Vibrational spectra of magnesite (MgCO₃) and calcite-III at high pressures

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ABSTRACT

Raman spectra of magnesite (MgCO₃) and infrared spectra of the highest pressure metastable phase of calcite (designated calcite-III) are presented to pressures of 34 and 32 GPa, respectively. We document that both phases persist at 300 K to the highest pressures of these measurements. Our results for magnesite are similar to previous data on dolomite, in that the two lowest frequency Raman-active modes of magnesite (at 329 and 216 cm⁻¹ at zero pressure) diverge as a function of pressure and that the mode Grüneisen parameters of the internal vibrations of the carbonate group are between five and seven times smaller than those of the low-frequency lattice modes. The spectra of calcite-III are consistent with the presence of carbonate environments that are distorted from trigonal symmetry, and this phase plausibly contains more than one distinct crystallographic environment of the carbonate unit.

INTRODUCTION

The alkaline earth carbonates have been a subject of considerable interest in the Earth sciences because they not only are the most abundant C-bearing species in the crust, but also may represent a major reservoir for C within the Earth's mantle (Berg, 1986; Canil, 1990; Katsura and Ito, 1990; Kraft et al., 1991). Among such carbonates, calcite represents a prototype that has shown extensive high-pressure polymorphism, whereas magnesite is the carbonate phase most likely to occur at depth within the Earth's mantle (Bridgman, 1939; Kushiro et al., 1975; Brey et al., 1983). The properties of metastable phases produced by compression of calcite have been examined at ambient temperature up to maximum pressures of 10 GPa using Raman spectroscopy (Liu and Mernagh, 1990); calcite undergoes two polymorphic phase transitions at pressures near 1.5 and 2.0 GPa, to the metastable phases calcite-II and calcite-III. For comparison, no in situ high-pressure spectral studies have been conducted on calcite-structured magnesite (MgCO₃).

The goals of this study are to characterize spectrally calcite-III and magnesite at high pressures in order to determine whether either material undergoes any phase transitions in the pressure range to 30 GPa, as well as to examine pressure-induced changes in the bonding properties of these phases. Our primary probes are vibrational spectroscopy: Raman spectra of magnesite, and infrared spectra of calcite-III. The latter data set complements and augments previous Raman spectra of calcite-III to 10 GPa (Liu and Mernagh, 1990). In presenting these data, we wish to establish the systematics of how alkaline earth carbonates respond to compression. When coupled with our prior Raman data on dolomite and infrared and Raman data on aragonite (Kraft et al., 1991), these data provide constraints on the behavior of all known carbon-

ate end-members in the CaCO₃-MgCO₃ system under pressures spanning those within the upper mantle of the Earth. The possible presence within the upper mantle of phases in this system both may provide a means by which C is retained in this region of the Earth, and may be correlated with the genesis of C-containing magmas. Thus, an understanding of the high-pressure stability and compressional behavior of these phases is of considerable importance.

EXPERIMENTAL DETAILS

Our starting material for the experiments on calcite was Iceland spar purchased from Ward's Natural Science Establishment, Inc.; this was powdered to a particle size of approximately 1 μm and diluted to 8 wt% in KBr, which served as both a pressure medium and infrared window. Samples of magnesite were polycrystalline natural samples from Snarum, Norway; both Raman spectra and X-ray diffraction confirmed that these were single-phase magnesite. All infrared spectra were conducted using a Bomem DA3.02 Fourier-transform infrared spectrometer, equipped with a liquid-He-cooled Cu-Ge detector and KBr beamsplitter. The Raman spectra were obtained using 488.0-nm Ar⁺ laser excitation, focused to a spot approximately 5 μm in diameter within the sample: estimated intensities at the sample are about 150–200 mW. A Spex Triplemate spectrograph coupled to a Quantar Technologies multichannel plate detection system was used to disperse and record spectra. All spectra are reported with a resolution of 4–5 cm⁻¹.

Pressures in the Raman experiments were generated using modified Merrill-Bassett diamond-anvil cells, with low-fluorescence Type I diamonds, and spring steel gaskets. Four samples were used in conducting the high-pressure Raman measurements. These experiments utilized
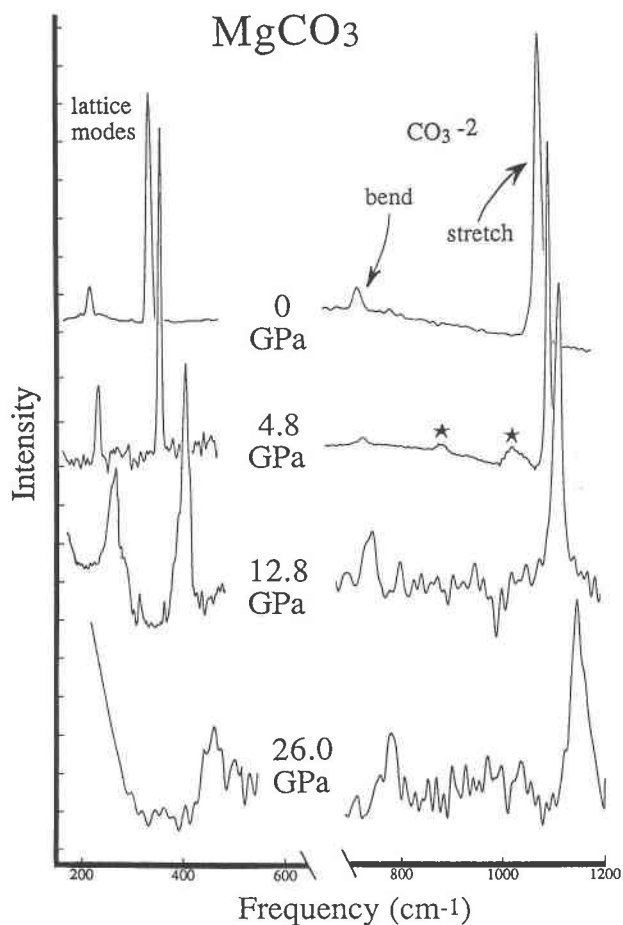
Fig. 1. Representative Raman spectra of magnesite (MgCO₃) at zero pressure and 4.8, 12.8, and 26.0 GPa. The stars on the spectrum at 4.8 GPa denote Raman peaks produced by the methanol-ethanol pressure medium.

