

THE H₂O-CO₂ SYSTEM UP TO 1.7 GPa: IMPLICATIONS FOR LARGE ICY MOONS. O. Bollengier¹, M. Choukroun², O. Grasset¹, G. Tobie¹, E. Le Menn¹, G. Bellino¹, L. Bezacier¹, Y. Morizet¹, A. Oancea¹, C. Taffin¹, ¹Université de Nantes, CNRS, Laboratoire de Planétologie et Géodynamique de Nantes, UMR 6112, 44322 Nantes Cedex 3, France, olivier.bollengier@univ-nantes.fr, ²Jet 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 H₂O-NH₃ binary system. As part of the further development of this high-pressure model, the present study focuses on the H₂O-CO₂ 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 CO₂ hydrates and CO₂-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 H₂O-CO₂ system. First, temperature-dependent experiments with samples of variable H₂O/CO₂ bulk compositions have been carried out at variable pressures to explore the stability of the known CO₂ sI clathrate hydrate in a water-rich, CO₂-saturated environment. Other experiments with bulk compositions close to the CO₂ sI clathrate hydrate ideal stoichiometry have been used to constrain the transition with pressure from the CO₂ sI clathrate hydrate to the unidentified CO₂ high-pressure hydrate phase recently reported [5]. Finally, the melting temperature of water ice VI in CO₂-saturated water was monitored through a third set of runs to estimate the effect of dissolved CO₂ on H₂O at saturation, and as a consequence the solubility of CO₂ 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 CO₂ sI clathrate hydrate (hereafter sI hydrate) and the recently reported CO₂ high-pressure hydrate (hereafter HP hydrate), along with the signature of mixed CO₂ dry ice and H₂O ice VI for comparison. The phase transition between the sI and HP hydrates around 0.7–0.8 GPa affects both the H₂O skeleton and CO₂ guest signatures of the sI hydrate with abrupt jumps (reversing the pressure-induced shift affecting the H₂O skeleton) at this pressure. Although the high-pressure phase has been recognized as a CO₂ 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.

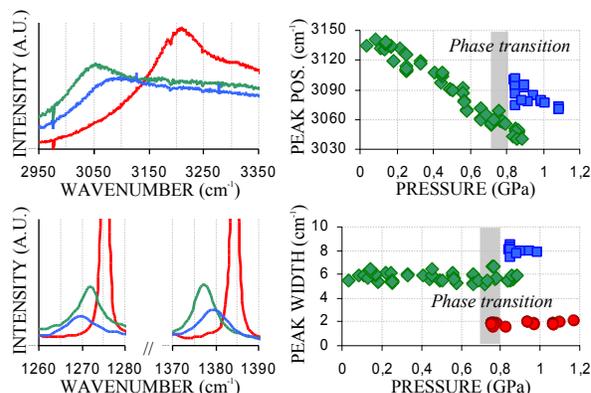


Figure 1. Typical Raman spectra of the sI (green, diamonds) and HP (blue, squares) CO₂ hydrates, and of H₂O-CO₂ ices mixture (red, circles), at 255–280 K and 0–1.2 GPa (pressures up to and past the hydrate transition). Upper part shows the O-H spectral range (H₂O skeleton for the sI hydrate) and pressure dependence of the bands positions. Lower part displays the CO₂ ν_1 and ν_2 vibrations region and pressure dependence of the ν_2 peak width.

Results: New stability data for the CO₂ sI and HP hydrates are reported on figure 2. The dissociation temperatures of the CO₂ sI hydrate (the "h-l₁-l₂" and "h-l₁-s₂" 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 H₂O/CO₂ 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 CO₂ 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.

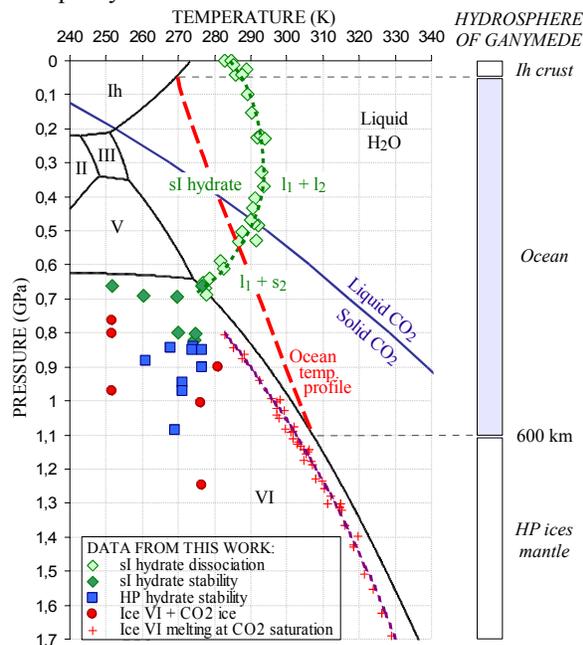


Figure 2. H₂O-CO₂ phase diagram with new data on the stability of the sl and HP hydrates. Plain curves are the pure phase equilibrium for H₂O (black) and CO₂ (blue). The violet dotted curve is the inferred equilibrium between ice VI and CO₂-saturated water. The green dotted line is the inferred equilibrium between the sl hydrate and the H₂O-rich liquid (l₁), CO₂-rich liquid (l₂) and solid CO₂ (s₂). 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 H₂O polymorphs in CO₂-saturated water must be evaluated as it describes the H₂O-CO₂ phase diagram at the condition most favorable to the CO₂ hydrate stability in a water-rich environment (CO₂ saturation); it may also be used to evaluate the maximum quantity of CO₂ that may be dissolved into water along this pressure/temperature profile. As no CO₂ 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 CO₂-saturated water between 0.8 and 1.7 GPa (figure 2). Compared to the pure H₂O 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 CO₂ dis-

solved in water. The CO₂ solubility have been estimated along the H₂O 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 CO₂ on the GPa range.

Implications: Although the simple H₂O-CO₂ 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, CO₂ 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 CO₂ present in the ocean may be trapped in the form of CO₂ clathrate hydrates. Above 0.6 – 0.7 GPa, CO₂ 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 CO₂ is unstable in the form of hydrates in these regions. CO₂ 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 CO₂ ice or carbonates, depending on the composition of the liquid phase. In this context, CO₂ may significantly affects the dynamics of the high-pressure mantle by favoring the presence of aqueous melts. CO₂ 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.

Acknowledgments: The research leading to these results has received funding from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013 Grant Agreement no. 259285). This work received funding from the PRES-UNAM.

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