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Thermal equation of state of post-aragonite $CaCO_3$-*Pmmn*

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Abstract

Calcium carbonate ($CaCO_3$) is one of the most abundant carbonates on Earth's surface and transports carbon to Earth's interior via subduction. Although some petrological observations support the preservation of $CaCO_3$ in cold slabs to lower mantle depths, the geophysical properties and stability of $CaCO_3$ at these depths are not known, due in part to complicated polymorphic phase transitions and lack of constraints on thermodynamic properties. Here we measured thermal equation of state of $CaCO_3$-*Pmmn*, the stable polymorph of $CaCO_3$ through much of the lower mantle, using synchrotron X-ray diffraction in a laser-heated diamond-anvil cell up to 75 GPa and 2200 K. The room-temperature compression data for $CaCO_3$-*Pmmn* are fit with third-order Birch-Murnaghan equation of state, yielding K_{T0} = 146.7 (±1.9) GPa and K'_0 = 3.4(±0.1) with V_0 fixed to the value determined by ab initio calculation, 97.76 Å^3. High-temperature compression data are consistent with zero-pressure thermal expansion $\alpha_T = a_0 + a_1T$ with $a_0 = 4.3(\pm0.3)\times10^{-5}$ K^{-1}, $a_1 = 0.8(\pm0.2)\times10^{-8}$ K^{-2}, temperature derivative of the bulk modulus $(\partial K_T/\partial T)_P = -0.021(\pm0.001)$ GPa/K; the Grüneisen parameter $\gamma_0 = 1.94(\pm0.02)$, and the volume independent constant $q = 1.9(\pm0.3)$ at a fixed Debye temperature $\theta_0 = 631$ K predicted via ab initio calculation. Using these newly determined thermodynamic parameters, the density and bulk sound velocity of $CaCO_3$-*Pmmn* and (Ca,Mg)-carbonate-bearing eclogite are quantitatively modeled from 30 to 80 GPa along a cold slab geotherm. With the assumption that carbonates are homogeneously mixed into the slab, the results indicate the presence of carbonates in the subducted slab is unlikely to be detected by seismic observations, and the buoyancy provided by carbonates has a negligible effect on slab dynamics.

Keywords: Carbonate, post-aragonite, thermal equation of state, lower mantle, X-ray diffraction