

# The significance of trace constituents in the solar system

Sushil K. Atreya

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Trace or minor constituents are key to the origin, maintenance, and the eventual fate of atmospheres of solar system objects. In this Introductory Paper, I illustrate this point by discussing certain cross cutting themes, including the chemistry of the formation and stability of a nitrogen atmosphere on Titan and the Earth, the chemical and biochemical origin of methane on the terrestrial planets and Titan, production and role of photochemical haze and aerosols, especially on Titan, and the significance of electro-photochemistry for habitability of Mars.

## 1. Introduction

Nitrogen is ubiquitous on terrestrial planets, comprising nearly three quarters by volume of the Earth's atmosphere and three percent each of the atmospheres of Mars and Venus today. However, the detection of a massive atmosphere of nitrogen with a surface pressure of 1500 millibar on a comparatively small and very cold moon Titan of Saturn by Voyager in 1980 was surprising. Even-smaller objects, Neptune's moon Triton and Pluto, are known to have a nitrogen atmosphere, but with a smaller and seasonally variable pressure ranging from less than 10 microbar to as large as 50 microbar. Plumes above the tiger stripes of Saturn's moon Enceladus might also contain traces of nitrogen. Nitrogen on planets and satellites could either have a primordial origin, or it could be secondary, *i.e.* a dissociation product of another nitrogen-bearing primordial molecule such as ammonia.

Nitrogen on Triton and Pluto is believed to be primordial, *i.e.* it was delivered as N<sub>2</sub> by the planetesimals that formed these objects. Triton and Pluto formed in the extreme cold regions of the solar nebula where the temperatures were below 40 K, allowing nitrogen to be trapped directly. Cold trapping of nitrogen in the Titan forming planetesimals was suggested also,<sup>48</sup> but is not supported by the Huygens Gas Chromatograph Mass Spectrometer (GCMS) measurement of primordial argon (<sup>36</sup>Ar). Direct capture of N<sub>2</sub> would be associated with <sup>36</sup>Ar also since the trapping temperature of argon is similar to that of nitrogen. This would result in the solar <sup>36</sup>Ar/N<sub>2</sub> = 0.11, whereas the GCMS measured this ratio to be  $2.1 \times 10^{-7}$ .<sup>46</sup> This clearly rules out direct capture of N<sub>2</sub> as the origin of Titan's nitrogen. It also implies that the planetesimals that formed Saturn's satellites, including Titan and Enceladus were warm, certainly too warm to trap nitrogen directly. This is even more of the case for the much warmer terrestrial planets. Thus the nitrogen on these bodies must be secondary.

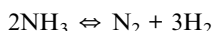
The amount of nitrogen in the plumes of Enceladus is controversial, perhaps below 0.1% based on the Cassini Ion and Neutral Mass Spectrometer (INMS) data on the plume composition (approximately 90% H<sub>2</sub>O, 5% CO<sub>2</sub>, 4% CO, 0.8% NH<sub>3</sub>, *etc.*<sup>64</sup>) and perhaps variable. The presence of volatiles above Enceladus is

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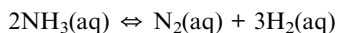
*Department of Atmospheric, Oceanic, and Space Sciences Space Research Building, University of Michigan, 2455 Hayward Street, Ann Arbor, MI, 48109-2143, USA*

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tioned to active plume sites, since the “atmosphere” of Enceladus is not permanent due to the moon’s low gravity and hence low escape velocity, such that its gases would disappear if the plumes became inactive.<sup>3</sup> Any amount of nitrogen in the plumes requires an explanation. Matson *et al.*<sup>41</sup> have proposed a mechanism for producing nitrogen from ammonia by endogenic process in the interior of Enceladus. The heating of the interior is assumed to result from tidal and radiogenic processes. For temperatures between 575 K and 850 K, they find rapid conversion of NH<sub>3</sub> to N<sub>2</sub>:



with a 70% efficiency at 800 K and 35 MPa, and, for temperatures below 575 K the process works best with metal or clay mineral catalysis:



where the reverse reaction is inhibited due reactant dispersal.

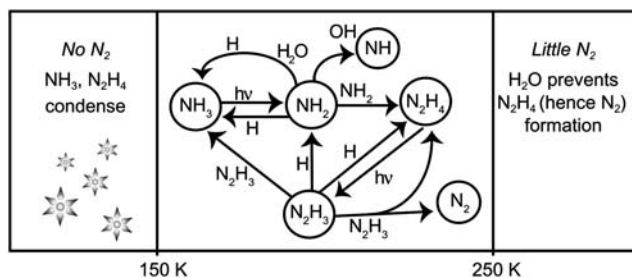
The above endogenic process is a straightforward thermal decomposition mechanism, except for the chemistry of metal or clay mineral catalysis, which is somewhat poorly constrained at high temperatures. The endogenic process could have had a role in producing some nitrogen on the terrestrial planets and Titan also, but photochemical conversion of ammonia was inescapable and far more effective, as will be discussed later. Ammonia is expected to have been a minor constituent of the primordial atmospheres on these bodies.

Another minor constituent of the atmosphere of Earth is methane, but it carries a profound significance as it is largely of biological origin. A small amount of methane is also reported to be present in the atmosphere of Mars, where it could be either geological or biological in origin. Methane and other organics are absent from Venus, which is not surprising considering the planet’s sulfur and halogen dominated thermochemistry and photochemistry. On Titan, methane has a particularly special role as the haze forming from the chemistry between methane and nitrogen in the ionosphere and the neutral atmosphere below result in up to 100 K warming of the stratosphere, and the collision-induced opacity of CH<sub>4</sub>-N<sub>2</sub>, H<sub>2</sub>-N<sub>2</sub> and N<sub>2</sub>-N<sub>2</sub> result in a 20 K increase in temperature at the troposphere. Without such warming Titan’s atmosphere would cool to the point that nitrogen would condense out as liquid, causing the atmosphere to collapse to very low pressure levels. Thus the very existence of an atmosphere on Titan is tied critically to trace constituents, which in turn result from the methane that comprises 5.65% (ref. 46, value supersedes ref. 47) of Titan’s atmosphere. The chemistry of the origin and fate of methane will also be reviewed in this paper.

## 2. The chemistry of the formation of nitrogen on terrestrial planets and Titan

Nitrogen is of a secondary origin on the terrestrial planets, Mars, Venus and Earth, as well as on Titan, *i.e.* it was produced originally from another nitrogen bearing compound, most likely ammonia. Thermal decomposition of ammonia in the past magmatic processes contributed to the ammonia of the terrestrial planets. Such a process was probably active in the interior of Titan also. However, the temperatures of primordial Mars, Earth, Venus and Titan were large enough to outgas large quantities of ammonia from their interiors to the atmosphere. This would naturally lead to the dissociation of ammonia by solar ultraviolet radiation. The solar UV flux in the dissociating region below 300 nm was as much as 10<sup>4</sup> times greater than today in the Sun’s pre-main sequence phase,<sup>72</sup> which resulted in large photolysis of NH<sub>3</sub> and a relatively fast production of N<sub>2</sub> as a consequence. The chemistry of the formation of nitrogen from ammonia for Titan is described below, and a similar process would have been at work on the terrestrial planets.

