In situ X-ray diffraction of aragonite and dolomite at high pressure and high temperature: Evidence for dolomite breakdown to aragonite and magnesite

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ABSTRACT

Energy-dispersive X-ray powder diffraction spectra have been collected for aragonite (CaCO₃) and dolomite [CaMg(CO₃)₂] at high pressure and high temperature, using synchrotron radiation and a cubic multi-anvil apparatus. Unit-cell volumes were measured up to 7 GPa and 1073 K along several isothermal paths. This study has confirmed previously determined but still debated values of the bulk incompressibilities at 298 K [65.4(5) GPa for aragonite and 90.7(7) GPa for dolomite] and thermal expansivities at 1 bar [6.7(5) × 10⁻⁵ K⁻¹ for aragonite and 4.1(5) × 10⁻⁵ K⁻¹ for dolomite]. New equation-of-state parameters were also measured: (0K/0P)ₚ = -0.013(2) and -0.025(4) GPa/K for aragonite and dolomite, respectively, and K₀ = 12.7(7) and 2.3(5) for aragonite and dolomite, respectively. These equation-of-state parameters could be used in the calculation of high-temperature, high-pressure thermodynamic properties of these carbonates.

At pressures exceeding 5 GPa, we observed that dolomite breaks down to aragonite and magnesite. We used the equation-of-state parameters measured in this study to calculate the position of the equilibrium curve: dolomite → aragonite + magnesite. This reaction could be important in the ultra-high-pressure metamorphism of carbonates. This decomposition reaction also provides a useful test of thermodynamic data sets of carbonates at high pressures and temperatures.

INTRODUCTION

To understand the stability of carbonates in the deep Earth as well as the CO₂ outgassing caused by meteorite impacts on the Earth’s surface, it is important to know the physical properties of carbonates at the high pressures and temperatures characteristic of the Earth’s mantle and of shock metamorphism. Following earlier work performed at P < 4 GPa (Irving and Wyllie 1975; Byrnes and Wyllie 1981), several experiments using diamond-anvil cells or multi-anvil apparatus have recently been conducted on carbonates (Katsura and Ito 1990; Canil and Scarfe 1990; Kraft et al. 1991; Williams et al. 1992; Biellmann and Gillet 1992; Ross and Reeder 1992; Biellmann et al. 1993a, 1993b; Gillet et al. 1993; Gillet et al. 1993; Fiquet et al. 1994; Redfern et al. 1993; Ross 1994). Most of these studies concluded that, although carbonates break down at high temperature under low-pressure conditions, they remain stable at simultaneous high pressures and high temperatures (e.g., 30 GPa and 2000 K).

More specifically, aragonite and dolomite have been studied at room temperature using high-pressure Raman and infrared spectroscopy (Kraft et al. 1991; Biellmann and Gillet 1992; Gillet et al. 1993) and P up to 30–40 GPa. In the study by Kraft et al. (1991), infrared spectra of dolomite were collected under high pressure and moderate temperature (up to 550 K), and Raman and infrared spectra were obtained from high-pressure samples quenched from high temperatures (800 K for dolomite and 2100 K for aragonite). Neither destabilization reactions nor phase transformations of dolomite or aragonite were reported in these studies. However, in an analytical transmission electron microscopy study of samples quenched from high temperature and pressures between 20 and 50 GPa, Biellmann et al. (1993b) reported the breakdown of dolomite into calcite and magnesite. In the presence of silicates (pyroxenes or olivines), they observed the formation of magnesite owing to dolomite decomposition, in agreement with petrologic work at lower pressures (Kushiro et al. 1975; Wyllie and Huang 1976; Eggle 1978; Wallace and Green 1988) and the high-pressure study of Katsura and Ito (1990). There is now a clear need for quantitative data to characterize the stability relations of these phases and to resolve the apparent contradictions in the literature. In addition to phase-equilibrium studies, an alternative approach for studying the poorly known phase relations of aragonite and dolomite at deep-mantle conditions is to measure their equations of state (EOS) at high pressures and temperatures.

Dynamic high-pressure studies have also been per-
THE C.T. FURNACE

FIGURE 1. Cell assembly used for high P-T X-ray diffraction study in the 6/4 system of the cubic-anvil press (SAM 85). T.C. = thermocouple, BE (4:1) = boron-epoxy mixture with weight ratio 4:1, BN = boron nitride, Re = rhenium foil, Pt = platinum wire, used to provide electrical contact.

We report the high P-T EOS of dolomite and aragonite as well as the high-pressure breakdown of dolomite to aragonite and magnesite. The high P-T EOS of magnesite is given in a separate study (Zhang et al. 1994).

