

Thermal behaviour of calcite-structure carbonates: a powder X-ray diffraction study between 83 and 618 K

MEILI WANG¹, GUANGHAI SHI^{1,*}, JIAQIAN QIN² and QING BAI¹

¹ State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

*Corresponding author, e-mail: shiguanghai@263.net.cn, shigh@cugb.edu.cn

² Metallurgy and Materials Science Research Institute, Chulalongkorn University, Bangkok 10330, Thailand

Abstract: The thermal behaviour of five calcite-structure carbonates (space group $R\bar{3}c$), magnesite (MgCO_3), smithsonite (ZnCO_3), rhodochrosite (MnCO_3), otavite (CdCO_3) and calcite (CaCO_3), was explored by *in situ* powder X-ray diffraction over the temperature range 83–618 K. The unit-cell and crystal-structure parameters relative to temperature in these carbonates were determined. All the carbonates in this study display obvious anisotropic thermal expansion: the values of the thermal expansion coefficients along the c -axis ($\alpha_0(c)$) are much larger than those along the a -axis ($\alpha_0(a)$). The a cell parameter of otavite increases slightly from 123 to 223 K and subsequently contracts at higher temperature. Negative thermal expansion along the a -axis is also observed in calcite. In contrast to those of magnesite and smithsonite, the $\text{O}_1\text{--O}_2$ bond distances of otavite and calcite do not expand with increasing temperature, which may explain their negative thermal expansion along the a -axis. Moreover, the values of $\alpha_0(V)$ and $\alpha_0(a)$ for the calcite-structure carbonates (MgCO_3 , ZnCO_3 , MnCO_3 , CdCO_3 , and CaCO_3) are shown to exhibit an inverse correlation with the cation radius. However, no obvious relationship is noted between the $\alpha_0(c)$ values and the size of the cations. Structural mechanisms for the systematic thermal behaviour of the five carbonates are also discussed.

Key-words: calcite-structure carbonates; low- and high-temperature X-ray diffraction; thermal expansion; crystal structure.

1. Introduction

The deep carbon cycle, involving the exchange of carbon-bearing phases between the Earth's surface and interior, has attracted considerable interest of geologists. Carbonates can be carried into the deep Earth through subduction process, and the carbon is partially released to Earth's surface via volcanism and related events (Javoy *et al.*, 1982; Zhang & Zindler, 1993; Sleep & Zahnle, 2001; Berner, 2003; Shi *et al.*, 2005; Dasgupta & Hirschmann, 2010; Hazen & Schiffries, 2013). Therefore, the high-temperature and high-pressure behaviour of the carbonates are essential for understanding the process of fixation, storage, migration, and outgassing of carbon between the interior and the surface (Gillet *et al.*, 1993; Liou *et al.*, 1995; Seto *et al.*, 2008; Boulard *et al.*, 2011; Hazen *et al.*, 2013; Shatskiy *et al.*, 2015).

The calcite-structure carbonates (space group $R\bar{3}c$), which include naturally occurring magnesite (MgCO_3), spherocobaltite (CoCO_3), smithsonite (ZnCO_3), rhodochrosite (MnCO_3), otavite (CdCO_3) and calcite (CaCO_3), represent a common carbonate mineral group. Most previous studies have focused on exploring the behaviour of the calcite-structure carbonates at high-pressure (e.g., Zhang & Reeder, 1999; Suito *et al.*, 2001; Fiquet *et al.*, 2002; Santillán & Williams, 2004; Ono *et al.*, 2007;

Oganov *et al.*, 2008; Minch *et al.*, 2010; Tao *et al.*, 2013; Gao *et al.*, 2014; Boulard *et al.*, 2015; Solopova *et al.*, 2015), whereas only a few data have been reported on their thermal behaviour (e.g., MgCO_3 : Markgraf & Reeder, 1985; Zhang *et al.*, 1997; Litasov *et al.*, 2008; ZnCO_3 : Rao & Murthy, 1974; MnCO_3 : Rao & Murthy, 1970; CdCO_3 : Bayer, 1971; Ballirano, 2016; CaCO_3 : Markgraf & Reeder, 1985; Antao *et al.*, 2009). In addition, several of these datasets have covered a limited temperature range because of the relatively low decomposition temperature, and some controversies still exist in the previous research. For example, the temperature dependence of thermal expansion of magnesite differs greatly among previous works (see Fig. 10 of Litasov *et al.* (2008)). Moreover, little systematic research has been performed to model the thermal behaviour of the calcite-structure carbonates, except for the work of Rao (1974). However, his thermal expansion data were determined from a narrow analysis range of the Bragg angles (55–80°). Therefore, further works on the thermal behaviour of the calcite-structure carbonates, especially systematic studies, are desirable.

In this study, *in situ* low- and high-temperature powder X-ray diffraction experiments were conducted between 83 and 618 K on five calcite-structure carbonates (MgCO_3 , ZnCO_3 , MnCO_3 , CdCO_3 and CaCO_3) to derive their axial and volumetric thermal expansion coefficients together

with the variations of crystal structure parameters with temperature. The mechanisms for the anisotropic thermal expansion of these carbonates, as well as the effects of the individual constituent atoms (*e.g.*, size and electronegativity) and the crystal structure on the thermal expansion are discussed, attempting to provide new insights into the systematics of the thermal expansion of calcite-structure carbonates.

2. Experimental methods

Three of the five calcite-structure carbonates used in this study are naturally sourced and optically homogeneous. Their chemical formulas are $(\text{Mg}_{0.994}\text{Ca}_{0.006})\text{CO}_3$, $(\text{Zn}_{0.995}\text{Ca}_{0.004}\text{Mg}_{0.001})\text{CO}_3$ and $(\text{Ca}_{0.981}\text{Mg}_{0.019})\text{CO}_3$, respectively, as measured by EPMA-1720 electron microprobe at China University of Geosciences (Beijing). The other two carbonates, synthesized MnCO_3 powder (purity of 99.9%) and CdCO_3 powder (purity of 99.99%), were purchased from Alfa Aesar.

For the magnesite sample, *in situ* X-ray diffraction experiments (83–598 K) were carried out at the 4B9A beamline of Beijing Synchrotron Radiation Facility (BSRF). The incident X-ray wavelength was 1.5401 Å. An oven chamber (Anton Paar TTK450) was used to heat or cool the samples, which was connected to a low-temperature N_2 gas stream. Temperatures were monitored by type Pt100 temperature sensor and controlled by a TCU-110 temperature control unit. Data for MnCO_3 from 83 to 203 K were also collected using the same method. For the other carbonates in this study, the *in situ* X-ray diffraction experiments (123–403 K for ZnCO_3 , 298–568 K for MnCO_3 , 123–593 K for CdCO_3 , and 123–618 K for CaCO_3) were conducted at Shanghai Institute of Ceramics, Chinese Academy of Sciences, using Bruker D8 Advance X-ray diffraction instrument, which also had an attached Anton Paar TTK450 oven. The system was equipped with a Cu target and was operated at 40 kV, 40 mA. Temperature calibration was performed with another type Pt100 temperature sensor placed at the sample position. The temperature uncertainty for both systems was approximately ± 3 K.

All samples were heated to a target temperature at a rate of 10 K/min and held for 5–10 min at the target temperature to allow the materials to relax sufficiently before collection of the powder diffraction patterns. Their patterns were collected in the 2θ range between 20° and 90° , with a scanning step width of 0.02° and step time of 1 s for MgCO_3 , ZnCO_3 , CdCO_3 , and CaCO_3 or 3 s for MnCO_3 . Following the data-processing procedure of Nie *et al.* (2017), the refinement of lattice parameters of the five carbonates was performed using the MDI's program Jade 6.0 (Material Data, Inc.). In addition, the obtained XRD data were modelled by the Rietveld method using the GSAS program (Larson & Von Dreele, 2000) coupled with the EXPGUI interface (Toby, 2001) to extract the crystal-structure parameters. The peak shapes were fitted using type-3 profile and the background was modelled with an 8-term shifted Chebyshev polynomial in the GSAS program.

