Role of a global ocean on the formation and evolution of an atmosphere on early Titan

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June, 9th 2016
1. Introduction

**Titan:**

- its radius is 2575 km
- its density is 1880 kg.m$^{-3}$: Titan is composed ~50%~ of water and ~50% of silicates
- Titan possess an atmosphere twice as massive as the Earth’s atmosphere
- this atmosphere is mainly composed of N$_2$ (~98%) and CH$_4$ (~2%)
- the origin of Titan’s atmosphere is still undetermined
1. Introduction


- discovering of the formation of complex molecules in the upper atmosphere (Waite et al. 2007)
- discovering of the methane cycle at Titan’s surface, similar to the water cycle on Earth (Stofan et al. 2007, Rodriguez et al. 2009)
- first *in situ* measurements of Titan’s atmosphere by Huygens (e.g. Niemann et al. 2005, 2010)
1. Introduction

Methane is irreversibly lost and destroyed by photochemistry in the upper atmosphere

- methane lifetime in the atmosphere is approximately 20 - 30 Ma (Griffith et al. 2013)
- the atmospheric $^{12}\text{C}/^{13}\text{C} (\text{CH}_4) = 91.1$ is close to the solar ratio (89) => methane is probably primordial and was recently injected in the atmosphere (<1Ga, Mandt et al. 2012)
- no surface methane reservoir was observed, inducing either a degassing from the interior of the satellite ($^{40}\text{Ar}=74-78$ ppb, origin: radioactive decay of $^{40}\text{K}$) or an existence of a subsurface reservoir
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Liquid methane in the porosity of the crust (Kossacki et Lorenz 1996, Hirai et al. 2001)

Clathrates of methane (Tobie et al. 2006)
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How methane-rich clathrates could integrate Titan’s icy crust?
1. Introduction

Nitrogen is weakly affected by the photochemistry and the atmospheric escape

- the ratio $^{36}\text{Ar}/\text{N}_2 = 2.7 \times 10^{-7}$ is $3 \times 10^5$ smaller than the solar value. $^{36}\text{Ar}$ and $\text{N}_2$ are incorporated in a fixed proportion in Titan’s building blocs:

![Graph showing mass comparison between $\text{N}_2$ and $^{36}\text{Ar}$]

Present-day $\text{N}_2$: $9 \times 10^{18}$ kg

If $\text{N}_2$ primordial: $7 \times 10^{17}$ kg

Present-day mass: $3.5 \times 10^{12}$ kg
1. Introduction

Nitrogen is weakly affected by the photochemistry and the atmospheric escape

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- the atmospheric $^{14}\text{N}/^{15}\text{N} (N_2) = 167$, close to the ratio measured in NH$_2$ radicals in comets (Rousselot et al. 2014, Shinnaka et al. 2014) and $^{14}\text{N}/^{15}\text{N}$ has probably not varied during Titan’s history (Mandt et al 2014)

At the time of Titan’s formation, nitrogen was probably incorporated as NH$_3$ in the satellite
1. Introduction

Possible conversion mechanisms of NH$_3$ into N$_2$:

1) Conversion by photochemistry (Atreya et al. 1978):
   - atmosphere saturated in NH$_3$
   - temperature > 150 K

2) Conversion by impact in the atmosphere (McKay et al. 1988, Ishimaru et al. 2011):
   - atmosphere dominated by CO$_2$ and NH$_3$

3) Conversion by impact in Titan's icy crust (Sekine et al. 2011):
   - NH$_3$-enriched icy crust
   - 1-5% of NH$_3$ expected in Titan's crust
   - high-velocity impacts (>3.5 km.s$^{-1}$)

4) Endogenic conversion (e.g. Glein et al. 2009):
   - water-silicate contact
   - temperature >400 K
1. Introduction

Formation of Titan

- warm surface because of the impact heating
- cold, icy surface
- high-velocity impacts

Late Heavy Bombardment (LHB)

Formation of Titan

- warm surface because of the impact heating
- cold, icy surface
- high-velocity impacts

Impact rate

Conversion by impact in the atmosphere

Photochemical conversion

Conversion by impact in Titan's crust

Endogenic conversion

adapted from Morbidelli et al. (2012)
1. Introduction

The efficiency of the NH$_3$ into N$_2$ conversion in the atmosphere is determined by the atmospheric composition.

Composition of the atmosphere is controlled by the dissolution of gases in water.

