Composition of the early Oligocene ocean from coral stable isotope and elemental chemistry

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ABSTRACT

A sectioned and polished specimen of the coral *Archohelia vicksburgensis* from the early Oligocene Byram Formation (~30 Ma) near Vicksburg, Mississippi, reveals 12 prominent annual growth bands. Stable oxygen isotopic compositions of 77 growth-band-parallel microsamples of original aragonite exhibit well-constrained fluctuations that range between −2.0 and −4.8‰. Variation in $\delta^{18}O$ of coral carbonate reflects seasonal variation in temperature ranging from 12 to 24 °C about a mean of 18 °C. These values are consistent with those derived from a bivalve and a fish otolith from the same unit, each using independently derived palaeotemperature equations. Mg/Ca and Sr/Ca ratios were determined for 40 additional samples spanning five of the 12 annual bands. Palaeotemperatures calculated using elemental-ratio thermometers calibrated on modern corals are consistently lower; mean temperature from Mg/Ca ratios are 12.5 ± 1 °C while those from Sr/Ca are 5.8 ± 2.2 °C. Assuming that $\delta^{18}O$-derived temperatures are correct, relationships between temperature and elemental ratio for corals growing in today's ocean can be used to estimate Oligocene palaeoseawater Mg/Ca and Sr/Ca ratios. Calculations indicate that early Oligocene seawater Mg/Ca was ~81% (4.2 mol mol^{-1}) and Sr/Ca ~109% (9.9 mmol mol^{-1}) of modern values. Oligocene seawater with this degree of Mg depletion and Sr enrichment is in good agreement with that expected during the Palaeogene transition from 'calcite' to 'aragonite' seas. Lower Oligocene Mg/Ca probably reflects a decrease toward the present day in sea-floor hydrothermal activity and concomitant decrease in scavenging of magnesium from seawater. Elevated Sr/Ca ratio may record lesser amounts of Oligocene aragonite precipitation and a correspondingly lower flux of strontium into the sedimentary carbonate reservoir than today.

INTRODUCTION

Secular variation in the textures and compositions of diverse sedimentary rock components attests to the importance of change in the intensity of global tectonism and attendant first-order oscillation in compositions of Phanerozoic atmospheres and oceans. Available information on the original mineralogy of abiotic carbonate precipitates such as ooids and synsedimentary marine cement (Sandberg, 1983) the composition of marine-derived evaporites (Hardie, 1996), the compositions of primary fluid inclusions (Lowenstein *et al.*, 2001), the strontium content of shallow marine limestones (Kahle, 1965), the magnesium content of fossil echinoderm debris (Dickson, 2002) and the abundance of dolostone (Mackenzie & Pigott, 1981) suggests that the divalent cation composition of seawater has varied on a scale of hundreds of millions of years in response to change in rates of seafloor spreading (Gaffin, 1987), plutonism and volcanism (Engel & Engel, 1964), and the concentration of carbon dioxide in global atmospheres (Lasaga *et al.*, 1985).

Because the composition of seawater is largely controlled by the balance of solutes that pass through global oceans, documentation of secular variation in either the textures or the compositions of carbonate or evaporite components serves to shed light on the nature of change in continental weathering rates and hydrothermal fluxes over Phanerozoic time. Accretionary biogenic carbonates are particularly useful in this regard.

Like abiotic mineral phases, their primary composition reflects the composition of seawater. In addition, one can be assured of the primary nature of skeletal material if high-resolution microsampling reveals regular intra-annual (seasonal) variation in composition, for diagenetic alteration would obliterate such small-scale inhomogeneities recorded in the skeleton during ontogeny. This is particularly true for aragonitic skeletons, for alteration is always associated with either dissolution or transformation to calcite with attendant loss of ontogenetic variation. Lastly, to the degree that assumptions about salinity are prerequisite to interpreting data, the taxonomic affinity of sampled specimens and coexisting species can provide useful constraints based on the tolerances of living relatives. Here we report stable isotopic and elemental data from an Oligocene aragonitic colonial coral collected near Vicksburg, Mississippi. Because $\delta^{18}O$ values of this specimen preserve an excellent record of seasonal variation in ambient seawater temperature, and because relations between temperature and elemental ratios are reasonably well constrained from modern corals, we use temperatures derived from isotope values in combination with elemental ratios to calculate Oligocene seawater Mg/Ca and Sr/Ca ratios.

