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FEASIBILITY OF USE OF VNIR REFLECTANCE SPECTROSCOPY FOR ANALYSIS OF WATER AND ORGANIC CONTENT IN SKELETONS OF SCLERACTINIAN CORALS

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ABSTRACT

Spectral and petrographic data show that water and organics in coral skeletons are intimately associated in both modern and Pleistocene samples. The water itself appears to be entrapped body fluids of the coral rather than sea water.

Relative band areas provide a more accurate indicator of total water and organic content than the relative band intensities used in previous studies. While the area of the 1.4-um absorption band provides a useful measure of the water content of samples, the 1.9-um band appears to provide a more sensitive indicator of their organic content. Spectra of skeletons of colonies of *Diploria strigosa* which were live when collected show there is significant intraskeletal variation in both water and organic content. Thecae commonly contain more water and organics than septa, but water contents of different portions of septa and thecae also show meaningful variations. Water and organics are lost rapidly after death of the coral. Amounts of organics and water in septa and thecae become more uniform throughout the skeleton, and differences between septa and thecae decrease.

Although organics are still present in dead and fossil skeletons, trends in areas of 1.4-um and 1.9-um water bands in their spectra show that both the absolute abundance of organics and abundance of organics relative to water has decreased. Changes in organic content are also indicated by the progressive decrease in intensity of the 0.67 um chlorophyll band in spectra of dead and Pleistocene samples.

INTRODUCTION

The chemical and mineralogical composition of skeletal carbonates is more complex and varied than the usual designations of "aragonite" and "high" or "low magnesian calcite" would suggest. Previous work has shown that water (liquid and bound H_2O and OH^-) is an important and ubiquitous component of all carbonate skeletal material (Gaffey, 1983, 1984a,b, 1985, 1988). Water in carbonate skeletons affects their solubility and stability, and can serve as a medium for diagenetic reactions (see Gaffey, 1988 for summary and references).

Organic compounds can also have a marked effect on diagenesis of carbonates (e.g. Gautier, 1985; Mitterer and Cunningham, 1985). Although it has been known for many years that carbonate skeletons contain organic material (see Weiner et al., 1983, for review) there is no tool routinely in use by carbonate petrologists for determining organic content, or for determining the relationship between water and organics in skeletal samples, and data on organic contents of carbonate skeletons is limited. Reflectance spectroscopy provides a rapid, non-destructive tool for characterization of water and organic content *in situ* (Gaffey, 1983, 1984a,b, 1985, 1988; Holden, 1988). Like X-ray diffraction, vibrational spectroscopy is non-selective, detecting all spectrally active components in a sample whether or not they are anticipated. Unlike X-ray diffraction, however, reflectance spectroscopy can detect liquid or amorphous phases, as well as those which have an ordered crystal structure.

The purpose of this study is to test the applicability of reflectance spectroscopy to studies of the effects water and organics on early diagenetic alteration of carbonate sediments. A

more detailed discussion of the spectral properties of water and organics can be found in Gaffey (1988 and this volume).

SAMPLES AND METHODS

All coral samples used in this study were collected during two visits to San Salvador, Bahamas, the first in January, 1988, and the second in June, 1988. Living corals were bleached in dilute clorox. Samples were identified at the generic, and, when possible, the specific level. Localities at which samples were collected and condition i.e., modern living, modern dead (whether still in place on the reef, in reef rubble, or in the intertidal zone on beaches), or fossil (from Pleistocene reefs on San Salvador) were recorded. Localities for and classification of samples used in this study are given in Table 1.

Thin sections of a radial section of coral heads, or longitudinal section of branches were prepared for each specimen. Acetate peels were also prepared for some samples. Septa of DSRBML-75, DSRBMD-92, and D-SPPL-84 were examined with SEM. Mineralogy of dead and fossil skeletons which might contain cements or sediment infill, or which might have been altered to calcite was determined using X-ray diffraction. Mineralogy of these samples is also given in Table 1.

Because grinding destroys some fluid inclusions, spectra were obtained from polished and bleached slabs. An 8-15mm thick slab was cut from the center of those specimens chosen for analysis. Each slab was polished to remove saw marks and bleached in 30% H_2O_2 (buffered to a neutral pH with NaOH) for 5 to 7 days to remove any organics freshly exposed by slabbing. The slabs were rinsed in tap water and dried in an oven at 37°C for at least one day before spectra were obtained. Samples were never subjected to temperatures above ~40°C as high temperatures can alter or destroy organics or hydrated mineral phases. Bidirectional VNIR (0.3 or 0.6 to 2.7 um) reflectance spectra were obtained with the spectrophotometer at RELAB at Brown University, described by Pieters (1983). Spectral resolution of all spectra is 5nm, and the area covered by each spectrum was about 2mm in diameter. Specimens were examined with hand lens and binocular microscope to ensure that all portions of the coral from which spectra were to be obtained were free of cements or sediment infill.

One species of scleractinian coral, *Diploria strigosa*, was studied in detail because good specimens from all three categories (living, modern dead, and fossil) were available. Also the structure and size of the corallites made it possible to study different structures, i.e. septa and thecae, within the skeleton to determine the amount of variability within one colony, enabling changes in water and organic content caused by diagenetic alteration to be distinguished from compositional variations inherent in the original

Table 1. Coral samples from which spectra were obtained.

Sample Number	Classification	Locality	Mineralogy
DSRBML-75	*Diploria strigosa*	Rice Bay, live specimen	aragonite
DSRBMD-92	" "	Rice Bay beach, marine vadose	thecae-aragonite septa-aragonite, minor HMC
DSQAPL-80	" "	Quarry A, Pleistocene	thecae-aragonite septa-aragonite, minor LMC
ACSTMD-86	*Acropora cervicornis*	Sandy Point, marine vadose	aragonite
DSBPML-77	*Diploria strigosa*	Bamboo Point, live specimen	aragonite
DLBPMD-81	*Diploria labyrinthiformis*	Bamboo Point, marine vadose	thecae-aragonite septa-aragonite + HMC
ACSPPL-82	*Acropora cervicornis*	Sue Point, Pleistocene	aragonite + LMC
D-SPPL-84	*Diploria sp.*	Sue Point Pleistocene	aragonite + LMC

