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Sampling Implications of Stable Isotope Variation in Holocene Reef Corals from the Mariana Islands

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Abstract—A sampling program was carried out on coral populations from 2 large emergent Holocene reef limestone outcrops in the Mariana Islands to estimate frequency distributions and sampling variation patterns in stable isotopes. At the "whole rock" level of sampling and analyses, both $\delta^{13}C$ and $\delta^{18}O$ appear to follow unimodal distributions among 8 genera across both localities, Guam and Pagan, but the curves are skewed toward lighter or more negative values. Conversion to low Mg-calcite of a small (< 5%) portion of 18 of the 85 analyzed specimens appears to account for that asymmetry.

Minimum sampling error is estimated at $\pm\ 0.44/\sqrt{n}$ for $\delta^{13}C$ and $\pm\ 0.67/\sqrt{n}$ for $\delta^{18}O$ (between samples within the same colony). There is a persistent increase in the experimental error introduced as the level of comparison changes from between samples within the same colony to between samples of different genera from different localities where the standard errors reach a maximum of $\pm\ 1.46/\sqrt{n}$ and $\pm\ 1.31/\sqrt{n}$ for $\delta^{13}C$ and $\delta^{18}O$, respectively. This change translates to a parallel increase in the minimum difference between stable isotope values that could be detected at any specific probability level.

The variation in isotopic composition at different sampling levels, i.e., colonies, genera, reef localities, etc. demands that the target population be carefully defined before sampling. This should ensure that an appropriate number of samples is analyzed at each level of comparison.

Introduction

Carbonate petrologists and geochemists have long attached paleo-environmental implications to values of oxygen and carbon isotopes from the skeletal components of limestones and, on these bases, have advanced both depositional and diagenetic interpretations (Hudson, 1977; Dickson and Coleman, 1980; Anderson and Arthur, 1983, and many others). Often, however, subtle environmental distinctions are ascribed to differences or trends in $\delta^{18}O$ and $\delta^{13}C$ values when, in fact, it is not at all apparent that statistical significance has been documented.

The aim of this report is to point out sources, levels, and relative magnitudes of stable isotope variation in coral populations which can be expected when sampling emergent Holocene carbonate rocks. Assessments of sampling errors can lead to more effective experimental designs (including the requisite number and levels of samples) and more efficient and rigorous data evaluation methods. This objective will be approached by first describing the frequency distributions of $\delta^{18}O$ and $\delta^{13}C$ in the targeted populations.

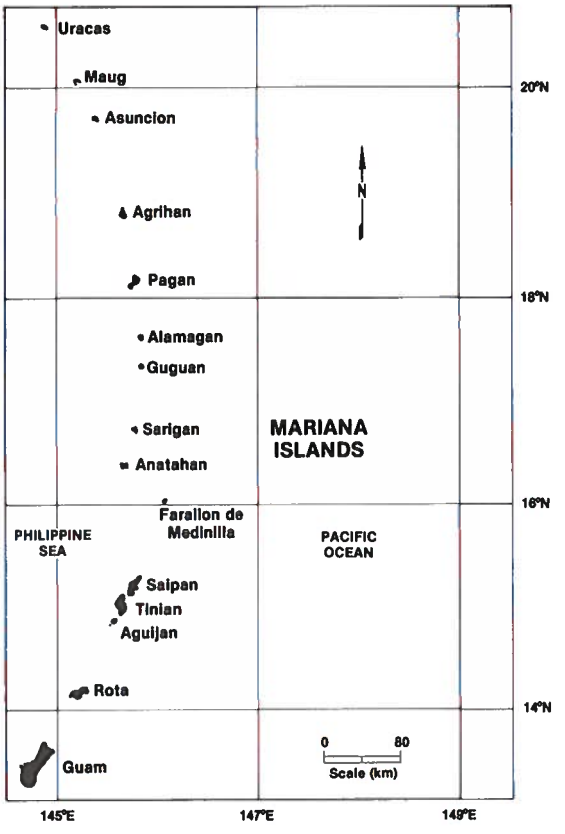

Figure 1. Map of Mariana Islands showing location of Pagan and Guam

Through a knowledge of the natural distribution of a variable, one can assert, with specified probability, that a particular value or the mean of a series of values is "unusual", and is thus either spurious or perhaps worthy of geologic interest.

Weber and Woodhead (1970) comment that, "isotopic information contained in ancient carbonate sediments cannot be fully utilized until the behavior of stable isotopes during the processes of organic and inorganic $CaCo_3$ precipitation, sediment transport, and diagenesis under various conditions is better understood". Of equal importance to meaningful interpretation is a thorough understanding of the sources and magnitudes of isotopic sampling variation associated with reef carbonates. This goal requires a careful assessment of the factors influencing primary isotopic composition in modern corals.

GEOLOGIC BACKGROUND

The results reported here stem from studies of the evolution of Neogene-to-Holocene reef and lagoonal limestones in the Mariana Island double arc system in the western Pacific basin (Fig. 1). There, since at least late Eocene, shallow-water limestones have been

accreting onto the "high islands" comprising the older southern arc. The only island in the younger arc to the north with any reported carbonate buildup is Pagan (Fig. 1), which has several raised Holocene reefs. With the exception of most of the Holocene deposits, all carbonates in the Marianas have undergone almost complete diagenetic alteration to low-Mg calcite.

