Front. Earth Sci.
DOI 10.1007/s11707-015-0503-x

RESEARCH ARTICLE

Patterns of coccolithophore pigment change under global acidification conditions based on *in-situ* observations at BATS site between July 1990–Dec 2008

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Abstract Coccolith production is an important part of the biogenic carbon cycle as the largest source of calcium carbonate on earth, accounting for about 75% of the deposition of carbon on the sea floor. Recent studies based on laboratory experiment results indicated that increasing anthropogenic CO_2 in the atmosphere triggered global ocean acidification leading to a decrease of calcite or aragonite saturation and calcium carbonate, and to decreasing efficiency of carbon export/pumping to deep layers. In the present study, we analyzed about 20 years of field observations of coccolithophore pigment, dissolved inorganic carbon (DIC), nutrients, and temperatures from the Bermuda Atlantic Time-series Study (BATS) site and satellite remote sensing to investigate the variable tendency of the coccolithophore pigment, and to evaluate the influence of ocean acidification on coccolithophore biomass. The results indicated that there was a generally increasing tendency of coccolithophore pigment, coupled with increasing bicarbonate concentrations or decreasing carbonate ion concentration. The change of coccolithophore pigment was also closely associated with pH, nutrients, mixed layer depth (MLD), and temperature. Correlation analyses between coccolithophores and abiotic parameter imply that coccoliths production or coccolithophore pigment has increased with increasing acidification in the recent 20 years.

Keywords dissolved inorganic carbon, BATS, MLD, coccolithophore pigments, the Bermuda

1 Introduction

Marine biogeochemical processes are largely controlled by phytoplankton because phytoplankton forms the basis of the food chain and affects sea surface CO_2 through photosynthesis. The biological carbon pump is one of the most important processes reducing CO_2 from the atmosphere through uptake of CO_2 and deposition of organic carbon to the deep ocean. It is very important to investigate the influence of increasing CO_2 on phytoplankton production and deposition of particle inorganic carbon (PIC) and particle organic carbon (POC) in the context of ocean acidification. Coccolithophores (or coccolithophorids) are single-cell algae, protists, and phytoplankton. They are distinguished by special calcium carbonate plates (or scales) called coccoliths, which are main sources forming microfossils. Coccolithophores are widely distributed in oceans and are observed in large numbers throughout the surface euphotic zone of the oceans (Heimdal, 1983). Thus coccolithophore plays an important role in the biogenic carbon cycle (Westbroek et al., 1985), with its production accounting for about 75% of the deposition of carbon on the sea floor having a marine origin, and as the largest source of calcium carbonate on earth (Honjo, 1986, 1990; Groom and Holligan, 1987). From the mid-Mesozoic, coccolithophores have been major calcium carbonate producers in the world's oceans, today accounting for about two-thirds of the total marine $CaCO_3$ production.

With increasing anthropogenic CO_2 in the world, ocean acidification, and global warming in response to rising atmospheric CO_2, partial pressures have attracted considerable attention from people, governments, scientists, and international organizations. It is widely expected that ocean acidification will reduce calcification or production of phytoplankton. Recent evidence suggests that the

Received August 24, 2014; accepted October 29, 2014

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increased absorption of CO_2 by the oceans, as a result of anthropogenic CO_2 release, will result in decreased calcification by corals, foraminifera, and coccolithophores (Bijma et al., 1999; Kleypas et al., 1999; Riebesell et al., 2000; Zondervan et al., 2001; Delille et al., 2005; Zeebe et al., 2008). The above viewpoint is rather popular in the world. However, Iglesias-Rodriguez et al. (2008) proved also that calcification and net primary production in the coccolithophore species *Emiliania huxleyi* (*E. huxleyi*) were significantly increased by high CO_2 partial pressures, based on their special laboratory evidence and field evidence from the deep oceans. Moreover, recent studies have already shown that different coccolithophore species exhibit different calcification responses: under increased pCO_2, a decrease in calcification for *E. huxleyi* and *Gephyrocapsa oceanica* (Bijma et al., 1999; Kleypas et al., 1999; Zondervan et al., 2001; Delille et al., 2005), a negligible calcification change with rising pCO_2 for Coccolithus pelagicus; and an increase followed by a decrease in calcification with rising pCO_2 for Calcidiscus leptoporus (Trimborn et al., 2007).

