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SKELETAL CARBONATE DIVERSITY: IMPLICATIONS FOR EARLY DIAGENESIS

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ABSTRACT

Skeletons produced by carbonate secreting organisms are not simple mineral systems of aragonite, or calcite with varying Mg contents, but are complex biological constructs which differ significantly from their physicochemically precipitated counterparts. Carbonate skeletons are not precipitated directly from and in equilibrium with sea water, but within the cells and/or tissues of carbonate secreting organisms in isolation from the ambient environment. Because carbonate skeletons are not precipitated in equilibrium with sea water, diagenetic alteration can begin within the marine environment immediately following death of the organism.

All characteristics of skeletal carbonates (i.e. mineralogy, microstructure, chemical and isotopic composition, and organic and water content) are controlled by the carbonate-secreting organism. The resulting sediments formed from skeletons produced by these organisms comprise a very diverse assemblage of materials, with significant variations occurring at least at the generic level. This diversity should result in similarly diverse responses to changes in diagenetic environments.

INTRODUCTION

Skeletons produced by carbonate secreting organisms form the major component of many modern and ancient marine carbonate sediments. The diagenetic history of carbonate sediments is a major factor controlling their porosity and permeability, and hence their ability to serve as reservoirs for water and petroleum. In particular, depositional textures and fabrics plus early surficial diagenetic processes, including dissolution, cementation, and dolomitization, are the major factors affecting the porosity and permeability of carbonate rocks (Moore, 1989).

Although a great deal of research in carbonate diagenesis has focussed on the cements and sediments which fill the pore spaces within and between skeletal components of carbonate sediments, far less work has been done on the diagenetic alteration of the skeletons themselves. A thorough understanding of the nature of the starting materials is a necessary prelude to any study of the diagenetic alteration of those materials. One purpose of this work was to mineralogically and chemically characterize some of the more common components of these starting materials, i.e. the skeletons of scleractinian corals, echinoids, Foraminifera, and coralline red algae, in order to better understand their responses to early diagenetic processes. The second goal was to investigate the ways in which skeletal materials produced by different organisms respond to an artificially induced, and therefor carefully controlled, change in one environmental parameter, in this case temperature.

MATERIALS AND METHODS

Samples for this study were obtained from live organisms, modern marine and intertidal sediments, and Holocene and Pleistocene rocks on and around the island of San Salvador, Bahamas. These included the scleractinian corals *Acropora cerivcornis* and *Diploria strigosa*, the echinoids *Lytechinus variegatus* and *Leodia sexiesperforata*, and the coralline red alga *Neogoniolithon sp.* Skeletons of the echinoids *Clypeaster rosacea* and *Encope emarginata*, the mollusc *Nautilus*, and the barnacle *Balanus* were purchased from commercial establishments. Skeletons of organisms collected live were cleaned in dilute or full strength (5%) commercial NaOCl immediately after collection. Skeletal material obtained from bottom sediments and from beaches was also cleaned in 5% NaOCl or 30% H_2O_2 before analysis. Some modern and fossil skeletal material was ground by hand in a ceramic mortar and pestle and seived into different particle size fractions. The 125-500 μm fraction, selected for use in heating experiments, was cleaned in an ultrasonic bath, bleached in

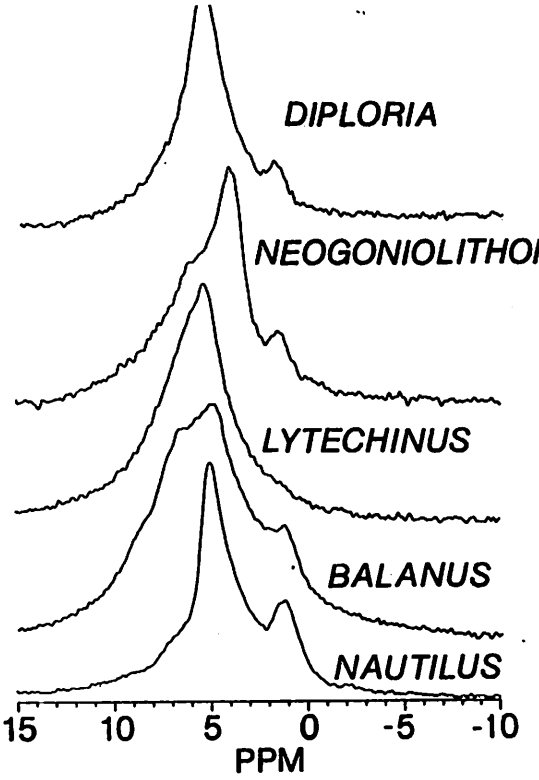

Fig. 1. ^1H CRAMPS NMR spectra of several biogenic carbonates. The PPM scale indicates chemical shift relative to a standard. The resonance near 1 ppm is produced by OH, that near 5 ppm by H_2O. The 4 and 6 ppm resonances in the *Neogoniolithon* spectrum, the resonances near 7 and 8 ppm in the *Balanus* spectrum, and the resonance near 6.5 ppm in the *Nautilus* spectrum are probably due to organics. The shoulder near 6 ppm in the *Lytechinus* spectrum is caused by bound H_2O.

