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1 **Title: Pluto's ocean is capped by gas hydrates**

2

3 **Authors: Shunichi Kamata^{1*}, Francis Nimmo², Yasuhito Sekine³, Kiyoshi**
4 **Kuramoto⁴, Naoki Noguchi⁵, Jun Kimura⁶, Atsushi Tani⁷**

5

6 **Affiliations:**

7 ¹Creative Research Institution, Hokkaido University, N21, W10, Kita-ku, Sapporo,
8 001-0021 Japan.

9 ²Department of Earth and Planetary Sciences, University of California, Santa Cruz,
10 1156 High St., Santa Cruz, CA 95064 USA.

11 ³Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama,
12 Meguro-ku, Tokyo, 152-8550 Japan.

13 ⁴Department of CosmoSciences, Hokkaido University, N10, W8, Kita-ku, Sapporo,
14 060-0810 Japan.

15 ⁵Graduate School of Technology, Industrial and Social Sciences, Tokushima University,
16 2-1 Minami-Jousanjima-cho, Tokushima, 770-8506 Japan.

17 ⁶Department of Earth and Space Science, Osaka University, 1-1 Machikaneyama-cho,
18 Toyonaka, 560-0043 Japan.

19 ⁷Department of Human Environmental Science, Kobe University, 3-11 Tsurukabuto,
20 Nada-ku, Kobe, 657-8501 Japan.

21

22 *Correspondence to: Shunichi Kamata, Hokkaido University, kamata@sci.hokudai.ac.jp

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24 Many icy solar system bodies possess subsurface oceans. At Pluto, Sputnik
25 Planitia's location near the equator suggests the presence of a subsurface ocean
26 and a locally thinned ice shell. To maintain an ocean, Pluto needs to retain heat
27 inside. On the other hand, to maintain large variations in ice shell thickness,
28 Pluto's ice shell needs to be cold. Achieving such an interior structure is
29 problematic. Here we show that the presence of a thin layer of clathrate hydrates
30 (gas hydrates) at the base of the ice shell can explain both the long-term survival of
31 the ocean and the maintenance of shell thickness contrasts. Clathrate hydrates act
32 as a thermal insulator, preventing the ocean from complete freezing while keeping
33 the ice shell cold and immobile. The most likely clathrate guest gas is methane
34 either contained in precursor bodies and/or produced by cracking of organic
35 materials in the hot rocky core. Nitrogen molecules initially contained and/or
36 produced later in the core would likely not be trapped as clathrate hydrates,
37 instead supplying the nitrogen-rich surface and atmosphere. The formation of a
38 thin clathrate hydrate layer capping a subsurface ocean may be an important
39 generic mechanism maintaining long-lived subsurface oceans in relatively large
40 but minimally-heated icy satellites and Kuiper Belt Objects.

41 Liquid water oceans are thought to exist inside icy satellites of gas giants such
42 as Europa and Enceladus and the icy dwarf planet Pluto¹. Understanding the survival of
43 subsurface oceans is of fundamental importance not only to planetary science but also to
44 astrobiology. One indication of a subsurface ocean on Pluto is Sputnik Planitia, a
45 ~1000-km-wide basin. It is a topographical low and is located near the equator,
46 indicating that it is a positive gravity anomaly. To make this basin a positive gravity
47 anomaly, a subsurface ocean beneath a locally thinned ice shell (by ~90 km) is inferred².

48 The presence of an ocean suggests a “warm” (i.e., not completely frozen) Pluto.
49 However, unlike icy satellites, tides do not play an important role in heating the dwarf
50 planet³, and radiogenic heating is insufficient to avoid complete freezing unless the ice
51 shell is highly viscous ($>\sim 10^{16}$ Pa s (ref. 4)). Heat may be retained inside Pluto owing to
52 a thick surface thermal insulating layer resulting from high porosity and a high
53 concentration of nitrogen ice⁵. However, if the ice shell is warm, its viscosity should be
54 low⁶. Substantial viscous flow of ice would then occur, eliminating any local thickness
55 contrasts⁷. Consequently, a locally thinned shell suggests a “cold” Pluto ($<\sim 200$ K at the
56 base of the ice shell²). One way to reconcile these contradictory requirements is to
57 depress the freezing point of water by contaminating the ocean with anti-freeze
58 molecules, such as ammonia². However, to avoid substantial viscous relaxation of the
59 ice shell, the ammonia concentration needs to be ~ 30 wt% (Supplementary Fig. 1). Such
60 a high concentration is hard to justify; the ammonia concentration in comets, whose
61 chemical composition should be representative of Kuiper Belt Objects (KBOs)
62 including Pluto⁸, are mostly less than 1 % with respect to water⁹. In addition, an
63 ammonia concentration >20 wt% leads to an ocean density <1000 kg/m³
64 (Supplementary Fig. 2, ref. 10), which makes it difficult for Sputnik Planitia to be a
65 positive gravity anomaly¹¹. Another possibility is that the viscosity of the ice shell is
66 high due to the presence of high-strength material, such as salts¹² or silicate particles¹³.
67 However, in a multiphase system, the weaker phase (i.e., water ice) dominates the
68 flow^{12,13}. Consequently, inhibiting substantial viscous relaxation requires the stronger
69 phase (i.e., salts) to be the dominant component. Such an ice shell would have a high
70 density (e.g., ~ 1.3 g/cm³ for a mixture of 50% H₂O ice and 50% epsomite). While the
71 density of the ocean might also be high due to the presence of salts in the ocean¹¹, their

72 concentrations would be largely controlled by the formation of clay minerals and
73 evaporates in the rocky core, keeping the ocean salinity $< 4\text{--}5$ mol/L or < 10 mol%
74 relative to H_2O (ref. 14) and, thus, the ocean density to be < 1.3 g/cm³. In order for the
75 ice shell to float on the ocean and for Sputnik Planitia to be a positive gravity anomaly,
76 the ice shell has a density much lower than the ocean (at least by ~ 0.2 g/cm³ (ref. 11)),
77 and its major constituent needs to be water ice.

78 Instead, we propose that the ice shell has a thin layer of clathrate hydrates at its
79 base (Fig. 1). Clathrate hydrates, or gas hydrates, are solids in which water molecules
80 create cages trapping gas molecules¹⁵. Because the formation temperatures of clathrate
81 hydrates are higher than the melting point of pure water ice¹⁵ and the subsurface ocean
82 is sufficiently pressurized by the overlying ice shell, a freezing ocean would form
83 clathrate hydrates rather than water ice if dissolved gas concentrations are sufficiently
84 high¹⁶. The thermal conductivity of clathrate hydrates is about a factor of 5–10 smaller
85 than that of water ice¹⁷ and the viscosity of clathrate hydrates is about an order of
86 magnitude higher than that of water ice¹⁸. Because of these physical properties, a cap of
87 clathrate hydrates would act as a highly viscous thermal insulator between a subsurface
88 ocean and an ice shell. The temperature difference across this layer allows the presence
89 of a subsurface ocean with a temperature near the melting point of pure water ice while
90 the overlying ice shell maintains a much lower temperature at the same time. Its high
91 viscosity would also maintain shell thickness contrasts for a long time.

92

93 **Global thermal evolution of Pluto:**

94 We first evaluate the effect of clathrate hydrates on the thermal evolution of
95 Pluto using the physical properties of methane hydrates^{15,17} ($\text{CH}_4 \cdot n\text{H}_2\text{O}$ where $n \sim 6$)

96 (Methods). In the absence of clathrate hydrates, a subsurface ocean is expected to freeze
97 completely because thermal convection in the ice shell removes heat effectively from
98 the deep interior⁴ (Fig. 2a, b). To maintain a thick subsurface ocean, the ice shell needs
99 to be conductive, requiring a reference viscosity about one or two orders of magnitude
100 higher than 10^{14} Pa s, which is a typical value for terrestrial ice sheets¹⁹. This may not
101 be impossible but would require an extremely large ice grain size (a few cm)²⁰.
102 Interestingly, a thicker surface porous layer⁵ leads to a shorter ocean lifetime, because
103 such a layer enhances thermal convection in the ice shell beneath (Supplementary Fig.
104 3).

