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Recent shoaling of the nutricline and thermocline in the western tropical Pacific

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[1] Long records of subsurface ocean observations are key to constrain our understanding of the climate response of the tropical Pacific to increasing greenhouse gases. Due to the lack of continuous ocean observations, proxies become essential to estimate changes in the tropical thermocline related to changes in Walker circulation. Here, we present high resolution stable nitrogen (δ^{15}N) and carbon (δ^{13}C) isotope records from three proteinaceous corals spanning the top 105 m of the euphotic zone from an offshore Palauan reef in the western tropical Pacific. Dated with radiocarbon-derived growth chronologies, these isotope records indicate a shoaling of the mean nutricline and thus the thermocline as well, and a likely increase in primary productivity in the western tropical Pacific since the mid-to-late 1970s. Thus, these are the first subsurface proxy data extending below 20 m to support a slowdown of the tropical Pacific Walker circulation during the 20th Century. **Citation:** Williams, B., and A. G. Grottoli (2010), Recent shoaling of the nutricline and thermocline in the western tropical Pacific, *Geophys. Res. Lett.*, *37*, L22601, doi:10.1029/2010GL044867.

1. Introduction

[2] The mean state of the tropical Pacific Ocean is a dominant driver of global climate through oceanic and atmospheric teleconnections [*Cane*, 1998]. The influence of increased greenhouse gases on the tropical Pacific Ocean is unknown, although recent modeling efforts suggest that the trade winds will weaken, the pattern of SST change is likely to have a zonally symmetric character with maximum warming on the equator, and the thermocline is likely to shoal and flatten [*Collins et al.*, 2010]. However, observational data are insufficient to validate these modeling results. In particular, reliable subsurface temperature profiles needed to test for changes in the thermocline depth are rare prior to the 1980s and absent prior to the 1950s. Unfortunately, current paleoceanographic proxy records are limited either in their resolution (i.e., ocean sediment records have centennial-to-millennial timescales resolution) or in their depth distribution (i.e., tropical scleractinian corals are restricted to the photic zone). Therefore, a novel method to reconstruct the subsurface physicochemical structure of the water column in the tropical Pacific is needed.

[3] Geochemical records derived from the skeleton of gorgonian alyconaceans (soft corals) and antipatharians (black corals) yield paleoceanographic information not available from carbonate-based climate archives or proxy records. Some species of these corals have a protein-rich internal skeleton that grows in concentric rings providing chronological control, similar to tree rings, and can grow for up to several thousands of years [*Roark et al.*, 2009]. The food source to these proteinaceous corals, particulate organic matter (POM) in the water column, drives the isotope geochemistry (δ^{15}N, δ^{13}C, and ^{14}C) of their organic skeleton [*Roark et al.*, 2005; *Sherwood et al.*, 2005; *Williams and Grottoli*, 2010; *Williams et al.*, 2007]. Widely distributed in the tropical Pacific from the near surface to thousands of meters deep [*Fabricius and Alderslade*, 2001], these corals are ideal for developing proxy records of subsurface stratification in the tropical Pacific.

[4] In the western tropical Pacific (WTP), the barrier layer lies between the warm (SSTs of ≥28°C) and fresh (sea surface salinity of ≤35) mixed layer and the thermocline (defined as the 20°C isotherm), and inhibits the transport of nutrients from deeper water into the mixed layer leaving the surface water depleted of nitrate [*Lukas and Lindstrom*, 1991; *Mackey et al.*, 1995; *Yoshikawa et al.*, 2006]. The depth of the 4 μmol kg^{-1} nitrate isopleth (hereafter called the nutricline) corresponds to the 28°C isotherm in the WTP, and like the thermocline, fluctuates both seasonally and on El Niño-Southern Oscillation (ENSO) timescales [*Colin*, 2001; *Matsumoto et al.*, 2004; *Radenac and Rodier*, 1996; *Zhang et al.*, 2007]. Below (above) the nutricline, the nitrate-rich (-poor) water is characterized by lower (higher) δ^{15}N nitrate (NO_3^-) values due to isotopic fractionation during nitrate uptake by phytoplankton [*Yoshikawa et al.*, 2006]. Accordingly, *in situ* POM produced throughout the euphotic zone in the nitrate-limited WTP [*Turk et al.*, 2001; *Yoshikawa et al.*, 2006] has δ^{15}N values resembling that of the ambient NO_3^- [*Altabet*, 1996]. Therefore, δ^{15}N values of organic matter below (above) the nutricline in nitrate-rich (-poor) water will be lower (higher). As the δ^{15}N values of ambient suspended particulate organic matter drive the proteinaceous coral skeletal δ^{15}N values here [*Williams and Grottoli*, 2010], we hypothesize that fluctuations in the nutricline depth above and below specimens collected from primarily within the barrier layer drive skeletal δ^{15}N values on seasonal to multi-decadal timescales.