Refined structure parameters include atom coordinates and displacement parameters.

3. Results and discussions

3.1. Unit-cell and crystal-structure parameters

Low- and high-temperature powder X-ray diffraction experiments for the five calcite-structure carbonates were conducted between 83 and 618 K, and several typical patterns are presented in Fig. 1. All the major peaks were assigned to the calcite structure, except for a few weak peaks that originated from the sample plate (*i.e.*, copper plate for MgCO_3 and Al-alloy plate for ZnCO_3 , CdCO_3 and CaCO_3). Their diffraction peaks gradually broaden with increasing temperature. Weak ice peaks were also observed in some of the low-temperature patterns of ZnCO_3 , CdCO_3 and CaCO_3 , which may have been caused by the relatively high air humidity in Shanghai.

Refined unit-cell parameters of the five calcite-structure carbonates at different temperatures are listed in Table 1. The unit-cell parameters under ambient conditions are in agreement with those reported in previous studies (Rao & Murthy, 1974; Markgraf & Reeder, 1985; Zhang & Reeder, 1999; Litasov *et al.*, 2008; Antao *et al.*, 2009; Ballirano, 2016), with discrepancies of less than 0.85%. In addition, the *a* and *c* unit-cell parameters at room temperature are plotted against the volume, indicating that both *a* and *c* axes increase linearly as functions of the volume (Fig. 2). Relative variations of the lattice parameters with temperature for the five carbonates imply that the thermal expansion for the carbonates is anisotropic, as the relative change along *a*-axis is different from that of *c*-axis in the investigated temperature range (Fig. 3).

Due to the existence of ice peaks in some low-temperature diffraction patterns of ZnCO_3 , CdCO_3 and CaCO_3 , reliable structure refinements were not obtained from the related data. It is also difficult to resolve the structure of MnCO_3 because of the broadening and weakening of its diffraction peaks. Accordingly, only the structural parameters of the reliable refinements (83–598 K for MgCO_3 , 243–403 K for ZnCO_3 , 298–593 K for CdCO_3 , and 223–573 K for CaCO_3) are used in the following discussions, as given in Table 2. The refinements yielded R_{wp} values ranging from 4.7 to 13.5% and R_p from 3.1 to 10.3%. The structure data in this study might be improved using high-quality XRD data. The M–O and C–O bond distances at room temperature in this study are broadly consistent with previous studies (*e.g.*, Effenberger *et al.*, 1981; Markgraf & Reeder, 1985; Ballirano, 2016). As the CO_3 group is expected to behave as a rigid body, the C–O bond distances are approximately independent on temperature. The M–O and $\text{O}_1\text{--O}_6$ bond distances increase with increasing temperature for the four calcite-structure carbonates (Fig. 4). In contrast, the $\text{O}_1\text{--O}_2$ bond distances of CdCO_3 and CaCO_3 are nearly constant with temperature, whereas the distance increases for MgCO_3 and increases slightly for ZnCO_3 .

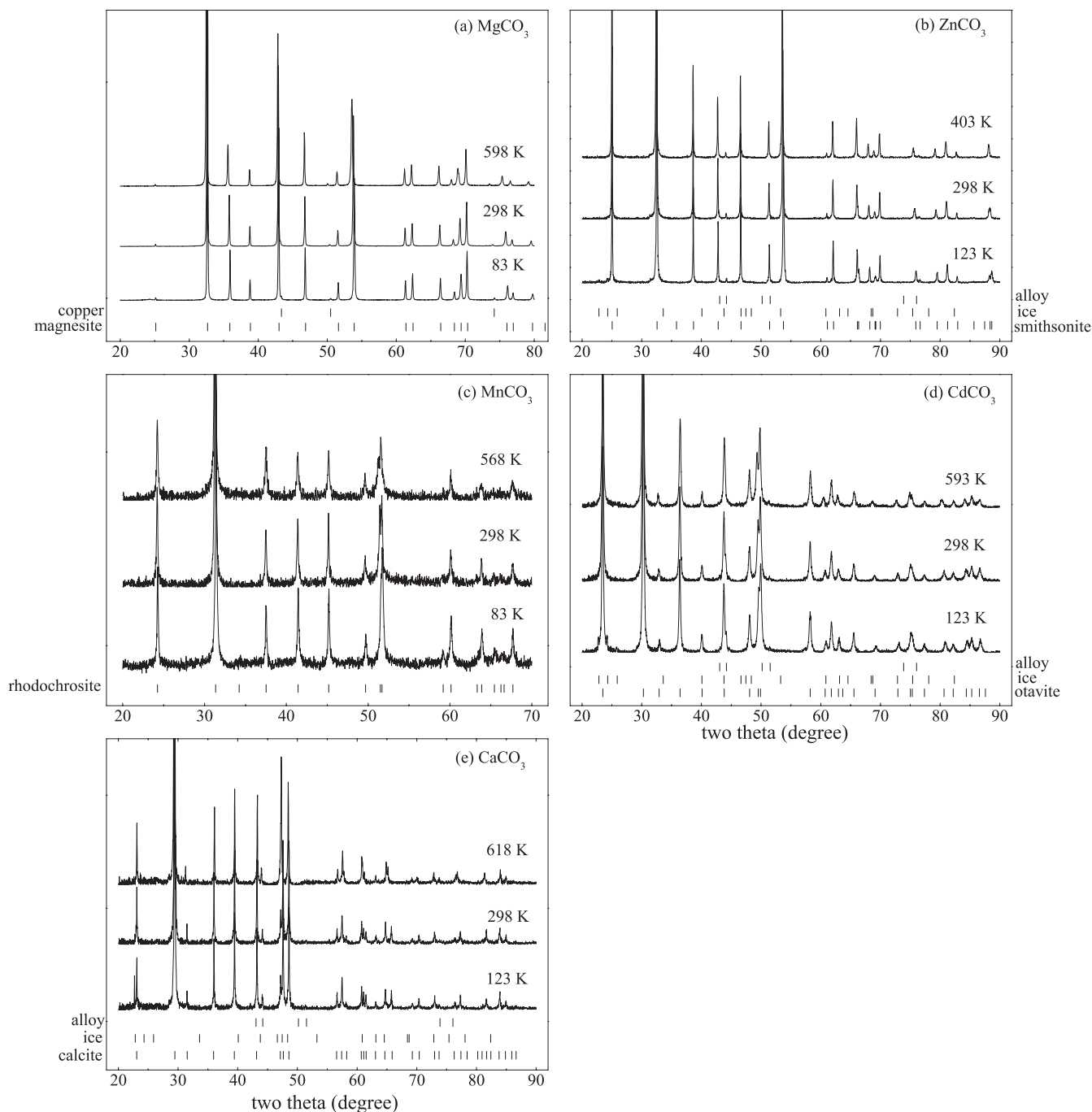


Fig. 1. Typical X-ray diffraction patterns collected at different temperatures. The background was subtracted from the original data. The short vertical lines indicate the positions of allowed reflections for the calcite-structure carbonates, the sample plate (Cu or Al-alloy), and ice.

3.2. Thermal expansion

To calculate the thermal expansion coefficient, the volume–temperature data were fitted to the following equations:

$$V_T = V_0 \exp\left(\int_{T_0}^T \alpha_T dT\right) \quad (1)$$

and

$$\alpha_T = a_0 + a_1 T + a_2 T^{-2} \quad (2)$$

where V_T , V_0 and α_T are the volume at temperature T , the volume at room temperature T_0 and the volumetric thermal expansion coefficient at temperature T , respectively; a_0 , a_1 and a_2 are the constants determined by fitting the experimental V – T data. In the cases that a_1 and a_2 could not be resolved, their values were fixed as zero. The fitting results are provided in Table 3 and the related fitting curves are shown in Fig. 5. Similarly, the axial thermal expansion coefficients were obtained by replacing the volume data in the equations above with the axial data; these fitting results are also listed in Table 3. Of note, subscript T is dropped

Table 1. Unit-cell parameters at various temperatures. Standard deviations are in parentheses.

