Coral
Calcification mechanism
$^{18}O/^{16}O$
Simulation

Coraux
Mode de calcification
$^{18}O/^{16}O$
Modélisation

Effects of calcification patterns on the oxygen isotope composition of the skeleton of the scleractinian coral *Acropora formosa*

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ABSTRACT

Oxygen isotope ratios were measured along the growth axis of branches of the scleractinian coral *Acropora formosa* collected at 2 and 12 metre depths at Yonge reef (Northern Great Barrier Reef, Australia). Measurements were made between two reference points separated by a distance corresponding to a growth period of six months, from mid-winter to mid-summer. For each of the two reference points, information concerning the environmental parameters controlling the development of the coral colonies was collected *in situ*. The variability of the isotopic values recorded from coral skeletons grown in identical physical and chemical conditions cannot be ascribed to technical problems, but may rather be induced by calcification mechanisms.

In order to define the influence of calcification processes on oxygen isotopic composition, a simple mathematical model is developed, simulating the behaviour of oxygen isotopes. According to Gladfelter's studies (1982, 1983, 1984), we infer that the main factors affecting the isotopic ratio of skeletal aragonite in the scleractinian coral *Acropora* genus are on the one hand the initial quantity of aragonite deposited at the apical part of the branch and consequently the relative amount of primary and secondary aragonite infilling residual pores during coral growth, and on the other hand, the duration of the secondary aragonite infilling. Comparisons between the measured and the calculated isotopic profiles reveal that differences in calcification processes account for isotopic discrepancies encountered in the different colonies analysed. This study stresses that care must be taken when using the oxygen isotope composition of coral skeleton as a paleoenvironmental proxy.

RÉSUMÉ

Variabilité de la composition isotopique en oxygène du squelette d'un corail scléractiniaire *Acropora formosa*, induite par le mécanisme de calcification.

Le rapport isotopique $^{18}O/^{16}O$ a été mesuré le long de l'axe de croissance de plusieurs branches de corail scléractiniaire *Acropora formosa* développées à deux profondeurs différentes, 2 et 12 m, et provenant de Yonge Reef (récif du Nord de la Grande Barrière, Australie). Les échantillons ont été pris entre deux points de chacune des branches, représentatifs des deux principales saisons (été et hiver) : l'un est souligné par un marquage à l'alizarine, l'autre correspond à l'extrémité de la branche. La variabilité des résultats isotopiques, obtenus pour des coraux qui se sont développés dans des conditions physico-chimiques totalement similaires, ne peut se justifier uniquement par l'imprécision de la méthode de mesure.

Nous avons utilisé un modèle mathématique, qui reproduit les fluctuations de la composition isotopique, afin de démontrer l'influence des processus de calcification sur les variations du rapport $^{18}O/^{16}O$. En nous basant sur des études effectuées par E. Gladfelter (1982, 1983, 1984) nous avons déduit que les facteurs responsables de la variabilité isotopique de l'aragonite du squelette des coraux sont essentiellement : la quantité initiale d'aragonite déposée à l'extrémité de la branche, et par la suite la quantité relative d'aragonite primaire et secondaire, et la durée de remplissage par l'aragonite secondaire. Par comparaison des profils isotopiques calculés et mesurés, il apparaît que la variabilité observée sur les mesures isotopiques est totalement justifiée par le mode de calcification. Cette étude souligne toutes les précautions à prendre lors de l'interprétation des données isotopiques en terme de reconstitution paléoclimatique.

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INTRODUCTION

While the role of the modern tropical ocean in global heat and water budgets is well identified, interactions between the tropical ocean and the atmosphere during the past are still poorly understood. Inconsistency between the reconstruction of sea-surface paleotemperature (CLIMAP, 1981) and continental paleoclimatic evidence (*i.e.* snowlines and vegetation changes) over the tropics, during the Last Glacial Maximum (Rind and Peteet, 1985), has been demonstrated by global circulation modelling. Corals could serve as accurate paleoenvironmental recorders, providing information about climatic conditions prevailing throughout the tropics, and notably the temperature of the superficial euphotic zone. However, as stressed by Barnes and Lough (1993) and Taylor *et al.* (1995), the use of geochemical proxies, such as $^{18}O/^{16}O$ or Sr/Ca in corals, presupposes knowledge of the physiological effects on the deposition of the skeletal carbonate. Corals collected by reef coring belong mainly to the branching colonies of the genus *Acropora*, particularly in the Indo-Pacific province. Therefore, it is of prime importance to obtain detailed information concerning the influence of biomineralization of *Acropora* skeletons on the geochemical signals.

More than 20 years ago, Weber and Woodhead (1972) defined the relationship between $\delta^{18}O$ and temperature for several coral genera, and in particular, for *Acropora*; their equation is: $\delta^{18}O = 3.43 - 0.28\ T\ °C$ (1), assuming that $\delta^{18}O$ water = 0. The deposition, in isotopic desequilibrium, of calcium carbonate from the coral skeleton is still poorly documented; McConnaughey (1989*b*) ascribed ^{18}O desequilibrium to kinetic effects during CO_2 hydration and hydroxylation, related to the calcification rate, but failed to explain why the different species yield different isotopic calibration *versus* temperature, or why the isotopic ratio of the superficial part of a single massive *Porites* head varies (McConnaughey, 1989*a*). However, oxygen isotopes are regarded as accurately reflecting variations in water temperature or/and in water isotopic composition (Swart, 1983*a*; Pätzold, 1984; McConnaughey, 1989*a*; Aharon, 1991). For instance, from experiments conducted on massive corals, McConnaughey (1989*a*) ascribed a 0.6 °C accuracy to temperature estimates. A few paleoenvironmental reconstructions are based on the study of branching corals (Fairbanks and Matthews, 1978; Dunbar and Wellington, 1981; Guilderson *et al.*, 1994). Dunbar and Wellington (1981) did not consider the factor driving the isotopic variability affecting different colonies grown in the same reefal environment, even though seasonal temperature changes were accurately reflected by variations in isotopic composition from modern branches of *Pocillopora damicornis*.

In order to understand such a variability, we examine the incorporation of oxygen isotopes into branches of colonies of the species *Acropora formosa* (Dana, 1846),

a non-banded branching species, subjected to similar environmental conditions over a six-month growth period. These corals were sampled on an outer shelf reef (Yonge reef) located in the northern part of the Australian Great Barrier Reef (14° 35' S, 145° 37' E). Variability of the oxygen isotopic profiles obtained from colonies grown in similar physico-chemical conditions could not be ascribed solely to poor instrumental accuracy, and we consequently assume that it could be attributed to mechanisms controlling calcification in *Acropora* colonies.

Gladfelter (1982, 1983, 1984) describes two processes involved in the skeletal development of *Acropora cervicornis*: (1) precipitation of a framework of aragonite fusiform crystals (*i.e.* primary aragonite); and (2) subsequent overgrowth of aragonite needles (*i.e.* secondary aragonite), progressively infilling residual intercrystalline spaces. This two-step mechanism could probably be applied to various *Acropora* species, even if *Acropora cervicornis* shows a greater skeletal strength than *Acropora formosa*, for which secondary calcification is less pronounced. However, no information is at present available concerning the respective content of every crystallographical variety (fusiform crystals and needles) and the time of deposition of secondary aragonite. Due to the size of the crystals, present-day techniques do not permit isotopic measurement of each crystal type; so we develop a simple mathematical model in order to estimate the respective oxygen isotopic composition of each crystalline deposit and the relevant variations along the growth axis of branches.

