

Single-crystal X-ray diffraction of $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0 \leq x \leq 0.79$) solid solutions from 100 to 500 K: Implications for thermal expansivity of disordered calcite

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ABSTRACT

Disordered CaCO_3 calcite is the high-temperature (high- T) polymorph of aragonite in the upper mantle. Its thermoelastic properties have not been determined since it cannot be quenched to the ambient conditions, although these properties are relevant to tracing carbonates in the Earth's deep interior by seismological methods. In the prior synthetic experiments at 2.5 GPa and 1473 K (Hu et al. 2024), $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions crystallized in the ordered ($0 \leq x \leq 0.19$) and disordered ($0.27 \leq x \leq 0.79$) calcite structures. In this study, in situ single-crystal X-ray diffraction (XRD) measurements were performed on these samples from 100 to 500 K. The volumetric thermal expansion coefficients for the disordered samples fall within a narrow range of $5.8 \sim 6.3 \times 10^{-5} \text{ K}^{-1}$, closely resembling those of aragonite and witherite, and systematically exceeding those in the ordered calcite-type structure. The presence of Ba^{2+} exhibits minimal influence on the thermal expansivities of disordered solid solutions, and the linearly extrapolated $\alpha_V(T)$ for disordered CaCO_3 calcite is quite similar to that for aragonite. The anisotropy of axial thermal expansivity follows the trend: ordered calcite > aragonite > disordered calcite. The MO_9 -polyhedra ($M = \text{Ca}$ and Ba) in both aragonite and disordered calcite could mitigate the anisotropy of thermal expansion, and are more sensitive to temperature variation, as compared with the MO_6 -octahedron in ordered calcite. The longer $M\text{-O}$ bonds exhibit larger thermal expansivity than the shorter ones in the disordered samples. The Kumar $V(T)$ equation, established on the Debye model, is adopted to extrapolate the $\alpha_V(T)$ models to higher temperatures, and the results for the disordered solid solutions still match well with aragonite and witherite at geologically relevant temperatures. Low-temperature measurements are necessary and important for a comprehensive investigation of pressure-volume-temperature (P - V - T) equations of state (EOS), as the α_V coefficient increases rapidly below 300 K, and progressively at higher temperatures. Conclusively, this study exemplifies the successful utilization of ambient-stable $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ analogs to explore the thermoelastic properties of disordered calcite.

Keywords: Disordered calcite, $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions, crystal structure, thermal expansion, high-temperature XRD

INTRODUCTION

Calcite (CaCO_3), the most abundant calcium carbonate mineral on the Earth's surface and crust, plays an important role in the global carbon cycle. It is conventionally designated as “calcite I” (ordered calcite in the $R\bar{3}c$ symmetry). At high- P and high- T conditions, several polymorphs of CaCO_3 have been identified (Fig. 1), including the high- P phases of calcite II, III, IIIB, VI, and VII at ambient temperature (Suito et al. 2001; Merlini et al. 2012; Pippinger et al. 2015; Koch-Müller et al. 2016; Gavryushkin et al. 2017), and the high- T polymorphs of calcite IV and V (Mirwald 1976, 1979; Dove and Powell 1989; Dove et al. 2005; Antao et al. 2009). Above 3 GPa and 500 K, calcite transforms to aragonite ($Pmcn$, orthorhombic), which is the stable polymorph of CaCO_3 from the top of the upper mantle to shallow lower mantle, and

further transforms to the post-aragonite structure around 40 GPa (Santillán and Williams 2004; Ono et al. 2007; Sekkal et al. 2008; Lv et al. 2020). Additionally, a new CaCO_3 phase, calcite Vb, is also identified in a narrow P - T range between calcite V and aragonite above 4 GPa and 1200 K (Druzhbin et al. 2022).

Recent studies on the P - T stability field of CaCO_3 indicate that aragonite transforms to disordered calcite (calcite V, $R\bar{3}m$) at higher temperatures from 3 to 13 GPa (Suito et al. 2001; Li et al. 2017; Hou et al. 2019; Gavryushkin et al. 2020; Druzhbin et al. 2022). The aragonite $\rightarrow$ disordered calcite phase transition initiates around 3 GPa and 1100 K with a Clapeyron slope of $\sim +7 \text{ MPa/K}$ (e.g., Suito et al. 2001). Hence, disordered calcite can be stable in hotter geological settings throughout the upper mantle above the 410 km seismic discontinuity (Katsura et al. 2010; Hasterok and Chapman 2011). Nevertheless, its thermodynamic properties, including P - V - T EOS and elasticity, remain uncharacterized due to its instability at the ambient conditions, as it rapidly reverts to ordered calcite upon cooling (e.g., Hu et al. 2024).

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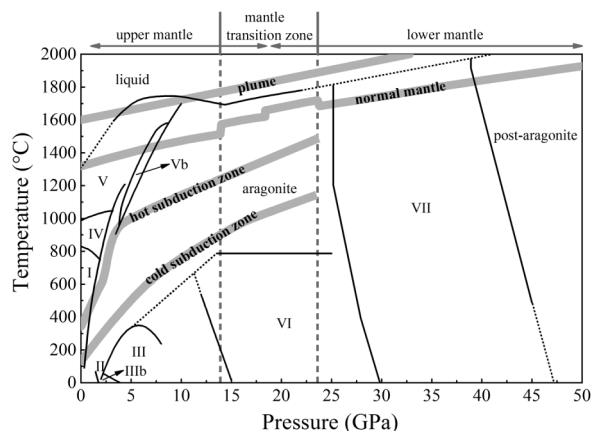


FIGURE 1. The P - T phase diagram of CaCO_3 revised based on Bayarjargal et al. (2018) and Druzhbin et al. (2022). The geotherms (gray bold curves) are plotted for the cold/hot subduction zones (Zhu and Sun 2021), normal mantle (Katsura 2022), and plume (Dasgupta 2013). The 410 and 660 km seismic discontinuities are also present as vertical dashed lines in the figure.

The reversible order $\rightarrow$ disorder transition in CaCO_3 calcite occurs at 1240 K under ambient pressure (e.g., Antao et al. 2009), and it took a century to elucidate the crystal structure of disordered calcite by in situ high-temperature XRD (Boeke 1912; Mirwald 1976, 1979; Dove and Powell 1989; Dove et al. 2005; Ishizawa et al. 2013; Ishizawa 2014). Although both the ordered and disordered calcites belong to the trigonal system, the CO_3 groups, stacked in layers perpendicular to the c axis, adopt disordered orientations in the $R\bar{3}m$ lattice. Subsequently, the occupancy in the O site decreases from 1 to 0.5, and the coordination number for Ca^{2+} increases from 6 to 9. The c axis is shortened to half of that for the ordered structure, and the a axis remains almost the same (e.g., Kawano et al. 2009; Ishizawa et al. 2013).

Although disordered CaCO_3 calcite is unquenchable at the ambient conditions, Ba-bearing disordered calcite powders [$\text{Ba}/(\text{Ba}+\text{Ca}) \geq 27$ mol%] were synthesized via precipitation from aqueous solutions at near-ambient temperatures (Whittaker and Joester 2017; Whittaker et al. 2018; Saito et al. 2020; Seknazi et al. 2020; Marugata et al. 2022). These metastable samples are poorly crystallized, limiting structural information derived from powder XRD data sets. Disordered and ordered calcites cannot be distinguished from each other by Raman or infrared spectra (e.g., Hu et al. 2024), and the disordered structure is typically identified by the extinction of the (113) and (211) reflection lines in XRD patterns, instead (Dove and Powell 1989; Dove et al. 2005; Cai et al. 2020).

