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# Aragonite-II and CaCO<sub>3</sub>-VII – new high-pressure phases of CaCO<sub>3</sub>

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## Abstract

Due to principal importance for mantle geology, high-pressure field of CaCO<sub>3</sub> phase diagram have been studying since invention of high-pressure technique. However, this investigation is far from been completed. In the present work, we show the results of targeted theoretical and experimental search which reveal two new polymorphs.

Calculations on crystal structure prediction were performed based on evolutionary algorithms (USPEX package) and density functional theory (VASP code) in the pressure range 20-100 GPa, with the most thorough search around aragonite to post-aragonite transformation (30-50 GPa). This calculations reveals the new structure with P21/c symmetry, which is most energetically favourable in the pressure range 32-46 GPa. Analysis of atomic arrangement shows that found P21/c structure is the analogue of deformed aragonite, based on which we called it aragonite-II. This analysis also shows that founded earlier P21/c-1 [Pickard and Needs, 2015] structure is similar to CaCO<sub>3</sub>-VI and can be considered as its superstructure with  $a = a$ ,  $b = b$ ,  $c = 2c$ . CaCO<sub>3</sub>-VI was synthesised experimentally on cold compression of calcite [Merlini et al., 2012], our calculations shows that it is metastable in all pressure-temperature range.

P-T phase diagram calculated based on density of states of phonons shows, that stability field of aragonite-II decreases with pressure, inclining at triple point aragonite-postaragonite-aragonite-II at 33 GPa and 1200K.

Performed at 13ID-D of GSECARS (Advanced Photon Source) in situ diamond anvil cell experiments confirm theoretical phase diagram and reveal a new polymorph of CaCO<sub>3</sub>, named CaCO<sub>3</sub>-VII, which is analogue of P21/c-1 with different unit cell parameters. Enthalpies and Gibbs energies of aragonite-II and CaCO<sub>3</sub>-VII are equal within the DFT error. On compression CaCO<sub>3</sub>-VII became more energetically favourable and in experiments we observe transformation of aragonite-II to CaCO<sub>3</sub>-VII on compression.

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