄) count rate. It was
336 determined from the noble gas scrubber cell data obtained in flight where methane was
337 the only non-noble atmospheric gas that was not removed by the chemical getters.

338 The mole fractions were computed using

339

$$340 \quad (2) \quad \text{CH}_4/(\text{N}_2+\text{CH}_4) = \frac{[16]/[28]/[cf_{16,28}]}{1 + [16]/[28]/[cf_{16,28}]}$$

341

342 or where m/z = 14 due to N₂ is used as a proxy for m/z = 28

343

$$344 \quad (3) \quad \text{CH}_4/(\text{N}_2+\text{CH}_4) = \frac{[16]/[14]/([28]/[14]_r)/[cf_{16,28}]}{1 + [16]/[14]/([28]/[14]_r)/[cf_{16,28}]}$$

345

346 where [16], [28], [14] are the actual pulse count rates at the respective mass values,
347 corrected for dead time. Residual background counts were subtracted. [cf_{16,28}] is the
348 calibration factor for the CH₄/N₂ ratio. [28]/[14]_r is the dead time corrected count ratio at
349 m/z = 28 and 14 in the range where both are valid.

350 The results are shown in Figure 6 as function of time from sequence initialization.

351 The section where the mass 14 proxy was used is marked in red. To improve the
352 statistical accuracy, data points were averaged over approximately 50 sample points also
353 shown in Figure 6. The error bars show the standard deviation. The vertical red dashed
354 line marks the time of surface impact. The variation of the mole fraction with altitude is
355 shown in Fig.7 A gradual increase in the mole fraction is noticed starting at 3000

356 seconds, about 40km above the surface, to 7500 seconds and about 7 km above the
357 surface. It then remained nearly constant until surface impact. After landing, it again
358 increased rapidly and remained nearly constant until close to the end of the data
359 transmission (Figure 6). The time averaged numerical data as shown in Figures 6 and 7
360 are tabulated in Table 1. The errors shown are one-sigma statistical errors only.
361 Additional systematic errors resulting from calibration and differences between the flight
362 instrument and the flight spare instrument are estimated to be $\pm 5\%$.

363 The increase of the mole fraction with decreasing altitude down to approximately 7
364 km is evidence for cloud formation (see section 4.1) and, after landing on the surface, of
365 evaporation of methane from the soils beneath the heated probe.
366

367 **3.2 Non - Methane Hydrocarbons and other Trace Gases**

368 Hydrocarbons of C_2 and higher order, and nitrogen containing species were not
369 reliably detected above the surface by the GCMS. Numerous heavy hydrocarbons and
370 nitriles, produced by photochemical reactions and energetic particle collisions, however,
371 were detected in situ at ionospheric altitudes above 900 km by the Cassini Ion and
372 Neutral Mass Spectrometer (INMS) [Waite et al., 2007] during Titan flybys of the
373 Cassini Orbiter and in the stratosphere remotely by the Cassini Composite Infrared
374 Spectrometer (CIRS) [Coustenis et al., 2007]. As the newly formed species descend, they
375 undergo additional chemical reactions to form more complex compounds and aerosols
376 while their parent mole fractions decrease. Ultimately, most gases condense or change to
377 aerosols as they reach the tropopause due to the decreasing temperature with decreasing
378 altitude between the stratosphere and troposphere [Wilson and Atreya, 2004].

379 When the GCMS measurements were initiated (below 146 km), only traces of C_2H_6
380 and C_2H_2 were near the detection threshold of the instrument but could not be quantified.
381 Evaporation of these materials from the surface was observed, however, after the probe
382 landed. In Figure 5c the mass spectra show more high mass peaks on the surface. Still
383 most of the count rates at higher mass values are close to the detection threshold and only
384 a few mass peaks stand out.

385 The probe came to rest on the surface in an upright position. In this position, the
386 sample inlet port of the GCMS could have been touching the surface or was inside of a
387 small cavity around the inlet port created by the settling motion. The interface geometry
388 of the inlet sample port and the surface is illustrated in the drawing shown in Figure 8.
389 The sample inlet line heated the inlet port on the surface either by conduction (direct
390 contact) or by conduction and radiation through the surrounding atmosphere. The exact
391 nature of the thermal contact of the inlet port with the surface is not known, nor is the
392 exact temperature or temperature distribution known of the surrounding surface area. It
393 can, however, be safely assumed that the temperature inside the probe and downstream in
394 the sample line was higher than the temperature of the surface and in the vicinity of the
395 capillary leak. The temperature at the entrance port of the inlet tube was not monitored.
396 On the surface, a value of 140 K was estimated from temperature modeling of the sample
397 inlet line [Lorenz et al., 2006].

398 The inlet port temperature, being higher than the ambient temperature, caused the
399 evaporation of low boiling point surface condensates followed by convective gas flow
400 through the heated sample line. In addition to methane, which showed the highest
401 evaporation rate and fastest time response, a number of other species were also

402 evaporating at different rates and with different starting times. This is shown in Figure 9.
 403 Increases in vapor concentrations after landing were identified for C₂H₆, C₂H₂ and C₂N₂,
 404 in addition to CH₄. A small increase in the C₆H₆, m/z = 78, 51 and 50 mass peaks, also
 405 occurred but it could not be identified unambiguously as originating from the surface.
 406 C₆H₆ was permanently present in the instrument as a trace background gas and the
 407 observed very small increase, which occurred before impact, could have been surface
 408 outgassing from the sampling system stimulated by the incoming atmospheric gas. The
 409 upper limit for the C₆H₆ mole fraction is 1x10⁻⁷. The list above is ordered in decreasing
 410 level of confidence of correct species identification. Pulse count rates were used from
 411 either parent and/or fractionation peaks and with application of the respective calibration
 412 factors, mole fractions were calculated. All reached quantifiable levels only after landing.
 413 The dashed vertical lines indicate the time of surface impact. The finite values above the
 414 surface seen in the figures are residuals at the detection threshold and are not valid
 415 numerical quantities. The detection threshold for C₂H₆ and C₂H₂ is relatively high with
 416 respect to the full dynamic range of the instrument because the mole fractions were
 417 derived by subtracting pulse count rates of interfering species from the total at m/z = 30
 418 and 26 respectively to obtain the plotted values. The upper limits of the mole fractions of
 419 the species in the atmospheric portions during the descent are estimated to be 1x10⁻⁵ for
 420 C₂H₆, 2x10⁻⁶ for C₂H₂ and 1x10⁻⁷ for C₂N₂.

