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A calibration of the oxygen isotope paleothermometer of coral aragonite from *Porites*

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Abstract. The oxygen isotopic composition ($\delta^{18}O_{aragonite}$) of coral aragonite is dependent upon two parameters, temperature and water oxygen isotopic composition. This tracer allows temperature reconstruction in tropical zones. Different published $\delta^{18}O$:temperature relationships show a slope derived from the regression $\delta^{18}O$ against T(°C) which varies between -0.16 and -0.23 for *Porites* genus. This implies greater uncertainty for paleoclimatic reconstruction. The calibrations were generated differently. They were obtained from several colonies, collected in different locations or the formula was derived from the same coral head following seasonal variations of temperature. The relationships took into account of $\delta^{18}O_{Sw}$ fluctuation or $\delta^{18}O_{Sw}$ were estimated from salinity or were not considered. We show by using isotopic data from Weber and Woodhead (1972) and assessing the $\delta^{18}O_{Sw}$ value by two different methods that a thermodynamically significant formula is generated.

Introduction

The coral isotopic composition ($\delta^{18}O_{aragonite}$) is a function of both temperature and water isotopic composition ($\delta^{18}O_{Sw}$). The strengh of the relationship between $\delta^{18}O_{aragonite}$ and SST is the basis of recent paleoclimatic reconstructions in tropical zones (Dunbar et al, 1994; Charles et al, 1997; Quinn et al, 1998). As a proxy indicator, coral $\delta^{18}O_{aragonite}$ thermometer is the result of the addition of a thermodynamic law dependent upon temperature and water isotopic composition($\delta^{18}O_{Sw}$, noise, essentially due to biological process and error implied by the multiple uncertainties of the measurements.

A calibration established from a large number of colonies collected from different sites which cover a large temperature range and also take into account the water isotopic value, could be regarded as the best "transfer" function, statistically reducing the metabolic influence. Weber and Woodhead (1972) published such a relationship for several genera, by comparing annual $\delta^{18}O_{aragonite}$ against annual temperature. Unfortunately in this study $\delta^{18}O_{Sw}$ was not considered. Therefore the formula only demonstrated the temperature dependence of $\delta^{18}O_{aragonite}$ and the "specific" isotopic fractionation of coral aragonite. By introducing the annual $\delta^{18}O_{Sw}$ value for each site, the new relationship could keep its statistical and thermodynamical significance. Since *Porites* coral is chosen for paleoclimatological reconstructions this paper will only consider this genus.

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Few $\delta^{18}O_{Sw}$ measurements have been published for the tropical belt. By using two different methods we assess $\delta^{18}O_{Sw}$ in the locations used by Weber and Woodhead (1972): the two series are very similar. In order to establish a relationship linking $\delta^{18}O_{Aragonite}$, $\delta^{18}O_{Sw}$ and temperature, we propose to introduce the $\delta^{18}O_{Sw}$ values in Weber and Woodhead data.

Coral $^{18}O/^{16}O$: an isotopic paleothermometer

Until now several formula T°C = f($\delta^{18}O_{aragonite}$, $\delta^{18}O_{Sw}$) have been published. Some relationships were based on different colonies developed in known environmental conditions. These colonies were collected from the field or from culture (Weil et al, 1981; Raynaud-Vaganay et al, 1998). We observe a great variability of oxygen isotopic values for one temperature even for a same genus; Raynaud-Vaganay et al (1999) who cultured colonies from the same mother colony showed a variability of 0.5‰ for *Acropora*. The great number of samples used by Weber and Woodhead for *Porites* (1972) avoids uncertainty but the relationship T °C = 11.21 - 3.31 ($\delta^{18}O_{aragonite}$) (1) is weakened because the $\delta^{18}O_{Sw}$ variability is not taken into account. It is estimated to be 0.80 to 1‰ vs SMOW over this latitudinal range.

The relationships obtained from only one coral head reflect the seasonal fluctuation of aragonite $\delta^{18}O$ including metabolic properties of each colony and the local environmental parameters such as seasonal $\delta^{18}O_{Sw}$ fluctuations. The sampling resolution (Leder et al, 1996) or a wrong time assignment to a sample may cause great variability. $\delta^{18}O_{Sw}$ is derived from salinity values (Carriquiry, 1994), or assimilated to an annual average (McConnaughey, 1989a) or not considered (Quinn et al, 1998). Only two studies take into account both the temperature, and $\delta^{18}O_{Sw}$ measurements, by using staining levels (Wellington et al, 1996; Leder et al, 1996). A strong correlation coefficient obtained by comparing $\delta^{18}O_{aragonite}$ and temperature does not reflect the isotopic dependence upon temperature. When temperature and $\delta^{18}O_{Sw}$ seasonal variations are strictly in or out of phase, the relationship between T (°C) and $\delta^{18}O_{aragonite}$ will be strong but the isotopic effect will include two factors. The absolute value of $\delta^{18}O$ measured from heads of the same genus collected in the same area show a possible offset of 0.2 to 0.5‰ (Linlsey et al, 1999). We notice that this offset is similar with the variability mentioned for cultures.