Fig. 2. Pressure shifts of the Raman vibrations of magnesite (MgCO₃) at room temperature. Data were obtained on both compression (open circles) and decompression (solid circles). Error bars in pressure are smaller than the symbols; this is because of the proximity of the ruby fluorescence pressure measurement to the sample areas in which the Raman spectra were taken, as well as the use of pressure media to reduce pressure gradients (see text). The four observed Raman modes all have positive mode shifts, which increase continuously with pressure, and no splitting of modes is observed.

both methanol-ethanol and Ar as pressure-transmitting media: results were indistinguishable between the two media. For the Raman experiments, pressures were calibrated using the ruby fluorescence technique (Mao et al., 1978), with the fluorescence being measured from a ruby chip within 10 μm of the location from which the Raman spectra were obtained. The infrared experiments were conducted in modified Mao-Bell type diamond-anvil cells with Inconel gaskets. Three to five ruby grains were included as calibrants in the sample; these were utilized to characterize the pressure variation within the sample chamber. The infrared results were generated from two samples.

RESULTS AND DISCUSSION

Magnesite spectra

The Raman spectrum of magnesite has been measured several times at ambient pressure, and, as with other phases isostructural with calcite, its spectrum is reasonably well understood (Bischoff et al., 1985; Yamamoto et
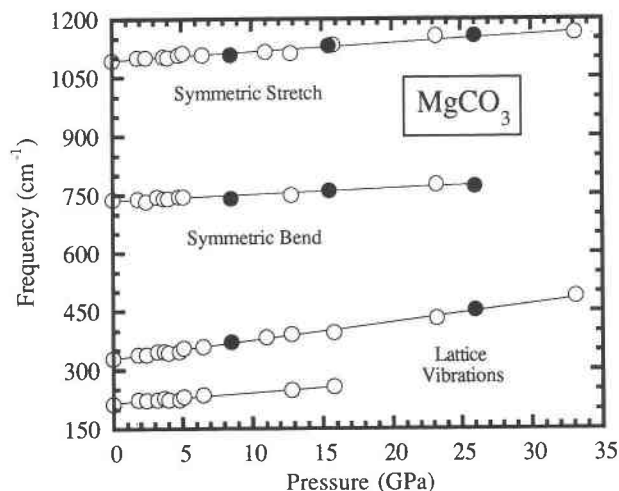
al., 1974, 1975; White, 1974). The bands with zero-pressure frequencies of 1095 and 735 cm⁻¹ are associated with the symmetric stretching vibration and in-plane bending vibration of the carbonate group, respectively. Some debate exists over the precise assignments of the two lower frequency bands at 329 and 216 cm⁻¹. Both White (1974) and Couture (1947) assigned the higher frequency of these bands to a translational motion of the carbonate groups relative to the divalent cation and the lower frequency band to a librational motion. However, Bischoff et al. (1985) proposed that the assignment of these bands be reversed, based upon an analogy with the spectrum of NaNO₃ (isostructural with calcite). We favor this latter assignment, primarily because it is consistent with the lattice dynamic simulations of Yamamoto et al. (1974).

Representative high-pressure Raman spectra of magnesite are shown in Figure 1 and mode shifts are plotted in Figure 2. We do not resolve the lowest frequency peak at pressures above about 13 GPa, possibly because of the role of nonhydrostaticity in broadening this peak. In the pressure range over which the spectrum of magnesite was measured, all observed bands shift continuously with pressure and do not undergo any resolvable splitting, as would be anticipated if a symmetry-lowering phase transition occurred in magnesite at high pressures. This high-pressure stability of magnesite is consistent with shock measurements, which show no change in the slope of the relationship between the shock velocity and the particle velocity of this material to ~120 GPa (Kalashnikov et al., 1973). Thus, the lack of phase transitions in both

TABLE 1. Magnesite (MgCO₃) Raman mode shifts

Magnesite (MgCO₃)		Dolomite* [CaMg(CO₃)₂]		
ν_0 (cm⁻¹)	dν/dP (cm⁻¹/GPa)	ν_0 (cm⁻¹)	dν/dP (cm⁻¹/GPa)	Assignment
1095	2.3 ± 0.1	1101	3.5 ± 0.3	ν_1: CO₃ symmetric stretch
735	1.5 ± 0.2	725	1.1 ± 0.2	ν_4: CO₃ in-plane bend
329	4.7 ± 0.1	301	4.4 ± 0.3	lattice mode
216	2.6 ± 0.2	177	1.4 ± 0.2	lattice mode

* Data from Kraft et al. (1991).

magnesite and dolomite at high pressures is in contrast to the behavior of calcite and is certainly induced by the presence of the smaller magnesium cation within their structures. We therefore anticipate that MgCO₃ in the calcite structure could be a stable carbonate phase to lower mantle depths, in accord with observations of magnesite in samples quenched from pressures of 26 GPa (Katsura and Ito, 1990).