T (K)	a (Å)	c (Å)	V (Å ³)
MgCO₃			
83	4.6335(1)	14.9638(7)	278.22(2)
123	4.6341(5)	14.9706(24)	278.42(8)
173	4.6353(3)	14.9835(17)	278.80(5)
223	4.6365(4)	15.0000(22)	279.26(7)
298	4.6395(2)	15.0311(11)	280.20(4)
373	4.6415(5)	15.0618(20)	281.01(7)
448	4.6440(4)	15.0965(18)	281.96(6)
523	4.6471(3)	15.1291(17)	282.95(5)
598	4.6503(7)	15.1560(28)	283.84(10)
ZnCO₃			
123	4.6543(8)	15.0052(12)	281.50(10)
163	4.6551(7)	15.0136(14)	281.75(8)
203	4.6559(9)	15.0261(14)	282.08(11)
243	4.6570(8)	15.0361(27)	282.41(11)
298	4.6585(5)	15.0543(13)	282.93(6)
333	4.6595(3)	15.0685(10)	283.32(5)
363	4.6606(2)	15.0796(8)	283.66(3)
403	4.6621(5)	15.0961(14)	284.16(6)
MnCO₃			
83	4.7890(17)	15.6551(91)	310.94(23)
143	4.7897(19)	15.6642(90)	311.21(31)
203	4.7902(11)	15.6818(46)	311.63(17)
298	4.7909(9)	15.7056(37)	312.19(14)
388	4.7916(10)	15.7317(51)	312.78(16)
478	4.7921(8)	15.7632(24)	313.49(12)
568	4.7926(19)	15.7917(56)	314.13(28)
CdCO₃			
123	4.9259(5)	16.2469(20)	341.41(8)
173	4.9260(5)	16.2598(20)	341.69(8)
223	4.9261(2)	16.2709(9)	341.93(4)
298	4.9259(4)	16.2955(16)	342.42(6)
353	4.9256(3)	16.3124(11)	342.74(5)
403	4.9254(1)	16.3317(4)	343.12(2)
453	4.9250(1)	16.3488(6)	343.41(2)
503	4.9244(4)	16.3637(25)	343.66(8)
553	4.9237(3)	16.3819(16)	343.94(6)
593	4.9232(4)	16.3981(15)	344.21(7)
CaCO₃			
123	4.9894(5)	16.9570(18)	365.57(8)
173	4.9875(5)	16.9750(21)	365.68(9)
223	4.9845(6)	17.0042(15)	365.87(9)
298	4.9828(6)	17.0315(11)	366.21(10)
373	4.9812(2)	17.0608(11)	366.61(4)
473	4.9792(2)	17.1023(9)	367.21(4)
573	4.9782(5)	17.1484(16)	368.04(8)
618	4.9773(4)	17.1713(19)	368.40(7)

off in most cases for the sake of brevity, *i.e.*, $\alpha_0(V)$ and $\alpha(V)$ represent the values of volumetric thermal expansion coefficients at room temperature and temperature T , respectively, and the same is true for the axial thermal expansion coefficients.

A few volume–temperature data from the literature have been processed using the same procedure as the corresponding sample; the fitting results are included in Table 3 for comparison. The $\alpha_0(V)$ value of magnesite in this study is consistent with those of Zhang *et al.* (1997), Litasov *et al.* (2008) and Merlini *et al.* (2016), within reciprocal uncertainties. In contrast, it is larger than that of Markgraf

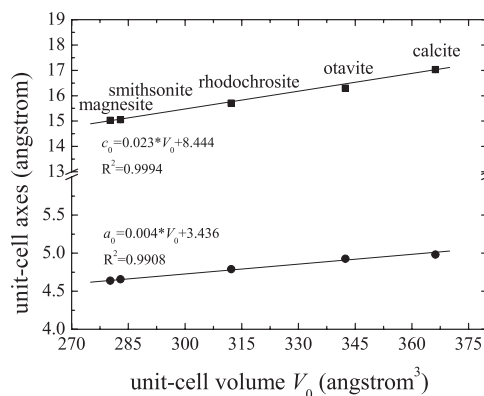


Fig. 2. The unit-cell parameters as a function of volume at ambient conditions. Positive linear trends exist between the a and c axes and the unit-cell volume, respectively. The filled circles and squares represent the values of the a - and c -axis, respectively.

& Reeder (1985), with a difference of 44%, which is likely attributed to the fact that no absorption correction was applied to MgCO₃ in their work. The relatively irregular volume–temperature data of ZnCO₃ from Rao & Murthy (1974) and MnCO₃ from Rao & Murthy (1970) yield large errors for the $\alpha_0(V)$ values (Table 3). The $\alpha_0(V)$ value of otavite from this work is 26% lower than that of Ballirano (2016). In addition, the $\alpha_0(V)$ value of calcite in this study agrees well with that of Merlini *et al.* (2016), while those from Antao *et al.* (2009) and Markgraf & Reeder (1985) are nearly identical and differ slightly from the value in this study, considering the uncertainties. The small discrepancy may result from the phase transition of calcite occurring at approximately 723 K (*e.g.*, Merlini *et al.*, 2016), as the upper limit of the fitting temperature range used in the work of Antao *et al.* (2009) and Markgraf & Reeder (1985) is much larger than 723 K.

Moreover, variations in thermal expansion coefficient with temperature for magnesite and calcite are compared with previous studies (Fig. 6). Although the temperature dependence of $\alpha(V)$ for magnesite in this study is close to that of Markgraf & Reeder (1985), some differences still exist among Markgraf & Reeder (1985), Zhang *et al.* (1997), Litasov *et al.* (2008), Merlini *et al.* (2016), and this study. In contrast, in the case of calcite, our results are almost the same as those of Merlini *et al.* (2016), and relatively small differences are noted compared with those of Antao *et al.* (2009) and Markgraf & Reeder (1985).

The thermal expansion coefficients of some bond distances in this study were also calculated using the method mentioned above (Table 4), with the a_1 and a_2 constants set to zero. There are relatively large estimated errors in the fitting results of O₁–O₂ bond distances for CdCO₃ and CaCO₃, as the O₁–O₂ bond distances nearly keep constant with temperature for these two samples. The related fitting curves are shown in Fig. 4.