421

422 3.3 Carbon Dioxide

423 Carbon dioxide, CO₂, is not expected to be present in any detectable abundance in
 424 the lower atmosphere of Titan. Evaporation from the surface, from CO₂ ice, is plausible
 425 and was observed from monitoring the peak intensity at m/z = 44. The m/z = 44 peak
 426 contained also contributions from a constant CO₂ background in the ion source and from
 427 propane, C₃H₈. Contributions from propane can be separated by observing the
 428 fractionation peaks of propane at m/z = 43 and 42. The CO₂ background, where
 429 measured, was constant and was subtracted. The result for CO₂ verses time is shown in
 430 Figure 9. Surface impact time is indicated in the figure by a vertical dashed line. As with
 431 the solid organic compounds on the surface the CO₂ mole fraction monotonically
 432 increases with time until the end of data transmission.

433

434 3.4 Hydrogen

435 Molecular hydrogen in the atmosphere was detected by the GCMS by observing the
 436 count rates at m/z = 2. The mole fraction was then calculated using the relation:

437

$$438 \quad (4) \quad \text{H}_2/(\text{N}_2+\text{CH}_4) = \frac{([2] - [16][cf\ 2,16])/[28]/[cf\ 2,28]}{1 + [16]/[28]/[cf\ 16,28]}$$

439

440 When the m/z = 28 counts were saturated the counts at m/z = 14 were used as proxy for
 441 mass 28 (corrected for CH₄ contributions)

442

$$443 \quad (5) \quad \text{H}_2/(\text{N}_2+\text{CH}_4) = \frac{([2] - [16][cf\ 2,16])/[14]/([28]/[14]_r)/[cf\ 2,28]}{1 + [16]/[14]/([28]/[14]_r)/[cf\ 16,28]}$$

444

445
446 where [2], [16], [28], and [29] are the pulse count rates at the respective mass values,
447 corrected for dead time, GC H₂ carrier gas crosstalk (leak L2 only) and residual ion
448 source background counts. [cf_{2,28}] is the calibration factor for the H₂/N₂ ratio at m/z = 2 to
449 m/z = 28. [cf_{16,28}] is the calibration factor for the CH₄/N₂ ratio at m/z = 16 to m/z = 28
450 and [28]/[14]_r is the dead time corrected count ratio at m/z = 28 and 14 in the range
451 where both are valid.

452 Contributions to the m/z = 2 count rate from dissociative ionized H₂⁺ ions of CH₄
453 were evaluated from laboratory calibration with CH₄ using the flight spare instrument.
454 The H₂⁺ ion fraction of the CH₄⁺ ion count rate was:

455
456 (6) $[cf_{2,16}] = [2]/[16]_{lab} = 1.05 \times 10^{-3}$

457
458 Species other than N₂ and CH₄ were not included in the mole fraction calculations. Their
459 contributions are negligible compared to other measurement errors.

460 The fixed (static) background in the ion source was determined for the leak L1
461 region before the sample inlet system was opened to the atmosphere. Fixed background
462 contributions in the leak L2 region were determined at the beginning of the leak L2
463 measurement phase when ambient hydrogen contributions were negligible. The carrier
464 gas contribution was determined by observing the increase in the m/z = 2 count rate at the
465 time when the hydrogen gas flow was started. It results from crosstalk of the hydrogen
466 pressure in the GC dedicated ion sources 3, 4 and 5 into ion source 1. The increase was of
467 the order of the residual ion source background. It does not vary with time since the
468 carrier gas pressure and hence the pressures in the GC dedicated ion sources were
469 constant. Contributions from other hydrogen carrying compounds were negligible.

470 The calibration factor [cf_{2,28}] was determined from laboratory calibration of the
471 flight spare instrument with representative gas mixtures of H₂, CH₄ and N₂. As described
472 in section 2.3 this calibration factor includes the pressure and mole fraction dependent
473 transmission through the capillary leak arrays of species with different molecular weight,
474 the ionization cross sections, the ion transmission through the mass filter and ion lens
475 system and conversion efficiency of the secondary electron multiplier ion detector. The
476 calibration factor was expressed in a closed form by fitting the laboratory calibration data
477 as function of pressure.

478 The mole fraction of hydrogen versus time from entry (all sampling points) is shown
479 in Figure 10 for the high altitude region (144 km to 66 km), leak L1, and the low altitude
480 and ground region (45 km to the ground), leak L2. Averaged data over approximately 50
481 sample points are also presented in Figure 10. The error bars shown are the standard
482 deviations. Figure 11 shows the altitude dependence of the mole fractions. On the
483 surface, the mole fraction remains constant until about 10000 seconds or 1300 seconds
484 after impact. The mole fraction then decreases gradually until the end of the mission.
485 Similar gradual decrease in mole fraction was observed also for methane. The cause is
486 not explained at this time. An instrument effect or a gradual change in the gas flow
487 through the sample inlet line because of the changes in temperature over time could be
488 contributing. The 50-point average data are tabulated in Table 2.

489
490 **3.5 Noble Gases**

491 ³⁶Ar and ²²Ne were the only non-radiogenic or “primordial” noble gases detected by
492 the instrument and only in sufficient abundance in the noble gas cell for quantitative
493 evaluation. Interference with peaks produced by organic molecules makes it impossible
494 to isolate them in the direct measurement sequence during the descent.

495 Noble gas cell data were collected during the descent from 77 km to 75 km and
496 analyzed during the descent from 64 to 61 km. Figure 12 shows the mass spectrum from
497 the noble gas cell. The function of the noble gas cell was to remove, or significantly
498 reduce, the concentration of the reactive gases in the cell that minimized the mass
499 spectral interference from these gas species, and enhanced the noble gas concentration
500 relative to molecular nitrogen. This was accomplished with a chemical getter that
501 pumped all reactive gases except methane. Mixing ratios of the noble gases with respect
502 to methane in the cell were then converted to mole fractions using the methane mole
503 fraction measured at the time when the noble gas and enrichment sample collection
504 occurred. More details on the operation of the noble gas cell can be found in Niemann et
505 al. (2002). Molecular nitrogen was only reduced in concentration. It could not be
506 removed completely from the cell. The pumping capacity of the getter is not sufficient to
507 remove all nitrogen. Carbon dioxide (CO₂), benzene (C₆H₆) and some other traces in the
508 low mass range were permanent background gases in the ion source which could not be
509 removed during the pre-flight processing. They did not originate from the cell.
510 Molecular hydrogen was not removed because of the diminished getter pumping
511 presumably due to the gas leak from the GC carrier gas reservoir as described in
512 section 2.3.

