

$\delta^{18}\text{O}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Mg ratios of Late Devonian abiotic marine calcite: Implications for the composition of ancient seawater

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Abstract—Late Devonian (Frasnian) abiotic marine calcite has been microsampled and analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, and minor element concentrations. Portions of marine cement crystals from the Alberta and Canning Basins have escaped diagenetic alteration and preserve original marine $\delta^{18}\text{O}$ values ($-4.8\text{‰} \pm 0.5$, PDB), $\delta^{13}\text{C}$ values ($+2.0$ to $+3.0\text{‰}$, PDB), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70805 ± 3), and Sr/Mg weight ratios (0.04 to 0.05). Marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are globally consistent and can be correlated within the Alberta Basin, and among the Alberta, Canning, and Williston Basins. Correlation of isotopic and chemical data strengthen the conclusion that marine cements from the Leduc Formation preserve original marine $\delta^{18}\text{O}$ values which are 3 to 4‰ lower than those of modern marine cements. These low $\delta^{18}\text{O}$ values are best explained by precipitation from ^{18}O -depleted seawater and not by elevated seawater temperature or diagenetic alteration.

For comparison with Devonian data, analogous data were collected from Holocene Mg-calcite and aragonite marine cements from Enewetak Atoll, Marshall Islands. Mg-calcite and aragonite marine cements are in isotopic equilibrium with ambient seawater, and Mg-calcite cements are homogeneous with respect to Sr and Mg contents. Empirically derived homogeneous distribution coefficients for Mg and Sr in modern, abiotic Mg-calcite from Enewetak Atoll are 0.034 and 0.15, respectively. An equation describing the dependence of D_{Sr} on Mg content was based on a compilation of Sr and Mg data from Holocene abiotic marine calcite ($D_{\text{Sr}} = 3.52 \times 10^{-6}$ (ppm Mg) + 6.20×10^{-3}). Unlike that derived from experimental data, this Sr-Mg relation is consistent over a range of 4 to 20 mol% MgCO_3 and may represent precipitation phenomena which are minimally controlled by kinetic effects. Comparison of Sr and Mg contents of analogous Devonian and Holocene marine cements suggests that the Mg/Ca ratio of Late Devonian seawater was significantly lower and that the Sr/Ca ratio was significantly higher than that of modern seawater.

INTRODUCTION

MECHANISMS RESPONSIBLE for the variation in $\delta^{18}\text{O}$ values of ancient marine minerals have long been the focus of debate among stable isotope geochemists, paleontologists, and geologists. MUEHLENBACHS and CLAYTON (1976) and GREGORY and TAYLOR (1981) argued that the $\delta^{18}\text{O}$ value of seawater is buffered at approximately 0‰ (SMOW) due to a balance of low- and high-temperature exchange reactions with crustal silicate minerals. However, BARRETT and FRIEDRICHSEN (1989) suggest that low temperature exchange reactions may dominate in some ophiolite sequences, implying a possible isotopic imbalance between the reactions controlling the $\delta^{18}\text{O}$ value of seawater. Re-evaluation of oceanic oxygen fluxes by HOLLAND (1984) indicates that the $\delta^{18}\text{O}$ value of seawater may change more rapidly than proposed by MUEHLENBACHS and CLAYTON (1976). In contrast to a constant $\delta^{18}\text{O}$ value for seawater, marine minerals from Phanerozoic age rocks have highly variable $\delta^{18}\text{O}$ values (e.g., SHEMESH et al., 1983; LUZ et al., 1984; KARHU and EPSTEIN, 1986; VEIZER et al., 1986). In the Phanerozoic record, Cambrian-Devonian marine carbonates have low $\delta^{18}\text{O}$ values ($< -4.0\text{‰}$ PDB) and post-Devonian marine carbonates have higher $\delta^{18}\text{O}$ values

($> -2.0\text{‰}$ PDB), indicating a rapid increase in $\delta^{18}\text{O}$ values at the end of the Devonian (VEIZER et al., 1986; POPP et al., 1986a; LOHMANN and WALKER, 1989; Fig. 1).

Explanations offered for the low $\delta^{18}\text{O}$ values of lower Paleozoic marine minerals range from elevated seawater temperatures (e.g., KARHU and EPSTEIN, 1986, 1990), to exchange with diagenetic fluids (e.g., DEGENS and EPSTEIN, 1962), to precipitation from ^{18}O -depleted seawater (e.g., WEBER, 1967; FRITZ, 1971; PERRY and TAN, 1972; VEIZER et al., 1986; LOHMANN and WALKER, 1989; PERRY, 1990). Using combined petrographic and chemical techniques, diagenetic alteration and/or preservation of marine calcite can be assessed directly (e.g., GIVEN and LOHMANN, 1985; POPP et al., 1986a,b; CARPENTER and LOHMANN, 1989). In addition, global correlation of anomalously low $\delta^{18}\text{O}$ values for marine calcite of a given age could narrow the range of possible explanations to elevated seawater temperatures and/or ^{18}O -depleted seawater.

Coordinated measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, and minor element concentrations from the same sample or identical splits provides a powerful method for quantifying water-rock interactions in marine carbonates (e.g., BANNER et al., 1988; MEYERS, 1989; MOLDOVANYI et al., 1990; GAO, 1990; BANNER and HANSON, 1990). In addition,

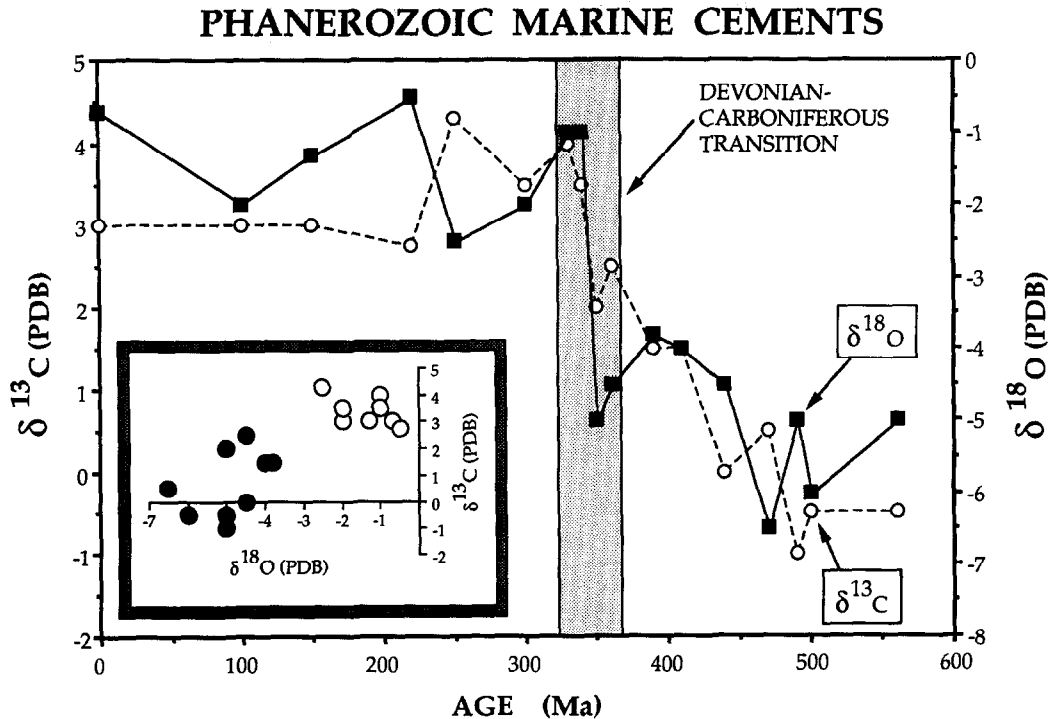


FIG. 1. $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ plot of Phanerozoic marine cement data depicting the dramatic change in the $\delta^{18}\text{O}$ values of marine calcite occurring at the end of the Devonian. Both the inset plot and the main plot indicate that $\delta^{13}\text{C}$ values also change at this time, thus dividing pre-Late Devonian and post-Late Devonian marine carbonates compositions. In the inset, filled circles represent Cambrian through Devonian marine cement data and open circles represent post-Devonian marine cement data. Modified from LOHMANN and WALKER (1989).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of well-preserved marine carbonates can also be used for chemostratigraphic correlation (e.g., KOEPNICK et al., 1985; DEPAOLO and INGRAM, 1985; PALMER and ELDERFIELD, 1985; CAPO and DEPAOLO, 1990). Compilation of such data can define long term secular variations in marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for examination of global strontium fluxes (e.g., VEIZER and COMPSTON, 1974; BRASS, 1976; BURKE et al., 1982). However, diagenetic alteration and poor temporal resolution of Paleozoic and Mesozoic samples make accurate definition of secular variations somewhat more difficult. In these cases, evaluation of diagenetic alteration, sampling with high temporal resolution, and global correlation of data are needed. Therefore, coordinated isotopic and minor element analysis of microsamples (below the scale of diagenetic heterogeneity) from carefully selected marine carbonates is imperative in accurately determining secular variations in the composition of seawater.

In recent years, there has been debate over the choice of analyzing abiotic or biotic marine carbonate as proxy indicators of ancient ocean chemistry. Due to their stable low Mg-calcite shells, brachiopods have been the focus of many geochemical studies (e.g., LOWENSTAM, 1961; VEIZER and COMPSTON, 1974; VEIZER et al., 1986; POPP et al., 1986a,b; BRAND, 1989; RUSH and CHAFETZ, 1990). However, the biochemical processes of brachiopod shell precipitation are still in question and shell calcite may or may not be in oxygen isotope equilibrium with ambient seawater (e.g., LOWENSTAM, 1961; HIEBERT et al., 1988; CARPENTER and LOHMANN, 1990). The $\delta^{13}\text{C}$ values and minor element contents

are biologically mediated and probably do not reflect the chemical and isotopic composition of the seawater from which they precipitate (e.g., WEFER, 1985; VEIZER et al., 1986; RUSH and CHAFETZ, 1990). To avoid possible biological fractionation or "vital effects" we have focused our analyses on abiotic marine calcite or marine cements (e.g., GONZALEZ and LOHMANN, 1985). For comparison, analyses of co-occurring brachiopod samples have been made when possible.

Attempts to constrain the isotopic and chemical composition of ancient seawater using a proxy indicator, such as marine calcite, rely on our understanding of processes which control the composition of the precipitated phase. Therefore, estimates of the $\delta^{18}\text{O}$ value and the Sr/Ca and Mg/Ca molar ratios of Devonian seawater are a function of sample preservation and our knowledge of distribution coefficients for calcite in experimental and natural systems.

The purpose of this study is to determine the primary $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and minor element contents of abiotic marine calcite in two Late Devonian (Frasnian) reefs from the Alberta Basin of western Canada (Fig. 2). For the purpose of global correlation, Late Devonian marine cements from the Canning Basin of Australia are also analyzed. To provide a comparative baseline for Devonian marine cements, Holocene abiotic high Mg-calcite (HMC) and aragonite (ARAG) from Enewetak Atoll are analyzed using a similar multi-tracer approach. These measurements, together with experimental and empirical data, are used to constrain the $\delta^{18}\text{O}$ value and Sr and Mg contents of Late Devonian seawater.

