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# Characterization of some biogenic carbonates with Raman spectroscopy

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## Abstract

Raman spectra are reported for biogenic carbonates from a scleractinian coral (*Porites* sp.), pink pigmented (*Corallium regale*) and unpigmented (*Corallium secundum*) precious corals, and natural and cultured pearls. Spectra of aragonitic *Porites* coral and pearls show Raman bands typical of aragonite; however, the bands of the natural pearl are slightly sharper than the corresponding bands from *Porites* and cultured pearl spectra. The broadening of the Raman bands of *Porites* is indicative of either small crystallite size or crystal structure disorder.

Spectra of the deep-sea, precious corals closely resemble Raman spectra of magnesian calcite, with the exception of the pink coral, which shows seven additional bands in the spectral region of 1020–3758 $cm^{-1}$. These extra bands arise from a carotenoid pigment that is responsible for the pink coloration of the coral skeleton. Lattice modes for these corals are much broader than the corresponding pure calcite bands but are similar to those of synthetic 9.9 mol% magnesian calcite. These increased halfwidths are attributed mainly to static positional disorder of the carbonate ion in the calcite. This static rotation of carbonate ions out of the basal plane results from the substitution of 10 mol% $Mg^{2+}$ for $Ca^{2+}$ in the calcite. The positional disordering of carbonate ions in biogenic magnesian calcite seems to be characteristic of these biominerals, irrespective of their source, and may affect the relative stabilities of these carbonates as they undergo diagenesis.

## Introduction

To date, nearly 60 different types of biogenic minerals have been recognized, but only a few of these biominerals have been examined in detail (Lowenstam and Weiner, 1989). Of this diverse assemblage of biominerals, the carbonates are the most important in terms of abundance, accounting for approximately 30% of the Phanerozoic sedimentary rock record after diagenesis (Chave, 1984; Lowenstam and Weiner, 1989; Morse and Mackenzie, 1990). These phases exert a major influence on the chemistry of sea water, the composition of sediments accumulating in the oceans, and the nature of diagenesis. In order to understand quantitatively the fate of these carbonates in sedimentary and diagenetic environments, information about their microstructures and chemical heterogeneities is essential.

Bischoff et al. (1985) used Raman spectroscopy to show that positional disordering of the carbonate ions is greater for biogenic magnesian calcites than for synthetic magnesian calcites with similar compositions. This disorder is an important factor affecting the thermodynamic stability of these biogenic phases. In the present study, Raman spectroscopy has been used to investigate the structures of biogenic aragonite and additional biogenic calcite. The results confirm previous findings (Bischoff et al., 1985) of carbonate ion positional disorder in biogenic calcites. Furthermore, our results show that the differences observed between biogenic and synthetic aragonite Raman spectra are much smaller than those of the magnesian calcite and that these differences may originate more from small crystallite size than crystal structure disorder.

## Experimental methods

The Raman spectra were recorded at room temperature with a Spex 1402 double monochromator and a computerized data acquisition system. The carbonate samples were excited with the 488.0-nm line of an $Ar^+$ ion laser. The biogenic calcite and aragonite samples were studied directly with no pretreatment, and the synthetic calcite and aragonite samples were powdered and placed in capillary tubes. Scattered radiation from the samples was measured in a 90° scattering geometry. The Raman spectra were obtained at intervals of 1 $cm^{-1}$ (100–1800 $cm^{-1}$) and 3 $cm^{-1}$ (2000–4000 $cm^{-1}$) and slit widths of 2 or 3 $cm^{-1}$. Selected anti-Stokes Raman spectra were recorded for calibration purposes and only Stokes Raman spectra are illustrated. Raman spectra of pink coral samples were also recorded with the 514.5-nm line of an $Ar^+$ ion laser to distinguish between Raman and fluorescence bands. Compositions of the magnesian calcite samples were determined using electron microprobe and X-ray diffraction analyses.

## Structure and band assignments

Calcite and aragonite are the two major polymorphs of calcium carbonate that have been identified as geologi-

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cally important biominerals. Aragonite is the thermodynamically favored phase at high pressure.

