THE ROLE OF CLATHRATE HYDRATES IN CLEANING THE NOBLE GASES OF TITAN'S ATMOSPHERE. O. Mousis[1], J. I. Lunine[2], S. Picaud[1], and D. Cordier[3,4], [1]Institut UTINAM, CNRS-UMR 6213, Observatoire de Besançon, BP 1615, 25010 Besançon Cedex, France (olivier.mousis@obs-besancon.fr), [2]Dipartimento di Fisica, Università degli Studi di Roma ''Tor Vergata'', Rome, Italy, [3]Institut de Physique de Rennes, CNRS, UMR 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France, [4]Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

Introduction: A striking feature of the atmosphere of Titan is that no primordial noble gases other than argon were detected by the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe during its descent to Titan's surface in January 2005. The detected argon includes primordial ^{36}Ar present in subsolar abundance in Titan's atmosphere (^{36}Ar/^{14}N is found to be about six orders of magnitude lower than the solar value) and the radiogenic isotope ^{40}Ar, which is a decay product of ^{40}K [1]. The other primordial noble gases ^{38}Ar, Kr and Xe were not detected by the GCMS instrument, yielding upper limits of 10^{-8} for their atmospheric mole fractions.

The interpretation of the noble gas deficiency measured in Titan's atmosphere has been the subject of several studies in the recent literature. It has thus been shown that the atmospheric depletion of xenon could be explained by its dissolution at ambient temperature in the liquid presumably present on Titan's soil while the fractions of argon and krypton incorporated in the liquid would be negligible [2]. Another interpretation of the Ar, Kr and Xe deficiencies is that the haze present in Titan's atmosphere could simultaneously trap these three noble gases in a way consistent with the observed atmospheric abundances [3]. In this mechanism, the open structure of the small aerosol particles would allow the noble gas atoms to fill their pores.

It has also been proposed that noble gases could be preferentially stored in clathrates present on the satellite's surface [4]. Preliminary investigation conducted by [4] and made with the CSMHYD commercial program [5] showed that such crystalline ice structures may act as a sink for Xe. However, the CSMHYD code [5] is not suitable below 140 K for gas mixtures of interest whereas the mean surface temperature of Titan is below 95 K [1], implying that the trapping efficiencies of Ar and Kr in clathrates were not explicitly calculated. Based on numerical codes designed for low temperatures, more recent studies showed that the trapping efficiency of clathrates is high enough to significantly decrease the atmospheric concentrations of Xe and Kr irrespective of the initial gas phase composition, provided that these clathrates are abundant enough on the surface of Titan [6][7]. However, these studies also showed that Ar remains poorly trapped in clathrates and that this mechanism alone could not explain the argon impoverishment measured in Titan's atmosphere. Here we use the same statistical thermodynamic model as the one employed by [6][7] but by including a set of recent parameters describing the intermolecular potentials derived from experiments [8]. This allows us to show that Ar, Kr and Xe can be trapped efficiently in a clathrate layer in contact with the atmosphere of Titan. This mechanism could explain in a consistent way the apparent deficiency of noble gases measured in Titan's atmosphere [1].

Methods: To calculate the relative abundances of guest species incorporated in a clathrate from a coexisting gas of specified composition at given temperature and pressure, we follow the method described by [6][7][9][10] which uses classical statistical mechanics to relate the macroscopic thermodynamic properties of clathrates to the molecular structure and interaction energies. It is based on the original ideas of van der Waals and Platteeuw [10] for clathrate formation, which assume that trapping of guest molecules into cages corresponds to the three-dimensional generalization of ideal localized adsorption.

In this formalism, the fractional occupancy of a guest molecule K for a given type t (t = small or large) of cage can be written as

$$y_{K,t} = \frac{C_{K,t} P_K}{1 + \sum_J C_{J,t} P_J} , \quad (1)$$

where the sum in the denominator includes all the species which are present in the initial gas phase. $C_{K,t}$ is the Langmuir constant of species K in the cage of type t, and P_K is the partial pressure of species K. This partial pressure is given by $P_K = x_K \times P$ (we assume that the sample behaves as an ideal gas), with x_K the mole fraction of species K in the initial gas, and P the total atmospheric gas pressure, which is dominated by N_2.

