nature geoscience

SUPPLEMENTARY INFORMATION
https://doi.org/10.1038/s41561-019-0369-8

In the format provided by the authors and unedited.

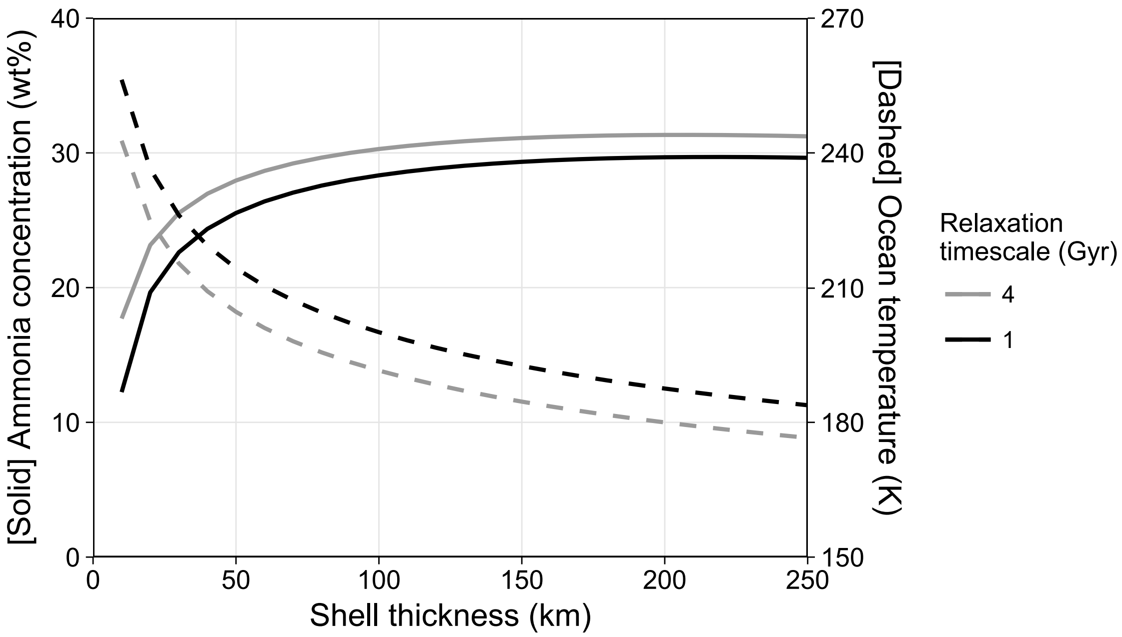
Pluto's ocean is capped and insulated by gas hydrates

Shunichi Kamata[1,8*], Francis Nimmo[2], Yasuhito Sekine[3], Kiyoshi Kuramoto[4], Naoki Noguchi[5], Jun Kimura[6] and Atsushi Tani[7]

