Carbon and Oxygen Isotope Fractionation in Scleractinian Corals: a Review

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ABSTRACT


The present theories on the fractionation of stable isotopes in scleractinian corals are critically discussed in the light of data available on primary productivity, respiration and stable isotope chemistry. These data support a model of fractionation in which the carbon and oxygen isotopes are decoupled. Calcification occurs from a reservoir of carbon dioxide derived from both organic and inorganic sources. Photosynthesis preferentially fixes $^{12}$C and thereby leaves behind $^{13}$C. Increases in the rate of photosynthesis therefore also enrich the carbon isotope ratio of the skeleton. From theoretical considerations, photosynthesis has little effect on the oxygen isotope ratio of the skeleton, a fact confirmed by available data. The process of respiration adds depleted carbon and oxygen to the calcification reservoirs. The varying correlations between carbon and oxygen isotopes seen in hermatypic corals are caused by changes in the relationship between photosynthesis and respiration at different geographical localities. The isotopic compositions in the skeletons of non-zooxanthellate corals, which show a consistent positive correlation, can also be explained by the above scenario.

INTRODUCTION

Scleractinian corals are the main framework and visual elements of modern coral reefs, particularly extensive in tropical latitudes. Although “reefs” have been recognised since the Precambrian, Scleractinians only emerged during the Early Mesozoic and did not become a dominant component until the Triassic (Stanley, 1981). As members of the Cnidaria they possess a diploblastic body structure comprising an ectoderm, mesoglea and endoderm. A skeleton is also secreted from a skeletogenic epithelium, the organisation of which has been extensively described (Wells, 1956; Barnes, 1970; Jell, 1974), but its relationship to the organic tissues is poorly understood and subject to varying interpretations (see Kinchington, 1981). Corals occur in ramose, incrusting, foliose and massive growth forms. Massive varieties form distinct growth bands of alternate dense and less dense
aragonite as an annual phenomenon (Dodge et al., 1974). The high-density band is thought to be formed during months of warmest temperature, although stress-related bands are also recognised. Such an annual chronology should enable scientists to subsample these bands in terms of geochemical parameters such as trace elements and/or stable isotopes in order to map out palaeotemperatures and other climatic events. However, a state of confusion exists in the literature as to the precise mechanisms whereby carbon and oxygen isotopes are fractionated in calcareous organisms. This situation is particularly true in the case of the hermatypic scleractinian corals because of the uncertain nature of the relationship between the endosymbiotic dinoflagellate Gymnodinium microadriaticum (zooxanthellae) inhabiting the gastrodermis and the coral; the gastroderm is a division of the endoderm. In this paper, I will attempt to describe the present state of knowledge regarding the scleractinian corals.

In describing carbon and oxygen isotope fractionation in scleractinian corals, distinction must be made between those containing zooxanthellae (hermatypic) and those which do not (ahermatypic). Although both these types of corals occur in a typical coral reef, only the ahermatypes are found in colder waters. The zooxanthellae exist within the gastrodermis of the coral host in a mutualistic symbiosis, although exactly how the coral derives its benefit, is not certain. It is clear that the presence of the zooxanthellae positively affects growth rate as measured by skeletal accretion and to this end the following theories, as summarized by Wilbur and Simkiss (1979), have been proposed:

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(1) zooxanthellae increase rate of skeleton formation by removing CO$_2$ (Goreau, 1959); (2) photosynthate is provided by the zooxanthellae which is subsequently used in matrix formation (Muscatine and Cernichiarri, 1969); (3) energy is provided by the zooxanthellae for the active transport of Ca$^{2+}$ and HCO$_3^-$ and for the synthesis of an organic matrix (Chalker and Taylor, 1975); (4) crystal poisons such as phosphate ions may be removed by the zooxanthellae (Simkiss, 1964).

The simplest of these alternatives proposes that carbon dioxide is removed by photosynthesis, thus shifting the equilibrium of the following equation to the right and thereby favouring the formation of CaCO$_3$:

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]  

However, while some CO$_2$ may be removed by the zooxanthellae, this mechanism does not explain why the growth tips of ramose corals, apparently depleted of zooxanthellae, also have higher rates of skeletal accretion (Goreau, 1959). The translocation of photosynthetic products from the zooxanthellae along the coral frond to the growth tip may provide an explanation, but the exact mechanisms remain to be discovered.

Neither ahermatypic nor hermatypic corals precipitate their skeletons in isotopic equilibrium with seawater (see Fig. 1 for range). Hermatypes, however, appear to have a much narrower range of values, indicating a connection between the activity of the zooxanthellae and the fractionation of C and O isotopes. Therefore, in order to understand what role zooxanthellae play in the fractionating process, we must first understand the behaviour of these

Fig. 1. The isotopic composition of various groups of calcareous organisms. Data from Keith and Weber (1965), Weber and Woodhead (1970), Swart and Coleman (1980), Emiliani et al. (1978), Land et al. (1977) and this study.
isotopes during photosynthesis. In the following discussion the concentra-
tions of carbon and oxygen isotopes are defined according to the conven-
tional notation as parts per thousand deviations from an international standard:

\[
\delta^{13}C = \left( \frac{^{13}C}{^{12}C} \text{sample} - \frac{^{13}C}{^{12}C} \text{standard} \right) / \frac{^{13}C}{^{12}C} \text{standard} \times 1000 \%
\]

For carbon and oxygen this standard is PDB (a belemnite from the
Cretaceous Peedee formation), but for oxygen only another standard is used
in some instances. This is SMOW or Standard Mean Ocean Water. When
the term "enriched" or "more positive" is used in the following text, then
more of the heavier isotope is present relative to the standard. Conversely,
"depletion" or "more negative" means more of the lighter isotope.

