High Pressure Phases of Gas Clathrate Hydrates and their Impact to the Habitability of the Icy Moons

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Introduction

Clathrate hydrates are proposed as constituents of the icy crusts and water rich reservoirs in the moons of the giant planets of the Solar System, e.g. as the source of CH_4 in Titan's atmosphere, or in Enceladus as the origin of the geyser compounds. Remote measurements show CO_2 presence on the surfaces of giant moons of Jupiter, though it is unclear whether it is in the interior and interacts with water. In Ganymede, aqueous layers are suggested to be deep within the moon, between layers of different water ice phases. Geophysical models show that the pressure in the ocean is up to 1.3 GPa, so we need to understand the interactions between H_2O and CO_2 under these conditions in order to constraint the carbon state in the aqueous layers. One way of interaction is forming clathrate hydrates.

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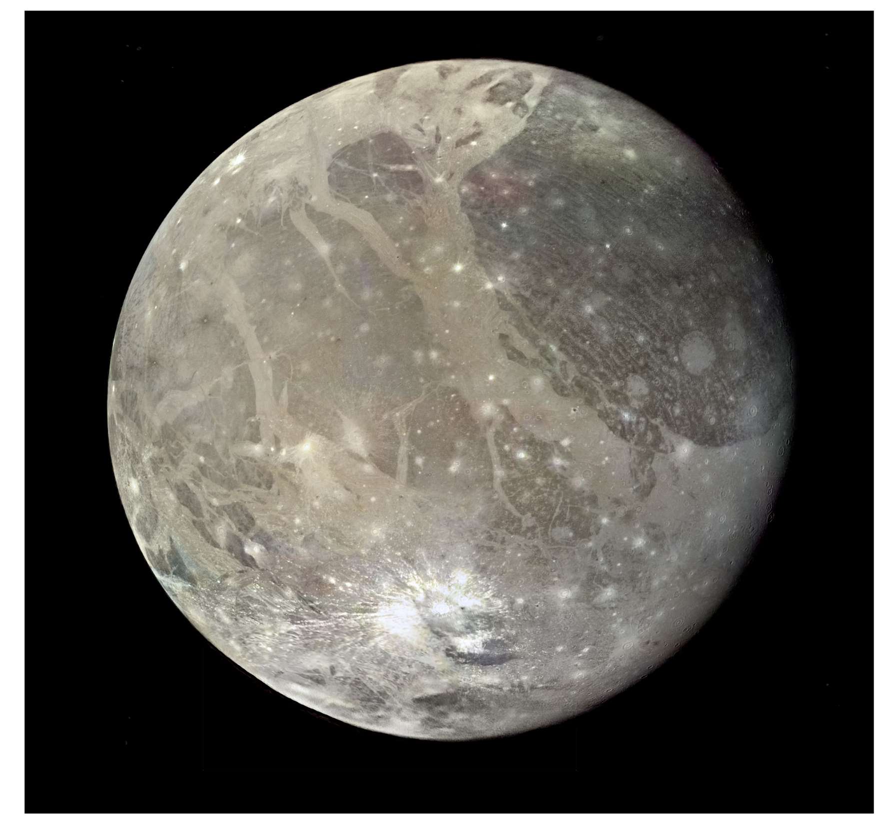
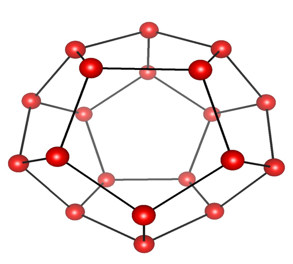