513 As in all other cases, laboratory calibration data for the instrument transmission
514 function were applied involving ionization cross sections, pulse counter dead times, gas
515 conductance of capillary leaks and effective pumping speed.

516 The ³⁶Ar mole fraction from the noble gas cell data is:

517

518 (7)
$$^{36}\text{Ar}/(\text{N}_2+\text{CH}_4) = (2.1 \pm 0.8) \times 10^{-7}$$

519 The presence of ³⁸Ar was confirmed qualitatively. The small number of pulse counts
520 collected was approximately correct for an isotope ratio for ³⁸Ar/³⁶Ar of 0.2. It also
521 provided assurance, that the mass peak at m/z = 36 was not a residual hydrocarbon peak.
522 The ³⁸Ar upper limit is $\sim 5 \times 10^{-8}$

523 The mole fraction of ²⁰Ne could not be determined at m/z = 20. Much larger peaks
524 of doubly ionized ⁴⁰Ar mask the peaks. The upper limit of the mole fraction for ²⁰Ne
525 is $\sim 4 \times 10^{-5}$.

526 The detection threshold of the isotope ²²Ne was also raised because of doubly
527 ionized CO₂ background interference at the m/z=22 peak. Although the interference peak
528 value was of the same order as the total peak count value (²²Ne⁺ and CO₂⁺⁺) it could be
529 subtracted from the total.

530 The remaining pulse count values were converted to a mole fraction of ²²Ne:

531

532 (8)
$$^{22}\text{Ne}/(\text{N}_2+\text{CH}_4) = (2.8 \pm 2.1) \times 10^{-7}$$

533

534 This result should be considered tentative because the signal level is low, close to the
535 detection threshold at m/z=22, which is also reflected in the large statistical error shown

536 Doubly ionized ^{20}Ne at $m/z = 10$ and ^{22}Ne at $m/z = 11$ were not detected. They occur in
537 an interference free region but their intensity would still be below the detection threshold
538 of the instrument.

539 CO_2 resided in the ion source as low-level permanent background gas. It is a
540 common contaminant in flight mass spectrometers and results from slow outgassing from
541 microscopic surface cracks and trapping volumes in the evacuated regions of the
542 instrument. Prolonged bake out periods, on a high vacuum pumping speed processing
543 system prior to launch, reduce it and other background gases but never do completely
544 eliminate them in the time available for processing.

545 Radiogenic ^{40}Ar was detected in the noble gas cell and directly during the descent.
546 The average mole fraction from 18 km altitude to the surface is:

547
548 (9)
$$^{40}\text{Ar}/(\text{N}_2+\text{CH}_4) = (3.35 \pm 0.25) \times 10^{-5}$$

549
550 Above 18 km altitude the direct measurement was obscured by the ^{40}Ar instrument
551 background. The mole fraction computed from the noble gas cell measurement is:

552
553 (10)
$$^{40}\text{Ar}/(\text{N}_2+\text{CH}_4) = (3.39 \pm 0.12) \times 10^{-5}$$

554
555 The mole fractions were computed from the $m/z = 40$ mass peak intensities. Laboratory
556 calibration data and corrections were applied for dead time and contributions from a
557 permanent ^{40}Ar instrument background. Contributions of hydrocarbons in the same mass
558 range, for example, C_3H_4 are negligible based on heights of the fractionation peaks.

559 Kr and Xe concentration levels were below the detection threshold of the instrument
560 as can also be seen from the mass spectrum shown in Figure 12. The upper limit is at a
561 mole fraction of 1×10^{-8} .

562 563 **3.6 Isotope Ratios for the Major Gas Constituents**

564 565 3.6.1 $^{14}\text{N}/^{15}\text{N}$ in Molecular Nitrogen

566 The isotopic ratio of nitrogen was derived from the pulse count ratio at, $m/z = 29$,
567 $^{14}\text{N}^{15}\text{N}$, and $m/z = 28$, $^{14}\text{N}_2$. The count ratios plotted versus time from entry are shown in
568 Figure 13 which also shows the count ratios plotted with $m/z = 14$, $^{14}\text{N}^+$, used as proxy
569 for $^{14}\text{N}_2$. The regions where leak L1 and leak L2 were used are shown in different colors
570 as indicated in the legend. At times later than 1500 seconds for leak L1 and later than
571 7000 seconds for leak L2 the $m/z = 28$ counts are no longer valid due to counter saturation
572 as can be seen by the slope changes. The species and molecular weight dependent gas
573 transmission through the capillary leaks was verified to be negligible for the difference of
574 one mass unit and the differential count resolution of the instrument. Corrections were
575 applied for the molecular weight depending on pumping speed of the vacuum pumps.

576 The results are listed in Table 3 from regions where the statistical fluctuations were
577 low and dead time corrections for the $m/z = 28$ peaks were also small. The average is:

578
579 (11)
$$^{14}\text{N}/^{15}\text{N} = 167.7 \pm 0.6.$$

580

581 As mentioned above, the range of usable data points during the descent was extended
582 by using dissociative ionized nitrogen $^{14}\text{N}^+$ at $m/z = 14$ as proxy for $^{14}\text{N}_2$. The
583 contributions from dissociative ionization of methane, CH_2^+ at $m/z = 14$ were subtracted.
584 The dissociation fractions were determined from flight data to be 0.0467 for N_2 and from
585 the noble gas cell data to be 0.0506 for CH_4 . The result is shown in Figure 14 where the
586 appropriately scaled pulse counts are plotted and the slope of the least square fit is the
587 isotope ratio $^{14}\text{N}/^{15}\text{N}$, after multiplication by the pumping speed ratio of $(29/28)^{0.5}$. The
588 results are 167.1 ± 3.9 for the leak L1 and 167.5 ± 2 for the leak L2 region. These
589 numbers are not listed in Table 3 and are presented only to show consistency of the data.