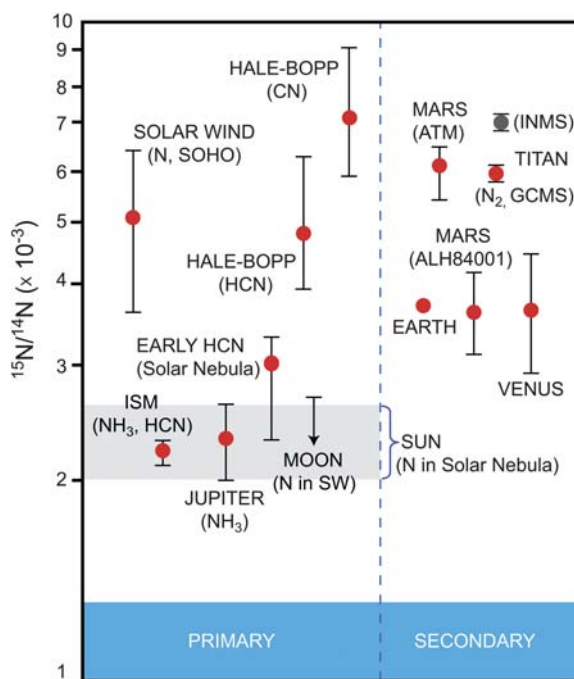
Atreya *et al.*<sup>5</sup> developed a photochemical model that showed production of large quantities of nitrogen from ammonia on primordial Titan. Voyager discovered nitrogen on Titan a couple of years later in 1980. Speculations of a nitrogen atmosphere resulting from the photolysis of ammonia existed as early as the early 1970s,<sup>34</sup> however. Considering Titan's density of  $1.8 \text{ g cm}^{-3}$ , it is believed that Titan is made of roughly 40% ice by mass, and the rest rock. Ammonia was trapped initially in ice of the Titan forming planetesimals. During the accretionary heating phase the volatiles were released to the atmosphere. Large quantities of water vapor, methane and ammonia, presumably in the solar O/C/N ratio, are believed to have been present in Titan's primordial atmosphere.<sup>36</sup> (In a relative sense, though, ammonia was a minor constituent of Titan's primordial atmosphere.) The photolysis of  $\text{NH}_3$  takes place at wavelengths below 300 nm, and peaks at around 195 nm. The photochemical scheme of ammonia on primordial Titan is shown in Fig. 1, after Atreya *et al.*<sup>5,6</sup> The model also contained methane, which played a central role in the radiative transfer hence the thermal structure of Titan's primordial atmosphere.<sup>1</sup> However, methane does not interfere with the chemical production of nitrogen from ammonia, as the photolysis of the two gases is both spectrally ( $\text{CH}_4$  largely at 121.6 nm, and  $\text{NH}_3$  largely around 200 nm) and spatially separated. As shown in Fig. 1, the photolysis of ammonia produces amidogen radicals ( $\text{NH}_2$ ). About a third of the ammonia so destroyed is recycled right back by the reaction of these radicals with hydrogen atoms also produced in the  $\text{NH}_3$  photolysis. The self-recombination of the remaining  $\text{NH}_2$  radicals results in hydrazine ( $\text{N}_2\text{H}_4$ ) molecules. At temperatures above 150 K, sufficient quantities of  $\text{N}_2\text{H}_4$  remain in the vapor phase, allowing its photolysis to proceed and form an intermediate radical, hydrazyl ( $\text{N}_2\text{H}_3$ ). The self-recombination reaction of these radicals leads to the production of  $\text{N}_2$ . Below 150 K, little  $\text{NH}_3$  is in the vapor form, and even the small amount of hydrazine formed from it condenses, preventing production of  $\text{N}_2$ . At temperatures greater than 250 K, a large quantity of water vapor coexists with the ammonia vapor. The photolysis of  $\text{H}_2\text{O}$  vapor results in the highly reactive hydroxyl molecules ( $\text{OH}$ ) and H atoms. The latter react with  $\text{NH}_2$  and recycle ammonia. Although some production of  $\text{N}_2$  from  $\text{NH}_2$  (from  $\text{OH} + \text{NH}_2$ ) and any small amount of  $\text{N}_2\text{H}_4$  that did form is still likely but the yield turns out to be extremely low. The ideal temperature range for producing  $\text{N}_2$  from  $\text{NH}_3$  on primordial Titan is thus 150–250 K,<sup>6</sup> slightly revised from the earlier range of 150–200 K<sup>5</sup> due to the inclusion of a radiatively controlled structure in the atmospheric temperature rather than an isothermal temperature. The temperature range also has an impact on the time scale for the formation of the currently observed pressure of nitrogen on Titan.



**Fig. 1** Photochemical production of  $\text{N}_2$  from  $\text{NH}_3$  in Titan's primordial atmosphere (updated from ref. 5. Below 150 K, little  $\text{NH}_3$  is in the vapor phase, and whatever small intermediate product hydrazine ( $\text{N}_2\text{H}_4$ ) forms from it condenses, thus preventing  $\text{N}_2$  formation. Above 250 K, water vapor has a sufficiently large vapor pressure, so that  $\text{OH}$  from its photolysis reacts with  $\text{NH}_2$  drastically decreasing the subsequent yield of  $\text{N}_2$ , while some recycling of  $\text{NH}_3$  occurs by the reaction of  $\text{NH}_2$  with  $\text{H}$  from  $\text{H}_2\text{O}$ .

The present nitrogen on Titan may be a relic of its original abundance because of escape from the atmosphere<sup>33,37</sup> that would result in the fractionation of nitrogen isotopes. The Huygens GCMS measures  $^{14}\text{N}/^{15}\text{N} = 167.7$  in Titan's  $\text{N}_2$ .<sup>46</sup> Assuming the Earth's  $^{14}\text{N}/^{15}\text{N} = 272$  as the reference (Fig. 2), this implies that Titan should have started out with approximately 5–10 bars of  $\text{N}_2$  to account for the current 1.5 bars present today.<sup>6</sup> The time scale for producing 10 bars of nitrogen photochemically from ammonia is calculated to be approximately 30 Myr.<sup>1</sup> Evolutionary models predict that Titan's surface temperature was in the 150–250 K range (the ideal temperature range, as explained above) for over 100 Myr,<sup>35</sup> which is more than that required for producing 10 bars of nitrogen thus allowing sufficient wiggle room to accommodate uncertainties in various model calculations.

The above time scale is based on the assumption that Titan's initial  $^{15}\text{N}/^{14}\text{N}$  ratio was the same as the Earth's, since, like the Earth, its nitrogen is secondary that was produced from ammonia photochemistry. As shown in the right panel of Fig. 2, the  $^{15}\text{N}/^{14}\text{N}$  ratio is the same on Venus, Earth and solid Mars (as reflected in ALH84001 meteorite). The higher  $^{15}\text{N}/^{14}\text{N}$  value in the atmosphere of Mars (ATM) indicates escape of nitrogen, which favors the lighter isotope. Likewise, escape would render the  $^{15}\text{N}/^{14}\text{N}$  value on Titan to be greater than terrestrial ( $^{15}\text{N}/^{14}\text{N} = 3.7 \times 10^{-3}$  or



**Fig. 2** Comparison of Titan's nitrogen isotope abundances from GCMS and INMS with those on the terrestrial planets and primary sources including the interstellar medium (ISM), Sun (SW: solar wind, SOHO: Solar and Heliospheric Observatory), Jupiter (which represents the protosolar value) and comet Hale-Bopp. For Titan, the GCMS value is more appropriate as the INMS result represents a model dependent extrapolation from the ionosphere at ~1000 km to the troposphere below 45 km. The  $^{15}\text{N}/^{14}\text{N}$  ratio in HCN in comet Hale-Bopp is based on reanalysis of the HCN data of Jewitt *et al.*<sup>31</sup> and Ziurys *et al.*<sup>74</sup> by Bockelee-Morvan *et al.*,<sup>11</sup> according to which the previous  $^{15}\text{N}/^{14}\text{N}$  ratio was revised up by about 35%. Bockelee-Morvan *et al.*<sup>11</sup> determine the nitrogen isotopes in another comet 17P/Holmes and find them to be quite different from Hale-Bopp (see text). For Mars, two values are shown, in the atmosphere (ATM) and Allan Hills meteorite (ALH84001), the latter presumably represents the solid Mars value. Prepared in consultation with Paul R. Mahaffy.

$^{14}\text{N}/^{15}\text{N} = 272$ ) provided that the initial nitrogen isotope ratio on Titan was same as that in the Earth's nitrogen. According to one model, however, hydrodynamic and sputtering loss may not have resulted in the fractionation in Titan's nitrogen isotopes so that the current  $^{15}\text{N}/^{14}\text{N}$  value is indicative of the initial value.<sup>40</sup> This idea needs to be investigated further as early loss processes especially during the T-Tauri phase are quite plausible.

