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H_2O and OH in echinoid calcite: A spectroscopic study

SUSAN J. GAFFEY
Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A.

ABSTRACT

Proton nuclear magnetic resonance (NMR) and visible and near-infrared (VNIR) reflectance spectral data and heating experiments indicate that the Mg-rich calcite (commonly referred to as high-Mg calcite and hereafter as HMC) that is produced by six different species of echinoids contains H_2O with mobilities and H bond strengths ranging from those characteristic of liquid H_2O to those observed in hydrated magnesium carbonate minerals. Total H_2O (inorganic OH^- and H_2O, i.e., that occurring in inorganic phases rather than organic compounds) contents of echinoid HMC range from 1.97 to 3.38 wt% and differ in amount from one species to another and, within one species, between different skeletal elements. The proportion of total H_2O that is rigidly bound is comparatively constant, ~0.4 in all samples. Total H_2O content shows no correlation with Mg/Ca ratio in these samples. Although echinoid ossicles are generally noted for their chemical homogeneity, the total H_2O content of echinoid HMC shows considerable variation within individual ossicles over distances of tens to hundreds of micrometers. Echinoid HMC contains small amounts of OH^- (a few tenths to hundredths of a percent by weight). Brucite does not occur, and OH^- is present either in solid solution or in a hydrated magnesium carbonate mineral.

INTRODUCTION

To monitor and understand the responses of carbonate sediments to early diagenetic alteration, the starting materials, including the skeletons produced by various carbonate secreting organisms, must be thoroughly characterized mineralogically and chemically. Skeletons produced by carbonate secreting organisms are not precipitated in equilibrium with sea water but within the organism's cells and tissues in isolation from the ambient environment. Because different organisms control the properties of their skeletons (i.e., skeletal mineralogy, chemical composition, crystal form and size, and H_2O and organic content) to varying degrees, carbonates formed by a given organism can differ significantly from those formed by other types of organisms as well as from abiogenic carbonates precipitated under the same ambient conditions of water temperature and chemistry. Thus, marine carbonate sediments are composed of a much more varied suite of materials with a wider range of diagenetic potentials than is generally recognized.

Skeletons of echinoderms are of geologic interest because they make important volumetric contributions to carbonate sediments and because they are preserved as fossils. Mg-rich calcite (hereafter referred to as HMC, following the common usage high-Mg calcite) produced by echinoids has long been of mineralogical interest because the high degree of organismal control exerted over their precipitation gives them several unusual properties, including external form and microstructure of crystals (e.g., Blake et al., 1984), unit-cell parameters (Bischoff et al., 1983), homogeneity of Mg distribution (Weber, 1969), fracture mechanics (e.g., Towe, 1967; O'Neill, 1981), and rate of alteration on heating (Gaffey et al., 1991).

Hydrated or hydroxylated phases incorporated into skeletal carbonates can affect their solubility, and fluid inclusions in biogenic materials can serve as a medium for diagenetic alteration. Although the major, minor, and trace element chemistry and organic-matrix content of echinoid HMC have been studied in some detail, OH^- and H_2O in echinoid HMC have received less attention. Here, all inorganic H_2O and OH^- are referred to collectively as total H_2O. Preliminary studies indicate that H_2O may make up as much as 2–3 wt% of echinoid skeletons (Gaffey, 1988; Gaffey et al., 1991). Alkalinity determinations (Busenberg and Plummer, 1985) and reflectance spectral data of heated samples (Gaffey et al., 1991) indicate that echinoid HMC may contain discrete OH^- as well. However, no hydrated or hydroxylated phases have been detected by X-ray diffraction (XRD), and the abundance and mode of occurrence of OH^- and H_2O in echinoid HMC are not well characterized. Spectroscopic techniques provide a direct measure of fundamental properties of OH^- and H_2O molecules, rather than an indirect measure of some secondary property such as weight loss on heating, and have been shown to be powerful tools for the study of OH^- and H_2O in geologic materials (e.g., Hunt and Salisbury, 1970; Aines and Rossman, 1984; Gaffey, 1988). Most biogenic carbonates contain significant amounts of organic matter, the spectral features of which overlap with those produced by OH^- and H_2O in inorganic phases, making quantitative characterization of OH^- and H_2O containing phases dif-

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TABLE 1. Specimens used in study and total H_2O contents as determined by ^1H NMR (see text for discussion)

Echinoid species	Skeletal element	wt% H_2O	wt% tightly bonded H_2O
Lytechinus variegatus	B	2.64	1.01
	C	2.88	1.09
	D	2.68	1.07
	E	2.81	0.99
Echinometra lucunter	B	2.69	0.98
	C	3.38	1.21
	D	2.92	1.18
	E	3.07	1.19
	F	1.97	0.95
	G	3.23	1.20
Leodia sexiesperforata	C	2.79	1.09
	E	2.34	1.00
Encope emarginata	C	2.61	1.02
	E	1.99	0.84
Clypeaster rosacea	C	2.27	0.92
	D	2.48	0.97
	E	2.23	0.85
Clypeaster rosacea	E	2.39	0.93
Mellita quinquiesperforata	D	2.41	1.02
	E	2.17	0.97

Note: letters in this table and all figures refer to skeletal elements as follows: B = spines, C = pyramid, D = ambulacral plates, E = interambulacral plates, F = teeth, and G = epiphysis.

ficult (Gaffey, 1990). However, the organic content of echinoid calcite is extremely low (<0.2 wt%) (Swift et al., 1986; Weiner, 1985), and so this calcite is particularly well suited to the study of OH^- and H_2O in biogenic HMC. One goal of this work is to use spectroscopic techniques to characterize the OH^- and H_2O contents of echinoid calcite qualitatively and quantitatively.

It has been suggested that the total H_2O content of biogenic HMC is positively correlated with Mg content (Mackenzie et al., 1983; Busenberg and Plummer, 1985; Gaffey, 1988). A second goal of this work is to examine the relationship between H_2O and Mg content of biogenic HMC.

MATERIALS AND METHODS

Samples used in the study are listed in Table 1. Specimens of *Lytechinus, Leodia,* and *Echinometra* were collected at San Salvador Island, the Bahamas, and treated with NaOCl to remove the bulk of the soft tissue. Samples of *Clypeaster, Mellita,* and *Encope* were purchased from commercial establishments. In the laboratory, skeletons were separated into their respective skeletal elements, which were crushed in a ceramic mortar and pestle and sieved in a sonic sifter to isolate the 125–500 μm fraction. Because some types of analyses were destructive and material analyzed by one technique could not be retrieved to be analyzed by another, composite samples were prepared with material obtained from several individuals of small (*Echinometra*) or thinly shelled (*Leodia, Lytechinus*) species. Use of composite samples was reasonable because the chemical composition of a given ossicle type (e.g., spines, ambulacral plates) is very similar in individuals of the same species from the same locality (Weber, 1969). The 125–500 μm particle-size fraction was treated with 5% NaOCl (full-strength commercial Clorox) for 3 d to remove remaining soft tissues (Gaffey and Bronnimann, 1993), rinsed thoroughly in distilled water, cleaned in an ultrasonic cleaner, and dried at temperatures <40 °C. The large skeletons of *Clypeaster* made it possible to include interambulacral plates from two individuals in this study. Because of the benthic life mode of these organisms and the porous structure of their ossicles, sand grains are frequently trapped within echinoid skeletons. Extraneous material was picked from the 125–500 μm fraction with a fine brush under a binocular microscope.

