Phase Equilibria of Solids in Pluto's Subsurface

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Background

Umurhan et al., Icarus 2017, 287, 301

- A basally wet glacier may have occurred on Pluto. Such glacier needs to have liquid phase at the base.
- Pluto's surface may have reached temperatures of 55-60 K in the past.
- For nitrogen ice, the vertical temperature gradient is 20 K/km.

Tan & Kargel, 2018, MNRAS 474, 4254:

- Total composition of $N_2/CH_4/CO$: {99.35%, 0.60% , 0.05%}
- The atmosphere with this total composition at 11 µbar collapses into N_2-rich solid on the Pluto's surface at temperatures below 36.9 K (density of 993.6 kg/m^3), and stays in gas phase above 43.3 K.
- At temperatures in between, the atmosphere is in equilibrium with CH_4-rich solid deposited on the surface (vapor-solid phase equilibrium). The solid's composition is {0.65%, 99.34% , 0.01%} at 40.5 K with a density of 529.1 kg/m^3.

Questions:

What is the progression of phase equilibria as we go deeper to subsurface Pluto? What is the depth where liquid appears?

Phase equilibria

- Equation of state: CRYOCHEM 2.0 (*Tan & Kargel, 2018, MNRAS 474, 4254*)
- Phase-equilibria requirements for a ternary mixture at temperature T and pressure P between two phases π and ω:

Chemical equilibrium

$$\mu_i^\pi(T, P, \mathbf{x}^\pi) = \mu_i^\omega(T, P, \mathbf{x}^\omega), \qquad i = 1, 2, 3$$

where the compositions are $\mathbf{x} = \{x_1, x_2, x_3\}$

Material balance

$$f^\pi\, \mathbf{x}^\pi + (1 - f^\pi)\, \mathbf{x}^\omega = \mathbf{z}, \qquad i = 1, 2$$

where f^π is the mole fraction of phase π and $\mathbf{z} = \{z_1, z_2, z_3\}$ is the total composition.

- Phase-equilibria calculations result in composition phase diagrams.

Phase diagrams

- Because the existing phases in the range of relevant temperatures in Pluto's subsurface are condense phases, i.e., solid and liquid, the phase boundaries on phase diagrams are not sensitive to pressure changes.
- Therefore, the resulting phase diagrams can be identified with their temperatures only, as the diagrams are almost identical even if the pressure is different.
- The temperature varies with depth δ due to the subsurface temperature gradient (20 K/km), while the pressure also varies with depth due to the gravity g (for Pluto, g = 0.62 m/s^2):