Ganymede. Credit: NASA

From Pressures and Cavities to Densities

Small

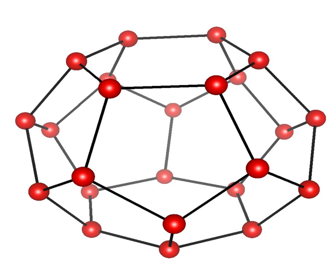


5^{12}

nCages per cell
sI 2
sII 16
sH 3

sI Large

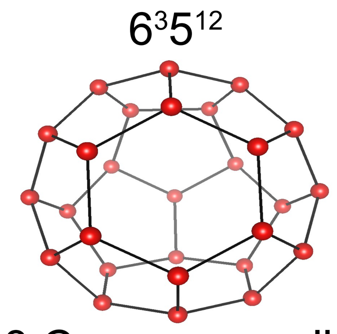
$6^2 5^{12}$



6 Cages per cell

sII Large

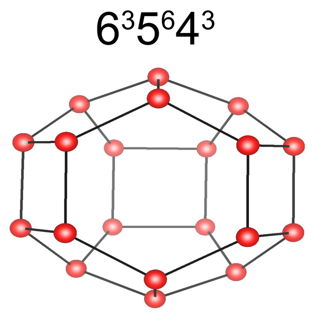
$6^3 5^{12}$



8 Cages per cell

sH Medium

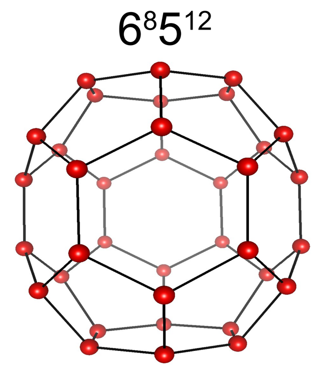
$6^3 5^6 4^3$



2 Cages per cell

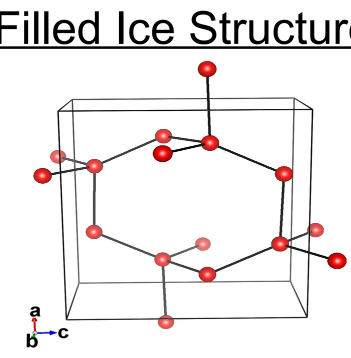
sH Large

$6^8 5^{12}$



1 Cage with 3 CH_4

FIS (Filled Ice Structure)



Channels

Host:Guest
$2H_2O$:1Guest

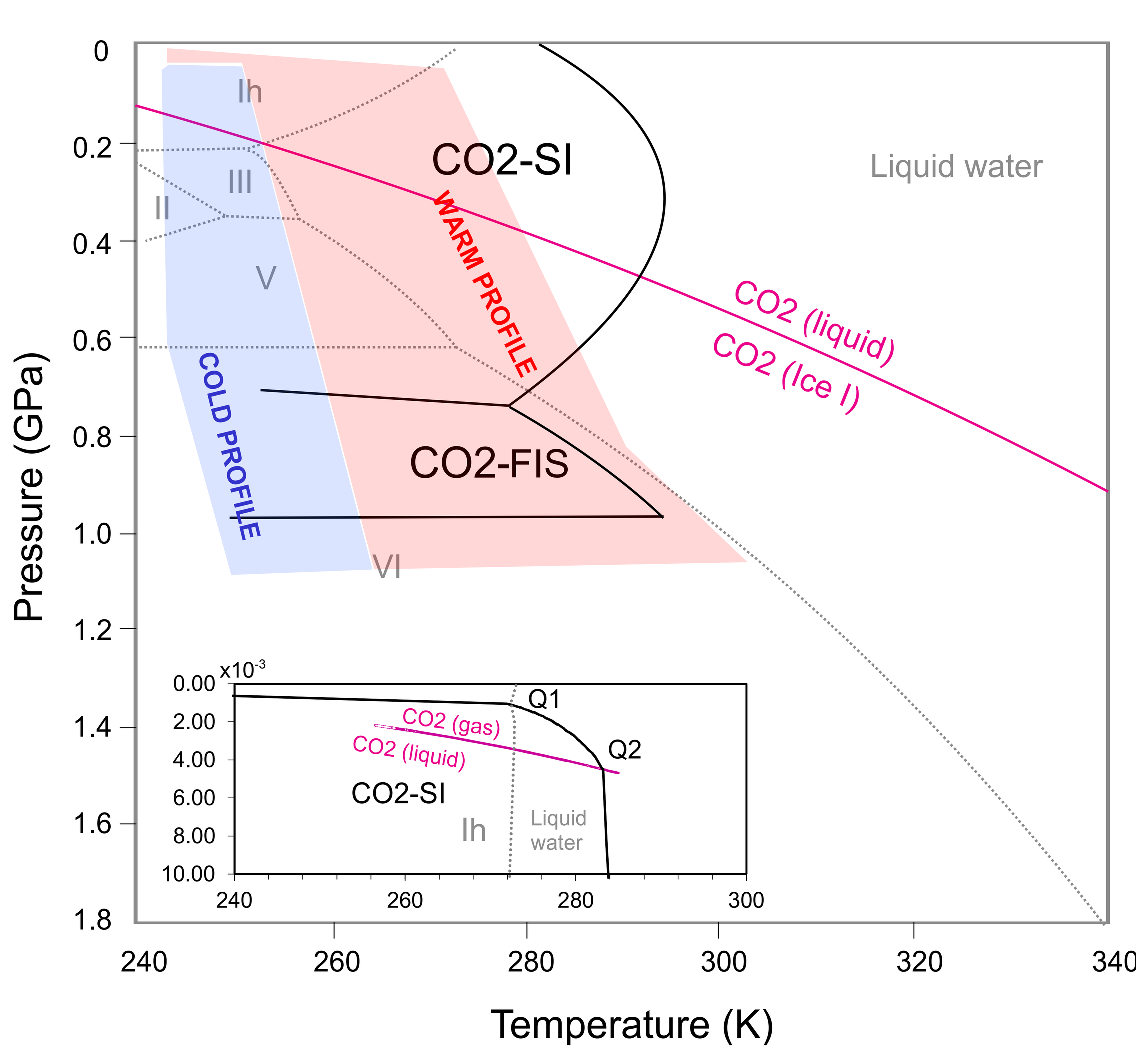
Type	Symm	nH_2O / cell	Press. Range (GPa)
sI	Pm3m	46	0—0.9 (CH_4) 0—0.7 (CO_2)
sII	Fd3m	136	0—0.5 (CH_4) metastable
sH	P6/mmm	34	0.9—1.6 (CH_4)
FIS	Imcm	8	1.6—42* (CH_4) 0.7—1.0 (CO_2)**

