HOKKAIDO UNIVERSITY

Title	Seasonal variations in the nitrogen isotope composition of Okinotori coral in the tropical western Pacific : A new proxy for marine nitrate dynamics
Author(s)	Yamazaki, Atsuko; Watanabe, Tsuyoshi; Ogawa, Nanako O. et al.
Citation	Journal of Geophysical Research, Biogeosciences, 116, G04005 https://doi.org/10.1029/2011JG001697
Issue Date	2011-10-14
Doc URL	https://hdl.handle.net/2115/49002
Rights	Copyright 2011 by the American Geophysical Union
Type	journal article
File Information	JGRB116_G04005.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Seasonal variations in the nitrogen isotope composition of Okinotori coral in the tropical western Pacific: A new proxy for marine nitrate dynamics

Atsuko Yamazaki,[1] Tsuyoshi Watanabe,[1] Nanako O. Ogawa,[2] Naohiko Ohkouchi,[2] Kotaro Shirai,[3] Mitsuhiro Toratani,[4] and Mitsuo Uematsu[5]

Received 23 February 2011; revised 14 June 2011; accepted 11 July 2011; published 14 October 2011.

[1] To demonstrate the utility of coral skeletons as a recorder of nitrate dynamics in the surface ocean, we collected coral skeletons of *Porites lobata* and determined their nitrogen isotope composition ($\delta^{15}N_{coral}$) from 2002 to 2006. Skeletons were collected at Okinotori Island in southwestern Japan, far from any sources of terrestrial nitrogen. Nitrogen isotope compositions along the growth direction were determined at 800 μm intervals (~1 month resolution) and compared against the skeletal carbon isotope composition ($\delta^{13}C_{coral\text{-}carb}$), barium/calcium ratio (Ba/Ca), and Chlorophyll-*a* concentration (Chl-*a*). From 2002 to 2004, ratios of the $\delta^{15}N_{coral}$ varied between +0.8 and +8.3‰ with inverse variation to SST (r = −0.53). Ba/Ca ratios and Chl-*a* concentrations were also observed to be high during seasons with low SST. These results suggested that the vertical mixing that occurs during periods of low SST carries nutrients from deeper water ($\delta^{15}N_{DIN}$; +5~+6‰) to the sea surface. In 2005 onward, $\delta^{15}N_{coral}$ and Ba/Ca ratios also had positive peaks even in high SST during periods of transient upwelling caused by frequent large typhoons (maximum wind speed 30 m/s). In addition, low $\delta^{15}N_{coral}$ (+0.8~+2.0‰) four months after the last typhoon implied nitrogen fixation because of the lack of typhoon upwelling through the four years record of $\delta^{15}N_{coral}$. Variations in the $\delta^{13}C_{coral\text{-}carb}$ and $\delta^{15}N_{coral}$ were synchronized, suggesting that nitrate concentration could control zooxanthellae photosynthesis. Our results suggested that $\delta^{15}N_{coral}$ holds promise as a proxy for reconstructing the transport dynamics of marine nitrate and thus also a tool for estimating nitrate origins in the tropical and subtropical oceans.

Citation: Yamazaki, A., T. Watanabe, N. O. Ogawa, N. Ohkouchi, K. Shirai, M. Toratani, and M. Uematsu (2011), Seasonal variations in the nitrogen isotope composition of Okinotori coral in the tropical western Pacific: A new proxy for marine nitrate dynamics, *J. Geophys. Res.*, *116*, G04005, doi:10.1029/2011JG001697.

1. Introduction

[2] Coral skeleton has been proposed to be a high-resolution recorder of past nutrient dynamics in the open ocean with a time scale of decades to millennia. Coralline Ba/Ca and Cd/Ca ratios have been used as recorders of upwelling events in the tropical ocean [e.g., *Lea et al.*, 1989; *Shen et al.*, 1987, 1991, 1992; *Matthews et al.*, 2008]. Concentrations of Ba and Cd increase with depth as nutrients distribute through the water column. *LaVigne et al.* [2008] reported that P/Ca ratios could be a direct nutrient proxy, observing that P/Ca cycles in a coral skeleton tracked variations in past seawater phosphate abundance in synchrony with seasonal upwelling.

[3] In addition to upwelling, nutrient concentrations in the surface ocean are determined by other processes such as ocean circulation, mixed-layer dynamics, atmospheric deposition, and the influences of biological pump. Conventional nutrient proxies have limitations in reconstructing these various nutrient sources. The nitrogen isotope of organic matter contained in coral skeletons ($\delta^{15}N_{coral}$) has the potential to record the origin of nitrogenous nutrients with their own nitrogen isotope compositions. Organic matrix in coral skeletons is biosynthesized in a prerequisite step of the calcification process [*Allemand et al.*, 1998], and preserved over a timescale of centuries [*Ingalls et al.*, 2003]. Reef-building corals seem well adapted to life in tropical waters that are poor in suspended particulate food. The $\delta^{15}N_{coral}$ in sym-

[1]Department of Natural History Sciences, Graduate School of Science, Hokkaido University, Sapporo, Japan.
[2]Institute of Biogeosciences, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan.
[3]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Tokyo, Japan.
[4]School of Engineering, Tokai University, Hiratsuka, Japan.
[5]Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Japan.

Copyright 2011 by the American Geophysical Union.
0148-0227/11/2011JG001697

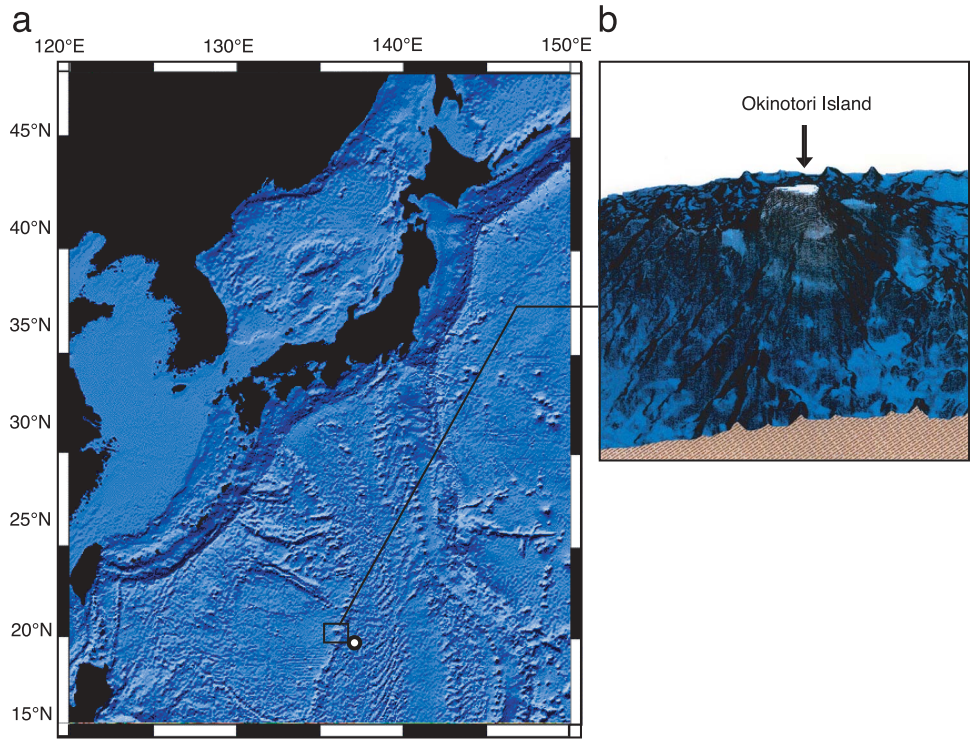

Figure 1. (a) Location of Okinotori Island (20°25′N, 136°05′E) and station 5-1 (open circle; 19°59′N, 137°01′E) during R/V *Hakuhoumaru* cruise KH-06-2. (b) Submarine topography in a bird's-eye view around Okinotori Island (Hydrographic and Oceanographic Department, Japan Coast Guard, 1991). The angle of depression is 45° northward in submarine topography.

biotic corals (+4.09 ± 1.51‰) was substantially lower than that in non-symbiotic corals (+12.25 ± 1.81‰) because the former exhibit both phototrophic and heterotrophic nutritional lifestyles [*Muscatine et al.*, 2005]. According to *Rahav et al.* [1989], 90% of the nitrogen assimilated by zooxanthellae is generated by the recycling of organic nitrogen within the host, and 10% is new nitrogen that must be assimilated from external sources to support new growth. These results imply that the nitrate absorbed by symbiotic algae is one of the main nutrient sources for corals.