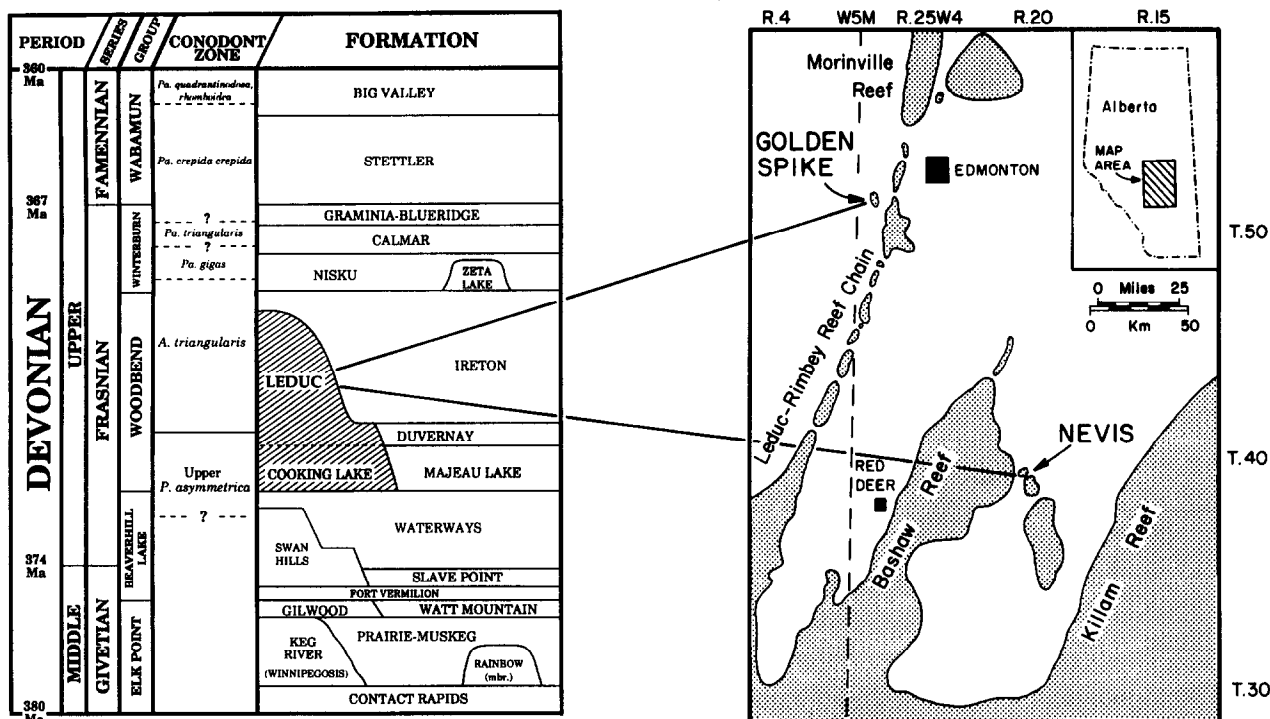


FIG. 2. Location map and generalized stratigraphic sequence. The diagonally ruled area of the stratigraphic cross-section is the Leduc Formation. Tentative conodont zones (ZIEGLER, 1962) are a compilation of data from MOUND (1968), POLLOCK (1968), and KOSCIUSKO (1987). Approximate absolute ages are from HARLAND et al. (1982). Modified from CARPENTER and LOHMANN (1989).

GEOLOGIC SETTING AND PREVIOUS RESEARCH

Golden Spike and Nevis are Upper Devonian (Frasnian) limestone reefs located approximately 35 km southwest and 170 km southeast of Edmonton, Alberta, Canada (Fig. 2). Both are located in the subsurface of the Alberta Basin and are part of the Middle Frasnian Leduc Formation (ANDRICHUK, 1958; MCGILLIVRAY and MOUNTJOY, 1975). Preliminary conodont biostratigraphy places the Leduc Formation in the *A. triangularis* conodont zone (MOUND, 1968; POLLOCK, 1968; KOSCIUSKO, 1987; Fig. 2). Both the Golden Spike and Nevis pinnacle reefs developed on the platform margin and are composed primarily of stromatoporoids, corals, and coralline algae. (MCGILLIVRAY and MOUNTJOY, 1975; WALLS et al., 1979). Both reefs have undergone similar burial histories and have escaped regional dolomitization.

Previous studies provide a detailed lithofacies description of the Golden Spike reef (MCGILLIVRAY and MOUNTJOY, 1975; WALLS, 1977; WALLS et al., 1979). WALLS et al. (1979) have divided the Golden Spike reef into reef interior facies, consisting of subtidal skeletal sand flats, peritidal laminites, and patch reefs, and reef margin facies, consisting of reef and reef flank debris. Reef margin facies contain abundant marine cement (radial fibrous calcite (RAFC)); WALLS et al., 1979; WALLS and BURROWES, 1985; CARPENTER and LOHMANN, 1989) due to the high initial porosity and the continuous, wave-induced flow of seawater through pores (e.g., LAND et al., 1989).

Previous workers have compiled a large quantity of petrographic and stable isotope data from the Golden Spike reef. Petrographic and stable isotope data of WALLS et al. (1979) and WALLS and BURROWES (1985) provided the basis for a subsequent study by CARPENTER and LOHMANN (1989) who documented the petrographic and geochemical ($\delta^{18}O$, $\delta^{13}C$, and minor element) variations in marine and diagenetic cements from the Golden Spike and Nevis reefs. These studies have outlined the diagenetic evolution of the reefs from early marine cementation to meteoric diagenesis, stylolitization, and burial-related cementation. Moreover, CARPENTER and LOHMANN (1989) found a positive correlation between inclusion density and diagenetic alteration of RAFC and proposed that inclusion-free samples preserve

original marine $\delta^{18}O$ and $\delta^{13}C$ values. Importantly, this study also indicated that other chemical tracers should be retained within the unaltered marine cements.

All data in this study are new analyses from previously described specimens. Unlike the previous study of CARPENTER and LOHMANN (1989), which used electron microprobe analyses, here we present minor element contents measured by ICP-AES (inductively coupled plasma atomic emission spectrometry) coupled with Sr, C, and O isotope ratios.

Holocene marine cement samples from Enewetak Atoll, Marshall Islands, are from cores taken from the windward reef flat of Enewetak (Fred) Island. Core E1 was taken from the algal ridge and core E2 was taken equidistant between the algal ridge and the beach. Magnesium contents of the calcite marine cements from these core samples have been described previously (VIDETICH, 1982, 1985).

METHODS

Previous studies of ancient marine chemistry have analyzed bulk or whole-rock samples (e.g., BURKE et al., 1982). Some multi-tracer studies have utilized up to 25 mg of calcite (POPP et al., 1986a,b) while others have utilized 1 to 5 mg samples (MOLDOVANYI et al., 1990). Due to the chemical heterogeneity of most ancient marine limestones, bulk or whole-rock analysis precludes measurement of a single homogeneous phase. To avoid mixing marine and non-marine phases, analytical procedures were optimized to analyze microsamples of $CaCO_3$ (1.0 to 1.5 mg of total sample) for Sr, O, and C isotope ratios as well as Mg, Sr, Fe, and Mn contents.

Strontium Isotope Analyses

Microsamples of powdered calcite were drilled from polished rock chips using a microscope-mounted drill assembly. A 500 μm dental burr and, when necessary, a faceted 20 μm drill bit were used for sampling. Approximately 1.0 mg of calcite was extracted for each sample, and approximately 0.2 to 0.5 mg was delivered to an acid-cleaned 1.5 mL polypropylene centrifuge tube for Sr isotope prepa-

ration, 0.2 to 0.5 mg to an acid-cleaned 1.5 mL polypropylene centrifuge tube for minor element analysis, and the remainder (approximately 0.2 mg) was delivered to a stainless steel sample container for C and O isotope analysis. Carbon and oxygen isotope samples were roasted *in vacuo* at 380°C to remove volatile contaminants. Strontium isotope samples were not treated until they were dissolved in 1 mL of 2.5 N HCl for approximately 10 min. Following dissolution, samples were loaded directly onto ion exchange columns.

Standard cation exchange procedures were used to separate Sr from interfering matrix elements (principally Ca) using 2.5 N HCl. As the matrix is dominated by Ca and the total mass of Sr is low (<100 ng), 3.5 mL of Biorad AG 1-X16 was used rather than the more conventionally used Biorad AG 1-X8 exchange resin. Evaporated separates were dissolved in dilute HNO₃ and loaded on a single zone-refined Re filament with a 1 µL drop of dilute H₃PO₄ containing a slurry of ultrapure Ta₂O₅. Such procedures yield blanks that contain less than 40 picograms of Sr. Strontium isotope ratios were measured on a VG Sector multi-collector mass spectrometer using peak hopping multidynamic analysis. The mean ⁸⁷Sr/⁸⁶Sr ratio for NBS-987 measured at the time of these analyses was 0.710245 ± 4 (2σ mean, N = 55) and the mean ⁸⁷Sr/⁸⁶Sr ratio for EN-1 (USGS Giant Clam Standard) measured at the time of these analyses was 0.709179 ± 7 (2σ mean, N = 22).

Carbon and Oxygen Isotope Analyses

Samples of Devonian CaCO₃ were reacted with anhydrous phosphoric acid at 55°C in an on-line gas extraction system coupled to the inlet of a Micromass VG-602E mass spectrometer. Samples of Holocene CaCO₃ were reacted at 73°C with 3 drops of anhydrous phosphoric acid in individual reaction vessels of an on-line, automated carbonate reaction device (Kiel Device) coupled to a Finnigan-MAT 251 mass spectrometer. Isotopic ratios were corrected for ¹⁷O contribution and are reported in per-mil (‰) relative to the PDB standard. Precision was monitored through daily analyses of the NBS-20 calcite standard and is better than 0.1‰ (1σ) for both C and O isotope compositions.

Minor Element Analyses

Samples of CaCO₃ were dissolved in 1 mL of dilute HCl-HNO₃. Concentrations of Ca, Mg, Sr, Fe, and Mn were determined simultaneously by ICP-AES using a Leeman Labs Plasma-Spec III. Analytical precision, based on gravimetric standards, was ±1.1% for Ca, ±1.7% for Mg, ±1.0% for Sr. The precision of trace metal analyses is typically worse for small CaCO₃ samples (5 to 10%). Detection limits (in solution) were 20 ppb for Fe and 2 ppb for Mn.

Raw cation concentration data were converted to weights of MeCO₃ and total weights of MeCO₃ species were used to convert to ppm. Data have not been normalized to a specific Ca concentration, because of significant amounts of MgCO₃ substitution. Mol% MgCO₃ was calculated using the contribution of all cations measured and was normalized to 100%. Sr/Mg ratios are calculated on a weight basis.

Location and Depth Information

All township and range locations of cores are abbreviated to the first two location numbers (e.g., 11-23 which refers to 11-23-51-27W4). All Golden Spike locations end with #-#-51-27W4 and the Nevis location is 6-13-38-22W4. To avoid future sampling confusion, all core depths are reported in feet below surface and have not been converted to SI units.

RESULTS

Abiotic Marine Calcite from the Alberta Basin, Canada

Inclusion-free RAFC was sampled from five well locations in the Golden Spike reef complex and one well location in the Nevis reef. Samples have been analyzed from various

depths within the reef and reef margin facies of both reefs to assess possible spatial and temporal heterogeneities (e.g., CARPENTER and LOHMANN, 1989). There are no measurable differences in the δ¹⁸O values or ⁸⁷Sr/⁸⁶Sr ratios between clear RAFC in either reef. These cements have the highest δ¹⁸O values (Golden Spike: -4.5 to -5.4‰ and Nevis: -4.3 to -5.2‰) and lowest ⁸⁷Sr/⁸⁶Sr ratios of all cements analyzed (Golden Spike: 0.70805 to 0.70809 and Nevis: 0.70801 to 0.70807; Table 1; Fig. 3). These low ⁸⁷Sr/⁸⁶Sr ratios and high δ¹⁸O values are from samples that do not luminesce under cathodoluminescence (CL) and, petrographically, show no signs of alteration. In general, clear RAFC has higher concentrations of Mg and Sr than its inclusion-rich counterpart. However, some overlap of clear and cloudy RAFC chemical compositions is apparent (Fig. 4; Table 1). These similarities may result from variable degrees of water-rock interaction and the inherent variability found among different crystals and locations.

Magnesium concentrations in clear RAFC from the Golden Spike and Nevis reefs range from 5000 to 8240 ppm (2.1 to 3.4 mol% MgCO₃) and 5720 to 8690 ppm (2.4 to 3.6 mol% MgCO₃), respectively (Fig. 4; Table 1), and are consistent with electron microprobe data of CARPENTER and LOHMANN (1989). Similarly, Sr contents of clear RAFC are comparable in both reefs (Golden Spike: 198 to 375 ppm, Nevis: 259 to 389 ppm; Fig. 4; Table 1). These values are the highest among the abiotically precipitated cements in both reefs. The Sr/Mg ratios of clear RAFC vary from 0.040 to 0.047 in the Golden Spike reef and from 0.037 to 0.068 in the Nevis reef. Iron and manganese contents of clear RAFC from both reefs are typically below 100 ppm and 25 ppm, respectively (Table 1).

Cloudy RAFC has lower and more variable δ¹⁸O values (Golden Spike: -5.1 to -7.9‰ and Nevis: -4.9 to -9.7‰) and higher, more variable ⁸⁷Sr/⁸⁶Sr ratios (Golden Spike: 0.70807 to 0.70823 and Nevis: 0.70808 to 0.70829) than does clear RAFC (Table 1; Fig. 3). With the exception of depth-related, temporal variations in the δ¹³C values of marine cements (i.e., δ¹³C values decrease with depth, CARPENTER and LOHMANN, 1989), there are no systematic isotopic or chemical variations with respect to facies or depth. Iron and manganese contents are slightly higher than those of clear RAFC (Table 1). Cloudy RAFC is typically depleted in Mg and Sr relative to clear RAFC. Although a few samples from the Nevis reef have Mg and Sr contents comparable to clear RAFC (Fig. 4; Table 1), the Sr and Mg contents of cloudy RAFC are always lower than those of clear RAFC in the same crystal. Despite alteration, cloudy RAFC retains Sr/Mg ratios similar to those observed in clear RAFC, varying from 0.034 to 0.082 in the Golden Spike reef and from 0.040 to 0.075 in the Nevis reef (Table 1).