Although there is consensus that Titan's nitrogen was produced from ammonia, the original source of ammonia is less clear. The Titan forming planetesimals could have originated in Saturn's subnebula or as comets in the outer solar nebula. If comets supplied the ammonia to Titan, the  $^{15}\text{N}/^{14}\text{N}$  ratio on Titan should be the same as on comets, in principle, provided that no escape of nitrogen occurred over geologic time. The  $^{15}\text{N}/^{14}\text{N}$  ratio from HCN and CN of comet Hale-Bopp (one of only two comets where the value has been determined from both molecules) shown in Fig. 2 does not match that on Titan as measured by the GCMS. (The INMS value shown in Fig. 2,  $^{15}\text{N}/^{14}\text{N} = 7.0 \times 10^{-3}$  ( $^{14}\text{N}/^{15}\text{N} = 143$ ), is about 15% greater than the GCMS value of  $^{15}\text{N}/^{14}\text{N} = 6.0 \times 10^{-3}$  ( $^{14}\text{N}/^{15}\text{N} = 167.7$ ). It could be due to the fact that the INMS value represents a model-dependent extrapolation from the ionosphere around 1000 km to the troposphere, unlike the *in situ* value in the troposphere measured by the GCMS. Thus it is more appropriate to use the GCMS value.) On another comet, 17P/Holmes, the nitrogen isotope ratio from HCN is about 30% different from that in Hale-Bopp ( $^{15}\text{N}/^{14}\text{N} = 7.2 \times 10^{-3}$  or  $^{14}\text{N}/^{15}\text{N} = 139$ , compared to  $^{15}\text{N}/^{14}\text{N} = 4.9 \times 10^{-3}$  or  $^{14}\text{N}/^{15}\text{N} = 205$  in Hale-Bopp) and about 20% different from CN ( $^{15}\text{N}/^{14}\text{N} = 6.1 \times 10^{-3}$  or  $^{14}\text{N}/^{15}\text{N} = 165$ , compared to  $^{15}\text{N}/^{14}\text{N} = 7.15 \times 10^{-3}$  or  $^{14}\text{N}/^{15}\text{N} = 140$  in Hale-Bopp, or a dozen other comets in which the value is available from CN) although the error bars around the central values are large.<sup>11</sup> The above example illustrates that not all comets are alike. Moreover, any comparison with cometary nitrogen isotopes must be carried out in the comet's  $\text{NH}_3$ , not its photochemical products (with  $\text{CH}_4$ ), HCN and CN, as parent–daughter fractionation in isotopes can and does occur. However, no measurement of nitrogen isotopes in the ammonia of comets is yet available. Even when it does become available, utmost caution needs to be exercised in comparing that value to Titan's, as the value in one or even a handful of comets may not reflect the diversity of cometary nitrogen (or other) isotopes.

The dissociation of ammonia (or a nitrogen bearing organic molecule) by impacts associated with or without shock induced chemistry during Titan's accretion or the late heavy bombardment has also been suggested as a possible origin of Titan's nitrogen. Although an intriguing idea, it does not satisfactorily explain a number of relevant observations such as (1)  $\text{H}_2$  and D/H: the cometary impact would result in excessive molecular hydrogen that cannot be removed from the atmosphere without introducing spurious fractionation in the hydrogen isotopes (D/H), not seen in the Huygens GCMS data, as discussed by Atreya *et al.*,<sup>6</sup> (2) conservation of CHONPS elements, *i.e.* absence or enrichment of species: the impacts would exhume many more trace or minor constituents besides  $\text{NH}_3$ , such as xenon and krypton (if sequestered in surface or subsurface), sulfur and phosphorus compounds, amongst others, and would create or enhance other constituents such as oxygen bearing species including CO, but the Cassini–Huygens data do not show evidence of any such effects of cometary impact either in the atmosphere or the surface of Titan, and (3) presence of species: certain species present on Titan such as primordial argon ( $^{36}\text{Ar}$ ) are absent from comets, which would be puzzling if comets were responsible for supplying Titan's volatiles either in the process of forming Titan or during the late heavy bombardment. (Except for a single report of  $^{36}\text{Ar}$  in comet Hale-Bopp,<sup>75</sup> which could not be confirmed independently,  $^{36}\text{Ar}$  has not been detected in any other comet.<sup>76</sup>) Considering the above difficulties, the origin of Titan's nitrogen (and methane) atmosphere from comets remains as an interesting hypothesis that needs testing with appropriate measurements in future missions to Titan.

In summary, the nitrogen of Earth, Mars, Venus and Titan is secondary. Its origin from ammonia, a minor constituent of their primordial atmospheres, to its subsequent chemical formation is controlled by trace constituents – $\text{N}_2\text{H}_4$ , OH and H in the case of Titan, and OH, H, Cl and perhaps sulfur and oxygen species in the case of the terrestrial planets.

### 3. The chemistry of the formation of methane on Earth, Mars and Titan

#### 3.1 Biotic and abiotic methane on Earth

Methane is considered as the most significant potential biomarker in the solar system, except where it is formed by inorganic chemical processes such as in the interiors of the giant planets or the primordial solar or planetary nebulae. On Earth, 90–95% of the 1775 ppbv  $\text{CH}_4$  present in the atmosphere is biogenic in origin, due either to current or past biology. A distribution of current sources of methane on Earth is shown in Fig. 3. Only oceans and lakes (3%) can be considered as essentially abiotic sources, whereas a portion of the methane from gas hydrates (1%) and the geologic sources (~8%, with about 1% each from mud volcanoes and other geothermal sources and 6% from seepage) could also be abiotic. Fully a quarter of all methane comes from swamps and wetlands. Grass eating ungulates belch out about 15% of the total terrestrial methane as a metabolic byproduct of the bacteria breaking down the organic matter in the guts of such animals. Leakage of natural gas, which is about 85% methane and the result of past or fossilized biology, and coal mines together make a similar contribution. Rice paddies, biomass burning and waste and landfill are responsible for about a tenth each. Termites make up the rest (4%). Thus, it is only natural to wonder whether biology is responsible when methane is detected on another planet or satellite. Such is the case with Mars where small amounts of methane are reported, and Titan where the gas comprises about 6% of the atmosphere.

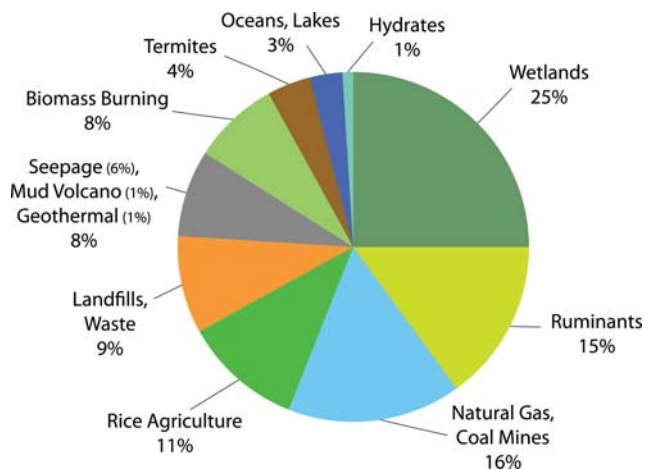


Fig. 3 Methane sources on Earth. Values used in this chart were compiled largely from the IPCC Report<sup>20</sup> and some recent updates (supersedes earlier values (ref. 53)).

#### 3.2 Chemistry of geologic and biogenic origin of methane on Mars

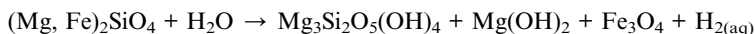
Ground-based<sup>32,44</sup> and Mars Express orbital observations<sup>26</sup> indicate trace amounts of methane in the atmosphere of Mars, with a global average abundance of 10–15 ppbv. Zahnle *et al.*<sup>73</sup> have questioned the validity of detection of methane and its seasonal

variability reported from the high resolution ground-based observations,<sup>44</sup> because of possible contamination of the blue-shifted Martian <sup>12</sup>CH<sub>4</sub> spectral signature by the twenty-times stronger telluric <sup>13</sup>CH<sub>4</sub> isotope signature. The criticism does not apply to the observations done from Mars orbit by the Planetary Fourier Spectrometer on Mars Express.<sup>26</sup> On the other hand, the latter data suffer from low resolving power issues including non- or ambiguous identification of several spectral features. Nevertheless, the above observations seem consistent with a small abundance of methane on Mars, amounting to a global average of 10–15 ppbv. However, claims of rapid variability and seasonal changes from either data set are far less convincing considering the marginal quality of all available data. One should recognize, however, that measurement of such trace quantities of methane in the Martian atmosphere is highly challenging. Dedicated, high precision techniques such as the tunable laser spectrometer with enrichment at front end by mass spectrometer on the 2011 Mars Science Laboratory rover<sup>38,66</sup> are required to unambiguously determine the presence, amount, isotope abundance, and variability of methane on Mars. The origin of even trace amounts of methane indicated by available observations needs to be understood. The associated chemical processes could provide some clues. Following is a brief discussion of the mechanisms for the production and fate of possible methane on Mars.