3.3. Anisotropic thermal expansion

As shown in Fig. 3, thermal expansion of magnesite, smithsonite, rhodochrosite, otavite, and calcite is strongly

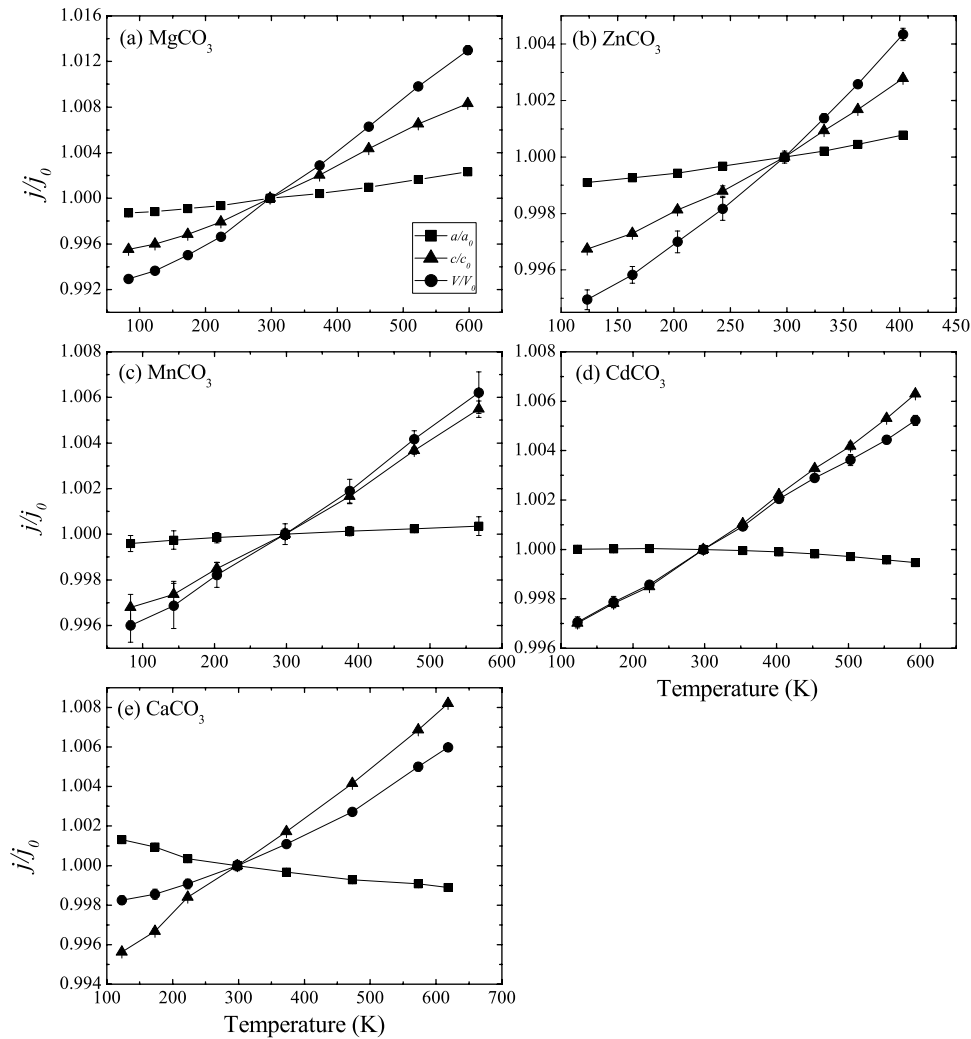


Fig. 3. Relative variations of the unit-cell parameters with temperature. Most of the error bars of these measurements are smaller than the size of the symbols. The solid curves are visual aids and have no physical significance.

Table 2. Selected interatomic distances (Å), atomic coordinates, and isotropic displacement parameters ($\times 10^2 \text{ Å}^2$).

T (K)	M–O	C–O	O ₁ –O ₂	O ₁ –O ₆	x_{O1}	U_M	U_C	U_O
MgCO₃								
83	2.0959(6)	1.293(1)	2.917(1)	3.0108(4)	0.2790(2)	1.08(6)	1.19(13)	0.81(6)
123	2.0973(5)	1.297(1)	2.918(1)	3.0138(4)	0.2796(2)	1.29(6)	1.48(12)	0.97(6)
173	2.0984(5)	1.295(1)	2.919(1)	3.0154(4)	0.2793(2)	1.32(6)	1.48(12)	1.03(6)
223	2.0993(8)	1.296(2)	2.920(2)	3.0175(6)	0.2794(3)	1.52(8)	1.51(18)	1.02(8)
298	2.1017(8)	1.298(1)	2.922(2)	3.0222(6)	0.2795(3)	1.61(8)	1.53(18)	1.02(8)
373	2.1036(6)	1.293(1)	2.924(1)	3.0247(4)	0.2786(2)	1.43(6)	1.53(13)	1.16(6)
448	2.1050(6)	1.294(1)	2.925(1)	3.0283(4)	0.2788(2)	1.45(6)	1.65(13)	1.21(6)
523	2.1066(6)	1.296(1)	2.926(1)	3.0320(4)	0.2789(2)	1.54(6)	2.02(13)	1.29(6)
598	2.1083(6)	1.295(1)	2.927(1)	3.0350(4)	0.2787(2)	1.85(6)	2.35(14)	1.56(6)
ZnCO₃								
243	2.1192(15)	1.277(3)	2.958(3)	3.0349(11)	0.2740(7)	0.48(5)	0.66(9)	–
298	2.1197(16)	1.278(3)	2.958(3)	3.0368(11)	0.2743(7)	0.61(4)	0.70(9)	–
333	2.1207(16)	1.278(3)	2.959(3)	3.0385(11)	0.2742(7)	0.73(5)	0.79(9)	–
363	2.1213(17)	1.279(3)	2.959(4)	3.0400(12)	0.2742(7)	0.74(5)	0.83(9)	–
403	2.1224(15)	1.277(3)	2.960(3)	3.0420(11)	0.2741(6)	1.45(5)	1.59(9)	–
CdCO₃								
298	2.2931(17)	1.289(3)	3.198(4)	3.2872(12)	0.2614(7)	0.57(4)	1.31(28)	0.64(13)
353	2.2951(17)	1.287(3)	3.200(4)	3.2907(12)	0.2611(7)	0.74(4)	1.40(28)	0.50(13)
403	2.2954(18)	1.289(4)	3.199(4)	3.2927(13)	0.2614(7)	0.76(5)	1.10(28)	0.55(14)

Table 2. (continued).

<i>T</i> (K)	M–O	C–O	O ₁ –O ₂	O ₁ –O ₆	<i>x</i> _{O1}	<i>U</i> _M	<i>U</i> _C	<i>U</i> _O
453	2.2962(18)	1.288(4)	3.199(4)	3.2951(13)	0.2613(7)	0.87(5)	1.71(29)	0.76(13)
503	2.2972(18)	1.288(4)	3.199(4)	3.2975(13)	0.2612(7)	0.96(5)	1.85(29)	0.76(13)
553	2.2990(22)	1.285(4)	3.201(5)	3.3002(16)	0.2606(8)	1.13(4)	2.58(37)	0.98(15)
593	2.2983(19)	1.288(4)	3.198(4)	3.3012(14)	0.2612(7)	1.05(5)	2.27(32)	1.07(14)
CaCO ₃								
223	2.3731(17)	1.250(3)	3.295(4)	3.4156(12)	0.2506(6)	1.64(10)	1.93(15)	–
298	2.3741(19)	1.248(4)	3.296(4)	3.4182(12)	0.2503(6)	1.78(9)	2.37(14)	–
373	2.3765(18)	1.245(4)	3.297(4)	3.4233(13)	0.2498(7)	1.97(10)	2.74(16)	–
473	2.3787(25)	1.245(5)	3.297(5)	3.4303(18)	0.2498(9)	3.12(14)	4.18(23)	–
573	2.3794(21)	1.246(4)	3.293(5)	3.4354(15)	0.2503(8)	2.65(11)	3.90(19)	–

