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

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The abundance of calcite at near surface conditions and findings of Ca-carbonates in diamond inclusions [1] triggers the interest in the high-*P* $CaCO_3$ phase diagram. Calculations and experiments show that there are 5 stable polymorphs at mantle *P-T* conditions: aragonite (< 30 GPa), $CaCO_3$-VII (30 -50 GPa), postaragonite (50-100 GPa) and sp^3-$CaCO_3$ (>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 (>15GPa) [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 $CaCO_3$ phase diagram. We investigated the $CaCO_3$-$SrCO_3$ solid solution up to 55 GPa and 800 K. Samples were first synthesized from the mixture of $CaCO_3$ and $SrCO_3$ 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 $(Ca,Sr)CO_3$ solid solution at room *T* are in good agreement with the metastable phase diagram of $CaCO_3$ 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 $CaCO_3$. 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.

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