The general behavior of the Raman bands of magnesite under compression are similar to those of the analogous bands in dolomite (Table 1). As in dolomite, the two lowest frequency vibrations diverge with increasing pressure, and the higher frequency internal carbonate vibrations shift at rates that are either comparable with, or slightly less than, those of the two low-frequency lattice modes. One of the primary differences lies in the considerably more rapid shift of the lowest frequency band in magnesite relative to that in dolomite. If we are correct in assigning this band to the E_g-symmetry carbonate translational band, then the square of its frequency is proportional to the force constant between the divalent cation and C within the carbonate lattice (Sherwood, 1972; Nicola et al., 1976). Accordingly, it is probable that within magnesite the C-divalent cation force constant increases significantly more rapidly with pressure than it does within dolomite.

Such a difference in the compressional mechanism may result from the greater stiffness and smaller distortion of the MgO₆ octahedron in magnesite relative to the CaO₆ octahedra present in dolomite. The compression of dolomite may involve a larger amount of distortion of the octahedra relative to that of magnesite, which could compress largely by simple decreases in Mg-C and Mg-O bond distances. Indeed, that this could be the case is supported by the response of these structures to temperature: as temperature is changed, the distortion of octahedra within dolomite shifts, whereas those within magnesite are

unchanged (Reeder and Markgraf, 1986; Markgraf and Reeder, 1985).

Mode Grüneisen parameters provide a means by which the relative contributions of each vibration to the thermochemical properties of these carbonates may be evaluated. We calculate these at ambient pressure conditions using

$$\gamma_i = K_T/\nu_0(\text{d}\nu/\text{d}P)_0 \qquad (1)$$

where γ_i is the mode Grüneisen parameter, K_T is the isothermal bulk modulus, ν_0 is the ambient-pressure mode frequency, and dν/dP is the mode shift with pressure (Table 1). For MgCO₃, we assume that K_T is equal to the isentropic bulk modulus and use a value of 117 GPa for this parameter (Christensen, 1972). Our calculated mode Grüneisen parameters are compatible with those of the analogous modes in dolomite (Table 2); again, that of the lowest frequency mode is significantly larger in magnesite than in dolomite. Also, in both materials the higher frequency internal modes of the carbonate group have mode Grüneisen parameters five to seven times smaller than those of the lower frequency lattice modes. As with dolomite, the largest contributions by optic modes to the thermodynamic Grüneisen parameter are produced by those at low frequencies.

For comparison with the mode Grüneisen parameters, the thermodynamic Grüneisen parameter (γ_{th}) of magnesite at 300 K may be calculated from the identity $\alpha K_s/\rho C_P$, where α is the thermal expansion, K_s is the isentropic bulk modulus, and C_P is the heat capacity. Here, we use a 300-K thermal expansion determined from a quadratic fit to the high-temperature volume data of Markgraf and Reeder (1985) (we utilize such a fit because the limited temperature range and number of these data preclude the use of a Mie-Grüneisen type formalism), the bulk modulus used above to calculate the mode Grüneisen parameters, and a heat capacity (C_P) from Kelley (1960). We thus derive a value of 0.91 for γ_{th} of magnesite, which is slightly larger than that of dolomite. The value of γ_{th} of dolomite is 0.84, calculated using the heat-capacity data of Krupka et al. (1985), a thermal expansion derived in an identical manner to that used for magnesite from the data of Reeder and Markgraf (1986), and a bulk modulus of 82 GPa. For magnesite, an average of the mode Grüneisen parameters of the Raman-active modes that we have characterized is 0.89, which compares favorably with the thermodynamic value.

TABLE 2. Mode Grüneisen parameters

Magnesite (MgCO₃)		Dolomite* [CaMg(CO₃)₂]	
ν_0 (cm⁻¹)	γ_i	ν_0 (cm⁻¹)	γ_i
1095	0.24 ± 0.02	1101	0.26 ± 0.03
735	0.24 ± 0.03	725	0.13 ± 0.03
329	1.67 ± 0.04	301	1.30 ± 0.08
216	1.4 ± 0.1	177	0.67 ± 0.08

* Data from Kraft et al. (1991).