[5] In contrast, δ^{13}C values of atmospheric carbon are expected to drive δ^{13}C values of the coral organic skeleton. Burning of ^{13}C-light fossil fuels (i.e., the ^{13}C-Suess effect) is decreasing atmospheric δ^{13}C values, resulting in a parallel decrease in the δ^{13}C values of dissolved inorganic carbon (DIC) in the surface ocean [*Quay et al.*, 2003]. As the DIC is incorporated into the marine carbon cycle, the δ^{13}C values

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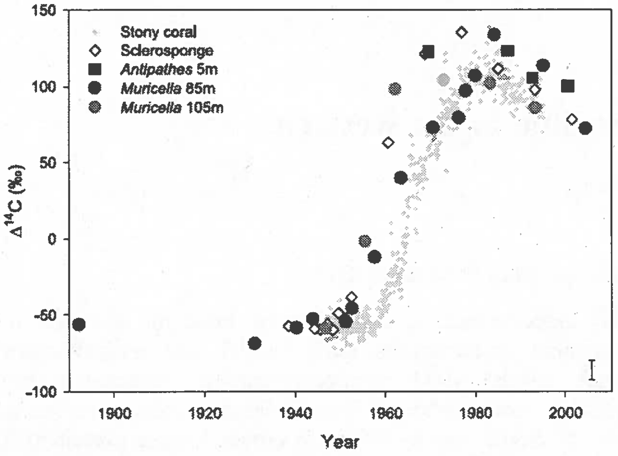

Figure 1. Radiocarbon values ($\Delta^{14}C$) for the *Antipathes* colony and *Muricella* colonies collected from 5 m, 85 m, and 105 m, respectively, measured across a radial transect and compared to published radiocarbon records from a *Porites* stony corals from 14 m depth offshore of Nauru Island [*Guilderson et al.*, 1998] and a Palauan *Ancanthocheatetes wellsi* sclerosponge from 17 m [*Grottoli et al.*, 2010]. Error bar of ±8‰ represents 2 standard deviations of the mean of the internal standard.

of the suspended POM pool and the coral colonies should also decrease. Therefore, we hypothesize that $\delta^{13}C$ values in the colonies will decrease in a manner consistent with the ^{13}C-Suess effect.

[6] In this study, we use high-resolution nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) stable isotope measurements from one *Antipathes* sp. black coral from 5 m and two *Muricella* sp. soft corals from 85 and 105 m depths to infer recent changes in the physicochemical oceanography of the WTP. The 5 m coral was collected from within the mixed layer. The 85 and 105 m coral were collected below the mixed layer but within the 55 to 200 m depth range where the thermocline vertically fluctuates [*Colin*, 2001; *Zhang et al.*, 2007]. As such, the two deeper specimens would have been within the barrier layer when the thermocline was at its deepest endpoint, and below the thermocline when it shoaled. Therefore, by measuring skeletal $\delta^{15}N$ and $\delta^{13}C$ values in these specimens, we can reconstruct vertical fluctuations in the nutricline, and the associated thermocline, above and below the specimens, as well as the ^{13}C-Suess effect in the WTP.

2. Methods

[7] One *Muricella* colony from 85 m and one *Antipathes* colony from 5 m were collected by diver using SCUBA in 2006, and a second *Muricella* colony from 105 m was collected by submersible in 2008. The corals were all collected live at Short Drop Off (7°16.4′N, 134°31.4′E), a 300 m vertical escarpment 2 km offshore of the island of Palau (see Figure S1 of the auxiliary material).[1] The site is well-flushed by the northward surface current flow driven by the North Equatorial Countercurrent in the winter and a southward flow driven by the Palau eddy in the summer and is subject to minimal terrestrial influence [*Heron et al.*, 2006].