590 591 3.6.2 $^{12}\text{C}/^{13}\text{C}$ in Methane

592 The carbon isotopic ratio was determined from methane, the major carbon-carrying
593 molecule in the atmosphere of Titan. Data were analyzed from all regions of the
594 atmosphere, the noble gas cell and the surface. As mentioned above, methane is retained
595 in the noble gas cell and it serves as reference gas to determine noble gas mixing ratios.
596 Pulse count ratios of $m/z = 17$ to $m/z = 16$ are plotted versus time from descent initiation
597 in Figure 15, for the upper atmosphere region sampled through leak L1 and the lower
598 atmosphere region and surface through leak L2. Methane ($^{12}\text{CH}_4$) is assumed to be the
599 only significant contributor to the $m/z = 16$ counts. Contributions of fractionations from
600 higher molecular weight species at $m/z = 16$ are negligible because of the high abundance
601 of methane. The counts at $m/z = 17$ are the sum of counts from $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$. Both
602 compounds cannot be separated by the mass spectrometer but the $^{12}\text{CH}_3\text{D}$ contribution
603 can be obtained from the results for the $^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$ ratio of the CIRS experiment on
604 the Cassini orbiter. A D/H ratio of 1.32×10^{-4} [Bezdard et al., 2007] was used to compute
605 the $^{12}\text{CH}_3\text{D}$ contribution to the $m/z = 17$ counts. Fractionations from high molecular
606 weight constituents do not add noticeably to the $m/z = 17$ count because none were seen
607 by the mass spectrometer in high enough concentrations to matter. Ammonia, NH_3 either
608 from the atmosphere or as chemical background is not expected to contribute to the
609 $m/z = 17$ peak because its atmospheric mixing ratio would be too low and the detection
610 would further be impeded by surface absorption in the instrument. A permanent ammonia
611 background in the ion source has never been observed. The regions from which the
612 isotopic ratios were computed are from 127 km to 67 km altitude for leak L1, from a grab
613 sample taken at 76.5 km for leak L3 (noble gas cell) and from 23 km to the surface and
614 on the surface for leak L2. The values are listed in Table 3.

615 The average atmospheric value is $^{12}\text{CH}_4/^{13}\text{CH}_4 = 91.1 \pm 1.4$, the noble gas cell
616 value is 91.7 ± 1.5 and the value for methane evaporated from the surface is 92.0 ± 0.5 .
617 These values are approximately 10% greater than the earlier preliminary results
618 [Niemann et al., 2005].

619 620 3.6.3 Deuterium in Molecular Hydrogen

621 The D/H ratio in hydrogen in the atmosphere was determined from molecular
622 hydrogen H_2 and deuterated hydrogen HD. The D/H isotope ratio is numerically very low
623 since the H_2 abundance in the atmosphere is also small. The low pulse count rate
624 at $m/z = 3$ (DH) reduces the time during the descent when the $m/z = 3$ pulse counts were
625 sufficiently above the detection threshold to yield a valid measurement. The leak L1
626 region was generally preferred because it was free from possible interference from the

627 molecular hydrogen that was used as a carrier gas later for the gas chromatograph
628 subsystem. It was determined, however, that the carrier gas interference was small, and
629 could be subtracted. The data were averaged for all of the leak L1 regions and all of the
630 leak L2 regions. Corrections were made for instrument carried hydrogen background, not
631 associated with the H₂ carrier gas for the GC, and contributions of dissociative ionized
632 H₂⁺ and HD⁺ from methane. The methane contributions were determined from post-flight
633 laboratory calibration of the flight spare GCMS instrument. The D/H ratios are listed in
634 Table 3.

635 Although it is of interest to see a height profile of the D/H ratio, the count rates at
636 m/z = 3 were too low to derive a meaningful profile.

637

638 **3.7 Oxygen**

639 Oxygen bearing constituents e.g. H₂O and CO₂ were not in sufficient abundance in
640 the atmosphere for an oxygen concentration and oxygen isotopic ratio measurement. CO
641 could not be separated from N₂, as discussed previously. However, as is shown in
642 Figure 9 and discussed in section 3.3, CO₂ was observed on the surface.

643

644 **4. Discussion**

645 Preliminary results from the GCMS have been reported previously [Niemann et al.,
646 2005]. All the preliminary results provided in that report have changed to various degrees
647 and are now superseded by the data provided in this paper. Calibration data applied from
648 a thorough calibration of the flight spare instrument, a more accurate accounting of mass
649 peak sizes (e.g. species interference) and dead time corrections of the pulse counting
650 system and a more thorough examination and better use of the complete data set led to
651 the results reported here.

652 Molecular nitrogen is the most abundant gas in the atmosphere of Titan followed by
653 a few percent in mole fraction of methane. The total pressure on the surface is 1500 hPa.
654 This was determined by many experiments using various techniques and refinements of
655 the measurements.

656 The GCMS results contributed a detailed altitude profile of the CH₄ and H₂ mole
657 fractions in the lower atmosphere, the isotope ratios of ¹⁴N/¹⁵N in molecular nitrogen,
658 ¹²C/¹³C in methane and D/H in molecular hydrogen.

659

660 **4.1 Methane (CH₄)**

661 The current CH₄ mole fraction of 5.5×10^{-2} just above the surface is subsaturated, at
662 a relative humidity of approximately 50%. While the mixing ratio of CH₄ remains nearly
663 uniform with altitude up to approximately 7 km, its saturation vapor mixing ratio
664 decreases rapidly with decreasing temperature above the surface (saturation vapor
665 pressure of CH₄ above a mixture of N₂ dissolved in liquid CH₄ was based on Kouvaris
666 and Flasar (1991)). Consequently, CH₄ reaches its lifting condensation level, or 100%
667 relative humidity, at an altitude of approximately 7 km. This represents the base of
668 condensation of CH₄ as liquid. The GCMS CH₄ data are consistent with saturation above
669 liquid CH₄ with N₂ dissolved in it up to about 13-14 km. Above this altitude, a phase
670 change to solid particles is expected, with the possible presence of supercooled droplets
671 of a two component (methane-nitrogen) liquid as well. The nearly constant CH₄ mole
672 fraction of 1.48×10^{-2} at the tropopause and above in the stratosphere is consistent with

673 saturation above CH₄ ice and with the departure of the measured CH₄ mole fraction from
674 the predicted Kouvaris and Flasar (1991) saturation values above approximately 14 km,
675 as discussed previously by Atreya et al. (2006), and confirmed recently by laboratory
676 simulation experiments [Wang et al., 2009].

677 The GCMS value is in agreement with the CIRS measurement of methane in the
678 stratosphere [Flasar et al., 2005]. Only at very high altitudes of ~600 km and higher does
679 photochemistry begin to erode methane, thus depleting its mole fraction [Wilson and
680 Atreya, 2004].

