The Chemical Origin and Evolution of Titan’s Volatiles

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Nitrogen: primordial, endogenic, photochemical
Methane: primordial, geological, biological
Trace volatiles: cycle of methane
Surface volatiles
What next?
$N_2$ origin

$NH_3$ primordial

$N_2$ by

impacts
photolysis
endogenic

$N_2$ primordial

trapped in planetesimals
N$_2$ trapped at Triton’s temperature (35 K)
$^{36}\text{Ar}/N_2$ Titan: $2.1 \times 10^{-7}$ \hspace{1em} solar: 0.11 \hspace{1em} Titan/Sun = $2 \times 10^{-6}$

(Niemann et al. 2005, 2010)
$N_2$ origin

$N_2$ primordial

NH$_3$ primordial

$N_2$ by

- impacts
- photolysis
- endogenic

trapped in planetesimals
Enceladus plume (%): H$_2$O 90, CO$_2$ 5, CO 4; NH$_3$ 0.8, CH$_4$ 0.9, CxHy, HCN ≤0.1
N$_2$ (%) : < 0.1 (INMS) < 0.3 (UVIS); 5-10 (CAPS) in magnetosphere

NH$_3$ dissociated in 500-800 K interior?
$N_2$ origin

$N_2$ primordial

NH$_3$ primordial

N$_2$ by

Impacts

Photolysis

Endogenic

Trapped in planetesimals
$N_2$ origin

$N_2$ primordial

$NH_3$ primordial

$N_2$ by

impacts  photolysis  endogenic

trapped in planetesimals
N$_2$ from NH$_3$ on primordial Titan
10 bars in 20-30 Myr

(Atreya et al. 1978; Atreya 1986; Adams and Atreya 2006; Adams 2006)
N\textsubscript{2} from comet impact dissociation of NH\textsubscript{3}: Are Titan’s nitrogen isotopes similar to Earth’s or comets?
nitrogen origin

• Cometary impact dissociation of NH\textsubscript{3} : *Unlikely for the bulk* of N\textsubscript{2}  
  ▪ Oxygen dilemma: excess CO produced, cannot be removed  
  ▪ Hydrogen dilemma: Excess (4 bars) H\textsubscript{2} produced, can’t be removed  
  ▪ Argon dilemma: \textsuperscript{36}Ar detected on Titan, but not in a single comet

*Nevertheless, it’s essential to determine* \textsuperscript{14}N/\textsuperscript{15}N in NH\textsubscript{3} and D/H in a wide variety of comets, and D/H in Titan’s H\textsubscript{2}O-ice to quantify the role of comets

• Direct delivery of N\textsubscript{2} in icy planetesimals (Owen, 1982) – *no* (\textsuperscript{36}Ar too low)  
• Endogenesis of NH\textsubscript{3} – *small contribution possible* (high T, N-isotopes?)

• Photolysis of NH\textsubscript{3} on primordial Titan (Atreya et al, 1978) – *most likely*  
  ▪ Nitrogen on Titan is secondary, as on Earth, Mars and Venus
methane controls nitrogen’s fate

On Titan, methane means “greenhouse”:
~100 K increase in stratosphere, due to hydrocarbon haze
~20 K increase in troposphere, due to CH\textsubscript{4}-N\textsubscript{2}, H\textsubscript{2}-N\textsubscript{2}, N\textsubscript{2}-N\textsubscript{2}
collision-induced opacity

Greenhouse (warming) critical to Titan’s N\textsubscript{2}:
\textit{no CH}_4 \rightarrow \textit{little to no N}_2;
\textit{N}_2 \textit{condenses and atmosphere collapses!}

Origin of Titan’s Methane:
Secondary, i.e. formed \textbf{on} Titan hydrogeochemically, or
Primordial, i.e. delivered \textbf{to} Titan directly as CH\textsubscript{4}, or
Biological, i.e. produced by methanogens
Titan’s methane: biogenic?

Essential for life: medium, nutrients & energy

- **Medium:** methane, not water, used as medium and solvent by Titan microbes (McKay & Smith, 2005; Schulze-Makuch & Grinspoon, 2005)
- **Nutrients:** Titanian microbes utilize H₂ and C₂H₂ as nutrients, and for
- **Energy:** C₂H₂ + 3H₂ → 2CH₄ (+334 kJ/mol, ok for microbial survival)
- **Methane** is released as a metabolic product (McKay & Smith, 2005)

**Caution...**

→ **Circular argument** for methane origin:
  CH₄ required to produce the nutrients, C₂H₂ and H₂

→ **No nutrient depletion** seen by GCMS:
  C₂H₂ present in surface, and H₂ uniformly mixed (1 Myr lifetime)

*Microorganisms do not produce Titan’s methane
However, life on the fringes is not ruled out*
H$_2$ uniformly mixed – no depletion

