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WATER AND ORGANICS IN SKELETAL CARBONATES: EARLY DIAGENETIC EFFECTS - A PROGRESS REPORT

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ABSTRACT

Water (liquid and bound H_2O and OH^-) and organic compounds are important primary constituents of all carbonate skeletons incorporated during growth. These phases may persist for long periods of time in the sediment column, either in their original form or as by-products of chemical or biological breakdown. Despite the fact that water and organic compounds play a central role in diagenesis of carbonate sediments, there are at present no techniques routinely in use by carbonate petrologists to detect, identify, or determine the abundances of these phases. Visible and near infrared (VNIR) (0.3 to 2.7 um) spectroscopy can potentially provide such a tool, affording a rapid, inexpensive, and non-destructive method for detecting the presence of many of the fluid and amorphous phases not accessible by X-ray diffraction, and for measuring the abundances of lighter elements such as H, C, O, and N not easily studied by more commonly used techniques such as microprobe, X-ray fluorescence, or AA. Spectral data show that there is considerable variation in the water and organic content of skeletons of different taxonomic groups, that water and organic compounds are found in fossil as well as modern skeletons, and that these phases are only partially removed by routine sample preparation techniques such as bleaching, grinding and heating. Routinely prepared carbonate samples are not representative of skeletal materials as they occur in nature, nor are they pure mineral samples of aragonite and calcite produced by organisms.

INTRODUCTION

The chemical and mineralogical composition of carbonate skeletons is more varied and complex than the usual terms "aragonite" and "high" or "low Mg calcite" imply. Water and organics, both an intrinsic part of all carbonate skeletons, can play a major role in diagenesis of carbonate sediments. Liquid water provides the medium for all diagenetic reactions (Bathurst, 1971). Presence of hydrated phases containing H_2O or OH^- can affect the stability and solubility of carbonate skeletons (e.g. Mackenzie and others, 1983; Mucci and Morse, 1984; Turner and others, 1986). Organic compounds themselves can facilitate precipitation of carbonates, and can affect the mineralogy, chemical composition, and crystal form of the precipitate (e.g. Loreau, 1982; Mitterer and Cunningham, 1985; Suess, 1973). Organic films on carbonate grains may also retard precipitation of carbonates (Suess, 1970). Organic compounds can form complexes with metal cations, affecting their mobility (Kharaka and others, 1986; Mitterer and Cunningham, 1985). Breakdown of organic compounds either by direct physicochemical oxidation or by bacteria can influence pore water chemistry, affecting Eh and pH as well as concentration of dissolved constituents such as NH_3^+, SO_4^{-2}, PO_4^{-3}, and CO_2 (Gautier, 1985; Kharaka and others, 1986) which can in turn affect the solubility and stability of carbonate phases (Walter, 1986). Although reefs occur in high energy environments where large volumes of water are circulated through the reef framework by waves and tides, anaerobic diagenesis can occur throughout reefs (Sansone, 1985; Sansone and others, 1988; Trichet and others, 1985).

Despite the importance of water and organic compounds in diagenetic reactions, and although water in various forms (liquid and bound H_2O and OH^-) and organic compounds are known to be important constituents not only of skeletal but also of non-skeletal grains such as ooids and peloids (e.g. Busenberg and Plummer, 1985; Crenshaw, 1982; Gaffey, 1983, 1984, 1985, 1988; Green and others, 1980; Mackenzie and others, 1983; Milliman, 1974; Mitterer and Cunningham, 1985; Schmalz, 1965; Weiner and others, 1983) there are at present no analytical techniques routinely in use by carbonate petrologists for identification and determination of abundances of these components. Organic contents of carbonate skeletons

reported the literature vary widely (see e.g. Milliman, 1974) and data on water contents are virtually non-existent. Although considerable work has been done on diagenesis of organics in clastic sequences (e.g. Gautier, 1986; Gautier and others, 1985) organics in carbonate sediments have received much less attention. The long term goals of this work are to identify and determine abundances of water-containing phases and of organic compounds in carbonate skeletons, and to relate changes in the types and abundances of these components to diagenetic processes within modern and Pleistocene reef sediments. An important first step in such a study is the development of analytical tools for studying water and organic compounds in geologic materials. VNIR reflectance spectroscopy can potentially provide one of these tools, and this paper summarizes the advances made to date in applying reflectance spectroscopy in studies of modern and ancient carbonate sediments. Application of this tool in a specific diagenetic study can be found in Zabielski and Gaffey (this volume).