NaOCl or H_2O_2 for at least 2 weeks, cleaned in the ultrasonic again, and dried in an oven. Samples were never subjected to temperatures above 40°C during preparation.

Organic contents and H_2O- and OH-containing phases were identified and their relative abundances determined using two spectroscopic techniques. ^1H CRAMPS (Combined Rotation and Multiple-Pulse Spectroscopy) NMR (Nuclear Magnetic Resonance) spectra were obtained at the Colorado State University Regional NMR Facility following the methods of Bronniman and others (1988) and Maciel and others (1990). NMR spectra of some samples are shown in Figure 1. Ultraviolet (UV), visible (V) and near-infrared (NIR) (0.3 - 2.7 μm) reflectance spectra of samples were obtained using the spectrophotometer at RELAB at Brown University described by Pieters (1983). Relative areas of the 1.4- and 1.9-μm absorptions produced by water, which provide a sensitive measure of total water and organic content were determined using methods outlined in Zabielski and Gaffey (1989).

Ca, Mg, Sr, and SO_4 contents of samples were determined using the electron microprobe at the Geology Department, R. P. I. Data given are averages of 15 or more analyses of each sample. Figure 2 shows relative area of the 1.4-μm band in spectra of biogenic calcites, which reflects the total water content of skeletons (Zabielski and Gaffey, 1989), plotted against Mg content.

Heating experiments were performed to determine the response of skeletal material to a change in a single environmental parameter. Samples were heated in a tube furnace using N_2 as an inert carrier gas to minimize reactions of organics with atmospheric O_2, and to remove any H_2O, CO_2, or other products evolved during heating. CO_2 was used at temperatures >300°C to prevent breakdown of $MgCO_3$ at these high temperatures. Samples were weighed before and after heating to monitor loss of water and breakdown of organics.

Heated and unheated samples were examined in thin section and with scanning electron microscope. SEM photos of some samples are shown in Figure 3.

Mineralogy of samples was determined using X-ray diffraction. Integrated peak areas were used to determine calcite/aragonite ratios in coral samples before and after heating. A calibration curve was constructed using samples of unheated *Acropora cervicornis* and *A. cervicornis* altered to calcite by heating to 400°C for 2 hours. Position of the major calcite peak was determined using a Si standard. Weight-loss data and X-ray diffraction data are shown in Figures 4 and 5.

DISCUSSION

Factors Controlling Water Content of Skeletons

Previous workers have established that the mineralogy, the crystal habit, orientation, and size, the major, minor, and trace element content, the stable C and O isotopic composition, and organic contents of skeletons are controlled, to a greater or lesser degree, by the carbonate-secreting organism (e.g. Chave, 1954; Lowenstam, 1981; Lowenstam and Weiner, 1989; Mann, 1983; Milliman, 1974; Weiner and others, 1983).

All carbonate skeletons also contain water in inclusions (Gaffey, 1985, 1988), with the possible exception of echinoderms (Blake and others, 1984). Most skeletons appear to contain OH^- as well, and some contain hydrated carbonate phases (Busenberg and Plummer, 1985; Gaffey, 1988, 1990 and references cited therein). It was previously suggested (e.g. Busenberg and Plummer, 1985; Gaffey, 1988; Mackenzie et al., 1983) that water content was related to mineralogy and chemical composition, i.e. that H_2O and OH^- content of carbonate skeletons was higher in calcites, particularly high Mg calcites, due to the difficulty of desolvating the Mg^{2+} ion.

NMR spectra indicate a lack of correlation between mineralogy and/or Mg content and water content of skeletons. OH^-- and H_2O-containing phases can be easily distinguished in NMR spectra because resonances produced by H_2O occur at about 5 ppm, while those due to OH^- occur near 1 ppm (Fig. 1). The 1 ppm resonance occurs in spectra of a variety of skeletal types, including coralline and molluscan aragonites and the low Mg calcite produced by the barnacle *Balanus*. The weakest OH^- resonance occurs in the spectrum of the echinoid *Lytechinus* which is 8.6 mole % $MgCO_3$.