* Max pressure studied but not decomposed
** Approximate values due to recent discovery

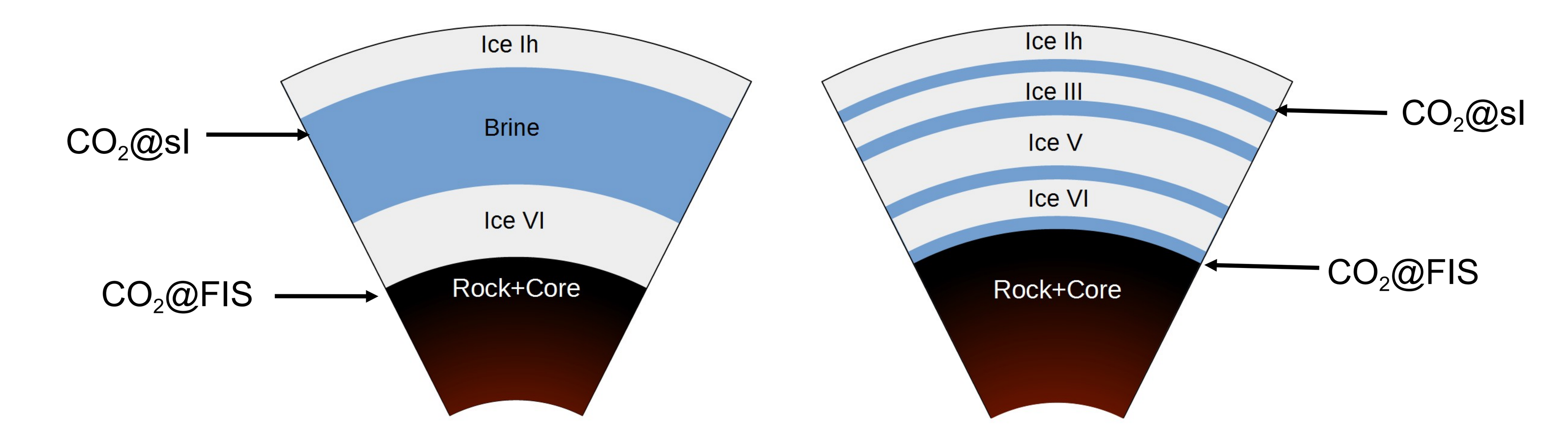
Guest	Phase	P(GPa)	T(K)	d(g/mL)
CH_4	sH	0.86—2.26	Room Temp.	1.018—1.083
	FIS	2.17—42.0	Room Temp.	1.117—1.962
CO_2	sI	—	77-240	1.119-1.154
	FIS	—	173	1.825