PREVIOUS RELATED GEOLOGIC STUDIES

Detailed general geology of the larger inhabited islands has been reported by Cloud et al. (1956) for Saipan; Corwin et al. (1957) for Pagan; Doan et al. (1960) for Tinian; and Tracey et al. (1964) for Guam. Sugawara (1934) briefly described the geology and geomorphology of Rota.

Schlanger (1964) described the depositional framework of the carbonates on Guam and related facies development to reef geomorphology using classical descriptive petrography. Diagenetic processes and textures of the Plio-Pleistocene Mariana Limestone on Orote Peninsula, Guam, have recently been described by Clayshulte and Ayres (1983). Reef-coral community structures, zonation, growth strategies, and both depositional and diagenetic facies development within the Holocene sections of Guam, Rota, and Pagan are a current research concern of this writer and collaborators (Siegrist, Randall, and Siegrist, 1984; Siegrist and Randall, 1985; Randall, Siegrist, and Siegrist, 1984; Bell and Siegrist, 1989).

The causes of stable isotope variability within modern benthic communities, especially within reef-building corals, have been well described (Keith and Weber, 1964; Weber, 1968; Weber and Woodhead, 1970, 1972; Hudson, 1977; Goreau, 1977a,b,c; Erez, 1978; Swart, 1983; Gonzalez and Lohmann, 1985; and many more). Species-specific responses in photosynthesis, respiration and rate of calcification to variations in ambient depths, temperatures and salinities contribute to the overall non-equilibrium isotopic compositions reported for hermatypic corals. We assume that these factors operated in much the same way with the same results during the Holocene. Stable isotope studies of Holocene carbonates support this notion (Gonzalez and Lohmann, 1985), but even minor diagenetic alteration will skew the dominant isotopic signal (Siegrist, 1986).

It is not our intention to attempt to ascribe causes to the isotopic compositions reported in this study. Unlike the previous works cited above, we are interested in how the variation changes with the level of sampling and how one must therefore compensate for those changes to assure reasonably precise estimates of composition.

Methods

STUDY SITES

Two locations were selected to study the distribution and sampling variation of stable isotopes in reef limestones: (1) Pagan (Fig. 1 and 2a): An emergent Holocene reef crops out for a distance of about 1500 m along a south-facing sector to the east coast of the caldera-dominated north end of Pagan. The fossil reef varies in width from about 10 to 65 m, averages about +1.0 m above low tide, and is situated within the high intertidal to

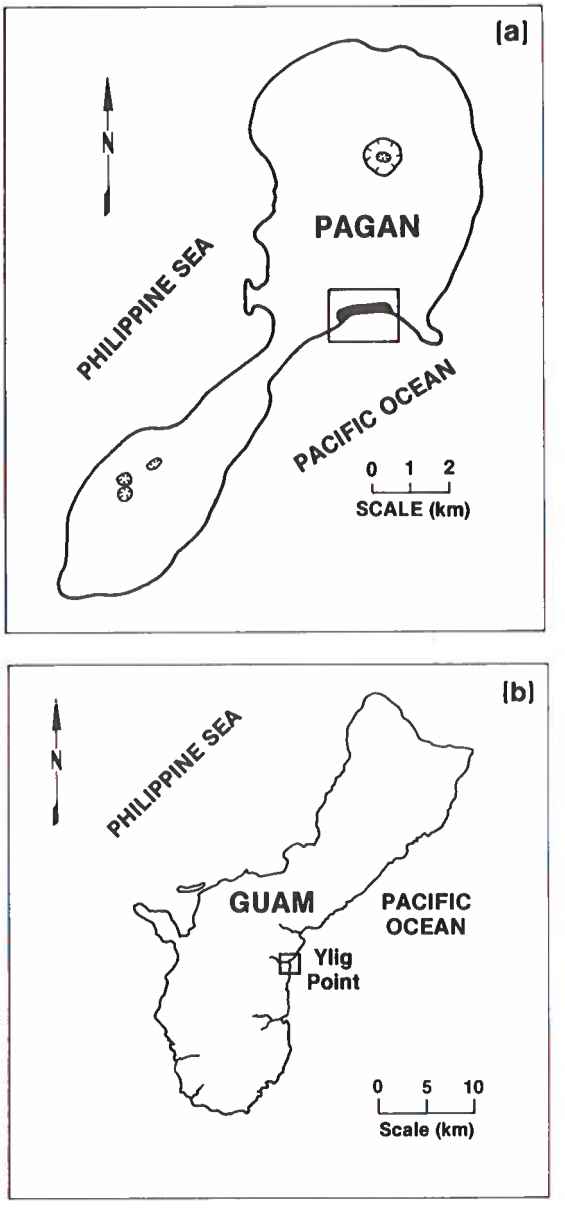

Figure 2. Maps showing location of sampled Holocene reefs. (a) Pagan. (b) Guam.

lowest supratidal zone. It lies directly upon basaltic substrate and is apparently no more than 1.5 to 2.0 m thick. (2) Guam (Fig. 1 and 2b): A raised Holocene reef comprises Ylig Point on the windward east-central coast of Guam. The nearly horizontal, wave-truncated outcrop measures roughly 500 by 150 m and rarely exceeds +1.2 m above low tide. As much as 7 m of Holocene section have been deposited on an irregular erosion surface of

the Plio-Pleistocene Mariana Limestone. Extensive surface and subsurface sampling reveal that an initial or "start-up" reef, predominantly of *Acropora*, evolved into two communities: a seaward, *Pocillopora*-rich, low diversity community and a landward, *Acropora*-rich, high diversity community (Siegrist et al., 1984).