Abiogenic mineral samples used in the study for comparison with biogenic materials include both an aragonite and a calcite speleothem rich in fluid inclusions, reagent-grade hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$], portlandite [$Ca(OH)_2$], and brucite [$Mg(OH)_2$], and a naturally occurring brucite from Nye County, Nevada. A magnesite sample from San Benito County, California, which contains a hydrated magnesium carbonate phase, was also included in the study. Initial XRD analysis of the sample (scanned from 10 to 52° 2θ at 0.03° 2θ/s) detected only magnesite. However, H atoms are relatively inefficient X-ray scatterers (Nuffield, 1966), and hydrated or hydroxylated phases could be present in amounts below detection limits for XRD. Three subsamples were therefore separated from the original material on the basis of crystal size and texture to isolate a fraction that might contain a higher proportion of any hydrated phases than the bulk sample. These were scanned from 5 to 40° 2θ at 0.01 or 0.02° 2θ/s, but magnesite was still the only mineral detected. Nevertheless, spectral data (see below) show that a hydrated mineral phase is present. A sufficient data base does not currently exist to allow identification of specific hydrous carbonate minerals from near-infrared reflectance or NMR spectral data. Even when hydrous carbonate minerals are identified by XRD, their OH^- and H_2O contents revealed by spectroscopic techniques can differ significantly from those given in their accepted chemical formulae (Pobeguin, 1959; White, 1971; Gaffey, 1990; Gaffey et al., 1993). It was concluded that the unidentified mineral is a hydrated magnesium carbonate phase because Mg has a tendency to form hydrous phases (Lippmann, 1973), the sample came from a locality known for the occurrence of hydrous magnesium carbonate minerals (Palache et al., 1951), and the numbers, positions, and widths of H_2O absorptions are similar to those in spectra of other hydrated alkaline-earth carbonates (Pobeguin, 1959; White, 1971).

Photomicrographs of heated echinoid plates were obtained using a JEOL Stereoscan 840 electron microscope. Ca, Mg, and Sr contents were determined by ICP on powdered splits of the bulk samples at the Department of Geological Sciences, University of Michigan, Ann Arbor. Quality assurance data on replicate control analyses showed Ca and Sr analyses were reproducible to 1.1% and Mg analyses to 0.9% (relative). Replicate analyses of echinoderm material indicate that variations within the bulk sample are less than analytical error even for the echinoid teeth, which are known to show wide ranges of Mg content within a single tooth (Schroeder et al., 1969).

High-precision visible and near-infrared (VNIR) (0.3–2.7 μm) spectra of samples were obtained at RELAB at Brown University, as described by Pieters (1983), and at the U.S. Geological Survey in Denver with a Beckman 5270 spectrophotometer, as described by Clark et al. (1990). Nearly all spectra were obtained at 5 nm resolution, although a few were measured at 10 nm. Errors in all reflectance spectra are smaller than the lines used to plot the data. Advantages of VNIR reflectance spectra over the more commonly employed mid-infrared (MIR) transmission spectra in studies of this type are discussed in Gaffey (1986, 1988, 1990) and Gaffey et al. (1993). VNIR spectral properties of calcite and aragonite are discussed in Gaffey (1986). VNIR spectral properties of liquid H_2O and of H_2O- and OH^--containing minerals are summarized in Gaffey (1988, 1990). Relative integrated intensities of the 1.4 and 1.9 μm H_2O bands, sensitive indicators of total H_2O content (Gaffey, 1988; Gaffey et al., 1991), were calculated using methods outlined in Zabielski and Gaffey (1989). Heating experiments were performed as described in Gaffey et al. (1991).

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained at the National Center for NMR applications at Colorado State University. Spectra of echinoid samples were obtained using a homebuilt NMR spectrometer operating at 360 MHz for ^1H. Spectra from which absolute total H_2O contents of echinoid samples were determined were obtained in the wide-line mode for samples of known mass using a wide-line pulse sequence; 99.3 at% D hexamethylbenzene-d_{18} was used as a standard. Each spectrum is the sum of 128 or 256 individual scans. Total H_2O abundances were calculated assuming all H was present as H_2O, an approximation justified by the low organic and OH^- content of these materials. For all samples, short experiments using relaxation delays of 10 and 5 μs gave the same absolute intensities, indicating all data correspond to fully relaxed spectra, and results should be quantitative. Total integrated peak intensities and intensities of the narrow-line component of the peak were calculated directly from the spectra. Integrated intensity of the wide-line portions of the resonances was determined by subtracting the integrated intensity of the narrow-line portion of the peak from total peak intensity. All spectral analyses and calculations for both VNIR reflectance and ^1H NMR spectra were performed using SPECPR, a package of spectrum processing routines originally developed by Clark (1980) and modified to operate on an IBM-compatible computer. Accuracy for abundances of H-containing species using NMR is usually within ±2% (Willard et al., 1981). The ^1H CRAMPS (Combined Rotation and Multiple Pulse Spectrometry) NMR spectra of echinoid samples were recorded using a 90° pulse of 1.25 μs and τ of 2.4 μs with the BR-24 pulse sequence. The ^1H CRAMPS NMR spectra of abiogenic mineral samples were obtained in this same mode, or as described in Gaffey et al. (1991). Spectra of minerals obtained in both modes were essentially identical. Chemical shifts were determined relative to a tetrakis(trimethylsilyl)methane (TTMSM) standard. Dipolar dephasing experiments were recorded with dephasing times of 2, 50, and 100 μs.

RESULTS AND DISCUSSION

Background

Echinoid skeletons contain many ossicles, including spines, test plates, and the feeding apparatus, all of which are composed of HMC. Most ossicles consist of an open meshwork, called stereom, with interconnected pore spaces, which may comprise >50% of its volume (Raup, 1966) (Fig. 1). Although both optical and XRD studies indicate that the vast majority of the skeletal elements behave as a single crystal (Raup, 1966; Donnay and Pawson, 1969), surfaces of ossicles are curved rather than being bounded by crystal faces, and fractures generally have a conchoidal (Fig. 1B) or whisker-like surface rather than typical calcite cleavages (Towe, 1967; O'Neill, 1981). SEM and TEM studies indicate that echinoderm calcites are composed of submicrometer-size crystallites in nearly perfect crystallographic alignment (Towe, 1967; O'Neill, 1981; Blake et al., 1984). With the exception of the teeth (Schroeder et al., 1969), distribution of Mg within individual ossicles, particularly those of echinoids growing at lower latitudes, is generally quite uniform. Although there can be significant differences in Mg content between different types of ossicles within a single skeleton, the Mg concentrations for a given type of ossicle (e.g., spines, ambulacral plates) from a single skeleton and from skeletons of other individuals of the same species from the same locality are very similar (Weber, 1969). Echinoid teeth differ from other skeletal elements in having a polycrystalline laminate structure and a very inhomogeneous Mg distribution, with variations of over 10 mol% magnesium carbonate reported within a single tooth (Schroeder et al., 1969).

Mode of occurrence of H_2O

VNIR reflectance spectra. Although spectral data for many types of carbonate skeletons indicate that most of the H_2O they contain occurs in fluid inclusions (Gaffey, 1988, 1990), spectral reflectance data indicate that H_2O in echinoid HMC occurs with H bond strengths ranging from those characteristic of liquid H_2O to those characteristic of H_2O in hydrated magnesium carbonate minerals.

With increased strength of H bonding, NIR absorption features produced by H_2O broaden, strengthen, and shift to longer wavelengths (see Gaffey, 1988, 1990, and references cited therein). Comparison of VNIR reflectance spectra of an echinoid HMC with spectra of abiogenic mineral samples (Fig. 2A) shows that the positions and widths of the 1.4 and 1.9 μm H_2O absorption features in the echinoid spectrum are intermediate between those of