[4] Previous studies have suggested that the time series of $\delta^{15}N_{coral}$ through the coral skeletons represent the history of nitrogen isotope in dissolved inorganic nitrogen ($\delta^{15}N_{DIN}$). *Marion et al.* [2005] reported that agricultural fertilizer flowing into a coral reef changed the $\delta^{15}N_{coral}$, while 30 year-tracks of the $\delta^{15}N_{coral}$ were found to decline with the increased introduction of chemical fertilizers with a low δ^{15}N value (−0.8‰). In the results of *Marion et al.* [2005], the temporal resolution of the $\delta^{15}N_{coral}$ was 3 to 6 months because the nitrogen abundance in the coral skeleton was too low (10 to 500 ppm) to be analyzed at a higher resolution; therefore, they targeted baseline changes in the $\delta^{15}N_{coral}$ at an annual time step. *Uchida et al.* [2008] analyzed 2 year-changes in the $\delta^{15}N_{coral}$ in Palau coral with a higher resolution (8 points/year) and suggested that the $\delta^{15}N_{coral}$ could be controlled by the seasonal mixing of a ^{15}N-depleted component from N_2 fixation and ^{15}N-enriched nitrate from the tropical open ocean. However, they did not demonstrate the occurrence of seasonal mixing with any observation data and other coral proxies.

[5] In this study, we measured the $\delta^{15}N_{coral}$ in a *Porites lobata* coral from Okinotori Island, a site located in the open ocean in the tropical western Pacific. Okinotori Island is an isolated island far removed from any sources of anthropogenic contamination. Coral reefs are mainly found in coastal areas that have been greatly affected by terrestrial inputs [*Bell*, 1992; *Fabricius*, 2005] and groundwater [*Szmant*, 2002], and these rich nutrient sources might mask the driving factor in the $\delta^{15}N_{coral}$ variability. However, in the Okinotori coral reef, nitrogen inputs come mainly from upwelling water and nitrogen fixation. The $\delta^{15}N_{coral}$ of Okinotori coral was analyzed at a high temporal resolution (approximately 1 month) to determine the seasonal variation of the $\delta^{15}N_{coral}$ and demonstrate the possibility of using $\delta^{15}N_{coral}$ as a new proxy for reconstructing nutrient transition in the oceans. Additionally, the Ba/Ca ratio was analyzed in parallel with the $\delta^{15}N_{coral}$ to detect upwelling water. We also used carbon isotopes in coral aragonite skeletons as a proxy for the photosynthetic activity of Okinotori coral. These coral geochemical data were compared with satellite data of Chl-*a* concentrations.

2. Materials and Methods

2.1. Okinotori Coral

[6] A specimen of a living coral colony of *Porites lobata* was collected at 2 m depth in the coral reef of Okinotori Island (20°25′N, 136°05′E) in Japan (Figure 1). Okinotori Island is the southernmost island in Japan and a solitary sea mountain with an elevation of 5700 m in the western Pacific Ocean. The

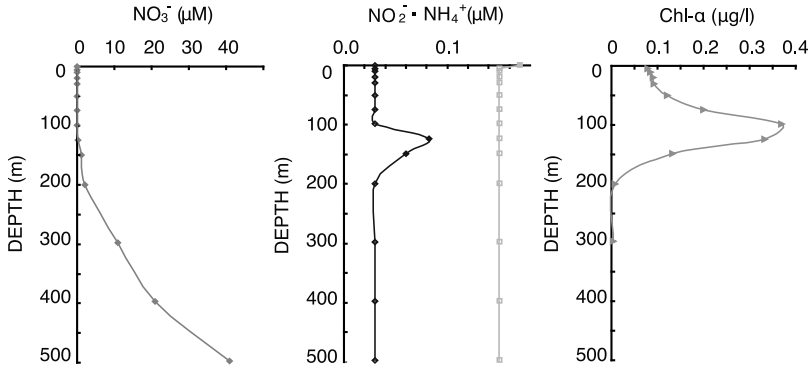

Figure 2. Vertical distribution of inorganic nitrogen (NO_3^-, NO_2^- and NH_4^+) and Chl-*a* at station 5-1. The concentrations of nutrients were very low and near the detection limit, especially in the surface layer (0 to 200 m) of the water column (euphotic zone).

island consists of two small tops over the sea surface inside a reef with a periphery of 11 km. Coral sampling was performed by scuba diving on June 5th, 2006, during cruise KH-06-2 of the Research Vessel (R/V) *Hakuhoumaru*. Figure 2 shows the vertical distributions of dissolved inorganic nitrogen and Chl-*a* near Okinotori Island (19°58.96′N, 137°00.87′E) on June 7th, 2006 (H. Ogawa, personal communication, 2008). Nitrate concentrations were below the detection limit in the euphotic zone (0 to 200 m depth) and increased in deeper layers. Okinotori coral is thus appropriate for estimating the origins of nitrogen uptake into corals and of nitrogenous nutrient dynamics in the tropical western Pacific.

2.2. Isotope Analysis

[7] An entire colony with a 60 cm wide diameter was sliced and ground to a thickness of 7 mm. X-ray photographs were taken at 55 kV, 3.5 mA, with an exposure time of 45 s. Based on visual inspections of the x-ray photographs, 28 annual bands were observed, and analytical lines were determined along the major growth axis (45.5 mm long from the coral surface). A 5 cm wide slab was cut from the sliced coral and further ground to a thickness of 3 mm; this thickness corresponds to the size of three individual corallites. The coral slab was cleaned by Milli-Q water in an ultra sonic bath for 20 min. The cleaning was repeated four times. The slab was dried in a 40°C oven. Microsampling for δ^{13}C and δ^{18}O analysis was conducted at 1 mm thickness from the slab edge, along a 1 mm width of the analysis line, and at 0.2 mm intervals toward the growth axis (corresponding to a temporal resolution of less than 1 week). Powdered samples (80 to 100 μg) were reacted with phosphoric acid at 70°C in a carbonate reaction device (Kiel device II). The CO_2 gas produced in this reaction was then introduced into a coupled mass spectrometer (Finnigan MAT 251). The δ^{13}C and δ^{18}O values were calibrated against NBS-19 and reported in standard δ notation relative to the Vienna Pee Dee Belemnite (VPDB) standard. Analytical error was estimated by 15 replicate measurements of a homogenized powder of crushed coral. The standard deviations (2σ; 95% confidence) are 0.05‰ and 0.08‰ for the δ^{13}C and δ^{18}O, respectively [*Watanabe et al.*, 2001].

[8] Powdered samples for the δ^{15}N and total nitrogen (TN) were obtained from a line parallel to the one used to collect the δ^{13}C and δ^{18}O samples. The total amount of nitrogen constituents in coral aragonite has been estimated to range from 0.001 to 0.05 wt% [*Marion et al.*, 2005]. The δ^{15}N and TN were microsampled from a 3 mm thick ledge every 0.8 mm (approximately 1 month resolution) to a depth of 3 mm, so as to obtain 3 mg of carbonate powder. To ensure no nitrogen loss during sample preparation, the skeletal powders were folded in tin capsules. We measured bulk δ^{15}N and TN in coral skeleton that includes both the soluble and the insoluble matrices. Previously, the insoluble matrix of nitrogen isotopes has been used as an indicator of marine pollution by *Marion et al.* [2005]. However, the soluble matrix of coral skeletons is rich in acidic amino acids [*Mitterer*, 1978; *Young*, 1971; *Cuif et al.*, 1999]. We therefore tried to detect the bulk $\delta^{15}N_{coral}$. The δ^{15}N and TN were measured using an online system of a Finnigan Delta Plus XP isotope-ratio mass spectrometer coupled to a Flash EA 1112 Automatic Elemental Analyzer through a Con-Flo III interface [*Ohkouchi et al.*, 2005; *Ogawa et al.*, 2010]. Isotope compositions were expressed in conventional δ notation against atmospheric N_2 for nitrogen. The analytical error for δ^{15}N was estimated to be within 0.2‰.

