

Sr/Mg ratios of modern marine calcite: Empirical indicators of ocean chemistry and precipitation rate

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Abstract—Holocene biotic and abiotic marine calcite have a similar range of Mg contents (0 to 22 and 4 to 21 mol% MgCO₃, respectively), yet biotic calcite has Sr²⁺ concentrations that are consistently 1250 ppm higher than those of abiotic calcite. As in laboratory experiments, a positive linear relation is observed between D_{Sr} and calcite Mg content. This produces two distinct linear trends on a plot of Sr²⁺ vs. Mg²⁺ concentrations. Principal axes of variation for both trends have similar slopes, yet distinctly different Sr²⁺ concentration intercepts. (Biotic: $y = 0.024x + 1298$, $r^2 = 0.70$; Abiotic: $y = 0.027x + 47$, $r^2 = 0.77$). The similar slopes of these trends reflect the constancy of Mg/Ca and Sr/Ca ratios of modern seawater. Equations describing the dependence of D_{Sr} on calcite Mg content are derived from both trends (Biotic: $D_{Sr} = 3.16 \times 10^{-6}$ (ppm Mg) + 0.169; Abiotic: $D_{Sr} = 3.52 \times 10^{-6}$ (ppm Mg) + 0.0062). Characterization of Sr-Mg trends for Holocene materials allows comparison with analogous trends from ancient samples to estimate relative changes in seawater Mg/Ca and Sr/Ca ratios.

The relatively high Sr contents of biotic calcite result from rapid precipitation rates associated with shell accretion in marine organisms. Calcites precipitated from seawater in laboratory experiments have D_{Sr} values that are similar to those of biotic marine calcite, suggesting that both precipitate at approximately the same rate. Our estimates of surface area-normalized precipitation rates in planktonic and benthonic foraminifera are comparable to those of seeded, pH-stat experiments. We conclude that the D_{Sr} values for biotic and experimental marine calcite are kinetically controlled, whereas the lower precipitation rates of abiotic marine calcite yield D_{Sr} values that approximate equilibrium conditions.

Experimentally derived equations describing the relation between D_{Sr} and calcite precipitation rate indicate that the offset in Sr content between biotic and abiotic calcite is the result of abiotic precipitation rates that are two to five orders of magnitude lower than those of biotic precipitates. However, observations of naturally occurring marine cements suggest that the five-order-of-magnitude offset best represents natural system processes.

INTRODUCTION

FOLLOWING THE EARLY CHEMICAL surveys by CLARK and WHEELER (1917, 1922) and VINOGRADOV (1953), various workers have analyzed marine carbonates for either Mg or Sr contents (e.g., KULP et al., 1952; CHAVE, 1954; THOMPSON and CHOW, 1955; ODUM, 1957). These studies provided the first minor element data for a wide variety of sediment-producing, calcareous marine organisms. The Sr and/or Mg contents of marine calcite were later examined using experimental (BERNER, 1975, 1978; MUCCI and MORSE, 1983; MUCCI, 1987; BURTON and WALTER, 1987, 1991) and empirical (GOLDSMITH et al., 1955; TUREKIAN and ARMSTRONG, 1960; LOWENSTAM, 1961; RUCKER and VALENTINE, 1961; DODD, 1965, 1967; LERMAN, 1965; GUNATILAKA, 1975; OHDE and KITANO, 1984; BRAND et al., 1987; CARPENTER et al., 1991) approaches. In our present study, results from laboratory precipitation experiments are used to interpret the Sr-Mg relations of Holocene abiotic and biotic marine calcite.

Nonthermodynamic homogeneous distribution or partition coefficients (i.e., D_{Mg} and D_{Sr}) are used in this study (e.g., HENDERSON and KRACEK, 1927). Here $D_{Me} = (mMe/mCa)_{solid} / (mMe/mCa)_{solution}$, where D_{Me} is the distribution coefficient of a minor element (Me), and mMe/mCa is the molar concentration ratio of the minor element relative to calcium in the solid or the solution. A detailed review of the

various types of distribution coefficients is found in MUCCI and MORSE (1990).

Laboratory precipitation experiments provide a basic understanding of the factors that control Sr and Mg incorporation into calcite from seawater and related fluids (e.g., MORSE and BENDER, 1990). It has been shown that the D_{Mg} value increases with increasing temperature and decreases with increasing PCO_2 and $[SO_4^{2-}]$ (e.g., KATZ, 1973; BURTON and WALTER, 1987, 1991; MUCCI, 1987; MUCCI et al., 1989), and increases exponentially with decreasing Mg/Ca ratios (e.g., MUCCI and MORSE, 1983). The influence of saturation state and precipitation rate on D_{Mg} has been highly debated (e.g., LAHANN and SIEBERT, 1982; MACKENZIE et al., 1983; GIVEN and WILKINSON, 1985a,b; MORSE, 1985; MUCCI and MORSE, 1983; BURTON and WALTER, 1987; MORSE and BENDER, 1990), yet there are no experimental data which suggest that D_{Mg} is precipitation rate dependent. In contrast, the D_{Sr} value increases with increasing precipitation rate (LORENS, 1981; MUCCI, 1986) and Mg content of the calcite (MUCCI and MORSE, 1983; see MORSE and BENDER, 1990, for summary).

Although these studies have added significantly to our understanding of physicochemical conditions controlling cation incorporation into calcite, elevated temperatures and/or low PCO_2 values must be employed in laboratory experiments to attain the Mg contents of naturally occurring high Mg-calcite (HMC) marine cements (e.g., GIVEN and WILKINSON,

1985a,b; MORSE, 1985; MORSE and BENDER, 1990; MUCCI and MORSE, 1990; BURTON and WALTER, 1991). Precipitation experiments, conducted at temperatures and PCO_2 values comparable to those of reefal environments, underestimate Mg contents by approximately 4 to 6 mol% $MgCO_3$ (e.g., VIDETICH, 1985; BURTON and WALTER, 1987, 1991). These inconsistencies do not diminish the value of laboratory experiments, but rather serve to highlight the need to examine materials from natural systems. Empirical studies of modern materials seem logical, given the existence of analogous materials in ancient carbonate rocks. Without some knowledge of modern natural systems, regardless of their chemical complexity, interpretation of chemical data from cements and allochems in ancient carbonate rocks may be severely compromised.

In the past, empirical studies of Sr and Mg contents of biotic marine calcite were conducted for a variety of reasons: (1) to examine the crystallographic effects of Mg incorporation into calcite (e.g., GOLDSMITH et al., 1955); (2) to examine the use of Sr and Mg contents as paleosalinity indicators (e.g., PILKEY and HOWER, 1960; LERMAN, 1965; DODD, 1965); (3) to examine the effect of temperature on Mg incorporation into calcite (e.g., CHAVE, 1954); and (4) to calculate distribution coefficients (D_{Sr} , D_{Mg}) for Holocene marine carbonates for use in determining ancient seawater Sr/Ca and Mg/Ca ratios from individual analyses. By assuming that these distribution coefficients are constant, ancient seawater Sr/Ca and Mg/Ca ratios can be directly calculated from analyses of well-preserved ancient analogues. Thus, secular trends in these tracers can be constructed to estimate the timing and magnitude of changes in the global processes controlling the Sr and Mg content of seawater (e.g., GRAHAM et al., 1982; RENARD, 1986).

Empirical data for biotic marine calcite have been produced using a wide variety of analytical techniques (i.e., arc spectrography, electron probe microanalysis (EPMA), atomic absorption spectrophotometry (AAS), X-ray fluorescence (XRF) and X-ray diffraction (XRD). However, in many cases, these data do not represent paired analysis of Mg^{2+} and Sr^{2+} . As a result, the data are not internally consistent; and direct comparison of these results with modern analytical data may be suspect due to inaccuracies and imprecision of the older methods (primarily for $[Sr^{2+}]$). To provide an analytically consistent data set, new analyses of Holocene biotic material are presented and compared with the previously published abiotic marine calcite data of CARPENTER et al. (1991). Here the term abiotic refers to nonskeletal, calcite cements that have precipitated from seawater (GONZALEZ and LOHMANN, 1985). Biotic marine calcite analyses were made using ICP-AES (inductively coupled plasma-atomic emission spectroscopy). Calcareous marine organisms representing several phyla from various geographic locations, water depths, and temperatures have been analyzed. Calcite was chosen due to its abundance in the rock record and its liberal minor element contents [i.e., up to thousands of ppm Sr^{2+} and more than 50,000 ppm Mg^{2+} (approx. 20 mol% $MgCO_3$)]. In addition, CARPENTER et al. (1991) have shown that the highly variable Mg content of abiotic aragonite cements precludes its use as a reliable indicator of seawater Mg/Ca ratios. As a result, only samples containing 100% calcite were analyzed.

