EFFICIENT TRAPPING OF NOBLE GASES BY CLATHRATES ON TITAN. C. Thomas, S. Picaud, O. Mousis and V. Ballenegger, Institut UTINAM, CNRS/INSU UMR 6213, 16 route de Gray, 25030 Besançon Cedex, France (caroline.thomas@univ-fcomte.fr)

Introduction: During its descent to Titan, the Gas Chromatograph Mass Spectrometer (GCMS) aboard the *Huygens* probe did not detect other noble gases than primordial ^{36}Ar and the decay product of ^{40}K, the radiogenic isotope ^{40}Ar. The molar fractions of other primordial noble gases (^{38}Ar, Kr and Xe) in Titan's atmosphere are therefore 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, with a $^{36}Ar/^{14}N$ ratio subsolar by several orders of magnitude [1].

One of the scenarios proposed to explain this deficiency is the trapping of atmospheric volatiles in multiple guest clathrates [2]. The program CSMHYD [3] available to predict the relative abundance of one gas trapped in such a structure does not allow calculations for the temperature and pressure conditions at the surface of Titan, and for mixtures with Ar and Kr. More accurate calculations of the trapping of noble gases in clathrates were performed using a hybrid model [4] based on the statistical thermodynamical model of van der Waals & Platteeuw [5], in which available experimental data [3,6] and an approximation of the dissociation pressure of a multiple guest clathrate [7] are employed. In particular, it was shown that the trapping of noble gases by those clathrates could be efficient enough to explain the deficiency in Xe and Kr in Titan's atmosphere [4].

In previous studies [2,4], the initial Titan's atmospheric composition was considered with only one noble gas at a time. In this work, we perform new calculations based on a more plausible gas mixture, in which Ar, Kr and Xe are simultaneously present.

Results and discussion: From our model, we calculate the relative abundances of CH_4, C_2H_6, N_2, Ar, Kr and Xe in multiple guest clathrates (structures I and II), as a function of the formation temperature, for three different atmospheric compositions. For the three cases, the initial gas phase abundance of CH_4 is taken equal to 4.92 % [1], whereas three different sets of initial abundances are considered for N_2, C_2H_6, Ar, Kr, and Xe. For the first case, data are determined from an atmospheric composition similar to that of our previous study [4]. For the second case, we consider that each ratio of noble gas to methane is solar [8] in the atmosphere of Titan, with all carbon in the form of methane. Finally, the third set of values is calculated under the assumption that each noble gas to methane gas phase ratio corresponds to the values calculated for solids produced in the feeding zone of Saturn, and ultimately accreted by the forming Titan [9].

In each case, the relative abundance of N_2 (approximately 95%) has been determined such that the molar fractions add to unity:

$$x_{CH4}+x_{Ar}+x_{Kr}+x_{Xe}+x_{N2}+x_{C2H6}=1.$$

The initial gas phase abundances for the three cases are given in Table 1.

Molecule	Molar fractions (%)		
	case 1	case 2	case 3
Ar	0.1	7.1264×10^{-2}	2.10506
Kr	0.1	3.44×10^{-5}	1.38×10^{-3}
Xe	0.1	3.8×10^{-6}	1.6×10^{-4}
CH_4	4.92	4.92	4.92
N_2	94.68	95	92
C_2H_6	0.1	8.6978×10^{-3}	0.9734

Table 1. Initial gas phase abundances corresponding to the three different systems considered: arbitrary data [2,4] (case 1), solar abundances (case 2), and Saturnian planetesimals (case 3).

In our previous study, we have shown that the trapping of Xe and Kr increased when the temperature decreased, whereas that of Ar decreased. By contrast, when considering the three noble gases included all together, the results obtained in the present study show a different behavior. Indeed, in the three cases, the fraction of encaged Xe is higher when the trapping occurs at lower temperatures. For Kr, the trapping diminishes in case 1 when temperature decreases, and it is almost constant in the two other cases. The differences between the results obtained from these two studies show that there is a strong competition in the trapping of Ar, Kr and Xe when they are simultaneously present. It is worth noting that the absolute values of the relative abundances within the multiple guest clathrates differ strongly for the three cases because of the very different initial gas phase abundances.

We have then calculated the ratio between the relative abundance of a noble gas in clathrates and its initial gas phase abundance. These ratios are calculated at a pressure P = 1.5 bar, corresponding to the present atmospheric pressure at the ground level of Titan, and at the corresponding dissociation temperature, in the three cases.

Case	Initial molar fraction in gas	Abundance ratio structure I	Abundance ratio structure II
	Ar		
1	0.1×10^{-2}	0.4	1.5
2	7.1264×10^{-4}	0.8	5
3	2.1051×10^{-2}	0.7	4.6
	Kr		
1	0.1×10^{-2}	7.6	35.3
2	3.44×10^{-7}	18.3	143.7
3	1.38×10^{-5}	11.6	89.5
	Xe		
1	0.1×10^{-2}	308	473
2	3.8×10^{-8}	863.4	2356
3	1.6×10^{-6}	269.2	948.7

Table 2. Abundance ratios of noble gas in clathrates to noble gas in the initial gas phase for Ar, Kr and Xe. These ratios are calculated at P=1.5 bar, and at the corresponding dissociation temperature (176 K for case 1, 167 K for case 2, and 187 K for case 3).

Table 2 shows that in such conditions, Xe trapped in clathrates is much more abundant than in the initial gas phase, irrespective of the initial gas phase composition, which means that its trapping is very efficient. A similar conclusion can be made for Kr, but to a lesser extent. As a consequence, the amount of Xe and Kr in Titan's atmosphere may be significantly diminished by trapping in clathrates. By contrast, the ratio for Ar is close to 1, which suggests that its trapping by clathrates is poor and does not significantly decrease its atmospheric concentration, which should remain almost constant.

Conclusion: The conclusions obtained here are similar to those of our previous study, despite the fact that Ar, Kr and Xe are considered simultaneously in the initial gas phase composition: trapping of noble gases by multiple guest clathrates can be efficient enough to explain the deficiency in Xe and Kr of Titan's atmosphere, but not that in Ar. To explain measurements made by the GCMS, this mechanism should work together with other scenarios, such as the formation of Titan from planetesimals that have been partially vaporized in the Saturn's subnebula [10].

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