Up to now, scientists have not reached an agreement on responses of Coccolithophere to increasing oceanic acidification. Further, previous studies (Marshall, 1968; Haidar and Thierstein, 2001; Sprengel et al., 2002) are mainly based on laboratory experiments and sparse field surveys with short cultivation periods or relatively short-term *in-situ* observation (Hulburt et al., 1960; Hulburt, 1990; Haidar and Thierstein, 2001) in relatively small regions, respectively. Satellite measurements have been also used in the study of coccolith variations (Strong and Eadie, 1978; Brown, 2000; Cokacar et al., 2004; Oguz and Ediger, 2006), and some interesting results have been presented in recent years. However, few studies were focused on longer-term change in coccolithophore/calcite of the northwest Atlantic Ocean near BATS in the sea surface water, and the possible mechanism of its responses to pH, dissolved inorganic carbon (DIC), nutrients, mixed layer depth (MLD), and sea surface temperature (SST).

Some pigments are exclusive for specific phytoplankton groups and can be used as taxonomic indicators (Jeffrey et al., 1997; Silva et al., 2013). For example, 19′-Hexanoyloxyfucoxanthin (Hex-fuco) (Silva et al., 2013) was used in this study as an indicator of coccolithophores with good positive correlation between Hex-fuco and coccolithophores cell counts ($r = 0.61$, $p < 0.05$) in the middle North Atlantic. In the present study, we plan to investigate seasonal/annual patterns of coccolithophore pigment (CP) using Hex-fuco as an indicator associated with ocean acidification, nutrients, winds, and SST in the Sargasso Sea of the northwest Atlantic Ocean, through analyzing pH, nutrients and MLDs based on relatively longer-term time-series observation data from BATS. Interesting results such as the seasonal and inter-annual variation of CP will be presented, and its responses to ocean acidification will also be discussed.

2 Study area, data and methods

2.1 Study area

Our study area, the Bermuda Atlantic Time-series Study station (BATS) (B in Fig. 1) located 82 km southeast of the island of Bermuda (31°40′N, 64°10′W) in the central northwestern Atlantic Ocean (Fig. 1(a)), belongs to one typical subtropical oceanic climate zone with mild weather all year round. Bottom depth at the BATS deployment area is ~4,680 m. The water column in the study area is stratified in summer, but well mixed in the winter (e.g., Joyce and Robbins, 1996) when mixing depths normally reach 100–200 m (Michaels, 1995). There are large seasonal temperature variations in the study area, generally with highest SST in August (~27.6 °C) and lowest SST in March (~19.1°C). The BATS core cruises consist of a single 4–5 day cruise monthly. On each core cruise, conductivity-temperature-depth profiles and water collections are made at 36–48 depths during a series of 4–7 casts from the surface to 4,200 m. Since June 1994, continuous surface seawater measurements of temperature, salinity, fluorescence, and pCO_2 have been made from a flow-through seawater system (Bates et al., 1998). Between January and April, an extra "bloom cruise" is added to increase sampling frequency to semimonthly during the spring-bloom period. A lot of *in-situ* hydrological-biological measurements have been carried out at BATS. In view of our study area being a typical subtropical region, our study possesses important significance in the investigation of the global carbon sink.

