Hydrated Carbonates under Pressure

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Abstract

Hydrated carbonates play an important role in the global carbon cycle and industrial carbon sequestration technologies. Understanding the fundamental crystallochemistry and mechanical properties of these minerals under different thermodynamic conditions is essential for predicting their phase stability. This work presents a comprehensive high-pressure investigation of two natural hydrated carbonates: the sodium sesquicarbonate trona ($Na_3H(CO_3)_2.2H_2O$) and the trihydrated magnesium carbonate nesquehonite ($MgCO_3.3H_2O$), and of a hydrated silicate-carbonate Y-kainosite ($Ca_2Y_2Si_4O_{12}(CO_3).H_2O$). Their high-pressure structural behavior was studied by a joint experimental and theoretical approach consisting of in-situ synchrotron single-crystal and powder X-ray diffraction (XRD) and complementary density functional theory (DFT) calculations.

Trona undergoes a phase transition at 12.8 GPa from its initial monoclinic structure to a dense triclinic polymorph. This phase transition was accompanied by an increase in the Sodium (Na) coordination number from 6 to 7–8. Nesquehonite, on the other hand, undergoes two pressure-induced phase transitions at the lower pressure thresholds of 2.4 GPa and 4 GPa, respectively. The transition to the second pressure-induced phase is marked by a distinctive coordination expansion of the Mg^{2+} cation from 6 to 7, forming distorted [MgO_7] pentagonal bipyramids. For Kainosite, the P-V data were fitted to the Birch–Murnaghan EOS to determine the bulk modulus: B_0 = 109.8(13) GPa. The effective coordination numbers of the Ca and Y atoms progressively increased with pressure, which entails the densification of the structure, due to the reorientation of [Si_2O_7] disilicate groups, the [CO_3] carbonate groups and the water molecules. The compressibility and anisotropy of low- and high-pressure phases were determined. Particularly interesting is the negative axial compressibility and negative thermal expansion observed in nesquehonite.

Across all the minerals, structural stability is observed to be heavily mediated by the dynamic reorganization of hydrogen-bonding networks. While trona exhibited 1D chain-like hydrogen bonding that reorganized into a localized 2D network at high pressure, nesquehonite's framework is sustained by highly directional 2D networks that accommodate significant polyhedral distortion. Together, these findings provide critical mechanistic insights into how pressure-induced coordination expansions and hydrogen-bond topologies dictate the stability of dense hydrated carbonate polymorphs in high-pressure environments.