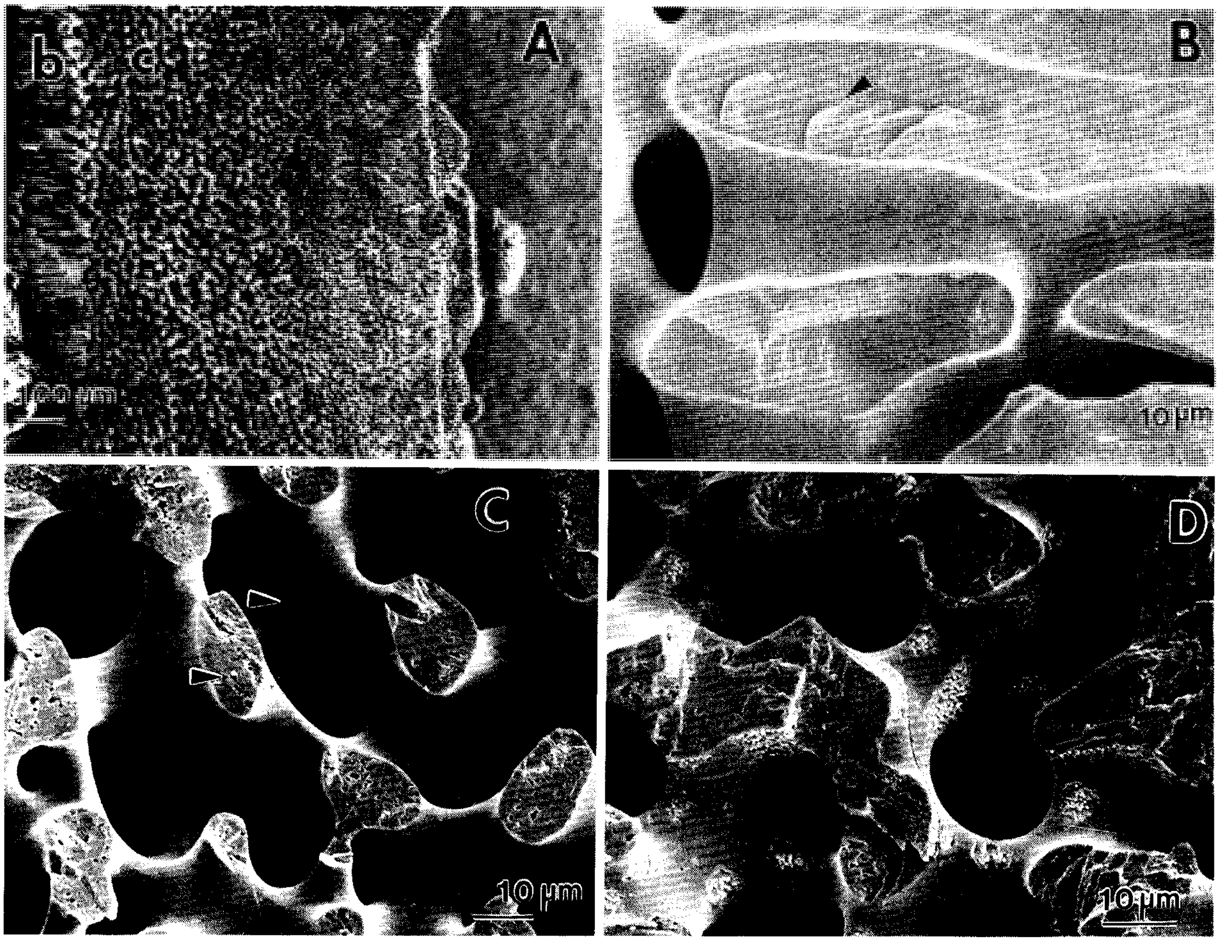


Fig. 1. SEM photomicrographs of *Lytechinus* plate heated to 250 °C for 24 h. (**A**) Cross section of plate, broken after heating, exterior surface to right. Letters b and c indicate horizon within plate from which photomicrographs in **B** and **C** were obtained. (**B**) Fracture surface of portion of plate undamaged by expulsion of H_2O on heating. Arrow indicates typical conchoidal fracture. (**C**) Moderate porosity and surface damage (arrows) caused by H_2O loss during heating. (**D**) Intense pitting and spalling affecting another fragment of the same plate.

absorptions produced by liquid H_2O in fluid inclusions and those of absorptions due to H_2O in hydrated magnesium carbonate phases.

Subtle differences in widths and relative intensities of H_2O absorption features exist between spectra of different echinoid samples (Fig. 2B), reflecting intersample variations in H bonding. For example, the 1.9 μm feature in the spectrum of the *Echinometra* teeth (*Ec.* F) is the shallowest and broadest of the three illustrated, whereas the same feature in the spectrum of the *Echinometra* epiphysis (*Ec.* G) is the most intense (Fig. 2B). In addition, the band minimum in the spectrum of the *Echinometra* epiphysis (*Ec.* G) (labeled 1a in Fig. 2B) occurs at slightly shorter wavelengths than that in the other two spectra. The 1.9 μm feature in echinoid spectra is composed of up to three overlapping absorptions (Fig. 2B). The position of the strongest absorption (1a in Fig. 2B) is similar to that produced by liquid H_2O, whereas the positions of the weaker features near 2.05 and 2.17 μm (labeled 1b and 1c, respectively) are similar to those produced by H_2O in spectra of hydrated magnesium carbonate phases (Fig. 2A). However, these three features are not evident in all echinoid spectra. For example, the weak feature near 2.17 μm (1c in Fig. 2B) is most evident in the spectrum of the *Echinometra* teeth (*Ec.* F) but is barely discernible in the other two spectra shown.

Heating experiments. Heating experiments also indicate that H_2O with a range of bond strengths occurs in echinoid HMC. Data and detailed discussion of earlier heating experiments are given in Gaffey et al. (1991). In a series of experiments, individual splits of samples of the coronal plates of *Lytechinus, Leodia, Echinometra,* and *Encope,* and spines of *Lytechinus* and *Echinometra* were heated to various temperatures (105, 150, 200, 300, or 400 °C) for times ranging from 2 to 24 h. Weight loss during heating was recorded, and VNIR reflectance spectra of the heated samples were obtained. Unlike other types of skeletal material, there is no weight loss or change in spectral properties of echinoid samples heated to 105 °C (although spectral and weight loss data show that H_2O

is expelled from echinoid samples at temperatures of 150 °C and higher). Also, in contrast to other types of skeletal material studied, spectra show that echinoid HMC heated to 400 °C still retains small amounts of H_2O, even though XRD and reflectance spectral data show that the HMC begins to dissociate to periclase (MgO) and CaO, the latter of which is rapidly hydrated to portlandite [$Ca(OH)_2$] by atmospheric H_2O. The high temperatures at which H_2O is released from echinoid HMC are similar to those observed in differential thermal analysis (DTA) of hydrated magnesium carbonate minerals such as nesquehonite and hydromagnesite (Webb and Kruger, 1970) and are consistent with the occurrence of some portion of the H_2O in echinoids in a form other than fluid inclusions.

Heating experiments performed by Gaffey et al. (1991) as well as additional heating experiments performed on *Echinometra* and *Lytechinus* spines and *Echinometra* teeth in the present study showed that the proportion of the H_2O lost from a sample on heating to a given temperature varies, which suggests interspecific variations in H_2O bonding strengths (Gaffey et al., 1991).

Wide-line NMR spectra. Wide-line NMR spectra provide information on the physical environments of protons. If H nuclei are in close proximity each is influenced by the magnetic field produced by the others, and dipole-dipole interactions split individual energy states into many closely spaced levels. If H nuclei are rigidly bound in a crystal structure, the many energy levels produced by dipole-dipole interactions result in many closely spaced absorptions giving a broad, unresolved spectral signal. In liquids, on the other hand, H-bearing molecules and ions can move freely, and random thermal motions average the dipolar interactions, producing a narrow line. A narrow line is also produced by isolated H nuclei separated too far from other protons for their dipole fields to interact, e.g., isolated OH^- in solid solution (Willard et al., 1981; Harris, 1983; Klinowski, 1984).

Wide-line NMR spectra of echinoids have both a wide- and a narrow-line component (Fig. 3), indicating the presence of both liquid-like and more rigidly bound H_2O. The width of the broad portion of these spectra is ~0.05 MHz, within the range typical of solids (Becker, 1980). These rigidly bound H_2O molecules may also produce the absorption features in reflectance spectra with band positions indicating H bond strengths similar to those of H_2O in hydrated mineral phases.

