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

Nadejda Marounina, Olivier Grasset, Gabriel Tobie and Sabrina Carpy

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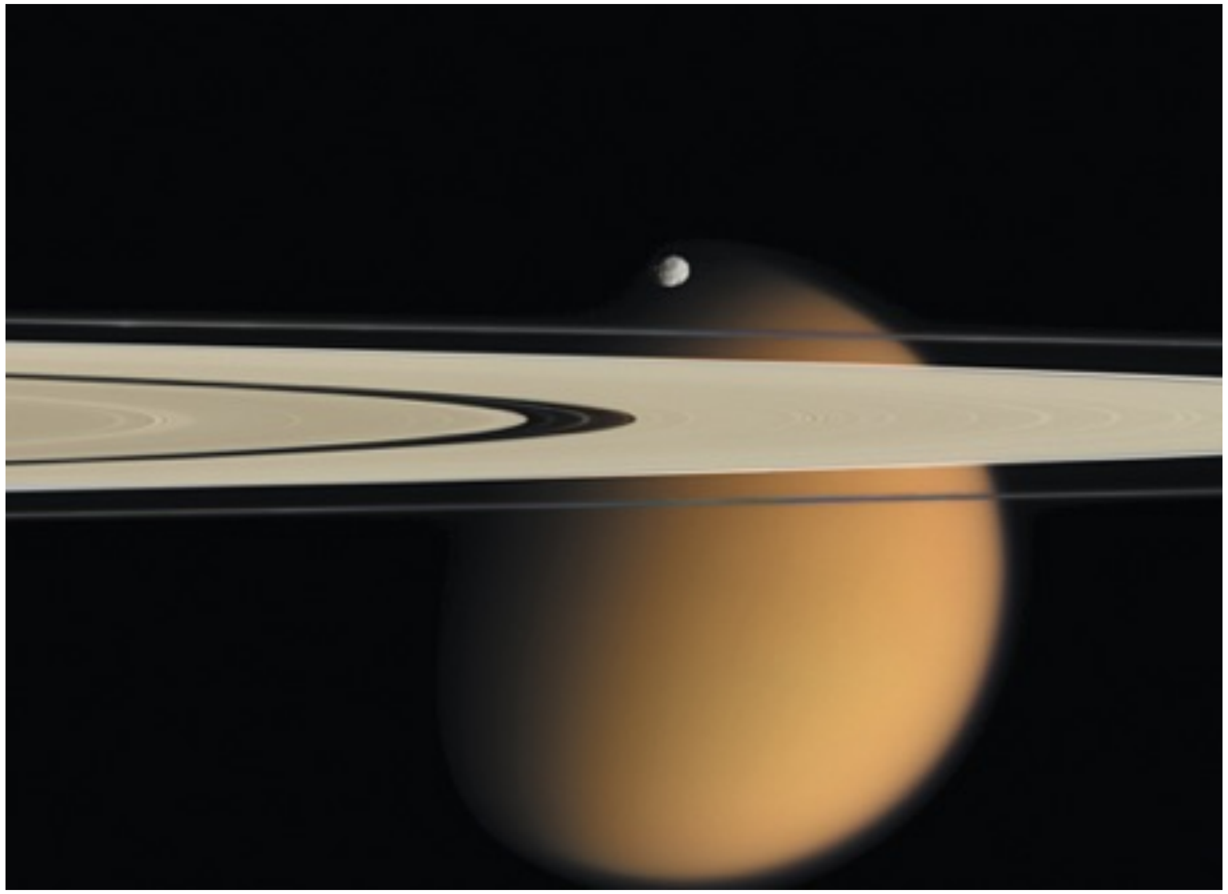
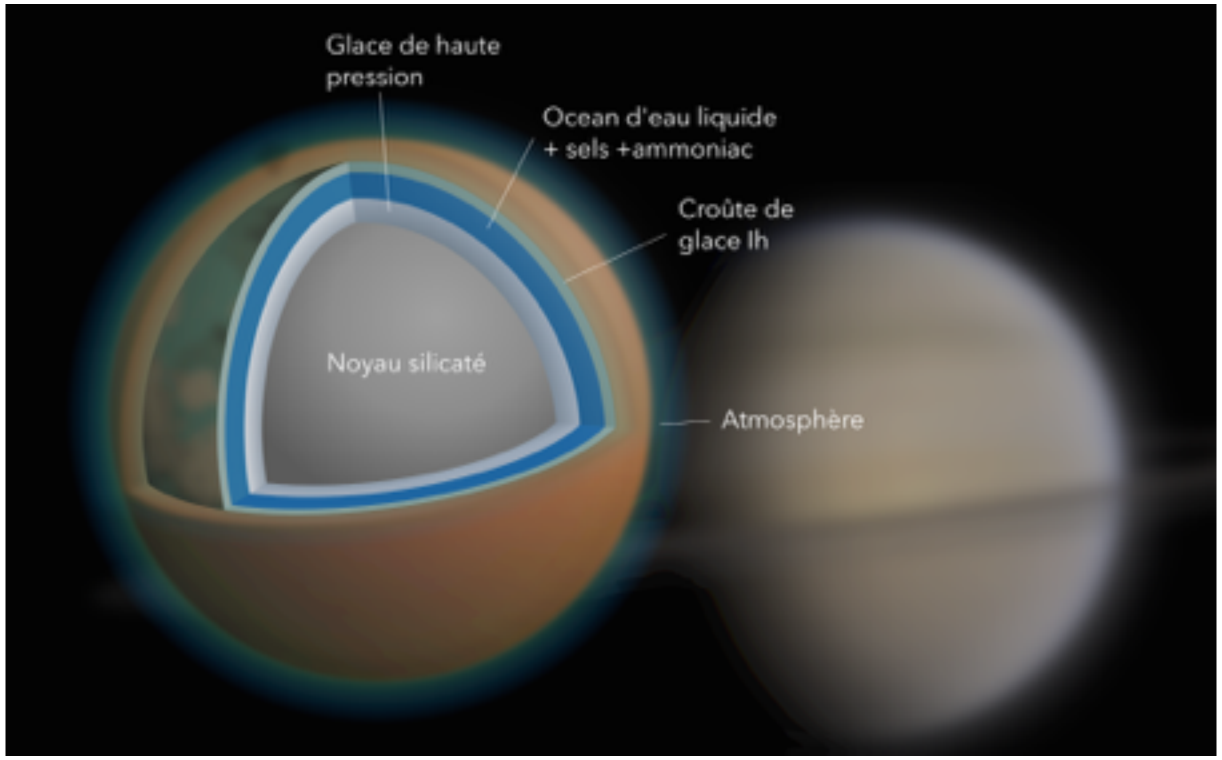
1. Introduction

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**

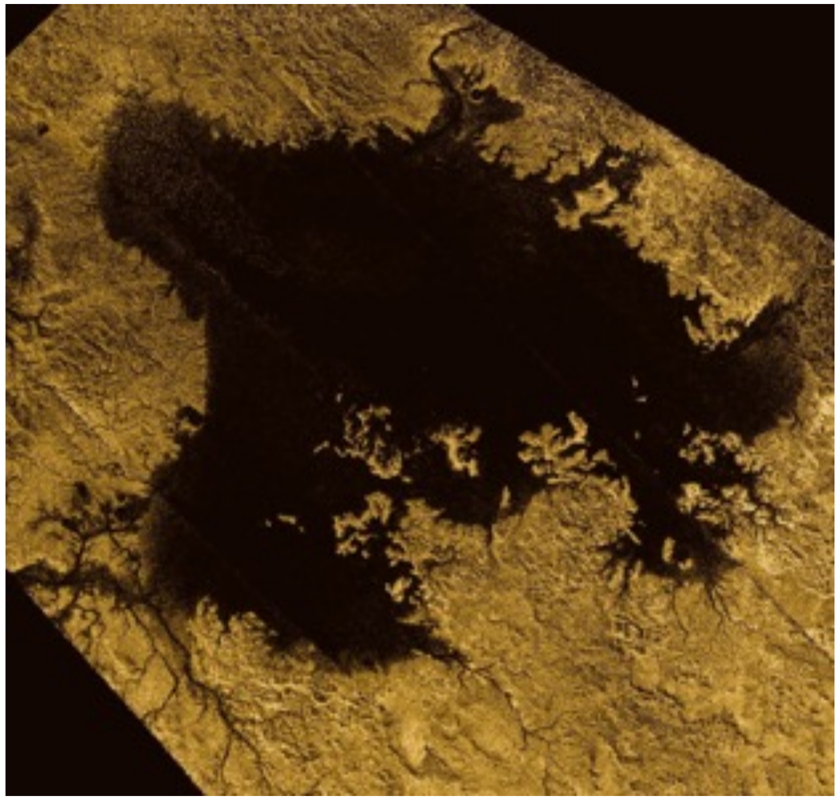




1. Introduction

Cassini-Huygens mission arrived in the system of Saturn in 2004, and Huygens probe landed at Titan's surface in January, 2005.

- 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 $^{12}C/^{13}C\ (CH_4) = 91.1$ 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}Ar=74-78 ppb**, origin: radioactive decay of ^{40}K) or an existence of a subsurface reservoir

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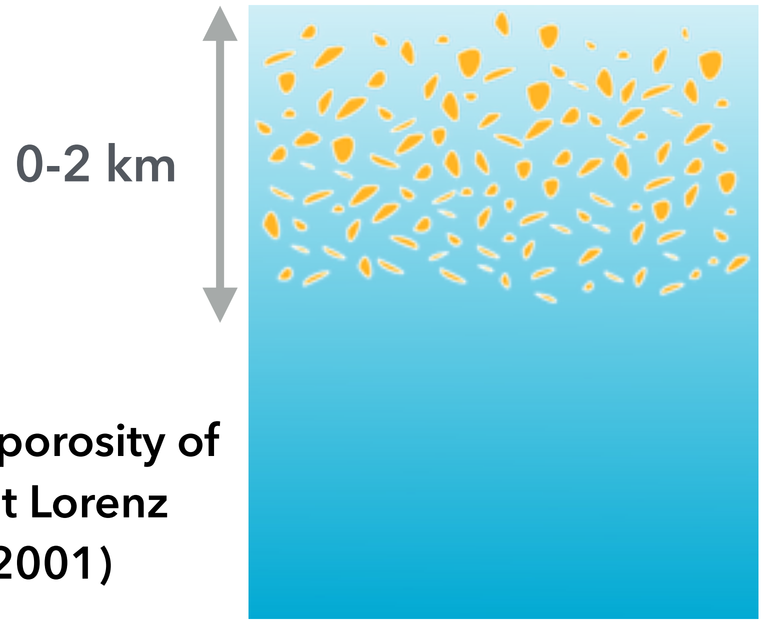
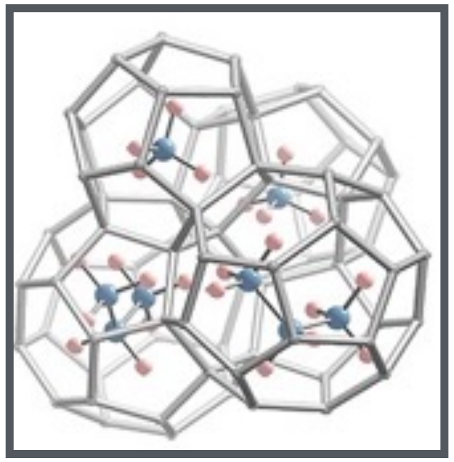
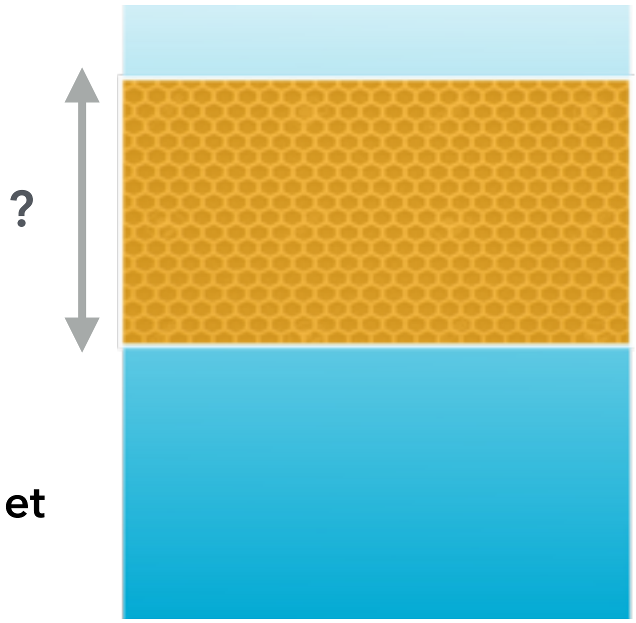


Liquid methane in the porosity of the crust (Kossacki et Lorenz 1996, Hirai et al. 2001)



Clathrates of methane (Tobie et al. 2006)



