Pressure induced phase transitions in Ca-carbonate and effect of cationic substitution on the phase behavior

N.S. MARTIROSYAN 1,2*, M. KOCH-MÜLLER 1, I. EFTHIMIOPOULOS 1, S. JAHN 2

1 GFZ, German Research Centre for Geosciences, Telegrafenberg, 14474 Potsdam, Germany (*correspondence: naira.martirosyan@gfz-potsdam.de)
2 Institut für Geologie und Mineralogie, Universität zu Köln, Cologne, Germany (s.jahn@uni-koeln.de)

The abundance of calcite at near surface conditions and findings of Ca-carbonates in diamond inclusions [1] triggers the interest in the high-P CaCO₃ phase diagram. Calculations and experiments show that there are 5 stable polymorphs at mantle P-T conditions: aragonite (< 30 GPa), CaCO₃-VII (30 - 50 GPa), postaragonite (50-100 GPa) and sp³-CaCO₃ (>100 GPa) [3, 4]. Cold compression of calcite leads to another sequence of phase transitions: cc-II (1.7-2.5 GPa), cc-IIIb (2-3 GPa), cc-III (4-15 GPa), and cc-VI (>15 GPa) [3, 5, 6]. P-induced phase transitions were studied by in situ XRD, and spectroscopic methods up to 50 GPa [3, 5, 6].

Here we studied the effect of Sr incorporation on the CaCO₃ phase diagram. We investigated the CaCO₃-SrCO₃ solid solution up to 55 GPa and 800 K. Samples were first synthesized from the mixture of CaCO₃ and SrCO₃ at 2 GPa and 1300 K in a multianvil apparatus. Microprobe analysis showed a homogeneous composition with the amount of Sr reaching 18 mol%. The powder XRD patterns can be described by a distorted calcite structure. All high-P experiments were conducted in situ in a diamond anvil cell using Raman-spectroscopy to detect phase transformations.

Phase transitions of the (Ca,Sr)CO₃ solid solution at room T are in good agreement with the metastable phase diagram of CaCO₃ and we observe all 4 known polymorphs: cc-II(1-2 GPa), cc-IIIb (2-4 GPa), cc-III (4-7 GPa) and cc-VI (16-55 GPa). An abrupt change in the frequencies of the Raman bands at 7 GPa indicates the formation of a new high pressure polymorph, cc-IIIc, which was not previously observed in pure CaCO₃. During heating to 600-800 K at 9 GPa we detected the re-entrance of cc-IIIb. At 10-11 GPa heating led to the formation of aragonite.