

## Phase transitions in CaCO<sub>3</sub> under hydrous and anhydrous conditions: Implications for the structural transformations of CaCO<sub>3</sub> during subduction processes

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### ABSTRACT

The transport of calcium carbonate (CaCO<sub>3</sub>) into the Earth's interior through subduction is one of the key processes in the global cycling of carbon. To develop a better understanding of the CaCO<sub>3</sub> structural stability during subduction processes, the phase transitions among CaCO<sub>3</sub>-I (calcite), CaCO<sub>3</sub>-II, -III/IIIb, and aragonite under pressure-temperature (*P-T*) conditions up to 2.5 GPa and 600 °C, in hydrous and anhydrous environments, were investigated using a hydrothermal diamond-anvil cell. One displacive and two reconstructive processes during the phase transitions among CaCO<sub>3</sub> polymorphs were confirmed from the results obtained from in situ observations and Raman spectroscopic measurements. Meanwhile, the effect of Ca-substitutional metal cations (e.g., Mg<sup>2+</sup>) in CaCO<sub>3</sub> and the presence of an aqueous fluid on the phase transition processes have been determined. Specifically, the CaCO<sub>3</sub>-I ↔ -II phase transition is a displacive process, occurring instantly at pressures varying from 1.6 GPa at room temperature to 1.5 GPa at 500 °C with the phase equilibrium boundary having a minimum *P-T* point at ~1.4 GPa at 300 °C, and is completely reversible upon cooling and decompression. The CaCO<sub>3</sub>-II → -III phase transition is a reconstructive process, observed at *P-T* conditions from 2.0 GPa at room temperature to 2.5 GPa at 150 °C, and is accomplished by solid recrystallization starting from CaCO<sub>3</sub>-II, transitioning through an intermediate CaCO<sub>3</sub>-IIIb, and ending at the CaCO<sub>3</sub>-III structure. The phase transition between CaCO<sub>3</sub>-I or -II and aragonite, which is also a reconstructive process, was found to occur by progressive solid recrystallization under high *P-T* hydrous and anhydrous conditions, or alternatively, via dissolution-precipitation under low-*P-T* hydrous conditions, depending on the presence of aqueous fluids and the heating rate of the system. The substitution for Ca<sup>2+</sup> by other metal cations (e.g., Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>) in CaCO<sub>3</sub> results in a significant increase in the pressures for the displacive and solid recrystallization reconstructive phase transitions, but has no detectable influence on the CaCO<sub>3</sub>-I/II ↔ aragonite transformation via a dissolution-precipitation process under hydrous conditions. Our results show that the presence of Ca-substitutional metal cations in CaCO<sub>3</sub> is a key factor controlling the phase stability of CaCO<sub>3</sub> under high *P-T* conditions, and suggest that aragonite should be the predominant phase in the upper mantle in subduction zones where the heating rate is very low and slab dehydration is prevalent.

**Keywords:** Calcite, CaCO<sub>3</sub>-II, CaCO<sub>3</sub>-III/IIIb, aragonite, phase transition, subduction