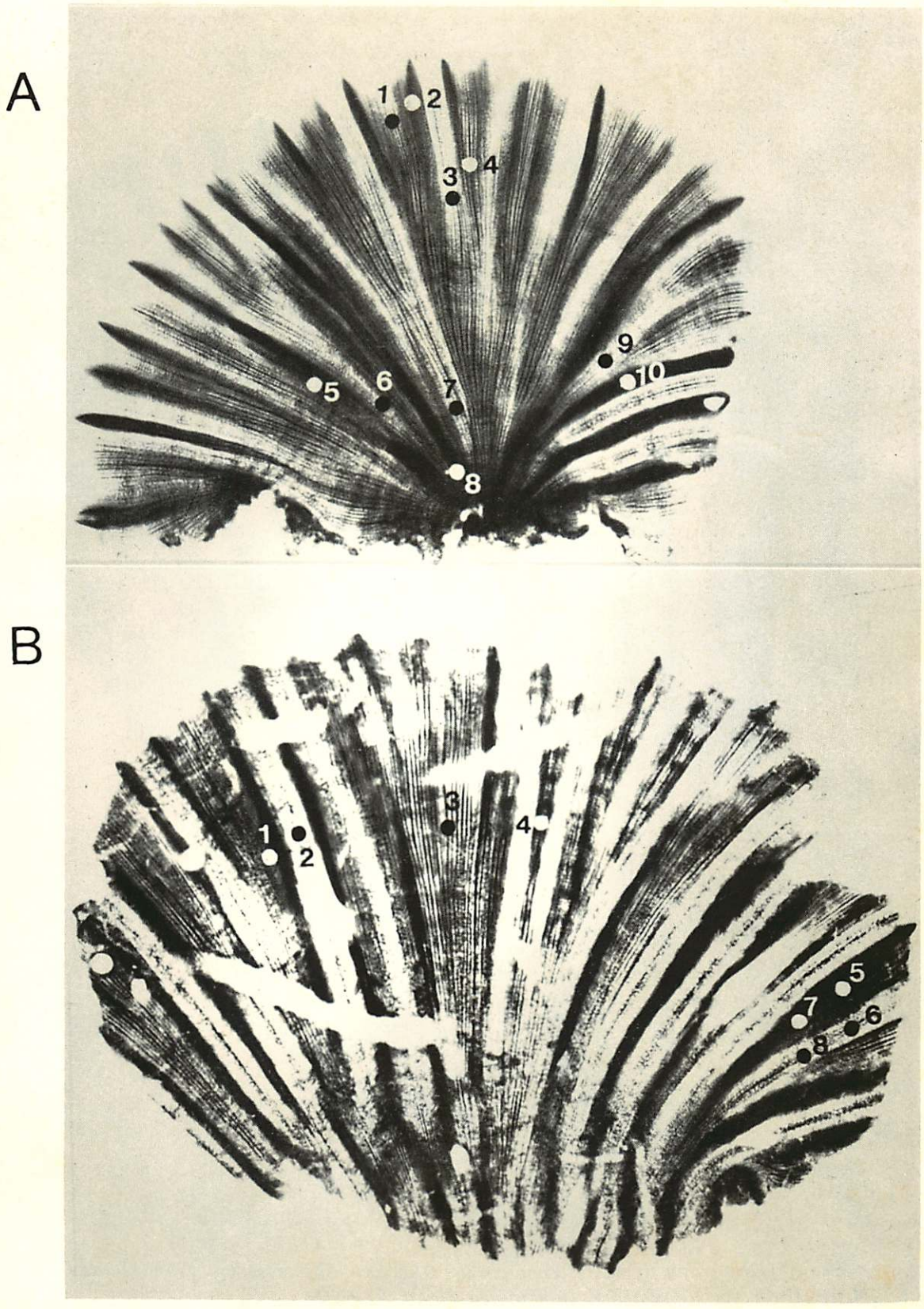

Fig. 1. X-ray radiographs of (A) skeleton of living coral collected in Rice Bay (DSRBML-75) and (B) dead coral skeleton collected on the beach, also at Rice Bay (DSRBMD-92). Dots indicate points from which spectra obtained.

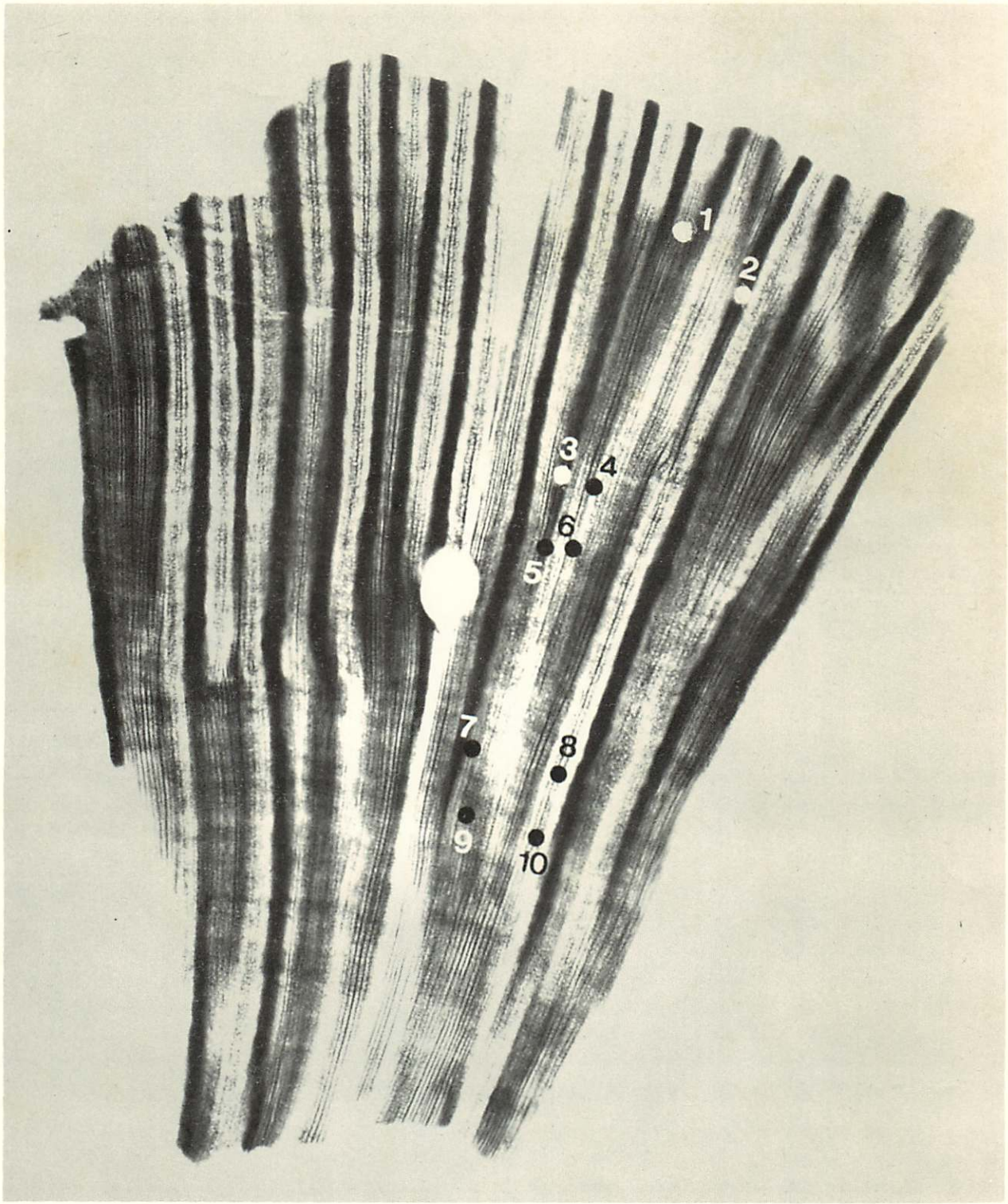

Fig. 2. X-ray radiograph of Pleistocene coral (DSQAPL-80) collected from Quarry A showing portions of skeleton from which spectra were obtained.