[8] A basal section, approximately 10 cm long, was removed from each colony from directly above the holdfast to just below the lowest branches. A one-centimetre thick cross-sectional slice was cut using a rock saw from the basal section of each colony, cleaned in an ultrasonic bath with 18mΩ Milli-Q®, rinsed, and dried overnight in an oven at 40°C. A radial sampling track that was parallel to the growth bands was selected for each colony based on clear banding patterns and the maximal radial distance across the cross-sectional slice then subsampled by milling at 0.1 mm increments in the *Muricella* colonies, and at 0.2 mm increments in the *Antipathes* colony using a high-precision, computer-driven Merchantek microdrill attached to an x, y, z controlled stage. The sampling interval was selected to maximize resolution of the resulting record and still obtain sufficient skeletal material for analysis. The depth (3 mm) and width of the drilling path were set to minimize temporal aliasing. At least 0.4 mg of skeletal material was milled for each subsample and analyzed for $\delta^{15}N$ ($\delta^{15}N$ = per mil deviation of the ratio of stable nitrogen isotopes ^{15}N:^{14}N relative to air) and $\delta^{13}C$ ($\delta^{13}C$ = permil deviation of the ratio of stable carbon isotopes ^{13}C:^{12}C relative to Vienna Peedee Belemnite Limestone Standard (VPDB)) isotopic composition. At selected locations along each sampling track, additional subsamples of 1.2 mg were milled for radiocarbon ($\Delta^{14}C$) analysis.

[9] The $\delta^{15}N$ and $\delta^{13}C$ values of each sample were measured by combusting each organic skeletal sample in a Costech Elemental Analyzer where the resulting N_2 and CO_2 gases were analyzed with a Finnigan Delta IV Plus isotope ratio mass spectrometer via a Finnigan ConFlow III open split interface. $\delta^{15}N$ values were reported relative to air. $\delta^{13}C$ values were reported relative to Vienna Peedee Belemnite Limestone Standard (VPDB). The standard deviation of the mean of repeated measurements of internal standards was ±0.15‰ for $\delta^{15}N$ and ±0.06‰ for $\delta^{13}C$. At least 10% of all samples were run in duplicate.

[10] $\Delta^{14}C$ was measured at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at the Woods Hole Oceanographic Institution using standard NOSAMS methods [*Osborne et al.*, 1994]. Values were reported as $\Delta^{14}C$ (the per mil deviation of $^{14}C/^{12}C$ of the sample relative to that of 95% Oxalic Acid-1 standard) and were blank corrected. The reported uncertainty of duplicate analyses of a known standard was typically ±5–8‰. (See Table S1 for radiocarbon results.)

[11] Measurements of bomb $\Delta^{14}C$ values in the coral skeleton were used in addition to the known date of collection to develop a growth chronology for each colony. The base of the bomb-curve was identified in the $\Delta^{14}C$ records for the *Muricella* colonies, and was anchored at ~1955. The growth rate in mm yr^{-1} was then calculated for both *Muricella* colonies using the anchored base of the bomb-curve and the year of collection. Assuming constant growth rates, the remainder of the skeletal $\Delta^{14}C$ values were plotted against time and were compared to known $\Delta^{14}C$ bomb-curve reconstructions from the tropical Pacific from scleractinian corals and sclerosponges (Figure 1). Skeletal $\Delta^{14}C$ values from the 5 m *Antipathes* colony indicated that the colony was <50 years old. Using the calculated growth rates and radial distances, colony ages of 38, 114, and 56 years were determined for the *Antipathes* colony

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2010GL044867.