105 In contrast, if clathrate hydrates form, a thick subsurface ocean can be
106 maintained for billions of years even if the reference viscosity of water ice is assumed to
107 be 10^{14} Pa s (Fig. 2c). This is because heat from the ocean cannot be removed efficiently
108 through the clathrate hydrate layer. As the clathrate layer thickens the overlying water
109 ice layer cools, leading to a higher viscosity. Thus, thermal convection in the ice shell
110 becomes less vigorous, further reducing the freezing rate of the ocean (Fig. 2d).
111 Consequently, the clathrate hydrate layer remains thin, while reducing the freezing rate
112 of the ocean. If the clathrate hydrate layer grows from the beginning, its current
113 thickness can reach ~30 km (Supplementary Fig. 4a, b). If its formation is delayed, its
114 current thickness would be reduced (Supplementary Fig. 4c, d). Nevertheless, the
115 efficiency of heat removal decreases significantly and the ocean thickness remains
116 approximately constant following the formation of a clathrate hydrate layer.

117 As the ocean freezes and the ice shell thickens, the radius and surface area of
118 Pluto increase, leading to the formation of normal faults on the surface⁴. Pluto's surface
119 is covered by many such faults²¹, and their pattern indeed supports global expansion of

120 Pluto²². A future detailed image analysis estimating the change of Pluto's radius would
121 provide a constraint on the clathrate hydrate layer thickness and the start timing and/or
122 the duration of clathrate hydrate formation, which would inhibit freezing and faulting.

123

124 **Viscous relaxation of the ice shell:**

125 We next examine the effect of clathrate hydrates on the timescale of viscous
126 relaxation of the ice shell using the physical properties of methane hydrates^{15,17,18}
127 (Methods). The origin of the local interior structure beneath Sputnik Planitia (a thin ice
128 shell above a thick ocean) is considered to be associated with the large impact that
129 formed the Sputnik Planitia basin^{2,11}. Although the age of this impact is unknown, the
130 eroded rim of the basin suggests that it is likely to be billions of years²³. Consequently,
131 the timescale of viscous relaxation should be at least one billion years.

132 If a clathrate hydrate layer does not exist, shell thickness contrasts can be
133 maintained for only a few million years unless an extremely viscous ice shell and/or an
134 extremely cold ocean is assumed (Fig. 3, Supplementary Fig. 5). In contrast, if a
135 clathrate hydrate layer of a few to 10 km in thickness exists at the base of the ice shell,
136 the timescale of ice shell relaxation is increased even by 3 to 4 orders of magnitudes and
137 can exceed one billion years even if we assume typical pure-water properties both for
138 the water ice layer and the ocean (Fig. 3). Such a large increase in the timescale results
139 from the combined effect of a low temperature in the water ice layer and the high
140 viscosity of clathrate hydrates (Supplementary Fig. 6). Thus, under the presence of a
141 thin clathrate hydrate layer, an extremely ammonia- or salt-rich Pluto is no longer
142 necessary to explain a long viscous relaxation timescale for the ice shell.

143

144 **Implications for geochemical evolution:**

145 Various gas species can form clathrate hydrates, though some species (e.g.,
146 CH₄) occupy clathrate hydrates more readily than others (e.g., N₂). This behavior may
147 explain the unique volatile composition observed on Pluto. Comets contain ~1 % of
148 CH₄ and a few % of CO with respect to water⁹, and even these low concentrations are
149 sufficient to form a clathrate hydrate layer several tens of km in thickness (Methods,
150 Supplementary Fig. 7). When Pluto formed, volatiles trapped in precursor bodies would
151 have been partitioned between the atmosphere, ice shell, and the subsurface ocean.
152 Gases may also have been initially trapped as clathrate hydrates near the surface²⁴,
153 which may also have happened at Titan²⁵. At an early stage, primordial CH₄ and CO
154 dissolved in the ocean would likely form mixed clathrate hydrates at depth. Although
155 precursor bodies of Pluto may be rich in CO₂ (ref. 9), CO₂ may not be major guest
156 molecules of clathrate hydrates above the ocean because its high density indicates that
157 CO₂-rich hydrates would not float on the ocean unless the ocean is highly salty
158 (Supplementary Table 1). CO₂ clathrate hydrates at the seafloor could have acted as a
159 thermostat to prevent heat transfer from the core to the ocean. Primordial CO₂, however,
160 may have been converted into CH₄ through hydrothermal reactions within early Pluto
161 under the presence of Fe-Ni metals²⁶. Because CH₄ and CO predominantly occupy
162 clathrate hydrates, the components that degassed into the surface-atmosphere system
163 would be rich in other species, such as N₂ (refs 8,27,28). Trapping of CO in deep
164 clathrate hydrates and degassing of N₂ may explain the low CO/N₂ on the surface of
165 Pluto²⁹. Further constraints on likely incorporation of cometary species, particularly CO,
166 into clathrate hydrates are desirable, either via experiments or a detailed statistical
167 thermodynamic approach¹⁵.

168 As clathrate hydrate formation continues, concentrations of dissolved gases
169 decrease if gases are not supplied to the ocean, eventually leading to the formation of
170 pure water ice instead of clathrate hydrates at the interface between the ocean and ice
171 shell. Thus, to form clathrate hydrates continuously in the ocean, secondary gases need
172 to be continuously supplied to the ocean in the later stages. One plausible mechanism to
173 supply gases is thermal cracking of organic materials in the rocky core, which would
174 mainly produce CH₄ (refs 30,31). Organic materials are abundant in cometary solids
175 (~45 wt% of dust grains of 67P/Churyumov-Gerasimenko³²). Thermogenic CH₄ can be
176 produced where temperatures exceed ~150 K (ref. 33), and such a condition can be
177 achieved in a large portion of Pluto's core for most of its history⁸ (Supplementary Fig.
178 8). A high-temperature origin of CH₄ would leave a trace in its isotopic composition³⁴.
179 N₂ can also be produced via pyrolysis of organic matter when temperatures exceed
180 ~350 K (ref. 35), though CH₄ would be preferentially trapped in clathrate hydrates²⁷.
181 Within a hot and porous core, high-temperature water-rock reactions would also occur.
182 These can produce various gas species depending on many factors, including the redox
183 state of the reactions, but the main gas species would be H₂ for chondritic rocks³⁶.
184 However, H₂ hydrates do not form unless H₂ is dominant in gases³⁷. If organic materials
185 within the rocky core contact with the hydrothermal fluids, a large quantity of C-bearing
186 gas species, such as CH₄, also would be included in the fluids through hydrothermal
187 decomposition³³. Thus, under the presence of abundant CH₄, H₂ would be degassed to
188 the surface and rapidly lost to the space because of its small mass. In contrast, heavier
189 N₂ becomes a major volatile at Pluto's surface^{38,39}. Gas production processes in a hot
190 rocky core are unlikely to occur in small icy bodies. This may be why CH₄ and N₂ are
191 found only on large KBOs such as Pluto and Eris but not on small KBOs such as

192 Charon^{38,40}. Furthermore, icy bodies possessing subsurface oceans may have low CO/N₂
193 and/or CH₄/N₂ ratios on their surface.

194 The current presence of subsurface oceans in outer solar system bodies is often
195 explained by a high concentration of ammonia^{1,41}, though it is only rarely detected^{9,38,42}.
196 In contrast, a thin clathrate hydrate layer is equally effective at maintaining subsurface
197 oceans and preventing motion of the ice shell, while requiring much lower
198 concentrations of secondary species (e.g., CH₄) whose presence is commonly inferred.
199 Such layers provide a likely explanation for minimally-heated but ocean-bearing
200 worlds.

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308

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312

313 **Author contributions:** S.K. developed the idea of this study, conducted thermal
314 evolution and viscous relaxation calculations, created all figures, and was the primary
315 author of the manuscript. F.N. participated in numerous discussions and co-wrote the
316 manuscript. Y.S. and K.K. provided information on gas production mechanisms and
317 likely guest gas species of clathrate hydrates. N.N. provided detailed information on
318 clathrate hydrates and calculated their densities. J.K. participated in numerous
319 discussions on thermal evolution models. A.T. provided detailed information on
320 clathrate hydrates formation. All the authors participated in interpretation of the results.