Abiotic Marine Calcite from the Canning Basin, Australia

Samples of RAFC from the Virgin Hills Formation have been categorized as altered and unaltered on the basis of petrographic characteristics. Unaltered RAFC crystals are a composite of distinct fibrous to bladed subcrystal domains, which are nonluminescent in CL and do not contain micro-

dolomite inclusions. Altered RAFC crystals contain ghost fabrics of composite subcrystals, have areas of bright luminescence, and contain microdolomite inclusions. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of unaltered marine cements from the Canning Basin of Australia are the same as those cements from the Alberta Basin ($\delta^{18}\text{O} = -4.5$ to -5.3‰ and $\delta^{13}\text{C} = +2.1$ to $+2.4\text{‰}$; e.g., HURLEY and LOHMANN, 1989; CARPENTER and LOHMANN, 1989). Three samples of unaltered RAFC from the Frasnian Virgin Hills Formation have $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which are within the analytical error of data from clear RAFC in the Golden Spike and Nevis reef of Alberta (-4.8 to -5.3‰ , 0.70808 to 0.70810; Fig. 3; Table 1). Altered samples of RAFC have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those of cloudy RAFC from the Alberta Basin (0.70814 to 0.70877; Fig. 3; Table 1). Like clear RAFC from Alberta, marine cements with the highest $\delta^{18}\text{O}$ values and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have the highest Mg and Sr contents (Table 1). Relative to RAFC from the Golden Spike and Nevis reefs of Alberta, Australian RAFC contains significantly more Mg and Sr, yet has comparable Sr/Mg ratios (0.040 to 0.075; Table 1, Fig. 4).

Brachiopod Shell Material

Brachiopods sampled from both the Golden Spike and Nevis reefs are generally well preserved, in most cases non-luminescent, and where possible, are from the same hand sample as marine cements. The variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ values is comparable to that observed in clear and cloudy RAFC (Fig. 3; Table 1). Relative to clear RAFC, brachiopod shell material from both the Golden Spike and Nevis reefs have lower Mg and higher Sr, Fe, and Mn concentrations. Unlike both clear and cloudy RAFC, the Sr/Mg ratios of brachiopod shell material are highly variable (Table 1).

Holocene Abiotic Marine Calcite and Aragonite from Enewetak Atoll

Calcite marine cement from the windward reef flat of Enewetak Atoll varies little in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values ($< \pm 0.3\text{‰}$; Fig. 5; Table 2). $\delta^{18}\text{O}$ values range from -1.1 to -1.6‰ and $\delta^{13}\text{C}$ values range from $+3.5$ to $+3.8\text{‰}$. These values are slightly higher than calculated equilibrium values (Fig. 5). Magnesium contents of calcite cements range from 15.7 to 20.5 mol% MgCO_3 and are consistent with electron microprobe analyses of the same materials by VIDETICH (1985). Strontium contents range from 970 to 1700 ppm. The Sr/Mg ratios range from 0.023 to 0.039 (Table 2).

Aragonite marine cement has $\delta^{18}\text{O}$ values comparable to those of co-existing calcite cements (-1.1 to -1.5‰), but has higher $\delta^{13}\text{C}$ values ($+4.6$ to $+4.9\text{‰}$) (Fig. 5; Table 2). The $\delta^{18}\text{O}$ values are higher than calculated equilibrium values (Fig. 5). Strontium contents range from 8,240 to 12,300 ppm and magnesium contents range from 181 to 4,170 ppm (Table 2). The Sr/Mg ratios are highly variable and range from 1.9 to 50. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of calcite and aragonite marine cements and skeletal material substrate are consistent with modern marine carbonate and EN-1 Standard ratios (0.70916 to 0.70920; Table 2).

DISCUSSION

Preservation of Primary $^{87}\text{Sr}/^{86}\text{Sr}$ Ratios and $\delta^{18}\text{O}$ Values and Sr/Mg Ratios

Several lines of petrographic and chemical evidence suggest that clear RAFC from the Golden Spike and Nevis reefs has escaped alteration by late diagenetic fluids and thereby preserves original marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ values. In contrast, cloudy RAFC has undergone variable amounts of diagenetic alteration. These conclusions are based on the following petrographic observations and chemical data (CARPENTER and LOHMANN, 1989):

- 1) Clear RAFC occurs in the interior of crystals, whereas cloudy RAFC occurs directly adjacent to inter-crystalline- and macro-pores, where the potential reaction with later diagenetic fluids is greatest.
- 2) Clear RAFC does not contain microdolomite or have neomorphic fabrics, whereas cloudy RAFC has abundant microdolomite (e.g., LOHMANN and MEYERS, 1977).
- 3) Clear RAFC is uniformly nonluminescent, whereas cloudy RAFC is brightly luminescent in CL.
- 4) Clear RAFC has the highest $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all co-occurring cement phases (Fig. 3; Table 1).
- 5) Clear RAFC has the highest Mg and Sr and lowest Fe and Mn content of all co-occurring cement phases (Fig. 4; Table 1).
- 6) The variation observed in both the $\delta^{18}\text{O}$ values and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all the clear RAFC data from both reefs (Golden Spike: 0.70806 ± 2 , $-4.9 \pm 0.5\text{‰}$ and Nevis: 0.70804 ± 3 , $-4.7 \pm 0.5\text{‰}$) is extremely small and comparable to that of analyses of modern marine carbonates and Sr isotope standards (Fig. 5; Table 2; e.g., BURKE et al., 1982; GONZALEZ and LOHMANN, 1985).
- 7) The isotopic composition of clear RAFC is similar to that of co-occurring LMC brachiopod shells (Fig. 3; Table 1).
- 8) Most importantly, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of clear RAFC from the Golden Spike and Nevis reefs can be correlated globally with those of well-preserved, time equivalent RAFC from the Canning Basin of Australia (Fig. 3; Table 1; CARPENTER and LOHMANN, 1989).

Preservation of clear RAFC may reflect its physical and chemical characteristics. Petrographic evidence of marine cement alteration adjacent to both inter-crystalline and macro pores indicates that alteration was related to flow of diagenetic fluids (e.g., meteoric water) yielding altered crystal margins (cloudy RAFC) and unaltered crystal centers (clear RAFC). If produced early in the diagenetic history of the reef, a stable (diagenetically altered) rind around crystal margins could serve to protect the inner portions of the crystals from further dissolution by later fluid migration (e.g., LOHMANN, 1978; CARPENTER and LOHMANN, 1989). In addition, the Mg content of clear RAFC may also serve to inhibit dissolution and diagenetic alteration; experimental data indicate that calcite with 2 to 5 mol% MgCO_3 is thermodynamically more stable than pure CaCO_3 (BUSENBURG and PLUMMER, 1989). If originally precipitated with these compositions, clear RAFC may be resistant to diagenetic alteration.

Table 1: Isotope and Minor Element Data--Devonian Marine Carbonates

LOCATION/DEPTH COMPONENT	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2 \sigma_{\text{m}}$	Mole % MgCO_3	Mg	Sr (ppm)	Fe	Mn	Sr/Mg
GOLDEN SPIKE REEF										
ALBERTA										
CLEAR RAFC										
15-23: 5365	-4.88	1.63	0.708053	± 17	---	---	---	---	---	---
15-23: 5365	-4.46	1.46	0.708073	± 38	---	---	---	---	---	---
15-23: 5365	-5.15	1.47	0.708064	± 17	---	---	---	---	---	---
15-23: 5375.5	-4.71	1.83	0.708049	± 27	---	---	---	---	---	---
15-23: 5574	-5.21	2.31	0.708082	± 17	---	---	---	---	---	---
9-23: 5811	-4.54	3.20	0.708045	± 14	2.1	5000	198	77	4	0.040
9-27: 5565	-4.93	2.31	0.708059	± 21	2.9	7090	322	36	21	0.045
9-27: 5837	-5.35	1.98	0.708075	± 16	---	---	---	---	---	---
9-27: 5853	-4.75	3.18	0.708047	± 18	3.3	8140	370	41	4	0.045
12-26: 5840.5	-4.92	1.98	0.708050	± 30	---	---	---	---	---	---
12-26: 5840.5	-4.78	1.82	0.708050	± 60	---	---	---	---	---	---
12-26: 5840.5	---	---	---	---	3.1	7430	312	---	---	0.042
12-26: 5840.5	---	---	---	---	2.8	6760	277	64	4	0.041
12-26: 5842	---	---	---	---	3.4	8240	344	< 23	< 5	0.042
12-26: 5842	-4.92	1.79	---	---	3.0	7420	310	49	8	0.042
3-27: 5599	-5.09	1.74	0.708086	± 13	---	---	---	---	---	---
3-27: 5599	-4.89	1.84	0.708088	± 16	---	---	---	---	---	---
3-27: 5599	-4.62	1.98	---	---	3.3	7950	375	81	10	0.047
3-27: 5609	-5.00	1.88	0.708065	± 16	---	---	---	---	---	---
BRACHIOPODS										
11-23: 5684	-5.49	2.11	0.708097	± 27	0.8	1840	150	442	47	0.082
12-26: 5864	-6.64	2.08	0.708070	± 14	1.7	4180	469	326	49	0.112
12-24: 5794	-4.19	3.70	0.708042	± 17	0.2	504	706	< 144	< 29	1.400
12-24: 5794	-4.44	4.62	0.708080	± 14	0.3	603	484	< 38	< 8	0.803
12-24: 5869	-4.66	3.46	0.708044	± 23	---	---	---	---	---	---
CLOUDY RAFC										
15-23: 5365	-4.99	1.49	0.708137	± 16	---	---	---	---	---	---
15-23: 5365	-6.45	1.58	0.708111	± 25	---	---	---	---	---	---
15-23: 5365	-7.90	1.70	0.708165	± 17	---	---	---	---	---	---
15-23: 5375.5	-6.76	1.74	0.708195	± 15	---	---	---	---	---	---
15-23: 5574	-5.45	2.63	0.708090	± 14	---	---	---	---	---	---
3-27: 5599	-7.39	1.95	0.708089	± 14	2.4	5590	221	170	45	0.040
3-27: 5609	-6.45	2.03	0.708153	± 28	---	---	---	---	---	---
12-26: 5840.5	-5.11	2.93	0.708068	± 25	---	---	---	---	---	---
12-26: 5840.5	-7.43	2.19	0.708236	± 14	---	---	---	---	---	---
12-26: 5840.5	-7.55	2.39	0.708102	± 21	---	---	---	---	---	---
12-26: 5840.5	---	---	---	---	0.8	1940	159	96	43	0.082
12-26: 5842	---	---	---	---	2.2	5430	208	70	19	0.038
12-26: 5842	-7.27	1.86	---	---	2.2	5310	180	144	43	0.034
11-23: 5688	-5.35	2.02	0.708232	± 20	---	---	---	---	---	---
9-27: 5565	-5.96	2.26	---	---	1.9	4630	244	104	21	0.053
9-27: 5837	-6.77	2.06	0.708085	± 20	---	---	---	---	---	---
9-27: 5853	-7.10	2.74	0.708329	± 14	1.7	4080	138	172	43	0.034
9-23: 5811	-5.78	3.29	0.708084	± 16	3.7	9060	379	369	16	0.042
11-27: 5980	-6.09	1.27	0.708075	± 13	---	---	---	---	---	---

Table 1: Isotope and Minor Element Data--Devonian Marine Carbonates (continued)

