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Coral skeletal chemistry: physiological and environmental regulation of stable isotopes and trace metals in *Montastrea annularis*

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[Plate 1]

A detailed study has been made of the ^{13}C, ^{18}O, calcium, magnesium, strontium, and iron contents of a coral skeleton deposited during a two-year period for which environmental data are available. Strong seasonal variations in ^{13}C and magnesium contents have been found. These appear to be linked to changes in growth rate, and should be considered in future work. ^{18}O content does not show equilibrium physicochemical temperature effects, and its lack of correlation with ^{13}C indicates complex metabolic isotope fractionation. Strontium content shows little variation. This difference from magnesium is predicted on grounds of biochemical ion transport. Iron is detrital in origin. Seasonal records of trace constituents in coral skeleton are shown to differ from those predicted by previous investigators, indicating that metabolic effects cannot be ignored in paleoenvironmental interpretation of carbonate skeletal chemistry. Stable isotopes are demonstrated to be useful tools in understanding overall carbon metabolism of photosynthetic calcifying organisms. A model of carbon isotope fractionation is developed, and used to place bounds on the sources of carbon used in photosynthesis and calcification. It is estimated that approximately 40 % of the carbon supply is from seawater bicarbonate and 60 % from recycled respiratory CO_2.

Introduction

Corals preserve a skeletal record of their environmental history. Recent work (Knutson, Buddemeier & Smith 1972; Dodge & Thompson 1974; Weber, White & Weber 1974) has shown that in many environments corals lay down skeletal bands of alternating high and low density, analogous to tree rings. These cycles have been demonstrated to be annual by measurement of natural (Dodge & Thompson 1974; Moore, Krishnaswami & Bhat 1973) and artificial (Knutson *et al.* 1972; Noshkin, Wong, Gatrousis & Eagle 1975) radionuclides. Seasonal variations in growth rate have been determined by direct weighing (Bak 1973) and alizarin staining techniques J. W. Porter, private communication) and were predicted by early work on coral physiology (Goreau & Goreau 1959, 1960*a*, *b*) showing calcification rates to be dependent on light intensity.

Various investigators have reported correlations between skeletal growth rate and skeletal density (Dodge & Thompson 1974); between growth parameters and temperature (Glynn & Stewart 1973; Clausen 1971; Weber & White 1974; Dodge & Vaisnys 1975), light (Goreau & Goreau 1959, 1960*a*, *b*), depth (Baker & Weber 1975), wind (J. W. Porter, private communication), rainfall (Rubinoff 1974), and suspended sediments (Dodge, Aller & Thompson 1974). Of particular interest has been the work of Bak (1974) in Curacao, who directly weighed corals and found that increase in mass correlated best with the number of 'sun hours' (that is, the integrated incident light intensity).

For detailed study of environmental and physiological effects on skeletal chemistry a living specimen of *Montastrea annularis* was chosen. The specimen was collected at a depth of 10 m in the upper fore reef, and was free of boring or epilithic organisms. Skeleton formed over two years was analysed in as fine detail as possible. These years (1969–70) were not chosen for any environmental circumstances such as unusual drought or hurricane rains, but because they were the only years for which water temperatures in the area were available (Reiswig 1971; Jackson 1972).

To ascertain whether chemical variations were responses of the whole organism or caused by local changes in growth rate and chemistry, the skeleton was sampled over the same deposition interval from opposite sides of the coral. These data give the first measure of the synchronous variability of chemical composition within a single coral colony. The results indicate that in general the coral records environmental information in a uniform manner, given that the specimen is one with fairly even growth.

Materials and methods

(*a*) *Sampling*

Live hemispherical specimens of *Montastrea annularis* (Ellis & Solander), a major reef building coral (Goreau & Goreau 1973), were collected at Discovery Bay and Pear Tree Bottom in St Ann, Jamaica, in March 1973. The tissue was washed off, the skeleton dried in sunlight, and 0.5 cm thick slabs were cut along the maximum growth axis with a rock saw. The slabs were X-rayed with clinical X-ray equipment to reveal the density banding pattern. Some specimens were radiochemically analysed (Dodge & Thompson 1974) using ^{228}Ra and ^{210}Pb techniques. Results showed that the banding was annual and that the growth rate was between 0.5 and 1.0 cm/year.

Based on time of specimen collection and the fact that a thin portion of low density skeleton overlies a band of dense skeleton (figure 1), it was concluded that the dense band had formed near the end of the year. This pattern has been consistently found by sampling through the year in Jamaica, Barbados, and Bermuda (R. E. Dodge, private communication). Years were assigned by counting bands back from the surface.

The skeletal slabs were carefully trimmed to select regions of the coral with locally flat growth surfaces, and tangential slices (about 0.02 cm × 0.5 cm × 3 cm) were cut

FIGURES 1*a*, *c*. For description see opposite.

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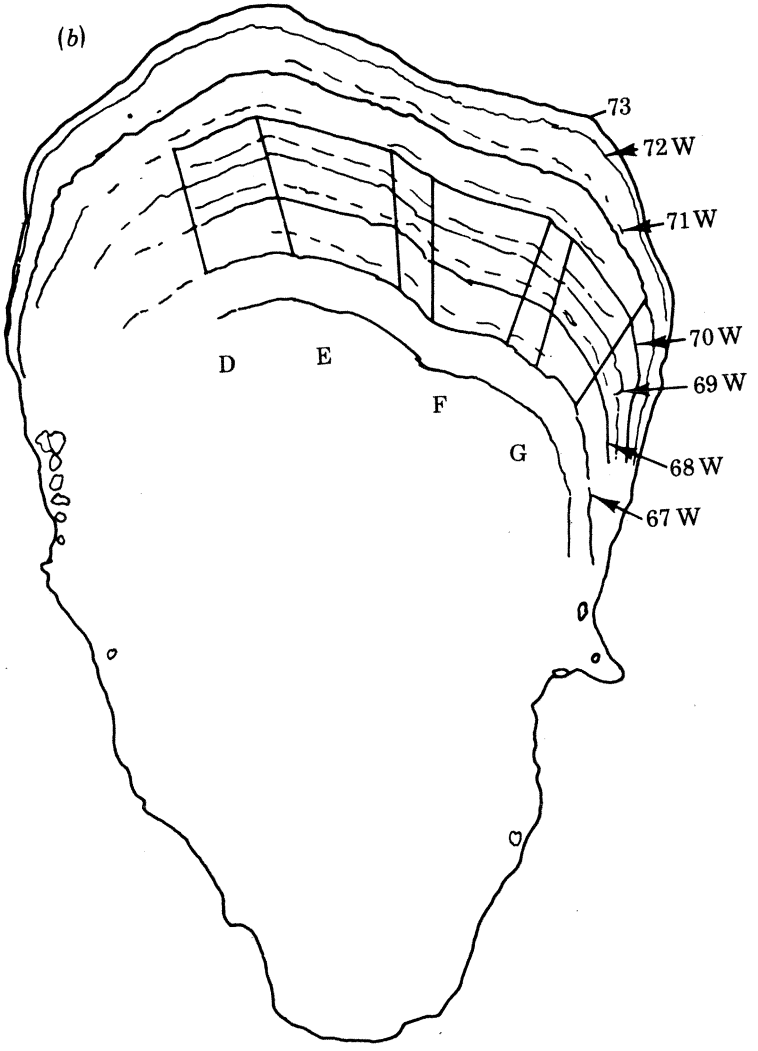