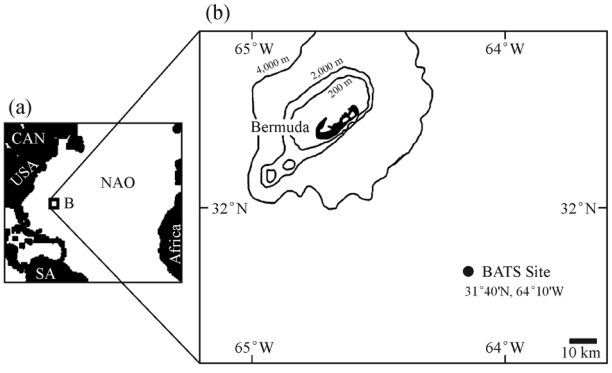

Fig. 1 (a) Location of the study area in the North Atlantic Ocean. (b) Bathymetric and geographic map of Bermuda Atlantic Time Series Study (BATS). CAN, Canada; NAO, North Atlantic Ocean; USA, United States of America; SA: South America.

2.2 Data and observations

In-situ vertical data of pH, nutrients, DIC, total alkaline, Hex-fuco (associated with coccolithophore), sediment fluxes, and algae blooms are derived from the BATS. In the study, we use Hex-fuco as a proxy of coccolithophore concentrations. The observation frequencies of data

were > 2 times per month. Measurements and sampling means have been described in previous works (Gardner, 1977; Knap et al., 1993, 1995; Dore et al., 1996; Bates et al., 1998; Hansell and Carlson, 2001); please refer to http://bats.bios.edu/ for detail.

SeaWiFS-derived Photosynthetic Available Radiation (PAR) data with 9 km resolution are obtained from the Distributed Archive Center of NASA (ftp://oceans.gsc.nasa.gov), which are available from 15 September 1997 to 10 March 2010. Here, monthly PAR data are used to display the depths of monthly CP peaks. ModisA-derived sea surface temperature data are also used with a high resolution (4 km) (ftp://modis.gsfc.nasa.gov/).

2.3 Methods

2.3.1 Time series data and power spectral Analysis

Due to missing values or sparse vertical resolution, data are interpolated into monthly time periods and 10 m vertical intervals. Time series of coccolithophore pigments and temperature were averaged for the depths from 10−150 m. Because of many values with default data or zero between 0−60 m, the time series of nutrients are averaged for 70−150 m. The values for pH, carbonate, and bicarbonate are derived from salinity, DIC, and alkalinity and temperature. We use only surface data of pH, carbonate, and bicarbonate to produce time series. MLD are determined by searching down the water column from 10 m below the sea surface until the sea water density has increased by 0.03 $kg \cdot m^{-3}$. At the same time, we use spectrum average power analysis to display seasonal and annual patterns of CP.

2.3.2 Seasonal pattern

Time series data were further processed into monthly climatologies of CP and abiotic factors based on averages of the data for 1990−2008. The seasonality of CP and abiotic factors were displayed here. The relations between CP and abiotic factors were discussed through analysis of the climatologies.

2.3.3 Time series profiles

Monthly vertical profiles during 1990−2008 were also presented based on CP, CTD temperature for the surface to 150 m, and nutrients for 60−150 m because most nutrients data such as nitrate and phosphate are missing or low in the upper 50 m layers. Due to relatively low concentrations of phosphate and numerous missing values, we only used one nitrate-nitrite profile as an index of nutrients.

2.3.4 Correlation analysis

In order to remove seasonal and periodic signals, and probe into the possible mechanism of CP responses to abiotic factors, we first calculated the differences of all above parameters from monthly climatologies, and then the correlation between CP and other parameters was calculated and analyzed respectively. In the analyses, we limited nutrients data for the upper 60 m layers, because dominant photosynthesis appeared generally in the upper 60 m layer. Finally, based on particulate inorganic carbon (PIC) data derived from MODISA, we also investigated the correlation between the monthly time series of satellite PIC averaged for the small region of 64°W−63°W, 31°N−32°N near BATS and *in-situ* Hex-fuco.

