

Stable isotope ratio variations in non-scleractinian coelenterate carbonates as a function of temperature

J. N. WEBER¹ and P. M. J. WOODHEAD²

¹ Pennsylvania State University; University Park, Pennsylvania, USA
and

² Discovery Bay Marine Laboratory; Jamaica

Abstract

Some coelenterates of the class Hydrozoa and some anthozoan coelenterates from the subclass Octocorallia secrete skeletons of calcium carbonate. Skeletal carbonates of three hydrozoans and of two octocorals were analyzed for the stable isotopes of carbon and oxygen. The results suggest that each of these coelenterates deposits CaCO₃ in oxygen isotopic equilibrium with seawater, and that at least one octocoral, *Heliopora*, has skeletal carbon in apparent isotopic equilibrium with atmospheric CO₂. Two of these coelenterates, *Millepora* and *Heliopora*, are significant contributors to the construction of coral reefs. Whereas δ¹⁸O of these corals is temperature dependent, δ¹³C is not obviously related to temperature. The δ¹⁸O-temperature relationship is not significantly different from the oxygen isotope paleotemperature scale developed by EPSTEIN et al. (1953). These findings contrast with numerous analyses of the carbonate in scleractinian coelenterates, which have long been reported to deposit CaCO₃ skeletons whose carbon and oxygen isotopic compositions are not in equilibrium with the external sea-water environment.

Introduction

When the oxygen isotope paleotemperature scale was established (EPSTEIN et al., 1951, 1953), it was noted that reef-building corals appear to fractionate oxygen isotopes in the process of depositing skeletal calcium carbonate. Subsequently, numerous analyses of scleractinian corals have confirmed that neither the carbon nor the oxygen of carbonate deposited by scleractinians is in isotopic equilibrium with the atmospheric CO₂ - seawater - seawater bicarbonate system at the temperature of formation (WEBER and WOODHEAD, 1970). In addition to the two variables, temperature and the ¹⁸O/¹⁶O ratio of the ambient water (which determine the oxygen isotopic composition of the calcareous shells of many invertebrates, including some foraminifera, brachiopods, and molluscs), in scleractinian corals the oxygen isotope ratio of the carbonate is apparently affected by some vital or physiological factors (EPSTEIN et al, 1951).

Coelenterates other than scleractinians also secrete a skeleton of calcium carbonate, but their carbon and oxygen isotopic compositions have received little attention, in contrast to the numbers of scleractinians

examined. Analyses of some hydrozoan and octocorals indicate that such coelenterates do precipitate skeletal CaCO₃ in oxygen isotopic equilibrium with seawater, and that at least for one genus, the carbon isotope ratio is similar to that predicted for isotopic equilibrium between CaCO₃ and atmospheric CO₂. Two of these, *Millepora* and *Heliopora*, are important contributors to coral-reef development in many parts of the world. The coelenterates considered here are: *Millepora* (order Milleporina), *Distichopora* (order Stylasterina), and *Stylaster* (order Stylasterina) in the class Hydrozoa; *Heliopora* (order Coenothecalia) and *Isis* (order Gorgonacea), both octocorals in the class Anthozoa.

Methods

Samples were collected at several localities (Table 1) in order to investigate the effect of temperature on isotopic composition. All analyzed specimens were obtained in coral-reef environments at water depths less than 8 m. Sample preparation techniques have been described by WEBER and WOODHEAD (1970), and a detailed account of the methods used for isotope ratio analysis by mass spectrometry has been published (WEBER and RAUF, 1966; DEINES, 1970). The mean annual surface-water temperatures listed in Table 1 were obtained from monthly charts of sea surface temperatures supplied by the U.S. Navy. Isotope data are reported in delta notation,

$$\delta^{18}\text{O} = \left(\frac{R_x}{R_s} - 1 \right) 1000, \quad (1)$$

where R_x is the ¹⁸O/¹⁶O ratio of CO₂ extracted at 25 °C from the carbonate sample by the phosphoric acid method, and R_s is the ¹⁸O/¹⁶O ratio of the PDB CO₂ standard. For δ¹³C values, R_x and R_s refer to the ratio ¹³C/¹²C.