EFFECT OF PHOTOSYNTHESIS ON CARBON ISOTOPE FRACTIONATION

Carbon dioxide is the active carbon species involved in photosynthesis. It
is fixed by ribulose bisphosphate carboxylase (RuBP) and subsequently
released to the Calvin cycle to form phosphoglyceric acid (PGA). The
fractionation accompanying this step has been measured to vary between
7.4‰ (Park and Epstein, 1960) to 89.2‰ (Deleens et al., 1974). A more
realistic value, however, is approximately 27‰. This large fractionation
means that any residual CO₂ is isotopically heavier and the CO₂ in cyto-
plasm may vary between 0 and −17.5‰, depending on the rate of CO₂
fixation and subsequent isotopic exchange with the atmosphere (Wong et al.,
1979). The establishment of such an equilibrium means that in spite of the
large fractionation (−27‰) accompanying CO₂ fixation by RuBP, the
actual isotopic composition of the PGA is heavier (−20 to −30‰). Plants
which fix CO₂ by this method are known as C₃ plants. In addition, there is a
group of plants with heavier isotopic compositions, the C₄ plants. In these
the CO₂ is initially fixed by another enzyme, PEP carboxylase. This fixation
does not involve as much fractionation and the CO₂ fixed is subsequently
totally released to RuBP. The C₄ plants are regarded as evolutionarily more
advanced and do not show the phenomenon of photorespiration seen in the
C₃ system. This involves a malfunctioning of the RuBP carboxylase which, in
the presence of oxygen, catalyzes a reaction between O₂ and RuBP to form
glyoxylate and PGA. This is eventually recycled back into the Calvin cycle
(see Fig. 2).

In photorespiration there are two stages at which isotope fractionation
could conceivably occur. The first takes place during the activity of RuBP
oxygenase when O₂ combines with RuBP, and the second as the cell recycles
the products of photorespiration. During the conversion of glycine to serine,
CO₂ is lost, a large portion of which is not recycled. Notwithstanding any
isotopic effects involved in the conversion of glycine to serine, the CO₂ will have an isotopic signature governed by the first step. If the released CO₂ has an isotopic composition which is at all different, it will result in a substantial isotopic effect as not all the released CO₂ is recycled via photosynthesis, whereas the subsequent products of photorespiration are. Isotopic fractionation at other stages in the photorespiration cycle is unlikely as not only would large reservoirs of the compounds not develop, but neither is there any quantitative loss of carbon. Some analyses of the isotopic composition of these compounds have been made by Abelson and Hoering (1960), but the results show that in some cases glycine is isotopically heavier than serine while in others the reverse is true. The evidence from this source is therefore inconclusive although theoretical calculations, based on the work of Galimov (1973), show there to be little difference between the two molecules. The participation of photorespiration in isotope fractionation is implied by the work of Troughton (1972). He has shown that the oxygen content of the atmosphere has no effect on the fractionation of carbon-13 in C₄ plants, whereas in Atriplex sp., a C₃ species, a fractionation of 0.25‰ per 1% increase in oxygen content was observed; changes in the δ¹³C were shown to behave in a non-linear manner with respect to oxygen content. Similarly it has been noted by others (Abelson and Hoering, 1961; Degens et al., 1968) that in aquatic environments, the degree of aeration is important in
fractionating carbon isotopes. This could be important in the supply of either CO$_2$ or O$_2$, the ratio of which controls the rate of photorespiration in the cell. Inter- and intra-molecular variation among cellular compounds also exists. Lipids, for example, are typically depleted in $^{13}$C relative to the remainder of the plant cellulose, a fractionation thought to be introduced by the oxidative decarboxylation of pyruvate to give acetyl Co-A (De Niro, 1977).

The data available for algae show them to be intermediate in isotopic composition between C$_3$ and C$_4$ plants (see Deines, 1980). The precise reasons for this were initially uncertain as CO$_2$ dissolved in the ocean is only 1%$_o$ heavier than atmospheric CO$_2$ (Emrich et al., 1970). Some kind of explanation may be offered by breaking down the overall fractionating process into several stages, as in the model proposed by Park and Epstein (1960). Their model, which is now subject to reinterpretation, allows for: (1) fractionation during initial assimilation of CO$_2$ into the cytoplasm, (2) incorporation into RuBP, and (3) translocation. The magnitude of the initial stage has now been called into question as a result of the findings that all the measured fractionation can be accounted for by incorporation into PGA; apparently Park and Epstein (1960) were not aware that CO$_2$ was the active carbon species involved in photosynthesis (Wong et al., 1979). In any case this stage would be absent in plants growing in an aqueous medium. The final fractionation stage, translocation, is probably also absent in algae which lack vascular systems. This step is responsible for removing isotopically heavier CO$_2$ from the region of photosynthesis and therefore plants without this step are likely to be heavier. It has been suggested that further fractionation effects may be introduced by the action of carbonic anhydrase promoting the dissociation of the predominant carbon species HCO$_3^-$ to CO$_2$ and OH$^-$ (Goreau, 1977b). Although as yet no experimental work has been conducted to determine if any isotope effects are involved, it is thought unlikely because of the very high activity of this enzyme. Carbonic anhydrase has been identified in a number of photosynthesising organisms, but as no differences have been detected between calcareous and non-calcareous algae (Okazaki, 1972), this enzyme does not appear to have a role in skeleton-forming processes. Indirectly, however, the dissociation of HCO$_3^-$ produces OH$^-$ ions, which may affect the availability of CO$_3^{2-}$ for skeleton production (Goreau, 1961). For an excellent review of carbon isotope fractionation during photosynthesis, see O'Leary (1981).

Zooxanthellae have an isotopic composition of $-17.5\%_o$ (Land et al., 1975b), a change in carbon content of only 9.5%$_o$ over the dissolved CO$_2$. This effectively means that either the composition of the internal carbon pool is heavier than the surrounding environment or that there is an absence of a large fractionation factor as measured by Wong et al. (1979) and others.
ENVIRONMENTAL EFFECTS ON PHOTOSYNTHESIS

\( \text{pH} \)

The species of carbon present in an aqueous environment is a function of \( \text{pH} \). Although it has been shown in terrestrial plants that \( \text{CO}_2 \) is the precursor of photosynthesis, some workers (Borowitzka and Larking, 1976; Schmidt and Winkler, 1979) have shown that aquatic plants may be able to utilize \( \text{HCO}_3^- \) as well as \( \text{CO}_2 \), although at a lower efficiency. The precursor of photosynthesis has important implications on the eventual isotopic composition of the photosynthate as \( \text{HCO}_3^- \) is approximately 8.2‰ heavier than \( \text{CO}_2 \) at 20°C (Emrich et al., 1970).