MATERIALS AND METHODS

Modern and fossil material used in this study was collected on Oahu, Hawaii, between 1980 and 1984, and from San Salvador Island, Bahamas in March, 1986 and January and June, 1988. Calcareous green algae such as *Halimeda* and *Penicillus*, and gorgonians were dried in an oven at a temperature of about 40°C. Coralline red algae, scleractinian corals, hydrozoans, and echinoids which were collected live were bleached in 5 % sodium hypochlorite solution before returning them to the laboratory for analysis. Sands from both beaches and the marine environment were collected so that samples of forams, plates of *Halimeda*, and segments of coralline red algae could be separated from them. *Homotrema rubrum* were removed from coral heads or rock slabs they encrusted. Some tests of live Foraminifera were also removed from *Penicillus* and *Halimeda*. Skeletons of dead echinoids, algae, and corals were collected from bottom sediments and from beaches.

Mineralogy of samples was determined using X-ray diffraction. All modern samples were bleached in H_2O_2 buffered to a neutral pH with NaOH or in sodium hypochlorite solution. Fossil specimens were examined in thin section and/or with SEM. VNIR (0.3 - 2.7 um) reflectance spectra were obtained both from whole samples and from bleached and unbleached powders. Spectra were obtained using the spectrophotometers at RELAB at Brown University, described by Pieters (1983) and at the U.S.G.S. in Denver, described by Clark and others (1988). Spectra of several samples were obtained on both instruments to verify subtle features.

BACKGROUND

VNIR spectroscopy provides a rapid, inexpensive, non-destructive technique for characterizing significant aspects of the mineralogical and chemical composition of geologic samples. Like X-ray diffraction it is non-selective, giving information on all optically active phases present in a sample. Unlike X-ray diffraction, however, it can be used to study many liquid and amorphous phases, and phases which occur in solid solution rather than as discrete mineral phases with an ordered lattice, providing a useful compliment to X-ray diffraction analyses. VNIR spectroscopy can also be used to study the lighter elements such as C, O, H, and N, which are not amenable to analysis by techniques such as microprobe or XRF which are more commonly employed by geologists.

Reflectance and transmission spectroscopy are not new techniques, but have been used routinely by chemists and physicists for about 60 years. All the basic principles used in interpretation of the spectra presented in this article and in Zabielski and Gaffey (this volume) are well established and are taken from the chemical literature cited below or in Gaffey (1988).

When light interacts with a compound certain wavelengths are preferentially absorbed. The number, positions, widths, and intensities of these absorptions are diagnostic of the mineralogical and chemical composition of the sample. Spectra of a sample may be obtained by reflecting light from its surface, or by transmitting light through it. The light is separated into its component wavelengths by a prism, diffraction grating or circular variable filter either before or after it has interacted with the sample, and the intensity of light reflected or transmitted at each wavelength is recorded. In the reflectance mode, the intensity of light reflected from the sample at each wavelength is ratioed to the intensity of that reflected from a standard, usually Halon in this spectral region. In the transmission mode, the intensity at each wavelength of a light beam which has passed through the sample is ratioed to the intensity of a beam which has not. In both

cases, spectra like those in Figure 1 are obtained, which show the percentage or proportion of light reflected from or transmitted through the sample as a function of wavelength. A perfect reflector would produce a straight line at 1.0 reflectance.