Results

As the oxygen isotopic composition of seawater is essentially constant throughout the ocean regions

Table 1. Localities sampled

Locality	Latitude	Longitude	Code for Fig. 1	Mean annual water temperature (°C)
Lady Musgrave Reef, Australia	24°S	152°E	LM	24.2
Heron Island, Australia	23°S	152°E	H	23.9
Gannet Reef, Australia	22°S	153°E	G	24.6
Hook Island, Australia	20°S	149°E	HK	24.9
Lizard Reef, Australia	15°S	146°E	L	26.3
Yonge Reef, Australia	14°S	146°E	Y	26.7
Torres Strait	10°S	142°E	T	28.0
Port Moresby, Papua	9°S	147°E	PM	28.4
Rabaul, New Britain	4°S	152°E	R	29.3
Buka, Solomon Islands	5°S	155°E	BK	28.6
Guadalcanal, Solomon Islands	10°S	160°E	HN	29.3
Noumea, New Caledonia	22°S	167°E	NU	26.0
Viti Levu, Fiji	18°S	178°E	FJ	26.8
Tonga	21°S	175°W	TG	25.0
Pago Pago, American Samoa	14°S	171°W	SM	28.1
Tahiti	18°S	149°W	TH	26.7
Bora Bora, French Polynesia	16°S	152°W	BB	26.3
Palau, Caroline Islands	7°N	134°E	KR	29.2
Guam	13°N	145°E	GM	28.5
Saipan, Mariana Islands	15°N	146°E	SP	28.2
Tarawa Atoll, Gilbert Islands	1°N	173°E	TR	28.1
Majuro Atoll, Marshall Islands	7°N	171°E	MJ	29.1
Key West area, Florida	24°N	82°W	K	25.5
Mauritius	20°S	58°E	MR	25.9

Table 2. Carbon and oxygen isotopic composition of skeletal carbonate of major genera of scleractinian corals from Heron Island (Australia) and Tarawa Atoll (Gilbert Islands). Mean δ value (standard deviation) number of specimens analyzed

Genus	Heron Island		Tarawa Atoll	
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
<i>Acropora</i>	-0.03(0.64)51	-3.20(0.32)51	-1.22(0.70)55	-4.34(0.32)55
<i>Favia</i>	0.19(0.67)12	-4.25(0.17)12	-2.22(0.92)19	-5.39(0.26)19
<i>Favites</i>	1.43(0.64)10	-4.25(0.19)10	-1.16(1.06)10	-4.72(0.22)10
<i>Fungia</i>	-0.50(1.06)17	-3.68(0.23)17	-2.82(0.62)37	-4.87(0.22)37
<i>Goniopora</i>	-2.55(0.85)13	-4.45(0.51)13	-3.07(0.35)4	-4.48(0.40)4
<i>Lobophyllia</i>	-0.71(1.44)7	-4.37(0.19)7	-2.42(0.84)8	-5.14(0.21)8
<i>Merulina</i>	-1.09(0.69)9	-4.29(0.31)9	-3.11(1.07)4	-5.48(0.17)4
<i>Montipora</i>	-0.21(0.83)19	-3.36(0.28)19	-0.37(0.93)21	-4.54(0.26)21
<i>Pavona</i>	-1.44(0.91)12	-3.98(0.46)12	-1.81(0.90)15	-4.45(0.70)16
<i>Platygyra</i>	1.66(1.01)22	-4.29(0.19)22	-1.82(1.13)12	-5.24(0.26)12
<i>Plesiastrea</i>	1.28(0.57)13	-4.21(0.11)13	—	—
<i>Pocillopora</i>	-2.38(0.54)9	-3.83(0.21)9	-2.79(0.58)21	-5.00(0.28)21
<i>Porites</i>	-0.09(0.74)24	-3.95(0.43)24	-1.34(1.42)38	-5.19(0.37)38
<i>Psammocora</i>	-0.78(0.64)10	-3.57(0.27)10	—	—
<i>Stylophora</i>	-0.22(0.27)10	-3.52(0.17)10	-1.33(0.42)11	-4.17(0.11)11
<i>Symphylia</i>	-1.21(0.94)10	-4.39(0.15)10	—	—

where samples were collected, variations in the $\delta^{18}\text{O}$ of CaCO_3 precipitated in isotopic equilibrium with seawater, hereafter designated CaCO_3 (eq.), are related to temperature differences according to the relationship determined by EPSTEIN et al. (1953). At Heron Island, Australia, and at Tarawa Atoll, for example, the $\delta^{18}\text{O}$

values of CaCO_3 (eq.) would be -1.65 and -2.52% respectively. Representative data for major scleractinian genera (Table 2) from these localities indicate considerable ^{18}O enrichment with respect to equilibrium values.