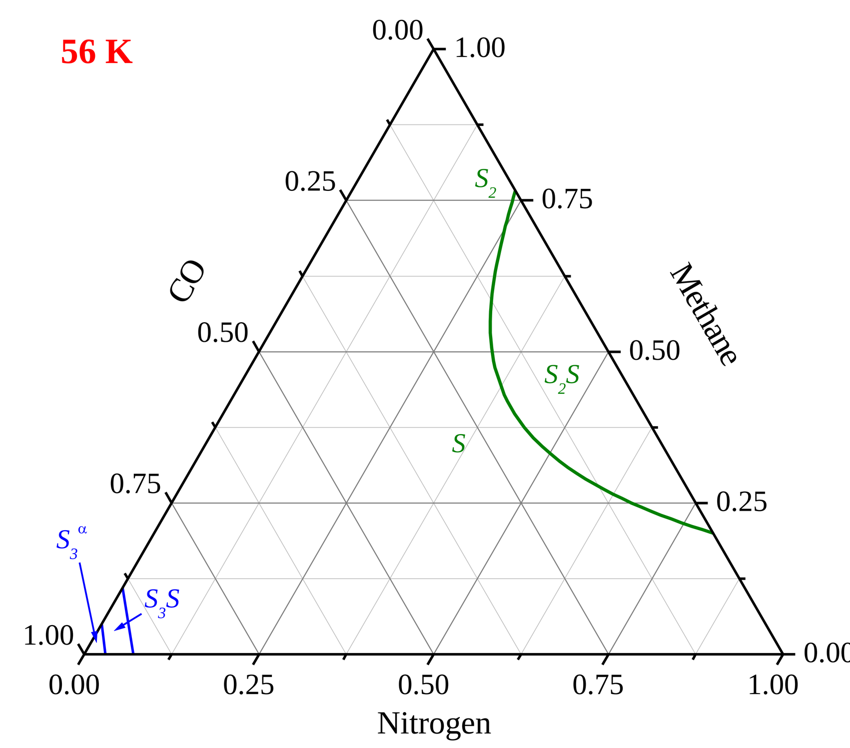
$$P = P_0 + \rho g \delta$$

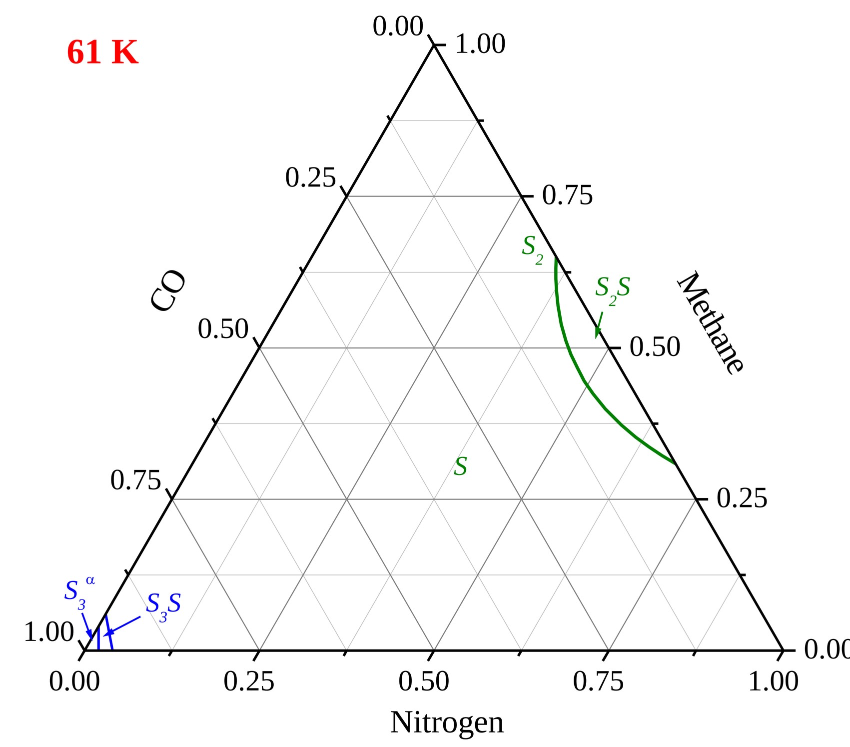
where P_0 is the pressure at surface and ρ is the N_2-rich-ice density (993.6 kg/m^3) that is assumed to be constant with depth.

