



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

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23

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 Pluto<sup>1</sup>. 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 inferred<sup>2</sup>.

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   planet<sup>3</sup>, 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 ice<sup>5</sup>. However, if the ice shell is warm, its viscosity should be  
54   low<sup>6</sup>. Substantial viscous flow of ice would then occur, eliminating any local thickness  
55   contrasts<sup>7</sup>. Consequently, a locally thinned shell suggests a “cold” Pluto ( $<\sim 200$  K at the  
56   base of the ice shell<sup>2</sup>). 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 ammonia<sup>2</sup>. However, to avoid substantial viscous relaxation of the  
59   ice shell, the ammonia concentration needs to be  $\sim 30$  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 Pluto<sup>8</sup>, are mostly less than 1 % with respect to water<sup>9</sup>. In addition, an  
63   ammonia concentration  $>20$  wt% leads to an ocean density  $<1000$  kg/m<sup>3</sup>  
64   (Supplementary Fig. 2, ref. 10), which makes it difficult for Sputnik Planitia to be a  
65   positive gravity anomaly<sup>11</sup>. Another possibility is that the viscosity of the ice shell is  
66   high due to the presence of high-strength material, such as salts<sup>12</sup> or silicate particles<sup>13</sup>.  
67   However, in a multiphase system, the weaker phase (i.e., water ice) dominates the  
68   flow<sup>12,13</sup>. 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.,  $\sim 1.3$  g/cm<sup>3</sup> for a mixture of 50% H<sub>2</sub>O ice and 50% epsomite). While the  
71   density of the ocean might also be high due to the presence of salts in the ocean<sup>11</sup>, 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  $\text{H}_2\text{O}$  (ref. 14) and, thus, the ocean density to be  $< 1.3$  g/cm<sup>3</sup>. 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  $\sim 0.2$  g/cm<sup>3</sup> (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 molecules<sup>15</sup>. Because the formation temperatures of clathrate  
81 hydrates are higher than the melting point of pure water ice<sup>15</sup> 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 high<sup>16</sup>. The thermal conductivity of clathrate hydrates is about a factor of 5–10 smaller  
85 than that of water ice<sup>17</sup> and the viscosity of clathrate hydrates is about an order of  
86 magnitude higher than that of water ice<sup>18</sup>. 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 ( $\text{CH}_4 \cdot n\text{H}_2\text{O}$  where  $n \sim 6$  (refs.

96 15,17)) (Methods). In the absence of clathrate hydrates, a subsurface ocean is expected  
97 to freeze completely because thermal convection in the ice shell removes heat  
98 effectively from the deep interior<sup>4</sup> (Fig. 2a, b). To maintain a thick subsurface ocean, the  
99 ice shell needs to be conductive, requiring a reference viscosity about one or two orders  
100 of magnitude higher than  $10^{14}$  Pa s, which is a typical value for terrestrial ice sheets<sup>19</sup>.  
101 This may not be impossible but would require an extremely large ice grain size (a few  
102 cm)<sup>20</sup>. Interestingly, a thicker surface insulating layer leads to a shorter ocean lifetime,  
103 because such a layer enhances thermal convection in the ice shell beneath  
104 (Supplementary Fig. 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 conductive clathrate hydrate layer. As the clathrate layer thickens the  
109 overlying water ice layer cools, leading to a higher viscosity. Thus, thermal convection  
110 in the ice shell becomes less vigorous, further reducing the freezing rate of the ocean  
111 (Fig. 2d). Consequently, the clathrate hydrate layer remains thin, while reducing the  
112 freezing rate of the ocean. If the clathrate hydrate layer grows from the beginning, its  
113 current thickness can reach ~30 km (Supplementary Fig. 4a, b). If its formation is  
114 delayed, its current thickness would be reduced (Supplementary Fig. 4c, d).  
115 Nevertheless, the efficiency of heat removal decreases significantly and the ocean  
116 thickness remains approximately constant following the formation of a clathrate hydrate  
117 layer.