EXPERIMENTAL TECHNIQUE AND RESULTS

Samples

The aragonite and dolomite samples were selected from pure single crystals from Eugui, Spain. The unit-cell parameters of the aragonite sample used in this work, refined at ambient conditions (P = 1 bar, T = 298 K), are a = 4.967(3), b = 7.961(3), c = 5.744(4) Å, in reasonably good agreement with the values given on the JCPDS card (5-453) of a = 4.959, b = 7.96, c = 5.741 Å. The a and c unit-cell parameters of dolomite at room pressure and room temperature are a = 4.804(2) and c = 15.99(1) Å, comparing well with the data from Ross and Reeder (1992), a = 4.8064(5) and c = 16.006(2) Å, for the same dolomite sample. Eugui dolomite has been used in several other studies (Barber et al. 1981; Reeder 1983; Reeder and Markgraf 1986). The 1 bar room-temperature work by Reeder and Wenk (1983) shows that the composition, Ca_{0.99}Mg_{0.01}Fe_{0.01}Mn_{0.002}(CO_3)_{2}, and cation ordering are nearly ideal. Moreover, transmission electron microscopy shows that Eugui dolomite is homogeneous, with very low density of dislocations (Barber et al. 1981; Reeder and Wenk 1983). Over the P-T range investigated in this study, it is unlikely that cation disorder ever occurred in the sample, even at the highest temperature of 1173 K. It has been shown that no significant disorder occurs in dolomite at 1 bar below 1173 K (Reeder 1983); moreover, at 1 GPa, complete disorder occurs at temperatures exceeding 1400 K (Reeder and Nakajima 1982).

High-pressure, high-temperature diffraction experiments

The high-pressure, high-temperature experiments were performed in a DIA-type, cubic anvil apparatus (SAM-85) operated at the superconductor wiggler synchrotron radiation beamline (X17B) of the National Synchrotron Light Source at Brookhaven National Laboratory. In these experiments the second-stage anvils were made of tungsten carbide, with 4 x 4 mm$^2$ square truncations, and the pressure medium was a 6 mm edge cube made of amorphous boron epoxy. Figure 1 is a schematic diagram of the cell assembly used in this system. The powdered sample, together with a layer of NaCl-BN powder mixture, was placed in a boron nitride sleeve in an amorphous carbon furnace. The EOS of NaCl (Decker 1971) was used to determine the pressure at any given temperature, whereas BN was used to prevent recrystallization of the salt during heating. Alumina sleeves and zirconia disks were used to separate the furnace from the pressure medium and the anvils; electrical contact between furnace and anvils was achieved with platinum wires and rhenium discs. A dc power supply was used to provide constant heating, and temperatures were directly measured.
in the sample with a W5%Re-W26%Re thermocouple. Pyrophyllite gaskets were used to protect the thermocouple. Previous studies have focused on the characterization of the sample environment both in terms of pressure and temperature gradients (Weidner et al. 1992). In those studies, the maximum temperature gradient at high temperatures (>900 K) and along a vertical axis was estimated to be 20 K from top to bottom of the cell assembly. However, this temperature gradient can be considered a maximum because X-ray diffraction spectra are collected on the portion of the sample closest to the thermocouple junction. As shown by Weidner et al. (1992), pressure gradients are negligible throughout the cell, especially when differential stresses are relaxed during and after heating.

The incident X-ray beam was collimated with 100 µm slits in the vertical direction and 200 µm slits in the horizontal direction. Energy-dispersive X-ray diffraction patterns were collected with a solid-state Ge detector, placed at a fixed 2θ angle of 7.5°, with a mean acquisition time of 200 s. The multichannel analyzer was calibrated before and after the experiment for both energy and 2θ position. The energy calibration and calculation of the 2θ angle were made in a one-step procedure (program “autocal”) using characteristic fluorescence lines of molybdenum and lead, as well as the positions of diffraction lines from an assemblage of standards, Si, Al₂O₃, and MgO. This calibration is accurate in the 25–75 keV energy range. During an experiment, the drift in 2θ and energy calibration did not exceed 0.05% and is thus considered as negligible.

The P-T paths followed in the experiments are shown in Figures 2a and 2b for aragonite and dolomite, respectively. The sample was first compressed at room temperature. Temperature was then increased slowly at constant ram load, leading to a decrease of the sample pressure because of both relaxation processes in the cell and gasket flow. The sample was then cooled; the cell pressure decreased again because of the loss of thermal pressure. Heating and cooling cycles were then repeated for several ram loads. After the first heating and cooling cycle, increasing temperature led to an increase in cell pressure because the cell had already relaxed. At chosen P and T conditions, reported in Tables 1 and 2 for aragonite and dolomite, respectively, we collected energy-dispersive X-ray spectra for both the sample and the NaCl.