Taking advantage of a piston-cylinder apparatus, Hu et al. (2024) successfully synthesized $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0.10 \leq x \leq 0.79$) solid solutions with roughly 10 mol% Ba^{2+} increments, which formed high-quality crystals in the ordered and disordered calcite structures with the Ba^{2+} concentrations of ≤ 19 mol% and ≥ 27 mol%, respectively. High-quality single-crystal XRD measurements at the ambient conditions revealed structural distinctions between these two structures, confirming that incorporation of significant Ba^{2+} (≥ 27 mol%) stabilizes the disordered calcite structure due to the large mismatch between the ionic radii

TABLE 1. The volumetric thermal expansion parameters fitted from 100 to 500 K

	α_1 (10^{-8} K^{-2})	α_0 (10^{-5} K^{-1})	R^2
Cal ₁₀₀	5.22(7)	0.027(6)	0.9921
Cal ₉₀ Wth ₁₀	4.42(5)	1.412(3)	0.9988
Cal ₈₁ Wth ₁₉	5.06(6)	3.164(7)	0.9986
Cal ₇₃ Wth ₂₇	19.06(13)	0.469(4)	0.9942
Cal ₆₁ Wth ₃₉	8.02(7)	3.683(4)	0.9990
Cal ₅₂ Wth ₄₈	6.78(6)	4.130(4)	0.9980
Cal ₄₄ Wth ₅₆	6.44(6)	3.833(3)	0.9992
Cal ₂₉ Wth ₇₁	11.24(10)	2.734(3)	0.9979
Cal ₂₁ Wth ₇₉	10.44(10)	2.637(3)	0.9978

of Ba^{2+} (IX) (1.47 Å in 9 coordination) (Shannon 1976) and Ca^{2+} (IX) (1.18 Å).

In this study, we conducted single-crystal XRD measurements on these crystals from 100 to 500 K to systematically investigate their thermal expansivities and internal structural evolution with temperature. The Ba^{2+} effect on thermal expansivity can be isolated since measurements are conducted on multiple compositions, and the thermal expansion coefficients could also be extrapolated to higher temperatures by some V - T equations developed based on the Debye model, which is widely adopted to reproduce the volume of solids at high temperatures. These findings enable the prediction of the thermal expansion behavior of disordered CaCO_3 calcite at high- T conditions of the upper mantle.

EXPERIMENTAL METHODS

The $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0 \leq x \leq 0.79$) solid solutions were synthesized at $P = 2.5$ GPa and $T = 1473$ K in a LPC250-300-50 piston-cylinder apparatus, with a duration of 24 h (Hu et al. 2024). The chemical compositions of the products were determined by electron probe microanalyzer (EPMA): CaCO_3 (Cal₁₀₀), $\text{Ba}_{0.10}\text{Ca}_{0.90}\text{CO}_3$ (Cal₉₀Wth₁₀), $\text{Ba}_{0.19}\text{Ca}_{0.81}\text{CO}_3$ (Cal₈₁Wth₁₉), $\text{Ba}_{0.27}\text{Ca}_{0.73}\text{CO}_3$ (Cal₇₃Wth₂₇), $\text{Ba}_{0.39}\text{Ca}_{0.61}\text{CO}_3$ (Cal₆₁Wth₃₉), $\text{Ba}_{0.48}\text{Ca}_{0.52}\text{CO}_3$ (Cal₅₂Wth₄₈), $\text{Ba}_{0.56}\text{Ca}_{0.44}\text{CO}_3$ (Cal₄₄Wth₅₆), $\text{Ba}_{0.71}\text{Ca}_{0.29}\text{CO}_3$ (Cal₂₉Wth₇₁), $\text{Ba}_{0.79}\text{Ca}_{0.21}\text{CO}_3$ (Cal₂₁Wth₇₉), where Cal and Wth are abbreviations for calcite and witherite (BaCO_3), respectively. High-quality crystals with diameters of 30–50 μm were selected for in situ single-crystal XRD measurements from 100 to 500 K.

Measurements were carried out on a Bruker D8 QUEST 4-axis motor-driven diffractometer equipped with a PHOTON III C14 detector, which adopted a rotating silver-anode X-ray generator (K_{α} average = 0.56086 Å) operated at 50 kV and 0.9 mA. The intensity data were collected in the 2θ range from 8 to 60° for both the unit-cell parameters determination and structure refinements. Temperature was controlled with uncertainties within ± 1 K by an OxfordCryosystems 800 Series Cryostream Cooler controller. Low temperatures were achieved by cooling with liquid nitrogen down to 100 K, and high temperatures were achieved by heating dry air streams up to 500 K. Experiments were conducted with an interval of 50 K and a heating rate of 6 K/min. At each step, the temperature was maintained for at least 15 min for the thermal equilibrium before measurement. Typically, ~ 160 –256 unique reflections were collected for the refinements on the unit-cell parameters (Online Materials¹ Table 1) and crystal structure at each temperature, utilizing the SHELXL refinement package (Sheldrick 2015) inside the software package of CryAlisPro/Olex2 (Dolomanov et al. 2009). The scattering factors for Ca^{2+} , Ba^{2+} , and C^{4+} cations (Cromer and Mann 1968) and O^{2-} anion (Tokonami 1965) are adopted. The intensity data collection parameters of R_1 (for the reflections with $I > 2\sigma$), R_{int} , and GooF are generally in the range of 2.5–4.9%, 3.5–6.2%, and 0.99–1.228, respectively (Online Materials¹ Table S2).

RESULTS AND DISCUSSION

Unit-Cell Parameters at Elevated Temperature

Consistent with the previous measurements at the ambient condition (Hu et al. 2024), the solid solutions with Ba concentrations < 20 mol% (i.e., Cal₁₀₀, Cal₉₀Wth₁₀, and Cal₈₁Wth₁₉)

crystallize in the ordered calcite structure ($Z = 6$, the number of formulas per unit cell), while those with higher Ba contents ($\text{Ca}_{73}\text{Wth}_{27}$, $\text{Ca}_{61}\text{Wth}_{39}$, $\text{Ca}_{52}\text{Wth}_{48}$, $\text{Ca}_{44}\text{Wth}_{56}$, $\text{Ca}_{29}\text{Wth}_{71}$, and $\text{Ca}_{21}\text{Wth}_{79}$) exhibit the disordered calcite structure ($Z = 3$). The thermal expansion coefficient (α) at the ambient pressure is defined as below:

$$\alpha_X = 1/X(\partial X/\partial T)_P \quad (1)$$

where X represents the volume V as well as the a or c axis for the samples in the trigonal system. The unit-cell volumes V for the disordered calcite samples ($V/2$ and $c/2$ for the ordered ones) are plotted as a function of temperature ($100 \leq T \leq 500$ K) in Figure 2, and variations of a and c axes with T are also exhibited in Online Materials¹ Figures S1a and S1b. Each data set is fitted to a second polynomial function of temperature with $R^2 > 0.992$, allowing the α_V coefficients to be expressed as a linear function of T (in K):

$$\alpha_V = a_1 \cdot T + a_0 \quad (2)$$

The fitted parameters of a_1 (10^{-8} K^{-2}) and a_0 (10^{-5} K^{-1}) are listed in Table 1.