skeleton. X-ray radiographs were obtained of the three samples which were studied in greatest detail (DSRBML-75, DSRBMD-92, and DSQAPL-80) and points from which spectra were obtained are shown on the X-ray radiographs of these specimens (Figs. 1 and 2). Spectra were obtained of ten points, five on the septa, and five on the thecae for samples DSRBML-75 and DSQAPL-80. Eight points, four each on the septa and thecae, were measured on DSRBMD-92. Points from which spectra were obtained were distributed uniformly between the basal interior and the outer edges of the coral skeletons. Spectra of samples of *Diploria labyrinthiformis*, and *Acropora cervicornis* were obtained as well.

Spectra of Iceland spar, liquid H_2O, and of a bleached coral slab are shown in Figure 3. The liquid water spectrum was provided by Steve Pratt at RELAB.

Spectra of organics were also obtained and are shown in Figure 4. One of the advantages of VNIR reflectance spectroscopy is that measurements may be made of unstable phases *in situ*, without subjecting them to extraction processes which may destroy or alter some of the components of interest (Holden, 1988). Differences in spectral properties of organics obtained from extracted organics and from organics *in situ* can be seen in Figure 4. The first spectrum is that of organics extracted from a sample of *Diploria*. Approximately 20 grams of skeleton were treated with 1M HCl to remove the $CaCO_3$, following the procedures of Kimber and Griffin (1987). The residual organics were removed from the HCl by filtration and gently rinsed with deionized water. Material retained on the filter was collected and air dried prior to analysis.

Spectra were also obtained from DSBPML-77, which was not bleached after slabbing. The second spectrum shown in Figure 4 was obtained from a portion of a coral polyp which remained in the skeleton after preliminary bleaching with clorox. Spectra were also obtained of portions of this skeleton which had been bored by endolithic algae, as well as portions which had not. A spectrum was also obtained of an unbleached powder from this skeleton. Subsequently any coral referred to as "bleached" was treated in H_2O_2 after slabbing.

ANALYSIS OF SPECTRAL DATA

Intensity of an absorption band increases with the increase in concentration of the ab-

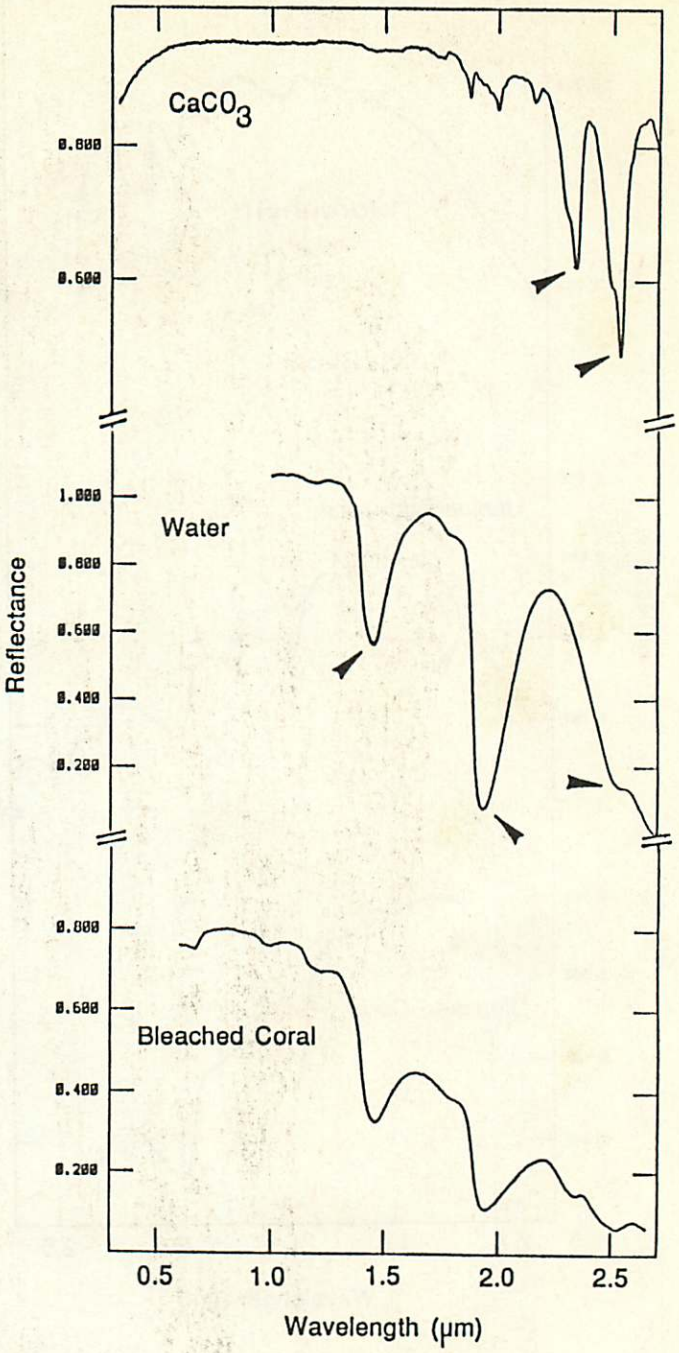

Fig. 3. Spectra illustrating absorption features due to vibrations of the carbonate ion and the H_2O molecule. The first spectrum is that of Iceland spar, the second spectrum is that of liquid H_2O. Arrows indicate the strong absorption features which indicate the presence of both these phases in the spectrum of the bleached coral also shown in this figure.