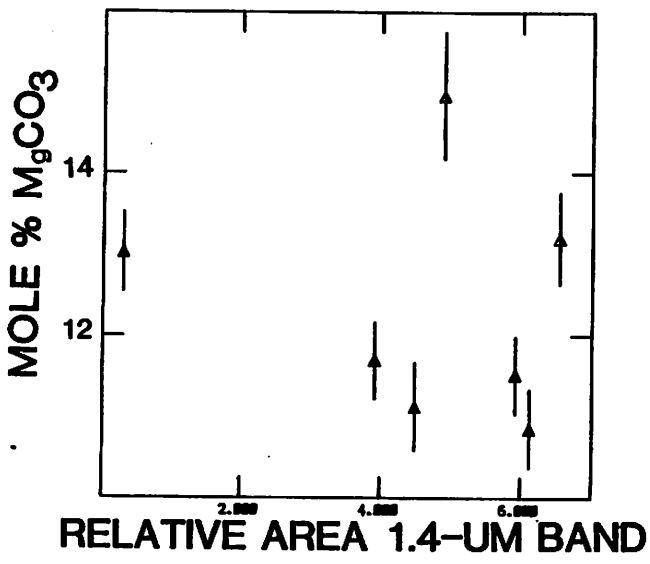

Fig. 2. Mg content of skeletal calcites as determined by microprobe plotted against the relative area of the 1.4-μm absorption band in UVVNIR reflectance spectra of these same samples. Relative areas of the 1.4-μm absorption band provides a measure of total water content (H_2O and OH) in samples.

Reflectance spectral data obtained to date indicate a lack of correlation between total water (H_2O + OH^-) content and Mg content of skeletal samples. Although data in Figure 2 are limited, they show no apparent trends relating Mg content to total water content, as indicated by the relative area of the 1.4-μm water band in reflectance spectra. Lowenstam and Weiner (1989) report the production of monohydrocalcite by molluscs and amorphous hydrated carbonate by molluscs and arthropods, indicating that hydrated and hydroxylated phases are not restricted to high Mg calcites.

Thus, water content, like the other mineralogical and chemical characteristics of carbonate skeletons is controlled by the carbonate-secreting organism, and water content is primarily a function of taxonomy.

Heterogeneous Distribution of Water and Organics

UVVNIR reflectance spectral and SEM data show that distribution of water is not uniform within a given skeleton, but can vary widley over distances of 10's of μm to millimeters. TEM work by Blake and others (1984) shows that echinoderm skeletons lack the minute intracrystalline inclusions characteristic of skeletal material produced by other types of organisms (e.g. Bruni and Wenk, 1985; Conger and others, 1977; Green and others, 1980), indicating all the H_2O in echinoderm skeletons occurs in hydrated carbonate phases. Spectral data indicate that relative variations in total water content of up to 30% can occur within a single skeleton of the echinoid *Lytechinus variegatus*. The SEM photo in Figure 3A also shows that water is quite unevenly distributed within echinoid skeletons. The pitting seen in this photo of a heated *Encope* sample is caused by the expulsion of water and organics on heating. The organic content of echinoid skeletons is very low, a few tenths of a % or less (Swift and others, 1986; Weiner and others, 1983). However, weight loss during heating of this sample was 1.2%, indicating the bulk of the weight loss was due to expulsion of water. Distribution of pits in the sample is not uniform, reflecting variations in the original water content of the sample.

Nor are H_2O inclusions evenly distributed within the skeletons which do contain them. Inclusions occur in inter- and intracrystalline voids ranging in size down to a few 10's of Ang-

