

N₂-C₂H₆ CLATHRATE SUBSTITUTION AND EXPLOSIVE N₂ DEGASSING AS A POSSIBLE FORMATION MECHANISM OF SMALL LAKES ON TITAN

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Introduction: Titan has unique surface environments in the Solar System, characterized as the presence of several oceans and thousands of small lakes of liquid hydrocarbons. The small lakes are usually formed within sharp-edged depressions (SEDs) [1]. SEDs have unique morphological characteristics with very steep and raised rims of hundreds-meters-height, and deep and flat floors [1–3], which may provide a key to reveal the surface evolution of Titan.

Since its discovery, several hypotheses, including karst lake, thermokarst lake, nitrogen explosion, and cryovolcanic models, have been proposed for formation of SEDs and small lakes on Titan [3–6]. The karst and thermokarst models propose dissolution of surface organic layer by hydrocarbon liquid [4,5] or dissolution of subsurface hydrocarbon ice layers; however, these models may suffer from interpreting formation of raised rims of SEDs [3,6]. The nitrogen explosion model [3] proposes that explosions of subsurface liquid nitrogen aquifers occurred due to a phase transition to gas phase on ancient, cold Titan. Although this model would explain raised rims, some small lakes with a circular shape appear to be geologically young, possibly calling for the formation mechanism that might work even in the present age [6]. Given geomorphic similarity with terrestrial maars and calderas, crater lakes formed by cryovolcanic collapse has been also suggested for formation of SEDs [6]. However, the fact that SEDs are mostly found in north-pole regions is not simply explained by cryovolcanic collapse and may call for an alternative mechanism for formation of SEDs.

Here, we propose a new formation mechanism of SEDs; that is, nitrogen (N₂)-hydrocarbon (CH₄ and C₂H₆) clathrate substitution and N₂ degassing in the subsurface. We hypothesize that on ancient cold Titan, liquid N₂ might have percolated into the icy crust in north-pole regions [7], creating N₂ clathrate hydrate in the subsurface. After a climate transition to the current state, liquid hydrocarbons (CH₄ and C₂H₆) would have then precipitated and infiltrated into the subsurface of north-pole regions. Subsurface N₂ clathrate hydrate is thermodynamically stable if pores of clathrate hydrates are filled with a N₂ atmosphere. However, this would become unstable when liquid hydrocarbon fills the surrounding pores, possibly causing substitution of clathrate hydrates in the subsurface and consequent release of N₂.

In this paper, we studied N₂-C₂H₆ clathrate substitution process using molecular dynamics (MD) simulations. The objective of this study is (1) to examine whether substitution of clathrate hydrate and consequent N₂ release occur via interactions of N₂ clathrate and liquid hydrocarbon, and (2) to estimate a timescale for N₂ release under Titan's low-temperature conditions.

Methods: To the objectives end, we conducted MD simulations with GROMACS version 5.1.5 [8] and 2020.4 [9], with molecular models of TIP4P/Ice [10], OPLS_AA [11], and TraPPE [12]. As for the initial condition, we constructed the hydrate–fluid interface system with a box size (3.4×3.4×~10 nm) (Fig. 1a), which is composed of N₂ clathrate hydrate of 2×2×3 of the unit cell (Fig. 1b) contacting with hydrocarbon liquid of 500 C₂H₆ molecules. We then ran simulations for a few thousand nanoseconds (Fig. 1c, d) in Berendsen thermostat and barostat [8, 9] at 3 MPa, corresponding to ~4,000 m in depth on Titan, and various temperatures (130 to 260 K).

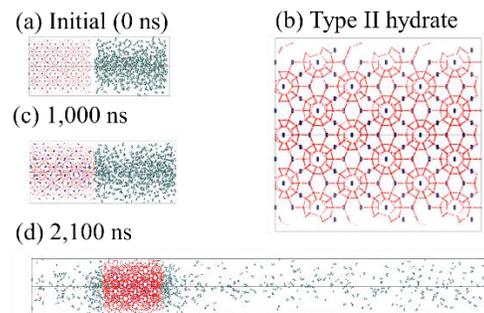


Fig. 1 Snapshots of the simulation at 3 MPa and 260 K: Initial configuration (0 ns) (a), type II nitrogen clathrate hydrate (b), configurations at 1,000 ns (c), and 2,100 ns (d). The dotted red lines indicate hydrogen bonds. N₂ molecules are in blue, while C₂H₆ molecules are green.

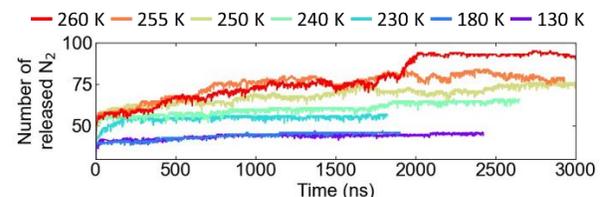


Fig. 2 Time evolution of N₂ number in the fluid phase at 3 MPa and various temperatures. The total N₂ number in the simulation is 288.