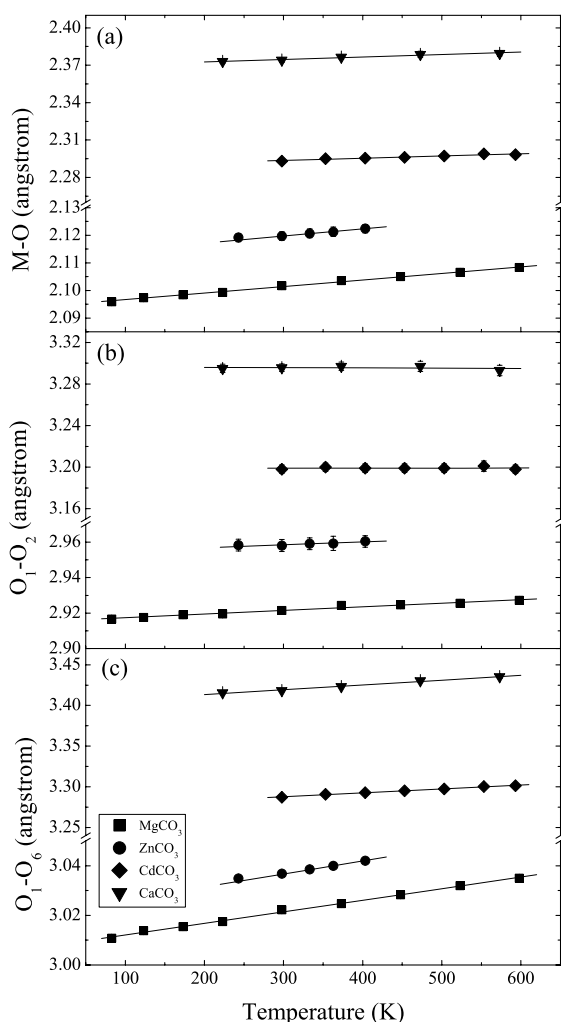
–: constraint, $U_O = U_C$ 

Fig. 4. Evolution of bond distances with temperature: (a) M–O bond; (b) O₁–O₂ bond; (c) O₁–O₆ bond. The solid lines are fitted by Equations (1) and (2), and the corresponding values used in these equations are presented in Table 4.

anisotropic. In the investigated temperature range, the relative change of *c*-axis is approximately 11.4 times that of *a*-axis for magnesite, 11.7 times for smithsonite, 37.9

times for rhodochrosite, 56.0 times for otavite, and 17.7 times for calcite. The variations of the *a/c* ratios for the five carbonates decrease with increasing temperature, which also reflects that the carbonates are thermally more expandable along *c*-axis than that of *a*-axis, as displayed in Fig. 7. In the crystal structures of these carbonates (Fig. 8), strongly bonded coplanar CO₃^{2–} groups are arranged parallel to the *ab*-plane and connected through much weaker bonds to 6-coordinated divalent cations M²⁺ (M: Mg, Mn, Zn, Cd, and Ca) (Graf, 1961; Maslen *et al.*, 1995). It implies that the expansion along the *c*-axis is relative to the variation of O₁–O₆ bond of the MO₆ octahedra, while the *ab*-plane is relative to that of O₁–O₂ bond where there exist resistances of the rigid CO₃^{2–} groups. All the calculated thermal expansion coefficients of O₁–O₆ bond distances are larger than those of O₁–O₂ bond distances for the five carbonates (Table 4); this kind of behaviour may account for the high anisotropy of thermal expansion for these carbonates.

In addition, the *a* cell parameters of otavite increase slightly from 123 to 223 K and then decrease at higher temperatures (Fig. 3). This reversal behaviour has been reported by Ballirano (2016); however, the reversal temperature is around 453 K in his data. The negative thermal expansion of the *a*-axis for calcite is also observed in the present study, which is consistent with the results of previous works (*e.g.*, Markgraf & Reeder, 1985; Dove *et al.*, 2005; Antao *et al.*, 2009). In this study, the O₁–O₂ bond distances for both otavite and calcite remain approximately constant with temperature, whereas those of magnesite and smithsonite increase (Fig. 4). Thus, this behaviour is expected to correlate with the negative thermal expansion along the *a*-axis. In addition, Markgraf & Reeder (1985) suggested that the basal edge O₁–O₂ of CaO₆ octahedra in calcite exhibited contraction if the libration of the CO₃ group along the *c*-axis was corrected. Therefore, the negative thermal expansion along *a*-axis for otavite and calcite is proposed to be caused by the relatively large libration motion of CO₃ groups. Furthermore, based on the data related to the vibrational ellipsoids of each atom in the calcite-structure carbonates (Reeder, 1983), the effect of libration motion of CO₃^{2–} groups on the

Table 3. Thermal expansion coefficients of the unit-cell parameters.

	f^a	j_0 (Å or Å ³)	α_0 (10 ⁻⁵ /K)	a_0 (10 ⁻⁵ /K)	a_1 (10 ⁻⁸ /K)	R ²	Reference
MgCO ₃	V	280.14(5) ^b	3.81(38)	2.22(26)	5.33(92)	0.9980	This study
	a	4.6391(2)	0.66(8)	0.39(6)	0.91(19)	0.9970	This study
	c	15.0307(18)	2.48(27)	1.42(19)	3.55(66)	0.9975	This study
	V	279.54(6)	4.18(8)	4.03(7)	0.49(10)		Litasov <i>et al.</i> (2008)
	V	279.32(15)	3.84(19)	3.15(17)	2.32(28)		Zhang <i>et al.</i> (1997)
	V	280.10(1)	3.33(10)	2.62(9)	2.39(16)		Merlini <i>et al.</i> (2016)
ZnCO ₃	V	279.31(6)	2.14(42)	0.16(37)	6.66(65)	0.9994	Markgraf & Reeder (1985) ^c
	V	282.94(1)	3.66(13)	1.14 (9)	8.44(32)	0.9999	This study
	a	4.6584(1)	0.66(6)	0.14(4)	1.75(15)	0.9994	This study
	c	15.0582(9)	2.14(7)	2.14(7)		0.9929	This study
MnCO ₃	V	284.87(13)	5.73(477)	8.19(390)	-8.26(922)	0.9757	Rao & Murthy (1974) ^c
	a	312.20(2)	2.09(19)	1.53(14)	1.88(43)	0.9989	This study
	c	4.7909(1)	0.16(2)	0.22(1)	-0.23(4)	0.9980	This study
CdCO ₃	V	15.7064(10)	1.79(22)	1.20(17)	1.99(49)	0.9985	This study
	V	308.48(7)	2.54(169)	1.25(138)	4.34(327)	0.9927	Rao & Murthy (1970) ^c
	a	342.45(2)	1.80(4)	1.80(4)		0.9961	This study
	c	4.9259(1)	-0.06(1)	0.19(1)	-0.84(4)	0.9973	This study
CaCO ₃	V	16.2970(8)	2.03(4)	2.03(4)		0.9969	This study
	a	342.84(5)	2.42(9)	2.42(9)		0.9739	Ballirano (2016) ^c
	V	366.20(1)	1.30(12)	0.23(9)	3.59(24)	0.9990	This study
	a	4.9831(2)	-0.57(8)	-0.99(8)	1.39(20)	0.9914	This study
	c	17.0308(1)	2.47(4)	2.47(4)		0.9977	This study
	V	367.66(10)	0.83(27)	-0.74(25)	5.28(34)	0.9940	Antao <i>et al.</i> (2009) ^c
	V	366.80(4)	1.34(7)	0.27(6)	3.59(11)		Merlini <i>et al.</i> (2016)
	V	367.57(6)	0.86(19)	-0.52(17)	4.63(26)	0.9986	Markgraf & Reeder (1985) ^c

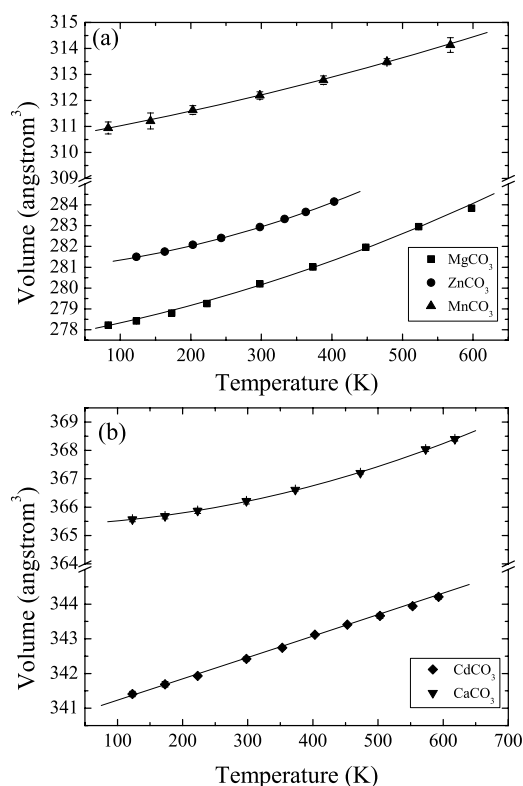
^a j stands for a , c or V .^b Data from the fitting results.^c Data obtained by reprocessing the original data from the literatures through the method of this study, and the a_1 and a_2 constants were selectively set to be zero, same as the corresponding sample.