METHODS

A number of specimens of the colonial coral *Archohelia vicksburgensis* (Family Oculinidae) were collected from shell beds of the early Oligocene Byram Formation (~30 Ma) near Vicksburg, Mississippi. Here, the Byram preserves four distinct shelly layers separated by muddy sands; each shell layer contains abundant branches of *Archohelia* (Fig. 1A), together with a diverse molluscan assemblage. The specimen we examined in greatest detail comes from the second shell layer above the contact with the underlying early Oligocene Glendon Limestone. Based on the lithology, stratigraphic position, taphonomy, and composition of associated faunal elements, it seems clear that these shelly
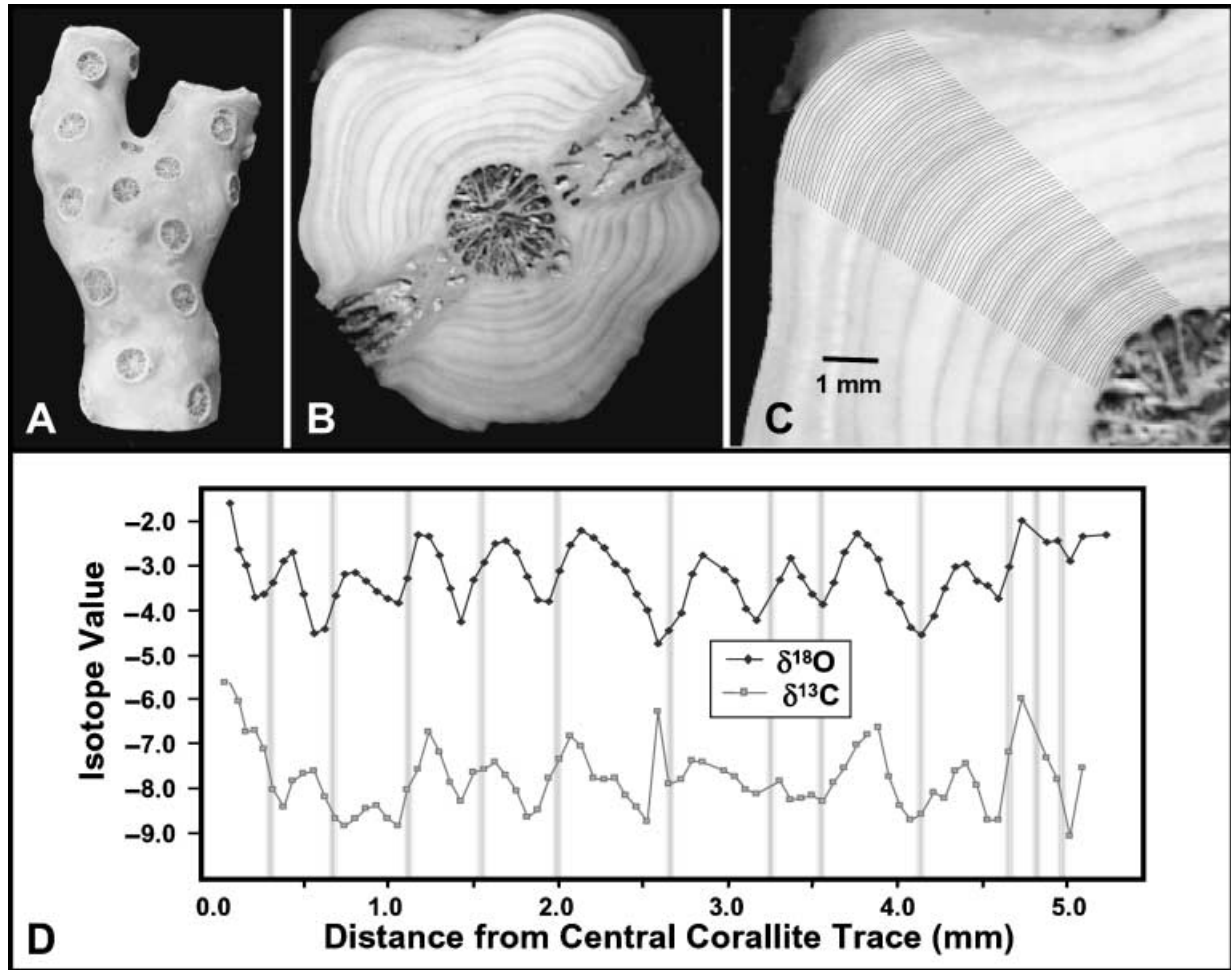

Fig. 1 (A) *Archohelia vicksburgensis* from the early Oligocene Byram Formation. This colony is 15 mm wide at base. (B) Cross-section through *Archohelia* showing prominent growth banding and dense skeletal structure. The outermost 3 annual bands are closely spaced near the coral margin and difficult to resolve in this image. (C) Sampling paths on *Archohelia* used to generate stable isotope data. (D) Variation in $\delta^{18}O$ and $\delta^{13}C$ of coral skeletal aragonite plotted from the centre of the colony to the growing margin. Gray bars indicate positions of annual growth bands.

units accumulated in shallow water on the Mississippi Oligocene shelf. The Byram Formation is part of a regressive sequence that begins within the underlying normal marine Glendon Limestone, and is overlain by laminated, dark, clay-rich lagoonal deposits of the Bucatunna Formation. All four beds consist of medium-to-coarse grained, somewhat muddy, glauconitic quartz sands, reflecting the increasing contribution of terrigenous components during the highstand. All contain nodules lithified by isopachous shallow-marine cements that are frequently rounded, wave-abraded, encrusted by hard bottom oysters, and/or penetrated by *Lithophaga* borings. Condition of associated mollusk shells is good, though bivalves are generally disarticulated and shells are concentrated, indicating some degree of winnowing or transport. Corals, too, are in good condition. While colony branches are broken, the breaks are clean and sharp, and alignment of colony fragments *in situ* suggests that at least some of the breakage occurred postburial. The abundance of the bivalves *Scapharca*, *Crassatella*, and *Callista* all suggest a nearshore, shallow shelf setting, while the overlying Buccatuna contains few if any marine fossils (Dockery, 1982). Foraminiferal faunas in the most normal marine facies of the Byram Formation suggest accumulation in offshore sand bars at water depths of no more than 5 meters (Fisher & Ward, 1984).