The ^1H CRAMPS NMR spectra. The ^1H CRAMPS NMR spectra, like VNIR reflectance spectra, indicate that H_2O in echinoid samples occurs with H bond strengths ranging from those typical of liquid H_2O to those characteristic of H_2O in hydrated carbonate minerals. Various techniques, including ^1H CRAMPS NMR, are used to narrow the broad resonances typical of spectra of solid-state samples to obtain a spectrum equivalent to those produced by liquids (Klinowski, 1984). Differences in the chemical shifts of resonances in NMR spectra provide information on the chemical environment of ^1H nuclei, making it possible to distinguish between OH^- and H_2O in samples. OH^- in minerals produces a resonance in the

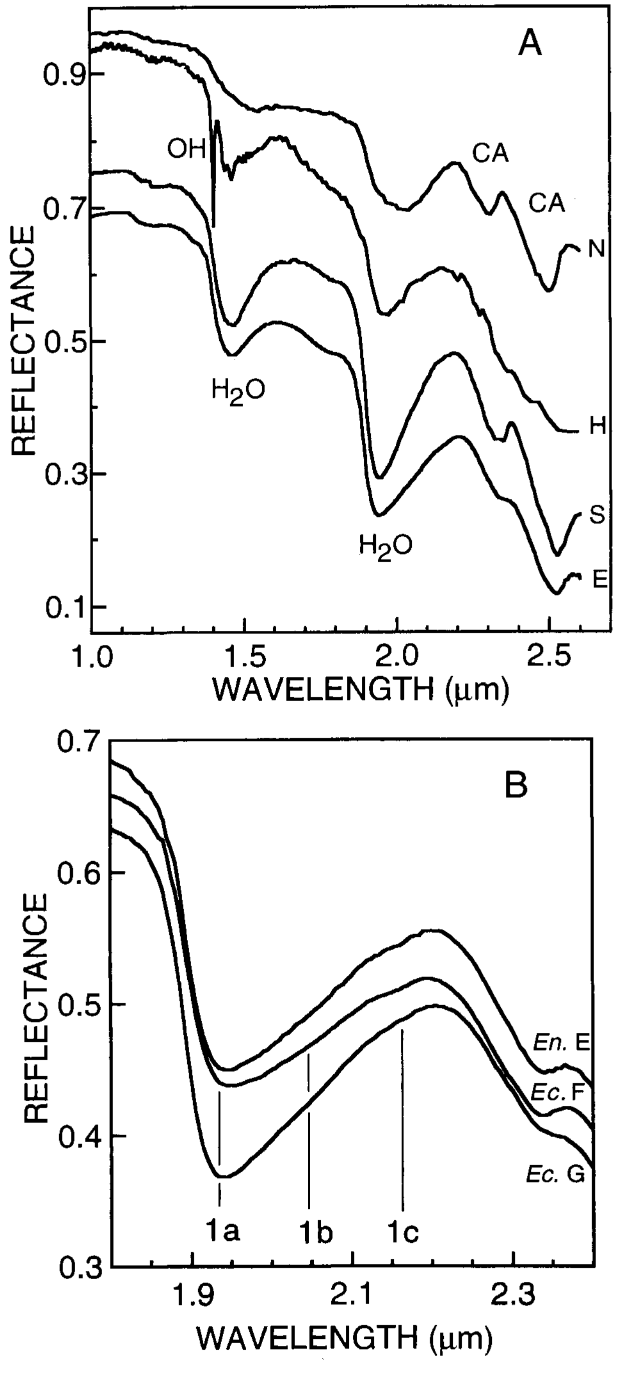


Fig. 2. Reflectance spectra of biogenic and abiogenic carbonates. (**A**) Comparison of spectrum of echinoid HMC (E) with spectra of abiogenic H_2O- and OH-containing carbonates: N = hydrated magnesium carbonate, H = hydromagnesite, S = speleothem containing aqueous fluid inclusions. Sharp narrow features near 1.4 µm are due to OH^-, broad features near 1.4 and 1.9 µm are due to H_2O, and those near 2.3 and 2.5 µm are due to carbonate (CA). Some spectra offset vertically for comparison. (**B**) The 1.9 µm H_2O features in three different types of ossicles from *Echinometra*. Different ossicle types in this and other figures are designated as in Table 1. Vertical lines indicate approximate positions of absorptions due to liquid-like (1a) and more strongly H bonded (1b and 1c) H_2O.

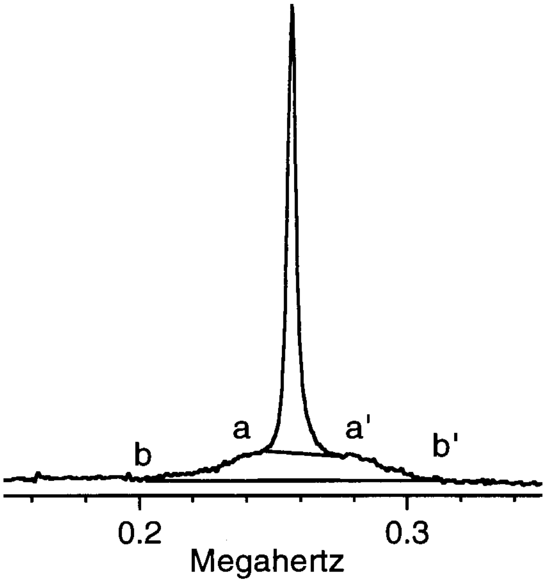


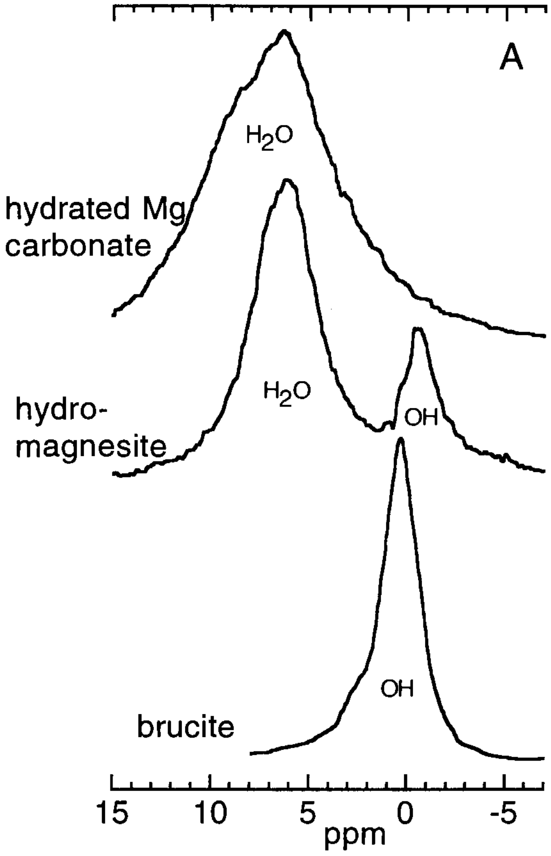
Fig. 3. Typical wide-line ^1H NMR spectrum of echinoid HMC. The narrow-line portion of the spectrum is that above the line a-a'; the wide-line portion is that between lines a-a' and b-b'. Integrated intensities of peak above background (b-b') were used to calculate total H_2O content, and that of the narrow-line portion (above a-a') to calculate amount of H_2O with liquid-like mobility.

0–1 ppm region, whereas liquid H_2O produces one near 5 ppm (Fig. 4A). The ^1H CRAMPS NMR spectra of echinoids show a strong resonance at 5 ppm owing to H_2O (Fig. 4B).

Increased strength of H bonding of OH^- or H_2O results in a shift of resonances to higher ppm (Berglund and Vaughn, 1980). In echinoid spectra the strong 5 ppm resonance characteristic of H_2O is asymmetric (Fig. 5), and the band maximum of this feature (1a in Fig. 5) in the spectrum of the *Echinometra* teeth (*Ec.* F) is shifted to slightly higher ppm. The asymmetry and the apparent shift of the 5 ppm resonance are both due to the presence of additional weaker resonances at higher ppm. In some echinoid spectra two additional resonances are identified near 6 and 7 ppm (1b and 1c in Fig. 5), chemical shifts similar to those of H_2O resonances in the spectra of hydromagnesite and the hydrated magnesium carbonate mineral (Fig. 4A).

As in VNIR reflectance spectra, subtle differences occur between ^1H CRAMPS NMR spectra of different echinoid samples. For example, the 7 ppm resonance identifiable in the spectrum of *Echinometra* spines (*Ec.* B) and teeth (*Ec.* F) is not evident in the other two spectra shown (Fig. 5).