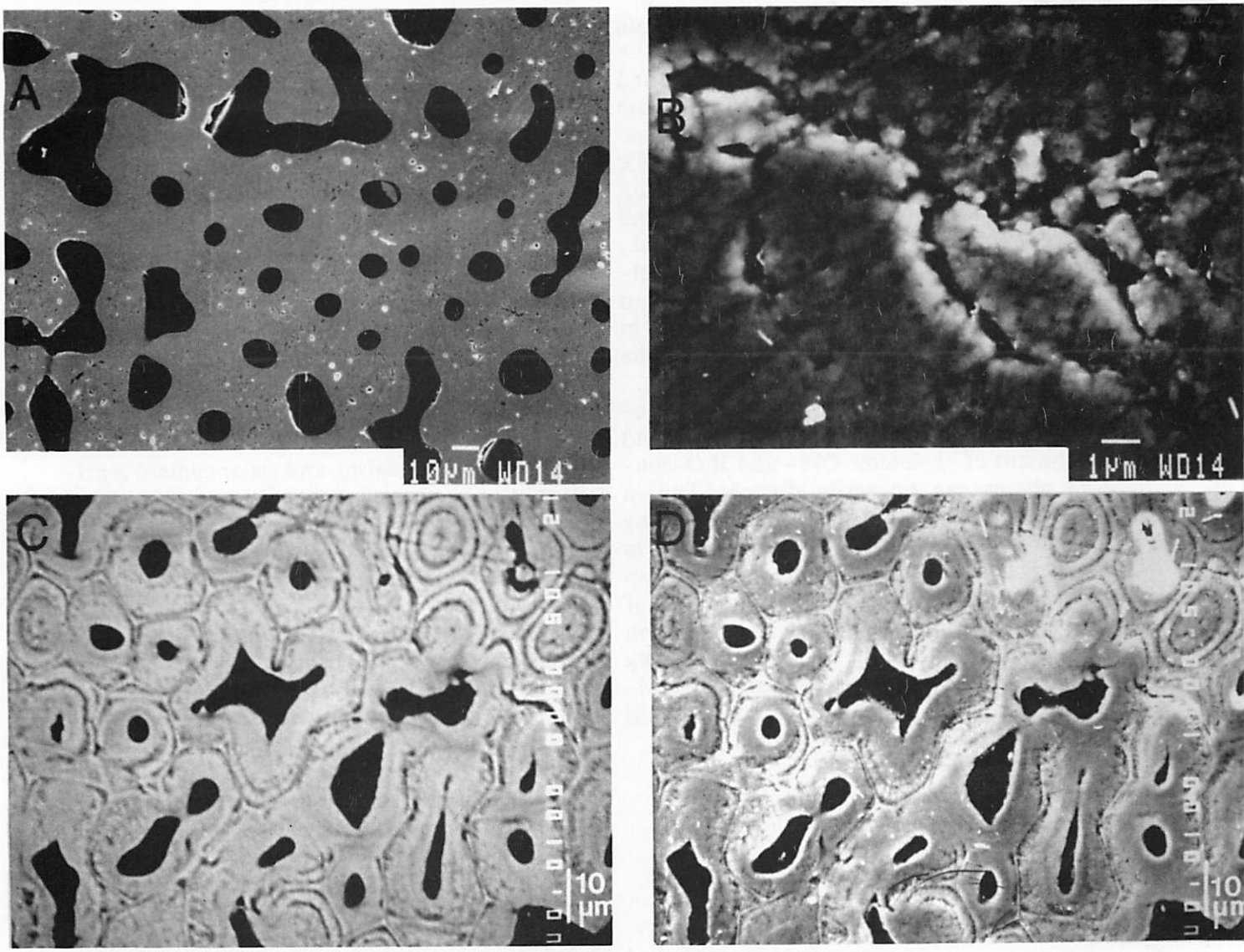

Fig. 3. SEM photomicrographs of skeletal samples heated to 200°C for 24 hours.
A) Heated speciment of *Encope* showing pitting caused by loss of water. Note uneven distribution of pitted areas reflecting original heterogeneities in water content within the skeleton.
B) Heated fragment of *Acropora* showing pitting and fracture of carbonate.
C) Backscatter electron image of heated *Neogoniolithon* showing concentric compositional zoning of cell walls and cements.
D) Secondary electron image of same field of view as C) showing pitting of cell walls and concentric zones in cements due to loss of organics and water on heating.

stroms (e.g. Bruni and Wenk, 1985; Green and others, 1980). Water in inclusions is often closely associated with organics in carbonate skeletons, and both are finely disseminated throughout the skeletal carbonate and can't be removed by grinding and bleaching (Gaffey, 1990 and references cited therein; Zabielski and Gaffey, 1989). Data in Zabielski and Gaffey (1989) show that relative variations in total water content of up to 65% occur within a modern *Diploria* skeleton. Figure 3B shows a heated *A. cervicornis* sample. Pitting and fracturing of *A. cervicornis* grains appears to be concentrated along trabeculae, where water and organics are most abundant (James, 1974).

Water and organics are also very unevenly distributed within *Neogoniolithon* skeletons. Figures 3C and D show SEM photomicrographs of heated samples of *Neogoniolithon* in which pitting occurs along the cell walls and within the cements which partially fill voids left after death of the vegetative cells. The high Mg calcite in this sample contains between 18 and 23 mole % $MgCO_3$. The backscatter electron image (Fig. 3C) shows concentric zoning of the carbonate making up the cell walls and cements. Moberly (1970) suggests this zoning may be due to variations in Mg, or in H_2O and OH^- content. Coralline red