The objective of this study is to characterize the Sr-Mg relations in Holocene marine calcite (abiotic and biotic) for use as a comparative tool in estimating the Sr/Ca and Mg/Ca ratios of ancient seawater via analysis of a suite of well-preserved ancient samples. This approach was used by CARPENTER et al. (1991) to compare modern and ancient abiotic marine calcites. Rather than analyzing a single specimen and calculating seawater Sr/Ca and Mg/Ca ratios based on an assumed distribution coefficient, the Sr and Mg covariation observed in analogous modern and ancient marine calcites (each having a range of Mg contents) are directly compared. To this end, we examine the Sr-Mg relations of Holocene biotic marine calcite and contrast them with similar relations for Holocene abiotic marine calcite described by CARPENTER et al. (1991). Specific emphasis is placed on the changes in the D_{Sr} value which varies as a function of precipitation rate and calcite Mg content.

PREVIOUS STUDIES

D_{Sr} -Mg Content Relations in Marine Calcite

Positive linear covariation of Sr and Mg contents of marine calcite has been described in both experimental and empirical studies (e.g., MUCCI and MORSE, 1983; OHDE and KITANO, 1984; Fig. 1a). Increases in the D_{Sr} value are the result of increasing amounts of Mg in the calcite crystal lattice. The correlation between increasing Mg content and decreasing d -values and cell volume in calcite has also been well documented (e.g., GOLDSMITH et al., 1955, 1958, 1961; KITANO and KANAMORI, 1966; BARNES and O'NEIL, 1971; BISCHOFF et al., 1983). At first glance, these findings seem contradictory, as decreases in cell volume might be expected to inhibit Sr incorporation. However, MUCCI and MORSE (1983) attributed the observed Sr-Mg relation to distortion of the calcite crystal structure via Mg^{2+} substitution for Ca^{2+} (ionic radii = 0.72 Å and 1.00 Å, respectively); this produces a localized increase in the size of nearby cation sites and increased incorporation of the larger Sr^{2+} ion (ionic radius = 1.18 Å; radii data from SHANNON and PREWITT, 1970, and SHANNON, 1976). Regardless of the exact position of Sr^{2+} (i.e., Mg-distortion sites, dislocations, grain boundaries, etc.), a systematic covariation of Sr^{2+} and Mg^{2+} is observed in various types of marine calcite (e.g., MUCCI and MORSE, 1983; OHDE and KITANO, 1984; CARPENTER et al., 1991).

D_{Sr} -Precipitation Rate Relations

LORENS (1978, 1981) and MUCCI (1986) found that D_{Sr} is positively correlated with increases in calcite precipitation rate. The relation described by LORENS (1978, 1981) indicates that low D_{Sr} values approximate equilibrium precipitation conditions and that high values are the result of kinetic effects (Fig. 1b). HOLLAND'S (1966) D_{Sr} value of 0.14 (± 0.02) for low Mg-calcite (LMC) (experimental precipitate from a Mg^{2+} -free solution) has generally been accepted as the "equilibrium" distribution coefficient for marine calcite (e.g., MUCCI and MORSE, 1983). For modern seawater, this distribution coefficient produces a LMC which contains approximately 1200 ppm Sr, which is consistent with the composition of planktonic foraminifera (e.g., BENDER et al., 1975). If, as the data of LORENS (1978, 1981) suggest, low

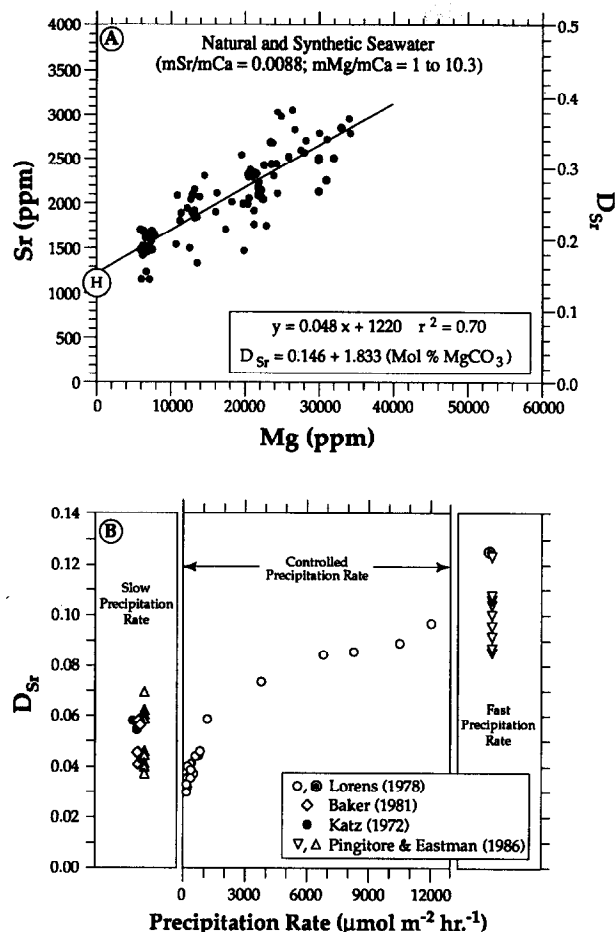


FIG. 1. (a) Plot of Sr vs. Mg content of inorganically precipitated calcite from natural and synthetic seawater at 25°C using a pH stat (Data from MUCCI and MORSE, 1983). D_{Sr} values corresponding to Sr contents are approximated on the right axis for reference. The mMg/mCa ratio of the synthetic seawater was varied from 1 to 10.3 (1, 2.5, 5.13, 7.5, 10.3) for these experiments (MUCCI and MORSE, 1983). The "H" represents the D_{Sr} value (0.14 ± 0.02) reported by HOLLAND (1966) for LMC inorganically precipitated from a Mg-free solution at 25°C. The Sr-Mg covariance of the MUCCI and MORSE (1983) data, exclusive of the HOLLAND (1966) data, is described by the equation: $y = 0.048x + 1220$; $r^2 = 0.70$. These data represent a variety of precipitation rates. MUCCI and MORSE (1983) have used these data together with the HOLLAND (1966) value to calculate the relation between D_{Sr} and Mg content ($D_{Sr} = 0.146 + 1.833 \times \text{mol\% MgCO}_3$ calcite; see inset). Note that Mg contents do not exceed approximately 34,000 ppm Mg or 12 mol% MgCO_3 . (b) Plot of D_{Sr} vs. precipitation rate for 0.5 or 0.7 M NaCl, Mg-free solutions for a range of temperatures. See inset for explanation of symbols. Precipitation rates apply only to the LORENS (1978) data set for controlled precipitation rate (O). (O) = spontaneous precipitation of LORENS (1978). The BAKER (1981) experiments were conducted at 60–80°C and the KATZ et al. (1972) experiments at 40–98°C. Other experiments were conducted at 25°C. (Δ) = "normal" precipitation rate of PINGITORE and EASTMAN (1986); (∇) = "very fast" precipitation rate of PINGITORE and EASTMAN (1986). Using the surface areas and seed masses reported by LORENS (1978), the controlled precipitation rate data have been recalculated. Modified from MORSE and BENDER (1990).

D_{Sr} values are indicative of equilibrium conditions, why do experimental and biotic marine LMC contain approximately 1200 ppm Sr rather than a value near 0 ppm?