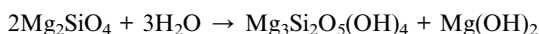
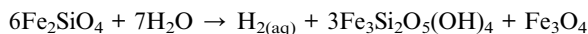
An extraplanetary origin such as that from comets, meteorites or interplanetary dust particles has been ruled out for the Martian methane as it would contribute less than 1% of the global value.<sup>7</sup> Volcanoes do not help either, as they put out 100–1000 times greater SO<sub>2</sub> at Earth, but SO<sub>2</sub> is actually less than one hundredths of the methane amount in the Martian atmosphere, besides the fact that the volcanoes have been extinct for over 100 Myr on Mars. Only geologic or biogenic origin is likely.<sup>7</sup> The production from either mechanism could be taking place now in the interior of Mars, or it could have occurred on the warmer and wetter Mars in the past. In either case, liquid water is essential for both biotic and geologic production of methane. The MARSIS radar on the Mars Express spacecraft and the SHARAD radar on Mars Reconnaissance Orbiter so far have found no trace of liquid water down to a few kilometres depth, but the water table could actually lie much deeper. Models of the Mars geotherms indicate a range of somewhere between 2 km and 25 km for the depth of aquifers,<sup>50</sup> deeper than the current radar data. Thus, current production of methane on Mars cannot be ruled out. Whether produced in the past or now, methane can be stored as clathrate-hydrate (CH<sub>4</sub>·6H<sub>2</sub>O molar proportions) in the subsurface ice and released from time to time when the clathrates are destabilized by any number of means including magmatic (large or small), thermal or mechanical stresses and impacts.

The geologic process is based on a set of hydrogeochemical reactions, involving first the reaction between water and rock (serpentinization) to liberate H<sub>2</sub>, followed by the reduction of primordial carbon in the form of CO, CO<sub>2</sub> or carbon grains to CH<sub>4</sub> by metal-catalyzed Fisher–Tropsch type reactions.<sup>7,50</sup> The principal chemical pathways are listed below.

1. Serpentinization: hydration of ultramafic silicates (Mg, Fe-rich) such as olivine and pyroxene results first in the formation of serpentine (Mg, Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, and molecular hydrogen (H<sub>2(aq)</sub>),

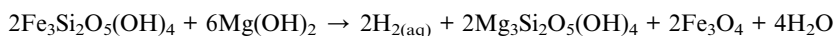


*i.e.*, olivine/pyroxene + water → serpentine + brucite + magnetite + hydrogen, where the key hydrogeochemical reactions are:

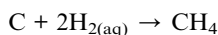
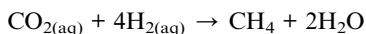
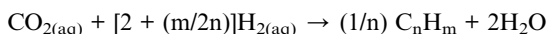


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followed by:



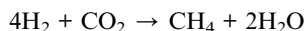
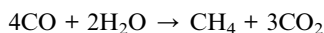
2. Methane by Fischer–Tropsch process: The  $\text{H}_{2(\text{aq})}$  liberated in above serpentinization process reacts with  $\text{CO}_2$ ,  $\text{CO}$  or  $\text{C}$  of the crustal rocks/pores to produce methane and possibly higher order hydrocarbons in decreasing abundances, *i.e.*



The above Fischer–Tropsch processes require metal catalysis by either Mg, Fe, Cr or their oxides, all of which are components of the ultramafic silicate rocks. Production of large quantities of methane is known to take place by above mechanism in the Black Smoker hydrothermal vents (300–500 °C, 300–400 bar) in terrestrial oceans as well as Lost City hydrothermal vents about 15 km from the spreading center where the temperatures are much milder, on the order of 30–120 °C (the upper range reflects the temperature of the underlying peridotite rock in contact with ocean water).

The above geochemical mechanism for producing methane can work in the interior of Mars if liquid water is present now or in the past when it almost certainly was. Both low and high temperature serpentinization processes are likely in either case, considering the low-high range of temperatures in the water table, according to the Martian geotherm models.<sup>50</sup> Finally, the recent detection of serpentine<sup>21</sup> on Mars lends some credibility to the above hydrogeochemical process for the formation of methane now or in the past. A biogenic source cannot be ruled out either.

Anaerobic, subterranean and oceanic chemolithotrophic microbial ecosystems on Earth are known to produce methane as a product of metabolism.<sup>15,57,51</sup> Coincidentally, the biochemical pathways involved<sup>67</sup> are similar to the above geochemical mechanism, and both require liquid water as the reactant, medium or solvent:



At Mars, the atmosphere is a large source of  $\text{CO}$  (~700 ppmv) and  $\text{H}_2$  (40–50 ppmv). The diffusion of these gases through the regolith to the subsurface aquifers would provide the nutrients to any microbial colonies that might exist in the subpermafrost aquifer environment of Mars. An abundant supply of  $\text{H}_2$  may also be available locally from serpentinization as discussed above. Fermentation is another process on Earth where various groups of microorganisms convert organic matter through a series of consecutive metabolic steps into acetic acid ( $\text{CH}_3\text{COOH}$ ) and then  $\text{CH}_4$  and  $\text{CO}_2$ . It is perhaps less likely at Mars, even if biology existed. As in the case of hydrogeochemical processes, the biotic production of methane on Mars need not be current. If microorganisms did exist on Mars in the past during its warmer and wetter phase, or if they exist in the aquifers now, the methane resulting from their metabolic activity can be stored in the permafrost or other ice for later release.

Irrespective of the production mechanism, once in the atmosphere the removal of methane occurs by photolysis largely above 50 km and by oxidation below, by OH from water vapor and  $\text{O}(^1\text{D})$  from ozone. The combined loss processes determine a timescale of 300–600 years against photochemical loss of methane in the Martian



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atmosphere.<sup>70</sup> A much more rapid loss is possible *via* heterogeneous processes involving a reactive surface, as will be discussed later (section 4.3). The photochemistry of methane in the atmosphere of Mars results mainly in the formation of ethane (C<sub>2</sub>H<sub>6</sub>), formaldehyde (CH<sub>2</sub>O) and methanol (CH<sub>3</sub>OH). However, their yield is very low with most products at pptv level or less, even if CH<sub>4</sub> were present at hundreds of ppmv levels.<sup>70</sup> Thus, for all practical purposes, methane is of little significance for the main chemistry of the Martian atmosphere, which is controlled by the CO<sub>2</sub>–H<sub>2</sub>O chemical pathways as will be discussed later (section 4.3).

### 3.3 Hydrogeochemical, primordial, and biochemical origin of methane on Titan

Potential sources of methane on Titan include: (i) direct delivery of CH<sub>4</sub> to Titan by the Titan forming planetesimals; (ii) formation of CH<sub>4</sub> on Titan either from primordial (non-methane) carbon; or (iii) biological. The abiotic production of methane in Titan's interior can be considered to be similar to the hydrogeochemical process discussed above for the Martian methane. During the accretionary heating phase of Titan the liquid water ocean in the interior is expected to have extended all the way to the core, where the rocks are. During that period, a good likelihood existed for both the high temperature serpentinization initially and the low temperature serpentinization later as the interior cooled. This was then followed by a Fischer–Tropsch process to produce sufficient quantities of methane.<sup>8</sup> The original carbon delivered to Titan in this scenario was in the form of primordial CO, CO<sub>2</sub> or carbon grains. As Titan cooled, the water ocean was gradually separated from the rocky core by a high-pressure ice barrier. Initially this ice, and subsequently the ice at shallower depths above the ocean, allowed the sequestration of methane as clathrate hydrate in Titan's interior. Methane was released to the atmosphere, perhaps episodically,<sup>60</sup> by cryovolcanism, impacts or other clathrate destabilizing processes, as also suggested above for Mars.

