Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.35455

Amorphous Carbonate Formation in Cryogenic Brines: Implications for Planetary Icy Surface Processes

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Carbonates from Gale Crater on Mars exhibit exceptionally high $\delta^{13}C$ (110 ± 3 ‰) and $\delta^{18}O$ (91 ± 4 ‰) values, which are difficult to explain by existing models of evaporation/Rayleigh processes and cryogenic brines [1]. In this study, we experimentally investigate one potential pathway for the rapid formation of carbonates under cold, low-pressure conditions similar to those impacting icy surface processes on Mars and other planetary bodies. We placed saturated bicarbonate solutions into a freeze-dryer. Once under vacuum, CO_2 degassing led to carbonate precipitation while evaporative cooling occurred simultaneously. As the solutions froze, additional carbonate formation was triggered by freeze concentration. We examined how freezing rates affect carbonate precipitation. Our findings show that even after several hours, the freezing of calcium (Ca) and calcium-magnesium (Ca-Mg) bicarbonate solutions continues to induce the precipitation of amorphous carbonates. In our setup, amorphous calcium carbonate (ACC) begins to nucleate at freezing rates greater than 0.3 vol% min^{-1}, which corresponds to approximately 6 hours for complete freezing. As freezing rates decrease, the ACC spherules coarsen. In magnesium-bearing brines, the freezing process produces unusually large domains of amorphous Ca-Mg carbonate. Cryogenic ACC forms during rapid freezing of bicarbonate solutions in liquid nitrogen [2]. Our study demonstrates that ACC and other amorphous carbonates can also form over longer freezing timescales, which may be significant for carbonate precipitation from cryogenic brines on Mars, particularly during day-night cycles. Preliminary carbon and triple oxygen isotope data support the notion that cryogenic ACC has a heavier isotope composition than what would be expected at equilibrium. Recent experiments suggest that transforming ACC into calcite could increase $\delta^{18}O$ by up to 8 ‰ [3]. If some Martian carbonates have passed through an amorphous carbonate precursor stage, this transformation could enhance isotope fractionation and provide an additional mechanism to account for the extremely high $\delta^{18}O$ isotope signatures observed in carbonates from Gale Crater.

[1] Burtt et al. (2024), *PNAS* 121.42, e2321342121. [2] Ihli, Kulak & Meldrum (2013), *AFM* 23.12, 1575-1585. [3] Asta et al. (2024), *GCA* 386, 96-109.