A polished cross section through this coral reveals a skeleton of densely packed laths of well-preserved aragonite with 12 prominent concentric annual growth bands (Fig. 1B). Such preservation is unusual in fossil corals because most other skeletons tend to exhibit greater porosities, and therefore more readily dissolve or alter to calcite during diagenesis. Micro-sampling across the growth axis produced carbonate powders from 77 successive growth-band-parallel milling paths (Fig. 1C); sampling resolution over the first 10 years of growth is 7–8 samples per year. Powders were analysed for their stable oxygen and carbon isotopic compositions at the University of Michigan's Stable Isotope Laboratory on a MAT 251 mass spectrometer coupled to a Kiel automated carbonate preparation system.

Forty additional microsamples spanning 5 of the 12 annual bands (indicated by the horizontal bar on Fig. 2) were digested in 50 μL of concentrated nitric acid, and elementa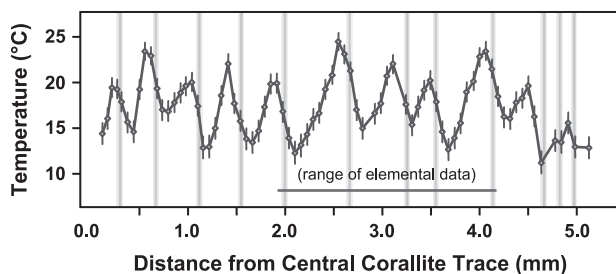l ratios measured using the Finnigan ELEMENT magnetic sector ICP-MS at the University of Michigan's Keck Environmental Geochemistry Laboratory. Instrumental parameters were similar to those described in Rosenthal *et al.* (1999), but with longer data integration times. During analysis, samples were bracketed and corrected using a laboratory calibration standard and drift-corrected using a bulk digest of this coral. Ratios were measured using ^{43}Ca, ^{26}Mg, and ^{88}Sr.

Temperature determinations based on δ^{18}O

Stable oxygen isotopic compositions of *Archohelia* show clear, well-constrained seasonal fluctuations ranging between −2.0 and −4.8‰ (Fig. 1D). Stable carbon isotope values generally covary with oxygen (Fig. 1D). Consistent intra-annual variation in stable isotope values preserved within an accretionary skeleton also confirms that diagenesis has not affected the isotopic composition of the carbonate, for aragonite is unreported as a diagenetic phase in carbonate rocks, and any neomorphic replacement by calcite would involve homogenization of isotope values. The δ^{18}O of coralline aragonite is known to vary with temperature, but the precipitation of coralline aragonite is not in equilibrium with seawater (Weber & Woodhead, 1972). Temperature equations for individual taxa must therefore be calibrated in the field or derived experimentally (e.g. McConnaughey, 1989b). Because this species of coral is extinct and a calibrated taxon-specific temperature equation is unavailable, we converted δ^{18}O values to temperature using four different temperature equations derived from a suite of modern corals (McConnaughey, 1989a; for *Porites* and *Pavona*; Roulier & Quinn, 1995; for *Solenastrea*; Leder *et al.*, 1996; for *Montastrea*; Table 1). While a number of other palaeotemperature equations are available in the literature, these four are explicit in their consideration of the effects of salinity on seawater δ^{18}O. To calculate palaeotemperatures, we assume that seawater δ^{18}O was − 0.5‰, consistent with estimates for the early Oligocene ocean at fully marine salinities (Zachos *et al.*, 1994; Lear *et al.*, 2000). While the Bryam Formation is a regressive near-shore unit, the benthic foraminiferan fauna of much of the unit is interpreted as normal marine (Fisher & Ward, 1984), and the lithofacies and associated molluscan fauna in the shell beds at this locality corroborate normal marine salinities. It should also be noted that while the colonial morphology of *Archohelia* is rather different from that of the large head corals generally used for palaeotemperature calibrations, its inferred shallow-shelf, normal marine environment might not have been substantially different. Large head corals are virtually absent from the Gulf Coast Palaeogene section.

Based on the presumption of normal marine salinities, we determined palaeotemperatures for each of the 77 samples analysed using each of the four temperature-δ^{18}O calibrations (Fig. 2). The difference between the maximum and minimum calculated palaeotemperature for a given isotope value ranged from 2.3 °C to 2.6 °C. The curve in Fig. 2 is based on the mean of all four palaeotemperatures calculated for each microsample;

Fig. 2 Temperature profile from *Archohelia* based on δ^{18}O of microsamples and four δ^{18}O palaeothermometers discussed in the text. Error bars reflect the standard deviation in oxygen isotope-derived palaeotemperature estimates. Gray bars indicate positions of annual growth bands.

