

PRESSURE DEPENDENCE OF THE INFRARED
ABSORPTION OF CALCITE

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ABSTRACT

The infrared absorption of calcite has been measured to over 20 kbar at 25°C in a Bridgman diamond-anvil squeezer, an apparatus in which intense shear produces large specimen deformation. Although observed changes in the absorption spectrum with increasing pressure near 4 kbar strongly suggest the calcite-aragonite transformation, neither optical study *in-situ* nor X-ray analysis on unloading confirms this interpretation. The observed changes may result from a minor structural distortion which is aided by shear stresses and related to the calcite-aragonite transformation.

INTRODUCTION

The pressure-temperature relationship of the natural polymorphs of CaCO_3 , calcite and aragonite, has been the subject of considerable study. Solubility experiments have shown that aragonite is the stable form above 3.8 kbar at 25°C (Jamieson, 1953). MacDonald (1956) in a Bridgman-anvil apparatus, and Clark (1957) and Crawford and Fyfe (1964) in hydrostatic pressure cells showed that calcite transforms irreversibly to aragonite with pressure, at temperatures above 100°C. Simmons and Bell (1963) also used a modified Bridgman-anvil apparatus and reported the irreversible formation of aragonite at 100°C above 7 kbar.

Several ultrasonic investigations bear on the high-pressure properties of calcite. Tozer and Birch (1960) reported an anomalous pressure dependence in the compressional wave velocity of calcite, at room temperature, in a hydrostatic pressure vessel. Ahrens and Katz (1963), using a Bridgman-anvil apparatus, found a maximum in both shear and compressional wave velocities in calcite beginning at a nominal pressure of about 4 kbar (25°C) with a marked decrease at higher pressures. Simmons and Bell (1963) interpreted the results of Tozer as a reversible, grain-size-dependent, calcite-aragonite transition. Gordon and Vaisnys (1964), using a hydrostatic bomb to 10 kbar, found no anomalous changes in the same materials as used by Ahrens and Katz. Wang (1966),

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in a similar experiment to 20 kbar, showed that the velocities are dependent upon crystallographic orientation, grain size, and porosity. He attributed a transition to either the calcite I-II or the II-III transformation occurring in the range of 15 to 18 kbar (Bridgman, 1939; Adadurov *et al.*, 1961). A recent determination of the elastic constants of single-crystal calcite under hydrostatic pressure at 25°C (Dandekar, 1968) has shown the existence of a possible minor structural change at approximately 4 kbar related only to shear strains.

Burns and Bredig (1956), Dacheille and Roy (1960a, 1964), and Jamieson and Goldsmith (1960) have reported forming aragonite after grinding calcite in a laboratory power mortar. Dacheille and Roy (1960b, 1962) have suggested that large shear stresses accelerate pressure-induced reactions which are otherwise sluggish at room temperature, without affecting the transition pressure. However the effect of frictional heating in these experiments may also be important.

PROCEDURE

In the present work, infrared absorption in a diamond-anvil cell (Van Valkenburg, 1963) is used to study the effect of pressure on calcite. Large shear stresses develop as a result of radially-outward flow of the sample during the first few kilobars of compression. The total quantity of specimen is of the order of 50 μg . A rough pressure calibration was obtained with materials having well-established transitions (Schock and Katz, 1967; Lippincott and Duecker, 1964). Pressure is normally a parabolic function of anvil radius, being highest at the center and diminishing to the edge of the anvil face, a distance of about 0.25 mm. However, for materials with high resistance to plastic flow the pressure distribution is more complex, with pressure increasing very steeply at the edge of the sample (Connell, 1966). Pressure reproducibility in successive runs is ± 1.0 kbar, with an estimated accuracy of ± 3.0 kbar due to the above-mentioned factors. Spectra were recorded on a Perkin-Elmer 421 dual-beam diffraction-grating instrument, with elliptical mirrors to focus the sample beam through the specimen. Because of the pressure gradient, the measured infrared absorption represents an average over a pressure range, limiting resolution for determining the pressure of any discontinuous spectral variation.

As a result of a change in the site symmetry of the carbonate ion (molecular symmetry D_{3h}), the infrared spectra of calcite (CO_3^{2-} site symmetry D_3) and aragonite (CO_3^{2-} site symmetry C_s) differ in several respects (Halford, 1946; Weir *et al.*, 1959). Of the six fundamental modes of vibration of the carbonate ion, the symmetric stretching mode (ν_1) is not active in the calcite structure, due to the high environmental symmetry. In the aragonite structure this symmetry is lowered, and the vibration becomes infrared active. The degeneracies in the doubly-degenerate antisymmetric stretching (ν_3) and doubly-degenerate planar bending (ν_4) modes are allowed in calcite, but not in aragonite, where they are split into non-degenerate vibrations. The out-of-plane bending (ν_2) mode is active in both structures.

