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# HIGH PRESSURE MID-INFRARED STUDIES OF CALCIUM CARBONATE

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## ABSTRACT

The infrared analysis of calcite to pressures of 61 kbar, obtained by means of a high-pressure diamond cell equipped with type II diamond anvils, has shown spectroscopicly that a new high pressure polymorph of calcium carbonate is produced at pressures above 30 kbars having a "vaterite-type" structure.

## INTRODUCTION

In this study, variations in the carbonate site symmetry due to pressure have been found to alter the calcite absorption spectra. These changes have led us to certain inferences regarding the ionic symmetry of calcite as a function of pressure.

*Terminology.* The point group notations used to identify molecular and site symmetries are the usual sets described by Herzberg (1945).

The *internal* symmetry of the molecules is established by the configuration of nuclei comprising the molecule. In the carbonate ion, the positions of the single carbon and three oxygen atoms determine this symmetry.

The *site* symmetry of the molecule is defined by the arrangement of any molecular ion and extramolecular nuclei to which it is bonded. It is, therefore, a function both of the symmetry of the molecule and its external environment.

For example, the ideal carbonate ion has the *internal* symmetry $D_3h$. However, if neighboring calcium atoms are also considered as in calcite. the *site* symmetry elements which define the configuration of one carbon, three oxygen and six calcium atoms are no longer $D_3h$, but $D_3$. Similarly for the aragonite structure, the divalent metallic ions provide still different site symmetry for the carbonate ion. In this case, the site symmetry for aragonite is $Cs$.

*Site symmetry of the $CaCO_3$ polymorphs.* Examination of the site symmetries of the various known calcium carbonate polymorphs substantiates the above.

*Calcite.* The carbonate ion has a site symmetry of $D_3$ which results in three infrared active bands and one infrared inactive band.

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| Mode or Vibration | Wave Number | IR Activity |
|---|---|---|
| $v_1$ = sym. str. | 1097 $cm^{-1}$ | inactive |
| $v_2$ = out-of-plane bend | 879 $cm^{-1}$ | active |
| $v_3$ = antisym. str. | 1432 $cm^{-1}$ | doubly degenerate[a] |
| $v_4$ = in-plane bend | 714 $cm^{-1}$ | doubly degenerate[a] |

[a] *i.e.*, each under certain symmetry conditions may split into two distinct vibrations of different frequency.

Weir, *et al.* (1959) propose that degenerate lattice frequencies of translational or rotational origin may interact with the degenerate fundamentals to produce a splitting or doubling. They observe a reversible splitting of the $v_3$ and a less apparent splitting of the $v_4$ fundamentals at pressures less than 30 kbar. At these pressures, the $v_1$ fundamental is observed and increases in intensity as pressure is applied. This suggests a deviation of the $D_3$ site symmetry selection rules; although, optically a change of phase is not observed.

*Aragonite.* Its carbonate ions have a $C_2$ site symmetry. Hence, six internal frequencies of the ion are now permitted in the infrared: the degeneracy is removed from $v_3$ and $v_4$, $v_1$ becomes active, and $v_2$ should remain unchanged. It is well to note that no changes are observed in aragonite by Weir, *et al.*, below 30 kbar.

*Vaterite.* This polymorph is reported to have a hexagonal unit cell containing two or more molecules per unit cell. However, structural details of the unit cell have not been established so far as can be ascertained. Therefore, the expected spectrum cannot be predicted.

All vaterite spectra obtained thus far agree with those previously published (Weir and Lippincott, 1961; Baron, 1959; Sterzel and Chorinsky, 1968). Comparison of the vaterite data with that of the calcite and aragonite types shows that the stretching force constant and out-of-plane bending constant are essentially unchanged. However, the in-plane constant has increased in vaterite.

|  | *Calcite* | *Aragonite* | *Vaterite* |
|---|---|---|---|
| $v_1$ | — | 1087 | 1090 |
| $v_2$ | 881 | 866 | 850–878 |
| $v_3$ | 1432 | 1430–1550 | 1450 |
| $v_4$ | 712 | 715–703 | 741–747 |

Weir and Lippincott (1961) suggest this marked change in the in-plane bending constant is indicative of repulsion between oxygen atoms in the plane of the ion if the analysis of the effects of different types of forces in solution by Benson and Drickamer (1957) is considered to apply here.

