Late Holocene variations in Pacific surface circulation and biogeochemistry inferred from proteinaceous deep-sea corals

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Abstract

$\delta^{15}N$ and $\delta^{13}C$ data obtained from samples of proteinaceous deep-sea corals collected from the North Pacific Subtropical Gyre (Hawaiian archipelago) and the central equatorial Pacific (Line Islands) document multi-decadal to century scale variability in the isotopic composition of surface-produced particulate organic matter exported to the deep sea. Comparison of the $\delta^{13}C$ data, where Line Island samples are 0.6‰ more positive than the Hawaiian samples, support the contention that the North Pacific Subtropical Gyre is more efficient than the tropical upwelling system at trapping and/or recycling nutrients within the mixed layer. $\delta^{15}N$ values from the Line Island samples are also more positive than those from the central gyre, and within the Hawaiian samples there is a gradient with more positive $\delta^{15}N$ values in samples from the main Hawaiian Islands versus French Frigate Shoals in the Northwestern Hawaiian Islands. The gradient in the Hawaiian samples likely reflects the relative importance of algal acquisition of metabolic N via dissolved seawater nitrate uptake versus nitrogen fixation. The Hawaiian sample set also exhibits a strong decrease in $\delta^{15}N$ values from the mid-Holocene to present. We hypothesize that this decrease is most likely the result of decreasing tradewinds, and possibly a commensurate decrease in entrainment of more positive $\delta^{15}N$-NO$_3$ subthermocline water masses.

1 Introduction

The central subtropical gyres comprise approximately 40% of the ocean’s surface and historically, given their low dissolved nutrient concentrations, have been perceived as desolate deserts. The last two decades of ocean observations have shown that this is not the case. While much of the carbon and nutrients (N, P, Si) fixed in the gyres are recycled within the mixed layer, about 10% of the primary productivity is exported out of the mixed layer to depth (Karl et al., 1996; Karl, 1999). Recent evidence has shown that high spatial and temporal variability in primary production also exists (Dore et al.,
The Hawaiian Ocean Time-series (HOT) observations show that primary production in the gyres is not limited by the nitrogen (Eppley et al., 1977; Ryther, 1959) delivered by the upward flux of NO$_3$ across the nutricline via diffusive and diapycnal entrainment events (Karl et al., 2008; Luo et al., 2012). The revised paradigm of the North Pacific Subtropical Gyre (NPSG), and the broader oceanic trades biome (Karl et al., 2008), incorporates significant nitrogen fixation by two microbial assemblages contributing to new production: a low and relatively constant nitrogen fixation rate by pico- and nanodiazotrophs, and a much higher rate by the diazotroph Trichodesmium (Church et al., 2009; Karl et al., 2008). Unicellular bacteria contribute to nitrogen fixation primarily during fall and winter months, whereas filamentous microorganisms (cyanobacteria and Trichodesmium) appear to be most important during summer blooms. Although nitrogen fixed by these taxa is only a few percent of total nitrogen use, it is a very significant (nearly half) contributor to annual new nitrogen (Church et al., 2009; Dore et al., 2002, 2008; Karl et al., 2008).

Global oceanic primary productivity appears to have declined over the past century, at the same time that sea surface temperatures have risen (Boyce et al., 2010). This is interpreted to reflect increasing hydrographic stability and reduced nutrient flux into the mixed layer. In contrast with the global trend of reduced primary productivity, in the North Pacific (and NPSG) marine productivity has slightly increased (Boyce et al., 2010). This large-scale observation is verified at HOT Station ALOHA (Fig. 1), where primary productivity has increased at a rate of $7.3 \pm 1.3$ mg C m$^{-2}$ d$^{-1}$ ($r = 0.6$) over the last $\sim 20$ yr. This is in addition to the near doubling of productivity of HOT-ALOHA relative to the CLIMAX study period (1965–1985) (Karl 1999) thought to be associated with the Pacific-Decadal Oscillation regime shift of 1976. Additionally, mean annual
mixed layer depth has increased by 0.7 m yr\(^{-1}\) \((r = 0.5)\), with winters seeing a larger depth increase than summers (cf. Quay and Stutsman, 2003). However, over the ~20 yr of observations the nitrogen export (as sinking POC) flux has only a small and relatively weak secular trend \((0.06 \text{ mg N m}^{-2} \text{ d}^{-1}, r = 0.16)\).