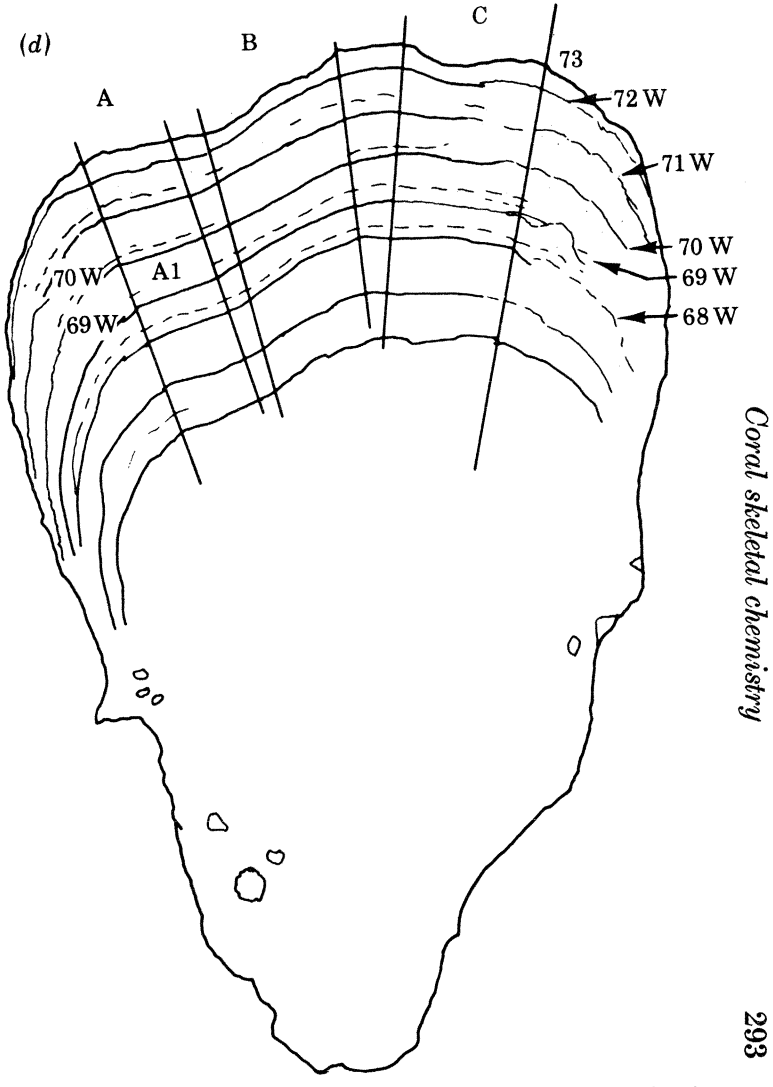

Figure 1. Shadow X-rays of radial slabs cut from specimen of *Montastrea annularis* (figures 1*a* and 1*c*). These slabs were adjacent to one another in the coral. The chronology of the banding pattern and the location of the sample series are shown in figures 1*b* and 1*d*.

with an ultra slow rotary blade. X-rays of coral slabs and the sampling schemes are shown in figure 1, plate 1.

Were the original slab cut at an angle θ to the maximum growth axis, then the apparent growth increment r_a would be related to the real increment r_r through

$$r_r = r_a \cos\theta \tag{1}$$

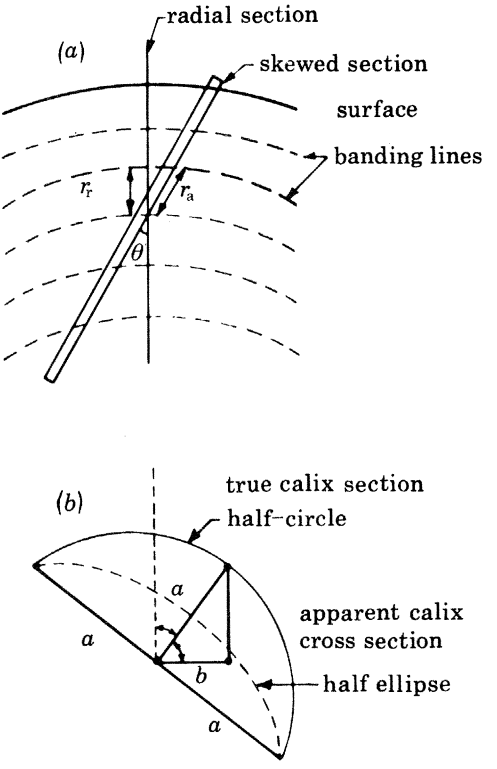

FIGURE 2. Geometrical construction showing the effect of skewed sections on the apparent annual growth rate (r_a) compared to the true linear growth rate (r_r) (figure 2*a*). Figure 2*b* shows the determination of the angle θ from the apparent calix cross section.

(figure 2*a*), where θ can be determined by measuring the ratio of the major and minor axes of calix cross sections $\overline{(a/b)}$ where they intersect the plane of the cut, where a and b are the major and minor axes respectively, and the bar denotes the average. Then

$$\cos\theta = \sqrt{(1 - \overline{(b/a)}^2)} \tag{2}$$

(figure 2*b*) from which the true growth increment can be determined. Inspection of the samples used indicated that θ was negligibly small.

(*b*) *Stable isotopes*

Samples were ground in agate mortar and then treated in a low temperature oxygen plasma furnace for 15 min to remove all organic matter. Weber, Deines,

Weber & Baker (1976) have pointed out the importance of pretreating carbonate samples to remove organic matter. Organic radicals and ions in the 44–46 mass range interfere with mass spectrometric determination of ^{13}C and ^{18}O, giving apparent enrichment of the heavy isotopes. Experimental work has shown that oxygen plasma treatment does not cause detectable isotopic exchange between carbonate and oxygen during 1 h runs (W. Deuser, private communication).

Samples were analysed by standard mass spectroscopic technique. Isotopic composition is expressed in the standard 'delta' per mille notation, where

$$\delta^{18}O = \left[\left\{\frac{\left(\frac{^{18}O}{^{16}O}\right)\text{sample}}{\left(\frac{^{18}O}{^{16}O}\right)\text{PDB standard}}\right\} - 1.000\right] \times 1000,$$

$$\delta^{13}O = \left[\left\{\frac{\left(\frac{^{13}C}{^{12}C}\right)\text{sample}}{\left(\frac{^{13}C}{^{12}C}\right)\text{PDB standard}}\right\} - 1.000\right] \times 1000.$$

Precision was measured by grinding and mixing a single sample, taking four splits, and treating each separately through oxygen plasma pretreatment, evolution of CO_2 with anhydrous H_3PO_4, and extraction into sample tubes. The resulting precision of the four samples measured as the standard deviation was 0.10 per mille for oxygen and 0.03 per mille for carbon.

(*c*) *Metals*

Specimens were dried at 125 °C and stored in a dessiccator. Each sample was ground to a fine powder in an agate mortar, homogenized with a stirring rod, and carefully weighed.

For the metal analyses samples were mixed with six times their mass of lithium metaborate ($LiBO_2$). Each sample was then fused in a platinum crucible for 15 min in a muffle furnace at 1000 °C, and quenched immediately to form a glass which was dissolved in roughly 5 ml of concentrated HCl and 20 ml of deionized distilled water. The resulting solution was carefully washed into a volumetric flask, and made up to 100 ml with deionized distilled water. Lanthanum stock solution was added to make the final solution up to 1 % La in order to remove interference with the calcium determination. The solutions were analysed for aluminium and iron; diluted 1:10 for strontium and magnesium determination; and diluted 1:200 for calcium determination. Each diluted solution was also made up to contain 1 % La. Metals were analysed by atomic absorption spectrophotometry.

Analytical precision was measured as the standard deviation of four replicate analyses of a large piece of coral which was ground and homogenized. The precision, expressed as the standard deviation percentage of the mean value was: Ca: 0.2 %; Mg: 0.4 %; Sr: 1.1 %; Fe: 0.5 % for three replicates and 26.2 % for all four. Precision was high for all measurements except for iron; for which three of the replicates were

almost identical with the fourth very different. It is suspected that this difference is not due to analytical error but represents a real variation due to the presence of a small lump of iron-rich detrital material. Leaching of a coral skeleton sample in dilute acid left a reddish residue, similar in colour to the iron-rich bauxites and terra rosa soils which overlie the limestone formations inland of the sample site.