LOCATION/DEPTH COMPONENT	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2 \sigma_m$	Mole % MgCO_3	Mg	Sr (ppm)	Fe	Mn	Sr/Mg
<i>NEVIS REEF</i>										
<i>ALBERTA</i>										
<i>CLEAR RAFC</i>										
6-13: 6015	-5.01	1.83	0.708074	± 17	---	---	---	---	---	---
6-13: 6015	-4.64	2.79	0.708055	± 13	---	---	---	---	---	---
6-13: 6015	-5.22	1.88	0.708052	± 16	---	---	---	---	---	---
6-13: 6015	-5.11	2.07	---	---	3.6	8680	318	---	---	0.037
6-13: 6015	---	---	---	---	2.4	5718	389	< 16	13	0.068
6-13: 6226	-4.57	2.66	0.708040	± 20	---	5720	---	---	---	---
6-13: 6226	-4.42	3.25	0.708014	± 11	---	---	---	---	---	---
6-13: 6226	-4.49	3.33	0.708039	± 14	3.1	7570	351	< 16	< 5	0.046
6-13: 6226	-4.57	2.42	0.708058	± 16	---	---	---	---	---	---
6-13: 6226	-4.26	3.28	0.708045	± 25	---	---	---	---	---	---
6-13: 6226	---	---	---	---	2.9	6960	296	< 27	11	0.043
6-13: 6226	---	---	---	---	2.5	6170	259	< 22	12	0.042
<i>BRACHIOPODS</i>										
6-13: 6030	-5.09	2.11	0.708132	± 21	1.2	2790	55	627	231	0.020
6-13: 6226	-4.90	3.21	0.708096	± 20	0.6	1506	254	143	< 32	0.168
6-13: 6226	-4.92	2.58	0.708046	± 16	0.6	1470	692	290	< 32	0.473
<i>CLOUDY RAFC</i>										
6-13: 6015	-9.72	1.63	0.708294	± 17	---	---	---	---	---	---
6-13: 6015	-5.48	1.79	0.708077	± 17	---	---	---	---	---	---
6-13: 6015	-7.51	1.97	0.708401	± 24	---	---	---	---	---	---
6-13: 6015	-7.35	1.95	0.708108	± 14	---	---	---	---	---	---
6-13: 6015	-4.89	1.97	0.708091	± 17	1.8	4490	232	460	76	0.052
6-13: 6015	-6.76	1.65	---	---	2.5	6110	257	124	75	0.042
6-13: 6226	-6.10	3.11	---	---	3.5	8480	301	157	108	0.036
6-13: 6226	-6.88	3.09	0.708084	± 17	---	---	---	---	---	---
6-13: 6226	-7.77	3.17	0.708179	± 21	3.4	8210	315	111	89	0.038
<i>VIRGIN HILLS FM.</i>										
<i>AUSTRALIA</i>										
<i>Unaltered RAFC</i>										
A1.01	-4.78	2.34	0.708084	± 17	6.5	15800	657	71	< 13	0.041
A1.02	-5.23	2.16	0.708094	± 16	5.8	14200	648	81	< 7	0.046
A1.03	-5.25	2.25	0.708097	± 14	7.1	17500	933	< 212	< 43	0.053
A1.04	-4.97	2.31	---	---	6.1	15000	729	120	26	0.049
A1.05	-4.54	2.35	---	---	5.8	14200	662	< 100	30	0.046
A1.06	-4.88	2.27	---	---	6.2	15100	709	< 88	< 18	0.047
A1.07	---	---	---	---	5.5	13400	658	137	< 14	0.049
A1.08	-5.08	2.34	---	---	5.3	12900	682	107	< 16	0.053
<i>Altered RAFC</i>										
A1.09	-5.13	2.42	0.708210	± 14	2.8	6920	310	---	---	0.045
A1.10	-4.81	2.44	0.708144	± 16	4.4	10800	435	308	24	0.040
A1.11	-5.70	2.50	0.708773	± 16	3.4	8320	412	116	25	0.050
A1.12	-4.67	2.69	0.708340	± 16	---	---	---	---	---	---
A1.13	-4.99	2.58	0.708154	± 13	---	---	---	---	---	---
A1.14	-6.62	1.33	0.708373	± 14	6.0	14700	615	376	< 68	0.042
A1.15	-5.86	2.32	---	---	2.4	5770	249	280	203	0.043
A1.16	-4.81	2.59	---	---	1.7	4060	302	162	28	0.075

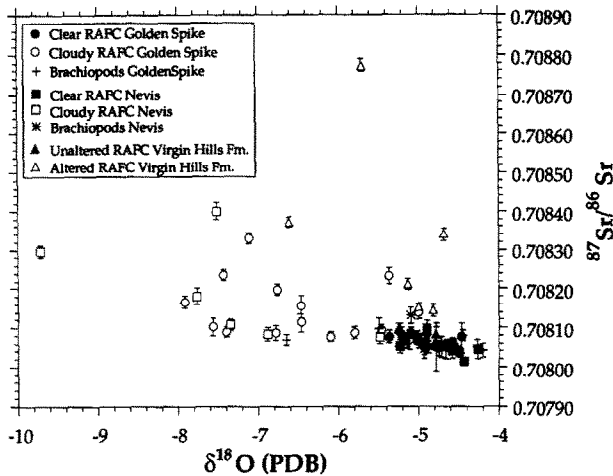


FIG. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ values of marine components from the Golden Spike and Nevis reefs (Middle Frasnian Leduc Formation) of the Alberta Basin and the Virgin Hills Formation (Frasnian) of the Canning Basin, Australia. Data plotted are from Table 1. See inset key for explanation of symbols. Analytical precision for individual Sr isotope analyses is represented by the error bars on each datum.

It has been suggested that the metastable composition of marine cements (HMC and ARAG in modern oceans) precludes their use as accurate isotopic indicators due to their reactivity in diagenetic environments (POPP et al., 1986a). To avoid this potential problem, many workers have chosen to analyze LMC brachiopod shell material which is assumed to be more resistant to diagenetic alteration than HMC and ARAG marine cements (e.g., VEIZER and COMPSTON, 1974; VEIZER et al., 1986; POPP et al., 1986a,b). The data presented here and in previous studies provide evidence that marine cements can preserve their original isotopic compositions despite the presence of diagenetic fluids and alteration of other marine components (e.g., GIVEN and LOHMANN, 1985; CARPENTER and LOHMANN, 1989). In this case, both brachiopod shell material and clear RAFC are equally well pre-

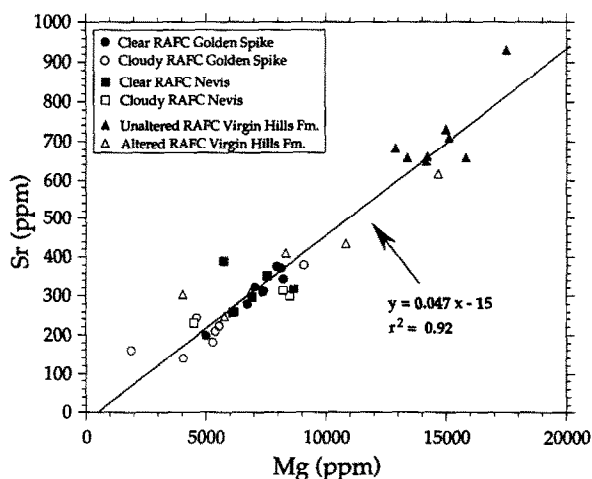


FIG. 4. Magnesium and strontium concentrations of RAFC from the Alberta and Canning Basins. Data from Table 1. See inset key for explanation of symbols.

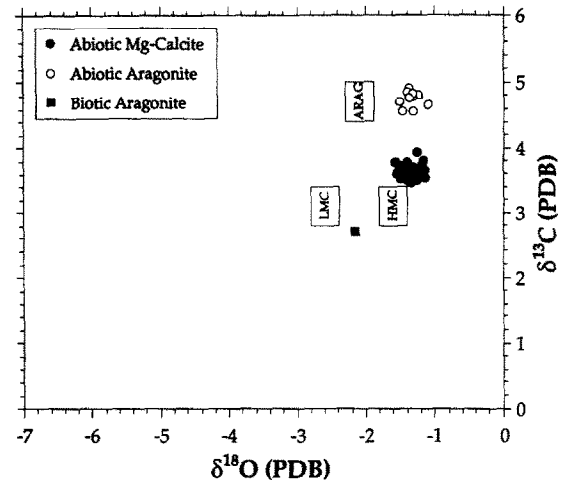


FIG. 5. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of Holocene marine cements from windward reef flat of Enewetak Atoll, Marshall Islands. Shaded rectangles are estimates of the composition of LMC, HMC, and ARAG precipitated in isotopic equilibrium with seawater. Size of the fields can be attributed to the range of observed temperatures ($27\text{--}29^\circ\text{C}$) and the possible variations in $\delta^{13}\text{C}$ values associated with biological activity. LMC $\delta^{18}\text{O}$ values were calculated using the fractionation factor of FRIEDMAN and O'NEIL (1977) for LMC- H_2O ($10^3 \ln \alpha = 2.78(10^6/T^2) - 2.89$); $\delta^{13}\text{C}$ values were calculated using a fractionation factor calculated from EMRICH et al. (1970) for LMC- HCO_3^- ($10^3 \ln \alpha = -0.81(10^6/T^2) + 10.69$). A $\delta^{13}\text{C}$ value of 1.65‰ for dissolved HCO_3^- was used assuming a $\Sigma\text{CO}_2 = 2.0 \times 10^{-5}$ mol/kg, pH of 8.1 and $T = 25^\circ\text{C}$ (e.g., KROOPNICK et al., 1972; KROOPNICK, 1980). HMC $\delta^{18}\text{O}$ values were calculated by adding 1.02‰ to the LMC values to adjust for the 17 mol% MgCO_3 composition (using the 0.06‰ per mol% MgCO_3 relation of TARUTANI et al., 1969). The ARAG field was positioned by using an aragonite-calcite fractionation of $+1.6\text{‰}$ for $\delta^{13}\text{C}$ (e.g., RUBINSON and CLAYTON, 1969) and 0.6‰ for $\delta^{18}\text{O}$ (TARUTANI et al., 1969). The measured aragonite-calcite fractionation for $\delta^{13}\text{C}$ is approximately $+1.2\text{‰}$.

served (Fig. 3; Table 1). Unlike examples of marine cement neomorphism, which involves mineral transformation in an isotopically closed system to preserve original isotopic compositions (e.g., GIVEN and LOHMANN, 1985), clear RAFC from the Golden Spike and Nevis reefs has escaped dissolution-precipitation processes.

An example of the preservation of clear RAFC is the small variability in $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Golden Spike and Nevis samples ($\pm 0.5\text{‰}$ for $\delta^{18}\text{O}$ values and ± 0.00002 for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for several locations and depths). While one could suggest diagenetic homogenization of isotopic and chemical compositions, the extremely variable $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in cloudy RAFC, which has undergone variable degrees of water-rock interaction, suggest otherwise (Fig. 3). In contrast to diagenetic homogenization, the low $\delta^{18}\text{O}$ values of late burial spars from the Golden Spike reef and the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (as low as -12.3‰ and as high as 0.71004 , respectively, CARPENTER, unpubl. data) indicate that diagenesis produces heterogeneous isotopic compositions. In addition, meteoric phreatic spars and vadose cements from the Golden Spike reef (byproducts of interaction between meteoric water and marine rock) have $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which are coincident with the clear and cloudy RAFC data of Fig. 3. The lowest $\delta^{18}\text{O}$ value- $^{87}\text{Sr}/^{86}\text{Sr}$ ratio pair is identical to that of clear RAFC