The water isotopic composition

Few water isotopic compositions from tropical belt have been published. The data given by Fairbanks et al (1996) are restricted to equatorial areas which are influenced by precipitations, while

Table 1. It seems that the model does not generate high salinity and waters isotopic values. The discrepancy observed in Tahiti or Lizard Reef could be due to island vicinity.

Site	Latitude	Longitude	Temp. °C (1)	Salinité (3)	$\delta^{18}O_{Sw}$ GEOSECS (4)	$\delta^{18}O_{Sw}$ OPA (5)	$\delta^{18}O_{Ar}$ (2)	$\delta^{18}O_{Sw}$-$\delta^{18}O_{Ar}$ GEOSECS	$\delta^{18}O_{Sw}$-$\delta^{18}O_{Ar}$ OPA
Guadalcanal	-10	160	29.3	34.70	0.25	0.26	-5.57	-5.55	-5.56
Rabaul	-4	152	29.3	34.40	0.14	0.27	-5.46	-5.33	-5.46
Koror, Palau	7	134	29.2	34.26	0.09	0.11	-5.43	-5.25	-5.27
Majuro	7	171	29.1	34.27	0.09	0.19	-5.35	-5.17	-5.27
Buka	-5	155	28.6	34.74	0.26	0.27	-5.28	-5.27	-5.28
Guam	13	145	28.5	34.59	0.21	0.14	-5.16	-5.10	-5.03
Port Moresby	-9	147	28.4	34.72	0.26	0.69	-5.20	-5.19	-5.62
Saipan	15	146	28.0	34.70	0.25	0.18	-5.24	-5.22	-5.15
AmericanSamoa	-14	-171	28.1	35.26	0.46	0.28	-5.28	-5.47	-5.29
Thursday Island	-10	142	28.0	34.84	0.30	0.17	-4.90	-4.93	-4.80
Torres Strait	1	173	28.1	34.92	0.33	0.32	-5.20	-5.26	-5.25
Viti Levu	-18	178	26.8	34.90	0.32	0.37	-4.75	-4.80	-4.85
Yonge Reef	-14	146	26.5	35.00	0.36	0.32	-4.64	-4.73	-4.69
Tahiti	-18	-149	26.7	36.02	0.74	0.43	-4.68	-5.15	-4.84
Lizard Reef	-16	-152	26.3	35.96	0.72	0.42	-4.57	-5.02	-4.51
Noumea	-22	167	26.0	35.49	0.54	0.54	-4.57	-4.84	-5.05
Mauritius	-20	58	25.9	35.06	0.38	0.29	-4.49	-4.60	-4.70
Key West	24	-82	25.5	36.06	0.75	1.24	-4.08	-4.56	-4.80
Tonga	-21	-175	25.0	35.49	0.54	0.40	-4.57	-4.84	-4.85
Hook Island	-20	149	24.9	35.36	0.49	0.91	-4.16	-4.38	-4.80
Gannet Reef	-22	153	24.6	35.37	0.50	0.38	-4.19	-4.42	-4.30
Lady Musgrave	-24	152	24.2	35.40	0.51	0.50	-4.04	-4.28	-4.27
Heron Island	-23	152	23.9	35.40	0.51	0.50	-3.97	-4.21	-4.20
Flinders	-27	154	23.0	35.47	0.53	0.51	-3.41	-3.67	-3.65
Coff's Harbour	-30	153	21.2	35.52	0.55	0.52	-2.74	-3.02	-2.99

(1), (2) are given in Weber and Woodhead (1972)
(3) is estimated from Levitus (1982)
(4) calculated by using δ=f(S) from GEOSECS (1987)
(5) calculated by using δ from OPA model

Weber and Woodhead coral locations (1972) cover latitudes between 15°N to 30°S where evaporation may also be important. The major knowledge of $\delta^{18}O_{Sw}$ is due to GEOSECS expeditions. Since salinity and isotopic composition changes are governed by the same processes, a relationship linking salinity and $\delta^{18}O_{Sw}$ may be calculated from GEOSECS measurements for latitudes between 40°N and 40°S (Östlund, 1987). From this we obtain $\delta^{18}O_{Sw}$ = -12.59 + 0.37 S (2). We estimated annual salinity for each site refered by Weber and Woodhead (1972) from the Levitus Atlas (1982) and we converted them into isotopic composition by using (2).