CARPENTER et al. (1991) suggested that abiotic marine

calcite contains substantially less Sr^{2+} than biotically and experimentally precipitated marine calcite because of its relatively low precipitation rates. This implies that biotic and experimental calcites precipitate at similarly rapid rates. Here we present new Sr and Mg content data for modern biotic calcite and discuss the similarities and differences between biotic, abiotic, and experimentally precipitated marine calcite.

METHODS

Samples of biotic marine calcite (<0.5 mg) were powdered using a microscope-mounted drill assembly and a 500 μm diameter dental burr as described by CARPENTER et al. (1991) and delivered to a 1.5 mL polypropylene centrifuge tube. In an attempt to provide an estimate of both mean composition and intraspecimen variability, microsamples (rather than bulk samples) were extracted to assess compositional variations within individual organisms. Ontogenetic variations were not assessed. All samples were rinsed once with ethanol and twice with deionized water and centrifuged between rinses. Following rinsing and centrifugation, calcite samples were dissolved in 1 mL of dilute HCl-HNO₃. Concentrations of Ca, Mg, and Sr were determined simultaneously by ICP-AES using a Leeman Labs Plasma-Spec III. Analytical precision, based on gravimetric standards, was $\pm 1.1\%$ for Ca, $\pm 1.7\%$ for Mg, and $\pm 1.0\%$ for Sr. Raw cation concentrations were converted to weights of MeCO_3 and total weights of MeCO_3 species were used to convert to ppm (where Me is the minor element in question). Data have not been normalized to a specific Ca concentration because of significant amounts of MgCO_3 substitution. Mol% MgCO_3 was calculated using the contribution of all cations measured and was normalized to 100%. Both the Mg^{2+} and Sr^{2+} concentrations of calcite are reported in ppm. By convention, Mg contents are also reported as mol% MgCO_3 . For consistency, all calculations and diagrams are made using Mg^{2+} concentrations in ppm.

Samples of the red alga *Amphiroa rigida* (specimen "b") were examined using XRD to assess the potential contribution of Mg^{2+} via dissolution of brucite ($\text{Mg}(\text{OH})_2$) during ICP-AES analyses (e.g., SCHMALZ, 1965; WEBER and KAUFMAN, 1965; MILLIMAN et al., 1971). Examination of d_{104} values of the *Amphiroa* calcite were consistent with a determinative curve of d_{104} vs. mol% MgCO_3 using the cell parameter calculations for biotic calcite from BISCHOFF et al. (1983). Calculated Mg contents from these d_{104} values (2.973 to 2.979) ranged from 21.5 to 19.5 mol% MgCO_3 , respectively. ICP-AES analyses of the same materials (~ 20 mg samples) range from 20.7 to 21.6 mol% MgCO_3 . No brucite was observed in these samples. Grinding and washing of samples had no noticeable effect on chemical analyses. Based on these findings, the Mg content of *Amphiroa* microsamples (<0.5 mg) using ICP-AES (Mean = 21.9 mol% MgCO_3 (± 0.5 , $N = 13$)), are presumed to be the result of Mg^{2+} substitution for Ca^{2+} in the calcite crystal lattice. If brucite is present, the abundance is below detection limits of XRD techniques.

RESULTS

Abiotic Marine Calcite

Abiotic marine calcite data used in this study were compiled by CARPENTER et al. (1991) and consist of data from MITCHELL et al. (1987), MAJOR and WILBER (1991), and CARPENTER et al. (1991) (Fig. 2). Materials are from Jamaica, Little Bahama Bank, and Enewetak Atoll, respectively. Descriptions of these materials can be found in the individual publications. Magnesium and strontium contents covary over a wide range of Mg contents [approximately 10,000 to 50,000 ppm Mg^{2+} (4 to 20 mol% MgCO_3); Fig. 2]. Correlation analysis has been conducted to assess the covariation of Sr and Mg contents (dependent variables) and the product moment correlation coefficient (r) (e.g., SOKAL and ROHLF, 1969). The correlation is highly significant ($r^2 = 0.77$, $\alpha - 1 = 0.99$) and is best represented by the slope and intercept of the prin-

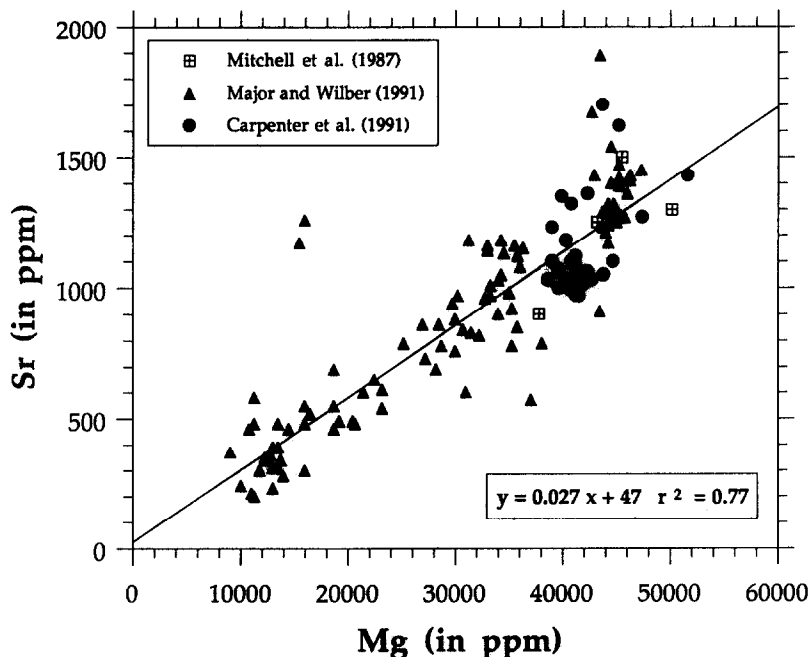


FIG. 2. Magnesium and strontium contents of Holocene abiogenic marine calcite. Data are from Little Bahama Bank (MAJOR and WILBER, 1991), Discovery Bay, Jamaica (MITCHELL et al., 1987), and Enewetak Atoll (CARPENTER et al., 1991). The equation at lower right describes the principal axis of variation of this trend. Modified from CARPENTER et al. (1991).

principal axis of variation with a 95% confidence interval (CARPENTER et al. (1991):

$$\text{ppm Sr}_{\text{calcite}} = 0.027_{(\pm 0.002)} (\text{ppm Mg}_{\text{calcite}}) + 47_{(\pm 93)}. \quad (1)$$

Biotic Marine Calcite

Biotic marine calcite data presented in this paper are new analyses from several geographic locations and water depths (Table 1, Fig. 3). Samples for this study include specimens from the phyla Protista (Foraminifera), Brachiopoda, Echinodermata, Bryozoa, Coelenterata and the algal division Rhodophyta (Table 1). Like abiogenic calcites, these samples represent a wide range of Mg contents [approximately 0 to 57,000 ppm Mg^{2+} (0 to 23 mol% MgCO_3); Fig. 3]. The covariation of Sr and Mg is also highly significant ($r^2 = 0.70$, $\alpha - 1 = 0.99$) and is best represented by the slope and intercept of the principal axis of variation with a 95% confidence interval:

$$\text{ppm Sr}_{\text{calcite}} = 0.024_{(\pm 0.004)} (\text{ppm Mg}_{\text{calcite}}) + 1298_{(\pm 121)}. \quad (2)$$

Differences in Mg contents among the different phyla have been observed previously (e.g., MILLIMAN, 1974; Table 1, Fig. 3). Calcareous algae (Rhodophyta) contain the most Mg of all biotic specimens analyzed (37,500 to 57,300 ppm; 15.1 to 22.8 mol% MgCO_3). Echinoderms have the most variable Mg contents (11,700 to 39,700 ppm; 4.8 to 15.9 mol% MgCO_3), with lower values from echinoid spines (Table 1). Octocorals (Coelenterata) and neritic benthic for-

minifera contain approximately the same amount of Mg (32,200 to 38,700 ppm; 13.0 to 15.6 mol% MgCO_3 and 33,300 to 37,900 ppm; 13.4 to 15.2 mol% MgCO_3 , respectively). The only Bryozoan analyzed, *Bugula neritina* contained from 24,000 to 27,100 ppm Mg^{2+} (9.7 to 11.0 mol% MgCO_3). The LMC biotic samples, planktonic foraminifera and brachiopods, contained 558 to 2350 ppm (0.23 to 0.96 mol% MgCO_3) and 1680 to 23,100 ppm (0.69 to 9.4 mol% MgCO_3 , respectively). Brachiopods containing relatively high amounts of Mg (*Thecidellina* sp.) are from a reefal setting in Curacao.