The \(\delta^{15}N\) of particles exported out of the mixed layer at HOT, which at steady state records the isotopic value of “new nitrogen”, exhibits an ~7‰ annual range, and the flux weighted mean annual values have varied by ~3‰ over the past 20 yr (Fig. 1). There is an opposing and significant secular trend in \(\delta^{15}N\) values \((-0.06 \text{‰ yr}^{-1}; r = 0.56)\), and also a linear relationship between \(\delta^{15}N\) of new production and overall primary productivity \((r = 0.7)\), where less positive \(\delta^{15}N\) corresponds to higher primary productivity. The variability in \(\delta^{15}N\) may in part reflect a much steeper rate of change prior to ~2002 (Dore et al., 2002), followed by a “reset” event of unknown origin (cf. Corno et al., 2007; Karl et al., 2008). The NO\(_3^-\) entering the mixed layer from the nutricline has a \(\delta^{15}N\) value of ~6.5‰, while that formed from nitrogen fixation has a \(\delta^{15}N\) value near 0‰ (Casciotti et al., 2008; Corno et al., 2007; Dore et al., 2002, 2008). Therefore, the balance of NO\(_3^-\) uptake versus fixation of new nitrogen supporting production is reflected in the \(\delta^{15}N\) value of exported particulate nitrogen. Together, these trends imply that the observed increase in primary productivity is the result of increased summer productivity supported by nitrogen fixation. This interpretation is supported by observations of summer blooms composed of Trichodesmium and other nitrogen fixing cyanobacters within the mixed layer, but well above the nutricline (Church et al., 2009; Karl et al., 2008 and references therein), and also both stoichiometric assemses of N and P dissolved and particulate pools (including < 10 nm NO\(_3^-\) concentrations; cf. Karl, 1999; Karl et al., 2008, among others) and in situ N\(_2\) fixation rates (e.g. Dore et al., 2002).

However, without a longer-term spatial and temporal context for these observations, it is very difficult to delineate the role of ecosystem changes vs. variable nutrient sources, or to understand if trends at HOT are linked to current global changes, or if they may simply reflect decadal scale natural fluctuation. Using deep-sea sediments for this
purpose is difficult as the flux of material to abyssal depths is severely reduced by remineralization in both the water column and at the seafloor, such that the ultimately “archived” material typically contains < 1% of the original exported production (e.g. Wakeham 1997). Open ocean cores in this region have very low accumulation rates (in general ≤ 2 cm kyr⁻¹), and are subject to significant bioturbation, which together vastly reduces the possible temporal resolution (e.g. Wheatcroft, 1990). Further, microbial degradation, trophic transfer, and diagenetic effects (e.g. Altabet, 1988, 2001, among many) can also act in concert to further confound the isotopic signal and thus the interpretation of what has occurred in the overlying surface waters. It is therefore necessary to turn to new archives to place the HOT and other instrumental observations in a longer context.

Deep-sea corals occur in all of the world’s oceans at depths ranging from 0 to 6200 m (Stanley and Cairns, 1988). Within the myriad of “deep-sea corals” are several taxa whose skeletons are completely or partly composed of a hard horny protein (gorgonin), that is well preserved and resistant to diagenesis (e.g. Sherwood et al., 2006). This group includes *Primnoa*, various bamboo genera (*Isidella, Keratoisis*), black (e.g., *Antipathes*) corals, and the gold coral *Gerardia*. *Gerardia* is a cosmopolitan colonial zoanthid that forms tree-like structures with heights of several meters and basal attachment diameters up to a few 10 s of cm. *Gerardia* have radial growth rates of < 100 µmyr⁻¹ and can attain “life spans” of centuries to millennia (Roark et al., 2006, 2009). In Hawaiian waters they are most abundant at ∼ 450 m, near the top of the regional low oxygen zone, and are directly attached to exposed, hard substrates. Radiocarbon (¹⁴C) analyses of polyps and a finely sectioned radial skeletal disk of a live harvested branch both documents incorporation of recently exported particulate organic carbon (Roark et al., 2009), while stable isotope analysis shows that polyps are ≤ 2 trophic levels relative to exported POC/PON (Roark et al., 2009). The close coupling between organic matter export and the growth of gorgonin in proteinaceous deep-sea coral skeletons indicates that these organisms are a source of information on past surface
biogeochemistry changes of potentially unsurpassed fidelity (cf. Heikoop et al., 2002; Roark et al., 2005, 2009; Sherwood et al., 2005, 2009, 2011; Williams et al., 2006).