Dephasing experiments. Dipolar dephasing NMR experiments (Fig. 6) of biogenic and abiogenic samples measure transverse (or spin-spin) relaxation times of protons, revealing the degree of molecular motion of H_2O molecules. The short relaxation times, about 50 μs, of the H_2O resonances in the hydromagnesite (Fig. 6A) and hydrated magnesium carbonate spectra indicate that mole-



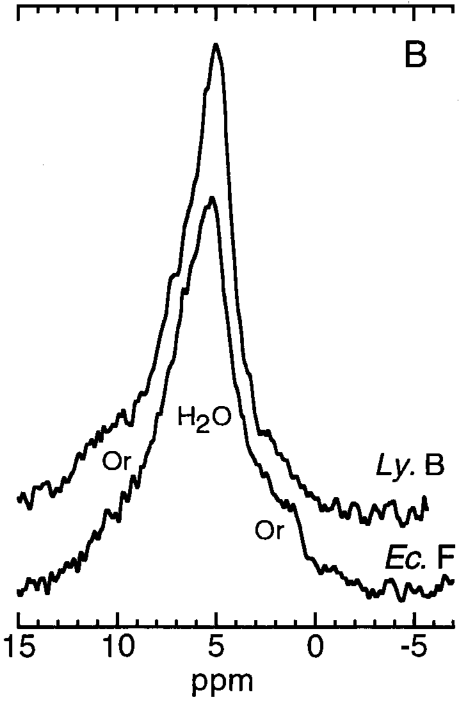


Fig. 4. The ^1H CRAMPS NMR spectra of abiogenic (A) and echinoid (**B**) carbonates show resonances produced by H_2O, OH^-, and organic phases (Or). *Ly.* = *Lytechinus*, *Ec.* = *Echinometra*. Some spectra offset vertically for comparison.

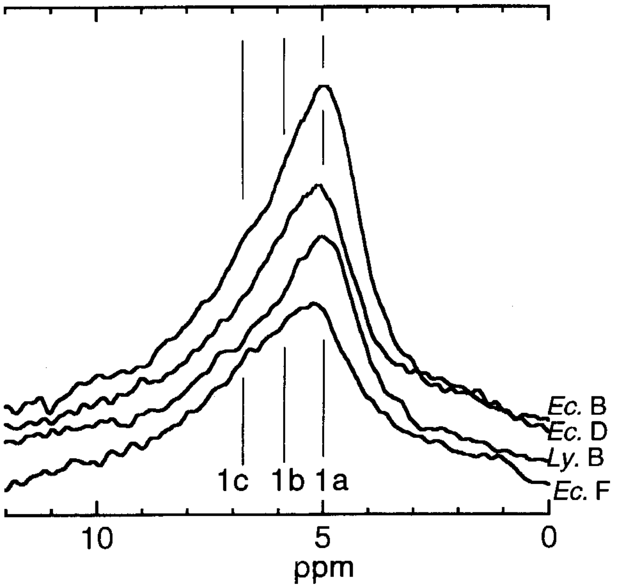


Fig. 5. Detail of 5 ppm peak in echinoid ^{1}H CRAMPS NMR spectra. See text for discussion. The same populations of H_2O molecules may produce the spectral features with the same labels in reflectance spectra in Fig. 2B. Some spectra offset vertically for comparison.

cules are rigidly bound in the solid (Lynden-Bell and Harris, 1969; Stone, 1982; Bronnimann et al., 1988). The small attenuation of the signal during the same period for the echinoid sample (Fig. 6B) indicates a long relaxation time similar to that characteristic of liquids. Because all features in the spectrum are attenuated at the same rate, it is evident that either all H_2O in the sample has a liquid-like mobility or H_2O molecules with greater bond strengths are close enough in proximity to liquid H_2O molecules to swap protons (Stone, 1982; Bronnimann et al., 1988). The latter case is more probable given the restricted molecular motions for ~40% of the H_2O, as evidenced by wide-line spectra.

Discussion. Prior work with VNIR reflectance spectra, many of which were of lower spectral resolution than those used in the present study, showed that biogenic HMC contained at least three structurally different populations of H_2O molecules with different H bond strengths. The positions of absorption features were consistent with H_2O bonded to both magnesium and calcium carbonate (Gaffey, 1988). The present data paint a more complex and less well-defined picture. NMR and reflectance spectral data demonstrate that H_2O with a range of bond strengths is present in all echinoid samples. The strongest absorption features in both types of spectra are produced by a population of H_2O molecules with bond strengths and mobilities similar to those of liquid H_2O. However, H_2O features in ^{1}H CRAMPS NMR and VNIR reflectance spectra of echinoid samples are broader than liquid H_2O features, with wings or tails that extend to longer wavelengths or higher ppm than are characteristic of features caused by liquid H_2O alone. In some reflectance and NMR spectra, spectral features in addition to those characteristic of liquid H_2O can be identified. The positions of these spectral features demonstrate the presence of populations of molecules with bond strengths characteristic of hydrated carbonate phases. In some spectra, however, the broad H_2O features cannot be readily subdivided into discrete, albeit overlapping, features. Such broad features may mean that H_2O occurs not in discrete populations with specific bonding energies but in a single population with a continuum of bond strengths.

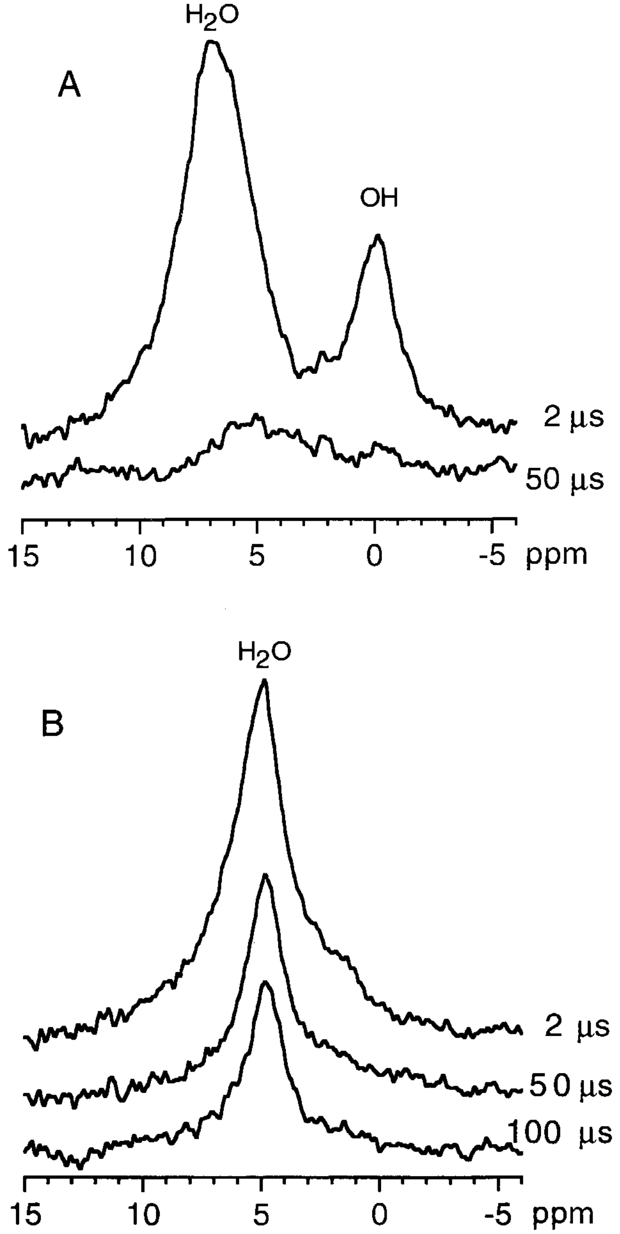


Fig. 6. NMR dephasing experiments: (**A**) hydromagnesite, no vertical offset of spectra; (**B**) echinoid HMC, spectra offset vertically for comparison. See text for discussion.