Previously Published Biotic Calcite Data

Previously published Sr and Mg analyses of biotic marine calcite were compiled and are plotted in Fig. 4. The covariation of Sr and Mg is highly significant ($r^2 = 0.47$, $\alpha - 1 = 0.99$) and is best represented by the slope and intercept of the principal axis of variation: $\text{ppm Sr}_{\text{calcite}} = 0.023 (\text{ppm Mg}_{\text{calcite}}) + 1245$. This relation closely approximates our biotic data presented in Fig. 3 and represented by Eqn. (2). However, the variability of Sr in our data is significantly less than that from the literature (i.e., $r^2 = 0.70$ vs. 0.47; Figs. 3 and 4). Variability of the older data may be the result of large sample sizes and thus possible incorporation of small amounts of aragonite in some bimineralic organisms. Less accurate measurement of Sr^{2+} concentrations by older analytical techniques may also account for some of this variability. Our data verify similar trends previously reported. However, the decreased variability of our data set allows a more precise characterization of Sr and Mg covariance.

DISCUSSION

Interpreting Sr-Mg Trends

For samples with equivalent Mg contents, modern biotic marine calcite contains significantly more Sr²⁺ than modern abiotic marine calcite (Table 1, Figs. 2, 3, 5). The biotic and abiotic trends are statistically distinct, due to their different Sr contents (offset by approximately 1250 ppm Sr), yet their slopes are indistinguishable [$0.024 (\pm 0.004)$ and $0.027 (\pm 0.002)$, respectively; Fig. 5]. Interpretation of these trends is based on our understanding of the factors that control D_{Sr} values in calcite. The relations described by LORENS (1981) and MUCCI and MORSE (1983) provide a basis for interpreting these trends (Eqs. 1, 2; Figs. 1, 2, 3, 5). Dependence of D_{Sr} on Mg content of the calcite defines the positive, linear co-variation of Sr and Mg in each trend (e.g., MUCCI and MORSE, 1983). Dependence of D_{Sr} on precipitation rate accounts for the offset between the biotic and abiotic trends (e.g., LORENS, 1981; Fig. 5); higher Sr contents of the biotic calcite are due to higher precipitation rates (LORENS, 1981; MUCCI, 1986). The similar slopes of both trends reflect the constant Mg/Ca and Sr/Ca ratios of modern seawater (e.g., CARPENTER et al., 1991).

Our interpretation of the biotic and abiotic trends focuses on the factors controlling D_{Sr} , and does not require discussion of the physical and chemical controls on Mg²⁺ incorporation into marine calcite (Fig. 5). Samples analyzed in this study do not have corresponding water data (i.e., no temperature or PCO_2 data) and as a result, variations in the factors controlling Mg²⁺ incorporation into marine calcite cannot be addressed. In the context of this study, the causes of the observed variations in Mg²⁺ content are relatively unimportant. However, the dependence of D_{Mg} on a variety of factors is of importance when trends for two temporally distinct data sets are compared (e.g., comparison of ancient and Holocene marine cement compositions; CARPENTER et al., 1991). For a discussion of the dependence of D_{Mg} on temperature, PCO_2 , $[SO_4^{2-}]$ and Mg/Ca ratios of ambient seawater see MUCCI and MORSE (1983) and BURTON and WALTER (1987, 1991). Suffice it to say that both modern biotic and abiotic marine calcite have a wide range of Mg contents (0 to 22 and 4 to 21 mol% MgCO₃, respectively) due to vital effects (e.g., CHAVE, 1954; Fig. 3) and variable PCO_2 and temperature (e.g., BURTON and WALTER, 1991). By virtue of these variable Mg contents (resulting from a variety of conditions) and the relation between D_{Sr} and the Mg content of calcite, the covariant trends observed in Fig. 5 are produced.

Given the possible range of Sr and Mg contents for marine calcite, why do the biotic and abiotic trends have similar slopes? The common factor linking these diverse samples (from a wide range of locations, depths, temperatures and PCO_2 values), is that all precipitated from seawater, a fluid that is relatively homogeneous with respect to Mg/Ca and Sr/Ca ratios (i.e., molar ratios of 5.1 and 0.0088, respectively). We propose that the slopes of both trends reflect the relative proportions of Sr, Mg, and Ca in modern seawater. Therefore, secular variations in ocean Sr, Mg, and/or Ca concentrations (relative to modern values) can be estimated by the change in slope of an analogous trend (e.g., comparing ancient and modern abiotic trends) and the absolute change

in concentration for analogous materials (e.g., the Mg content of ancient and modern reefal marine cements, CARPENTER et al., 1991).

To provide a basis for comparison, the relation between D_{Sr} and Mg content in modern biotic and abiotic marine calcite must be quantified. From Eqn. (1), CARPENTER et al. (1991) have derived an equation for the dependence of D_{Sr} on the Mg content of modern abiotic marine calcite:

$$D_{Sr} = 3.52 \times 10^{-6} (\text{ppm Mg}_{\text{calcite}}) + 0.0062. \quad (3)$$

Using Eqn. (2), a similar equation can be derived for biotic marine calcite:

$$D_{Sr} = 3.16 \times 10^{-6} (\text{ppm Mg}_{\text{calcite}}) + 0.169. \quad (4)$$

Equations (3) and (4) are the best estimates of Sr-Mg relations for modern, natural systems. Unlike the work of MUCCI and MORSE (1983), these empirical relations cover the widest possible range of Mg contents for both types of marine calcite and represent precipitation from a fluid with constant Mg/Ca and Sr/Ca ratios (Fig. 1a). The distinctions between the MUCCI and MORSE (1983) data (Fig. 1a) and the abiotic data of CARPENTER et al. (1991; Fig. 2) are the markedly higher Sr and lower Mg contents of the experimentally precipitated calcite. Higher Sr contents can be explained by relatively rapid precipitation rates (see next section), yet the limited range of Mg contents (a maximum of ~12 mol% MgCO₃) cannot be easily explained (Figs. 1a and 2). Although Mg/Ca ratios of the fluids in the MUCCI and MORSE (1983) experiments were adjusted to produce variable Mg contents in the calcite precipitates, these marked increases in Mg/Ca ratios (from 1 to 10.3 at 25°C) did not yield the same range of Mg contents observed in naturally occurring carbonates (e.g., reefal marine cements of VIDETICH, 1985). Such discrepancies between experimental and empirical Sr and Mg contents require further examination of both precipitation processes.

Equations describing the relation between D_{Sr} and precipitation rate have been used to calculate the difference in precipitation rate responsible for the 1250 ppm offset in Sr content between biotic and abiotic calcite [$D_{Sr} = 0.0339 \times (\log \text{ppt. rate}) + 0.157$ (LORENS, 1981) and $D_{Sr} = 0.0622 \times (\log \text{ppt. rate}) + 0.539$ (MUCCI, 1986), where ppt. rate is in moles/m² hr. To effect a change in D_{Sr} of approximately 0.16 to 0.17 (which corresponds to the Sr content offset), the equation of LORENS (1981) requires a difference in precipitation rate of five orders of magnitude, whereas the equation of MUCCI (1986) requires a difference of two orders of magnitude.