MATERIAL AND METHODS

Field investigations

Sets of branches of the scleractinian coral *Acropora formosa* from individual colonies were cemented on plots in November 1988 at depths of 2 and 12 m on the reef flat and the inner reef slope, covering a 2 m^2 area at each site. In July 1989, gross production and respiration of each sample were measured (Juillet-Leclerc *et al.*, submitted). The branches were subsequently stained using Alizarin red-S, as described by Barnes (1970). The same metabolic parameters were again measured in January 1990. The branches were then collected and dried for subsequent determination of growth rate and isotopic compositions. Colonies # 42, 45, 61, 63 and 66 were grown at a depth of 2 m, while Colonies # 17, 18, 67, 68, 69 and 70 were grown at 12 m.

Yonge Reef is a shelf-edge reef 5400 m long and 450-1100 m wide. The sea water temperature was recorded *in situ* during the physiological investigations in July 1989 (austral winter) and January 1990 (austral summer) at the two reef sites (Tab. 1). As the reef front is exposed, as a consequence of SE trade-wind generated waves and oceanic swell, to high levels of hydrodynamic energy for 9 to 10 months of the year, the experimental area (*i.e.* the shelf edge reef) is subjected to the direct influence of the open ocean, thereby preventing isotopic fluctuations due to severe evaporation or dilution by rainfall (Swart *et al.*, 1983b). Additional information about interannual and seasonal variability of temperature, salinity and light could be inferred from the continuous record of environmental parameters obtained in 1991 from Agincourt Reef, 85 nautical miles south of Yonge Reef, and from the data obtained near Lizard Island (14° 40' S, 143° 28' E) between 1974 and 1983. Monthly records of the environmental parameters staggered over several years near Lizard Island showed that the only noticeable changes in salinity occurred in this area from February to April; the period singled out in this study (July to January) is not affected by such changes. So although $\delta^{18}O$ of the ambient sea water has not been measured, we estimate, from salinity changes, that the isotopic variation between winter and summer cannot exceed 0.3 ‰.

The data obtained in July 1989 refer to the Alizarin-stained zone, while those obtained in January 1990 refer to the apex of the branches (Tab. 1). Comparisons of these data with water temperature on Agincourt reef confirmed the considered values as representative of mean summer or winter conditions. January is one of the months of highest temperature during the year; the lowest temperatures occur in July (and August). While sea water temperatures vary seasonally (5 °C on average), there was very little depth-controlled gradient of temperature at the times of measurement. Variations in daily irradiation exhibit a clear seasonality, which is much more marked at the depth of 2 m than at 12 m.

The linear extension rates of the branches, measured for the period July 1989-January 1990, range from 14 to 26 mm/6 months at the depth of 2 m, and from 20 to 31 mm /6 months at 12 m (Tab. 1).

Laboratory investigations

Subsampling of coral branches

Several branches from different colonies were sawn carefully into two parts along the growth axis, keeping the relevant apex undamaged; each branch is considered as representative of one colony. Some 80 µg of carbonate (referred to as *subsamples*) were removed for isotopic analysis, using a 0.6 mm drill (with low drill speed to avoid any mineralogical conversion by heating (Gill *et al.*, 1995)), in proximity to and along the growth axis, close to the deposition area of the first crystal generation, at the tip of the branch. Since the linear growth rates of each branch are known (Tab. 1), every subsample could be regarded as encompassing a period of extension varying approximately from four days for a growth rate of 14 mm/6 months (Colony # 63) to eight days for a growth rate of 31 mm /6 months (Colony # 70). All the branches were subsampled at 4 mm intervals, between the Alizarin-stained band and the apex, with the exception of Colony # 61, on which the subsampling resolution was 2 mm. Since the apical point of coral branches is very fragile, it may be broken during extraction; in this case (as for Colony # 70), an apex was removed from another branch belonging to the same colony. Subsampling must be performed strictly along the growth axis; we checked isotopic variations laterally to the axis: aragonite can exhibit changes in $\delta^{18}O$ up to 0.2 ‰ *vs* PDB just 1 mm away from the axis. The

Table 1

Average environmental conditions (depth, temperature) at the sites of the Acropora specimens studied. $\delta^{18}O$ values refer to the subsamples collected from the Alizarin-stained zone (austral winter, July 1989) and at the tip of branches (austral summer, January 1990), respectively. $\Delta^{18}O$ values refer to differences between oxygen isotopic ratios between winter and summer. Average growth rates of the acroporid branches studied are given.

Sample number	Growth rate (mm. 6-months)	Depth (m)	Austral Winter July 89		Austral Summer Jan 90		
			Temperature (°C)	$\delta^{18}O$ (‰)	Temperature (°C)	$\delta^{18}O$ (‰)	$\Delta^{18}O$
42	23.5	2	26.0	– 4.32	30.5	– 5.04	0.72
45	21	2	26.0	– 4.31	30.5	– 5.13	0.82
63	14	2	26.0	– 4.47	30.5	– 5.15	0.68
66	26	2	26.0	– 4.14	30.5	– 4.91	0.77
61	24	2	26.0	– 4.17	30.5	– 4.72	0.55
				δ = – 4.28 (σ = 0.15)		δ = – 4.99 (σ = 0.18)	Δ = 0.71
17	19.5	12	25.6	– 3.92	30.8	– 4.71	0.79
18	22.5	12	25.6	– 3.82	30.8	– 4.62	0.8
67	30	12	25.6	– 3.83	30.8	– 4.57	0.74
68	28	12	25.6	– 3.85	30.8	– 4.64	0.79
69	21	12	25.6	– 3.99	30.8	– 5	1.01
70	31	12	25.6	– 4	30.8	– 4.47	0.47
				δ = – 3.90 (σ = 0.08)		δ = – 4.67 (σ = 0.18)	Δ = 0.77

subsamples taken from the stained and the apical zones were considered to be time (or season) reference points, *i.e.* days of alizarin-staining and of collection respectively.

Isotopic measurements

Both $\delta^{18}O$ and $\delta^{13}C$ values were measured on all the samples. Only the results of $^{18}O/^{16}O$ ratios are presented and discussed in the present study. The isotopic analyses were performed using a FINNIGAN MAT 251, coupled with a standard FINNIGAN "Carbonate Device". This permits automatic processing of the subsamples with an individual acid bath. In the case of aragonite material, the reproducibility of a coral subsample is 0.07 ‰ for $\delta^{18}O$. The isotopic composition $\delta^{18}O$ is expressed as:

$$\delta^{18}O = [(^{18}O/^{16}O)\ \text{sample}/(^{18}O/^{16}O)\ \text{standard}-1]^* 10^3$$

in delta notation, working standard referred to PDB using as reference NBS 19, $\delta^{18}O$ of – 2.20 ‰ *vs* PDB (Hut, 1987; Coplen, 1988) .

After subsampling, since the coral aragonite considered herein is modern, the obtained powder was treated for 20 min in an oven at 400 °C, under vacuum, in order to destroy organic matter. As we know that such a treatment may convert aragonite into calcite, the isotopic composition of some subsamples was compared before and after heat treatment, in order to assess the effect of oven-drying. In many cases, there was no noticeable difference, while in few others an isotopic offset was observed which did not exceed 0.2 ‰.