### Calcite

Calcite has rhombohedral space group $D_{3d}^6$ ($R\bar{3}c$) with $Z = 2$. Cations have $C_{3i}$ site symmetries, and C atoms occupy sites with $D_3$ symmetry. Factor-group analysis predicts that 27 optical modes will be distributed among the following symmetry species (Bhagavantam and Venkatarayudu, 1939; Wilkinson, 1973; White, 1974):

lattice modes

$$\Gamma_{rot} = A_{2g}(i.a.) + E_g(R) + A_{2u}(IR) + E_u(IR)$$

$$\Gamma_{trans} = A_{2g}(i.a.) + E_g(R) + A_{1u}(i.a.) + A_{2u}(IR) + 2E_u(IR)$$

internal modes

$$\Gamma_{int} = A_{1g}(R) + A_{2g}(i.a.) + 2E_g(R) + A_{1u}(i.a.) + A_{2u}(IR) + 2E_u(IR)$$

where $\Gamma_{rot}$ and $\Gamma_{trans}$ refer to the rotational and translational lattice modes, and R, IR, and i.a. refer to Raman-active, infrared-active, and inactive modes, respectively. In the Raman spectrum of calcite, a total of five fundamental vibration modes, two lattice modes and three internal modes, are expected to be active (White, 1974). The first overtone of the infrared-active $2 \times \nu_2$ mode at 1740–1750 $cm^{-1}$ is also allowed in the Raman spectrum.

### Aragonite

Aragonite has orthorhombic space group $D_{2h}^{16}$ (*Pnma*) with $Z = 4$. In calcite, C in the carbonate anions occupies sites with $D_3$ symmetry, but in aragonite C has $C_s$ symmetry. Factor-group analysis predicts that 57 optical modes in aragonite will be distributed among the following symmetry species (Couture, 1947; Yamamoto et al., 1974):

lattice modes

$$\Gamma_{rot} = A_{1g}(R) + 2B_{1g}(R) + 2B_{2g}(R) + B_{3g}(R) + 2A_{1u}(i.a.) + B_{1u}(IR) + B_{2u}(IR) + 2B_{3u}(IR)$$

$$\Gamma_{trans} = 4A_{1g}(R) + 2B_{1g}(R) + 2B_{2g}(R) + 4B_{3g}(R) + 2A_{1u}(i.a.) + 3B_{1u}(IR) + 3B_{2u}(IR) + B_{3u}(IR)$$

internal modes

$$\Gamma_{int} = 4A_{1g}(R) + 2B_{1g}(R) + 2B_{2g}(R) + 4B_{3g}(R) + 2A_{1u}(i.a.) + 4B_{1u}(IR) + 4B_{2u}(IR) + 2B_{3u}(IR).$$

In the Raman spectrum of aragonite, 30 fundamental vibration modes are expected to be active. The rotational and translational lattice modes appear in the low-frequency region (100–350 $cm^{-1}$), whereas the internal fundamental modes of vibration of the carbonate ions appear in the high-frequency region (600–1800 $cm^{-1}$).

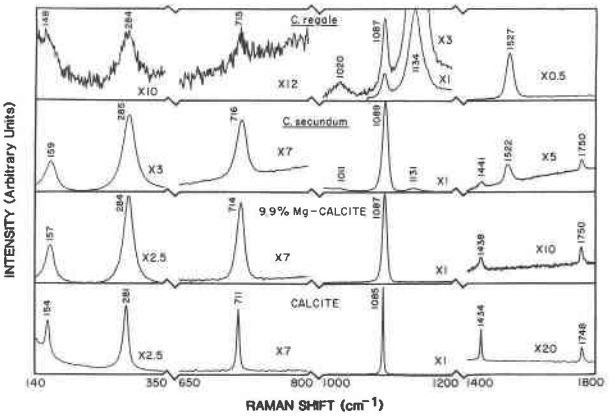


Fig. 1. Portions of the Raman spectra for pink (*C. regale*) and white (*C. secundum*) precious corals, synthetic magnesian calcite (9.9 mol% $MgCO_3$), and calcite over the region of 140–1800 $cm^{-1}$. Scaling factors for the various intervals are relative to the $\nu_1$ mode (~1085 $cm^{-1}$) of each sample.

## Results and Discussion

### Biogenic calcite

Selected portions of the region from 140–1800 $cm^{-1}$ of the Raman spectra of deep-sea corals, calcite, and magnesian calcite with 9.9% Mg are shown in Figure 1. Additional high-frequency Raman spectra in the interval of 2000–4000 $cm^{-1}$ for pink (*Corallium regale*) and white (*Corallium secundum*) precious corals are shown in Figure 2.