The non detection of heavy noble gases, Xe and Kr, by Huygens GCMS seems to provide support to the above hypothesis of production of methane on Titan. Had methane arrived at Titan directly as CH<sub>4</sub>, the same planetesimals would have delivered much greater quantities of Xe and Kr than the GCMS upper limit of 10 ppbv. However, suggestions have been made that Xe and Kr might be sequestered as clathrates in the ice below Titan's purported ocean several hundred kilometres beneath the surface. It is surprising that no outgassing of these volatiles occurred in Titan's 4.5 Gyr geologic history, considering that even <sup>40</sup>Ar produced in Titan's rocks some 2000 km below the surface gets out to the atmosphere where it has been detected. Sequestration of Xe and Kr in the aerosols in the stratosphere is another idea, but it is not evident why degassing does not occur once the aerosols descend to the surface where the temperature is twenty degrees warmer. Moreover, impacts of micrometeorites and charged particles such as the galactic cosmic rays (GCR) are also likely to release them. Perhaps there is a way out of this dilemma, but none satisfactory has been found yet.

Assuming that the absence of Xe and Kr in Titan's atmosphere has some as yet unknown explanation, another model has been proposed for the origin of Titan's methane. According to this model, Titan forming planetesimals originated from the outer solar nebula, not Saturn's subnebula, and they delivered methane directly to Titan.<sup>43</sup> In their best case scenario, these authors<sup>43</sup> find that if methane was produced by the abovementioned serpentinization process, to explain the current D/H ratio in Titan's CH<sub>4</sub> ( $1.32 \times 10^{-4}$ ) the D/H ratio in Titan's initial H<sub>2</sub>O ice would be only 0.7 times the D/H found from H<sub>2</sub>O on Enceladus, and worse yet if photochemistry enriched primordial D/H in Titan's methane. The model is based on several assumptions, notably: (a) D/H in Titan's ice must be same as in Enceladus' ice, which is far from certain as the volatile history of these two objects is very different; (b) Enceladus and the comets have the same D/H in their H<sub>2</sub>O, which is based on only three comets (Halley, Hyakutake, Hale-Bopp) all belonging to the

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same family of Oort cloud comets; (c) fractionation in D/H did not occur in the chemistry of serpentinization or the Fischer–Tropsch process or post CH<sub>4</sub> formation, which still needs to be demonstrated. Finally, since <sup>36</sup>Ar is not present in comets, the cometary origin of Titan's volatiles hypothesis also implies that no measurable amount of primordial argon (<sup>36</sup>Ar) can be present on Titan, contrary to the Huygens GCMS detection of 200 ppb of <sup>36</sup>Ar in Titan's atmosphere (see also end of Sec. 2). On the other hand, the direct detection of CO<sub>2</sub> in the surface of Titan<sup>46</sup> may be an indicator of the formation of methane on Titan. Nevertheless, direct delivery of methane by planetesimals from the outer solar nebula is an attractive hypothesis that deserves testing by determining the D/H ratio in the surface ice of Titan in future missions, as well as the D/H ratio in the ice of multiple and diverse comets. Much theoretical and laboratory work under Titan-specific conditions is also needed to fully comprehend the various chemical fractionation scenarios.

It has also been suggested that Titan's methane might be produced by methanogens.<sup>42,55</sup> Life as we know it requires a source of energy, nutrients, and water – a solvent or medium for the biochemical reactions and the transport of nutrients. McKay and Smith<sup>42</sup> proposed new types of microorganism that use Titan's liquid methane, instead of water, which is frozen solid at 94 K, as the medium, and utilize H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> from Titan's atmosphere as nutrients. Methane is released in turn. They also calculated an energy release of 334 kJ mol<sup>-1</sup> in the above biochemical process:



Considering that this energy is sufficient for survival of methanogenic bacteria on Earth, they suggested the possibility of widespread methanogenic life in Titan's methane liquid.

Even if the above scenario works, it would not be responsible for the origin of methane on Titan, because in order for the bacteria to generate methane, they need methane in the first place as the nutrients, C<sub>2</sub>H<sub>2</sub> + 3H<sub>2</sub>, are photochemical products of methane.<sup>8</sup> Titan's methane must have another origin. Whether or not methanogens are present on Titan is another matter. If they did exist, they would severely deplete the nutrients, H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>. The Huygens GCMS determines a uniform mole fraction of 0.001 for H<sub>2</sub>,<sup>46</sup> in good agreement with the Cassini Composite Infrared Radiometer Spectrometer value<sup>18</sup> and the Voyager value,<sup>17</sup> as well as various photochemical models according to which H<sub>2</sub> arises from CH<sub>4</sub> and is expected to be uniformly mixed because of its one million year lifetime in Titan's atmosphere. Furthermore, the Huygens GCMS detected acetylene (amongst other molecules) evaporating from Titan's surface in the measurements made for over an hour after the probe landed. Thus, no perceptible depletion in the nutrients, C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>, is recorded, which argues against widespread methanogenic life in Titan's surface, at least in the Huygens landing site, as was suspected previously from preliminary analysis of the Cassini-Huygens data.<sup>6</sup> It should be mentioned, however, that the INMS reported an H<sub>2</sub> mole fraction in the lower thermosphere<sup>65</sup> that is four times greater than every other measurement or models. This puzzling result warrants an independent analysis of the INMS H<sub>2</sub> data, especially considering its potential implication to Titan's biology.

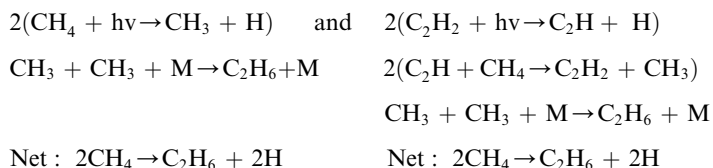
#### **4. Chemistry in the atmosphere and ionosphere, formation of aerosols, surface processes**

In the atmospheres of planets, numerous trace gases result from the chemistry of and between major and minor constituents. Here I will limit the discussion to the two constituents nitrogen and methane, whose chemistry is intertwined at Titan but is

rather separate at Mars. As mentioned previously, the chemistry of methane in the atmosphere of Mars can produce higher order hydrocarbons, *etc.* but in insignificant quantities and with relatively short lifetimes. In contrast to Mars, a rich chemistry is triggered by the solar ultraviolet flux and the charged particles in Titan's neutral atmosphere below approximately 800 km and the ionosphere above.

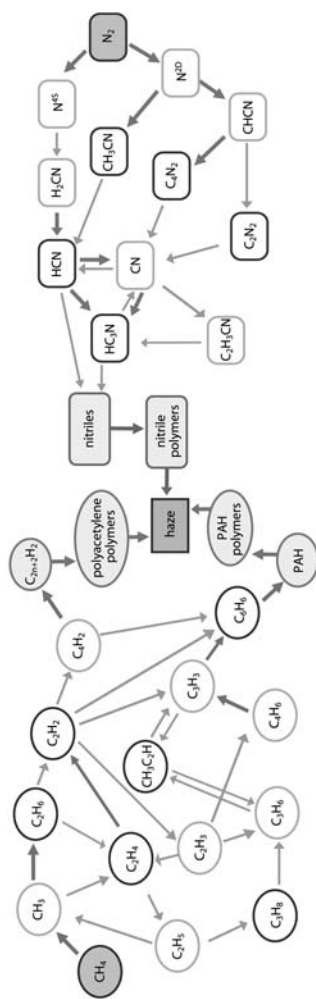
#### 4.1 The neutral atmosphere of Titan – hydrocarbon and nitrile chemistry and hazes