Assuming a value of -6.4% for the $\delta^{13}\text{C}$ of at-

mospheric CO₂ over the oceans (CRAIG and KEELING, 1963), the carbon isotopic composition of CaCO₃ (eq.) can be calculated from the isotope fractionation factor (α) in the CO₂-CaCO₃ system measured by EMRICH et al. (1970). $\delta^{13}\text{C}$ values at 20° and 30 °C are

Table 3. Carbon and oxygen isotopic composition of skeletal carbonate of *Millepora*, *Distichopora*, *Heliopora*, *Stylaster*, and *Isis*. Mean δ value (standard deviation) number of specimens analyzed

Genus	Locality (Table 1)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
<i>Millepora</i>	H	0.81(0.33)11	-1.60(0.27)11
	LM	0.80(-)2	-1.66(-)2
	G	0.17(0.28)5	-1.65(0.20)5
	K	-0.01(0.38)12	-1.85(0.46)12
	FJ	0.45(0.48)8	-2.22(0.30)8
	TH	1.34(0.12)3	-1.97(0.04)3
	NU	0.51(0.37)14	-2.05(0.31)14
	GM	-0.23(0.38)4	-2.58(0.17)4
	SM	0.55(0.22)7	-2.14(0.31)7
	Y	0.24(0.95)6	-2.66(0.29)6
	L	1.00(0.29)5	-2.26(0.48)5
	KR	1.32(-)2	-2.66(-)2
	SP	0.51(0.86)3	-2.61(0.09)3
	T	1.48(-)2	-2.33(-)2
	PM	0.70(0.58)16	-2.70(0.40)16
	TR	0.97(0.42)19	-2.36(0.24)19
	R	1.42(0.20)3	-3.04(0.12)3
	BK	0.79(0.27)7	-2.77(0.13)7
	HN	1.27(0.27)6	-2.88(0.19)6
	TG	1.20(0.48)15	-1.71(0.25)15
MJ	0.80(0.89)6	-2.89(0.27)6	
MR	1.11(0.29)3	-1.64(0.17)3	
BB	1.17(0.26)9	-2.07(0.26)9	
HK	0.94(0.79)3	-1.78(0.10)3	
<i>Distichopora</i>	H	1.87(0.16)9	-1.37(0.26)9
	FJ	1.87(-)2	-2.01(-)2
	TH	2.21(0.13)3	-1.64(0.18)3
	NU	1.70(0.17)9	-1.66(0.14)9
	KR	2.06(-)2	-2.54(-)2
	PM	1.21(0.21)10	-2.63(0.16)10
	TG	1.32(0.46)4	-1.55(0.10)4
<i>Heliopora</i>	GM	4.52(-)1	-2.60(-)1
	KR	4.38(-)2	-2.47(-)2
	SP	4.59(0.04)3	-2.37(0.05)3
	PM	4.50(0.24)9	-2.19(0.17)9
	TE	4.52(0.27)15	-2.12(0.19)15
	BK	5.00(0.29)5	-2.50(0.23)5
	HN	4.65(0.24)4	-2.60(0.12)4
	MJ	4.18(0.34)7	-2.74(0.10)7
<i>Stylaster</i>	H	2.08(0.24)6	-1.39(0.14)6
	Isis	2.50(-)1	-1.61(-)1

+3.70 and +3.07%, respectively. Using calculated values of α (BOTTINGA, 1968), the $\delta^{13}\text{C}$ of CaCO₃ (eq.) is +4.23% at 20 °C. In each case, the carbonate of scleractinian coral skeletons contains much less ¹³C than predicted for conditions of isotopic equilibrium (Table 2).