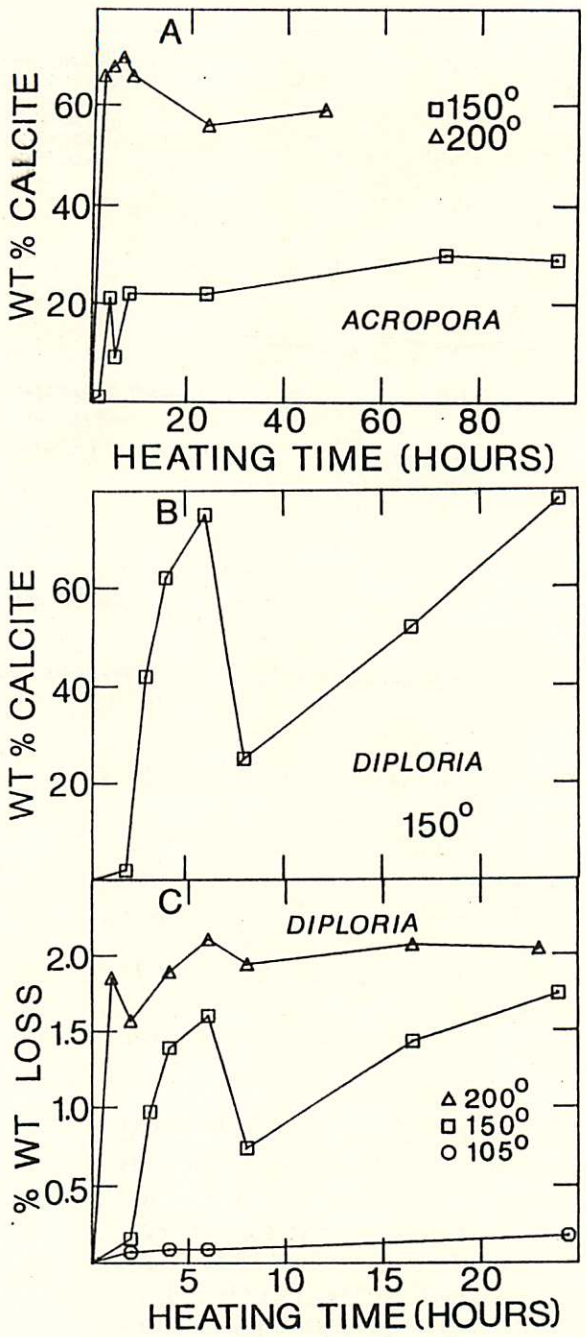

Fig. 4. Calcite content and weight loss of heated samples of coralline aragonites.
A) Calcite content of heated samples of *Acropora cervicornis*.
B) Calcite content of heated samples of *Diploria strigosa*.
C) Weight loss on heating of samples of *Diploria strigosa*. Note similarity in trend of weight loss (i.e. water loss, see discussion in text) and calcite content of *Diploria* samples heated to 150°C.

algae calcify by impregnating their cell walls with high Mg calcite, and precipitation of carbonate is controlled by a polysaccharide matrix (Cabioch and Giraud, 1986). Breakdown of this organic matrix (reflectance spectra show loss of OH and CH groups from polysaccharides) causes the observed pitting along the cell walls. Pitting within the cements filling the voids is presumably due to expulsion of water, indicating the compositional zoning is due, at least in part, to variations in H_2O content, as suggested by Moberly (1970).

Mineralogical Alteration and Water Loss on Heating

Skeletal carbonates may show significant changes in mineralogy on heating. Because biogenic aragonites contain a large number of lattice defects (Busenberg and Plummer, 1989) as well as water in inclusions, they may be partially or completely altered to calcite at temperatures much lower than the 400°C at which the reaction occurs in dry, abiogenic aragonites. Figures 4A and B show calcite content of *Diploria* and *Acropora* samples after heating. While neither coral showed any detectable calcite after heating at 105°C, samples heated to 150°C or higher were partially or completely altered to calcite. However, these data show that the two corals do not alter to the same degree on heating. While *Acropora* samples heated to 150°C and 200°C for ~24 hr contained ~78 and 44 wt % aragonite respectively, *Diploria* samples heated at the same temperatures and times contained 25 and 5 wt % aragonite, respectively.

Although complete weight loss data were not obtained for *Acropora* samples, Figure 4C shows weight loss of *Diploria* samples during heating. Coralline aragonites contain about 0.1 wt % organics (Lowenstam and Weiner, 1989; Weiner and others, 1983), so the observed weight loss is due primarily to expulsion of water from the skeletons. Data in Figures 4B and C show the calcite content of *Diploria* samples heated at 150°C parallels weight loss (i.e. water loss) at the same temperature. Thus, increased water loss is correlated with increased alteration of aragonite to calcite. When samples were completely altered to calcite, reflectance spectra show that all water had been removed from the samples (detection limits for water in carbonate samples are approximately 0.01 wt % [Gaffey, 1985]).

Rate of alteration in both samples slows

markedly after the first 6 to 8 hours. However, data in Figure 4 show that water loss and alteration to calcite are not a smooth function of time, but vary considerably from one run to another, despite the fact that all material was taken from the same homogenized bulk sample. This reflects the heterogeneities in microstructure (Constantz, 1985) and water content of coralline aragonites.

Experimental work has shown that high Mg calcites can be altered to dolomite and a calcite of lower Mg content by heating (Goldsmith, 1960; Graf and Goldsmith, 1955, 1956; Grover and Kubanek, 1983; Land, 1967). Figure 5 shows X-ray diffraction data for heated and unheated samples of echinoids and *Neogoniolithon*. None of the high Mg calcites studied here showed any alteration on heating to 105°C for 24 hours. However, at higher temperatures, significant changes occurred in echinoid samples (Figs. 5A, B). After heating at 300°C for 2 hours, samples of the echinoid *Leodia* (14.0 mole % $MgCO_3$), contained dolomite detectable by X-ray diffraction. Position of the major dolomite peak shows the dolomite is calcian, containing ~40 mole % $MgCO_3$, using the curves summarized by Milliman (1974). X-ray diffraction data show that with time, the $MgCO_3$ of the dolomite phase increases, while the major calcite peak produced by these same samples breaks down into 2 or more peaks, and shifts to lower angles °2Θ, indicating the presence of multiple calcite phases with decreased Mg content (Fig. 5A). At lower temperatures and shorter times (Fig. 5B), detectable dolomite was not produced, but the major calcite peak did show a significant shift to lower angles.