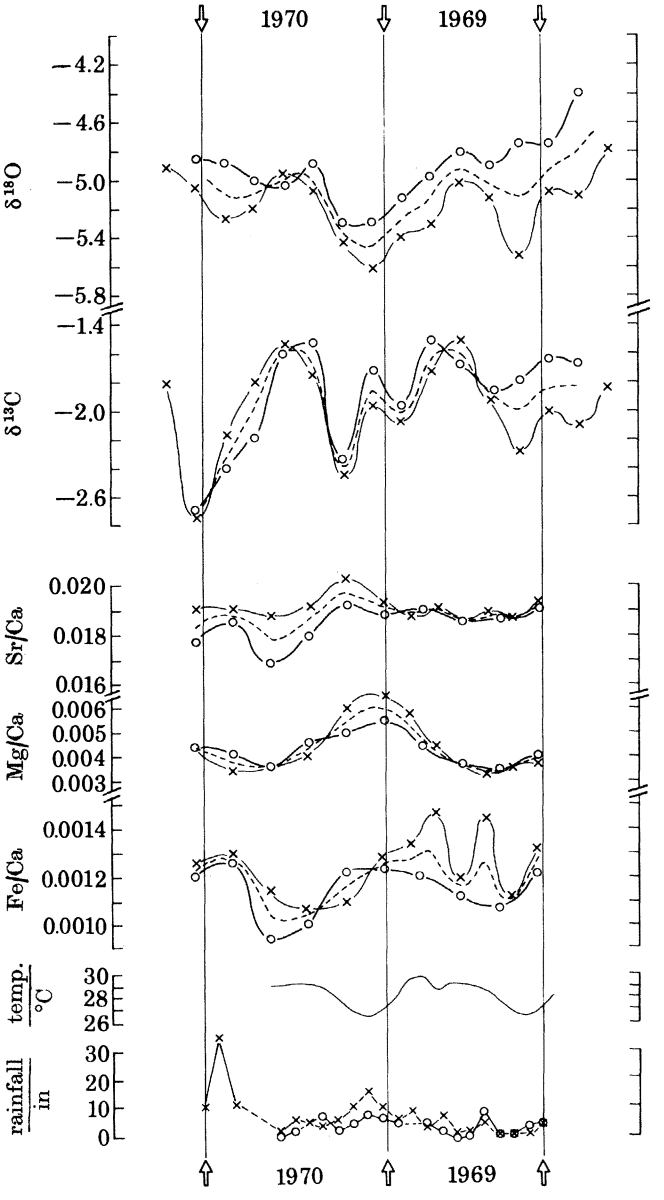

FIGURE 3. For description see facing page.

Observations

(*a*) *Stable isotopes*

The ^{13}C content has a mean δ-value of around -2.0 per mille (figure 3), several per mille lower than inorganically precipitated calcium carbonate. Strong annual variations are apparent, with the minima falling close to the dense skeletal bands. Both sample series, although from different sides of the coral, agree closely with one another except for the 1968 samples. The ^{13}C content of the skeleton seems to reflect the physiological and/or environmental circumstances of the animal as a whole. While the summer values reach a high of about -1.5 per mille, each succeeding winter sampled results in a somewhat lower value, to a minimum of -2.7 per mille in late 1970. While the detailed features of the curve are hard to explain without more detailed information on relevant environmental and physiological variables, the basic feature of enrichment in the heavy carbon isotope in summer and depletion in winter can be logically correlated to growth rate. Faster growth results in the use of a larger fraction of the available light carbon in photosynthesis by the zooxanthellae. This leaves an inorganic carbon pool in the tissues that is depleted in the light carbon isotope, which is used in skeleton formation (figure 5). Proper confirmation of this hypothesis would require measurements of tissue growth rate and of tissue carbon isotope composition through the year. Such data are not available.

^{18}O

In contrast to the carbon isotope pattern, the oxygen isotope distribution is not clear. The mean value of about -5.0 per mille is lower than that for calcium carbonate inorganically precipitated from seawater. Values range from -4.4 to -5.6, but

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Figure 3. Measured values of skeletal chemical composition and environmental data. Carbon and oxygen isotopes are plotted as delta per mille values, metals are given as metal/calcium mass ratios. Isotopic data points plotted as circles are from sample series F, crosses are from series C. Metal data plotted as circles are from series B, crosses are from series E. All metal or isotope values marked by the same symbol were measured on identical samples, and the different data series are plotted so that samples corresponding to the dense skeletal bands (whose position is indicated by the arrows at top and the vertical lines) coincide. Although dense band values coincide temporally, variations in annual growth rate over the coral surface result in a slight shift of points from different sample series with respect to one another in mid year. For instance the two ^{13}C sample series are considered to be almost identical, although two maxima are slightly displaced from one another in the way they are plotted. Seawater temperatures are after the measurements of Reiswig (1971) and Jackson (1972). The 1969 temperature dip represents a large storm. Rainfall data for Discovery Bay (2 miles west of sample site) and Runaway Bay (2 miles east of sample site) are courtesy of the Jamaica Meteorological Service. Crosses mark Discovery Bay rainfall, circles indicate Runaway Bay. The vertical lines in the environmental data mark December values, and so are not coincident with the dense band values in the data. Due to growth rate variations, the horizontal data scale is not a linear time scale. It is difficult to match chemical and environmental data precisely unless skeletal growth rate is known through the year. Dashed lines represent average data values.

the cross correlation between sample series is not nearly as good as for carbon and one side of the coral is generally about 0.3 per mille lighter than the other (figure 3). There is no obvious explanation for this unless it is caused by metabolic differences between the two sides that are not seen in the carbon record. The data seems to contain a very weak annual trend with minor lows in the dense band, superimposed on a larger long-term variation. There is little sign of the physicochemical temperature effect usually found in carbonates. Calcium carbonate inorganically precipitated from seawater is systematically depleted in ^{18}O as the temperature increases, providing a well calibrated 'paleotemperature curve' of carbonate $\delta^{18}O$ against temperature that is the basis of much of paleoclimatology. If such a temperature dependent variation (about 1 per mille) were present in these data it would be detectable. Spatial inhomogeneity of ^{18}O seen here, and its apparent biological control, is at variance with assumptions of 'equilibrium' inorganic precipitation that have generally been used in the environmental interpretation of the $\delta^{18}O$ content of biogenic carbonates.

$^{13}C/^{18}O$ *correlation*

There is no clear relation between the carbon and oxygen isotopes. A plot of ^{18}O content against ^{13}C content shows considerable scatter (figure 4), since the small inferred annual variation of the oxygen is buried in a longer term variation (figure 3).

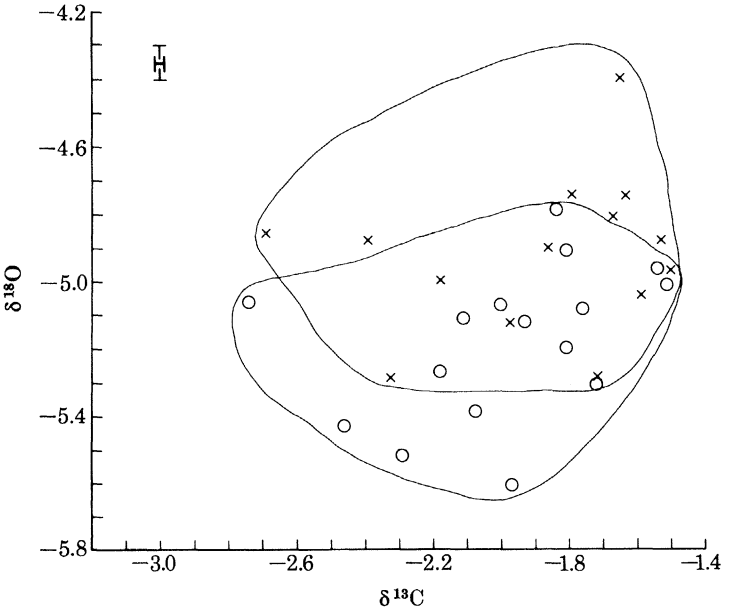

FIGURE 4. Scatter plot of $\delta^{18}O$ against $\delta^{13}C$. There is no clear correlation between the isotopes, although the F series (crosses) is somewhat enriched in ^{18}O compared to the C series (circles). It is inferred from the lack of correlation between the two isotopes that different processes are involved in their fractionation.

It does not seem that these two isotopes are utilized in a similar fashion. Possible reasons and implications of this are discussed later.

(*b*) *Metals*

Magnesium

Measured magnesium concentrations vary between 1100 and 2100 parts per million. This twofold variation is smoothly seasonal with a high in the 1969 dense band (figure 3). Values on both sides of the coral show the same pattern, but the absolute difference between the two sets of data is greater than the analytical precision. Consequently these differences are probably real, but no explanation can be offered without further knowledge of tissue metabolism on both sides of the coral. Skeletal magnesium content seems inversely related to overall growth rates, although further study is required clearly to relate such variations to growth rate and environment.