The five fundamental bands and the overtone band at 1740–1750 $cm^{-1}$ predicted from the group theory analysis of calcite are observed in the synthetic and biogenic calcite spectra. The bands at 154 $cm^{-1}$ and 281 $cm^{-1}$ in the calcite spectrum have been assigned to translational ($E_g$) and rotational ($E_g$) modes, respectively (Bischoff et al., 1985). It should, however, be emphasized that a considerable degree of mixing occurs between the translational and rotational lattice modes of calcite (Rousseau et al., 1968). The weak bands at 711 $cm^{-1}$ and 1434 $cm^{-1}$ are internal $E_g$ modes corresponding to in-plane bending ($\nu_4$) and antisymmetric stretching ($\nu_3$) modes of carbonate ions. The strongest band, at 1085 $cm^{-1}$, is an $A_g$ internal mode that derives from the symmetric stretching mode ($\nu_1$) of the carbonate ion.

The general features of the Raman spectra of the pink and white corals closely resemble the spectra of calcite and synthetic magnesian calcite with 9.9% Mg, even though the pink coral spectrum has a low signal-to-noise ratio because of the strong fluorescence background. In addition to the expected calcite bands, Raman bands were also observed at 1011, 1131, and 1522 $cm^{-1}$ in the spectrum of white coral and at 1020, 1134, and 1527 $cm^{-1}$ in the spectrum of pink coral. The band at 1134 $cm^{-1}$ for pink coral is nearly three times stronger than the 1087-$cm^{-1}$ ($A_{1g}$) mode of the carbonate ion that dominates the other calcite spectra. Raman spectra of biogenic carbon-

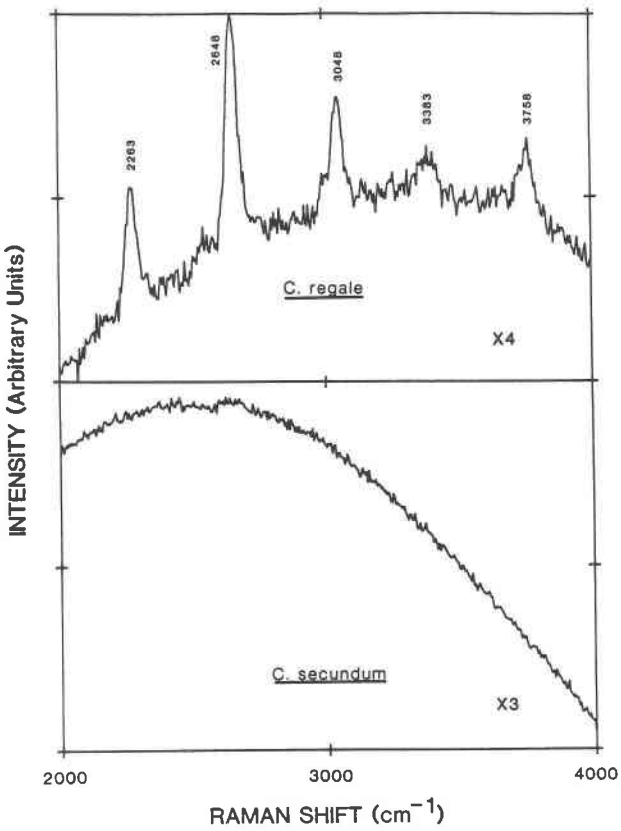


Fig. 2. Raman spectra in the region of 2000–4000 cm$^{-1}$ of pink *C. regale* and white *C. secundum* precious corals showing the characteristic combination and overtone bands of the carotenoid pigment in the *C. regale* spectrum.

ates usually contain a weak band near 1014 cm$^{-1}$ that has been attributed to bicarbonate ion ($HCO_3^-$) (Bischoff et al., 1985), which occurs in biogenic carbonates as a possible charge balance for an equivalent amount of $Na^+$ (White, 1975; Veizer, 1983; Bischoff et al., 1983). The Raman band at 1011 cm$^{-1}$ in the *C. secundum* spectrum can be assigned to bicarbonate ion. The origins of those bands that are not assignable to vibrations of carbonate and bicarbonate ions in calcite will be discussed in the following section.