The unit-cell parameters for this Ca_{100} sample align well with the previous experiments below 500 K (Antao et al. 2009; Wang et al. 2018), with discrepancies typically within the experimental uncertainties (Online Materials¹ Figs. S2a–S2c). The a axis exhibits slightly negative thermal expansivity [$-0.47(2) \times 10^{-5} \text{ K}^{-1}$], and the α_c coefficient [$+2.54(9) \times 10^{-5} \text{ K}^{-1}$] is positive. In both the ordered and disordered structures, rigid CO_3 groups are stacked in layers perpendicular to the c direction, rendering the

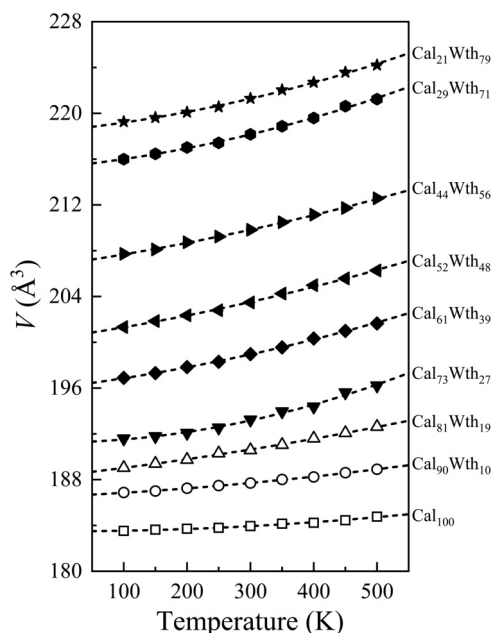


FIGURE 2. Variation of volumes with temperature from 100 to 500 K, and a second-order polynomial curve (dashed) is fitted for each sample ($R^2 > 0.992$). The unit-cell volumes for the disordered samples (solid symbols) and half of the unit-cell volumes for the ordered ones (open symbols) are plotted in the figure. The experimental uncertainties are smaller than the sizes of the symbols.

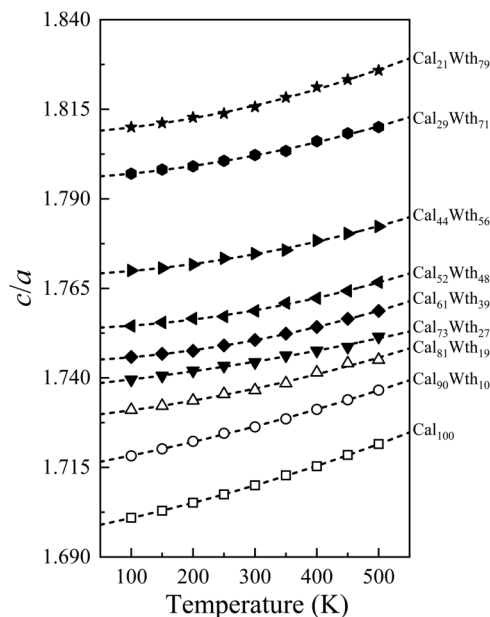


FIGURE 3. The axial ratios of c/a plotted as a function of temperature, and second-order polynomial curves (dashed) are fitted for the $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0 \leq x \leq 0.79$) solid solutions in both the ordered (open symbols) and disordered (solid symbols) calcite-type structures. Half of the c -axis is adopted for the ordered samples so as to be consistent with the disordered ones. The sizes of the symbols are larger than the uncertainties of measurement.

c axis more temperature-sensitive, and the axial c/a ratios systematically increase at elevated temperature (Fig. 3). For the ordered samples of Ca_{100} , $\text{Ca}_{90}\text{Wth}_{10}$, and $\text{Ca}_{81}\text{Wth}_{19}$, the averaged axial and volumetric thermal expansion coefficients increase at elevated Ba^{2+} concentration (Figs. 4a–4c; Online Materials¹ Table S3). The α_V coefficient for $\text{Ca}_{81}\text{Wth}_{19}$ is nearly triple that of Ca_{100} . This enhancement in the thermal expansivity arises from lattice distortion and expansion caused by the incorporation of larger Ba^{2+} cations [$r(\text{VI}) = 1.35 \text{ \AA}$] (Shannon 1976) into 6-coordinated cationic sites.

For the disordered samples with 9-coordinated M^{2+} ($M = \text{Ca}$ or Ba) sites, the volumetric thermal expansion coefficients fall within a narrow range of $5.8 \sim 6.2 \times 10^{-5} \text{ K}^{-1}$ (Fig. 4c). Their α_a and α_c coefficients typically exceed those of $\text{Ca}_{81}\text{Wth}_{19}$ by 37–76% and 4–10%, respectively. Notably, single-crystal XRD measurements were also performed on the aragonite-type carbonates in a comparable T -range from 143 to 586 K, including aragonite (CaCO_3), strontianite (SrCO_3), and witherite (BaCO_3) (Ye et al. 2012). The averaged α_V coefficients for these end-member carbonate samples coincide at the value of $6.5(2) \times 10^{-5} \text{ K}^{-1}$, which are also quite close to those for the disordered solid solutions. Then, the averaged α_a and α_V coefficients for disordered Ca_{100} , linearly extrapolated from the disordered $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0.27 \leq x \leq 0.79$) samples, align with the α_a (Fig. 4a) and α_V (Fig. 4c) values for aragonite (Ye et al. 2012), respectively. Hence, the composition of M^{2+} ($M = \text{Ca}$, Sr , and Ba) has minimal impact on the volumetric thermal expansivity, as the cations are 9-coordinated in both aragonite and disordered calcite structures. In contrast, the MCO_3 carbonates with