H$_2$ lifetime
1 million yrs

(Niemann et al., 2010)
C$_2$H$_2$ in Titan’s surface – lots of it
Titan’s methane secondary? clue from GCMS: Kr and Xe <10 ppbv

(Niemann et al., 2010)
**Abiotic** methane by serpentinization + F-T process:
liberate hydrogen, mix carbon, make methane on Earth, Mars, Titan

hydration of ultramafic silicates (olivine/pyroxene) produces serpentine, hydrogen, and methane

$$[[\text{Mg,Fe}]_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4]$$
serpentine

metal-catalyzed Fischer-Tropsch process

**Diagram:**
- Fe + H₂O → H₂
- H₂ + CO, CO₂, C → CH₄
**Abiotic** methane by **high** temperature serpentinization: 
*Black Smoker hydrothermal vents*

Juan De Fuca Ridge

- **depth**: 2222 m
- **exit temp**: 342°C
- **pressure**: 200 bar
- **chimney ht.**: 10 m

Mid Atlantic Ridge

- **temperature**: 300-500°C, sulfur-rich, highly acidic (~lemon juice)
*abiotic* methane by *low* temperature serpentinization:

*Lost City*

- 15 km from Mid-Atlantic Ridge
- 30-90 C (120 C peridotite)
- highly alkaline (~ammonia, milk of magnesia)
- little sulfur minerals
- 20 m high carbonate towers
Titan’s methane primordial? xenon and krypton hiding

• buried as clathrates below Titan’s ocean
  -destabilization? outgassing? $^{40}$Ar?

• in shallow subsurface clathrathes
  -destabilization? outgassing?

• trapped in aerosols (Jacovi, Bar-Nun)
  -surface degassing? selective?
  -lab conditions very different from Titan
    (CH$_4$ too low by $10^4$, UV too high…)
Methane’s fate - neutral photochemistry: hydrocarbons, nitriles, aerosols

Methane destroyed irreversibly in 10’s - 100 Myr

Ions

Neutrals

(Waite et al., 2007 INMS)
negative ions at Titan: CAPS/ELS

electron attachment:
\[ \text{HCN} + e \rightarrow \text{CN}^- + \text{H} \]

followed by,
dissociative attachment:
\[ \text{CN}^- + \text{HC}_3\text{N} \rightarrow \text{C}_3\text{N}^- + \text{HCN} \]

\[ \text{C}_5\text{N}^- \cdots \text{to } 10^4 \text{ Da?} \]

(similarly,
\[ \text{CH}_4 + e \rightarrow \text{CH}_3^- + \text{H}, \text{etc.} \]

(Vuitton et al., 2009,
Andrew Coates, 2009)
where does Titan’s methane go?

- \( \text{loss rate} \approx 1.3 \times 10^{10} \)

- \( \text{C}_2\text{H}_6 \)
  - Condensation
  - \( 5.3 \times 10^9 \) (40%)

- \( \text{Condensation of other Organics} \)
  - \( 3.6 \times 10^9 \) (30%)

- \( \text{Haze} \)
  - \( 1.2 \times 10^9 \) (10%)

- \( \text{CH}_4 \) Escape
  - \( 2.9 \times 10^9 \) (0-20%)

(in C atoms cm\(^{-2}\) s\(^{-1}\) normalized to the surface.
15% of total \( \text{CH}_4 \) destroyed in ionosphere)

Methane destroyed, *irreversibly*, in 10’s - 100 Myr

(Wilson & Atreya, 2009)
Volatile compounds evaporate from Titan’s surface at 146 K:

- **Methane (liq)**
  - +40% from evaporation
  - *Triple point 90.67 K*

- **Ethane (liq)**
  - 10x strato mole fraction
  - *Triplet point 90.3 K*

- **Acetylene (solid)**
  - >10x strato mole fraction

- **Cyanogen (solid)**
  - >100x strato mole fraction

- **Carbon dioxide (solid)**
  - >100x strato mole fraction

(Niemann et al. 2010)
Take Home

• *Nitrogen originated from*
  • ammonia photolysis – most likely
  • comet impacts and endogenesis less important

• *Methane originated from*
  • hydrogeochemical, primordial and endogenic processes, in TBD amounts
Methane cycles through
  - photochemical destruction in 10’s-100 Myr, and
  - replenishment, essential for sustaining $N_2$
  - billions of years of supply – no energy crisis!

Life as we don’t know it
  - can’t be ruled out, but perhaps on the fringes
  - prebiotic molecule formation quite likely
Surface composition provides a window into atmospheric processes
- GSFC Titan cryo chamber (M. Trainer)
- Simulation (S. Atreya, H. Niemann)

Haze and gas (suggest PANH, clusters, O-chem)
- Observations (CIRS, INMS, CAPS/ELS)
Surface is key to Titan’s mysteries!