Infrared spectra and structure of CaCO₃-III

Previous work. Although the phase of calcite metastable at the highest pressure known, CaCO₃-III, was discovered over five decades ago by Bridgman (1939), the structure of this phase remains unknown. This is in spite of three high-pressure X-ray diffraction studies (Davis, 1964; Cifrulak, 1970; Merrill and Bassett, 1972), three high-pressure Raman investigations (Fong and Nicol, 1971; Gillet et al., 1988; Liu and Mernagh, 1990), and four high-pressure infrared studies on calcite-structured starting material (Weir et al., 1959; Schock and Katz, 1968; Cifrulak, 1970; Adams and Williams, 1980). Indeed, the only indexing of the X-ray pattern of this phase that is consistent with spectroscopic data indicated that the unit cell of calcite-III is monoclinic, with several possibilities for the space group of this phase (Merrill and Bassett, 1972). As the local environments of the carbonate groups and the compressional behavior of calcite-III are unconstrained, we focus here on vibrational spectroscopic constraints on the structure, bonding, and compressional mechanisms within this phase.

Of the previous infrared studies, none exceeded claimed pressures of 6 GPa, and the three earlier studies utilized no gasket: as such the spectra in these studies represent superpositions of the spectra of calcite-III, calcite-II, and calcite. Indeed, even the spectra of Adams and Williams (1980) to 3.9 GPa may contain some contribution from residual calcite-II, as this phase is often retained within the pressure range within which calcite-III is metastable (e.g., Fong and Nicol, 1971; Adams and Williams, 1980). Schock and Katz (1968) proposed on the basis of studies to 2.0 GPa, that a transition related to the calcite-aragonite transformation occurred within their sample; Fong and Nicol (1971) similarly emphasized the similarity between the Raman spectrum of calcite-III and aragonite. Using infrared spectra to a nominal pressure of 6.0 GPa, Cifrulak (1970) proposed that calcite-III had a vaterite-type structure, similar to a low-density metastable phase of calcium carbonate that can form at ambient pressures and temperatures. Finally, Adams and Williams (1980) refrained from assigning a specific structure to calcite-III but concluded on the basis of band multiplicities that the unit cell of CaCO₃-III has two crystallographically distinct anion sites and probably contains eight formula units.

Infrared data. Our infrared spectra of this phase are both better resolved than any of the previous spectra (Fig. 3) and access pressures at which we anticipate that any residual calcite-II will have converted to the higher pressure calcite-III phase. Our measured mode shifts are shown in Figure 4 and tabulated in Table 3. The asymmetric stretching vibrations (ν_3) lying between 1400 and 1550 cm⁻¹ at low pressure are particularly interesting, as these vibrations are particularly sensitive to the site symmetry of the carbonate group. Furthermore, only Weir et al. (1959) have previously presented high-pressure spectra of calcite in this spectral region. Our spectra below 15 GPa show clear evidence of three distinct bands in this
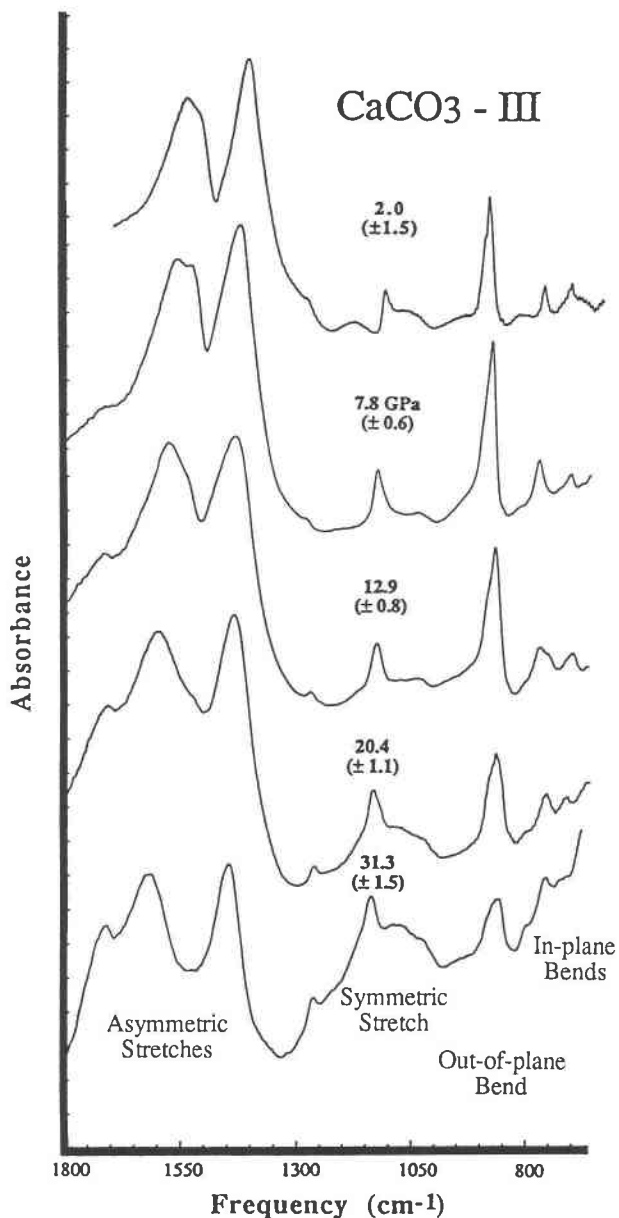

Fig. 3. Representative midinfrared spectra of calcite-III as a function of pressure.

