From CO_2 clathrate hydrate to solid carbonic acid: high-pressure chemistry in astrochemical ices

Demetrio SCELTA (LENS and ICCOM-CNR Italy),
Selene BERNI (IFAC-CNR, Italy)
Sebastiano ROMI (LENS and Università di Firenze, Italy)
Samuele FANETTI (LENS and ICCOM-CNR, Italy)
Frederico G. ALABARSE (ELETTRA Sincrotrone Trieste, Italy)
Bjorn WEHINGER (ESRF, France)
Roberto BINI (LENS and Università di Firenze, Italy)

Abstract

Water-rich ices containing simple volatile molecules are widespread throughout the Solar System and the interstellar medium, making their chemistry highly relevant to astrochemical processes [1]. Among these systems, carbon dioxide (CO_2)–water (H_2O) mixtures are of particular interest due to the abundance of CO_2 on icy planetary bodies, comets, and interstellar ices [2]. Moreover, the chemical reactivity between CO_2 and H_2O may result in the formation of their 1:1 adduct, carbonic acid (H_2CO_3), a key intermediate in carbon chemistry. The synthesis of H_2CO_3 from its constituents has long remained challenging and has often been carried out under very drastic conditions starting from fluids: only a few recent works have encompassed high-pressure in this complex framework [3-5].

We recently identified a particularly effective route for the formation of solid hydrated carbonic acid through the cold compression of pristine CO_2 clathrate hydrate [6-7]. Under moderate pressure and temperature conditions (130–270 K, <5 GPa), this process leads to the formation of diverse hydrated phases, including crystalline ε-H_2CO_3, amorphous ε-H_2CO_3, and crystalline ε_m-H_2CO_3. These phases were characterized using Raman spectroscopy together with synchrotron and laboratory X-ray diffraction. A detailed investigation of the ε_m-H_2CO_3 formation pathway [7] reveals a complex multistep mechanism involving dense amorphous intermediates with remarkable thermal and pressure stability, as well as the transient appearance of metastable ice phases [8]. The observed transformations highlight the rich structural landscape accessible in compressed CO_2–H_2O systems and provide new insight into the behavior of carbon-bearing ices under planetary interior conditions.

The relatively mild pressure–temperature regime required for these reactions is compatible with processes occurring within icy worlds, such as the subduction of surface materials into deeper layers. These findings therefore suggest previously unrecognized pathways for carbonic acid formation and storage in extraterrestrial environments, with important implications for the chemical evolution of icy bodies and the diversity of astrochemical processes beyond Earth.

[1] A.M. Shaw, Astrochemistry: From Astronomy to Astrobiology, Wiley, 1st edition, 2006

[2] H.Y. McSweenJr, G.R. Huss, Cosmochemistry, Cambridge University Press, 2010

[3] H. Wang *et al.*, Sci. Rep. 2016, 6, 19902

[4] E.H. Abramson *et al.*, Sci. Rep. 2017, 7, 821

[5] E.H. Abramson *et al.*, Am. Mineral. 2018, 103, 1468

[6] S. Berni *et al.*, Angew. Chem. Int. Ed. 2024, 63, e202403953

[7] S. Berni *et al.l,* Chem. Sci. 2025,16, 22769

[8] D. Scelta *et al.*, under peer review