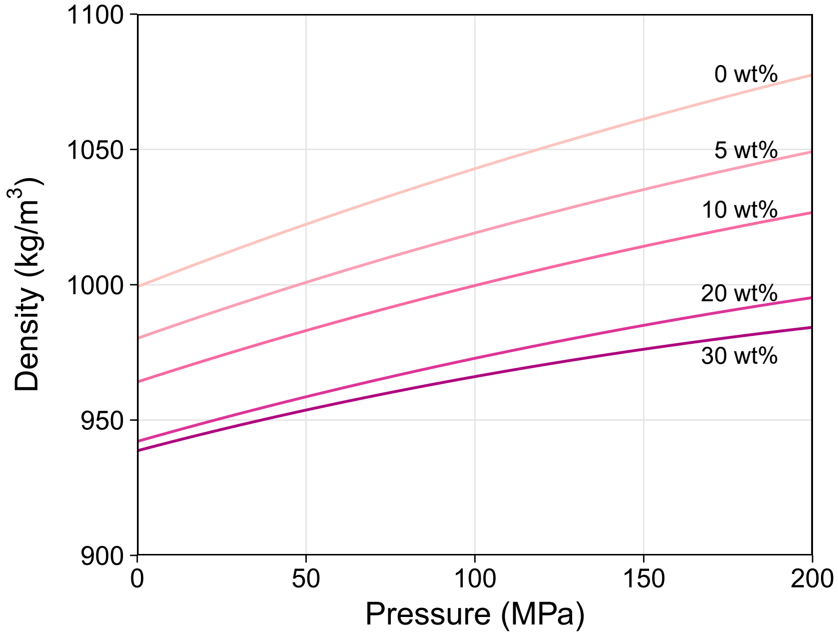
[1]Creative Research Institution, Hokkaido University, Sapporo, Japan. [2]Department of Earth and Planetary Sciences, University of California, Santa Cruz, Santa Cruz, CA, USA. [3]Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan. [4]Department of Cosmosciences, Hokkaido University, Sapporo, Japan. [5]Graduate School of Technology, Industrial and Social Sciences, Tokushima University, Tokushima, Japan. [6]Department of Earth and Space Science, Osaka University, Toyonaka, Japan. [7]Department of Human Environmental Science, Kobe University, Kobe, Japan. [8]Present address: Department of Earth and Planetary Sciences, Hokkaido University, Sapporo, Japan. *e-mail: kamata@sci.hokudai.ac.jp

Supplementary Information for: Pluto's ocean is capped and insulated by gas hydrates

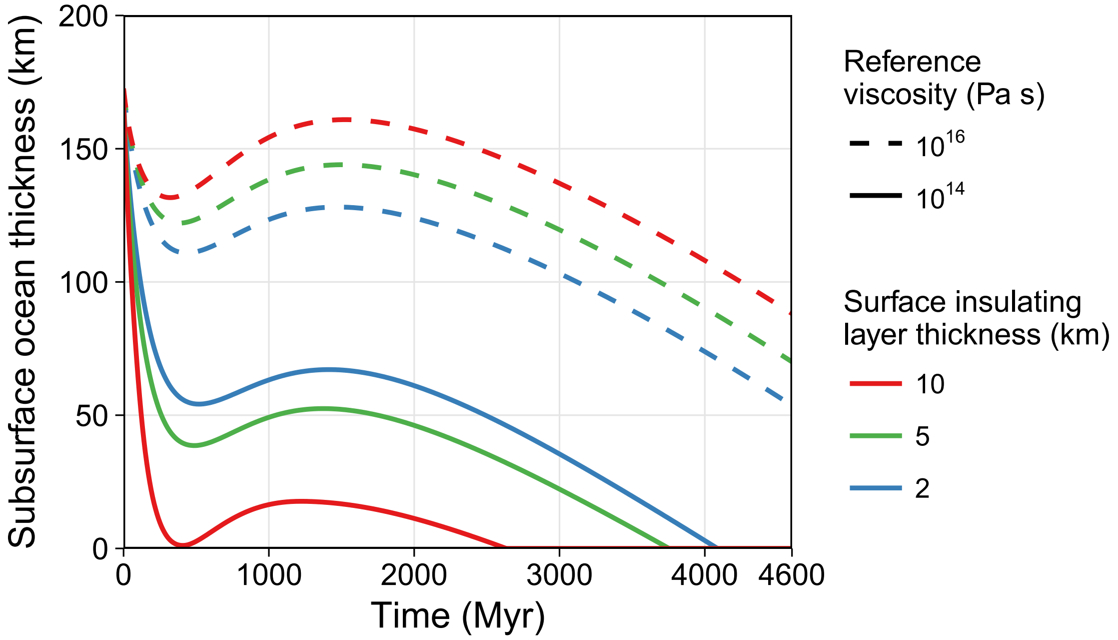
Shunichi Kamata, Francis Nimmo, Yasuhito Sekine, Kiyoshi Kuramoto, Naoki Noguchi, Jun Kimura, Atsushi Tani