Spectral variations between different samples make it difficult to determine whether the strongly H-bonded H_2O is associated with magnesium carbonate, calcium carbonate, neither, or both. The H_2O in echinoid samples with H bond strengths stronger than those typical of liquid H_2O could occur in one or more of three forms: (1) H_2O could occur in a discrete, hydrated mineral phase in crystallite sizes too small, or in abundances too low, to be detected with XRD. The anomalous behavior of echinoid skeletal material during heating observed by Gaffey et al. (1991) (i.e., the retention of H_2O at high temperatures and the rapid formation of dolomite and the dissociation of carbonate at comparatively low temperatures) could also be related to the presence of a hydrous carbonate phase not present in other biogenic HMC samples. (2) Molecules of H_2O could exist along the boundaries between the small crystallites comprising the stereom. Echinoderm HMC apparently lacks the minute fluid inclusions, lattice defects, and dislocation features (Blake et al., 1984) that provide sites for H_2O in other biogenic materials. H_2O in sites between crystallites that can accommodate only one or a few molecules, or perhaps a thin layer of H_2O associated with the organic matrix, would have restricted molecular motion and H bonding energies similar to those of adsorbed rather than liquid water. (3) H_2O could occur in solid solution distributed throughout the carbonate. Neutron diffraction and TEM studies of echinoid skeletal material will provide additional information on the mode of occurrence of H_2O in biogenic HMC.

OH^- in echinoid calcites

Small amounts (a few tenths to hundredths of a percent by weight) of OH^- occur in echinoid HMC either in solid solution or in a hydrated magnesium carbonate mineral.

Presence and abundance of OH^-. Although some data have indicated that echinoid HMC contains OH^- (Busenberg and Plummer, 1985; Gaffey et al., 1991), its presence has not been unequivocally demonstrated. Busenburg and Plummer (1985) subtracted alkalinity contributed by carbonate from total alkalinity of HMC samples to determine OH^- content in a suite of biogenic samples. However, they noted that this approach is valid only if no HCO_3^- or other anions that could contribute to alkalinity are present. Although ^1H CRAMPS NMR spectra of some echinoid samples contain features near 1 ppm (Fig. 4B), these could be due to aliphatic CH in organic compounds in addition to OH^- in minerals (Wade, 1987). Many NMR spectra of echinoid HMC lack a 1 ppm resonance, but ^1H NMR is less sensitive than some other spectroscopic techniques and might not detect trace amounts of OH^- (Becker, 1980).

Reflectance spectra of OH^--bearing minerals contain sharp, narrow features near 1.4 μm (Fig. 7A) and 2.7 μm (Mara and Sutherland, 1953; Ryskin, 1974) produced by the first overtone and fundamental mode of the O-H stretching vibration, respectively. However, they lack the 1.9 μm feature produced by a combination of the H-O-H bending and O-H stretching fundamentals that characterizes spectra of H_2O. No OH^- features are discernable in spectra of unheated echinoid HMC (e.g., Fig. 2A). However, the broad, strong 1.4 and 3.0 μm features produced by H_2O in echinoid samples can mask features produced by small amounts of OH^-. Because H_2O is generally driven off at lower temperatures than OH^- in minerals (Smykatz-Kloss, 1974), H_2O absorption features are considerably weakened in spectra of heated samples, but OH^- features remain. Sharp, narrow OH^- features are evident in spectra of echinoid samples heated to 300 °C (Figs. 7B and 8). Positions of OH^- features vary depending on the metal with which the OH^- is associated (Ryskin, 1974), and positions of OH^- features in the spectra of the heated HMC samples are very similar to those of the strongest absorptions produced by OH^- in brucite (Figs. 7B and 8), suggesting the association of OH^- with Mg.

It is not possible to quantify OH^- content in these samples from the spectral data at present. No data are available in the literature on absorption coefficients for OH^- absorptions in spectra of brucite. Breakdown of carbonate begins before all H_2O and OH^- are driven off by heating, rendering weight-loss data at these high temperatures inaccurate. Dissociation of carbonate at comparatively low temperatures also affects the results of differential thermal and thermogravimetric analyses. It is evident from the lack of clear OH^- resonances in the NMR spectra of echinoid HMC with well-defined H_2O absorptions that OH^- concentration is low, a few tenths of a percent by weight or less.

Mode of occurrence of OH^-. HMC skeletons of some types of coralline red algae contain brucite (Schmalz, 1965; Weber and Kaufman, 1965), and it is possible that other biogenic HMC samples could contain brucite as well. Dehydration of brucite occurs at temperatures of 400 °C or higher (Smykatz-Kloss, 1974), and brucite could be the phase producing the sharp 1.4 μm absorption in the spectra of heated echinoid samples. However, in addition to the strong 1.4 and 2.7 μm features, VNIR reflectance spectra of brucite also contain features near 1.36 μm (Fig. 7A) and several sharp narrow features in the 2.0–2.6 μm region (Mara and Sutherland, 1953). The spectra of heated echinoid samples lack these additional absorption features characteristic of a discrete brucite phase (Figs. 7B and 8), suggesting that echinoid HMC does not contain brucite. Spectral data are consistent with the occurrence of OH^- in solid solution, in agreement with Busenberg and Plummer's (1985) conclusions based on dissolution experiments with biogenic HMC. However, loss of OH^- from hydrated carbonate minerals such as artinite $[Mg_2(CO_3)(OH)_2 \cdot 3H_2O]$ and hydromagnesite also occurs at temperatures higher than those used in this study (Smykatz-Kloss, 1974). In addition, the 3 μm region of spectra of some hydrous carbonate minerals (e.g., artinite), like the echinoid spectra in Figure 8, contains a broad absorption due to H_2O and a single sharp absorption due to OH^- (Pobeguin, 1959; White, 1971). Thus, OH^- in echinoid HMC could also occur in a hydrated magnesium-bearing mineral phase not yet identified.

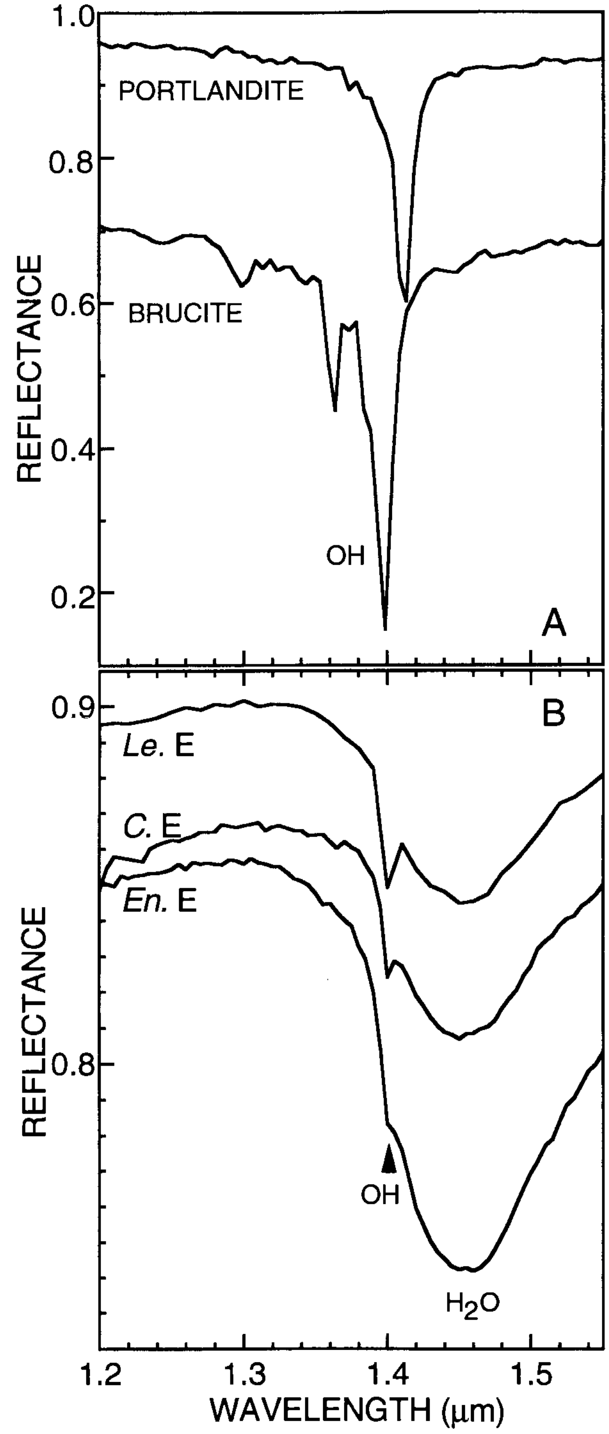


Fig. 7. Reflectance spectra of OH-containing abiogenic (**A**) and heated echinoid (**B**) samples. Position of OH feature in spectra of heated echinoids is the same as the strongest feature in brucite, indicating OH^- is associated with Mg. *Le.* = *Leodia*, *C.* = *Clypeaster*, and *En.* = *Encope.*