## EXPERIMENTAL

The calcite used in this study was the Iceland Spar variety. It was obtained from Ward's Natural Science Establishment, Inc. Its high purity was established by an emission spectroscopic analysis.

All spectra were obtained on a Beckman IR-9 Infrared Spectrophotometer utilizing a 5X beam condenser equipped with potassium bromide lenses. Sample pressure was effected by means of a High Pressure Diamond Optics diamond-anvil cell equipped with type II diamonds. A rough pressure calibration was obtained with materials having well established transitions. Errors in pressure calculations exist due to inherent incapabilities of the cell. A uniform pressure cannot be applied to the sample due to an effect of concentrically-decreasing pressure at the diamond faces. This is to say that the highest pressure exerted will be at the center of the cell and decrease toward its outer edges.

The vaterite polymorph used in this study was synthesized by the method of McConnell (1959). An X-ray powder pattern confirmed the presence of vaterite in large quantities [minor amounts (10–15 percent) of calcite were also found].

X-ray patterns of the compressed calcium carbonate in the diamond cell at a pressure of 61 kbar was obtained by a flat camera with a sample to film distance of 45 mm using molybdenum radiation and exposed for eighteen hours. In that this work is an infrared study, the X-ray data was used only to supplement the infrared evidence of a high pressure polymorph.

## RESULTS OF PRESSURE EFFECTS TO 60 KBAR ON THE SYMMETRY OF THE CARBONATE ION IN CALCITE

Pressure to approximately 30 kbars produces effects similar, though significantly different, to those observed by Weir, *et al.*, and Schock and Katz (1968) in experiments covering this pressure range. However, due to poor transmission of the diamond pressure cell in the $v_3$ region (approximately 1400 cm$^{-1}$), confirmation of degeneracy of this mode was not attempted. The results of Weir, *et al.*, concerning this mode are plausible and have been accepted as valid.

A splitting of the doubly degenerate $v_4$ mode is observed as pressure is increased. In view of the fact that weak bands are observed on both sides of this mode (approximately 715 cm$^{-1}$) at approximately 745 cm$^{-1}$ and approximately 690 cm$^{-1}$, assignment of the degenerate components of this mode is formidable.

Schock and Katz assign the 714 cm$^{-1}$ and 695 cm$^{-1}$ bands as the components of the $v_4$ split which results in a $\Delta\ v_4 \cong 19\ \text{cm}^{-1}$; a reasonable assumption. Weir, *et al.*, fail to observe the 695 $\text{cm}^{-1}$ band and tentatively assign the $v_4$ split to the 714 $\text{cm}^{-1}$ and 740 $\text{cm}^{-1}$ band. A larger $\Delta\ v_4$ ($\cong$26 $\text{cm}^{-1}$) results. Schock and Katz offer no assignment of the 740 $\text{cm}^{-1}$ band and only note that it increases with pressure. We favor the degenerate split of the $v_4$ mode at 714 $\text{cm}^{-1}$ and 690 $\text{cm}^{-1}$ for *Cs* site symmetry of aragonite and propose the 740 $\text{cm}^{-1}$ band, which we also observe to increase with pressure, as being due to a change in the inplane bending constant indicative of repulsion between oxygen atoms in the plane of the carbonate ion. It should be noted that the effect of concentrically decreasing pressure inherent in the pressure cell can produce this change due to a mixture of polymorph species.

Due to the fact that the $v_4$ fundamental is not a triple degenerate band it is believed to split due to a mixture of two polymorphic forms produced: one resulting in a 740 $\text{cm}^{-1}$ band for an as yet unnamed polymorph and the other resulting in a 690 $\text{cm}^{-1}$ band due to production of an aragonite polymorph. (The possibility of polymorphic mixtures due to uneven pressure has been previously described.) It has been observed that the 740 $\text{cm}^{-1}$ band is the first to form; the 690 $\text{cm}^{-1}$ band forms almost immediately after and remains stable, as we shall later show, under pressures from 25 kbar to 60 kbar. The 740 $\text{cm}^{-1}$ band changes considerably under high pressure; this is to be expected if the causal interpretation of the band is correct.