2.3. Analysis of Barium/Calcium Ratios

[9] Barium and calcium concentrations were analyzed along the same sampling line that was used for nitrogen isotope sampling. Concentrations were measured using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [Agilent 7500CS ICP-MS coupled with a 213 nm Nd-YAG laser ablation system (New Wave Research)]. The flow rate for the laser ablation cell output gas (He) was 600 ml/min. Ablated sample was also mixed with additional Ar before injection into the mass spectrometer. The slab sample was ablated using a 30 μm laser spot at 50 μm intervals. All laser spots avoided pores on the coral skeletons (Figure S1 in the auxiliary material).[1] The distance from the top of the slab to each ablation spot was calculated as if each spot was on a straight line. Before data acquisition, the sample surface was cleaned by five seconds of pre-ablation. The calibration of the signal intensity to the Ba/Ca ratio was performed using three

[1]Auxiliary materials are available in the HTML. doi:10.1029/2011JG001697.

standard materials: NIST 612 standard glass distributed by the National Institute of Standards and Technology, pressed pellets of certified reference materials of powdered coral (JCp-1), and powdered giant clam (JCt-1), both distributed by the National Institute of Advanced Industrial Science and Technology [*Shirai et al.*, 2008]. The isotope ^{44}Ca was used as an internal standard, and ^{138}Ba was expressed in terms of its molar ratio to ^{44}Ca. The analytical error for the Ba/Ca ratio was 0.42 μmol/mol (n = 34, 1σ), estimated by replicate measurements of JCp-1. The Ba/Ca data were filtered through a five-point running median function to remove the occasional extreme outliner points resulting from dust or other discrete particle contamination entering the plasma [*Sinclair et al.*, 1998]. The resolution of the filtered Ba/Ca data was approximately 10 days.

2.4. Environmental Data

[10] Data on temporal chlorophyll-a concentrations (8-day binned data available at NASA's Ocean Color Web, http://oceancolor.gsfc.nasa.gov/) were obtained from a 9 km by 9 km pixel containing Okinotori Island in SeaWiFS (Sea-viewing Wide Field-of-view Sensor) [*McClain et al.*, 2004]. Isotopic and elemental analyses were converted to time series using the relationship between the skeletal δ^{18}O and sea surface temperature (SST) observed by the Japan Agency for Marine-Earth Science and Technology (SST data available at the JAMSTEC Okinotorishima Web site, http://www.jamstec.go.jp/j/database/okitori/index.html). The SST was measured at intervals of either 40 min or 1 h at an automatic observatory in Okinotori Island. These data were converted to weekly averages to better compare with the temporal resolution of the isotope analysis. The $\delta^{15}N_{coral}$ and TN were also plotted with the outgoing long-wave radiation (OLR) obtained from satellite observation data collected by the National Oceanic and Atmospheric Administration (NOAA) [*Liebmann and Smith*, 1996]. The OLR is the intensity of infrared emission from the ocean surface, which decreases with increasing cloud cover. Surfaces covered by clouds emit relatively short-wave radiation, reflecting the cooling temperature of the cloud surface. In contrast, long-wave radiation is emitted from warming surfaces. The OLR could be used as an indicator of high sunlight-like OLR in strong sunlight [*Shupe and Intrieri*, 2004]. We also described typhoon passed over Okinotori Island. Typhoons defined from the past positions of typhoons (Japan meteorological agency) and wind speed at Okinotori Island observed by JAMSTEC (wind speed data available at http://www.jamstec.go.jp/j/database/okitori/index.html).

2.5. Chronology for Okinotori Coral

[11] The age model was established using the relationship between the coral δ^{18}O profiles and SST (Figures 3d and 3h). The δ^{18}O profile was compared with density bands in x-radiographs to detect annual variations. High-density

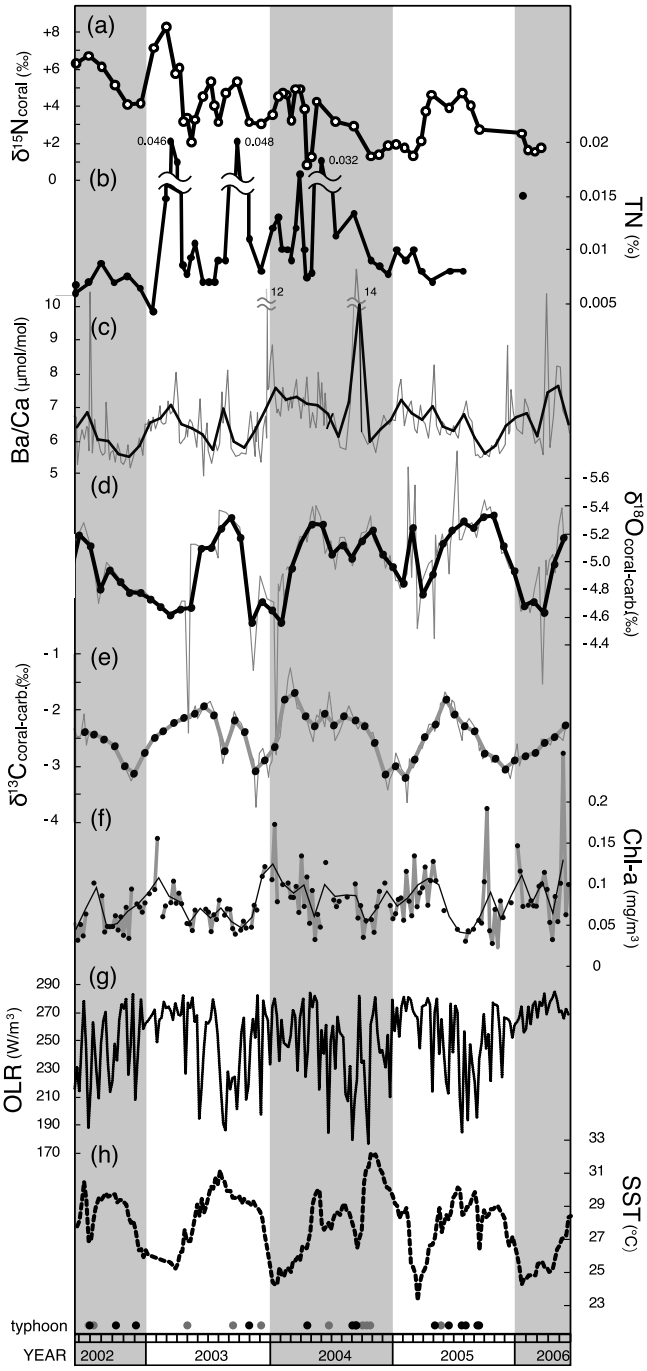

Figure 3. Time series of coral isotope analysis and meteorological data for Okinotori Island. Duration of the typhoons passing above Okinotori Island was shown as black circles (maximum wind speed larger than 30 m/s) and gray circles (maximum wind speed larger than 20 m/s) above the *x* axis. (a) Nitrogen isotope ratio in the organic matrix of coral skeletons ($\delta^{15}N_{coral}$), (b) total nitrogen in coral skeletons (TN), (c) row plots of coral skeletal Ba/Ca ratios; solid line, and 12 samples/yr resampling; thin line, (d) oxygen isotope ratio in skeletal carbonate ($\delta^{18}O_{coral\text{-}carb.}$), 12 samples/yr resampling; open circle with solid line, row plots; thin line, (e) carbon isotope ratio in skeletal carbonate ($\delta^{13}C_{coral\text{-}carb.}$), 12 samples/yr resampling; open circle with solid line, row plots; thin line, (f) Chl-*a* concentration calculated from 8-day composite images of SeaWiFS, (g) weekly outgoing long-wave radiation (OLR) from satellite data of NOAA, and (h) weekly sea surface temperature (SST) from the observatory of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC).

bands appeared at the minima of the δ^{18}O (high SST). The skeletal δ^{18}O variation in Okinotori coral included both positive and negative spikes. To clarify the seasonal variation of the δ^{18}O, the data were resampled at a resolution of 12 points/year. The majority of the seasonal variation of the δ^{18}O in coral was between −5.4 and −4.5‰. The resampling profile was compared against the SST. As time control points, the minima and maxima for the δ^{18}O were tied to the maxima and minima for SST, respectively. To convert distances into dates, the growth rate was assumed to be constant during each of the tied points.