681

682 **4.2 Molecular hydrogen, (H₂)**

683 The H₂ mole fraction determined from the GCMS data is in good agreement with
684 previous determinations of the H₂ mole fraction in Titan by Voyager IRIS and Cassini
685 CIRS experiments. The Voyager determination by Courtin et al., (2005) from S₀ (0) and
686 S₀ (1) transitions of the H₂-N₂ dimers indicated a mole fraction of $(1.0 \pm 0.4) \times 10^{-3}$.
687 The CIRS-Cassini determination is equal to $(9.6 \pm 2.4) \times 10^{-4}$ [Courtin et al., 2007].

688 Since Titan's atmosphere is mainly composed of N₂ and CH₄, substantial amounts of
689 atomic hydrogen are produced by photochemical reactions during the formation of
690 organic products. Theoretical models predict that atomic hydrogen recombines to form
691 H₂ molecules [Yung et al., 1984; Wilson and Atreya 2004; Strobel et al., 2009; Cui et al.
692 2008; Strobel, 2009]. The models predict a constant volume mixing ratio of H₂ in the
693 homosphere, consistent with the 1Myr photochemical lifetime of H₂

694 In laboratory measurements, Sekine et al (2008a) investigated heterogeneous
695 reactions of atomic hydrogen with synthetic Titan tholins. Results suggested to the
696 authors that these reactions might remove atomic hydrogen in the stratosphere and
697 mesosphere of Titan. In a subsequent work, Sekine et al. (2008b) proposed a model of
698 the total H₂ production and loss rate in the stratosphere, with an H loss peaking around
699 500 km altitude. As a consequence, the H₂ mixing ratio might not be constant with
700 height. Thus, it may be premature to conclude that the INMS measurements of H₂ made
701 at altitudes above 900 km [Waite et al., 2005; Yelle et al., 2006, 2008; Cui et al., 2008]
702 can be extrapolated monotonically to those measured in the lower atmosphere in situ
703 by the Huygens GCMS and remotely by CIRS from the Cassini orbiter.

704

705 **4.3 Carbon Dioxide, (CO₂)**

706 Carbon dioxide was first detected in the atmosphere of Titan by the Voyager
707 Infrared Radiometer Spectrometer at 667 cm⁻¹ in the ν₂ band of the Q branch
708 [Samuelson et al., 1983]. These observations yielded an average mole fraction
709 of 1.5 (+1.5,-0.8) ppbv above 110 hPa, later revised to approximately 14 ppbv between
710 100-200 km altitude following further analysis of the same data [Coustenis et al., 1991].
711 This revision agrees with the Cassini CIRS results at the peak of the contribution function
712 at 6.2 hPa [Coustenis et al., 2007]. The CIRS data showed little change in CO₂ with
713 latitude. While CO₂ remains subsaturated down to low stratospheric altitudes [Baines et
714 al., 2006], it is expected to condense at the tropopause where the temperature is 74 K,
715 provided that some unknown process does not deplete it in the lower stratosphere. Some
716 re-evaporation of dry ice particles is expected during sedimentation below the tropopause
717 down to the 94K surface of Titan but, some CO₂ could be expected to survive in
718 condensed form at the surface. The presence of solid CO₂ in the surface of Titan was

719 reported from an analysis of the Cassini Visible and Infrared Mapping Spectrometer
720 [McCord et al., 2008].

721 The GCMS detected CO₂ on the surface of Titan as described in section 3.3.

722 This CO₂ could have originated from one or more of the following sources: A reaction in
723 the atmosphere between CO and externally delivered water vapor by way of

724 CO+OH → CO₂+H [Samuelson et al. 1983] where OH is derived from water vapor
725 detected in Titan's upper atmosphere by ISO [Feuchtgruber et al., 1999]; or it could have
726 been trapped as condensate on planetesimals that made Titan [e.g.Hersant et al. 2008]; or
727 left over and outgassed from the interior if methane was produced in Titan's interior
728 [Atreya et al., 2006].

729 CO is uniformly mixed in Titan's atmosphere, and believed to be primordial and
730 outgassed from the interior in cryovolcanic events [Baines et al., 2006]. A detailed
731 height profile for CO₂ is not yet available. The measured CO/CO₂ ratio in Titan's
732 stratosphere is approximately 2300, with CO at 33 ppm based on the Cassini Visual and
733 Infrared Mapping Spectrometer (VIMS) measurements [Baines et al., 2006; Bellucci et
734 al., 2009] and 32 ppm from ground based measurements [Lellouch et al., 2004], This is
735 nearly a factor of 2000 greater than the value of 1.3 estimated for comets [Boice and
736 Huebner, 1997].

737 Any outgassing of CO₂ (and CO) from the interior might be expected to be
738 associated with traces of other volatiles, especially H₂O, NH₃ and H₂S. The GCMS
739 surface data do not show evidence of these gases. This does not imply that they are not
740 present on the surface. The GCMS only samples the warmed area of Titan's surface in the
741 immediate vicinity of the inlet. The H₂O saturation vapor pressure at the suspected
742 evaporation temperature of 145 K [Lorenz et al., 2006] is only 1.3x10⁻⁸ hPa, or a mole
743 fraction of 8.7x10⁻¹² relative to the 1500 hPa atmospheric pressure at the surface. This is
744 well below the normal GCMS detection capability. The NH₃ vapor pressure is 67.7 hPa,
745 or a mole fraction of 4.5x10⁻⁵, which is within the detection range of the GCMS.
746 However, the m/z = 17 peak is masked by much higher contributions from ¹³CH₄ and
747 ¹²CH₃D that made the detection impossible. Although a saturated mole fraction of H₂S
748 (2x10⁻³) would be detectable by the GCMS, the measured H₂S at m/z = 34 was below the
749 detection threshold of the GCMS in this mass range. The GCMS derived upper limit is
750 5x10⁻⁸. The threshold is raised above 1x10⁻⁸ because of background counts occurring at
751 high ion source pressures
752

753 **4.4 Protosolar noble gases**

754 The Huygens GCMS spectra clearly show the presence of the protosolar isotope of
755 argon, ³⁶Ar, with a mixing ratio of (2.1 ± 0.8) x10⁻⁷. There are no indications of Kr and
756 Xe with their upper limits being 10 ppb [Niemann et al., 2005; this paper]. This led
757 several investigators to suggest models for the evolution of the atmosphere that would
758 account for the absence of these two gases. These models included formation of
759 clathrates on the surface of Titan [Thomas et al., 2007; Osegovich and Max, 2005] or
760 formation and sequestration of clathrates in a putative sub-surface ocean [Tobie et al.,
761 2006], or capture by aerosols with subsequent precipitation. [Jacovi and Bar-Nun, 2008].