\( \text{Temperature} \)

The temperature-dependent fractionation of carbon (see Fig. 3) between \( \text{CO}_2-\text{HCO}_3^- \) system is 0.109‰ per °C (Emrich et al., 1970). As \( \text{CO}_2 \) is the carbon species involved in photosynthesis, this temperature effect should be translated to the isotopic composition of the plant tissues (Degens et al., 1968). Other researchers, however, have found no clear correlation between temperature and photosynthate (Troughton, 1972; Calder and Parker, 1973), although Whelan et al. (1978) determined that there were different fractionation effects during the incorporation of \( \text{CO}_2 \) into PGA at 25 and 35°C.

\( \text{Light} \)

As yet there are no data to suggest light-dependent fractionation of carbon in \( \text{C}_3 \) plants (Park and Epstein, 1960).

\[ \text{Fig. 3. Carbon isotopic fractionation (after Garlick, 1974). Data from Emrich et al. (1970); Mook (1968); Vogel et al. (1970).} \]
Environmental CO₂ concentration

It has been suggested that an examination of tree rings can reveal past changes in the global atmosphere CO₂ concentration (Francey, 1980, and others). Farquhar (1980), however, has proposed that CO₂ increases per se have little effect on the cellulose δ¹³C. He argues that the carbon isotopic composition is primarily controlled via the ratio of intercellular to atmospheric CO₂. Factors which reduce CO₂ assimilation as a result of primary effects, i.e., such as a reduction in photosynthesis, reduce the δ¹³C while a reduced CO₂ supply increases δ¹³C.

PHYSIOLOGICAL EFFECTS ON OXYGEN ISOTOPE FRACTIONATION DURING PHOTOSYNTHESIS

Discussion of the fate of oxygen during metabolic and photosynthetic processes is a subject which has received considerably less attention than that of carbon despite the fact the ¹⁸O/¹⁶O ratio is widely used for palaeotemperature work. Oxygen in the photosynthate has a δ¹⁸O of approximately +28‰ SMOW (Epstein et al., 1977), but is dependent on local isotopic and temperature regimes. It may be derived from three sources: H₂O and CO₂ used during photosynthesis, or O₂ consumed during photorespiration.

The incorporation of CO₂ into PGA proceeds by the following equation:

\[
\text{RuBP} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{PGA}
\]

(The values underneath the above and following equations are the calculated theoretical isotopic compositions of the molecules relative to Standard Mean Ocean Water, SMOW.) As may be observed from this equation, there appears to be only a slight fractionation of the oxygen involved in photosynthesis. The values shown in eq. 2 are based on the following assumptions:

1. RuBP and PGA have approximately the same isotopic composition as cellulose in marine algae as measured by Epstein et al. (1977);

2. The values shown in eq. 2 are those of the components used in photosynthesis (relative to SMOW), and are based on the assumption that H₂O and CO₂ maintain their characteristic fractionation of 1.0412 at 25°C (Friedman and O’Neil, 1977).

The process of photosynthesis also releases oxygen from the breakdown of H₂O which is depleted in ¹⁸O. This reaction is induced by light according to the following generalized equation and provides energy for the fixation of CO₂:

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2
\]
The released hydrogen ions are captured by ferroxin and ultimately passed via the cytochrome cycle to NADP; this provides energy for the fixation of CO₂. The oxygen released during this process is depleted in ¹⁸O (Lane and Dole, 1956) and therefore the residual H₂O becomes enriched in ¹⁸O. However, it has been shown experimentally that, no matter what is the isotopic composition of the CO₂, it rapidly comes into equilibrium with the plant water (De Niro and Epstein, 1979) and it is therefore this reservoir which is the principal isotopic determining force, even though, as may be observed in eq. 2, 2/3 of the oxygen involved in photosynthesis is derived from CO₂. De Niro and Epstein altered the δ¹⁸O of the CO₂ in their experiments from +6.8‰ to +985‰ with only a 9‰ change in the isotopic ratio of the cellulose. From this research it may be appreciated that whatever the small differences in the isotopic composition of the CO₂ derived from photosynthesis is, it will come into equilibrium with a much larger amount of H₂O and therefore have only a very small effect on the isotopic composition of the system.

**PHOTORESPIRATION**

Photorespiration proceeds by the following equation:

\[
\text{RuBP} + \text{O}_2 \rightarrow \text{PGA} + \text{phosphoglycolate}
\]  

(4)

The role of photorespiration in the fractionation of oxygen isotopes is particularly intriguing as photorespiration is dependent on light intensity and CO₂/O₂ ratio. Although there is as yet no information on the isotopic effects involved in photorespiration, it has been shown that under increased illumination there is a decrease in the competitive uptake of CO₂ by RuBP carboxylase. Coincident with this a large increase in the uptake of ¹⁸O¹⁶O was also observed (Gerster et al., 1979). However, in these same experiments total inhibition of the photosynthesising system did not change this pattern indicating the involvement of O₂ in other parts of the metabolic cycle, and therefore the fractionation associated with photorespiration, remains unresolved. If, however, it is assumed that there is an isotopic fractionation of the O₂ similar in magnitude to that accompanying normal respiration (i.e., 1.016, Lane and Dole, 1956), then the resultant phosphoglycolate and CO₂ released during the conversion of glycine to serine will be lighter than other plant constituents. As photorespiration in some instances can be as high as 40% of primary production (Zelitch, 1971), such an effect could result in large changes in the oxygen isotope ratio of the plant compounds.
RESPIRATION

The generalized respiration equation is given below. It has been shown that oxygen depleted in $^{18}$O is used in this process and a fractionation factor of 1.016 has been proposed (Lane and Dole, 1956):

$$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (4)$$

If it is again assumed that the fractionation between $\text{CO}_2$ and $\text{H}_2\text{O}$ is maintained, then both $\text{CO}_2$ and $\text{H}_2\text{O}$ are depleted with respect to the original $\text{CO}_2$ and $\text{H}_2\text{O}$ in the cell. In such a situation this excess $\text{CO}_2$ and $\text{H}_2\text{O}$ is excreted into the intercellular spaces.