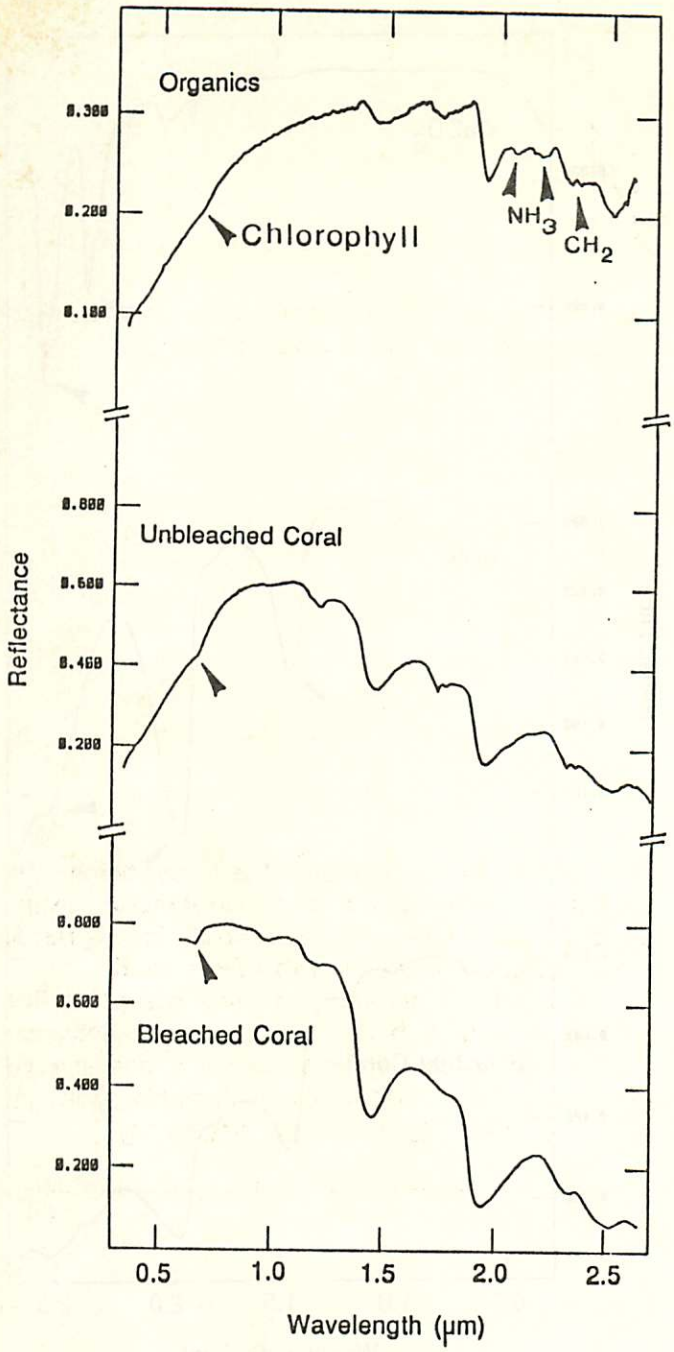

Fig. 4. Spectra illustrating absorption features due to organics. The first spectrum is that of organics extracted from a bleached Diploria strigosa *skeleton using HCl. The second spectrum is that of a portion of a coral polyp remaining after preliminary bleaching with clorox and exposed upon slabbing of the skeleton. The second spectrum contains a feature near 0.67 um due to organic pigments in symbiotic zooxanthellae. It also contains sharp narrow features near 1.2, 1.7, and 2.3 due to overtones and combination tones of the C-H stretching fundamental and broader bands near 2.1 and 2.2 um due to overtones and combination tones of the N-H stretching fundamental (see Gaffey, this volume for further discussion). The third spectrum is that of a coral skeleton which, despite prolonged bleaching in H_2O_2 still retains absorption features due to organic compounds near 0.67, 2.2 and 2.3 um.*

sorbing species (Herzberg, 1945; Burns, 1970). However, as previous work by Gaffey (1988) has shown that relative water band intensity alone does not accurately reflect the total water content of samples when water is present in more than one phase, it was decided that band areas would be used. Although calibration work still remains to be done which will allow water and organic contents to be quantitatively determined from band areas, these data show relative differences in water content within and between samples.

Two methods of band area calculation were employed in this study. The first used a straight line continuum, extended from the 0.6 to 1.3-um portion of spectra, as shown in Figure 5. Gaffey (1986) found the assumption of a straight-line continuum provided a useful model for determining positions, widths, and intensities of carbonate absorption bands in carbonate spectra. Log intensities were used because the Beer-Lambert law more accurately reflects behavior of absorption features than other models which have been employed (Clark and Roush, 1984; Gaffey,

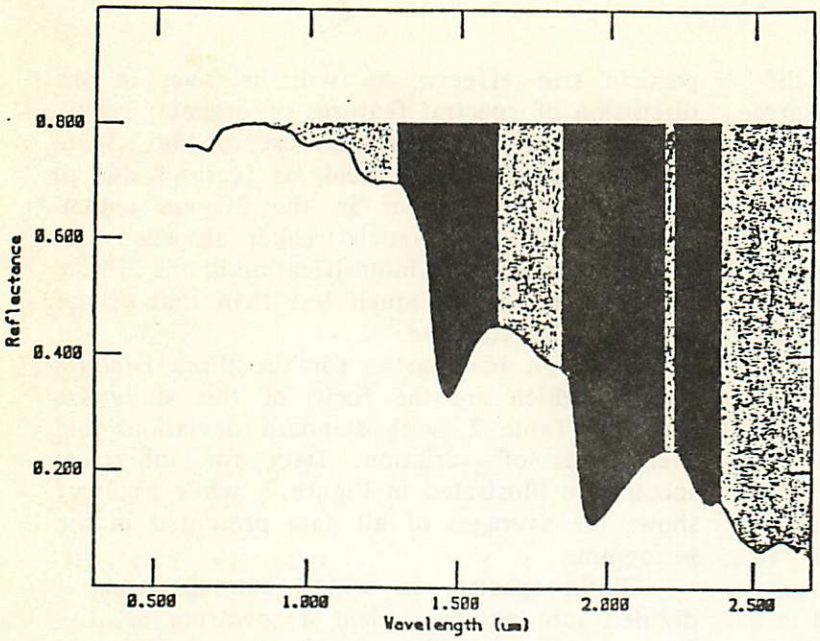

Fig. 5. Illustration the continuum-area method of calculating band areas.

1986). The edges of the absorption bands in the spectra in this study were determined by visual estimate on an expanded printout of the log of each spectrum. Several different criteria for defining band edges, e.g. a reflectance maximum, an inflection point on the curve, or a particular wavelength, may be used. However, the same criterion must be used for all analyses to minimize errors in calculation. The area below the continuum between the two wavelengths designated as band edges, colored black in Figure 5, represents the continuum area of the band.