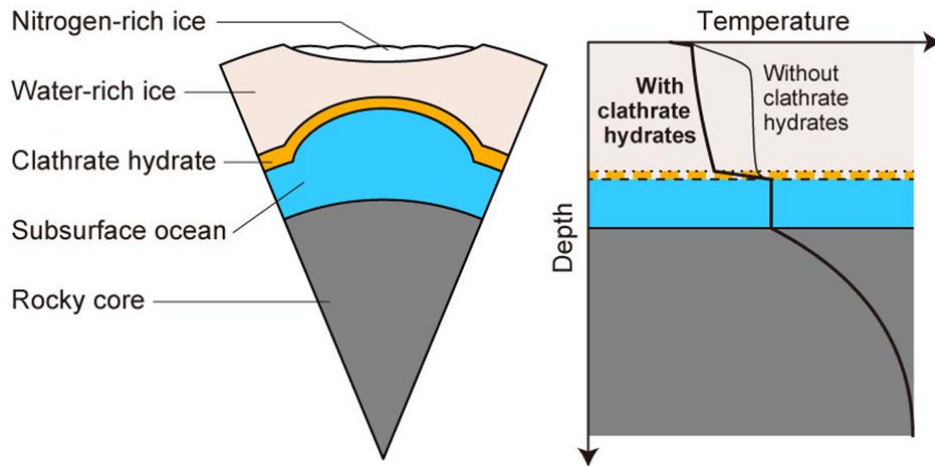
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323 **Author Information:** The authors declare no competing financial interests.
324 Correspondence and requests for materials should be addressed to S.K.
325 (kamata@sci.hokudai.ac.jp).

326

327 **Figures:**

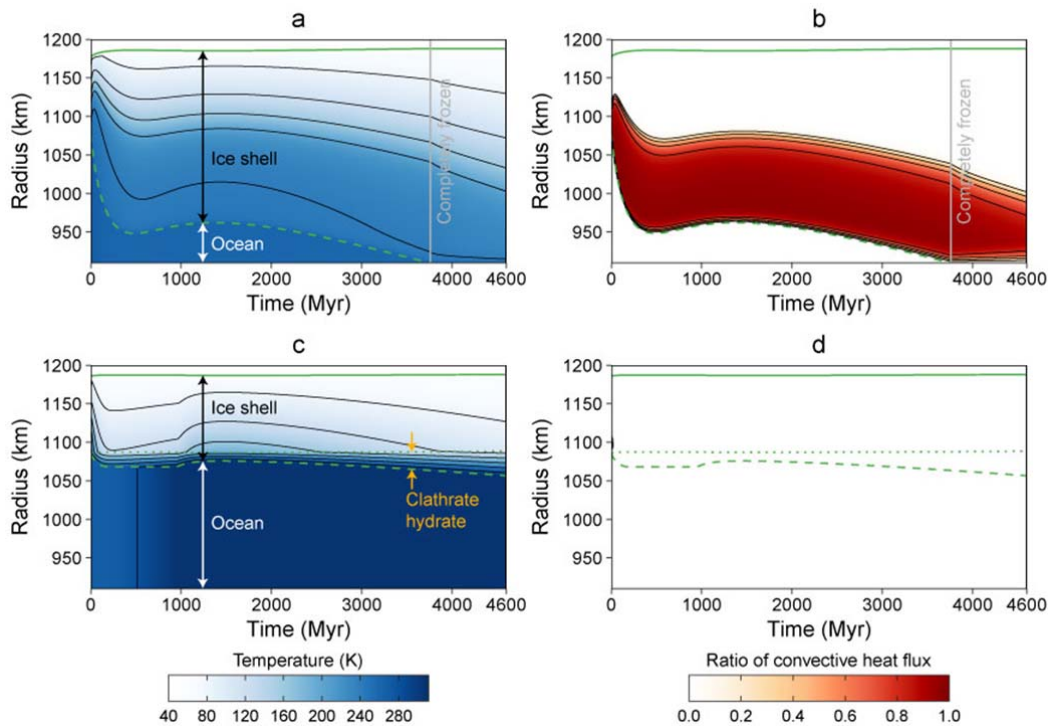


328

329 **Figure 1 | Schematic diagram of the interior structure of Pluto.** The ice shell has a
330 thin clathrate hydrate layer at its base. Temperature changes substantially across
331 this layer immediately above the subsurface ocean, leading to a conductive shell
332 rather than a convective shell. Nitrogen-rich ice on the surface is the bright surface
333 of Sputnik Planitia.

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337 **Figure 2 | Time evolution of the interior thermal profile above the rocky core.** Here

338 the reference viscosity of water ice is 10^{14} Pa s, the initial ice shell thickness is 100

339 km, and the surface insulating layer thickness is 5 km. The green solid, dashed, and

340 dotted curves indicate the surface of Pluto, the boundary between the ice shell and

341 the ocean, and the boundary between the water ice layer and the clathrate hydrate

342 layer, respectively. **a**, The temperature profile for the case without clathrate hydrate

343 formation. The subsurface ocean becomes thin rapidly and freezes completely at

344 ~ 3.8 Gyr. **b**, The ratio of the convective heat flux to the total heat flux (the sum of

345 the convective and conductive heat fluxes) for the case of **a**. The lower part of the

346 ice shell where temperature is nearly constant is highly convective. **c**, The

347 temperature profile for the case with clathrate hydrate formation. Clathrate hydrate

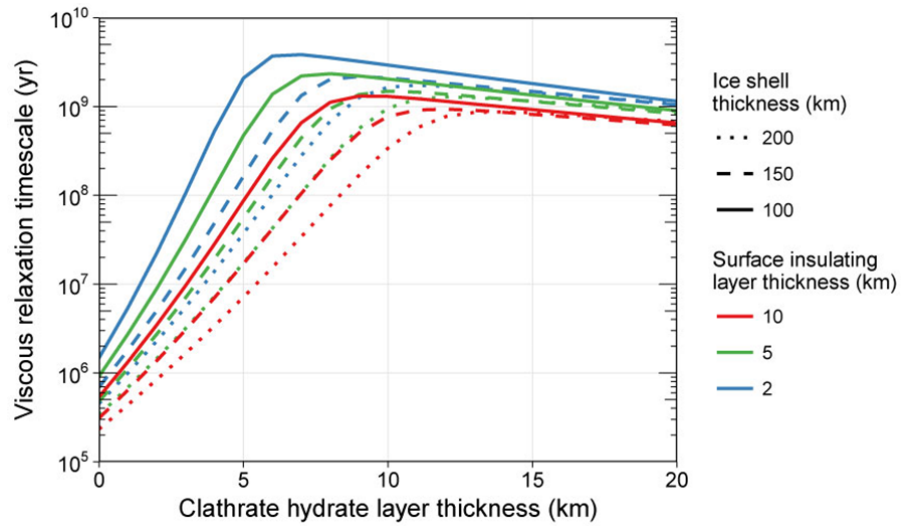
348 formation starts from the beginning (0 yr). The subsurface ocean remains thick,

349 and the water ice layer is cold throughout. **d**, The ratio of the convective heat flux

350 to the total heat flux for the case of **c**. Convection does not occur in the ice shell.

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354 **Figure 3 | Timescale of viscous relaxation of the ice shell.** Results for different layer
 355 thicknesses are shown. The reference viscosity of water ice is 10^{14} Pa s, and
 356 freezing-point depression due to impurities in the ocean is not considered. The
 357 presence of a clathrate hydrate layer ~ 5 – 10 km in thickness leads to a timescale of
 358 viscous relaxation longer than 10^9 yr.

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360

361 **Methods:**

362 **Thermal evolution:**

363 To calculate the time evolution of the radial temperature profile of Pluto, we used the
364 code developed by ref. 43. We modified the code to incorporate the effects of a clathrate
365 layer and those of a surface thermal insulating layer.