We propose to model the chemical exchanges between an ocean and an atmosphere, which was never done before for primitive Titan.
1. Introduction

- modeling of the chemical exchanges between an ocean and an atmosphere

- we account for:
  - \( \text{NH}_3 \) as a main carrier of nitrogen
  - \( \text{CH}_4 \) to investigate its fate for early Titan
  - \( \text{CO}_2 \) as one of the main volatiles possibly accreted in Titan (Tobie et al. 2012)

- we account for the formation of a \( \text{CH}_4+\text{CO}_2 \) clathrate crust
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

For an element $i$, in thermodynamical equilibrium in a liquid and a vapor phases:

\[ y_i P = H_{solvant,i} x_i \]

- no interaction between dissolved chemical species: only 2 compounds
- valid only for low molar fractions $x_i$
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

For an element $i$, in thermodynamical equilibrium in a liquid and a vapor phases:

\[
\frac{f_i^g}{f_i^L} = \frac{\phi_i}{L_i} P = \gamma_i x_i f_i^0
\]

**Fugacity coefficient:**
Non-ideal behavior of the gas, Peng-Robinson equation of state

- used successfully for vapor mixtures that contain water (Englezos, 1993; Pazuki et al. 2006)

**Activity coefficient:**
Non-ideal behavior of the dissolved species, Universal quasi-chemical model (UNIQUAC)

- reproduce the vapor-liquid equilibrium of NH$_3$, CO$_2$ and H$_2$O (Thomsen et Rasmussen 1999, Darde et al. 2012)
- UNIQUAC could not be used for CH$_4$: we used Henry’s law instead

**Reference fugacity:**
is fixed by the choice of a model of the activity coefficient

- for the solvent it is the saturation vapor pressure
- for the dissolved species, it is their Henry’s constant
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

For CO$_2$-NH$_3$-H$_2$O system:

Prediction of the model, that account only for the vapor-liquid equilibrium:
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

For CO$_2$-NH$_3$-H$_2$O system:

\[
\begin{align*}
\text{GAS} & \quad \text{LIQUID} \\
\text{CO}_2 & \quad \text{H}_2\text{O} \\
\text{NH}_3 & \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\end{align*}
\]

Vapor-liquid equilibrium

\[
\begin{align*}
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{NH}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \\
\text{HCO}_3^- + \text{NH}_3 & \rightleftharpoons \text{NH}_2\text{COO}^- + \text{H}_2\text{O} \\
\end{align*}
\]

Chemical equilibrium

Prediction of the model, that account only for the vapor-liquid equilibrium:

A. $T=333.15$ K

B. $T=333.15$ K

~100 bar

~1-3 bar
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

Comparison of the model to the experimental data for T=60°C:

- chemical interactions in water considerably increase the solubility of CO₂ and NH₃ in liquid water
- our model reproduce accurately (within 10%) the CO₂ and NH₃ partial pressures
- a precipitation of a carbon-rich salts is observed for high NH₃ and CO₂ concentrations
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

Summary for the CO\textsubscript{2}-NH\textsubscript{3}-H\textsubscript{2}O system:

- NH\textsubscript{3} partial pressure remains low and decreases with the increasing CO\textsubscript{2} concentration.
- CO\textsubscript{2} d partial pressure depends on the relative concentrations of CO\textsubscript{2} and NH\textsubscript{3}:
  - if $m_{\text{CO2}}/m_{\text{NH3}} < 1$ then $P_{\text{CO2}}$ remains low
  - if $m_{\text{CO2}}/m_{\text{NH3}} > 1$ then $P_{\text{CO2}}$ increases with $m_{\text{CO2}}$
2. Role of a global ocean on the atmospheres of water-rich bodies

2.2 Vapor-liquid equilibrium model in planetary context:

- melt fraction of primitive Titan is still poorly constrained. Here we consider $x_{\text{melt}}=50\%$
2. Role of a global ocean on the atmospheres of water-rich bodies

2.3 Size and chemical composition of the atmospheres for the CO₂-NH₃-H₂O system

- if \( m_{\text{CO}_2}/m_{\text{NH}_3} < 1 \), the atmosphere is tenuous and the main compound of the atmosphere is water;

- if \( m_{\text{CO}_2}/m_{\text{NH}_3} > 1 \), CO₂ the size of the atmosphere increases because the CO₂ partial pressure rises. CO₂ become the main atmospheric compound;

- NH₃ atmospheric abundance decreases with the increasing CO₂ concentration.
2. Role of a global ocean on the atmospheres of water-rich bodies