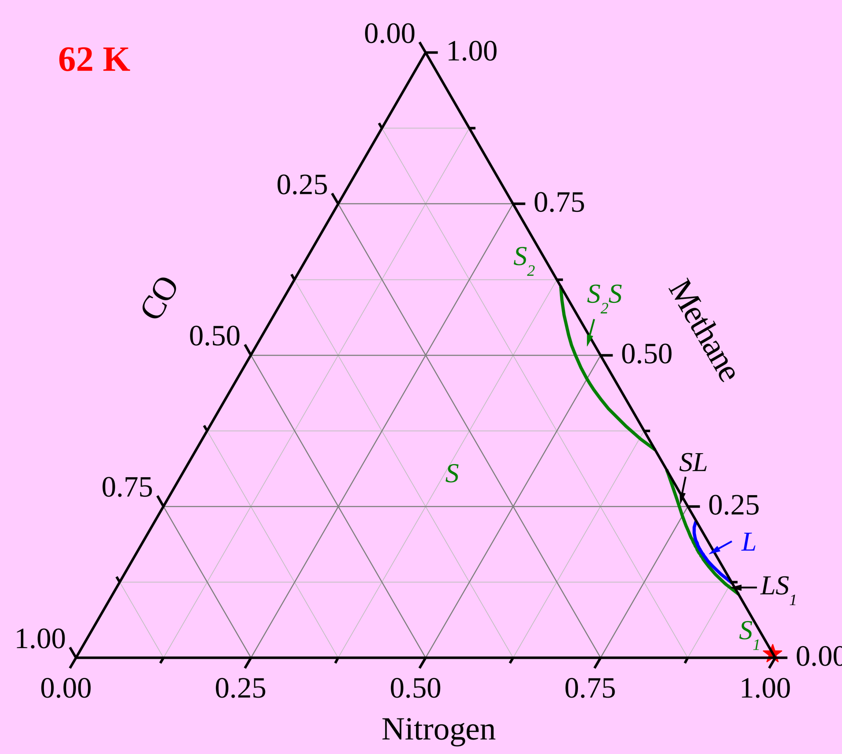
- Two cases of different surface temperatures T_0 (55 K and 60 K) are presented. Even though the mixture sublimates at the surface in the temperature range of 55-60 K due to the currently low pressure of 11 µbar, the ice survives in the subsurface due to higher pressures as shown on the phase diagrams.
- The corresponding pressures and depths for the presented phase diagrams are tabulated below:

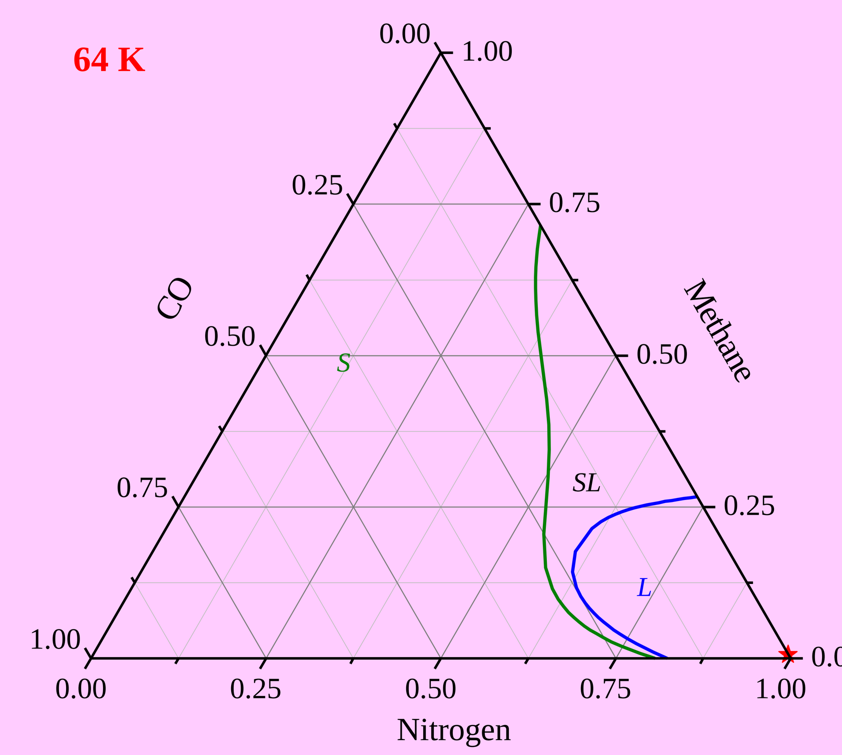
Temperature [K]	Pressure [bar], depth [m]	
	For T_0 = 55 K	For T_0 = 60 K
56	0.308, 50 m	-
61	1.848, 300 m	0.308, 50 m
62	2.156, 350 m	0.616, 100 m
64	2.772, 450 m	1.232, 200 m
66	3.388, 550 m	1.848, 300 m
68	4.004, 650 m	2.464, 400 m
70	4.620, 750 m	3.080, 500 m