RESULTS AND DISCUSSION

With increasing pressure (Fig. 1), the ν_1 fundamental of the carbonate ion, absent in calcite at atmospheric pressure, is excited at 1087 cm^{-1} . Its absorbance ($A = -\log I/I_0$, where I is the observed and I_0 the reference intensity) increases with a slight shift to the blue of approximately 2 cm^{-1} in 10 kbar. The ν_2 fundamental is observed to shift discontinuously from 882 cm^{-1} to 865 cm^{-1} . The ν_4 fundamental, originally at 710 cm^{-1} , splits into two distinct bands at approximately 715 cm^{-1} and 690 cm^{-1} . No change can be observed in the ν_3 fundamental due to the absorption of the diamond in this region. The qualitative changes in the ν_1 and ν_4 fundamentals have been reported by Weir *et al.* (1959). The weak bands at 835 cm^{-1} and 740 cm^{-1} are unaccounted for, although the former is observed to decrease and the latter to increase in absorbance with pressure.

These changes, together with the above observations of Dachille and Roy, and Jamieson and Goldsmith, appear to suggest the formation of aragonite with increasing pressure in an apparatus with large shear stresses. In apparent confirmation of this interpretation, spectra of natural calcite and aragonite specimens (Adler and Kerr, 1963) reveal that the ν_2 fundamental occurs at approximately 885 cm^{-1} in calcite and 858 cm^{-1} in aragonite, and the splitting $\Delta\nu_4 \approx 15\text{ cm}^{-1}$, with a new

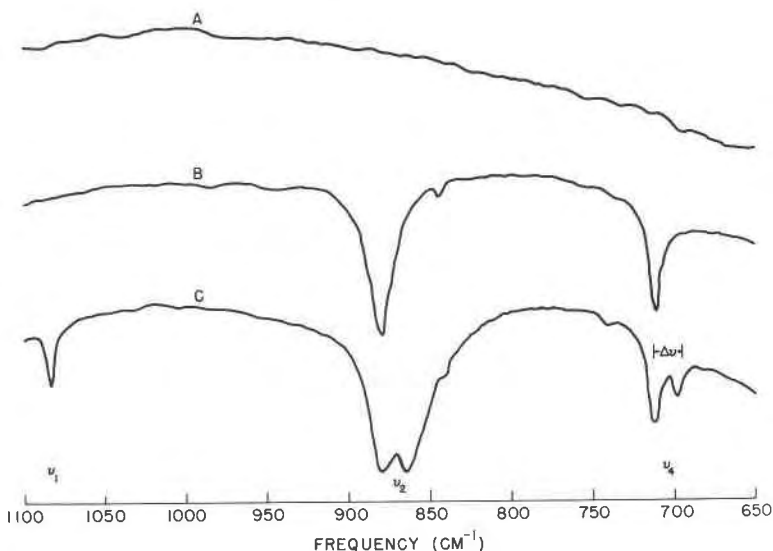


FIG. 1. Infrared spectral changes in calcite with pressure. (A) blank diamond spectra, (B) calcite at 1 bar, (C) calcite at 20 kbar central pressure.

band appearing to the low-frequency side of the original, degenerate ν_4 . In addition the ν_1 fundamental occurs at approximately 1085 cm^{-1} in aragonite. To test this interpretation, the diamond-cell was placed in a petrographic microscope and calcite was observed optically with increasing pressure. However, none of the effects usually observed during a phase transformation appeared; *e.g.*, a discontinuous change in refractive index and in birefringence, and the growth of single crystals. In addition, samples X rayed after unloading using conventional powder techniques showed no new phases. These results suggest that the infrared results should be attributed to a change in the calcite lattice not involving a structural reorganization of the type characteristic of low-order phase transformations. This does not preclude the formation of aragonite in amounts too small to be detected optically or with X rays.

Of the possible carbonate-ion site symmetries resulting from deformation of the calcite lattice, C_{2v} and C_{3v} seem most likely. These involve a slight lowering in symmetry, but not of the degree associated with the transformation to the C_s aragonite symmetry. With both C_{2v} and C_{3v} the ν_1 mode is infrared active but only with C_{2v} is the degeneracy in ν_4 removed. In several carbonate structures with known C_{2v} site symmetry for the carbonate ion, this splitting has not been resolved (Nakamoto *et al.*, 1957).

To determine the pressure-dependence of the absorption spectrum with greater precision, the ν_1 fundamental was continuously scanned and the change in intensity $\Delta I/I_0$ plotted as a function of pressure (Fig. 2). The ν_4 fundamental would have given more useful information. However, the response of the spectrophotometer is poor in this region. In addition the new position of the ν_2 fundamental is within the limits of the original absorption band, thereby limiting resolution for determining the absorption of ν_2 as a continuous function of pressure. There is a suggestion of partial irreversibility with pressure in both the splitting in the ν_4 fundamental and in the shift of the ν_2 fundamental. In addition, instrument performance and transmission in the diamonds are excellent in the region of the ν_1 fundamental.