The oxygen isotopic composition of the hydrozoan coral *Millepora* is distinctly different from that of the scleractinians (Table 3). This genus was collected at 24 localities (total of 171 specimens), which represent a temperature range extending from 23.9° to 29.3 °C. $\delta^{18}\text{O}$ is negatively correlated with temperature (T), and least squares regression, using DEMING's (1943) method where both variables are equally weighted, yields the relation:

$$T (^{\circ}\text{C}) = 17.18 - 4.31 \delta^{18}\text{O} (\text{‰}).$$

Within the limits of uncertainty in the isotope and temperature data, the $\delta^{18}\text{O}$ values of CaCO₃ (eq.) and CaCO₃ secreted by *Millepora* are virtually identical at a given temperature.

$T (^{\circ}\text{C})$	$\delta^{18}\text{O}$ <i>Millepora</i>	$\delta^{18}\text{O}$ CaCO ₃ (eq.)	Difference
24	-1.58	-1.65	0.07
26	-2.05	-2.07	0.02
28	-2.52	-2.48	0.04

Mean $\delta^{18}\text{O}$ values for *Millepora* from various localities are plotted as a function of temperature in Fig. 1. The line shown on this figure represents the oxygen isotope paleotemperature scale (EPSTEIN et al., 1953). For 19 of the 24 localities, the difference between the mean $\delta^{18}\text{O}$ value and $\delta^{18}\text{O}$ of CaCO₃ (eq.) is less than 0.2%.

A total of 39 specimens of *Distichopora* was obtained from 7 localities whose mean annual water temperatures span the same range as *Millepora*. The least squares regression line calculated from the data in Table 3 is almost parallel to the isotopic paleotemperature curve, but is displaced by about 0.2% towards greater ¹⁸O/¹⁶O at a given temperature.

Heliopora (46 specimens from 8 localities) was found over a much smaller range of temperature (minimum 28.1; maximum 29.3 °C) than *Millepora* and *Distichopora*. As a result, the slope of the least squares regression line is less reliable, because the error in determining mean temperature is large relative to the total range of temperature. Nevertheless, $\delta^{18}\text{O}$ of *Heliopora* and $\delta^{18}\text{O}$ of CaCO₃ (eq.) are not greatly different, especially for samples at higher temperatures:

$T (^{\circ}\text{C})$	$\delta^{18}\text{O}$ <i>Heliopora</i>	$\delta^{18}\text{O}$ CaCO ₃ (eq.)	Difference
29.3	-2.74	-2.76	0.02
28.7	-2.51	-2.63	0.12
28.1	-2.27	-2.50	0.23

Samples of *Stylaster* and *Isis* from only one locality were available for analysis (Table 3). The results suggest that the oxygen isotopic composition of the

skeletons of these corals is also in equilibrium with seawater, quite unlike the scleractinians from the same reefs.

For *Millepora*, $\delta^{13}\text{C}$ is generally in the range +0.5 to +1.5‰. *Distichopora*, *Stylaster*, and *Isis* tend towards higher ^{13}C contents ($\delta^{13}\text{C} = +1$ to +2.5‰). The carbon isotopic composition of each of these four corals is intermediate between that of most scleractinians and that of CaCO_3 (eq.). Only *Heliopora* ($\delta^{13}\text{C} = +4$ to +5‰) approaches equilibrium values. No evidence of a relationship between $\delta^{13}\text{C}$ and temperature is indicated by the data.

