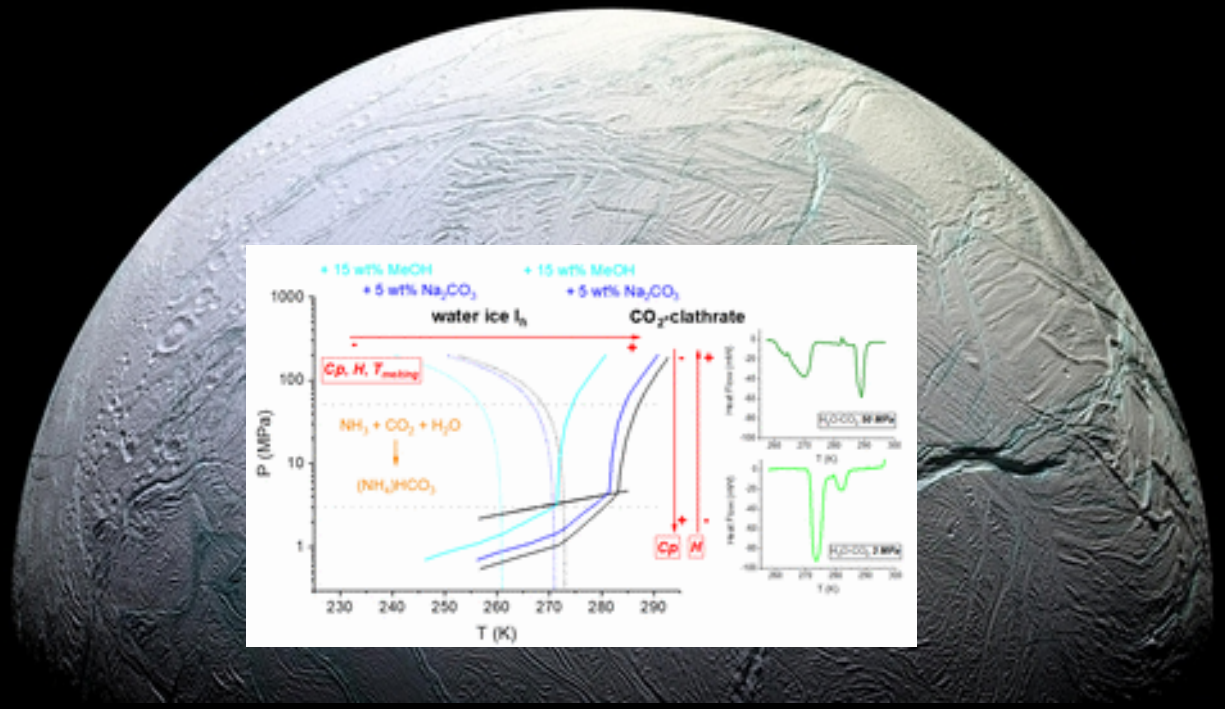
Thermal properties of the H_2O-CO_2-Na_2CO_3/CH_3OH/NH_3 systems at low temperatures and pressures up to 50 MPa



Images (credits): Front, graphical abstract (Muñoz-Iglesias, CAB-INTA-CSIC); back, Enceladus (NASA/JPL-Caltech)

KEYWORDS: CO_2-clathrates, carbonates, methanol, ammonia, enthalpy, heat capacity, calorimetry, Raman spectroscopy

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 (ΔH_d) of **CO_2-clathrates in the presence of sodium carbonate, ammonia, and methanol at temperatures ≥ 233 K and pressures ≤ 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}).

Muñoz-Iglesias V. and Prieto-Ballesteros O. 2021 *ACS Earth Space and Chemistry*