The crystal structure of calcite III

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Abstract. The crystal structure of calcite III has been deduced from existing high pressure powder X-ray diffraction patterns, based on the assumption that it is a displacive modification of the calcite I structure. The structure is monoclinic with space group $C2$ and a Z of 6. There are two Ca and two C positions, and five O positions, and atom coordinates have been refined by distance-least-squares methods to give reasonable octahedral coordination for Ca and parallel, planar CO_3 groups. Unit cell parameters refined from a published powder diffraction pattern at 4.1 GPa are: $a = 8.746(8)$Å; $b = 4.685(5)$Å; $c = 8.275(8)$Å; and $\beta = 94.4°$. The structure has a calculated density of 2.949 Mg/m^3 at 4.1 GPa which is less than that of aragonite at this pressure and consistent with early piston cylinder studies. This implies that calcite III is indeed a metastable intermediary between calcite I and aragonite.

Introduction

Calcite ($CaCO_3$) is one of the most abundant mineral species on the surface of this planet. It occurs in biogenic and inorganically precipitated sediments and sedimentary rocks. It occurs as the principal mineral constituent in metamorphic marbles. And, it occurs in igneous carbonatites and kimberlites thought to be derived from deep mantle sources. Although it is the major source and sink for atmospheric CO_2, there are major uncertainties about how it is stored in the planet's interior and how it might be released to the atmosphere in a cataclysmic eruptive cycle or impact event [*Tyburczy and Ahrens*, 1986]. In particular, we do not know the structure of one of its high pressure polymorphs formed at modest pressures, and we do not know its high pressure phase diagram.

Calcite was first observed to undergo phase transitions at pressure by *Bridgman* [1939]. Measuring volume in a piston-cylinder, he observed a transition to a slightly denser phase (calcite II) at 1.44 GPa and a transition to a significantly denser phase (Calcite III) at 1.77 GPa. These phase changes were also observed upon shock compression of single-crystal calcite by *Ahrens and Gregson* [1964]. *Singh and Kennedy* [1974] placed the calcite I - calcite II transformation at 1.45 GPa and the calcite II - III transformation at 1.74 GPa at room temperature. *Merrill and Bassett* [1975] placed the calcite I - II transition at 1.5 GPa and the II - III transition at 2.2 GPa. Curiously, calcite II was observed in all of these studies to be more compressible than either calcite I or III.

The crystal structure of calcite II was determined by *Merrill and Bassett* [1975] based on single-crystal X-ray data. Most workers have assumed that Calcite II and III are metastable intermediaries, and that the stable high pressure phase is aragonite. However, this assumption is dependent on the structure and density of calcite III which are unknown. This assumption has recently been called into serious question by a study of calcite at high pressure using diffraction of synchrotron X-rays. *Fiquet et al.* [1994] report an extrapolated zero pressure density of 3.14 Mg/m^3 for calcite III. The crystal structure of aragonite is well known, and its equation of state parameters have recently been refined at pressures to 7GPa and temperatures to 800°C [*Martinez* et al., 1996].

Structural Considerations

Several structures have been proposed for calcite III, but none has been confirmed by high pressure powder or single crystal diffraction experiments. *Merrill and Bassett* [1972] proposed a cell for calcite III that is between calcite I and aragonite in density (Table 1), but have not determined the structure. *Davis* [1964] indexed a high pressure X-ray powder diffraction pattern on an orthorhombic unit cell with a Z of 10 (Table 1) and proposed that calcite III might have a structure similar to what he proposed for KNO_3 (IV) [*Davis and Adams*, 1962]. However, the KNO_3(IV) structure has not been confirmed. The space group and atom locations have not been determined for either calcite III or KNO_3(IV).

Fiquet et al. (1994) indexed a high pressure synchrotron X-ray powder pattern on Davis' cell and obtained good internal consistency at several pressures and an extrapolated zero pressure density of 3.14 Mg/m^3 which is 7.2% denser than aragonite. This implies that calcite III, and not aragonite, is the stable high pressure phase. Indeed, shock compression of aragonite [*Vizgirda and Ahrens*, 1984] indicate a post-aragonite phase at pressures above 8 GPa with a relatively small volume change. Whereas aragonite is preserved metastably on geologic time scales, the calcite I - II - III transformations appear to be displacive, so that calcite II and III are not preserved on release of pressure [*Liu and Murnagh*, 1990] except for tiny amounts of calcite II preserved on shear boundaries [*Biellmann et al.*, 1993]. The structure proposed by Davis (1964) based on high pressure X-ray powder diffraction patterns, is orthorhombic with a Z of 10 and gives a density of 3.10 Mg/m^3 which is greater than estimates of 2.88 to 2.93 Mg/m^3 obtained from the piston-cylinder studies.

Numerous workers have noted that calcite III reverts to calcite I on release of pressure [*Bridgman*, 1939; *Singh and Kennedy*, 1972; *Merrill and Bassett*, 1975], whereas aragonite persists metastably at ambient conditions for millions of years. *Merrill and Bassett* [1972] showed that the

Table 1. Proposed unit cell parameters for calcite III compared to cells for calcite I, calcite II and previous cells for calcite III.

