

**THE H<sub>2</sub>O-CO<sub>2</sub> SYSTEM UP TO 1.7 GPa: IMPLICATIONS FOR LARGE ICY MOONS.** O. Bollengier<sup>1</sup>, M. Choukroun<sup>2</sup>, O. Grasset<sup>1</sup>, G. Tobie<sup>1</sup>, E. Le Menn<sup>1</sup>, G. Bellino<sup>1</sup>, L. Bezacier<sup>1</sup>, Y. Morizet<sup>1</sup>, A. Oancea<sup>1</sup>, C. Taffin<sup>1</sup>, <sup>1</sup>Université de Nantes, CNRS, Laboratoire de Planétologie et Géodynamique de Nantes, UMR 6112, 44322 Nantes Cedex 3, France, [olivier.bollengier@univ-nantes.fr](mailto:olivier.bollengier@univ-nantes.fr), <sup>2</sup>Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California 91109.

**Introduction:** Understanding the evolution and present state of the water-rich icy bodies of the outer solar system requires a robust description of the behavior of the hydrated phases and other present volatiles at the relevant pressure and temperature conditions. This can be achieved through the use of thermodynamic models, from simple, pure phase systems to more complex, multi-components ones, provided enough experimental data are available. For example, the FREZ-CHEM model [1] is able to describe a complex, water-based chemistry; it is, however, limited to moderate pressures (0–0.1 GPa) relevant to small icy bodies or to the subsurface environment of more massive ones, like the subsurface ocean of Europa.

Another model was developed recently [2] to describe the high pressures (0–2.2 GPa) that may have affected the hydrospheres of the largest of those icy bodies (e.g. Titan, Ganymede, Callisto...), from their early evolution to their present state (for the more massive and/or less differentiated ones). However, it is currently limited to the H<sub>2</sub>O-NH<sub>3</sub> binary system. As part of the further development of this high-pressure model, the present study focuses on the H<sub>2</sub>O-CO<sub>2</sub> system, as carbon dioxide is widely detected on icy surfaces [3] and is expected to be the most abundant carbon species inside the largest icy moons [4]. Experiments have been focused on the elevated pressures (> 0.2 GPa) and low temperatures (280–330 K) relevant for the largest icy moons. This study provides data required on CO<sub>2</sub> hydrates and CO<sub>2</sub>-bearing aqueous solutions to include this important compound in the high-pressure thermodynamic model.

**Experiments:** Sapphire and diamond anvil cell experiments have been conducted to explore the H<sub>2</sub>O-CO<sub>2</sub> system. First, temperature-dependent experiments with samples of variable H<sub>2</sub>O/CO<sub>2</sub> bulk compositions have been carried out at variable pressures to explore the stability of the known CO<sub>2</sub> sI clathrate hydrate in a water-rich, CO<sub>2</sub>-saturated environment. Other experiments with bulk compositions close to the CO<sub>2</sub> sI clathrate hydrate ideal stoichiometry have been used to constrain the transition with pressure from the CO<sub>2</sub> sI clathrate hydrate to the unidentified CO<sub>2</sub> high-pressure hydrate phase recently reported [5]. Finally, the melting temperature of water ice VI in CO<sub>2</sub>-saturated water was monitored through a third set of runs to estimate the effect of dissolved CO<sub>2</sub> on H<sub>2</sub>O at saturation, and as a consequence the solubility of CO<sub>2</sub> in water.

**Phase identification:** The phases present in the samples are identified via in-situ Raman spectroscopy. In figure 1 are reported Raman spectra for the CO<sub>2</sub> sI clathrate hydrate (hereafter sI hydrate) and the recently reported CO<sub>2</sub> high-pressure hydrate (hereafter HP hydrate), along with the signature of mixed CO<sub>2</sub> dry ice and H<sub>2</sub>O ice VI for comparison. The phase transition between the sI and HP hydrates around 0.7–0.8 GPa affects both the H<sub>2</sub>O skeleton and CO<sub>2</sub> guest signatures of the sI hydrate with abrupt jumps (reversing the pressure-induced shift affecting the H<sub>2</sub>O skeleton) at this pressure. Although the high-pressure phase has been recognized as a CO<sub>2</sub> hydrate, its exact nature is still unknown. Our Raman spectra show that the signatures of the two hydrates are very similar, which may suggest the clathrate hydrate nature of the HP hydrate.