spectral region, with frequencies at 2.0 GPa of 1537, 1513, and 1403 cm⁻¹. Were the carbonate ions in this phase present in a single, low-symmetry site, we would anticipate that this band would be split into two components, as the ν_3 vibration is doubly degenerate within the ideal carbonate group (e.g., White, 1974). That three components exist confirms the inference of Adams and Williams (1980) that at least two crystallographically distinct carbonate ions are present within this phase. Notably, we would thus expect that a fourth component should be present in this spectral region, and it may be that the asymmetry of the peak at 1403 cm⁻¹ toward its higher energy side may be associated with this missing fourth
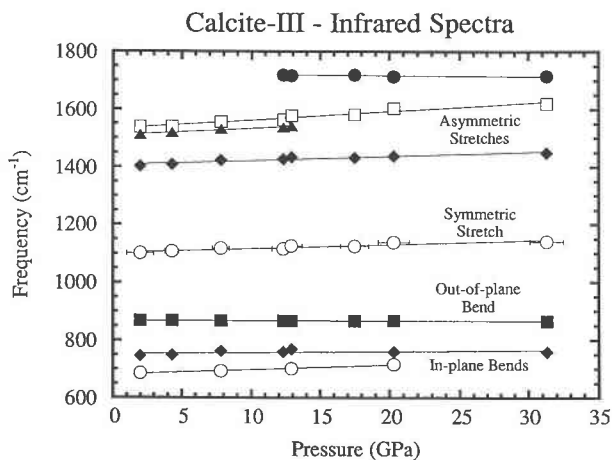
Calcite-III - Infrared Spectra

Fig. 4. Pressure shifts of the infrared frequencies of calcite-III at 300 K. The spectrum at 2.0 GPa was taken on decompression; all other points were taken on compression. Error bars at each pressure are shown on the symmetric stretching vibration ($\nu_0 = 1100$ cm^{-1}).

ment with less than trigonal symmetry. We observe compelling evidence for only one such vibration within the infrared, at 1100 cm^{-1} at 2 GPa; for comparison, Adams and Williams (1980) claimed that an unresolved shoulder was present to the low-energy side of this peak in their highest pressure spectra. We do observe some assymetry toward the low-energy side of the 1100-cm^{-1} peak in our lower pressure spectra, which could be associated with an additional unresolved band at 3–8 cm^{-1} lower frequency than the primary peak; this asymmetry decreases with pressure. Liu and Mernagh (1990) observe three distinct peaks in the frequency range between 1080 and 1102 cm^{-1} within the Raman spectrum of calcite-III at 2.0 GPa (note that this is the strongest peak in the Raman spectra of carbonates), and we would accordingly expect this vibration to produce a multiplet in the infrared spectrum. That it does not implies that the additional infrared bands are likely to be degenerate in frequency with one another, indicating again that the carbonate environments in this phase are similar in their distortion at high pressure.

The presence of two low-symmetry crystallographic environments of the carbonate group would plausibly produce a doubling of this vibration in both the infrared and Raman spectra. Thus, the presence of three closely spaced symmetric stretching bands in the Raman spectrum is probably a consequence of either three or more distinct carbonate units being present in the unit cell of calcite-III or of the Raman spectra resolving either one or two bands induced by factor-group or correlation-field splitting (e.g., White, 1974). As none of the other vibrational bands associated with the carbonate group shows compelling evidence for three or more crystallographically distinct carbonate environments, we view the latter explanation as being more plausible.

Extrapolating the pressure shifts of Liu and Mernagh for the three observed Raman components of the ν_1-derived Raman bands yields essentially identical frequencies (1187 and 1188 cm^{-1}) for two of these Raman bands at 30 GPa, with the third lying only 10 cm^{-1} lower (1177 cm^{-1}). Thus, if two of these bands are generated by the presence of two distinct crystallographic sites in calcite-III (rather than both additional bands being generated by factor-group splitting), then the decreased separation between these bands at high pressure is also compatible with the difference between carbonate sites in this phase decreasing with increasing pressure.

component. Yet, the evolution of the 1513-cm^{-1} peak into a shoulder of the 1537-cm^{-1} peak and its ultimate disappearance as pressure is increased (and the highest frequency feature broadens: Fig. 3) above 15 GPa imply that the effect of pressure is to reduce the crystallographic differences between these two sites. That the lower frequency peak at 1403 cm^{-1} becomes more symmetric at high pressures further supports this interpretation.

Utilizing a semiempirical correlation between the splitting of the asymmetric stretching vibrations and the angular distortion of the carbonate group, we calculated a difference between the minimum and maximum O-C-O angles present in the carbonate groups in this phase of 6.3° (± 0.9°) at low pressure to 7.8° (± 0.9°) at 31 GPa (Greenaway et al., 1986). Thus, from the increase in splitting of the asymmetric stretching vibrations in calcite-III, we infer that the carbonate groups become increasingly distorted in this phase with compression. Yet, from the disappearance of the 1513-cm^{-1} feature, we believe that the two distorted carbonate environments become progressively more similar at high pressures.