The tendency to form dolomite is not related to the Mg content of these skeletal samples. *Neogoniolithon* (19.6 mole % $MgCO_3$) showed no evidence of alteration when heated to 300 or 400°C, and no shift in position of the major calcite peak (Fig. 5C). Two samples of foraminifera were heated to 300°C for 28 hours. Neither sample produced detectable dolomite in that time, and the X-ray diffractogram of *Quinqueloculina* (13.0 mole % $MgCO_3$) showed no change in the major calcite peak. However, the major peak produced by the *Homotrema rubrum* sample (13.2 mole % $MgCO_3$) did broaden into multiple peaks and showed a small shift to lower angles. As with the coralline aragonites and foraminiferal calcites, high Mg calcites produced

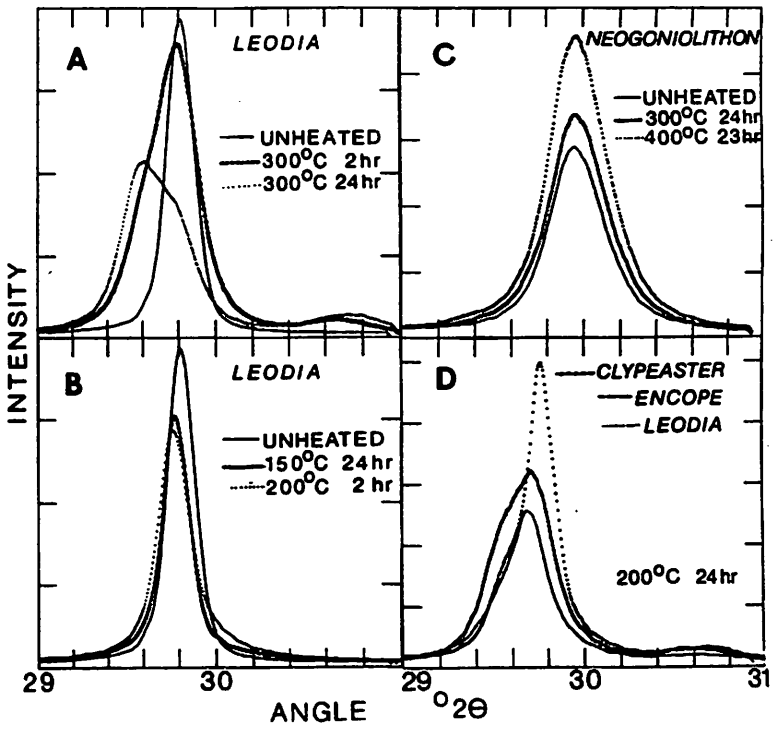

Fig. 5. X-ray diffractograms of magnesian calcites before and after heating.
A) Echinoid *Leodia* unheated and heated to 300°C for 2 and 24 hours.
B) Echinoid *Leodia* heated to 150°C for 24 hours and 200°C for 2 hours.
C) *Neogoniolithon* unheated and heated to 300°C and 400°C for 24 hours.
D) Three different echinoids heated to 200°C for 24 hours.

by different genera of echinoids also altered at different rates on heating. Of the three echinoids studied, *Clypeaster* (11.7 mole % $MgCO_3$) formed dolomite the most readily, producing a detectable dolomite peak after heating to 200°C for 6 hours. *Encope* (11.5 mole % $MgCO_3$) altered the least readily (Fig. 5D). As with the coralline aragonites, mineralogical change is correlated with water loss in echinoids. For example, on heating to 300°C for 24 hours, *Encope* lost ~1.46 wt % water (2 measurements), while *Clypeaster* lost ~2.38 wt % (average of 4 measurements), despite the fact that spectral data indicate that the total water contents of the two echinoid samples are similar.

Early Diagenetic Alteration of Carbonate

Skeletal carbonates, which are the subject

of this study, are not precipitated directly from sea water, but are produced by biologically controlled mineralization (Mann, 1983), in which the site of mineral formation is sealed off from the surrounding environment (Lowenstam and Weiner, 1989). Since skeletal carbonates are precipitated in isolation from the marine environment, they are not necessarily in equilibrium with normal marine waters, and diagenesis can begin in the marine environment immediately after death of the organism.

NMR spectral data in Figure 6 provide an example of diagenetic alteration of "pristine" coralline aragonites. The spectra in Figure 6 were obtained from two of the samples of *Diploria strigosa* described in Zabielski and Gaffey (1989).