Measurements of pressure and nonhydrostatic stress in the cell

The d_{202} values of NaCl were obtained by nonlinear least-squares fitting of the recorded X-ray diffraction spectra using a program called GPLS (General Purpose Least Square) and by use of our own calibration program. Then, the unit-cell parameters and volume were refined by a least-squares fitting of the values of Q_{202} = 1/d^2 using the 111, 200, 220, 222, and 420 diffraction lines. The Decker EOS (Decker 1971) was then used with volume and temperature measurements to determine pressure. The use of other EOS for NaCl (e.g., Birch 1978) does not change the pressure within this pressure and temperature range (Meng et al. 1993), and the precision of the pressure determination is estimated to be better than 0.2 GPa (Meng et al. 1993; Wang et al. 1994).

Nonhydrostaticity in the cell is a very crucial parameter because it affects the determination of both pressure and unit-cell volume of the sample. Nonhydrostatic stresses are removed by heating the sample above the temperature at which it yields and begins to deform plastically. The differential stresses can be estimated quantitatively in the NaCl using the method developed by Weidner et al. (1992) and are given in Tables 1 and 2. In these tables, the differential stress is the difference between the axial and radial stresses, both being negative.
for compression. We generally observe in this cell assembly that compression at room temperature induces negative differential stresses (i.e., axial stress greater than radial stress in absolute values), whereas both cooling and decompression result in positive differential stresses. It appears that in these particular experiments, most of the differential stresses were relaxed when the cell was heated above 700–800 K. When the cell assembly was loaded with materials such as olivine or garnet, higher temperatures were required to remove the nonhydrostatic stress. It should be noted that the absence of differential stress in the NaCl does not necessarily imply zero differential stress in the sample. Weidner et al. (1994) showed that the line width of diffraction peaks in the sample is a good indicator of local deviations from hydrostaticity. This effect is also apparent in carbonates as shown in Figure 3,
which compares the X-ray diffraction spectra of aragonite after pure compression (Fig 3a) and heating at 873 K (Fig 3b). Empirically, differential stress-free spectra are characterized by line widths similar to or even narrower than those in the sample at ambient conditions. Only data with narrow diffraction lines as well as reasonably low nonhydrostaticity measured in the NaCl (typically when the absolute value of the differential stress is smaller than 0.1 GPa) were used for EOS determinations.

**Measurement of lattice parameters and EOS**

The $d_{	ext{hkl}}$ values of aragonite and dolomite were obtained by nonlinear least-squares fitting of the recorded X-ray diffraction spectra and our own calibration program. Then, the unit-cell parameters and volume were refined by least-squares fitting the values of $Q_{	ext{hkl}} = 1/d^2$ (program “celrer”) using 10–14 and 6–8 diffraction lines for aragonite and dolomite, respectively. For aragonite we used 111, 021, 121, 012, 200, 031, 112, 130, 022, 211, 221, 202, 132, and 113; and for dolomite we used 1014, 0006, 0115, 1120, 1123, 2022, 0118, and 1126. Unit-cell volumes and lattice parameters are reported in Tables 3 and 4 for aragonite and dolomite, respectively. Some of the aragonite data points, obtained with calcite as a starting material, loaded in the same cell and transformed in situ during the experiment, are also reported in Table 3. This calcite was loaded a few millimeters above the aragonite. The very small differences in unit-cell parameters and volume measurements between these two sets of data confirm the small pressure and temperature gradients in the cell assembly.

**Breakdown of dolomite into aragonite and magnesite**

In our first attempt to determine the high $P$-$T$ EOS of dolomite, we compressed the sample to 8 GPa and heated it. Above 673 K (7.2 GPa), the X-ray diffraction spectra changed dramatically (Figs. 4a and 4b); aragonite and magnesite peaks appeared. At 973 K (7 GPa), all dolomite peaks had disappeared, indicating that the breakdown of dolomite into aragonite and magnesite was complete (Fig. 4c). The unit-cell volumes of aragonite and magnesite in the assemblage are shown in Table 5. They differ only marginally from the unit-cell volumes of pure magnesite, also measured in the same experiment, and those of pure aragonite, determined in a separate experiment at similar conditions. This suggests that the amounts of Mg in aragonite and of Ca in magnesite are very low because the unit-cell parameters of the two phases would have been significantly affected otherwise. In Figure 4, it is interesting to note that the diffraction lines of the new phases are sharper than those of the dolomite, suggesting that magnesite and aragonite grains grew in an environment that was relatively free of differential stress. In a second experiment performed to locate the breakdown conditions more precisely, we followed a different $P$-$T$ path (path 4 in Fig. 2b). Dolomite was compressed to $P = 5.5$ GPa, heated to 873 K ($P = 5$ GPa), and then recompressed at constant temperature until the breakdown reaction was observed. Onset of the decomposition occurred at 5.7 GPa after these conditions were maintained for more than 90 min. Further compression at 873 K up to 7.4 GPa did not significantly change the proportions between reacted and unreacted material. It was necessary to heat the sample to 1073 K to complete the reaction, suggesting that the breakdown kinetics are quite sluggish at conditions close to equilibrium. For the same reason, attempts to reverse the breakdown reaction at 1073 K and lower pressure suffered kinetic problems.