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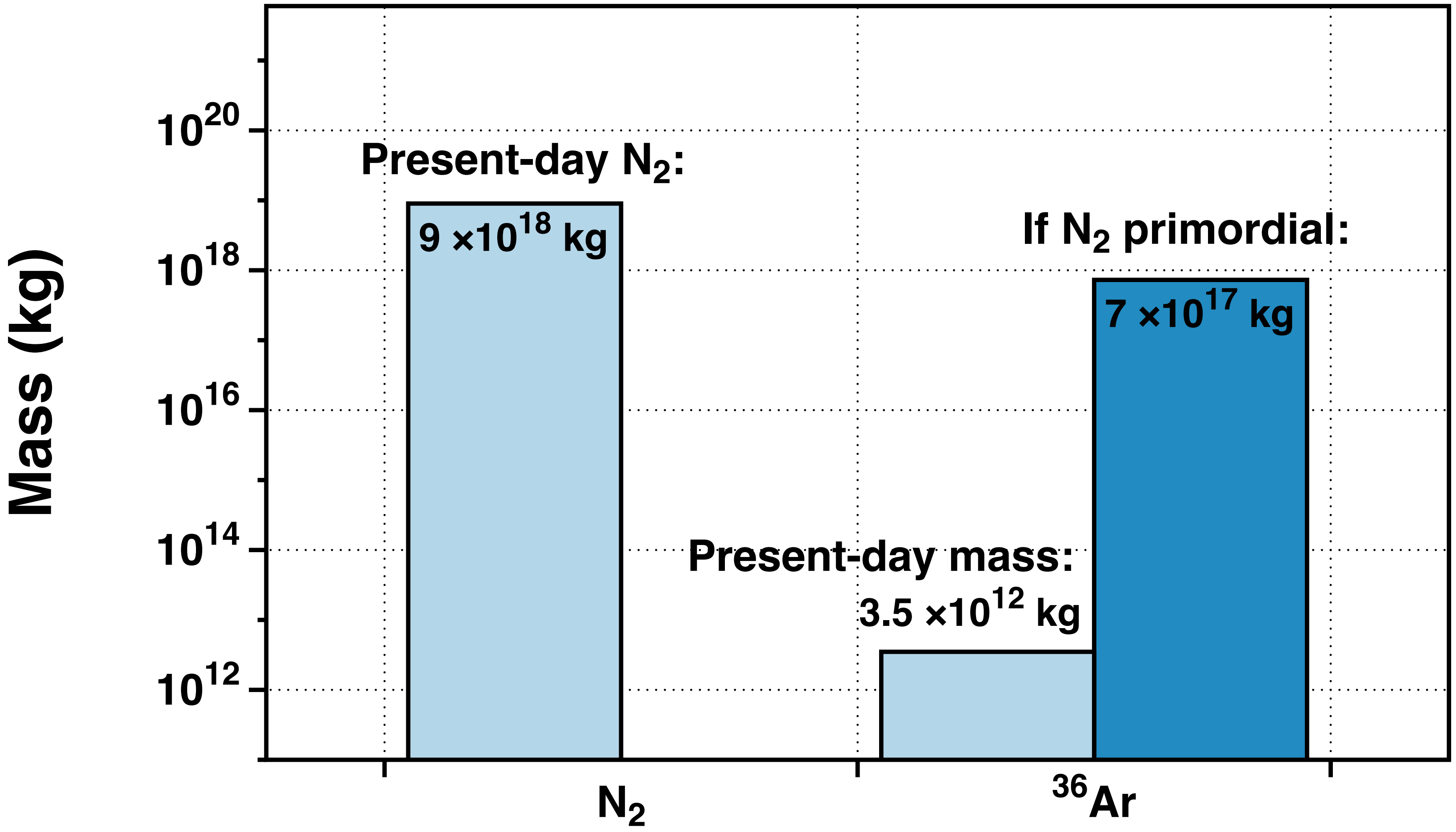
How methane-rich clathrates could integrate Titan's icy crust ?

Nitrogen is weakly affected by the photochemistry and the atmospheric escape

- the ratio **$^{36}Ar/N_2$ = 2.7x10^{-7}** is 3x10^{5} smaller than the solar value. ^{36}Ar and N_2 are incorporated in a fixed proportion in Titan's building blocs:



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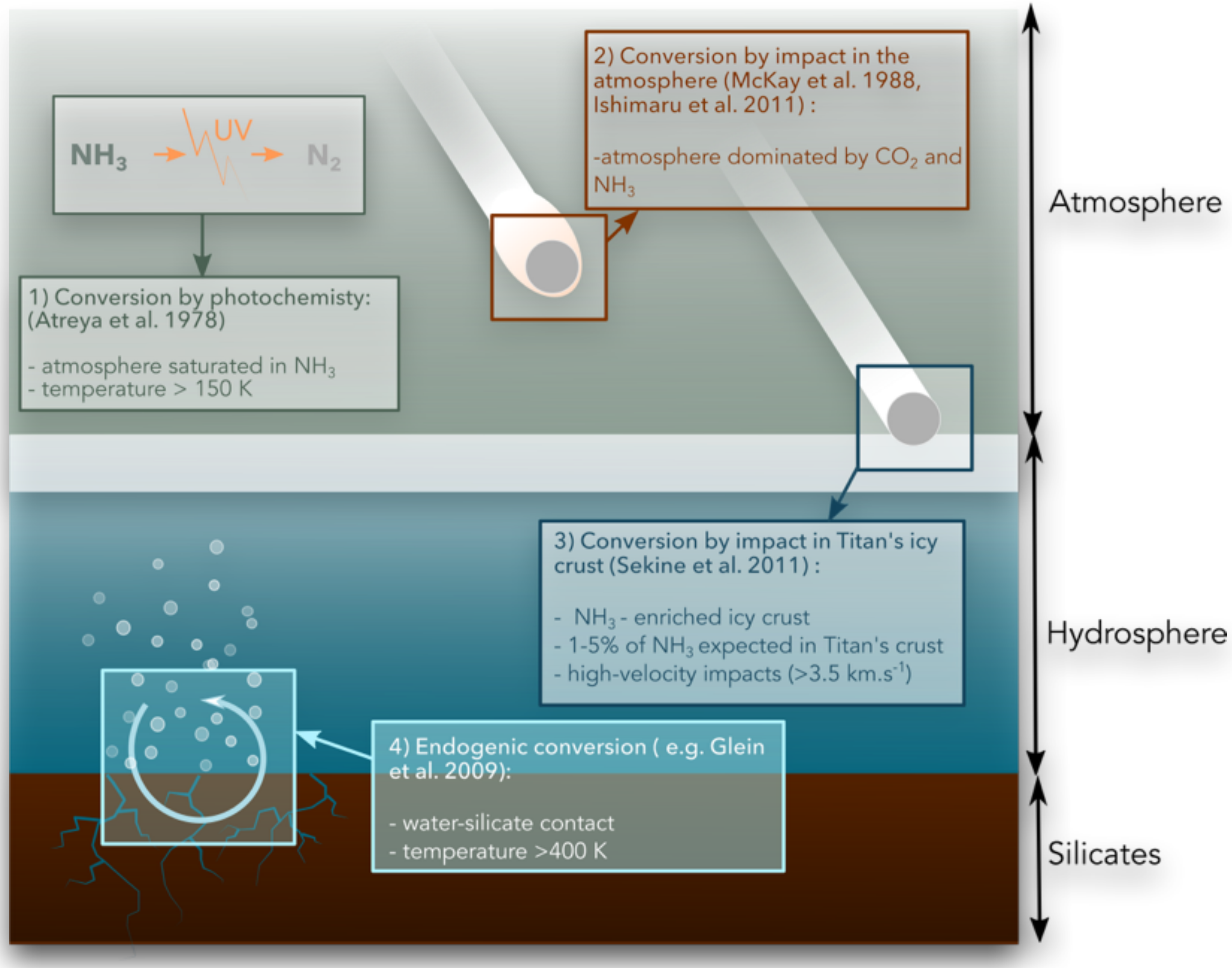
- the atmospheric $^{14}N/^{15}N$ (N_2) = 167, close to the ratio measured in NH_2 radicals in comets (Rousselot et al. 2014, Shinnaka et al. 2014) and $^{14}N/^{15}N$ has probably not varied during Titan's history (Mandt et al 2014)

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 photochemisty: (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

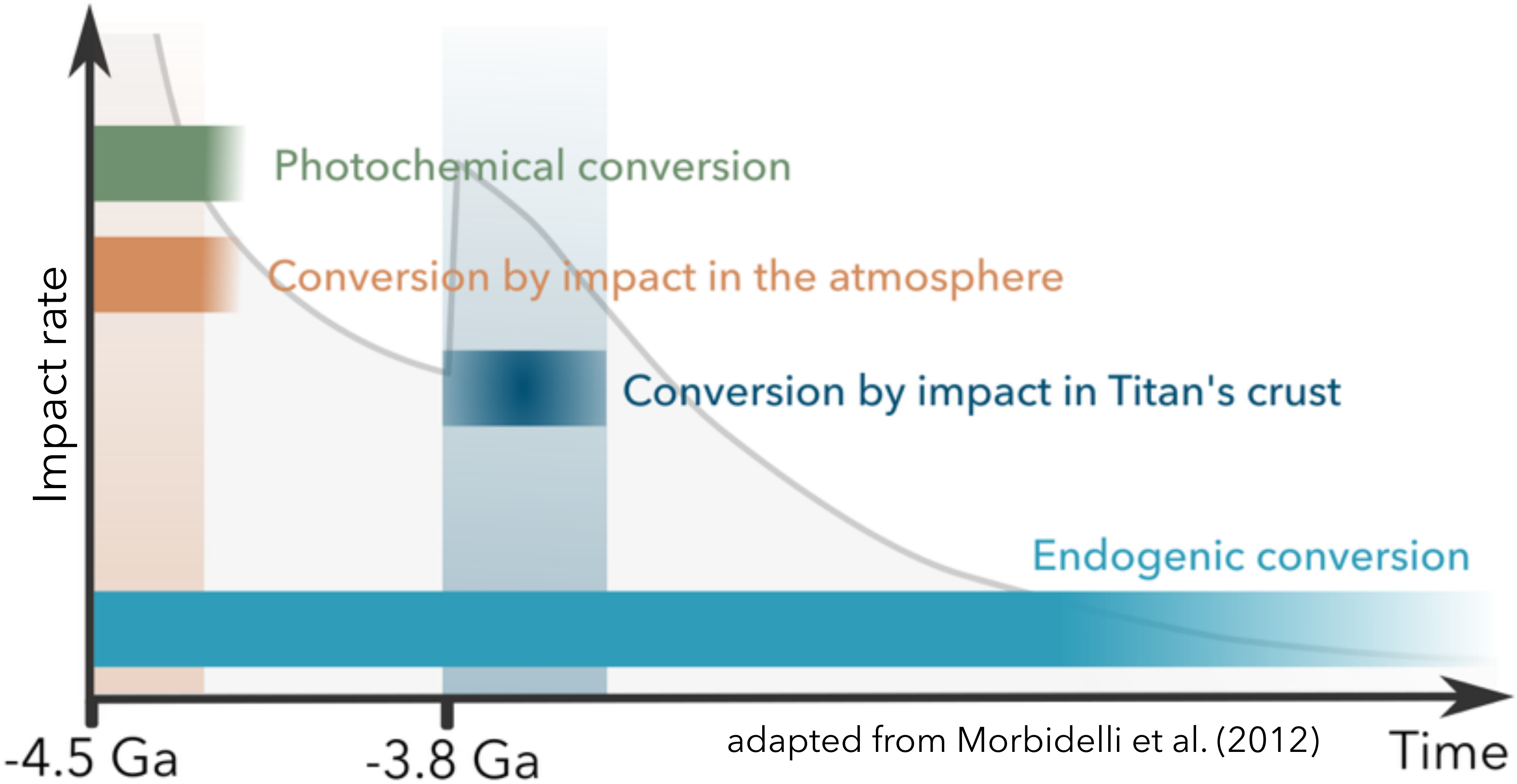
3) Conversion by impact in Titan's icy crust (Sekine et al. 2011) :

- 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



adapted from Morbidelli et al. (2012)

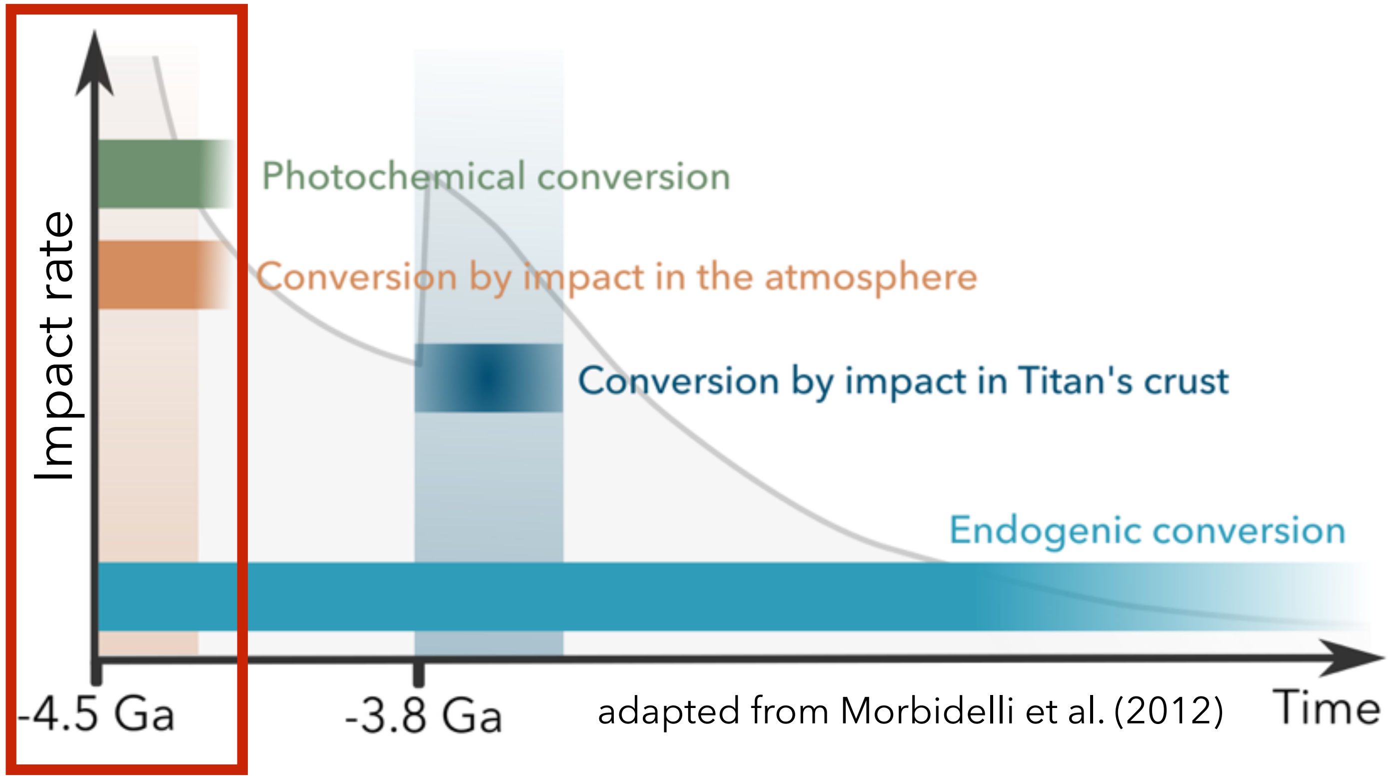
Formation of Titan

- warm surface because of the impact heating

Late Heavy Bombardment (LHB)