## 2 Methods

Deep-sea coral samples, both living and fossil were collected using the Hawai’ian Undersea Research Laboratory’s DSRV Pisces IV and V. Results presented here include mainly samples collected from the Hawai’ian archipelago (Big Island, Cross Seamount, Oahu in the Main Hawai’ian Islands; MHI, and French/East French Frigate Shoals and Brooks Bank in the North West Hawai’ian Islands; NWHI), as well as a smaller sample set from Kingman Reef and Palmyra in the Line Islands (∼ 6° N, 161° W) (Fig. 2). Upon recovery, the external polyps and tissue were removed using a seawater hose from all live-collected individuals. After removing the tissue layer, the skeletons (live collected and sub-fossil) were washed with seawater followed by fresh water and allowed to air dry on deck. Stumps were cut into ∼ 0.7 cm thick cross-section disks taken close to the basal attachment. In a small number of cases additional disks were also taken higher on the branch (or stump) to confirm growth longevity and radial growth rate. “Range finder” sampling of the skeleton was done by microdrilling center (inner) and outer samples from radial transects using a 1.8 mm spherical carbide bur. Depending on the size of the cross-section disk sub-samples between the inner and outer samples were also taken.

Milled sub-samples were decarbonated using 1N HCl, rinsed three-times with milliQ water and dried overnight on a heating block. Samples were transferred to tin boats and the mass determined. Carbon and nitrogen stable isotope analyses were made via continuous-flow IRMS using a Carlo-Erba elemental analyzer connected to an Optima IRMS in the UCSC Light Isotope Facility. Results are reported in conventional per mil notation relative to V-PDB (δ¹³C) and air (δ¹⁵N). Reproducibility of the isotope results is ±0.12 ‰ and ±0.06 (1-sd) based on reproducibility of standards (acetanilide, n = 20).
and replicate analyses \( (n = 29) \) of coral samples for \( \delta^{13} \)C and \( \delta^{15} \)N, respectively. C : N ratios determined during analysis were ±0.15 (1-sd).

Radiocarbon samples were first converted to CO\(_2\) via sealed-tube combustion, and the resulting purified CO\(_2\) reduced to graphite in the presence of an iron catalyst. Individual graphite-catalyst mixtures were pressed into aluminum target holders and analyzed via accelerator mass spectrometry. Results include a background subtraction based on similarly prepared \(^{14}\)C-free coal and wood, sample specific \( \delta^{13} \)C corrections, and are reported as conventional radiocarbon years as per Stuiver and Polach (1977). Conventional radiocarbon years were converted to calendar ages using the IntCal09 data product (Reimer et al., 2009). For Hawai’ian samples, and based on a ~ 40 yr average of reef-building hermatypic coral data, a \( \Delta R \) of −28 ± 4 was used (Druffel et al., 2001). For the Line Islands we use 0 ± 50 yr which is consistent with reef-building coral results presented in Zaunbrecher et al. (2010). Radiocarbon results of a sub-set of the Hawai’ian samples included here have been previously reported in Roark et al. (2006, 2009).

3 Results

Range finder ages and implied radial growth rates for the Hawai’ian samples are presented in Fig. 3a and for the Line Island specimens in Fig. 3b. Average radial growth rate for the Hawai’ian sample suite is 38 ± 21 \( \mu \)m yr\(^{-1} \) \( (n = 58) \), with age ranges per specimen collected of 225 to 2740 yr. The average radial growth rate of the Line Island specimens is 33 ± 15 \( \mu \)m yr\(^{-1} \) \( (n = 14) \), with age ranges per specimen of 290 to 1600 yr. The distribution of specimen ages is clustered in the late Holocene (< 6000 yr BP). At Cross Seamount we collected a specimen dated from the late deglacial, ~ 10 500 to ~ 11 300 calendar years BP. The majority of the samples are subfossil branches and not trunks. These data therefore represent minimum age-ranges and should not be used to estimate population dynamics and ultimate longevity. Based on the average linear
growth rate and the milled sample size, isotopic results are representative of 50–100 yr integrations. The average C : N ratio of all Gerardia samples was 2.82 ± 0.16.