Bischoff et al. (1985) evaluated in detail some of the possible mechanisms for interpreting the variations in half width (full width at the half-maximum peak height) and band positions in Raman spectra of magnesian calcite; only a brief summary is given here. The systematic variations in the Raman spectra of magnesian calcite may be potentially explained by changes in unit-cell dimensions because of the random substitution of $Mg^{2+}$ for $Ca^{2+}$ in the magnesian calcite solid-solution series, heterogeneities in the distribution of $Mg^{2+}$ in the biogenic calcite, or the presence of trace constituents, such as $SO_4^{2-}$, $Na^+$, and $OH^-$ (Busenberg and Plummer, 1985), in the biogenic samples. Bischoff et al. (1985) evaluated these potential mechanisms and showed that they are either not plausible on the basis of other observations or are not sufficiently significant to account for the differences observed between the half widths of synthetic and biogenic magnesian calcite samples having similar $Mg^{2+}$ contents. Instead, they proposed that the static positional disorder of carbonate ions in the calcite structure can provide a mechanism to explain the variations in the Raman spectra of the biogenic calcite. This disorder is physically manifested as a tilting of the planar carbonate groups out of the basal plane toward the c axis in order to accommodate the shorter Mg-O bonds in the crystal structure. This mechanism is supported by measurements of the *c*/*a* axial ratios for magnesian calcite, which shows positive deviations of the ratio from the ideal behavior (Bischoff et al., 1983; Mackenzie et al., 1983). Thus, although other factors may in part account for the increases in half width and changes in band positions in Raman spectra of biogenic magnesian calcite, the static positional disordering of the carbonate groups in the calcite crystal structure largely accounts for this behavior (Bischoff et al., 1985).

Observed half widths and positions of prominent Raman bands for the calcite samples are summarized in Table 1. The half widths and positions of the Raman bands in the pink and white coral spectra are found to be significantly different from the corresponding bands of the synthetic calcite, and to more closely resemble those of the synthetic 9.9 mol% magnesian calcite spectrum (Fig. 1). The spectra for the pink coral in the low frequency region are much degraded in comparison to the other calcite spectra in Figure 1. Biogenic magnesian calcite typically yields noisy spectra because of fluorescence from trace impurities (Bischoff et al., 1985), and the reduced precision in data for these spectra may, in part, be responsible for some scatter in the trends of spectral

**TABLE 1.** Raman frequencies and half widths (cm$^{-1}$) for synthetic and biogenic calcites

| Sample | T | L | $\nu_4$ | | $\nu_1$ | | $\nu_3$ | | $2 \times \nu_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Calcite | 154 | 281 | 711 | | 1085 | | 1434 | | 1748 |
| | (6.7) | (9.5) | (4.5) | | (2.5) | | (5.5) | | (8.0) |
| 9.9 mol% | 157 | 284 | 714 | | 1087 | | 1438 | | 1750 |
| Magnesian calcite | (14.7) | (18.3) | (9.7) | | (7.6) | | (14) | | (10.8) |
| White coral | 159 | 285 | 716 | 1011 | 1089 | 1131 | 1441 | 1522 | 1750 |
| (*C. secundum*) | (19.4) | (23.1) | (13.4) | nm | (9.4) | nm | (13.9) | (23.9) | (13.9) |
| Pink coral | 148 | 284 | 715 | 1020 | 1087 | 1134 | nm | 1527 | nm |
| (*C. regale*) | nm | (26) | nm | (22.9) | (9.0) | (21.4) | | (25.9) | |

*Note:* Half widths given in parentheses. The abbreviation nm = not measured. T = translational mode; L = librational mode.

properties obtained from biogenic carbonates. The skeletal pigment in the pink coral skeleton is the most likely cause for the degraded signal-to-noise ratio in the low-frequency region of this sample. The large half widths for the lattice modes (140–350 $cm^{-1}$ region in Fig. 1) of the precious corals are similar in magnitude to half widths measured for other biogenic magnesian calcite (Bischoff et al., 1985) and are primarily attributed to the static positional disordering of the carbonate ion in the calcite crystal structure. This disordering results from the presence of 10 mol% $Mg^{2+}$ in these biogenic samples as determined by electron microprobe and X-ray diffraction analyses. For a given mol% of $Mg^{2+}$, the biogenic calcites also show slightly greater half widths than the compositionally equivalent synthetic calcites (Bischoff et al., 1985), which suggests the possibility of greater positional disorder along with greater compositional heterogeneities in the biogenic magnesian calcite.