118 As the ocean freezes and the ice shell thickens, the radius and surface area of  
119 Pluto increase, leading to the formation of normal faults on the surface<sup>4</sup>. Pluto's surface

120 is covered by many such faults<sup>21</sup>, and their pattern indeed supports global expansion of  
121 Pluto<sup>22</sup>. A future detailed image analysis estimating the change of Pluto's radius would  
122 provide a constraint on the clathrate hydrate layer thickness and the start timing and/or  
123 the duration of clathrate hydrate formation, which would inhibit freezing and faulting.

124

#### 125 **Viscous relaxation of the ice shell:**

126 We next examine the effect of clathrate hydrates on the timescale of viscous  
127 relaxation of the ice shell using the physical properties of methane hydrates<sup>15,17,18</sup>  
128 (Methods). The origin of the local interior structure beneath Sputnik Planitia (a thin ice  
129 shell above a thick ocean) is considered to be associated with the large impact that  
130 formed the Sputnik Planitia basin<sup>2,11</sup>. Although the age of this impact is unknown, the  
131 eroded rim of the basin suggests that it is likely to be billions of years<sup>23</sup>. Consequently,  
132 the timescale of viscous relaxation should be at least one billion years.

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

144

145 **Implications for geochemical evolution:**

146 Various gas species can form clathrate hydrates, though some species (e.g.,  
147 CH<sub>4</sub>) occupy clathrate hydrates more readily than others (e.g., N<sub>2</sub>) (refs. 15,16). This  
148 behavior may explain the unique volatile composition observed on Pluto. Comets  
149 contain ~1 % of CH<sub>4</sub> and a few % of CO with respect to water<sup>9</sup>, and even these low  
150 concentrations are sufficient to form a clathrate hydrate layer several tens of km in  
151 thickness (Methods, Supplementary Fig. 7). When Pluto formed, volatiles trapped in  
152 precursor bodies would have been partitioned between the atmosphere, ice shell, and the  
153 subsurface ocean. Gases may also have been initially trapped as clathrate hydrates near  
154 the surface<sup>24</sup>, which may also have happened at Titan<sup>25</sup>. At an early stage, primordial  
155 CH<sub>4</sub> and CO dissolved in the ocean would likely form mixed clathrate hydrates at depth.  
156 Although precursor bodies of Pluto may be rich in CO<sub>2</sub> (ref. 9), CO<sub>2</sub> may not be a major  
157 guest molecule of clathrate hydrates above the ocean because its high density indicates  
158 that CO<sub>2</sub>-rich hydrates would not float on the ocean unless the ocean is highly salty  
159 (Supplementary Table 1). CO<sub>2</sub> clathrate hydrates at the seafloor could have acted as a  
160 thermostat to prevent heat transfer from the core to the ocean. Primordial CO<sub>2</sub>, however,  
161 may have been converted into CH<sub>4</sub> through hydrothermal reactions within early Pluto  
162 under the presence of Fe–Ni metals<sup>26</sup>. Because CH<sub>4</sub> and CO predominantly occupy  
163 clathrate hydrates, the components that degassed into the surface-atmosphere system  
164 would be rich in other species, such as N<sub>2</sub> (refs. 8,27,28). Trapping of CO in deep  
165 clathrate hydrates and degassing of N<sub>2</sub> may explain the low CO/N<sub>2</sub> on the surface of  
166 Pluto<sup>29</sup>. Further constraints on likely incorporation of cometary species, particularly CO,  
167 into clathrate hydrates are desirable, either via experiments or a detailed statistical



168 thermodynamic approach<sup>15</sup>.