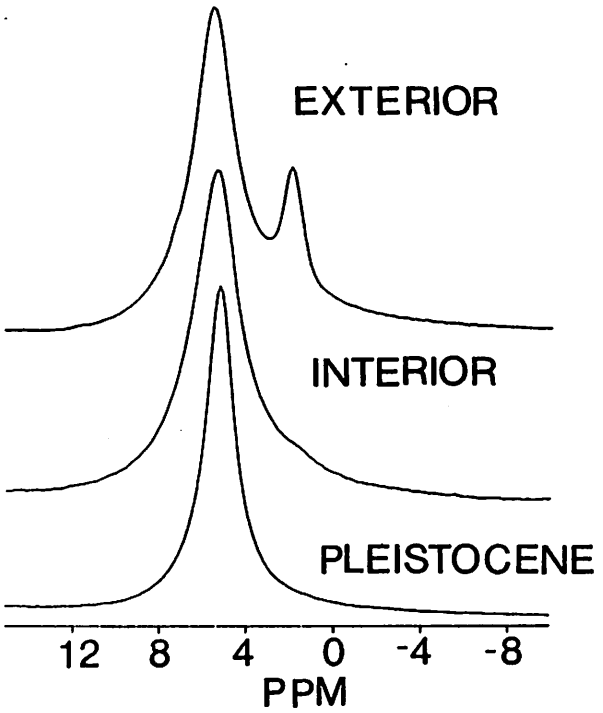

Fig. 6. ^{1}H CRAMPS NMR spectra of samples of *Diploria strigosa*. The PPM scale indicates chemical shift relative to a standard. The first was obtained from the outer portion of a skeleton still occupied by the coral polyps at time of collection, the second from an inner portion of the same colony infested with microbial endoliths, and the third from a Pleistocene sample from Quarry A.

Two spectra were obtained from the skeleton of the live coral, one from the outer portion of the skeleton still occupied by the coral polyps, the other from the inner portion infested with microbial endoliths. The reduced intensity of the 1 ppm resonance in the spectrum of the sample from the interior of the skeleton indicates a drop in hydroxyl content of the skeleton. Growth banding revealed by X-ray radiography (Zabielski and Gaffey, 1989) shows the coral head was approximately 25 years old, indicating the hydroxyl was lost very rapidly from the skeleton, perhaps as a result of endolith acitivity. These data show that the minerals in skeletal carbonates are not necessarily stable in the marine environment.

The spectrum of the Pleistocene skeleton shows a further loss of hydroxyl, as well as the decrease in H_2O content revealed by reflectance spectroscopy (Zabielski and Gaffey, 1989). In addition, the 5 ppm peak in the spectrum of the Pleistocene sample has narrowed, indicating an increase in the mobility or liquid-like behavior of the water in the fossil skeleton apparently due to breakdown of the organics with which the water is associated (Charles Bronnimann, personal communication, 1990). Thus, although X-ray diffraction and petrographic studies in thin section and with SEM indicate these coralline aragonites are "pristine", they differ significantly from the original material precipitated by the coral polyps. This type of alteration could potentially affect the results of isotopic and trace element studies used in paleoecological interpretations.

CONCLUSIONS

1. Carbonate skeletons are not simple mineral systems of aragonite or calcite with varying Mg contents, but are complex, heterogeneous composite materials containing organics, H_2O in inclusions, and hydrated and hydroxylated mineral phases.

2. As with all other physical, mineralogical, and chemical attributes of skeletal carbonates, the primary control of water content of skeletons is taxonomic.

3. Heating experiments show that the varied compositions and structures produced by different organisms result in varied responses to changes in a single environmental parameter. Differences in response to heating occur at least at the generic level.

4. Mineralogical changes resulting from heating coralline aragonites and echinoid calcites are related to loss of water, greater mineralogical alteration being observed in samples which showed the greatest water loss.

5. Because skeletal carbonates are formed within the cells and tissues of the carbonate secreting organism, they are not precipitated in chemical equilibrium with sea water, and diagenetic alteration can begin immediately following the death of the organism in the marine environment.

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REFERENCES CITED

Blake, D.F., Peacor, D.R., and Allard, L.F., 1984, Ultrastructural and microanalytical results from echinoderm calcite: Implications for biomineralization and diagenesis of skeletal material: Micron and Microscopica Acta, v. 15, p. 85-90.

Bronnimann, C.E., Hawkins, B.L., Zhang, M., and Maciel, G.E., 1988, Combined rotation and multiple pulse spectroscopy as an analytical proton nuclear magnetic resonance technique for solids: Analytical Chemistry, v. 60, p. 1743-1750.

Bruni, S.F., and Wenk, H.-R., 1985, Replacement of aragonite by calcite in sediments from the San Cassiano Formation (Italy): Journal of Sedimentary Petrology, v. 55, p. 159-170.

Busenberg, E., and Plummer, L.N., 1985, Kinetic and thermodynamic factors controlling the distribution of SO_4^{2-} and Na^+ in calcites and selected aragonites: Geochimica et Cosmochimica Acta, v. 49, p. 713-725.

Busenberg, E., and Plummer, L.N., 1989, Thermodynamics of magnesian calcite solid-solutions at 25°C and 1 atm total pressure: Geochimica et Cosmochimica Acta, v. 53, p. 1189-1208.

Cabioch, J., and Giraud, G., 1986, Structural aspects of biomineralization in the coralline algae (calcified Rhodophyceae), in Leadbeater, Barry S. C., and Riding, Robert, eds., Biomineralization in the Lower Plants and Animals, Oxford, Clarendon Press, p. 141-156.