Over the past 6000 yr, the δ13C of the Line Island specimens tend to have more positive values (−15.9 ± 0.4‰, n = 39) relative to the Hawaiian samples (−16.5 ± 0.6‰, n = 47) (Fig. 4a). Over the late Holocene there is no obvious secular trend to the δ13C values (r =< 0.01, 0.13 for the Line Islands and Hawai’ian Islands respectively). However, the deglacial specimen from Cross Seamount exhibits a δ13C increase from −18% to nearly −16‰ from 11 300 to 10 500 cal yr BP (Fig. 4a, r = 0.89).

The δ15N values of Line Island samples exhibit no trend (8.3 ± 4.8 × 10−6‰ yr−1, r = 0.03), and over the late Holocene are substantially more positive than all of the NPSG samples, particularly those from the NWHI: (Line Isl: +16.9 ± 0.5‰, n = 39 vs. NWHI: +9.4 ± 0.8‰, n = 47) (Fig. 4b). Within the Hawai’ian archipelago there is also a much smaller geographic trend in values, where samples from the southern and main islands are more positive and those from the NWHI are less positive (Fig. 4b: Big Island/Cross: +12 ± 1‰; Lanikai; +10.9 ± 0.6‰; NWHI +9.4 ± 0.8‰). In contrast with the Line Islands samples, most records from the Hawai’ian islands exhibited significant temporal trends. In a specimen from Cross Seamount spanning the end of the last deglaciation (11 300–10 500 calendar years BP), we document a 4‰ δ15N increase, beginning at ∼11‰ at 11.3 kyr BP and peaking at ∼15‰ before decreasing slightly at 10.5 kyr BP. Unfortunately, no samples span the interval between 10 500 and ∼3850 calendar years BP from this location. Values from samples at ∼3850 calendar years BP are similar to those at 10 500 calendar years BP, however they systematically decrease through the present day, with values of ∼10.6‰ for 14C-modern gorgonin (8.9 × 10−4 ± 1.1 × 10−5‰ yr−1, r = 0.87, n = 27, p < 0.005). Similar decreases in δ15N values in the late Holocene, although of differing magnitudes, are also observed at all other HI and NWHI sites. A ∼1.5‰ decrease between ∼5080 and ∼350 calendar years BP is observed at the Big Island (3.3 × 10−4 ± 7.3 × 10−6‰ yr−1, r = 0.62, n = 34, p < 0.005). Samples from the windward side of Oahu, spanning ∼570 to ∼5500 calendar years BP, also experience a smaller and nearly insignificant decrease in δ15N values.
(6.4 \times 10^{-5} \pm 7.4 \times 10^{-5} \% \text{yr}^{-1}, r = 0.18, n = 24) over the same interval. Finally, samples from the NWHI (~ 5780 calendar years BP to present) exhibit more variability than the other Hawaiian locations, and record a decrease in $\delta^{15}$N of just over 1 $\%$, equivalent to $2.0 \times 10^{-4} \pm 0.07 \times 10^{-5} \% \text{yr}^{-1}, r = 0.38, n = 47, p < 0.01$).