ENVIRONMENTAL SIGNIFICANCE OF OXYGEN ISOTOPIC COMPOSITION

Isotopic ratios of the reference subsamples

Oxygen isotope values obtained from the season reference subsamples (*i.e.* from the Alizarin-stained zone and the apex of the coral specimens studied) are given in Table 1.

Since there is very little change in temperature between the two sites (0.3-0.4 °C), the oxygen isotopic values obtained should be identical for all the aragonite samples deposited at the same time. In fact, the averaged discrepancy measured between the depths of 2 m and 12 m is around 0.4 ‰ both in winter and summer, which exceeds the expected error ranges, supposing the total error on isotopic value due to the precision of subsampling and the instrumental accuracy to be of the order of 0.15 ‰. Dispersion is higher in the case of the subsamples taken from the apex of the branches, due to the difficulty of sampling. It is noteworthy that the isotopic values recorded in July 1989 exhibit a lower dispersion, namely 0.30 ‰ and 0.15 ‰ respectively for samples grown at 2 m and 12 m, than isotopic compositions measured for January 1990, which show a dispersion of 0.32 ‰ irrespective of depth.

If the temperature dependence estimated by Weber and Woodhead (1972) applied (– 0.28 ‰ per °C), then seasonal temperature differences of around 4.5 °C would produce $\delta^{18}O$ changes of – 1.26 ‰; this is considerably larger than the observed isotopic mean change of – 0.74 ‰ (Tab. 1).

Several problems arise from the previous observations:

– differences in temperature between winter and summer do not account for differences in oxygen isotopic composition measured from each *Acropora* colony, at either 2 or 12 m, assuming the Weber and Woodhead calibration (1972) to be correct.

– the observed variability of 0.33 ‰ (in winter at 2 m depth), 0.43 ‰ (in summer at 2 m depth), 0.18 ‰ (in winter at 12 m depth) and 0.63 % (in summer at 12 m depth) considerably exceeds dispersion due to measurements.

– a systematic $\delta^{18}O$ discrepancy is recorded for an identical season between the 2 m and 12 m depths.

– there is no clear relationship between extension rate and oxygen isotope composition.

Isotopic variations along the *Acropora* branches from July 1989 to January 1990

In order to understand why the amplitude of isotopic variation is systematically lower than that due to a simple isotopic response to a temperature effect, an analysis was performed on subsamples drilled along some *Acropora* branches, from the stained zone to the apex (Colonies # 42, 45, 61 and 63 for the 2 m deep site and Colonies # 68, 69 and 70 for the 12 m deep site). Figure 1 indicates changes in the isotopic composition obtained between July 1989 and January 1990. The growth rate of a given coral branch is assumed to remain constant throughout the six-month period. For each colony collected, the isotopic signal shows a similar seasonal trend (*i.e.* depletion in ^{18}O from July 1989 to January 1990), on which variations specific to every branch are superimposed, although the local conditions at each site were strictly similar.

In isotopic terms, the samples from the reef flat site, at 2 m depth (Colonies # 42, 45, 61 and 63) (Fig. 1A) behave differently:

– for Colonies # 42 and 63, the isotopic profiles are very similar, whereas the respective growth rates of the relevant

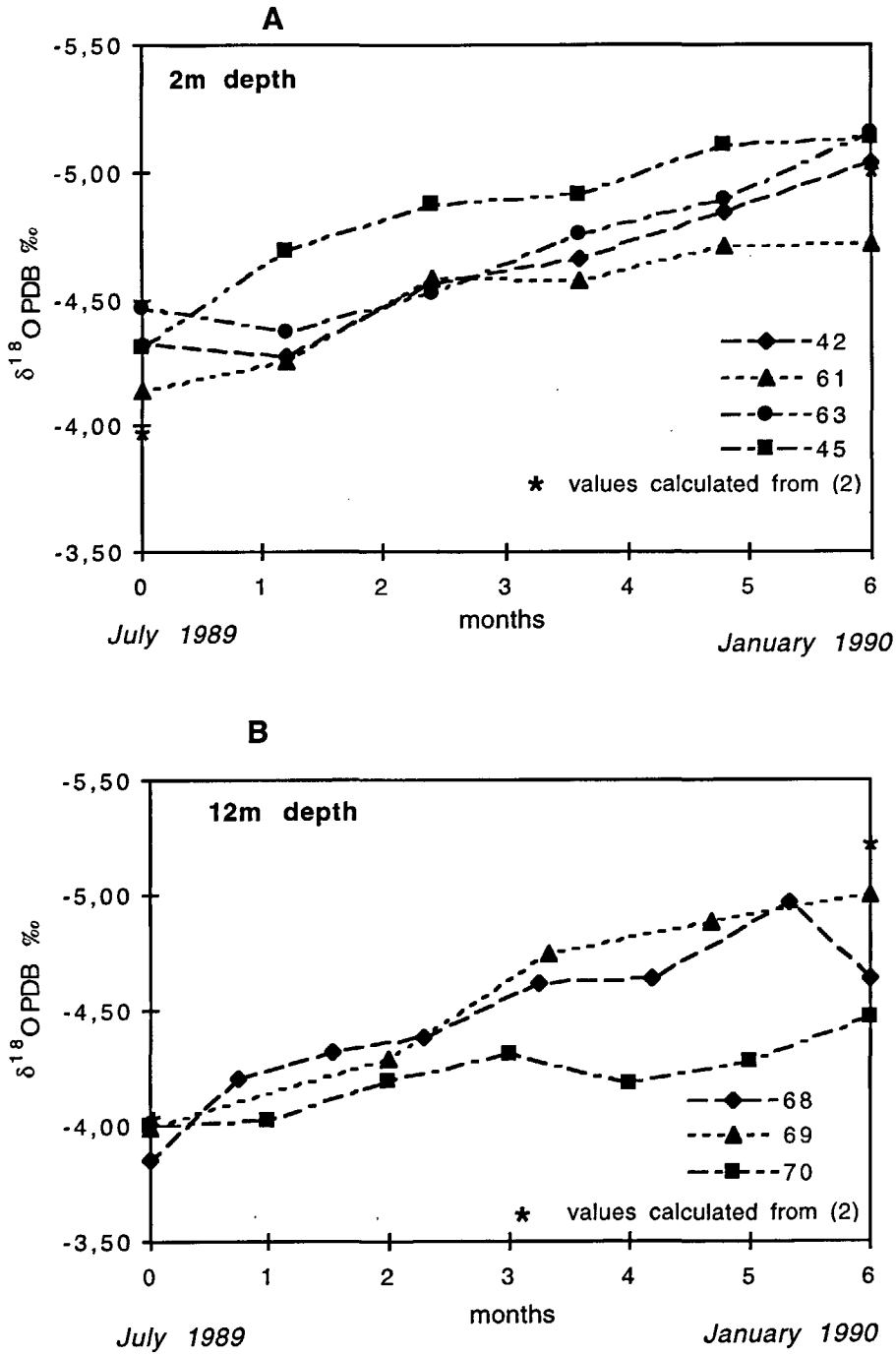

Figure 1

Oxygen isotope profiles from the growth axis of Acropora *branches, for a growth period of six months. The reference points (July 1989, January 1990) correspond to the Alizarin-stained band and to the apex of the branches, respectively. A. Profiles of the four specimens grown at 2 m depth; B. Profiles of the three specimens grown at 12 m depth.*

colonies differ substantially (24 mm and 14 mm/6 months).