- cold, icy surface
- high-velocity impacts

1. Introduction



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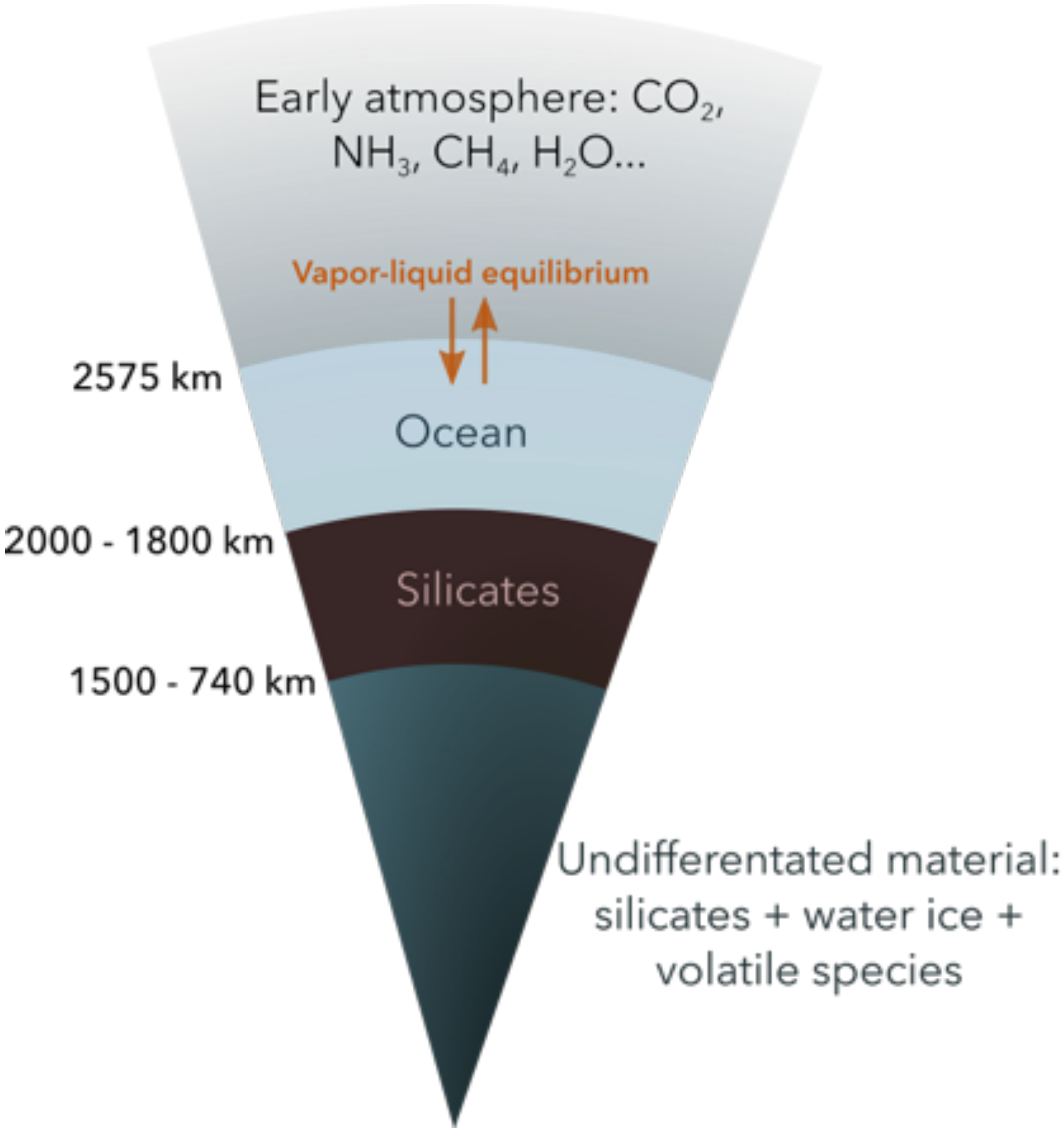


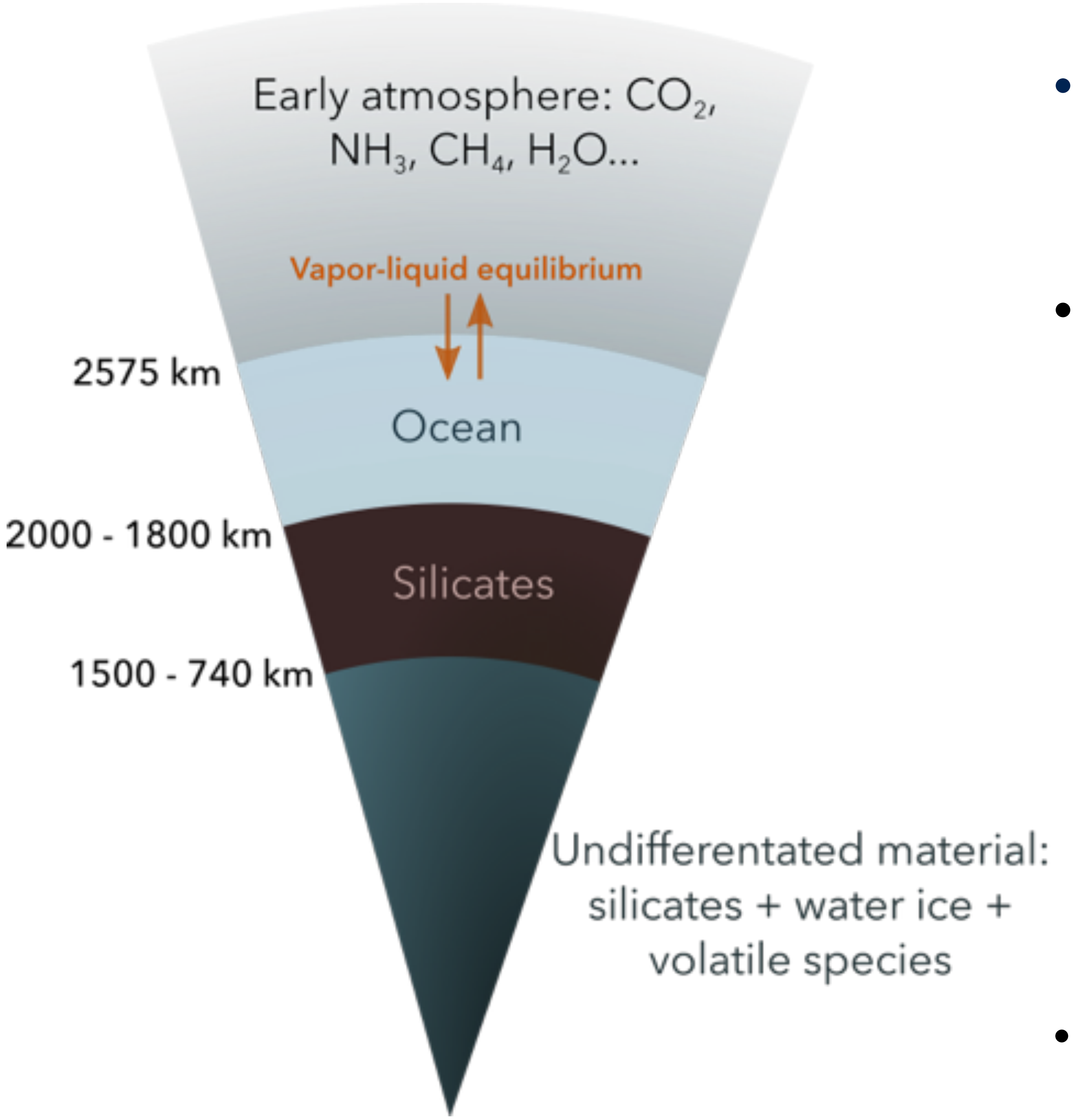
The efficiency of the NH_3 into N_2 conversion in the atmosphere is determined by the atmospheric composition

Internal structure of primitive Titan (from Lunine and Stevenson 1987)

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:
  - **NH_3** as a main carrier of nitrogen
  - **CH_4** to investigate its fate for early Titan
  - **CO_2** as one of the main volatiles possibly accreted in Titan (Tobie et al. 2012)

- we account for the formation of a CH_4+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:

$$f_i^g = f_i^L$$

$$\boxed{y_i \ P} = \boxed{H_{solvant,i} \ x_i}$$

Ideal gas

Henry's law

- no interaction between dissolved chemical species: only 2 compounds
- valid only for low molar fractions x_i

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$$f_i^g = f_i^L$$

$$\phi_i \; y_i \; P \; = \; \gamma_i \; x_i \; f_i^0$$

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_2O (Thomsen et Rasmussen 1999, Darde et al. 2012)
- UNIQUAC could not be used for CH_4: we used Henry's law instead

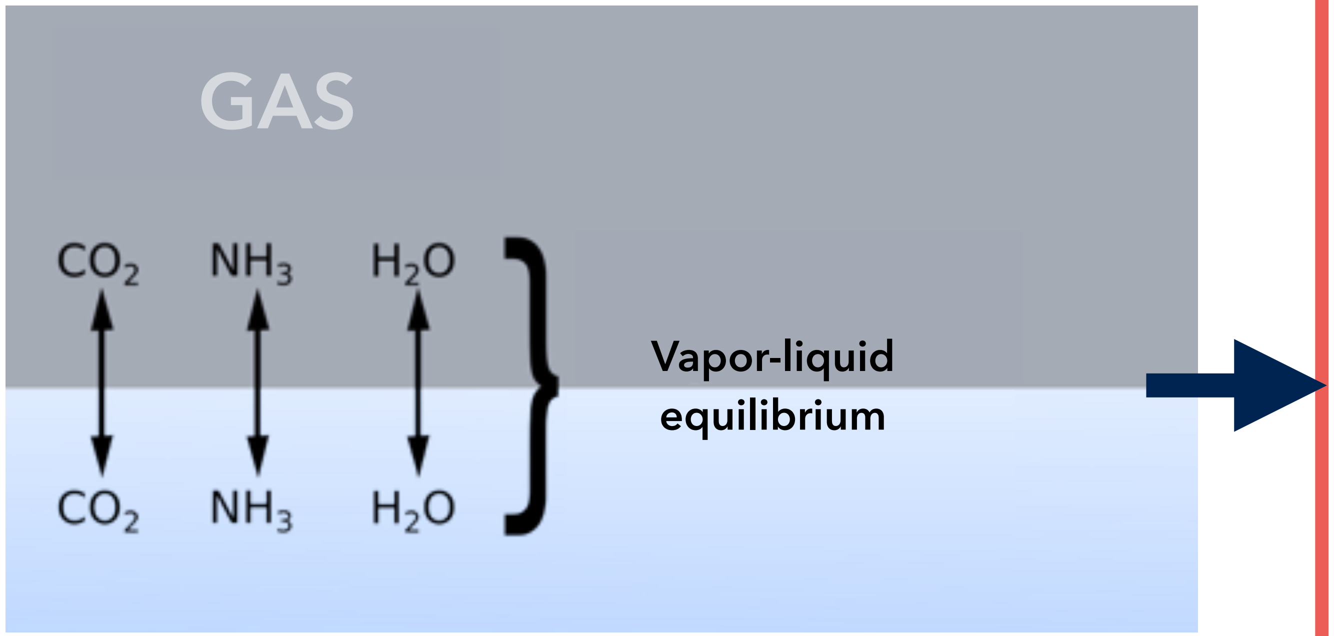
Reference fugacity:
is fixed by the choice of a model of the activity coefficient

- for the solvent it is the saturation vapor pressure
- for the dissolved species, it is their Henry's constant