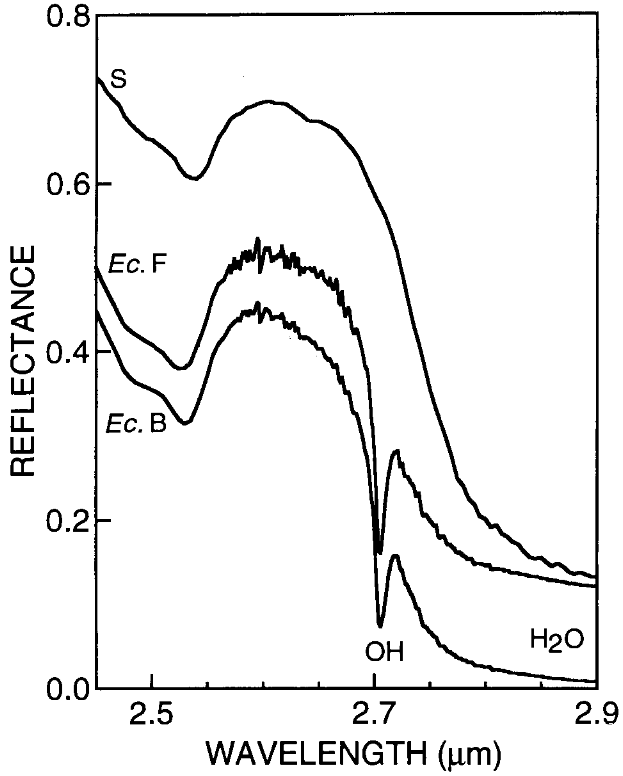


Fig. 8. OH^- features in spectra of heated *Echinometra* spines (B) and teeth (F). Compare to the spectrum of a calcite speleothem (S), which contains features due to carbonate and H_2O alone. The strongest brucite absorption occurs at 2.704 µm, whereas portlandite produces one at 2.744 µm (Ryskin, 1974). The position of the OH^- feature in spectra of heated echinoid samples is similar to that of brucite. Noise in the 2.6 µm region in the echinoid spectra is due to variations in atmospheric H_2O in the path of the spectrometer beam. The positions of carbonate bands in this spectral region are a function of cation mass (Gaffey, 1987). The 2.5 µm carbonate feature occurs at shorter wavelengths in echinoid spectra than in the speleothem spectrum because of the Mg content of the former. Spectra offset vertically for comparison. *Ec.* = *Echinometra.*

Amount of total H_2O

Total H_2O contents of echinoid HMC samples in this study range from 1.97 to 3.38 wt%. The total H_2O contents of skeletons vary between species and, within a given species, from one skeletal element to another.

Reflectance and NMR spectra provide two independent measures of the total H_2O contents of biogenic samples, and with a few exceptions, both techniques show the same relative variations in total H_2O content between different species and ossicle types (Table 1; Fig. 9). Although relative areas of the 1.4 µm bands in reflectance spectra are very sensitive to differences in total H_2O content of skeletal samples (Gaffey, 1988; Gaffey et al., 1991), calibration curves for determination of total H_2O content from reflectance spectra have not yet been developed. Wide-line NMR spectra, however, make it possible to

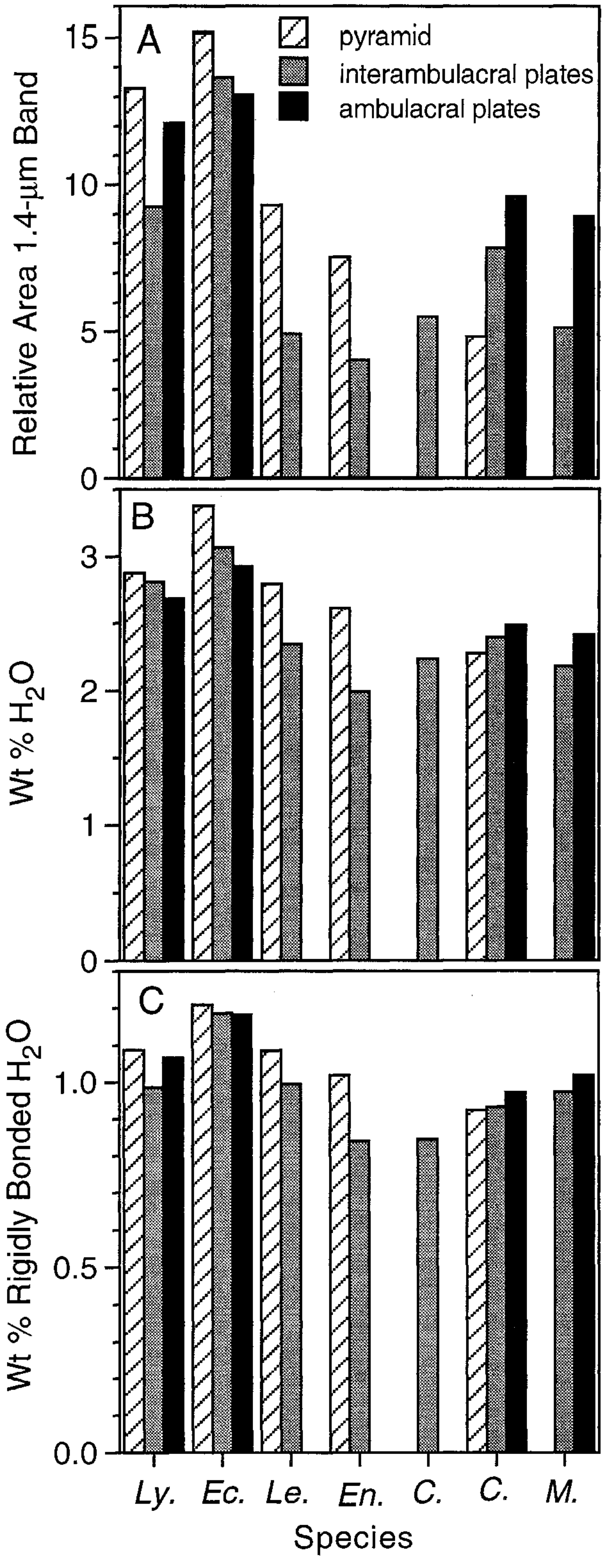


Fig. 9. Total H_2O content of different skeletal elements determined from reflectance spectra (**A**) and NMR spectra (**B** and **C**). *Ly.* = *Lytechinus*, *Ec.* = *Echinometra*, *Le.* = *Leodia*, *En.* = *Encope*, *C.* = *Clypeaster*, and *M.* = *Mellita*.

quantify abundances of total H_2O in samples because the integrated peak intensity is proportional to the number of H nuclei producing the absorption. Total H_2O content and amount of H_2O with liquid-like mobility, which produces the narrow portion of the peak (Fig. 3), were calculated from spectra. The latter value was subtracted from the total H_2O content to determine the concentration of the rigidly bound phase.

Total H_2O contents in the echinoid HMC samples in this study range from 1.97 to 3.38 wt%. The H_2O contents of the spines and coronal plates of *Echinometra* are somewhat higher than those of the same ossicles in other species (Table 1). However, differences in total H_2O content between ossicle types within a given species are commonly greater than those between species (Table 1; Fig. 9A and 9B). Among the types of ossicles studied, the pyramid, part of the feeding apparatus, tends to have the highest total H_2O content. However, more species must be studied to verify any trends in total H_2O content among different types of ossicles.

Abundances of rigidly bound H_2O vary from 0.84 to 1.19 wt% (Table 1). The proportion of total H_2O that is rigidly bound is fairly constant ($\sim$40%) and shows no correlation with total H_2O content or species (Table 1, Fig. 9C).