The Langmuir constant depends on the strength of the interaction between each guest species and each type of cage, and can be determined by integrating the molecular potential within the cavity as

$$C_{K,t} = \frac{4\pi}{k_B T} \int_0^{R_c} \exp\left(-\frac{W_{K,t}(r)}{k_B T} \right) r^2 dr , \quad (2)$$

where Rc represents the radius of the cavity assumed to be spherical, k_B the Boltzmann constant, and $W_{K,t}(r)$ is the spherically averaged Kihara potential representing the interactions between the guest molecules *K* and the H_2O molecules forming the surrounding cage *t*.

Results and Discussion: We have calculated the composition of structure II clathrates (favored structure for N_2-dominated clathrates) which are expected to form on the surface of Titan by using Kihara parameters derived from [8] for available species (N_2, CH_4, C_2H_6 and Xe) and from [11] for the remaining ones (Ar and Kr). We assume that all noble gases were initially present in the atmosphere of Titan, with Ar/N, Kr/N and Xe/N ratios assumed to be solar [12]. Table 1 gives the resulting composition of Titan's atmosphere used in our calculations.

Table 1: Assumed composition of Titan's atmosphere at the ground level.

Species X	Mole fraction f_X	Reference
N_2	8.80×10^{-1}	This work
CH_4	4.92×10^{-2}	[1]
C_2H_6	1.49×10^{-5}	[11]
Ar	7.07×10^{-2}	This work
Kr	5.01×10^{-5}	This work
Xe	4.89×10^{-6}	This work

The dissociation temperature of clathrates formed at a pressure of 1.46 bar on the surface of Titan is about 166 K. This implies that, if they exist, these clathrates either formed (i) in ancient times where the atmosphere of the satellite of Saturn was warmer or (ii) during more recent release events of hot and porous cryolava towards the surface. We will assume here that, once formed, the composition of these clathrates does not change during the cooling of Titan's surface. Table 2 shows the composition of the clathrates formed in these conditions on the surface of Titan.

Table 2: Composition of clathrate calculated at P = 1.46 bar and T = 166 K.

Species	Mole fraction F_X	F_X / f_x
N_2	3.93×10^{-1}	0.45
CH_4	3.74×10^{-1}	7.60
C_2H_6	4.86×10^{-2}	3261.74
Ar	1.78×10^{-1}	2.52
Kr	3.60×10^{-3}	71.86
Xe	2.42×10^{-3}	494.89

In addition, given the Ar, Kr and Xe abundances assumed in the atmosphere of Titan, it is possible to evaluate the amount of clathrates needed to trap all these noble gases. Indeed, the total number of Ar, Kr and Xe atoms that would exist in the atmosphere of Titan is order of 1.06×10^{43}, 3.23×10^{39} and 2.02×10^{38}, respectively. The equivalent volume of clathrate needed to fully trap argon, i.e. the most abundant noble gas, would be then about 2.29×10^{15} m^3, with a cell owning a total of 24 cages and a unit volume of $(17.3 \times 10^{-10}$ m$)^3$. On the other hand, since the mole fraction of Ar in structure II clathrates has been calculated to be about 1.78×10^{-1}, we then obtain a total clathrates volume of 1.28×10^{16} m^3 on Titan that is needed to trap simultaneously the three noble gases. This volume translates into a multiple guest clathrates layer owning the composition given by Table 2 and with an equivalent thickness of about 154 m all over the surface of Titan. The calculated thickness of the clathrates layer is such that cryovolcanism is probably required to create substantial amounts of porous icy material that spread on the surface, analogous to basaltic lava flows [13]. Long periods of active cryovolcanism on Titan, as previously suggested by [14], should lead to the continuous build up of consecutive layers of cryolava.

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