The dual-fractionation of the oxygen isotopes from coral skeleton

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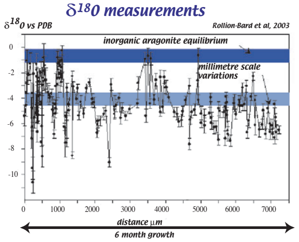
It is commonly accepted that the oxygen isotopic composition of aragonite ($\delta^{18}O$), the most often used proxy for temperature in corals, is governed by the isotopic thermometer equation established for carbonaceous organisms like foraminifera:

$\delta^{18}O_{arag} - \delta^{18}O_{sw} = a$ SST (°C) + b (McConnaughey, 1989).

Empirical relationships obtained by linear regression of seasonal $\delta^{18}O$ values against instrumental SST data, revealed that each coral colony has its own $\delta^{18}O$/SST relationship (Leder et al., 1996; Wellington et al., 1996). These equations are strongly influenced by biological activity, which is not compatible with a reliable proxy. Moreover, the relationships obtained from a few year measurements, fail in predicting temperature reasonably well on a long time scale (Crowley et al., 2001).

SIMS measurement

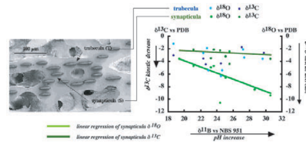
$\delta^{18}O$ measurements



Boron, carbon and oxygen isotopic compositions were determined at the micrometre scale by high-resolution ion microprobe in a sample of modern coral (massive hermatypic coral, Porites lutea) collected in New Caledonia (Rollion-Bard et al, 2003)
In order to explain low $\delta^{18}O$, we suppose that $CaCO_3$ precipitation occurs faster than O isotopic equilibration.

Low $\delta^{18}O$ values derive from kinetic fractionation

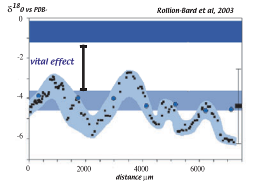
$\delta^{18}O$ and $\delta^{13}C$ versus $\delta^{11}B$ (a pH tracer) with respect to microstructure



the pH influence on carbon species cannot explain the low $\delta^{18}O$ values

In synapticula, $\delta^{18}O$ and $\delta^{13}C$ kinetic fractionation is pH mediated

Smoothed $\delta^{18}O$



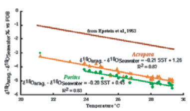
$\delta^{18}O$ values measured by ion microprobe along the growth axis of the coral with an artificially degraded spatial resolution obtained by smoothing the data using asliding mean over 400µm.

Intra-annual isotopic variations are modulated by monthly growth cycles and cannot be expressed by a linear equation

The $\delta^{18}O$ disequilibrium is caused by kinetic fractionation

When biologic variability is statistically removed,

Mean annual $\delta^{18}O$



- Mean annual $\delta^{18}O$ are corresponding to 27 sites (Weber and Woodhead, 1972), temperature variability being provided by the spatial distribution.
- Mean annual $\delta^{18}O$ is calculated from about 20 Porites colonies and 40 Acropora colonies, reducing the isotopic variability due to the biological activity.
- By taking into account annual $\delta^{18}O_{sw}$ values, Juillet-Leclerc and Schmidt (2001) improved the Weber and Woodhead calibration.

annual $\delta^{18}O$ is governed by a quasi-equilibrium equation

Annual mean $\delta^{18}O$ results of the average of highly variable values
Annual $\delta^{18}O$ isotopic fractionation is due to a quasi-equilibrium + a kinetic process
Annual $\delta^{18}O$ and $\delta^{13}C$ are both affected by kinetic fractionation
The $\delta^{18}O$ and $\delta^{13}C$ kinetic fractionations are biologically mediated
The $\delta^{18}O$ and $\delta^{13}C$ kinetic fractionations are modulated by external factors through photosynthesis

Culture

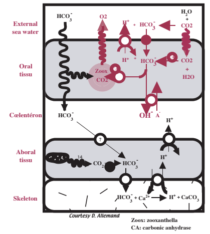
The sources and mechanisms of inorganic carbon transport for scleractinian coral calcification and photosynthesis were studied using a double labelling technique with $H^{14}CO_3$ and ^{45}Ca (Furla et al, 2000).

Summary of the main characteristics of Ca^{2+} and dissolved inorganic carbon metabolism in Stylophora pistillata microcolonies in the dark or in light

	Dark	Light
Rate of respiration (nmol h-1mg-1protein)	194	>194
Rate of photosynthesis (nmol h-1 1 mg-1 protein)		- 179
Rate of calcification (14Ca) (nmol h-1 mg-1 protein)	12.31	49.25
Rate of calcification (14C) (nmol h-1 mg-1 protein)	3.77	17.14
14C/ 45Ca in the skeleton (%)	26	37
Fraction of metabolic CO2 used for calcification (%)	4.4	17
Water volume of the coelenteron (mlmg-1 protein)	10.8	8.6
Coelenteric pH*	**7.5**	**8.5**
Total coelenteric DIC (mmol 1-1)	2.29	1.29
[HCO3-] in the coelenteron (mmol 1-1) ‡	2.17	1.02
[CO2] in the coelenteron (mmol 1-1)‡	66	3
Calcite oversaturation in the coelenteron (%)‡	143	672
Aragonite oversaturation in the coelenteron (%)‡	**79**	**372**
[HCO3-] in tissues (mmol 1-1)	3.7	147
[DIC]intracellular/[DIC]extracellular	1.56	61.30
Passive transepithelial oral DIC flux (nmol h-1 mg-1 protein)	132	62

*Values obtained by Kühl et al. (1995) and Furla et al. (1998b).
‡Calculated using the CO2 program of M. Frankignoulle (University of Liège, Unité d'Océanographie Chimique) by assuming values of coelenteric pH similar to those measured by Kühl et al. (1995) and Furla et al. (1998b).
The light level was 250 mmol photonsm-2 s-1.
DIC, dissolved inorganic carbon.