Determining which equation is more applicable to our data is not straightforward. In the case of the LORENS (1981) equation, the solution used for calcite precipitation is a Mg-free, NaCl, CaCl₂ solution, whereas the solution for the MUCCI (1986) experiments was artificial seawater, with variable amounts of Na₂HPO₄. Application of the LORENS (1981) data to Mg-calcite precipitated from seawater may not be appropriate, yet his study examines the effects of precipitation rate on D_{Sr} , without superimposing the effects of Mg incorporation on D_{Sr} or orthophosphate ion on precipitation rate (e.g., MUCCI and MORSE, 1983; MUCCI, 1986). In the LOR-

Table 1. Sr²⁺ and Mg²⁺ Contents of Holocene Biotic Marine Calcite

Phylum/Division	Genus/Species	Location	Mol % MgCO ₃	Mg ²⁺ (ppm)	Sr ²⁺ (ppm)
Rhodophyta	<i>Amphiroa rigida</i> (a)	Florida Keys	20.1	50400	2640
Rhodophyta	<i>Amphiroa rigida</i> (a)	Florida Keys	20.3	50900	2690
Rhodophyta	<i>Amphiroa rigida</i> (a)	Florida Keys	17.2	42800	2960
Rhodophyta	<i>Amphiroa rigida</i> (a)	Florida Keys	18.4	46000	2460
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	21.5	54000	2470
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.7	57100	2540
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.2	55800	2300
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.4	56400	2520
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	21.5	53900	2430
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.8	57300	2570
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.0	55300	2520
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.5	56600	2640
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	21.9	54900	2800
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	21.5	54000	2520
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	21.3	53500	2520
Rhodophyta	<i>Amphiroa rigida</i> (b)	Florida Keys	22.1	55600	2530
Rhodophyta	<i>Neogoniolithon</i> sp. (a)	Florida Keys	16.9	42200	2100
Rhodophyta	<i>Neogoniolithon</i> sp. (b)	Florida Keys	19.4	48500	2490
Rhodophyta	<i>Neogoniolithon</i> sp. (b)	Florida Keys	18.8	47100	2750
Rhodophyta	<i>Neogoniolithon</i> sp. (b)	Florida Keys	17.1	42700	2230
Rhodophyta	<i>Neogoniolithon</i> sp. (b)	Florida Keys	15.1	37500	2600
Rhodophyta	<i>Neogoniolithon</i> sp. (b)	Florida Keys	15.2	37900	2680
Brachiopoda	<i>Kraussina rubra</i>	Cape of Good Hope	0.92	2250	706
Brachiopoda	<i>Megerlea truncata</i>	Sicily	2.93	7140	1090
Brachiopoda	<i>Notosaria</i> sp.	New Zealand	2.58	6290	1160
Brachiopoda	<i>Terebratella cruenta</i>	New Zealand	0.75	1820	883
Brachiopoda	<i>Stethothyris</i> sp.	Antarctica	0.69	1680	1060
Brachiopoda	<i>Thecidellina</i> sp.	Curacao	8.92	22000	1390
Brachiopoda	<i>Thecidellina</i> sp.	Curacao	9.37	23100	1270
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	9.73	24000	2380
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	11.7	28900	2250
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	11.2	27700	2640
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	11.5	28500	2420
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	10.2	25000	2590
Bryozoa	<i>Bugula neritina</i>	East Coast Florida	11.0	27100	2360
Echinodermata	Unidentified Asteroid (Starfish)	Florida Keys	12.2	30200	1950
Echinodermata	<i>Bathycrinus</i> sp.	8°42'N, 55°48'W; 3014-3239 m	10.0	24600	1870
Echinodermata	<i>Bathycrinus</i> sp.	8°42'N, 55°48'W; 3014-3239 m	9.81	24200	1940
Echinodermata	<i>Comanthus bennetti</i>	-----	15.2	37800	1890
Echinodermata	<i>Dendraster excentricus</i>	Northern California	9.49	23400	1990
Echinodermata	<i>Dendraster</i> sp. (test)	Northern California	10.6	26300	2030
Echinodermata	<i>Echinometra lacunter</i>	Molasse Key, Florida	13.9	34400	1960
Echinodermata	<i>Echinus</i> sp. (test)	-----	12.4	30600	2180
Echinodermata	<i>Echinus</i> sp. (test)	-----	13.3	32900	2280
Echinodermata	<i>Endoxocrinus parrae</i>	-----	12.1	29900	1990
Echinodermata	<i>Eucidaris tribuloides</i> (spine)	Molasse Key, Florida	5.76	14100	1940
Echinodermata	Unidentified Echinoid (spine)	Florida	5.72	14000	1730
Echinodermata	Unidentified Echinoid (test)	Florida	12.3	30500	2070
Echinodermata	<i>Lytechinus variegatus</i>	Lona Key, Florida	6.75	16600	1880
Echinodermata	<i>Mellita</i> sp.	-----	12.6	31300	1940
Echinodermata	<i>Mellita</i> sp.	-----	10.6	26300	2030
Echinodermata	<i>Protosocrinus ruberrimus</i>	-----	11.3	27900	1730
Echinodermata	Unidentified Echinoid (spine)	Florida	4.78	11700	1880
Echinodermata	Unidentified Echinoid (test)	Florida	12.1	29800	2310
Echinodermata	Unidentified Crinoid	-----	14.5	35900	2020
Echinodermata	Unidentified Ophiuroid	Rodriguez Key, Florida	15.8	39300	1950
Echinodermata	Unident. Ophiuroid (Brittle Star)	Florida, Keys	15.9	39700	1940
Coelenterata	<i>Tubipora musica</i>	Phillipines	15.6	38700	2610
Coelenterata	<i>Tubipora musica</i>	Phillipines	13.9	34400	2280
Coelenterata	<i>Tubipora musica</i>	Phillipines	13.0	32200	2420
Coelenterata	<i>Tubipora</i> sp.	Western Pacific	13.8	34300	2390

Table 1 (continued). Sr²⁺ and Mg²⁺ Contents of Holocene Biotic Marine Calcite

Phylum/Division	Genus/Species	Location	Mol % MgCO ₃	Mg ²⁺ (ppm)	Sr ²⁺ (ppm)
Protista	<i>Archais sp.</i>	Sugarloaf Key, Florida	15.2	37900	1640
Protista	<i>Archais sp.</i>	Sugarloaf Key, Florida	13.4	33300	1710
Protista	<i>Archais sp.</i>	Sugarloaf Key, Florida	13.8	34400	1710
Protista	<i>Archais sp.</i>	Sugarloaf Key, Florida	14.6	36300	1600
Protista	<i>Globigerinella siphonifera</i>	Rio Grand Rise (AII.107 Site 63)	0.62	1500	1190
Protista	<i>Globigerinoides ruber</i> (red)	Nicauraguan Rise (CHO 288, BC-122)	0.91	2210	1650
Protista	<i>Globigerinoides ruber</i> (red)	Nicauraguan Rise (CHO 288, BC-122)	0.96	2350	1660
Protista	<i>Globigerinoides ruber</i> (white)	Nicauraguan Rise (CHO 288, BC-122)	0.59	1440	1460
Protista	<i>Globigerinoides ruber</i> (white)	Nicauraguan Rise (CHO 288, BC-122)	0.69	1680	1370
Protista	<i>Globigerinoides sacculifer</i>	Nicauraguan Rise (CHO 288, BC-122)	0.50	1230	1370
Protista	<i>Globigerinoides sacculifer</i>	Nicauraguan Rise (CHO 288, BC-122)	0.64	1570	1400
Protista	<i>Globorotalia menardii</i>	Bahamas (OCE 205 Site 7)	0.55	1340	1310
Protista	<i>Globorotalia truncatulinoides</i>	Rio Grand Rise (AII.107 Site 63)	0.23	558	1340
Protista	<i>Globorotalia unguolata</i>	Rio Grand Rise (AII.107 Site 63)	0.33	805	1340
Protista	<i>Hastigerina pelagica</i>	Rio Grand Rise (AII.107 Site 63)	0.58	1420	1230
Protista	<i>Hastigerina pelagica</i>	Nicauraguan Rise (CHO 288, BC-122)	0.67	1630	1210
Protista	<i>Orbulina universa</i>	Rio Grand Rise (AII.107 Site 63)	0.94	2290	1350
Protista	<i>Orbulina universa</i>	Nicauraguan Rise (CHO 288, BC-122)	0.75	1830	1190