366 We assume a 3-layer Pluto, consisting of an ice shell (solid), a subsurface
367 ocean (liquid), and a rocky core (solid). The time evolution of temperature in the solid
368 parts is obtained by solving the equation:

$$369 \quad \rho C_p \frac{dT}{dt} = -\frac{1}{r^2} \frac{d}{dr} (r^2 F_{\text{cond}} + r^2 F_{\text{conv}}) + Q \quad (1)$$

370 where ρ is density, C_p is specific heat, T is temperature, t is time, r is radial distance
371 from the center, F_{cond} is conductive heat flux, F_{conv} is convective heat flux, and Q is
372 volumetric heating rate. F_{cond} is given by the product of thermal conductivity and the
373 local thermal gradient while F_{conv} is estimated using a modified mixing length theory⁴³
374 (see below).

375 The core is assumed to be purely conductive ($F_{\text{conv}} = 0 \text{ W/m}^2$) and to be
376 uniformly heated from within due to the decay of long-lived radioactive elements. The
377 heating rate for carbonaceous chondrites^{4,43} is used. The density, specific heat, and
378 thermal conductivity of the core are 3000 kg/m^3 , 1000 J/kg/K , and 3 W/m/K ,
379 respectively. The radius of the core is $\approx 910 \text{ km}$, which is calculated from eq. (2) of ref. 5
380 assuming the mean density of Pluto⁴⁴ (1854 kg/m^3), the present-day radius of Pluto⁴⁴
381 (1188 km), and the density of ices (including clathrate hydrates; 920 kg/m^3).

382 The subsurface ocean is assumed to be an inviscid fluid, and the ocean
383 temperature is assumed to be uniform. For the case without clathrate hydrate formation,
384 the ocean temperature is calculated from the pressure-dependent melting point of pure

385 water ice⁴⁵. For the case with clathrate hydrate formation, it is between the melting point
 386 of pure water ice and the dissociation temperature of methane hydrate¹⁵. No heat
 387 production in the ocean is assumed.

388 The ice shell is divided into 3 layers: a surface insulating layer (i.e., a top
 389 low-conductivity layer), a water ice layer, and a basal clathrate hydrate layer. The
 390 thickness of the top layer is assumed to be constant and to be 5 km unless otherwise
 391 noted. The thin top and basal layers are assumed to be purely conductive, and the thick
 392 intermediate layer is assumed to be convective or conductive depending on the viscosity.
 393 The thermal conductivities from the top to the bottom layers are 1 W/m/K (ref. 5),
 394 $0.4685 + 488.49/T$ W/m/K where T is temperature in Kelvin (ref. 46), and 0.6 W/m/K
 395 (ref. 17), respectively. The temperature-dependent specific heat of water ice⁴⁷ and that
 396 of methane hydrate⁴⁸ are used. No heat production ($Q = 0$ W/m³) in the ice shell is
 397 assumed. F_{conv} for the intermediate part is given by

$$398 \quad F_{\text{conv}} = \begin{cases} -\frac{\alpha C_p \rho^2 g l}{18\eta} \left\{ \frac{dT}{dr} - \left(\frac{dT}{dr} \right)_s \right\} & \left(\text{for } \frac{dT}{dr} \leq \left(\frac{dT}{dr} \right)_s \right) \\ 0 & \left(\text{for } \frac{dT}{dr} > \left(\frac{dT}{dr} \right)_s \right) \end{cases} \quad (2)$$

399 where $\alpha = 10^{-4}$ /K is thermal expansivity of ice, g is gravitational acceleration, l is the
 400 mixing length, η is viscosity of ice, and $(dT/dr)_s$ is the adiabatic thermal gradient. dT/dr
 401 is calculated by local thermal gradient, while $(dT/dr)_s$ is given by $-\alpha g T / C_p$. l is chosen so
 402 that it reproduces a scaling law between the Rayleigh number and the Nusselt number
 403 based on 3D numerical calculations^{43,49}. l is updated at each time step since it depends
 404 on the thickness of the layer, rheological parameters, and the temperature difference
 405 across the layer⁴³. η is given by

$$406 \quad \eta = \eta_{\text{ref}} \exp \left(\frac{E_a}{R_g T_{\text{ref}}} \left(\frac{T_{\text{ref}}}{T} - 1 \right) \right) \quad (3)$$

407 where η_{ref} is reference viscosity of ice, $E_a = 60$ kJ/mol is the activation energy, R_g is the

408 gas constant, $T_{\text{ref}} = 273 \text{ K}$ is the reference temperature^{4,43,50}. The nominal value of η_{ref} is
409 10^{14} Pa s (ref. 19). Note that we assume a Newtonian rheology. This assumption is
410 appropriate under typical conditions for terrestrial ice sheets (i.e., grain size $\sim 1 \text{ mm}$,
411 stress $\sim 10^{-3} \text{ MPa}$, temperature near the melting point) (ref. 51). Nevertheless, Pluto's
412 ice shell may exhibit non-Newtonian behavior (due to a large grain size, for example).
413 The effect of non-Newtonian flow can be imitated by a Newtonian fluid with a smaller
414 activation energy^{52,53}. Calculation results using different activation energies are shown
415 in Supplementary Fig. 9. We find that a smaller activation energy leads to a faster
416 freezing of a subsurface ocean beneath a convective ice shell. Consequently, our model
417 calculations using a Newtonian rheology provide the longest ocean lifetime for cases
418 without a clathrate hydrate layer. On the hand, for cases with a clathrate hydrate layer,
419 different activation energies lead to nearly the same result because the ice shell is
420 conductive. Thus, our conclusion does not change even if Pluto's ice shell exhibits
421 non-Newtonian behavior. It is noted that results shown in Supplementary Fig. 9 assume
422 the reference viscosity of water ice of 10^{14} Pa s . Although different creep mechanisms
423 may lead to different reference viscosities, its quantification is left for another study.

424 The initial thickness of the ice shell is assumed to be 100 km. Initial
425 temperature in the ice shell linearly increases with depth from 40 K at the surface to the
426 pressure-dependent melting point of water ice⁴⁵ at the base of the ice shell. The initial
427 temperature of the ocean and the rocky core is assumed to be uniform (i.e., the melting
428 point of water ice). Different initial conditions do not affect the long-term evolution^{4,43}.
429 The exception is an initially completely frozen case; ref. 4 reported that a subsurface
430 ocean does not appear if an initially completely frozen Pluto and $\eta_{\text{ref}} \leq 10^{15} \text{ Pa s}$ are
431 assumed. However, the conditions required for the formation of a subsurface ocean

432 based on their results are too strict because a freezing-point depression due to pressure
433 is not incorporated in their calculations. A detailed investigation of such conditions is
434 beyond the scope of this study and is left for another study.

435 The temporal change in the thickness of the ice shell is calculated from the
436 difference between the outgoing and incoming heat fluxes at the base of the ice shell.
437 Note that this difference in heat flux is used not only to change the thickness of the ice
438 shell but also to change the temperature of the ocean. For the case without clathrate
439 hydrate formation, the effect of the ocean temperature change caused by a change in the
440 ice shell thickness is incorporated by using an effective latent heat⁴³. For the cases with
441 clathrate hydrate formation, the change in the thickness of the ice shell is interpreted as
442 that of the clathrate hydrate layer. If the outgoing heat flux is higher than the incoming
443 heat flux, the clathrate hydrate layer becomes thicker, keeping the ocean temperature
444 constant. If the outgoing heat flux is lower than the incoming heat flux, the ocean
445 temperature increases, keeping the layer constant until the ocean temperature reaches
446 the pressure-dependent dissociation temperature of methane hydrate¹⁵. If the ocean
447 temperature reaches the dissociation temperature, the clathrate hydrate layer becomes
448 thinner. As the clathrate hydrate layer becomes thinner and the pressure at the top of the
449 ocean decreases, the ocean temperature decreases because of the pressure dependence of
450 dissociation temperature. Similar to the case without clathrate hydrate formation, the
451 effect of pressure dependence of dissociation temperature is included by using an
452 effective latent heat. Latent heats of water ice and methane hydrate are 333 kJ/kg and
453 437 kJ/kg (ref. 54), respectively. Note that the radius of Pluto changes as the thicknesses
454 of the ice shell and the ocean (the density of 1000 kg/m³ is assumed for the latter)
455 change in order to conserve the total mass of Pluto. The initial radius of Pluto is

456 determined so that the final radius becomes the present-day value through trial and
457 error.