Table 1 Microsampled coral $\delta^{18}O$ and $\delta^{13}C$ values

distance from centre (mm)	$\delta^{18}O$	$\delta^{13}C$	distance from centre (mm)	$\delta^{18}O$	$\delta^{13}C$
5.26	−2.33	–	2.40	−3.13	−8.14
5.11	−2.35	−7.53	2.34	−2.98	−7.76
5.04	−2.90	−9.05	2.27	−2.63	−7.81
4.97	−2.46	−7.81	2.21	−2.39	−7.75
4.90	−2.49	−7.32	2.14	−2.22	−7.07
4.76	−1.99	−5.99	2.08	−2.55	−6.83
4.69	−3.05	−7.17	2.01	−3.15	−7.35
4.62	−3.76	−8.7	1.95	−3.80	−7.75
4.55	−3.47	−8.7	1.88	−3.79	−8.49
4.49	−3.37	−7.92	1.82	−3.27	−8.65
4.42	−2.99	−7.44	1.75	−2.72	−8.05
4.36	−3.03	−7.59	1.69	−2.45	−7.69
4.29	−3.51	−8.21	1.62	−2.53	−7.40
4.23	−4.14	−8.08	1.56	−2.94	−7.57
4.16	−4.55	−8.58	1.49	−3.34	−7.62
4.10	−4.41	−8.71	1.43	−4.26	−8.30
4.03	−3.86	−8.38	1.37	−3.52	−7.85
3.97	−3.61	−7.74	1.30	−2.78	−7.18
3.90	−2.89	−6.64	1.24	−2.36	−6.73
3.84	−2.56	−6.81	1.17	−2.34	−7.58
3.77	−2.29	−7.02	1.11	−3.29	−8.04
3.71	−2.70	−7.53	1.05	−3.84	−8.83
3.64	−3.39	−7.87	0.99	−3.74	−8.67
3.58	−3.88	−8.28	0.92	−3.58	−8.37
3.51	−3.65	−8.16	0.86	−3.36	−8.43
3.45	−3.27	−8.21	0.80	−3.17	−8.68
3.38	−2.85	−8.26	0.74	−3.20	−8.82
3.32	−3.32	−7.83	0.68	−3.69	−8.67
3.19	−4.25	−8.13	0.62	−4.44	−8.19
3.12	−3.98	−8.03	0.55	−4.54	−7.62
3.06	−3.35	−7.73	0.49	−3.66	−7.66
2.99	−3.12	−7.59	0.43	−2.70	−7.83
2.86	−2.77	−7.4	0.37	−2.91	−8.4
2.79	−3.20	−7.38	0.31	−3.39	−8.04
2.73	−4.09	−7.81	0.26	−3.67	−7.11
2.66	−4.47	−7.91	0.20	−3.71	−6.7
2.60	−4.77	−6.26	0.15	−3.00	−6.72
2.53	−4.00	−8.74	0.10	−2.66	−6.04
2.47	−3.66	−8.43	0.05	−1.63	−5.62

Table 2 Coral elemental ratios

Sample #	Mg/Ca43 (mmol/mol)	Sr/Ca43 (mmol/mol)
1	2.60	9.79
2	2.78	9.58
3	2.88	9.87
4	2.49	9.89
5	2.70	9.87
6	2.65	9.87
7	3.54	9.95
8	2.94	10.11
9	2.65	10.22
10	2.70	10.18
11	–	9.90
12	2.86	9.82
13	2.51	10.05
14	2.46	10.21
15	2.47	10.26
16	2.50	10.10
17	2.72	9.87
18	3.52	9.82
19	2.60	9.89
20	2.54	9.98
21	2.42	9.81
22	2.57	9.84
23	2.48	9.87
24	2.75	9.72
25	3.00	9.82
26	2.59	9.77
27	2.81	9.70
28	–	9.63
29	3.02	9.64
30	3.09	9.78
31	2.57	9.81
32	2.59	9.82
33	2.80	9.78
34	–	9.75
35	3.88	9.94
36	2.71	9.87
37	2.65	9.86
38	3.80	9.78
39	3.25	9.87
40	2.69	9.76

mean temperature and seasonal range derived from each individual equation are presented in Fig. 4. Temperature estimates vary seasonally between 12 and 24 °C.

To increase our confidence in coral palaeotemperatures, we also sectioned and microsampled the venerid bivalve *Callista sobrina*, collected from the same horizon of the Byram Formation at the same locality. Because bivalve shell compositions generally do not suffer from the taxon-specific vital effects that influence coral isotope values (Anderson & Arthur, 1983), they have been more widely used in deep-time palaeoclimate studies. Palaeotemperatures derived from this clam using the temperature-$\delta^{18}O$ relation for molluscan aragonite from Grossman & Ku (1986) vary seasonally between 15 and 25 °C (Fig. 3). In addition, temperatures from a Byram Formation benthic fish otolith using the temperature-$\delta^{18}O$ equation of Patterson *et al.* (1993) range from 12 to 24 °C (Ivany *et al.*,
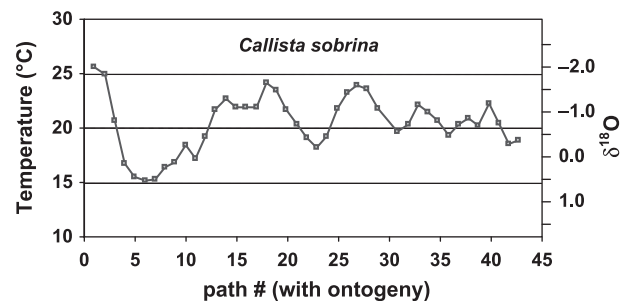

Fig. 3 Variation in $\delta^{18}O$ and inferred palaeotemperature based on microsampling of the bivalve *Callista sobrina* from the Bryam Formation. Note that mean temperature and seasonal range of temperature variation are comparable to that derived from the coral *Archohelia*. Seasonality is likely reduced later in ontogeny because of a reduction in the number of calcifying days per year with age.