The second method used was the point-line method. The area below a straight line connecting the two points on the spectrum which marked the edge of the band, was calculated (Fig. 6).

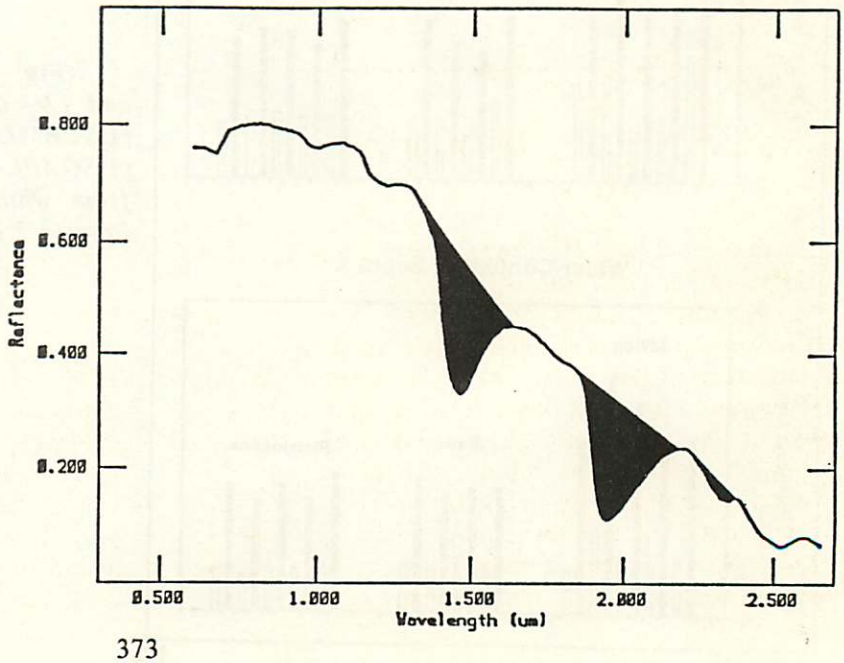

Fig. 6. Illustration of the point-line method for calculating band areas.

Comparison of data obtained by these two different methods showed that the continuum area method (Fig. 5) failed to show any consistent trends. The continuum-area method was therefore discarded and all band areas shown in this paper were calculated using the point-line method.

Areas were calculated for three bands in each spectrum: the 1.4- and 1.9-um water bands and the 2.3-um carbonate band. Band intensities and areas are a function not only of the concentration of the absorbing species, but of the particle size and packing or porosity of the sample as well. However, the intensity of an absorption feature relative to intensities of other features in the same spectrum remain constant, regardless of particle size (Gaffey, 1986). To correct for differences in grain size or porosity between samples, the area of each H_2O band in a spectrum was divided by the area of one of the strong carbonate absorption features in the same spectrum. Gaffey (1988) previously used the intensity of the 2.5-um carbonate band to correct for particle size effects. However, as can be seen from Fig. 3, liquid H_2O also has a strong 2.5-um feature. For this reason, areas of the 1.4- and 1.9-um water bands were ratioed to the area of the 2.3-um carbonate band to correct for particle size effects. As will be seen in the discussion of spectral features of organics below, and in Gaffey (this volume) use of the 2.3-um band is also less than ideal, as features due to CH_2 in organics occur in the 2.3-um region. However, CH_2 is a much weaker absorber than H_2O, so the apparent intensification of the 2.3-um carbonate feature is much less than that of the 2.5-um carbonate band.

Data on band areas for the three *Diploria* samples which are the focus of this study are listed in Table 2, with standard deviations and coefficients of variation. Data for individual spectra are illustrated in Figure 7, while Figure 8 shows the averages of all data presented in the histograms.

Ratio spectra, in which one spectrum is divided into another, yield a spectrum of differences in types and abundances of contained phases between two samples. Ratio spectra for the three *Diploria* samples are shown in Figure 9. The short-wavelength portion of three spectra (Fig. 10) show features due to organic pigments.

RESULTS AND DISCUSSION

Coral skeletons contain both intra- and

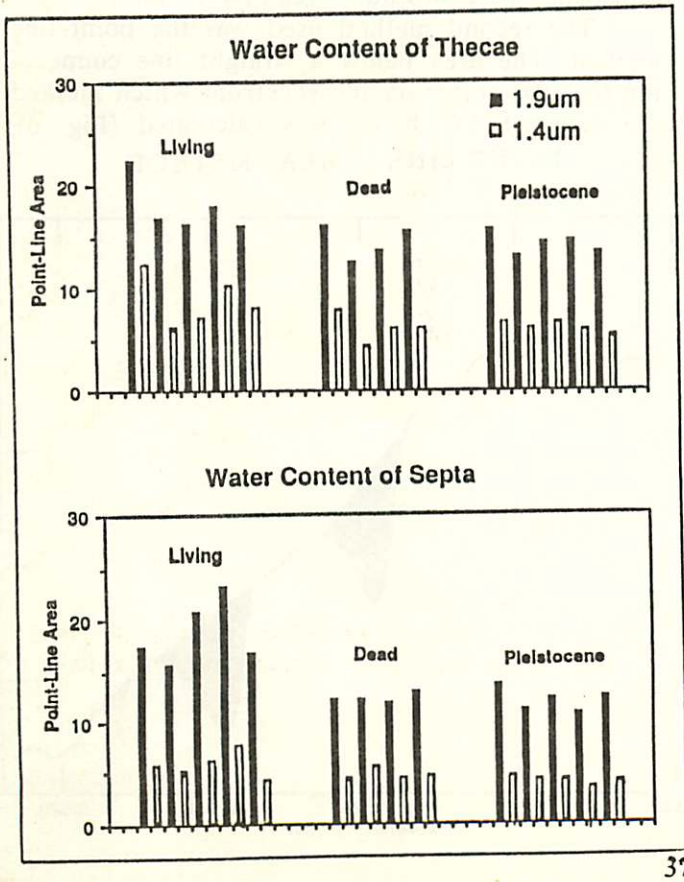

Fig. 7. Band areas calculated for the 1.4- and 1.9- um band in spectra obtained from living (DSRBML-75), dead (DSRBMD-92) and Pleistocene (DSQAPL-80) samples of Diploria strigosa. *Points from which spectra were obtained illustrated in Figures 2 and 3. Localities listed in Table 1.*

Table 2. Relative band areas calculated for each spectrum. These are ratios and therefore dimensionless numbers.