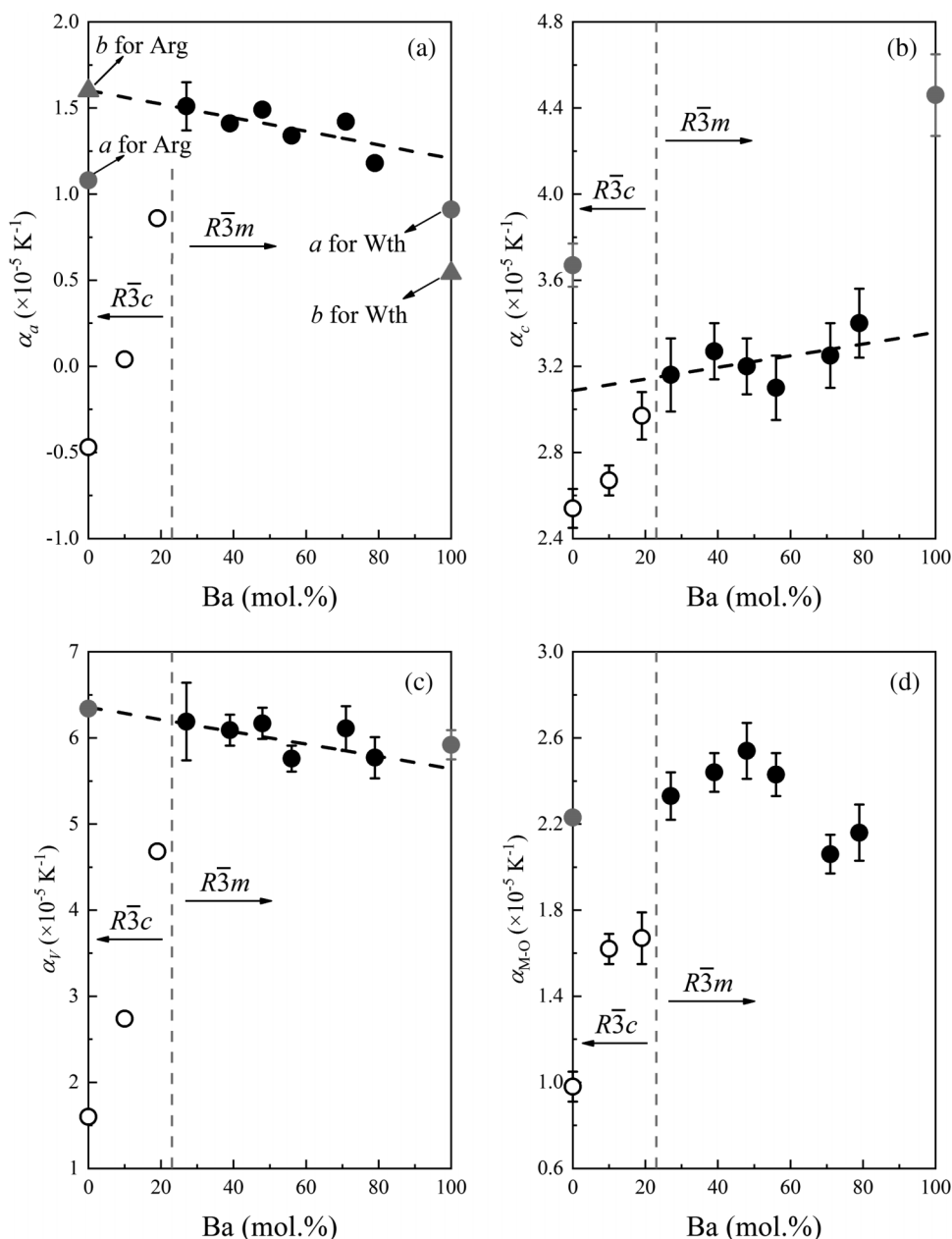


FIGURE 4. The averaged thermal expansion coefficients (100–500 K) of the (a) a axis, (b) c axis, (c) volume, and (d) $\langle M-O \rangle$ for the $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions in both the ordered (open symbols) and disordered (solid black symbols) calcite samples. Comparison is made with aragonite and witherite (gray symbols) (Ye et al. 2012), which were measured from 143 to 586 K. Linear regressions (dashed line) are fitted for the disordered samples in (a, b, and c). The propagated uncertainties for the α values are shown as vertical error bars if larger than the sizes of the symbols.

6-coordinated M^{2+} generally exhibit smaller α_v values ($< 4.5 \times 10^{-5} \text{ K}^{-1}$), including calcite, magnesite (MgCO_3), and dolomite [$\text{CaMg}(\text{CO}_3)_2$] (Markgraf and Reeder 1985; Reeder and Markgraf 1986; Fei 1995; Zhang et al. 1997; Litasov et al. 2008; Antao et al. 2009; Merlini et al. 2016; Wang et al. 2018 and 2019; Karunadasa et al. 2019; Floquet et al. 2020).

Although $\text{Ca}^{2+} \rightarrow \text{Ba}^{2+}$ (Sr^{2+}) substitution negligibly affects the α_v coefficients among the aragonite-type carbonates, the axial thermal expansivity exhibits obvious compositional

dependence. The α_c values follow the sequence of aragonite < strontianite < witherite (Ye et al. 2012). Similar trends, although slightly, can also be observed in the synthetic samples in the disordered calcite structure. Their α_a coefficients progressively decrease, while the α_c values increase at elevated Ba^{2+} concentration. Despite the fact that lattice distortion is reduced by the incorporation of Ba^{2+} in the MO_9 polyhedron (Antao and Hassan 2009), the anisotropy for the axial thermal expansivity becomes more pronounced.

Structural Variation with Temperature

The order $\rightarrow$ disorder transition in the calcite structure involves disordered orientations for CO_3 groups, and an increment in M^{2+} coordination number from 6 to 9 (Antao et al. 2009; Ishizawa et al. 2013; Ishizawa 2014; Hu et al. 2024). In the structure refinements, the C atoms are fixed at the special positions of (0, 0, 0.25) and (0, 0, 0.5) in the ordered and disordered calcite samples, respectively. The M^{2+} cations are consistently fixed at the position of (0, 0, 0) in both symmetries, and the occupancies of Ca^{2+} and Ba^{2+} are fixed according to the measured compositions by EPMA (Hu et al. 2024). The refined O^{2-} positions (x, y, z) at various temperatures are listed in Online Materials¹ Table S4. The O_y and O_z are fixed at 0 and 0.25 in the ordered calcites, respectively. The O occupancy is full (fixed at 1) in the ordered calcite structure and reduced to half (0.5) when its arrangement becomes disordered.

Based on the refined atomic coordinates, the M -O and C-O bond lengths are computed in Online Materials¹ Tables S5 and S6, respectively. In the ordered structure, MO_6 octahedra exhibit uniform M -O bond lengths (2.35–2.42 Å). Conversely, MO_9 polyhedra in the disordered samples display three short (2.28–2.51 Å) and six long M -O bonds (2.85–2.95 Å). Temperature dependences for the averaged M -O bond lengths ($\langle M\text{-O} \rangle$) are compared in Figure 5 among these synthetic samples. For the ordered samples of Ca_{100} , $\text{Ca}_{90}\text{Wth}_{10}$, and $\text{Ca}_{81}\text{Wth}_{19}$, the thermal expansion coefficients for $\langle M\text{-O} \rangle$ increase at elevated Ba^{2+} content, following the trends of the axial and volumetric α values. It reflects significant lattice distortion caused by Ba^{2+} substitution in MO_6 octahedra site. Alternatively, the disordered samples exhibit larger thermal expansion coefficients for $\langle M\text{-O} \rangle$ ($2.1 \sim 2.5 \times 10^{-5} \text{ K}^{-1}$), as compared with the ordered ones ($< 1.7 \times 10^{-5} \text{ K}^{-1}$) (Fig. 4d), and the $\langle M\text{-O} \rangle$ in aragonite also exhibits a similar α value of $2.33(2) \times 10^{-5} \text{ K}^{-1}$ (Antao and Hassan 2010; Ye et al. 2012).

The short and long M -O lengths in the disordered samples are further plotted as a function of temperature (Figs. 6a–6f). The thermal expansion coefficients for the long M -O bonds ($\alpha_{M\text{-O}} = 2.34 \sim 3.02 \times 10^{-5} \text{ K}^{-1}$) are systematically larger than those for the short ones ($0.73 \sim 2.17 \times 10^{-5} \text{ K}^{-1}$), consistent with the structural investigations on aragonite (Antao and Hassan 2010; Ye et al. 2012). Therefore, the MO_9 polyhedra in both disordered calcite- and aragonite-type structures are more sensitive to temperature variation, as compared with the MO_6 octahedron in the ordered calcite. This highlights the dominant role of the M^{2+} -centered polyhedra in the bulk thermal expansivity.

The atomic thermal vibrations cannot be ignored in the lattice, especially for O^{2-} , and the isotropic displacement parameter of O [$U_{\text{eq}}(\text{O})$] is quite larger than that for C [$U_{\text{eq}}(\text{C})$] (Online Materials¹ Table S7). Therefore, thermal correction is conducted to the covalent C-O bond length as below (Downs et al. 1993; Hazen et al. 2000):

$$R_{\text{SRB}}^2 = R^2 + 3 \cdot [U_{\text{eq}}(\text{O}) - U_{\text{eq}}(\text{C})] \quad (3)$$

where R is the apparent bond length directly calculated from the atomic coordinates between C and O, and R_{SRB} is the simple rigid bond length with chemical significance. The corrected C-O bonds typically exceed the apparent ones by 0.03–0.06 Å in the solid

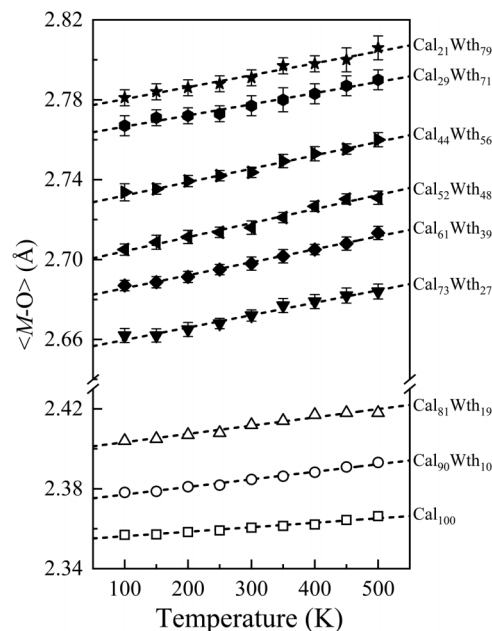


FIGURE 5. The averaged M -O bond lengths vs. temperature for the synthetic samples in this study with linear regressions (dashed lines). The experimental uncertainties for $\langle M\text{-O} \rangle$ are shown as vertical error bars if larger than the sizes of the symbols.

solutions, and the formers are plotted as a function of temperature (Figs. 7a–7i). The C-O bond length in calcite (Ca_{100}) shows a thermal expansion coefficient smaller than $1 \times 10^{-5} \text{ K}^{-1}$, which is consistent with the observations in aragonite (Antao and Hassan 2010; Ye et al. 2012). Additionally, the C-O bonds in the some of the disordered calcite samples become more sensitive to temperature variation, and the $\alpha_{\text{C-O}}$ values are $3.90 \times 10^{-5} \text{ K}^{-1}$ for $\text{Ca}_{29}\text{Wth}_{71}$ and $2.67 \times 10^{-5} \text{ K}^{-1}$ for $\text{Ca}_{21}\text{Wth}_{79}$, which is abnormally large among carbonate minerals.