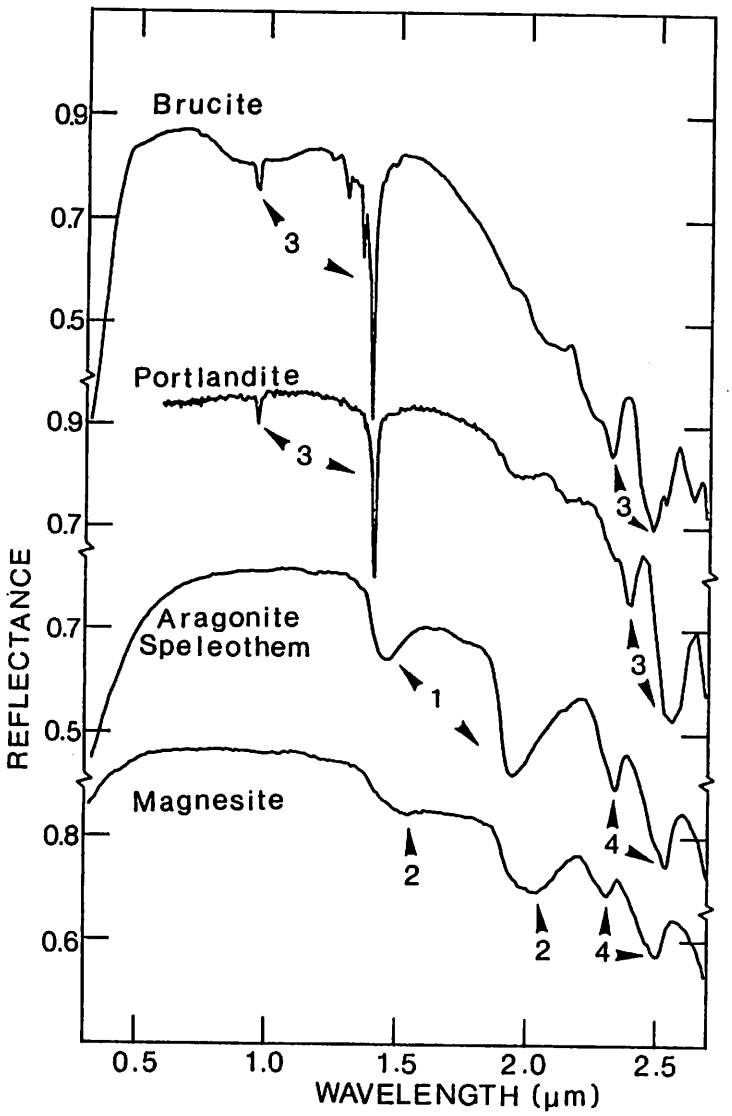

Fig. 1. Spectra of nonbiogenic mineral samples containing liquid and bound H_2O and OH^-. Arrows indicate absorption features due to: 1 - Liquid H_2O, 2 - Bound H_2O, 3 - OH^-.

Several different processes in compounds and crystals can cause absorption of light: (1) electronic transitions in molecular orbitals in compounds; (2) electronic transitions between unfilled d-shells in transition metal ions such as Fe^{2+} and Fe^{3+}; (3) internal vibrational transitions in molecules and molecular ions such as H_2O or NH_3^+ in which bond lengths and bond angles change; (4) external vibrational transitions in which the molecule or molecular ion moves as a unit. Fundamental internal vibrational modes are those in which the atoms in a molecule move in straight line paths causing a change in bond length (stretching modes) or bond angle (bending modes). External vibrational modes in crystals such as calcite or aragonite consist of librational or rocking motions of the carbonate ion, or translational motions analogous to P and S waves. Overtones and combination tones are analogous to the overtones of a vibrating violin string. In these vibrational modes the atoms do not follow straight line paths. However, these more complex motions can all be resolved into their component fundamentals. More may be learned about spectroscopy from excellent references such as those of Farmer (1974), Harris and Bertolucci (1978), Herzberg (1945), Wheatley (1968), and Wilson and others (1955).

The VNIR region of the spectrum employed in the present study and in Zabielski and Gaffey (this volume) has a number of advantages over the more commonly used mid-infrared (MIR) (3 to 20 um) and far infrared (FIR) (>20 um) regions. (1) Because the types of particle size effects which hamper work in the MIR and FIR (Estep-Barnes, 1977; Farmer and Russell, 1966; Russell, 1974; Tuddenham and Lyon, 1960) are absent in the VNIR, spectra can be obtained from samples in any form (Gaffey, 1986). Unstable or soluble phases such as organics and hydrated mineral phases can be studied *in situ*, without subjecting materials to grinding, heating, bleaching, or extraction techniques which may alter, remove, or destroy the phases of interest. (2) The VNIR region contains absorptions due to all four types of transitions discussed above, unlike the MIR and FIR which only contain features due to vibrational transitions. (3) A great deal of overlap between absorption bands occurs in the 3 um region which contains absorptions due to the fundamental O-H, C-H, and N-H stretching modes and the first overtones of the H-O-H and H-N-H bending modes. However, in the VNIR energy differences between different vibrational modes are amplified, and a useful separation occurs between absorptions due to overtones and combination tones of these modes.

Spectral Properties of Carbonates

All anhydrous carbonate minerals produce a series of sharp, narrow absorptions at wavelengths

>1.6 um, whose precise positions and widths vary with mineralogy and chemical composition. All but the two strongest bands near 2.3 and 2.5 um are usually masked by water bands in spectra of skeletal carbonates, although in spectra of some samples the carbonate band near 2.17 um can also be seen. See Gaffey (1984, 1985, 1986, 1987) for more complete discussions of the VNIR spectral properties of anhydrous carbonate minerals.

Spectral Properties of Water

As used here, "water" refers to all inorganic liquid and bound H_2O and OH^-. Spectra of some H_2O- and OH^--containing phases are shown in Figures 1 and 2. The brucite, aragonite speleothem, and magnesite are naturally occurring mineral samples. The portlandite, hydrocerussite, hydrozincite, and hydromagnesite samples are reagent grade chemicals.

