

High Pressure Phases of Gas Clathrate Hydrates and their Impact to the habitability of the icy moons. F. Izquierdo-Ruiz^{1,2}, A.S.J. Méndez. J.M. Recio² and O. Prieto-Ballesteros¹. ¹Centro de Astrobiología, INTA-CSIC, Madrid, 28850, Spain, ²Dept. Química Física y Analítica, U.Oviedo, Oviedo, 33006, Spain. fizquierdo@cab.inta-csic.es

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 [1], for example methane clathrate hydrates as the source of CH₄ in Titan's atmosphere, or in Enceladus as the origin of the geyser compounds.

The outer solar system is rich in carbon dioxide (CO₂). As remote measurements show, it is present on the surfaces of giant moons of Jupiter [2-5], while 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 [6], so we need to understand the interactions between H₂O and CO₂ under these conditions in order to constraint the carbon state in the aqueous layers. One form of interaction is forming clathrate hydrates. Here we show the results of some theoretical calculations about density of clathrates. We suggest some implications of the clathrate formation to the moon structure and the habitability of the deep aqueous layers.

Cavities for volatiles at different pressures: Gas clathrate hydrates are crystals formed by water molecules, held together by hydrogen bonds, which form cavities in where a guest volatile molecule resides. Among all the possible structures, there are four: the cubic structures I and II (sI, sII), the hexagonal structure (sH) and a filled ice type structure (FIS). They have 46, 134 34 and 8 water molecules per unit cell and space groups Pm3n, Fd3m, P6/mmm and Imcm, respectively.

In the former 3 structures, several types of cages compose the unit cell. In the sI type there are two type of cages: 5¹²(2), 12 faces of five vertex (two per unit cell) and 6²5¹²(6), bigger. When all cages are occupied, the hydration number is 5.75:1. In the case of the sII, there are 5¹²(16), small, and 6⁴5¹²(8), big cages. Its hydration number when fully occupied is 5.58:1. Finally, the sH has (from smaller to bigger) 5¹²(3), 4³5⁶6³(2) and 5¹²6⁸(1) cages. In simple clathrates it is proved that the biggest cage can accept several guests inside and, for example, in the case of CH₄ the ideal hydration number is 3.4:1, with 3 CH₄ molecules inside the big cage. The FIS structure is derived from the ice Ih structure and it does not have cages but channels in which the guests fill the space. Loveday and Nelmes published a review about several simple hydrates depicting their properties [7] though they did not include some important systems, such as CO₂ clathrates. This latter

system is studied recently using XRD and Raman spectroscopy [8, 9] and has two known phases. The low pressure phase (0-0.7 GPa) is an sI type clathrate while the high pressure (0.7-1.0 GPa) has been unidentified until very recently and is a FIS structure [10].

Density of High Pressure Phases: In the table below we present a summary of our calculations about clathrates density. They are obtained from XRD measurements to have the cage occupation of each clathrate structure [7, 10, 11, and refs. therein]

Guest	Phase	P(GPa)	T(K)	d(g/cm ³)
CH ₄	sH	0.86-2.26	Room Temp.	1.018-1.083 0.972-1.035 [10]
	FIS	2.17-42.0	Room Temp.	1.117-1.962
CO ₂	sI	-	77-240	1.119-1.154 1.049-1.075 [10]
	FIS	-	173	1.825

CH₄@sH has a density around 1.03 g/cm³ at 1.0 GPa CH₄@FIS has a density starting around 1.10 g/cm³. In the case of CO₂ the referenced studies are focused on thermal expansion. For CO₂@sI we find a density around 1.14 at 173 K and for CO₂@FIS there is only one point so far [10]. In the case of the FIS structure, occupations are assumed as the ideal relation of 2 water molecules per guest.

Effect on the habitability: The influence of these phases in the evolution of giant icy moons is considered since they were discovered [12]. Clathrates are stable on a wide range of pressures. We predict some implications such as: 1) The variation in density of clathrates supports a multilayered structure similar than that proposed in [13]. 2) Volatiles released from differentiation of the icy moons might be retained by clathrates. Keeping them trapped, volatiles would not react with aqueous layers or escape until any process activate their dissociation.

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