### Calcite pigments

The most prominent bands in the Raman spectrum of the pink precious coral *C. regale* are a number of bands that are not attributable to the carbonate skeleton of the coral (Figs. 1, 2). The dominant Raman bands, between 1020 and 1527 $cm^{-1}$, are characteristic of resonance Raman spectra from *trans* conjugated carotenoid pigments (Rimai et al., 1973; Hoskins and Alexander, 1977). The intensities of the carotenoid Raman bands are much enhanced over the bands of the calcite matrix owing to the resonant coupling of the vibrational and electronic transitions with the laser source. Thus Raman spectra of carotenoids may be obtained at very low in situ pigment concentrations.

The characteristic vibrational modes of the carotenoid pigment are assigned as follows (Saito and Tasumi, 1983; Merlin, 1985; Merlin and Delé-Dubois, 1986). The fundamental Raman bands are at 1527 $cm^{-1}$ ($\nu_1$), which is produced by the stretching vibrations of -C=C- double bonds, and at 1134 $cm^{-1}$ ($\nu_2$) because of the stretching of -C-C- single bonds. The low intensity band at 1020 $cm^{-1}$ ($\nu_3$) is attributable to the rocking mode of the $-CH_3$ functional group. The other Raman bands of the carotenoid are combinations or overtones of the fundamental modes: 2263 $cm^{-1} = 2\nu_2$; 2648 $cm^{-1} = \nu_1 + \nu_2$; 3048 $cm^{-1} = 2\nu_1$ or $3\nu_3$; 3383 $cm^{-1} = 3\nu_2$; and 3758 $cm^{-1} = \nu_1 + 2\nu_2$.

As part of a wide-ranging Raman spectroscopic investigation of a variety of natural pigments in mollusc shells and corals, Merlin and Delé (1983) and Merlin and Delé-Dubois (1986) examined the pigments of a sample of the precious coral *Corallium rubrum,* which has a deep red coloration, both in situ and in solution extracts. Previous attempts to characterize the nature of the pigmentation of *C. rubrum* using chemical techniques were unsuccessful because the pigment could not be extracted from the skeleton (Fox, 1972). By using Raman spectroscopy, Merlin and Delé (1983) successfully identified a carotenoid as the type of pigment responsible for the coloration of this coral. Based on a comparison with the Raman spectra of other carotenoids, a *trans* configured carotenoid with a ROOC-$(CH{=}CH)_n$-COOR′ ($n = 11 \pm 1$) structure was proposed for the pigment in *C. rubrum* (Merlin, 1985; Merlin and Delé-Dubois, 1986).

A comparison of our Raman spectra from *C. regale* with the spectra from *C. rubrum* (Merlin and Delé-Dubois, 1986) reveals that the spectra are essentially identical, and the band positions differ by only 2–3 $cm^{-1}$ for the fundamental carotenoid modes. The intensities of the carotenoid bands relative to the carbonate bands are significantly greater for *C. rubrum* than for the *C. regale* bands in our spectra. The $\nu_1$ calcite peak at 1087 $cm^{-1}$ is a separate and distinct peak in the Raman spectrum for *C. regale* (Fig. 1), but the same $\nu_1$ calcite band is barely discernible as a shoulder on the much more intense $\nu_2$ carotenoid band of *C. rubrum* (Merlin and Delé-Dubois, 1986). These intensity differences are attributable to corresponding differences in the relative concentrations of the same carotenoid pigment; the pink coloration of *C. regale* results from a lower concentration of carotenoid in the calcite skeleton than in the deep red colored *C. rubrum.*

Further support for the contention that a carotenoid is responsible for coloration of the coral is obtained from examination of white parts of the same coral skeleton (Merlin and Delé-Dubois, 1986) and a white member of the same genus (*C. secundum*). Our Raman spectra for *C. secundum* do not exhibit the intense bands characteristic of the carotenoid pigment found in the *C. regale* spectra. The weak bands in the *C. secundum* spectrum at 1131 $cm^{-1}$ and 1522 $cm^{-1}$ (Fig. 1) are presumably due to trace amounts of pigment in the skeletal matrix, although none of the characteristic combination or overtone bands were observed at higher frequencies because of their very low intensities (Fig. 2). The resonance Raman scattering of carotenoids can serve as a useful nondestructive and diagnostic technique for identifying this class of pigment in biogenic minerals.