**Discussion**

**Methods for EOS data processing**

**Isothermal Birch-Murnaghan equation of state.** The measured unit-cell volumes of aragonite and dolomite were fitted along isothermal curves with a Eulerian finite-strain Birch-Murnaghan EOS (Fig. 5):

$$
P = \frac{1}{2} K_0 T \left[ \left( \frac{V_{0,T}}{V} \right)^{7/3} - \left( \frac{V_{0,T}}{V} \right)^{5/3} \right] \cdot \left[ 1 + \frac{4}{3} \left( K_0 T - 4 \right) \left( \frac{V_{0,T}}{V} \right)^{2/3} - 1 \right].$$

(1)
The three parameters \( V_{0,T}, K_{0,T}, \) and \( K'_{0,T} \) (the volume, the bulk modulus, and the pressure derivative of the bulk modulus, respectively) were derived from this equation, all at 1 bar and at the temperature of the specific isotherm. In the present study, the investigated compression range combined with the relatively few data points for each isotherm did not allow us to determine all three parameters independently and with reasonable accuracies. Therefore, we decided to adopt the common assumption that \( K'_{0,T} \) is a constant equal to 4, which is identical to restricting the Birch-Murnaghan EOS to second order (e.g., Poirier 1991). The \( K_{0,T} \) and \( V_{0,T} \) parameters were thus determined for temperatures ranging from 298 to 973 K and are reported in Table 6 together with the uncertainties of the fit to a second-order Birch-Murnaghan equation. The temperature dependence of \( K_{0,T} \) can be simply described by

\[
K_{0,T} = K_{0,298\text{ K}} + (dK_{0,T}/dT)(T - 298) \tag{2}
\]

as is shown in Figure 6, in which the average value of \( dK_{0,T}/dT \) deduced from a linear fit as well as the standard deviation to the fit are given. It is also possible (Fig. 7) to obtain an average thermal expansion coefficient \( \langle \alpha \rangle_{298-1000\text{ K}} \) between 298 and 1000 K, defined by

\[
V_{0,T} = V_{0,298\text{ K}} \{1 + \langle \alpha \rangle_{298-1000\text{ K}} [T(K) - 298]\}. \tag{3}
\]

The difference between this linear fit and a more exact exponential fit is negligible in the temperature range considered in the study. Values of \( K_{0,T}, K'_{0,T}, dK_{0,T}/dT, \) and \( \langle \alpha \rangle_{298-1000\text{ K}} \) are summarized in Table 7, along with EOS parameters from earlier work for comparison. Strictly speaking, the parameter \( dK_{0,T}/dT \) is different from the usual \( (\partial K/\partial T)_P \), but it is likely that this difference is small and contained within the experimental error bars.

**High-temperature Birch-Murnaghan equation of state.** To crosscheck the EOS analysis, we also performed for each phase an inversion of the whole set of experimental data, on the basis of the third-order Birch-Murnaghan
equation of state at high temperature (HTBM), proposed by Saxena and Zhang (1990). This equation is modified from Equation 1 in the following way: \( V_{0,T} \) is written as

\[
V(0, T) = V_{0,298} \exp \left[ \int_{298}^{T} \alpha(T) \, dT \right]
\]

and the isothermal incompressibility is given by Equation 2. To test the sensitivity to the functional forms used in the EOS, other temperature dependencies of \( \alpha \) were checked, such as

\[
\alpha(T) = \alpha_0 + \alpha_1/T^2.
\]

Because of the limited pressure and temperature ranges of this study, \( K_{0,T} \) was assumed to be independent of temperature. With this procedure, six parameters are refined, namely \( V_{0,298} \), \( K_{0,298} \), \( K_{0,T} \), \( dK_{0,T}/dT \), \( \alpha_0 \), and \( \alpha_1 \), on the basis of 64 data points for aragonite and 42 data points for dolomite. The results of this inversion are shown in Table 7, together with the uncertainty of the fit. They compare very well with the results obtained using the second-order isothermal Birch-Murnaghan EOS (Table 7). Use of a different functional form for \( \alpha \) by substituting Equation 6 for Equation 5 did not significantly change the results for the other parameters.
TABLE 5. Determination of unit-cell volume of aragonite and magnesite formed in the dolomite breakdown reaction