2003). The agreement with these other proxies, each using independently calibrated palaeotemperature equations, provides confirmation of temperature estimates from coral δ^{18}O values.

Temperature determinations based on elemental ratios

Sr/Ca and Mg/Ca ratios of skeletal aragonite have also been used successfully as temperature proxies in modern and Pleistocene corals; therefore, we initially anticipated that temperature estimates based on elemental ratios from this Oligocene coral would be consistent with those from δ^{18}O values. This proved not to be the case.

A number of coral palaeotemperature equations using either Mg/Ca or Sr/Ca are available in the literature, and a consensus is not yet available on which of these are more robust or appropriate in a given setting. Rather than arbitrarily choosing one of each, we calculate temperatures using a suite of coral thermometers for Mg/Ca (Mitsuguchi *et al.*, 1996; for *Porites*; and Wei *et al.* 2000, for *Porites*) and Sr/Ca (Beck *et al.*, 1992; corrected in 1993; Alibert & McCulloch, 1997; Heiss *et al.*, 1997; Gagan *et al.*, 1998; Sinclair *et al.*, 1998; Crowley *et al.*, 1999; Fallon *et al.*, 1999; Correge *et al.*, 2000; Marshall & McCulloch, 2001, 2002; all based on *Porites*) such that the range of palaeotemperatures could be evaluated. We chose not to use the Mg/Ca equations of Fallon *et al.* (1999) and Sinclair *et al.* (1998) because they both yield a significantly lower correlation coefficient between Mg/Ca and temperature than the other two. Likewise, we chose not to use Sr/Ca equations of Smith *et al.* (1979), de Villiers *et al.*, 1994), Schrag (1999b),

Shen *et al.* (1996), and Wei *et al.* (2000) due to concerns about analytic precision, the distance between coral and temperature collection sites, or significant divergence from other calibration studies, as discussed by Marshall & McCulloch (2002).

The mean and range of palaeotemperatures derived from elemental ratios (Table 2) were compared to the 37 δ^{18}O-derived temperatures over the same 4-year interval of coral growth (indicated on Fig. 2). Early Oligocene temperature estimates derived from Mg/Ca and Sr/Ca ratios are all significantly lower than those determined using δ^{18}O values (Fig. 4). Nevertheless, in all cases the *range* of temperatures represented by coral aragonite was 11.5–13.5 °C (Fig. 4), a similarity suggesting that isotopic and elemental chemistry are both capturing the same range of seasonal temperature variation, but one in which values are shifted toward cooler temperatures for both elemental systems.

We also drilled an additional 15 time-averaged transects from 13 different but similarly well-preserved *Archohelia* colonies collected from 4 different stratigraphic levels within the Byram Formation at the Vicksburg locality and repeated the analysis. Four of these were from the same bed as the coral subjected to detailed analysis; the others included 3 samples each from similar shell beds ~1.5 and 2.5 meters above, and 2 meters below. Mean Sr/Ca and Mg/Ca ratios of the original specimen fall within the range of values obtained from this broader sample, and analysis of variance revealed no compositional differences between stratigraphic levels (P = 0.665 and p = 0.706, for Sr/Ca and Mg/Ca, respectively; Table 3). Elemental ratios derived from these corals apparently reflect ambient marine conditions during the accumulation of the
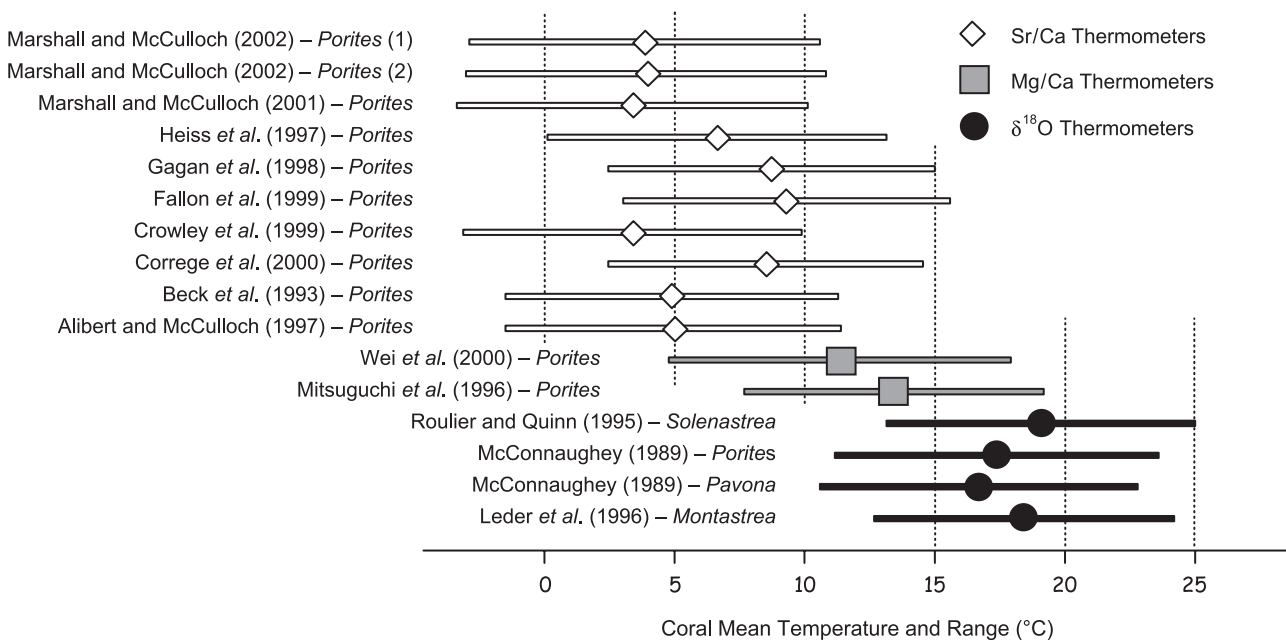

