European Mineralogical Conference
Vol. 1, EMC2012-490, 2012
European Mineralogical Conference 2012

High pressure polymorphs of carbonates and their possible occurrence in the inner Earth.

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Calcite, $CaCO_3$, undergoes several high pressure phase transitions, known since the pioneering works of Bridgman (1939). We report the crystal structure determination of the $CaCO_3$-III and $CaCO_3$-VI high-pressure polymorphs obtained by single-crystal synchrotron X-ray micro-diffraction, recently optimized to afford the possibility of collecting single-crystal data suitable for structure determinations, *in-situ* at non-ambient conditions, even after multiphase transitions with first-order character. $CaCO_3$-III and $CaCO_3$-IV are both triclinic, and are characterised by the presence of non-coplanar CO_3 groups. The density of $CaCO_3$-III is lower than aragonite, in agreement with the currently accepted view of aragonite as the thermodynamically Ca-carbonate stable phase at these pressures. The density of the $CaCO_3$-VI structure, on the contrary, is higher than aragonite. For this reason it could be supposed that a region may exist where this polymorph replaces aragonite in the Earth's intermediate mantle. This polymorph could also clarify the old observations of Vizgirda and Ahrens (1982) and Tyburczy and Ahrens (1986) of phase transitions detected with shock wave experiments both on calcite and aragonite starting material at these pressures. The lower coordination number for Ca site [7+2] instead of [9] in aragonite suggests that these structures could be easily adopted by an extended solid-solution range from calcite towards the dolomite [$CaMg(CO_3)_2$] - ankerite [$CaFe(CO_3)_2$] compositional join. Similar structures have been in fact also observed also in Fe-dolomite compositions, but shifted at higher pressures.

The transitions from calcite to $CaCO_3$-III and $CaCO_3$-VI are perfectly reversible and after pressure release we always observe the calcite structure, with the sample recovered as a single-crystal. Indeed, it is highly unlikely that these structures can be observed in samples recovered from high-pressure environments.

References:

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