

First evidence of CaCO₃-III and CaCO₃-IIIb high-pressure polymorphs of calcite: Authigenically formed in near surface sediments

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ABSTRACT

Calcite is one of the most ubiquitous minerals in the Earth's crust and is mostly present as calcite or the slightly denser polymorph aragonite. In addition five different phases of CaCO₃ (calcite II–VI), which display similar structural features as calcite, have been observed with increasing pressure in different experiments by several authors. Experimentally, the CaCO₃-III and CaCO₃-IIIb polymorphs have recently been observed by Merlini et al. (2012) applying pressures between 2.5–15 GPa on natural samples of calcite using single-crystal synchrotron X-ray diffraction.

Here we report an occurrence of metastable authigenic CaCO₃-III and CaCO₃-IIIb nanocrystals for the first time in nature. Using transmission electron microscopy, idiomorphic, 50–150 nm sized crystals were observed within several meters from the surface in quaternary loess deposits in Central Asia.

Nanocrystals contain higher surface energy per volume compared to coarse-grained materials due to their larger surface area. The internal pressure of a solid, P_s , is at equilibrium with the surface stress, which increases with decreasing particle size. We estimated internal pressures inside the observed nanocrystals between 2.54–4.06 GPa, assuming spherical crystals with 1 nm diameter and specific surface energies, between 1.27–2.03 J/m² (Forbes et al. 2011).

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