762 However, Owen and Niemann (2009) demonstrated that the relative abundances of
763 noble gases in known reservoirs in the solar system -- the Sun, Venus, Earth, Mars and
764 meteorites -- would allow the Huygens GCMS to detect ³⁶Ar, but not the other two gases.

765 The instrument simply did not have the sensitivity to detect Kr and Xe given the observed
766 abundance of ^{36}Ar in any of these reservoirs. Although the processes proposed for the
767 non-detection of krypton and xenon may be operating on Titan, the available data do not
768 reveal or require them [Owen and Niemann, 2009]. Of course, Titan might have collected
769 its noble gases from a completely different mixture from those we know. The only
770 constraint we can offer on such unknown mixtures is that the depletion of argon relative
771 to krypton could not be greater than it is on Mars or the Earth.

772 The origin of argon on Titan can be explored by comparing the solar value of
773 $^{14}\text{N}/^{36}\text{Ar}$ with the values in the atmospheres of Titan, Mars and Earth, once they have
774 been reconstructed for escape [Lunine et al. 1999]. The solar value of $^{14}\text{N}/^{36}\text{Ar}$ is 30
775 [Grevesse et al., 2007]. On Earth and Mars it is $\sim 4 \times 10^4$ while on Titan it is $\sim 1 \times 10^7$.
776 There are several ways of explaining these differences but a detailed treatment of
777 appropriate models is beyond the scope of this paper.

778 The discovery of ^{22}Ne provides yet another perspective. On Titan, $^{22}\text{Ne}/^{36}\text{Ar} \sim 1$,
779 but with the caveat that the ^{22}Ne is tentative and has a large uncertainty (Section 3.5). On
780 the Sun it is 3, on Earth and Venus 0.04, in the C3V meteorite Allende the ratio is 0.02. It
781 is virtually impossible to trap Ne in ice except in amorphous ice at ambient temperatures
782 of about 20 to 25 K [Laufer et al., 1987]. There are not yet any detections of Ne or any
783 other noble gases in comets [Weaver et al., 2002]. The implications of the detection of
784 neon in Titan's atmosphere require further investigation.

785 The cold outer solar nebula should duplicate chemical conditions in the interstellar
786 cloud from which it formed. The basic features of these conditions should be captured in
787 comets. Yet comets do not reveal either the abundances or molecular species in the
788 interstellar medium as expected. In the ISM, N_2 is typically ten times more abundant than
789 NH_3 whereas in the comae of comets NH_3 is the dominant carrier of N. There is only an
790 upper limit on N_2 that is orders of magnitude below the expected abundance. Argon was
791 not detected either, with an upper limit of about 10% of the solar value for Ar/O
792 [Weaver et al., 2002]. The presence of NH_3 , and the strong depletion of N_2 are clear and
793 striking [Cochran et al., 2000; Bockelee-Morvan et al., 2004]. This suggests that an
794 efficient process precluded the trapping of detectable (so far!) amounts of N_2 and Ar in
795 cometesimals.

796 However, ^{36}Ar was clearly measured in Titan's atmosphere by the Huygens GCMS
797 and N_2 has been known to be the major atmospheric constituent since Voyager
798 discovered it. The tiny amount of ^{36}Ar must be primordial, but N_2 is currently assumed to
799 be the product of NH_3 photodissociation in the warm early atmosphere of Titan [Atreya et
800 al.; 2009]. There are several possible processes that could lead to the value of $^{36}\text{Ar}/^{14}\text{N}$
801 that is observed in Titan's atmosphere today, both in the capture of these gases from the
802 solar nebula and in their pre-appearance histories on Titan [Bar-Nun et al., 1988;
803 Huebner and McKay 1991; Iro et al., 2003; Hersant et al., 2008]. The discovery of ^{36}Ar
804 therefore provides a new basis for future studies of Titan. The acquisition of new noble
805 gas data from Titan must wait a decade or more. Meanwhile our best hope for some
806 enlightenment is perhaps the measurement of noble gases and nitrogen from Comet
807 Churyumov-Gerasimenko by the Rosetta mission.

808
809

4.5 Radiogenic Argon

810 Radiogenic ^{40}Ar is a decay product of potassium 40 (^{40}K), which has a half-life of
811 1.28 billion years. Thus, over the age of the solar system most of the radiogenic argon on
812 Titan has been produced and its abundance in the atmosphere is potentially an indicator
813 of the extent to which outgassing of volatile elements has occurred from the deep interior,
814 where the rock (hence the potassium) should reside. If the rocky component of the
815 interior of Titan has the same composition as that of the Earth and has outgassed to the
816 same extent, ^{40}Ar should be much more abundant than measured, comprising $\sim 0.05\%$ of
817 the atmosphere [Owen, 1982] (corrected for loss of N). Evidently the outgassing or
818 cycling of volatiles to the surface was not as much as on the Earth. Nevertheless the
819 presence of the ^{40}Ar at the levels seen in Titan's atmosphere is a strong indication that
820 Saturn's largest moon has had a geologically active past, and is consistent with the view
821 that methane has been outgassed from Titan's interior over geologic time, replacing that
822 depleted in the atmosphere by chemistry energized by ultraviolet photons and by charged
823 particles.

824

825 **4.6 Nitrogen $^{14}\text{N}/^{15}\text{N}$ isotope ratio**

826 The revised GCMS result confirms that the $^{14}\text{N}/^{15}\text{N}$ ratio of 167.7 in N_2 on Titan
827 today is substantially different from the telluric value of 272 [Anders and Grevesse,
828 1989]. This is additional information to help understand the isotope ratios measured in
829 the solar system that suggests large scale isotope heterogeneity in the early solar nebula
830 [Marty et al., 2010]. Using data from the Cassini Ion and Neutral Mass Spectrometer
831 (INMS) Mandt et al. (2009) arrive at a value of $^{14}\text{N}/^{15}\text{N} = 143$ for the lower, mixed,
832 atmosphere. The discrepancy between the GCMS and the INMS could be the result of
833 model-dependent extrapolation of the INMS data from the region of measurements above
834 1000 km to the homosphere

835 It is difficult to determine the value of $^{14}\text{N}/^{15}\text{N}$ in the primitive atmosphere of Titan.
836 There is a large consensus for the hypothesis that NH_3 not N_2 was the dominant form of
837 nitrogen in the solar nebula and in the Saturn sub nebula where Titan was formed
838 [Atreya et al., 2009]. The nitrogen isotope ratios in NH_3 in comets and representative
839 protosolar bodies which contributed nitrogen to the atmosphere e.g. in icy grains have not
840 yet been measured so that we do not know the value in NH_3 on early Titan.