3 Results

3.1 Monthly coccolithophore pigment

The time series (Fig. 2) averaged for the upper 150 m during 1990−2008 indicated evidently the seasonality of CP with peak concentrations in spring (March−April) and lowest in autumn (September−November). An overall trend of increase was observed from 1990−2008. The concentrations increased from 1990−1995, decreased from 1995−2001, and increased again from 2001 to present. Highest values occurred in the spring of 1990 (0.105 $\mu g \cdot kg^{-1}$), 1995 (0.15 $\mu g \cdot kg^{-1}$), and 2006 (0.11 $\mu g \cdot kg^{-1}$), respectively, with lowest concentrations in 2001−2003. Analysis of the power spectrum (Fig. 2(b)) indicated dominant CP variations at one-year and ten-year cycles. In the following subsection, the abiotic time series data (Fig. 3) will be presented to investigate the trend in CP.

The monthly climatologies (Fig. 4) indicated the characteristics of high (low) CP concentration coincided with high (low) bicarbonate, low (high) pH, high (low) DIC, low (high) calcite saturation (Ω), low (high) temperature, and high (low) nitrate. Unlike the relation between CP and nitrate, that between CP and phosphate is not good. In addition, the seasonal peak of phosphate lagged one month compared with nitrate and MLDs.

3.2 Dissolved inorganic carbon, nutrients, and physical conditions

DIC concentration (Fig. 3(a)) shows a trend of increase (Fig. 3(a), left) with a strong seasonal and inter-annual variation (Fig. 3(a), right). There is positive coincidence between DIC and CP: higher DIC concentrations associated with higher CP in late winter–spring, and lower DIC with lower CP in boreal autumn, especially in October. DIC also shows a strong 1-year cycle (Fig. 3(a), right), closely coinciding with that of CP.

Seasonal and annual cycles of MLDs, temperature, and salinity (Figs. 3(b)−3(d)) were evident, with highest temperature, highest salinity, and shallowest MLDs in late summer−early autumn, and the lowest temperature and

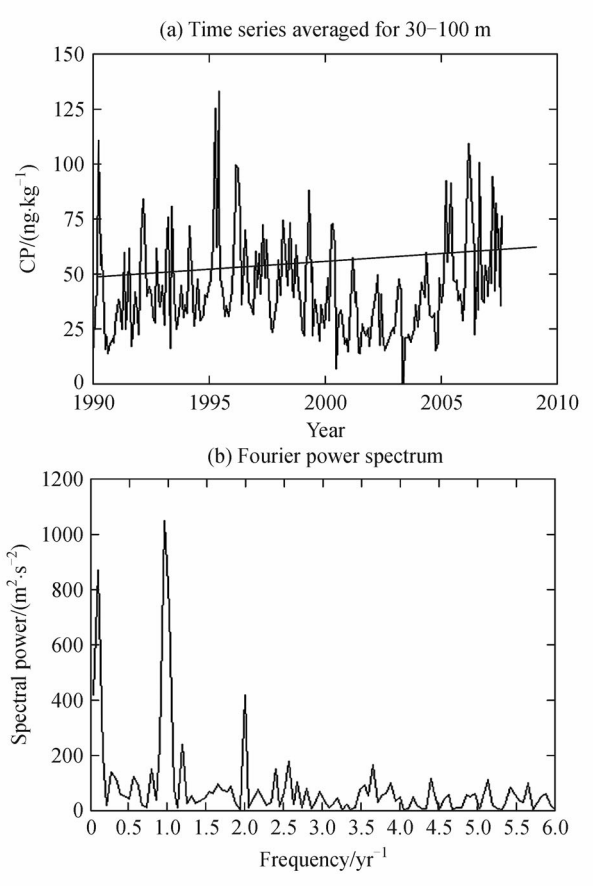

Fig. 2 (a) Time series of coccolithophore and (b) its discrete Fourier power spectrum based on one sample period of 1/12 year.

deepest MLDs in late winter−early spring. Generally, there were higher nutrients with deeper MLDs.

Nutrients (i.e., P, N) revealed approximately an annual cycle and seasonal change (Fig. 3(e)). Especially, the N concentration coincided closely with that of CP with roughly 1 month lag of CP. The ratio of N:P was generally over 16:1. The concentration of P is relatively low, approaching zero in most of the measurement period. However, results of the power spectrum showed that the cycle of 1 year was much stronger than the cycles over 1 year.