CH_4@sI (Fortes '12): d(mean)=0.962 g/mL

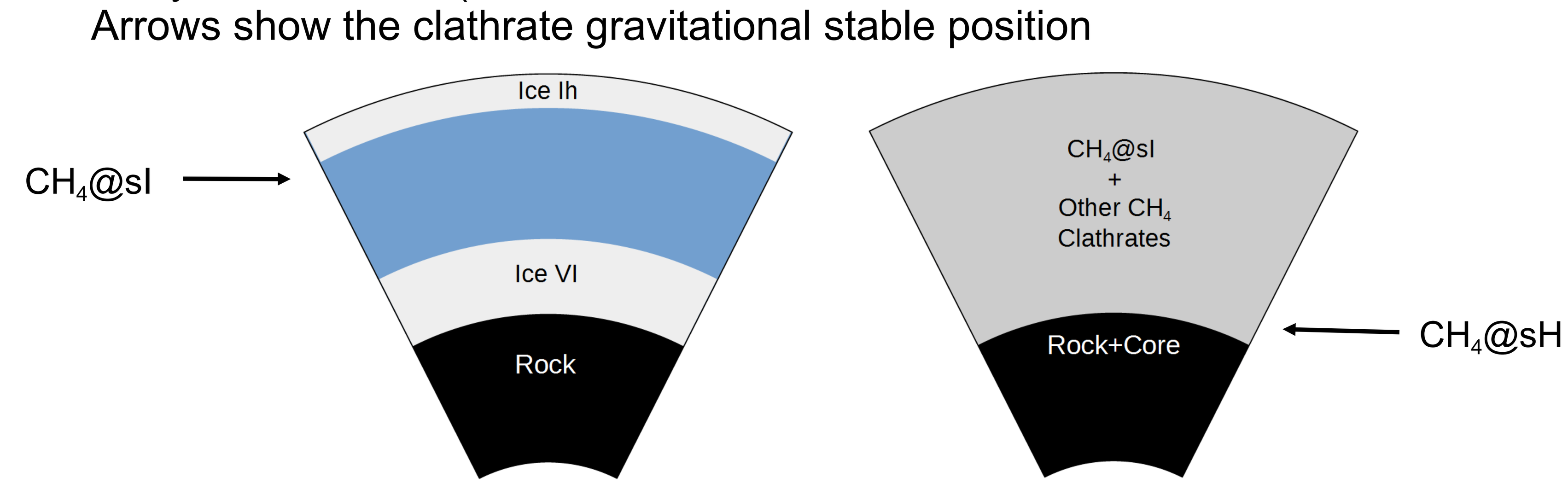
Effect of high pressure phases on the giant icy moons



Phase diagram of water ice (dotted line) and CO_2 clathrate (solid thick line), where thermal profiles of Ganymede are shown (modified from Sohl et al. 2010, Bollengier et al. 2013). Low pressure phase diagram of CO_2-clathrate sI is in the inset.



Ganymede models (after Sohl et al. 2002, Vance & Brown 2013, Vance et al. 2014)
Arrows show the clathrate gravitational stable position



Titan geophysical models (after Fortes 2012)
Arrows indicate gravitational stable position of clathrates

High density of CO_2 clathrates might support a multilayered structure. However, it is not clear if high pressure clathrates can form at depth from its separate components. It is known that they can be transformed from low pressure phases in solid-solid phase transitions. Laboratory experiments are running to shed light on the former process.

The sI to FIS transition require a convective behavior of the icy layer in order to sink the sI phase to deeper levels. If it occurs, this transition is associated with a remarkable change in volume and other thermo-dynamical parameters.

Molecules containing essential elements for life, which would be released during early differentiation of the satellite, could have been retained at upper clathrate layers. Clathrate components would react in aqueous layers if they dissociate during further heating episodes.

Future JUICE mission will help to understand the structure and habitability of Ganymede.

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