H_2O has three strong absorption features near 1.4 (the first overtone of the O-H stretch), 1.9 (a combination of the H-O-H bend and O-H stretch) and 2.5 um (a combination of the O-H stretch and an external mode). H_2O also produces weaker absorptions near 0.9, 1.2, and 1.8 um (Bayly et al., 1963). The aragonite speleothem spectrum (Fig. 1) illustrates absorption features due to $CaCO_3$ and liquid H_2O.

When H_2O is incorporated into a crystal lattice, hydrogen bonding causes absorption bands to broaden, intensify, and shift to longer wavelengths (Falk and Knop, 1973; Hamilton and Ibers, 1968). OH^--containing mineral phases produce absorptions near 0.9, 1.4 and 2.2 to 2.3 um, but do not produce a features in the 1.2- and 1.9-um regions (Chapman and Nacey, 1957; Miller and Willis, 1956). OH^- features in mineral spectra tend to be sharper and narrower than H_2O features.

Spectra in Figures 1 and 2 illustrate the usefulness of VNIR spectroscopy for characterizing water in geologic samples. For example, although X-ray diffraction indicates the magnesite sample (Fig. 1) contains only magnesite, its spectrum indicates the presence of bound H_2O, in addition to water in fluid inclusions which occurs in nearly all mineral samples. The hydrozincite and hydrocerussite samples of Figure 2 are reagent grade $ZnCO_3$ and $PbCO_3$, respectively. X-ray diffraction shows the "$PbCO_3$" sample is ~50% hydrocerussite, chemical formula $Pb_3(CO_3)_2(OH)_6$ (Fleischer, 1980), and its spectrum shows the expected narrow sharp OH^- absorptions near 0.9, 1.4, and 2.3 um. However, although X-ray diffraction analysis of the "$ZnCO_3$" sample shows it is composed of hydrozincite, formula $Zn_5(CO_3)_2(OH)_6$ (Fleischer, 1980), the strong 1.9-um band and positions of both the 1.4- and 1.9-um bands indicate the presence of bound H_2O. The chemical composition of many hydrated carbonate mineral phases, including hydrated $MgCO_3$ minerals such as nesquehonite and hydromagnesite, are poorly known (e.g. White, 1971) and additional data is needed before hydrated species in carbonate skeletons can be related to specific mineral phases.

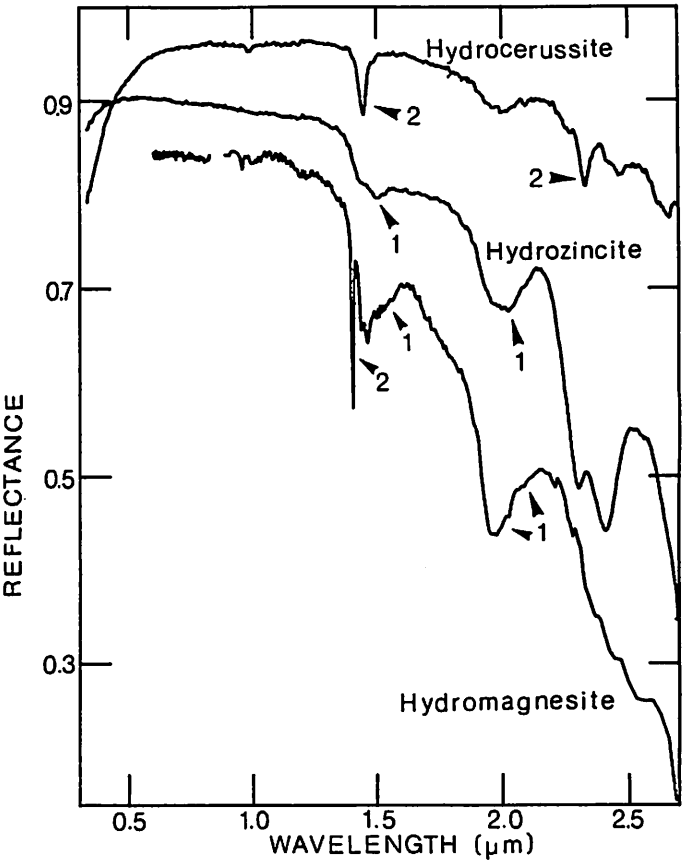

Fig. 2. Spectra of reagent grade chemicals showing features due to bound H_2O and OH^-. Note that although the chemical formula for hydrozincite indicates this mineral contains only OH^-, bound H_2O is actually the form of hydrogen present. Arrows indicate absorption features due to: 1- Bound H_2O, 2- OH^-.

Spectral Properties of Organics

A variety of organic compounds have been identified in carbonate skeletons. Mollusks have been most intensely studied, but information is

also available on organics in skeletons of other organisms. The following discussion is not intended to give a complete analysis of the spectral properties of all organic compounds, but to briefly outline the spectral characteristics of broad classes of compounds known to occur in skeletal carbonates. Spectra of some organic materials are shown in Figure 3.