Fig. 5. Temperature–volume relationships of the five calcite-structure carbonates. The solid curves are fitted by Equations (1) and (2), and the corresponding values used in these equations are presented in Table 3.

a parameters is expected to decrease with decreasing cation size, explaining why the negative thermal expansion is restricted to otavite and calcite.

3.4. Systematics of thermal expansion at ambient condition

For a variety of isostructural compounds, properties of constituent atoms (*e.g.*, size and electronegativity) and parameters of crystal structures (*e.g.*, bond length) have an important effect on their physico-chemical behaviour. The related properties of the five calcite-structure carbonates used in this study are listed in Table 5. In calcite-structure carbonates (*e.g.*, Reeder, 1983; Maslen *et al.*, 1995), as the unit-cell only has one 6-coordinated cation site, we used the values of ionic radius for M²⁺ (Mg²⁺, Zn²⁺, Mn²⁺, Cd²⁺ and Ca²⁺) with 6-fold coordination (Shannon, 1976) in this study. Relationships between the thermal expansion coefficients and the cation size for the calcite-structure carbonates are presented in Fig. 9.

In accordance with the suggestions of Reeder (1983) and Ballirano (2016), the $\alpha_0(a)$ values exhibit an inverse relation with ionic radius of the cations (r), as roughly expressed by $\alpha_0(a)$ (10⁻⁵ K⁻¹) = -4.075 $\cdot$ r + 3.624 (Fig. 9a). Notably, the $\alpha_0(\text{O}_1\text{--O}_2)$ values also show an approximately inverse linear relation with the ionic radius, which may be the cause of the linear trend between the $\alpha_0(a)$ values and cation size in the calcite-structure

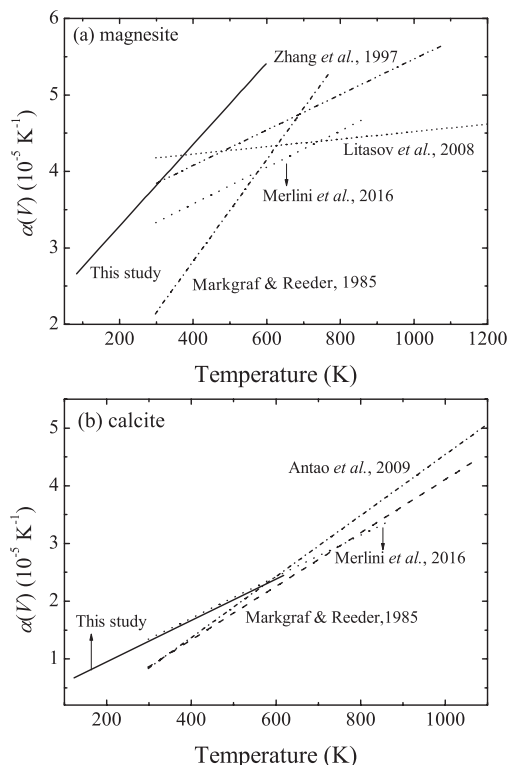


Fig. 6. Comparisons of the variations of thermal expansion coefficients with temperature for (a) magnesite and (b) calcite with previously reported results. Data are from Markgraf & Reeder (1985), Zhang *et al.* (1997), Litasov *et al.* (2008), Antao *et al.* (2009), and Merlini *et al.* (2016). The data from Markgraf & Reeder (1985) and Antao *et al.* (2009) are refitted by Equations (1) and (2) using absolute temperature.

Table 4. Thermal expansion coefficients of selected bond distances at room temperature ($\times 10^{-5}/\text{K}$).

	M–O	O ₁ –O ₂	O ₁ –O ₆
MgCO ₃	1.13(3)	0.70(4)	1.54(3)
ZnCO ₃	1.22(3)	0.56(11)	1.73(7)
CdCO ₃	0.79(9)	0.02(13)	1.45(5)
CaCO ₃	0.82(9)	−0.08(19)	1.71(10)

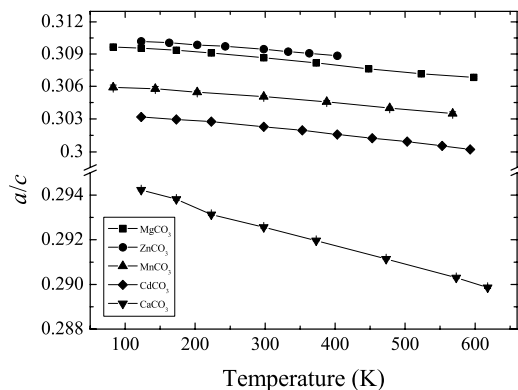


Fig. 7. Variation of the a/c ratios with temperature. The error bars are smaller than the symbol sizes of most data. The solid curves are visual aids and have no physical significance.

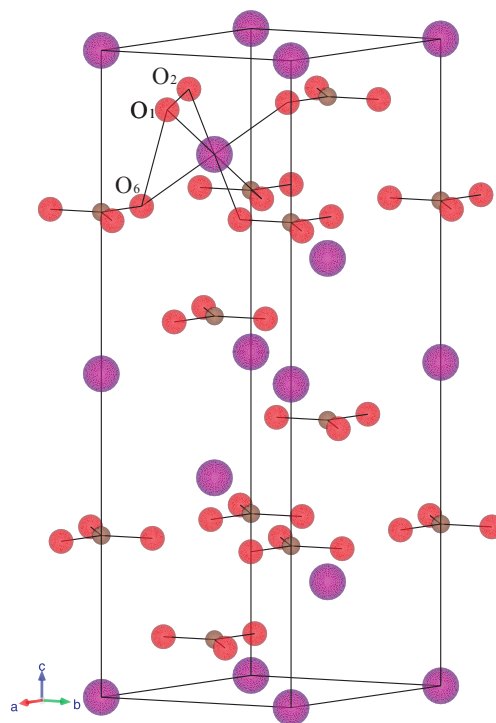


Fig. 8. Crystal structure of calcite-structure carbonates plotted with rhodochrosite as an example. Large spheres represent metal cations (Mg, Zn, Mn, Cd, and Ca), intermediate spheres represent O, and the smallest spheres represent C.

Table 5. Summary of two properties of Mg²⁺, Zn²⁺, Mn²⁺, Cd²⁺, and Ca²⁺.

Cation	Radius (Å) ^a	Electronegativity ^b
Mg ²⁺	0.72	1.31
Zn ²⁺	0.74	1.65
Mn ²⁺	0.83	1.55
Cd ²⁺	0.95	1.69
Ca ²⁺	1.0	1.0

^a Data from Shannon (1976).

^b Data from Ride (1998).

carbonates. No obvious regular correlation is noted between the $\alpha_0(c)$ values and the radius. Although the $\alpha_0(c)$ values decrease from magnesite to rhodochrosite as the cation size increases, otavite and calcite have relatively larger $\alpha_0(c)$ values than that predicted from this trend (Fig. 9b). This phenomenon is inferred to be related to the thermal behaviour of O₁–O₆ bond in these carbonates. As noted in Fig. 9b, CdCO₃ and CaCO₃ display relatively large $\alpha_0(\text{O}_1\text{–O}_6)$ values and the two values exhibit a positive correlation with the ionic radius, which could also be attributed to the relatively large libration motion of CO₃^{2−} groups along c -axis in these two samples. However, the data for ZnCO₃ appear to diverge from the speculative trend from the $\alpha_0(c)$ values, which requires further exploration.