Relationship between Mg/Ca ratio and total H_2O content

Previous work (Mackenzie et al., 1983; Gaffey, 1988) indicated a positive correlation between H_2O and Mg content in biogenic HMC. Total H_2O content in these studies was determined by measuring weight loss and changes in absorbance of a 3400 cm^{-1} feature in transmission spectra (Mackenzie et al., 1983) or by measurement of H_2O evolved (Gaffey, 1988) on heating of samples. Because many of the samples on which measurements were made contained organic matter (Gaffey, 1990; Gaffey and Bronnimann, 1993), which degrades on heating contributing to weight loss and evolving H_2O (Gaffey et al., 1991), additional investigation into the relationship, if any, between Mg and total H_2O contents of HMC samples was needed.

Both NMR and reflectance spectral data in the present study indicate there is no correlation between Mg/Ca ratio and abundance of total H_2O in echinoid HMC (Fig. 10). Correlation between Mg/Ca ratio and H_2O content are equally poor for three measures of H_2O content, and linear fits to the data in Figure 10A, 10B, and 10C give r^2 of 0.01, 0.00, and 0.08, respectively.

Inspection of sample damage in heated echinoid plates (Fig. 1) gives visual evidence of this lack of correlation. Although the distribution of Mg within individual echinoid ossicles is known to be quite homogeneous, the H_2O content, as reflected in the sample damage, is quite variable.

Heterogeneous distribution of H_2O

With the exception of the teeth (Schroeder et al., 1969), echinoid ossicles are generally regarded as chemically ho-

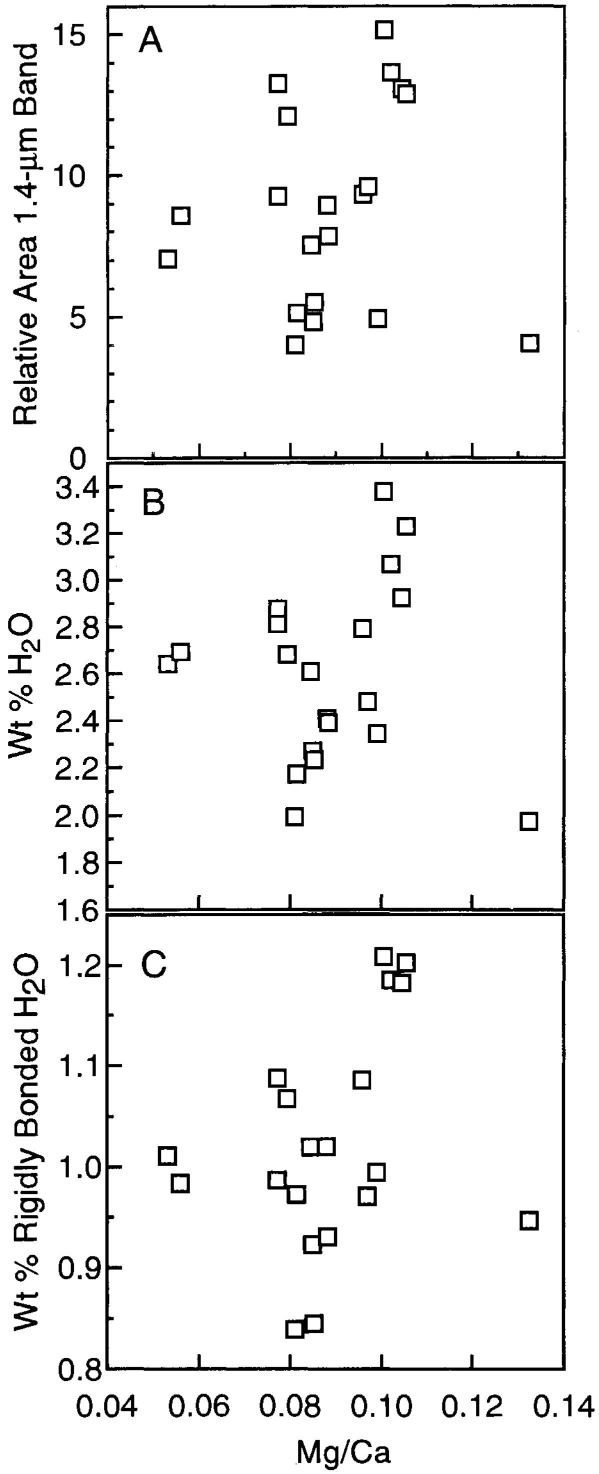


Fig. 10. Relationship between Mg/Ca ratio of echinoid HMC and total H_2O content indicated by reflectance spectra (A) and NMR spectra (B and C).

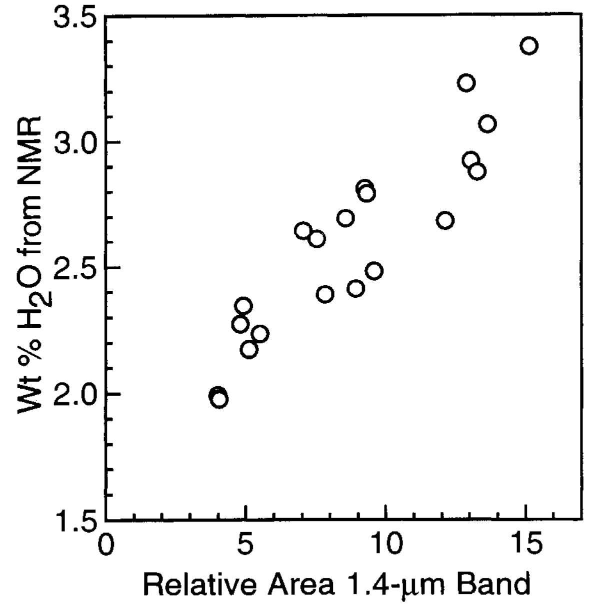


Fig. 11. Relationship between two independent measures of total H_2O content of echinoid HMC samples. Scatter in data is due to differences in total H_2O content of different subsamples of a given ossicle type.

mogeneous (Raup, 1966). Although H_2O is more homogeneously distributed within echinoid HMC than in some other types of skeletal material such as coralline aragonite or red algal HMC (Gaffey et al., 1991), VNIR reflectance data and heating experiments reveal significant inhomogeneities in H_2O distribution within individual echinoid ossicles.

Variation in the amount of H_2O in different portions of a single echinoid plate is seen visually in Figure 1. Pitting, spalling, and fracturing of the material are caused by expulsion of H_2O on heating (Gaffey et al., 1991). Note that although some portions of the plate show no pitting (Fig. 1B), others are moderately (Fig. 1C) or even severely (Fig. 1D) damaged during heating. This variability in the amount of damage reflects variations in the amount of H_2O in samples, its strength of bonding, or both.

Limited spectral data indicate that significant differences in total H_2O content exist between subsamples taken from the 125–250 µm fraction of some ossicle samples. The 1.4 µm band in reflectance spectra of two subsamples of the pyramid of *Lytechinus* had relative areas of 13.28 and 8.38, and in spectra of two subsamples of the interambulacral plates of *Leodia*, 4.92 and 7.97. Because these are high-precision spectra and error bars are narrower than the lines used to plot the data, these differences reflect real variations in the total H_2O content of these HMC samples.

Similar differences in total H_2O content between different splits of the same bulk material probably also explain the relatively poor correlation between VNIR reflectance and NMR data in Figure 11. Both VNIR reflectance and NMR spectral data provide accurate measures of the H content of samples. There is an excellent correlation between the total H_2O content, measured by weight loss on heating, and the relative area of the 1.4 μm band in reflectance spectra of heated samples (data in Gaffey et al., 1991). H contents determined from NMR spectra are accurate to within ±2% (Willard et al., 1981). Despite the accuracy and precision of the two techniques, the correlation between the data obtained from them ($r^2 = 0.84$ for linear fit to the data) is relatively poor (Fig. 11), probably because reflectance and NMR spectra in this study were obtained from two different splits of the bulk echinoid HMC samples.

Intraossicle heterogeneities in total H_2O content and the lack of correlation between H_2O and Mg/Ca ratios may mean that total H_2O content is related to ossicle structure or to growth rate. Additional studies are needed to determine the controls of H_2O content in echinoid skeletons.

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