ENS (1981) experiments precipitation rate was varied by three orders of magnitude, whereas that of MUCCI (1986) was varied by approximately 1.5 orders of magnitude. Furthermore, incorporation of Mg into calcite will yield a higher D_s value than that for LMC precipitated at the same rate (e.g., LORENS, 1981; MUCCI and MORSE, 1983; MUCCI, 1986). Regardless of the Mg content of the calcite, variations in precipitation rate should produce commensurate changes in D_s (and ul-

timately Sr²⁺ concentration) for calcites containing equal amounts of Mg²⁺ (e.g., MUCCI, 1986; Fig. 5). The relation between precipitation rate and D_s for various solutions may change with additional experimental and empirical studies, but at present, the relations described by LORENS (1981) and MUCCI (1986) are the only ones available for this purpose. Although the correlation coefficient for the LORENS (1981) data is considerably better than that for the MUCCI (1986)

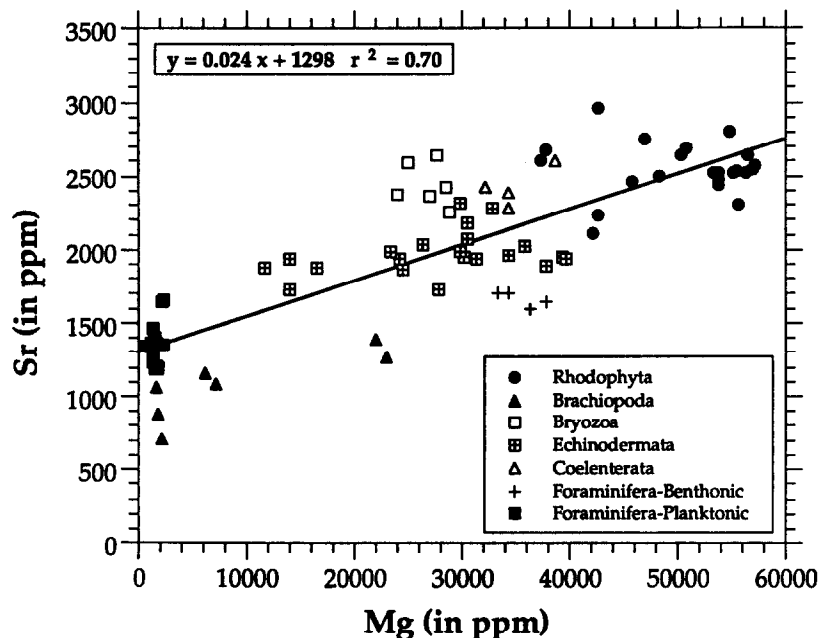


FIG. 3. Magnesium and strontium contents of Holocene biotic marine calcite. Inset legend indicates the biotic classification for individual analyses. Data are from Table 1. The equation at upper left describes the principal axis of variation of this trend.

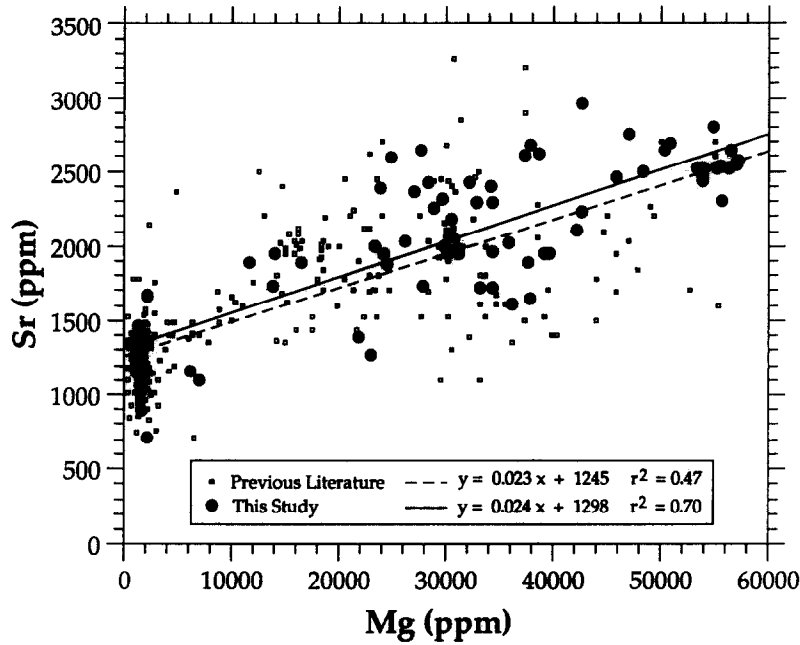


FIG. 4. Magnesium and strontium contents of Holocene biotic marine calcite (Data from Fig. 3, Table 1) plotted with similar data from the literature. Equations describing each data set are at the bottom of the diagram. Data from this study have a higher correlation coefficient yet similar slopes and intercepts. Literature data are from BENDER et al. (1975), BRAND et al. (1987), DELANEY et al. (1989), EMILIANI (1955), GAFFEY et al. (1991), GOLDSMITH et al. (1955), GUNATILAKA (1975), JONES and JENKINS (1970), KEITH and WEBER (1965), KRINSLEY (1960), LIPPS and RIBBE (1967), LOWENSTAM (1961), MATTHEWS (1966), OHDE and KITANO (1984), PILKEY and HARRISS (1966), RUCKER and VALENTINE (1961), SCHOPF and ALLAN (1970), SCHOPF and MANHEIM (1967), and TUREKIAN and ARMSTRONG (1960).

data, there is no reason to exclude either set of results. Therefore, both relations have been used to constrain precipitation rate based on differences in D_{Sr} and Sr^{2+} concentrations in marine calcite (Fig. 5).

Biotic and Experimental Precipitation Rates

Using the relations of LORENS (1981) and MUCCI (1986), the relative difference in precipitation rate between abiotic

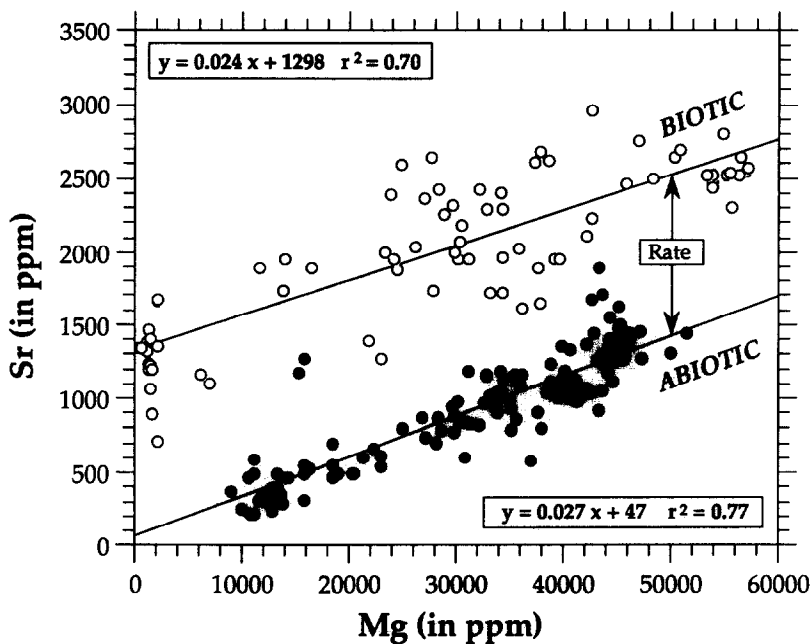


FIG. 5. Magnesium and strontium contents of Holocene biotic and abiotic marine calcite (Figs. 2, 3, Table 1). Equations at upper left and lower right describe the principal axes of variation for the biotic and abiotic trends, respectively. The nearly parallel trends are offset by approximately 1250 ppm Sr. This offset is interpreted as a higher precipitation rate in the biotic calcite.

and biotic calcite can be calculated (Fig. 5). However, to assign an absolute value to abiotic calcite precipitation rates, it is first necessary to calculate precipitation rates for biotic calcite. The following discussion examines biotic precipitation rates and compares them with measured precipitation rates from laboratory experiments.