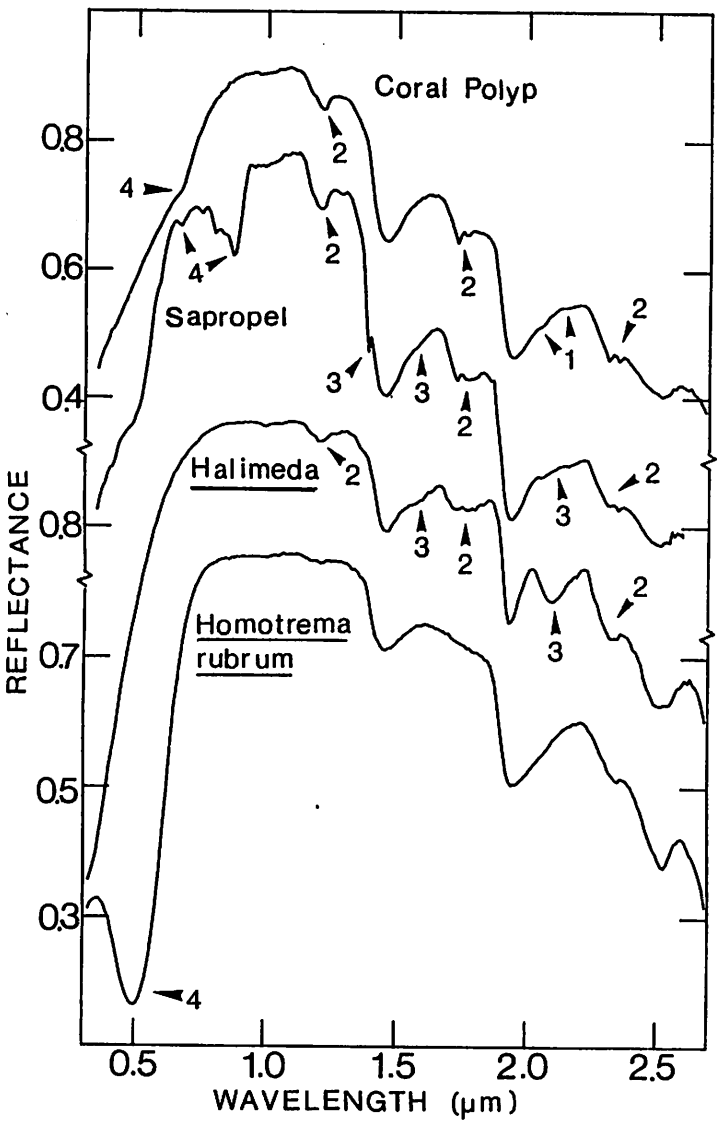

Fig. 3. Spectra of organic samples. Arrows indicate absorption features due to: 1- NH_3^+, 2- CH_2, CH_3, 3- OH, 4- organic pigments.

The near infrared portion of the spectrum is dominated by overtones and combination tones of the N-H, C-H, and O-H stretching fundamentals of functional groups in organic compounds. Despite the large size and structural complexity of organic molecules, small groups of atoms such as NH_3^+, OH, or CH_2 within those molecules will consistently produce absorption bands of similar intensities in approximately the same spectral region, called characteristic group frequencies. Precise positions of these absorption features will vary somewhat depending on the way the atomic group is bonded to the larger molecule (Colthup and others, 1964; Kaye, 1954; Wheatley, 1968).

While assignments of a single absorption feature to a given compound can't be made with confidence, suites of features considered together reduce the ambiguity in identification of absorbing species (Adams, 1975; Huguenin, 1987). Although the MIR is the wavelength region of choice for chemists, there is some data available in the literature on the NIR spectral properties of organics. In addition, because absorptions in the NIR are overtones and combination tones of fundamental modes, extrapolations can be made from the more readily available data on fundamental modes in the MIR (Herzberg, 1945).

Proteins

Proteins rich in aspartic acid are a characteristic component of many carbonate skeletons. Glutamic acid, glycine, and alanine may also be important constituents (e.g. Crenshaw, 1982; Mitterer and Cunningham, 1985; Weiner and others, 1983; Wilbur and Simkiss, 1979). NH_3^+ and CH_2 are the principle functional groups in proteins producing absorptions in the NIR (Colthup and others, 1964; Davies and Littlewood, 1979; Weber and Teale, 1965; Whetsel and others, 1958).