4 Discussion

4.1 Carbon ($\delta^{13}$C) isotopes

Over the time interval for which we have data (late Holocene ~ 5000 yr BP to present), the Line Island specimens average 0.6 $\%$ more positive than the NPSG samples: $-15.9 \pm 0.4$ $\%$ ($n = 39$) versus $-16.5 \pm 0.6$ $\%$ ($n = 47$) ($p < 0.0001$). There are no consistent trends as a function of time in either data set. The inferred late Holocene latitudinal gradient of $\geq 0.5$ $\%$ is larger than observed from modern surface $\delta^{13}$ΣCO$_2$ analyses (e.g. Kroopnick, 1974, 1985; Quay and Stutsman, 2003). Modern sinking particulate organic carbon in the equatorial region and the NPSG have similar values, in the range of $-18$ to $-22$ $\%$ (Altabet, 2001; Georicke and Fry, 1994; Laws et al., 1995), with a flux weighted average of $-21$ $\%$ for HOTS samples (cf. Fig. 1). The latitudinal $\delta^{13}$C gradient recorded in Gerardia not surprisingly implies that “nutrient trapping” in the equatorial region is less efficient than in surface waters of the NPSG. The Line Islands are within the equatorial waveguide where upwelling of high nutrient, low $\delta^{13}$ΣCO$_2$ water occurs in the eastern equatorial Pacific, as well as locally, but due to iron limitation nutrients are not completely consumed. Westward advection and/or entrainment of the upwelled water allows the surface reservoir to become enriched in $^{13}$C with increasing distance from the upwelling center, and with continued phytoplankton preferential fixation/consumption of $^{12}$C (e.g. Zhang and Quay, 1997). A leaky system, one that exports POC out of the mixed layer, will (therefore) leave the residual DIC pool with more positive $\delta^{13}$C values. More efficient recycling in the NPSG would minimize net $^{12}$C flux out of the mixed layer, yielding values that are less enriched relative to the original
dissolved inorganic carbon “stock”. The Line Islands also experience seasonal to interannual sea surface temperature (SST) and nutrient variability associated with El Niño-Southern Oscillation and SST and sea level pressure variations on longer timescales (e.g. Tourre et al., 2001). This variability has the ability to impart potential biases in discrete or infrequent samples. We argue that the density of modern POC and DIC data from the equatorial region is not sufficient to unequivocally define a ∼ 0.5‰ regional difference in sinking POC or DIC over long (multi-decadal) timescales whereas the observations presented herein are.

The late deglacial sample (Cross Seamount) records a nearly monotonic 2‰ increase in δ13C values between ∼11.5 and ∼10.3 kyr BP, i.e. at the very end of the Younger-Dryas-PreBoreal transition. This shift exceeds the ∼ 0.5‰ increase observed in CO2 trapped in ice cores (Taylor Dome, Smith et al., 1999) and thus cannot strictly be explained by air-sea δ13C-CO2 equilibration. This shift is also counter to the temperature effect of δ13C composition expected during the transition from cooler (glacial/Younger Dryas) to warmer (PreBoreal) time. During the deglaciation along nearly the whole of the west coast of North America, a consistent pattern of increased burial of organic carbon occurred in the oxygen minimum zone (e.g. Dean et al., 2006; Kienast et al., 2002). We offer an explanation based on changes in carbon burial rates where sequestration of the isotopically more negative organic carbon (∼ −20‰) would tend to increase the δ13C of the remaining DIC pool. The Cross δ15N data (Fig. 4) provides further evidence for the δ13C change as a signal that is propagated into the NPSG from the margin via advection and entrainment of subthermocline water masses. The δ15N pattern between 11.5 and 10.3 kyr BP is, in fine-scale detail, similar to that observed in oxygen minimum zone sediments (e.g. Kienast et al., 2002). Based on transient tracer data, the timescale of lateral advection and isopycnal diffusion of NPSG thermocline and subthermocline waters is several decades (e.g. Jenkins, 1996; Warner et al., 1996). This timescale is sufficient to allow for advection of δ15N-NO3 signals from the low oxygen zones in the eastern Pacific having substantial denitrification (e.g. Rafter et al., 2011 and references therein) into the NPSG.
4.2 Nitrogen ($\delta^{15}N$) isotopes

The Palmyra and Kingman Reef samples have an average value of $+16.9\%$ (gorgonin) relative to $\sim +8\%$ for sinking POC near Palmyra (Altabet, 2001). Polyp and gorgonin $\delta^{15}N$ are expected to be similar (Heikoop et al., 2002; Roark et al., 2009). Thus, these offsets allow us to infer that, like Hawai’ian Gerardia, the Line Island Gerardia are likely low order consumers.