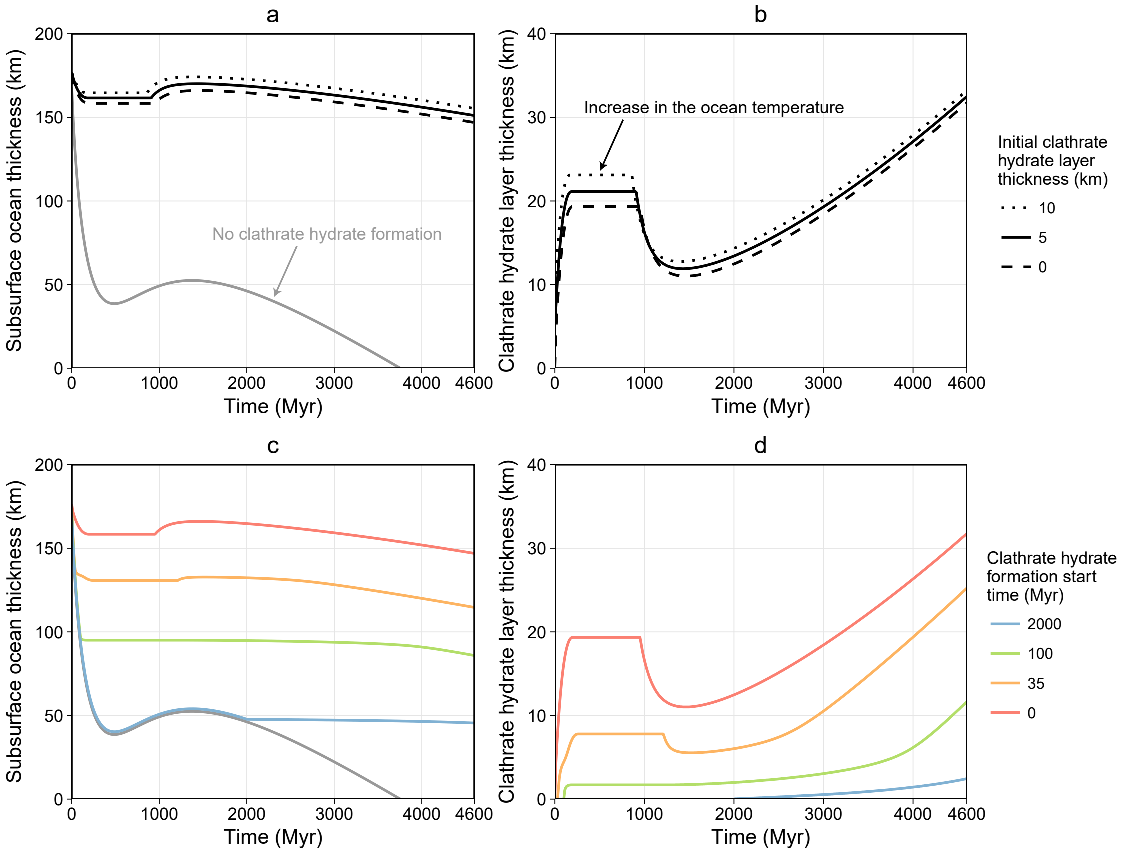
Supplementary Fig. 1: Ammonia concentration and temperature of the subsurface ocean required for avoiding substantial lateral flow in the ice shell without clathrate hydrates. The ocean temperature is calculated analytically by using the method of ref. 2. The corresponding ammonia concentration is calculated from an equation based on laboratory experiments[45]. A shell thickness less than ~100 km is unlikely because the height of the thickened portion of the ocean is expected to be ~80 km for an isostatically compensated basin 7 km in depth[2,11] before the loading of nitrogen ice sheet.