Table 2: Isotope and Minor Element Data--Holocene Marine Carbonates

LOCATION/AGE COMPONENT	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\sigma_{\text{m}}$	Mole % MgCO_3	Mg	Sr	Fe (ppm)	Mn	Sr/Mg
<i>Enewetak Atoll</i>										
<i>Holocene</i>										
Abiotic Mg-Calcite										
E2.01	-1.40	3.66	---	---	16.9	42100	1060	186	120	0.025
E2.02	-1.25	3.71	---	---	16.7	41700	1060	< 113	34	0.025
E2.03	-1.38	3.75	---	---	15.5	38600	1030	340	64	0.027
E2.04	-1.45	3.70	---	---	16.6	41400	1060	< 502	< 100	0.026
E2.05	-1.13	3.67	---	---	16.3	40700	996	< 212	< 42	0.024
E2.06	---	---	---	---	16.3	40500	1020	429	< 54	0.025
E2.07	-1.38	3.79	---	---	---	---	---	---	---	---
E2.07	-1.26	3.67	0.709156	± 11	17.1	42700	1030	< 161	< 32	0.024
E2.08	-1.47	3.68	---	---	---	---	---	---	---	---
E2.08	-1.48	3.59	0.709172	± 17	16.0	39900	1350	210	47	0.034
E2.09	-1.57	3.78	---	---	18.9	47400	1270	< 190	< 38	0.027
E2.10	-1.18	3.74	---	---	16.5	41200	1120	221	53	0.027
E2.11	-1.47	3.73	---	---	16.5	41100	1100	153	46	0.026
E2.12	-1.31	3.71	---	---	16.9	42300	1060	< 204	< 41	0.025
E2.13	-1.51	3.67	---	---	16.6	41300	1050	< 228	< 46	0.025
E2.14	-1.15	3.81	---	---	17.9	44700	1100	529	< 34	0.025
E2.15	-1.24	3.93	---	---	16.5	41200	972	< 231	< 46	0.024
E2.16	-1.29	3.70	---	---	15.7	39000	1230	< 150	< 30	0.032
E2.17	-1.33	3.62	---	---	15.7	39000	1100	368	< 41	0.028
E2.18	-1.25	3.59	---	---	16.3	40800	1100	192	52	0.027
E1.01	-1.42	3.65	0.709203	± 14	20.5	51600	1430	308	< 56	0.028
E1.02	-1.27	3.58	0.709174	± 13	17.5	43700	1700	300	< 60	0.039
E1.03	-1.55	3.60	---	---	17.5	43800	1050	357	< 51	0.024
E1.04	-1.32	3.59	---	---	17.0	42300	1360	< 205	< 41	0.032
E1.05	-1.24	3.49	---	---	18.1	45200	1620	< 311	< 62	0.036
E1.06	-1.14	3.53	---	---	16.2	40300	1180	310	< 62	0.029
E1.07	-1.49	3.51	---	---	15.9	39600	1000	532	< 37	0.025
E1.08	-1.39	3.49	---	---	16.6	41300	1050	177	27	0.025
E1.09	-1.38	3.56	---	---	16.8	41800	1010	< 163	33	0.024
E1.10	-1.27	3.66	---	---	16.6	41500	1000	270	34	0.024
E1.11	-1.32	3.45	---	---	16.7	41500	970	< 170	< 34	0.023
E1.12	-1.47	3.54	---	---	16.3	40600	1000	308	< 28	0.025
E1.13	-1.34	3.47	---	---	16.4	40800	1320	< 101	< 20	0.032
E1.14	-1.28	3.56	---	---	15.9	39600	1070	267	62	0.027
E1.15	-1.21	3.56	---	---	16.4	40800	1030	< 223	< 45	0.025
Abiotic Aragonite										
E2.19	-1.46	4.55	---	---	0.4	1040	8940	< 452	< 90	8.6
E2.20	-1.31	4.55	---	---	0.2	566	9000	< 246	< 49	16
E2.21	-1.23	4.81	---	---	0.6	1490	12300	< 786	< 157	8.2
E2.22	-1.39	4.91	---	---	0.2	476	8680	< 111	< 22	18
E2.23	-1.36	4.91	0.709181	± 13	1.4	3290	10300	< 214	< 43	3.1
E2.24	-1.51	4.70	---	---	0.6	1480	9870	< 185	< 37	6.7
E2.25	-1.31	4.78	---	---	1.7	4170	7820	< 156	< 31	1.9
E2.26	-1.38	4.85	---	---	0.2	498	8370	151	< 23	17
E2.27	-1.31	4.84	---	---	0.1	246	8620	< 112	< 22	35
E2.28	-1.37	4.76	---	---	0.1	181	9000	117	< 21	50
E2.29	-1.10	4.67	---	---	0.5	1190	8240	209	< 42	6.9
Biotic Aragonite										
E2.30	-2.15	2.72	0.709167	± 13	0.2	559	2300	< 224	< 45	4.1

(-4.6‰ and 0.70807, CARPENTER et al., 1990; CARPENTER, unpubl. data). Intersection of these data trends at the same $\delta^{18}\text{O}$ value and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio suggests that clear RAFC accurately records an original marine rock isotopic composition. As such, clear RAFC either escaped alteration altogether or experienced water-rock interaction under extremely low W/R ratio conditions (Fig. 3).

Comparison of inherent isotopic heterogeneity in modern marine carbonates also suggests preservation of clear RAFC. Variability observed in clear RAFC $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is comparable to the range of ratios measured in modern seawater and marine carbonates (e.g., BURKE et al., 1982; our analyses of the USGS EN-1 standard and other Holocene marine carbonates; Fig. 3; Tables 1, 2). The variability of $\delta^{18}\text{O}$ values in individual samples of recent marine cement is approximately $\pm 0.3\text{‰}$ (e.g., GONZALEZ and LOHMANN, 1985; Fig. 5). Considering the range of temperatures in the upper 100 m of tropical seawater today and the possible admixture of small amounts of diagenetically altered material during sampling, the variability of $\pm 0.5\text{‰}$ observed in clear RAFC, is not unreasonable for an unaltered marine calcite. In comparison, the total variation in $\delta^{18}\text{O}$ values of modern marine cements from the Marshall Islands and Bermuda (representing two different oceans and latitudes with a temperature range of approximately 5°C) is approximately $\pm 1.0\text{‰}$ (GONZALEZ and LOHMANN, 1985). Although intra-basin isotopic variability should be somewhat smaller due to similar temperature and salinity conditions (e.g., variation between the Golden Spike and Nevis reefs), global correlation of marine cement $\delta^{18}\text{O}$ values may still be valid within a $\pm 1.0\text{‰}$ range of values.

Correlation of isotopic data for the Golden Spike and Nevis reefs indicates coeval precipitation of marine cements at two locations in the Alberta Basin (Figs. 2, 3; Table 1). More importantly, unaltered RAFC from the Frasnian of the Canning Basin of Australia have O, C, and Sr isotope ratios which are the same as those of clear RAFC from the Alberta Basin (Fig. 3; Table 1; e.g., HURLEY and LOHMANN, 1989; CARPENTER and LOHMANN, 1989). Although the Sr and O isotope data from both basins have distinctly different diagenetic alteration trends, due to differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr content of local diagenetic fluids, these trends diverge from the same marine composition (Fig. 3). A complicating factor in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio correlation is the potential for absolute age differences between two units which are biostratigraphically correlated. Considering that the Middle Frasnian (~ 370 Ma) is a period of increasing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (e.g., BURKE et al., 1982) and that both the Leduc reefs of Alberta and the Virgin Hills Formation of Australia occur in a time window of approximately 3 to 5 m.y., we conclude that agreement of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to within 0.00003 is a good correlation (e.g., 0.70805 ± 2 vs. 0.70808 ± 2 ; Fig. 3; Table 1). Additional confirmation of global $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is found in the comparison of our unaltered marine cement data with similar age carbonate and anhydrite data from the Duperow Formation of the Williston Basin (ROARK, 1989; Table 3).

The different alteration trends illustrated in Fig. 3 for the Alberta and Australia marine cement data indicate that although the original marine calcite in both sites was of the same composition, the diagenetic fluids were not; diagenetic fluids at the Australia location had higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and

Table 3: $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Late Devonian Fms. -- Williston Basin (Roark, 1989)

FORMATION	Ma*	$^{87}\text{Sr}/^{86}\text{Sr}^{**}$	COMPONENT
Three Forks Fm.	365	0.708153	Nodular Anhydrite
Birdbear Fm.	367	0.708115	Massive Anhydrite
Birdbear Fm.	369	0.708100	Stromatopora
Duperow Fm.	371	0.708074	Laminated Anhydrite
Duperow Fm.	371	0.708092	Stromatopora
Duperow Fm.	372	0.708108	Stromatopora
Duperow Fm.	372	0.708083	Laminated Anhydrite
Duperow Fm.	372	0.708077	Laminated Anhydrite
Souris River Fm.	373	0.708019	Stromatopora
Dawson Bay Fm.	377	0.707956	Stromatopora
Dawson Bay Fm.	377	0.707923	Crinoid

*Ages from North Dakota Geological Survey Correlation Chart (Bluemle et al., 1981). Ages within formations determined by linear interpolation as stated in Roark (1989).

**Corrected from reported data by adding 0.000036 to correct for normalization and inter-laboratory differences.

higher Sr contents (e.g., BANNER and HANSON, 1990). This difference can be explained by the proximity of Proterozoic gneiss which underlies the reef complex. Additionally, interbedding of Proterozoic age lithoclasts with Devonian peritidal carbonates is a likely source for the radiogenic Sr observed in diagenetic calcites (e.g., HURLEY, 1986). Although quantitative modeling of these alteration or water-rock interaction trends will be presented elsewhere, it should be noted that the intersection of different diagenetic trends can be used to evaluate the composition of marine carbonate, and should not be viewed as an obstacle in determining original marine isotopic compositions (e.g., GIVEN and LOHMANN, 1985).

Preservation of original $\delta^{18}\text{O}$ values has significant implications for other tracers. Water-rock interaction models for carbonate systems indicate that the $\delta^{18}\text{O}$ value of the rock undergoing dissolution-precipitation is the most sensitive indicator of diagenetic alteration in a system with a low Sr content and low $^{87}\text{Sr}/^{86}\text{Sr}$ fluid (e.g., meteoric water; BANNER et al., 1988; BANNER and HANSON, 1990; GAO, 1990). Such is the case of the marine cement alteration trend from the Golden Spike and Nevis reefs (Fig. 3). Preservation of $\delta^{18}\text{O}$ values indicates closure with respect to tracers such as $\delta^{13}\text{C}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and Sr, Mg contents (i.e., the point at which the composition of the secondary diagenetic phase equals that of the initial rock).

Scenarios can be constructed whereby $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are an equally sensitive indicator of diagenetic alteration. For example, if diagenetic fluids have elevated Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as was the case for the Virgin Hills Formation, the W/R (water/rock) ratios necessary for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio closure approaches that for closure with respect to $\delta^{18}\text{O}$ values. Likewise, closure for both isotopic tracers would require preservation of marine $\delta^{13}\text{C}$ values and Mg and Sr contents. Therefore, correlation of primary $\delta^{18}\text{O}$ values in clear RAFC, indicates that primary Sr and Mg contents are also preserved.

Comparison of Sr/Mg Ratios between Holocene and Devonian Marine Cements

Laboratory precipitation experiments provide a basic understanding of the factors which control Sr and Mg incorporation into calcite abiotically precipitated from seawater and related solutions (i.e., MORSE and BENDER, 1990). It has been shown that D_{Mg} values increase with increasing temperature and decrease with increasing PCO_2 and $[\text{SO}_4^{2-}]$ (KATZ, 1973; BURTON and WALTER, 1987; MUCCI, 1987; MUCCI et al., 1989; BURTON and WALTER, 1991). D_{Mg} in-

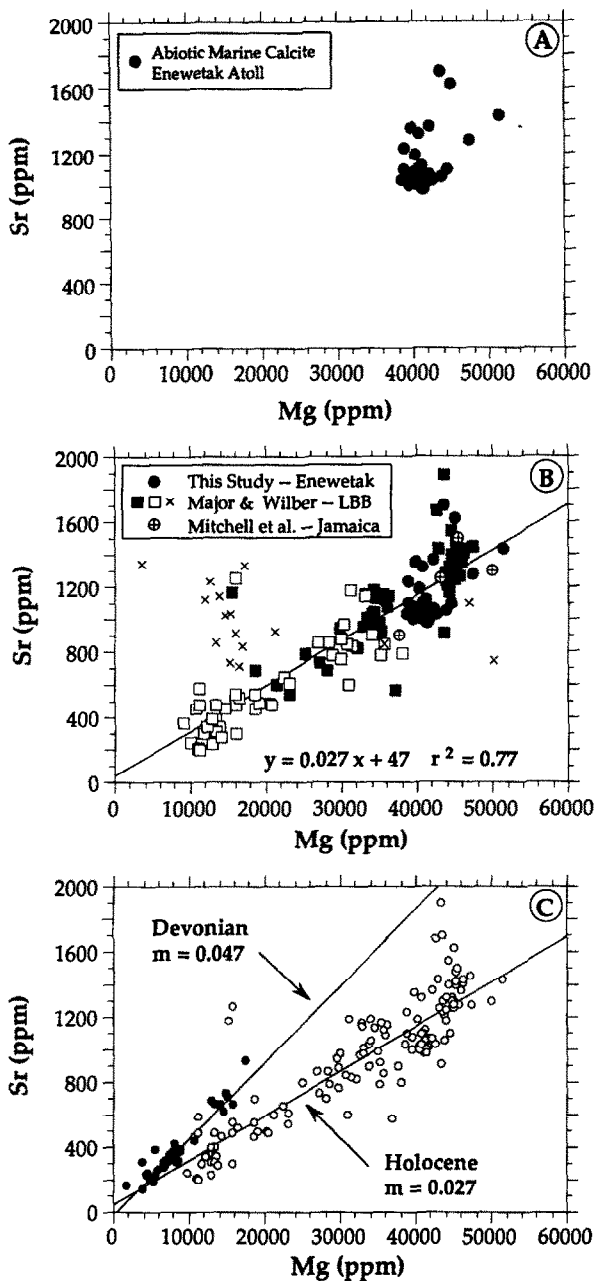


FIG. 6. (a) Magnesium and strontium concentrations of modern HMC marine cement from Enewetak Atoll. Mean values are 42,100 and 1,150 ppm, respectively (See Table 2). (b) Magnesium and strontium concentrations of Holocene marine calcite. Data are from Little Bahama Bank (MAJOR and WILBER, 1991), Discovery Bay, Jamaica (MITCHELL et al., 1987), and Enewetak Atoll (Table 2, this study). Open Squares and \times 's of the MAJOR and WILBER (1991) data set are luminescent in CL, and filled squares are non-luminescent. \times 's have not been used in the statistical calculations as they have been described as "recrystallized" (MAJOR and WILBER, 1991). (c) Magnesium and strontium concentrations of Devonian and Holocene marine calcite data. Data are from Figs. 4 and 6b, respectively. The "recrystallized" samples (\times 's) of the MAJOR and WILBER (1991) data set have been removed from the plot.