3.3 CP, nitrate, and temperature

CP, nitrate, and temperature (Fig. 5) also showed strong vertical difference/variation in the annual cycle from 1990−2008. Monthly peak values (Figs. 4(a), 4(b) and 5) of CP did not appear generally at the surface, but at 40−100 m. Peak values in spring (Figs. 4 and 5) are closer to surface layers. Nitrate is generally very low except in late winter–early spring. Temperature is higher near the surface, except that during the winter−spring period there was uniformly low temperature in the upper layer.

3.4 Analysis of correlation

Through analyses of correlation, CP has a positive relationship (Fig. 6) with bicarbonate ($r = 0.32$, $p < 0.005$), DIC ($r = 0.28$, $p < 0.05$) and nitrate ($r = 0.24$, $p < 0.05$). In contrast, it has a negative relationship with carbonate ($r = 0.24$, $p < 0.05$), pH and Ω ($r = 0.24$, $p < 0.05$). The bicarbonate has a more significant correlation with CP than other abiotic factors.

4 Discussion

4.1 Seasonality and annual tendency in CP

As shown in Figs. 2 and 3, significant seasonal signals were presented in CP, temperature, light, nutrients (here, P and N as the indicators), salinity, pH, and HCO_3^- and CO_3^{2-}. The CP pattern was regulated possibly by seasonal cycles of DIC, nutrients, light, and temperature. Though there was roughly a similar seasonal tendency between CP and nutrients (Figs. 2−4), it was observed that monthly mean nutrients for the upper layer were generally high in winter, in contrast with low CP. The results may be attributed to low sea water temperature and weak light irradiance (Fig. 7) and strong mixing (Figs. 4 and 5), which were probably unfavorable to (restraint) growth of phytoplankton (Haidar and Thierstein, 2001). High nutrients, increasing light irradiance, and increasing stable stratification induced by elevated SST from winters to springs triggered frequent occurrences of seasonal CP peaks in later winters or early springs, implying biophysical influence of abiotic factors on coccolithophore. The present result is consistent with the results of Haidar and Thierstein (2001). Nutrients (Figs. 4(a) and 4(i)) for the upper 60 m are possibly a limiting factor (e.g., [N] < 0.03 μmol·kg^{-1}) from late spring to early winter versus (> 0.1 μmol·kg^{-1}) in winter−spring, leading to monthly CP peak value occurring in the deeper layer outside of the winter−spring transit season. Due to generally low nutrients (Fig. 5) and strong light PAR (Fig. 7) at the surface layer, the monthly peak lies at the deeper layer compared with that in late winter−early spring. Thus, the change in depth of the monthly CP peaks may be attributed to a compromise of nutrients, light irradiance, and sea water temperature.

Considering the fact that there are no strong mesoscale eddies controlling regional dynamics around BATS (Steinberg et al., 2001), we can ignore the influence of upwelling or downwelling triggered by mesoscale eddies. Thus, MLDs triggered by perturbation can be generally treated as a good index of the upper-layer mixing and the uptake of nutrients (Figs. 3(c), 3(e), 4(h), and 4(i); Conte et al., 2001; Haidar and Thierstein, 2001; Steinberg et al., 2001), which was supported by the good correlation ($r = 0.31$, $p < 0.001$) between MLDs and CP (one month lag of