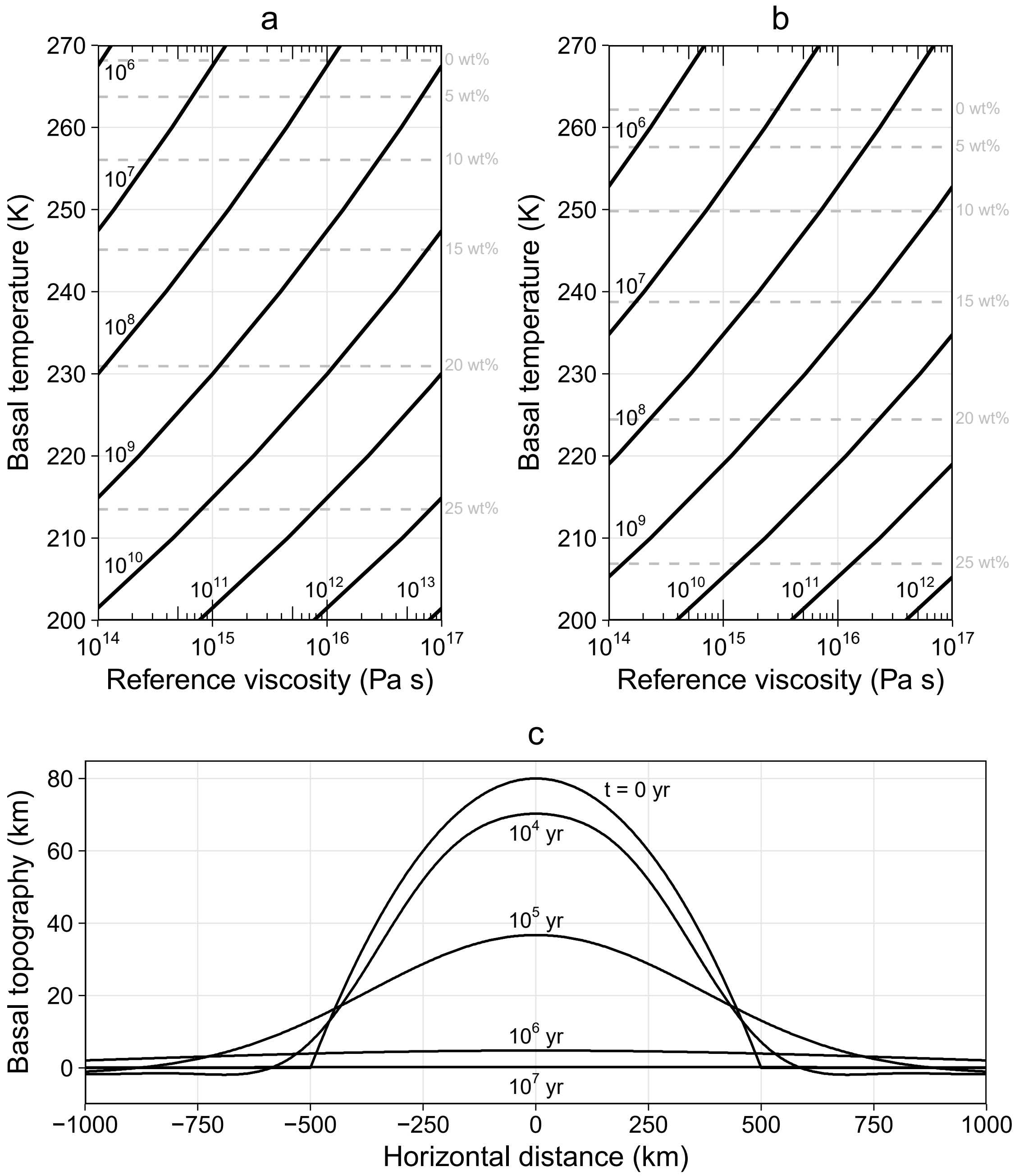
Supplementary Fig. 2: Density of ammonia-water liquid. The density is calculated analytically by using the method of ref. 10. The temperature is assumed to be the melting point depending on pressure and ammonia concentration[45]. An ammonia concentration ≥20 wt% is unlikely because the ocean density becomes <1000 kg/m^3, which will make the Sputnik Planitia basin a negative gravity anomaly[11].