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$T$ (K)</th>
<th>Unit-cell V magnesite in mix. ($\text{Å}^3$)</th>
<th>Unit-cell V aragonite in mix. ($\text{Å}^3$)</th>
<th>Unit-cell V pure magnesite* ($\text{Å}^3$)</th>
<th>Unit-cell V pure aragonite* ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.02</td>
<td>873</td>
<td>269.2(6)</td>
<td>214.9(3)</td>
<td>267.2(3)</td>
<td>213.1</td>
</tr>
<tr>
<td>6.99</td>
<td>973</td>
<td>267.0(5)</td>
<td>214.0(2)</td>
<td>268.7(1)</td>
<td>214.2</td>
</tr>
<tr>
<td>6.86</td>
<td>1073</td>
<td>271.6(6)</td>
<td>215.4(1)</td>
<td>269.6(2)</td>
<td>215.4</td>
</tr>
<tr>
<td>6.78</td>
<td>1173</td>
<td>270.7(2)</td>
<td>216.7(2)</td>
<td>272.8(6)</td>
<td>216.4</td>
</tr>
<tr>
<td>6.74</td>
<td>1273</td>
<td>274.8(2)</td>
<td>218.2(3)</td>
<td>272.5(1)</td>
<td>217.5</td>
</tr>
</tbody>
</table>

* Measured at the same $P$-$T$ conditions in the same experiment; see Zhang et al. (1994).
** Calculated from the closest experimental conditions at the same temperature, in pure aragonite experiment, corrected for the pressure difference with a $K_o$ value estimated at these $P$-$T$ conditions.

**TABLE 6.** Determination of $K_{0,T}$, $V_{0,T}$ along isotherms, assuming $K_{0,T} = 4$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_{0,T}$ (GPa)</th>
<th>$V_{0,T}$ ($\text{Å}^3$)</th>
<th>$\delta V_{0,T}$* ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>91.3</td>
<td>320.6</td>
<td>0.4</td>
</tr>
<tr>
<td>373</td>
<td>88.3</td>
<td>321.6</td>
<td>0.75</td>
</tr>
<tr>
<td>473</td>
<td>82</td>
<td>324.2</td>
<td>0.03</td>
</tr>
<tr>
<td>573</td>
<td>83.4</td>
<td>324.2</td>
<td>0.5</td>
</tr>
<tr>
<td>673</td>
<td>74.9</td>
<td>326.4</td>
<td>0.3</td>
</tr>
<tr>
<td>773</td>
<td>79.2</td>
<td>326.7</td>
<td>0.2</td>
</tr>
<tr>
<td>873</td>
<td>70.9</td>
<td>329.1</td>
<td>0.4</td>
</tr>
<tr>
<td>973</td>
<td>75.3</td>
<td>329.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Thermal pressure. The thermal pressure formalism has been successfully used to analyze high-temperature EOS data [e.g., Anderson (1984) and his subsequent studies]. The differential thermal pressure is determined by subtracting the pressure at volume $V$ and room temperature obtained using Equation 1 from that measured at the same $V$ but at temperature $T$. The differential thermal pressure $\Delta P_{V}$ is thus the difference between the thermal pressure at $T$ and the thermal pressure at room temperature:

$$\Delta P_{V} = P_{V}(V, T) - P_{V}(V, 298 \text{K}) = P(V, T) - P(V, 298 \text{K}).$$

Results of thermal pressure analysis on aragonite and dolomite are shown in Figure 8.

EOS parameters of aragonite and dolomite

Aragonite. Unit-cell volumes of aragonite are shown in Figure 5 along different isothermal curves. The results of the isothermal second-order Birch-Murnaghan analysis are shown in Table 6 and Figures 6a and 7a. The value of $K_{0,T} = 64.8(4.3)$ GPa determined in this work is consistent with previously determined values of 64.5 GPa (Birch 1966), 66.7 GPa (Salje and Viswanathan 1976), and 64.5 GPa (Martens et al. 1982). The average thermal expansion coefficient between 298 and 1000 K is $\langle \alpha \rangle_{298-1000 K} = 6.5(1) \times 10^{-5}$ K$^{-1}$. In the specific case of aragonite, thermal expansion had never been studied over such a wide range of temperature because at ambient pressure aragonite transforms back to calcite upon heating. The value given in Salje and Viswanathan (1976), measured up to 573 K, compares well with our value. A linear fit with Equation 2 suggests that the temperature derivative of the bulk modulus is close to $-0.018$ GPa/K (Fig. 6a). The analysis using the high-temperature, third-order Birch-Murnaghan EOS confirms these results and provides ad-
The bulk modulus as a function of temperature. Each value of \( K_{0,T} \) has been determined from fitting the volume data along an isotherm. A linear fit of these data leads to the value of \( dK_{0,T}/dT \) shown for (a) aragonite and (b) dolomite with \( K_{0,T} = 4 \). The numbers in parentheses correspond to residuals of the linear fit.