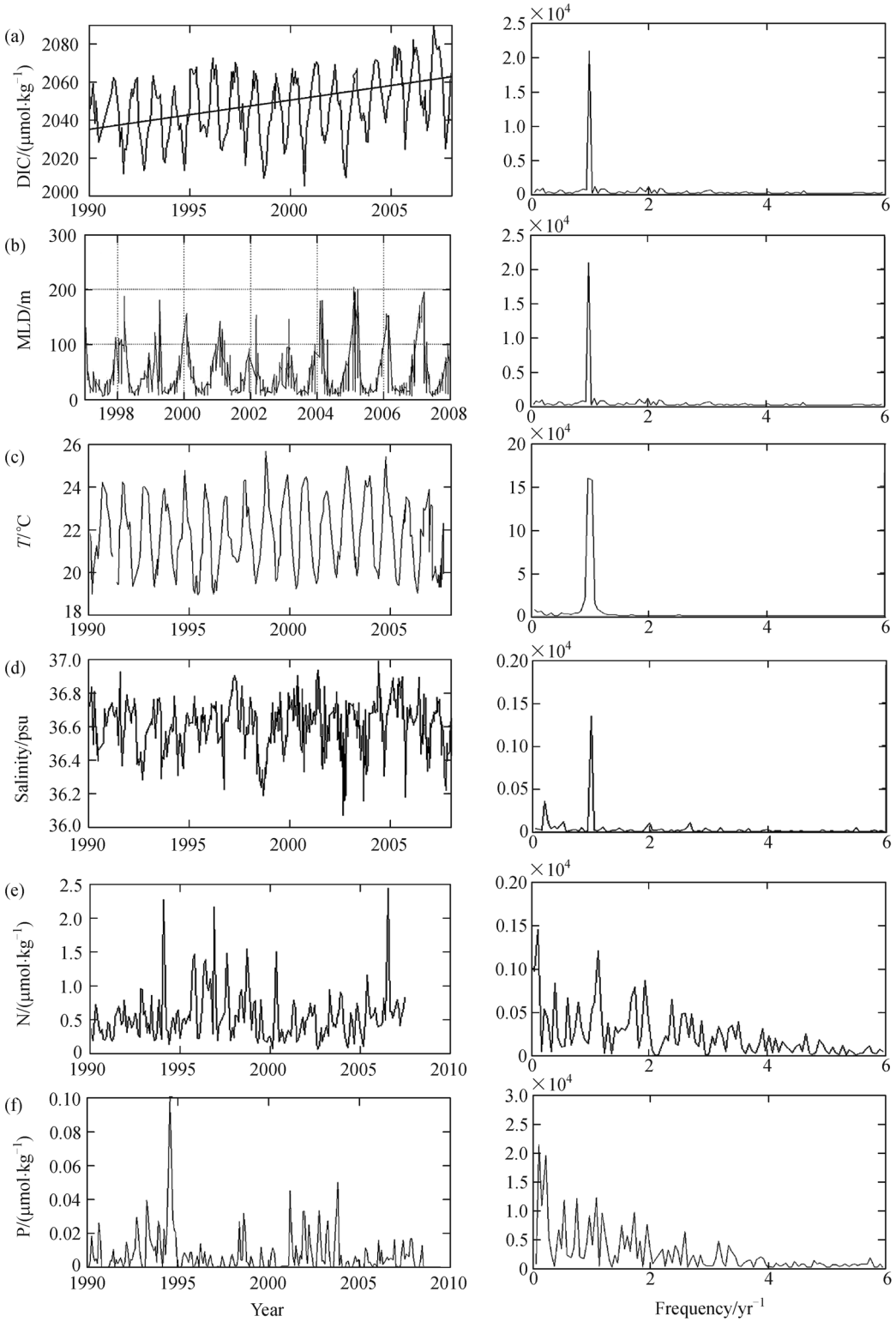

Fig. 3 Time series and power spectrum of abiotic factors (a) dissolved inorganic carbon (μmol·kg^{-1}); (b) mixed layer depth (m); (c) temperature (°C); (d) salinity; (e) nitrate and nitrite (μmol·kg^{-1}); (f) phosphate (μmol·kg^{-1}). Left: time series; right: power spectrum based on detrended data.