SAMPLE	Pt. No.	Description	1.4 um band	1.9 um band
DSRBML-75	1	septa	5.73	17.43
	2	theca	12.34	22.33
	3	septa	5.32	15.79
	4	theca	6.23	16.80
	5	theca	7.17	16.28
	6	septa	6.22	20.80
	7	septa	7.77	23.18
	8	theca	10.28	17.90
	9	septa	4.29	16.89
	10	theca	8.20	16.14
DSRBMD-92	1	theca	7.98	16.10
	2	septa	4.45	12.19
	3	septa	5.71	12.19
	4	theca	4.52	12.54
	5	theca	6.20	13.77
	6	septa	4.41	11.84
	7	theca	6.04	15.52
	8	septa	4.66	12.93
DSQAPL-80	1	septa	4.74	13.77
	2	theca	6.68	15.75
	3	theca	6.18	13.21
	4	septa	4.32	11.12
	5	theca	6.73	14.50
	6	septa	4.38	12.10
	7	theca	5.90	14.67
	8	septa	3.57	10.78
	9	theca	5.37	13.60
	10	septa	4.19	12.38

	Mean	Standard deviation	Coefficient of variation
DSRBML-75			
1.4-um band, septa	5.87	1.15	0.195
1.9-um band, septa	18.82	7.57	0.402
1.4-um band, thecae	8.84	4.87	0.550
1.9-um band, thecae	17.89	5.30	0.296
DSRBMD-92			
1.4-um band, septa	4.81	0.28	0.059
1.9-um band, septa	12.29	0.16	0.013
1.4-um band, thecae	6.18	1.51	0.243
1.9-um band, thecae	14.48	1.99	0.138
DSQAPL-80			
1.4-um band, septa	4.24	0.15	0.034
1.9-um band, septa	12.03	1.11	0.092
1.4-um band, thecae	6.17	0.26	0.042
1.9-um band, thecae	14.35	0.79	0.055

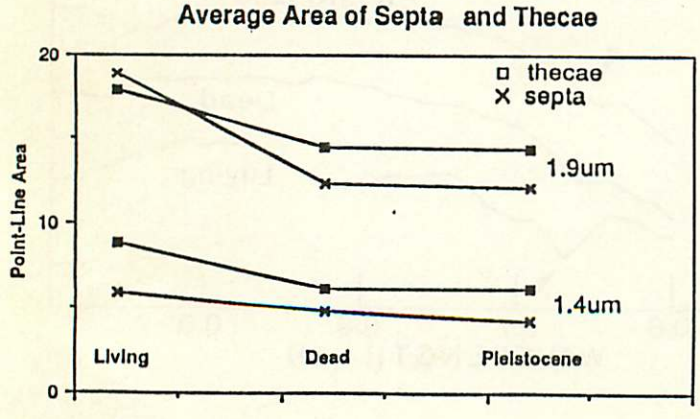

Fig. 8. Average band areas calculated for 1.4- and 1.9-um bands in spectra of septa and thecae of each specimen.

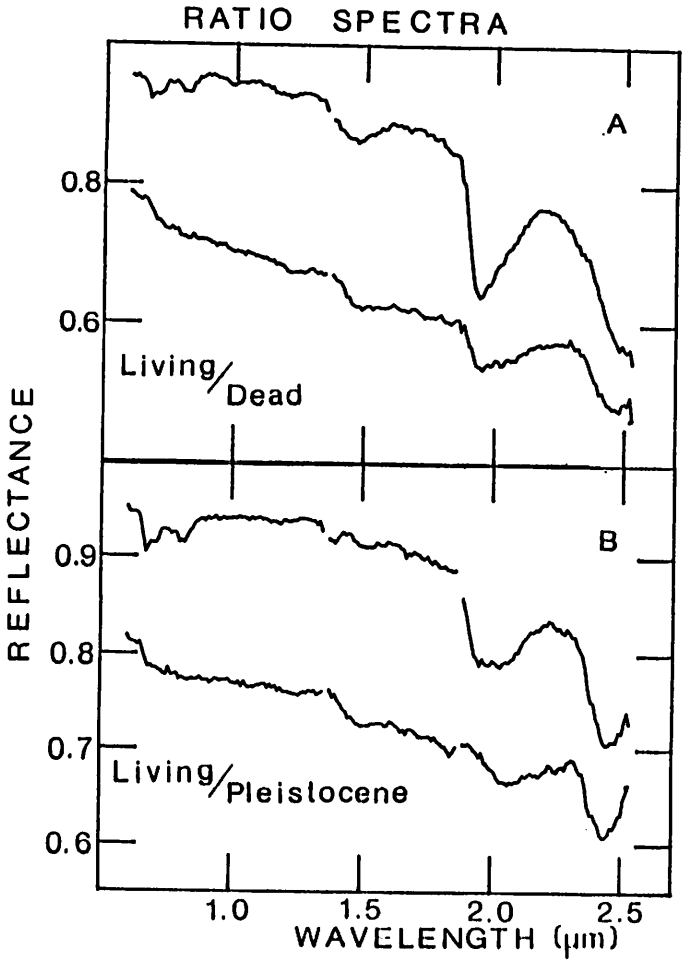

Fig. 9. Ratios of spectra obtained of skeletons of live (DSRBML-75) and dead (DSRBMD-92) (A) and live and Pleistocene (DSQAPL-80) (B) coral skeletons. Each spectrum is obtained by dividing a reflectance spectrum obtained from one skeleton into that obtained from another. Compare to spectra shown in Figures 1 and 4. Spectra show that the skeleton of the dead and Pleistocene samples have lost liquid H_2O as well as the organics which produce the CH_2 features near 1.7 and 2.3 um, the NH_3 features near 2.1 and 2.2 um, and organic pigments which produce features near 0.67 um. However, amount and form of organics lost vary within as well as between skeletons from the Recent and Pleistocene.

interskeletal voids described by Gvirtzman and Friedman (1977). Interskeletal voids, those portions of the corallite once occupied by the coral polyp, contain organic material (Gvirtzman and Friedman, 1977). The centers of sclerodermites, the bundles of radiating aragonite crystals which form the skeleton, contain small (<1 um) equant carbonate crystals surrounded by soluble organic material (James, 1974). In addition, the aragonite crystals making up the skeleton contain minute intracrystalline voids which contain organics (Green et al., 1980) and/or liquid water as fluid inclusions (Bruni and Wenk, 1985; Gaffey, 1983, 1984a,b; 1985, 1988). The organic matter in coral skeletons is composed of proteins and polysaccharides (Johnston, 1980; Wilbur and Simkiss,

