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High-pressure behaviour and equation of state of calcite, $CaCO_3$

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Abstract The high-pressure response of the cell parameters of calcite, $CaCO_3$, has been investigated by single crystal X-ray diffraction. The unit cell parameters have been refined from 0 to 1.435 GPa, and the linear and volume compressibilities have been measured as $\beta_a = 2.62(2) \times 10^{-3}$ GPa^{-1}, $\beta_c = 7.94(7) \times 10^{-3}$ GPa^{-1}, $\beta_v = 13.12 \times 10^{-3}$ GPa^{-1}. The bulk modulus has been obtained from a fit to the Birch-Murnaghan equation of state, giving $K_0 = 73.46 \pm 0.27$ GPa and $V_0 = 367.789 \pm 0.004$ Å^3 with $K' = 4$. Combined with earlier data for magnesite, ankerite and dolomite, these data suggest that K_0V_0 is a constant for the Ca-Mg rhombohedral carbonates.

Introduction

Calcite is the dominant C-bearing phase in the Earth's crust, and acts as a buffer for the long-term cycling of CO_2 between the atmosphere, oceans and solid Earth (Berner 1994; Bickle 1996). It is unsurprising, therefore, that the high-pressure stability and behaviour of $CaCO_3$ and related phases has attracted considerable interest. There have been a number of investigations into the pressure response of the structure of calcite as well as its higher-pressure metastable polymorphs, ranging from the pioneering work of Bridgman (1939) to the more recent static X-ray study of Fiquet et al. (1994). Measuring the compressibility of calcite by X-ray diffraction has, however, proven to be a taxing experiment: the range of its metastability at ambient temperature is limited to pressures below approximately 1.5 GPa, at which pressure the rhombohedral calcite structure transforms to a monoclinic polymorph via an elastic instability (Bridgman 1939; Singh and Kennedy 1974; Vo-Thanh and Lacam 1984; Barnett et al. 1985). Most of the high-pressure studies of calcite have, therefore, focused on the transition to monoclinic calcite-II, and the higher-pressure transition to the elusive and unknown structure of calcite-III. The transformations to higher-pressure metastable polymorphs also mean that static crystallographic measurements of the linear compressibilities and bulk modulus of rhombohedral calcite can only be obtained from a very limited range of change in cell parameters: reliable determination of the bulk modulus and compressibility of the cell edges of calcite is highly dependent on the precision and accuracy to which the cell parameters can be obtained as a function of pressure. They are also limited by errors in the measurement of pressure itself.

In this study, we report the first high precision measurements of the pressure response of the unit cell parameters of calcite, exploiting a novel single crystal diffraction system tailored to the determination of cell parameters at high pressure. The unit cell parameters have been measured between 0 and 1.5 GPa, and the isothermal bulk modulus has been obtained from the Birch-Murnaghan equation of state. The anisotropic nature of the structural changes of calcite with pressure is compared with the behaviour of some other rhombohedral carbonates.

Experimental method

The calcite crystal used in this study was taken from an optically clear specimen. A cleavage rhomb, of dimensions of approximately 70 μm, was mounted in a BGI-type diamond anvil cell (Allan et al. 1996), together with a single crystal fragment of twin-free natural quartz and a chip of ruby, used as pressure calibrants. The pressure medium was a 4:1 methanol:ethanol mixture, and the gasket material was 750X inconel. The unit cell parameters of the sample at ambient pressure ($a = 4.9891(3)$ Å, $c = 17.0611(7)$ Å) are in close

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agreement with other measurements of end-member calcite. They indicate that the stoichiometry is $CaCO_3$, with any impurities (in particular $MgCO_3$, but also Fe, Mn, Zn or Cd on the M-site, all of which lower the cell parameters) at less than 1 mol% (Reeder 1983).

Measurement of the shift of the R_1 fluorescence line of ruby, relative to its room pressure value, was used as a preliminary indication of the pressure of the cell on changing pressure. This method is, however, particularly susceptible to the effects of temperature variations between the site of the diffractometer, where diffraction data are obtained, and that of the spectrometer, where pressure readings are obtained: typical temperature variations between instruments can routinely limit the pressure determination to ± 0.05 GPa. An internal diffraction standard, however, provides a means of obtaining pressures to a precision of considerably less than 0.01 GPa. Since the range of pressures over which we can measure the compressional behaviour of calcite is limited (due to the small pressure range of stability), we adopted the more precise method of obtaining pressure data from the compressibility of quartz (Angel et al. 1997).