Fig. 4 Mean temperature vs. temperature range determined from Sr/Ca and Mg/Ca palaeothermometers and δ^{18}O of *Archohelia* microsamples. Note that elemental ratios produce temperatures significantly cooler than δ^{18}O values, yet exhibit similar seasonal ranges.

Table 3 Bulk elemental ratios from corals in Byram Formation shell beds 1 through 4 (from base of unit)

Sample	Stratigraphic Position	Mg/Ca43 (mmol/mol)	Sr/Ca43 (mmol/mol)
OC1	3	3.09	9.49
OC2	3	2.56	9.59
OC3	4	2.58	9.53
OC4	2	3.20	9.69
OC5	2	3.31	9.48
OC6	2	2.38	9.76
OC7	2	2.62	9.55
OC8A	2	2.97	9.38
OC8B	2	3.04	9.48
OC8C	2	2.92	9.37
OC9	3	2.42	9.47
OC11	4	2.89	9.26
OC12	1	2.58	9.41
OC13	1	2.95	9.58
OC14	1	3.08	9.55

Byram Formation, yet yield palaeotemperatures much cooler than corresponding estimates based on $\delta^{18}O$.

Early Oligocene seawater chemistry

How might differences in these seemingly robust isotope-derived and element-derived palaeotemperatures be resolved? Perhaps the most probable explanation for the apparent differences is that seawater composition has changed since the Oligocene, such that temperature calibrations based on corals living in today's oceans are not applicable to deep time. Sr/Ca and Mg/Ca ratios of skeletal aragonite depend on both the temperature of precipitation and the ratios of these elements in seawater at the time of formation. If the latter were different during the Oligocene, temperature equations based on living corals would not be valid. However, because we have an independent constraint on temperature from $\delta^{18}O$ data, we can invert elemental thermometers from modern seas and use $\delta^{18}O$-derived temperatures to calculate Sr/Ca and Mg/Ca ratios that would be expected had this Oligocene coral lived in seawater of modern composition. Differences between observed Oligocene and predicted Modern coralline elemental ratios therefore reflect differences between Modern and early Oligocene seawater compositions.

Assuming that the $\delta^{18}O$-derived palaeotemperatures are correct, we calculate predicted Sr/Ca and Mg/Ca ratios for coralline aragonite using each combination of the four $\delta^{18}O$ thermometers and the two Mg/Ca and 10 Sr/Ca thermometers noted above (Fig. 5). On average, expected coralline aragonite Sr/Ca ratios are 9.4 ± 0.2 mmol mol^{-1} and Mg/Ca ratios are 3.6 ± 0.4 mmol mol^{-1}, while observed values are 10.2 mmol mol^{-1} and 2.9 mmol mol^{-1}, respectively. This implies that early Oligocene seawater Sr/Ca ratios were 109% of today's value (9.9 vs. 9.1 mmol mol^{-1}) and Mg/Ca ratios were 81% of today's value (4.2 mol mol^{-1} vs. 5.2 mol mol^{-1}).

Oligocene seawater was evidently depleted in magnesium and enriched in strontium relative to calcium in comparison to today's ocean.

Because $\delta^{18}O$-derived palaeotemperatures depend on the value of $\delta^{18}O$ presumed for seawater, and because the volume of early Oligocene ice (and hence seawater $\delta^{18}O$) likely varied during this time interval, we also calculated palaeotemperatures assuming a seawater value of −1, the end-member value for an ice-free world (Zachos *et al.*, 1994). Under this condition, mean palaeotemperatures are cooler by 1.7 °C, still far above those determined using elemental ratios. A more negative composition of regional seawater associated with reduced salinity would also serve to reduce calculated palaeotemperatures; however, in order to bring isotope-derived palaeotemperatures into line with Sr/Ca-derived temperatures, the $\delta^{18}O$ of seawater would have to be as negative as −4‰. In the Gulf Coast region, this is the estimated composition of Palaeogene coastal rivers (Ivany *et al.*, 2004). Corals are generally stenohaline marine organisms, and there is absolutely no evidence that the diverse associated fauna in these Byram Formation shell beds reflect sediment accumulation in freshwater settings.