NH_3^+ groups produce two or more broad, rather diffuse absorptions between 2.0 and 2.2 um and broad bands near 1.5 and 1.1 um (Colthup and others, 1964; Miller and Willis, 1956; Weber and Teale, 1965; Whetsel and others, 1958). Sharp, narrow bands due to CH_2 occur in the 2.3 to 2.4-um region and near 1.7 um. Narrow bands also occur near 1.2 um (Colthup and others, 1964; Kaye, 1954; Miller and Willis, 1956; Weber and Teale, 1965).

Hydrogen bonding causes absorption bands due to functional groups to intensify and shift to longer wavelengths. NH_3^+ and CH_2 absorptions are several orders of magnitude weaker than those produced by an equal concentration of H_2O or OH^- (Bayly and others, 1963; Russell and Thompson, 1955a,b). Thus absorptions due to NH_3^+, CH_2, and CH_3 may be partially or completely masked by absorptions due to liquid H_2O in fluid inclusions (e.g. Hotta, 1969), or in polysaccharides. Absorptions due to weakly absorbing

species will be detected most readily in the more transparent regions of the spectrum where absorptions due to H_2O, OH^-, and carbonate are weak or lacking.

Polysaccharides

Polysaccharides also occur in many carbonate skeletons (Borowitzka, 1986; Cabioch and Giraud, 1986; Krumbein, 1979; Weiner et al., 1983). OH^- groups in polysaccharides produce broad bands between 2.0 and 2.3 um and near 1.5 and 1.0 um (Perlin and Casu, 1982; Zhbankov, 1966). Sharp, narrow bands near 0.9 and 1.4 um indicate the presence of a weakly bound OH^- group (Zhbankov, 1966), illustrated in the sapropel spectrum in Figure 3. CH_2 groups produce narrow, sharp absorption features near 2.3 and 1.7 um, and narrow absorptions near 1.4 and 1.2 um (Colthup and others, 1964; Evans and Hibbard, 1951; Zhbankov, 1966).

Lipids

Lipids have been identified in some carbonate skeletons (Johnston, 1979, 1980). Spectra of lipids are dominated by absorptions of CH_2 and CH_3 groups near 1.2, 1.4, 1.7 and 2.3 - 2.4 um (Chapman, 1965; Colthup and others, 1964; Davenport, 1971).

Organic Pigments

Organic pigments such as chlorophyll and carotene produce very intense absorption features in the visible region due to electronic transitions in molecular orbitals. These pigments and/or the products resulting from their breakdown can persist in sediments for geologically long periods of time, and absorptions due to these pigments are found in oils and organic-rich sediments in ancient rocks (Baker and Louda, 1986).

PHASES IN MODERN SKELETONS

Inorganic H_2O and OH^-

Spectra of all skeletal carbonates studied to date show absorption features due to liquid H_2O in fluid inclusions (Gaffey, 1983, 1984, 1985, 1988). Chemical analyses of the organic component of mollusk shells also indicate the presence of H_2O in fluid inclusions (Hudson, 1967). SEM and TEM studies of a variety of types of skeletal material have shown that rapid growth of crystals results in abundant twinning and growth dislocations, and produces a polycrystalline material with numerous inter- and intracrystalline voids (Bruni and Wenk, 1985; Constantz, 1986a,b) filled with organic material and/or liquid water (e.g. Bruni and Wenk, 1985; Conger and others, 1977; Green and others, 1980; Gvirtzman and Friedman, 1977; Hudson, 1967; James, 1974; Towe and Thompson, 1972).

Spectral and other properties of skeletal carbonates indicate the presence of bound H_2O- and OH^--containing phases in many skeletons, particularly the high Mg calcites (e.g. Busenberg and Plummer, 1985; Gaffey, 1984, 1985, 1988; Mackenzie and others, 1983; Mucci and Morse, 1984; Schmalz, 1965; Turner and others, 1986; Weber and Kaufman, 1965). Lowenstam (1981) also reports the presence of hydrated amorphous $CaCO_3$ and monohydrocalcite in some mollusks and arthropods.

Lippmann (1973) notes that Mg has a marked tendency to form hydrous carbonate mineral phases, and attributes this to strong bonds which exist between Mg^{2+} and water molecules in aqueous solutions. Rapid precipitation of mineral phases from concentrated solutions, both in nature and in chemical laboratories, apparently produces these unstable, hydrated phases. During precipitation of biominerals, an amorphous or hydrated phase is often precipitated first and later reverts to a more stable anhydrous phase (Mann, 1986). It may be that some of these unstable, intermediate phases remain in skeletons.

Skeletons of *Lytechinus variegatus*, like those of most echinoids, contain very little organic matter, organics comprising < 0.1% of the skeleton by weight (Swift and others, 1986). All absorption features in the *Lytechinus* spectrum in Figure 4a can be attributed to liquid and bound H_2O.