3. Results

3.1. $\delta^{15}N_{coral}$ and TN in Okinotori Coral

[12] Figure 3 shows the analytical results of the Okinotori coral analysis and meteorological data for Okinotori Island. The $\delta^{15}N_{coral}$ profile from May 2002 to June 2006 showed seasonal variations ranging between +0.8 and +8.3‰ (Figure 3a). The average values of the $\delta^{15}N_{coral}$ (+3.7‰) agree with the symbiotic coral skeletal value (+4.09 ± 1.51‰) reported by *Muscatine et al.* [2005]. The δ^{15}N in coral tissues and skeletons has been used as an indicator of the $\delta^{15}N_{DIN}$ [*Sammarco et al.*, 1999; *Heikoop et al.*, 2000; *Risk et al.*, 1994; *Marion et al.*, 2005; *Uchida et al.*, 2008]. The DIN assimilated by zooxanthellae is assumed to be the main source of nitrogen for coral, according to *D'Elia and Cook* [1988]. At the subtropical North Pacific Station ALOHA, the δ^{15}N values of DIN increase from +1.9‰ at a 150 m depth to +7.1‰ at a 500 m depth [*Casciotti et al.*, 2008]. In deeper water (below 500 m), the $\delta^{15}N_{DIN}$ is typically +5 to +6‰ in the north Pacific [e.g., *Cline and Kaplan*, 1975; *Liu et al.*, 1996; *Sigman et al.*, 2005; *Casciotti et al.*, 2008]. Previous studies have suggested that the DIN sources for surface water in the subtropical North Pacific are biological fixation of N_2 and nitrate from deep water upwelling [e.g., *Liu et al.*, 1996; *Dore et al.*, 2002; *Casciotti et al.*, 2008]. The $\delta^{15}N_{DIN}$ from N_2 fixation was assumed to be around 0‰, and the $\delta^{15}N_{DIN}$ from deeper water was assumed to be +5 to +6‰. The $\delta^{15}N_{DIN}$ in subsurface water depends on the mixing ratio of these two sources as well as biological fractionation in the euphotic zone [*Sigman et al.*, 1999]. The $\delta^{15}N_{coral}$ of the Okinotori coral (+0.8~+8.3‰) varied within a similar range of $\delta^{15}N_{DIN}$ in tropical and subtropical North Pacific. The $\delta^{15}N_{coral}$ values obtained intra-annual highs when SSTs were low (29°C below): in the summer of 2002, the beginning of 2003, the beginning of 2004, May to September in 2004, and the beginning of 2005 (Figure 3h). From June of 2002 to November of 2004, monthly $\delta^{15}N_{coral}$ and SST had negative correlation ($r^2 = 0.28$, $p < 0.003$) (Figure S2). In this term, $\delta^{15}N_{coral}$ had gradually decreasing with increasing annual mean SST (27.7°C in 2002, 27.9°C in 2003, and 28.4°C in 2004). On the other hand, from November of 2004 onward, monthly $\delta^{15}N_{coral}$ and SST had positive correlation ($r^2 = 0.43$, $p = 0.01$) although significance (p-value) was smaller than the former term. This correlation mainly attribute to the positive peaks (~5‰) of $\delta^{15}N_{coral}$ in summer of 2005, when Ba/Ca had positive peaks similarly. The $\delta^{15}N_{coral}$ values were extremely low (between +0.8 and +2.0‰) in May 2003, April and November 2004, and February 2005.

[13] The total nitrogen (TN) content in coral ranged from 0.007 to 0.048%, with a mean value of 0.015% (Figure 3b). The mean value of TN agrees with that of the previous studies (0.001 ~ 0.1‰ [*Marion et al.*, 2005; *Uchida et al.*, 2008]). The TN profile generally trended high with high $\delta^{15}N_{coral}$ values, with the exception of August 2003. The TN could capture the quantity of nitrogenous nutrients assimilated by corals. Absorption of nitrogen by symbiotic algae could cause coral metabolism to be more active and consequently lead to organic nitrogen being fixed in coral skeletons. In addition to physiological changes, higher TN values might also be caused by organic matter such as endolithic algae adhering to the surface of the skeletons [e.g., *Odum and Odum*, 1955; *Fork and Larkum*, 1989]. However, we did not find algae on the skeletal surface under the microscope. We also have to consider that whether TN changed with the skeletal density. Extension rate in massive *Porites* is inversely related to average skeletal density [*Lough and Barnes*, 2000]. From 2003 to 2005, annual extension rate and annual average of TN were 13.6 mm/year −0.016%, 10.2 mm/year −0.012%, and 12.5 mm/year −0.013%, respectively. TN increased with increasing extension rate; decreasing skeletal density. This result suggested an accumulation of skeletal organic matter was not dependent on the skeletal structure in Okinotori coral.

3.2. Ba/Ca in Okinotori Coral

[14] The Ba/Ca in Okinotori coral ranged from 5 to 14 μmol/mol and averaged 6.6 μmol/mol (Figure 3c). The Ba/Ca had the highest peak in August to September 2004 when six typhoons passed across Okinotori Island in succession. The Ba/Ca ratios were also high during each of the typhoon seasons from 2002 to 2005. Okinotori Island rises steeply from the deep sea (approximately 2500 m) (Figure 1), which causes upwelling [*Genin and Boehlert*, 1985]. Typhoons formed off the equatorial areas often pass across Okinotori Island as they move toward East Asia. According to *Price* [1981], the heavy winds that occur during these hurricanes cause upwelling. The Ba/Ca was high during periods of low SST and low during periods of high SST, with the exception of May to August 2003. The Ba/Ca profile also oscillated with temporal variations in Chl-*a* (Figure 3f). When the Ba/Ca, Chl-*a* and SST were converted to a monthly resolution by resampling at 12 points/yr, correlation coefficients (r^2) were 0.27 and 0.26 for coral Ba/Ca versus Chl-*a* and Ba/Ca versus SST, respectively, with the exception of six typhoons in September 2004. From April to September of 2005, Ba/Ca has continuously more than 6 μmol/mol even in summer, when large typhoons (maximum wind speed >30 m/s) passed on Okinotori Island every month (April to September) and cooled SST 29°C below.

3.3. Seasonal Variation in the $\delta^{13}C_{coral\text{-}carb}$ and $\delta^{15}N_{coral}$

[15] Skeletal δ^{13}C has previously been used as a proxy of solar irradiance [e.g., *Fairbanks and Dodge*, 1979]. Annual variation of the $\delta^{13}C_{coral\text{-}carb}$ did not, however, display any oscillation with OLR (Figures 3e and 3g). The $\delta^{13}C_{coral\text{-}carb}$ positively correlated with the $\delta^{15}N_{coral}$, and this correlation was 0.27 (r^2) from October 2003 onward. Similar variations between the $\delta^{13}C_{coral\text{-}carb}$ and $\delta^{15}N_{coral}$, with the exception of a low $\delta^{15}N_{coral}$ period in May 2003, suggest that the

$\delta^{13}C_{coral\text{-}carb}$ changes with nutrient concentration. The $\delta^{13}C_{coral\text{-}carb}$ is determined by the δ^{13}C of DIC and isotope fractionation—kinetic and metabolic fractionation. Rapid skeletal calcification often appears to be associated with strong kinetic disequilibria [*McConnaughey*, 1989b]. Kinetic fractionation during CO_2 hydration and hydroxylation produces a simultaneous depletion of ^{13}C and ^{18}O [*McConnaughey*, 1989b]. No correlation between the $\delta^{18}O_{coral\text{-}carb}$ and $\delta^{13}C_{coral\text{-}carb}$ in Okinotori coral (r^2 = 0.02) suggested that metabolic effects might control the $\delta^{13}C_{coral\text{-}carb}$ variation much more strongly than kinetic fractionation. Metabolic fractionation produces the skeletal $\delta^{13}C_{coral\text{-}carb}$ changes that reflect those in symbiont photosynthesis and host respiration [*Swart*, 1983; *Muscatine et al.*, 1989; *McConnaughey*, 1989a, 1989b; *McConnaughey et al.*, 1997; *Grottoli and Wellington*, 1999]. Because a low rate of photosynthesis decreases the $\delta^{13}C_{coral\text{-}carb}$ values, the values have been used as a proxy of solar irradiance [*Cole and Fairbanks*, 1990; *Grottoli and Wellington*, 1999; *Reynaud-Vaganay et al.*, 2001; *Grottoli*, 2002]. However, the $\delta^{13}C_{coral\text{-}carb}$ of Okinotori coral was high during the season with low sunlight. Synchronous variation of the $\delta^{15}N_{coral}$ and $\delta^{13}C_{coral\text{-}carb}$ suggested that the $\delta^{13}C_{coral\text{-}carb}$ was controlled by photosynthesis and that zooplankton consumption of coral varied with nutrient concentration. High nutrient concentrations enhance coral symbiont photosynthesis, and the $\delta^{13}C_{coral\text{-}carb}$ values will increase with increasing nitrogen assimilation. *Grottoli and Wellington* [1999] reported that the $\delta^{13}C_{coral\text{-}carb}$ values significantly increased when zooplankton (δ^{13}C; −14 to −25‰) density was reduced. Increases in zooplankton resulting from a nutrient rich environment must decrease the $\delta^{13}C_{coral\text{-}carb}$ if zooplankton concentration is the main factor controlling the $\delta^{13}C_{coral\text{-}carb}$. The $\delta^{13}C_{coral\text{-}carb}$ in Okinotori coral, however, increase with increased $\delta^{15}N_{coral}$ values. This result implies that photosynthesis was activated with nitrogen assimilation because of increasing nutrient supply and that zooplankton consumption did not affect the $\delta^{13}C_{coral\text{-}carb}$ variations. The $\delta^{13}C_{coral\text{-}carb}$ and $\delta^{15}N_{coral}$ were synchronized, suggesting that the nitrate concentration could control zooxanthellae photosynthesis in nutrient-limited and isolated environments.