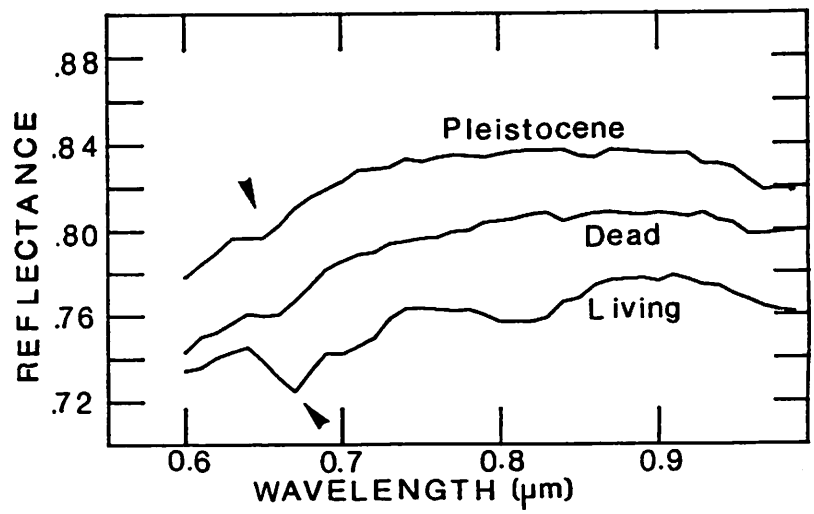

Fig. 10. Short-wavelength portion of spectra of living, dead and Pleistocene Diploria *skeletons showing progressive weakening of the 0.67- um chlorophyll absorption and loss of 0.7-um H_2O band.*

1979). These organic compounds may include some or all of the following: the organic matrix used in forming the skeleton, soft tissues of the coral polyp, and compounds produced by the endolithic algae. All of these components can contribute features to VNIR spectra of corals.

Spectral properties of carbonates and liquid H_2O are shown in Figure 3. The first spectrum in Figure 3 is that of Iceland spar. Spectra of all anhydrous carbonate minerals show these same absorption features, but precise positions of these features vary with mineralogy (Gaffey, 1986, 1987). Liquid H_2O (Fig. 3) has three strong absorptions in the VNIR region, near 1.4, 1.9 and 2.5 um (see Gaffey, 1988, for discussion and references to the chemical literature). Simple addition or multiplication of the $CaCO_3$ spectrum and the H_2O spectrum will approximate that of the bleached coral. The number, positions, and widths of the 1.4- and 1.9-um bands in the coral spectrum show that all the water is present as liquid H_2O.

Spectra of coral tissue and of organics isolated from the coral skeleton are shown in Figure 4. Spectra of organic compounds in the VNIR region contain features due to NH_3^+, NH_2, OH^-, and CH_2 (see Gaffey, this volume, for discussion and references to the chemical literature). Overtones and combination tones of the stretching vibrations of CH_2 in amino acids or polysaccharides produce the sharp narrow features near 2.35, 1.7 and 1.2 um. Overtone and combination tones of the stretching modes of NH_3^+ in proteins produce the broader, more diffuse features near 2.1 to 2.2 um. OH^- in organic compounds generally produces broad features near 1.45 and 2.1 um. In addition, absorptions occur at visible wavelengths (0.3 - 0.7 um) in coral spectra. These are due to organic pigments in symbiotic zooxanthellae, and endolithic algae.

Petrographic and Mineralogical Data

All coral skeletons studied appear to be composed primarily of aragonite, any high magnesian calcite (HMC) being present in marine cements and the bulk of low magnesian calcite (LMC) occurring in fresh water vadose cements similar to those described from the Cockburn Town reef by White et al. (1984) and from the Mosquito Marsh reef described by Vierma et al. (1984).

Examination with petrographic microscope shows DSRBML-75 contains minor amounts of fibrous aragonite cement. DSRBMD-92 contains both fibrous aragonite and micritic HMC cements. Pleistocene samples from Quarry A show some marine cements (fibrous aragonite and micritic calcite, presumably now LMC) and marine sediment infill, primarily composed of ooids. Septa and dissepiment have undergone considerable dissolution.

Examination of septa of DSRBML-75, DSRBMD-92, and D-SPPL-84 showed a reduction in amount of organics with time. Large areas of the septa of the living skeleton (DSRBML-75) are covered with organic films and filaments, which in many areas are penetrated by acicular crystals of marine aragonite cements. Areas of septa of the dead coral (DSRBMD-92) covered by organics are much smaller than those in the living sample, and organics appear to be partially calcified by subspheric nannograins, as described by Loreau (1982). The surfaces of septa from the Pleistocene sample are almost entirely free of organics. A few small, scattered rhombs can be seen replacing aragonite in the Pleistocene sample, as well as some platy crystals ~1.0 um in diameter which may be hematite. Additional work is needed to completely characterize the mineralogy of these samples.

Loss of Water and Organics

The histograms in Figure 7 and data in Table 2 show considerable variation in band areas for both the 1.4- and 1.9-um features in spectra of different portions of the skeleton of the live coral. In general there is a decrease both in individual and average band areas for both the 1.4- and 1.9- um bands in spectra of the dead and Pleistocene samples relative to those in spectra of the living sample. However, areas of the two bands, and band areas for septa and thecae do not decrease by the same amount or at the same rate. The decrease in area is greater for the 1.9-um band than for the 1.4-um band. The trend for both the 1.4- and 1.9-um band areas for the thecae are similar, but for the septa, the decrease in area of the 1.9-um band is more pronounced than that of the 1.4-um band. The area of the 1.9-um band is greater in spectra of the septa than of the theca in the live coral, but the reverse is true for the dead and Pleistocene samples.

Spectra of other samples of *Diploria* studied showed these same trends in band areas. Spectra of *Acropora* showed less variability in band areas

between different portions of the skeleton of the same colony, probably because their skeletons have a more porous open structure throughout, and because the smaller corallite size made it impossible to isolate different structures within the skeleton for analysis.

In general, the standard deviations and coefficients of variation also show a decrease for data obtained from spectra of dead and Pleistocene samples relative to these values for spectra of the living sample, the 1.9-um band in the spectra of septa of DSRBMD- 92 being the exception.

Because there are a number of NH_3^+ and organic OH^- absorptions in the 2.0-2.2-um region which overlap with the 1.9-um water band, the areas determined for the 1.9-um band in part reflect the organic content of the skeletons. The 1.4-um band shows less overlap of absorption features due to different phases, and appears to reflect the H_2O content of the skeletons more accurately. Comparison of the data for living samples with that for dead and Pleistocene samples (Figs. 7 and 8) support this conclusion. Greater organic content in a sample is reflected by an anomalous increase in area of the 1.9-um band without a similar increase in the area of the 1.4-um band. Differences in trends in areas for the 1.9-um band in spectra of septa and thecae, and differences in the magnitude of changes in areas of the 1.4- and 1.9-um bands from one sample to another indicate that more than one phase is contributing to these spectral features. If only one phase, e.g. liquid H_2O were present, the 1.4- and 1.9-um bands would show the same trends in band area. Effect of organic content on band areas is most clearly illustrated in spectra of the septa of the living coral.