Strontium

Strontium values of 6700 ± 200 p.p.m. were measured. The values for the two sides were identical in 1969, but one side had significantly more strontium in 1970 (figure 3), the difference exceeding the analytical precision. No annual variation in strontium content occurred in 1969, and the variation in 1970 is difficult to interpret. No obvious growth rate or environmental control is apparent.

Iron

Iron values between 360 and 560 p.p.m. were measured. The pattern is complicated (figure 3) and there is great variation between the two sample series. Since iron is likely to be detrital in origin, its pattern reflects unhomogeneous incorporation of suspended sediment into the coral skeleton. Its distribution is not directly correlated to physiological variables but to water turbidity, resuspended sediments, heavy rain runoff, and land erosion. Interpretation of iron contents is difficult unless the temporal and spatial distribution of suspended sediments in the water is known and are correlatable with environmental parameters. Spatial inhomogeneity of iron and lack of correlation with rainfall (figure 3) demonstrates that it is at best a crude environmental indicator.

Aluminium

All samples measured contained aluminium concentrations at or below the limit of detection, about 125 p.p.m.

Discussion

(*a*) *Carbon isotopes*

Weber & Woodhead (1970) have predicted that fast growing corals should be isotopically heavier than slow growing corals. The seasonal data presented here confirms their hypothesis within individual corals. They measured bulk ^{13}C content

of corals collected in areas of different mean temperature. The strong seasonal variation reported here is probably responsible for the large scatter of their data, which lacked seasonal control of sampling.

While the carbon isotope skeletal record indicates seasonally changing composition and utilization rates of organismic carbon pools, tissue carbon isotope measurements needed to complete the picture, are lacking.

(*b*) *A model for metabolic carbon isotope fractionation in corals*

A model of carbon isotope cycling in corals can be made by considering the different carbon pools (figure 5). A simpler version of this model was first presented by Weber & Woodhead (1970).

The coral contains an inorganic carbon pool in its tissues that is made up of carbon dioxide, bicarbonate, and carbonate ions. Some is derived from seawater, and some from tissue respiration. This carbon pool is utilized both in photosynthesis of the endosymbiotic dinoflagellates (zooxanthellae) and in skeleton deposition by the calicoblastic epidermis. Other carbon comes from direct feeding on zooplankton and uptake of suspended and dissolved organic matter (Goreau, Goreau & Yonge 1971).

Let $\delta_{c.p.}, \delta_{s.w.}, \delta_{m.}, \delta_{o.}, \delta_{s.}$, be the ^{13}C δ-value of the organism's inorganic carbon pool, of seawater inorganic carbon, of respired metabolic CO_2, of carbon fixed into organic matter by photosynthesis, and of the skeleton respectively (figure 5). Let X be the fraction of the inorganic carbon pool that comes from seawater as opposed to tissue respiration, and let Y be the fractional of inorganic carbon used in skeleton formation as opposed to photosynthesis. Then

$$\delta_{c.p.} = X\delta_{s.w.} + (1-X)\delta_{m}. \tag{3}$$

This carbon pool is partitioned between calcification and photosynthesis, so that

$$\delta_{c.p.} = Y\delta_{s.} + (1-Y)\delta_{o}, \tag{4}$$

when all of the inorganic carbon pool is ultimately consumed. It is possible that some of the carbon pool is not used but is exchanged out of the system. In this open-system case

$$\delta_{c.p.i.} = Y\delta_{s.} + (1-Y-Z)\delta_{o.} + Z\delta_{c.p.f.}, \tag{5}$$

where $\delta_{c.p.i.}$ is the initial isotopic composition of the carbon pool, $\delta_{c.p.f.}$ is the final isotopic composition of the unused (excreted) carbon pool, and Z is the proportion of the carbon pool that is excreted unused. There is no information on the size of such a carbon pool, but it is argued to be small on the grounds that the coral-alga-symbiosis is a net autotroph. Most hermatypic corals produce net oxygen (Kanwisher & Wainwright 1967; Roffman 1968) and consume more CO_2 than they produce. Hermatypes must actively take up CO_2 from seawater to provide enough carbon for zooxanthellar photosynthetic fixation, so that all of their internal pool is ultimately utilized. Hence it will be assumed that Z is small enough to be ignored, or that if it is appreciable, the inorganic pool is not fractionated in excretion. That is, $\delta_{c.p.i.} = \delta_{c.p.f.}$. This would result from straight exchange of internal inorganic

carbon with the seawater inorganic carbon reservoir, and would not affect estimates of the relative proportions used in photosynthesis and skeletogenesis. Until direct physiological measurements of Z are made, it will be hard to improve estimates of $\delta_{c.p.}$.

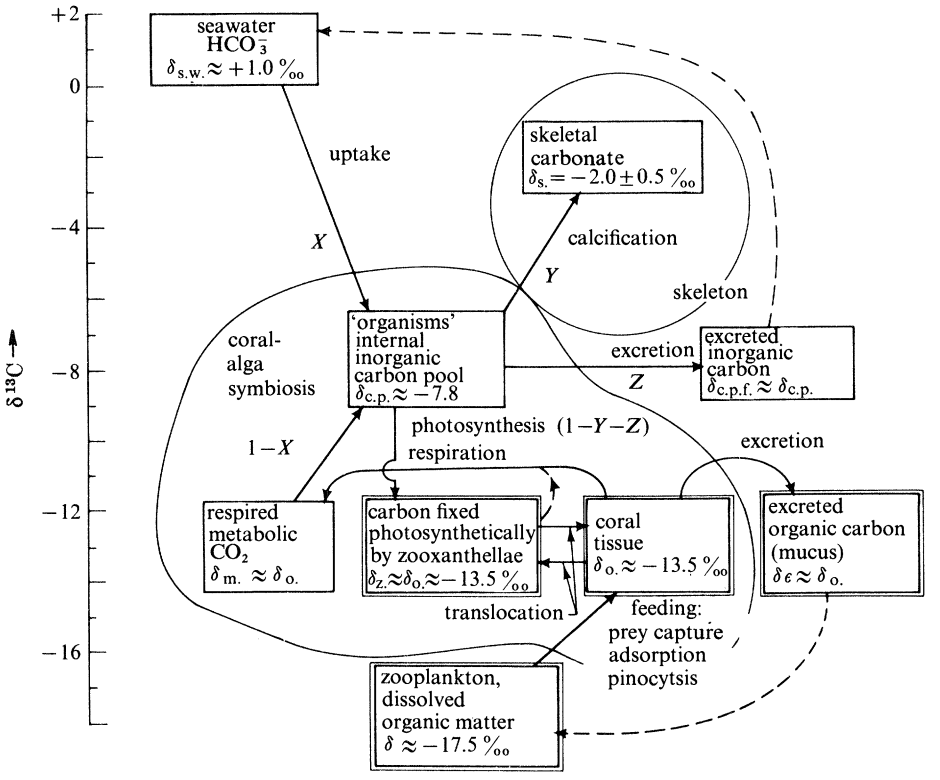

FIGURE 5. Model for carbon isotope fractionation in corals, showing carbon pools plotted against their $\delta^{13}C$, and the processes (arrows) which interconnect them. The upper right circle is the skeleton, and the coral-alga tissue is represented by the other closed figure. Inorganic carbon pools are shown as single line rectangles, while organic carbon pools are denoted by double line rectangles. Each process of material exchange (arrows denote direction of exchange) that is not horizontal involves isotopic fractionation. Dashed arrows are not explicitly discussed in the text, but represent ultimate sinks for excreted pools. This model follows the essential features of T. F. Goreau's model for carbon metabolism (1961).

Evidence from many organisms (summarized in Smith 1972) demonstrates that the isotopic composition of respired CO_2 is very close or equal to the mean isotopic composition of the organism's tissues. Hence, $\delta_{o.} = \delta_{m.}$. The only circumstance that could conceivably affect this would be for the coral to excrete large quantities of mucus with an isotopic composition greatly different from the animal as a whole which is most improbable. As long as the excreted mucus is isotopically similar to the organic tissue that secretes it, excretion will not affect the isotopic mass balance of inorganic carbon.