– Colonies # 45 and 61, display similar trends and similar growth rates (21 mm and 24 mm /6 months respectively), but show different $\delta^{18}O$ values.

For the samples taken from the backreef slope, at 12 m depth (# 68, 69 and 70) (Fig. 1B), the isotopic compositions vary from branch to branch. In particular, Colony # 70 displays a limited seasonal variation.

Reliability of the oxygen ratio/temperature calibration by Weber and Woodhead (1972)

The quantity of calcium carbonate extracted from *Acropora* branches by Weber and Woodhead (1972) for isotope analysis represented approximately a year's growth and, therefore, the relevant results provide information on the average annual temperature. The 10 °C amplitude of the average temperature values recorded strengthened confidence in the reliability of their calibration.

However, as the isotopic composition of water is neglected in formula (1) given in the introduction, we estimated annual salinity for each site from Levitus' Atlas (1982); this salinity value was converted into isotopic composition by using the relationship between salinity and $\delta^{18}O$ corresponding to the tropical Pacific Ocean, calculated from the GEOSECS Atlas (Östlund, 1987):

$$\delta^{18}O_{water} = -11.20 + 0.33\ S \quad (2).$$

For *Acropora*, the resulting equation is:

$$\delta^{18}O_{aragonite} - \delta^{18}O_{water} = 1.62 - 0.22\ T\ °C \quad (3).$$

For the *Acropora formosa* colonies considered, the isotopic composition value calculated at 2 m depth in summer, using the modified Weber-Woodhead equation, is – 4.96 °/oo, while the mean value measured is – 4.99 °/oo; in winter, the calculated value is – 3.97 °/oo while the average value is – 4.28 °/oo, considering that, at Yonge Reef, the mean $\delta^{18}O_{water}$ is 0.35 °/oo *vs* SMOW from (2). Taking into account the analytical error range, we consider that these values are quite identical for summer, but different for winter. This discrepancy could be attributed to a $\delta^{18}O_{water}$ change but this parameter does not justify the high isotopic variability observed for colonies grown in identical conditions.

CALCIFICATION DEPENDENCE OF OXYGEN ISOTOPE COMPOSITION IN *ACROPORA*: A MODEL

As emphasized by Dodge *et al.* (1992), Barnes and Lough (1993) and Taylor *et al.* (1995), the aragonite deposition mechanism may specifically influence the distributional patterns of isotopic variations within coral skeletons. Since this assumption cannot be directly proven from isotopic analyses, due to the minute quantities of crystal deposits involved, a simple mathematical model is developed below, to account for the role of biomineralization in isotopic composition.

The growth model

Prior to the calculation of isotopic distribution, the main characteristics of carbonate accretion in *Acropora* have to be defined. Gladfelter (1982) reported patterns of calcium carbonate accretion along axial corallites in *Acropora cervicornis*. Two phases of calcification were described: (1) an initial deposition phase (primary calcification), mainly characterized by growth of micritic fusiform crystals; and (2) a subsequent deposition phase (secondary calcification), resulting in a gradual infilling of intercrystal space by aragonite needles. The branch tips are initially slightly mineralized, then thicken regularly; the thickening of corallites is accompanied by an increase in density and a decrease in porosity. However, the relative importance of primary and secondary calcification and the degree and rate of intraskeletal infilling vary from colony to colony. These mechanisms seem to apply to various *Acropora* species (Gladfelter, 1982) with variable secondary calcification. What is the effect of these processes on isotopic ratios ?

The isotopic model

As the analysed powder is the result of a mixture of two types of aragonite (primary and secondary), we may express the measured isotopic composition as:

$$\text{measured } \delta = M_I\ \delta_I + M_{II}\ \delta_{II} \quad (4),$$

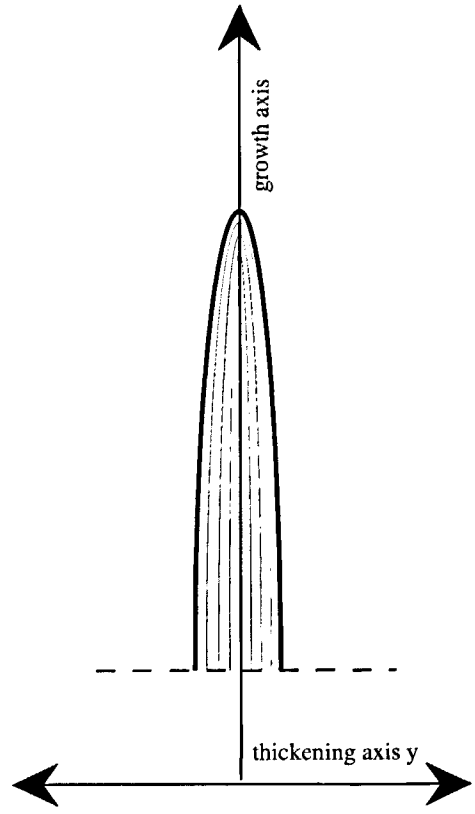

Figure 2

Modelling of growth of Acropora *branches. A given branch extends linearly along z axis and correlatively thickens along y axis. z is the distance of a given pinpoint along growth axis to the initial tip of the branch. At the starting time of growth, z is equal to zero. At the time t, the apex has reached the position z; at the time* t_{end}*, the apex has covered a distance L from the starting point.*

where M_I and M_{II} are the relative amounts of respectively the primary and the secondary aragonite, at any time $M_I + M_{II} = 1$, and at the end of the experiment, for the sample extracted at the tip of the branch, $M_I = 1$. The final content of primary aragonite at the base of the branch, obtained after a growth period and then an infilling of several months, has never been estimated; this value is one of the variables which will be tested in the simulation described here. As shown in Figure 2, the building of a framework of micritic fusiform crystals contributes to the linear extension of the axial corallite, while the second step of aragonite infilling contributes essentially to the growth of lateral corallites; considering that alizarine staining implies coloration of the whole branch, we infer that M_{II} is organic aragonite. Along the growth axis of the acroporid branches, primary aragonite is assumed to be the dominant mineralogical form (Gladfelter, 1984) but its amount decreases from the tip to the base. At a rough estimate (Gladfelter, 1984) we consider that the extension rate is constant throughout the year, and that secondary infilling is higher during months when illumination is at its greatest. In order to keep this model as simple as possible, and as the considered species do not show density bands, the effect of light will be not taken into account here; infilling will be regarded as constant through time. M_I and M_{II} vary as assymptotic laws (Fig. 3).

In the above equation, δ_I is the isotopic composition of primary aragonite formed "instantaneously", and δ_{II} is the isotopic composition of secondary aragonite progressively formed.

We may express the isotopic composition of each aragonite phase according to the respective temperatures of deposition. The precipitation temperature of primary aragonite is related to the extension rate and inferred from local temperature variation. The isotopic composition of secondary aragonite reflects the integration of $\delta^{18}O$ of $CaCO_3$ deposited progressively throughout the period of infilling, corresponding to temperature changes during the same period. Equations are reported in the Appendix. In the study area, the annual temperature variability can be approximated to a sine curve. As an example, we plotted, on Figure 3, simulation of M_I, M_{II}, δ_I and δ_{II} and the resulting isotopic profile along a branch, calculated for a progressive and continuous infilling over a period of six months, and a final amount of 40 % of primary aragonite at the base of a branch.