Biotic and laboratory precipitation processes occur over similar time periods. Seeded, pH-stat experiments typically last 2 to 24 hours (e.g., LORENS, 1981, MUCCI and MORSE, 1983; MUCCI, 1986; BURTON and WALTER, 1987, 1991) and foraminifera chambers form in approximately 6 to 24 hours (e.g., BÉ et al., 1979; ANDERSON and FABER, 1984). Similarly, daily growth increments have also been observed in molluscs (e.g., LUTZ and RHOADS, 1980), barnacles (e.g., BOURGET, 1980) and corals (e.g., DODGE and VAISNYS, 1980). Although the nature of growth increments varies between organisms (e.g., usually marked by incorporation of organic matter in the carbonate), it is generally accepted that most marine fauna produce daily to fortnightly increments in their calcareous exoskeletons (e.g., LOWENSTAM and WEINER, 1989). In contrast, the duration of marine cement precipitation is on the order of hundreds to thousands of years (e.g., GRAMMER et al., 1991). Although quantification of calcite precipitation rate depends on the mass of CaCO_3 precipitated per period of time and surface area, the durations of these processes place upper limits on precipitation rates.

Several studies of calcification in planktonic and benthonic foraminifera provide the basis for our discussion of biotic calcite precipitation rates (e.g., DUGUAY and TAYLOR, 1978; EREZ, 1982; ANDERSON and FABER, 1984; KUILE and EREZ, 1984). Calcite accretion rates for the planktonic foraminifera *Globogerinoides sacculifer* range from 3.2×10^{-5} to 1.1×10^{-3} $\mu\text{mol/h}$ (EREZ, 1982) and from 2.6×10^{-3} to 3.9×10^{-3} $\mu\text{mol/h}$ (ANDERSON and FABER, 1984). Rates for the benthonic foraminifera *Amphistegina lobifera* and *Amphisorus hemprichii* range from 1.7×10^{-3} to 8.6×10^{-3} $\mu\text{mol/h}$ and 8.3×10^{-3} to 2.3×10^{-2} $\mu\text{mol/h}$, respectively (KUILE and EREZ, 1984). Rates of approximately 1.7×10^{-2} to 4.2×10^{-2} $\mu\text{mol/h}$ (incubated in light) and 2.0×10^{-3} to 1.3×10^{-2} $\mu\text{mol/h}$ (incubated in darkness) were measured for *Archais angulatus* (DUGUAY and TAYLOR, 1978).

Because precipitation rate is a function of seed crystal surface area, laboratory precipitation rates are normalized to surface area (i.e., in $\text{mol/m}^2 \text{h}$, see MUCCI and MORSE, 1983; MUCCI, 1986; BURTON and WALTER, 1987, 1991). Therefore, to compare calcite precipitation rates in biotic and laboratory settings directly, estimates of surface area associated with biotic calcite precipitation are required. We have chosen to model the surface area associated with foraminifera chamber formation because this calcification process is relatively well documented and the Mg content of foraminifera is similar to that of experimentally precipitated calcites.

Our first model estimates the surface area of a smooth sphere, with a radius of $80 \mu\text{m}$ (surface area = $8.0 \times 10^{-8} \text{m}^2$). Based on the observations of chamber morphology by BÉ et al. (1979), this shape approximation seems reasonable for many planktonic foraminifera. A chamber radius of $80 \mu\text{m}$ has been used to estimate surface areas for both planktonic and benthonic foraminifera and is typical for *Globogerinoides sacculifer* (i.e., EREZ, 1982; ANDERSON and FABER, 1984).

In cases where multiple chambers have formed, surface area is multiplied by the number of chambers. We have assumed that one chamber is produced in a 24-hour period. Because a smooth sphere model provides a minimum surface area, calculated precipitation rates are maximized. These surface areas yield relatively high precipitation rates for the foraminifera mentioned above (Planktonic: 400 to $48,900 \mu\text{mol/m}^2 \text{h}$; Benthonic: 800 to $260,000 \mu\text{mol/m}^2 \text{h}$).

SEM and TEM observations by BÉ et al. (1979) and HEMLEBEN et al. (1977) indicate that the surface area available for calcite precipitation may be considerably larger than that of a smooth sphere. Numerous calcareous "plaques" ($5 \mu\text{m}$ in diameter and $3 \mu\text{m}$ thick) form within the "anlage" during initial chamber formation and coalesce to form a thin bilamellar wall which later thickens by lamellar accretion (BÉ et al., 1979). These numerous sites of calcite formation serve to increase the available surface area by approximately one order of magnitude. We have modeled chamber surface area using multiple cylindrical "plaques" with the dimensions described above. Assuming a porosity of 22%, approximately 19,300 plaques are needed to construct a chamber with a radius of $80 \mu\text{m}$. This yields a surface area of $9.1 \times 10^{-7} \text{m}^2$. Using this surface area, precipitation rates for *Globogerinoides sacculifer* range from 35 to $1800 \mu\text{mol/m}^2 \text{hr}$ (EREZ, 1982) and 1100 to $4300 \mu\text{mol/m}^2 \text{h}$ (ANDERSON and FABER, 1984). Similar rates are observed for the benthonic foraminifera *Amphistegina lobifera* and *Amphisorus hemprichii*; these range from 70 to $1100 \mu\text{mol/m}^2 \text{h}$ and 440 to $2800 \mu\text{mol/m}^2 \text{h}$, respectively (KUILE and EREZ, 1984). Using data from DUGUAY and TAYLOR (1978) for *Archais angulatus*, precipitation rates of 110 to $2300 \mu\text{mol/m}^2 \text{h}$ are calculated. Given approximations of surface area, these calculations represent our best estimates of calcite precipitation rates in foraminifera.

Importantly, these rates are comparable to those of seeded, pH-stat experiments. Precipitation rates associated with experimentally precipitated calcite are on the order of 10 to $10,000 \mu\text{mol/m}^2 \text{h}$ (e.g., LORENS, 1978; 1981, Fig. 1b). Calcite precipitation rates from seawater solutions are typically 50 to $1500 \mu\text{mol/m}^2 \text{h}$ (e.g., MUCCI and MORSE, 1983; MUCCI, 1986; BURTON, 1988; BURTON and WALTER, 1987, 1991). Given the similarity in D_{sr} values for biotic and laboratory calcite precipitated from seawater and our estimates of precipitation rates in foraminifera, we conclude that biotic and laboratory calcite precipitate at comparable rates (e.g., Figs. 1a, 3).

These estimates of biotic precipitation rates can be used to estimate the relative rate of abiotic calcite precipitation. If we assume that biotic precipitation rates are approximately $1500 \mu\text{mol/m}^2 \text{h}$, then using the relations of LORENS (1981) and MUCCI (1986), abiotic precipitation rates range from 0.015 to $15 \mu\text{mol/m}^2 \text{h}$, respectively. To check these estimates, volumes of marine cement can be calculated and compared with observations in natural systems. For example, if we use a duration for marine cement precipitation of 1000 years, an abiotic precipitation rate of $0.015 \mu\text{mol/m}^2 \text{h}$ (using the LORENS, 1981, equation) and the density of calcite (2.71g/cm^3), then the volume of marine cement precipitated over this time interval is 4.9cm^3 per m^2 of substrate. This estimate seems reasonable given the volume of marine cements observed in reefal environments (e.g., LAND and GOREAU, 1970;

GINSBURG and JAMES, 1976; LIGHTY, 1985; SALLER, 1986; AISSAOUI, 1988). However, if the higher rate of $15 \mu\text{mol}/\text{m}^2 \text{ h}$ (using the MUCCI, 1986, equation) is used, then the volume of marine cement is an unreasonable 4900 cm^3 per m^2 of substrate. In addition, we have observed a range of biotic and experimental calcite precipitation rates (10^1 to $10^3 \mu\text{mol}/\text{m}^2 \text{ h}$) which do not produce large variations in D_{Sr} values. As a result, we conclude that the difference between the biotic and abiotic trends of Fig. 5 results from precipitation rate differences that are more than two orders of magnitude. As a result, the D_{Sr} -precipitation rate relation of LORENS (1981) may best represent natural system processes.

D_{Mg} and Precipitation Rate

It has been suggested previously that Mg^{2+} incorporation into marine calcite may, in part, be controlled by precipitation rate (e.g., LAHANN and SIEBERT, 1982; GIVEN and WILKINSON, 1985a,b). If the difference in precipitation rate estimated from the disparate Sr contents of biotic and abiotic marine calcite is correct, one concludes that Sr^{2+} is a more sensitive indicator of precipitation rate than Mg^{2+} . This is consistent with the findings of laboratory precipitation experiments [see MORSE (1985) and MORSE and BENDER (1990) for reviews]. However, this observation does not exclude the possibility that Mg^{2+} incorporation may be a function of precipitation rate.