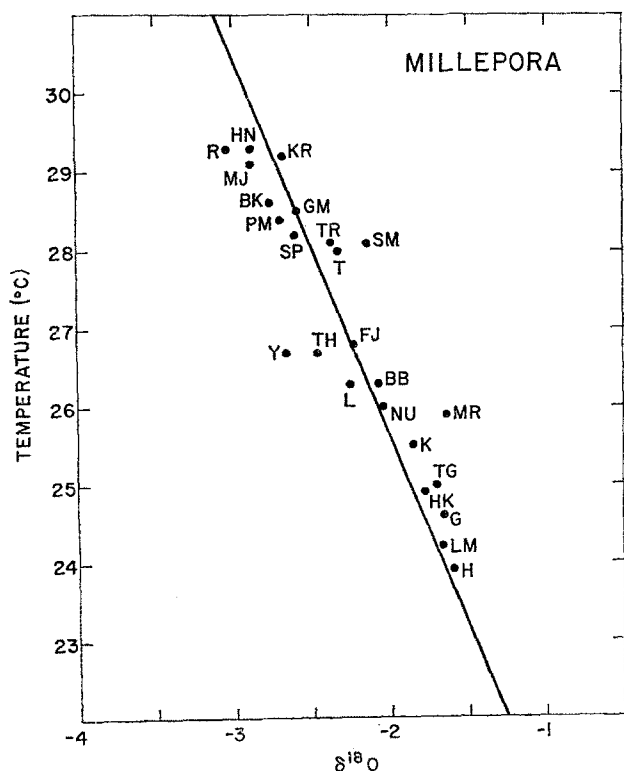


Fig. 1. *Millepora*. Mean $\delta^{18}\text{O}$ values of skeletal carbonate of hydrozoan coral from 24 localities plotted against mean annual water temperature. Locality codes are listed in Table 1

Discussion and conclusions

Higher concentrations of ^{12}C and ^{16}O in coral carbonates than in CaCO_3 (eq.) are attributed to the relatively primitive and inefficient respiratory mechanisms of coelenterates which permit the incorporation of metabolic carbon dioxide into the calcareous skeleton. This process was first proposed by H. CRAIG (cited in REVELLE and FAIRBRIDGE, 1957), and has subsequently been supported by studies of PEARSE (1970) and WEBER and WOODHEAD (1970). All samples of the

more than 80 genera of hermatypic and ahermatypic scleractinian skeletons analyzed have isotopic compositions significantly different from CaCO_3 (eq.). At least three hydrocorals and two octocorals, however, deposit calcium carbonate in apparent oxygen isotopic equilibrium with ambient seawater, and one of these, *Heliopora*, consistently yields $\delta^{13}\text{C}$ values, suggesting carbon isotopic equilibrium between skeletal CaCO_3 and atmospheric CO_2 . These findings are puzzling, in that the five non-scleractinian corals investigated appear to excrete metabolic carbon dioxide through the same respiratory mechanisms as the isotopically anomalous scleractinians, that is, by diffusion of the metabolite through the tissues and/or uptake by zooxanthellae. The polyps of the hydrozoans and also of *Heliopora*, however, are very much smaller than those of scleractinian corals, and it is possible that, with faster excretion of CO_2 to seawater, little or no metabolic carbon dioxide is incorporated in the skeleton. This is, at present, speculation, and why some coelenterates precipitate skeletal carbonate in apparent isotopic equilibrium with the external environment, whereas others do not, is a challenging aspect of the overall problem of calcification processes in the corals which build reefs.

Summary

1. Measurements of carbon and oxygen isotopic compositions of the skeletal calcium carbonate in the non-scleractinian coelenterates, *Millepora*, *Distichopora*, *Stylaster*, *Heliopora*, and *Isis*, are compared with carbon and oxygen stable isotope data for scleractinian corals.

2. Skeletal carbonate of none of the more than 80 genera of scleractinian corals analyzed is in isotopic equilibrium with the seawater system; all such carbonates are enriched in the lighter isotopes, ^{12}C and ^{16}O , with respect to CaCO_3 precipitated in isotopic equilibrium with seawater.

3. *Millepora* skeletons (171 specimens from 24 localities representing a temperature range of 23.9° to 29.3 °C), however, appear to be in oxygen isotopic equilibrium with seawater. $\delta^{18}\text{O}$ is negatively correlated with temperature and the relationship is virtually identical to that predicted by the "paleotemperature equation". Similar results were found for the other non-scleractinian coelenterates analyzed.

4. Of all coelenterates studied, only *Heliopora* has skeletal carbon isotope ratios suggesting carbon isotopic equilibrium between CaCO_3 and atmospheric CO_2 .

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First author's address: Dr. J. N. WEBER
Pennsylvania State University
Department of Geosciences
Geology Section
303 Deike Building
University Park
Pennsylvania 16802
USA

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