Enewetak Atoll are comparable to these findings, and our analyses provide the first reported Sr contents for these cements (Fig. 6a). Taken alone, there is no distinct trend in the

Enewetak data, but when compared to Sr and Mg contents of HMC marine cement from Discovery Bay, Jamaica (MITCHELL et al., 1987), and abiotic marine calcite from the Little Bahama Bank (MAJOR and WILBER, 1991), a positive correlation between Sr and Mg is apparent (Fig. 6b).

The Sr and Mg contents reported by MAJOR and WILBER (1991) are interpreted as having been precipitated from seawater or shallow burial fluids (with Mg/Ca and Sr/Ca ratios equal to that of seawater) at depths of 504 to 700 m and temperatures of approximately 12 to 6°C, respectively. Samples with the highest Mg contents occur in the shallowest and warmest water. In general, samples which exhibited CL banding, due to variable Eh conditions in fluids below the sediment-water interface, had lower Mg and Sr contents and higher Fe and Mn contents than nonluminescent samples (Fig. 6b). MAJOR and WILBER (1991) attribute the covariance of Sr and Mg in their samples to kinetic effects or differences in precipitation rates, where higher rates incorporate more Sr and Mg. An alternative explanation can be presented.

By combining our HMC data from Enewetak Atoll with those of MITCHELL et al. (1987) and MAJOR and WILBER (1991) a covariation of Sr and Mg is observed over the range of 4 to 20 mol% MgCO₃ (Fig. 6b). The covariation of Sr and Mg is highly significant ($r^2 = 0.77$, $\alpha - 1 = 0.99$) and is best represented by the slope and intercept of the principal axis of variation with a 95% confidence interval (Fig. 6b):

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

Causes for the variable Mg contents of Holocene abiotic marine calcite, and therefore D_{Mg} , cannot be uniquely determined without direct measurement of fluid chemistries and temperatures and precipitation rates. However, in light of experimental data, the causes for the variable Mg contents observed in the Holocene marine calcite (Fig. 6b) are more easily explained by variable temperature and PCO_2 than by variable precipitation rates (e.g., BURTON and WALTER, 1991). Warm shallow waters of reefal settings (25–29°C) with potentially low PCO_2 values (due to high photosynthetic activity) may serve to increase D_{Mg} values relative to cool (6°C) deeper waters. Although higher saturation states of surface waters may increase precipitation rates (e.g., WALTER, 1986), experimental data suggest that changes in precipitation rate alone cannot produce the observed changes.

Regardless of the factor or factors which control Mg incorporation into marine calcite, it is important to note that given a constant fluid Sr/Ca ratio, D_{Sr} is primarily dependent on the Mg content of calcite (controlled by the calcite crystal lattice) and secondarily dependent on precipitation rate (e.g., MUCCI and MORSE, 1983; LORENS, 1981). It has been shown experimentally that there is a positive, linear correlation between Mg content and D_{Sr} (and therefore Sr content) (MUCCI and MORSE, 1983). Such a relation can be derived for modern abiotic marine calcite from Eqn. (1):

$$D_{\text{Sr}} = 3.52 \times 10^{-6} (\text{ppm Mg}_{\text{calcite}}) + 6.20 \times 10^{-3}. \quad (2)$$

The slope of the line described by Eqn. (2) is similar to that of MUCCI and MORSE (1983), yet the range of values for D_{Sr} are systematically lower. This is probably due to the rel-

actively rapid precipitation rates of the MUCCI and MORSE (1983) experiments. Given that D_{Sr} is precipitation rate dependent, the low Sr contents in the abiotic marine calcite indicate that their precipitation rates (on the order of years or longer?) are apparently lower than biotic and experimental precipitation rates (on the order of hours and days; e.g., LORSENS, 1981; OHDE and KITANO, 1984; MUCCI and MORSE, 1983). Unlike the experimental data of MUCCI and MORSE (1983) and the natural system biotic data of OHDE and KITANO (1984), the line described by Eqn. (1) intersects near the origin (Fig. 6b). This relation predicts a pure calcite end-member, rather than a calcite containing 0 ppm Mg and 1000 ppm Sr. Given the range of Mg contents (4 to 20 mol% $MgCO_3$), we present Eqns. (1) and (2) as our best estimate of the relation of Sr and Mg in marine abiotic calcite precipitated at the relatively slow rates typical of marine cements.

Covariation of Sr and Mg in Devonian marine cements was evaluated in the same manner as Eqn. (1) (Fig. 4). This covariation is also highly significant ($r^2 = 0.92$, $\alpha - 1 = 0.99$) and is best represented by the slope and intercept of the principal axis of variation with a 95% confidence interval (Fig. 4):

$$\text{ppm Sr}_{\text{calcite}} = 0.047_{(\pm 0.004)} (\text{ppm Mg}_{\text{calcite}}) - 15_{(\pm 45)} \quad (3)$$

Like the D_{Sr} dependence on Mg content of the Holocene samples, there is a similar relation in Devonian samples. However, significance tests were performed to determine if the slopes of the principal axes of the Holocene and Devonian data were the same; both are significantly different (0.027 and 0.047, respectively; Figs. 4, 6b,c). We attribute this difference to a variation in the Mg/Ca and Sr/Ca ratios of seawater. As the calcite crystal structure places liberal upper and lower limits on the amount of Mg and Sr substitution for Ca, the systematic variation of both Sr and Mg reflects variation in fluid compositions and commensurate adjustments of distribution coefficients. That is, for a given set of Mg/Ca and Sr/Ca ratios for seawater there will be a unique Sr-Mg trend for marine calcite.

Before comparing the Holocene and Devonian data sets, a qualitative distinction between them must be made. The Devonian trend, described by Eqn. (3), is composed of data from unaltered and partially altered marine cement data and the Holocene trend, described by Eqn. (1), is composed of data from unaltered marine calcite (Figs. 4, 6b,c). The CL in the Holocene samples (constructional zones on crystal faces MAJOR and WILBER, 1991) is thought to result from fluctuations in Eh due to shallow burial, whereas CL in the Devonian samples (cloudy RAFC) is directly related to partial alteration (water-rock interaction) by non-marine fluids (CARPENTER and LOHMANN, 1989). Addition of data from partially altered Devonian samples does not change the covariance between Sr and Mg present among the unaltered samples (Fig. 4). Admittedly, the processes that preserve original Sr/Mg ratios during diagenetic alteration are not fully understood. Apparently, partial alteration (at low W/R ratios) produces a proportional decrease of Mg and Sr, while retaining primary Sr/Mg ratios (Fig. 3; Table 1). Like the Holocene trend, the principal axis of the Devonian trend passes near

the origin, suggesting a similarity in marine cement precipitation rates (Figs. 4, 6b,c).

Assuming that the Mg/Ca ratio of Devonian seawater was the same at the Alberta and Australia locations, the higher Mg content of well-preserved RAFC from Australia must represent locally higher D_{Mg} values. As a result of higher Mg contents, D_{Sr} and Sr contents are also higher (e.g., MUCCI and MORSE, 1983), in part, producing the relation described by Eqn. (3) (Fig. 4). Several conditions at the Australian site could increase the D_{Mg} values: (1) higher temperature, (2) lower PCO_2 , (3) lower sulfate concentration, (4) higher precipitation rate, or (5) increased saturation state. Based on $\delta^{18}O$ values of well-preserved marine cements, a temperature difference between sites seems unlikely. Given the scope of this research, determination of the other variables such as PCO_2 and $[SO_4^{2-}]$ cannot be made. Even without knowledge of the mechanism controlling local variations in D_{Mg} values, the consistent relation between Sr and Mg contents can still be used to estimate Sr/Ca and Mg/Ca ratios of late Devonian seawater.

As a whole, well-preserved Devonian marine cements have low Mg contents (<7 mol% $MgCO_3$) relative to modern HMC marine cements (14–18 mol% $MgCO_3$). These anomalous Devonian compositions could result from precipitation at relatively low seawater temperatures, yet this is not compatible with the low $\delta^{18}O$ values of the clear RAFC or the shallow water tropical setting of reefal facies. Elevated PCO_2 values also could be invoked due to higher atmospheric PCO_2 at this time (e.g., SANDBERG, 1985). For example, BERNER (1990) has suggested that Devonian atmospheric PCO_2 was approximately 10 to 13 times higher than today. However, BURTON and WALTER (1991) have shown that increases of $10^{-4.5}$ to 10^{-1} (at a constant temperature and Mg/Ca ratio) yield a decrease of at most, 5 mol% $MgCO_3$. Unless Late Devonian seawater had PCO_2 values well above 10^{-2} , lower Mg contents (approximately 10–15 mol% $MgCO_3$, lower) cannot be ascribed solely to elevated PCO_2 .

Estimating Mg/Ca and Sr/Ca Ratios of Late Devonian Seawater

Comparison of Sr and Mg contents of marine cements of Holocene and Devonian age indicates two important differences (Fig. 6c). First, Sr and Mg contents of reefal abiotic marine calcite are lower in the Devonian samples (Figs. 6a,b,c). Second, the slope of the Devonian trend (0.047) is 1.7 times greater than the Holocene trend (0.028; Figs. 4, 6b,c). By assuming that reefal water temperatures and PCO_2 values in the Devonian were not dramatically different from Holocene conditions and by using the D_{Sr} and D_{Mg} values calculated from Holocene marine cements compositions with the relations of Eqns. (1), (2), and (3), we can constrain the Mg/Ca and Sr/Ca ratios of Late Devonian seawater (Fig. 7; Table 4). Distribution coefficients used in these calculations are derived from the mean Sr and Mg contents of Enewetak HMC cements. The Mg contents of Leduc Formation RAFC were initially modeled using the mean D_{Mg} from Enewetak HMC cements; a commensurately higher value was used for RAFC from the Virgin Hills Formation. D_{Sr} values were calculated according to calcite Mg contents and Eqn. (2) (Table

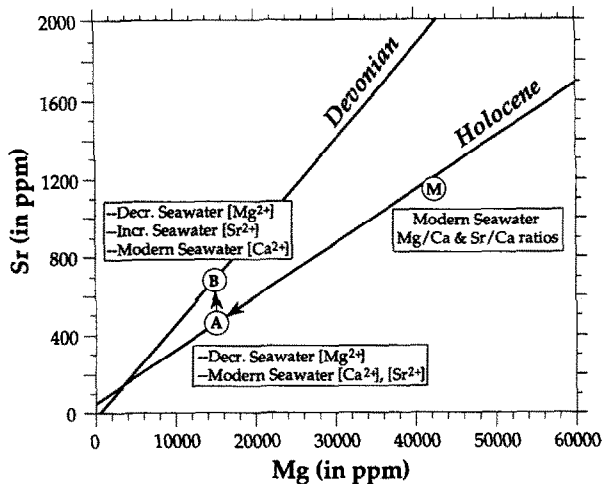


FIG. 7. Schematic diagram depicting the changes in Sr and Mg contents of Holocene and Devonian abiogenic marine calcite due to possible changes in the Sr, Mg content of seawater. Devonian and Holocene trends are from Figs. 4 and 6. M is the mean composition of modern abiogenic marine calcite from Enewetak, Atoll (Fig. 6a; Table 4). A is the composition of calcite precipitated from conditions described in scenario #2 of Table 4 (only Virgin Hills Formation, Australia). B is the composition of calcite precipitated from conditions described in scenarios #3 and #4 of Table 4 (only Virgin Hills Formation, Australia). Australian compositions serve as conservative estimates. Alberta compositions are not plotted.