841 Several scenarios for interpreting the $^{14}\text{N}/^{15}\text{N}$ ratio measured on Titan today can be
842 envisaged. The first scenario was to assume that a very large nitrogen escape occurred
843 during the evolution of Titan [Lunine et al. 1999; Lammer et al., 2000]. This permits us to
844 assume a large initial isotopic ratio, even the telluric ratio of 272 [Anders and Grevesse,
845 1989]. However, Mandt et al. (2009) have calculated that, considering the large amount
846 of N_2 that must be fractionated, the initial $^{14}\text{N}/^{15}\text{N}$ cannot have changed much due to
847 atmospheric processes and the initial isotopic ratio should have been close to 167. A
848 detailed treatment of the subject is given by Atreya et al. (2009).

849

850 **4.7 Carbon $^{12}\text{C}/^{13}\text{C}$ isotope ratio**

851 The value of $^{12}\text{C}/^{13}\text{C}$ determined in the local interstellar medium is 43 ± 4 [Hawkins
852 and Jura, 1987]. In evaluating this determination it is important to remember that the Sun
853 has revolved around the center of the galaxy 15-20 times since the origin of the solar

854 system. Thus the “local” Interstellar Medium today is not the one in which the solar
855 system formed. Furthermore, galactic evolution will lower the ratio with time. There is,
856 however, a remarkable uniformity of $^{12}\text{C}/^{13}\text{C} = 90 \pm 5$ in every solar system object that
857 has been measured with sufficient precision (Table 4). Accordingly, we adopt the solar
858 value of 90 as our standard reference [Anders and Grevesse, 1989]. This choice is
859 strongly supported by the most recent observations of the coma of comets. Manfroid et
860 al., (2009) give 91.0 ± 3.6 for the ratio in 23 comets of various dynamical classes. We
861 therefore expect to find a value of $^{12}\text{C}/^{13}\text{C}$ close to 90 in Titan’s hydrocarbons. Indeed the
862 GCMS found $^{12}\text{C}/^{13}\text{C} = 91.4 \pm 1.5$ for methane in Titan’s atmosphere and 92.0 ± 0.5 at
863 the surface. [Niemann et al. this work].

864 These values can be compared with measurements made by remote sensing.
865 Analyses of 15 IR spectra covering bands of CH_4 , C_2H_2 and C_2H_6 with the Cassini
866 orbiter Composite Infrared Spectrometer (CIRS) by Nixon et al. (2008a) produced an
867 average value of $^{12}\text{C}/^{13}\text{C} = 80.8 \pm 2$. Individual measurements were CH_4 : 76.6 ± 2.7 ; C_2H_2 :
868 84.8 ± 3.2 ; C_2H_6 : 89.8 ± 7.3 . Nixon et al. (2008b) found a value of 84 ± 17 for this ratio
869 in CO_2 . Jennings et al., (2009) reported $^{12}\text{C}/^{13}\text{C} = 89 \pm 8$ from ground-based observations
870 of C_2H_6 . It is too soon to attempt an analysis of the reason(s) for the disagreement among
871 these different measurements.

872 The preliminary reported value of $^{12}\text{C}/^{13}\text{C}$ in methane derived from GCMS data
873 was 82.3 ± 1 . [Niemann et al., 2005]. This value is noticeably lower than the terrestrial
874 value of the reference inorganic standard value of 89.4 (NIST or Vienna-Pee Dee
875 Belemnite – V-PDB). Since terrestrial carbon-based biological activity is usually
876 associated with an isotopic fractionation that favors light carbon [Farquhar et al., 1989],
877 we suggested that this preliminary value of $^{12}\text{C}/^{13}\text{C}$ did not support a possible biological
878 origin for CH_4 . It is now clear that the stand alone ratio $^{12}\text{C}/^{13}\text{C} = 91.4 \pm 1.5$ [Niemann et
879 al., this work] in Titan’s methane does not allow any conclusions to be drawn on the
880 existence of biological activity on Titan past or present.

881

882 **4.8 Deuterium - hydrogen isotope ratio**

883 The D/H ratio in hydrogen obtained by the GCMS is $(1.35 \pm 0.3) \times 10^{-4}$. As
884 outlined in section 3.6, the D/H ratio is determined from the measurement of the ratio of
885 HD to H_2 present in the atmosphere of Titan. These gases are presumably products of
886 photolysis of CH_4 . Therefore, it may not be too surprising that the ratio derived from
887 GCMS measurements agrees with the value of $1.32(+0.15/-0.11) \times 10^{-4}$ derived from
888 $\text{CH}_3\text{D}/\text{CH}_4$ measured by the CIRS instrument in the stratosphere of Titan [Bezard et al.,
889 2007].

890 The low enhancement of this Titan D/H ratio for hydrogen relative to the protosolar
891 D/H ratio in hydrogen of $(2.1 \pm 0.5) \times 10^{-5}$ [Geiss and Gloeckler, 1998] or $(2.6 \pm 0.7) \times 10^{-5}$
892 [Mahaffy et al., 1998] is, however, difficult to interpret. The Titan D/H ratio is lower than
893 the D/H ratios in cometary water, which varies from 2.9×10^{-4} to 4.1×10^{-4} as measured in
894 four comets [Villaneuva et al., 2009], and in the water plumes escaping from Enceladus,
895 as measured by the INMS experiment, which is $2.9(+1.5/-0.7) \times 10^{-4}$ [Waite et al; 2009]. A
896 more efficient deuterium exchange between water and protosolar hydrogen relative to
897 methane with H_2 is unattractive because laboratory measurements have provided
898 evidence that in a neutral environment the isotopic exchange is weaker than that of water
899 with hydrogen [Lecluse and Robert, 1994].