An "Equilibrium" D_{Sr} value

The concept of an "equilibrium" D_{Sr} value for LMC is generally accepted (e.g., HOLLAND, 1960; 1962, 1966; LERMAN, 1965; MUCCI and MORSE, 1983). HOLLAND'S (1960) D_{Sr} value of $0.14 \pm (0.02)$, for calcite precipitated from a Mg-free, non-seawater solution has been accepted as the equilibrium D_{Sr} value for marine calcite because of its agreement with the Sr content of marine LMC (e.g., BENDER et al., 1975). In light of the findings of LORENS (1978, 1981), MUCCI and MORSE (1983), OHIDE and KITANO (1984), and CARPENTER et al. (1991), the concept of a fixed value seems untenable. KATZ et al. (1972), LORENS (1978), BAKER et al. (1982), and more recently, APITZ et al. (1990) have obtained D_{Sr} values for LMC of less than 0.06. The lowest value, 0.026 ± 0.003 is comparable to the D_{Sr} values associated with the slowest precipitation rates of the LORENS (1978, 1981) experiments (Fig. 1b). Therefore, we conclude that these lower values most closely represent "equilibrium" D_{Sr} values for LMC. Although true chemical equilibrium may not be achieved at temperatures near 25°C , biotically and experimentally precipitated marine calcite containing from 1000 to 3000 ppm Sr must be interpreted as the result of kinetically controlled precipitation (Fig. 5; LORENS, 1981; MUCCI, 1986). In contrast, abiotic marine calcite, with its low Sr contents, more closely approximates equilibrium conditions. To characterize abiotic precipitation rates, future laboratory experiments should attempt to replicate the Sr and Mg contents observed in Fig. 2. Even though the low precipitation rates needed to reproduce abiotic calcite compositions may yield small quantities of calcite overgrowths, attempts at approaching these rates should be made.

The observation that abiotic marine cements are precipitated in carbon and oxygen isotope equilibrium with ambient seawater (e.g., GONZALEZ and LOHMANN, 1985; CARPENTER et al., 1991), and that biotic carbonates are often not in isotopic equilibrium or have vital effects often due to kinetic fractionation (e.g., MCCONNAUGHEY, 1989), is consistent with the rate-controlled offset in D_{Sr} values seen in Fig. 5. Given the significant difference between the Sr contents of biotic and abiotic marine calcite and the relation between D_{Sr} and precipitation rate, the relation between D_{Sr} and kinetic fractionation of carbon and oxygen isotopes in biotic marine calcite should be examined.

Marine Crustaceans: An Exception to the Rule?

One biotic marine calcite which deviates from the trend of Fig. 3 is that of marine crustaceans. As a group, crustaceans which include barnacles (1.0 to 1.6 mol% MgCO_3 ; PILKEY and HARRISS, 1966), ostracodes (0.8 to 10.8 mol% MgCO_3 ; CADOT et al., 1972; BURKE and BISCHOFF, 1989) and decapods (2.0 to 13.2 mol% MgCO_3 ; MILLIMAN, 1974), have significantly higher Sr contents than other biotic marine calcite. LMC barnacles contain from 2300 to 2600 ppm Sr (PILKEY and HARRISS, 1966). Ostracodes contain from 2800 to 3700 ppm Sr (BURKE and BISCHOFF, 1989) and decapods (*Cancer sp.* and *Carcinus sp.*) contain from 3000 to 5500 ppm Sr (Compilation of data from MILLIMAN, 1974). Although a crude Sr-Mg covariance is observed for crustacean calcite ($y = 0.05x + 2600$; $r^2 = 0.41$), the accuracy of this trend is suspect as few reliable analyses of decapod calcite are available. We anticipate that additional analyses of marine crustacean calcite will produce a Sr-Mg covariance with a slope comparable to that of other biotic calcite data, yet with higher Sr contents.

The relatively high Sr content of marine crustaceans suggests that their mode of calcite precipitation differs significantly from other marine organisms. Based on the arguments previously presented, elevated Sr contents suggest very rapid precipitation rates. This is supported by the rapid shell accretion in the barnacle *Balanus triganus* (3.9 mm of growth in its first two weeks of life; MILLIMAN, 1974). Many workers have reported shell accretion in barnacles of 15 to 30 mm per year (MILLIMAN, 1974). Rapid growth is attributed to the relatively short life span of many barnacles (approximately one year). We conclude that the observed difference in the Sr contents of foraminifera and barnacles, both short-lived organisms composed of LMC, is the result of higher precipitation rates for barnacle calcite.

Other crustaceans also undergo rapid shell formation (e.g., LOWENSTAM and WEINER, 1989; DALINGWATER and MUTVEI, 1990). Periodic molting or loss and re-growth of ostracode and decapod exoskeletons necessitates extremely rapid production of skeletal material and thus, calcite precipitation (e.g., BURKE and BISCHOFF, 1989). In a discussion of rapid skeletogenesis in crustaceans, LOWENSTAM and WEINER (1989) describe Crustaceans as "the champions of mineral mobilization and deposition in the animal kingdom." Although we have not presented a comprehensive discussion of crustacean physiology and chemistry, further examination of the relation between precipitation rates and D_{Sr} in organ-

isms with rapid skeleton accretion rates, such as crustaceans, may be warranted.

Future Applications

Characterization of Sr-Mg trends for Holocene marine calcite provides a means of comparing analogous trends from ancient materials to help constrain the Sr, Mg, and Ca content of ancient oceans. CARPENTER et al. (1991) provide a description of this method in their comparison of Sr/Mg ratios of Holocene and Devonian marine cements. This method requires analysis of well-preserved ancient materials with a range of Mg contents. Given such a data set, Holocene trends can be compared with analogous trends from other time periods to provide estimates of seawater Sr/Ca and Mg/Ca ratios. These in turn can be used to model global processes controlling the Sr, Mg, and Ca content of seawater (i.e., sea floor hydrothermal activity, evaporite and dolomite formation, continental weathering, and changes in riverine fluxes, glaciation, and the dominance of aragonite vs. calcite precipitation from seawater).

CONCLUSIONS

- 1) On the basis of Sr and Mg contents of Holocene biotic and abiotic marine calcite, it is apparent that for samples with equivalent Mg contents, biotic calcite contains significantly more Sr²⁺ than abiotic calcite. The biotic and abiotic trends are distinct, due to their different Sr contents, yet their slopes are indistinguishable [0.024 (±0.004) and 0.027 (±0.002), respectively]. This produces two parallel Sr-Mg trends (over a wide range of Mg contents) that are offset by approximately 1250 ppm Sr. This offset is the result of precipitation rates in biotic calcite that are five orders of magnitude higher than that of the abiotic calcite. It is proposed that the slopes of these trends are indicative of the Mg/Ca and Sr/Ca ratios of modern seawater and that secular variations in these ratios would produce trends with different concentrations and slopes. Comparison of modern trends (either biotic or abiotic) with analogous ancient trends provides a means of estimating the Mg/Ca and Sr/Ca ratios of ancient seawater.
- 2) Similarities between the D_{Sr} values for biotic and experimental marine calcite suggest that both precipitate at approximately the same rate. This is confirmed by estimates of surface-area normalized precipitation rates in foraminifera. Laboratory precipitation rates for abiotic calcite are too high to reproduce the Sr contents found in natural system, abiotic marine calcite. Attempts at lowering precipitation rates in laboratory experiments to replicate natural system D_{Sr} values are recommended.
- 3) The Sr content of naturally occurring abiotic marine calcite more closely approximates equilibrium conditions than biotic or experimental precipitates. This is consistent with previous findings that, unlike many biotic precipitates, abiotic marine cements are precipitated in isotopic equilibrium with ambient seawater. Further characterization of precipitation rates, D_{Sr} values, and carbon and oxygen isotope fractionation is warranted.

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