The temperatures we report here are comparable to those suggested for the early Oligocene low-mid latitude surface ocean in general and the Gulf of Mexico in particular as determined from the $\delta^{18}O$ of planktonic foraminifera (Zachos *et al.*, 1994). Yet these and other values have more recently been challenged as being anomalously cool because of bias introduced by preservation (Pearson *et al.*, 2001) or diagenesis (Schrag, 1999a). Likewise, our coral temperatures are also several degrees cooler than those reported specifically from the Byram Formation by Kobashi *et al.*, 2001) based on the composition of molluscan carbonate. The difference in the latter case arises from the fact that those authors presumed that Oligocene Gulf Coast waters were somewhat enriched due to evaporation (e.g. Zachos *et al.*, 1994). At this juncture, it is unclear whether Byram waters were depleted relative to global oceans due to mixing of freshwater from the ancestral Mississippi River, comparable to the global ocean, or enriched due to evaporation. However, if Kobashi *et al.* (2001) are correct and these waters were evaporatively enriched, this would serve to raise calculated palaeotemperatures by several degrees and thereby further enhance the incongruity between isotope-derived and element-derived palaeotemperatures, making the composition of the Oligocene ocean even more different than today's.

We also acknowledge here that the mechanisms by which minor elements are incorporated into skeletal carbonates are not yet fully understood. It is likely that the composition of seawater and the temperature of crystallization are not the only controls on Sr/Ca and Mg/Ca. Growth rate may have a significant effect on the Sr/Ca of corals (Thompson & Livingston, 1970; de Villiers *et al.*, 1994), as also suggested for bivalves (Stecher *et al.*, 1996) otoliths (Sadovy & Severin, 1992), and coccolithophorids (Stoll & Schrag, 2001). In addition, Marshall & McCulloch (2002) suggest that physiological
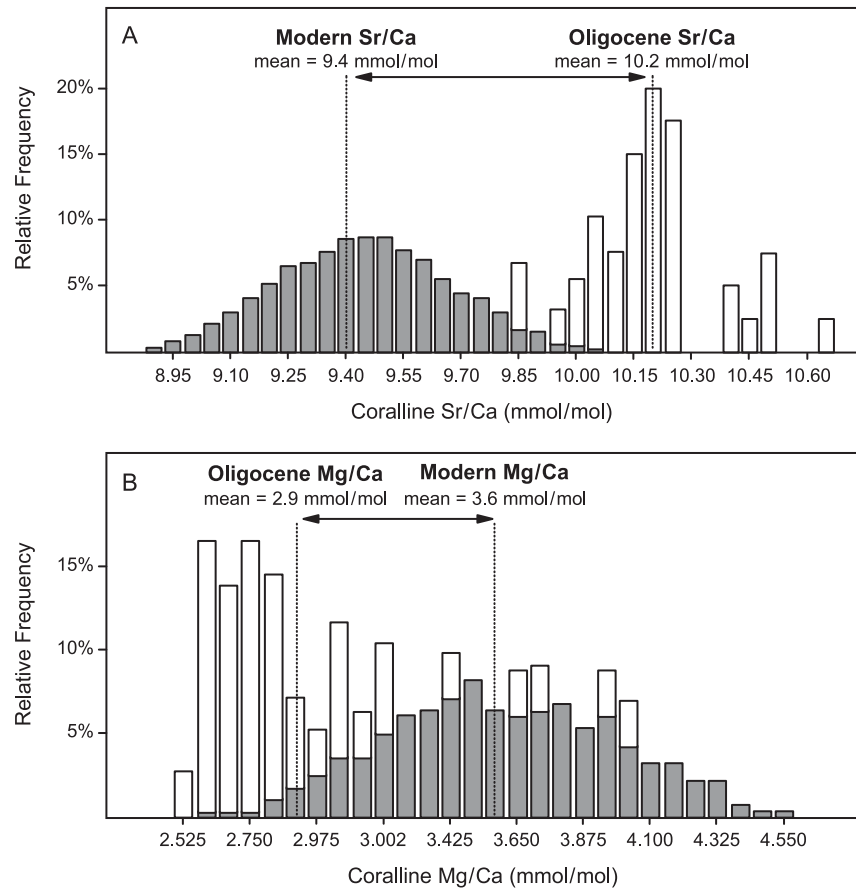
Fig. 5 Comparison of observed Oligocene Sr/Ca (A) and Mg/Ca (B) ratios with those predicted for corals growing in the modern ocean. Disparity between these estimates reflects the difference between early Oligocene and modern seawater compositions.