Estimation of Y, the fraction of the inorganic carbon pool used in skeletogenesis, is difficult. Careful analysis of the tracer kinetics of ^{14}C-labelled bicarbonate in the manner done for ^{45}Ca in the green calcareous alga *Halimeda* (Böhm & Goreau 1973), or double labelling with both ^{14}C and ^{45}Ca labels (Goreau 1963) can be used. However ^{45}Ca and ^{14}C spikes are diluted into metabolic pools of very different sizes and controlled in different fashions. As a result there is a short-term lack of stochiometry in skeletal fixation of these isotopes (Goreau 1963) that can only be resolved by following the tracer kinetics of both isotopes over the course of time, in order to estimate both pool sizes and instantaneous uptake rates. This problem seems to lie at the heart of the recent suggestion by Crossland & Barnes (1974) that stochiometric deficiency of ^{14}C incorporation into the skeleton requires a further source of carbon.

An estimate of Y can be made by requiring that charge balance be maintained. In this case, for each molecule of carbon dioxide fixed in photosynthesis, one molecule of calcium carbonate is precipitated (Goreau 1961). While it seems reasonable to require charge balance, it is possible that cation pumping and other metabolic processes that affect acid-base homeostasis in the coral tissue could allow Y to be other than the value of 0.5 which would be predicted in their absence.

Hermatypic corals are known to excrete ammonia and phosphate into seawater at low rates in light compared to ahermatypes (Yonge 1963). In hermatypes these metabolic wastes are recycled to the zooxanthellae and fixed into new organic matter (Lewis & Smith 1971). Hence it is possible that internal cycling of charged nitrogen and phosphorus species are involved in charge balance. Crossland & Barnes (1974) have suggested that ammonia plays such a rôle in coral calcification. In the absence of solid evidence for the rôle of nitrogen metabolism in regulating Y, consideration of this possible effect must be postponed. Determination of Y requires far more sophisticated physiological experiments than those hitherto performed.

A value of $Y = 0.5$ will be used here. The only previous estimate of Y (around $\frac{1}{3}$) is for the calcareous freshwater filamentous alga *Cladophora* (Wood 1975). This should have a lower value of Y since its shape offers more exchange surface with the external medium. This makes it possible to maintain charge balance by excretion of carbonate alkalinity, and would reduce the amount of carbonate precipitated, but would be more difficult in massive corals.

From equations (3) and (4) we derive the general expression

$$X = \frac{Y(\delta_{s.} - \delta_{o.}) + \delta_{o.} - \delta_{m.}}{(\delta_{s.w.} - \delta_{m.})}. \tag{6}$$

For the special case when $\delta_{o.} = \delta_{m.}$ and $Y = 0.5$ we find that:

$$\delta_{c.p.} = \tfrac{1}{2}(\delta_{s.} - \delta_{o.}), \tag{7a}$$

and

$$X = \frac{\delta_{s.} - \delta_{o.}}{2(\delta_{s.w.} - \delta_{o.})}. \tag{7b}$$

The isotopic composition of the inorganic carbon pool and the fraction of it derived from seawater and from respiration can then be estimated from $\delta_{s.}$, $\delta_{o.}$ and $\delta_{s.w.}$.

The $\delta^{13}C$ of *Montastrea annularis* tissue has been measured by Land, Lang & Smith (1975) in corals collected in similar habitat a few miles from our sample locations. They found that corals have an isotopic composition similar to their zooxanthellae, and concluded that coral tissue was largely derived from translocated photosynthetic products. Although it is well established that organisms have the isotopic composition of their food (Smith 1972), Land *et al.* found that zooplankton collected near the ocean surface in daytime were several per mille lighter than coral tissue. However, corals take up dissolved organic matter directly through pinocytosis of the epithelia which is covered with flagella and microvilli (Goreau, Goreau & Yonge 1971), and feed extensively at night on a demersal fauna that is largely cryptic during the day (Porter 1974). The isotopic composition of these food sources was not measured.

Land *et al.* also concluded that little or no respiratory CO_2 was used in photosynthesis. It is well established that light carbon is preferentially fixed during photosynthesis and that respiratory CO_2 has a similar carbon isotopic composition to bulk respiring tissue (Smith 1972), so that zooxanthellae using respiratory CO_2 should be enriched in ^{12}C relative to their hosts. The identical composition found by Land *et al.* led them to suggest that zooxanthellae discriminate against metabolic CO_2 and use only seawater bicarbonate as a carbon source.

The model (figure 5) indicates that the relative enrichment of ^{13}C in corals compared to zooplankton is due to the fact that *some* coral tissue carbon is photosynthetically fixed inorganic carbon originally derived from seawater. The model suggests that similarity of coral and zooxanthellar δ-values reflects the isotopic composition and turnover rates of the linked carbon pools, and is best explained by efficient internal cycling of carbon between the symbiotic partners that is fairly rapid compared with time scales of replacement of the internal pool by uptake of seawater bicarbonate. The system is a partially closed one in which most of the inorganic carbon is *ultimately* consumed. Consequently, that zooxanthellae take up a larger fraction of ^{13}C than they would if they used seawater directly, and their discrimination against the heavy isotope is reduced. Analogous phenomena have been observed in an algal bloom that began to deplete its available CO_2 supply (Deuser 1970), and in experiments and field measurements in which increased algal growth rates resulted in photosynthetic fixation of isotopically heavier carbon (Degens, Guillard, Sackett, & Hellebust 1968; Deuser, Degens & Guillard 1968; Sackett, Ecklemann, Bender & Bé 1965).

Weber (1974*b*) and Woodhead & Weber (1973) have proposed that skeletal isotopic differences between hermatypes and ahermatypes can be explained by accumulation of isotopically light metabolic CO_2 in the larger hermatypes due to a reduced surface/volume ratio. Contrary to Land *et al.* they argue that the light metabolic CO_2 is efficiently scavenged by the hermatype's zooxanthellae, leaving behind an isotopically heavier source pool for calcification than is found in ahermatypes. An alternative but related explanation seems more consistent with the physiology of the organisms: that hermatypes are isotopically heavier than aherma-

types not because they eliminate metabolic CO_2 to their endosymbionts more efficiently than ahermatypes do to seawater, but because of the greater uptake rate of isotopically heavy seawater bicarbonate to meet the carbon demands of the zooxanthellae.

Direct measurements of the δ-value of seawater bicarbonate in the area are not available (L. S. Land, private communication). Land *et al.* used the mean seawater value of 0 per mille (Deuser & Hunt 1969). Data from coral reef environments generally give higher values; between plus 1–2 per mille in the Bahamas (Lowenstam & Epstein 1957), and in Pacific reefs (Weber & Woodhead 1971). In the absence of direct measurements in the sample area, a value of $\delta_{s.w.} = +1.0$ per mille will be used.

It is possible that there are small seasonal changes in the carbon isotope composition of dissolved seawater bicarbonate due to changes in overall rates of photosynthesis, respiration, and calcification of the entire reef ecosystem, or to changes in evaporation and rainfall. Such effects are probably small since the specimen came from 10 m depth on the fore reef slope facing a well mixed reservoir of Caribbean water.

If we use these data in equation (7) the δ-value of the coral's inorganic pool is found to be about -7.8 per mille, and X is found to be almost 0.4. That is, 60 % of the coral's inorganic carbon pool is derived from respiration, and 40 % from seawater. Unlike most animals, which must eliminate metabolic CO_2, the coral must take up bicarbonate from seawater at a considerable rate. Efficient internal cycling of carbon is insufficient to maintain an organic productivity that is among the highest known in any ecosystem (Odum & Odum 1956) without active uptake of seawater inorganic carbon.