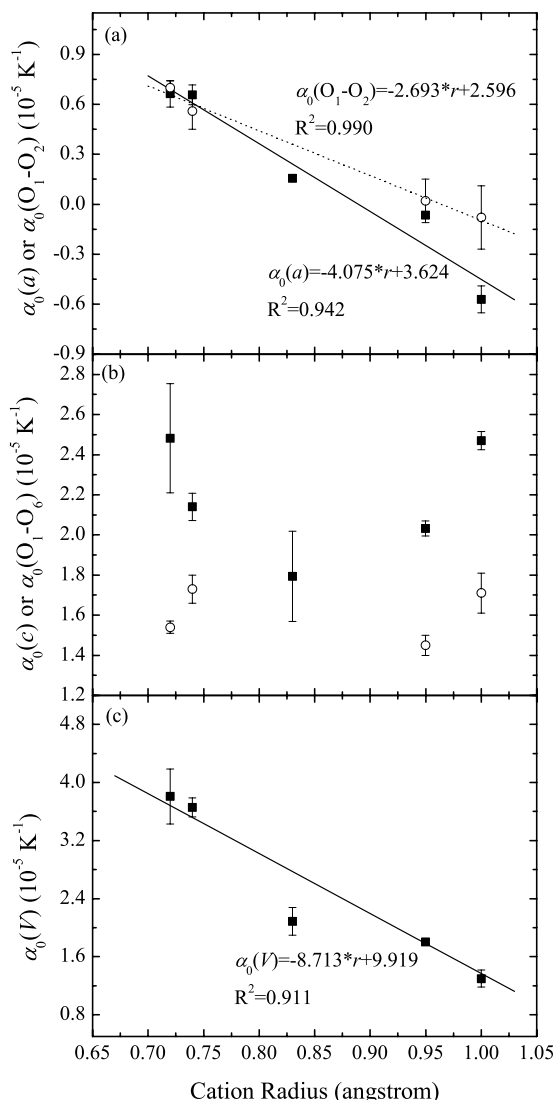


Fig. 9. Effect of cationic radius on the thermal expansion coefficients (room temperature) of the five calcite-structure carbonates. The filled solid squares represent the results from the cell parameters, and the open circles represent those from the structure parameters. The ionic radius data are from [Shannon \(1976\)](#).

Moreover, an inverse correlation between the $\alpha_0(V)$ values and the ionic radius is observed in this study and fits the approximate expression $\alpha_0(V) (10^{-5} \text{ K}^{-1}) = -8.713 * r + 9.919$. The variation of $\alpha_0(V)$ values with the cationic radius is suggested to be clearly related to those of a parameters, owing to the higher weight of a parameters on the volume with respect to that of c parameters, and the trend between the $\alpha_0(V)$ and $\alpha_0(a)$ values is presented in [Fig. 10](#). The $\alpha_0(V)$ values increase with increasing $\alpha_0(a)$, however, the trend is close to an exponential instead of linear relationship. No clear dependence of the $\alpha_0(V)$ values on the ionic radius was reported by [Reeder \(1983\)](#) and [Ballirano \(2016\)](#).

An approximately linear trend of volume thermal expansion with (M–O) bond length is also observed,

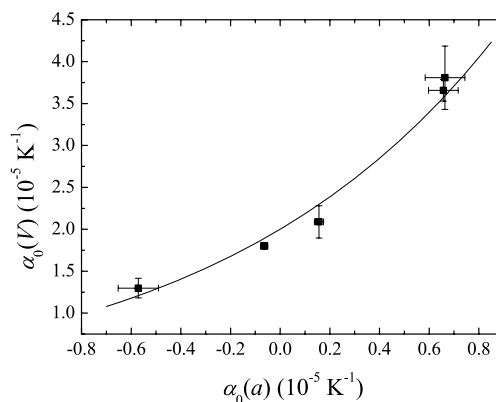


Fig. 10. Dependence of the $\alpha_0(V)$ values on $\alpha_0(a)$ values. The solid curve is a visual aid and has no physical significance.

whereas no clear correlation exists between the volume thermal expansion and electronegativity.

4. Conclusions

Unit-cell and crystal structure parameters of five calcite-structure carbonates (magnesite (MgCO_3), smithsonite (ZnCO_3), rhodochrosite (MnCO_3), otavite (CdCO_3), and calcite (CaCO_3)) were acquired via *in situ* powder X-ray diffraction over a temperature range from 83 to 618 K. Thermal expansion of these carbonates displays strong anisotropy, *i.e.*, larger expansion coefficients along the c -axis than those of the a -axis for magnesite, smithsonite, and rhodochrosite; positive expansion coefficients along the c -axis with reversal and negative expansion coefficients along the a -axis for otavite and calcite, respectively. Such behaviour could be explained by their featured crystal structure. In addition, negative thermal expansion along the a -axis of otavite and calcite is attributed to their relatively large libration motion of CO_3 groups along the c -axis, as the corresponding $\text{O}_1\text{--O}_2$ bond distances remain approximately constant with temperature in contrast to the increase observed for magnesite and smithsonite. Experimental results in this investigation show that the $\alpha_0(V)$ and $\alpha_0(a)$ values exhibit negative relations with the ionic radius of the cations, which can be roughly expressed by $\alpha_0(V) (10^{-5} \text{ K}^{-1}) = -8.713 * r + 9.919$ and $\alpha_0(a) (10^{-5} \text{ K}^{-1}) = -4.075 * r + 3.624$, respectively, and it is proposed to be correlated to the systematic thermal behaviour of $\text{O}_1\text{--O}_2$ bond with the cation size. However, due to the effect of relatively large libration motion of CO_3 groups along c -axis, the $\alpha_0(c)$ values of otavite and calcite are larger than those predicted from the inverse linear trend among magnesite, smithsonite and rhodochrosite.