Schmidt (1998) demonstrated that over a tropical zone, the salinity and $\delta^{18}O_{Sw}$ do not necessarily vary in phase. Thus the salinity and $\delta^{18}O_{Sw}$ relationship is assessed in another way. G Delaygue et al (2000) proposed to simulate the sea surface water isotopic composition by using the OPA oceanic GCM in which the atmospheric fluxes are prescribed by the isotopic version of the NASA/GISS atmospheric model; thus the $\delta^{18}O_{Sw}$ is estimated in each grid corresponding to islands considered by Weber and Woodhead (Table 1).

By comparing these data, obtained independently, we observe the values deduced by OPA are comparable with GEOSECS data except for some sites (Figure 1). The $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{Sw}$ distribution versus temperature is very similar whichever the $\delta^{18}O_{Sw}$ series.

The modified calibration

Usually temperature is plotted as a function of isotopic composition, $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ being the independent variable and temperature the dependent one following the predictive sense. Despite the good agreement of $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ obtained from the two approaches, the error concerning annual temperature is lower. Thus we consider temperature as the independent variable.

By introducing the calculated $\delta^{18}O_{Sw}$ values in the coral data (taking into account PDB ‰ ≈ SMOW ‰ - 0.27 ‰), we obtain: $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ = 1.85 - 0.25 T °C (3) with a correlation coefficient r^2 of 0.87 and an error on the slope of 0.02 (1σ) for a confidence level of 95%.

The residual values are higher for the two lower temperatures. These isotopic values result from compilation of measurements made on *Porites* located in the southern part of GBR. By studying great number of coral heads in the Coral Sea from 10 to 21°S, Lough and Barnes (2000) observed that temperature and calcification rate decrease with increasing latitude. Following the McConnaughey assumption (1989b), low calcification rate could drive a kinetic effect implying a higher $\delta^{18}O_{aragonite}$ and justifying the discrepancy.

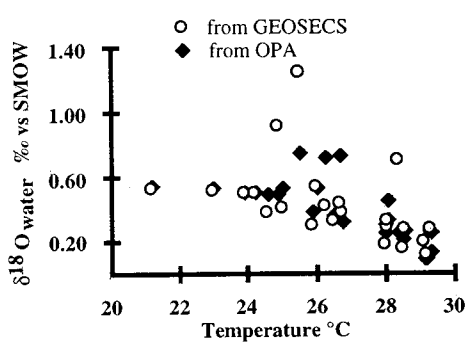

Figure 1. The water isotopic composition assessed by the two approaches plotted against temperature.

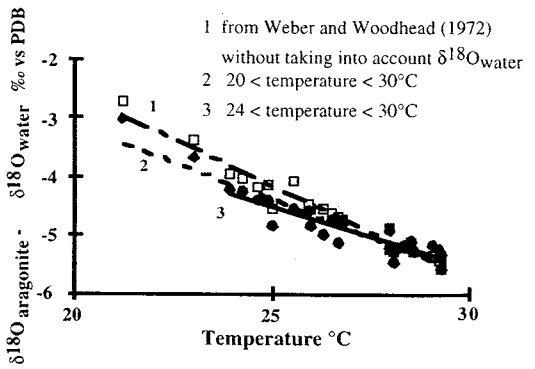

Figure 2. The linear relationships obtained by considering $\delta^{18}O_{aragonite}$ from Weber and Woodhead (1972) ($\delta^{18}O_{aragonite}$ = 3.61 - 0.31T°C), $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{water}$ for temperatures between 20 and 30°C ($\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ = 1.85 - 0.25 T °C) and between 24 and 30°C ($\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ = 0.45 - 0.20 T °C).

By neglecting these two sites the relationship on a temperature range comprised between 24 and 30°C becomes $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ = 0.45 - 0.20 T °C (4) (r^2 =0.82 and the error on the slope is 0.02).

Figure 2 compares the linear relationships obtained by Weber and Woodhead without taking into account $\delta^{18}O_{Sw}$, the formula (3) and (4), respectively, with slopes increasing from -0.31, -0.25 and -0.20‰/°C. The residual values for the relationship obtained by Weber and Woodhead are comprised between -0.4 and 0.3, for (3) between -0.6 and 0.5 and for (4) between -0.3 and 0.2. These different values applied to 0.5‰ isotopic amplitude could drive temperature estimates from 1.6 to 2.5°C which limits precision of temperature assessment. As the isotopic reconstructions require high accuracy we have to discreminate the best value. The annual temperature average over tropical zones is more often higher than 23°C; thus -0.20‰/°C may be applied in most cases and (4) is the most thermodynamically significant formula. We now have to compare this slope value with the previous ones calculated from seasonal variations.

