# HEAT STORAGE OF CRYOGENIC FLUIDS OF OCEAN WORLDS: PART II

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## 1. Introduction

"Ocean worlds" are those planetary bodies that had or have potential stable deep aqueous environments beneath their surfaces. In the last decades, the data obtained in the space missions reveal that the solar system is richer in these systems than previously expected [1,2]. Hence, from Ceres, to icy satellites of the Gas and Icy Giants, and even Pluto, can have liquid reservoirs at their interior that influence in their geological processes and thermal evolution.

Nevertheless, due to this wide region in the solar system where these bodies are found, several are the chemical compositions that may be considered and studied at the time to try to understand their properties. In systems closer to the Sun, dissolved salts may have an important presence in the aqueous reservoirs. While volatiles start to increase their abundance at the interior of those systems located far because the decrease in temperature.

In this research we are characterizing spectroscopically and thermodynamically several aqueous solutions with planetological interest, at temperature-pressure (T-P) ranges that can be found in the upper layers of the icy crusts. Salts like sulfates, carbonates and chlorides, and volatiles like ammonia, methanol and carbon dioxide are being dissolved in water in different proportions depending on the planetary body where we want to perform the experimental simulation.

### 2. Experimental setup

Solutions are studied in two facilities: (a) the high pressure  $\mu$ DSC7 evo calorimeter (Setaram), that allows to determine the thermal history and specific heat (Cp) values, and (b) the high-pressure cell coupled to the Raman spectrometer iHR550 (Horiba Jobin Yvon), from which we can know the chemicophysical state and the reactions that occur with the P-T changes.

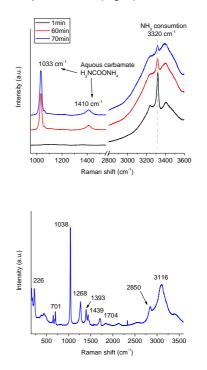
The systems studied so far at a temperatures down to 233 K have been: (1) salty aqueous solutions of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, MgCO<sub>3</sub>, MgSO<sub>4</sub> and NaCl, (2) aqueous solutions of 10-30wt% NH<sub>3</sub>, (3) aqueous solutions of 10-100wt% MeOH, (4) mixtures NH<sub>3</sub> +

MeOH, and (5) previous systems with the addition of  $CO_2$  up to 500 bar.

#### 3. Results

The initial results are shown in recent works [3,4]. Here, as an example, we present the research focuses on the  $NH_3$  aqueous solutions when they coexist with different carbon species. On the one hand  $CO_2$ , and, on the other hand,  $Na_2CO_3$ .

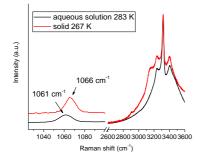
When  $CO_2$  is added to an NH<sub>3</sub> aqueous solution the formation of ammonia carbonate is highly favorable and the reaction occurs fast. The consumption of aqueous NH<sub>3</sub> is followed by the appearance of aqueous carbamate and, finally, teschemacherite (NH<sub>4</sub>HCO<sub>3</sub>) precipitates (confirmed by XRD). No change was observed in the solid when it was pressurized up to 500 bar (Fig. 1).



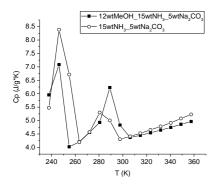
**Figure 1.** Consumption of  $NH_3$  and formation of aqueous carbamate (top). Raman spectrum of teschemacherite (bottom).

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Conversely, the dissolution of  $Na_2CO_3$  in the  $NH_3$  aqueous solutions does not consume aqueous  $NH_3$  and only  $Na_2CO_3$  is measured as final precipitate (Fig. 2). Calorimetry shows how the Cp changes according to the  $Na_2CO_3$  phase stabilized, which is related to the temperature (Fig. 3).



**Figure 2.** Raman spectra of H<sub>2</sub>O-NH<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> before and after precipitation of solid.



**Figure 3.** Cp versus Temperature of  $H_2O$ -NH<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> and  $H_2O$ -NH<sub>3</sub>-MeOH-Na<sub>2</sub>CO<sub>3</sub> systems.

#### 4. Discussion and conclusions

This work has the aim to characterize the deep environments of icy bodies where cryogenic fluids can potentially stabilize. The combination of the data from calorimetry and Raman spectroscopy allow to link the thermal properties of the systems with their chemicophysical state at a temperatures down to 233 K and pressures up to 500 bar. A wide range of different chemical behaviors are being studied. Depending on the system, we can observe: no change in the P-T range studied (e.g. H<sub>2</sub>O-MeOH-CO<sub>2</sub>), a variation in the aqueous speciation without precipitation (e.g. H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub>-CO<sub>2</sub>), or the formation of solids (e. g. H<sub>2</sub>O-NH<sub>3</sub>-CO<sub>2</sub>). All these processes are reflected in the Cp and thermal characteristics of the systems. The combination of these techniques will be a support for the interpretation of the data taken in future space missions, especially in those able to study by radar the upper layers of icy satellites, as JUICE from ESA and Europa Clipper from NASA.

## 5. References

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[3] Muñoz-Iglesias V., et al. (2019) LPSC, Houston, TX.

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## 6. Acknowledgments

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