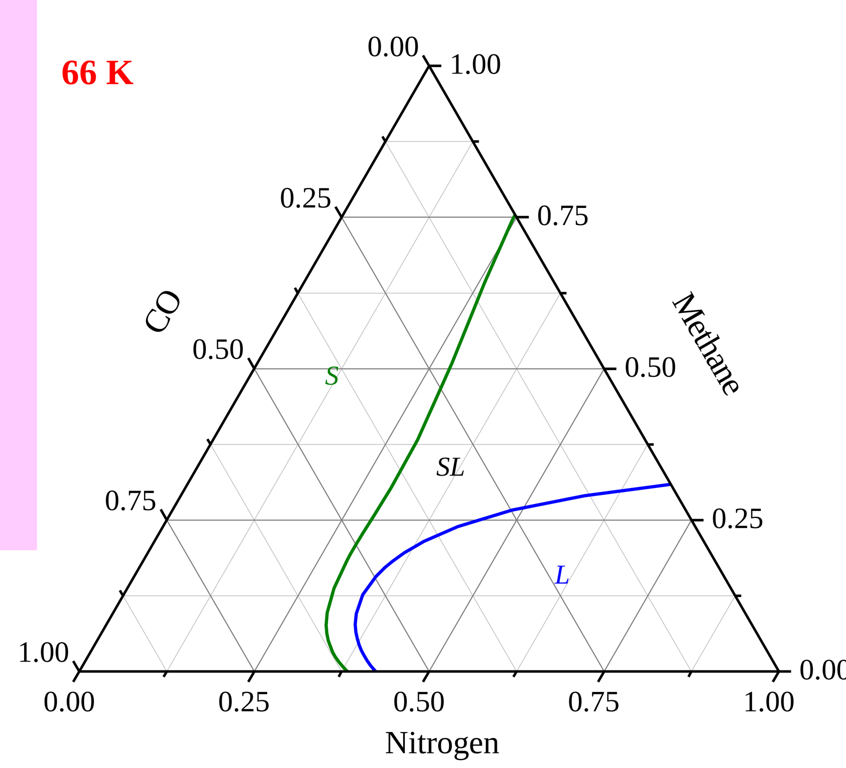
- If a basally wet glacier occurred on Pluto, the liquid would have been at a temperature between 62-64 K, where the composition of ice (red star) entered the solid-liquid (SL) region.
- The corresponding depth is 100-200 m for a surface temperature of 60 K and 350-450 m for a surface temperature of 55 K, thus confirming the estimation by *Umurhan et al.* (*Icarus 2017, 287, 301*).