EXPERIMENTAL QUESTIONS AND FIELD SAMPLING DESIGNS

This study is designed to address some basic questions concerning the distribution and sampling variation of $\delta^{18}O$ and $\delta^{13}C$ in emergent Holocene corals. These questions are: (1) What is the variation in $\delta^{18}O$ and $\delta^{13}C$ within the same colony or within the same genus (but different colony) of coral? (2) What is the overall variation in $\delta^{18}O$ and $\delta^{13}C$ in corals from the surface of one or more large reef outcrops of Holocene limestones? (3) Do frequency distributions and sampling variability patterns in stable isotopes permit statistical discrimination between populations of reef corals? (4) Are the frequency distributions sufficiently defined to give insight into the evolution of these populations and to enable the development of more efficient (less biased) sampling designs?

Within-colony variation was addressed by sampling along a transect across a single, huge colony (diameter = 9.3 m) of *Porites* lying in the highest intertidal-lowest supratidal

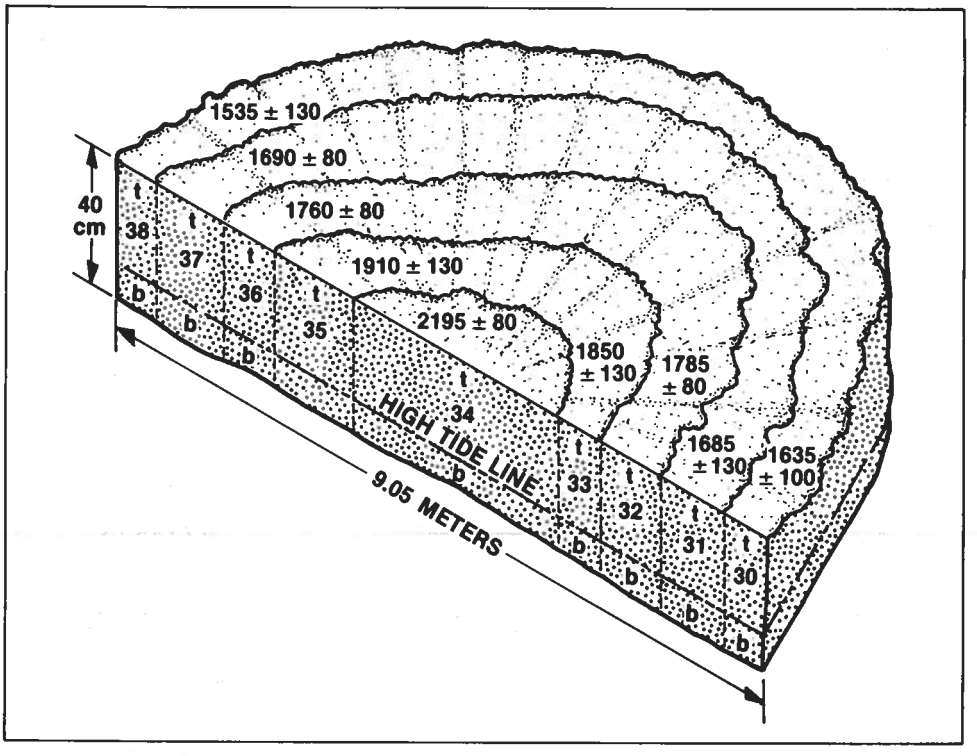

Figure 3. Sampling structure, implemented on large *Porites* colony on Pagan. From each numbered segment, a supratidal (t) and an intertidal (b) sample were collected.

zone on Pagan. The upper two-thirds of the .40 m thick colony is in the freshwater vadose zone except during unusual tidal intervals and storm surges, whereas the bottom portion is in marine waters, except during lowest (spring) tide.

Eighteen samples (roughly 4 × 4 × 6 cm) were collected from this colony along a single diameter as indicated in Figure 3. This size was collected to average out variations in isotopic values arising from seasonal paleotemperature variability. Samples generally equidistant from the center and within the identical macroscopically defined concentric growth segment were assumed in the field to be roughly the same age, an assumption that seems valid as indicated by ^{14}C age dates (Fig. 3). One set of samples was collected across the upper surface ("t" on Fig. 3); the other set came from the corresponding segments within the wet zone near the lower edge of the exposure ("b" on Fig. 3). From this design, the two main sources of variation are Location (broadly, the diagenetic environment: freshwater vs. marine vadose) and Age (distance from colony center).