169           As clathrate hydrate formation continues, concentrations of dissolved gases  
170 decrease if gases are not supplied to the ocean, eventually leading to the formation of  
171 pure water ice instead of clathrate hydrates at the interface between the ocean and ice  
172 shell. Thus, to form clathrate hydrates continuously in the ocean, secondary gases need  
173 to be continuously supplied to the ocean in the later stages. One plausible mechanism to  
174 supply gases is thermal cracking of organic materials in the rocky core, which would  
175 mainly produce CH<sub>4</sub> (refs. 30,31). Organic materials are abundant in cometary solids  
176 (~45 wt% of dust grains of 67P/Churyumov-Gerasimenko<sup>32</sup>). Thermogenic CH<sub>4</sub> can be  
177 produced where temperatures exceed ~150°C (ref. 33), and such a condition can be  
178 achieved in a large portion of Pluto's core for most of its history<sup>8</sup> (Supplementary Fig.  
179 8). A high-temperature origin of CH<sub>4</sub> would leave a trace in its isotopic composition<sup>34</sup>.  
180 N<sub>2</sub> can also be produced via pyrolysis of organic matter when temperatures exceed  
181 ~350°C (ref. 35), though CH<sub>4</sub> would be preferentially trapped in clathrate hydrates<sup>27</sup>.  
182 Within a hot and porous core, high-temperature water-rock reactions would also occur.  
183 These can produce various gas species depending on many factors, including the redox  
184 state of the reactions, but the main gas species would be H<sub>2</sub> for chondritic rocks<sup>36</sup>.  
185 However, H<sub>2</sub> hydrates do not form unless H<sub>2</sub> is dominant in gases<sup>37</sup>. If organic materials  
186 within the rocky core contact with the hydrothermal fluids, a large quantity of C-bearing  
187 gas species, such as CH<sub>4</sub>, also would be included in the fluids through hydrothermal  
188 decomposition<sup>33</sup>. Thus, under the presence of abundant CH<sub>4</sub>, H<sub>2</sub> would be degassed to  
189 the surface and rapidly lost to the space because of its small mass. In contrast, heavier  
190 N<sub>2</sub> becomes a major volatile at Pluto's surface<sup>38,39</sup>. Gas production processes in a hot  
191 rocky core are unlikely to occur in small icy bodies. This may be why CH<sub>4</sub> and N<sub>2</sub> are

192 found only on large KBOs such as Pluto and Eris but not on small KBOs such as  
193 Charon<sup>38,40</sup>. Furthermore, icy bodies possessing subsurface oceans may have low CO/N<sub>2</sub>  
194 and/or CH<sub>4</sub>/N<sub>2</sub> ratios on their surface.

195         The current presence of subsurface oceans in outer solar system bodies is often  
196 explained by a high concentration of ammonia<sup>1,41</sup>, though it is only rarely detected<sup>9,38,42</sup>.  
197 In contrast, a thin clathrate hydrate layer is equally effective at maintaining subsurface  
198 oceans and preventing motion of the ice shell, while requiring much lower  
199 concentrations of secondary species (e.g., CH<sub>4</sub>) whose presence is commonly inferred.  
200 Such layers provide a likely explanation for minimally-heated but ocean-bearing  
201 worlds.

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313

314

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

323

324

325 **Competing interests:** The authors declare no competing interests.

326

327

328 **Figure captions:**

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 this  
331 layer immediately above the subsurface ocean, leading to a conductive shell rather than  
332 a convective shell. Nitrogen-rich ice on the surface is the bright surface of Sputnik  
333 Planitia.

334

335 **Figure 2: Time evolution of the interior thermal profile above the rocky core.** Here

336 the reference viscosity of water ice is  $10^{14}$  Pa s, the initial ice shell thickness is 100 km,  
337 and the surface insulating layer thickness is 5 km. The green solid, dashed, and dotted  
338 curves indicate the surface of Pluto, the boundary between the ice shell and the ocean,  
339 and the boundary between the water ice layer and the clathrate hydrate layer,  
340 respectively. **a**, The temperature profile for the case without clathrate hydrate formation.  
341 The subsurface ocean becomes thin rapidly and freezes completely at  $\sim 3.8$  Gyr. **b**, The  
342 ratio of the convective heat flux to the total heat flux (the sum of the convective and  
343 conductive heat fluxes) for the case of **a**. The lower part of the ice shell where  
344 temperature is nearly constant is highly convective. **c**, The temperature profile for the  
345 case with clathrate hydrate formation. Clathrate hydrate formation starts from the  
346 beginning (0 yr). The subsurface ocean remains thick, and the water ice layer is cold  
347 throughout. **d**, The ratio of the convective heat flux to the total heat flux for the case of **c**.  
348 Convection does not occur in the ice shell.