4. Discussion

4.1. Possible Factors Controlling $\delta^{15}N_{coral}$

[16] Nitrogen sources for reef corals include seawater DIN assimilated by zooxanthellae, coral consumption of PON (particulate organic nitrogen, e.g., zooplankton) and DON (dissolved organic nitrogen), and nitrogen fixation of symbiotic cyanobacteria [*Rahav et al.*, 1989; *Heikoop et al.*, 1998; *Lesser et al.*, 2004, 2007]. The $\delta^{15}N_{coral}$ might depend on 1) the flux and δ^{15}N of DIN from terrestrial, open ocean, and atmospheric sources into coral reefs; 2) nitrogen fixation due to nutrient depletion in coral reefs; and 3) the proportional changes of autotrophic and heterotrophic metabolism in corals. In the Okinotori coral reef, new DIN supplies are derived from nitrate upwelling in the open ocean and/or atmospheric anthropogenic nitrogen [e.g., *Doney et al.*, 2007; *Duce et al.*, 2008]. According to *Duce et al.* [2008], the ratio of total atmospheric nitrogen (NOx, NH_3, organic N) to upwelled DIN into the upper 130 m of the ocean was 0.11 to 0.30 in the eastern tropical Pacific around Okinotori Island, making upwelled DIN dominant over atmospheric inputs. Nitrogen fixation is also a major source of new nitrogen for tropical coral reefs. In coral reefs, significant nitrogen fixation is activated by microalgae living in the reef sediment and by other reef organisms having the capability to fix nitrogen [*Wiebe et al.*, 1975; *Larkum et al.*, 1988]. Corals also have symbiotic cyanobacteria [*Lesser et al.*, 2004, 2007]. Coral consumption of plankton might increase the $\delta^{15}N_{coral}$. The δ^{15}N of phytoplankton and zooplankton are +3 to 12‰ and +5 to 14‰, respectively [*Owens*, 1985]. The autotrophic status of the coral-algal symbiosis must exhibit the stepwise trophic δ^{15}N enrichment (+3.4‰) characteristic of nitrogen across trophic levels in food webs [*Minagawa and Wada*, 1984]. However, *Yamamuro et al.* [1995] reported the δ^{15}N of coral tissue in Ishigaki and Palau (+4 to +6‰) and suggested that zooplankton were not the main source of nitrogen for corals. *Uchida et al.* [2008] suggested that feeding PON may not affect the $\delta^{15}N_{coral}$ in more insolated environments because photoautotrophy was suggested for symbiotic coral living at 0 to 30 m water depth, while heterotrophy was suggested for coral at 50 m for a reef in Jamaica [*Muscatine and Kaplan*, 1994]. As the insolation for Okinotori coral (2 m depth) may have been enough for photoautotrophy, heterotrophy might not exert a controlling effect on the $\delta^{15}N_{coral}$. For Okinotori coral, possible factors controlling the $\delta^{15}N_{coral}$ were DIN from the upwelling of nitrate and/or nitrogen fixation in the coral reef.

4.2. Nitrate Supply From Deeper Water

[17] Nitrates supplied by vertical mixing in periods of low SST might control seasonal variation of the $\delta^{15}N_{coral}$. Because of the similarity between the vertical distributions of Ba and nutrients [e.g., *Lea et al.*, 1989], the Ba/Ca ratio in the coral skeleton has also been used as a tracer of variability in upwelling and entrainment of nutrient-rich subsurface water to the surface ocean. *Alibert and Kinsley* [2008a, 2008b] reported that coralline Ba enrichment during low SST seasons was caused by thermocline shoaling, allowing cold, deep, and Ba-rich waters to mix into the surface layer. These authors suggested that the Ba/Ca ratio might be a tracer of vertical mixing. The vertical flux of nitrate from the deeper layer through eddy diffusion and turbulent mixing is generally considered to be the main source of new nitrogen in highly stable, non-upwelling, open-ocean regions [*Lewis et al.*, 1986]. Seasonal variations in 8-day averaged Chl-*a* concentrations were also higher during low SST seasons. These data indicated that primary production during low SST periods was active around Okinotori Island. Not only seasonal vertical mixing, transient upwelling of typhoon could also supply nitrate to ocean surface. $\delta^{15}N_{coral}$ and Ba/Ca had positive peaks from April to September in 2005 with large typhoons. From June of 2002 to November of 2004, $\delta^{15}N_{coral}$ and SST correlation coefficient without typhoon months was 0.35 (r^2, $P < 0.003$). These results suggested that nitrate supply due to typhoon upwelling could influence on $\delta^{15}N_{DIN}$ in ocean surface. As the $\delta^{15}N_{DIN}$ beneath the thermocline is +5 to +7‰, the positive $\delta^{15}N_{coral}$ values from 2003 to 2006 (+4.6 ~ +5.3‰) imply that subsurface nutrient-rich water was supplied to the surface water and mixed with ^{15}N-

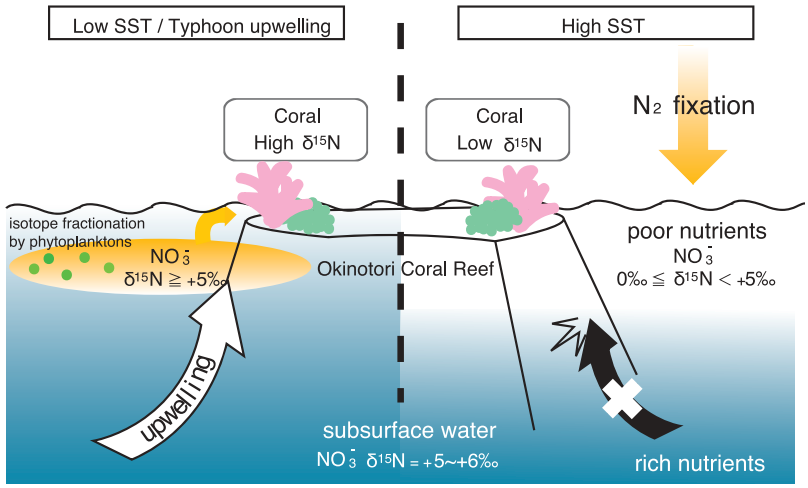

Figure 4. Schematic diagram of nitrate dynamics recorded in Okinotori coral ($\delta^{15}N_{coral}$). $\delta^{15}N_{nitrate}$ referenced from ALOHA station [*Casciotti et al.*, 2008].

depleted water from N_2 fixation. $\delta^{15}N_{coral}$ showed decreasing trend with increasing annual mean SST except 2005, indicating that the influence of nitrogen fixation became stronger through the three years. It is also important to consider that the isotope fractionation associated with the nitrate assimilation by zooxanthellae may change the $\delta^{15}N_{coral}$ values [*Muscatine and Kaplan*, 1994; *Heikoop et al.*, 1998]. When nitrogen assimilation is enhanced as a result of elevated nutrient concentrations, the ^{15}N-discrimination becomes low [*Muscatine and Kaplan*, 1994; *Heikoop et al.*, 1998] and the $\delta^{15}N_{coral}$ is increased by the $\delta^{15}N_{DIN}$ value in seawater. Such fractionation is expected to be minimal because DIN is rapidly incorporated into internal coral pools typical to N-limited coral reef waters [*Marion et al.*, 2005; *Heikoop et al.*, 2000].

4.3. N_2-Fixation

[18] Nitrogen input from marine N_2-fixation enhances primary production in subtropical oceans [*Karl et al.*, 1997; *Capone et al.*, 2005; *Casciotti et al.*, 2008]. In coral reefs, N_2-fixation of free-living or benthic cyanobacteria supplies both dissolved and particulate organic nitrogen, and coral reef ecosystems act as sustainable organic matter producers in oligotrophic tropical oceans [*Wiebe et al.*, 1975; *Yamamuro et al.*, 1995]. The δ^{15}N of new nitrogen from N_2 fixation is close to that of atmospheric N_2 (−2 to 0‰) [*Hoering and Ford*, 1960; *Minagawa and Wada*, 1986; *Carpenter et al.*, 1997]. The $\delta^{15}N_{DIN}$ of the surface ocean will therefore decrease as N_2 fixation increases relative to the δ^{15}N of mean ocean NO_3^- (+5‰) [*Knapp et al.*, 2008]. The $\delta^{15}N_{coral}$ was extremely low in May 2003 (+2.0‰), April 2004 (+0.8‰), February 2005 (+1.3‰), and February to March 2006 (+1.5 to +1.6‰). These periods each occurred four months after a typhoon. Typhoon upwelling supplies nutrients to the sea surface and enhances ocean primary production [*Lin et al.*, 2003; *Toratani*, 2008]. In high SST periods, nutrient starvation could occur outside of the typhoon season and trigger decreases in the coral δ^{15}N due to nitrogen fixation.