There are two samples at each combination of Location and Age. For example, P36t and P32t (fig. 3), are about equidistant from the colony center along the sampling transect and include the same growth interval. Because the growth intervals between traceable concentric rings can be demonstrated by ^{14}C analysis to be coeval, these paired samples such as P36t and P32t represent quasi-duplicate samples and as such serve as the basis for computing the experimental error in the statistical analyses that follow.

To compare differences between populations of corals, at Pagan and at Ylig Point, Guam, seaward-to-landward line transects were run across the top of the reefs. Three line transects were run at Pagan, about 250 m apart, and at Ylig, 24 transects, each about 75 m long, 3 m apart, were run. At both locations, samples were collected every 0.75 m along the transects. From the over 200 corals collected, 85 individual specimens were randomly selected, enabling the accumulation of sufficient coral genera to establish both within- and between-genera variation in stable isotope values and to estimate overall variation in surface sampling. Also the data developed from this sampling program were used to estimate the isotopic frequency distributions from the coral populations. The experimental design can be visualized from the scheme in Figure 4.

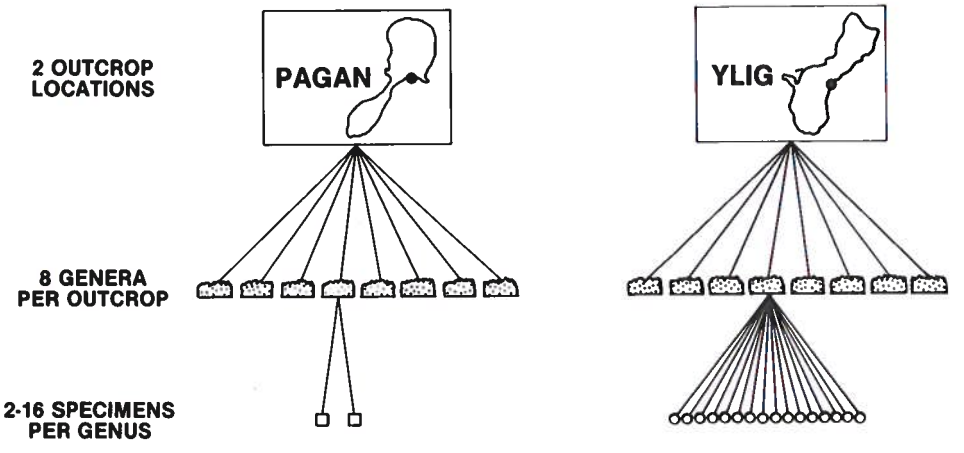

Figure 4. Experimental design used to evaluate line-transect data set in ANOVA in Table 3.

An important experimental question for future study is whether the variation in stable isotope values across a Holocene outcrop is random or systematic and, if systematic, whether the pattern is ascribable to depositional or diagentic controls. To address this question requires considerably more samples and resources than were available for the current study. As reported above (Siegrist, 1986), landward meteoric influences tend to mask between-genera differences such that a spatial variation data set would require careful filtering and interpreting.

STABLE ISOTOPE ANALYSIS

The 85 coral samples were classified to the generic level, and along with the 18 Pagan *Porites* specimens were split, cleaned in hydrogen peroxide and HCl, and approximately 75 gram (1 × 1 × 4 cm) subsamples were shipped for isotopic analyses to the U.S. Geological Survey, Menlo Park, California. All coral samples were completely ground and analyzed by x-ray diffraction to identify the presence of secondary calcite. Isotope analyses were then performed on a Finnegan MAT 251 60-degree sector mass spectrometer; values are reported with reference to PDB.

Results and Discussion

PETROGRAPHY

The petrography of detrital fractions associated with the coral populations at Ylig and Pagan has been previously reported (Siegrist et al., 1984, Siegrist & Randall, 1985). Briefly, they consist mainly of poorly-sorted coral, coralline algal, molluscan, foraminiferal, and echinoidal fragments (average size about 1-phi) cemented by light-tan high-Mg calcite (HMC) micrite. Isopachous rim cements, body-cavity linings and peloidal fills of HMC and aragonite are pervasive yet rarely exceed 3% of any specimen. Low-Mg calcite (LMC) is absent in Pagan specimens, but occurs in about 5% of the detrital samples from Ylig, although it never exceeds 5% in any individual specimen.

FREQUENCY DISTRIBUTIONS

Isotopic analyses are given in Table 1. Histograms of the frequency distributions of stable isotopes are presented in Figure 5; the familiar $\delta^{13}C$ vs. $\delta^{18}O$ cross plot is given in Figure 6. The distributions indicate that the parent populations of $\delta^{13}C$ and $\delta^{18}O$ are unimodal and perhaps follow a Normal Distribution as Chi-Square Goodness-of-Fit test gave values of 17.05 for $\delta^{13}C$ and 23.4 for $\delta^{18}O$ at 7 and 10 degrees of freedom, respectively (Davis, 1986). The departure from a Normal Distribution at the "whole rock" level can be traced quite clearly to those samples shown in Figure 5 and marked with asterisks in Table 1(b) that have detectable amounts of diagenetically produced LMC.

Averages of 11 stable isotope values from closely associated detrital carbonate specimens are indicated on both histograms. They point to generally more positive isotopic signatures in detrital fractions than in coral framework on the same outcrop, a result previously reported by other workers (Gonzalez and Lohmann, 1985).