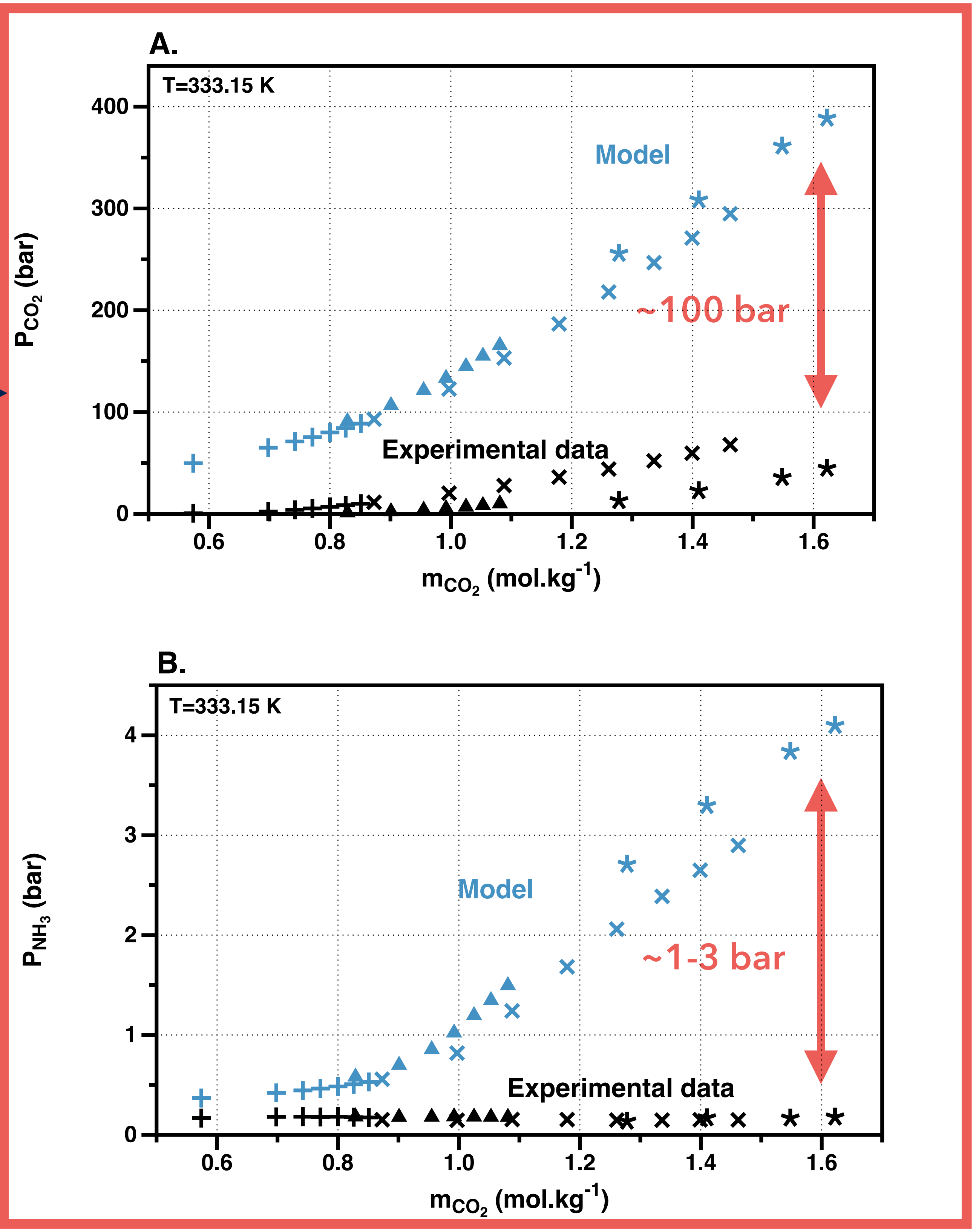
2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

For CO_2-NH_3-H_2O 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

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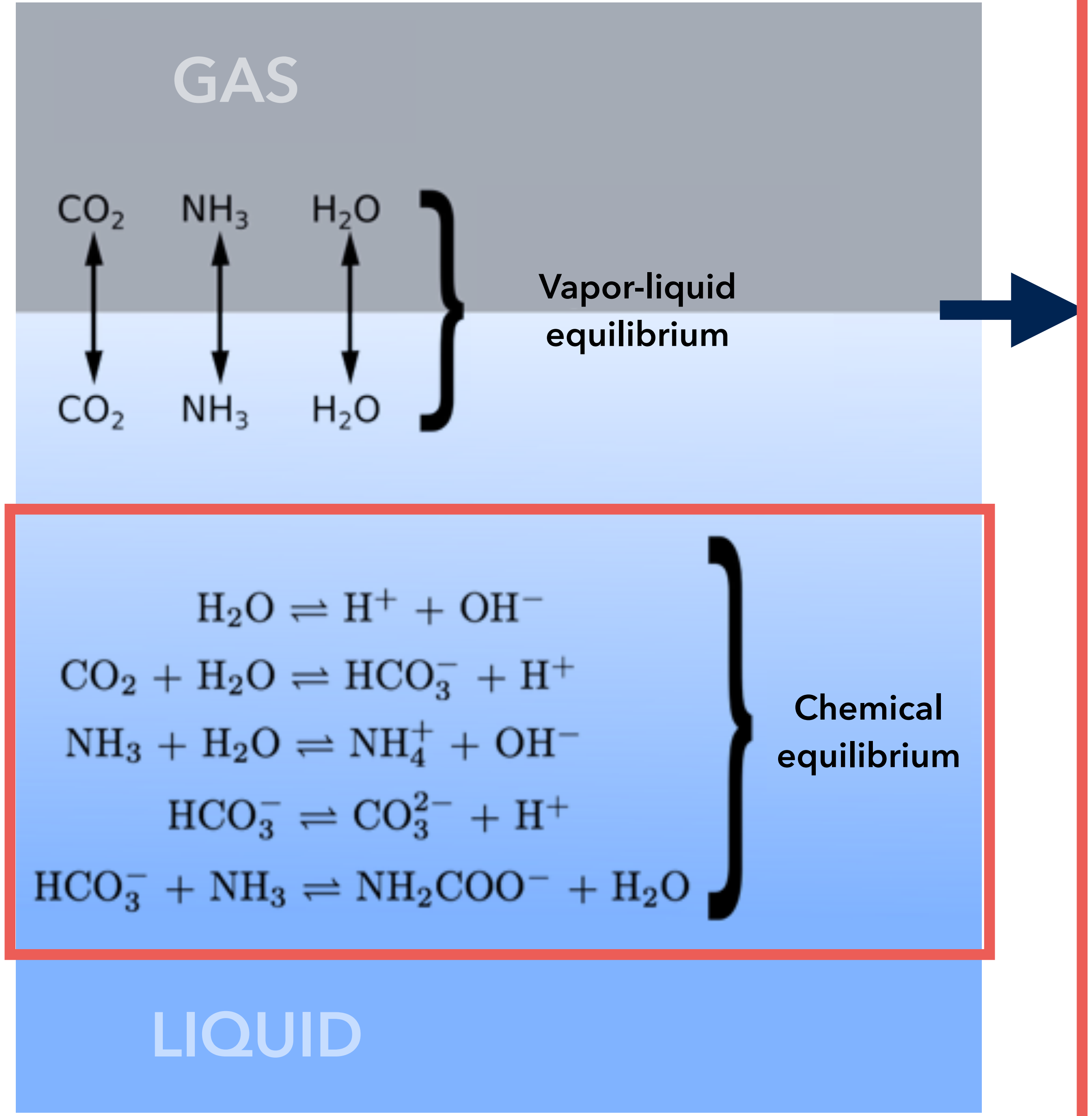
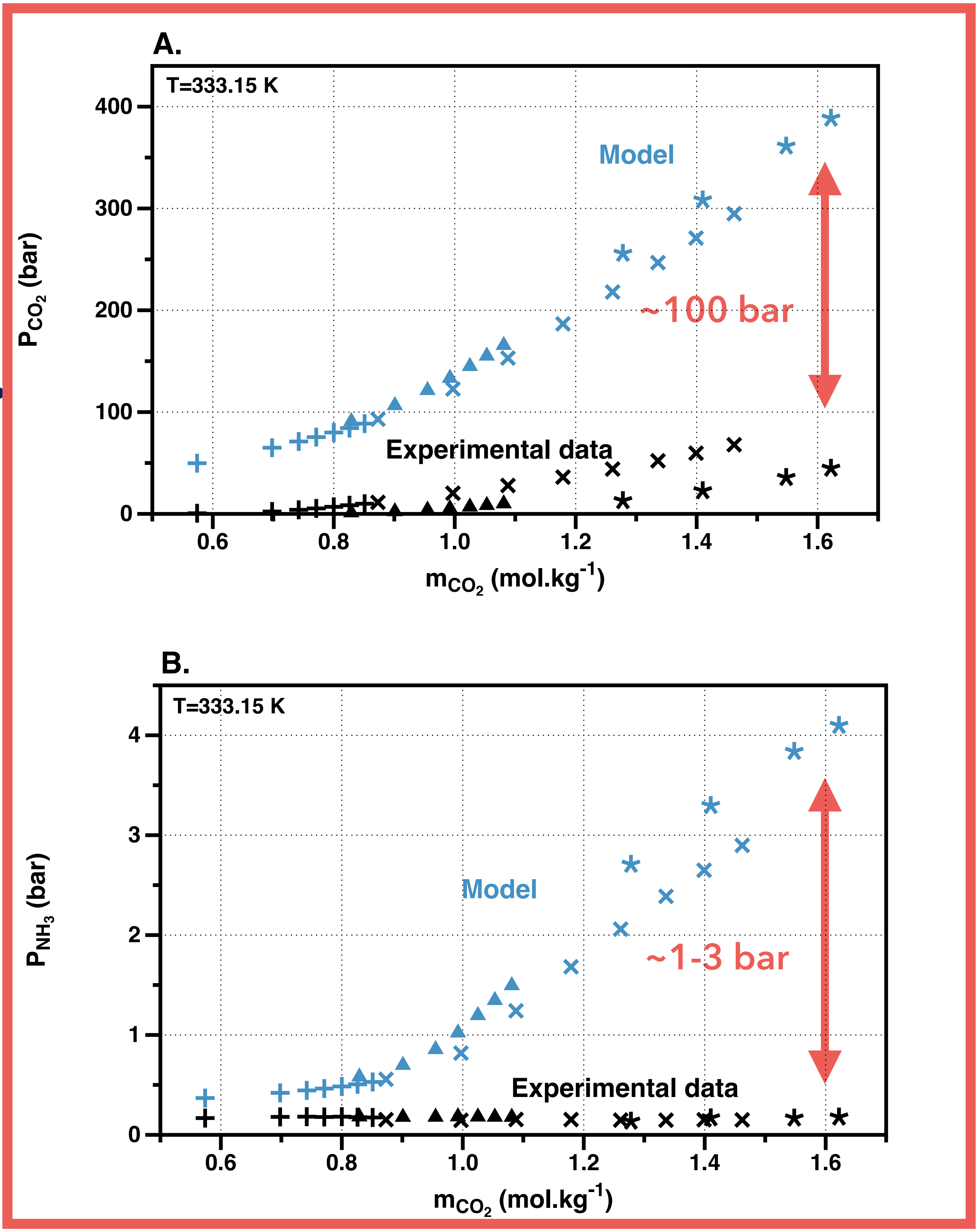


Vapor-liquid equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$
$$HCO_3^- + NH_3 \rightleftharpoons NH_2COO^- + H_2O$$

Chemical equilibrium

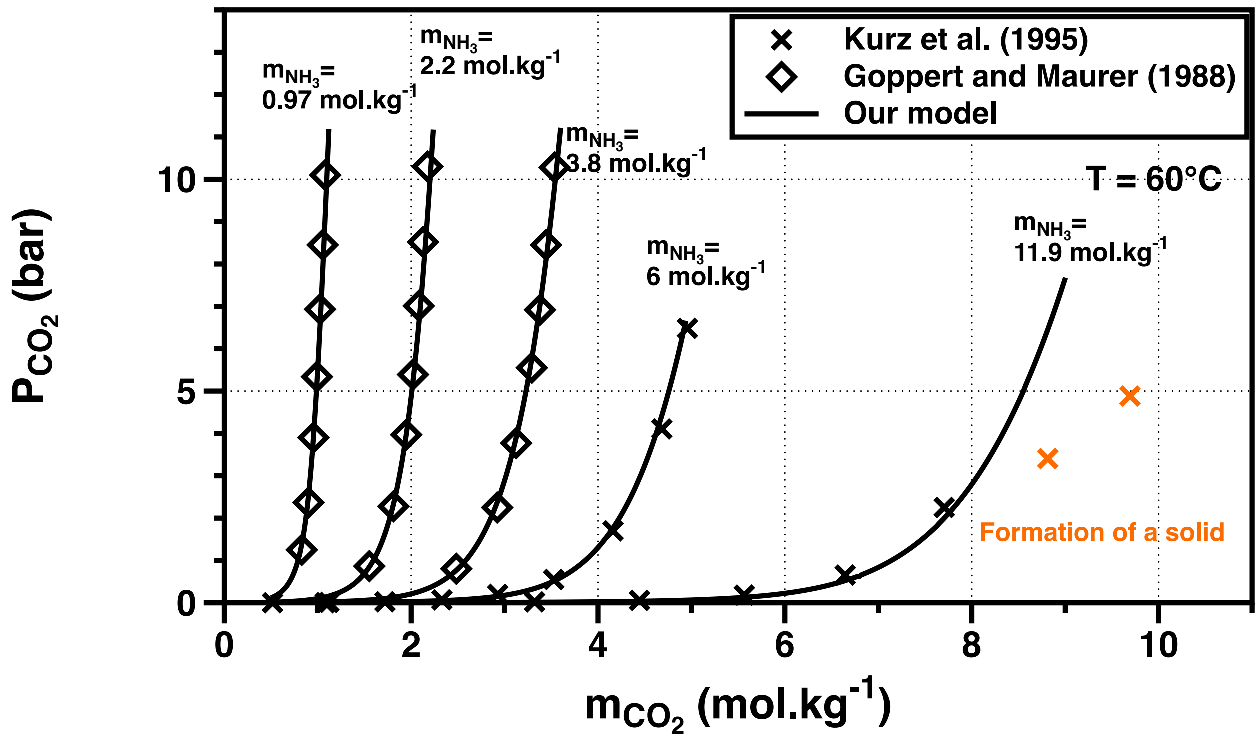
Prediction of the model, that account only for the vapor-liquid equilibrium:

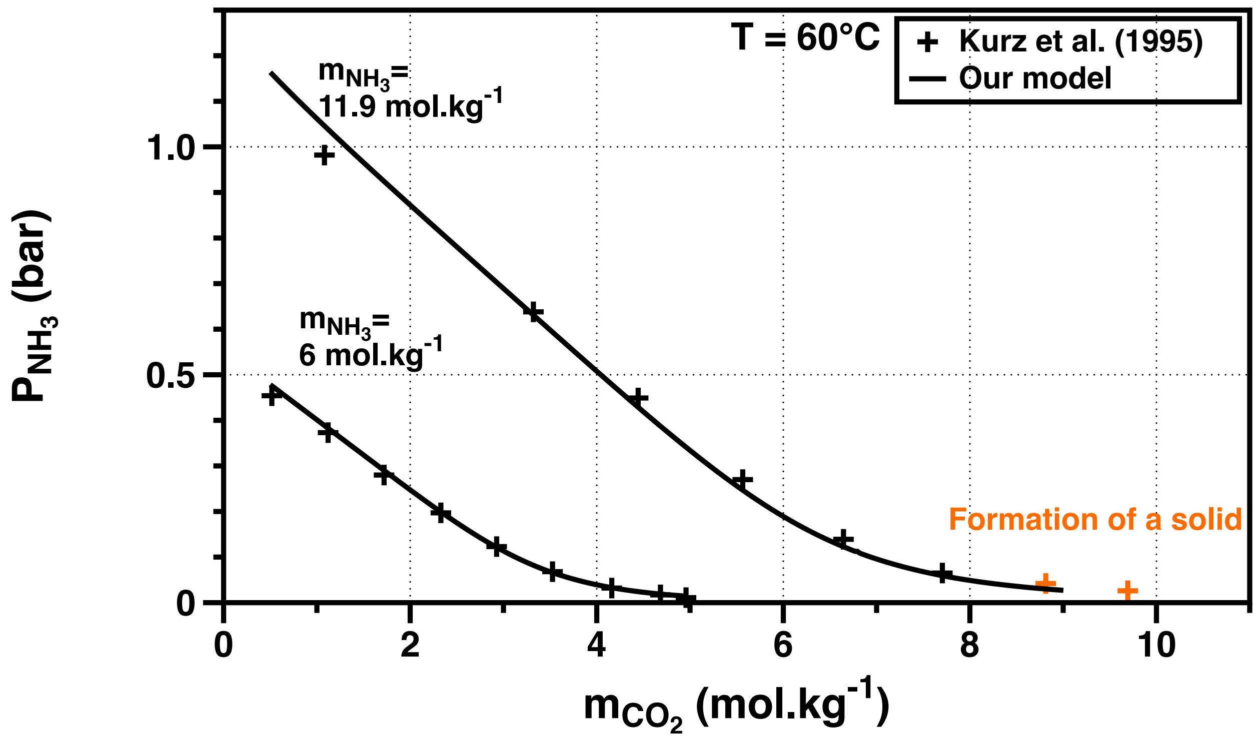


2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

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

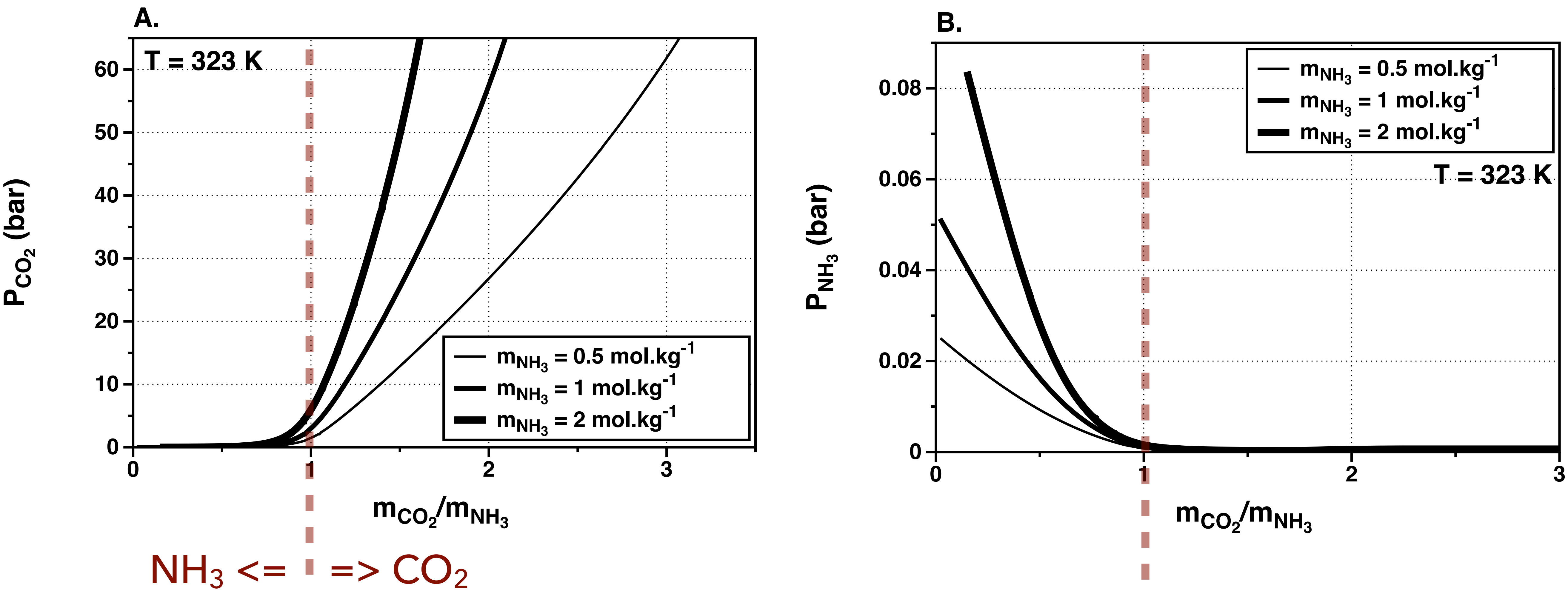




- **chemical interactions in water considerably increase the solubility of CO_2 and NH_3 in liquid water**
- our model reproduce accurately (within 10%) the CO_2 and NH_3 partial pressures
- a precipitation of a carbon-rich salts is observed for high NH_3 and CO_2 concentrations

2. Role of a global ocean on the atmospheres of water-rich bodies

2.1 Vapor-liquid equilibrium model

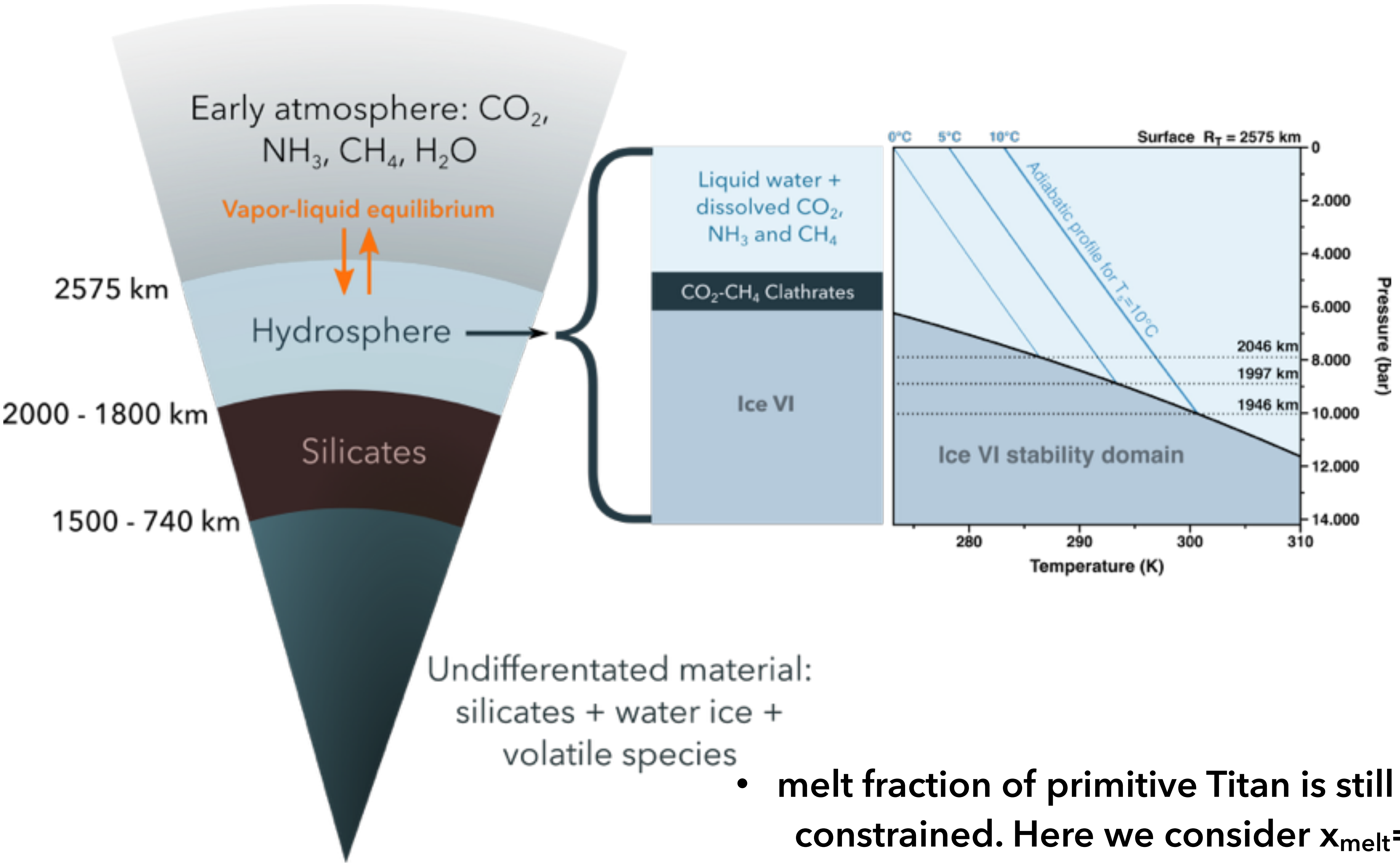


Summary for the CO_2-NH_3-H_2O system:

- NH_3 partial pressure remains low and decreases with the increasing CO_2 concentration
- CO_2 d partial pressure depends on the relative concentrations of CO_2 and NH_3 :
  - if $m_{CO2}/m_{NH3} < 1$ then P_{CO2} remains low
  - if $m_{CO2}/m_{NH3} > 1$ then P_{CO2} increases with m_{CO2}

2. Role of a global ocean on the atmospheres of water-rich bodies

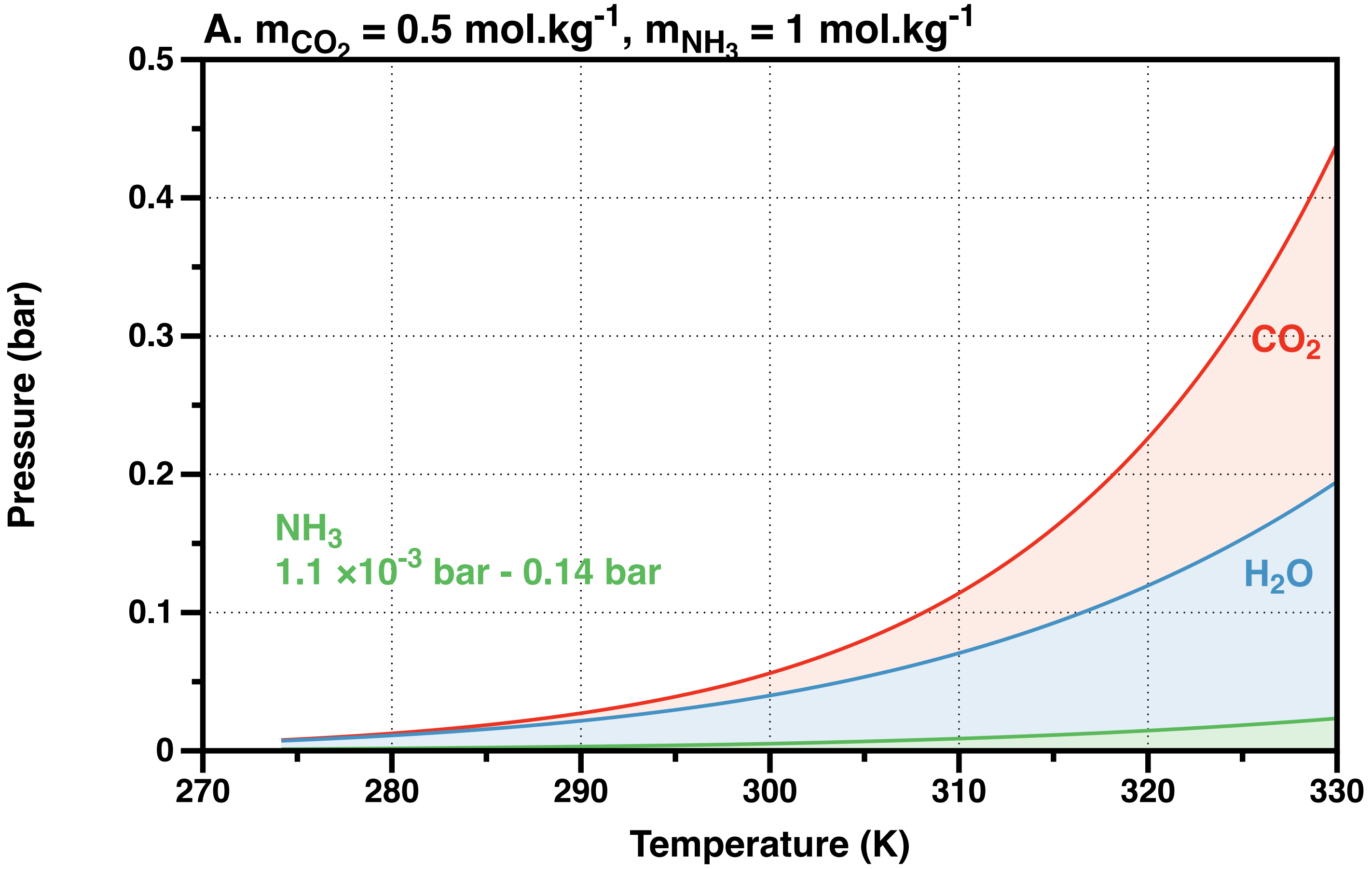
2.2 Vapor-liquid equilibrium model in planetary context:



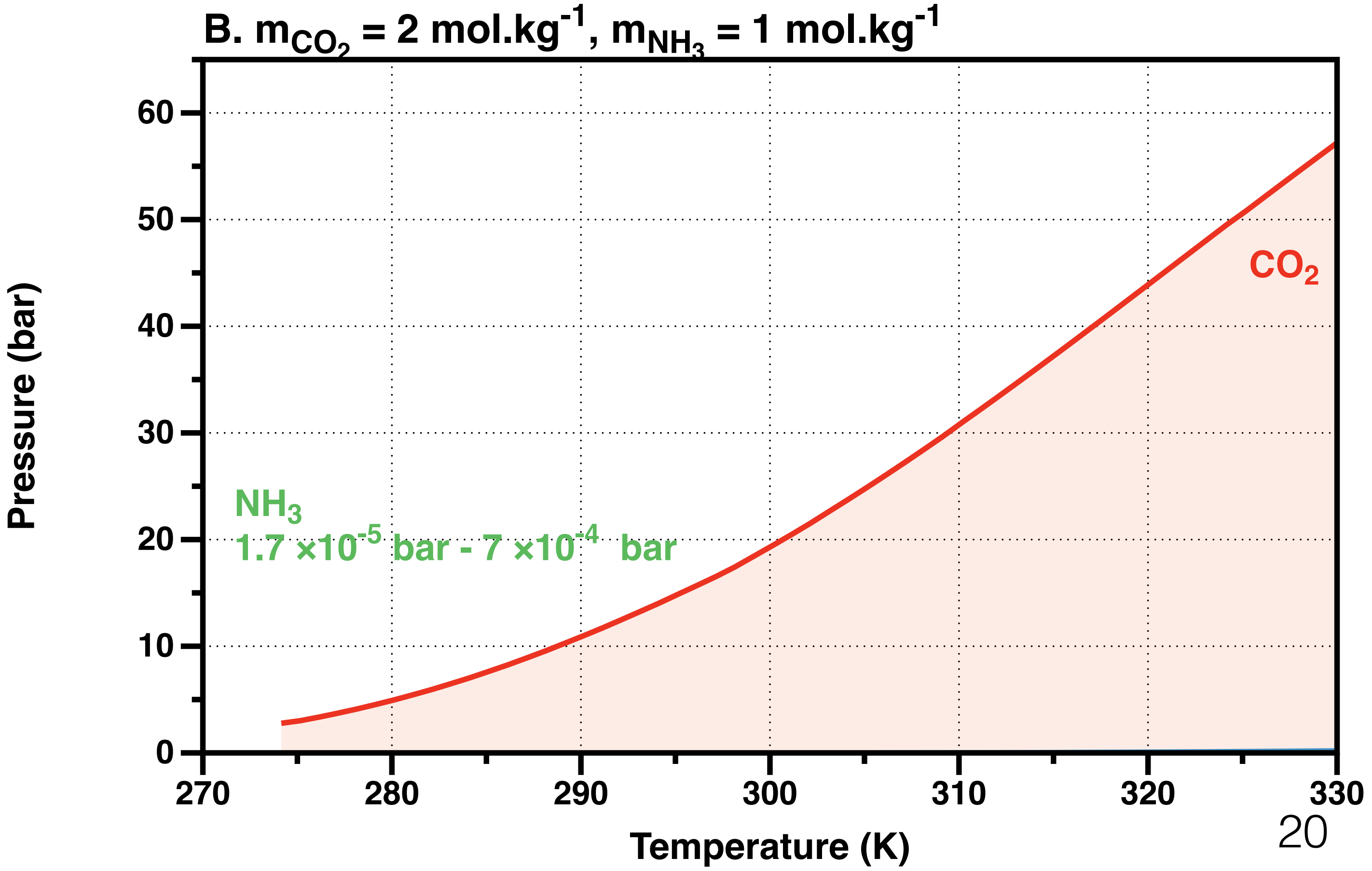
- melt fraction of primitive Titan is still poorly constrained. Here we consider x_{melt}=50%

2. Role of a global ocean on the atmospheres of water-rich bodies

2.3 Size and chemical composition of the atmospheres for the CO_2-NH_3-H_2O system



A. $m_{CO_2} = 0.5$ mol.kg^{-1}, $m_{NH_3} = 1$ mol.kg^{-1}



B. $m_{CO_2} = 2$ mol.kg^{-1}, $m_{NH_3} = 1$ mol.kg^{-1}

- **if m_{CO2}/m_{NH3} <1**, the atmosphere is tenuous and the main compound of the atmosphere is water;

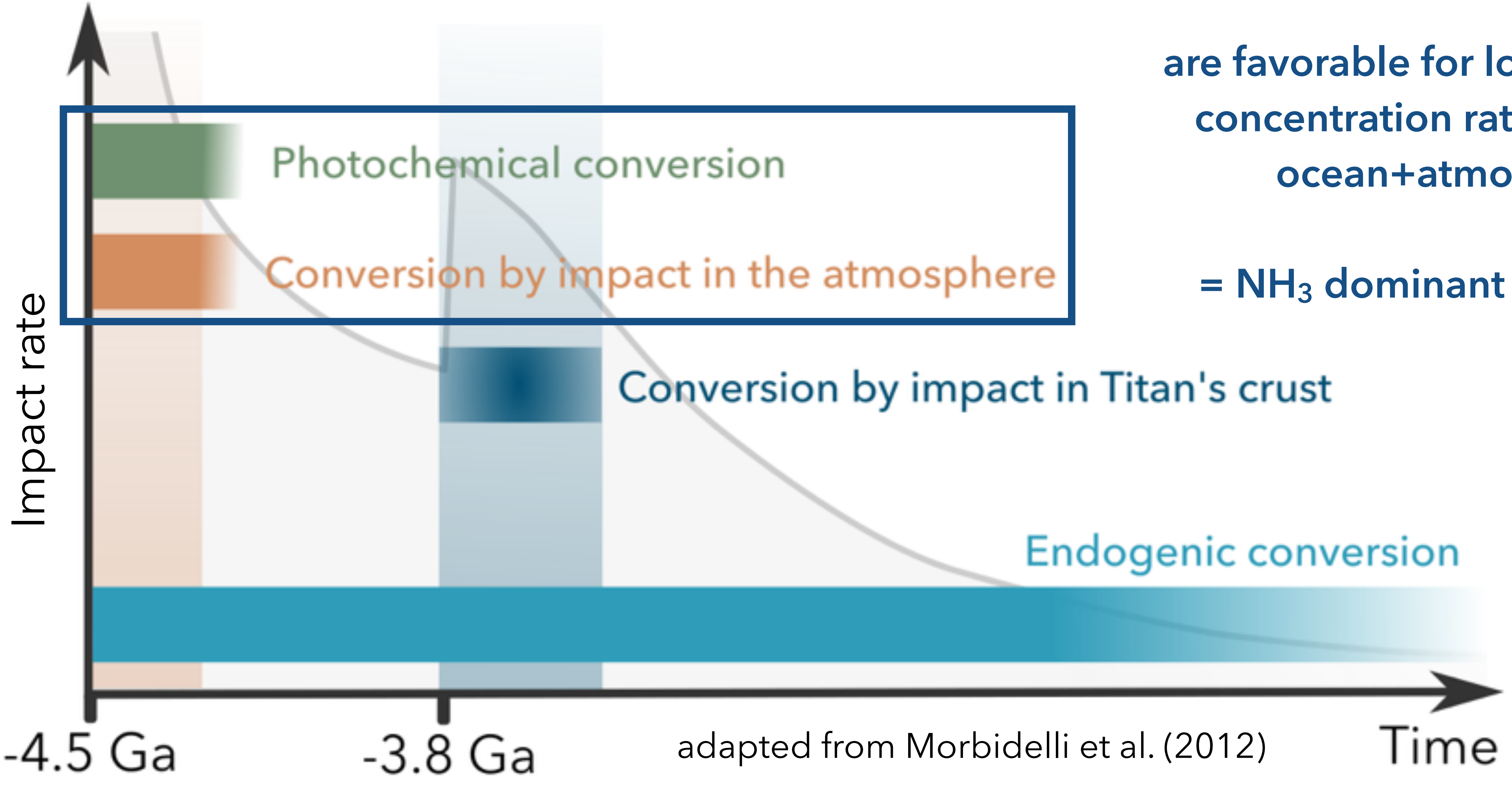
- **if m_{CO2}/m_{NH3} >1**, CO_2 the size of the atmosphere increases because the CO_2 partial pressure rises. CO_2 become the main atmospheric compound;

- NH_3 atmospheric abundance decreases with the increasing CO_2 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_2O system

- NH_3 influence considerably the abundance of CO_2 in atmospheres of early Titan



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

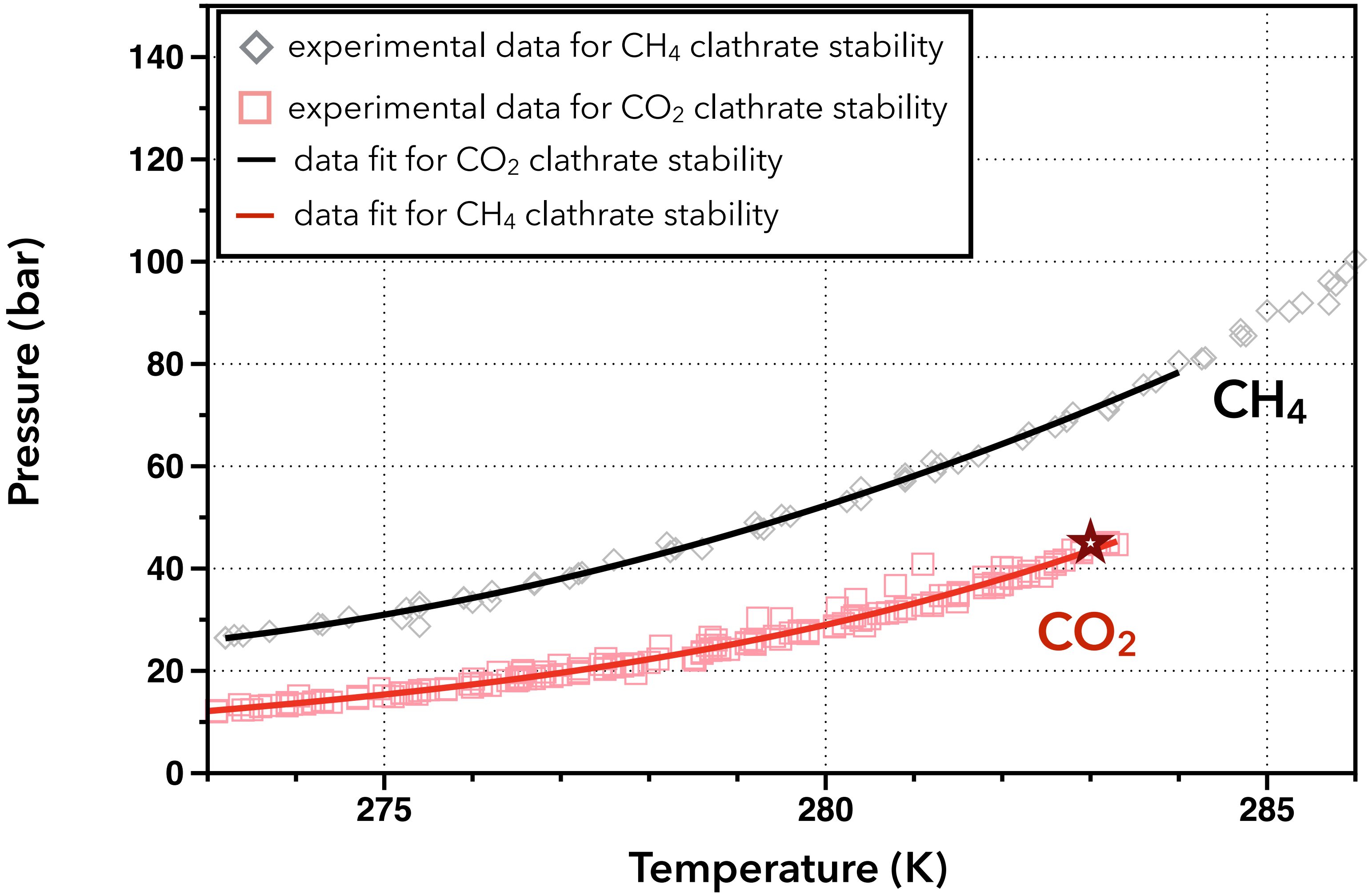
2. Role of a global ocean on the atmospheres of water-rich bodies