[19] From October 2004 to February 2005, the $\delta^{15}N_{coral}$ values continued to be low (+1.3~+1.9‰) even though six typhoons had successively passed through the area from August to October 2004, and the maximum values of Ba/Ca were seen during this period. In addition, Ba/Ca and Chl-*a* values remained high during this period, indicating large nutrient concentrations. Except for nitrogen fixation, the external source of low δ^{15}N for the open ocean is atmospheric deposition [*Duce et al.*, 2008]. The δ^{15}N composition of rain NO_3^- is −15 to +3.6‰ [e.g., *Peterson and Fry*, 1987; *Paerl and Fogel*, 1994; *Hastings et al.*, 2003]. The large amounts of precipitation caused by typhoons might supply rich nitrogenous components and decrease the δ^{15}N at the sea surface.

4.4. Nitrate Dynamics in Okinotori Coral Reef

[20] The $\delta^{15}N_{coral}$ in Okinotori coral exhibited the potential to record the history of the $\delta^{15}N_{DIN}$ in the tropical open ocean (Figure 4). Higher values of the $\delta^{15}N_{coral}$ coinciding with periods of low SST suggest that vertical mixing brought nutrients up from the subsurface water to the sea surface. The $\delta^{15}N_{coral}$ maxima from late 2003 to 2006 were approximately +5.0‰, implying the existence of new nitrogen production. The largest $\delta^{15}N_{coral}$ value of +8.3‰ occurred in February 2003 and is attributed to the $\delta^{15}N_{DIN\text{-}water}$ increasing by isotopic fractionation via phytoplankton in the euphotic zone during a few month vertical mixing with no typhoon upwelling. Concentrations of coralline Ba and Chl-*a* increased in seasons with low SST and in typhoon seasons, which indicated the timing of nitrate supply from the deeper ocean layer. However, high SST might also prevent the upwelling of deeper water. The sea surface then becomes nutrient poor, triggering N_2 fixation in the sea surface and in the coral reef. Mixing of the $\delta^{15}N_{DIN}$ from the deeper ocean layer (+5‰~) and N_2 fixation (−2~0‰) made the $\delta^{15}N_{DIN}$ range from 0 to +5‰ in the surface water, which yielded low $\delta^{15}N_{coral}$.

5. Conclusions

[21] We presented seasonal variations of $\delta^{15}N_{coral}$ compared with coralline Ba/Ca, skeletal δ^{13}C, and detailed observation data - SST, Chl-a, OLR, and typhoon records. In Okinotori Island, $\delta^{15}N_{coral}$ and SST had an inverse rela-

tionship seasonally and inter-annually from 2002 to 2004. This result suggested that nitrate in ocean surface was supplied by vertical mixing from cold ^{15}N-rich water from deeper layer and by N_2 fixation due to nutrient deficiency in high SST. Transient upwelling with typhoons could influence $\delta^{15}N_{coral}$ changes depending on typhoon frequency and wind strength in Okinotori Island. Although preservation of organic matter required examining for further works to apply $\delta^{15}N_{coral}$ to long cores or fossils, this study suggested that $\delta^{15}N_{coral}$ record nutrient dynamics in open oceans for decade to millennia scales.

[22] **Acknowledgments.** We acknowledge Chika Sakata and Tomohisa Irino for their analyses of carbon and oxygen isotopes. Sampling of Okinotori coral took place with the help of the crew on R/V *Hakuhoumaru* KH-06-2. Coral identification was performed with the guidance of Toru Nakamori. Slabs of the specimen were made with the technical support of Hidehiko Nomura and Kousuke Nakamura. Hiroshi Ogawa tendered the data for the vertical distribution of nutrients at Station 5-1. We really thank the helpful comments of Associate Editor, two reviewers, and Dennis Baldocchi, Editor of *Journal of Geophysical Research-Biogeosciences*.

References

Alibert, C., and L. Kinsley (2008a), A 170-year Sr/Ca and Ba/Ca coral record from the western Pacific warm pool: 1. What can we learn from an unusual coral record?, *J. Geophys. Res.*, *113*, C04008, doi:10.1029/2006JC003979.

Alibert, C., and L. Kinsley (2008b), A 170-year Sr/Ca and Ba/Ca coral record from the western Pacific warm pool: 2. A window into variability of the New Ireland Coastal Undercurrent, *J. Geophys. Res.*, *113*, C06006, doi:10.1029/2007JC004263.

Allemand, D., É. Tambutté, J. P. Girard, and J. Jaubert (1998), Organic matrix synthesis in the scleractinian coral stylophora pistillata: Role in biomineralization and potential target of the organotin tributyltin, *J. Exp. Biol.*, *201*, 2001–2009.

Bell, P. R. F. (1992), Eutrophication and coral reefs—Some examples in the Great Barrier Reef lagoon, *Water Res.*, *26*(5), 553–568, doi:10.1016/0043-1354(92)90228-V.

Capone, D. G., J. A. Burns, J. P. Montoya, A. Subramaniam, C. Mahaffey, T. Gunderson, A. F. Michaels, and E. J. Carpenter (2005), Nitrogen fixation by *Trichodesmium* spp.: An important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, *Global Biogeochem. Cycles*, *19*, GB2024, doi:10.1029/2004GB002331.

Carpenter, E., H. Harvey, B. Fry, and D. Capone (1997), Biogeochemical tracers of the marine cyanobacterium Trichodesmium, *Deep Sea Res., Part I*, *44*, 27–38, doi:10.1016/S0967-0637(96)00091-X.

Casciotti, K. L., T. W. Trull, D. M. Glover, and D. Davies (2008), Constraints on nitrogen cycling at the subtropical North Pacific station ALOHA from isotopic measurements of nitrate and particulate nitrogen, *Deep Sea Res., Part II*, *55*, 1661–1672, doi:10.1016/j.dsr2.2008.04.017.

Cline, J. D., and I. R. Kaplan (1975), Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean, *Mar. Chem.*, *3*, 271–299, doi:10.1016/0304-4203(75)90009-2.

Cole, J. E., and R. G. Fairbanks (1990), The Southern Oscillation recorded in the δ^{18}O of corals from Tarawa Atoll, *Paleoceanography*, *5*(5), 669–683, doi:10.1029/PA005i005p00669.

Cuif, J. P., Y. Dauphin, A. Freiwald, P. Gautret, and H. Zibrowius (1999), Biochemical markers of zooxanthellae symbiosis in soluble matrices of skeleton of 24 *Scleractinia* species, *Comp. Biochem. Physiol., Part A*, *123*, 269–278, doi:10.1016/S1095-6433(99)00059-8.

D'Elia, C. F., and C. B. Cook (1988), Methylamine uptake by zooxanthellae-invertebrate symbioses: Insights into host ammonium environment and nutrition, *Limnol. Oceanogr.*, *33*, 1153–1165, doi:10.4319/lo.1988.33.5.1153.

Doney, S. C., N. Mahowald, I. Lima, R. A. Feely, F. T. Mackenzie, J. Lamarque, and P. J. Rasch (2007), Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Proc. Natl. Acad. Sci. U. S. A.*, *104*(37), 14,580–14,585, doi:10.1073/pnas.0702218104.

Dore, J. E., J. R. Brum, L. M. Tupas, and D. M. Karl (2002), Seasonal and interannual variability in sources of nitrogen supporting export in the oligotrophic subtropical North Pacific Ocean, *Limnol. Oceanogr.*, *47*, 1595–1607, doi:10.4319/lo.2002.47.6.1595.

Duce, R. A., et al. (2008), Impacts of atmospheric anthropogenic nitrogen on the open ocean, *Science*, *320*, 893–897, doi:10.1126/science.1150369.

Fabricius, K. E. (2005), Effects of terrestrial runoff on the ecology of corals and coral reefs: Review and synthesis, *Mar. Pollut. Bull.*, *50*, 125–146, doi:10.1016/j.marpolbul.2004.11.028.

Fairbanks, R. G., and R. E. Dodge (1979), Annual periodicity of the ^{18}O/^{16}O and ^{13}C/^{12}C ratios in the coral *Montastraea annularis*, *Geochim. Cosmochim. Acta*, *43*, 1009–1020, doi:10.1016/0016-7037(79)90090-5.