The chemistry of Titan's neutral atmosphere has been modeled by several groups (see ref. 59 for a review). Here I will highlight the salient points. Fig. 4 illustrates the basic chemical processes at work in the stratosphere and the upper atmosphere of Titan. On the left side are shown the pathways for an isolated CH<sub>4</sub> chemistry, which are in fact very similar to those in the atmosphere of Jupiter. Methane undergoes photolysis largely at the Lyman-alpha wavelength of 121.6 nm due to the large solar flux at this wavelength. Nearly 50% of the products are in the form of methyl radicals (CH<sub>3</sub>), while the rest are in the form of <sup>1</sup>CH<sub>2</sub>, <sup>3</sup>CH<sub>2</sub> and CH. The quantum yields of these latter radicals are not well constrained, especially at the non Lyman-alpha wavelengths. CH<sub>3</sub> is the precursor to all complex organics at Titan and the giant planets. Photolysis in the upper atmosphere accounts for nearly a third of the CH<sub>4</sub> destruction rate on Titan ( $4.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ , or  $8.7 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$  when referenced to surface.<sup>68</sup> The other two-thirds is due to catalytic destruction by C<sub>2</sub>H<sub>2</sub> in the stratosphere below. The escape from the atmosphere results in an additional 15–20% loss of methane from Titan's atmosphere. Thus, the total irreversible loss of methane takes place at a rate of approximately  $1.3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ , referenced to the surface.<sup>68</sup> At this rate methane would be irreversibly converted to other forms or lost from the atmosphere in approximately 10–30 Myr.<sup>68</sup> The continued presence of methane in the atmosphere, which is critical for maintaining the very atmosphere on Titan, thus requires its replenishment from time to time.<sup>60</sup> It is estimated that the interior of Titan may hold tens of billions of years worth of supply of methane in the form of clathrate hydrates, while only about 5% of the available supply has been consumed by photochemistry in Titan's geologic history.<sup>6</sup> Even accounting for uncertainties in the storage estimate, it is safe to assume there is little likelihood of an energy crisis on Titan to power Titan's chemistry through the life of the solar system. In Titan's present atmosphere, the two above-mentioned main dissociating chemical pathways of methane are elaborated below. They convert methane to ethane at a rate of about 40%, whereas ethane condenses out of the atmosphere, first as solid ice particles in the stratosphere and then turning to liquid droplets in the middle troposphere.



[M is the concentration of the background atmosphere]

As shown in Fig. 4, further chemistry results in the formation of stable heavier hydrocarbons, including C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, polyacetylenes or polyynes (C<sub>2n+2</sub>H<sub>2</sub>, n = 1,2,3...), *etc.* Laboratory and theoretical work by Gu *et al.*<sup>28</sup> shows formation of triacetylene (C<sub>6</sub>H<sub>2</sub>) from a reaction between C<sub>2</sub>H and C<sub>4</sub>H<sub>2</sub>, *i.e.* by the usual pathway for polyyne formation. Polyacetylenes higher than diacetylene have not been detected yet, perhaps because of their low vapor phase concentrations. Polymerization of the polyynes is expected to result in haze layers at higher elevations in the upper atmosphere. Benzene (C<sub>6</sub>H<sub>6</sub>) results on self-recombination of the propargyl radicals (C<sub>3</sub>H<sub>3</sub>). The continued H-abstraction C<sub>2</sub>H<sub>2</sub>-addition reaction sequence subsequent to the formation of benzene as well as the continued



**Fig. 4** Basic schematic of coupled methane-ammonia chemistry in the neutral atmosphere of Titan below ~800 km, showing the production of stable hydrocarbons and nitriles, and subsequently the photochemical haze.<sup>8</sup>

$C_2H_2$ -addition to close the second ring are expected to form polycyclic aromatic hydrocarbons (PAH) that subsequently polymerize to form haze at lower elevations in the stratosphere, according to photochemical models (e.g. ref. 69). The presence of nitrogen as Titan's main atmospheric component couples the chemistry of methane with that of nitrogen, as illustrated on the right side of Fig. 4. Reactive nitrogen atoms ( $N^{2D}$  and  $N^{4S}$ ) form from the solar UV and charged particle dissociation of  $N_2$ . Their reaction with methane and its products results in the most abundant nitrile, HCN, as well as smaller abundances of  $CH_3CN$ ,  $HC_3N$ ,  $C_2N_2$ ,  $C_4N_2$ , etc. The polymerization of HCN and other nitriles results in additional haze layers. The total hydrocarbon and nitrile polymer haze formed in the neutral atmosphere photochemistry accounts for about a 10% rate of destruction of methane, while the condensation of non-ethane organics as aerosols accounts for 30%.<sup>68</sup> The combined polymer-aerosol haze is key to maintaining a stable atmosphere of nitrogen on Titan, as discussed earlier.

## 4.2 Titan's ionospheric processes – cations, anions, hazes and aerosols

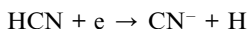
In addition to the hazes formed in the neutral atmosphere, the ionosphere may be a significant source, perhaps even the major source, of haze in Titan's atmosphere. The fast ion-molecule reactions in the ionosphere can ultimately result in heavy hydrocarbon and nitrile positive ions. In fact, the Cassini INMS detects such ions in the instrument's 100 Da mass range, with a one-to-one correspondence between the neutrals below and the resulting ions above, such as  $CH_4$  and  $CH_5^+$ ,  $C_6H_6$  and  $C_6H_5^+/C_6H_7^+$ , etc.<sup>63</sup> A significant finding of the INMS was the first ring molecule, benzene, at a mole fraction that is up to 1000 times greater than in the neutral atmosphere below. Even after considering the lower densities of the ionospheric region, it is obvious that the resulting haze from PAHs and other heavy organics would compete in importance with similar hazes produced in the neutral atmosphere.<sup>4</sup> Ionospheric reactions also have the potential of introducing nitrogen into the PAHs, thus creating PANHs. Vuitton *et al.*<sup>61</sup> have developed a comprehensive model to interpret the above INMS data. The kinetics of reactions beyond simple molecules is poorly constrained, however. Nevertheless it is apparent the heavy molecules formed from cation-molecule reactions would make a significant contribution to Titan's haze. Even larger molecules and subsequent aerosols and soot could result from the anion chemistry, as discussed below.

One of the most intriguing findings about the ionosphere came from observations made with the Electron Spectrometer (ELS) of the Cassini Plasma Spectrometer (CAPS), which provided evidence for negative ions ranging to 10 000 Da at  $\sim 1000$  km in Titan's ionosphere.<sup>13,14,63</sup> Distinct anion peaks were identified at  $22 \pm 4$  Da,  $44 \pm 8$  Da, and a less certain identification at  $82 \pm 14$  Da (ELS was not designed for detecting ions, hence the low mass resolution). Model calculations (e.g. ref. 62) identified, these peaks, respectively, as  $CN^-$ ,  $C_3N^-/C_4H^-$  and  $C_5N^-$ . The concentration of the negative ions was determined to be about  $200 \text{ cm}^{-3}$ <sup>13,14</sup> or about 10% of the positive ion concentration. The presence of massive negative ions has important implications for Titan's haze.

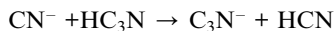
While negative ions have been known to be prevalent in the relatively dense D-region of the Earth's ionosphere below 80 km, and indeed small densities of the negative ions  $CH_3^-$  and  $H^-$  were predicted below 200 km in Titan's atmosphere from the impact of galactic cosmic rays,<sup>12</sup> the existence of massive organic anions at nanobar levels was unexpected. In the Earth's D-region, 3-body electron attachment to atoms and molecules results in the formation of  $O_2^-$ , and halogens  $Cl^-$  and  $Br^-$ , all with large electron affinity. Subsequent reactions with neutral atoms and molecules result in other anions. For example,  $O_2^-$  reactions form  $O^-$ ,  $O_3^-$ ,  $O_4^-$ ,  $CO_3^-$ ,  $NO_3^-$ , etc. The loss of negative ions occurs primarily by: (i) photodetachment ( $X^- + h\nu \rightarrow X + e^-$ ), such as  $H^-$  in stellar atmospheres;<sup>10</sup> (ii) associative detachment ( $X^- + Y \rightarrow XY + e^-$ ); or (iii) cation-anion recombination. The latter (iii) can be

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more important at Titan, where the solar flux is only 1% of that at the Earth. In Titan's ionosphere, dissociative electron attachment of HCN seems to be the trigger for more complex anions, *i.e.*



followed by charge transfer to neutral nitriles and hydrocarbons, such as



and the loss of the resulting anions mainly by associative detachment.

The simple negative ions so formed and identified from the CAPS/ELS data ( $\text{CN}^-$ ,  $\text{C}_3\text{N}^-/\text{C}_4\text{H}^-$  and  $\text{C}_5\text{N}^-$ ) could be precursors to more complex negative ions and subsequently high mass neutrals in the ionosphere.