In the ordered samples, CO_3 groups remain planar, in which the O-C-O angles are consistently 120° . Nevertheless, the CO_3 groups are aplanar in the disordered structures and the O-C-O angles decrease with increasing Ba concentration. The aplanarity in the disordered samples is more severe than those for the aragonite-type carbonates with the O-C-O angles in the range of $119.95^\circ \sim 119.98^\circ$ (Antao and Hassan 2009). This aligns well with the “umbrella distortion” for CO_3 groups observed in disordered CaCO_3 calcite around 1250 K (Ishizawa et al. 2013; Ishizawa 2014). The CO_3 groups tend to become coplanar with typically increasing O-C-O angles at elevated temperature (Figs. 8a–8f).

Comparison of α_V Coefficients at Higher Temperatures

The volumetric thermal expansion coefficients for solids typically increase at elevated temperatures, and numerous functional formulas have been proposed for $\alpha_V(T)$ (e.g., Fei 1995; Kroll et al. 2012; Trots et al. 2012; Ye et al. 2022). Notably, there is no universal thermodynamic framework dictating the functional form of $\alpha_V(T)$; model validity can only be assessed by its ability to reproduce measured high- T volumes. The Mie-Grüneisen-Debye model (e.g., Wallace 1998) is widely

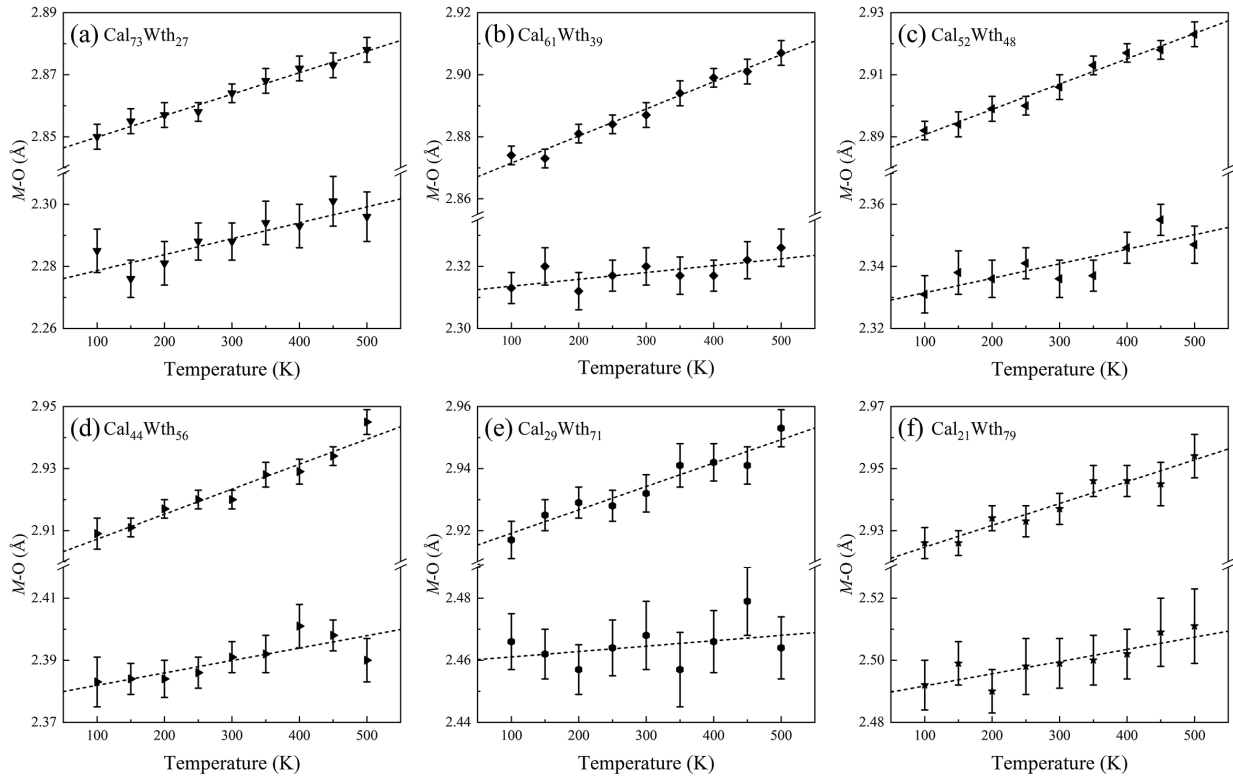


FIGURE 6. The short and long $M\text{-O}$ bond lengths plotted as a function of temperature for the disordered calcite samples: (a) $\text{Cal}_{73}\text{Wth}_{27}$, (b) $\text{Cal}_{61}\text{Wth}_{39}$, (c) $\text{Cal}_{52}\text{Wth}_{48}$, (d) $\text{Cal}_{44}\text{Wth}_{56}$, (e) $\text{Cal}_{29}\text{Wth}_{71}$, and (f) $\text{Cal}_{21}\text{Wth}_{79}$. Linear regression (dashed line) is fitted for each bond, and the vertical error bars stand for the uncertainties of the $M\text{-O}$ lengths.

used to construct high- T thermodynamic properties, including P - V - T EOS. In this section, comparison will be further made for the thermal expansivities between the $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions and the end-member carbonates (aragonite, witherite, and calcite), all of which are extrapolated to geologically relevant temperatures.

Among the $\alpha_V(T)$ functions related to the Debye model, the Kumar equation (Eq. 4) (Kumar 2003) has been proven valid to reproduce the volumes of various silicates at high temperatures (e.g., Kroll et al. 2012; Ye et al. 2022):

$$V(T) = V_0(0) \cdot \left[1 - \frac{\ln(1 - (2k+2) \cdot E_{th}(T)/Q_0)}{2k+2} \right] \quad (4)$$

where $Q_0 = V_0(0) \cdot K_T(0)/\gamma_{\text{MGD}}$ and $k = (K'_T - 1)/2$. $V_0(0)$, $K_T(0)$, and K'_T are the unit-cell volume, the isothermal bulk modulus, and its P -derivative taken at $T = 0$ K and $P = 0$ GPa, respectively. The Grüneisen parameter of γ_{MGD} is fitted from the Mie-Grüneisen-Debye EOS (Barron et al. 1980), and the thermal energy, $E_{th}(T)$, can be treated as a function of temperature:

$$E_{th}(T) = \frac{9nRT}{(\Theta_D/T)^3} \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \quad (5)$$

where $n = 5$ is the number of atoms per MCO_3 unit and $R = 8.314$ J/K/mol is the gas constant. Θ_D is the Debye temperature calculated in the form of acoustic Debye temperature Θ_{ac} in this discussion:

$$\Theta_{ac} = \frac{h}{k} \cdot \left(\frac{3N \cdot n \cdot \rho}{4\pi \cdot M} \right)^{1/3} \cdot V_m \quad (6)$$

where h , k , and N are Planck, Boltzmann, and Avogadro's constants, respectively. M is the molar mass, and the mean velocity V_m is derived from the elastic velocities as follows:

$$V_m = \left(\frac{2}{3 \cdot V_S^3} + \frac{1}{3 \cdot V_P^3} \right)^{-1/3} \quad (7)$$