The duration of infilling is the other variable that we investigate by this model. It depends probably on the connection between the calcicoblastic epithelium and the skeleton; surprisingly, the relevant process is poorly documented. Two scenarios have to be considered, namely total or partial infilling of skeletal pores over the growth period. Unfortunately, little is known concerning the duration of the infilling phase. According to Gladfelter (1982), this phase in *Acropora cervicornis* presumably extends over many years, occurring more actively over the first 2.5 years and subsequently declining. Since no data about the species *Acropora formosa* are available, both scenarios were considered in the model.

Simulated oxygen isotopic profiles calculated from (4), for different amounts of primary and secondary aragonite and different infilling periods, are given in Figure 4, compared to the isotopic profile calculated for an "instantaneous" deposited aragonite with equation (3).

COMPARISON BETWEEN THE MEASURED AND THE CALCULATED ISOTOPIC PROFILES

The calcification process induces marked variations in oxygen isotope composition, thus explaining the isotopic variability observed in the different colonies of the same *Acropora* species. By calculating the oxygen isotope composition of skeletal aragonite, we first intend to account for the isotopic ratios obtained from the reference samples (*i.e.* the stained zone and the apex), which reflect the minimal and maximal temperature conditions occurring in the reef area studied. By comparing measured and calculated isotopic profiles we should also be able to estimate the relative quantity of primary and secondary aragonite in the branches studied. Then, we interpret the six-month isotopic profiles in the context of the model.

Simulation for a six-month growth period

To explain the dispersion of the measured oxygen isotope ratios obtained from July 1989, we suggest that varying amounts of secondary aragonite, deposited over the six month period of coral growth, affect the final isotopic composition of aragonite. As shown in Figure 4A, the greater the abundance of primary aragonite, the greater the enrichment in ^{18}O of the isotopic ratio at the stained zone. The isotopic amplitude calculated for the base of the branch, on the basis of 20 and 80 % deposition of primary aragonite over six months, corresponds to a measured amplitude of around 0.35 ‰.

However, the isotopic value recorded in July 1989 may also depend on the duration of skeletal infilling, assuming this infilling to be constant. For instance, for a 40 % final amount of primary aragonite, variation of the infilling rate affects skeletal $\delta^{18}O$ at most by 0.1 % (Fig. 4B). Compared to the isotopic value of a branch subjected to continuous infilling during six months, $\delta^{18}O$ of a branch completely infilled over a four-month period is enriched. The isotopic effect of infilling duration is reduced in comparison with that of the respective amounts of primary and secondary aragonite.

Certain parameters, such as coral growth rate or porosity, may contribute indirectly to variations in oxygen isotope composition. The ability of coral skeletons to be infilled depends directly on initial porosity: the higher the initial porosity, the greater the potential for the deposition of secondary aragonite. The data obtained from the specimens growing at the depth of 2 m exhibit a correlation between the isotopic composition of the relevant stained zone and linear extension rate. Even if the oxygen isotopic ratios are not directly controlled by growth rate, a link may exist between the degree of skeletal infilling (or porosity) and elongation rate. For a given temperature range and for the same amount of aragonite deposited, it is assumed that the

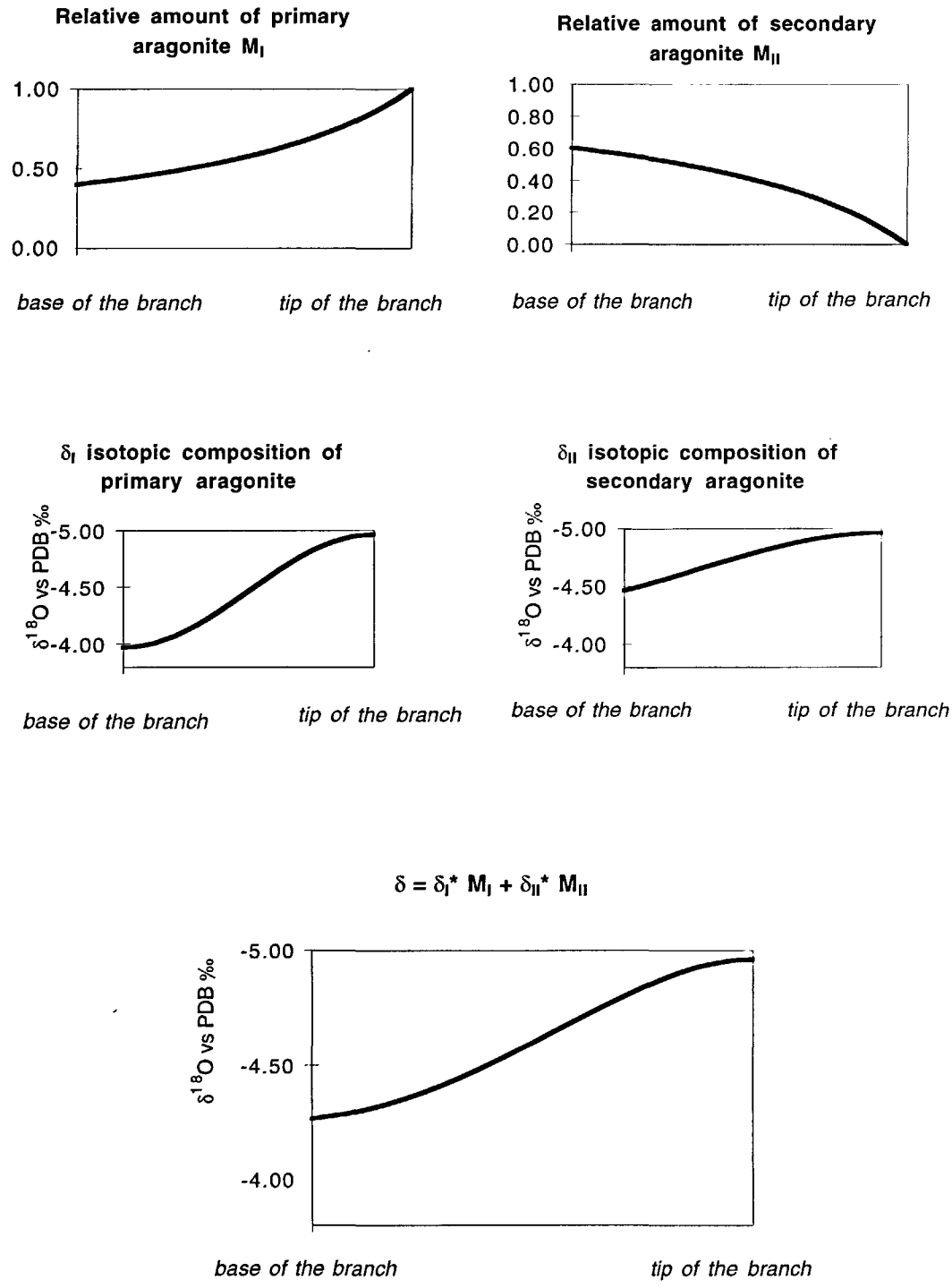

Figure 3

Simulation of M_I, M_{II}, δ_I and δ_{II} and the resulting isotopic profile along a branch, calculated for a progressive and continuous infilling over six months, and a final amount of 40 % of primary aragonite at the base of a branch.

faster the growth rate, the less important the secondary infilling and, consequently, the more abundant the primary aragonite accretion and the higher the residual porosity (Fig. 4A). Therefore, rapid elongation should be associated with ^{18}O-enriched ratios, which is verified in Table 1, specially for samples taken at the apex of the branches.