(e.g. thermal) stress and age of a coral colony may affect the way strontium is partitioned into the skeleton. In this context, we note that all the palaeotemperature equations employed here are derived from hermatypic (zooxanthellate) corals. Yet, based on its colonial morphology (comparatively small branching skeleton with few, widely spaced corallites) and the fact that δ^{13}C is quite depleted (Fig. 1D; McConnaughey *et al.*, 1997), it is possible that *Archohelia* was ahermatypic. Living representatives of the family Oculinidae include both zooxanthellate and azooxanthellate forms, but a documented living species of *Archohelia*, *A. rediviva*, is an ahermatype (Wells & Alderslade, 1979; Cairns *et al.*, 2001). Ahermatypic corals appear to have higher Sr/Ca ratios than hermatypes (Thompson & Livingston, 1970), perhaps a result of slower calcification rates in combination with a distribution coefficient for Sr in aragonite slightly greater than one. This may contribute to the offset seen in predicted vs. observed Sr/Ca and to the anomalously cooler temperatures derived from *Archohelia*. Presumably, Mg/Ca ratios might be expected to be lower in ahermatypes due to the distribution coefficient slightly less than one. However, a recent Sr/Ca temperature equation for the ahermatypic coral *Astrangia* (Cohen *et al.*, 2002) yields palaeotemperatures even lower than those reported here (mean = −3.0 °C), with a range (22.1 °C) much higher than all other equations, suggesting

that it is not at all an appropriate temperature equation for *Archohelia* despite the potential ecological similarity. One way to validate the use of these palaeotemperature equations on *Archohelia* might be to find specimens of that genus that coexist with colonies of *Porites*, such that elemental (and isotopic) ratios of the two can be compared.

Calcite to aragonite seas

Despite the uncertainties, the suggestion of lower Mg/Ca and higher Sr/Ca seawater compositions during the Oligocene is consistent with a Palaeogene transition from 'calcite' to 'aragonite' seas (Sandberg, 1983). Various authors have suggested that first-order variation in the rates of continental weathering (e.g. Berner, 1991), seafloor spreading (Gaffin, 1987; but see Rowley, 2002), and submarine hydrothermal activity (e.g. Wolery & Sleep, 1976; Humphries & Thompson, 1978) have resulted in significant changes in ambient Mg/Ca and Sr/Ca of the global ocean. From these (and other) studies, it has been concluded that Phanerozoic variation in oceanic Mg/Ca primarily reflects change in the intensity of largely mole-for-mole Mg-for-Ca exchange during the hydrothermal alteration of basaltic ocean crust. First-order models of such global cycling (e.g. Wilkinson & Algeo, 1989; Hardie, 1996;

Arvidson *et al.*, 2000) imply an increase in oceanic Mg/Ca since sometime in the Cretaceous, and data on compositions of echinoderm ossicles (Dickson, 2002), rudist bivalve shells (Steuber, 2002), and evaporite fluid inclusions (Lowenstein *et al.*, 2001; Horita *et al.*, 2002) confirm an increase from about unity to a present value of about 5.2 over the past 100 million years. An Oligocene Mg/Ca ratio of 4.2 is in good agreement with this hypothesized trend. Although this value is somewhat higher than the Oligocene Mg/Ca values interpolated by Lowenstein *et al.* (2001) based on Eocene and Neogene analyses, it is higher than their measured late Eocene value, hence consistent with a rising trend toward the present. It is within the error bars for, and hence statistically indistinguishable from, their Neogene values.

The Phanerozoic history of strontium variation is less clear (e.g. Stoll & Schrag, 1998, 2001; Martin *et al.*, 1999). Steuber & Veizer (2002) suggest that the seawater Sr/Ca ratio has decreased from a Cretaceous high of about 12.2 mmole/mol to a modern value of 9.1 mmol mol^{-1} in response to an increase in the precipitation of (Sr-enriched) aragonite and an associated increase in Sr sequestration during the burial of marine carbonate. Lear *et al.* (2003) have recently suggested that late Cretaceous Sr/Ca was about 1.5 times modern values (~13.5 mmole/mole), primarily because of higher Sr delivery via global rivers. Lear *et al.* (2003) also suggest, however, that seawater Sr/Ca dropped to a value of about 8.0 mmol mol^{-1} by the early Oligocene, and then recovered to modern values. This is somewhat lower than the early Oligocene ratio of 9.9 suggested by our coral.

Owing to a general dearth of additional proxy data on Palaeogene ocean compositions, it is not possible at this time to resolve these smaller differences. However, isotope and elemental compositions from the Byram Formation coral do yield Mg/Ca and Sr/Ca ratios that are in good agreement with major changes anticipated from predictions of elemental cycling during an overall transition from shallow Cretaceous seas dominated by calcite precipitation to Neogene seas dominated by the precipitation of aragonite. The early Oligocene represents an interval of time approximately midway between these two states; elemental seawater ratios inferred from isotope and elemental compositions of the Byram Formation coral are in agreement with those anticipated from first-order models, and are generally supported by available data.

The methodology employed here of constraining palaeotemperature with $\delta^{18}O$ and back-calculating the Mg/Ca and Sr/Ca ratios of seawater using well-constrained equations from Modern taxa offers promise for helping to decipher the still-murky history of secular variation in the composition of seawater. This is particularly true if fossil taxa can be chosen for which palaeotemperature equations already exist, or if they can be cross-calibrated with known taxa. While corals are notoriously poorly preserved, enough taphonomic windows likely exist to allow reasonable coverage of at least the Cenozoic in this manner. A better understanding of the history of variation in seawater chemistry will provide important insight into the relative roles of tectonism and weathering through time. And, in addition, to the degree that ocean composition has had an impact on the relative dominance of calcite vs. aragonite-producing organisms in the ocean (e.g. Stanley & Hardie, 1998), revealing these variations may allow us to better interpret the record of biological diversity of skeletonized taxa.

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