Application of the model can be made to published depth profiles of organic carbon in *Montastrea annularis* (Land *et al.* 1975) and of skeletal carbon in the same species (Weber *et al.* 1976). The calculated values of X obtained as a function of depth are:

depth/m	X
0	0.48
10	0.41
20	0.39
30	0.43

When the coral grows faster it produces more metabolic CO_2, but the deficiency of this CO_2 compared to that needed for photosynthesis is also greater, so that the coral must take up a higher proportion of seawater bicarbonate. Despite possible photoinhibition, surface corals take up most seawater bicarbonate (and hence inferred to be growing fastest) with corals from 30 m next. Corals from 20 and 10 m show the smallest proportional uptake of seawater carbon. This is in accord with the *in situ* ^{14}C and ^{45}Ca uptake data of Barnes & Taylor (1973). They found that growth rates of *Montastrea annularis* were higher at 9 m and 33.5 m than they were at intermediate depths of 15 and 24.5 m, and suggested the existence of shallow and deep adapted races of *M. annularis*.

(c) *Relationship of the model to calcification mechanism*

The equation used to describe the internal partitioning of the carbon pool:

$$2HCO_3^- \rightleftharpoons CO_2 + CO_3^{2-} + H_2O \quad (8)$$

(Goreau 1961) represents the overall reaction, and is not intended to imply that photosynthesis and calcification are temporally and physically juxtaposed, as has been inferred by some workers (Pearse & Muscatine 1971; Vandermeulen & Muscatine 1974). This representation of the *overall* reaction is justified on the grounds that it is the CO_2 molecule and *not* the bicarbonate ion that is fixed. The question of which chemical species is actually used affects both the charge balance and the isotopic fractionation, since isotopic equilibrium between CO_2 and HCO_3^- is more slowly achieved than chemical equilibrium. The estimate of Y used here depends on the assumption that it is the CO_2 species that is photosynthetically fixed in photosynthesis and the carbonate ion in calcification. The enzyme Ribolose diphosphate carboxylase, which catalyses carbon fixation, is known to have a very high affinity for the CO_2 molecule and very little for the bicarbonate ion (Hochachka & Somero 1973). Isotopic enrichment consistent with the limitation of photosynthetic carbon fixation by the rate of formation of CO_2 from bicarbonate is documented in the literature for algae (Metzner 1975).

At physiological pH, bicarbonate is the dominant carbon species, and it is in chemical equilibrium with carbonic acid through the ionization reaction:

$$H_2CO_3 = H^+ + HCO_3^-$$

which is kinetically rapid. Carbonic acid dehydration:

$$H_2CO_3 = H_2O + CO_2$$

is kinetically slow, and so the enzyme carbonic anhydrase, which catalyses the hydration reaction, is an important protein constituent of algae (Hochachka & Somero 1973). Inhibitors of the enzyme reduce photosynthetic fixation, and algal cultures contain carbonic anhydrase as a constitutive enzyme, repressing its synthesis when grown under conditions of unusually high P_{CO_2} (Metzner 1975). The fact that carbonic anhydrase levels are similar in calcareous and non-calcareous algae (Okazaki 1972) implies that its primary rôle is in photosynthetic CO_2 supply, and only indirectly in calcification. However in order to maintain charge balance, carbonic anhydrase, by producing CO_2 from bicarbonates indirectly regulates the rate at which carbonate ion is made available for calcification (Goreau 1961). Under these conditions isotopic equilibrium lags behind chemical equilibrium, reducing the carbon isotope fractionation between CO_2 and CO_3^{2-}, and ultimately between organic matter and calcium carbonate.

No study of isotopic fractionation at the carbonic anhydrase step seems to have been made. Such work would help provide a mechanistic explanation for carbon isotope fractionations found in calcifying and photosynthetic organisms, as has been done for sulphur isotope metabolism in bacteria (Goldhaber & Kaplan 1974).

Equation (8) implicitly conceals the mechanism that translocates carbon to sites

of calcification and photosynthesis. Metabolic inhibitor studies show that a light dependent reaction (such as carbon fixation or photophosphorylation) (Vandermeulen, Davis & Muscatine 1972), and oxidative phosphorylation (Chalker & Taylor 1975) are involved in calcification. Despite clear evidence of energy requiring mechanisms it will be hard to improve the overall equation (8) until chemical forms and transport mechanisms of carbon and calcium are known.

Calcium binding proteins have been isolated from various systems by Wasserman, Corradino, Taylor & Morrissey (1971). Calcium deposition in the tips of growing *Acropora cervicornis* is dependent on photosynthesis in distal portions of the branch (Pearse & Muscatine 1971), and calcification in vertebrates does not depend on the concentration of free calcium ion, but varies directly with the quantity of calcium-protein complex (Urist, Meyer & Merickel 1971). In the aragonitic alga *Halimeda*, non-skeletal calcium is largely bound to acidic mucopolysaccharides (Böhm 1972*b*, 1973). It seems likely that active calcium transport plays an important regulatory rôle in coral calcification, so that skeleton deposition is intimately linked to carbon metabolism which is reflected in the skeleton ^{13}C content.

(*d*) *Oxygen isotopes*

Skeletal ^{18}O contents have been measured in large numbers of coral specimens from areas of different mean temperature (Keith & Weber 1965; Weber 1973*b*; Weber & Woodhead 1970, 1972*a*, *b*; Woodhead & Weber 1973). The $\delta^{18}O$ against temperature curve is displaced from the 'paleotemperature curve' by species specific amounts, although paralleling it. The irregular seasonal trend reported here is probably responsible for much of the reported scatter in the data.

If individual corals adjusted their ^{18}O content to temperature in the same manner as the bulk content of mean populations do to mean temperature changes, then a clear one per mille seasonal variation would be seen, with isotopically lighter values in summer deposited skeleton. However, no such variation is seen in these data. This predominance of metabolic fractionation over physicochemical equilibrium effects is analogous to seasonal changes of deuterium content in trees (Wilson & Grinstead 1975), where wood becomes isotopically lighter in summer even though the ambient rain is heavier.

Weber, Deines, White & Weber (1975) have noted a slight correlation between $\delta^{18}O$ and the proportion of less dense skeleton. They did not know the season of dense band formation in their samples, and assumed that ^{18}O variations in skeleton paralleled the equilibrium effect, with isotopically lighter skeleton being deposited at warmer temperature. As a result, they concluded that the dense bands were formed in summer. The present data confirms that dense skeleton seems weakly associated with lighter isotopic composition. Since the dense band in Jamaican corals forms near the end of the year (R. E. Dodge, private communication) it does not support Weber *et al.* on ^{18}O enrichment in winter.

In order to interpret the ^{18}O content of the skeleton, a model of oxygen isotope mass balance is desirable. Since dissolved (atmospherically derived) oxygen,

dissolved carbon dioxide, and the oxygen of marine H_2O are all isotopically lighter than seawater bicarbonate, there are many possible sources for light oxygen in the skeleton even without considering photosynthetically produced oxygen and organic oxygen pools. There is no information on any of these pools in corals, and more work is needed before skeletal oxygen isotope variations can be used to place bounds on oxygen metabolism in symbiotic systems.

(*e*) *Carbon and oxygen isotope correlation*

A plot of $\delta^{13}C$ against $\delta^{18}O$ (figure 4) shows considerable scatter, implying that different processes are involved in carbon and oxygen isotope fractionation. Although a weak seasonal trend in ^{18}O may be present, the irregular long-term variation in ^{18}O content dominates.

In photosynthesis the oxygen of CO_2–HCO_3^- pools does not end up in evolved oxygen even though bicarbonate ion stimulates oxygen evolution (Stemler & Radmer 1975). The photosynthetically evolved oxygen is believed to come from water, although there is some controversy on this point (Metzner 1975). If the oxygen derived from CO_2 is incorporated into an oxygen pool that is not translocated to the coral host along with photosynthetically fixed carbon (Trench 1971; Muscatine & Cernichiari 1969; Goreau & Goreau 1960*c*; Lewis & Smith 1971; Barnes & Taylor 1973; Cooksey & Cooksey 1972), then correlation between ^{18}O and ^{13}C might not result.

Keith & Weber (1965), Weber & Woodhead (1970), and Woodhead & Weber (1973) have analysed bulk composition of large numbers of corals from areas of significantly different temperature and growth rate. They found a correlation between ^{13}C and ^{18}O that contained a good deal of scatter. Seawater bicarbonate uptake, in diluting the internal pool, could give a correlation between the two isotopes that depends on the extent of dilution. Complex metabolic differences in the fractionation and skeletal incorporation of these isotopes seem to have outweighed any possible seasonal dilution effects in the present data.