458 The surface temperature is fixed to 40 K, and the thermal gradient at the center
459 is fixed to 0 K/m. The temperatures at the base of the ice shell and the top of the rocky
460 core are the same and are given by temperature of the ocean if a subsurface ocean exists.
461 If the ocean is completely solidified, the temperature at the boundary between the ice
462 shell and the rocky core is obtained by equating the heat flux at the top of the rocky core
463 to that at the base of the ice shell. Temperatures and heat fluxes at the boundaries within
464 the ice shell are assumed to be continuous. For the case with clathrate hydrate formation,
465 the start time of clathrate hydrate formation of 0 yr and no pre-existing clathrate hydrate
466 layer are assumed unless otherwise noted. We calculate the thermal evolution for 4.6
467 Gyr for each calculation.

468

469 **Viscous relaxation:**

470 To calculate the timescale of viscous relaxation for the ice shell of Pluto, we
471 followed the procedure adopted by ref. 7. We assume that the thinned portion of the ice
472 shell has a bowl-shaped topography at the base of the ice shell. More specifically, the
473 cross section can be described using a quadratic function, and the height and radius of
474 the bowl are assumed to be 80 km and 500 km, respectively. These values are chosen
475 assuming a nearly (Airy) isostatically compensated basin before the loading of
476 nitrogen-rich ice^{2,11}. The shape of the basal topography is then expressed as a
477 superposition of zonal components of spherical harmonic functions. In this study, we
478 consider spherical harmonic degrees from 1 to 20. The time evolution of the amplitudes
479 (coefficients) of each spherical harmonic for 10^{10} yr is obtained using the numerical

480 code calculating spheroidal viscoelastic deformation of a planetary body developed by
 481 ref. 55 (see below). The time evolution of the basal topography can be calculated by
 482 superposing the spherical harmonics with time-dependent amplitudes. The timescale of
 483 viscous relaxation is defined as the time when the volume of the bowl becomes $1/e$ of
 484 the initial condition where e is Napier's constant.

485 The governing equations are the linearized equation of momentum
 486 conservation given by

$$487 \quad \nabla_j \cdot (\sigma_{ij} - P\delta_{ji}) + \rho \nabla_i \phi = 0, \quad (4)$$

488 the Poisson's equation for the gravitational field given by

$$489 \quad \nabla^2 \phi = -4\pi G\rho, \quad (5)$$

490 and the constitutive equation for a Maxwell medium given by

$$491 \quad \frac{d\sigma_{ji}}{dt} + \frac{\mu}{\eta} \left(\sigma_{ji} - \frac{\sigma_{kk}}{3} \delta_{ji} \right) = \left(\kappa - \frac{2\mu}{3} \right) \frac{de_{kk}}{dt} \delta_{ji} + 2\mu \frac{de_{ji}}{dt}, \quad (6)$$

492 where ∇_i is a spatial differentiation in direction of i ($= x, y, z$), σ_{ji} is stress tensor, e_{ji} is
 493 strain tensor, P is hydrostatic pressure, δ is the Kronecker delta, ϕ is gravitational
 494 potential, G is the gravitational constant, ρ is density, μ is shear modulus, η is viscosity,
 495 κ is bulk modulus. Application of spectral harmonic expansion to the governing
 496 equations leads to a six-component, time-dependent, inhomogeneous first-order
 497 ordinary differential equation system. The major assumptions are a
 498 spherically-symmetric steady-state interior structure, small deformation amplitudes, and
 499 a linear viscoelasticity⁵⁵. These assumptions are valid to estimate the timescale of
 500 viscous relaxation, though more detailed numerical calculations would be necessary for
 501 precisely estimating the shape of the ice shell.

502 Following the thermal evolution calculations, we use a 3-layer Pluto model,
 503 though a steady-state thermal profile is adopted because what we calculate is the

504 timescale of viscous relaxation under a given interior structure. We assume that the ice
505 shell consists of Maxwell viscoelastic material, that the subsurface ocean is an inviscid
506 liquid, and that the rocky core consists of purely elastic material. The radius of the core
507 is determined in the same manner as that done in thermal evolution calculations.
508 Different ice shell thicknesses, clathrate hydrate layer thicknesses, and surface
509 insulating layer thicknesses are considered.

510 The densities of the ice shell, the ocean, and the core are 920 kg/m^3 , 1000
511 kg/m^3 , and 3000 kg/m^3 , respectively, which are used in the thermal evolution
512 calculations. The shear moduli of the ice shell, the ocean, and the core are 3.3 GPa , 0
513 GPa , and 10 GPa , respectively. We adopt an incompressible ($\kappa \rightarrow \infty$ and $e_{kk} \rightarrow 0$) limit
514 because of the small size of Pluto. The viscosity in the ice shell is calculated from the
515 temperature profile adopting the same rheological model. The surface temperature is
516 fixed to 40 K . The temperature at the base of the ice shell is assumed to be the
517 pressure-dependent melting point of pure water ice⁵⁶ unless otherwise noted. Assuming
518 a steady-state conductive profile with given boundary temperatures, we calculate the
519 temperature profile in the ice shell analytically. The thermal conductivity profile is the
520 same as that used in thermal evolution calculations. The reference viscosities of water
521 ice and clathrate hydrates are 10^{14} Pa s (ref. 19) and $2 \times 10^{15} \text{ Pa s}$ (ref. 18), respectively,
522 unless otherwise noted. The activation energy of water ice and clathrate hydrates are 60
523 kJ/mol (ref. 50) and 90 kJ/mol (ref. 18), respectively, unless otherwise noted. The upper
524 limit of the viscosity is 10^{30} Pa s , though the choice of this value does not affect the
525 timescale of viscous relaxation of topography at the base of the ice shell.

526

527 **Mass balance:**

528 We calculate the amount of methane with respect to water in the ice shell and subsurface
529 ocean. The thicknesses of these layers are determined in the same manner as in viscous
530 relaxation calculations; the thickness of the ice shell is a free parameter while that of the
531 ocean is calculated so that the mean density becomes the observed value. The ice shell
532 is divided into an outer pure water ice layer and a deeper methane hydrate layer. We
533 assume methane hydrate (Structure I) of full cage occupancy (i.e., $\text{CH}_4 \cdot 5.75 \text{H}_2\text{O}$) (ref.
534 15). The ocean is assumed to consist of water and methane only. We use the pressure at
535 the top of the ocean and the melting point of pure water ice⁵⁶ to calculate the (pressure-
536 and temperature-dependent) solubility of methane in the ocean⁵⁷.

537

538

539 **Data availability:**

540 The data that support the plots within this paper and other findings of this study
541 are available from the corresponding author on reasonable request.

542

543

544 **Code availability:**

545 Codes for the thermal evolution and viscous relaxation calculations are
546 available upon reasonable request from S.K.