Single crystal diffraction was conducted using a Huber four-circle diffractometer, purpose designed for precise cell parameter determination. All measurements were made in fixed-phi mode, following the approach of Angel et al. (1997). Unfiltered Mo radiation from a sealed tube source was used, and the large source to crystal and crystal to detector distances allow low FWHM in omega. Eight-position centring was used to determine the setting angles of the crystal and eliminate the effects of zero- and crystal-offsets (King and Finger 1979). At each pressure, the cell parameters of both the calcite sample and quartz internal standard crystals were obtained from the positions of 14 low-angle reflections. Initial cell parameters were obtained as triclinic, without symmetry constraints, as a test of deviations from hexagonal symmetry, but none showed statistically significant deviations. Final cell parameters were determined, for both quartz and calcite, with hexagonal constraints by the vector least-squares method of Ralph and Finger (1982).

Cell parameter behaviour and the I–II transition

The unit cell parameters for calcite at pressures between 0 and 1.5 GPa are reported in Table 1. The cell parameters show a monotonic decrease with pressure, up to 1.435 GPa. At a pressure slightly higher than this, the sample transformed to the monoclinic "calcite-II" structure, at which point it twins and undergoes a spontaneous strain with a shear ε_{13}. Although this transition is ferroelastic in character, with softening of certain elastic constants (Vo Thanh and Lacam 1984), it is strongly first order and we saw no evidence for anomalous compressibility along either the *x* or *z* axes in the rhombohedral calcite structure at pressures approaching the transition, as would be anticipated for a less discontinuous elastically driven transition.

At room temperature and pressure, calcite displays strong neutron inelastic scattering at the F-point of the Brillouin zone, which appears to be a signature of the high-pressure monoclinic calcite-II phase (Dove et al. 1992). In particular, critical phonons at the F-point of the Brillouin zone correspond to a distortion pattern akin to that of the calcite-II polymorph. The transition of calcite-I to calcite-II results from two displacements. First, an 11° rotation in opposite directions of the adjacent CO_3 groups along the *c* axis, and second small antiparallel displacements of adjacent Ca ions. The CO_3 group rotational displacements are thought to drive the transition, just as they drive the high-temperature orientational disordering transition in calcite-I (Redfern et al. 1989). We attempted an investigation of possible pre-cursor ordering and critical phenomena in calcite-I on approaching the I–II transformation, not only by looking for anomalies in the cell-edge compression, but also by looking for diffuse scattering at positions where monoclinic superlattice reflections appear, where the critical F-point fluctuations are assumed important although not fully understood. We searched for diffuse intensity associated with inelastic scattering at a point in reciprocal space (X, Y, Z) with $X = -2.5$, $Y = 0$, $Z = 2$, equivalent to the F-point in the Brillouin zone, which becomes the zone centre (a Bragg reflection) in the monoclinic structure. Scanning between the $\bar{2}04$ reflection and the 300 reflection (the mid-point of this line in reciprocal space shows a peak in diffuse scattering at ambient pressure and temperature) we were unable to detect any additional intensity above the background at any point, despite very long scan times of over 24 hours. We attribute this null result to the difficulties of detecting diffuse intensity from samples held in a diamond anvil cell, where Compton scattering from the diamond increases the