Table 1. Stable isotope data from (a) large *Porites* colony on Pagan and (b) line-transects and grid sampling at Ylig and Pagan.

(a)

Sample Number	$\delta^{13}C$	$\delta^{18}O$	Sample Number	$\delta^{13}C$	$\delta^{18}O$
P30t	+2.34	−3.31	P34b	+2.03	−2.58
P30b	+1.04	−4.82	P35t	+0.98	−4.57
P31t	+0.34	−4.55	P35b	+0.91	−4.83
P31b	−0.20	−5.16	P36t	+0.61	−1.09
P32t	+0.84	−4.40	P36b	+0.56	−4.81
P32b	+0.68	−4.92	P37t	−0.19	−4.52
P33t	+0.97	−4.54	P37b	+0.66	−4.87
P33b	+1.02	−4.82	P38t	+1.07	−4.15
P34t	+2.16	−2.00	P38b	+0.38	−4.75
			Average	+0.95	−4.32

(b)

Acanthastrea	$\delta^{13}C$	$\delta^{18}O$	*Favia*	$\delta^{13}C$	$\delta^{18}O$
AcG1[1]	+1.15	−4.76	FG1[1]	+0.47	−4.31
AcG2	−0.08	−4.41	FG2	+0.38	−4.51
AcP1	+1.41	−2.27	FG3	−0.34	−4.28
Acp2	+1.20	−3.00	*FG4	−0.85	−4.69
Average	+0.92	−3.61	FG5	+0.31	−4.51
			*FG6	−0.77	−4.65
			FG7	+0.05	−4.80
			*FG8	−2.80	−5.31
			FG9	+0.92	−3.60
			FP1	−0.01	−4.03
			FP2	−0.42	−3.55
			FP3	+0.80	−3.40
			Average	−0.12	−4.30
Acropora	$\delta^{13}C$	$\delta^{18}O$	*Goniastrea*	$\delta^{13}C$	$\delta^{18}O$
ArG1	+0.84	−2.56	GG1	−0.30	−2.84
ArG2	+0.59	−3.25	*GG2	−0.69	−5.27
ArG3	+1.93	−3.53	*GG3	−1.33	−5.63
ArG4	+2.20	−3.57	*GG4	−2.21	−4.97
ArP1	−0.50	−3.56	GG5	−0.13	−5.07
ArP2	+0.27	−3.40	*GG6	−1.64	−3.04
ArP3	+0.55	−3.77	GP1	−0.10	−4.64
ArP4	+0.07	−2.94	GP2	+1.18	−3.86
ArP5	+1.58	−3.33	GP3	+0.83	−4.33
ArP6	+0.22	−3.51	GP4	+1.84	−4.06
ArP7	+0.92	−3.22	GP5	+1.18	−4.32
ArP8	−0.14	−3.32	GP6	+1.00	−4.57
ArP9	−0.45	−3.57	GP7	+0.65	−4.68
ArP10	−0.30	−2.27	*Average*	+0.02	−4.40
ArP11	+1.02	−2.20			
ArP12	−0.05	−3.63			
Average	+0.55	−3.23			
Hydnophora	$\delta^{13}C$	$\delta^{18}O$	*Platygyra*	$\delta^{13}C$	$\delta^{18}O$
HP1	+0.87	−3.96	PyG1	+0.49	−4.97
HP2	+1.83	−3.57	PyG2	+0.57	−4.86

Table 1.
(*continued*)

(b)

Hydnophora	$\delta^{13}C$	$\delta^{18}O$	*Platygyra*	$\delta^{13}C$	$\delta^{18}O$
HP3	+0.44	−3.40	PyP1	+0.81	−4.42
Average	+1.05	−3.64	PyP2	+0.59	−4.73
			Average	+0.62	−4.75
Leptoria	$\delta^{13}C$	$\delta^{18}O$	*Pocillopora*	$\delta^{13}C$	$\delta^{18}O$
LG1	+1.23	−3.11	*PcG1	−1.89	−4.11
LG2	+1.20	−0.93	*PcG2	−1.15	−3.93
LG3	+0.38	−4.90	PcG3	+1.03	−2.41
LG4	+3.24	−2.29	PcG4	+1.23	−2.45
LG5	+1.86	−3.08	*PcG5	−2.01	−3.83
*LG6	−3.30	−5.22	PcG6	+0.57	−2.71
LG7	+0.30	−3.93	*PcG7	−0.71	−4.71
*LG8	+1.30	−4.54	*PcG8	−1.99	−3.99
LP1	+1.06	−2.97	*PcG9	−1.36	−4.37
LP2	−0.10	−4.00	PcG10	−0.56	−3.28
LP3	+1.18	−4.33	PcG11	+1.15	−3.79
LP4	−0.20	−3.64	PcG12	+0.34	−3.88
Average	+0.46	−3.58	*Average*	−0.35	−3.62
			Porites	$\delta^{13}C$	$\delta^{18}O$
			*PrG1	−2.87	−4.99
			*PrG2	−3.14	−4.59
			PrG3	−0.28	−5.16
			PrG4	+0.99	−4.35
			PrP1	+2.53	−3.40
			PrP2	+2.35	−3.56
			PrP3	+1.23	−4.40
			PrP4	+0.71	−4.07
			PrP5	+0.05	−3.86
			Average	+0.17	−4.27

[1] Last letter of sample number, G or P, refers to Guam or Pagan.
* LMC detected by XRD analysis.