Comparison with other calibrations

By regressing annual $\delta^{18}O$ extrema against temperature extrema McConnaughey (1989a) published the following equation: $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{Sw}$ = 0.594 - 0.209 T°C for a *Porites* collected in Galapagos, considering a $\delta^{18}O_{Sw}$ annual average of 0.4 ‰ vs SMOW. Wellington et al (1996) calculated T °C = 3.97 - 4.48 $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{Sw}$) in the same site with measured $\delta^{18}O_{Sw}$; this slope corresponds with -0.22‰/°C. This study showed that with an annual temperature amplitude of more than 6°C, $\delta^{18}O_{Sw}$ contribution represents around 10% of $\delta^{18}O_{aragonite}$ variability. $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{Sw}$ = 1.36 - 0.22 T°C for monthly values and $\delta^{18}O_{aragonite}$ - $\delta^{18}O_{Sw}$ = 1.72 -0.235 T°C for trimestrial values. Carriquiry (1994) acquired these results from a coral collected in Costa Rica where temperature annual amplitude is 4°C and by using the relationship $\delta^{18}O_{Sw}$ = f(S) assessed for this area. Gagan et al (1994), estimated this value to be 0.18‰/°C.

The results from Leder et al (1996) and Linsley et al (1999) suggest that for the same genus and similar temperature the isotopic offset may vary by 0.5; thus the estimation of the constant in (4) may be the primary source of error. It appears that -0.20‰/°C is the average slope value previously published for *Porites*. We observe that the most reliable study has been performed in Galapagos where the annual temperature amplitude is greatest. Concerning the area where $\delta^{18}O_{Sw}$ is neglected (Linsley et al, 1999) we remarked that in these sites, often, the highest temperature is synchronous with maximum rainfall. Both effects drive $\delta^{18}O_{aragonite}$ values lower, amplifying the annual amplitude. In these conditions the slope estimate is higher than -0.20 expected.

We applied formula (4) to environmental data of 3 sites described in literature: Moorea (Boiseau et al, 1998), Galapagos (Wellington et al, 1996) and Clipperton (Linsley et al, 1999) to compare measurements and calculations (Table 2). Taking into account of the possible offset of 0.5‰, the mean annual $\delta^{18}O_{aragonite}$ calculations are in agreement with the data. But adding the temperature and $\delta^{18}O_{Sw}$ isotopic effects, the calculated isotopic annual amplitude is higher than the measurements: the more annual amplitude is reduced, the higher the discrepancy. This calibration, being assessed from annual values, the deviation -0.20‰/°C may only be used for estimating the temperature variations given by interannual $\delta^{18}O_{aragonite}$ and not for seasonnal fluctuations.

This confirms previous studies, -0.23‰ per 1°C is the calibration obtained with annual isotopic values (Boiseau et al, 1998) in Moorea Island, assuming the annual water isotopic value roughly the same over the time. At this site where annual temperature amplitude is 2°C, it is emphasized that the calibration established from the seasonal isotopic values exhibit a lower deviation per 1°C. Similar considerations were previously made by Quinn et al (1998) and Crowley et al (2000).

Table 2. Comparison of the isotopic values obtained by applying the modified Weber and Woodhead calibration and considering $\delta^{18}O_S$, with measurements performed in three locations. Taking into account the possible 0.5‰ shift the calculated isotopic values are in good agreement with the data, whereas the calculated annual amplitude is much higher than the measurements.

	Moorea (1)		Galapagos (2)		Clipperton (3)	
Mean annual temperature °C	26.75		23.6		28	
Annual temperature amplitude °C	2.5		6.8		2	
Mean annual _ δ_{Sw} ‰vs SMOW	1.2		0.26		-0.15	
Annual _ δ_{Sw} amplitude ‰ vs SMOW	0.2		0.38		0.3	
T and _ δ_{Sw} are out of phase						
	Measured	calculated	measured	calculated	measured	calculated
Mean annual _ $\delta_{aragonite}$ ‰vs PDB	-4.2	-3.7	-4.1	-4.00	-5.6<	<-6 -5.3
Annual $\delta_{aragonite}$ amplitude ‰ vs PDB	0.5	0.7	1.25	1.74	0.4	0.7

(1) data from Boiseau et al, 1998; we considered composited data from 1958 to 1990
(2) data from Wellington et al, 1996
(3) data from Linsley et al, 1999; we considered the last 4 years (1990-1994)

Summary

- Weber and Woodhead $\delta^{18}O_{aragonite}$ values are the most statistically significant data series.
- The $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ values obtained for the 2 lowest temperatures are higher than others; this could be justified by kinetic effect.
- The relationship: $\delta^{18}O_{aragonite}$- $\delta^{18}O_{Sw}$ = 0.45 - 0.20 T °C is calculated for temperatures between 24 and 30°C (tropical temperature range). Two close colonies belonging to the same genus may show an offset of 0.5 ‰ due to isotopic desequilibrium.
-0.20‰/°C is similar to the value published by Wellington et al (-0.22‰/°C). But it can be used to estimate temperature changes only for annual reconstruction.

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