Table 1 Unit cell parameters of calcite to 1.425 GPa

P (GPa)		*a* (Å)		*c* (Å)		Volume (Å^3)	
0.000	± 0.000	4.98914	± 0.00030	17.06107	± 0.00067	367.787	± 0.004
0.902	± 0.005	4.97759	± 0.00022	16.93936	± 0.00051	363.468	± 0.031
0.832	± 0.004	4.97846	± 0.00019	16.94497	± 0.00044	363.715	± 0.027
0.136	± 0.006	4.98768	± 0.00041	17.04437	± 0.00093	367.205	± 0.058
0.633	± 0.005	4.98134	± 0.00033	16.97161	± 0.00086	364.708	± 0.047
0.226	± 0.004	4.98621	± 0.00037	17.03038	± 0.00086	366.688	± 0.053
0.589	± 0.005	4.98164	± 0.00033	16.98032	± 0.00075	364.940	± 0.046
0.274	± 0.005	4.98555	± 0.00039	17.02863	± 0.00096	366.553	± 0.055
0.548	± 0.003	4.98189	± 0.00037	16.98481	± 0.00086	365.073	± 0.053
0.465	± 0.006	4.98288	± 0.00029	16.99760	± 0.00064	365.493	± 0.041
1.077	± 0.006	4.97532	± 0.00026	16.91495	± 0.00056	362.612	± 0.038
1.340	± 0.006	4.97146	± 0.00032	16.87915	± 0.00077	361.284	± 0.045
1.354	± 0.006	4.97148	± 0.00026	16.87817	± 0.00055	361.266	± 0.036
1.425	± 0.008	4.97062	± 0.00027	16.87164	± 0.00065	361.001	± 0.039

background signal and swamps out the diffuse intensity of interest.

Compressibility of calcite

While the null result in our attempt to detect anomalies in diffuse scattering below the I–II transition was disappointing, we were nevertheless able to determine the pressure response of the unit cell to a very high precision, and far more accurately than has been obtained previously. The axial compressibilities, a/a_0 and c/c_0, are shown as a function of pressure in Fig. 1. The mean (linear) compressibilities of the a and c axes are $2.62(2) \times 10^{-3}$ GPa^{-1} and $7.94(7) \times 10^{-3}$ GPa^{-1} respectively. The ratio of the compressibilities (that along the z axis being approximately three times that along x and y) is similar to that found in other calcic carbonates (Ross and Reeder 1992; Martinez et al. 1996), but greater than that suggested by the study of calcite conducted by Fiquet et al. (1994) using energy-dispersive powder diffraction. Fiquet et al. (1994) do, however, point to the large error bars on their individual cell parameters, and the small pressure range over which they were able to obtain data.

The volume compressibility of calcite is also shown in Fig. 1. To a first approximation, the pressure-dependent behaviour can be described in terms of a linear volume compressibility, β_v, with (in this case) $\beta_v = 13.12 \times 10^{-3}$ GPa^{-1}. We note that $\beta_v = 2\beta_x + \beta_z$, as anticipated for a hexagonal crystal. Our value of the volume compressibility agrees well with that of Singh and Kennedy (1974), who measured the compression of calcite using a piston cylinder apparatus and obtained a value of $\beta_v = 14.07 \times 10^{-3}$ GPa^{-1}. The pressure-volume relationship is better described by the Birch-Murnaghan equation of state, which describes pressure in terms of K_0, the bulk modulus, and K_0' its first derivative with respect to pressure. We fitted our P-V data to the Birch-Murnaghan equation by minimising residuals in both volume and pressure (with a fully weighted fit). We found it was not possible to refine a value of K_0' (the estimated errors in the refined value were as large as the value of K_0' itself). With K_0' set as 4 (Bridgman 1925, and Singh and Kennedy 1974, obtained K_0' as close to 4 by experiment), we obtain a value for K_0 of 73.46 ± 0.27 GPa and a value of V_0 of 367.789 ± 0.004 Å^3 ($\chi^2_W = 1.19$), which agrees well with the earlier reported values for the bulk modulus of calcite (Table 2).

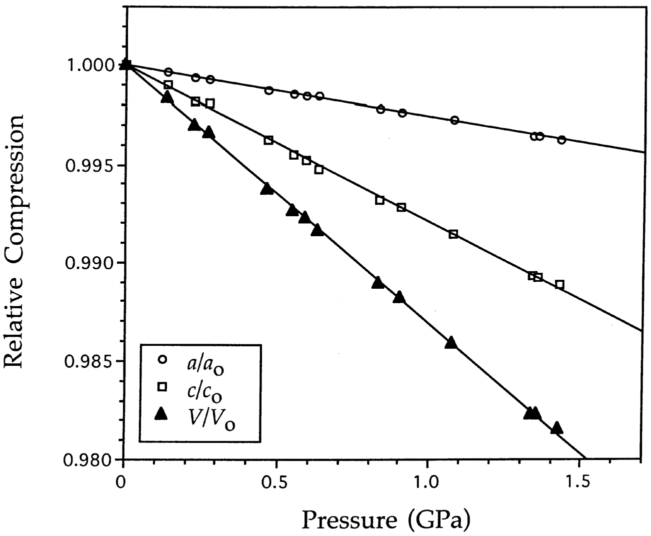

Fig. 1 The variation of a/a_0, c/c_0 and V/V_0 as a function of pressure in calcite