Structure	Pressure (GPa)	a (Å)	b (Å)	c (Å)	β (°)	vol. (Å³)	Z	ρ (Mg/m³)	Reference
Calcite I	0	4.9896		17.061		367.8	6	2.711	Reeder [1983]
Calcite II	1.5	6.334	4.948	8.033	107.9	239.6	4	2.775	Merrill and Bassett [1974]
Calcite III	2.3	8.75	8.37	7.08	90.	518.5	10	3.205	Fiquet et al. [1994]
Calcite III	1.9	8.9	8.42	7.14	90.	535.1	10	3.106	Davis [1964]
Calcite III	2.0	8.46	9.216	6.005	106.	450.2	8	2.954	Merrill and Bassett [1972]
Calcite III	1.87	8.827	4.785	8.342	98.5	348.5	6	2.862	Re-index of Davis [1964]
Calcite III	4.1	8.746	4.685	8.275	94.4	338.1	6	2.949	Re-index of Fiquet et al [1994]

calcite I-II transformation is displacive, involving only small distortions of the Ca octahedra and rotation of the CO_3 groups. This implies that the calcite II-III transformation is similarly displacive. So, the question arises: is it possible to index the powder X-ray diffraction patterns of *Davis* [1964] and *Fiquet et al.* [1994] on a unit cell that is a relatively simple distortion of calcite I or II so that we can calculate a density for calcite III and compare it to values measured in the early piston-cylinder experiments.

Calcite I is trigonal-rhombohedral, $R\bar{3}c$, with trigonal axes $a = 4.99$Å and $c = 17.06$Å. The structure has Ca at the origin, and in layers every $c/6$ along c. The planar CO_3 groups are oriented perpendicular to c. Comparison of these cell parameters with those proposed for calcite III by Davis (1964) show an obvious geometric relation. The b of the Davis cell is about one-half of c of calcite; the a of the Davis cell is about $\sqrt{3}$ times a of calcite, and c of the Davis cell is 1.5 times a of calcite. If calcite topology is maintained, this cell would have a Z of 9, not 10. But, as *Davis* [1964] pointed out, it is difficult to put an odd number of formula units in an orthorhombic cell.

Looking at the calcite structure, if the a and b relations noted above are valid, the repeat along c of the Davis cell cannot be correct. It must be either twice this value or 2/3 of this value to maintain calcite topology. The smaller cell is simpler, and so is preferred for our model. It also has a Z of 6 which is consistent with orthorhombic or monoclinic symmetry. Converting the cell of *Fiquet et al.* [1994] at 2.3GPa, we obtain cell parameters of $a = 8.75$, $b = 8.37$, and $c = 4.72$, and calculate a density at of 2.885 Mg/m³, compared to 3.205 Mg/m³ using the Davis cell.

Given these cell relations, we deduced a model for the structure and tested it by calculation of diffracted intensities. Calcite has a repeat of 17Å on c, but the Ca and C cations repeat every third layer or one-half the cell spacing (8.5Å). However, the CO_3 group related by the half cell translation is rotated by 60° relative to the first. The Ca has a very symmetric octahedron in calcite with $\bar{3}$ symmetry. If we lower this symmetry, we can counter-rotate the carbonate groups above and below the Ca layer at $z/c = 0$ by about 10°, so that they give a distorted but reasonable six coordination for Ca. To achieve a repeat of 8.5Å instead of 17Å we would have to rotate the CO_3 groups in the upper half of the calcite I cell by about 60°. This results in a reduction in symmetry and a

significant distortion of the octahedra, but cuts the c-repeat in half. The resultant structure is end-centered with diads parallel to one axis, and no mirrors or glides. The maximum symmetry would be monoclinic, space group $C2$. To be consistent with standard setting of the monoclinic system (b-unique), we would re-label the axes so that $a = 8.75$Å; $b = 4.72$Å (= c_{Fiquet} • 2/3); and $c = 8.37$Å (= b_{Fiquet}). This cell also maintains the c axis as perpendicular to the planar carbonate groups as in calcite I.

There are two different Ca sites and two different carbonate groups consistent with the Raman spectra of *Williams et al.* [1992]. The relative rotations of the carbonate groups are poorly constrained. The model does, however, satisfy the criteria of fitting within an orthogonal cell, and specifies six-fold coordination for Ca^{+2}. The model also yields parallel, planar carbonate groups, and a density consistent with the piston-cylinder data. The model also predicts X-ray powder patterns consistent with observation. Finally, our proposed calcite III structure is achievable via displacive distortion of the calcite I and calcite II structures as suggested by static and dynamic compression data.