900 The D/H ratio in cometary methane might be smaller than the D/H ratio in cometary
901 water [Mousis et al. 2002] implying a similar behavior in the protosolar cloud. According
902 to available isotope chemistry models, this seems unlikely. Our best chance to improve
903 the situation would be to determine the D/H ratio in methane in a comet from ground-
904 based observations or from the Rosetta mission. Equally of value would be to measure
905 the D/H ratio in water ice at the surface of Titan [Coustenis et al. 2009].
906

907 **4.9 Organic species evaporating from the surface.**

908 The different volatilities of each component either in pure form or in mixtures with
909 other species including nitrogen and the large uncertainty about the surface contact
910 parameters make it difficult to relate the observations quantitatively to surface
911 concentrations. It is noticeable though, that those molecules which would be on the
912 surface at the landing site in liquid form as possibly droplets, reach a constant partial
913 pressure. CH₄ and C₂H₆ fall into that group. The others, which would be sublimating from
914 solids (ices), never reached a constant level through the end of the GCMS surface
915 measurements. This indicates that the temperature environment in the sampling area on
916 the surface was transient for the duration. A reservoir of the evaporating liquids must
917 have been able to hold enough liquids to last for the duration of the surface sampling.
918 Flash evaporation from thin layer condensation on stable aerosols is less likely because
919 the rate would vary more with time. It is thus likely that there was a reservoir of
920 condensed species on the surface at the Huygens landing site.
921

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935

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1202
1203
1204 Figure Captions.
1205
1206 Figure 1.
1207 Schematic of the Huygens GCMS gas sampling and mass spectrometer assembly .
1208 The subsystems and their interfaces and functions are indicated on the left.
1209 The multi ion source mass spectrometer subsystem is shown on the right
1210 IS 1to IS5 are the ion sources. GC1 to GC3 are the gas chromatograph channels.
1211
1212 Figure 2.
1213 Illustration of the locations of the atmosphere sample inlet and outlet ports on the
1214 Huygens probe.
1215
1216 Figure 3.
1217 Ambient pressure, descent velocity and probe dynamic pressure versus altitude during
1218 probe descent. The descent velocity and dynamic pressure share the common left-hand
1219 ordinate while the ambient pressure uses the right-hand ordinate as indicated by the

1220 horizontal arrows next to each curve. The ambient pressure was measured by the HASI
1221 experiment. The descent velocity was determined by the DWE experiment and the
1222 Descent Trajectory Working Group (DTWG). The dynamic pressure was computed from
1223 the ambient mass density and the descent velocity.

1224
1225 Figure 4.
1226 Ambient pressure-temperature-altitude and event profiles versus time from measurement
1227 sequence initiation. Panel a: Ambient pressure and temperature. Panel b: Raw count rates,
1228 uncorrected for pulse-pileup and/or dead-time, from ion source 1 for $m/z = 28$ and 16.
1229 The gaps in the $m/z = 28$ trace are events when the rare gas (Rg) and enrichment cell
1230 (EC) were analyzed and the ACP data were transferred and analyzed with ion source 2.
1231 Panel c: The time intervals when the inlet leaks L1 and L2 were used are shown in the
1232 shaded areas. Panel d: The gas chromatograph cycles.

1233
1234 Figure 5.
1235 Examples of averaged mass spectra obtained at high and low altitude and on the surface. 5a:
1236 Average from 130 to 120 km, ~ 4 to 6 hPa ambient pressure (leak L1). 5b: Average from 20
1237 to 10 km ~ 500 to 900 hPa ambient pressure (leak L2). 5c: Average surface spectra (leak L2)
1238 from 9000 seconds to 13000 seconds.

1239
1240
1241 Figure 6.
1242 Methane mole fraction all sample points, diamonds and squares averaged over 50 sample
1243 points versus time from sequence initiation. The analysis was divided into regions for leak
1244 L1 and leak L2. N_2 $m/z = 14$ counts, (corrected for methane contribution) are a proxy for m/z
1245 $=28$ for the leak L2 data because at lower altitudes the pulse counts at $m/z = 28$ are no longer
1246 valid. The regions are marked in the figure and the legend. The time of surface impact is also
1247 marked. The error bars are the standard deviation.

1248
1249 Figure 7.
1250 Methane mole fraction averaged over 50 sample points versus altitude. The error bars are the
1251 standard deviation. Leak L1 data are blue diamonds and leak L2 data are red squares.

1252
1253 Figure 8.
1254 A schematic of the GCMS sample inlet and its mounting in the Huygens Probe.

1255
1256 Figure 9.
1257 Mole fractions of CH_4 , C_2H_6 , C_2H_2 , C_2N_2 and CO_2 versus descent time..
1258 Error bars are standard deviation. The time of surface impact is indicated by a vertical dashed
1259 red line.

1260
1261 Figure 10.
1262 The mole fraction of molecular hydrogen versus time from sequence initiation. All data points
1263 and 50 sample points averages are shown for the leak L1 and leak L2 regions. The error bars
1264 are standard deviations. The time of surface impact is indicated by a vertical dashed red line.

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1266 Figure 11.
1267 The mole fraction of molecular hydrogen versus altitude. The data points shown are 50 sample
1268 point averages. The error bars are standard deviations.
1269
1270 Figure 12.
1271 Average mass spectrum of the rare gas cell contents. CO₂ (at m/z=44) and C₆H₆ (at m/z = 78)
1272 were permanent background gases in the ion source.
1273
1274
1275 Figure 13.
1276 Pulse count ratios of m/z = 29 (¹⁵N¹⁴N⁺) to m/z = 28 (¹⁴N₂⁺) (red and blue) and m/z = 29 to
1277 m/z = 14 proxy (black and red) versus time from sequence initiation shown for the leak L1 and
1278 leak L2 regions. The increase in the m/z =29 to m/z =28 count ratios at ~1500 seconds and
1279 7000 seconds results from counter saturation at high count rates for m/z = 28.
1280
1281 Figure 14.
1282 M/z = 28 counts multiplied by two (m/z = 14 is used as proxy) versus m/z =29 counts. Leak L1
1283 counts are dark blue diamonds and leak L2 counts are red squares. The straight lines are least
1284 square fits. The m/z=29 counts were multiplied by molecular mass ratio (28/29)^{1/2} to account
1285 for the gas flow difference in free molecular flow to the pumps.
1286
1287 Figure 15.
1288 Pulse count ratios of all sample points of m/z =17 to m/z =16 due to CH₄, versus time from
1289 sequence initiation. Dark blue is from the leak L1 region and red is from the leak L2 region.
1290 Surface impact is indicated by the vertical dashed red line.
1291
1292 Table 1. CH₄ mole fraction, 50 data point averages. The grayed area indicates the data points
1293 averaged near the surface as noted in the table at the bottom. Pressure and temperature derived
1294 from the HASI experiment.
1295
1296 Table 2. H₂ mole fraction, 50 data point averages. Pressure and temperature derived from the
1297 HASI experiment.
1298
1299
1300 Table 3. Isotope ratios and noble gas abundances
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1302 Table 4. Carbon isotope ratios ¹³C/¹²C in the solar system
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