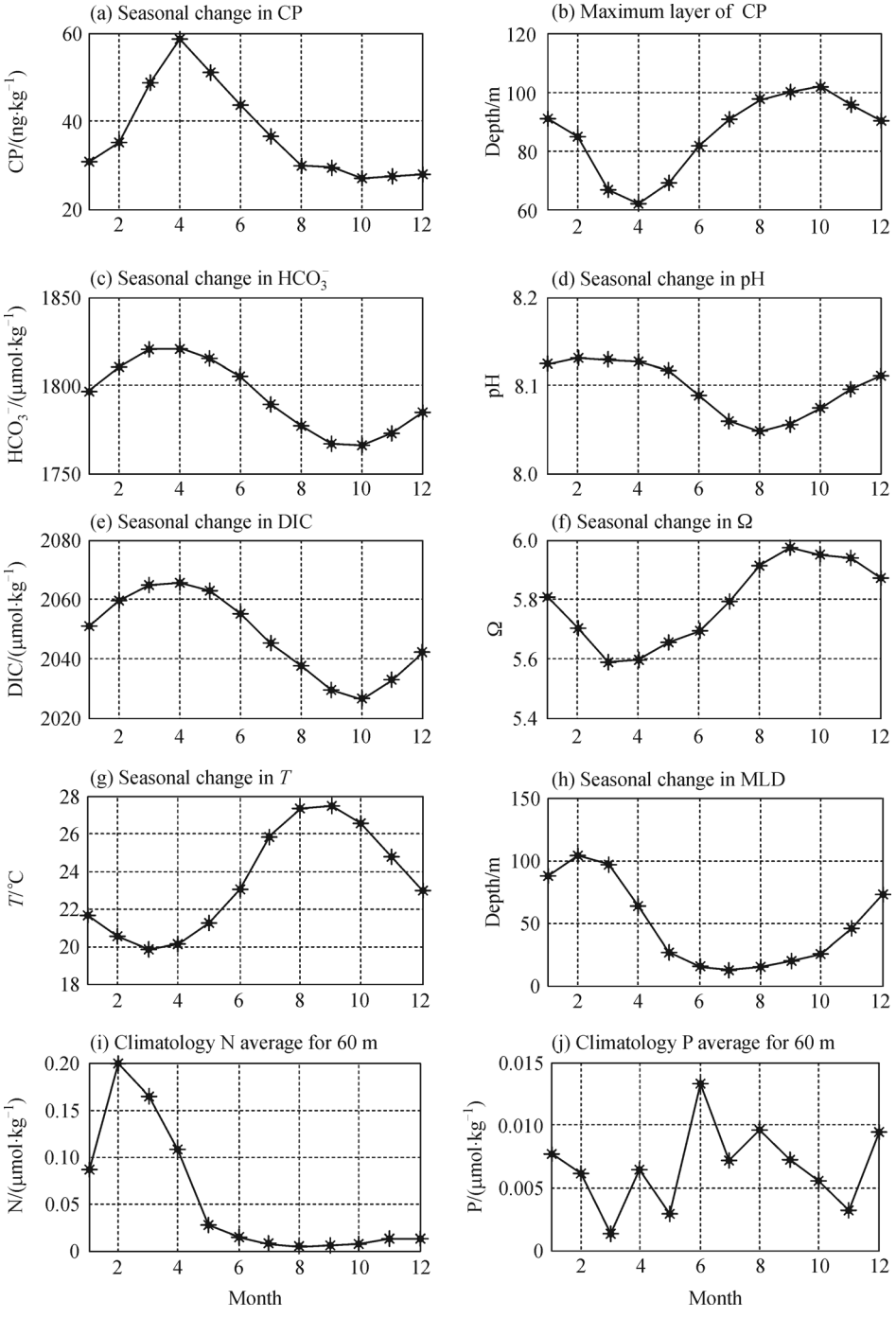

Fig. 4 Monthly climatologies of biophysical factors. (a) Coccolithophore pigments (CP) (ng·kg^{-1}); (b) depth of CP peak (m); (c) bicarbonate (μmol·kg^{-1}); (d) pH; (e) DIC (μmol·kg^{-1}); (f) calcite saturation Ω; (g) sea surface temperature (at 10 m) (°C); (h) MLD (m); (i) nitrate and nitrite (μmol·kg^{-1}) averaged for the upper 60 m; (j) phosphate (μmol·kg^{-1}) averaged for the upper 60 m.