In summary, metabolic processes may either increase or decrease the oxygen isotope composition of the residual $\text{H}_2\text{O}$-$\text{CO}_2$-$\text{HCO}_3^-$ pool from which calcification takes place. The fixation of $\text{CO}_2$ has little effect on the isotopic composition of the $\text{H}_2\text{O}$-$\text{CO}_2$ system, although the light-induced breakdown of $\text{H}_2\text{O}$ yields water enriched in $^{18}$O. However, it is likely that this $\text{H}_2\text{O}$ would soon mix with intra- and extracellular water and as the zooxanthellae are located in the gastrodermis of the coral, one cell layer away from the skeletogenic epithelium, breakdown of $\text{H}_2\text{O}$ is likely to have only a small effect. Respiration on the other hand may produce a depleted pool from which calcification may occur (eq. 4).

ENVIRONMENTAL EFFECTS ON PHOTOSYNTHESIS, RESPIRATION AND CALCIFICATION RATES

Photosynthesis and respiration have been effectively measured in scleractinian corals by rates of $\text{O}_2$ consumption and evolution (see McCloskey et al., 1978, for review). Photosynthesis shows saturation at comparatively low light levels (650 ft. candles) and calcification exhibits typical peaks in early morning and late afternoon (Chalker, 1977). This cyclical nature could be related to photoinhibition which occurs at high light intensities (Barnes and Taylor, 1973). The P/R ratio (ratio of photosynthesis to respiration), however, does not change with depth, but if anything is slightly higher near the surface at some localities (Svoboda, 1977). Similarly, even though Barnes and Taylor showed extensive photoinhibition under conditions of high light, quantities of carbon fixed in the surface corals were still higher than in those occurring at greater depths. Other measurements using the same species of coral as Barnes and Taylor studied, have shown similar trends (Spencer-Davis, 1977).

Raising the temperature increases both the rates of respiration and photosynthesis, although the temperature at which photosynthesis reaches its
optimum, is generally 10°C lower than respiration (see Fig. 4). As photosynthesis acts to increase the isotopic composition of the internal carbon pool and respiration to decrease it, at temperatures above the photosynthesizing optimum, the internal pool will become negative in spite of other environmental factors which may favour photosynthesis. It has been discovered that corals from different geographical localities show varying correlations between temperature and P/R ratio (Coles and Jokiel, 1977). For example, in Hawaiian corals P/R was negatively correlated with temperature, whereas in the Enewetak specimens a curvilinear relationship was observed. Changes in rates of respiration and photosynthesis do not necessarily correspond to absolute growth variations. Rates of skeletal accretion have been measured by a wide variety of methods and the effect of environmental variables has been reviewed by Buddemeier and Kinzie (1976). Generally corals show a growth optimum around 27–29°C, but are able to withstand much wider ranges. Such an optimum coincides with that for photosynthesis, but is well below that for respiration. Other variables likely to be influential in growth are salinity, sedimentation and light. Salinity or changes in water chemistry affect growth rates (Maragos, 1972) and skeletal composition (Swart, 1981). However, variability in the carbon and oxygen isotope composition of water while affecting skeletal composition does not influence growth itself. Depth has often been quoted as an environmental variable, but really it reflects a combination of conditions, temperature, light, sedimentation, salinity and environmental stability. Correlations between depth and isotopic composition are therefore not as simplistic as previously assumed.

CALCIFICATION MECHANISMS

In corals, both extracellular (Goreau, 1959) and intracellular (Hayes and Goreau, 1976) mechanisms of calcification have been proposed. Sites of
calcification and hence the mechanisms whereby ions are transported have important implications on both the energy requirement (Wilbur and Simkiss, 1979) and the fractionation of carbon and oxygen isotopes. The intracellular site of crystal initiation necessarily implies that Ca\(^{2+}\) and HCO\(_3^-\) are transported into the cell by some unidentified mechanism, held in vesicles and subsequently released to the crystal-bearing sites. However, an examination of the ultrastructure of one particular coral has revealed insufficient calcium storage to account for observed skeletogenesis (Vandermeulen, 1975) and subsequent electron microprobe analysis of the so-called crystal-bearing vesicles has failed to locate any large amounts of calcium (Kinchington, 1979). Although the problem may well be one of technique (Hayes et al., 1980), such evidence would tend to favour an extracellular site in which the ions pass intra- or intercellularly. Crosslands and Barnes (1974) suggested that allantoins may be the medium by which CO\(_2\) and Ca\(^{2+}\) are transported to the sites of calcification. The breakdown of the allantoins would yield CO\(_2\) and NH\(_3\), of which the latter may neutralise the protons formed during the precipitation of CaCO\(_3\). Such a pathway could be a mechanism whereby so-called “metabolic” CO\(_2\) would be introduced into the skeleton without directly involving photosynthesis or respiration. The activity of zooxanthellae in this process may be implicated by the presence of urease in the dinoflagellates promoting the removal of NH\(_3\) by the formation of urea.

Evidence from the chemical composition of scleractinian corals shows that while some cations in the seawater are accurately reflected by their concentrations in the skeleton (Ca, Sr and U: Swart, 1979, 1980), the coral, as well as exerting a species effect, is able to exclude others. This may conceivably be exerted by either: (1) uptake by a selective carrier molecule, or (2) exclusions at intercellular junctions. Isotopic data suggest that HCO\(_3^-\) may arrive at the site of skeletogenesis from both pathways, although the extracellular route is probably more important. It is also conceivable that cations in skeletogenesis can utilise inter- and/or intracellular routes. The open nature of the system is suggested by the fact that corals secrete aragonite rather than calcite. If the coral was able to exclude all the ions other than those it required, then calcite would be secreted as it is the stable form under low magnesium concentrations.