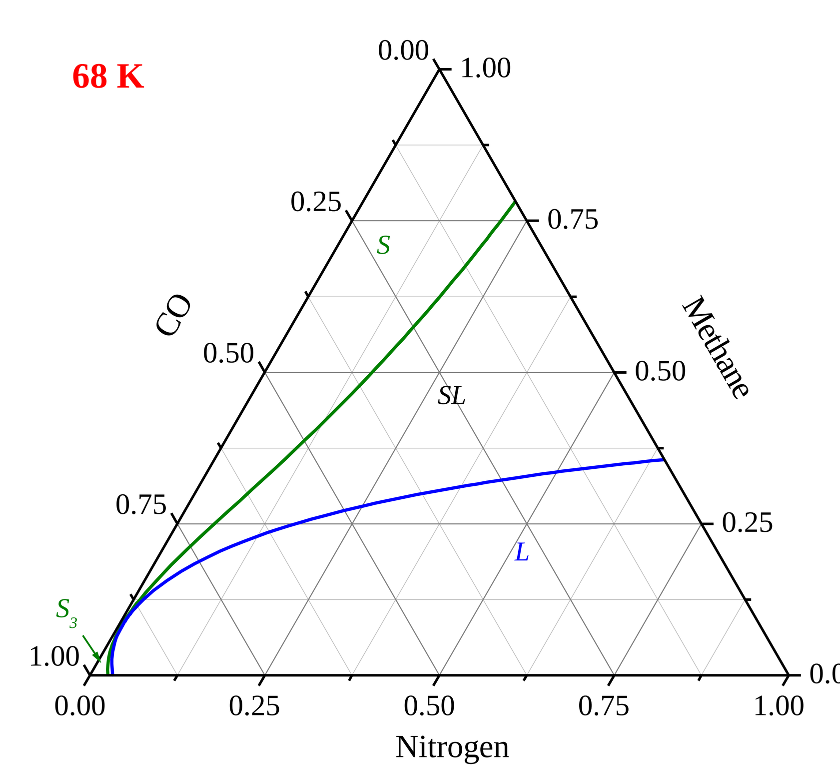


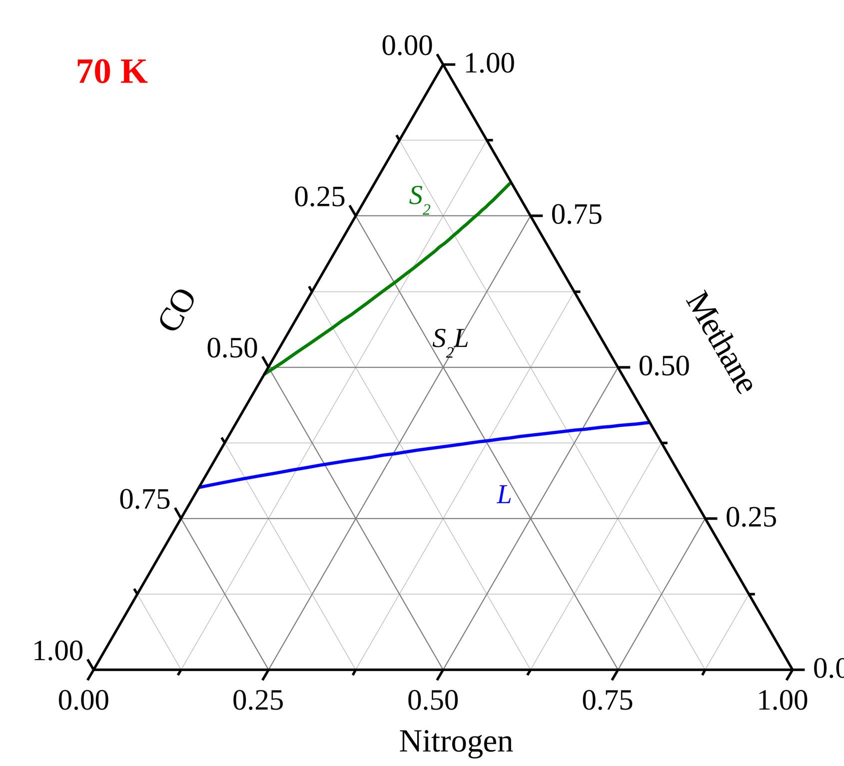












Phase-diagram legend

S: solid L: liquid

Labels with subscript

1: rich with nitrogen

2: rich with methane

3: rich with CO

Labels without subscript denote regions that may be rich with two or more components.

Superscript α denotes the solid phase with cubic crystalline structure, while the other solids have hexagonal structures.

- At 56 and 61 K, the phase diagrams show two solid-solid regions: S_2S and S_3S. The latter is due to the phase transition of CO from β phase to α phase due to cooling across 61.5 K. The phase boundaries of S_3S on the diagrams are not calculated because CRYOCHEM currently only models CO in β phase; the boundaries are hypothetically added for illustration purposes.
- Liquid phase appears above 61 K such as shown on the diagram of 62 K, where a tiny "lagoon" appears near the pure N_2 vertex and becomes larger as the temperature increases.
- In the meantime, the solid-solid S_3S disappears as the temperature increases while the S_2S merges with the solid-liquid (SL) region at temperatures between 62-64 K.
- At higher temperatures, the solid is methane rich, and the liquid is methane lean in the composition space such as shown at 70 K.