

CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

***P-V-T* equation of state and high-pressure behavior of CaCO₃ aragonite†**

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ABSTRACT

The equation of state of aragonite was determined by in situ synchrotron X-ray diffraction experiments on a hot-pressed polycrystalline specimen of aragonite within its stability field up to 5.8 GPa and 1173 K. As a complement to this experimental study, first-principle density functional theory calculations were performed up to 20 GPa at 0 K. Thermoelastic parameters for aragonite (CaCO₃) were derived by a least-squares fit of the experimental *P-V-T* data to the third-order Birch-Murnaghan equation of state (EOS), yielding the bulk modulus and its pressure and temperature derivatives $K_0 = 65.24 \pm 0.24$ GPa, $K'_0 = 4.95 \pm 0.12$, $(\partial K_T / \partial T)_P = -0.024 \pm 0.002$ GPa/K and volume thermal expansion $\alpha_{300} = (6.1 \pm 0.7) \times 10^{-5}$ K⁻¹. The analyses of the axial compressibility at ambient temperature show that the *c*-axis is much more compressible than the *a*- and *b*-axes. Based on first-principle calculations, the anisotropic compression behavior of aragonite structure is explained by the heterogeneous shortening of <Ca-O> and <C-O> bond lengths and the rotation of <O-C-O> angles along the *a*-, *b*-, and *c*-axes, whereas the unit-cell volume change of aragonite under compression is accommodated by comparable compression rate of the CaO₉ polyhedra and the voids in the crystal lattice. The results attained from this study provide important thermoelastic parameters for understanding the thermodynamic behavior and chemical reactions involving aragonite at subduction zone conditions.

Keywords: Aragonite, X-ray diffraction, equation of state, axial compressibility, high pressure and high temperature, first-principle density functional theory calculation