**CARBON AND OXYGEN ISO TOPE FRACTIONATION IN CORALS**

It is well established that temperature, through normal equilibrium fractionation processes, affects the \(\delta^{18}O\) of coral skeletons (Weber and Woodhead, 1972; Dunbar et al., 1980; Weil et al., 1981). However, attempts by subsequent workers to either use this relationship as a palaeotemperature indicator (Weber, 1977) or even to map out recent variations have led to
conflicting conclusions (Swart and Coleman, 1980). For example, Emiliani et al. (1978) recorded only half the observed temperature variation, by examining the skeletal $\delta^{18}$O value. It has been suggested that physiological variables and/or variations in water isotope ratio might be responsible for masking the temperature dependence of the $\delta^{18}$O value. Others have put the lack of variation down to imprecise sampling of the coral's growth bands (Fairbanks and Dodge, 1979). The literature, however, contains a number of varying hypotheses concerning the origin of the carbonate portion of its skeleton. First observations by Goreau (1961) noted that calcification rates as measured by $^{14}$C techniques were consistently lower than those made by $^{45}$Ca methods. He concluded that inorganic bicarbonate containing the radioactive tracer was being diluted, findings subsequently confirmed by Pearse (1971) and Erez (1978). A large number of workers who have measured the $^{13}$C/$^{12}$C ratio of coral skeletal material have noticed that it is depleted with respect to inorganic aragonite precipitated under similar conditions. Weber and Woodhead (1970) proposed that the skeleton was formed from an internal pool of carbon and oxygen, the isotopic composition of which was determined by a simple mixture of organic and inorganic sources. Although subsequent models have become more complex there is broad agreement that corals contain both types of carbon and oxygen in their skeletons. Differences in opinion arise, however, as to the magnitude, the effect of photosynthesis, and growth processes in general have on the isotopic composition. At present the following models for carbon and oxygen partitioning have been suggested.


The original fractionation model as described above, devised by Weber and Woodhead (1970), proposed that isotopically light respired CO$_2$ was being efficiently scavenged by the zooxanthellae, thus preventing it from decreasing the overall isotopic composition of the internal pool. Consequently an increase in photosynthesis would increase the uptake of isotopically light CO$_2$, thereby increasing the $\delta^{13}$C of the skeleton. This means that corals growing under optimum photosynthesizing conditions, i.e., near the surface, would have higher $\delta^{13}$C values. The data of Weber and Woodhead (1970), Weber et al. (1976) and Swart and Coleman (1980) do show this effect, but others have questioned the interpretation offered by Weber and Woodhead. Other consequences of this model were: (1) carbon and oxygen isotopes would be positively correlated; (2) carbon and oxygen isotopes would become increasingly depleted with depth, although in the case of oxygen this may become obscure as a result of temperature gradients; (3) corals with larger polyps would have more variable $\delta^{13}$C values; (4) dif-
ferences in isotopic composition would be caused by variations in growth form and tissue thickness.

Model 2: Goreau (1977a, b)

The second model, described by Goreau (1977a,b), deals with carbon only as he argues that carbon and oxygen are probably fractionated by different mechanisms. This model shows that the isotopic composition of the internal carbon pool is determined by the cycling of carbon from of a number of sources (see Fig. 5).

In this figure it may be observed that corals have an isotopic composition heavier than their supposed diet of zooplankton. Heterotrophs, however, normally have an isotopic composition of the tissues which is similar to their

Fig. 5. Carbon isotope fractionation model as proposed by Goreau (1977a). Approximate $\delta^{13}C$ values of the pools are shown on the vertical scale.
diet (De Niro and Epstein, 1976) and it is therefore likely that the coral derives a large portion of its carbon directly from the zooxanthellae which are similar in isotopic composition (Land et al., 1975b). Because of this similarity Land et al. (1977) suggested that zooxanthellae may utilize bicarbonate as a carbon source rather than the isotopically lighter CO$_2$. Similarly, other researchers, investigating photosynthesis in green algae, have concluded that HCO$_3^-$ could be the species of carbon involved in the Calvin cycle. Ribulose bisphosphate carboxylase, however, is specific to CO$_2$ or O$_2$ and the lack of difference in photosynthesis shown by previous workers may be due to the activity of carbonic anhydrase, promoting the dissociation of

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![Graph](image.png)

**Fig. 6.** Data from various sources on the relationship between depth, isotopic composition and carbon production in *Montastrea annularis*. In A and B the top line (round symbols) are data for the distal portions of the skeleton; the bottom line (square symbols) are data for the apical regions. C shows the $\delta^{13}C$ for organic material, and D the data for photosynthesis, respiration and skeletal production. The general trend in all these figures is a decrease in $\delta^{13}C$ with increasing depth. Fig. 6D shows some of the wealth of data on photosynthesis, respiration and skeletal production. Both respiration and photosynthetic rates decline with depth in the data of Spencer-Davis (1977). The skeletal production data of Barnes and Taylor (1973) shows little depth-related variation, although this was cited by Erez (1978) as support for Model 3. The variation in the work of Barnes and Taylor is smaller than the experimental error associated with the analytical technique and is probably not significant (D.J. Barnes, personal communication).
HCO$_3^-$ As regards the lack of difference in the isotopic compositions of zooxanthellae and the coral tissue, this is probably achieved through rapid cycling of the carbon pools (Goreau, 1977a). The rapid cycling could also account for the failure of the large amount of lipid transported between the symbionts to deplete the isotope ratio of the coral; lipids are known to be depleted relative to bulk tissues. In Goreau's model he used a $\delta^{13}$C for the coral tissues of $-13.5\%$, data obtained from Land et al. (1975b). However, Land et al. measured three species of corals and found not only differences between species but also more negative values increasing with depth (Fig. 6).