Simulation of the isotopic profile for one-year growth

Figures 5A and 5B display the effects of relative amount of primary and secondary aragonite and of infilling duration on the isotopic composition of acroporid skeletons after one year of growth. The plotted isotopic curves are calculated from sine temperature variations over one year, with a continuous infilling of intraskeletal pores on Figure 5A and with a varying infilling duration on Figure 5B. The more abundant the primary aragonite, the greater the annual isotopic amplitude and the less important the difference between isotopic composition for summer 1989 and summer 1990. As a general rule, the faster the infilling, the more subdued the isotopic amplitude. As we noticed previously, infilling duration does not affect

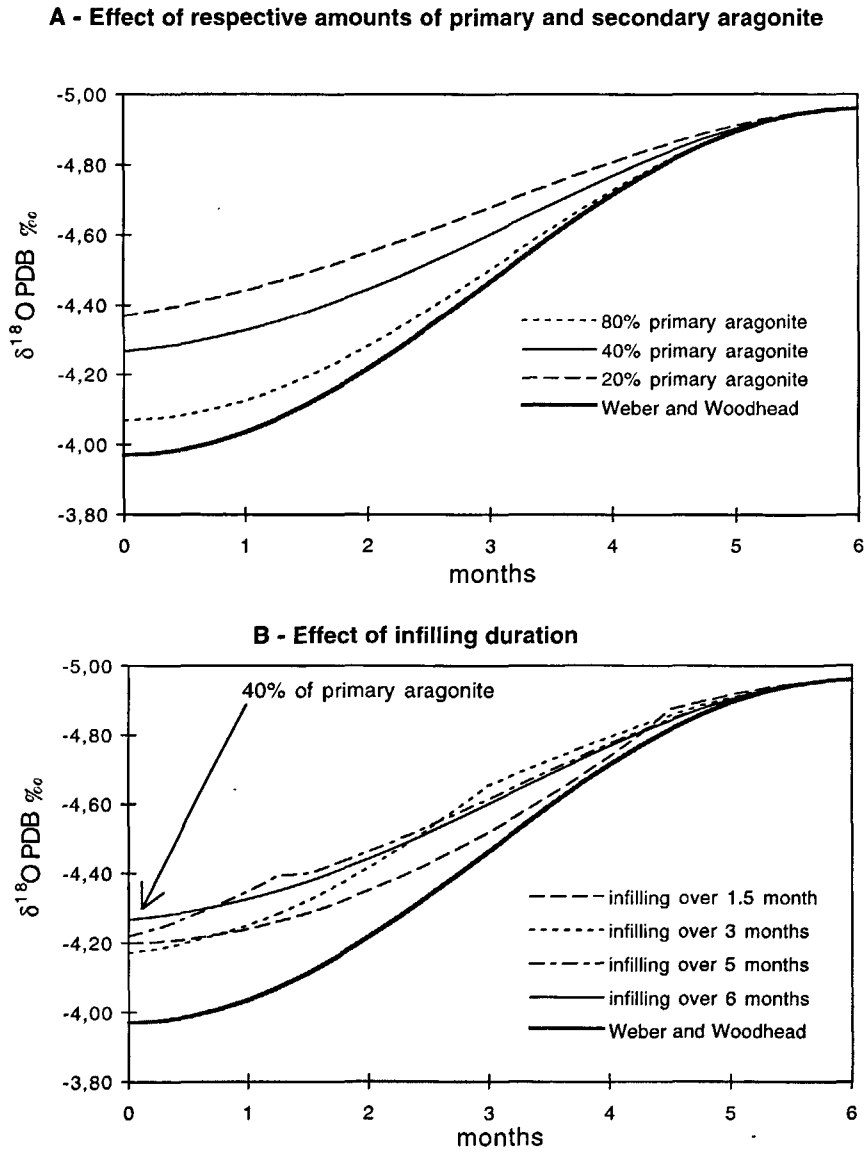

Figure 4

Simulated oxygen isotopic profiles of Acropora *branches for a six-month growth period, compared to that obtained from the modified Weber and Woodhead equation (1972). A. Simulation as a function of the relative amount of primary aragonite (20, 40, 80 % of the total skeletal volume) deposited during skeletogenesis. B. Simulation as a function of the infilling time of residual pores by secondary aragonite.*

significantly the isotopic composition. However, infilling duration enhances trends in the isotopic profiles; thus, the maximum $\delta^{18}O$ values, which are only slightly affected by the respective amounts of primary and secondary aragonite, are shifted.

Comparison of simulated and measured one-year isotopic profiles

Since the acroporid branches studied developed over a period of approximately one year in the test areas, Figures 6A and 6B present a comparison of simulated isotopic profiles with those obtained from analysis of the acroporid branches over this period. As we have no chronological reference before the staining mark, we estimated that the most negative isotopic value recorded at the base of a branch corresponds to summer 1989. Consequently, an accurate comparison will be possible for the final six months only.

Figure 6 shows data from colonies grown in the reef flat environment (2 m deep) compared with the simulated profiles obtained for final primary aragonite amounts of 20 and 40 %.

– Colony # 45 is systematically ^{18}O-impoverished in comparison with the other samples. Such an isotopic discrepancy cannot be attributed to difference in growth rate.

– Colonies # 63 and 42 display similar isotopic profiles, whereas their elongation rates are different. Infilling of the relevant branches by secondary aragonite is believed to have been important, but residual porosity is probably higher in Colony # 42 than in Colony # 63. A slight isotopic