349

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

355

356

357 **Methods:**

358 **Thermal evolution:**

359 To calculate the time evolution of the radial temperature profile of Pluto, we used the



360 code developed by ref. 43. We modified the code to incorporate the effects of a clathrate  
361 layer and those of a surface thermal insulating layer.

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

$$365 \quad \rho C_p \frac{dT}{dt} = - \frac{1}{r^2} \frac{d}{dr} (r^2 F_{\text{cond}} + r^2 F_{\text{conv}}) + Q \quad (1)$$

366 where  $\rho$  is density,  $C_p$  is specific heat,  $T$  is temperature,  $t$  is time,  $r$  is radial distance  
367 from the center,  $F_{\text{cond}}$  is conductive heat flux,  $F_{\text{conv}}$  is convective heat flux, and  $Q$  is  
368 volumetric heating rate.  $F_{\text{cond}}$  is given by the product of thermal conductivity and the  
369 local thermal gradient while  $F_{\text{conv}}$  is estimated using a modified mixing length theory<sup>43</sup>  
370 (see below).

371 The core is assumed to be purely conductive ( $F_{\text{conv}} = 0 \text{ W/m}^2$ ) and to be  
372 uniformly heated from within due to the decay of long-lived radioactive elements. The  
373 heating rate for carbonaceous chondrites<sup>4,43</sup> is used. The density, specific heat, and  
374 thermal conductivity of the core are  $3000 \text{ kg/m}^3$ ,  $1000 \text{ J/kg/K}$ , and  $3 \text{ W/m/K}$ ,  
375 respectively. The radius of the core is  $\approx 910 \text{ km}$ , which is calculated from eq. (2) of ref. 5  
376 assuming the mean density of Pluto<sup>44</sup> ( $1854 \text{ kg/m}^3$ ), the present-day radius of Pluto<sup>44</sup>  
377 ( $1188 \text{ km}$ ), and the density of ices (including clathrate hydrates;  $920 \text{ kg/m}^3$ ).

378 The subsurface ocean is assumed to be an inviscid fluid, and the ocean  
379 temperature is assumed to be uniform. For the case without clathrate hydrate formation,  
380 the ocean temperature is calculated from the pressure-dependent melting point of pure  
381 water ice<sup>45</sup>. For the case with clathrate hydrate formation, it is between the melting point  
382 of pure water ice and the dissociation temperature of methane hydrate<sup>15</sup>. No heat  
383 production in the ocean is assumed.

384 The ice shell is divided into 3 layers: a surface insulating layer (i.e., a top  
385 low-conductivity layer), a water ice layer, and a basal clathrate hydrate layer. The  
386 thickness of the top layer is assumed to be constant and to be 5 km unless otherwise  
387 noted. The thin top and basal layers are assumed to be purely conductive, and the thick  
388 intermediate layer is assumed to be convective or conductive depending on the viscosity.  
389 The thermal conductivities from the top to the bottom layers are 1 W/m/K (ref. 5),  
390  $0.4685 + 488.49/T$  W/m/K where  $T$  is temperature in Kelvin (ref. 46), and 0.6 W/m/K  
391 (ref. 17), respectively. The temperature-dependent specific heat of water ice<sup>47</sup> and that  
392 of methane hydrate<sup>48</sup> are used. No heat production ( $Q = 0$  W/m<sup>3</sup>) in the ice shell is  
393 assumed.  $F_{\text{conv}}$  for the intermediate part is given by

$$394 \quad F_{\text{conv}} = \begin{cases} -\frac{\alpha C_p \rho^2 g l^4}{18\eta} \left\{ \frac{dT}{dr} - \left( \frac{dT}{dr} \right)_s \right\} & \left( \text{for } \frac{dT}{dr} \leq \left( \frac{dT}{dr} \right)_s \right) \\ 0 & \left( \text{for } \frac{dT}{dr} > \left( \frac{dT}{dr} \right)_s \right) \end{cases} \quad (2)$$