The same general features (Fig. 2) were observed with the following starting materials: reagent CaCO_3 powder, 98 percent calcite from X-ray analysis; powdered Iceland spar; and Iceland spar crystals $80\ \mu$ thick, oriented perpendicular and parallel to the crystallographic c axis. All specimens showed a slight increase in absorbance of the ν_1 fundamental up to a central pressure in the neighborhood of 4 kbar. This is attributed to deformation of the calcite lattice. Above 4 kbar, the absorbance rapidly increases nearly linearly, with a gradual decrease in

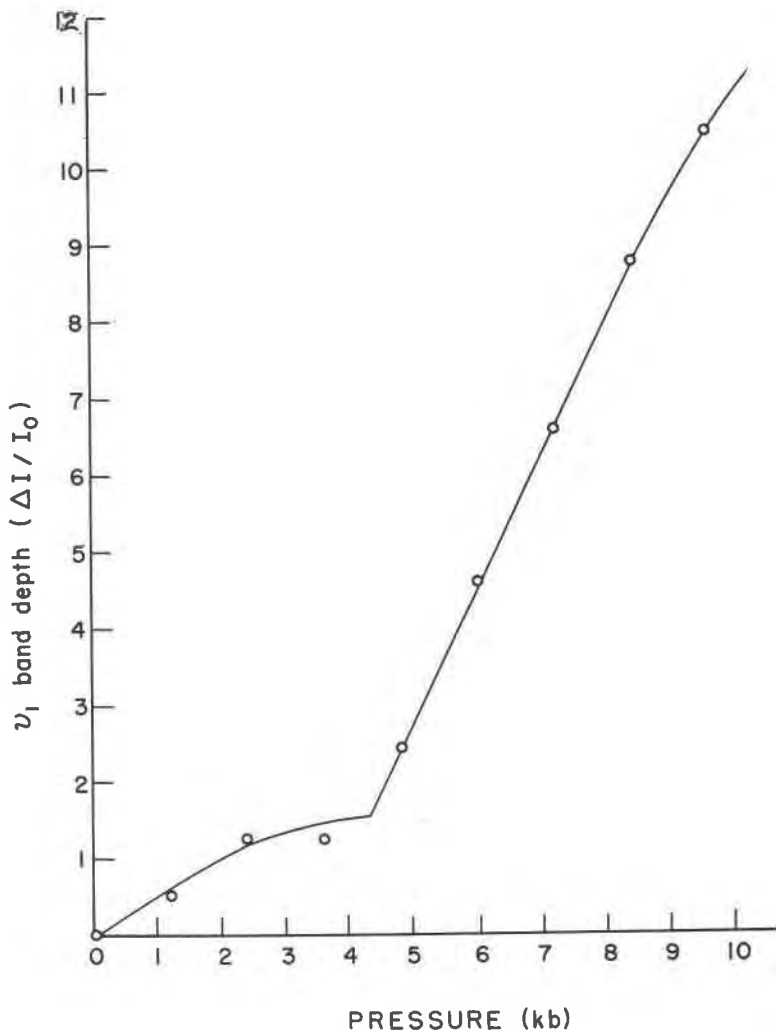


FIG. 2. Carbonate ν_1 absorbance versus central pressure for samples of calcite.

slope above 10 kbar central pressure. No orientation effect was observed either in the position of the knee or in the shape of the curve (Fig. 2). For every specimen, 40–60 percent of the pressure-induced absorbance of the ν_1 fundamental remained upon release of pressure. Due to large hysteresis in the pressure apparatus, data could not be obtained during decompression. No changes in slope (Fig. 2) or in the gross spectra of calcite or aragonite were observed in the vicinity of

14.6 or 17.7 kbar, the reported transition pressures for calcite II and III at 25°C (Bridgman, 1939), phases which Jamieson (1957) suggested are metastable with respect to aragonite. This has been confirmed in the case of calcite II by Boettcher and Wyllie (1967). The possibility that the effect (Fig. 2) is the calcite I-II transformation is inconsistent with the demonstrated reversibility of this transformation (Bridgman, 1939).

CONCLUSIONS

The high-pressure spectrum of calcite indicates a lowering of the carbonate ion site-symmetry. The discontinuous change, both in the position of the ν_2 fundamental and in the absorbance of the ν_1 fundamental at approximately 4 kbar may be related to the calcite-aragonite transformation. It is not unreasonable to expect a minor structural distortion in the calcite lattice to occur discontinuously at or near the calcite-aragonite equilibrium pressure at 25°C. The present experiments, and the elastic shearing stress maximum under hydrostatic pressure (Dandekar, 1968), suggest that shear stresses are an important factor, the directional stress creating a structural distortion which is part of the mechanism of transformation. It is possible that the solid-state transformation involves more than one rate-controlled mechanism, one step being related to shear instability. The observations of strained calcite formed from aragonite (Dasgupta, 1964; Boettcher and Wyllie, 1967b) are compatible with the concept of a distortion being at least partly responsible for the calcite-aragonite transformation. As in the grinding experiments, the effect of frictional heating in these experiments is not known. At local sites the temperature may be increased enough to affect significantly the rate of any reaction. However, the rate at which the force was applied did not alter the results (Fig. 2) to rates as low as 0.1 kbar central pressure min^{-1} .

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