While our volume compressibility data simply serve to confirm previous measurements made by other methods, our measurements of the unit cell compressibilities allow the first sensitive measure of the change in the axial ratio, c/a, of calcite with pressure. The rhombohedral carbonates are sometimes described in terms of their relationship to the NaCl structure, the packing of the Ca^{2+} cations and CO_3^{2-} oxy-anions conforming approximately to a distorted "NaCl" arrangement (so long as one ignores the orientational arrangement of the oxy-anions). Reeder (1983) has, however, pointed out the shortcomings in this, a "traditional", crystal chemical description of calcite. He stresses that, in particular, the comparison of the array of orientational ordered CO_3^{2-} oxy-anions with spherically symmetric anions in the rocksalt structure is far from helpful. Indeed, Megaw (1973) noted that the array of oxygen atoms in calcite more closely (although still far from ideally) corresponds to that of hexagonal close packing. Perfect hexagonal packing of oxygens would lead to the relationship $4a = \sqrt{2}c$. The ratio $t = 4a/\sqrt{2}c$, therefore, provides a measure of the distortion of the oxy-anion-cation packing away from an ideal hexagonal close packed oxygen arrangement. At ambient temperature and pressure this ratio, t, is 0.873 for magnesite, 0.849 for dolomite, and 0.827 for calcite, showing that these carbonates are more expanded along c than along a, com-

Table 2 Bulk modulus of calcite

Reference	K_0 (GPa)	K_0'	Method
Bridgman (1925)	73.15	4.17	Piston cylinder
Peselnick and Robie (1963)	71.7	–	Acoustic
Dandekar (1968)	73.3	–	Acoustic
Humbert and Plicque (1972)	72.5	–	Acoustic
Singh and Kennedy (1974)	71.1	4.15	Piston cylinder
Fiquet et al. (1994)	69.5 ± 2.1	4	Powder ED XRD
This study	73.46 ± 0.27	4	Single crystal XRD

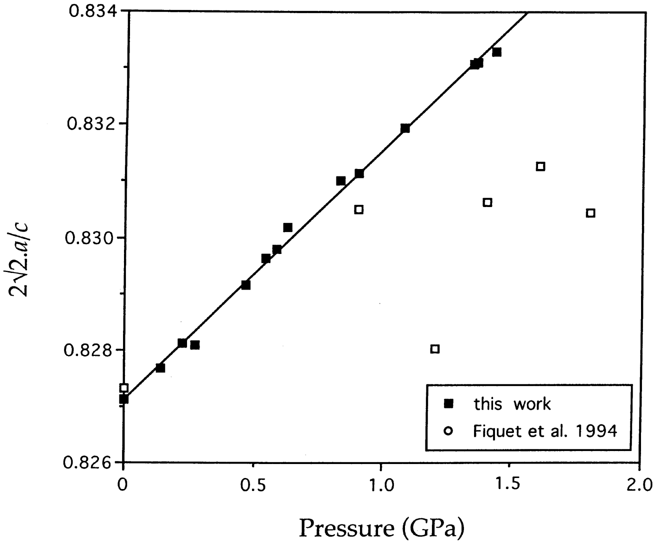

Fig. 2 Variation of the ratio $t = 4a/\sqrt{2}c$ with pressure in calcite. This ratio is unity for the NaCl structure, to which the rhombohedral calcite structure has been compared

