From [CO_3] towards [CO_4]: a high-pressure study of two novel hydrous carbonates

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Abstract

Carbonates are ionic compounds that are typically known to feature $[CO_3]^{2-}$ groups, in which the sp^2 hybridization of the orbitals of carbon leads to a trigonal planar geometry of the carbonate anions. Many examples of metal carbonates with the general chemical formula $MeCO_3$ (Me = Ca, Fe, Mg, etc.) have been reported at ambient conditions. Owing to the rotations of the carbonate anions $[CO_3]^{2-}$, such sp^2 carbonates exhibit a wide range of polymorphs even at pressures below 20 GPa.

At pressures higher than 20 GPa, the definition of carbonates has been expanded to include compounds based on $[CO_4]^{4-}$ tetrahedra, where the central carbon atoms form sp^3 hybridized orbitals with their four neighboring oxygen atoms. These compounds become more common at pressures above 50 GPa with examples[1, 2] exhibiting a wealth of structural diversity due to tetrahedra polymerizing via common vertices. Alike the chemistry of silicates[3, 4], this results in the formation of various structural units of various dimensionalities. The dominance of the sp^3 hybridization for carbonates above 50 GPa was predicted by calculations[5, 6] and has been experimentally well-documented [7].

However, the mechanisms that lead to this transition are still not fully understood. Merlini at al. [8] have demonstrated that $CaCO_3$-II begins to exhibit an intermediate state of the carbonate anions between 40 and 60 GPa, with the carbon atoms gradually moving away from the plane of the $[CO_3]^{2-}$. Another factor that affects the displacement of carbon from the ideal trigonal configuration is the hydrogen interactions in the structure. This effect was demonstrated in nuclear magnetic resonance spectroscopy[9] studies of monohydrocalcite and ikaite, two naturally occurring calcium carbonate hydrates.

To further study the effect of pressure and hydrogen on the structural evolution of carbonates, we performed high-pressure, high-temperature experiments on the $CaCO_3$(s) + H_2O(l) system at 38(2) GPa and 2000(200) K using a laser-heated diamond anvil cell. Usage of multi-grain, single crystal X-Ray diffraction at ID27 and ID11 beamlines of European Synchrotron Radiation Facility allowed us to identify new hydroxide and hydroxy-hydrate carbonates, namely tR45 $Ca_3(CO_3)_2(OH)_2$ and mP104 $Ca_4(CO_3)_3(H_2O)_2(OH)_2$, as products of the reaction. Compression of the discovered phases up to 74 GPa revealed a gradual evolution of the central carbon from trigonal to tetrahedral, a change that is more pronounced for tR45 $Ca_3(CO_3)_2(OH)_2$ (Figure 1). In the current contribution we will present the pressure-induced evolution of both phases and discuss the mechanism of this structural change enhanced by the presence of OH^- groups interacting with the carbonate anions.

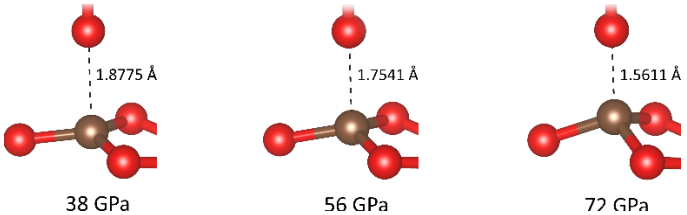

Figure 1: Schematic representation of the effect of compression on the geometry of CO_3 triangular units in tR45 $Ca_3(CO_3)_2(OH)_2$, showing the gradual evolution of the geometry of central carbon position.

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