# Structural Evolution and Decarbonation Reaction of Calcium Carbonate during Subduction Processes

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One key aspect of the Earth Carbon Cycle is how carbon stored in marine sediments and altered oceanic crust are transported into the Earth's mantle and then recycled at subduction zones. Calcium carbonate ($CaCO_3$) is one of the most abundant carbonates in the crust and shows complicated phase transitions under pressure-temperature conditions. Several high-pressure polymorphs including calcite (*R*-3*c*, *Z*=6), $CaCO_3$-II, $CaCO_3$-III (*P*-1, *Z*=10), $CaCO_3$-IIIb (*P*-1, *Z*=4), $CaCO_3$-V (disordered, *R*-3m), $CaCO_3$-VI (*P*-1, *Z*=2), aragonite (*Pmcn*, *Z*=4), $CaCO_3$-VII ($P2_1/c$) and post-aragonite (*Pmmn*, *Z*=2) have been reported, among which $CaCO_3$-III and $CaCO_3$-IIIb are of particular interest. They are characterized with different cell parameters, but display structural connections in similar stability field. Here using Diamond Anvil Cells (DACs) and micro-Raman Spectroscopy, we observed a transformation from calcite to $CaCO_3$-II at ~1.5 GPa and 27 °C with a negative slope to ~1.3 GPa and 250 °C, and it further evolves to $CaCO_3$-IIIb at ~2.0 GPa. Increasing pressure to 3.38 GPa, a sluggish transition from $CaCO_3$-IIIb to $CaCO_3$-III occurred. But for crystals with developed internal cracks, $CaCO_3$-II directly converts to $CaCO_3$-III at ~2.0 GPa. It thus can be concluded that $CaCO_3$-IIIb is a metastable intermediate phase during the reconstructive transformation from $CaCO_3$-II to $CaCO_3$-III. Splitting of C-O in-plane bending and symmetric stretching vibrations, and appearance of new lattice vibrations in Raman spectra suggest a lower crystal symmetry of $CaCO_3$-IIIb and $CaCO_3$-III relative to calcite. Besides, two types of phase transition mechanism to aragonite is observed: (1) under lower pressure-temperature conditions (~0.8 GPa and 200 °C), aragonite forms slowly with an outgrowth aragonite morphology via

dissolution-precipitation transformation; (2) at pressures in excess of 1.39 GPa with temperatures above 435 °C, aragonite grows by replacement of calcite/$CaCO_3$-II via solid-solid transformation. During the subsequent cooling and decompression processes, the reverse conversion is not achieved; instead aragonite preserved back-to ambient conditions. In addition, decarbonation of $CaCO_3$ (including calcite, $CaCO_3$-II and aragonite) by quartz took up under hydrothermal conditions. The proceeding of this reaction exhibits a positive slope beginning from 0.2 GPa and 438 °C to 1.71 GPa and 535 °C. This is a dominant process that leads to the release of $CO_2$ fluid and generation of considerable porosity that permits fluids transport through rock. Our study on structural evolution and decarbonation reaction of calcium carbonate shed lights on carbon recycle and storage in the deep Earth.