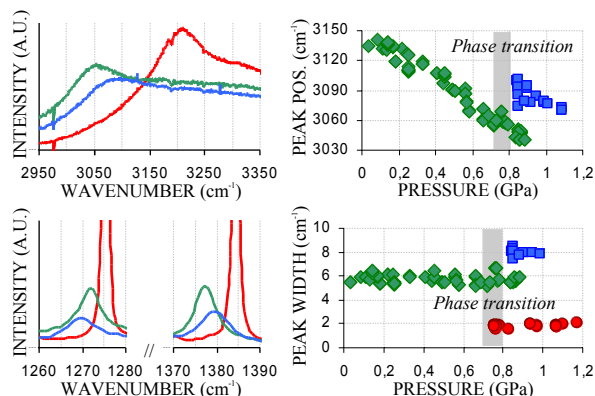


Figure 1. Typical Raman spectra of the sI (green, diamonds) and HP (blue, squares) CO<sub>2</sub> hydrates, and of H<sub>2</sub>O-CO<sub>2</sub> ices mixture (red, circles), at 255–280 K and 0–1.2 GPa (pressures up to and past the hydrate transition). Upper part shows the O-H spectral range (H<sub>2</sub>O skeleton for the sI hydrate) and pressure dependence of the bands positions. Lower part displays the CO<sub>2</sub> ν<sub>1</sub> and ν<sub>2</sub> vibrations region and pressure dependence of the ν<sub>2</sub> peak width.

**Results:** New stability data for the CO<sub>2</sub> sI and HP hydrates are reported on figure 2. The dissociation temperatures of the CO<sub>2</sub> sI hydrate (the "h-l<sub>1</sub>-l<sub>2</sub>" and "h-l<sub>1</sub>-s<sub>2</sub>" equilibrium curves) observed during our experiments are in good agreement with the previous studies reporting this equilibrium up to 0.2 and 0.5 GPa [6,7]. Recently, another study monitored this transition with variable H<sub>2</sub>O/CO<sub>2</sub> sample compositions [8]. Although the results from this third study did not reproduce those of the two first reports, the general bow-shaped outline of the transition was clearly identified up to the highest stable pressures for the sI hydrate. Our results agree with this third report, leading to a maximum stability pressure for the sI hydrate of about 0.7–0.8 GPa.

At higher pressures, our results agree with the recent report of a CO<sub>2</sub> high-pressure hydrate [5]. The phase was found to be stable beyond 0.7 – 0.8 GPa and at least up to 1 GPa, below 280 K, in the water ice VI domain. However, an unexpected behavior was observed during our experiments, as this phase was not found stable below 255 K, in contradiction to what was first reported. Experiments are ongoing to explain this discrepancy.

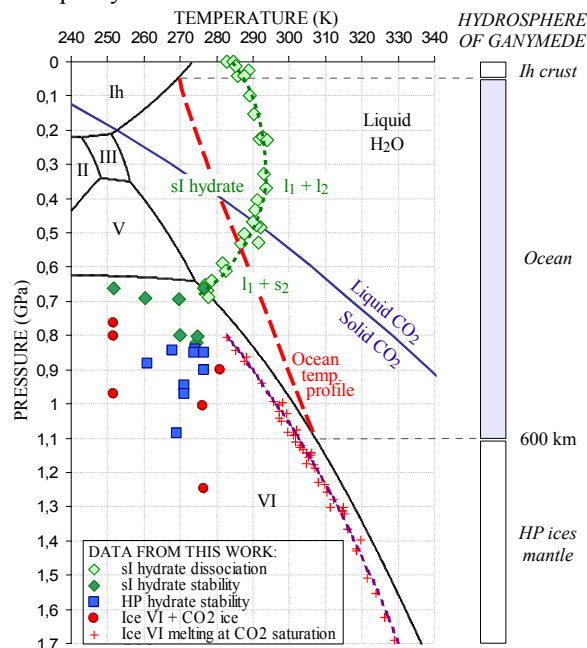


Figure 2. H<sub>2</sub>O-CO<sub>2</sub> phase diagram with new data on the stability of the sl and HP hydrates. Plain curves are the pure phase equilibrium for H<sub>2</sub>O (black) and CO<sub>2</sub> (blue). The violet dotted curve is the inferred equilibrium between ice VI and CO<sub>2</sub>-saturated water. The green dotted line is the inferred equilibrium between the sl hydrate and the H<sub>2</sub>O-rich liquid (l<sub>1</sub>), CO<sub>2</sub>-rich liquid (l<sub>2</sub>) and solid CO<sub>2</sub> (s<sub>2</sub>). The right part of the diagram is a possible past hydrosphere of Ganymede as a function of pressure, after [9]. The corresponding temperature profile in the liquid layer is the red dashed line in the phase diagram.