2.3 Size and chemical composition of the atmospheres for the CO$_2$-NH$_3$-H$_2$O system

- NH$_3$ influence considerably the abundance of CO$_2$ in atmospheres of early Titan

![Graph showing the evolution of conversion types over time.](image)

- Photochemical conversion
- Conversion by impact in the atmosphere
- Conversion by impact in Titan's crust
- Endogenic conversion

adapted from Morbidelli et al. (2012)

are favorable for low CO$_2$ / NH$_3$ concentration ratio in Titan's ocean+atmosphere

= NH$_3$ dominant compound
2. Role of a global ocean on the atmospheres of water-rich bodies
2.4 Formation of clathrates at the surface of primitive Titan

- we add the dissolution of CH$_4$ in water to the previous model using the Henry’s law, because the necessary experimental data for UNIQUAC is not available

- we observe the formation of CH$_4$-CO$_2$ clathrate hydrates at Titan’s surface

- clathrate hydrate are commonly observed on Earth (e.g. gas pipelines) and forms easily at low temperatures, when an appropriate gas is in contact with water and the pressure is high enough
2. Role of a global ocean on the atmospheres of water-rich bodies
2.4 Formation of clathrates at the surface of primitive Titan

- no interaction of (NH$_3$, CO$_2$) and CH$_4$ in the liquid, therefore the results obtained for the previous ternary system are also valuable here

- if m$_{CO2}$/m$_{NH3}$ < 1 CH$_4$ is the main compound trapped in clathrates

- if m$_{CO2}$/m$_{NH3}$ > 3 CO$_2$ is the main compound trapped in clathrates
2. Role of a global ocean on the atmospheres of water-rich bodies

2.4 Formation of clathrates at the surface of primitive Titan

- if CH$_4$ is the main compound trapped in clathrates, clathrates form a crust at Titan’s surface
- if CO$_2$ is the main compound trapped in clathrates, the clathrates that form at Titan’s surface are denser than water
we observe a formation of a clathrate crust at Titan’s surface only when NH$_3$ concentration is higher than CO$_2$ concentration in Titan’s building blocks (or Titan’s ocean+atmosphere).
3. Discussion

- cometary abundances and Enceladus plume abundances indicate us that CO₂ was probably the main compounds in Titan’s building blocks

- lead to a low abundance of NH₃ in the atmosphere and therefore to an inefficient the NH₃ into N₂ conversion in the atmosphere

- lead to a formation of CO₂-rich, dense clathrates - no clathrate CH₄-rich crust at Titan’s surface
3. Discussion

- cometary abundances and Enceladus plume abundances indicate us that CO$_2$ was probably the main compounds in Titan’s building blocks.

- however, it is still unclear what fraction of volatile compounds in comets was lost or modified during the accretion processes.

- the volatile inventory in Enceladus may have been re-processed due to aqueous alteration processes.

figure from Tobie et al. (2014)
3. Discussion

Evolution of a CO$_2$-CH$_4$ atmosphere:

- CH$_4$ is rapidly lost by photochemistry
- when the surface temperature is low enough, CO$_2$ condenses at Titan’s surface
- for the case $m_{\text{CO}_2}/m_{\text{NH}_3} = 3$, ~10 bar of CO$_2$ in the atmosphere, the condensed CO$_2$ forms a ~500 m layer of ice and could influence the dynamic of Titan’s crust during all its history
4. General conclusion

- chemical interactions of CO$_2$ and NH$_3$ in water allow an efficient dissolution of both compounds in water

- atmospheric abundances of both CO$_2$ and NH$_3$ depend on their relative abundances in atmosphere+ocean system

- efficient conversion of NH$_3$ into N$_2$ in Titan’s primitive atmosphere is possible only when NH$_3$ is the main compound relative to CO$_2$ in ocean+atmosphere system

- the same constraint applies for the formation of the clathrate crust enriched in CH$_4$ at Titan’s surface
5. Perspectives:

Use an atmospheric model to account for the radiative equilibrium: explore the lifetime of the liquid water at the surface of the planetary bodies

Chemical exchanges between the ocean and the atmosphere

Explore the influence of water-rock interactions on the atmospheric composition: water-rock interactions buffer the pH of the ocean, which could influence the solubility of all volatile species ...

Add new chemical compounds to the solubility model: H$_2$S, CH$_3$OH ... are also abundant in comets and partially dissociate in water