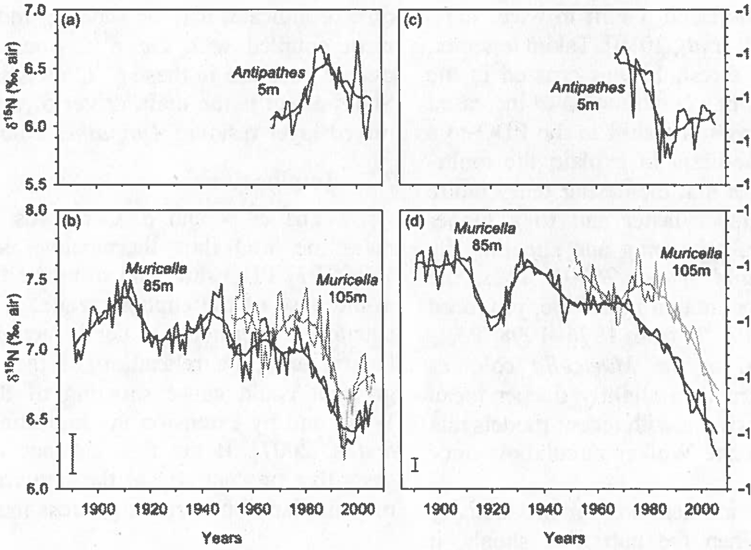

Figure 2. Annually resolved stable nitrogen isotope (δ^{15}N) values for (a) one *Antipathes* colony collected from 5 m and (b) two *Muricella* colonies collected from 85 and 105 m. Stable carbon isotope (δ^{13}C) values for the same (c) *Antipathes* colony and (d) *Muricella* colonies. The smoothed 11-year running mean is plotted as bold line in each panel to highlight the decadal-scale rates of change. Isotope values have been corrected for depth- and genus- specific variability according to *Williams and Grottoli* [2010]. Error bars represent 2 standard deviations of the mean δ^{15}N and δ^{13}C of the internal standards, respectively. Offsets between the different colonies reflect specimen-specific variability. δ^{15}N values in both *Muricella* colonies begin decreasing in 1976/1977 (±2 years).

from 5 m and the *Muricella* colonies from 85 and 105 m, respectively (a more detailed discussion of the growth chronologies is given in the auxiliary material). The Δ^{14}C-derived chronologies for each colony were then applied to the stable isotope records and each stable isotope measurement represented 6 to 9 months of growth.

[12] To account for the different collection depths of each colony and that the isotope composition of suspended POM changes with depth, a depth correction of −0.013‰ m^{-1} was applied to the δ^{15}N records [*Williams and Grottoli*, 2010]. An order-specific correction of +1‰ was applied to the *Antipathes* δ^{13}C values and a depth correction of +0.023‰ m^{-1} was applied to the δ^{13}C records [*Williams and Grottoli*, 2010]. Data were annually interpolated using AnalySeries software so that each record had the same resolution. Regression analyses were performed between the annually-resolved δ^{15}N records and annually resolved subsurface temperature dataset and the Southern Oscillation Index (see auxiliary material). To compare the decadal changes in δ^{15}N values and δ^{13}C values in all three records, the annually-resolved data were smoothed with an 11-year running mean (Figure 2).

3. Results and Discussion

3.1. Nitrogen Isotope Records

[13] The skeletal δ^{15}N values in the *Antipathes* colony increased by 0.5‰ starting in early-1970s, peaked in the mid-1980s, and decreased 0.3‰ by 1997 (Figure 2a). The skeletal δ^{15}N values in the 85 m *Muricella* colony varied on decadal timescales by up to ~0.4‰ prior to 1970 (Figure 2b). In both of the *Muricella* colonies, δ^{15}N values steadily decreased by ~0.6‰ from 1976/1977 (±2 years) to the late 1990s, and then increased by 0.15‰ through to the end of the records (Figure 2b). Thus, the decadal and longer-term trends in the two deeper *Muricella* records differed from that of the shallow *Antipathes* record. The availability of only one record within the mixed layer prevents rigorous interpretation of the decadal changes in the *Antipathes* δ^{15}N values. However, as nitrate is limiting within the mixed layer [*Mackey et al.*, 1995] and deeper water never upwells to the surface at this site [*Colin*, 2001], changes in the source water characterized by nitrate and subsequently ***in situ*** POM with different δ^{15}N values upon which the *Antipathes* feeds, drives the fluctuations in the *Antipathes* skeletal δ^{15}N values. For the two *Muricella* colonies, the similarity of the δ^{15}N values from the mid-to-late 1970s to the end of the records strongly indicates a common environmental forcing on the decreasing skeletal δ^{15}N values. The decreasing values in the two *Muricella* colonies from the 1970s suggest a shoaling of the mean nutricline depth such that both corals increasingly fed on organic matter with low δ^{15}N values from below the nutricline. In addition, since the nutricline closely corresponds with the thermocline in the WTP [*Yoshikawa et al.*, 2006], the data suggests a similar multi-decadal shoaling of the mean thermocline depth. This is consistent with the modeled response of the tropical Pacific Ocean to global warming, which includes a shoaling and flattening thermocline [*Collins et al.*, 2010; *DiNezio et al.*, 2009]. Furthermore, the records here indicate that this shoaling is unprecedented over the past 115 years.

