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CLATHRATE HYDRATES AS A TRAPPING MECHANISM OF NOBLE GASES IN TITAN'S ATMOSPHERE

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Abstract. In January 2005, Huygens probe landed on Saturn's largest Moon, Titan. The atmospheric measurements carried out during the descent of the probe showed that, except for some tiny amounts of ^{36}Ar, no other primordial noble gases were detected in Titan's atmosphere : their mole fractions may be smaller than the GCMS instrument's sensibility (Niemann et al. 2005). It has been recently proposed that the formation of clathrate hydrates on the surface of Titan may act as a sink for atmospheric gases (Osegovic & Max 2005). In the case of noble gases, their trapping in such hydrates can deeply modify their atmospheric concentration. To test this hypothesis, we have used the model of van der Waals & Platteeuw (1959) to calculate the relative abundance of noble gases in clathrate hydrates on the surface of Titan. We show there is a strong correlation between the evolution of Titan's climate and the efficiency of the noble gases trapping in hydrates. Moreover, we find that, when the Titan's atmospheric temperature and pressure conditions decrease, the capture of Kr and Xe in hydrates becomes more efficient, whereas that of Ar diminishes.

1 Introduction

During its descent to Titan, the Gas Chromatograph Mass Spectrometer (GCMS) aboard the *Huygens* probe didn't detect other noble gases than primordial ^{36}Ar and the decay product of ^{40}K, the radiogenic isotope ^{40}Ar. The lack of detection of other primordial noble gases (^{38}Ar, Kr and Xe) means that their molar fractions in Titan's atmosphere are inferior to 10^{-8}, which is the instrument's detection limit. Furthermore, although ^{36}Ar has been detected, its abundance within Titan's atmosphere is very low. Indeed, the ratio ^{36}Ar/^{14}N is about six orders of magnitude lower than the solar value (Niemann et al. 2005).

Several scenarios have been proposed to explain this deficiency of Titan's atmosphere in primordial noble gases. The one we have studied is the trapping of atmospheric volatiles in multiple guest clathrate hydrates (Osegovic & Max 2005 – hereafter OM05). In such ice structures, cages formed by water molecules are stabilized by trapping volatiles. Thus, OM05 used the program CSMHYD developed by Sloan (1998) to calculate clathrate hydrates composition on the surface of Titan. They concluded that noble gases from Titan's atmosphere might have been completely trapped by multiple guest clathrate hydrates. However, they expressed reservations about their conclusions for several reasons. First, they had to assume similar trapping efficiencies for Xe, Ar and Kr, because the program CSMHYD doesn't allow the study of the two latter. And they had to extrapolate their results to the surface temperature of Titan (about 94 K), because this program cannot simulate clathrate hydrate formation at temperature and pressure conditions of Titan's atmosphere at ground level.

Because of these limitations, we used another approach, based on the statistical model of van der Waals & Platteeuw (1959) and described by Lunine & Stevenson (1985), to reinvestigate OM05's assumptions and calculate more accurately the trapping of noble gases in multiple guest clathrate hydrates. Thus, we have explicitly calculated the amount of Xe, Kr, and Ar trapped in such structures, at the present temperature and pressure of the surface of Titan.

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2 Model

The first stage of this approach is to represent interactions between guest and host with the spherically averaged Kihara potential. For a spherical guest molecule, this potential can be written as (McKoy & Sinanoğlu 1963)

$$w(r) = 2z\epsilon \frac{\sigma^{12}}{R_c^{11} r}\Big(\delta^{10}(r) + \frac{a}{R_c}\delta^{11}(r)\Big) - \frac{\sigma^6}{R_c^5 r}\Big(\delta^4(r) + \frac{a}{R_c}\delta^5(r)\Big), \tag{2.1}$$

with

$$\delta^N(r) = \frac{1}{N}\Big[\Big(1 - \frac{r}{R_c} - \frac{a}{R_c}\Big)^{-N} - \Big(1 + \frac{r}{R_c} - \frac{a}{R_c}\Big)^{-N}\Big]. \tag{2.2}$$

Table 1 gives the Kihara parameters a, σ and ϵ for the species we have studied.