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

$$402 \quad \eta = \eta_{\text{ref}} \exp \left( \frac{E_a}{R_g T_{\text{ref}}} \left( \frac{T_{\text{ref}}}{T} - 1 \right) \right) \quad (3)$$

403 where  $\eta_{\text{ref}}$  is reference viscosity of ice,  $E_a = 60$  kJ/mol is the activation energy,  $R_g$  is the  
404 gas constant,  $T_{\text{ref}} = 273$  K is the reference temperature<sup>4,43,50</sup>. The nominal value of  $\eta_{\text{ref}}$  is  
405  $10^{14}$  Pa s (ref. 19). Note that we assume a Newtonian rheology. This assumption is  
406 appropriate under typical conditions for terrestrial ice sheets (i.e., grain size  $\sim 1$  mm,

407 stress  $\sim 10^{-3}$  MPa, temperature near the melting point) (ref. 51). Nevertheless, Pluto's  
408 ice shell may exhibit non-Newtonian behavior (due to a large grain size, for example).  
409 The effect of non-Newtonian flow can be imitated by a Newtonian fluid with a smaller  
410 activation energy<sup>52,53</sup>. Calculation results using different activation energies are shown  
411 in Supplementary Fig. 9. We find that a smaller activation energy leads to a faster  
412 freezing of a subsurface ocean beneath a convective ice shell. Consequently, our model  
413 calculations using a Newtonian rheology provide the longest ocean lifetime for cases  
414 without a clathrate hydrate layer. On the other hand, for cases with a clathrate hydrate  
415 layer, different activation energies lead to nearly the same result because the ice shell is  
416 conductive. Thus, our conclusion does not change even if Pluto's ice shell exhibits  
417 non-Newtonian behavior. It is noted that results shown in Supplementary Fig. 9 assume  
418 the reference viscosity of water ice of  $10^{14}$  Pa s. Although different creep mechanisms  
419 may lead to different reference viscosities, their quantification is left for another study.

420         The initial thickness of the ice shell is assumed to be 100 km. Initial  
421 temperature in the ice shell linearly increases with depth from 40 K at the surface to the  
422 pressure-dependent melting point of water ice<sup>45</sup> at the base of the ice shell. The initial  
423 temperature of the ocean and the rocky core is assumed to be uniform (i.e., the melting  
424 point of water ice). Different initial conditions do not affect the long-term evolution<sup>4,43</sup>.  
425 The exception is an initially completely frozen case; ref. 4 reported that a subsurface  
426 ocean does not appear if an initially completely frozen Pluto and  $\eta_{\text{ref}} \leq 10^{15}$  Pa s are  
427 assumed. However, the conditions required for the formation of a subsurface ocean  
428 based on their results are too strict because a freezing-point depression due to pressure  
429 is not incorporated in their calculations. A detailed investigation of such conditions is  
430 beyond the scope of this study and is left for another study.