The presence of the ν_1 symmetric stretching vibration also dictates that the carbonate group is in an environ-

TABLE 3. Calcite-III midinfrared mode shifts

ν_0* (cm^{-1})	dν/dP (cm^{-1}/GPa)	γ_i	Assignment
1718	−0.2 ± 0.2	−0.01 ± 0.01	2 × out-of-plane bend
1537	3.0 ± 0.3	0.15 ± 0.02	ν_3: asymmetric stretch
1513	~3.5 ± 0.2	0.17 ± 0.01	ν_3: asymmetric stretch
1403	1.5 ± 0.2	0.08 ± 0.01	ν_3: asymmetric stretch
1100	1.4 ± 0.2	0.10 ± 0.01	ν_1: symmetric stretch
868	−0.08 ± 0.03	−0.01 ± 0.003	ν_2: out-of-plane bend
745	1.8 ± 0.6**	0.18 ± 0.06	ν_4: in-plane bend
685	1.7 ± 0.2	0.19 ± 0.02	ν_4: in-plane bend

* Calcite-III frequencies at 2.0 GPa.
** Fit to data below 13 GPa: see text.

As in aragonite, the out-of-plane bending band appearing near 868 cm^{-1} in the infrared spectra is quite insensitive to pressure (Fig. 4, Table 3; Kraft et al., 1991). We attribute this lack of shift to this vibration's known sensitivity to intercarbonate ion coupling (Decius et al., 1963; Sterzel, 1969). This coupling is certainly enhanced by pressure, and any compression-induced increase in the force constant of this vibration is counteracted by this coupling. In passing, we observe that the location of this band in calcite-III is more similar to that of the strongest ν_2 bands in calcite or vaterite (each near 870 cm^{-1}) than to those of aragonite-structured carbonates, which characteristically lie below 855 cm^{-1} in the infrared (e.g., Sato and Matsuda, 1969; Healy and White, 1973; White, 1974).

The ν_4 in-plane bending vibrations appear as two peaks at 685 and 745 cm^{-1} in the infrared spectrum at 2 GPa; Adams and Williams' (1980) spectra contained an additional shoulder near 730 cm^{-1}, but we see no evidence for such a feature. The ν_4-derived vibration is split into two components, as we would expect from a carbonate group in lower than trigonal symmetry. Unfortunately, splittings of the in-plane bending vibrations are less easily correlated with crystallographic distortions of the carbonate group than those of the asymmetric stretching vibrations (Greenaway et al., 1986). In contrast with the asymmetric stretching bands, no further splitting beyond the doubling expected from site group effects is observed; indeed, this vibration appears to be insensitive to the apparent presence of two distinct carbonate groups in the unit cell of this phase. We note that the higher frequency of these two peaks is the only band in the spectra whose frequency shows significant nonlinearity with pressure; its frequency increases to 760–765 cm^{-1} at 8–12 GPa and then remains relatively constant in frequency to higher pressures. Thus, the splitting between these bands appears to increase initially but may decrease at pressures above 8–12 GPa. Unfortunately, the lower frequency of these bands becomes more difficult to resolve at high pressures, probably because of interference from lower frequency lattice vibrations. That these two peaks initially diverge is consistent with the behavior of the asymmetric stretching vibration, whose two primary components (ν_0 of 1537 and 1403 cm^{-1}) also diverge at high pressure. Thus, the initial divergence of these bands is consistent with a greater distortion of the carbonate groups at high pressure.

We note two aspects of our high-pressure spectra that we believe may be produced by overtone vibrations. First, there is an increase in amplitude observed in our higher pressure spectra between 1000 and 1150 cm^{-1}. Second, a peak appears in our high-pressure spectra near 1718 cm^{-1}, which steadily increases in amplitude as pressure is increased and is essentially invariant in frequency with increasing pressure. We attribute the latter feature to a two-phonon vibration associated with the $2 \times \nu_2$ transition. Both the frequency of this band and its pressure shift are consistent with this explanation (it is expected that anharmonicity will cause the frequency of a two-phonon

vibration to be lower than twice the frequency of the one-phonon vibration). We have no simple explanation for the pressure-induced increase in the intensity of this band but note that it may be produced by enhanced Fermi resonance, as the higher frequency and higher intensity asymmetric stretching bands become closer in energy to this mode as pressure is increased (e.g., Nakamoto, 1986). More speculatively, we also attribute the enhanced intensity between 1000 and 1150 cm^{-1} to overtones involving lattice modes, possibly enhanced in intensity by proximity to the symmetric stretching vibration; such combinations of both the out-of-plane and in-plane bending vibrations of the carbonate group with lattice modes are observed in calcite, and calcite-III has a large number of lattice modes that could generate such combinations (Hellwege et al., 1970; White, 1974; Liu and Mernagh, 1990).

Structural implications. The structure of calcite-III remains elusive: yet we can draw some inferences on its pressure dependence from the present data and preclude a close affinity of this structure with those of known calcium carbonate phases. Both Schock and Katz (1968) and Fong and Nicol (1971) have emphasized possible similarities of their high-pressure spectra with those of aragonite; yet, we do not believe that the high-pressure phase of calcite is closely related structurally to aragonite. On the basis of a comparison of our spectra in Figure 3 with our prior high-pressure spectra of aragonite (Kraft et al., 1991), we believe that the primary affinity between these two phases lies in that they both contain somewhat distorted carbonate groups. We are thus in accord with Schock and Katz (1968) that any transition to an aragonite-like structure observed in their samples may have been initiated by shear stress. Specifically, the location of the ν_2 out-of-plane bending vibration, which is often a sensitive probe of the environment of the carbonate ion (Healy and White, 1973), is notably different between the two phases. The splitting of the ν_3 asymmetric-stretching vibration in calcite-III is at least twice as large as that of aragonite at all pressures between 0 and 31 GPa [note that this splitting is unresolvable in aragonite at ambient pressure (Kraft et al., 1991)], and the two components of the ν_4-derived in-plane bending vibrations are split by 60 cm^{-1} in calcite-III, in comparison with ~14 cm^{-1} in aragonite. Thus, although the symmetries of the carbonate groups in calcite-III are probably low (as in aragonite), the level of distortion of the carbonate groups in calcite-III is significantly larger than that present in aragonite.