Table 1. Parameters of Kihara potential: a is the radius of the impenetrable core, ϵ is the depth of the potential well, and σ is the Lennard-Jones diameter. These parameters are taken from Jager (2001)(a) and Diaz Peña et al. (1982)(b).

Molecule	σ(Å)	a(Å)	ϵ/k_B(K)	Ref.
CH_4	3.1514	0.3834	154.88	(a)
C_2H_6	3.2422	0.5651	189.08	(a)
N_2	3.0224	0.3526	127.67	(a)
Ar	2.829	0.226	155.30	(b)
Kr	3.094	0.307	212.70	(b)
Xe	3.3215	0.2357	192.95	(a)

In Eq. (2.1), z is the coordination number of the cell (see Table 2), and r is the distance of the guest molecule from the cavity center.

Table 2. Parameters for the cavities. b represents the number of small (b_s) or large (b_ℓ) cages per unit cell for a given structure of clathrate, R_c is the radius of the cavity (parameters taken from Sparks et al. 1999), and z the coordination number in a cavity.

Clathrate structure	I		II	
Cavity type	small	large	small	large
b	2	6	16	8
R_c(Å)	3.905	4.326	3.902	4,682
z	20	24	20	28

The integration of this potential within the cavity enables the calculation of Langmuir constants $C_{K,t}$ of species K in the cage of type t (t = small or large) in a given type of clathrate hydrate structure (I or II) :

$$C_{K,t} = \frac{4\pi}{k_B T}\int_0^{R_c} \exp\Big(-\frac{w(r)}{k_B T}\Big) r^2 dr, \tag{2.3}$$

where R_c is the radius of the cavity assumed to be spherical (see Table 2). The occupancy fraction of a cage t by the guest molecule K is given by the following expression,

$$y_{K,t} = \frac{C_{K,t} P_K}{1 + \sum_J C_{J,t} P_J}, \tag{2.4}$$

where P_K is the partial pressure of K, and the sum at the denominator includes all the species which are present in the initial gas phase.

The relative abundance f_K of a guest molecule K in a clathrate hydrate can then be calculated as

$$f_K = \frac{b_s y_{K,s} + b_\ell y_{K,\ell}}{\sum_J (b_s y_{J,s} + b_\ell y_{J,\ell})}, \tag{2.5}$$

where b_s and b_ℓ are the number of small and large cages per unit cell, for the considered clathrate hydrate structure (I or II). The sum in the denominator includes all species present in the system.

3 Results and discussion

We study a gas with a composition similar to that of Titan's atmosphere : we assume that the main atmospheric compounds of the initial gas phase are (see Table 3) N_2, CH_4, C_2H_6 and only one noble gas (Xe, Kr or Ar). We then calculate the relative abundances of Xe (f_{Xe}), Kr (f_{Kr}) and Ar (f_{Ar}) trapped in clathrate hydrates formed from this gas, with respect to all guests incorporated. The conclusions of our calculations are similar for both structures I and II, and we present here only the results obtained for structure I.

Table 3. Initial gas phase abundances considered in the atmosphere of Titan.

Molecule	Molar fractions (%)
Noble gas	0.1
CH_4	4.8
N_2	95
C_2H_6	0.1

From this model, we represent the evolution of f_{Xe}, f_{Kr} and f_{Ar} in a multiple guest clathrate hydrate as a function of T, the formation temperature (Figs. 1). Figure 1a shows that the relative abundances of Xe and Kr are higher in clathrate hydrates at low (T), and they progressively decrease when this formation temperature increases. By contrast, the relative abundance of Ar in clathrate hydrates is higher at high T, and it strongly decreases with this formation temperature, as shown in Fig. 1b. Moreover, note that the scale is multiplied by 10^{-4} for f_{Ar}, which means that Ar is poorly trapped in clathrate hydrates irrespective of the formation temperature.