431           The temporal change in the thickness of the ice shell is calculated from the  
432 difference between the outgoing and incoming heat fluxes at the base of the ice shell.  
433 Note that this difference in heat flux is used not only to change the thickness of the ice  
434 shell but also to change the temperature of the ocean. For the case without clathrate  
435 hydrate formation, the effect of the ocean temperature change caused by a change in the  
436 ice shell thickness is incorporated by using an effective latent heat<sup>43</sup>. For the cases with  
437 clathrate hydrate formation, the change in the thickness of the ice shell is interpreted as  
438 that of the clathrate hydrate layer; we assume the growth and dissociation rates of  
439 clathrate hydrates are simply controlled by heat transfer<sup>15</sup>. If the outgoing heat flux is  
440 higher than the incoming heat flux, the clathrate hydrate layer becomes thicker, keeping  
441 the ocean temperature constant. If the outgoing heat flux is lower than the incoming  
442 heat flux, the ocean temperature increases, keeping the layer constant until the ocean  
443 temperature reaches the pressure-dependent dissociation temperature of methane  
444 hydrate<sup>15</sup>. If the ocean temperature reaches the dissociation temperature, the clathrate  
445 hydrate layer becomes thinner. As the clathrate hydrate layer becomes thinner and the  
446 pressure at the top of the ocean decreases, the ocean temperature decreases because of  
447 the pressure dependence of dissociation temperature. Similar to the case without  
448 clathrate hydrate formation, the effect of pressure dependence of dissociation  
449 temperature is included by using an effective latent heat. Latent heats of water ice and  
450 methane hydrate are 333 kJ/kg and 437 kJ/kg (ref. 54), respectively. Note that the radius  
451 of Pluto changes as the thicknesses of the ice shell and the ocean (the density of 1000  
452 kg/m<sup>3</sup> is assumed for the latter) change in order to conserve the total mass of Pluto. The  
453 initial radius of Pluto is determined so that the final radius becomes the present-day  
454 value through trial and error.

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

465

#### 466 **Viscous relaxation:**

467           To calculate the timescale of viscous relaxation for the ice shell of Pluto, we  
468 followed the procedure adopted by ref. 7. We assume that the thinned portion of the ice  
469 shell has a bowl-shaped topography at the base of the ice shell. More specifically, the  
470 cross section can be described using a quadratic function, and the height and radius of  
471 the bowl are assumed to be 80 km and 500 km, respectively (Supplementary Fig. 5c).  
472 These values are chosen assuming a nearly (Airy) isostatically compensated basin  
473 before the loading of nitrogen-rich ice<sup>2,11</sup>. The shape of the basal topography is then  
474 expressed as a superposition of zonal components of spherical harmonic functions. In  
475 this study, we consider spherical harmonic degrees from 1 to 20. The time evolution of  
476 the amplitudes (coefficients) of each spherical harmonic for  $10^{10}$  yr is obtained using the  
477 numerical code calculating spheroidal viscoelastic deformation of a planetary body  
478 developed by ref. 55 (see below). The time evolution of the basal topography can be

479 calculated by superposing the spherical harmonics with time-dependent amplitudes. The  
 480 timescale of viscous relaxation is defined as the time when the volume of the bowl  
 481 becomes  $1/e$  of the initial condition where  $e$  is Napier's constant.

482 The governing equations are the linearized equation of momentum  
 483 conservation given by

$$484 \quad \nabla_j \cdot (\sigma_{ij} - P\delta_{ji}) + \rho\nabla_i\phi = 0, \quad (4)$$

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

$$486 \quad \nabla^2\phi = -4\pi G\rho, \quad (5)$$

487 and the constitutive equation for a Maxwell medium given by

$$488 \quad \frac{d\sigma_{ji}}{dt} + \frac{\mu}{\eta} \left( \sigma_{ji} - \frac{\sigma_{kk}}{3} \delta_{ji} \right) = \left( \kappa - \frac{2\mu}{3} \right) \frac{de_{kk}}{dt} \delta_{ji} + 2\mu \frac{de_{ji}}{dt}, \quad (6)$$

489 where  $\nabla_i$  is a spatial differentiation in direction of  $i$  ( $= x, y, z$ ),  $\sigma_{ji}$  is stress tensor,  $e_{ji}$  is  
 490 strain tensor,  $P$  is hydrostatic pressure,  $\delta$  is the Kronecker delta,  $\phi$  is gravitational  
 491 potential,  $G$  is the gravitational constant,  $\rho$  is density,  $\mu$  is shear modulus,  $\eta$  is viscosity,  
 492  $\kappa$  is bulk modulus. Application of spherical harmonic expansion to the governing  
 493 equations leads to a six-component, time-dependent, inhomogeneous first-order  
 494 ordinary differential equation system. The major assumptions are a  
 495 spherically-symmetric steady-state interior structure, small deformation amplitudes, and  
 496 a linear viscoelasticity<sup>55</sup>. These assumptions are valid to estimate the timescale of  
 497 viscous relaxation, though more detailed numerical calculations would be necessary for  
 498 precisely estimating the shape of the ice shell.