ANALYSIS OF VARIANCE

Isotopic ratios from Table 1(a), taken from the single *Porites* colony on Pagan were evaluated by the analysis of variance (ANOVA) shown in Table 2 (Davis, 1986). The ANOVAs demonstrate that both carbon and oxygen variation between *Porites* segments (AGE) are significant as compared to respective ERROR terms; furthermore, $\delta^{18}O$ varies significantly between intertidal and supratidal diagenetic environments (LOCATIONS) when compared to (ERROR) variation. This variation is consistent for all paired (b vs. t) samples (Table 1a) and averages about 1.0%.

The experimental error may be expressed as the square root of the ERROR mean square (standard deviation) or 0.4436 for $\delta^{13}C$ and 0.6749 for $\delta^{18}O$. Thus the average of n replicates taken from a single *Porites* colony would have a theoretical standard error of

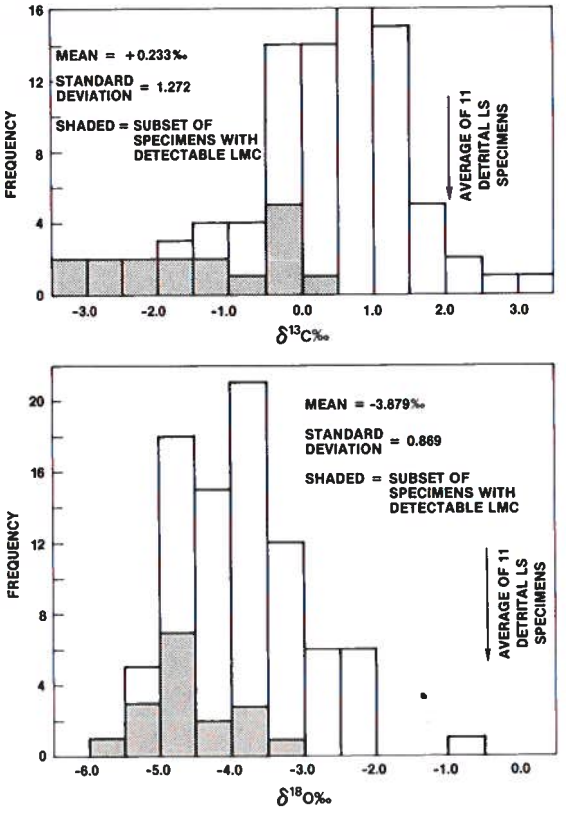

Figure 5. Frequency distribution histograms for $\delta^{13}C$ (above) and $\delta^{18}O$ (below). Data from Table 1 (b).

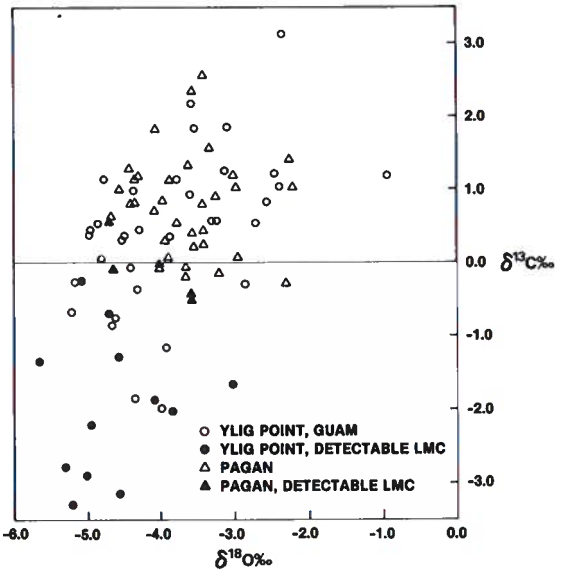

Figure 6. Cross-plot of $\delta^{13}C$ vs. $\delta^{18}O$ data from Table 1 (b).

Table 2. ANOVA for $\delta^{13}C$ and $\delta^{18}O$ from single *Porites* colony on Pagan

Source of Variation	Degrees of Freedom	Mean Squares	F	Pr F
		(a) Carbon		
AGE (between segments)	4	1.4240	7.24	.0091
LOCATION (wet/dry)	1	0.2312	1.17	Not Significant
INTERACTION	4	0.2006	1.02	Not Significant
ERROR (replicate)	8	0.1968		
TOTAL	17			
		(b) Oxygen		
AGE	4	2.4658	5.41	.0001
LOCATION	1	1.6395	3.60	.0007
INTERACTION	4	0.0829	0.18	Not Significant
ERROR	8	0.4555		
TOTAL	17			

Table 3. ANOVA of carbon and oxygen isotopes from transects on Pagan and Ylig

Source of Variation	Degrees of Freedom	Mean Squares	F	P F	Estim. Mean Sq.
		(a) Carbon			
LOCALITIES (Ylig vs. Pagan)	1	15.5869	6.87	.02	0.3065
GENERA (Between Genera)	12	2.2695	1.77	.09	0.1961
ERROR	71	1.2835			1.2835
TOTAL	84				
		(b) Oxygen			
LOCALITIES	1	2.7689	1.61 5.22	Not. Sig. .03	0.0125
GENERA	12	1.7192	3.24	.002	0.2364
ERROR	71	0.5304			0.5304
TOTAL	84				

$+0.4436/\sqrt{n}$ and $+0.6749/\sqrt{n}$ for $\delta^{13}C$ and $\delta^{18}O$, respectively (Davis, 1986). Although the actual numbers apply strictly to Pagan *Porites*, we have no reason to believe that other colonies of other coral genera are any more or less homogeneous with respect to the distribution of stable isotopes.