Subsequent measurements of $\delta^{13}$C in coral tissues (Swart, 1982) also show them to vary in isotopic composition. Such differences may reflect diet or effectiveness of the zooxanthellae-host relationship. As far as the depth effect is concerned, this is probably a reflection of the decreased photosynthesis, resulting from a reduction in light intensity, and a more dominant influence of diet in determining isotopic composition of the tissues. The $\delta^{13}$C values of non-zooxanthellate organic tissues have been measured by Land et al. (1977) and were found to be much more negative, around $-19.5\%$. This would appear to confirm both that corals derive a large portion of photosynthetic CO$_2$ from the zooxanthellae, and that hermatypic corals have a heavier internal carbonate pool.

Goreau used his model to account for heavy isotopic values shown in corals growing near the surface and at 30 m (Weber et al., 1976); Weber et al. interpreted the change in carbon-13 according to the original model (Weber and Woodhead, 1970) and postulated that the increase in isotopic composition at 30 m was a result of the existence of another polymorph of Montastrea annularis. However, Goreau (1977b) concluded that although corals produce more metabolically light CO$_2$ when they grow faster, the deficiency compared to that needed for photosynthesis was also greater, and therefore the coral was forced to take up a greater portion of bicarbonate. The skeletons would therefore be isotopically heavier.

Model 3: Erez (1978)

The third school of opinion, favoured by Erez (1978) and Emiliani et al. (1978), suggests that increased photosynthesis is linked to increased isotopic fractionation. Erez proposed that photosynthesis enhances the overall metabolic activity of the coral thereby increasing the amount of metabolic CO$_2$ added to the coral's internal pool. This would cause the skeleton to adopt a more negative isotopic composition during periods of higher photosynthesis. However, data from Erez (1978) shown in Fig. 9 do not convincingly support this theory. Erez also proposed that a decrease in $\delta^{18}$O with depth was similarly a result of increase in photosynthesis at intermediate depths.
Fig. 7. Schematic carbon flow in a non-zooxanthellate coral. Two arrows indicate isotopic exchange reactions, a double-sided arrow diffusion in both directions and a single arrow input only. Vertical scale indicates possible ranges only of $\delta^{13}C$. The isotopically light-respired CO$_2$ ($-19\%$) mixes with inorganic CO$_2$ ($-7\%$). HCO$_3^-$ in equilibrium with this CO$_2$ has a range of isotopic compositions between $-12\%$ and $+1\%$. A skeleton precipitated without other isotopic effects, possibly induced by the secretion process itself, could have an isotopic composition of between $-11\%$ and $+3\%$, depending on the relative contribution of each source. This agrees with the data shown in Fig. 10. Such a flow scheme could also be present in the ectodermis of a hermatypic coral.

However, as shown above, photosynthesis per se has no effect on isotopic composition of oxygen, a finding confirmed by the absence of a depth vs. $\delta^{18}O$ relationship shown by other workers. Changes in respiration or photorespiration, on the other hand, could produce such changes, but it must be remembered that the overwhelming influence on the oxygen isotope com-
position of the skeleton is still exerted by the seawater. The fact that corals growing near the surface have been shown to be enriched in carbon-13 was suggested by Erez (1978) to be a result of the photoinhibition of zooxanthellae at light intensities over 600 ft. candles (Barnes and Taylor, 1973). However, in view of the large errors associated with the $^{45}$Ca technique of growth rate measurement, it is possible that such measurements may not represent normal phenomena (Barnes, 1982, and personal communication). As previously discussed, in all cases examined, production of carbon and hence P/R ratios were still higher in surface corals than at lower depths (Svoboda, 1977; Spencer-Davis, 1977). Although this theory cannot be categorically ruled out, present data from a wide range of sources tend to favour the idea that increases in photosynthesis isotopically enrich the residual pool from which calcification takes place.

DISCUSSION

In order to achieve isotopic compositions of the order shown in Fig. 1, mechanisms must be invoked which will take into consideration all of the various factors discussed in this paper. Of the models proposed so far, the one suggested by Goreau (1977a) best agrees with the available data, but although he was the first to point out that photosynthesis can drive the residual pool from which calcification occurs, isotopically heavy, this was not incorporated into his model. Goreau also made no distinction between the various dissolved species of carbon, the relative fractionations of which are shown in Fig. 5. The most significant of these is between HCO$_3^-$ and CO$_2$ (8.2‰). HCO$_3^-$ will dissociate into CO$_2$, which will be isotopically heavier than that produced by respiration. As the eventual isotopic composition of the skeleton will be determined by mixing between inorganic CO$_2$ (-7‰) and respired CO$_2$ (-13.5 to -19.5‰), logically the skeleton should have a carbon-13 value between approximately 1 and -10‰. In fact, only ahermatypic corals show such a range (Fig. 7). This points to the zooxanthellae either removing metabolically light CO$_2$ or fractionating the carbon pool during the incorporation of CO$_2$ to form PGA. If the former were the case, then the isotopic composition of the zooxanthellae would surely be much more negative than -17.5‰, the same composition as its supposed CO$_2$ source. Alternatively, during the incorporation of CO$_2$ into PGA, fractionation factors as high as 35‰ and higher have been proposed. If one considers a lower fractionation, say only 9‰, the remaining carbon will become isotopically enriched in carbon-13. As the value of the pool increases, the fractionation needed to maintain a zooxanthellae composition of -17.5‰ will increase towards the often-quoted values. Eventually, an equilibrium will
Carbon balance in the endodermis of a hermatypic coral

Fig. 8. Schematic carbon flow in the gastrodermis of a zooxanthellate coral as in Fig. 7. This figure differs from that of Goreau (1977a) in that the intracellular carbon pool is shown to be isotopically heavier than the external one. The range of the intracellular CO₂ pool shown is based on a fractionation of CO₂ by RuBP carboxylase of approximately 10%. The intracellular pool may therefore be very much heavier.

be established between incoming CO₂ – HCO₃, respired CO₂ and CO₂ being incorporated into PGA (see Fig. 8).