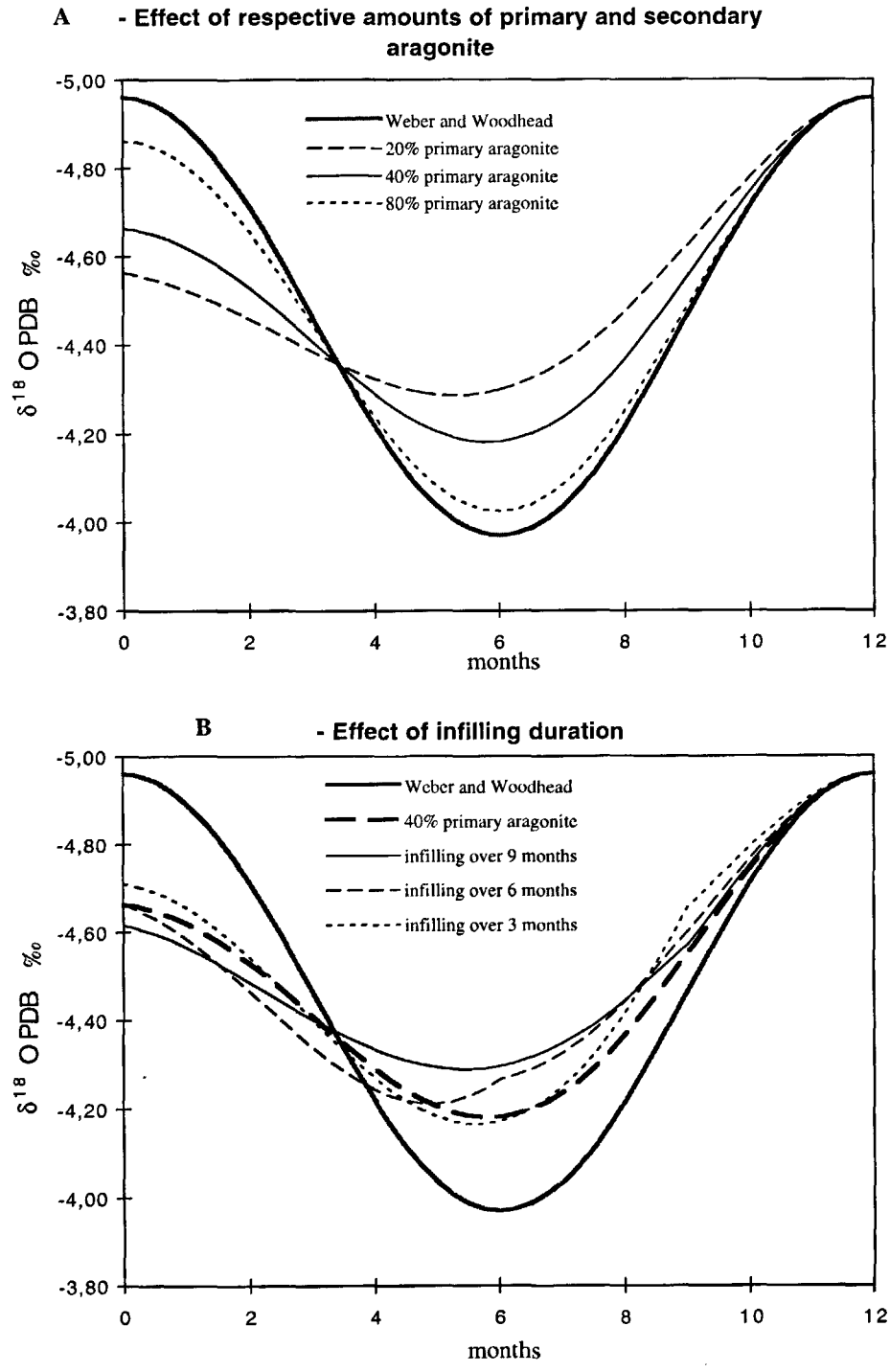

Figure 5

Simulated oxygen isotopic profiles of Acropora *branches for a one-year growth period, compared to that obtained from the modified Weber and Woodhead equation (1972). A. Simulation as a function of the relative amount of primary aragonite (20, 40, 80 % of the total skeletal volume) deposited during skeletogenesis. B. Simulation as a function of the infilling time of residual pores by secondary aragonite.*

decrease is observed at the stained zone of both samples. Assuming that analytical resolution was good for these branches, the ^{18}O depletion may be a specific response to a staining-induced stress. Colony # 63 shows a good consistency with the simulated isotopic profile calculated for a primary aragonite amount of 20 % at the base of the branch (Fig. 6A).

Similarly, the consistency between the isotopic profile from Colony # 42 and the relevant simulated curve is good for the final six months, despite the discrepancy recorded for the earlier four months; this could be due to a few months delay as a consequence of the assumption of a constant extension rate.

– In Figure 6B, Colony # 61 exhibits the same profile as the simulated curve calculated from 40 % of primary aragonite at the base of the branch, except for the two final months. High isotopic values measured on the apex of this specimen could be attributed to the bent shape

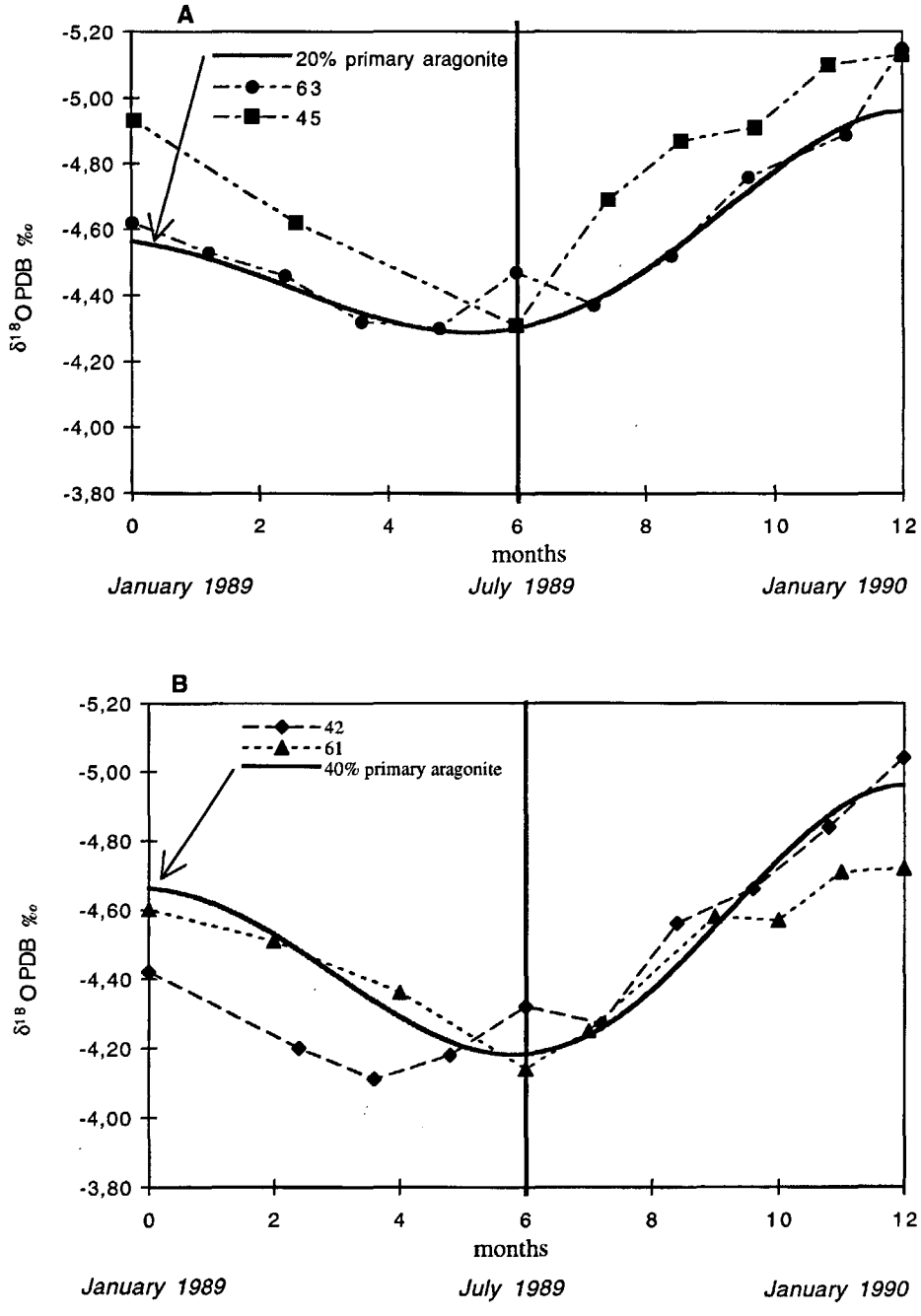

Figure 6

Comparison between the simulated oxygen isotopic profiles constrained by the amount of primary aragonite deposited and the measured profiles in Acropora *branches grown at 2 m depth, for a one-year growth period. A. The amount of primary aragonite deposited at the base of the branch is 20 %. B. The amount of primary aragonite deposited at the base of the branch is 40 %.*

of its growth axis, which rendered a regular saw cut difficult; in these subsamples, the amounts of primary and secondary aragonite may be different from the amounts deposited along the long axis, and crystal nucleation has been probably delayed by one to two months compared to that of the extension axis.

