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# On the Possible Interplay Between Liquid and Clathrate Reservoirs on Titan

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#### **Abstract**

We investigate the interplay that would happen between a reservoir of liquid hydrocarbons located in Titan's subsurface and a hypothetical clathrate reservoir that progressively forms when the liquid mixture diffuses throughout a coexisting porous icy layer.

#### 1. Introduction

Hundreds of lakes and a few seas are observed to cover the polar regions of Titan [1]. While a significant number of these lakes and seas should be regularly filled by hydrocarbon rainfalls [2], some of them could be also renewed via their interconnection with liquid reservoirs of alkanes located in the subsurface [3]. These lakes could result from the interaction between subsurface liquid and clathrate reservoirs and possess a composition differing from that of lakes and rivers engendered by precipitations. As a liquid reservoir occupies a finite volume, the progressive transfer and fractionation of the molecules in the forming clathrate reservoir could alter the lakes' chemical composition. In order to explore this possibility, we use a statisticalthermodynamic model [4] to compute the composition of the clathrate reservoir that forms as a result of the progressive entrapping of the species present in the liquid mixture. This allows us to track the evolution of the mole fractions of species present in the liquid reservoir as a function of their progressive entrapment in the clathrate layer.

## 2. Modeling approach

We assume that the liquid reservoir is in contact with porous ice and that clathrates form at the liquid/ice interface. We consider an isolated system composed of a clathrate reservoir that progressively forms and replaces the H<sub>2</sub>O crustal material with time and a liquid reservoir that correspondingly empties due to the net

transfer of molecules to the clathrate reservoir. Based on this approach, we have elaborated a computational procedure with the intent to determine the mole fractions of each species present in the liquid reservoir and trapped in the forming clathrate reservoir, as a function of the fractions of the initial liquid volume (before volatile migration) remaining in lake and present in clathrates, respectively. At the beginning of our computations, the liquid reservoir's composition is derived from those computed by [5] for lakes at polar and equator temperatures, which result from models assuming thermodynamic equilibrium between the atmosphere and the lakes.

#### 3. Results

Figure 1 represents the evolution of the mole fractions of species present in a subsurface liquid reservoir of Titan as a function of their progressive entrapping in structures I and II clathrate reservoirs located at the poles (T = 90 K) and at the equator (T = 93.6 K). The evolution of the liquid reservoir's composition varies significantly if one assumes the formation of a structure I or a structure II clathrate reservoir. In particular, the change of clathrate structure in our model alters the number of dominant species present in the liquid phase at high mole fractions of entrapped liquid. It also drastically affects the evolution of the abundances of secondary species during the progressive liquid entrapping. When considering the formation of a structure I clathrate, and irrespective of the liquid reservoir's temperature, the dominating species is C<sub>2</sub>H<sub>6</sub> until that a liquid mole fraction of 0.85 has been trapped into clathrate. Above this value, and because of the entrapping of the other molecules in structure I clathrate, C<sub>3</sub>H<sub>8</sub> becomes the only remaining species in the liquid reservoir. At both temperatures considered, the initial abundance of CH<sub>4</sub> in the liquid phase is close to that of C<sub>3</sub>H<sub>8</sub>. However, as the liquid progressively forms clathrate with ice, the mole fraction of CH<sub>4</sub> rapidly decreases and finally converges towards zero after a mole fraction of 0.3-0.5 of the initial liquid reservoir has been entrapped. Meanwhile, the mole fractions of  $N_2$ , Ar and CO form plateaus and finally drop towards zero at the same mole fraction of entrapped liquid that corresponds to the disappearance of CH<sub>4</sub>. When considering the formation of a structure II clathrate, the dominant species remains C<sub>2</sub>H<sub>6</sub>, irrespective of the mole fraction of liquid entrapped in clathrate and the temperature of the reservoirs. Instead of increasing with the progressive liquid entrapment in clathrate as in the previous case, the abundance of C<sub>3</sub>H<sub>8</sub> decreases and suddenly drops when the mole fraction of entrapped liquid is 0.15-0.23. The abundances of CH<sub>4</sub>, N<sub>2</sub>, Ar and CO also decrease with the progressive formation of structure II clathrate and suddenly drop at mole fractions of entrapped liquid in the 0.11-0.18 range. The temperature of the liquid and clathrate reservoirs also plays a role in the determination of their composition, but in a less important man-ner than the modification of the clathrate structure. Figure 1 shows that the rise of temperature decreases by several per cents the mole fraction of entrapped liquid at which the abundances of minor species drop in the solution. Compared to the change of clathrate structure, a temperature variation also affects (to a lower extent) the mole fractions of secondary species in the liquid reservoir but does not influence those of major compounds.

#### 4. Conclusions

If subsurface liquid reservoirs equilibrated with clathrate layers, then our computations should allow disentangling in situ measurements of lakes and rivers flowing from subsurface liquid reservoirs from those of liquid areas directly engendered by precipitations. In the case of structure I clathrate formation, and irrespective of the temperature considered, the solution is dominated by ethane at mole fractions of the initial liquid reservoir trapped in clathrate lower than 0.9. At higher mole fractions, propane becomes the only species remaining in the liquid phase. In the case of structure II clathrate formation, ethane is the only dominant species in solution, irrespective of the temperature considered and mole fraction of entrapped liquid.

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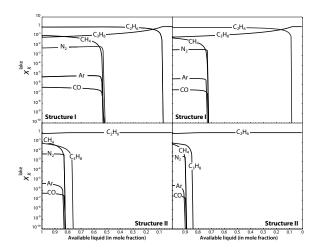


Figure 1: Composition of alkanofers located at the pole (left panels) and at the equator (right panels) in contact with forming clathrate layers. Mole fractions of various species K in solution depend on the mole fraction of available liquid (number of moles still present in the liquid phase to the total number of moles present in the initial liquid reservoir). Top and bottom panels correspond to the formation of structure I and II clathrates, respectively.

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