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



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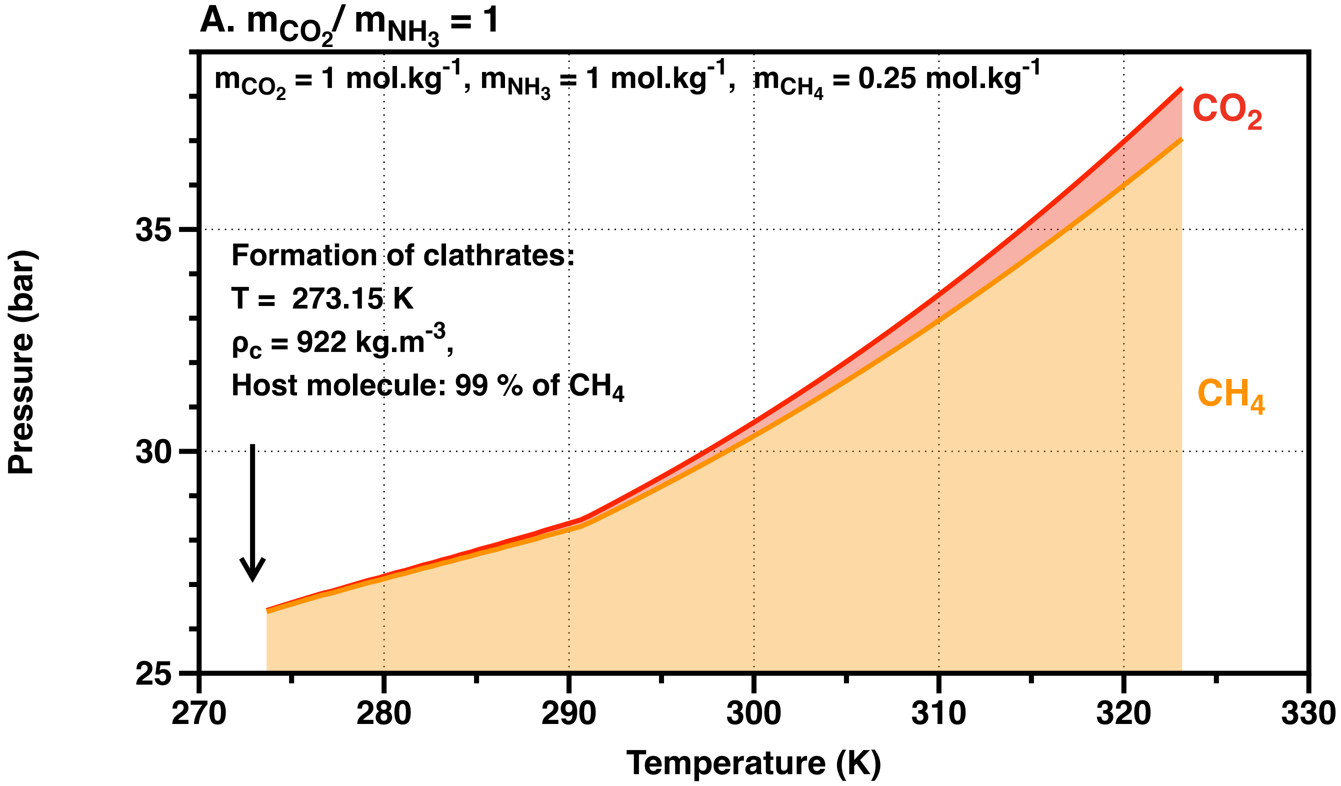
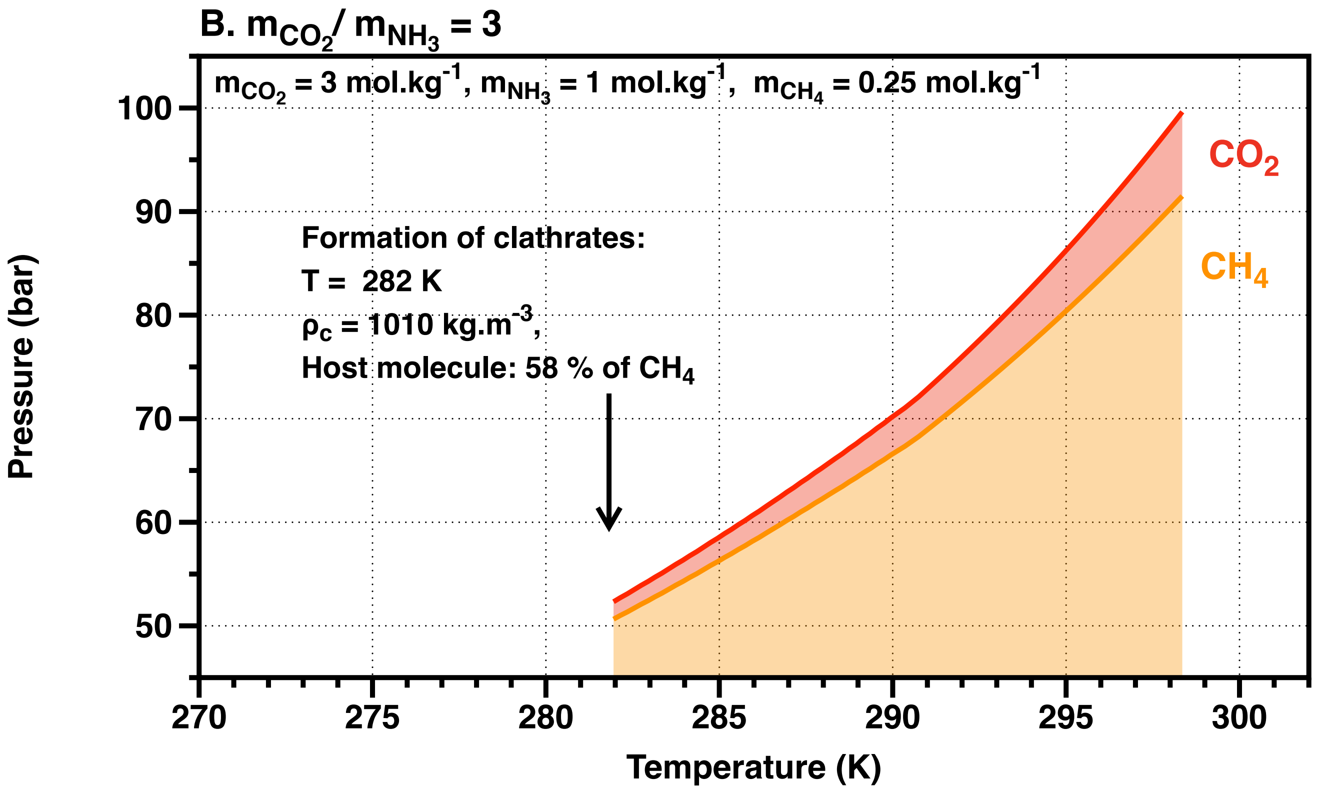

A. $m_{CO_2}/m_{NH_3} = 1$

- no interaction of (NH_3, CO_2) and CH_4 in the liquid, therefore the results obtained for the previous ternary system are also valable here

- if m_{CO2}/m_{NH3} <1 CH_4 is the main compound trapped in clathrates


B. $m_{CO_2}/m_{NH_3} = 3$

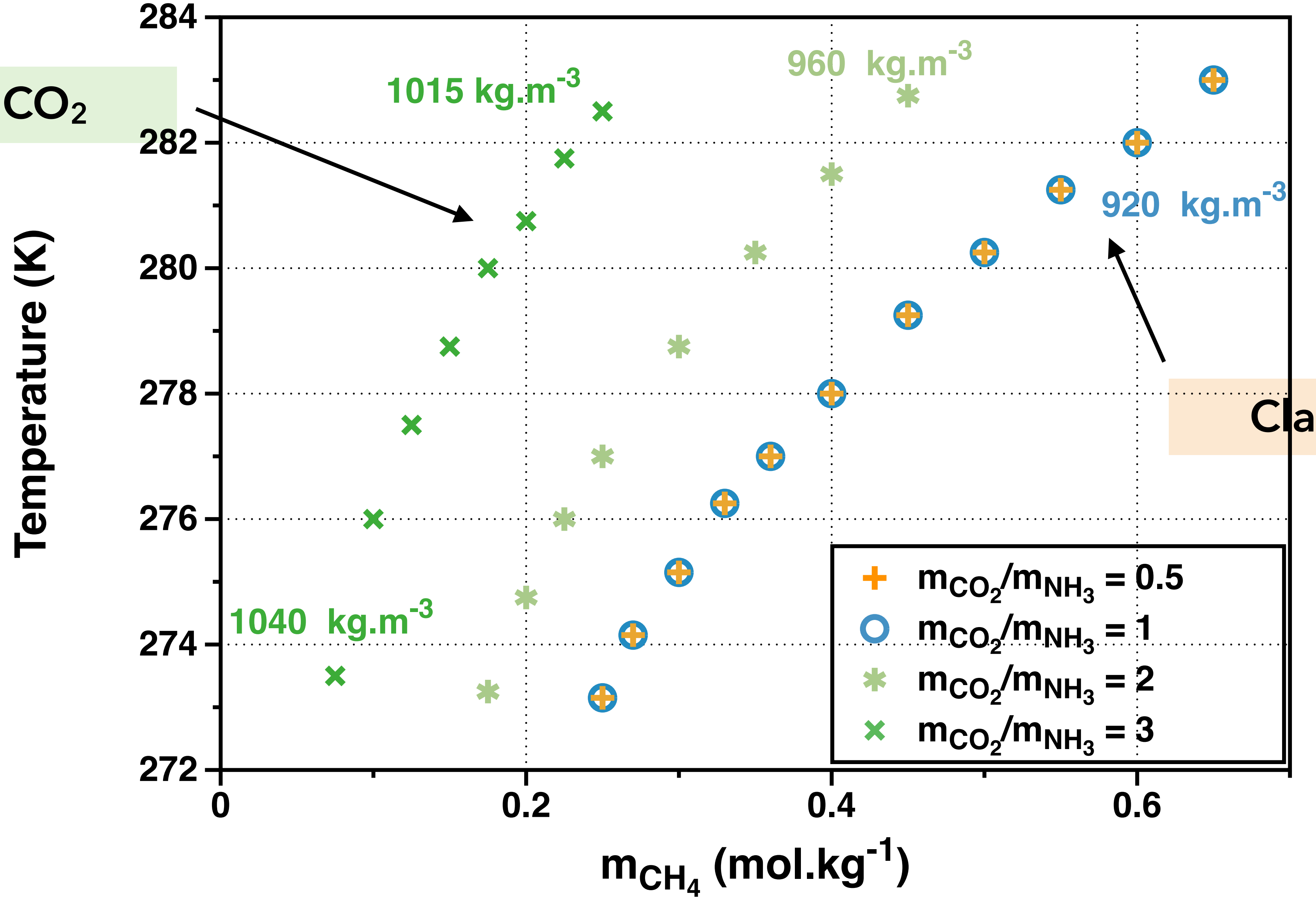
- if m_{CO2}/m_{NH3} >3 CO_2 is the main compound trapped in clathrates

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 forms at Titan's surface are denser than water



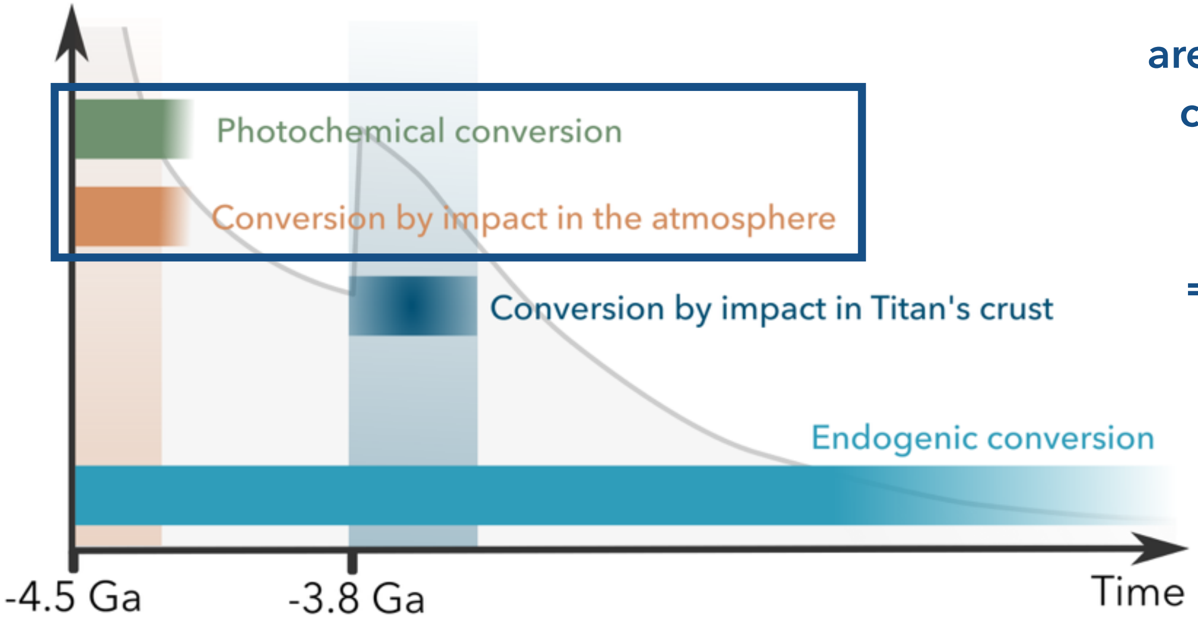
Clathrates of CO_2

Clathrates of CH_4

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 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 blocs (or Titan's ocean+atmosphere)