4). Because of the large number of variables, several scenarios can be envisaged. We have outlined only those that are most plausible. In each scenario, we have tried to reproduce the approximate Sr and Mg contents of well-preserved marine cements from both the Alberta and Australia locations (Table 4).

The first scenario is one in which the molar Mg/Ca and Sr/Ca ratios of Devonian seawater are the same as the modern ocean, 5.14 and 0.0088, respectively (Table 4). Given these seawater ratios, and the composition of unaltered RAFC from Alberta and Australia, calculated D_{Mg} and D_{Sr} values are unreasonably low compared to values for modern reefal marine cements and precipitation experiment data. Therefore, it appears reasonable to conclude that the Mg/Ca and Sr/Ca ratios of Devonian seawater differ from those of modern seawater.

In scenario 2, Ca and Sr contents of Devonian seawater are the same as modern seawater and the Mg content is decreased, thus reducing the Mg/Ca ratio by 81% (Table 4). A reasonable D_{Mg} value for modern reefal marine cements has been used and D_{Sr} values have been calculated using Eqn. (2) for the appropriate calcite Mg contents. This scenario yields Mg contents equivalent to those of Devonian samples. However, Sr contents lie on the Holocene trend of Fig. 6c and are still much lower than measured Devonian values (A of Fig. 7; Table 4).

Scenario 3 holds the Ca content of Devonian seawater at its modern concentration while Mg and Sr contents are decreased and increased, respectively. This produces a decrease in the Mg/Ca ratio of 81% and an increase in the Sr/Ca ratio of 55% (Table 4). As in scenario 2, a reasonable D_{Mg} value for modern reefal marine cements has been used and D_{Sr} values have been calculated using Eqn. (2) for the appropriate

calcite Mg contents. Although this scenario yields the observed Devonian marine cement compositions (B of Fig. 7; Table 4), experimental data indicate that decreases in the Mg/Ca ratio of seawater from 5.14 to 1.0 yield an increase in the D_{Mg} value of approximately 50% (MUCCI and MORSE, 1983). Therefore, the calculations of scenario 3 may slightly overestimate the Mg/Ca of Devonian seawater. In its basic design, scenario 4 is the same as scenario 3, except that the values for D_{Mg} are increased by 50%, thus requiring a commensurate 50% decrease in the seawater Mg/Ca ratio over scenario 3.

Decreases in fluid Mg/Ca ratios are also known to increase calcite precipitation rate at a given saturation state (e.g., BERNER, 1975; MUCCI and MORSE, 1983; WALTER, 1986). Therefore, the low Mg/Ca ratios estimated by scenarios 3 and 4 for the Devonian, could produce more rapid precipitation rates assuming an equivalent degree of surface ocean saturation. This, in turn, could yield higher D_{Sr} values. If the effect of precipitation rate on D_{Sr} values was important, one would expect a Devonian trend with a slope equal to that of the Holocene trend, yet with higher Sr contents. However, as noted before, the Devonian Sr-Mg trend passes near the origin and is not parallel to the Holocene trend (Fig. 6c). On this basis, we conclude that the increase in precipitation rate produced by low fluid Mg/Ca ratio, does not appreciably effect Sr incorporation.

Given our knowledge of distribution coefficients, Sr-Mg relations, and the assumptions regarding Devonian reefs and preservation of original chemistry in marine cements, scenario 4 appears to best estimate the Mg/Ca and Sr/Ca of Late Devonian seawater (Table 4). Our estimate of Mg/Ca and Sr/Ca ratios of Late Devonian seawater indicate that there was less Mg (80 to 90% less) and more Sr (50 to 60% more) than in modern seawater. Although these scenarios do not preclude simultaneous variations in the Sr, Mg, and Ca content of seawater, all of the more complex permutations cannot be described here.

We recognize that there are uncertainties associated with our estimates of the chemistry of Late Devonian seawater. Further examination of well-preserved, ancient, marine minerals is needed to test their validity. Abiogenic marine calcite provides material from which Mg/Ca and Sr/Ca ratios of ancient seawater can be simultaneously estimated. Based on analysis of modern analogues, marine cement compositions are relatively unaffected by kinetic and vital effects.

Constraining the $\delta^{18}O$ Value of Late Devonian Seawater

Clear RAFC from the Alberta Basin retains an original marine $\delta^{18}O$ value which is 3 to 4‰ lower than post-Devonian analogues (Figs. 1, 5). Therefore, it is necessary to explain these low $\delta^{18}O$ values in a context of precipitation from either warmer or isotopically lighter Late Devonian seawater. A variety of observations and data can be used to constrain both the temperature and $\delta^{18}O$ value of Late Devonian seawater. These include (1) examination of the possible $\delta^{18}O$ values of marine calcite precipitated from a range of seawater temperatures and $\delta^{18}O$ values, (2) comparison of marine calcite $\delta^{18}O$ values and water temperatures to the maximum lethal temperatures limit for modern marine organisms, (3)

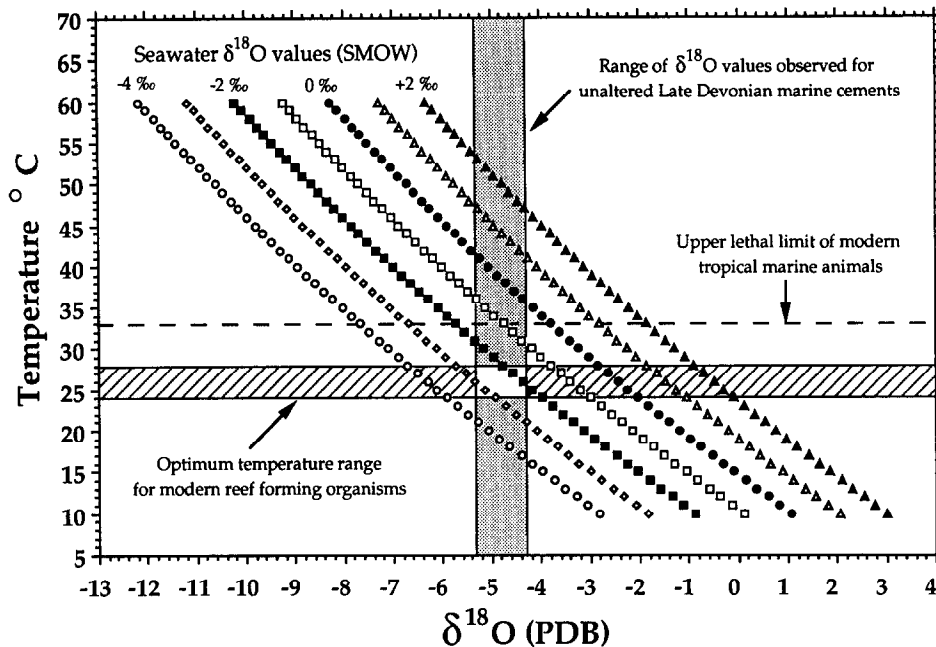


FIG. 8. Theoretical $\delta^{18}\text{O}$ values of a 3 mol% MgCO_3 calcite cement precipitated from seawater of variable temperature (10 to 60°C) and $\delta^{18}\text{O}$ value (+2 to -4‰ (SMOW)). Calcite $\delta^{18}\text{O}$ values were calculated using the calcite-water fractionation factor of FRIEDMAN and O'NEIL (1977) and correcting for Mg content using the data of TARUTANI et al. (1969). The upper lethal temperature limit for subtidal marine animals is taken from THOMPSON and NEWTON (1988) and the optimum temperature range for reef-forming organisms is from MILLIMAN (1974).

assessment of the plausibility of dramatically elevated seawater temperatures, and (4) comparison of paleolatitudes, seawater temperatures, and the isotopic composition of marine cements, meteoric phreatic spars, and syngedimentary dolomite.

A hypothetical 3 mol% MgCO_3 calcite precipitated from modern seawater (0‰ (SMOW)) at 25°C would have a $\delta^{18}\text{O}$ value of -2.2‰ (PDB) rather than the -4.8‰ of Late Devonian RAFC (Fig. 8). Assuming that the oxygen fractionation factor for calcite-water is correct (FRIEDMAN and O'NEIL, 1977), the $\delta^{18}\text{O}$ value or temperature of our hypothetical seawater is incorrect. This discrepancy must be reconciled by higher seawater temperatures, lower seawater $\delta^{18}\text{O}$ values, or some combination of both.

In a study of modern marine cements from Enewetak and Bikini atolls, GONZALEZ and LOHMANN (1985) found that ARAG and HMC marine cements have $\delta^{18}\text{O}$ values which are consistently 1.0 to 1.5‰ higher than predicted equilibrium values. New data from Enewetak Atoll HMC cements indicate that they are, at most, 0.5‰ higher than equilibrium $\delta^{18}\text{O}$ values (Fig. 5). GONZALEZ and LOHMANN (1985) have attributed this difference to errors in water $\delta^{18}\text{O}$ values, biological effects due to associated bacteria (?), or underestimation of equilibrium values due to kinetic fractionation during carbonate precipitation in the TARUTANI et al. (1969) experiments. Therefore, we use a range of $\delta^{18}\text{O}$ values for our modern theoretical 3 mol% MgCO_3 calcite (-2.2‰ to -1.2‰ to be conservative). This leaves a difference between calculated and measured values of 2.6 to 3.6‰ which must be explained by either changes in temperature or seawater $\delta^{18}\text{O}$ values. We have calculated the $\delta^{18}\text{O}$ values of 3 mol% MgCO_3 calcite over a range of seawater temperature and $\delta^{18}\text{O}$

values (10 to 60°C and +2 to -4‰ (SMOW); Fig. 8). To precipitate a 3 mol% MgCO_3 calcite with a $\delta^{18}\text{O}$ value of -4.8‰ \pm 0.5 (PDB) from seawater with a $\delta^{18}\text{O}$ value of 0 to -1‰ (SMOW), it is necessary to have seawater temperatures which range from 42 to 31°C. However, if the $\delta^{18}\text{O}$ value of seawater was between -2 and -3‰ (SMOW), temperatures between 31 and 21°C would be required (Fig. 8).

The optimum temperature range for modern reef-forming organisms is between 24 and 28°C (MILLIMAN, 1974; THOMPSON and NEWTON, 1988; Fig. 8). More importantly, the maximum lethal temperature limit of modern tropical, subtidal marine animals is 33°C (e.g., THOMPSON and NEWTON, 1988; Fig. 8). The maximum lethal temperature of upper littoral molluscs is approximately 40 to 45°C (HENDERSON, 1929; EVANS, 1948) while for lower littoral molluscs it is approximately 35°C (HENDERSON, 1929). However, upper lethal temperatures of 32 to 35°C have been observed for subtidal molluscs (HENDERSON, 1929). In fact, tropical, subtidal marine animals can withstand lower temperatures more easily than higher temperatures (10°C lower lethal limit; THOMPSON and NEWTON, 1988). Although these temperature limits do not exclude the possibility of ancient reefal organisms evolving an adaptation to higher temperatures, the choice of extremely high ancient seawater temperatures seems implausible.

KARHU and EPSTEIN (1986) have suggested that Late Devonian seawater was extremely warm (55 to 65°C). If, as they suggest, seawater temperatures were approximately 60°C and its $\delta^{18}\text{O}$ value was -1‰ (SMOW), then the $\delta^{18}\text{O}$ of our marine cements should be between -8 and -10‰ (PDB; Fig. 8). We must conclude that the seawater temperatures calculated by KARHU and EPSTEIN (1986) are extreme overestimates.

Such warm tropical surface waters would not be stable for long periods of time as storm systems could be produced to dissipate heat away from equatorial regions (e.g., BARRON, 1987).

Such warm seawater temperatures are seemingly in direct opposition to the reports of glacial deposits in lower Paleozoic sediments, including Late Devonian glacial sediments from South America (CAPUTO, 1985; CAPUTO and CROWELL, 1985; FRAKES and FRANCIS, 1988). It is possible that such high temperatures would inhibit the formation of sea ice and polar ice caps regardless of continental positions. Evidence has been compiled which indicates that large areas of South America were affected by continental glaciation during the Late Devonian (CAPUTO, 1985). Although these findings are controversial, as many glacial features can be produced by both alpine and continental glaciations, the large land area affected by these sediments suggests continental glaciation (CAPUTO, 1985). Regardless of the origin of these glacial sediments, the possibility of continental glaciation and its effect on the $\delta^{18}\text{O}$ value of seawater must be considered.