547

548

549 **References (Methods):**

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551 modified mixing length theory: Application to Saturnian icy satellites. *J. Geophys.*

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1 **Supplementary Information: Pluto's ocean is capped by gas hydrates**

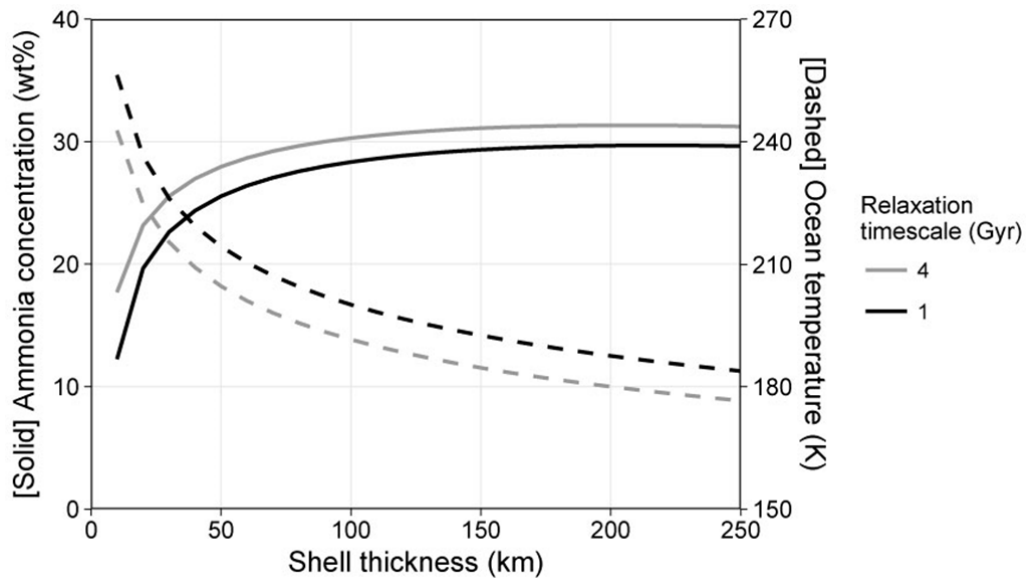
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3 Shunichi Kamata, Francis Nimmo, Yasuhito Sekine, Kiyoshi Kuramoto, Naoki Noguchi,

4 Jun Kimura, Atsushi Tani

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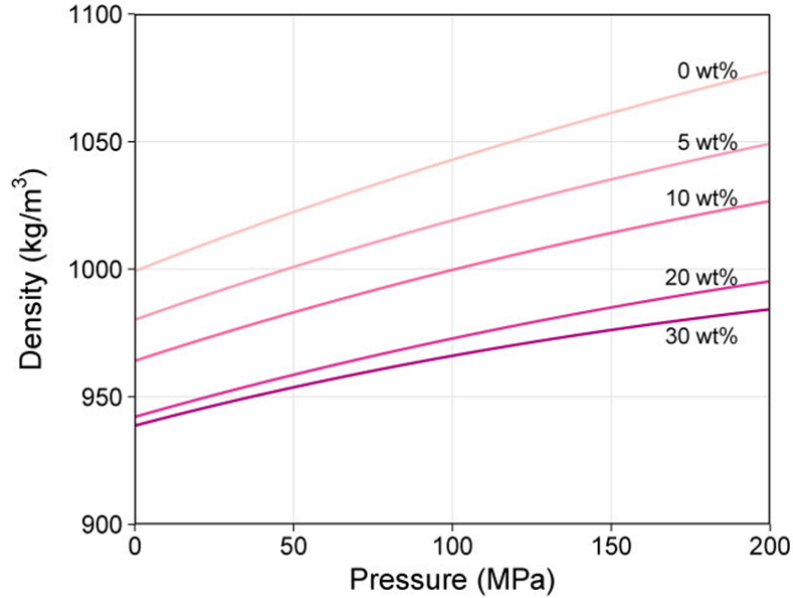


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8 **Supplementary Fig. 1 | Ammonia concentration and temperature of the subsurface**
9 **ocean required for avoiding substantial lateral flow in the ice shell without**
10 **clathrate hydrates.** The ocean temperature is calculated analytically by using the
11 method of ref. 2. The corresponding ammonia concentration is calculated from an
12 equation based on laboratory experiments⁴⁵. A shell thickness less than ~100 km is
13 unlikely because the height of the thickened portion of the ocean is expected to be ~80
14 km for an isostatically compensated basin 7 km in depth^{2,11} before the loading of
15 nitrogen ice sheet.

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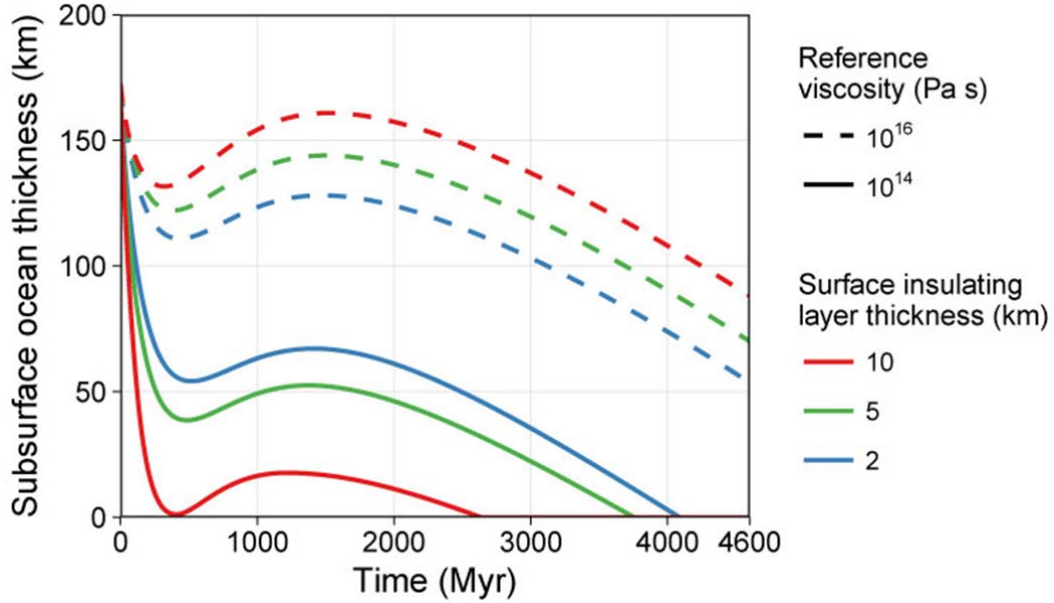


18

19 **Supplementary Fig. 2 | Density of ammonia-water liquid.** The density is calculated
20 analytically by using the method of ref. 10. The temperature is assumed to be the
21 melting point depending on pressure and ammonia concentration⁴⁵. An ammonia
22 concentration ≥ 20 wt% is unlikely because the ocean density becomes < 1000 kg/m³,
23 which will make the Sputnik Planitia basin a negative gravity anomaly¹¹.