The *Halimeda* spectrum in Figure 4a provides another example. The narrow feature near 2.3 um, superimposed on the 2.3-um carbonate band, could be attributed to CH_2. However, the more easily detected CH_2 absorptions near 1.7 and 1.2 um are lacking (compare to *Homotrema* spectrum, Fig. 4a), indicating that this absorption is best attributed to $Ca(OH)_2$. Broadening and apparent shift to longer wavelengths of the 1.4- and 1.9-um bands may be attributed to bound H_2O.

Organic Compounds in Skeletons

Organic compounds in skeletons may be part of an organic matrix used to construct the

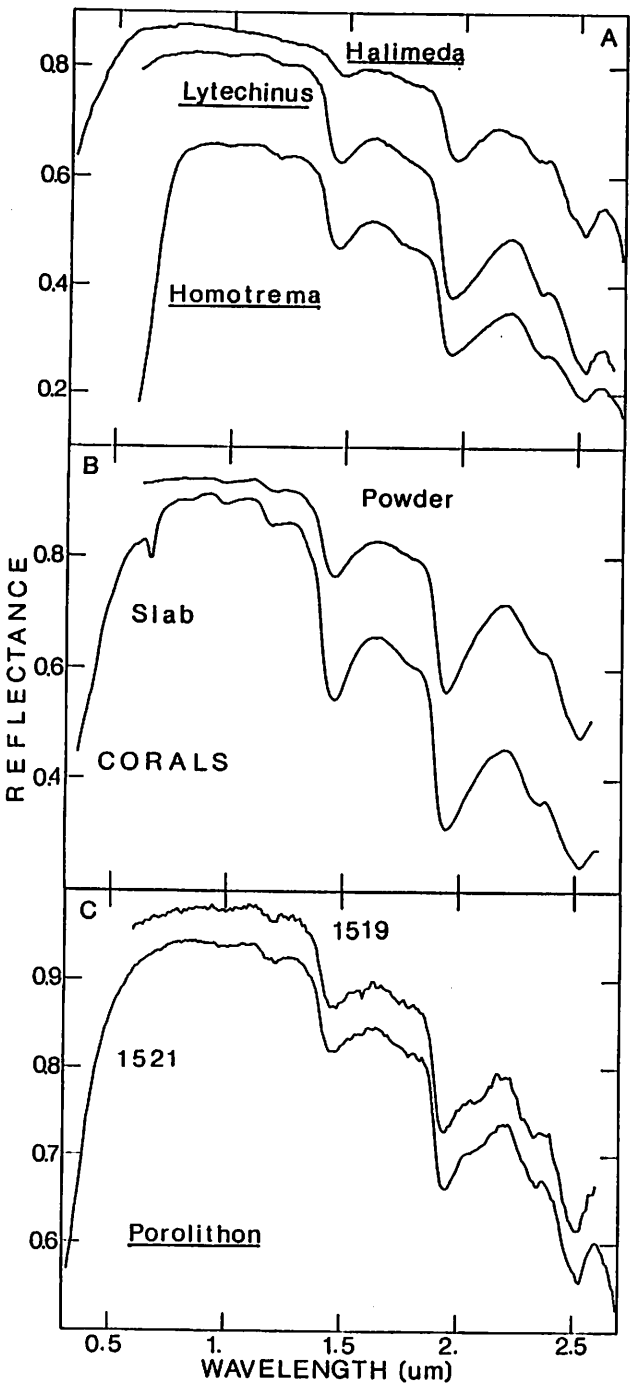

Fig. 4. Spectra of powdered and whole samples of skeletal carbonates showing absorption features due to water and organics. A. Spectra of whole plates of Lytechinus variegatus, *whole tests of* Homotrema rubrum *and bleached powder of* Halimeda. *Spectra offset vertically:* Lytechinus *0.05*, Homotrema *- 0.05. B. Spectra of bleached slab and bleached powder of scleractinian coral skeletons. C. Spectra of bleached powders of coralline red algae* Porolithon. *Spectra offset vertically: 1521 - 0.03, 1519 - 0.02.*

skeleton and perhaps to give it added strength (e.g. Crenshaw, 1982; Lowenstam, 1986; Weiner and others, 1983), soft tissues and body fluid of the organism entrapped during growth (Constantz, 1986a,b; Johnston, 1979, 1980) or material introduced by endoliths (Johnston, 1980). All skeletons contain some organic material, even after bleaching and grinding (e.g. Young, 1971). However, because many of the functional groups in organic compounds are weak absorbers, spectra of carbonate skeletons may not always indicate the presence of organics. For example, Figure 4b shows spectra obtained from a powdered, bleached coral sample and from a slab of a coral head. The spectrum of the slab shows some weak absorptions in the 2.2 - 2.3-um region due NH_3^+, a weak shoulder on the 2.3-um carbonate band and weak features near 1.7 and 1.2 um due to CH_2, as well as features near 0.67 and 0.40 um due to organic pigments introduced by endolithic algae (Baker and Louda, 1986; Lukas, 1974). However, in the powdered, bleached sample, only features due to liquid H_2O and carbonate can be seen. Additional work is needed to determine the detection limits for various organic compounds in spectra of intimate mixtures with water and carbonates.