Although nitrogen isotope values of the Line Island specimens do not exhibit a trend over the last $\sim 7000$ yr, there is $2–3\%$ variability recorded by individual multi-decadal average samples. An explanation for this is suggested by variable nitrogen dynamics observed in the modern ocean. During the JGOFS EqPac/EPOC experiments surface nitrate concentrations were found to vary by a factor of two, with five-fold variations in nitrogen flux, whereas suspended and sinking POC $\delta^{15}N$ was much less variable (Altabet, 2001). An exception was observed in sediment trap samples collected at $5^\circ$ N and $2^\circ$ N, where a $\sim 5\%$ change in $\delta^{15}N$ of sinking POC approximately covared with nitrogen flux, spanning the termination of the 1992 El Niño event. This shift is the consequence of changing surface circulation when an El Niño transitions to “normal” or La Niña conditions bringing a northward expansion of recently upwelled (higher nutrient) water and intensification of the North Equatorial Current.

Although ENSO variability cannot explain all tropical oceanographic variability, it is a useful model to further explore our paleo-observations. Based on the observations of Altabet (2001) the deep sea coral data could be reflecting multi-decadal variability of the relative frequency of El Niño events. Although the vertical gradient in $\delta^{15}N$ of water sourced by upwelling is weak (Rafter et al., 2011) we cannot, over long timescales, uniquely exclude systematic changes in $\delta^{15}NO_3$ due to isopycnal and diapycnal mixing of waters sourced from the denitrifying zones of the eastern Pacific. That being said, it is interesting to note that the less positive coral $\delta^{15}N$ values at $\sim 2000$ and $\sim 1000$ yr BP are consistent with fewer El Niño events, and conversely more positive $\delta^{15}N$ associated with more frequent El Niño events as reconstructed from an Ecuadorean lake record by...
Moy et al. (2002). A piece-wise linear interpolation monte carlo assessment (Blaauw, 2010) of the Moy et al. (2002) age model yields an average 95% confidence range for the late Holocene of ±250 yr. Therefore these two data sets are synchronous within calibration and age-model uncertainties. However, without further refinement of the Pallcacocha timescale, or a continuous bulk isotope analyses from the Line Island specimens, a more detailed comparison is premature.

In contrast to the Line Islands, the Hawai’ian corals reveal an interesting geographic pattern of Late Holocene δ¹⁵N variability. A Late Holocene decrease in δ¹⁵N (secular trend) is strongest in the southern Hawaiian Islands (Cross Seamount 3‰ change; Big Island 1.5‰ change to ~ 350 yr BP), and less apparent in the NWHI (Table 1). Modern and near modern δ¹⁵N values from Cross Seamount and the Big Island approach those of the NWHI. If we were to apply the HOT δ¹⁵N-productivity relationship, the trend to less positive δ¹⁵N values would imply an increase in primary productivity to the west of the Big Island, at least to Cross Seamount, and little to no change in productivity in the NWHI and east of Oahu. Additionally, if we use the 1-D NO₃-nitrogen fixation end-member model (Fig. 1), then the observed decrease in δ¹⁵N implies an increase in nitrogen fixation in excess of 30% over the late Holocene.

Both of these interpretations, however, require constant δ¹⁵N-NO₃ source values, which over these multi-millenial timescales, far in excess of the advective timescale of subsurface waters, may not be valid. An alternate explanation to the 1-D NO₃-nitrogen fixation model would also be to consider changes in the source of NO₃ as a function of water mass (cf. Fig. 4 in Casciotti et al., 2008). The decrease in δ¹⁵N values observed at Cross and the Big Island could be accommodated by an increase in the proportion of subtropical salinity maximum water (STSMW; less positive δ¹⁵N) relative to shallow salinity minimum and North Pacific intermediate water (SSMW/NPIW; more positive δ¹⁵N). The lack of a similar decrease to the east of Oahu, as well as the trend in the NWHI, implies that the decrease in δ¹⁵N values is associated with the permanent mesoscale anticyclonic eddy centered at ~ 19° N (e.g. Flament, 1996), or the production of anticyclonic cold core eddies off the Hawai’ian Islands which are
accompanied by entrainment of higher nutrient water from below (e.g. Bidigare et al., 2003).