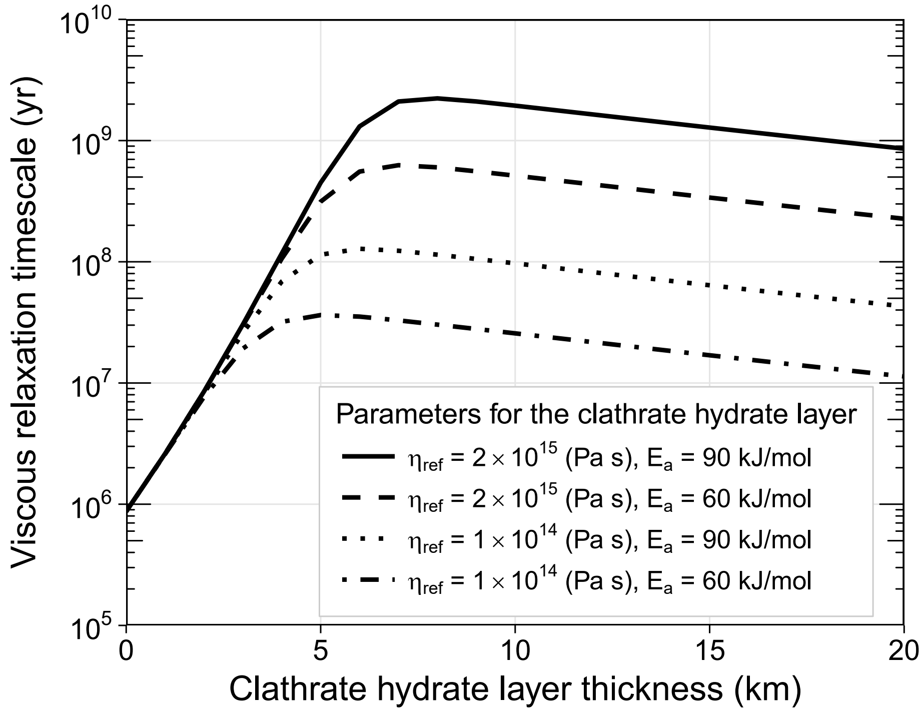
Supplementary Fig. 3: Time evolution of the subsurface ocean thickness for cases without clathrate hydrates. Results for different reference viscosities of water ice and different thicknesses of a surface insulating layer are shown. A high reference viscosity results in a conductive ice shell. In such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



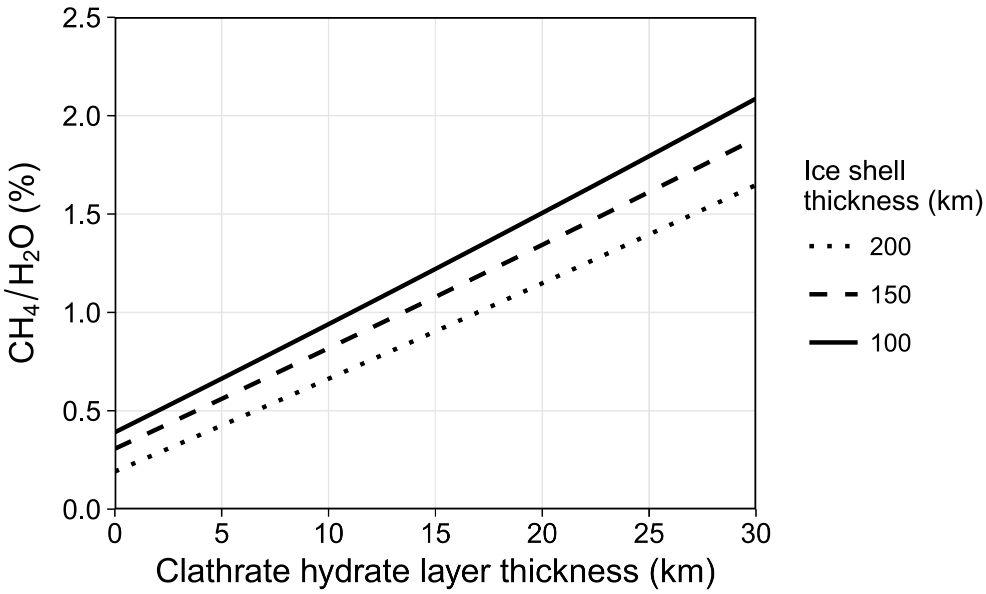
Supplementary Fig. 4: Time evolution of Pluto's interior structure for cases with and without clathrate hydrate layers. Here the reference viscosity of water ice is 10^{14} Pa s, the initial ice shell thickness is 100 km, and the surface insulating layer thickness is 5 km. **a**, The evolution of the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