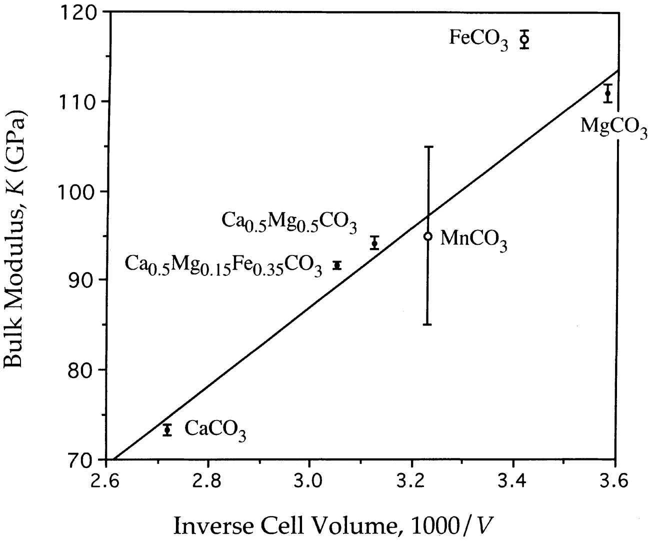

Fig. 3 Bulk modulus-volume relationships for rhombohedral carbonates. Data for ankerite and dolomite are from Ross and Reeder (1992), magnesite from Ross (1997), rhodochrosite from Martens et al. (1982), siderite from Zhang et al. (1998), calcite from this study. The reciprocal volume and bulk modulus both decrease with increasing Ca-content

pared with the packing of spherical ions. On increasing pressure, the ratio of the compressibilities along *a* and *c*, for calcite, leads to an increase in *t* towards the values of the more Mg-rich carbonates. Hence, by 1.425 GPa, just below the calcite I–II transition, *t* has increased to 0.833 (Fig. 2). The change in the *c*/*a* ratio reflects the relative incompressibility of the C—O bonds compared with the more compressible Ca—O bonds.

Anderson and Anderson (1970) have noted that, to a first approximation, many oxides and silicates with the same crystal structure display the relationship that $K_0 V_0$ is a constant. Using the results of this study, together with the results of previous single crystal compression studies of the iron- and magnesium-bearing carbonates ankerite, dolomite (Ross and Reeder 1992) and magnesite (Ross 1997), we can explore the applicability of this assumed behaviour to the rhombohedral carbonates. For this series of carbonates we see that reciprocal volume and bulk modulus both decrease with increasing Ca-content (Fig. 3). We note that ankerite and dolomite lie approximately mid-way on the trend defined by magnesite and calcite, as might reasonably be expected from simple mixing behaviour. The datum for rhodochrosite comes from Martens et al. (1982): it was obtained by observing the deformation of a steel gasket containing $MnCO_3$ in a diamond anvil cell and is subject to greater error than the single crystal static compressibility measurements. The volume compressibility relationship for this set of samples does indeed approximate to the $K_0 V_0 = \text{constant}$ conjecture. The datum for siderite, however, comes from an energy-dispersive powder diffraction study, using a large volume apparatus (Zhang et al. 1998), and appears to lie off the trend of the other samples. Weidner et al. (1982) have noted that the elastic properties of minerals are particularly sensitive to replacement of Mg^{2+} by 3-*d* transition elements. It seems, for the case of the rhombohedral carbonates, that this may be because of crystal field effects, given that $MnCO_3$ lies on the expected volume compressibility trend (and Mn^{2+}, with five 3-*d* electrons, has no crystal field stabilisation) whereas siderite (in which octahedral Fe^{2+} gains crystal field stabilization) is anomalously incompressible. Such stabilisations would be extremely sensitive to local (inhomogeneous) distortions of the coordination polyhedra, which could conceivably influence the bulk pressure-dependent behaviour. Further experimental and theoretical work on the pressure-dependent behaviour of siderite seems to be called for.

Our results, therefore, show that the pressure response of rhombohedral calcite (below the transformation to the monoclinic polymorph) is similar to that of other rhombohedral carbonates. We have obtained data not only on the volume-pressure relations for calcite, but also (for the first time) on the anisotropy of compression in calcite, which we find is akin to that in dolomite, ankerite and magnesite.