The V_P and V_S velocities can be computed from the adiabatic bulk (K_S) and shear (G) moduli and density (ρ) as in Equations (8a and 8b):

$$V_P = \sqrt{\frac{K_S + 4 \cdot G/3}{\rho}} \quad (8a)$$

$$V_S = \sqrt{\frac{G}{\rho}} \quad (8b)$$

Based on the elastic measurements on carbonates (Liu et al. 2005; Lin 2013; Zhuravlev and Korabel'nikov 2022) (Online Materials¹ Table S8), the Debye acoustic temperatures are calculated (from Eqs. 6–8) for aragonite [516(8) K], calcite [498(5) K], and witherite [293(4) K]. Next, the Kumar equation (Eq. 4) is adopted to fit the measured unit-cell volume vs. temperature for aragonite (Figs. 9a and 9b) (Lucas et al. 1999; Antao and Hassan 2010; Ye et al. 2012; Palaich et al. 2016) and witherite (Figs. 9c and 9d) (Antao and Hassan 2007;

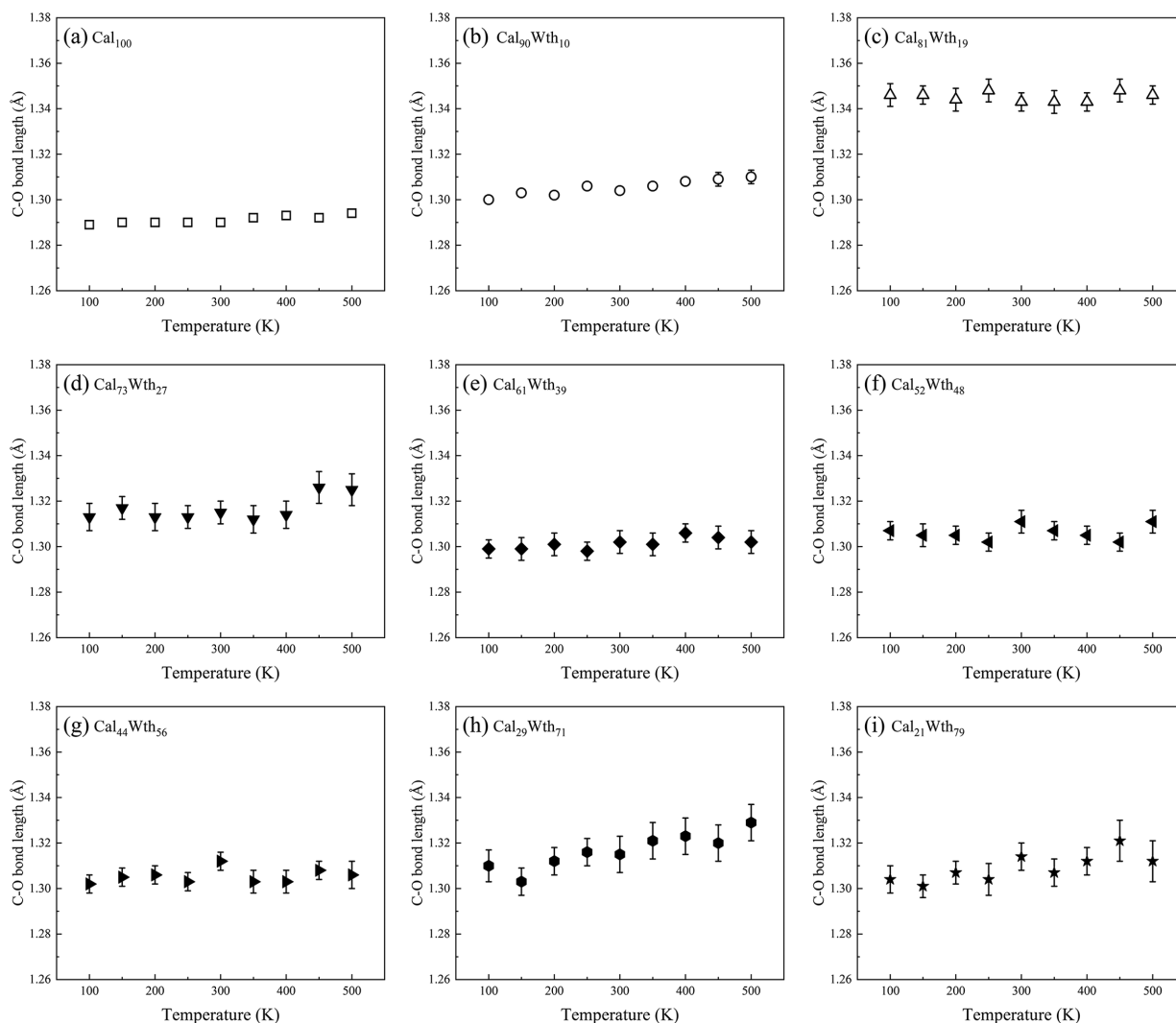


FIGURE 7. (a–i) The simple rigid C–O bond lengths (corrected through Eq. 2) at elevated temperature for the synthetic $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ ($0 \leq x \leq 0.79$) samples. The experimental uncertainties are shown as vertical error bars if larger than the sizes of symbols.

Ye et al. 2012) from 143 K to the high temperatures right below phase transitions. At the ambient pressure, aragonite completely transforms to calcite at 773 K, and the $Pmcn \rightarrow R3m$ phase transition in witherite occurs at 1084 K (Antao and Hassan 2007, 2010). The high- T volumes have been normalized to that at the ambient temperature [i.e., $V(T)/V(298 \text{ K})$] for each data set, so as to avoid systematic discrepancies among different experiments. The modeled curves match well with the data points, with the fitting residuals $\{\Delta[V(T)/V(298 \text{ K})] = [V(T)/V(298 \text{ K})]_{\text{measured}} - [V(T)/V(298 \text{ K})]_{\text{fit}}\}$ typically within $\pm 1.0 \times 10^{-3}$. The fitted $V(0 \text{ K})/V(298 \text{ K})$ ratios are 0.9899(6) (aragonite) and 0.9878(5) (witherite), and the Q_0 (10^6 J/K/mol) parameters are 1.92(3) and 2.08(3) for aragonite and witherite, respectively.

According to the high- T XRD measurement on calcite (Antao et al. 2009), a partial order-disorder transition initiates at 681 K, marked by progressively decreasing O^{2-} occupancy (x_0) down to 0.711 at 1234 K. The order $\rightarrow$ disorder phase

transition completes at 1240 K (Ishizawa et al. 2013; Ishizawa 2014) with $x_0 = 0.5$ in the disordered structure. Consequently, the volume increases rapidly due to the partial order $\rightarrow$ disorder transition above 681 K, and the Fei equation (Eq. 9) (Fei 1995) turns out to be valid to reproduce the measurements on calcite in the whole T -range from 173 to 1200 K (Figs. 9e and 9f) (Antao et al. 2009; Wang et al. 2018, 2019; this study), rather than the Kumar equation:

$$\alpha(T) = a_0 + a_1 \cdot T + \frac{a_2}{T^2} \quad (9)$$

where the fitted parameters are $a_1 = 7.22(8) \times 10^{-8} \text{ K}^{-2}$, $a_0 = -2.63(6) \times 10^{-5} \text{ K}^{-1}$, and $a_2 = 1.71(3) \text{ K}$, yielding fitting residuals typically within $\pm 1.0 \times 10^{-3}$ except for a few extreme points below 173 K (Wang et al. 2018; this study) or above 1200 K (Antao et al. 2009).