The volume of Devonian glacial ice relative to modern ice volume is difficult to estimate. Based on the $\delta^{18}\text{O}$ value and volume of modern glacial ice, SHACKLETON and KENNETT (1975) have calculated that complete melting would decrease the $\delta^{18}\text{O}$ value of modern oceans by approximately 1‰. In such a scenario, the discrepancy between calculated and measured marine cement $\delta^{18}\text{O}$ values would be reduced to 1.6 to 2.6‰. However, the findings of CAPUTO (1985) make lowering the $\delta^{18}\text{O}$ value of seawater due to melting of glacial ice and dramatic increases in the temperature of seawater less likely. On the other hand, storage of more glacial ice than today would drive seawater $\delta^{18}\text{O}$ values higher, thus exacerbating the discrepancy between low $\delta^{18}\text{O}$ values of marine cements and high $\delta^{18}\text{O}$ values seawater.

OPDYKE and WILKINSON (1990) have found that marine cements and ooids occur over a relatively narrow range of paleolatitudes throughout the Phanerozoic (within 35° N/S) and is similar to their distribution in modern oceans. Over this range of latitudes today, surface seawater temperatures are approximately 20 to 30°C (CLIMAP Members, 1976, 1981). Therefore, if seawater temperatures were significantly warmer in the Lower Paleozoic, the range of paleolatitudes for ooid and marine cement occurrences should have widened. However, this trend does not occur for the wide variety of continent configurations of the Phanerozoic (OPDYKE and WILKINSON, 1990). A similar latitudinal distribution (within 35° N/S) is found for modern zooxanthellate corals (ROSEN, 1984). This latitudinal range is controlled primarily by the temperature of tropical surface water being within the optimum temperature range of corals (24 to 28°C). A typical occurrence of marine cements is within the framework pores of reef-building organisms whether they be corals or stromatoporoids (e.g., JAMES et al., 1976; GINSBURG and JAMES, 1976; WALLS et al., 1979; GIVEN and LOHMANN, 1985). Therefore, in most cases, the distribution of marine cements closely tracks that of reefs and shelf carbonates. Based on these observations, we conclude that the temperature for marine cement precipitation (tropical surface waters) has not changed dramatically during the Phanerozoic.

An additional constraint on the $\delta^{18}\text{O}$ value of seawater comes from the $\delta^{18}\text{O}$ values of Late Devonian calcite precipitated from meteoric water. The $\delta^{18}\text{O}$ value of modern rain water in subtropical coastal settings is approximately 2 to 6‰ lower than that of seawater (e.g., YURTSEVER, 1975). Given this approximate difference in water compositions and relatively invariant mean annual temperatures (<6°C variation for most tropical settings, CLIMAP Members, 1976, 1981), the $\delta^{18}\text{O}$ value of marine and meteoric calcite should also be separated by 2 to 6‰ (assuming similar fractionation factors and neglecting fractionation due to MgCO_3 contents). Based on the O and C isotope data of meteoric calcite, HURLEY and LOHMANN (1989) and CARPENTER and LOHMANN (1989) have defined meteoric calcite lines ($\delta^{18}\text{O}$ values of calcite precipitated from water-dominated meteoric fluids) for both the Alberta and Canning Basins. Both locations have approximately the same $\delta^{18}\text{O}$ values (-8.0 to -9.0‰ PDB) and are coastal settings within 15° of the equator (HURLEY and VAN DER VOO, 1987; VAN DER VOO, 1988). Using the $\delta^{18}\text{O}$ value of clear RAFC (-4.8‰), the difference between marine and meteoric calcite is approximately 4.0‰. This is similar to the difference between seawater and rain water in tropical settings in the western Pacific Ocean today (YURTSEVER, 1975).

If, for the sake of argument, we assume that Late Devonian seawater had a $\delta^{18}\text{O}$ value of approximately $0 \pm 1\%$ (SMOW; e.g., MUEHLENBACHS and CLAYTON, 1976; GREGORY and TAYLOR, 1981), and that clear RAFC precipitated at elevated temperatures, then the $\delta^{18}\text{O}$ value of meteoric water in these reefs (Devonian rainwater) would be 8.0 to 9.0‰ lower than seawater. Given modern latitudinal distributions of rainwater with these low $\delta^{18}\text{O}$ values, such a seawater-meteoric water difference would be compatible with latitudes above 45° (YURTSEVER, 1975). Such a large difference between seawater and meteoric water seems unreasonable given paleolatitudes of 15°N and S for the Alberta and Canning Basins. While this argument alone is not conclusive, we consider a $\delta^{18}\text{O}$ value of $0 \pm 1\%$ (SMOW) for Late Devonian seawater to be unreasonable.

Further evidence of ^{18}O -depleted seawater comes from the $\delta^{18}\text{O}$ values of symsedimentary dolomite from Late Devonian (Early Famennian ?) carbonate units from the southeast margin of the Fitzroy trough in the Canning Basin (WALLACE, 1990). Compared with time equivalent marine cement data from the nearby Lennard shelf (HURLEY and LOHMANN, 1989), the $\delta^{18}\text{O}$ values of symsedimentary dolomites are 2 to 4‰ higher. A similar relation is found between recent marine cements and sabkha dolomites of Abu Dhabi (GONZALEZ and LOHMANN, 1985; MCKENZIE, 1981; WALLACE, 1990). While the relative difference between calcite and dolomite $\delta^{18}\text{O}$ values is the same in both recent and Late Devonian examples, Late Devonian samples are approximately 4‰ lower than Holocene values. We attribute this difference to lower $\delta^{18}\text{O}$ values of Late Devonian seawater.

Causes of Anomalous Devonian Seawater Chemistry

The common mechanism which links, in varying degrees, the Mg and Sr concentrations and the $\delta^{18}\text{O}$ value of seawater

is seafloor hydrothermal activity. Although the global Mg, Sr, and O systems are ultimately related, each will respond differently to a change in global processes due to different reservoir sizes and residence times. In addition, each system has a unique set of fluxes which control both the chemical and isotopic composition of seawater. As the time needed for each system to reach steady state is different ($Sr < Mg < O$), each system will respond to the same flux perturbation at different rates. Therefore, a dramatic change in the seafloor hydrothermal activity would produce changes in each system, yet would be recorded in the rock record at different times.

A possible cause of low $\delta^{18}O$ values of Late Devonian and Lower Paleozoic seawater is the dominance of low temperature alteration of oceanic and continental crust over high temperature seawater-basalt exchange reactions (e.g., LOHMANN and WALKER, 1989; WALKER and LOHMANN, 1989). This explanation is opposed to the concept of isotopic balance between low and high temperature exchange reaction fluxes which keep the $\delta^{18}O$ value of seawater fixed near 0‰ (MUEHLENBACHS and CLAYTON, 1976; GREGORY and TAYLOR, 1981; MUEHLENBACHS, 1986). The $\delta^{18}O$ values of Phanerozoic marine minerals imply that the $\delta^{18}O$ value of seawater was variable. If so, modern flux estimates may either be incorrect or inapplicable to ancient ocean systems.

HOLLAND (1984) re-evaluated the continental, submarine, and hydrothermal oxygen isotope fluxes assuming that these processes are proportional to sea floor spreading rates. These calculations suggest that decreases in spreading rate would increase the dominance of low temperature silicate exchange reactions, thereby lowering the $\delta^{18}O$ value of seawater. To produce a seawater $\delta^{18}O$ value of $-2‰$, a 75% decrease in current spreading rates would be necessary (HOLLAND, 1984). Using these calculations the time needed for the oceans to reach steady state is 46 m.y. The dramatic change in $\delta^{18}O$ values of marine carbonate at the Devonian-Carboniferous boundary suggests that the $\delta^{18}O$ value of seawater increased by approximately 2 to 3‰ in approximately 10 to 20 m.y. (Fig. 1). This change occurs approximately twice as fast as previously estimated (MUEHLENBACHS and CLAYTON, 1976; HOLLAND, 1984). To effect such a change, the volume of rock involved in high temperature alteration would need to be increased disproportionately to that experiencing low temperature weathering. Ultimately, a marked increase in global heat flow and/or volume of high temperature ridge material would be required to produce these changes.

The only model estimates of Mg variation for Phanerozoic oceans are those of WILKINSON and ALGEO (1989) which suggest that marked decreases in Devonian Mg/Ca ratios are possible. Our calculations of Mg/Ca ratios between 0.6 and 1.0 are consistent with their estimates for this time period. Furthermore, they indicate that lower Mg contents of ancient oceans is controlled primarily by Mg removal during dolomite formation and to a lesser extent by Mg removal by high temperature alteration of oceanic basalt. Although BERNER et al. (1983) and LASAGA et al. (1985) discuss variations in Mg and Ca over the last 100 m.y., they exclude dolomite formation from their calculations. Given this, they estimate much smaller variations in Mg/Ca ratios. Application of their estimates to the Devonian is somewhat difficult.

Preferential removal of ^{16}O and Mg from seawater during high temperature seawater-basalt interactions seems inconsistent with our findings of low Mg, low $\delta^{18}O$ value Late Devonian marine calcite. The relatively long residence time for O (10 to 50 m.y. (?)) may allow the Mg content of seawater to respond to a global flux change well before the seawater $\delta^{18}O$ value responds. Such conditions could be attained if the dominant fluxes controlling seawater Mg contents and $\delta^{18}O$ values are dolomite formation and low temperature silicate weathering, respectively. While removing Mg from seawater, dolomite formation would have little effect on seawater $\delta^{18}O$ values. Alternatively, the Late Devonian could be a time of transition between dominance of low-temperature silicate alteration (lower Paleozoic) and dominance of high-temperature basalt alteration (post Devonian) (e.g., LOHMANN and WALKER, 1989; WALKER and LOHMANN, 1989). As such, the "onset" of sea floor hydrothermal activity may occur well before the ocean reaches steady state with respect to its $\delta^{18}O$ value. If the time required to reach steady state for Mg is much shorter (<15 m.y.), then Mg contents may decrease without a concomitant change in the $\delta^{18}O$ value.

A 50 to 60% increase in the Sr/Ca ratio of seawater could be attributed, in part, to the dominance of calcite precipitation during the early Paleozoic (e.g., WILKINSON et al., 1985; SANDBERG, 1985). SCHLANGER (1988) has suggested that the flux associated with storage of Sr in aragonitic marine carbonates during the recent rise in sea level is approximately twice that of riverine input (e.g., PALMER and EDMOND, 1989). If, as in the early Paleozoic, calcite was the dominant $CaCO_3$ polymorph during periods of relatively high sea level, an increase in the seawater Sr/Ca ratios could be attained. The Sr/Ca ratios also could rise due to an increase in the hydrothermal vent flux from oceanic crust (PALMER and EDMOND, 1989). While carbonate precipitation, riverine and hydrothermal input are possible contributors to seawater Sr, only riverine and hydrothermal fluxes affect the $^{87}Sr/^{86}Sr$ ratio of seawater. The decrease in the $^{87}Sr/^{86}Sr$ ratio of marine minerals at the end of the Devonian (e.g., BURKE et al., 1982) may suggest that a hydrothermal flux played a role in determining the Sr/Ca ratio of Late Devonian seawater.

SUMMARY

Late Devonian marine cements (radial fibrous calcite) from the subsurface of Alberta have escaped alteration by diagenetic fluids and retain original marine $^{87}Sr/^{86}Sr$ ratios, $\delta^{18}O$ and $\delta^{13}C$ values, and Sr/Mg ratios. The $\delta^{18}O$ values of Devonian marine cements are approximately 3.5‰ lower than those of analogous Holocene marine cements. Comparison of the Sr/Mg ratios of Holocene and Devonian abiotic marine calcite indicates that the Mg/Ca and the Sr/Ca ratios of Late Devonian seawater were approximately 80 to 90% lower and 50 to 60% higher than modern seawater, respectively. The low Mg/Ca ratios and $\delta^{18}O$ values of Late Devonian seawater can be explained by dolomite formation and low temperature silicate weathering fluxes during the Early Paleozoic, respectively. High Sr/Ca ratios may be a response to the dominance of calcite over aragonite precipitation during the Lower Paleozoic and increased hydrothermal input from

oceanic crust during the Devonian. As the residence time of O in seawater is much longer than Sr, it is conceivable that an increase of hydrothermal activity could change the Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater over the course of 3–5 m.y., while the $\delta^{18}\text{O}$ value does not change for up to 50 m.y. Therefore, the transition from an ocean system dominated by low temperature silicate alteration to one dominated by high temperature exchange reactions between seawater and basalt may occur earlier in the Devonian without an actual change in the seawater $\delta^{18}\text{O}$ value until the end of the Devonian.

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