Fork, D. C., and A. W. D. Larkum (1989), Light harvesting in the green alga *Ostreobium* sp., a coral symbiont adapted to extreme shade, *Mar. Biol. Berlin*, *103*, 381–385, doi:10.1007/BF00397273.

Genin, A., and G. W. Boehlert (1985), Dynamics of temperature and chlorophyll structures above a seamount: An oceanic experiment, *J. Mar. Res.*, *43*, 907–924, doi:10.1357/002224085788453868.

Grottoli, A. G. (2002), Effect of light and brine shrimp on skeletal δ^{13}C in the Hawaiian coral *Porties compressa*: A tank experiment, *Geochim. Cosmochim. Acta*, *66*, 1955–1967, doi:10.1016/S0016-7037(01)00901-2.

Grottoli, A. G., and G. M. Wellington (1999), Effect of light and zooplankton on skeletal δ^{13}C values in the eastern Pacific corals *Pavona clavus* and *Pavona gigantean*, *Coral Reefs*, *18*, 29–41, doi:10.1007/s003380050150.

Hastings, M. G., D. M. Sigman, and F. Lipschultz (2003), Isotopic evidence for source changes of nitrate in rain at Bermuda, *J. Geophys. Res.*, *108*(D24), 4790, doi:10.1029/2003JD003789.

Heikoop, J. M., J. J. Dunn, M. J. Risk, I. M. Sandeman, H. P. Schwarcz, and N. Waltho (1998), Relationship between light and the δ^{15}N of coral tissue: Examples from Jamaica and Zanzibar, *Limnol. Oceanogr.*, *43*, 909–920, doi:10.4319/lo.1998.43.5.0909.

Heikoop, J. M., M. J. Risk, A. V. Lazierb, E. N. Edinger, J. Jompa, G. V. Limmon, J. J. Dunn, D. R. Broune, and H. P. Schwarcz (2000), Nitrogen-15 signals of anthropogenic nutrient loading in reef corals, *Mar. Pollut. Bull.*, *40*, 628–636, doi:10.1016/S0025-326X(00)00006-0.

Hoering, T., and H. T. Ford (1960), The isotope effect in the fixation of nitrogen by Azotobacter, *J. Am. Chem. Soc.*, *82*, 376–378, doi:10.1021/ja01487a031.

Ingalls, A. E., C. Lee, and E. R. M. Druffel (2003), Preservation of organic matter in mound-forming coral skeletons, *Geochim. Cosmochim. Acta*, *67*, 2827–2841, doi:10.1016/S0016-7037(03)00079-6.

Karl, D., R. Letelier, L. Tupas, J. Dore, J. Christian, and D. Hebel (1997), The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, *388*, 533–538, doi:10.1038/41474.

Knapp, A. N., P. J. DiFiore, C. Deutsch, D. M. Sigman, and F. Lipschultz (2008), Nitrate isotopic composition between Bermuda and Puerto Rico: Implications for N_2 fixation in the Atlantic Ocean, *Global Biogeochem. Cycles*, *22*, GB3014, doi:10.1029/2007GB003107.

Larkum, A. W. D., I. R. Kennedy, and W. J. Muller (1988), Nitrogen fixation on a coral reef, *Mar. Biol. Berlin*, *98*, 143–155, doi:10.1007/BF00392669.

LaVigne, M., M. P. Field, E. Anagnostou, A. G. Grottoli, G. M. Wellington, and R. M. Sherrell (2008), Skeletal P/Ca tracks upwelling in Gulf of Panamá coral: Evidence for a new seawater phosphate proxy, *Geophys. Res. Lett.*, *35*, L05604, doi:10.1029/2007GL031926.

Lea, D. W., D. T. Shen, and E. A. Boyle (1989), Coralline barium records temporal variability in equatorial Pacific upwelling, *Nature*, *340*, 373–376, doi:10.1038/340373a0.

Lesser, M. P., C. H. Mazel, M. Y. Gorbunov, and P. G. Falkowski (2004), Discovery of symbiotic nitrogen-fixing cyanobacteria in corals, *Science*, *305*, 997–1000, doi:10.1126/science.1099128.

Lesser, M. P., L. I. Falcón, A. Rodríguez-Román, S. Enríquez, O. Hoegh-Guldberg, and R. Iglesias-Prieto (2007), Nitrogen fixation by symbiotic cyanobacteria provides a source of nitrogen for the scleractinian coral *Montastraea cavernosa*, *Mar. Ecol. Prog. Ser.*, *346*, 143–152, doi:10.3354/meps07008.

Lewis, M. R., W. G. Harrison, N. S. Oakey, D. Herbert, and T. Platt (1986), Vertical nitrate fluxes in the oligotrophic ocean, *Science*, *234*, 870–873, doi:10.1126/science.234.4778.870.

Liebmann, B., and C. A. Smith (1996), Description of a complete (interpolated) outgoing longwave radiation dataset, *Bull. Am. Meteorol. Soc.*, *77*, 1275–1277.

Lin, I., W. T. Liu, C. C. Wu, G. T. F. Wong, C. Hu, Z. Chen, W. D. Liang, Y. Yang, and K. K. Liu (2003), New evidence for enhanced ocean primary production triggered by tropical cyclone, *Geophys. Res. Lett.*, *30*(13), 1718, doi:10.1029/2003GL017141.

Liu, K. K., M. J. Su, C. R. Hsueh, and G. C. Gong (1996), The nitrogen isotopic composition of nitrate in the Kuroshio Water northeast of Taiwan: Evidence for nitrogen fixation as a source of isotopically light nitrate, *Mar. Chem.*, *54*, 273–292, doi:10.1016/0304-4203(96)00034-5.

Lough, J. M., and D. J. Barnes (2000), Environmental controls on growth of the massive coral *Porites*, *J. Exp. Mar. Biol. Ecol.*, *245*, 225–243, doi:10.1016/S0022-0981(99)00168-9.

Marion, G. S., R. B. Dunbar, D. A. Mucciarone, J. N. Kremer, J. S. Lansing, and A. Arthawiguna (2005), Coral skeletal δ^{15}N reveals isotopic traces of an agricultural revolution, *Mar. Pollut. Bull.*, *50*, 931–944, doi:10.1016/j.marpolbul.2005.04.001.

Matthews, K. A., A. G. Grottoli, W. F. McDonough, and J. E. Palardy (2008), Upwelling, species, and depth effects on coral skeletal cadmium-to-calcium ratios (Cd/Ca), *Geochim. Cosmochim. Acta*, *72*, 4537–4550, doi:10.1016/j.gca.2008.05.064.

McClain, C. R., G. C. Feldman, and S. B. Hooker (2004), An overview of the SeaWiFS project and strategies for producing a climate research quality global ocean bio-optical time series, *Deep Sea Res., Part II*, *51*, 5–42, doi:10.1016/j.dsr2.2003.11.001.

McConnaughey, T. (1989a), ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns, *Geochim. Cosmochim. Acta*, *53*, 151–162, doi:10.1016/0016-7037(89)90282-2.

McConnaughey, T. (1989b), ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects, *Geochim. Cosmochim. Acta*, *53*, 163–171, doi:10.1016/0016-7037(89)90283-4.

McConnaughey, T. A., J. Burdett, J. F. Whelan, and C. K. Paull (1997), Carbon isotopes in biological carbonates: Respiration and photosynthesis, *Geochim. Cosmochim. Acta*, *61*, 611–622, doi:10.1016/S0016-7037(96)00361-4.

Minagawa, M., and E. Wada (1984), Stepwise enrichment of ^{15}N along food chains: Further evidence and the relation between δ^{15}N and animal age, *Geochim. Cosmochim. Acta*, *48*, 1135–1140, doi:10.1016/0016-7037(84)90204-7.

Minagawa, M., and E. Wada (1986), Nitrogen isotope ratios of red tide organisms in the East China Sea: A characterization of biological nitrogen fixation, *Mar. Chem.*, *19*, 245–259, doi:10.1016/0304-4203(86)90026-5.

Mitterer, R. M. (1978), Amino acid composition and metal binding capability of the skeletal protein of corals, *Bull. Mar. Sci.*, *28*(1), 173–180.

Muscatine, L., and I. R. Kaplan (1994), Resource partitioning by reef corals as determined from stable isotope composition. II. ^{15}N of symbiotic dinoflagellates and animal tissue versus depth, *Pac. Sci.*, *48*, 304–312.

Muscatine, L., J. W. Porter, and I. R. Kaplan (1989), Resource partitioning by reef corals as determined from stable isotope composition. I. d^{13}C of zooxanthellae and animal tissue vs depth, *Mar. Biol. Berlin*, *100*, 185–193, doi:10.1007/BF00391957.