### Biogenic aragonite

Portions of Raman spectra in the 140–1800 $cm^{-1}$ region for aragonite of the reef-building coral *Porites,* of cultured and natural pearl, and of synthetic aragonite are shown in Figure 3. Only 14 bands out of the 30 predicted Raman-active modes were detected in the Raman spectra of the polycrystalline aragonite samples. The lower-than-predicted number of observed bands may be attributed to a number of factors, such as low intensities, accidental degeneracies, or very small displacements of the trigonal anions to give a near-trigonal symmetry [$D_{3d}^3$ ($P\bar{3}m1$) and $Z = 2$] (Ismail et al., 1982) that yields a simpler spectrum than expected for crystals with the aragonite structure. The positions of the observed Raman bands are in agreement with those reported by Couture (1947) for the polarized Raman spectrum of aragonite. The most intense band near 1085 $cm^{-1}$ ($A_{1g}$) in the aragonite spectra corresponds to the $\nu_1$ symmetric stretching mode of the carbonate ion. The low to medium intensity bands in

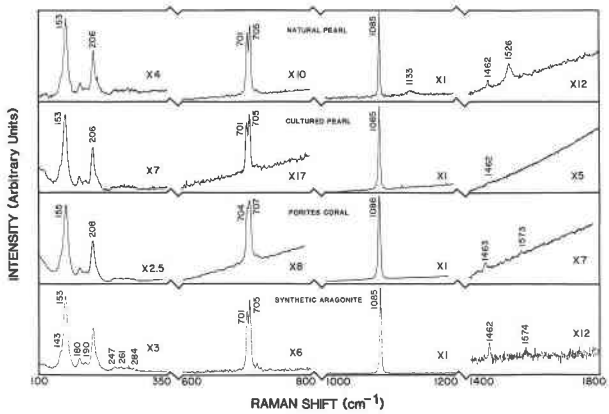


Fig. 3. Selected portions of the Raman spectra in the interval of 100–1800 $cm^{-1}$ for natural and cultured pearls, the scleractinian coral *Porites* sp., and synthetic aragonite. The scaling factors are relative to the $\nu_1$ mode (~1085 $cm^{-1}$) for each sample. The $\nu_2$ band of the carbonate ion in the region of 800–850 $cm^{-1}$ is very weak and is not shown in the figure.

the region of 100–300 $cm^{-1}$ of the aragonite spectra arise from translational and rotational modes of lattice vibration. The $\nu_4$ in-plane bending mode of the carbonate ion in aragonite occurs as a doublet consisting of bands at ~701 $cm^{-1}$ ($B_{1g}$) and ~705 $cm^{-1}$ ($A_{1g}$) (Fig. 3, Table 2), which is in contrast to the single band at ~711 $cm^{-1}$ found in the calcite spectra (Fig. 1, Table 1). We were able to observe only a single band at 1462 $cm^{-1}$ in the $\nu_3$ region, rather than a doublet (1464 and 1466 $cm^{-1}$) as reported by Couture (1947). We also detected a very weak $\nu_2$ band at ~852 $cm^{-1}$ (Table 2); this vibrational mode is permitted for the aragonite crystal structure but is not allowed in the Raman spectra of crystals with a calcite structure. An additional weak band at ~1574 $cm^{-1}$ was observed in some of the aragonite spectra (Fig. 3, Table 2). The ~1574-$cm^{-1}$ band probably arises from a combination mode.

The Raman spectrum measured for the natural pearl sample contains two bands at 1133 $cm^{-1}$ and 1526 $cm^{-1}$ that are not observed in the cultured pearl spectrum (Fig. 3, Table 2) and that are not assignable to vibrations of the carbonate ions in the aragonite crystal. These respective bands originate from the vibrations of single and double C bonds. Such bands may result from a diffuse matrix of protein that pervades the carbonate matrix of the natural pearl (Alexander, 1940). Although no coloration of the sample was noticed, these bands might also be caused by the type of carotenoid pigment discussed in the previous section, particularly as in the case of the white *C. secundum* coral. The intensity ratio of the two bands in the natural pearl ($I_{1526}/I_{1133} = 1.1$) is identical to the ratio of the equivalent peaks of the carotenoid pigment in the pink coral carbonate. This evidence indicates that trace amounts of carotenoid are likely present in the aragonite matrix of the natural pearl, and one might predict that for pearls with some coloration, the pigmentation may originate from a carotenoid.