499 Following the thermal evolution calculations, we use a 3-layer Pluto model,  
 500 though a steady-state thermal profile is adopted because what we calculate is the  
 501 timescale of viscous relaxation under a given interior structure. We assume that the ice  
 502 shell consists of Maxwell viscoelastic material, that the subsurface ocean is an inviscid

503 liquid, and that the rocky core consists of purely elastic material. The radius of the core  
504 is determined in the same manner as that done in thermal evolution calculations.  
505 Different ice shell thicknesses, clathrate hydrate layer thicknesses, and surface  
506 insulating layer thicknesses are considered.

507         The densities of the ice shell, the ocean, and the core are  $920 \text{ kg/m}^3$ ,  $1000$   
508  $\text{kg/m}^3$ , and  $3000 \text{ kg/m}^3$ , respectively, which are used in the thermal evolution  
509 calculations. The shear moduli of the ice shell, the ocean, and the core are  $3.3 \text{ GPa}$ ,  $0$   
510  $\text{GPa}$ , and  $10 \text{ GPa}$ , respectively. We adopt an incompressible ( $\kappa \rightarrow \infty$  and  $e_{kk} \rightarrow 0$ ) limit  
511 because of the small size of Pluto. The viscosity in the ice shell is calculated from the  
512 temperature profile adopting the same rheological model. The surface temperature is  
513 fixed to  $40 \text{ K}$ . The temperature at the base of the ice shell is assumed to be the  
514 pressure-dependent melting point of pure water ice<sup>56</sup> unless otherwise noted. Assuming  
515 a steady-state conductive profile with given boundary temperatures, we calculate the  
516 temperature profile in the ice shell analytically. The thermal conductivity profile is the  
517 same as that used in thermal evolution calculations. The reference viscosities of water  
518 ice and clathrate hydrates are  $10^{14} \text{ Pa s}$  (ref. 19) and  $2 \times 10^{15} \text{ Pa s}$  (ref. 18), respectively,  
519 unless otherwise noted. The activation energy of water ice and clathrate hydrates are  $60$   
520  $\text{kJ/mol}$  (ref. 50) and  $90 \text{ kJ/mol}$  (ref. 18), respectively, unless otherwise noted. The upper  
521 limit of the viscosity is  $10^{30} \text{ Pa s}$ , though the choice of this value does not affect the  
522 timescale of viscous relaxation of topography at the base of the ice shell.

523

#### 524 **Mass balance:**

525 We calculate the amount of methane with respect to water in the ice shell and subsurface  
526 ocean. The thicknesses of these layers are determined in the same manner as in viscous

527 relaxation calculations; the thickness of the ice shell is a free parameter while that of the  
528 ocean is calculated so that the mean density becomes the observed value. The ice shell  
529 is divided into an outer pure water ice layer and a deeper methane hydrate layer. We  
530 assume methane hydrate (Structure I) of full cage occupancy (i.e.,  $\text{CH}_4 \cdot 5.75 \text{H}_2\text{O}$ ) (ref.  
531 15). The ocean is assumed to consist of water and methane only. We use the pressure at  
532 the top of the ocean and the melting point of pure water ice<sup>56</sup> to calculate the (pressure-  
533 and temperature-dependent) solubility of methane in the ocean<sup>57</sup>.

534

535

536 **Data availability:**

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

539

540

541 **Code availability:**

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

544

545

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