(*f*) *Magnesium*

The magnesium concentrations measured (table 1) compare with reported values of 700–1600 p.p.m. (Milliman 1974) for *Montrastrea cavernosa* in Bermuda (Amiel, Friedman & Miller 1973), and with 800–2500 p.p.m. for various Pacific coral genera (Weber 1974*a*). The marked seasonality of Mg content found here does not support Weber's conclusion that 'there is no evidence that...the rate of calcification exert(s) any influence on skeletal magnesium chemistry'. His samples did not have seasonal control, and averaged out seasonal variations which may have been present.

The seasonal variation noted here is a potentially useful tool for measuring seasonal environmental variations recorded in coral skeletons. Since the Mg/Ca ratio of seawater is constant, changes in the skeleton are due exclusively to biological effects in skeleton formation modulated by environmental variations affecting coral physiology.

TABLE 1. METAL CONCENTRATIONS (P.P.M.)

sample no.	calcium	strontium	magnesium	iron
B-1	357912	6334	1544	427
B-2	352333	6526	1442	441
B-3	385573	6483	1357	363
B-4	370121	6640	1673	371
B-5	348340	6695	1716	422
B-6	351334	6620	1907	432
B-7	353815	6745	1565	426
B-8	354757	6586	1317	397
B-9	354423	6637	1233	382
B-10	354523	6792	1435	430
E-1	356173	6788	1495	442
E-2	355132	6761	1198	456
E-3	351156	6575	1242	397
E-4	352012	6726	1416	374
E-5	354447	7162	2116	388
E-6	349079	6754	2253	448
E-7	354126	6639	2020	471
E-8	351783	6693	1541	513
E-9	360680	6729	1318	430
E-10	351391	6652	1148	506
E-11	358386	6698	1272	401
E-12	347278	6732	1285	455

(*g*) *Strontium*

Strontium contents of corals have long been regarded as a potential paleoecological tool, and numerous investigators have searched for environmental correlates of this metal. The present results imply that this metal is a poor environmental indicator compared to magnesium, an element to which less attention has been paid.

The values obtained (table 1) compare with 6000–8000 p.p.m. for *M. cavernosa* in Bermuda (Amiel *et al.* 1973), with 7550 and 8020 for *M. annularis* (Livingston & Thompson 1971), with 7800 ± 530 p.p.m. for six different coral species (Thompson & Livingston 1970), with 8540 ± 640 p.p.m. for Bahamian corals of the same species (by microprobe and EDTA titration (Scherer 1974)), with an average of 6800 p.p.m. (range 6300–7200) for *Montastrea* genus (Milliman 1974), and with an average of about 7200 p.p.m. for 2020 specimens of various species (Weber 1973*a*). The slightly lower values found here for *M. annularis* is in accord with the data tabulated by Milliman (1974) showing *Montastrea* to have a lower Sr concentration than other genera of Scleractinia. The mean skeletal Sr/Ca ratio measured in this work was 0.0188 ± 0.0006, which compares with the mean seawater ratio of 0.0188 ± 0.0009 (Kinsman & Holland 1969). The seawater Sr/Ca ratio is constant except for very slight depletion in some surface waters where celestite ($SrSO_4$) skeletons are deposited by the acantharian Radiolaria (Brass & Turekian 1972).

Sr/Ca ratios found here indicate that corals do not discriminate between strontium and calcium during uptake, active transport, and deposition. Calcium ions are

involved in many aspects of cellular regulation (Williams 1974; Simkiss 1974) and are carefully regulated at concentrations of only 10^{-6}–10^{-7} mol/l in cells. Most is bound to the endoplasmic reticulum or the mitochondria (Simkiss 1974). Strontium ions compete with calcium for active transport across membranes while magnesium ions do not (Bray & Clark 1971); and strontium is not discriminated from calcium in mitochondrial uptake (Lehninger 1970). Since strontium ions appear to be transported by the same biochemical ion pumps as calcium, while magnesium content is regulated by a different transport system, it follows that variations in skeletal Mg/Ca ratio are more probable and more physiologically meaningful than changes in Sr/Ca ratios.

Strontium contents of inorganically precipitated aragonites decrease with increasing temperature (Kinsman & Holland 1969) and it has been suggested that strontium should be depleted in summer deposited skeleton (Weber 1973*a*). Most investigators have concluded that there is little temperature or growth effect on Sr in corals (Thompson & Livingston 1970; Harriss & Almy 1964). Weber, on the basis of statistical analysis of large numbers of samples from areas of different mean temperature, reported that strontium content was lower in faster growing corals from warmer waters (Weber 1973*a*). He predicted that corals should show seasonal variations of around 300 p.p.m. but no clear seasonal distribution has been found.

(*h*) *Iron and aluminium*

Iron values measured (table 1) compare with reported values of 5–170 p.p.m. for corals (Milliman 1974), 200–300 p.p.m. for aragonitic algae (Böhm 1972*a*), 5–900 p.p.m. for various coral species (Livingston & Thompson 1971), 10–110 p.p.m. in Pacific corals (Tokuyama, Kitano & Kanemisha 1972), 500–510 p.p.m. in *Millepora* (St John 1970), and 1–4 p.p.m. in corals from the Coral Sea, an area presumably remote from detrital accumulations (St John 1972).

The distribution of iron in this specimen is complicated. During periods of high rainfall red soil material can be seen suspended in the water, and some is presumably incorporated into the skeleton, producing the red residue discussed earlier. Direct microscopic confirmation of trapped detrital phases in coral skeleton has recently been published (Barnard, Macintyre & Pierce 1974). The likely local source material, Jamaican bauxite and terra rosa, is made up of the minerals gibbsite, boehmite, haematite, and goethite, with minor quantities of other minerals. Alumina contents are commonly approximately 50%, 5–25% iron, and 5–15% silica (Comer 1974).

Aluminium was measured in Jamaican aragonitic algae by Böhm, who found an Al/Fe ratio similar to that of clays (Böhm 1972*a*). Values of 180–1900 p.p.m. were reported in Okinawan corals (Tokuyama *et al.* 1972). The low (less than 125 p.p.m.) content of aluminium measured in this work suggests that the included detrital phases in the area are rich in the iron minerals goethite and haematite rather than in the alumina minerals boehmite and gibbsite. Detrital magnetite can be found in the mouths of streams in the area. R. K. Trench (private communication) has observed that the zoanthid *Palythoa* in Bermuda takes up detrital magnetite

particles and incorporates them into the mesentary indicating that coelenterates can transport small particles through their tissues and deposit them in structural units.

(*i*) *Environmental significance and paleoecological implications*

This work presents measurements of the annual changes in coral skeletal chemistry. As the first such information, it indicates some unexpected relationships between skeletal chemistry and environmental parameters that require further work to be sufficiently understood both in biological terms and as indicators of the environment.

The sampling scheme was chosen to determine whether skeleton chemistry is a whole-organism response to the environment, or affected by local heterogeneity. Restriction of sampling to a period in which water temperature was measured resulted in data from an insufficiently long time span. This failure is particularly severe in interpretation of the trace metal analyses. Future work should analyse samples from longer time intervals, and include years with hurricanes, winter 'northers', droughts, unusual cloudiness, and banding pattern abnormalities. Many interesting problems regarding the environmental correlates of skeletal chemistry cannot be addressed with the present data.

The seasonal trends reported here differ from variations in bulk skeletal chemistry between areas of different average temperature. This suggests that the fine scale environmental history recorded by the chemistry of long-lived recent corals or by unaltered Pleistocene fossils, will be quite different from that predicted by previous workers. Bulk skeletal chemistry reflects differences in *mean* incorporation rates of trace constituents, and may average out quite different seasonal patterns of *relative* incorporation. If this is the case, then detailed sampling of seasonal patterns in corals from different environments may allow the separation of changes that are primarily physiological from those that are environmentally affected.

Strong biological influence on patterns of skeletal chemistry indicate that environmental implications made from trace metal and stable isotope concentrations in biogenic carbonates cannot be safely drawn without knowledge of the metabolic processes affecting them. Much of our knowledge of ancient environments comes from precisely such measurements in calcareous fossils, which has been interpreted with minimal reference to the biology of skeleton formation.