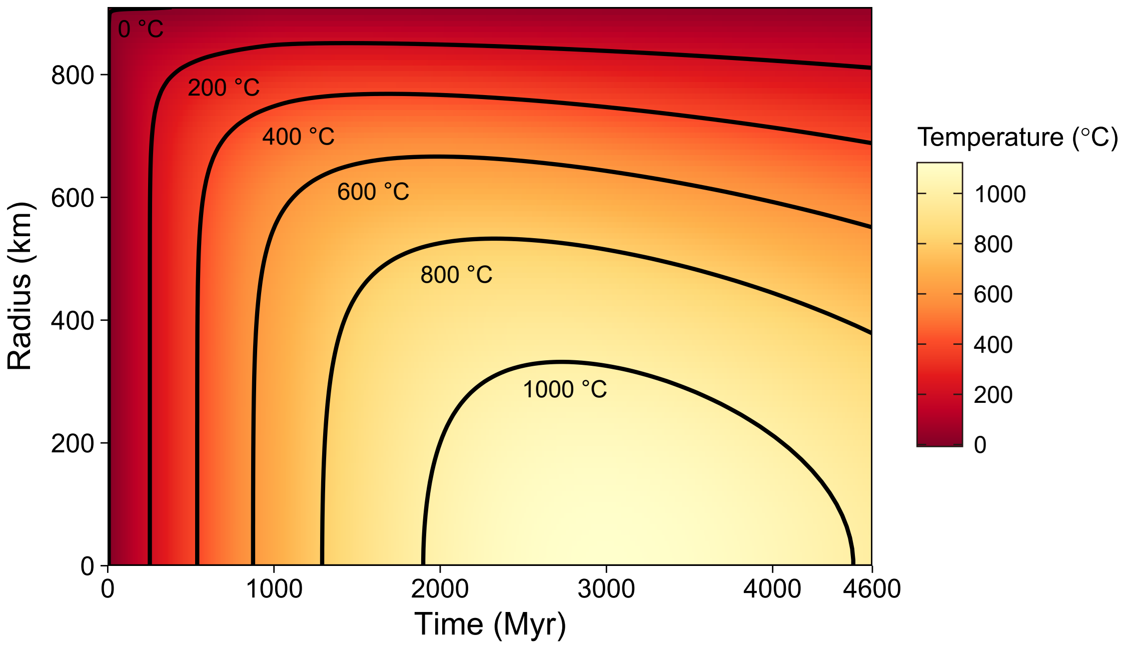
Supplementary Fig. 5: Viscous relaxation of the ice shell without clathrate hydrates. **a**, Relaxation timescale for the ice shell thickness of 100 km. The surface insulating layer thickness is 5 km. Numbers indicate the relaxation timescale in yr. Horizontal gray lines show corresponding ammonia contents in the ocean[45]. **b**, The same as **a** but for the ice shell thickness of 200 km. **c**, The temporal change of topography at the base of the ice shell. Results for the ice shell thickness of 100 km, the surface insulating layer thickness is 5 km, and the reference viscosity of 10^{14} Pa s. The relaxation timescale for this case is ~9×10^5 yr.