The very large mass of negative ions is still puzzling. It is likely that cluster ions form in Titan's thermosphere, as they do in the Earth's atmosphere. Once formed, the cluster ions would eventually lead to macromolecules, nanometre size aerosols and soot in Titan's thermosphere. The chemistry of cluster ion formation in the Earth's atmosphere has been studied extensively since the 1960s, observationally, theoretically and experimentally. Water molecules participate in first forming mainly positive cluster ions, such as  $\text{O}_2^+ \cdot \text{H}_2\text{O}$  below 80 km that go on to produce  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  in subsequent reactions, while  $\text{NO}^+ \cdot (\text{H}_2\text{O})_n$  clusters dominate above 80 km.<sup>45,30</sup> Negative cluster ions such as  $\text{O}_2^- \cdot (\text{H}_2\text{O})_2$  are seen in the D-region.<sup>56</sup> High electric fields can produce  $\text{OH}^- \cdot (\text{H}_2\text{O})_n$  negative cluster ions.<sup>58</sup> Several molecules at ionospheric heights of Titan including  $\text{NH}_3$  and  $\text{H}_2\text{O}$  as well as aerosols can serve as ideal candidates for cluster ion formation, both positive and negative. Negative ions detected in the plume of Enceladus during Cassini's E3 encounter plausibly correspond to water clusters.<sup>14</sup> As mentioned earlier, ion-ion recombination is expected to be an important process in Titan's ionosphere, and it could result in large molecular clusters. Nigel Adams suggests (see the Discussion section) that since ion-ion recombination is an order of magnitude slower and less energetic than electron-ion recombination, there is more time for clusters to build up rapidly on both positive and negative ions. Much of the relevant laboratory chemical kinetics data on the formation of ion clusters and just ordinary ions at Enceladus and Titan is presently lacking other than that for the very simplest ones. However, progress has been made recently. For example, the Selected Ion Flow Tube measurements of a series of ring molecules, benzene, toluene and pyridine, with  $\text{CH}_3^+$  and  $\text{C}_3\text{H}_3^{+2}$  represent an important step in the right direction.

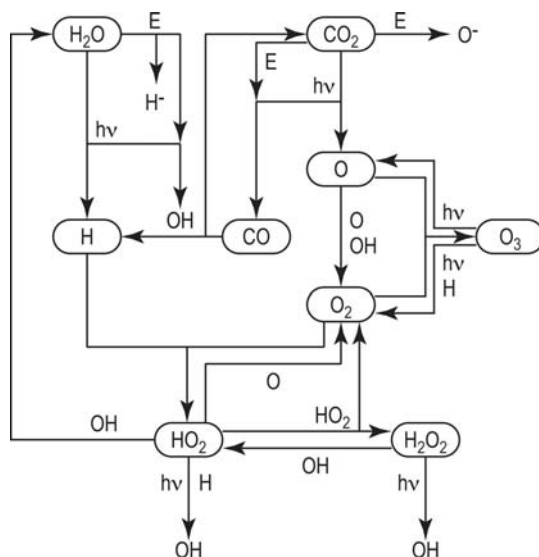
### 4.3 Electrochemistry, negative ion pairs, oxidants, and organics at Mars

At Mars, negative ion chemistry could have profound implications for habitability of the planet. Storm electric fields on Mars create negative ion pairs that might lead to excessive oxidant production. An oxidized surface was invoked to explain the data from Life Sciences Experiment on the 1976 Mars Viking landers, but the amount of surface oxidizer required was too large. The background of this problem is that the Viking GCMS found no trace of organics on the surface of Mars – which was surprising even if Mars has no indigenous organics, since 9000 tons of micrometeoritic material enters Mars each year ( $300 \text{ g s}^{-1}$ ), a quarter of which survives to the surface,<sup>25</sup> and a few percent of that is organic material – while the other Life Sciences Experiments discovered a highly reactive surface. When nutrients were added to the soil, the Labeled Release (LR) experiment found that gas was given off and the Gas Exchange (GEX) found that both  $\text{O}_2$  and  $\text{CO}_2$  were released from the soil. Microbes were suggested, but the rapidity of reactions implied an unrealistic metabolism. The seemingly contradictory findings of the Viking GCMS: absence of organics, and the LR and GEX experiments: possible presence of microorganisms, hence organics,

could be reconciled if a powerful oxidizer were present in the Martian surface. Oyama *et al.*<sup>49</sup> proposed hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as that oxidizer. A quarter century later, hydrogen peroxide was eventually detected in the atmosphere.<sup>16,22</sup> However, the observed abundance of 20 ppbv (and highly variable seasonally) was too low by a factor of 1000 (ref. 39) to destroy the surface organics (see ref. 7 for a detailed discussion). The answer could lie in the ion chemistry driven by triboelectric processes in convective dust storms and dust devils that are ubiquitous on Mars.

Taking a cue from their measurements of electric fields in terrestrial dust devils, Delory *et al.*<sup>19</sup> and Farrell *et al.*<sup>23</sup> developed a collisional plasma model for the Martian dust devils and storms. They find that negatively charged dust, not sand (ref. 24), particles are critical for generating large electrostatic fields of up to  $25 \text{ kV m}^{-1}$  that extend to high altitudes. In the ensuing collisional plasma, three new product sets result from two key molecules of the Mars atmosphere,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Electron impact of  $\text{CO}_2$  results in  $\text{CO}_2^+$  ions ( $>14 \text{ eV}$ ). More importantly to the oxidant question, dissociative attachment by electrons produces  $\text{CO/O}^-$  from  $\text{CO}_2$  (4.4 eV) and  $\text{OH/H}^-$  from  $\text{H}_2\text{O}$  (6.5, 8.6, 11.8 eV). These ion pairs are crucial to the electrochemical production of  $\text{H}_2\text{O}_2$ , as discussed below.

Atreya *et al.*<sup>9</sup> developed an electrochemical model, based on the ion pair production rates of Delory *et al.*,<sup>19</sup> and found an  $\text{H}_2\text{O}_2$  production rate that exceeded its photochemical production rate by up to a factor of  $10^4$  for the highest electrostatic fields of  $25 \text{ kV m}^{-1}$ . The chemical scheme is illustrated in Fig. 5. The photolysis of  $\text{CO}_2$  below 320 nm produces CO and O. The recombination of O atoms produces  $\text{O}_2$  molecules. The reaction between O and  $\text{O}_2$  yields  $\text{O}_3$  molecules as in the Earth's atmosphere. The photolysis of  $\text{H}_2\text{O}$  below 200 nm produces OH and H. The reaction between the H atoms (from  $\text{H}_2\text{O}$ ) and  $\text{O}_2$  molecules (from  $\text{CO}_2$ ) results in peroxy radicals ( $\text{HO}_2$ ). The self-recombination of two  $\text{HO}_2$  radicals produces  $\text{H}_2\text{O}_2$  in the atmosphere of Mars. In electrochemistry, triboelectric processes break down  $\text{H}_2\text{O}$  to produce additional OH, and  $\text{CO}_2$  to produce additional CO. Since the process takes place near the surface, a maximum amount of water vapor is available to produce the OH, unlike photochemistry, which occurs well above the water



**Fig. 5** Electro-photochemical scheme for production of hydrogen peroxide in the atmosphere of Mars.  $\text{CO/O}^-$ ,  $\text{OH/H}^-$  ion pairs result from action of triboelectric fields generated in the Martian dust devils and storms.

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condensation level on Mars. The addition OH so produced combine with the additional CO to produce additional H atoms. The rest of the pathways are the same as in photochemistry, with the end result being excess H<sub>2</sub>O<sub>2</sub> production. The H<sup>-</sup> and O<sup>-</sup> ions produced in the above electrochemical process are neutralized by photodetachment and added to the volume affected. The H atoms produced here are also part of the above excess production of H<sub>2</sub>O<sub>2</sub> by electrochemistry. In the steady state there is little change in the CO–CO<sub>2</sub> balance, as the excess CO is simply recycled into CO<sub>2</sub> that previously underwent triboelectric destruction. This would occur from a CO + OH reaction both in the affected volume and subsequently in the surface/subsurface upon the breakdown of H<sub>2</sub>O<sub>2</sub>.