A reduction in the production of eddies could be the result of a reduction of the tradewinds and an increased frequency of midlatitude frontal systems which tend to block the trades. In general, a complementary effect of a reduction in the trade winds is decreased rainfall. On seasonal, inter-annual, and decadal timescales Hawai‘ian Islands rainfall is influenced by large-scale atmospheric circulation changes exemplified by the correspondence of winter-time (rainy season) drought associated with El Niño events, and over longer periods a strong relationship is observed with the negative phase of the Pacific Decadal Oscillation (Chu and Chen, 2005; Diaz and Giambelluca, 2012). Paleoclimate reconstructions from Oahu and Laysan (located in the far NWHI) indicate a reduction in precipitation since the mid-Holocene (Athens et al., 2007; Uchikawa et al., 2010). The most parsimonious explanation for the observed multi-millennial scale trends in $\delta^{15}$N values may therefore be a reduction in tradewinds, leading to reduced anticyclonic eddy production. This would have reduced the entrainment of more positive $\delta^{15}$N-NO$_3$ water masses from depth, although the possibility also exists for either a reduction in overall entrainment or sourcing of less positive $\delta^{15}$N-NO$_3$ waters that are more shallow. A reduction in tradewinds and an overall drying in the Hawai‘ian region is also consistent with modeling studies which link the orbital pacing of the seasonal cycle of solar radiation, and the suppression of ENSO during the mid-Holocene boreal summer insolation maximum (Clement et al., 2000). Finally, this interpretation is also consistent with ice core dust proxies, which indicate the mid-Holocene had slightly higher dust deposition than the late Holocene (Osterberg et al., 2008). Deposition of dust would be expected to stimulate N-fixation leading to less positive $\delta^{15}$N values (i.e. increased input of fixed N near 0 ‰), not the more positive values that we observe in the mid-Holocene.

However, even taking into account the secular decrease in $\delta^{15}$N, the variability in $\delta^{15}$N from the NWHI samples was larger than any of the MHI locations. The mixed layer currents in the lower NWHI near French Frigate Shoals are extremely variable,
and are dominated by mesoscale eddies, where the variability in current velocity amplitude exceeds the mean (Firing and Brainard, 2006). We hypothesize that in periods when $\delta^{15}$N is more positive, the longer-term circulation is dominated by northwestern flow bringing the influence of higher $\delta^{15}$N-NO$_3$ waters from the MHI to French Frigate Shoals. In contrast, when $\delta^{15}$N is less positive, longer-term circulation is likely dominated by southern and eastward flow from farther in the center of the gyre where $\delta^{15}$N-NO$_3$ is dominated by nitrogen fixation.

5 Conclusions

Bulk $\delta^{13}$C analyses of Gerardia skeletal material, spanning the mid-late Holocene, document a 0.6 ‰ gradient between the Line Islands in the Equatorial Pacific and samples from the Hawai’ian archipelago in the NPSG, where the values of Line Island samples are more positive. During the mid-late Holocene there are no consistent trends in the data as a function of time. The latitudinal gradient of $\geq$ 0.5 ‰ is larger than observed from somewhat limited modern surface $\delta^{13}\Sigma$CO$_2$ analyses. The fossil results are perhaps a better integrated signal particularly for the Equatorial region which experiences large seasonal to interannual variability. With similar $\delta^{13}$C-$\Sigma$CO$_2$ as the source, these results imply that “nutrient trapping” in the equatorial region is less efficient than in surface waters of the NPSG.

The long-term $\sim$ 20 yr average $\delta^{15}$N of sinking POC at the Hawai’ian Ocean Time-series is $+3.4 \pm 0.7$ with a (annual weighted) range of $\sim 3$‰. 50–100 yr $\delta^{15}$N averages reconstructed from Gerardia skeletons spanning the past 6,000 yr indicate that multi-decadal $\delta^{15}$N variability in the Hawai’ian Islands in the NPSG is of similar amplitude to the annual variability captured by HOTS and related cruises. The $\delta^{15}$N values in Hawai’ian Gerardia skeletons document a general decrease in sinking POC $\delta^{15}$N values since the mid-Holocene. Direct explanations for these data include both changes in primary production, relative increases in N fixation, as well as a systematic change in the $\delta^{15}$N-NO$_3$ of sub-thermocline water-masses, or an overall decrease
in the entrainment of sub-thermocline waters or entrainment of waters that are more shallow (less positive $\delta^{15}$N-NO$_3$). Less entrainment of deeper and more positive $\delta^{15}$N-NO$_3$ water masses, or a change to entraining shallower water masses, most likely also would have been associated with a decrease in the tradewinds, and a decrease in the formation of anticyclonic eddies in the passages between the main and southern Hawaiian Islands. Modern observations, which show a strong atmospheric dynamic linkage between tradewinds and precipitation, suggest that this decrease in tradewinds was likely also accompanied by a decrease in precipitation, a feature observed in Hawaiian paleorecords.