While stable isotopic measurements have considerable power as a biological tool that places constraints on metabolism, their future use should be more closely tied to direct physiological measurements. Improvement of the carbon model presented here (which is substantially derived from the work of the late T. F. Goreau) requires better knowledge of coral-alga metabolism. The best available estimates at the present state of the art have been used for the biological parameters of the model. Many are clearly known to an unsatisfactory extent, and further work is needed along these lines.

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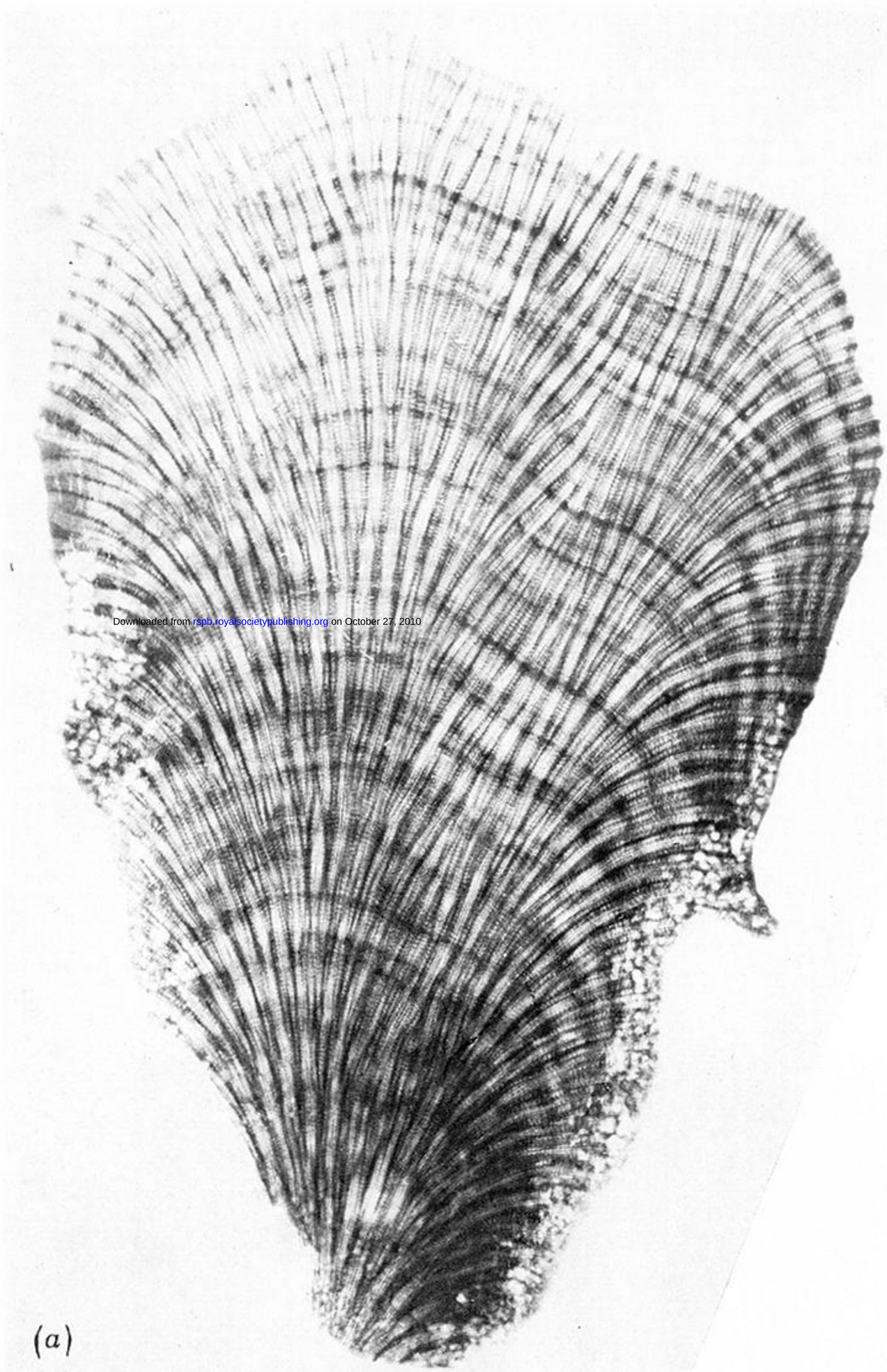

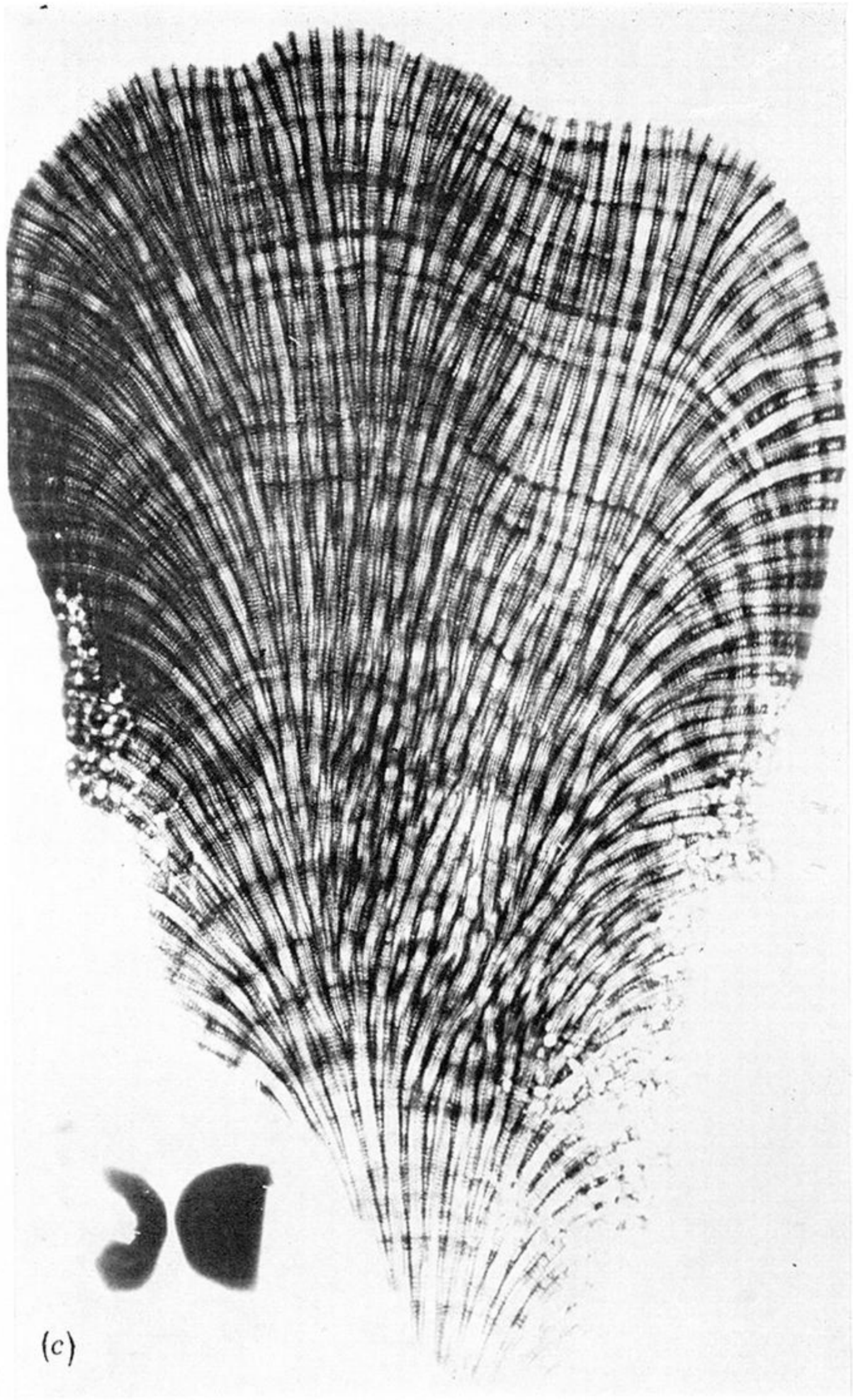

FIGURES 1*a*, *c*. For description see opposite.