In hermatypic corals, the zooxanthellae are situated in the gastrodermis, two body layers away from the skeletogenic epithelium. It is not known how CO₂ and HCO₃⁻ are transferred between the gastroderm and ectoderm, but each layer can be considered as a separate system adsorbing and secreting carbon species into the intercellular spaces. The proposed carbon budget of the gastrodermis is shown in Fig. 8. The range of isotopic values shown
assumes that there is a fractionation between CO₂ and RuBP of only 10‰, much less than previously quoted. The possible range of intercellular HCO₃⁻ may therefore be larger than actually shown on the diagram. The bicarbonate in the intercellular spaces moves to the site of skeletogenesis by mass diffusion processes where it mixes with CO₂ excreted from the ectoderm. This has an isotopic composition similar to the respiring tissues and is therefore negative. The skeleton will be formed from a mixture of these two sources.

_Intraskeletal variation_

Intraskeletal isotopic variation typically takes the form of isotopic depletion in the rapidly growing areas of the coral (Keith and Weber, 1965; Land et al., 1975a; Weber et al., 1976). These areas are also depleted in zooxanthellae (see Fig. 6). Such evidence would tend to confirm the relationship between zooxanthellae and skeletal isotopic composition. In ahermatypic corals, even greater intraskeletal heterogeneity exists. Emiliani et al. (1978) measured values between -8 to -1‰ for carbon and -5 to +.5‰ for oxygen in one specimen (see Fig. 10). These workers concluded that the differences reflected variations in growth rate during the life span of the coral with more negative values occurring at the base. As the growth rate of the coral decreased, the isotopic values approached equilibrium with seawater. In a similar study on _Lophelia pertusa_ (Swart, this study) extreme negative
values were measured at the edge of the calice. These probably also reflect
growth variations.

*Photorespiration*

A further potential source of CO$_2$ arises from that produced by photorespiration. Although the isotopic effects involved are not known, the potential of this contribution may be considerable as in some plants 40% of primary productivity may be lost by photorespiration. Possible effects of photorespiration in corals have been discussed by Benson et al., (1978) and Tolbert (1976), although in their studies the only conclusion reached was that the evaluation of such relationships could only be made with difficulty. Both Crosslands and Barnes (1977) and Burris (1977) were unable to measure appreciable amounts of CO$_2$ evolution by isolated zooxanthellae in the light. It may be that, (1), CO$_2$ is rapidly refixed, in which case no isotopic effect would be visible or that, (2), glycolate is being excreted by the algae which in turn reduces the availability of glycine and hence CO$_2$ production. A feature of photorespiration, the increased production of glycine under high oxygen concentrations, has not been observed in any micromarine algae (Burris, 1977). It was concluded that these algae may have one or more of the following: (1) a different photorespiration pathway; (2) more than one photorespiration pathway; (3) small pool sizes of glycine and serine; (4) no or little photorespiration at all.

Although data available at the moment tend to preclude photorespiration as an important component of carbon metabolism in zooxanthellae, there are arguments that the experiments carried out so far are non-physiological and therefore do not truly represent natural conditions. Similarly, it has been observed that isolated zooxanthellae change their physiological state with time (Trench, 1971) and thus results obtained so far may be incorrect.

*Role of calcification mechanisms*

A factor as yet not mentioned by previous workers, is how various proposed calcification mechanisms may affect isotopes. Transport across cellular membranes by a "carrier molecule" will almost invariably mean greater fractionation than simple diffusive processes. Although there are still many uncertainties concerning the calcification processes, I favour the idea that Ca$^{2+}$ and HCO$_3^-$ move through the intercellular spaces at a rate controlled by the secretion of an organic matrix or the formation of cavities between the skeleton and skeletogenic epithelium. During movement through these spaces, kinetic fractionation occurs with the lighter molecules moving at a faster rate. The concept of being either a carbon importer or exporter
has important implications on the isotopic composition. For example, ahermatypes export CO$_2$, therefore, $^{13}$CO$_2$ will move out at a slower rate than $^{12}$CO$_2$. Conversely, hermatypes import CO$_2$ and thus the reverse process will apply. Land et al. (1977) concluded that because of the wide range of isotopic compositions shown in the ahermatypes, inorganic bicarbonate could not be instrumental in skeletal formation, as no matter what isotopic composition was assigned to the metabolic component, simple mixing with inorganic CO$_2$ would not be able to explain the observed isotopic distribution. They further suggested that removal of respiratory CO$_2$ would be influenced by metabolic processes such as active transport, opening and closing of the polyp mouth. Such processes, although removing CO$_2$, will promote maximum fractionation and consequently will result in a more positive intercellular CO$_2$ pool. The idea of an active CO$_2$ disposal mechanism can probably be ruled out because of the energy involved (Wilbur and Simkiss, 1979). Proponents of the idea that zooxanthellae act to increase carbon isotope fractionation point to evidence obtained from corals which can exist in either the zooxanthellate or non-zooxanthellate form. One of these, Madracis pharensis, has a more depleted skeletal $\delta^{13}$C in the hermatypic form (Land et al., 1977). However, while this apparently lends credence to Model 3, it should be realised that all hermatypic corals are able to shed their zooxanthellae under periods of stress and survive, but grow then at a very much reduced level. The reduced input of respiratory CO$_2$ would result in a heavier skeletal $\delta^{13}$C. Although it is not certain whether the two forms of M. pharensis are the same species, it may not be valid to compare them, because the species lacking the zooxanthellae may do so for some other reason which influences the carbon balance. The same argument may well be leveled against recent data on Astrangia danae, a scleractinian also able to grow in either form (Cummings and McCarthy, 1982). This study showed the opposite trend to M. pharensis, i.e., the zooxanthellate individuals had isotopically heavier carbon in their skeletons.