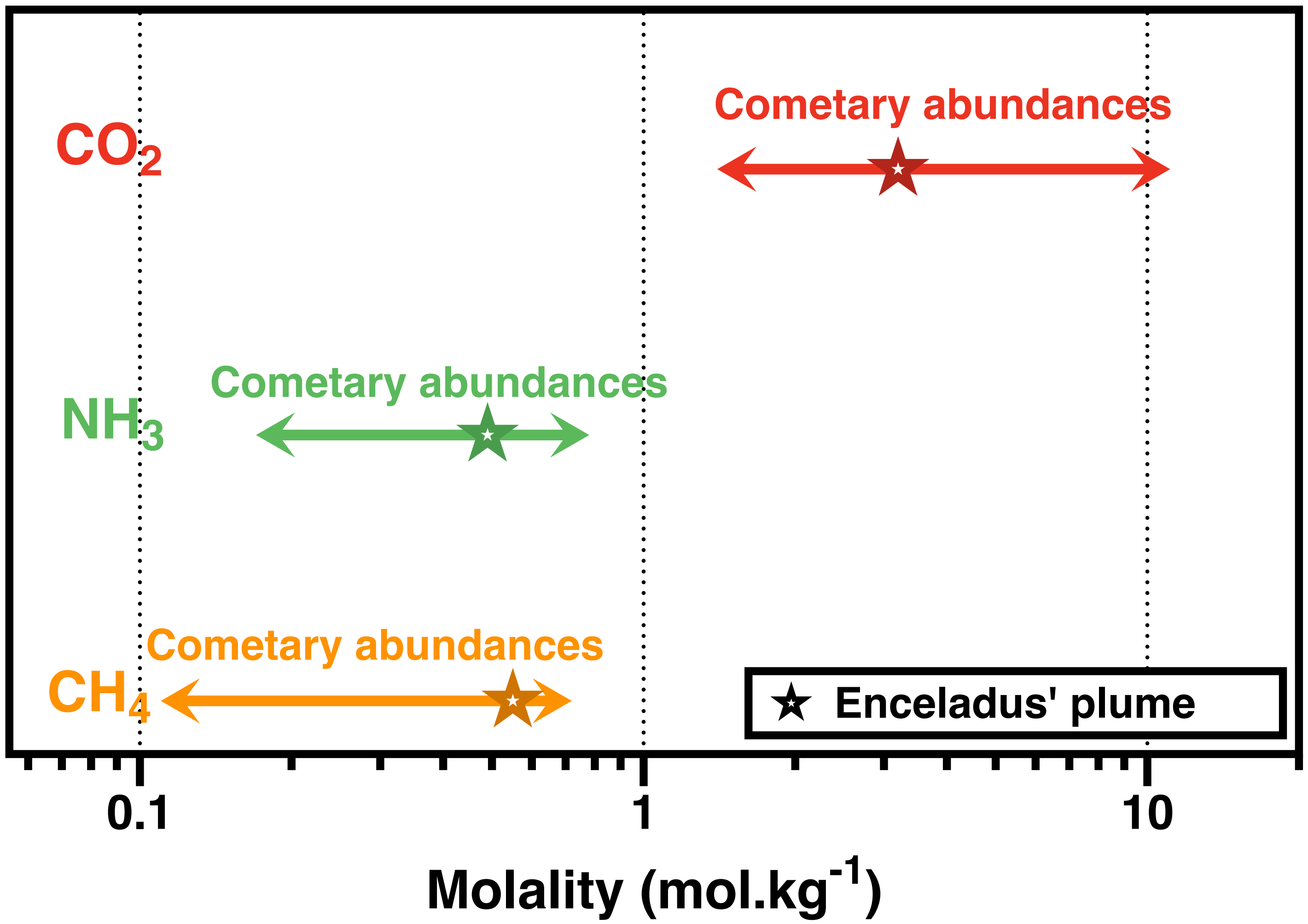


are favorable for low CO_2 / NH_3 concentration ratio in Titan's ocean+atmosphere

= NH_3 dominant compound

3. Discussion

- cometary abundances and Enceladus plume abundances indicate us that CO_2 was probably the main compounds in Titan's building blocks



- lead to a low abundance of NH_3 in the atmosphere and therefore to an inefficient the NH_3 into N_2 conversion in the atmosphere

- lead to a formation of CO_2-rich, dense clathrates - no clathrate CH_4-rich crust at Titan's surface

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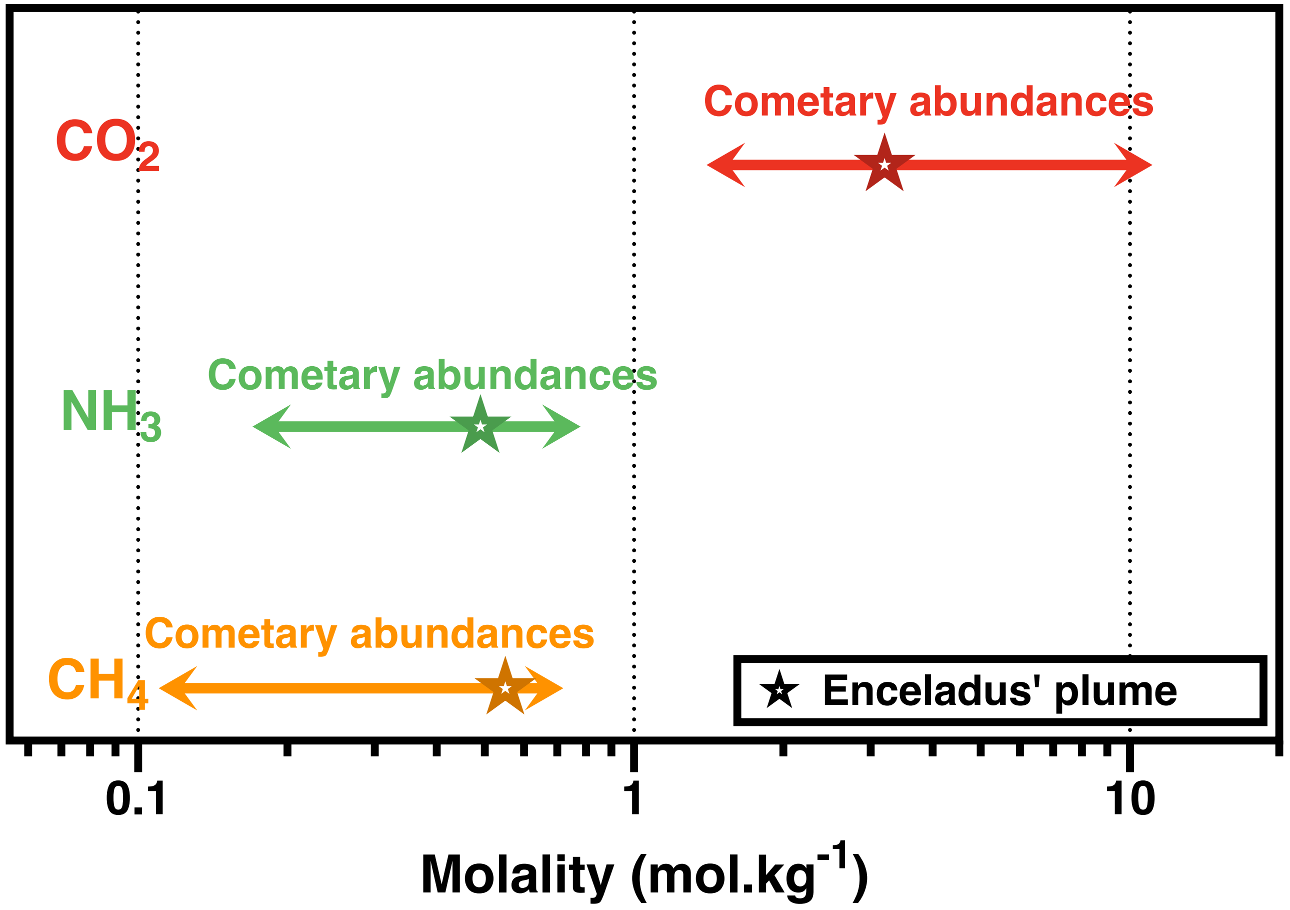


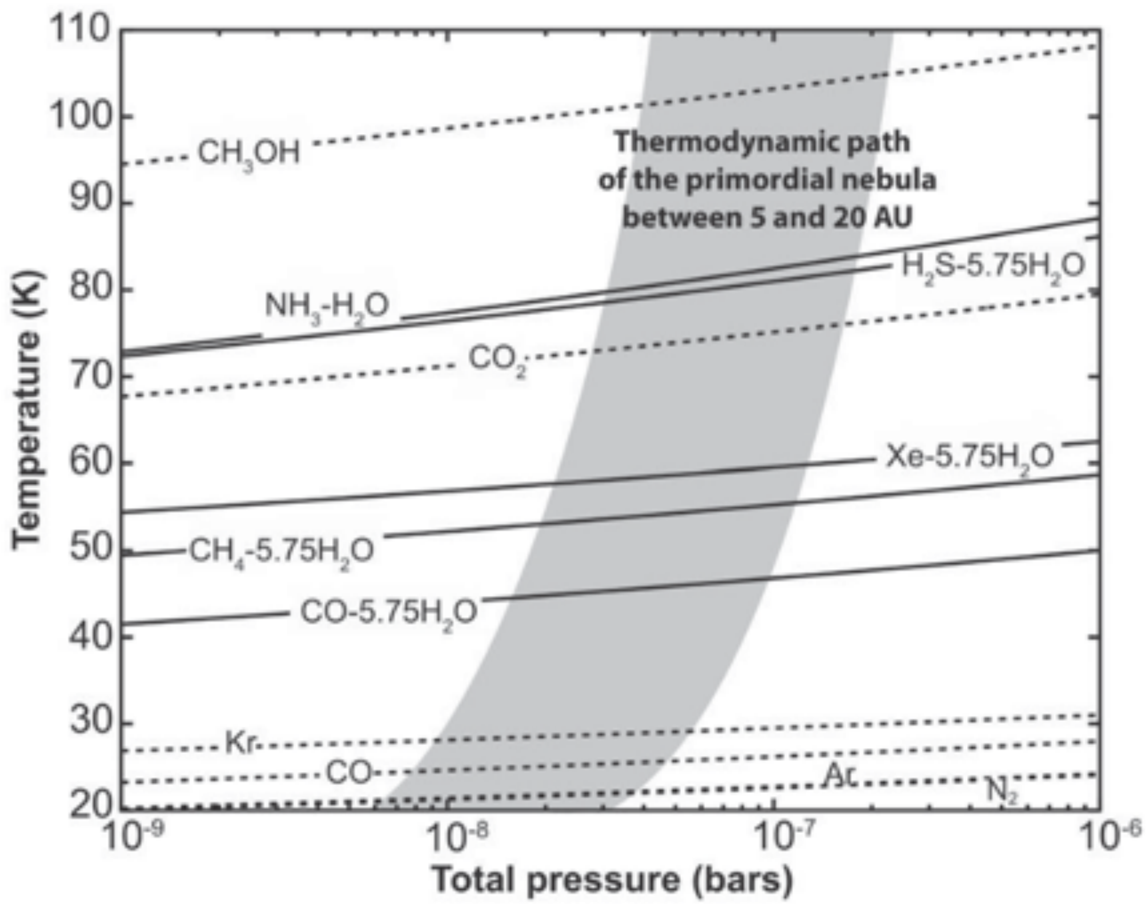


figure from Tobie et al. (2014)

- 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

3. Discussion

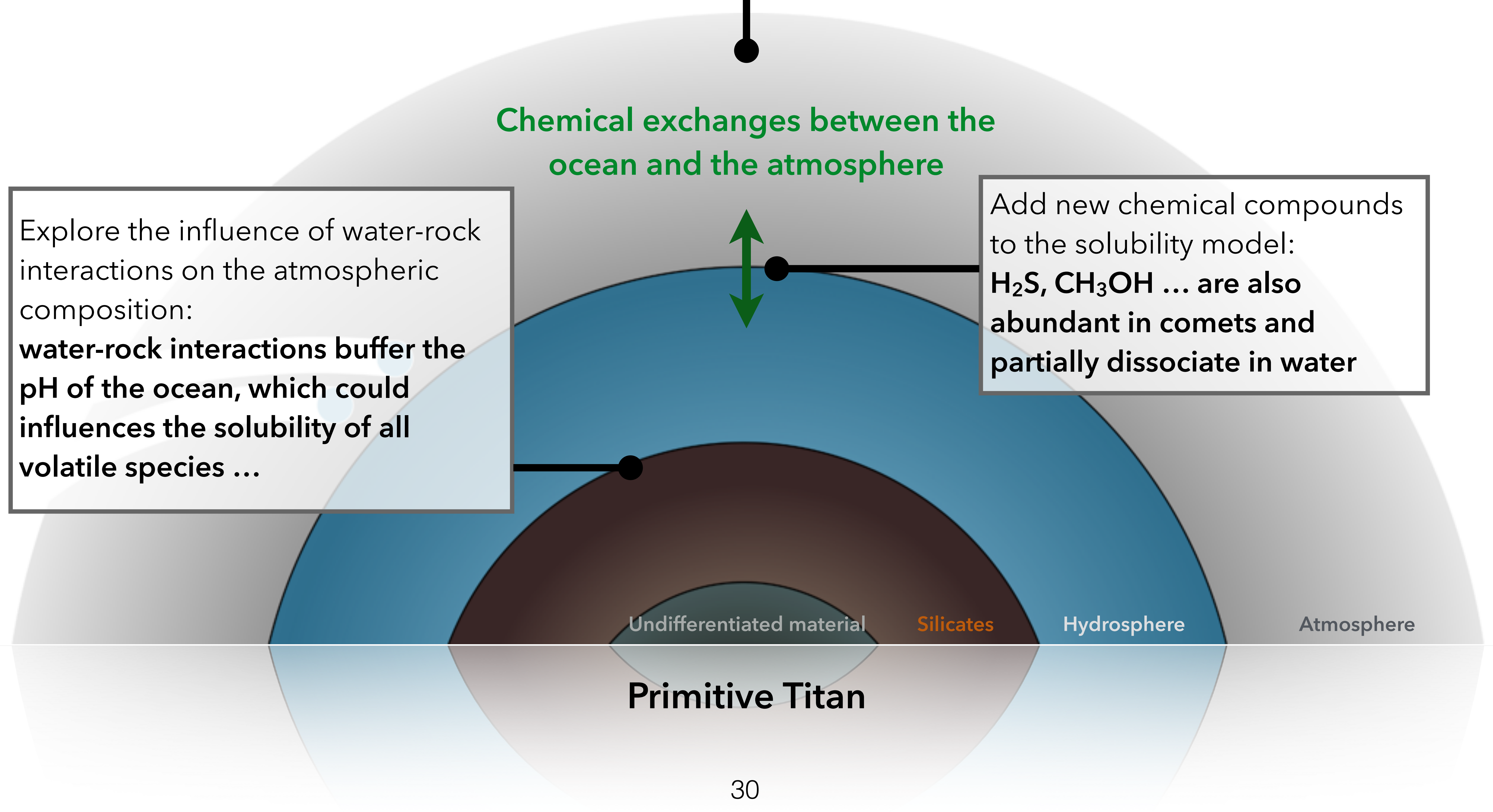
Evolution of a CO_2-CH_4 atmosphere :

- 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_{CO2}/m_{NH3} =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 fo 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 influences the solubility of all volatile species …

Add new chemical compounds to the solubility model:
H_2S, CH_3OH … are also abundant in comets and partially dissociate in water