The line-transect sample data from Pagan and Guam (Table 1) are shown in Table 3. The ERROR term in this design is within-genera isotope variation and is considerably larger in each case than the ERROR term indicated from the Pagan *Porites* colony in Table 2.

F tests indicate that, compared to the ERROR variance, there is statistically signifi-

cant between-genera isotope variability (GENERA), taken over both Pagan and Ylig; there is also a significant overall difference in carbon isotopes between Pagan and Ylig (LOCALITIES) compared either to ERROR or GENERA variance, an inference that can be drawn from Figure 6 as well. On the other hand, the variation in $\delta^{18}O$ between the two localities is not significantly greater than that between coral genera.

If the 17 specimens from Ylig that display detectable calcite conversion were eliminated (Table 1(b), and Fig. 6), and a simple Student's "t" test (Davis, 1986) were run between average carbon values from Pagan vs. Ylig, the differences indicated in the ANOVA in Table 3 vanish. This would then justify combining the Pagan and Ylig data sets as was done to construct Figure 5.

DISTRIBUTION OF HOLOCENE STABLE ISOTOPE VALUES

Frequency distributions provide excellent objective rationale for deciding whether an individual coral should be included for analytical purposes in a defined population or for comparing two (or more) populations to each other. Although the Chi-Square tests show that neither isotope population follows at the "whole rock" level of sampling and analysis a Normal distribution, Normal probability statements can be used in accepting or rejecting hypotheses, and for comparing data if one deals with means of several analyses, instead of an individual analysis (Davis, 1986). One can set up confidence intervals around the mean of a population of either carbon or oxygen isotopes or a joint confidence interval around the means of both. For example, 6 corals from the base of a drill core punched through the lower contact of the Holocene at Ylig have an average $\delta^{18}O$ of $-5.11‰$ and a standard deviation of 1.15‰. Using the population standard deviation estimated from this study (0.869‰ from Fig. 5) or the 1.15‰ from the sample of 6 corals, one can assert with a probability exceeding 0.95 that the material from the bottom of the drill core is not part of the parent Holocene population of oxygen isotopes described in this study.

The form of the sampling distribution is itself important. A symmetric unimodal distribution such as a Normal Distribution implies that a relatively homogeneous parent material has remained unaltered or has been acted upon uniformly by diagenetic processes. Bimodality, on the other hand, could arise because the targeted population was originally heterogeneous with respect to isotope fractionation. This situation has been cited by Weber (1970, 1972) and Weber et al. (1976) who demonstrated the depth dependency of isotope signatures in modern corals and other organisms. If an emergent reef represents a series of coral communities that grew in progressively shallower water it is possible, because of the karstic terrain of the outcrops, that the specimens sampled would have grown at different water depths. The result would then be polymodal and/or skewed frequency distributions.

Bimodality or polymodality and skewed distributions could also arise even if the original population were relatively homogeneous. Siegrist and Randall (1985) and Siegrist (1986) have shown that the external controls on diagenesis do not operate uniformly on emergent Holocene outcrops in the Mariana Islands. The permeability and the configuration of the rock unit underlying the reef, the proximity and development of the Ghyben-Herzberg lens, tidal pumping, and of course, the geochemistry of the pore-waters are the major variables influencing the intensity, style, and distribution of diagenetic al-

teration products. Results may be random or systematic, but in either case, the isotope sampling distribution, reflecting both a depositional and diagenetic signature, will neither be unimodal nor symmetrical.

This situation is well illustrated in the case of the large *Porites* colony on Pagan. Within a distance of less than 0.4 m, oxygen isotopes show systematic and significant differences between two adjacent but not quite identical diagenetic environments.

SAMPLING VARIATION AND EFFICIENCY

Levels and magnitudes of variability related to outcrop sampling of Holocene corals for stable isotope analysis are indicated in Table 4. Variance estimates for each level of sampling, expressed as cumulative standard deviation, are calculated from the Estimated Mean Square column of the Table 3 ANOVAs using methods outlined in statistics texts (Davies, 1958, for example). They represent the increasing uncertainty associated with an observation or statistical comparison as the scope of the sampling grows from replicates within a single colony to descriptions or comparisons of Holocene corals along the Mariana Arc. As such, Table 4 also emphasizes, after Krumbein and Graybill (1957), the absolute need to define carefully the target population.