Muscatine, L., C. Goiran, L. Land, J. Jaubert, J. P. Cuif, and D. Allemand (2005), Stable isotopes (δ^{13}C and δ^{15}N) of organic matrix from coral skeleton, *Proc. Natl. Acad. Sci. U. S. A.*, *102*(5), 1525–1530, doi:10.1073/pnas.0408921102.

Odum, H. T., and E. P. Odum (1955), Trophic structure and productivity of a windward coral reef community on Eniwetok Atoll, *Ecol. Monogr.*, *25*(3), 291–320, doi:10.2307/1943285.

Ogawa, N. O., T. Nagata, H. Kitazato, and N. Ohkouchi (2010), Ultra-sensitive elemental analyzer/isotope ratio mass spectrometer for stable nitrogen and carbon isotope analyses, in *Earth, Life and Isotopes*, edited by N. Ohkouchi et al., pp. 339–353, Kyoto Univ. Press, Japan.

Ohkouchi, N., Y. Nakajima, H. Okada, N. O. Ogawa, H. Suga, K. Oguri, and H. Kitazato (2005), Biogeochemical processes in a meromictic lake Kaiike: Implications from carbon and nitrogen isotopic compositions of photosynthetic pigments, *Environ. Microbiol.*, *7*, 1009–1016, doi:10.1111/j.1462-2920.2005.00772.x.

Owens, N. J. P. (1985), Variations in the natural abundance of ^{15}N in estuarine suspended particulate matter: A specific indicator of biological processing, *Estuarine Coastal Shelf Sci.*, *20*, 505–510, doi:10.1016/0272-7714(85)90092-7.

Paerl, H. W., and M. L. Fogel (1994), Isotopic characterization of atmospheric nitrogen inputs as sources of enhanced primary production in coastal Atlantic Ocean waters, *Mar. Biol. Berlin*, *119*, 635–645, doi:10.1007/BF00354328.

Peterson, B. J., and B. Fry (1987), Stable isotopes in ecosystem studies, *Annu. Rev. Ecol. Syst.*, *18*, 293–320, doi:10.1146/annurev.es.18.110187.001453.

Price, J. F. (1981), Upper ocean response to a hurricane, *J. Phys. Oceanogr.*, *11*, 153–175, doi:10.1175/1520-0485(1981)011<0153:UORTAH>2.0.CO;2.

Rahav, O., Z. Dubinsky, Y. Achituv, and P. G. Falkowski (1989), Ammonium metabolism in the zooxanthellate coral, *Stylophora pistillata*, *Proc. R. Soc. London, Ser. B*, *236*, 325–337, doi:10.1098/rspb.1989.0026.

Reynaud-Vaganay, S., A. Juillet-Leclerc, J. Jaubert, and J. P. Gattuso (2001), Effect of light on skeletal δ^{13}C and δ^{18}O, and interaction with photosynthesis, respiration and calcification in two zooxanthellate scleractinian corals, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *175*, 393–404, doi:10.1016/S0031-0182(01)00382-0.

Risk, M. J., P. W. Sammarco, and H. P. Schwarcz (1994), Cross-continental shelf trends in δ^{13}C in coral on the Great Barrier Reef, *Mar. Ecol. Prog. Ser.*, *106*, 121–130, doi:10.3354/meps106121.

Sammarco, P. W., M. J. Risk, H. P. Schwarcz, and J. M. Heikoop (1999), Cross-continental shelf trends in coral δ^{15}N on the Great Barrier Reef: Further consideration of the reef nutrient paradox, *Mar. Ecol. Prog. Ser.*, *180*, 131–138, doi:10.3354/meps180131.

Shen, G. T., E. A. Boyle, and D. W. Lea (1987), Cadmium in corals as a tracer of historical upwelling and industrial fallout, *Nature*, *328*, 794–796, doi:10.1038/328794a0.

Shen, G. T., T. M. Campbell, R. B. Dunbar, G. M. Wellington, M. W. Colgan, and P. W. Glynn (1991), Paleochemistry of manganese in corals from the Galapagos Islands, *Coral Reefs*, *10*, 91–100, doi:10.1007/BF00571827.

Shen, G. T., J. E. Cole, D. W. Lea, L. J. Linn, T. A. McConnaughey, and R. G. Fairbanks (1992), Surface ocean variability at Galapagos from 1936–1982: Calibration of geochemical tracers in corals, *Paleoceanography*, *7*(5), 563–588, doi:10.1029/92PA01825.

Shirai, K., T. Kawashima, K. Sowa, T. Watanabe, T. Nakamori, N. Takahata, H. Amakawa, and Y. Sano (2008), Minor and trace element incorporation into branching coral *Acropora nobilis* skeleton, *Geochim. Cosmochim. Acta*, *72*, 5386–5400, doi:10.1016/j.gca.2008.07.026.

Shupe, M. D., and J. M. Intrieri (2004), Cloud radiative forcing of the arctic surface: The influence of cloud properties, surface albedo, and solar zenith angle, *J. Clim.*, *17*, 616–628, doi:10.1175/1520-0442(2004)017<0616:CRFOTA>2.0.CO;2.

Sigman, D. M., M. A. Altabet, D. C. McCorkle, R. Francois, and G. Fischer (1999), The δ^{15}N of nitrate in the southern ocean: Consumption of nitrate in surface waters, *Global Biogeochem. Cycles*, *13*, 1149–1166, doi:10.1029/1999GB900038.

Sigman, D. M., J. Granger, P. J. DiFiore, M. M. Lehmann, R. Ho, G. Cane, and A. van Geen (2005), Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin, *Global Biogeochem. Cycles*, *19*, GB4022, doi:10.1029/2005GB002458.

Sinclair, D. J., L. P. J. Kinsley, and M. T. McCulloch (1998), High resolution analysis of trace elements in corals by laser ablation ICP-MS, *Geochim. Cosmochim. Acta*, *62*, 1889–1901, doi:10.1016/S0016-7037(98)00112-4.

Swart, P. K. (1983), Carbon and oxygen isotope fractionation in scleractinian corals: A review, *Earth Sci. Rev.*, *19*, 51–80, doi:10.1016/0012-8252(83)90076-4.

Szmant, A. M. (2002), Nutrient enrichment on coral reefs: Is it a major cause of coral reef decline?, *Estuaries Coasts*, *25*(4), 743–766, doi:10.1007/BF02804903.

Toratani, M. (2008), Primary production enhancement by typhoon Ketsana in 2003 in western North Pacific, *Proc. SPIE Int. Soc. Opt. Eng.*, *7150*, 715013, doi:10.1117/12.806426.

Uchida, A., M. Nishizawa, K. Shirai, H. Iijima, H. Kayanne, N. Takahata, and Y. Sano (2008), High sensitivity measurements of nitrogen isotopic ratios in coral skeletons from Palau, western Pacific: Temporal resolution and seasonal variation of nitrogen sources, *Geochem. J.*, *42*, 255–262, doi:10.2343/geochemj.42.255.

Watanabe, T., A. Winter, and T. Oba (2001), Seasonal changes in sea surface temperature and salinity during the Little Ice Age in the Caribbean Sea deduced from Mg/Ca and ^{18}O/^{16}O ratios in corals, *Mar. Geol.*, *173*, 21–35, doi:10.1016/S0025-3227(00)00166-3.

Wiebe, W. J., R. E. Johannes, and K. L. Webb (1975), Nitrogen fixation in a coral reef community, *Science*, *188*, 257–259, doi:10.1126/science.188.4185.257.

Yamamuro, M., H. Kayanne, and M. Minagawa (1995), Carbon and nitrogen stable isotopes of primary producers in coral reef ecosystems, *Limnol. Oceanogr.*, *40*, 617–621, doi:10.4319/lo.1995.40.3.0617.

Young, S. D. (1971), Organic material from scleractinian coral skeletons—I. Variation in composition between several species, *Comp. Biochem. Physiol., Part B*, *40*, 113–120.

N. O. Ogawa and N. Ohkouchi, Institute of Biogeosciences, Japan Agency for Marine-Earth Science and Technology, 2-15 Natsushima-cho, Yokosuka 237-0061, Japan.

K. Shirai, Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1, Bunkyo-ku, Tokyo 133-0033, Japan.

M. Toratani, School of Engineering, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan.

M. Uematsu, Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa-shi, Chiba 277-8568, Japan.

T. Watanabe and A. Yamazaki, Department of Natural History Sciences, Graduate School of Science, Hokkaido University, N10W8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan. (zaki@mail.sci.hokudai.ac.jp)