The $v_1$ fundamental is activated at high pressures and is reversible below 25 kbar in this work and that of Weir, *et al.* and is indicative of a deviation of the $D_3$ site symmetry rules. Schock and Katz found that for every specimen tested, 40 percent to 60 percent of the pressure induced absorption of the $v_1$ fundamental remained upon release of pressure. The significance of these results will be discussed shortly.

It is our belief that the pressure induced changes in the fundamentals observed below 20 kbar are calcite I→II or II→III transitions, which many workers have suggested are metastable with respect to aragonite. The pressures of our transitions compare favorably with those proposed by Bridgman (1925): calcite I→II at 14.6 kbar and II→III at 17.7 kbar. Jamieson (1957) later demonstrated that as the pressure is increased calcite shows a diminuition in the intensities of the high-angle X-ray reflections and a decrease in the relative intensity of the $11\overline{2}3$ reflection. This phenomena was estimated to start at approximately 15 kbar. Between 20 kbar and 22 kbar, the $11\overline{2}3$ became extinguished, possibly indicating a halving of the *c*-axis. Their experimental evidence suggests that calcite II is an anion-disordered form of normal calcite.

Davis (1964) however, differs with the suggested mechanism of rotational anion disorder for the production of calcite polymorphs. He sites experimental evidence to show that such disorder results in *c*-axis expansion, not contraction, and hence is doubtful that anion rotation can be the mechanism of transformation of calcite I to calcite II.

Recalling that Schock and Katz found their pressure induced $v_1$ fundamental irreversible, a plot of carbonate $v_1$ absorbance vs. central pressure of the cell was provided by them to show that the effect of a calcite I—II or II—III transition is inconsistent with the above interpreted reversibility of this transformation. In that the $v_1$ mode in our study is not preserved when pressure is released, we cannot comment on the validity of this conclusion but only suggest the remote possibility that the irreversible aragonite polymorph may have been produced even though their X-ray data show no evidence of aragonite. In this study, and that of Weir, *et al.*, a shift in the $v_1$ band to a higher wavenumber as pressure is increased is observed suggesting a change in the orientation or center of gravity of the carbonate ion. Weir, *et al.*, go on to interpret this shift as a result of a decrease in the C—O bond distance in the carbonate ion under pressure. This is not to say that the C—O bond is easily compressed but only that the calculated parameter of compressibility compares favorably with that of Bridgman. $[(-1/R)(\Delta R/\Delta P)] = 2.8\times10^{-7}$ atm.; calculated by use of the internuclear potential function (Lippincott and Schroeder, 1956). The increase of the 740 $cm^{-1}$ band with pressure, previously interpreted as a repulsion between oxygen atoms in the plane of the carbonate ion, further confirms a change in the ion orientation. The change in the $v_4$ (740 $cm^{-1}$) mode, however, does not appear to be due entirely to repulsion of oxygen atoms in the plane of the carbonate ion. If the 740 $cm^{-1}$ band is due entirely to repulsion of the oxygen atoms resulting from a decrease of the carbon-oxygen bond distance, the $v_1$ mode (symmetric stretching) should also shift to a much larger wavenumber. This is not observed to be the case. At a pressure of 61 kbar the $v_1$ mode has shifted from 1087 $cm^{-1}$ to 1105 $cm^{-1}$, whereas the $v_4$ mode has shifted from 715 $cm^{-1}$ to 747 $cm^{-1}$. The $v_4$ mode (an in-plane bend) may interact with the calcium by intraionic bonding with the oxygen of the carbonate, resulting in a change of only the in-plane bending constant. The $v_1$ mode will be essentially unaffected by this bond. It is, therefore, necessary to consider the position of the calcium atoms in the crystal lattice and their effect on the carbonate ion. Investigation of these lattice modes under pressure in the region below 400 $cm^{-1}$ will be attempted later. At the present, the mid-infrared data suggests ample evidence of a change in the ion orientation for our purposes.

The above observations have shown themselves to be reversible below approximately 20 kbar of pressure. On the basis of the infrared evidence an irreversible aragonite structure or $C_s$ symmetry is not produced until pressures above 20 kbar are attained. It is our belief that pressure induced spectral changes below this pressure are calcite I→II or II→III transitions. Interpretation of the spectral data suggests anion-disorder and the reversibility of this transition is consistent with the findings of Bridgman and Jamieson.