Additional evidence that \( K_{0,T} \) is very likely to be <4 (Table 7). The thermal pressure in aragonite at temperatures above 298 K is shown in Figure 8a as a function of temperature. The trend is approximately linear, yielding an average \( aK \) value of 0.0039(2) GPa/K, in qualitative agreement with the values of both (\( aK \))_{298-1000K} and \( K_{0,T} \) determined above. Within the precision of the present data at a given temperature, it is impossible to detect any significant volume dependence.

Dolomite. The value of \( K_{0,298} \) reported in this study \([K_{0,298 K} = 90.7(7)\), Table 7] is slightly lower than the value of \( K_{0,298 K} = 112.9(2.2) \), with \( K_{0,T} = 4 \), reported by Fiquet et al. (1994). The high value of \( K_{0,298 K} \) reported in this room-temperature diamond-anvil cell study might be due to nonhydrostatic conditions that can significantly affect the \( V \) measurements. This difference might also be due to the existence of a change in compression mechanism detected at 4 GPa in the study of Fiquet et al. (1994). The small number of data points collected in dolomite in our study at room temperature and pressures exceeding 4 GPa does not allow us to resolve this issue. Our value compares well with \( K_{0,298 K} = 94.1(7) \), \( aK = 4 \), obtained by Ross and Reeder (1992), and \( K_{0,298 K} = 94.9 \) GPa derived from single-crystal ultrasonic measurement of Humbert and Plique (1972). The variations of \( aK \) and \( V_{0,T} \) with temperature are plotted in Figures 6b and 7b. A linear fit with Equation 2 suggests that the temperature derivative of the bulk modulus is close to \(-0.026 \) GPa/K (Fig. 6b). The analysis using the high-temperature, third-order Birch-Murnaghan EOS provides a similar value for \( dK_{0,T}/dT \) of \(-0.025(4) \) GPa/K (Table 7). The average thermal expansion coefficient between 298 and 1000 K, \( (aK)_{298-1000K} = 4.2(3) \times 10^{-5} \) K^{-1}, is in reasonable agreement with the value of \( 3.79 \times 10^{-5} \) K^{-1} determined by Reeder and Markgraf (1986). The inversion with the high-temperature, third-order Birch-Mur-
Table 7. Equation-of-state parameters of aragonite and dolomite

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$K_o (\text{GPa})$</th>
<th>$K_o^{*}$</th>
<th>$(\text{d}K_o/\text{d}T) (\text{GPa/K})$</th>
<th>$(\alpha)_{300-1000}^o (10^{-9}\text{K}^{-1})$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.5</td>
<td>4</td>
<td>---</td>
<td>---</td>
<td>sample dimensions</td>
</tr>
<tr>
<td>2</td>
<td>66.66</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>piston displacement</td>
</tr>
<tr>
<td>3</td>
<td>64.52</td>
<td>2.7 ± 0.7</td>
<td>-0.018(2)</td>
<td>6.5 ± 0.1</td>
<td>ultrasonic</td>
</tr>
<tr>
<td>4</td>
<td>64.8 ± 4.3</td>
<td>4</td>
<td>-0.013(2)</td>
<td>6.7 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>5*</td>
<td>65.4 ± 0.5</td>
<td>2.7 ± 0.7</td>
<td>-0.025(4)</td>
<td>4.2 ± 0.3</td>
<td>X-ray</td>
</tr>
<tr>
<td>6</td>
<td>112.9 ± 2.2</td>
<td>4</td>
<td>-0.026(2)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>7</td>
<td>94.1 ± 0.7</td>
<td>4</td>
<td>-0.022(4)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>8</td>
<td>94.9 ± 0.2</td>
<td>4</td>
<td>-0.025(4)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>9</td>
<td>81.96</td>
<td>4</td>
<td>-0.025(4)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>4*</td>
<td>91 ± 4</td>
<td>4</td>
<td>-0.026(2)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
<tr>
<td>5*</td>
<td>90.7 ± 0.7</td>
<td>2.7 ± 0.7</td>
<td>-0.025(4)</td>
<td>4.1 ± 0.5</td>
<td>X-ray</td>
</tr>
</tbody>
</table>

Note: References are as follows: 1 = Martens et al., 1982; 2 = Sahle and Viswanathan, 1976; 3 = Birch, 1966; 4 = this work, second-order B-M; 5 = this work, third-order B-V; 6 = Fiquet et al., 1994; 7 = Reeder and Markgraf, 1986; 8 = Ross and Reeder, 1992; and 9 = Humbert and Plicque, 1997.

