



# Titan's bulk volatile inventory constrained by Cassini-Huygens

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## 1 Introduction

The origin of Titan's thick nitrogen atmosphere and the source of its present-day methane has long been debated. Measurements performed these last years by the *Cassini-Huygens* mission now provide key constraints to determine what is the most likely scenario for the origin of nitrogen and the recycling process of methane. The very low abundance of primordial argon,  $^{36}\text{Ar}$ , relative to nitrogen, measured by the Gas Chromatograph Mass Spectrometer (GCMS) onboard Huygens indicates that nitrogen has been most probably brought on Titan in the form of ammonia and has been converted *in situ* [1]. A variety of chemical processes has been proposed to explain the conversion of  $\text{NH}_3$  into  $\text{N}_2$ , however the exact mechanism still remains uncertain. The presence of methane in today's atmosphere is also problematic as it should disappear in less than 100 millions of years owing to photochemical destruction. The absence of extensive reservoir of liquid methane onto the surface implies that exchanges with the subsurface have probably occurred in order to maintain several percents of methane in the atmosphere [2]. Outgassing from the interior is supported by the detection of radiogenically-derived  $^{40}\text{Ar}$ , the decay product of  $^{40}\text{K}$  presumably contained in the rocky core, by the Huygens GCMS [1]. Although a variety of models has been proposed for the release of volatiles from the interior, the initial composition as well as the exact mechanism and the timing of outgassing remain unconstrained. Here we combine existing observational constraints with thermodynamical modeling of Titan's interior in order to determine the possible bulk composition of Titan and the chemical exchange between the interior and the atmosphere since the accretion.

## 2 Initial composition and early evolution

Based on a series of data collected by Cassini-Huygens, we quantify the chemical exchanges that occurred on Titan between the interior and the atmosphere during the satellite accretion and during the subsequent cooling stage, and we address the possible link between the present-day volatile inventory and the initial composition of Titan's building bricks [3,4]. We determine the possible composition of the post-accretional atmosphere on Titan and investigate the role of clathration processes on its early evolution. We predict that Titan's primordial bricks contain about 1-1.5% of  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{S}$  and less than 0.3% of  $\text{CH}_4$ , and we provide upper limits for their content in noble gases (Table 1, [4]). We show that the atmosphere possibly generated during accretion is dominated by  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  and has a surface pressure exceeding 10 bars.

Table 1: Upper and lower limits for molar fraction (in %) of several volatiles with respect to water ice in the primordial bricks that formed Titan

Species	Lower limits	Upper limits
$\text{CH}_4$	0.001	0.3
$\text{CO}_2$	-	1.5
$\text{H}_2\text{S}$	0.002	1.3
$\text{NH}_3$	0.04	1.1
$\text{CO}$	$3.0 \times 10^{-6}$	$2.0 \times 10^{-4}$
$\text{Ar}$	$2.7 \times 10^{-9}$	$3.0 \times 10^{-6}$
$\text{Xe}$	-	$5.1 \times 10^{-5}$

During the post-accretional cooling stage, large amounts of atmospheric gas compounds are predicted to be reincorporated in the interior in the form of clathrate hydrates. Most of the methane is

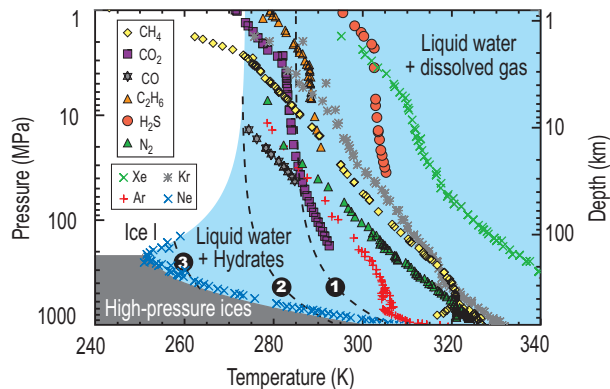


Figure 1: *Compilation of experimentally-derived dissociation temperatures of clathrate hydrate of pure gas compounds relevant for Titan's interior as a function of confining pressure, compared to the temperature profile (black dashed curves) through the ocean at different periods of Titan's evolution (1: just after accretion ( 10 Myr) when the first clathrates form at the surface; 2: when the water ice crust forms 3: present).*

predicted to be within the interior after the accretion, whereas large amounts of  $\text{CO}_2$  are predicted to precipitate and accumulate at the surface in the form of  $\text{CO}_2$  ice. Moreover, we show that argon and neon mainly remain in the atmosphere, whereas xenon is almost entirely re-incorporated in the interior.

### 3 Long-term evolution and internal outgassing

After the early epoch, large quantities of volatiles are still retained in the interior: dissolved in the ocean, in the form of clathrate hydrate mixed with water ices, or in silicate minerals. The composition of gases released during the rest of the evolution is determined by the stability of each gas species relative to the clathrate phase (Fig. 1) and is expected to be dominated by  $\text{CH}_4$  and  $\text{CO}_2$ , and to contain small amounts of argon and CO. It can be anticipated from our analysis that flows and deposits of  $\text{CO}_2$ -rich materials would be associated to cryovolcanic events.

Although the detection of  $^{40}\text{Ar}$  clearly support that interaction with the silicate phase has occurred during Titan's history, it is still unclear if significant chemical exchanges has occurred with the rocky core. Only

detection of  $^{38}\text{Ar}$  and of the other noble gas isotopes by a future mission [5] will permit us to determine how the silicate phase has contributed to the volatile budget of Titan. Such informations will give clear informations about the differentiation state of Titan and the degree of chemical exchanges with the rocky core. Isotopic ratios in the surface materials ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$  ice, organic matters, gas clathrate ammonia hydrate) will also permit us to better identify the probable subsurface volatile reservoir as well as the release mechanism.

### References

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