A smaller data-set of Late Holocene Gerardia based $\delta^{15}$N values from the Line Islands does not exhibit any long-term trend across the late Holocene. The 2–3‰ $\delta^{15}$N variability hints at multi-decadal ENSO variability, through ocean dynamics, influencing the $\delta^{15}$N of sinking POC at $\sim 5^\circ$ N.

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References


Flament, P.: The Ocean Atlas of Hawai’i, School of Ocean and Earth Science and Technology, University of Hawai’i, Honolulu, HI, 1996.


### Table 1. Trends in Late Holocene Gerardia $\delta^{15}$N values as a function of location.

<table>
<thead>
<tr>
<th>Location</th>
<th>Youngest (cal yr BP)</th>
<th>Oldest (cal yr BP)</th>
<th>Trend ($%$ yr$^{-1}$)</th>
<th>$r$</th>
<th>$N$</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Islands</td>
<td>Post-bomb</td>
<td>7200</td>
<td>$8.3 \pm 4.8 \times 10^{-6}$</td>
<td>0.03</td>
<td>39</td>
<td>na</td>
</tr>
<tr>
<td>NWHI</td>
<td>Post-bomb</td>
<td>5800</td>
<td>$2.0 \times 10^{-4} \pm 0.07 \times 10^{-5}$</td>
<td>0.38</td>
<td>47</td>
<td>$&lt; 0.01$</td>
</tr>
<tr>
<td>Lanikai</td>
<td>570</td>
<td>5550</td>
<td>$6.4 \times 10^{-5} \pm 7.4 \times 10^{-5}$</td>
<td>0.18</td>
<td>24</td>
<td>na</td>
</tr>
<tr>
<td>Big Island</td>
<td>350</td>
<td>5100</td>
<td>$3.3 \times 10^{-4} \pm 7.3 \times 10^{-6}$</td>
<td>0.62</td>
<td>34</td>
<td>$&lt; 0.005$</td>
</tr>
<tr>
<td>Cross</td>
<td>Post-bomb</td>
<td>3850</td>
<td>$8.9 \times 10^{-4} \pm 1.1 \times 10^{-5}$</td>
<td>0.87</td>
<td>27</td>
<td>$&lt; 0.005$</td>
</tr>
</tbody>
</table>
Fig. 1. Composite HOT-ALOHA data (http://hahana.soest.hawaii.edu/hot/hot-dogs/) including (upper panel) nitrogen export, primary productivity, annual mixed layer depth and (lower panel) $\delta^{15}N$ and $\delta^{13}C$ of sinking POC.
Fig. 2. Annual surface nitrate (µmolL$^{-1}$) concentration (NODC World Ocean Atlas 2009 accessed via iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA09/), “X” denotes Kingman Reef/Palmyra Island complex. Inset figure: mean annual sea surface temperatures (WOA, 2009) and surface currents. Locations discussed in the text: HOT-Aloha (H), Cross Seamount (C), Big Island – windward (K), Oahu – leeward (O), and the Northwest Hawai’ian Islands (NWHI) which includes samples from near French Frigate Shoals (French and East French Frigate Shoals, Brooks Bank).
Fig. 3. (A) Upper panel Hawai’ian *Gerardia* longevity (calendar years BP) and average radial growth rate (µm/yr⁻¹) and (B) lower panel equivalent plot for Line Island samples.
Fig. 4. (A) (upper) Bulk *Gerardia* δ¹³C (‰ VPDB) and (B) (lower) δ¹⁵N (‰ air) as a function of time and location. Each sample represents approximately 50–100 yr.