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References

Allan DR, Miletich R, Angel RJ (1996) A diamond anvil cell for single crystal X-ray diffraction studies to pressures in excess of 10 GPa. Rev Sci Instrum 67:840–842

Anderson DL, Anderson OL (1970) The bulk modulus-volume relationship for oxides. J Geophys Res 75: 3494–3500

Angel RJ, Allan DR, Miletich R, Finger LW (1997) The use of quartz as an internal pressure standard in high-pressure crystallography. J Appl Crystallogr 30: 461–466

Barnett JD, Nelson HM, Tyagi SD (1985) High-pressure EPR study of the calcite-$CaCO_3$(II) displacive phase transformation near 1.6 GPa. Phys Rev B 31: 1248–1257

Berner RA (1994) Geocarb II: a revised model of atmospheric CO_2 over Phanerozoic time. Am J Sci 291: 339–376

Bickle MJ (1996) Metamorphic decarbonation, silicate weathering and the long-term carbon cycle. Terra Nova 8: 270–276

Bridgman PW (1925) Linear compressibility of fourteen natural crystals. Am J Sci 210: 483–498

Bridgman PW (1939) The high-pressure behavior of miscellaneous minerals. Am J Sci 210: 483–498

Dandekar DP (1968) Variation of the elastic constants of calcite with temperature. J Appl Phys 39: 3694–3699

Dove MT, Hagen ME, Harris MJ, Powell BM, Steigenberger U, Winkler B (1992) Anomalous inelastic neutron scattering from calcite. J Phys Condens Matter 4: 2761–2774

Fiquet G, Guyot F, Itie JP (1994) High-pressure X-ray diffraction study of carbonates: $MgCO_3$, $CaMg(CO_3)_2$, and $CaCO_3$. Am Mineral 79: 15–23

Humbert P, Plicque F (1972) Propriétés élastiques de carbonates rhomboédriques monocristallins: calcite, magnésite, dolomite. C R Acad Sci Paris 275: 391–394

King H, Finger LW (1979) Diffracted beam crystal centring and its application to high-pressure crystallography. J Appl Crystallogr 12: 374–378

Martens R, Rosenhauer M, Von Gehlen K (1982) Compressibilities of carbonates. In: W Schreyer (ed) High-pressure researches in geoscience. Schweizerbartsche Verlagbuchhandlung, Stuttgart, Germany, pp 235–238

Martinez I, Zhang J, Reeder RJ (1996) In situ X-ray diffraction of aragonite and dolomite at high pressure and high temperature: evidence for dolomite breakdown to aragonite and magnesite. Am Mineral 81: 611–624

Megaw HD (1973) Crystal structures: a working approach. W Saunders, Philadelphia

Peselnick L, Robie RA (1963) Elastic constants of calcite. J Appl Phys 34: 2494–2495

Ralph RL, Finger LW (1982) A computer program for refinement of crystal orientation matrix and lattice constants from diffractometer data with lattice symmetry constraints. J Appl Crystallogr 15: 537–539

Redfern SAT, Salje E, Navortsky A (1989) High-temperature enthalpy at the orientational order-disorder transition in calcite: implications for the calcite/aragonite phase equilibrium. Contrib Mineral Petrol 101: 479–484

Reeder RJ (1983) Crystal chemistry of rhombohedral carbonates. In: Reeder RJ (ed) Carbonates: mineralogy and chemistry. (Reviews in mineralogy, 11) Mineral Soc Am, Washington, DC, pp 1–48

Ross NL (1997) The equation of state and high-pressure behaviour of magnesite. Am Mineral 82: 682–688

Ross NL, Reeder RJ (1992) High-pressure structural study of dolomite and ankerite. Am Mineral 77: 412–421

Singh AK, Kennedy GC (1974) Compression of calcite to 40 kbar. J Geophys Res 79: 2615–2622

Vo-Thanh D, Lacam A (1984) Experimental study of the elasticity of single crystal calcite under high pressure (the calcite I–calcite II transition at 14.6 kbar). Phys Earth Planet Inter 34: 195–203

Weidner DJ, Bass JD, Vaughan MT (1982) The effect of crystal structure and composition on elastic properties of silicates. In: Akimoto S, Manghnani M (eds) High-pressure research in geophysics. Center for Academic Publications, Japan, pp 125–133

Zhang J, Martinez I, Guyot F, Reeder RJ (1998) Effects of Mg-Fe^{2+} substitution in calcite-structure carbonates: thermoelastic properties. Am Mineral 83: 280–287