[14] The start of the decrease in δ^{15}N values in the mid-to-late 1970s coincides with a shift to a positive phase of the PDO in 1976/1977 [*Mantua et al.*, 1997]. Interestingly, the previous shift to a positive phase of the PDO in ~1925 was not recorded in the coral δ^{15}N records (Figure 2b). Similarly, the 1976/1977 shift is well-documented in tropical ENSO records while the 1925 and 1947 PDO shifts are typically absent in the same records [*Deser et al.*, 2004]. Furthermore, a Palauan sclerosponge δ^{18}O record from the

same location as our corals indicated a shift in water mass circulation post-1977 [*Grottoli et al.*, 2010]. Taken together, these findings suggest that a threshold was crossed in the mid-to-late 1970s resulting from a combination of increased global sea surface temperatures and a shift in the PDO to a warm phase. A possible hypothesis to explain the multi-decadal shoaling at that time is that increasing temperature warmed the surface mixed layer faster and to a higher degree than the deeper water, enhancing and shoaling the tropical thermocline [*Yang and Wang*, 2009]. Thus, the shoaling thermocline, and concomitant nutricline, produced the observed decrease in coral δ^{15}N from 1976–1998. Post-1998, δ^{15}N values increased in the *Muricella* colonies (Figure 2b) indicating a return to a slightly deeper mean thermocline depth. This is consistent with recent models that indicate a modest increase in the Walker circulation since 1998 [*Vecchi et al.*, 2006].

[15] Our findings also have implications for productivity in the oligotrophic WTP. When the nutricline shoals, it brings nitrate-rich water higher in the water column and into the base of the euphotic zone, and stimulates primary productivity [*Radenac and Rodier*, 1996]. Therefore a shoaling in the mean nutricline depth as recorded by our proteinaceous corals will bring more nitrate-rich water to the base of the euphotic zone fueling primary productivity. Thus, these coral records suggest that primary productivity has increased over the past 30 years, enhancing the biological pump, and increasing the amount of carbon dioxide removed from the atmosphere in the WTP.

3.2. Carbon Isotope Records

[16] Within the mixed layer, mean δ^{13}C values from the *Antipathes* coral decreased by an average of ~0.45‰ per decade from the late-1960s to the late-1980, and then increased by 0.2‰ through to the end of the record (Figure 2c). Below the mixed layer, δ^{13}C values in the 85 m *Muricella* coral decreased by an average of ~0.4‰ for the 80-year period spanning 1890 to 1970 with a ~0.5‰ negative anomaly from 1912 through 1932 (Figure 2d). Afterwards, the average decadal rate of δ^{13}C decline for both *Muricella* colonies was 0.05‰ for the 1970s, 0.25‰ for the 1980s, and 0.45‰ for the 1990s, and an additional 0.2‰ for the last 5 years of the record (Figure 2d). However, post-1976/1977, these δ^{13}C rates of decrease in the 85 and 105 m *Muricella* colonies are higher than those recorded in oceanic DIC-δ^{13}C [*Quay et al.*, 2003] and Indo-Pacific coral records [*Swart et al.*, 2010] over the past several decades. This is consistent with an increase in primary productivity within and below the barrier layer associated with a shoaling of the nutricline. The progressive depletion of CO_2 over time with increasing productivity below the mixed layer results in increasing fractionation and progressively lower δ^{13}C values of the *in situ* produced POM. Thus the δ^{13}C values in the *Muricella* colonies feeding on this POM decrease at a greater rate than expected by the δ^{13}C-Suess effect alone. While the decadal rate of change in δ^{13}C record from the *Antipathes* colony that is within the mixed layer and not subject to nutrient-enhanced productivity does contain some variability, the overall average decrease of 0.7‰ over the entire record is generally consistent with the decline measured in tropical Pacific corals due to the δ^{13}C-Suess effect [*Swart et al.*, 2010]. The average 1‰ decrease in δ^{13}C values for the two deeper *Muricella* colonies over the same period of time of indicates that the shoaling-induced nutrient enhancement coupled with the δ^{13}C-Suess effect is driving the overall decrease in these δ^{13}C records while only the δ^{13}C-Suess effect is the main driver of the δ^{13}C decrease in the mixed-layer residing *Antipathes* colony.

3.3. Implications

[17] The δ^{15}N and δ^{13}C records here indicate that the nutricline, and thus thermocline, shoaled following the 1976/1977 PDO shift, and stimulated enhanced productivity at the base of the euphotic zone. A decrease of the mean equatorial thermocline depth across the entire tropical Pacific and/or a relaxation of the east-west thermocline gradient could cause shoaling of the thermocline in the WTP, and by extension the nutricline as well [*Vecchi and Soden*, 2007]. If the first instance is occurring, this suggests that productivity at the bottom of the euphotic zone may similarly be increasing across the entire tropical Pacific.

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