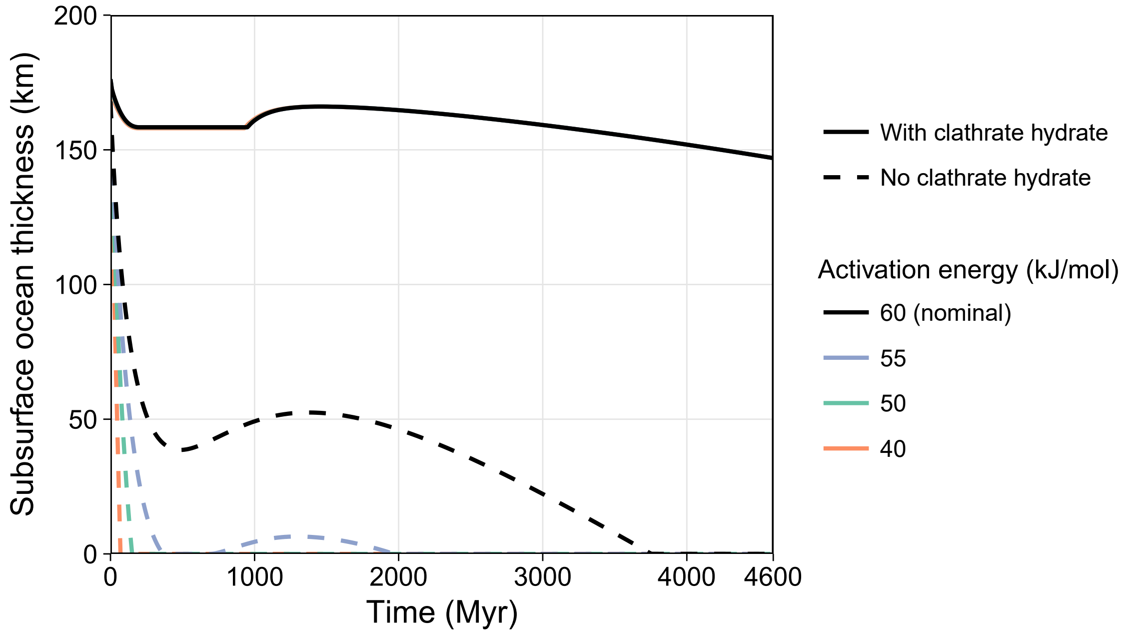
Supplementary Fig. 6: Timescale of viscous relaxation of the ice shell assuming different rheological parameters for the clathrate hydrate layer. Here the reference viscosity of water ice is 10^{14} Pa s, the ice shell thickness is 100 km, the surface insulating layer thickness is 5 km, and freezing-point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



Supplementary Fig. 7: The amount of methane with respect to water required to form a methane hydrate layer. Results for different ice shell thicknesses are shown. Methane hydrate (Structure I) of full cage occupancy is assumed (i.e., $CH_4 \cdot 5.75\ H_2O$). A thinner ice shell requires a larger amount of methane because of a thicker subsurface ocean that can dissolve methane. One percent of methane is sufficient to form a clathrate hydrate layer >10 km in thickness.



Supplementary Fig. 8: Time evolution of temperature in the rocky core. The result for the nominal case with clathrate hydrate formation (i.e., the lower panels in Fig. 2) is shown. Different calculation conditions lead to similar temperature profiles in the core. A large portion of the core has temperature higher than ~150°C (CH_4 production) and ~350°C (N_2 production) for billions of years[8].



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

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

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

Supplementary Discussion: CO hydrate formation.

The present study suggests the formation of CO clathrate at the interface between the ice shell and subsurface ocean to explain the low CO/N_2 ratio on Pluto's surface. We are implicitly assuming that CO conversion to clathrates is favoured over catalytic reaction of CO to reduced carbon species in the ocean. Although there are large uncertainties in the relevant conditions, available experimental data of high activation energy of catalytic reactions to form reduced carbon species (refs. 26,58,59) suggest that CO clathrate formation is much faster than CO reduction over the likely range of temperatures in the ocean.

Supplementary References:

58. Sekine, Y., Sugita, S., Shido, T., Yamamoto, T., Iwasawa, Y., Kadono, T. & Matsui, T., S. The role of Fischer–Tropsch catalysis in the origin of methane-rich Titan. *Icarus* **178**, 154–164 (2005)
59. Vannice, M. A. The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the Group VIII metals. *J. Catal.* **37**, 449–461 and 462–473 (1975)