Estimates of the population mean and standard deviation are extremely useful when planning future studies that compare a new section with the one under study. If, for example, we intend to compare corals from another Holocene emergent reef in the Mariana Islands with those reported here we can use our estimates of the mean and standard deviation to effect more efficient sampling. If we let h = the difference between the mean coral isotope ratio (oxygen or carbon) from this study and that anticipated from a comparative reef, the minimum number of samples required to detect that difference, n, is:

$$n = (ts/h)^2 \text{ (Krumbein and Graybill, 1957)}$$

where s is the standard deviation and t is from the Student's "t" distribution with $n - 1$ degrees of freedom at some pre-specified probability level. In practice, we would specify a minimum value of h, e.g. 0.75‰, that we would like to be able to detect 95% of the time, and calculate the number of samples needed to assure us of that goal. In a more rigorously statistical sense, h is equal to ½ "the pre-specified confidence interval around the population mean". It is also important to note that the number of samples n varies as the square of the standard deviation, a point that will be addressed below.

The right-hand column in Table 4 presents the calculated minimum detectable difference in $\delta^{13}C$ and $\delta^{18}O$ when comparing the mean of n corals from the specified populations at a probability level = 0.95. As an example, in random sampling 5 times from a single coral colony for $\delta^{13}C$ and $\delta^{18}O$, one could hope to detect isotope differences of about $1.13/\sqrt{5} = \pm 0.5$‰ and $1.89/\sqrt{5} = \pm 0.85$‰, respectively. On the other hand, in sampling at the outcrop level 5 random coral samples (presumably different genera) could resolve mean differences in $\delta^{13}C$ and $\delta^{18}O$ of only about $2.85/\sqrt{5} = \pm 1.28$‰ and $2.56/\sqrt{5} = \pm 1.14$‰. Thus, to achieve comparable sensitivity in resolving isotopic differences at these two levels of sampling, one must analyze between 2 ($\delta^{18}O$) and 7 ($\delta^{13}C$) times as many outcrop samples as one would analyze samples within a single colony.

Finally, a glance at the Mean Squares column in Table 2 shows that except for the meaningless INTERACTION, $\delta^{18}O$ mean square values exceed those of $\delta^{13}C$. An F test

Table 4. Levels and magnitudes of isotope variation in Holocene corals (P = .95)

Level of coral population to be compared	ANOVA Table Number	Cumulative s		Minimum Detectable Difference ($ts/\sqrt{n}$)	
		$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
Replicate (same colony, age and diagenetic environment)	2	.4436	.6749	$.8695/\sqrt{n}$	$1.3228/\sqrt{n}$
Between coral specimens in same colony and diagenetic environment irrespective of age.	2	.4626	.9218	$.9067/\sqrt{n}$	$1.8067/\sqrt{n}$
Between specimens in the same colony irrespective of diagenetic environment or age.	2	.5773	.9648	$1.1315/\sqrt{n}$	$1.8910/\sqrt{n}$
Between corals of the same genus in the same reef outcrop.	3	1.2715	1.2088	$2.4921/\sqrt{n}$	$2.3692/\sqrt{n}$
Between corals of the same genus but from more than one outcrop.	3	1.3464	1.3029	$2.6389/\sqrt{n}$	$2.5603/\sqrt{n}$
Between corals of different genus, from more than one outcrop.	3	1.4558	1.3078	$2.8534/\sqrt{n}$	$2.5633/\sqrt{n}$

(Davis, 1986) comparing $\delta^{13}C$ and $\delta^{18}O$ mean squares indicates that ERROR and LOCATION differences are significant (P = .95). This implies that at these levels of sampling *Porites* colonies, oxygen isotope values appear to be more sensitive to colony-level subenvironments than are carbon isotopes. This apparent difference is masked at higher levels of sampling where, in general, $\delta^{13}C$ exceeds $\delta^{18}O$ variation.

Obviously, values of variation at any level are simply estimates and are only applicable to isotope comparisons between Holocene corals in the Mariana Islands. However, the relative magnitudes expressed at each level may well be reflected in unaltered Holocene coral populations elsewhere.

Conclusions

To arrive at valid inferences from stable isotope data sets, it is important to understand how each of the variables, $\delta^{18}O$ and $\delta^{13}C$, is distributed and how they covary. The form of the distribution is sensitive to both depositional and diagenetic factors and could be useful in developing environmental models. It is also important to be aware of the relative magnitudes of experimental errors introduced at all levels of field sampling.

In the Mariana Islands, $\delta^{13}C$ and $\delta^{18}O$ values in unaltered coral populations within emergent Holocene reef outcrops would appear to follow a fairly symmetrical unimodal

function, although it could not be demonstrated that the parent population was normal. Although primary growth-depth variation in corals could account for the distorted distributions obtained, in all likelihood, they are the result of low-level conversion of a minority of specimens to low Mg-calcite.

Isotope variation increases markedly with the complexity of the sampling population, e.g., going from within-colony to between-colony to between-genera to between-reef outcrop comparisons. The increase is somewhat more obvious in $\delta^{13}C$ analyses because the replicate error for $\delta^{13}C$ is only about 67% as large as for $\delta^{18}O$. This progressive growth in uncertainty associated with successively higher levels of sampling translates to an exponential (squared) increase in the number of samples required to affect equal resolution at each level of sampling.

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