Active DIC uptake to support symbiont photosynthesis

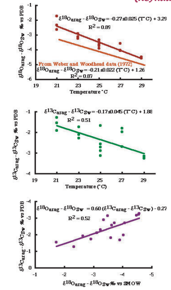


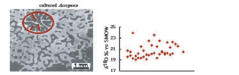
this mechanism could explain the coelenteric pH

Coelenteric pH variations are likely related to photosynthetic activity

Temperature effect on $\delta^{18}O$ and $\delta^{13}C$

Acropora has been cultured under temperature controlled conditions (Reynaud-Vaganay et al., 1999)





cultured Acropora grown with constant conditions also shows high isotopic variability

- $\delta^{18}O$ and $\delta^{13}C$ are temperature dependent
- $\delta^{18}O$ and $\delta^{13}C$ are likely kinetically fractioned

- we know from Weber and Woodhead data (1972) that annual $\delta^{18}O$ is governed by the quasi-equilibrium law
- the slope obtained by cultures is 0.27 higher than 0.20

- temperature affects $\delta^{18}O$ and $\delta^{13}C$
- $\delta^{18}O$ and $\delta^{13}C$ data are scattered

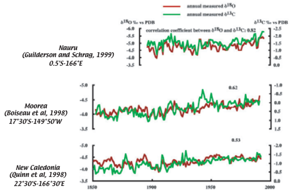
$\delta^{18}O$ and $\delta^{13}C$ are kinetically fractioned through biologic activity

Possible mechanism: temperature enhances photosynthesis
coelenteric pH increases
$\delta^{18}O$ and $\delta^{13}C$ decreased

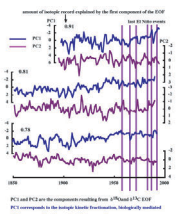
Assessment of annual $\delta^{18}O$ signal related to the quasi-equilibrium fractionation

Statistically, the best tool to identify the common signal between two time series $\delta^{18}O$ and $\delta^{13}C$ is the Principal Component (PC) or empirical orthogonal function (EOF) analysis which provides the time series which maximized the covariance. The first component corresponds to the kinetic fractionation and explain the majority of the measured $\delta^{18}O$ value. The second component corresponds to the quasi-equilibrium relationship.

measured $\delta^{18}O$ and $\delta^{13}C$

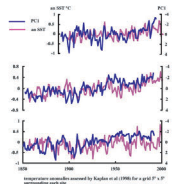


PC1 and PC2



the measured $\delta^{18}O$ signal is mainly due to the kinetic fractionation

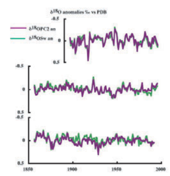
PC1 compared with SST anomalies



Temperature anomalies assessed by Kaplan et al (1998) for a grid 5° x 5° surrounding each site

PC1 is influenced by temperature and other factors

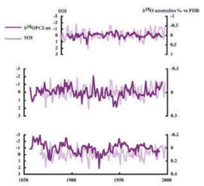
$\delta^{18}O$PC2 and calculated $\delta^{18}O$SW



the first step of EOF being the normalization:
$\delta^{18}O$PC2 = PC2 * std dev ($\delta^{18}O$)
$\delta^{18}O$Sea water is calculated using the quasi-equilibrium equation with SST anomaly assessment from Kaplan et al (1998)

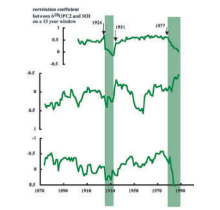
PC2 variations are governed by: $\delta^{18}O_{arag} + \delta^{18}O_{Sw} = -0.20$ SST (°C) + 0.45
$\delta^{18}O$PC2 variability is essentially due to water $\delta^{18}O$ changes

$\delta^{18}O$PC2 and SOI



$\delta^{18}O$PC2 negative peaks are associated with abundant precipitation
The correlation between $\delta^{18}O$PC2 and SOI essentially indicates precipitation during El Niño

a shift of oceanic regime?



Most often, at Nauru, abundant precipitation are associated with the warm phase of El Niño, except from 1977 to1990 and from 1924 to 1931.
These anomalies are also recorded by Moorea and New Caledonia corals.
These anomalies are likely due to the convergence zones migration or oceanic advection.
The 1977 climatic shift is well documented.
What is the origin of the 1924 shift?

The $\delta^{18}O$ signal corresponding to the quasi-equilibrium equation is masked by an other signal PC1 which cannot be considered as a quantitative proxy.
By comparing the "quasi-equilibrium $\delta^{18}O$" signal with SOI we underline the well documented 1977 climatic shift and we point out an anomaly between 1924 and 1931, affecting the south western Pacific Ocean.

All the $\delta^{18}O$ and $\delta^{13}C$ coral records need to be revisited taking into account the dual fractionation

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