We may note that, after comparing simulated and measured isotopic profiles and assessing relative amounts of primary and secondary aragonite, primary aragonite amount does not always prevail; in the final analysis, secondary aragonite may be found in greater quantity than primary aragonite.

Figure 7 gives the results for oxygen isotopic profiles measured from colonies grown in the backreef environment (12 m deep).

– The isotopic ratios measured from Colony # 70 vary very slightly. Direct examination of the skeleton indicates that Colony # 70 is highly porous.

– The profiles of Colonies # 68 and 69 show the same evolutionary trend; the isotopic value recorded on the apex of Colony # 68 emphasizes the difficulty of sampling this part of a coral branch. As we remarked for Colony # 42, the response given by Colony # 69 could be delayed

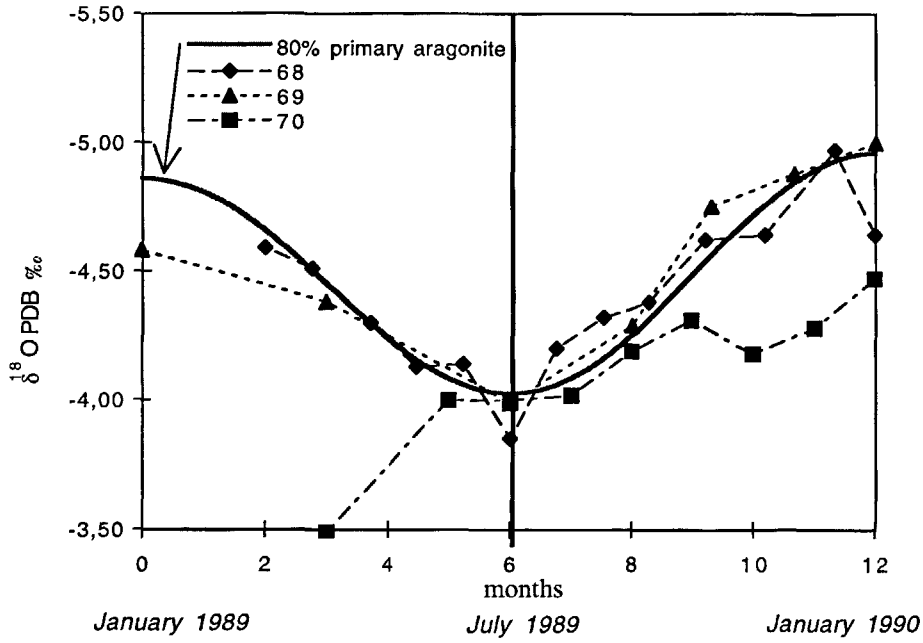

Figure 7

Comparison between the simulated oxygen isotopic profiles constrained by an amount of 80 % of primary aragonite deposited at the base of the branch and the measured profiles in Acropora *branches grown at 12 m depth, for a one-year growth period.*

by two months. Isotopic profiles from Colonies # 68 and 69 are in a good agreement with the simulated curve calculated for an 80 % rate of primary aragonite deposited at the base of the branches after a year's growth. This high primary aragonite content estimated for the deeper branches is sufficient to account for the isotopic difference observed between the two depths. We could assume that infilling by secondary aragonite is less active for deep sites, where light is reduced, but more data are necessary to confirm this assumption.

Overall, except for Colonies # 70 and 45, the mathematical model presented offers a meaningful simulation of the oxygen isotopic behaviour during *Acropora* skeletogenesis, even in the deeper environment.

PALEOENVIRONMENTAL SIGNIFICANCE OF THE OXYGEN ISOTOPE COMPOSITION IN *ACROPORA* SKELETONS

The present study raises the question of using isotopic composition from *Acropora* material in paleoenvironmental reconstruction. Since this coral genus is one of the main reef builders, in both the Caribbean and the Indo-Pacific province (see Davies and Montaggioni, 1985), Holocene reef sequences contain numerous beds of *in situ* or detrital acroporid branches. The understanding of the effects of skeletogenesis on the oxygen isotopic composition of coral aragonite is a prerequisite to judicious sampling, to the assessment of paleotemperatures and, more generally, to meaningful interpretation of the isotopic data. As in the case of modern colonies, aragonite sampling along the growth axis of fossil specimens provides a record of isotopic patterns through time. However, calcification effects on the oxygen isotopes have to be modulated according to various species of *Acropora* genus (Gladfelter, 1982). Although the curve provides information about annual paleotemperature variability, it is preferable to calculate the median value from the measurements obtained along the branch axis rather than the mean value. Then, the value obtained is close to the annual mean value, which is always slightly overestimated. A compromise has to be found between optimal information and minimal analyses.

CONCLUSIONS

Measurements of the oxygen isotope composition of the reef-building coral *Acropora formosa* permit elucidation of some fundamental aspects of the oxygen isotopic behaviour of branching acroporids; a better understanding would require further research on the consequences of skeletogenesis processes on isotopic ratios.

– The oxygen isotopic composition of aragonite sampled all along the growth axis of a branch, results from $\delta^{18}O$ of primary aragonite at the time of construction of the apex, combined with $\delta^{18}O$ of secondary aragonite progressively precipitated in the residual space. A mathematical model simulating the mechanism of deposition of $CaCO_3$ accounts for the smoothed isotopic profiles gained by subsampling at regular intervals along the growth axis.

– Isotopic variations along a given profile are controlled essentially by the relative contents of primary and secondary aragonite; the duration of skeletal infilling plays a minor role.

Isotopic measurements obtained after several months of growth show that at shallow depth, infilling by secondary aragonite is very active (secondary aragonite may exceed

primary aragonite amounts), whereas infilling remains reduced at greater depths.

The reliability of the environmental record is conditional upon the calcification patterns of every coral form. In order to extract the most significant information in terms of paleoenvironmental reconstruction, we have to improve our understanding of biomineralization processes and their effects on the isotopic composition of carbonates.

APPENDIX

Isotopic composition calculation

The annual temperature T(t) varies as a sine curve:

$T(t) = T_{median} + a/2 * \sin(\omega_0 t + \Pi/2)$

t being the time

ω_0 corresponding to initial conditions

T_{median} is the median temperature

a is the total temperature amplitude

$\delta_I(t)$ is the isotopic composition of primary aragonite formed at t; from equation (3):

$\delta I(t) = A + B * T(t)$

with

$A = 1.62 - \delta^{18}O_{water}$

$B = -0.22$

$\delta_I(t) = A + B * [T_{median} + a/2 * \sin(\omega_0 t + \Pi/2)]$

δ_{II} is the isotopic composition of secondary aragonite progressively formed.

$$\delta_{II}(t) = 1/t * \int [A + B * [T_{median} + a/2 * \sin(\omega_0 t + \Pi/2)]]\, dt$$

$$\delta_{II}(t) = [A + B * T_{median} + aB/2\ t * \cos(\omega_0 t + \Pi/2)]_t^0$$

– if the infilling is complete for $t_{max} > t$

$$\delta_{II}(t) = [A + B * T_{median} + aB/2\ t * \cos(\omega_0 t + \Pi/2)]_t^0$$

– if the infilling is complete for $t_{max} < t$

$$\delta_{II}(t) = [A + B * T_{median} + aB/2\ t * \cos(\omega_0 t + \Pi/2)]_t^{t-t_{max}}$$

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