Spectra of other samples, however, do show absorptions attributable to organic compounds even after grinding and bleaching. Comparison of the spectrum of whole *Homotrema* tests (Fig. 4a) with the spectrum of powdered, bleached *Homotrema* (Fig. 3) shows that in the spectrum of the powdered sample the C-H features near 2.3 and 1.7 um are not evident. However, the C-H feature near 1.2 um is still present, although weakened, in the spectrum of the powdered sample, as well as the strong band near 0.5 um caused by the organic pigments which give this foram its distinctive red color.

Spectra of calcareous red algae in Figure 4c may also show some features due to organic compounds. Calcification in the coralline red algae results from impregnation of the cell wall with high Mg calcite (HMC), a process controlled by a polysaccharide matrix (Cabioch and Giraud, 1986). Comparison of spectra of coralline red algae with spectra of organic materials (Fig. 3) and nonbiogenic mineral samples (Figs. 1 and 2) show that features in these spectra could be assigned either to organic and or to inorganic phases. It has been known for some time that skeletons of coralline red algae contain brucite (Busenberg and Plummer, 1985; Schmalz, 1965; Weber and Kaufman, 1965). Grinding and bleaching

aid in distinguishing between absorption features due to organics and those due to mineral phases. Grinding and bleaching will weaken features due to liquid water and organics, making those due to mineral phases more prominent. Some features originally attributed to hydrated mineral phases (Gaffey, 1988), now appear to be better assigned to organic compounds. For example, the feature near 2.2 um in the spectrum of sample 1521 in Figure 4c is probably due to OH in polysaccharides. These features are weakened in the spectrum of 1519 which was bleached more thoroughly, and features due to liquid and possibly to bound H_2O and OH^- become more evident.

Spectra clearly indicate that routine grinding and bleaching do not remove all the water and organic materials from skeletons. Routinely prepared samples are not pure specimens of aragonite and calcite produced by organisms.

Water and organics are present in Pleistocene and even older samples (e.g. Gaffey, 1983, 1984, 1985, 1988; Wyckoff, 1972; Zabielski and Gaffey, this volume), and fluid inclusions may still be abundant in fossils even after alteration of aragonite and high Mg calcite to low Mg calcite (Gaffey, 1984, 1985, 1988; Sandberg, 1984). Thus, organic compounds and liquid water incorporated in skeletons during their formation may remain to play important roles in carbonate diagenesis for geologically long periods of time. Organic pigments which produce absorption features in the visible region of the spectrum also persist in geologic samples even after considerable breakdown and heating of organic materials, providing biomarkers for determining the history and origin of organic materials (e.g. Baker and Louda, 1986).

UNRESOLVED QUESTIONS

The complexity and variability in composition of skeletal carbonates and the sensitivity of VNIR reflectance spectroscopy to these variations have combined to slow progress in this diagenetic study. The water and organics in skeletons are strongly affected by routine sample preparation such as bleaching, grinding, and heating. However, despite routine bleaching and grinding, samples still contain significant quantities of water and organics. Spectra indicate that routinely processed samples are not representative of the original materials as they occur in nature, nor are they pure samples of aragonite and calcite produced by various organisms. This is true even of fossil specimens from which much organic material is presumably lost.

Additional information is needed on the effects of grinding, bleaching, and heating on the composition of carbonate samples. In addition, because spectral data available in the literature of physics and chemistry are generally inadequate for studies of geologic materials, additional spectra of organic compounds and hydrated mineral species must be obtained. Additional work is needed employing other analytical techniques (e.g. NMR, ESR, Raman spectroscopy, FTIR, coulomtery) to completely characterize the water and organic content of skeletons. These techniques should provide a quantitative measure of the water and organics in skeletons, and should make it possible to develop calibration curves allowing abundances of these phases to be determined from spectra. More work is needed using reflectance spectra in the visible region, where absorptions due to electronic transitions in molecular orbitals occur.

In addition, all phases present in skeletons must be characterized. Much of the previous work on organics in carbonate skeletons has focused on those compounds believed to make up the organic matrix used by organisms to construct their skeletons. However, organic compounds may affect diagenesis of carbonates regardless of their source, and skeletons may also contain organics derived from other tissues or body fluids of plants and animals which build the skeletons, as well as from endoliths which infest skeletons after death.

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