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References

- Antao, S.M., Hassan, I., Mulder, W., Lee, P.L., Toby, B.H. (2009): *in situ* study of the *R*-3*c* to *R*-3*m* orientational disorder in calcite. *Phys. Chem. Miner.*, **36**, 159–169.
- Ballirano, P. (2016): Thermal behaviour of otavite, CdCO_3 . *Eur. J. Mineral.*, **28**, 285–293.
- Bayer, G. (1971): Thermal expansion anisotropy of dolomite-type borates $\text{Me}^{2+}\text{Me}^{4+}\text{B}_2\text{O}_6$. *Z. Kristallogr.*, **133**, 85–90.
- Berner, R.A. (2003): The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature*, **426**, 323–326.
- Boulard, E., Gloter, A., Corgne, A., Antonangeli, D., Auzende, A. L., Perrillat, J.P., Guyot, F., Fiquet, G. (2011): New host for carbon in the deep Earth. *P. Natl. Acad. Sci.*, **108**, 5184–5187.
- Boulard, E., Goncharov, A.F., Blanchard, M., Mao, W. (2015): Pressure induced phase transition in MnCO_3 and its implications on the deep carbon cycle. *J. Geophys. Res.*, **120**, 4069–4079.
- Dasgupta, R. & Hirschmann, M.M. (2010): The deep carbon cycle and melting in Earth's interior. *Earth Planet. Sci. Lett.*, **298**, 1–13.
- Dove, M.T., Swainson, I.P., Powell, B.M., Tennant, D.C. (2005): Neutron powder diffraction study of the orientational order-disorder phase transition in calcite, CaCO_3 . *Phys. Chem. Miner.*, **32**, 493–503.
- Effenberger, H., Mereiter, K., Zemmann, J. (1981): Crystal structure refinements of magnesite, calcite, rhodochrosite, siderite, smithsonite, and dolomite, with discussion of some aspects of the stereochemistry of calcite type carbonates. *Z. Kristallogr.*, **156**, 233–244.
- Fiquet, G., Guyot, F., Kunz, M., Matas, J., Andrault, D., Hanfland, M. (2002): Structural refinements of magnesite at very high pressure. *Am. Mineral.*, **87**, 1261–1265.
- Gao, J., Zhu, F., Lai, X.J., Huang, R., Qin, S., Chen, D.L., Wu, X. (2014): Compressibility of a natural smithsonite ZnCO_3 up to 50 GPa. *High Pressure Res.*, **34**, 89–99.
- Gillet, P., Biellmann, C., Reynard, B., McMillan, P. (1993): Raman spectroscopic studies of carbonates Part I: High-pressure and high-temperature behaviour of calcite, magnesite, dolomite and aragonite. *Phys. Chem. Miner.*, **20**, 1–18.
- Graf, D.L. (1961): Crystallographic tables for the rhombohedral carbonates. *Am. Mineral.*, **46**, 1283–1316.
- Hazen, R.M. & Schiffrins, C.M. (2013): Why deep carbon. *Rev. Mineral. Geochem.*, **75**, 1–6.
- Hazen, R.M., Downs, R.T., Jones, A.P., Kah, L. (2013): Carbon mineralogy and crystal chemistry. *Rev. Mineral. Geochem.*, **75**, 7–46.
- Javoy, M., Pineau, F., Allègre, C.J. (1982): Carbon geodynamic cycle. *Nature*, **300**, 171–173.
- Larson, A.C. & Von Dreele R.B. (2000): GSAS-General Structure Analysis System. Los Alamos National Laboratory, Los Alamos.
- Liou, J.G., Zhang, R.Y., Ernst, W.G. (1995): Occurrences of hydrous and carbonate phases in ultrahigh-pressure rocks from east-central China: Implications for the role of volatiles deep in cold subduction zones. *Isl. Arc*, **4**, 362–375.
- Litasov, K.D., Fei, Y., Ohtani, E., Kuribayashi, T., Funakoshi, K. (2008): Thermal equation of state of magnesite to 32 GPa and 2073 K. *Phys. Earth Planet. Int.*, **168**, 191–203.
- Markgraf, S.A. & Reeder, R.J. (1985): High-temperature structure refinements of calcite and magnesite. *Am. Mineral.*, **70**, 590–600.
- Maslen, E.N., Streltsov, V.A., Streltsova, N.R., Ishizawa, N. (1995): Electron density and optical anisotropy in rhombohedral carbonates. III. Synchrotron X-ray studies of CaCO_3 , MgCO_3 and MnCO_3 . *Acta Crystallogr.*, **51**, 929–939.
- Merlini, M., Sapelli, F., Fumagalli, P., Gatta, G.D., Lotti, P., Tumiat, S., Abdellatif, M., Lausi, A., Plaisier, J., Hanfland, M., Crichton, W., Chantel, J., Guignard, J., Meneghini, C., Pavese, A., Poli, S. (2016): High-temperature and high-pressure behavior of carbonates in the ternary diagram CaCO_3 - MgCO_3 - FeCO_3 . *Am. Mineral.*, **101**, 1423–1430.
- Minch, R., Seoung, D.H., Ehm, L., Winkler, B., Knorr, K., Peters, L., Borkowski, L.A., Parise, J.B., Lee, Y., Dubrovinsky, L., Depmeier, W. (2010): High-pressure behavior of otavite (CdCO_3). *J. Alloy. Compd.*, **508**, 251–257.
- Nie, S., Liu, Y., Liu, Q., Wang, M., Wang, H. (2017): Phase transitions and thermal expansion of BaCO_3 and SrCO_3 up to 1413 K. *Eur. J. Mineral.*, **29**, 433–443.
- Oganov, A.R., Ono, S., Ma, Y., Glass, C.W., Garcia, A. (2008): Novel high-pressure structures of MgCO_3 , CaCO_3 and CO_2 and their role in Earth's lower mantle. *Earth Planet. Sci. Lett.*, **273**, 38–47.
- Ono, S., Kikegawa, T., Ohishi, Y. (2007): High-pressure transition of CaCO_3 . *Am. Mineral.*, **92**, 1246–1249.
- Rao, K.K. (1974): Thermal expansion and crystal structure. *Am. Inst. Physics. Conf. Proc.*, **17**, 219–230.
- Rao, K.K. & Murthy, K.S. (1970): Thermal expansion of manganese carbonate. *J. Mater. Sci.*, **5**, 82–83.
- , — (1974): Thermal expansion of zinc carbonate. *J. Mater. Sci.*, **9**, 1196–1197.
- Reeder, R.J. (1983): Crystal chemistry of the rhombohedral carbonates. *Rev. Mineral. Geochem.*, **11**, 1–47.
- Ride, D.R. (1998) Handbook of Chemistry and Physics (79th edition). CRC Press, Boca Raton.
- Santillán, J. & Williams, Q. (2004): A high-pressure infrared and X-ray study of FeCO_3 and MnCO_3 : comparison with $\text{CaMg}(\text{CO}_3)_2$ -dolomite. *Phys. Earth Planet. Int.*, **143**, 291–304.
- Seto, Y., Hamane, D., Nagai, T., Fujino, K. (2008): Fate of carbonates within oceanic plates subducted to the lower mantle and a possible mechanism of diamond formation. *Phys. Chem. Miner.*, **35**, 223–229.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, **A32**, 751–767.
- Shatskiy, A.F., Litasov, K.D., Palyanov, Y.N. (2015): Phase relations in carbonate systems at pressures and temperatures of lithospheric mantle: review of experimental data. *Russ. Geol. Geophys.*, **56**, 113–142.
- Shi, G.H., Tropper, P., Cui, W.Y., Tian, J., Wang, C.Q. (2005): Methane- (CH_4) -bearing fluid inclusions in Myanmar jadeites. *Geochem. J.*, **39**, 503–516.
- Sleep, N.H. & Zahnle, K. (2001): Carbon dioxide cycling and implications for climate on ancient Earth. *J. Geophys. Res.*, **106**, 1373–1399.

- Solopova, N.A., Dubrovinsky, L., Spivak, A.V., Litvin, Y.A., Dubrovinskaia, N. (2015): Melting and decomposition of MgCO_3 at pressures up to 84 GPa. *Phys. Chem. Miner.*, **42**, 73–81.
- Suito, K., Namba, J., Horikawa, T., Taniguchi, Y., Sakurai, N., Kobayashi, M., Kikegawa, T. (2001): Phase relations of CaCO_3 at high pressure and high temperature. *Am. Mineral.*, **86**, 997–1002.
- Tao, R., Fei, Y., Zhang, L. (2013): Experimental determination of siderite stability at high pressure. *Am. Mineral.*, **98**, 1565–1572.
- Toby B.H. (2001): EXPUGI, a graphical user interface for GSAS. *J. Appl. Cryst.*, **34**, 210–213.
- Zhang, J. & Reeder, R.J. (1999): Comparative compressibilities of calcite-structure carbonates: Deviations from empirical relations. *Am. Mineral.*, **84**, 861–870.
- Zhang, Y. & Zindler, A. (1993): Distribution and evolution of carbon and nitrogen in Earth. *Earth Planet. Sci. Lett.*, **117**, 331–345.
- Zhang, J., Martinez, I., Guyot, F., Gillet, P., Saxena, S.K. (1997): X-ray diffraction study of magnesite at high pressure and high temperature. *Phys. Chem. Miner.*, **24**, 122–130.
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