Thermal properties of the H$_2$O-CO$_2$-Na$_2$CO$_3$/CH$_3$OH/NH$_3$ systems at low temperatures and pressures up to 50 MPa

The results shown in this research have important planetary implications related to the thermal behavior of bodies rich in the compounds of the systems studied, as can be the case of Enceladus. We show that the level of cage occupancy in clathrates plays a key role in their thermal behavior. Highly-occupied clathrates will be robust and will contribute to the retention of heat inside the planetary bodies due to their characteristic low thermal conductivity. However, poorly-occupied clathrates will dissociate more easily than water ice, allowing greater heat fluxes through the icy crust and favoring the dissipation of heat to the exterior.

We used differential scanning calorimetry (DSC) to determine the values of specific heat capacity ($C_p$) and enthalpy of dissociation ($\Delta H_d$) of CO$_2$-clathrates in the presence of sodium carbonate, ammonia, and methanol at temperatures $\geq 233$ K and pressures $\leq 50$ MPa. We also monitored the physico-chemical evolution of the systems along the pressure–temperature paths through Raman spectroscopy.

Final fluids richer in dissolved CO$_2$ had a lower $C_p$. Addition of carbonates and methanol led to a decrease in the melting temperature of both ice and clathrates. Ammonia reacted with CO$_2$ to rapidly form ammonium bicarbonate, however, ice and CO$_2$-clathrates could also stabilize in parallel.

The protocol used to form the CO$_2$-clathrates influenced the thermal behavior of the system. The formation of clathrates from aqueous solutions without the application of clathrate-stabilizers, mechanical agitation, or synthesis from crushed ice led to a low guest occupancy, forming less stable clathrates with low enthalpies of dissociation (130–275 J g$^{-1}$).

**KEYWORDS:** CO$_2$-clathrates, carbonates, methanol, ammonia, enthalpy, heat capacity, calorimetry, Raman spectroscopy