Results: Figure 1 shows that N_2 is released from cages of clathrate hydrate into a liquid C_2H_6 phase over time; meanwhile, some C_2H_6 molecules are entrapped into the cages. These results indicate substitution of N_2 to C_2H_6 occurs in clathrate hydrate.

Release of N_2 (~50 molecules) in the outermost cage (i.e., two monolayers of clathrate hydrate) occurs very rapidly ($< \sim 10^2$ ns) after interaction with C_2H_6 liquid. On the other hand, N_2 in deeper parts of clathrate hydrate is released slowly (order of 10^3 ns), with a temperature dependence (Fig. 2) which is possibly controlled by diffusion of molecules in clathrate hydrate.

In our simulation at 260 K, we found that rapid volume expansion occurred at $\sim 2,000$ ns (Fig. 1c). The rapid expansion seems to occur immediately after a sudden increase of N_2 in a fluid phase at $\sim 1,900$ ns (Fig. 2). We consider that the rapid volume expansion occurred due to degassing of N_2 from the liquid phase, resulting from a thermodynamic instability of C_2H_6 - N_2 liquid mixtures owing to low N_2 solubility. This instability occurs when the number of N_2 in the fluid is greater than ~ 85 (N_2 fraction $> \sim 15\%$ in the fluid) in our simulation, leading to an explosive expansion.

To understand the nature of N_2 release, we assume that N_2 release from clathrate hydrate at a depth (d) can be expressed as one-dimensional diffusion [13]:

$$d = \sqrt{Dt} \quad (1)$$

$$D = D_0 e^{-\frac{E_A}{RT}} \quad (2)$$

where D and D_0 are the diffusion coefficient at a finite temperature and the fitted maximal diffusion coefficient, respectively, t is time when a molecule comes out from depth d , E_A is the activation energy of diffusion, R is the gas constant, and T is temperature. By fitting our data at temperatures ≥ 230 K (Fig. 2), we obtain D_0 and E_A as $1.0 \times 10^{-2} - 1.6 \times 10^3$ cm²/s and 33 ± 12 kJ/mol, respectively. The obtained E_A is higher than but within a range of the assumed value of E_A (5–23 kJ/mol) for CH_4 - C_2H_6 clathrate substitution [13] based on gas diffusion through the ice [14,15], CO_2 clathrate growth [16], and strength of hydrogen bond [17].

Discussion: Using the obtained E_A , we estimate timescale for N_2 degassing under Titan's surface/subsurface conditions for different grain sizes of clathrate hydrate and temperatures (Fig 3). Figure 3 shows a strong dependence of the timescale on temperature and grain size. For instance, for a grain with a radius of 0.1 mm, N_2 release would take only 10^4 years at 130 K; whereas, more than $\sim 10^9$ years are necessary at 90 K. This suggests that substitution of N_2 - C_2H_6 clathrate would proceed ineffectively on Titan's surface at ~ 90 K; however, this may take place in geologically short times (e.g., $< 10^4$ years) in the subsurface if the subsurface temperature is higher than 110 K, which is achieved in 100 m depth with high thermal gradient

more than 0.2 K/m. The high thermal gradients on Titan can be achieved if the surface is covered with a layer of porous organic matter (e.g., haze particles).

We suggest that infiltration of liquid hydrocarbon in north-pole regions of Titan would have caused clathrate substitution and consequent N_2 degassing in the subsurface. This could have enhanced pressure locally (e.g., along with fractures or faults) due to volume expansion, which, in turn, may have led to a gas explosion when pressure exceeded strength of crustal ice, forming SEDs with raised rims and deep floors. If this is the case, SEDs could be served as geological evidence of a volatile exchange between the surface and subsurface of Titan, in response to a dramatic climate transition in the past.

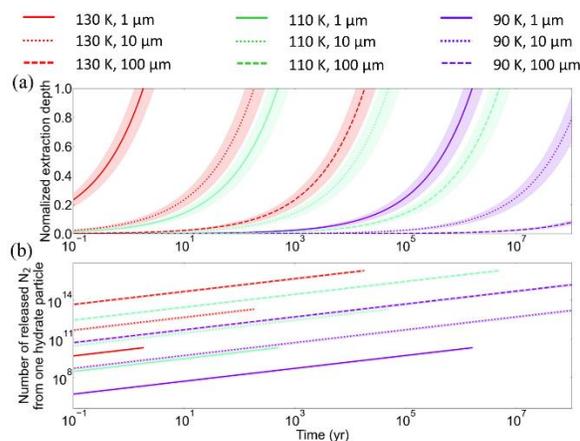


Fig. 3 (a) Depths of clathrate grain, where N_2 is released, normalized by grain radius (r) at different temperatures as a function of time; (b) the number of released N_2 from a clathrate hydrate grain.

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References:

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