Relationships between the fractionation of carbon and oxygen isotopes

In order to explain the apparent coupling of the carbon and oxygen isotopes in ahermatypes (Fig. 10), one must again return to the effect of photosynthesis on oxygen and carbon fractionation. Oxygen, according to the above discussion, does not appear to be influenced by photosynthesis. Carbon, however, is fractionated during the incorporation of CO$_2$ into PGA and, therefore, processes which increase the rate of photosynthesis will act to increase the isotopic composition of the residual carbon reservoir, without affecting the isotopic composition of the oxygen. Superimposed on the effects of photosynthesis, are those of respiration which will act to deplete
both carbon and oxygen isotopes. In the ahermatypes, respiration and thermodynamic fractionation are the only processes affecting carbon and oxygen (without invoking any activity of carbonic anhydrase or uptake by a hypothetical carrier molecule) and therefore the overall fractionation of the isotopes will be positively correlated. In hermatypes, photosynthesis when combined with the effects of respiration obscures the relationship between the two isotopes as in the data of Weber and Woodhead (1970), or even causes the data to become totally random (Goreau, 1977a; Swart and Coleman, 1980). In some instances a negative correlation may result (Emiliani et al., 1978; Fairbanks and Dodge, 1979). Fairbanks and Dodge concluded that the degree of correlation between oxygen and carbon was determined by the relationship between insolation and temperature; such a conclusion would appear to fit available data. The fractionation of both carbon and oxygen isotopes is temperature-dependent, although carbon is affected to a much lesser extent. In inorganic precipitates, therefore, the isotopes will be negatively correlated; photosynthesis acts to enhance this correlation. However, at higher temperatures when rates of photosynthesis relative to respiration are reduced, the contribution of negative carbon from respiration
increases and a positive correlation can result. Similarly, the P/R data collected by Coles and Jokiel (1977) show the varying relationships which exist between P/R and temperature at different localities. Furthermore, any environmental process which will tend to increase the rate of photosynthesis, while not affecting respiration will result in a negative correlation between the isotopes. Examples of such processes are evident in the data of Fairbanks and Dodge (1979). In corals collected from localities where insolation and temperature did not vary in phase, the isotopes were negatively correlated, whereas in areas where insolation and temperature did coincide, the reverse was the case.

The wide range of isotopic compositions of the ahermatypic corals reflect variations in geometry, water temperature, growth rates and even local isotopic regimes. In contrast, the carbon balance of hermatypes is much more under control, evident in the narrower range of isotopic values.

**Isotope fractionation in other calcareous organisms**

The major difference in the geochemistry of coral-reef components, originates in their mineralogies: calcite and aragonite. It has been shown that under normal marine conditions aragonite is the stable form of precipitation and calcite formation is inhibited as a result of the presence of magnesium ions. It is likely, therefore, that organisms that form calcitic skeletons are able to exert a greater control on the trace elements in their skeletons although the presence or nature of an organic matrix may be instrumental (Matheja and Degens, 1968). Such controls are also likely to induce greater isotopic fractionation. An examination of published isotopic compositions (see Fig. 1) shows that generally aragonitic organisms are less fractionated than calcitic ones.

Although this review has been concerned primarily with scleractinian corals, many of the principles involved apply to other calcareous organisms. In particular, isotopic compositions of foraminifera have been extensively examined. Erez (1978) has shown isotopic depletion in foraminifera growing in association with symbiotic dinoflagellates to increase with increasing light-intensity. Similar results have been shown by Williams et al. (1981), although the data of both these workers show contradictions in that some of the species studied have shown no trend between $\delta^{13}C$ and photosynthesis. As with corals, analogies can be drawn between groups of foraminifera containing endosymbionts and those which do not. If a similar type of calcification mechanism existed in these organisms, then a positive correlation might be expected in the case of the non-zooxanthellate foraminifera. The fact that such a relationship has been found to be absent in some deep-sea benthic forms has led Belanger et al. (1981) to suggest that respired
CO₂ may not be instrumental in skeletal formation, and differing hypotheses for isotopic fractionation have been proposed for planktonic and benthonic forms. Alternatively, carbon isotope flow regimes in benthic environments, which have been shown to be anomalous (Rau, 1981), could cause this lack of correlation.

SUMMARY

The data presented in this paper support, with amendments, many of the ideas suggested by Weber and Woodhead (1970) in their original model of fractionation, later modified by Goreau (1977a). However, consideration of the respiration and photosynthesis equations, shows different processes to operate in the fractionation of stable isotopes and, therefore, a correlation between carbon and oxygen is not a necessary prerequisite to any fractionation model. In hermatypic corals, increases in photosynthesis relative to respiration can cause changes in the observed correlation of these two isotopes. These changes occur because, although photosynthesis increases the concentration of the heavier isotope of carbon in the residual pool, it has little if any effect on oxygen fractionation. Respiration adds depleted carbon and to a lesser extent oxygen to the calcification pool. Because of the location of the zooxanthellae and the overwhelming influence of H₂O in the determination of the isotopic composition of any coexisting carbonate phases, these symbionts will probably have little if any effect on the oxygen isotopic composition of the skeleton.

The depth vs. δ¹³C correlation shown by many previous researchers, probably reflects a reduction in light-intensity with depth. The absence of this correlation in some localities is probably a result of the fact that depth itself is not a quantifiable environmental variable, but merely a combination of many parameters. Changes in the depth profile of the δ¹³C of the organic material of the coral indicates both the increased role of zooplankton in the nutritional requirements of the coral and the decreased activity of zooxanthellae. Further changes in the isotopic ratio of the coral's internal pool may be induced through the activities of photorespiration. Variations in this parameter can be caused by changes in light and or CO₂/O₂ ratio.

Although differences in the magnitude of carbon and oxygen isotopes between ahermatypes and hermatypes are not consistent in direction, the removal of the influence of photosynthesis in ahermatypes causes the isotopes to be positively correlated. Such consistent correlations are not found in hermatypes. This provides a valuable geochemical tool for distinguishing between ahermatypes and hermatypes in the fossil record.
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