Next, the volumetric thermal expansion coefficients are plotted as a function of temperature for calcite (in the Fei equation), aragonite, and witherite (in the Kumar equation) in Figure 10.

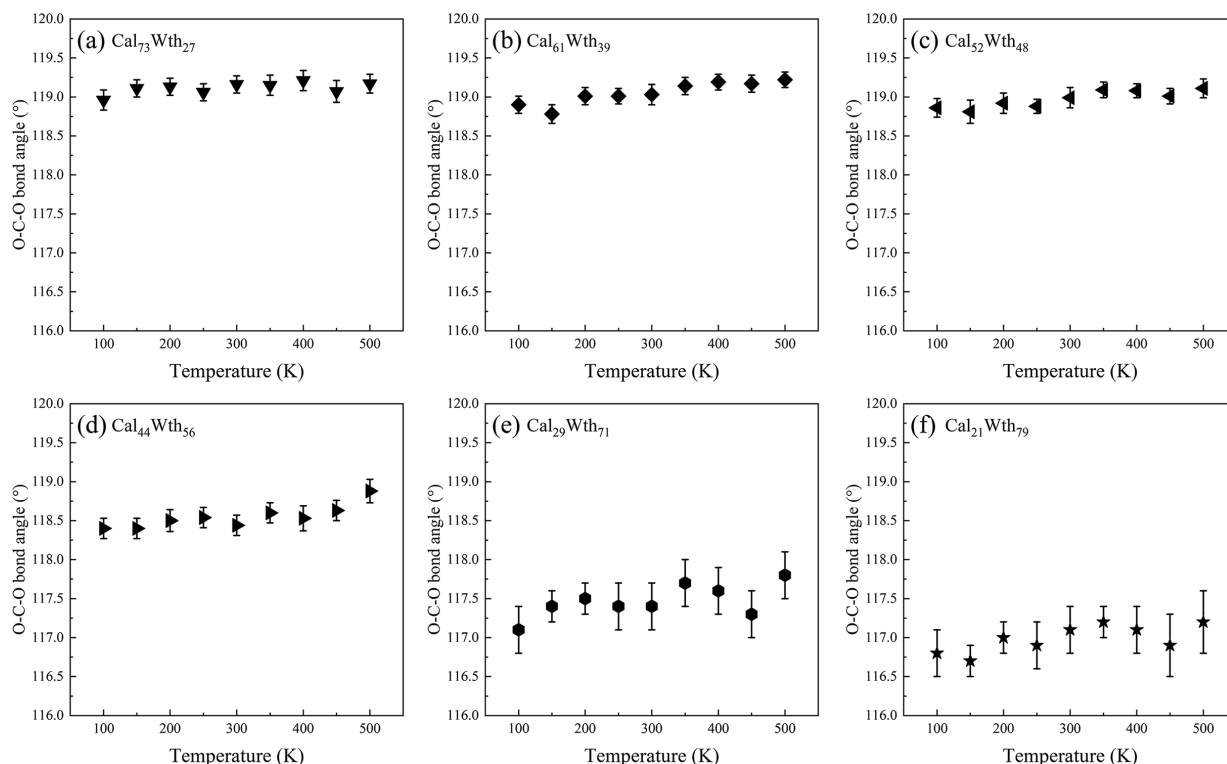


FIGURE 8. (a–f) The O–C–O bond angles at elevated temperature for the disordered calcite samples, and the uncertainties are exhibited as vertical error bars.

The α_V curve for calcite is exhibited in the T -range above 300 K, since the Fei equation predicts artificially small volume (Fig. 9e) and large thermal expansion coefficient at lower temperatures. At $T = 1500$ K, the extrapolated α_V values are 43% (in aragonite) and 12% (in witherite) larger than that for calcite. On the other hand, the Kumar equation is also adopted to fit the $V(T)$ data sets of the $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions measured from 100 to 500 K. The $\alpha_V(T)$ profiles are also illustrated in the figure for the representatives of $\text{Cal}_{81}\text{Wth}_{19}$, $\text{Cal}_{73}\text{Wth}_{27}$, and $\text{Cal}_{44}\text{Wth}_{56}$. $\text{Cal}_{81}\text{Wth}_{19}$ exhibits the largest thermal expansivity among the samples in the ordered calcite structure, and the α_V coefficients for $\text{Cal}_{73}\text{Wth}_{27}$ and $\text{Cal}_{44}\text{Wth}_{56}$ define the upper and lower bounds for the disordered ones, respectively. The k parameters (in Eq. 4) are assumed to be 3/2, since K'_T is fixed at 4 for calcite (Redfern and Angel 1999) and witherite (Wang et al. 2015). The fitted Θ_{ac} temperatures, $V(0 \text{ K})/V(300 \text{ K})$ ratios and Q_0 parameters are listed in Online Materials¹ Table S9.

The modeled $\alpha_V(T)$ values for the disordered $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ solid solutions are also very close to those for aragonite and witherite up to 1500 K. Additionally, the Kumar equations are also fitted for aragonite and witherite based on the $V(T)$ data sets in a narrower T -range of 143–586 K (Ye et al. 2012), and the extrapolated $\alpha_V(1500 \text{ K})$ values are approximately 7–9% higher than those fitted from all the data sets combined as shown in the figure. Hence, the predicted α_V values for the disordered solid solutions could be overestimated at higher temperatures, but the differences are expected to be no more than 10%.

IMPLICATIONS

As illustrated in Figure 10 for carbonates, the $\alpha_V(T)$ models based on the Kumar equation increase rapidly at temperatures below 200 K and progressively at higher temperatures. Similar trends are also observed for the volumetric thermal expansivities in silicate minerals (e.g., Kroll et al. 2012; Trots et al. 2012; Ye et al. 2022). Besides, the isochoric (C_V) and isobaric (C_P) heat capacities also increase at much quicker rates below 200 K (e.g., Zhu et al. 2019; Liu et al. 2024), which could further affect the thermodynamic Grüneisen parameter (γ) (e.g., Anderson 1995):

$$\gamma(T) = \left(\frac{\partial P}{\partial U} \right)_V \cdot V = \frac{\alpha(T) \cdot K_T(T) \cdot V(T)}{C_V(T)} \quad (10)$$

In the previous studies on cordierite (Hu et al. 2022) and olivine (Liu et al. 2024), the γ parameters decrease rapidly up to ~ 500 K and then increase slowly at higher temperatures. Overall, these thermodynamic properties are modeled on the basis of the Debye model (Eq. 5), in which the temperature derivative of the thermal energy, $\partial E_{th}(T)/\partial T$, grows rapidly at $T \ll \Theta_D$ but stabilizes when T is near or above Θ_D . Notably, the Debye temperatures are typically lower than 1000 K for most silicates and carbonates (e.g., Ye et al. 2022; this study). Therefore, low-temperature measurements should also be necessary and important for accurately modeling the thermodynamic and thermoelastic properties of minerals at various P - T conditions, like P - V - T EOS and heat capacities.

