High-pressure compressibility and thermal expansion of aragonite

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ABSTRACT

The structure and isothermal equation of state of aragonite were determined to 40 GPa using synchrotron single-crystal X-ray techniques. In addition, powder diffraction techniques were used to determine thermal expansion between 298–673 K. At room temperature, aragonite has orthorhombic Pnma structure to 40 GPa, with an isostructural bulk modulus of 66.5(7) GPa and \( K' = 5.0(1) \). Between 25–30 GPa the aragonite unit cell begins to distort due to a stiffening of the c-axis compressibility, which is controlled by the orientation and distortion of the carbonate groups. The ambient pressure thermal expansion measurements yielded thermal expansion coefficients \( a_0 = 4.9(2) \times 10^{-4} \) and \( a_1 = 3.7(5) \times 10^{-4} \). The combined results allow the derivation of a thermal equation of state. The new data provide constraints on the behavior of carbonates and carbon cycling in the Earth’s crust and mantle.

Keywords: Aragonite, high pressure, thermal expansion, compressibility, equation of state, single crystal, X-ray diffraction

INTRODUCTION

Carbon in the deep Earth consists of a primordial component plus carbonate that has recycled into the Earth’s mantle via subduction zones (Dasgupta and Hirschmann 2010; Kellemen and Manning 2015). In the solid state, carbon has limited solubility in mantle silicates and therefore resides chiefly in carbon-rich accessory phases, either as oxidized carbonate or reduced graphite, diamond, or carbide (Shcheka et al. 2006). Aragonite is one of the two most common forms of calcium carbonate found at the Earth’s surface and is formed by both biological and physical processes. Although aragonite is metastable at ambient conditions at the surface of the Earth, its biological formation and contribution to ocean floor deposits and high-pressure stability make it the predominant form of calcium carbonate contributing to deep-Earth recycling at subduction zones. Therefore, understanding the phase stability and compressibility of aragonite at high pressures and temperatures will help constrain the behavior of a key potential carbon reservoir in the deep carbon cycle.

At ambient conditions, aragonite has an orthorhombic \( 2/m \) \( 2/m \) \( 2/m \) structure and an average unit-cell volume of 226.93(6) Å³ and a Z of 4 (Fig. 1) (Martínez et al. 1996; Santillán and Williams 2004; Ono et al. 2005; Antao and Hassan 2010; Ye et al. 2012). Aragonite becomes stable relative to calcite at ~0.3 GPa (e.g., Johannes and Puhan 1971); however, the pressure of its transformation to a higher pressure (post-aragonite) phase is the subject of debate (Vizgirda and Ahrens 1982; Kraft et al. 1991; Santillán and Williams 2004; Ono et al. 2005; Martínez et al. 1996; Liu et al. 2005). Early shock compression experiments suggested that aragonite undergoes a phase transition around 6 GPa with the possibility of another transition at ~16 GPa (Vizgirda and Ahrens 1982). However, subsequent vibrational spectroscopy experiments found no sign of these phase transitions to 40 GPa (Kraft et al. 1991). X-ray diffraction studies by Santillán and Williams (2004) and Ono et al. (2005) indicated a phase transition near 35–40 GPa but found differing behavior near the transition pressure. Santillán and Williams (2004) noted that strong lattice strain developed between 26 and 40 GPa and suggested that it marked the onset a sluggish transition to a trigonal structure that became complete at 40 GPa. In contrast, Ono et al. (2005) proposed that the transition was a new orthorhombic structure with \( Z = 2 \). Studies of high-pressure CaCO₃ by ab initio methods focused chiefly on the transition to post-aragonite and pyroxene-type polymorphs (Oganov et al. 2006, 2008; Arapan et al. 2007; Arapan and Ahuja 2010; Pickard and Needs 2015), but in some cases results identify additional potentially stable structures in the vicinity of the aragonite to post-aragonite transition (e.g., Pickard and Needs 2015).

Insights into the nature and location of the transition to a higher pressure phase can be gained by study of the compressional behavior of aragonite. However, existing X-ray diffraction studies (Martínez et al. 1996; Santillán and Williams 2004; Ono et al. 2005) disagree and lack sufficient detail in the pressure range of the transition.

To address these issues, we conducted a single-crystal synchrotron X-ray diffraction study of aragonite under hydrostatic compression to 40 GPa at ambient temperature in a diamond-anvil cell (DAC). We supplemented compressional results with thermal expansion data from powder X-ray diffraction at ambient pressure. The combination of these studies enables the creation...