THE FATE OF ETHANE IN TITAN’S HYDROCARBON LAKES AND SEAS. Olivier Mousis\(^1\), Jonathan I. Lunine\(^2\), Alexander Hayes\(^2\), and Jason Hofgartner\(^2\), \(^1\)Aix Marseille Université, CNRS, LAM (Laboratoire d’Astrophysique de Marseille) UMR 7326, 13388, Marseille (olivier.mousis@lam.fr), \(^2\)Center for Radiophysics and Space Research, Space Sciences Building Cornell University, Ithaca, NY 14853, USA.

Introduction: Titan has a thick atmosphere dominated by nitrogen and methane. The dense orangebrown smog hiding the satellite’s surface is produced by photochemical reactions of methane, nitrogen, and their dissociation products with solar ultraviolet, which lead primarily to the formation of ethane and heavier hydrocarbons [Lavvas et al., 2008]. On Titan, the temperature and atmospheric pressure conditions prevailing at the ground level permit clathrate formation when liquid hydrocarbons enter in contact with the exposed water ice [1]. Assuming a high porosity for Titan’s upper crust, clathrates with hydrocarbon guest species are stable and expected to occur down to several kilometers from the surface [1,2]. These clathrates may contain a significant fraction of the ethane and propane generated in Titan’s atmosphere over the solar system’s lifetime [1]. On the other hand, hundreds of lakes and a few seas of liquid hydrocarbons have been observed by the Cassini spacecraft to cover the polar regions of Titan [3-5]. If they are isolated from the subsurface, these lakes and seas should display compositions reflecting those of the precipitates--ethane, implying that they should contain a significant fraction of ethane. Alternatively, if the basins containing liquids are in contact with the icy crust of Titan, their compositions may be altered by interactions with clathrate reservoirs that progressively form if the liquid mixtures diffuse throughout preexisting porous icy layers [6]. Here we investigate the evolution of the ethane mole fraction in a lake that interacts with a forming clathrate layer under these circumstances.

Model description: Our liquid reservoir consists of a mixture of CH\(_4\) and C\(_2\)H\(_6\), and its equilibration is assumed faster with clathrate than with the atmosphere. We follow the approach proposed by [6] in which a hydrocarbon liquid reservoir is assumed to be in contact with porous ice and clathrate formation is expected to occur at the liquid/ice interface. We consider an isolated system composed of a clathrate reservoir that progressively forms and replaces the crustal material with time and a liquid reservoir that correspondingly empties due to the net transfer of molecules to the clathrate reservoir.

We use the numerical procedure defined in [6] with the intent to determine the mole fractions of each species present in the liquid reservoir and trapped in the forming clathrate reservoir. These mole fractions depend on the fractions of the initial liquid volume (before volatile migration) remaining in the liquid and present in clathrates. Our computation starts from a predefined composition of the liquid reservoir. It uses an iterative process for which the number of moles in the liquid phase being trapped in clathrates between each iteration is equal to 10\(^{-6}\) the total number of moles available. The numerical procedure utilized to calculate at each step the relative abundances of guest species incorporated in clathrates is based on a statistical mechanical model that relates their macroscopic thermodynamic properties to the molecular structures and interaction energies [6-9]. The computation presented here is based on the assumption that only structure I clathrates form at equilibrium from a mixture of CH\(_4\) and C\(_2\)H\(_6\), supported by experiments [10].

Results: Figure 1 represents the evolution of the mole fractions of species present in the liquid reservoir and its associated clathrate as a function of the progressive liquid entrapment. Our computation has been conducted at a surface temperature of 91 K and the starting mole fractions of CH\(_4\) and C\(_2\)H\(_6\) have been set to 0.7 and 0.3 in the liquid reservoir, respectively. The mole fraction of C\(_2\)H\(_6\) in the liquid significantly decreases with progressive entrapment of the liquid reservoir, forcing this reservoir to become methane-pure when more than half (in mole fraction) of the initial reservoir has been trapped in clathrates. In this case, the mole fraction of C\(_2\)H\(_6\) is below 5\% in the liquid phase when more than ~40\% of the initial liquid reservoir is trapped in clathrate. C\(_2\)H\(_6\) is drawn out of the liquid phase because it is more efficiently trapped in clathrate than is CH\(_4\). The mole fraction of C\(_2\)H\(_6\) decreases progressively in the forming clathrate because of its sharp abundance decline in the liquid reservoir. At the end of the liquid reservoir enclathration, the mole fractions of CH\(_4\) and C\(_2\)H\(_6\) trapped in clathrate converge towards their starting values in the liquid, while the latter is methane rich.

Discussion: No direct measurement of the chemical composition of Titan’s lakes or seas has been done to date. Cassini Visual and Infrared Mapping Spectrometer data indicate the presence of liquid ethane in Ontario Lacus [11] but this only pertains to the topmost portion of the lake and it remains unclear how deep is that reservoir. On the other hand, indirect measurements (radar backscattering) of the composition of the much larger Ligeia Mare suggest that this sea is...
This apparent ethane deficiency in Ligeia Mare could have resulted from its interaction with an underlying clathrate layer that progressively formed from the entrapment of ethane.

Circumstantial evidence from a variety of geologic features and isotopic ratios of carbon, hydrogen, and potassium in the atmosphere suggest that methane resupply from the interior has been extensive, enough to produce vastly more ethane than is seen on the surface [13]. Our model shows that the ethane will then naturally be incorporated in the clathrate. One issue is how to “renew” the crustal water ice once saturated with ethane clathrate; the subduction model of Choukroun and Sotin [2] seems promising in this regard.

It is quite likely that Titan’s water ice crust has been largely methane clathrate hydrate over its history [15]. In this case, our model is unchanged, because ethane’s preferential incorporation in clathrate relative to methane means that the latter is driven out of the ice as the former is incorporated. In this way, methane will slowly work its way out of the crust and into the atmosphere—possibly mostly by way of the seas if indeed these are the most active sites of ethane-methane exchange as we suggest above. A signature of such mediation of the exchange of ethane and methane over time might be heterogeneity of the isotopic signature of methane in the seas over fracture zones where the methane is outgassing—or disequilibrium between the isotopic composition of methane in the sea and in the atmosphere. Either way, testing this requires a sea lander.

expressed as a function of the remaining fraction of the initial liquid reservoir.

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**References:**