24

25

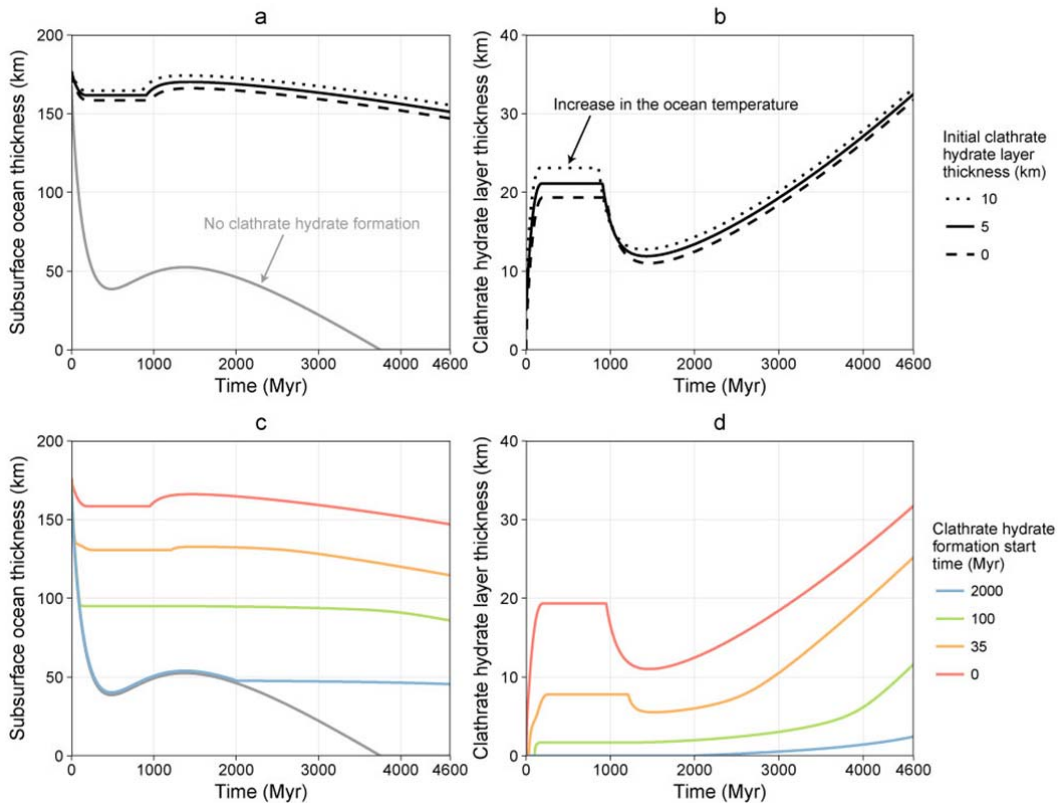


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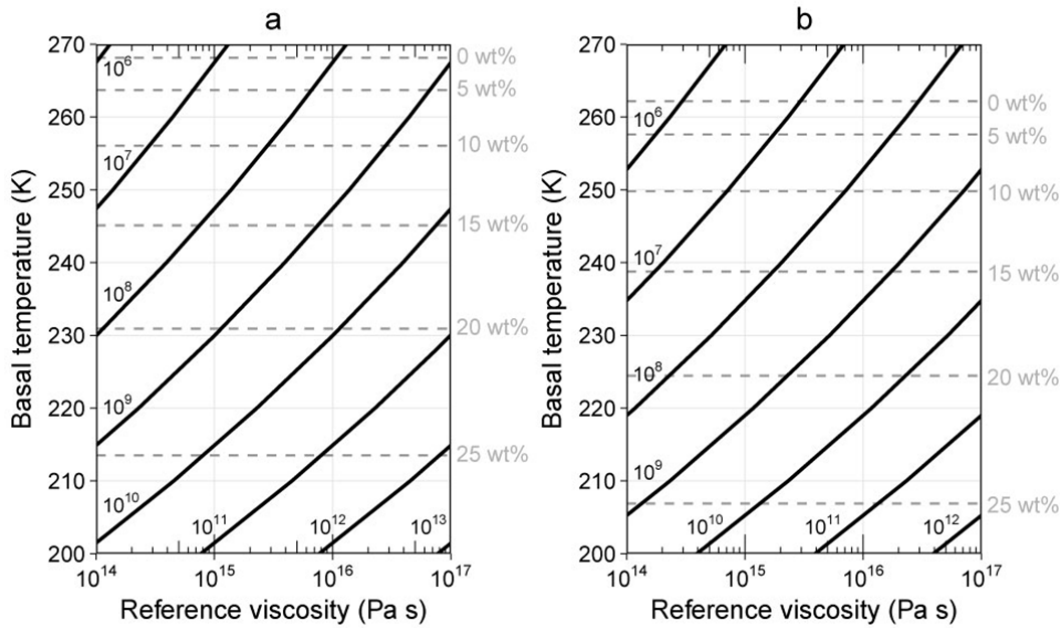
27 **Supplementary Fig. 3 | Time evolution of the subsurface ocean thickness for cases**
 28 **without clathrate hydrates.** Results for different reference viscosities of water ice and
 29 different thicknesses of a surface insulating layer are shown. A high reference viscosity
 30 results in a conductive ice shell. In such a case, a thicker surface insulating layer leads
 31 to a thicker ocean. In contrast, a low reference viscosity results in a convective ice shell,
 32 and the effect of a surface insulating layer becomes opposite from the case of a
 33 conductive shell (see text).

34

35



36
 37 **Supplementary Fig. 4 | Time evolution of Pluto's interior structure for cases with**
 38 **and without clathrate hydrate layers.** Here the reference viscosity of water ice is 10^{14}
 39 Pa s, the initial ice shell thickness is 100 km, and the surface insulating layer thickness
 40 is 5 km. **a**, The evolution of the subsurface ocean thickness for different pre-existing
 41 clathrate hydrate layer thicknesses. Clathrate hydrate formation starts from the
 42 beginning (0 yr). The gray line represents the result without clathrate hydrates. **b**, The
 43 evolution of clathrate hydrate layer thickness for the results shown in **a**. The thickness
 44 of the clathrate hydrate layer reaches ~ 30 km. **c**, The same as **a** but for different start
 45 timings of the clathrate hydrate formation. No pre-existing clathrate hydrate layer is
 46 assumed. **d**, The same as **b** but for the results shown in **c**. An earlier start of clathrate
 47 hydrates formation leads to a thicker clathrate hydrate layer.
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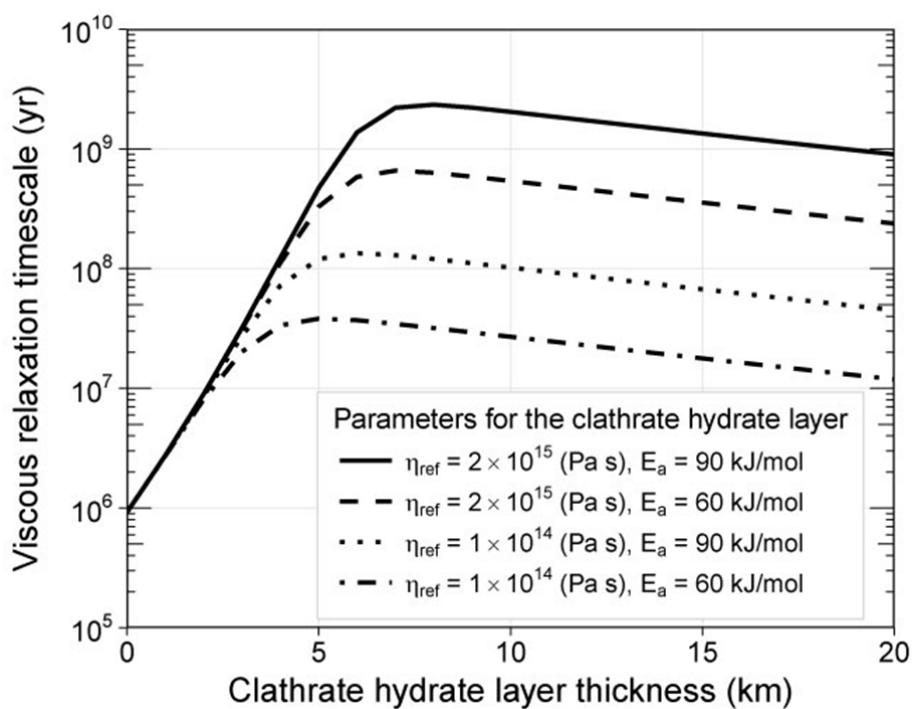


50

51 **Supplementary Fig. 5 | Timescale of viscous relaxation of the ice shell without**
 52 **clathrate hydrates.** Results for the ice shell thickness of **a** 100 km and of **b** 200 km,
 53 respectively, are shown. The surface insulating layer thickness is 5 km. Numbers
 54 indicate the relaxation timescale in yr. Horizontal gray lines show corresponding
 55 ammonia contents in the ocean⁴⁵. The nominal model (i.e., a reference viscosity of 10^{14}
 56 Pa s and an ammonia concentration of 0 wt%) leads to a relaxation timescale of only
 57 $\sim 10^6$ yr.