As the pressure exerted is increased above 20 kbar (Fig. 1), the 690 $cm^{-1}$ band becomes stable and does not increase in intensity or shift. The $v_1$ mode shifts to a higher wavenumber as expected when pressure is increased. The striking feature produced by pressures above 25 kbar is the change resulting in the 740 $cm^{-1}$ band relative to the 715 $cm^{-1}$ fundamental. The 740 $cm^{-1}$ band increases in intensity, indicative of a higher concentration of the polymorph producing this band, and shifts to a higher wavenumber with increasing pressure. The 715 $cm^{-1}$ fundamental decreases with increasing pressure; at the end point of our experiment, 60 kbar, it is the weakest band in the spectrum (Fig. 1).

Recalling the stability of 690 $cm^{-1}$ band, we have interpreted this band to be indicative of a constant volume of aragonite since it is unique to only the aragonite structure. The increasing ratio of the 740 $cm^{-1}$ to 690 $cm^{-1}$ band has been interpreted as being indicative of an increasingly higher concentration of the polymorph that produces the 740 $cm^{-1}$ band. This unknown polymorph has been observed by its infrared spectrum to be reversible to the aragonite structure upon release of the pressure.

This is not to imply that the new polymorph is derived from aragonite although this is a possibility. It seems more likely that all the calcite has not been converted to aragonite, that which has not is converted to an unstable polymorph. The detection of calcite in aragonite would be difficult due to overlap of concurrent bands. The above results perhaps can be more easily visualized by the graph in Figure 2.

The observed forward reflection (transmission) powdered diffraction pattern of the compressed calcium carbonate is consistent with the high pressure infrared data. A "vateritelike" structure is the principal polymorph at 61 kbar; calcite and aragonite are also present but in lesser quantities. Table 2 lists the observed *d* Å of the pattern for the high pressure polymorph, giving their assignments and appropriate ASTM powder data file value correlation for calcite, aragonite and vaterite.

## CONCLUSION

It is obvious that the frequency trends observed in this study are attributable to changes in the carbonate ion; specifically, arising from

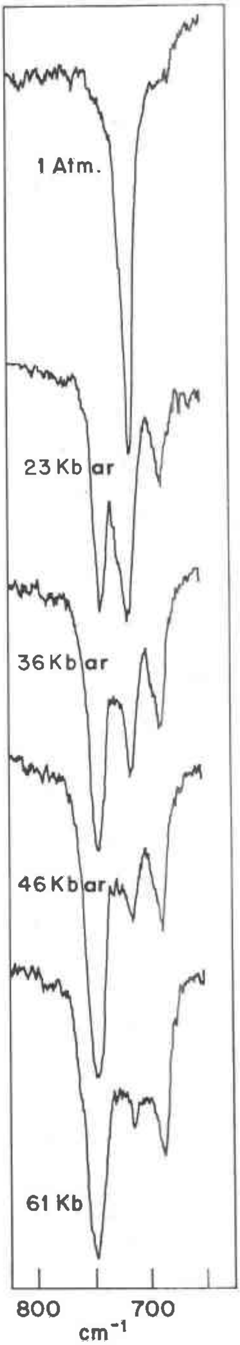

FIG. 1. High Pressure Changes of the $\nu_4$ Fundamental in Calcite.

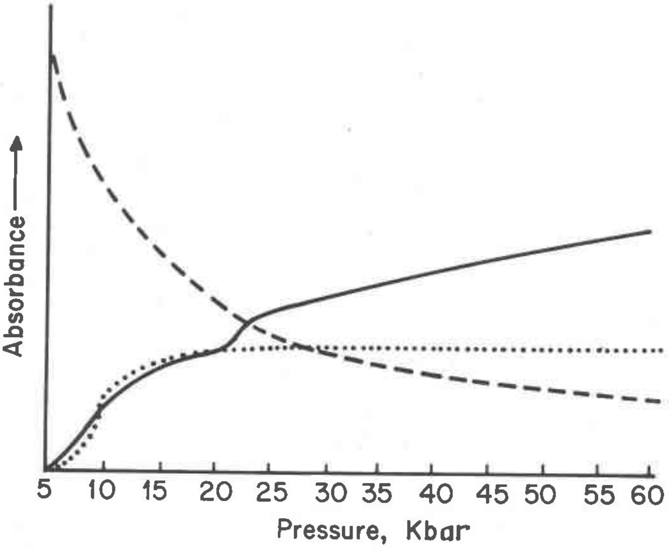

FIG. 2. Relative Intensity Changes in the $v_4$ Fundamental as a Function of Pressure [- - - -, 715 cm$^{-1}$; . . . , 690 cm$^{-1}$; —— 740 cm$^{-1}$ .