The melting curve of the H<sub>2</sub>O polymorphs in CO<sub>2</sub>-saturated water must be evaluated as it describes the H<sub>2</sub>O-CO<sub>2</sub> phase diagram at the condition most favorable to the CO<sub>2</sub> hydrate stability in a water-rich environment (CO<sub>2</sub> saturation); it may also be used to evaluate the maximum quantity of CO<sub>2</sub> that may be dissolved into water along this pressure/temperature profile. As no CO<sub>2</sub> hydrate is stable near the melting curve of water beyond 0.8 GPa, experiments allowed to monitor the melting curve of water ice VI in CO<sub>2</sub>-saturated water between 0.8 and 1.7 GPa (figure 2). Compared to the pure H<sub>2</sub>O system, these experiments revealed a temperature depletion of the melting curve of about 5 K between 0.8 and 1.4 GPa and up to 6 K at 1.7 GPa. The available thermodynamic model [2] suggests that, under an ideal solution assumption, this temperature depletion can be correlated to the quantity of CO<sub>2</sub> dis-

solved in water. The CO<sub>2</sub> solubility have been estimated along the H<sub>2</sub>O melting curve to range from 4 to 5 molar percents between 0.8 and 1.7 GPa. These values are very close to those below 0.2 GPa at similar temperatures [10], which suggests that pressure has little effect on the solubility of CO<sub>2</sub> on the GPa range.

**Implications:** Although the simple H<sub>2</sub>O-CO<sub>2</sub> binary system is not fully representative of the complex chemistry (ammonia, salts, other gas species...) expected inside the outer solar system icy bodies, the present results provide new constraints on planetary environments. As illustrated on Figure 2, CO<sub>2</sub> is stable in the form of clathrate hydrates throughout an internal ocean on Titan, Ganymede or Callisto (typically comprised between 0.1 and 0.6 GPa and up to 1 GPa). This implies that a significant fraction of CO<sub>2</sub> present in the ocean may be trapped in the form of CO<sub>2</sub> clathrate hydrates. Above 0.6 – 0.7 GPa, CO<sub>2</sub> clathrate hydrates are stable at temperatures significantly smaller than the melting point of high-pressure ices. Current evolution models predict that the temperature in the high-pressure layer should be close to the melting point of ice (e.g. [11]), implying that CO<sub>2</sub> is unstable in the form of hydrates in these regions. CO<sub>2</sub> in the high-pressure layer may exist dissolved in liquid water pockets at temperatures down to 5-6 K below the melting point of pure water ice, and in the form of solid CO<sub>2</sub> ice or carbonates, depending on the composition of the liquid phase. In this context, CO<sub>2</sub> may significantly affects the dynamics of the high-pressure mantle by favoring the presence of aqueous melts. CO<sub>2</sub> is therefore expected to play a key role in the thermo-chemical evolution of large outer solar system icy moons like Titan, Ganymede and Callisto.

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**References:** [1] Marion G.M. et al. (2010) *Computers & Geosciences*, 36, 10-15. [2] Choukroun M. and Grasset O. (2010) *J. Chem. Phys.*, 133, 144502. [3] Dalton J.B. (2010) *Space Sci. Rev.*, 153, 219-247. [4] Scott H.P. et al. (2002) *EPSL*, 203, 399-412. [5] Hirai H. et al. (2010) *J. Chem. Phys.*, 133, 124511. [6] Takenouchi S. and Kennedy G.C. (1965) *J. Geol.*, 73, 383-390. [7] Nakano S. et al. (1998) *J. Chem. Eng. Data*, 43, 807-810. [8] Manakov A.Y. et al. (2009) *J. Phys. Chem. B*, 113, 7257-7262. [9] Bland M.T. et al. (2009), *Icarus*, 200, 207-221. [10] Duan Z. and Sun R. (2003) *Chemical Geology*, 193, 257-271. [11] Sotin C. and Tobie G. (2004) *C. R. Physique* 5, 769-765.