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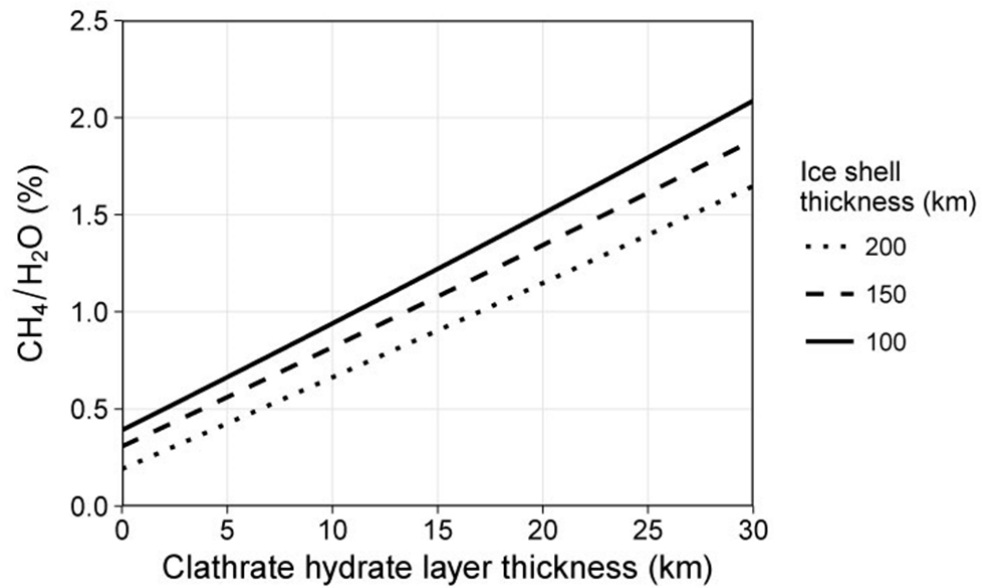


60

61 **Supplementary Fig. 6 | Timescale of viscous relaxation of the ice shell assuming**
 62 **different rheological parameters for the clathrate hydrate layer.** Here the reference
 63 viscosity of water ice is 10^{14} Pa s, the ice shell thickness is 100 km, the surface
 64 insulating layer thickness is 5 km, and freezing-point depression due to impurities in the
 65 ocean is not considered. The presence of a clathrate hydrate layer ~ 5 km in thickness
 66 increases the relaxation timescale by a factor of ~ 30 . Both a reference viscosity and an
 67 activation energy of clathrate hydrates higher than those of pure water ice increase the
 68 relaxation timescale.

69

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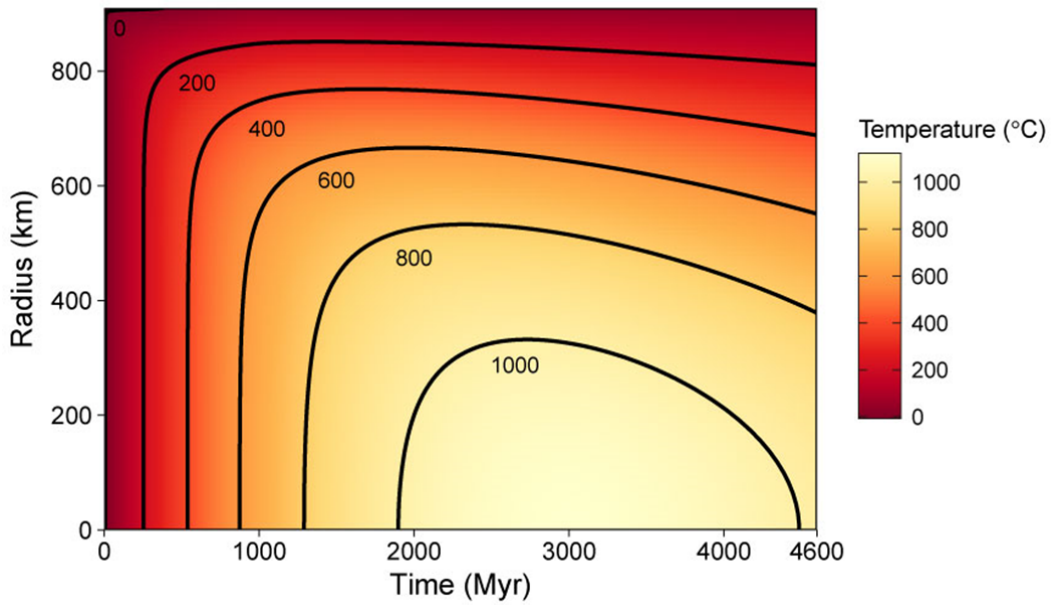


71

72 **Supplementary Fig. 7 | The amount of methane with respect to water required to**
 73 **form a methane hydrate layer.** Results for different ice shell thicknesses are shown.
 74 Methane hydrate (Structure I) of full cage occupancy is assumed (i.e., CH₄·5.75 H₂O).
 75 A thinner ice shell requires a larger amount of methane because of a thicker subsurface
 76 ocean that can dissolve methane. One percent of methane is sufficient to form a
 77 clathrate hydrate layer >10 km in thickness.

78

79

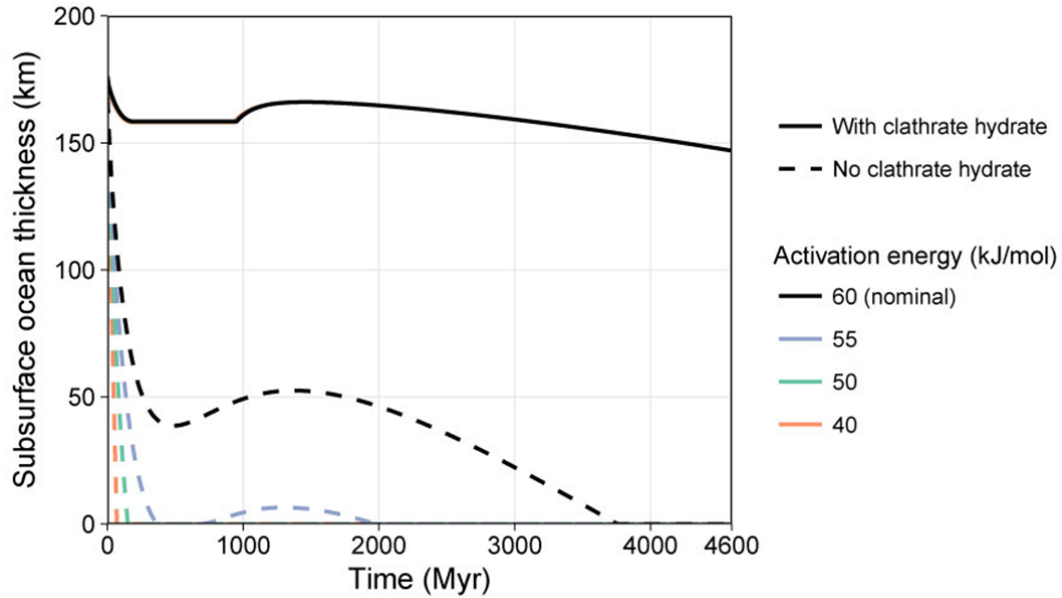


80

81 **Supplementary Fig. 8 | Time evolution of temperature in the rocky core.** The result
 82 for the nominal case with clathrate hydrate formation (i.e., the lower panels in Fig. 2) is
 83 shown. Different calculation conditions lead to similar temperature profiles in the core.
 84 A large portion of the core has temperature higher than $\sim 150^\circ\text{C}$ (CH_4 production) and
 85 $\sim 350^\circ\text{C}$ (N_2 production) for billions of years⁸.

86

87



88

89 **Supplementary Fig. 9 | Time evolution of the subsurface ocean thickness for**
 90 **different activation energies.** Results for cases with and without clathrate hydrates
 91 under a given reference viscosity (i.e., 10^{14} Pa s) are shown. The use of a smaller
 92 activation energy can approximately reproduce the thermal structure assuming a
 93 non-Newtonian rheology^{52,53}. If a clathrate hydrate layer does not exist, a smaller
 94 activation energy leads to a faster freezing of a subsurface ocean. In contrast, if a
 95 clathrate hydrate layer exists, different activation energies leads to nearly the same
 96 result because the ice shell is conductive (see Fig. 2).

97

98

99 **Supplementary Table 1 | Density of clathrate hydrates.**

Guest molecules	Structure	Density (kg/m ³)
CH ₄	Structure I	918.55
CO	Structure I	1010.8
CO	Structure II	1000.5
CO ₂	Structure I	1133.8
N ₂	Structure II	1000.5

100 Each density is calculated by the method of ref. 15. The cage occupancies of the guest
101 molecules are assumed to be 1.0.

102