Linear compressibilities and thermal expansions of crystallographic axes

Aragonite. The relative compressions $a/a_0, b/b_0,$ and $c/c_0$ are plotted in Figure 9a for two temperatures, 298 K (solid symbols) and 873 K (open symbols). At room temperature, the $c$ axis of aragonite [mean linear compressibility: $5.8(2) \times 10^{-3} \text{GPa}^{-1}$] is about three times more compressible than the $a$ axis [mean linear compressibility: $2.4(2) \times 10^{-3} \text{GPa}^{-1}$]. The $b$ axis, with a mean linear compressibility of $4.2(2) \times 10^{-3} \text{GPa}^{-1}$, is intermediate between $a$ and $c$. At higher temperatures, within the precision of the present measurements, the same relative order of the linear compressibilities of $a$, $b$, and $c$ is preserved. The relatively high compressibility of the $c$ axis

FIGURE 8. Thermal pressure, calculated using Equation 7, as a function of temperature. (a) Aragonite. Open circles and solid diamonds correspond to calcite and aragonite starting material, respectively. Linear fits of these data (shown here as lines) give a mean value for $\alpha K = 0.0039(2)$ GPa/K. (b) Dolomite. A mean value for $\alpha K = 0.0032(2)$ GPa/K is deduced by a linear fit (solid line) of the data. (c) Dolomite. Thermal pressure as a function of volume at 673, 773, and 873 K, showing volume dependence of thermal pressure at a given temperature.
is readily explained by the fact that it is perpendicular to the planar CO$_2^-$ groups and that this direction does not contain short O-O distances.

Isobaric thermal expansivities of crystallographic axes are represented in Figure 9b for pressures of 3.5 and 8 GPa. They were obtained by a simple and small isothermal pressure correction to the experimental points with pressures close to these two values. The average linear thermal expansion coefficients of $a$ and $b$ between 298 and 1000 K are similar [$<\alpha_{a,b}>_{298-1000\text{ K}} = 1.3(2) \times 10^{-5} \text{ K}^{-1}$ at 3.5 GPa and $<\alpha_{a,b}>_{298-1000\text{ K}} = 1.0(2) \times 10^{-5} \text{ K}^{-1}$ at 8 GPa]. The $c$ axis has a mean linear thermal expansion coefficient that is on average three times larger [$<\alpha_c>_{298-1000\text{ K}} = 3.0(2) \times 10^{-5} \text{ K}^{-1}$ at 3.5 GPa and $<\alpha_c>_{298-1000\text{ K}} = 2.5(2) \times 10^{-5} \text{ K}^{-1}$ at 8 GPa]. The decrease of the thermal expansion coefficient with pressure is quite evident for the $c$ axis. The relative high thermal expansivity of the $c$ axis is related to the same factors giving it a high compressibility. Inverse relation of bond thermal expansivities and bond compressibilities are common, and such relationships often hold for crystallographic axes (e.g., Hazen and Finger 1982).

**Dolomite.** The relative compressions $a/a_0$ and $c/c_0$ at room temperature are plotted in Figure 10a. The abrupt hardening along the $a$ axis observed at room temperature by Fiquet et al. (1994) is not seen here probably because only one data point has been collected at room temperature above 4 GPa in this study. Such a hardening is not
Table 8. Calorimetric data for magnesite, aragonite, and Eugui dolomite

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\text{f}$ (kJ/mol)</th>
<th>$S$ [J/(mol·K)]</th>
<th>$C_p = a + bT + cT^2 + dT^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td>-1111.8*</td>
<td>65.10**</td>
<td></td>
</tr>
<tr>
<td>Aragonite</td>
<td>-1208.16**</td>
<td>88**</td>
<td></td>
</tr>
<tr>
<td>Eugui-dolomite</td>
<td>-2328.34†</td>
<td>155.20**</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from Chai and Navrotsky 1993.
** Holland and Powell 1990.
† Calculated from Chai et al. 1995.

detected at 873 K either. The linear compressibilities at 298 K of the a and c axes are $2.0(1) \times 10^{-3}$ and $5.5(1) \times 10^{-3}$ GPa$^{-1}$, which are consistent with the values $1.9487 \times 10^{-3}$ and $5.7588 \times 10^{-3}$ GPa$^{-1}$ from Ross and Reeder (1992). These results confirm that the c axis is two to three times more compressible than the a axis. This same behavior holds at higher temperatures, and the axial compressibilities at 873 K are also reported in Figure 10. The linear compressibilities of the a and c axes increase with increasing temperature and equal $2.5(2) \times 10^{-3}$ and $6.2(2) \times 10^{-3}$ GPa$^{-1}$ at 873 K, respectively. The structural explanation for the higher compressibility of the c axis in dolomite was discussed by Ross and Reeder (1992).