The Raman spectra for the synthetic and biogenic aragonite samples are all very similar (Table 2, Fig. 3) and the biogenic aragonite spectra are not as variable as the spectra of biogenic magnesian calcite. The positions of the Raman bands are all similar, and the only differences are found in the peak half widths. The lattice modes of the natural pearl have half widths that are narrower than in the synthetic aragonite (Table 2). The half widths for some lattice modes and the $\nu_1$ symmetric stretching band of the carbonate ions in the *Porites* coral sample are greater than for the synthetic and other biogenic aragonite. The slight broadening of the *Porites* bands may possibly be attributed to a difference in the aragonite crystal size and habit. For a typical scleractinian coral, the skeletal matrix is made up of small acicular aragonite crystals on the order of 1–4 $\mu$m in diameter (Constantz, 1986). Although such aragonite crystals are sufficiently small to cause line broadening, the *Porites* band positions are, however, shifted to higher frequencies, which is opposite to the shift expected from reduced particle sizes (Sharma and Urmos, 1987). Variability in the Raman spectra of biogenic aragonite may, perhaps, be attributed more to variations in crystallite size or other factors than to crystal structure disorder, which, if it occurs in aragonite, is certainly not as pronounced as the disorder found in magnesian calcite.

## Summary and conclusions

The Raman spectroscopic results presented in this paper and previously by Bischoff et al. (1985) reveal that carbonate ion positional disordering is ubiquitous in both biogenic and synthetic magnesian calcite. An important

**Table 2.** Raman frequencies and half widths ($cm^{-1}$) for synthetic and biogenic aragonite

| Sample | Lattice modes | | | | | | | | $\nu_4$ | | $\nu_2$ | $\nu_1$ | | $\nu_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aragonite (synthetic) | 143 | 153 (8.7) | 180 (7.4) | 190 | 206 (7.4) | 247 | 261 | 284 | 701 | 705 | 853 | 1085 (2.1) | | 1462 (6.0) | 1574 |
| *Porites* coral | 145 | 155 (9.6) | 182 (7.4) | 192 | 208 (8.1) | 249 | 264 | 286 | 704 | 707 | nm | 1086 (4) | | 1463 (10) | 1573 |
| Cultured pearl | 144 | 153 (8.7) | 180 (6.0) | 190 | 206 (7.4) | 246 | 261 | 283 | 701 | 705 | nm | 1085 (2.2) | | 1462 (6.5) | |
| Natural pearl | 143 | 153 (7.4) | 180 (5.6) | 190 | 206 (6.8) | 248 | 259 | 284 | 701 | 705 | 852 | 1085 (2.1) | 1133 | 1462 (5.0) | 1526 (19.9) |

*Note:* Half widths given in parentheses. The abbreviation nm = not measured.

aspect of these observations is that biogenic magnesian calcite phases exhibit greater positional disorder of the carbonate ion than does synthetic magnesian calcite with the same $Mg^{2+}$ content (Fig. 1). A significant geological consequence of these different degrees of disordering is that these differences are, in part, responsible for different relative chemical reactivities of these phases during diagenesis. Disordering and other physical and chemical factors affecting the relative stabilities of various carbonate phases have been used by Bischoff et al. (in preparation) to propose a number of different possible reaction pathways for the diagenetic stabilization of magnesian calcite to more stable carbonates containing smaller concentrations of trace element impurities and less structural disorder.

As might be predicted from the typically low degree of trace element substitution in aragonite, which at most is ~1% for $Sr^{2+}$ (Veizer, 1983), the Raman spectra for the biogenic aragonite samples do not show evidence of the type of carbonate ion positional disordering that typifies biogenic magnesian calcite. Thus other factors, such as crystallite size, may need to be considered when assessing the chemical reactivities of aragonite undergoing diagenesis.

Raman spectroscopy is a valuable tool for characterizing the microstructure of biogenic and synthetic carbonates. This method can also detect organic material, such as carotenoid pigment, that is closely associated with the mineral matrix of biogenic carbonate. Variations in the positions and half widths of the Raman-active modes provide evidence of the presence of rotational disordering of the carbonate ion in carbonates. This rotational disorder is evident in calcite, but not in aragonite, owing to the presence of solid solution between $Ca^{2+}$ and $Mg^{2+}$ and the greater concentration of trace impurities in calcite. Raman studies of biogenic magnesian calcite show that it typically has some degree of disorder that is greater than that in the equivalent synthetic materials. This disordering in biogenic materials has not been a widely recognized phenomenon. Such disordering in biogenic carbonates may play an important role in influencing the diagenetic behavior of these minerals.

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