At low pressures, the spectra of calcite-III bear a somewhat closer resemblance to vaterite than to aragonite (e.g., Cifrulak, 1970), implying that the carbonate environment in calcite-III is more similar to that in vaterite. Unfortunately, unlike for aragonite, there are no high-pressure spectra available of vaterite with which to make a direct comparison between calcite and vaterite under identical pressure conditions. Yet, in detail, the resemblance at low pressures is not compelling. For example, while the splitting of the two most intense components of the asym-

metric stretching vibration of calcite-III is most similar among the known $CaCO_3$ polymorphs to that present within vaterite, this splitting is significantly larger in calcite-III ($\sim$134 cm^{-1} at 2.0 GPa, as opposed to 70 cm^{-1} in vaterite at zero pressure according to Sato and Matsuda, 1969). Also, although only one carbonate environment exists in vaterite, there are clearly at least two in calcite-III, as manifested by the presence of three components of its asymmetric stretching bands in the infrared and multiple components of the symmetric stretch in the Raman. Furthermore, whereas the ν_4 vibration in vaterite is not resolvably split, that in calcite-III clearly has two widely separated components.

With regard to higher pressure polymorphism, we note that the pressure-temperature path followed in our experiments does not intersect the phase boundary between calcite-III and calcite-VI. This transition, to a phase with physical properties similar (although perhaps not identical) to aragonite, has been proposed to exist at pressures near 10 GPa on the basis of shock wave experiments on calcite (Tyburczy and Ahrens, 1986; Kerley, 1989).

The mode Grüneisen parameters of the internal modes of the carbonate group in calcite-III are also reported in Table 3; we utilize a bulk modulus of 75 GPa for this phase, as determined from piston-displacement studies (Singh and Kennedy, 1974). All the measured pressure shifts of the internal modes correspond to γ_i values of less than 0.2: this magnitude of mode Grüneisen parameter is generally similar to those of the infrared-active internal modes of aragonite under pressure (Kraft et al., 1991). As with aragonite, the asymmetric stretching and symmetric stretching vibrations have comparable average γ_i values, whereas the average mode Grüneisen parameter of the in-plane bending vibrations is slightly larger than those of the higher frequency modes. Again, as with magnesite, the low values of the Grüneisen parameters of these modes imply that the compaction in this phase is primarily produced in the divalent cation sites.

ACKNOWLEDGMENTS

REFERENCES CITED

Adams, D.M., and Williams, A.D. (1980) Vibrational spectroscopy at very high pressures. Part 26. An infrared study of the metastable phases of Ca[CO₃]. Journal of the Chemical Society, Dalton Transactions, 1482–1486.

Berg, G.W. (1986) Evidence for carbon in the mantle. Nature, 324, 50–51.

Bischoff, W.D., Sharma, S.K., and Mackenzie, F.T. (1985) Carbonate ion disorder in synthetic and biogenic magnesian calcites: A Raman spectral study. American Mineralogist, 70, 581–589.

Brey, G., Brice, W.R., Ellis, D.J., Green, D.H., Harris, K.L., and Ryabchikov, I.D. (1983) Pyroxene-carbonate reactions in the upper mantle. Earth and Planetary Science Letters, 62, 63–74.

Bridgman, P.W. (1939) The high pressure behavior of miscellaneous minerals. American Journal of Science, 237, 7–18.

Canil, D. (1990) Experimental study bearing on the absence of carbonate in mantle-derived xenoliths. Geology, 18, 1011–1013.

Christensen, N.I. (1972) Elastic properties of polycrystalline magnesium, iron, and manganese carbonates to 10 kilobars. Journal of Geophysical Research, 77, 369–372.

Cifrulak, S.D. (1970) High-pressure mid-infrared studies of calcium carbonate. American Mineralogist, 55, 815–824.

Couture, L. (1947) Etudes des spectres de vibrations de monocristaux ioniques. Annales de Physique, 12, 5–94.

Davis, B.L. (1964) X-ray diffraction data on two high-pressure phases of calcium carbonate. Science, 145, 489–491.

Decius, J.C., Malan, O.G., and Thomson, H.W. (1963) The effect of intermolecular forces upon the vibrations of molecules in the crystalline state. I. The out-of-plane bending of the carbonate ion in aragonite minerals. Proceedings of the Royal Society of London, 275A, 295–309.

Fong, M.Y., and Nicol, M. (1971) Raman spectrum of calcium carbonate at high pressures. Journal of Chemical Physics, 54, 579–585.

Gillet, P., Malezieux, J., and Dhamelincourt, M. (1988) Micro-Raman multichannel spectroscopy up to 2.5 GPa using a sapphire-anvil cell: Experimental set-up and some applications. Bulletin de Minéralogie, 111, 1–15.