Chave, K.E., 1954, Aspects of the biogeochemistry of magnesium 1.Calcareous marine organisms: Journal of Geology, v. 62, p. 266-283.

Conger, S.D., Green, H.W., and Lipps, J.H., 1977, Test ultrastructure of some calcareous Foraminifera: Journal of Foraminiferal Research, v. 7, p. 278-296.

Constantz, B.R., 1986, The primary surface area of corals and variations in their susceptibility to diagenesis, in Purser, Bruce H., ed., Reef Diagenesis, New York, Springer-Verlag, p. 53-76.

Gaffey, S.J., 1985, Reflectance spectroscopy in the visible and near-infrared (0.35-2.55 μm):Applications in carbonate petrology: Geology, v. 13, p. 270-273.

Gaffey, S.J., 1988, Water in skeletal carbonates: Journal of Sedimentary Petrology, v. 58, p. 397-414.

Gaffey, S.J., 1990, Chapter 5: Skeletal versus nonbiogenic carbonates: UV-Visible-Near IR (0.3-2.7-μm) reflectance properties, in Coyne, L.M., McKeever, S.W.S., and Blake, D.F., eds., Spectroscopic Characterization of Minerals and Their Surfaces, American Chemical Society Symposium Series No. 415, p. 94-116.

Goldsmith, J.R., 1960, Exsolution of dolomite from calcite: Journal of Geology, v. 68, p. 103-109.

Graf, D.L., and Goldsmith, J.R., 1955, Dolomite-magnesium calcite relations at elevated temperatures and CO_2 pressures: Geochimica et Cosmochimica Acta, v. 7, p. 109-128.

Graf, D.L., and Goldsmith, J.R., 1956, Some hydrothermal syntheses of dolomite and protodolomite: Journal of Geology, v. 64, p. 173-186.

Green, H.W., Lipps, J.H, and Showers, W.J., 1980, Test ultrastructure of fusulinid Foraminifera: Nature, v. 283, p. 853-855.

Grover, J., and Kubanek, F., 1983, The formation of ordered dolomite from high magnesium calcite at 250°C to 350°C and 1500 bars: Epitactic growth with optimal phase orientation, and implications for carbonate diagenesis: American Journal of Science, v. 283-A, p. 514-539.

James, N.P., 1974, Diagenesis of scleractinian corals in the subaerial vadose environment: Journal of Paleontology, v. 48, p. 785-799.

Land, L.S., 1967, Diagenesis in skeletal carbonates: Journal of Sedimentary Petrology, v. 37, p. 914-930.

Lowenstam, H.A., 1981, Minerals formed by organisms: Science, v. 211, p. 1126-1131.

Lowenstam, H.A., and Weiner, S., 1989, On Biomineralization: New York, Oxford University Press, 324 p.

Maciel, G.E., Bronnimann, C.E., and Hawkins, B.L., 1990, High-resolution ^1H nuclear magnetic resonance in solids via CRAMPS, in Warren, W.S., ed., Advances in Magnetic Resonance, v. 14, p. 125-50.

Mackenzie, F.T., Bischoff, W.D., Bishop, F.C., Loijens, M., Schoonmaker, J., and Wollast, R., 1983, Magnesian calcites: Low-temperature occurrence, solubility and solid-solution behavior, in Reeder, R.J., ed., Carbonates: Mineralogy and Chemistry, Mineralogical Society of America Reviews in Mineralogy Vol. 11, p. 97-144.

Mann, S., 1983, Mineralization in biological systems: Structure and Bonding, v. 54, p. 125-174.

Milliman, J.D., 1974, Marine Carbonates: New York, Springer-Verlag, 375 p.

Moberly, R., Jr., 1970, Microprobe study of diagenesis in calcareous algae: Sedimentology, v. 14, p. 113-123.

Moore, C.H., 1989, Carbonate Diagenesis and Porosity: New York, Elsevier, 338 p.

Pieters, C.M., 1983, Strength of mineral absorption features in the transmitted component of near-infrared reflected light: First results from RELAB: Journal of Geophysical Research, v. 88, p. 9534-9544.

Swift, D.M., Sikes, S., and Wheeler, A.P., 1986, Analysis and function of organic matrix from sea urchin tests: The Journal of Experimental Zoology, v. 240, p. 65-73.

Weiner, S., Traub, W., and Lowenstam, H.A., 1983, Organic matrix in calcified exoskeletons, in Woestbroek, P., and de Jong, E. W., eds., Biomineralization and Biological Metal Accumulation, New York, Reidel Publishing, p. 205-224.

Zabielski, V.P., and Gaffey, S.J., 1989, Feasibility of use of VNIR reflectance spectroscopy for analysis of water and organic content in skeletons of scleractinian corals, in Mylroie, J. E., ed., Proceedings of the Fourth Symposium on the Geology of the Bahamas, Port Charlotte, Florida, Bahamian Field Station, p. 367-381.