Effect of cationic substitution on the pressure-induced phase transitions in calcium carbonate

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ABSTRACT

The high-pressure CaCO₃ phase diagram has been the most extensively studied within the carbonates group. However, both the diverse mineralogy of carbonates and the abundance of solid solutions in natural samples require the investigation of multi-component systems at high pressures (P) and temperatures (T). Here we studied a member of the CaCO₃-SrCO₃ solid-solution series and revealed the effect of cationic substitution on the pressure-induced phase transitions in calcium carbonate.

A synthetic solid solution Ca₀.₈₂Sr₀.₁₈CO₃ was studied in situ by Raman spectroscopy in a diamond-anvil cell (DAC) up to 55 GPa and 800 K. The results of this work show significant differences in the high-pressure structural and vibrational behavior of the (Ca,Sr)CO₃ solid solution compared to that of pure CaCO₃. The monoclinic CaCO₃-II-type structure (Sr-calcite-II) was observed already at ambient conditions instead of the “expected” rhombohedral calcite. The stress-induced phase transition to a new high-pressure modification, termed here as Sr-calcite-IIic, was detected at 7 GPa. Sr-calcite-VII formed already at 16 GPa and room T, which is 14 GPa lower compared to CaCO₃-VII. Finally, crystallization of Sr-aragonite was detected at 540 K and 9 GPa, at 200 K lower T than pure aragonite. Our results indicate that substitution of Ca²⁺ by bigger cations, such as Sr²⁺, in CaCO₃ structures can stabilize phases with larger cation coordination sites (e.g., aragonite, CaCO₃-VII, and post-aragonite) at lower P-T conditions compared to pure CaCO₃. The present study shows that the role of cationic composition in the phase behavior of carbonates at high pressures should be carefully considered when modeling the deep carbon cycle and mantle processes involving carbonates, such as metasomatism, deep mantle melting, and diamond formation.

Keywords: Deep carbon cycle, calcium carbonate, solid solution, phase diagram, phase transition, high pressure, vibrational spectroscopy

INTRODUCTION


At atmospheric pressure, CaCO₃ crystallizes predominantly in the rhombohedral calcite structure [space group R̄3c] with coplanar CO₃²⁻ groups and Ca²⁺ in sixfold coordination (Ca⁶⁰). Compression of calcite leads to a complex polymorphism with several phase transitions. Previous experimental and computational studies revealed four stable high-pressure polymorphs of calcite: aragonite (Pnma, Ca⁶⁰), CaCO₃-VII (P2₁/c, Ca¹⁰⁹), post-aragonite (Pmnm, Ca¹²³), and sp²-CaCO₃ (P2₁/c, Ca¹²³, C4(i)) (Fig. 1) (Ono et al. 2005, 2007; Gavryushkin et al. 2017; Lobanov et al. 2017; Bayarjargal et al. 2018). The formation of these high-pressure phases is kinetically hindered at ambient temperature and occurs only above 773 K (500 °C) (Bayarjargal et al. 2018).

Cold compression of calcite, on the contrary, leads to a different sequence of high-pressure polymorphs: CaCO₃-II (P2₁/c, Ca⁶⁰); CaCO₃-III and -IIb (PT, Ca⁶⁰ and Ca⁶⁰); CaCO₃-VI (PT, Ca¹²³) (Fig. 1) (Suito et al. 2001; Merlino et al. 2012, 2018; Koch-Müller et al. 2016; Bayarjargal et al. 2018). All of these high-pressure modifications are considered metastable (Suito et al. 2001; Merlino et al. 2012, 2018; Koch-Müller et al. 2016; Bayarjargal et al. 2018). Such consideration arises from the fact that those polymorphs appear within the stability fields of