By applying the same kind of isothermal pressure correction as described for aragonite, we obtain the isobaric mean linear thermal expansivities at different pressures. Figure 10b gives the value of mean linear thermal expansivities at 1 bar obtained by Reeder and Markgraf (1986), as well as our data for 2 and 4 GPa. The anisotropy in the linear thermal expansion ($\alpha_c \approx 2.5 \alpha_a$) does not seem to be affected by pressure up to 4 GPa.

**Thermodynamics of the breakdown reaction of dolomite into aragonite and magnesite**

In addition to the determination of the equation of state for dolomite, we also found that dolomite was metastable vs. aragonite and magnesite above 5-6 GPa (see Fig. 4). Using existing calorimetric data and the EOS determined in this study for dolomite and aragonite, and the EOS for magnesite determined by the same technique (Zhang et al. 1994), we computed the thermodynamic equilibrium for the reaction

$$\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{MgCO}_3.$$  

The Gibbs free energy of reaction, which equals zero at equilibrium, is

$$\Delta_r G^0_{T,P} = \Delta_r G^0_{T,0} + \int_{P_0}^P \Delta_r V_{T,\nu} \, dP$$

where $\Delta_r G^0_{T,0}$ is the standard Gibbs free energy of reaction at room pressure and high temperature and $\Delta_r V(T,P)$ is the volume of reaction at $P$ and $T$, determined from the equations of state. $\Delta_r G^0_{T,P}$ is given by

$$\Delta_r G^0_{T,P} = \Delta_r H^0_{T,0} + \int_{T_0}^{T} \Delta_r C_{P,\nu} \, dT - T \left( \Delta_r S^0_{T,0} + \int_{T_0}^{T} \frac{\Delta_r C_{P,\nu}}{T} \, dT \right)$$

where $\Delta_r H^0_{T,0}$ and $\Delta_r S^0_{T,0}$ are the standard enthalpy and entropy of reaction at 298 K, respectively, and $\Delta_r C_{P,\nu}$ is the heat capacity of reaction. Different values have been reported for standard enthalpies and entropies of carbonates.
ates at 298 K (e.g., Holland and Powell 1990; Saxena et al. 1993), and there are some discrepancies between databases, especially for magnesite (see Table 8). Recent calorimetric measurements of the enthalpy of formation of magnesite have been used here (Chai and Navrotsky 1993). In the case of dolomite, we were careful to use an enthalpy of formation measured for the specific material that we used in this study (i.e., Eugui dolomite) (Chai et al. 1995). The other thermochemical values were taken from Holland and Powell (1990), and all the thermochemical data are summarized in Table 8. In an alternate calculation, we used the data set of Saxena et al. (1993).

The second term on the right side of Equation 9 is obtained by integrating numerically the high-temperature third-order Birch-Murnaghan EOS using our experimental results for dolomite and aragonite and those of Zhang et al. (1994) for magnesite. We also used an analytical form obtained by integrating a Murnaghan EOS (e.g., Fei and Saxena 1986):

$$V(P, T) = V(T_0)\left[1 + a(T - T_0)\left(1 + \frac{K_{0,T}^*}{K_{0,T}}P\right)\right]^{-\frac{1}{K_{0,T}}}$$

Because of the relatively small pressure range, the difference between the two procedures is negligible (a few joules for $\Delta G$). The calculated equilibrium curves are shown in Figure 11. The sensitivity to calorimetric parameters is shown by the difference between the two curves, which were calculated with the use of different calorimetric parameters only. Linear fits lead to $P$ (GPa) = 3.2 + 0.0023$T$ (K) and $P$ (GPa) = 4.2 + 0.019$T$ (K), using the calorimetric data of Chai and Navrotsky (1993) and Chai et al. (1995) and those of Saxena et al. (1993), respectively. The experimentally observed occurrences of dolomite and of the assemblage aragonite + magnesite in the experiments are also reported in Figure 11. The agreement is good overall, but from our experimental data there is no basis for determining which curve is better. More phase-equilibrium data are needed to resolve this issue; so far our attempts to reverse the reaction in situ at the synchrotron beamline were unsuccessful because of the relatively slow reaction rates. In addition to the use of this reaction for testing consistency of thermodynamic data sets involving solid carbonates, the reaction might be important in the ultra-high-pressure metamorphism of carbonates. Evidence for it remains to be detected in ultra-deep metamorphic rocks or in shocked carbonatic materials.

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