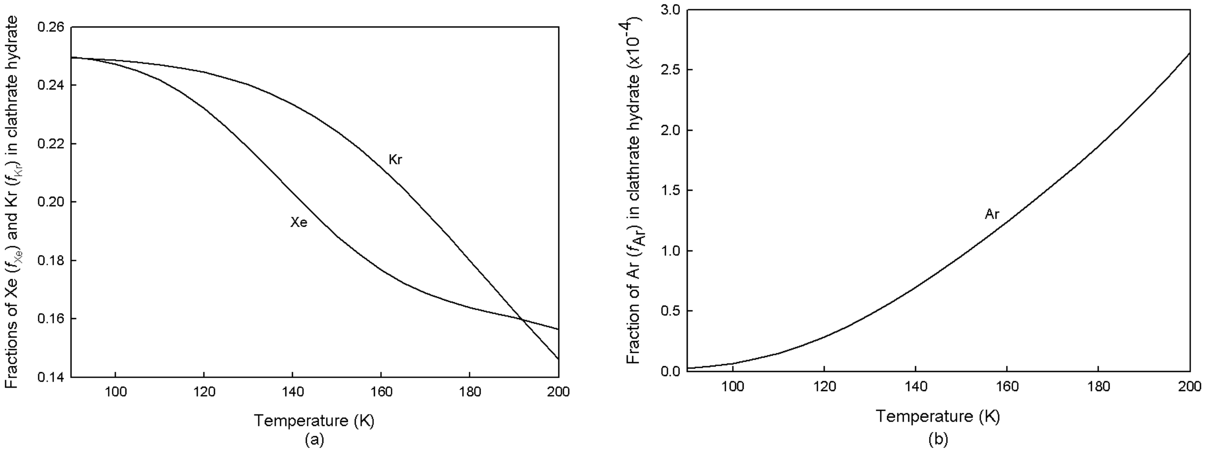

Fig. 1. f_{Xe} and f_{Kr} (a), and f_{Ar} (b) in a multiple guest clathrate hydrate, as a function of temperature.

The values of the Kihara parameters of Ar are lower than those of Xe and Kr (see Table 1). Consequently, the interaction energy with the surrounding water molecules in clathrate hydrate cages is stronger for the two latter molecules, which may explain this huge difference between the trapping of Ar, Xe and Kr in clathrate hydrates.

To show the trapping efficiency, we have calculated the ratio between the relative abundance f_K of a given noble gas in the multiple guest clathrate hydrate and its initial gas phase abundance x_K (see Table 3). This abundance ratio has been calculated at $P = 1.5$ bar, which is the present atmospheric pressure at the ground level of Titan (see Table 4).

Table 4 shows that in such conditions, Xe and Kr trapped in clathrate hydrates are almost 200 times more abundant than in the initial gas phase, which means that their trapping is very efficient. As a consequence, the amount of Xe and Kr in Titan's atmosphere may be significantly decreased. By contrast, the ratio for Ar is inferior to 1. This noble gas is less abundant in clathrate hydrates than in the initial gas phase. Such an inefficient trapping can't decrease significantly Ar's atmospheric concentration, which remains almost constant.

Table 4. Abundance ratios of noble gas in clathrate hydrate (f) to noble gas in the initial gas phase (x) for Xe, Kr and Ar. These ratios are calculated at $P = 1.5$ bar.

	Xe	Kr	Ar
x	0.001	0.001	0.001
f/x	168	195	1.577×10^{-1}

4 Conclusions

Trapping of noble gases by multiple guest clathrate hydrates could be efficient enough to explain the deficiency in Xe and Kr of Titan's atmosphere. On the contrary, Ar clathration efficiency can't explain, alone, the tiny amount of Ar detected by *Huygens*. This mechanism should work together with other scenarios to explain measurements made by the GCMS.

5 The bibliography

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