Greenaway, A.M., Dasgupta, T.P., Koshy, K.C., and Sadler, G.G. (1986) A correlation between infrared stretching mode absorptions and structural angular distortions for the carbonato ligand in a wide variety of complexes. Spectrochimica Acta A, 42, 949–954.

Healy, P.C., and White, A.H. (1973) The ν_2 vibration of the carbonate species. Spectrochimica Acta A, 29, 1191–1195.

Hellwege, K.H., Lesch, W., Plihal, M., and Schaack, G. (1970) Zweiphononenabsorptionsspektren und Dispersion der Schwingungszweige in Kristallen der Kalkspatstruktur. Zeitschrift für Physik, 232, 61–86.

Kalashnikov, N.G., Pavlovskiy, M.N., Simakov, G.V., and Trunin, R.F. (1973) Dynamic compressibility of calcite-group minerals. Physics of the Solid Earth, 2, 23–29.

Katsura, T., and Ito, E. (1990) Melting and subsolidus phase relations in the MgSiO₃-MgCO₃ system at high pressures: Implications to evolution of the Earth's atmosphere. Earth and Planetary Science Letters, 99, 110–117.

Kelley, K.K. (1960) Contributions to the data on theoretical metallurgy: XIII. High-temperature heat-content, heat capacity, and entropy data for the elements and inorganic compounds. U.S. Bureau of Mines Bulletin 584, 1–232.

Kerley, G.I. (1989) Equations of state for calcite minerals. I. Theoretical model for dry calcium carbonate. High Pressure Research, 2, 29–47.

Kraft, S., Knittle, E., and Williams, Q. (1991) Carbonate stability in the Earth's mantle: A vibrational spectroscopic study of aragonite and dolomite at high pressures and temperatures. Journal of Geophysical Research, 96, 17997–18009.

Krupka, K.M., Hemingway, B.S., Robie, R.A., and Kerrick, D.M. (1985) High-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, dolomite, enstatite, bronzite, talc, tremolite, and wollastonite. American Mineralogist, 70, 261–271.

Kushiro, I., Satake, H., and Akimoto, S. (1975) Carbonate-silicate reactions at high pressures and possible presence of dolomite and magnesite in the upper mantle. Earth and Planetary Science Letters, 28, 116–120.

Liu, L.G., and Mernagh, T.P. (1990) Phase transitions and Raman spectra of calcite at high pressures and room temperature. American Mineralogist, 75, 801–806.

Mao, H.K., Bell, P.M., Shaner, J.W., and Steinberg, D.J. (1978) Specific volume measurements of Cu, Mo, Pd and Ag and calibration of the ruby R₁ fluorescence pressure gauge from 0.06 to 1 Mbar. Journal of Applied Physics, 49, 3276–3283.

Markgraf, S.A., and Reeder, R.J. (1985) High-temperature refinements of calcite and magnesite. American Mineralogist, 70, 590–600.

Merrill, L., and Bassett, W.A. (1972) Crystal structures of the high pressure phases of calcite. Eos, 53, 1121.

Nakamoto, K. (1986) Infrared and Raman spectra of inorganic and coordination compounds. Wiley, New York.

Nicola, J.H., Scott, J.F., Couto, R.M., and Correa, M.M. (1976) Raman spectra of dolomite [CaMg(CO₃)₂]. Physical Review B, 14, 4676–4678.

Reeder, R.J., and Markgraf, S.A. (1986) High-temperature crystal-chemistry of dolomite. American Mineralogist, 71, 795–804.

Sato, M., and Matsuda, S. (1969) Structure of vaterite and infrared spectra. Zeitschrift für Kristallographie, 129, 405–410.

Schock, R.N., and Katz, S. (1968) Pressure dependence of the infrared absorption of calcite. American Mineralogist, 53, 1910–1917.

Sherwood, P.M.A. (1972) Vibrational spectroscopy of solids, p. 62–73. Cambridge University Press, Cambridge, England.

Singh, A.K., and Kennedy, G.C. (1974) Compression of calcite to 40 kbar. Journal of Geophysical Research, 79, 2615–2622.

Sterzel, W. (1969) Der Einfluss der Kristallstruktur auf die Kopplung der ν_2-Schwingung von Carbonationen. Zeitschrift für anorganische und allgemeine Chemie, 368, 308–316.

Tyburczy, J.A., and Ahrens, T.J. (1986) Dynamic compression and volatile release of carbonates. Journal of Geophysical Research, 91, 4730–4744.

Weir, C.F., Lippincott, E.R., van Valkenberg, A., and Bunting, E.N. (1959) Infrared studies in the 1- to 15-micron region to 30,000 atmospheres. Journal of Research of the National Bureau of Standards, 65A, 173–183.

White, W.B. (1974) The carbonate minerals. In V.C. Farmer, Ed., The infrared spectra of minerals, p. 227–279. Mineralogical Society Monograph, London.

Yamamoto, A., Utida, T., Murata, H., and Shiro, Y. (1974) Optically-active vibration and elastic constants of calcite and aragonite. Bulletin of the Chemical Society of Japan, 47, 265–273.

Yamamoto, A., Shiro, Y., and Murata, H. (1975) Optically-active vibrations and effective charges of calcite and magnesite. Bulletin of the Chemical Society of Japan, 48, 1102–1106.