To test and refine this model, we first calculated diffracted intensities to see if they are consistent with the published powder diffraction patterns [*Davis*, 1964, *Fiquet et al.*, 1994]. A powder diffraction pattern was calculated for the model structure using the estimated cell parameters with $\beta = 90°$, using the program XPOW [*Downs et al.*, 1993]. A fit adequate to index the pattern at 4.1GPa was obtained, which allowed refinement of the cell parameters in the deduced monoclinic space group. Least squares refinement of the unit cell parameters gave an excellent fit to the observed pattern and successfully indexed 10 of 11 lines readily discernible from the published analogue pattern, with no strong calculated lines unobserved. The observed and calculated lattice spacings and intensities are reported in Table 2. Only one relatively weak line at 2.608Å in the observed pattern was not indexed. The refined unit cell parameters are reported in Table 1. The pattern reported by Davis was also indexed and the cell parameters refined (Table 1).

The excellent fit between observed and calculated intensities and spacings gives confidence that the essential features of the model are correct. The model contains 20 unconstrained atom position parameters. With only ten or so observed intensities, it is not possible to refine the position

Table 2. Observed powder diffraction data of calcite III from analogue pattern at 4.1 GPa by Fiquet et al. [1994] with spacings and intensities calculated from structure model in space group $C2$ with $a = 8.746$Å; $b = 4.685$Å; $c = 8.275$Å; $\beta = 94.4°$.

d_{obs}(Å)	I_{obs}	h	k	l	d_{calc} (Å)	I_{calc}
3.978	5	-2	0	1	3.983	5
		1	1	1	3.639	7
2.964	100	-1	1	2	2.972	100
2.883	40	2	0	2	2.888	48
2.757	5	0	0	3	2.750	3
2.608	10					
2.484	15	3	1	0	2.470	17
2.418	10	-3	1	1	2.410	4
2.319	5	3	1	1	2.325	5
2.182	4	-3	1	2	2.183	5
		4	0	1	2.069	7
2.014	10	-2	2	1	2.019	14
		-2	0	4	1.922	11
		-3	1	3	1.900	10
		1	1	4	1.818	17
1.785	5	0	2	3	1.783	9
		3	1	3	1.781	8

Figure 1. The crystal structure of calcite III: polyhedral representation; a*- projection, c-vertical. The Ca1 octahedron at the origin is more distorted than Ca2.
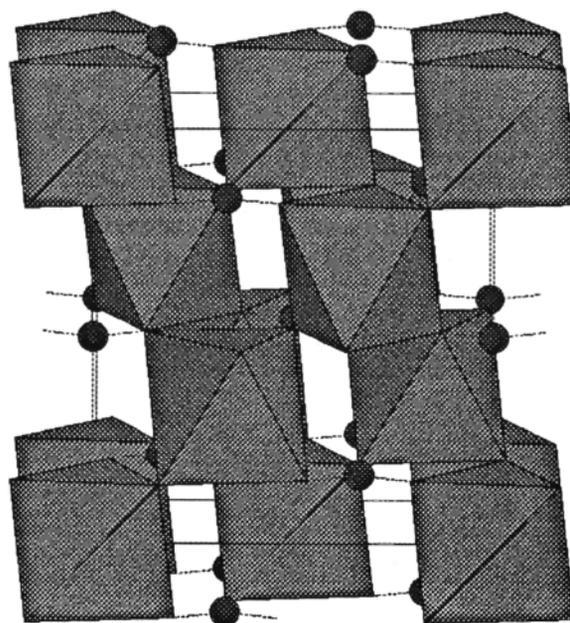
parameters from the intensities directly. We used the distance least squares code DLS (*Baerlocher*, 1976) to refine atom positions. The CO_3 groups were constrained to be planar and parallel by constraining the z/c position coordinate. The final position parameters are reported in Table 3. They differ only slightly from those of the initial model obtained by rotating the CO_3 groups about the second carbon atom, C2, by about 10° relative to calcite, consistent with the symmetry operators of space group $C2$. The structure is illustrated in Figure 1. The X-ray diffracted intensities were then re-calculated using the refined atom coordinates with no significant changes observed. Meaningful further refinement of these positions will require more precise diffracted intensity data.

Conclusion

In conclusion, we have deduced a model for the crystal structure of calcite III that satisfies the criteria of giving reasonable six-fold coordination for Ca, of having parallel,

planar carbonate groups, of yielding a density consistent with piston-cylinder studies, of successfully predicting spacings and intensities of published powder diffraction patterns, and of being reachable via displacive distortion of the calcite I structure. We have refined the unit cell parameters from published powder X-ray diffraction patterns at 1.87 and 4.1 GPa to yield densities of 2.862 and 2.949 Mg/m^3 respectively which are less than aragonite at these pressures. This structure resolves the uncertainty of the density and stability of calcite III relative to other polymorphs of $CaCO_3$. Further high pressure diffraction studies will be required to refine nearest-neighbor distances to high precision.

Table 3. Atom Coordinates for calcite III model in $C2$ from DLS refinement.

Atom	Wyckoff	x/a	y/b	z/c
Ca 1	2a	0	0	0
Ca 2	4c	0.161	0.483	0.333
C1	2b	1/2	0.494	1/2
C2	4c	0.331	-0.021	0.167
O1	2b	0	0.266	1/2
O2	4c	0.373	0.364	0.500
O3	4c	0.204	0.136	0.167
O4	4c	0.308	0.696	0.167
O5	4c	0.464	0.096	0.167

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