The electrochemical production of peroxide can be so large that most of the peroxide would rapidly diffuse into the regolith where it could be sequestered for hundreds to millions of years depending on the depth of penetration, which can be several meters.<sup>9</sup> Laboratory experiments show that peroxide destroys organics quite efficiently.<sup>54,27</sup> In a generic sense, peroxide could also destroy simple organic molecules, such as methane. Observations indicate localized destruction and rapid temporal and seasonal changes of methane on Mars, implying a lifetime on the order of a less than a year to a few years instead of the photochemical lifetime of a few hundred years. As mentioned earlier, one needs to be cautious not to over interpret the marginal data available now, but if the above characteristics of methane distribution are confirmed by precise measurements in the future, the answer might lie in its destruction also by surface oxidants as the gas diffuses into the regolith from the atmosphere. It is important to note the boundaries and location of the Martian aeolian processes that are proposed for the excess oxidant production electrochemically also shift over time, which would result in a non uniform distribution of oxidants in the surface.

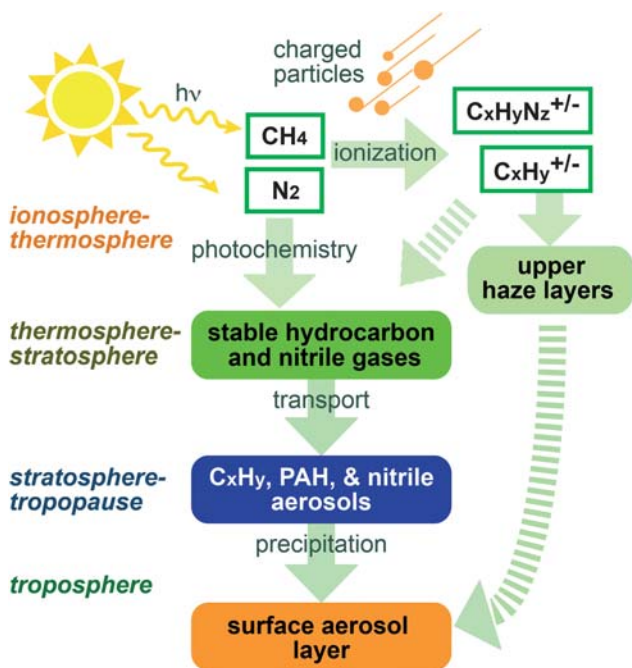
Direct oxidation of CH<sub>4</sub> by hydrogen peroxide is kinetically inhibited in the atmosphere of Mars,<sup>70</sup> and the encounter of CH<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> in the soil would not change that. However, mineral reactions in the soil are likely to change H<sub>2</sub>O<sub>2</sub> into much more potent oxidants,<sup>52,71</sup> such as superoxides (O<sub>2</sub><sup>-</sup>), peroxy (HO<sub>2</sub>), or hydroxyl (OH) radicals. It is these latter oxidants, produced from the mineral processing of H<sub>2</sub>O<sub>2</sub> in the regolith, that are likely to destroy simpler organics such as CH<sub>4</sub>, as well as more complex ones. The long lifetime of H<sub>2</sub>O<sub>2</sub> in the regolith is a major advantage for the mineral reactions to proceed to completion to above oxidants. Although peroxide was proposed to explain the absence of organics in the surface of Mars, it has not yet been detected in the surface because of the lack of appropriate instruments on spacecraft missions to Mars. On the other hand, another type of oxidant, perchlorate was detected in the north polar region of Mars with the Wet Chemistry Laboratory (WCL) on Phoenix Mars Lander.<sup>29</sup> No perchlorate data are available at other sites. WCL found 0.4–0.6 wt% of perchlorate salts (Mg(ClO<sub>4</sub>)<sub>2</sub>, NaClO<sub>4</sub>, and smaller amounts of Ca(ClO<sub>4</sub>)<sub>2</sub> and KClO<sub>4</sub>), with the maximum comparable to the largest deposits on Earth such as those in the perchlorate flats of the Atacama Desert in Chile. Unlike hydrogen peroxide, perchlorates are, paradoxically, highly stable, a characteristic that makes them suitable as an oxidizer in rocket fuel where controlled combustion, not explosion, is essential. This is most likely the reason why direct destruction of organics by perchlorates is not seen.<sup>27</sup> On the other hand, there is the possibility that they too could also change to more reactive forms by mineral processing in the Martian surface. Mineralogical and chemical processing of potential oxidants at Mars is an area in need of laboratory work.

## 5. Summary and concluding remarks

Trace constituent chemistry plays a critical role in planetary atmospheres, from the very formation of the atmospheres to their evolution over geologic time to their current structure, composition and stability. A minor component of the primordial atmosphere, ammonia, together with its trace products was responsible for the



atmosphere of nitrogen we have on Titan and the Earth today and for the nitrogen component of Venus and Mars atmospheres. Although biogenic methane dominates on Earth, either hydrogeochemical or biochemical or both processes could be at work on Mars. Trace gases produced in the photochemistry of the atmosphere as well as the primordial ones are believed to participate in the relevant processes to produce methane geologically or biochemically in the interior of Mars. Methane is not generated by photochemistry in the atmosphere of Mars. The origin of methane at Titan is not biogenic, and the relevant data sets all taken with the same instrument rule out widespread methanogenic life, at least in the Huygens landing site. Hydrogeochemical, primordial and endogenic processes could each contribute to the methane on Titan, but critical data are presently lacking to determine their relative contributions. Chemistry triggered by charged particles plays a crucial role in numerous planetary phenomena. On Mars, triboelectric processes in convective dust activity create negative ion pairs that are predicted to produce strong oxidants by electrochemistry, which would subsequently destroy the organics. Negative ion chemistry in the aeolian processes could have implications for other (non oxidant) chemistry also. Negative and positive ion chemistry in Titan's upper atmosphere is a major, perhaps even dominant, contributor to the moon's upper atmospheric haze layer/s as well as the total atmospheric aerosol. Although very massive (negative) ions to 10 000 Da are detected in the ionosphere, only simple hydrocarbons and nitriles have been found in the neutral atmosphere below. This is actually not completely surprising considering that the more complex organics are expected to be below the detection limit of current instruments on spacecraft and the ground. Moreover, with the exception of nitrogen, they would all condense in Titan's lower atmosphere and the tropopause (70 K, 100 mb, 45 km), resulting in a drastic reduction in their vapor phase concentrations. On the other hand, aerosols and haze produced in Titan's ionosphere and the neutral atmosphere fall on to the



**Fig. 6** Cartoon of the photochemical processes in the neutral and ionospheric regions of Titan, showing that all stable hydrocarbons, nitriles, aerosols and hazes either precipitate or sediment out of the atmosphere on to the surface of Titan.

surface, as illustrated in Fig. 6. In fact, the mass spectrum of the material evaporated from the surface after Huygens landed is extremely rich. Since the GCMS was designed as an atmospheric sampler, its mass range was limited to 140 Da and the instrument was not optimized for analyzing the surface material. Thus identification of the large mass peaks in the surface spectrum, many of which undoubtedly represent fractionation of molecules much heavier than 140 AMU, is presently not possible. Nevertheless the spectrum clearly demonstrates the presence of complex organic molecules in the surface, perhaps even prebiotic molecules, which began their journey from above but built up in far greater concentration at the surface over time. The secrets of Titan's atmosphere and the ionosphere lie in its surface!<sup>4</sup> Processing of the surface material by galactic cosmic rays (GCR) and impact gardening is a possibility that needs to be investigated carefully in the laboratory and by modeling. The GCRs could be important also in shaping the nitrile chemistry in the lower stratosphere where the GCRs reach their unit optical depth (e.g. ref. 69). The oxygen chemistry in Titan's atmosphere is puzzling. While various photochemical models predict detectable abundance of several molecules including aldehydes, it is surprising that other than the simple oxygen bearing molecules, H<sub>2</sub>O in the thermosphere and CO and CO<sub>2</sub> in the lower atmosphere and the surface, none other have yet been identified. Clearly, deficiencies exist in either modeling or the relevant laboratory and theoretical work. Great strides are being made recently in all areas of planetary chemistry, however, as is evident from papers in this *Faraday* volume. Studies that mimic as closely as possible the relevant environmental conditions of the atmosphere and ionosphere including temperature, pressure, bath gas, thermodynamic phase and conductivity, and, where applicable, the geochemical and mineralogical characteristics of the surface and the interior are most relevant and valuable to the interpretation of planetary and satellites observations.

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