On the other hand, the rigid CO_3 groups are stacked in the layers perpendicular to the c -axis for MCO_3 carbonates,

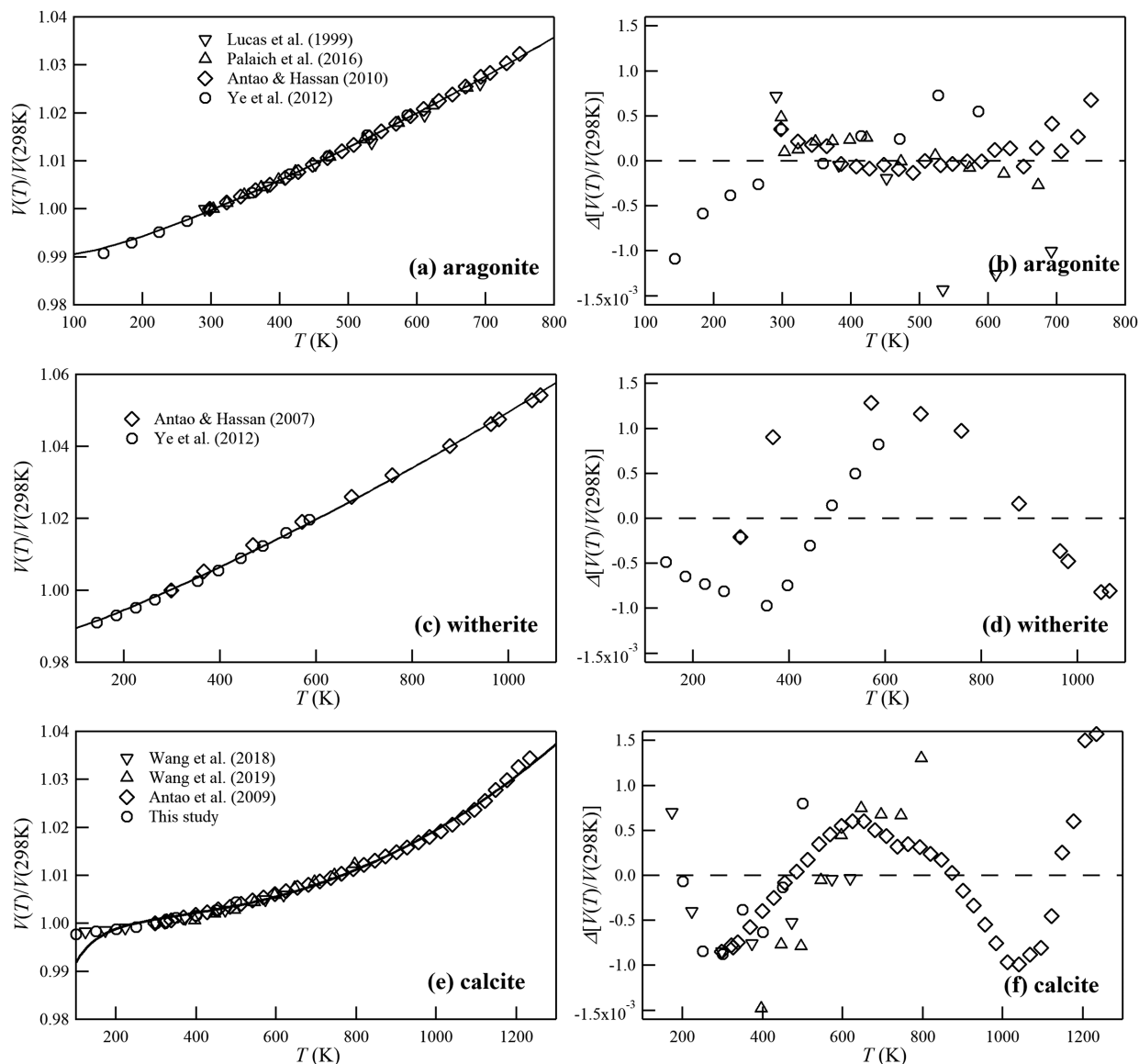


FIGURE 9. The measured volumes at various temperatures for (a, b) aragonite (Lucas et al. 1999; Antao and Hassan 2010; Ye et al. 2012; Palaich et al. 2016), (c, d) witherite (Antao and Hassan 2007; Ye et al. 2012), and (e, f) calcite (Antao et al. 2009; Wang et al. 2018, 2019; this study). The $V(T)$ values are normalized to that at the ambient temperature [i.e., $V(T)/V(298\text{K})$] in each study, and the experimental uncertainties are smaller than the sizes of the symbols. The solid curves are fitted based on the Kumar equation (Eq. 4) for (a) aragonite and (c) witherite, and the Fei equation (Eq. 9) for (e) calcite, with the fitting residuals exhibited in (b, d, and f).

including the aragonite-type, ordered and disordered calcite-type structures. Consequently, the c -axis exhibits significantly larger thermal expansivities (e.g., Antao and Hassan 2007, 2009; Ye et al. 2012; Wang et al. 2018, 2019) and compressibilities [$\beta = -1/V \cdot (\partial V/\partial P)_T$] (e.g., Fiquet et al. 1994; Zhang et al. 1997; Redfern and Angel 1999; Palaich et al. 2016; Litasov et al. 2017), compared with the a/b axes. The anisotropies of axial thermal expansivities in ordered calcite are greater than those in aragonite due to its negative α_a coefficient (Antao et al. 2009; Wang et al. 2018). This study identified the trend for the axial thermal expansivity: $\alpha_a(\text{disordered calcite}) \approx \alpha_b(\text{aragonite}) > \alpha_a(\text{aragonite})$ (Fig. 4a) and $\alpha_c(\text{disordered}$

calcite) $< \alpha_c(\text{aragonite})$ (Fig. 4b). Thus, the anisotropy of axial thermal expansivity in disordered calcite should be even smaller than that in aragonite. Notably, the ratio of $3\beta_c/\beta_V$ in calcite (in its stable P -range < 2 GPa) (Redfern and Angel 1999) also exceeds that for aragonite (Palaich et al. 2016). These findings suggest that MO_9 polyhedra in carbonates mitigate the anisotropies in both axial thermal expansivity and compressibility. Further compressional and elastic experiments on disordered $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ crystals could be helpful to predict the anisotropic elasticity for disordered CaCO_3 calcite. The Ba^{2+} effect could also be isolated if measurements are conducted on multiple compositions, analogous to this study. Understanding the anisotropic

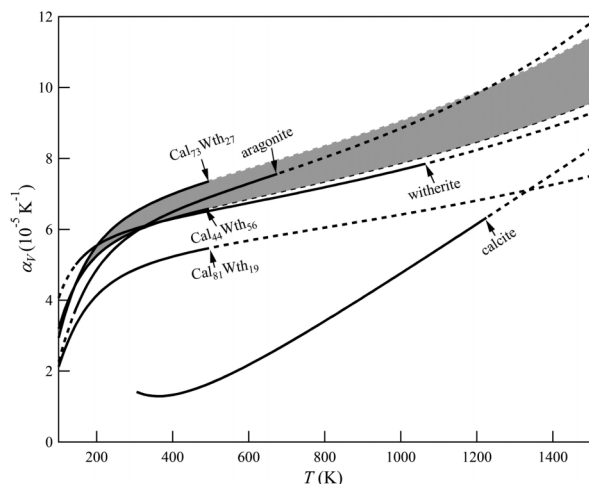


FIGURE 10. The volumetric thermal expansion coefficients, $\alpha_V(T)$, for the end-members of carbonates, as illustrated in Figure 9, as well as the selected solid solutions ($\text{Ca}_{81}\text{Wth}_{19}$, $\text{Ca}_{73}\text{Wth}_{27}$, and $\text{Ca}_{44}\text{Wth}_{56}$), which are also derived based on the Kumar equation. The solid and dotted parts of a curve stand for the T -ranges of measurement and extrapolation, respectively. The gray area represents the extrapolated $\alpha_V(T)$ values for the $\text{Ba}_x\text{Ca}_{1-x}\text{CO}_3$ samples ($0.27 \leq x \leq 0.79$) in a disordered calcite structure.

elasticities for carbonates is relevant to tracing distributions of carbonates in the upper mantle by seismological observations (e.g., Yuan and Beghein 2013; French and Romanowicz 2014).

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