repulsion of oxygen atoms in the plane of the ion resulting from both a decrease in the carbon-oxygen bond distance and intraionic bonding with calcium as a function of increasing pressure. The new polymorph exhibits infrared bands having frequencies similar to those of known "vaterite-type" polymorphs (Table 1); the X-ray powder pattern also confirms the existence of a "vaterite-type" structure (Table 2). The repulsive force explanation is consistent with Weir and Lippincott's interpretation of the calcium carbonate vaterite spectrum. The theory of intraionic bonding of oxygen and calcium supplies the mechanism neces-

TABLE 1. KNOWN VATERITES AS COMPARED TO THE HIGH PRESSURE (61 kbar) POLYMORPH

| | Sterzel and Chorinsky (1968) | Weir and Lippincott (1961) | This work, synthetic | This work, calcite at 61 kbar |
|---|---|---|---|---|
| $v_1$ | 1089 | 1090 | 1089 | 1100 |
| $v_2$ | 877 | 850–878 | 877 | 878 |
| $v_3$ | 1450 | 1450 | 1450 | N.A. |
| $v_4$ | 744 | 741–747 | 746 (715) | 747 (715) (690) |

Frequencies in parentheses are believed to be due to calcite and/or aragonite.
N.A. = not available.

TABLE 2. X-RAY DIFFRACTION PATTERN OF CALCITE AT 61 KBAR

| High-pressure polymorph (*d* Å) | Assignment (*d* Å—*I*/*I* ASTM value) |
|---|---|
| 4.26 | vaterite (4.26–75) |
| 3.87 | calcite (3.86–12) |
| 3.64 | vaterite (3.58–100) |
| 3.35 | vaterite (3.30–100) and aragonite (3.40–100) (?) |
| 3.04 | calcite (3.04–100) |
| 2.72 | vaterite (2.73–100) and aragonite (2.70–46) (?) |
| 2.32 | vaterite (2.33<br>2.30–50) and calcite (2.285–18) (?) |

sary to initiate a repulsive force for an in-plane bending mode ($v_4$) of this nature without considerably affecting the symmetric stretching ($v_1$) mode. The production of a new polymorphic transition produced by a change in pressure is extremely complex in that kinetic as well as potential energies are involved. A complete structural picture of the new polymorphic transition will require consideration of these energies. Hopefully, this will be accomplished when all the infrared data below 400 cm$^{-1}$ has been collected. Due to the correlative features of the high pressure polymorph with known vaterite as evidenced by both infrared and X-ray data, it is believed that "vaterite-type" structure is a stable polymorph of calcium carbonate under pressure of 60 kbar to 65 kbar. High pressure experiments on the vaterite polymorph indicate that it is very stable under high pressure. Only minor frequency shifts of the bands are noted, with no evidence of new band production.

However, to even remotely suggest that calcium carbonate vaterite is a high pressure polymorph of calcite is precarious, McConnel's (1962) density of 2.60 for vaterite makes it thermodynamically impossible for vaterite to form from calcite I, II, or III at high pressure as a reversible equilibrium product unless it is sufficiently compressible so as to overcome the density difference and thus Gibb's Free Energy differences among these phases. Bridgman's compression data give an increase in density of 10 percent at 50–60 kbar for $CaCO_3$. Jamison (1957) has also shown that vaterite is less compressible than calcite at about 20 kbar.

As suggested by Davis (1964), many calcite polymorph structures may be isostructural with various nitrate structures. Confirmation of these suggestions are beyond the scope of data collected in the mid-infrared spectral region (5000 to 400 cm$^{-1}$). Studies in the far-infrared spectral region (750–33 cm$^{-1}$) will be attempted to obtain insight into the lattice vibrations of this high-pressure polymorph.

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