The marked decrease in areas of both the 1.4- and 1.9-um bands in spectra of the septa probably represents loss of organics which were part of the tissue of the coral polyp. The thecae would be expected to contain fewer organics, perhaps only those employed in formation of the coral skeleton, and those contributed by endoliths (Additional work will be needed to further characterize the organic contents of septa and thecae). The dense structure of the thecae, however, would prevent rapid loss of organics seen in the septa of the dead and Pleistocene samples. Water and organics trapped within intracrystalline voids and within the centers of sclerodermites remain in place until the voids are breached by dissolution or physical destruction of the skeleton.

The persistence of organics in corals of Pleistocene age is also shown by the chlorophyll absorption feature near 0.67 um in all the spectra in Figures 4 and 10, as well as in most of the spectra obtained in this study. This chlorophyll is probably the result of assimilation of products from the symbiotic zooxanthellae (Von Holt and Von Holt, 1968; Muscatine and Cernichiari, 1969) or from the alga *Ostreobium* which is the predominant endolith infesting coral skeletons (Lukas, 1973).

There is great variation in the amounts and types of phases being lost, both at different points within the same skeleton, and at different stages during its diagenetic history. Ratio spectra in Figure 9 illustrate some of these differences in organic and water content between skeletons. As mentioned above, when one spectrum is divided into another, the resulting curve is a spectrum of differences between the two samples, i.e. of the phases which one contains that the other does not. Comparison of these ratio spectra with the spectra of organics and of liquid H_2O shows that not only is H_2O being lost, but other phases containing OH^-, NH_3^+, and CH_2 as well. The first spectrum in Figure 9A shows that water is the principle phase lost in this portion of the septa of the dead coral. The 0.67-um region of the spectrum shows that chlorophyll has also been lost. The second spectrum in Figure 9A shows that at another location on the septa, proteins as well as water have been lost. The ratio spectra in Figure 9B show that water and organics (proteins and possibly polysaccharides) have all been lost in both portions of the septa from which these spectra were obtained, but in differing amounts.

The high degree of variability in water and organic content between different portions of the living and dead coral colonies, and the variation in amount and types of phases being lost, indicates that early alteration is taking place within microenvironments which are not in equilibrium with each other or with the ambient environment, a model proposed by Pingitore (1982). As diagenesis proceeds in the subaerial environment all voids in the skeleton are enlarged by dissolution until they are interconnected (Gvirtzman and Friedman, 1977). At this stage all portions of the skeleton tend toward equilibrium reflected in the low coefficients of variability for band areas, and in the similarity in band areas for septa and thecae in the Pleistocene sample.

The SEM and spectral data also indicate

that prolonged bleaching does not remove all of the organics in skeletons, a fact which has important repercussions for other types of chemical analyses.

Dissolution and Cementation

Water and organics in coral skeletons undoubtedly play an important role in their diagenesis. The centers of the sclerodermites and the seed crystals which they contain are preferentially dissolved, even when there are no visible conduits to the outer surface of the coral (Gvirtzman and Friedman, 1977; James, 1974; Pingitore, 1976). Gvirtzman and Friedman (1977) also noted that centers of the sclerodermites retain water longer than any other portion of the skeleton. Constantz (1986b) noted that aragonite crystals in coral skeletons are more susceptible to dissolution than adjacent aragonitic marine cements. It is our contention that the inclusions of organics and liquid water are in part responsible for the decreased stability of skeletal aragonites, and, as suggested by Gvirtzman and Friedman (1977) for the apparently anomalous dissolution of sclerodermites from the center outwards. Water is present to serve as a medium for diagenetic reaction, and breakdown of organics may increase the CO_2 content of solutions facilitating dissolution of skeletal aragonites.

Organics can serve as a substrate for precipitation of carbonate (e.g. Loreau, 1982; Mitterer and Cunningham, 1985). Calcification of organic films appears to have occurred in the skeleton of the dead colony. Decay of organics can also change pore water chemistry. For example NH_3^+ may be released, increasing the pH of pore waters and promoting precipitation of carbonate. While the occurrence of aragonite cements penetrating organic films does not provide conclusive evidence, it does suggest a relationship between the two.

It is important to note that the liquid H_2O and organic compounds involved in these reactions are an intrinsic part of the skeleton incorporated during growth. During formation of the skeleton, the sites of calcification are isolated from surrounding sea water (Wilbur and Simkiss, 1979; Crenshaw, 1982), and inclusions in the crystals of the skeleton probably contain the mineralizing fluids of the animal. Johnston (1980) notes that some of the organics in coral skeleton are intimately bound with and completely dispersed within the skeletal aragonite. Organics are probably trapped within the crystal during growth as suggested by Barnes (1970) and Constantz (1986a). This is not surprising as organic matrices are used to facilitate formation of the skeleton and water provides a medium for transport of Ca^{2+} and HCO_3^- to the site of deposition (Crenshaw, 1982).

CONCLUSIONS

Although both water and organics can potentially have a marked affect on the diagenesis of carbonate skeletons, there is at present no tool routinely in use by sedimentary petrologists for their detection and identification, or for determination of their abundances. Visible and near-infrared (VNIR) (0.3 - 2.7 um) reflectance spectroscopy can provide a rapid, inexpensive, non-destructive tool for characterizing water and organic contents of skeletons. This technique has the added advantage of allowing organics to be studied *in situ*, without deleterious effects of the standard techniques employed for their extraction (Holden, 1988).

In spectra of coral skeletons relative area of the 1.9-um absorption band calculated by the point-line method appears to reflect total H_2O and organic content, while the relative area of the 1.4-um band appears to more accurately reflect the H_2O content alone. At present, only relative changes in water and organic contents of skeletons can be studied in this way, and calibration curves must be developed so that water and organic contents of skeletons can be quantitatively characterized from spectral data. In addition, other techniques such as NMR, ESR, Raman spectroscopy, and coulometry will help to better characterize the water and organic phases contained in these skeletons. In addition, because organics are lost so rapidly after death of the colony, skeletons found in place on reefs and in reef rubble should be studied as well, to give a more complete picture of early diagenetic changes.

Water and organics are primary components incorporated during growth, and are intimately associated in skeletons of scleractinian corals. Some of the water and organics occur in interskeletal voids which are in communication with the environment surrounding the coral head. Organics in these portions of the skeleton are lost rapidly after death of the coral. Other organics, and the water with which they are associated, are isolated within intracrystalline and intraskeletal voids. These are retained for a

longer period within the skeleton. Water and organics in intracrystalline voids are retained until the crystals are dissolved or physically destroyed.

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