CP). Better coincidence between CP and MLDs may reflect the uptake and entrainment of nutrients from below the eutrophic layer. However, due to consumption of phytoplankton photosynthesis, present nutrients in stock cannot represent synchronous phytoplankton biomass, leading to relatively weak correlation ($r = 0.24$, $p < 0.001$) between CP and nutrients (nitrate and nitrite) compared with that between CP and MLDs.

4.2 Influence of DIC, light, temperature, and nutrients on CP

Recent evidence has shown that increased absorption of CO_2 by the oceans as a result of anthropogenic CO_2 release will result in decreased calcification by coccolithophores (Riebesell, et al., 2000; Zondervan et al., 2001; Delille et al., 2005). However, Iglesias-Rodriguez et al. (2008)

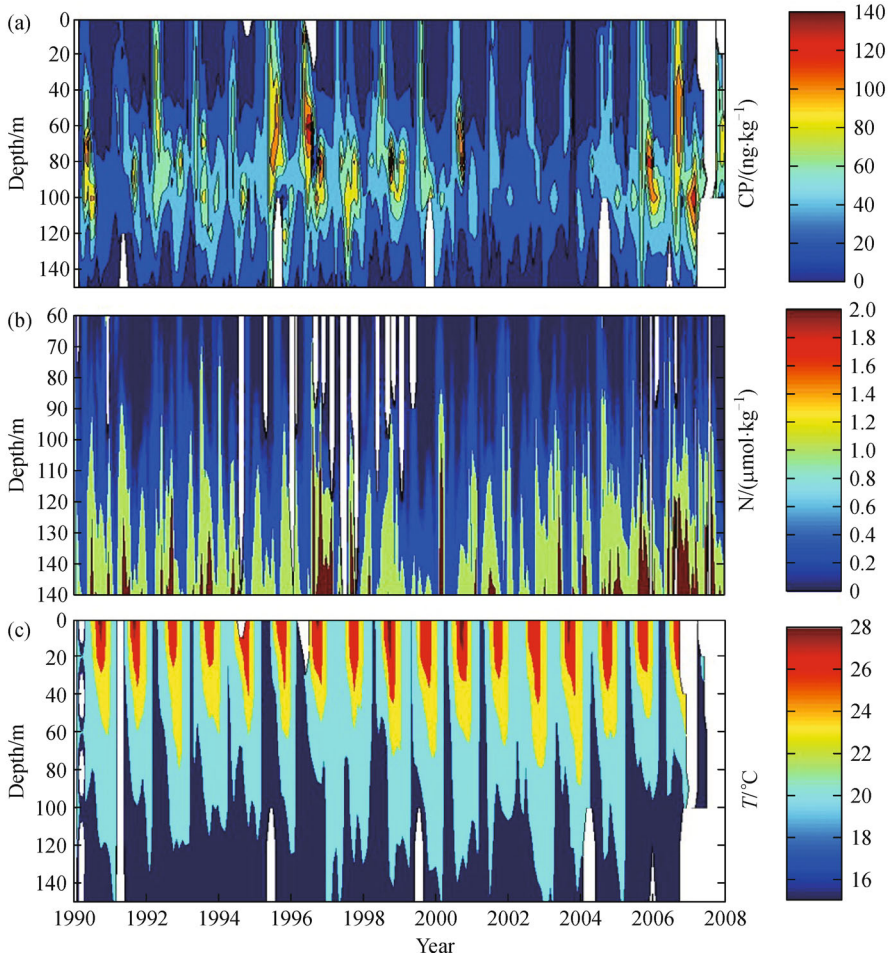

Fig. 5 Depth-time plot from 1990−2008. (a) Coccolithophore pigments (CP); (b) the total N of NO_3^- and NO_2^- (μmol·kg^{-1});

suggested that some coccolithophore species increased significantly due to high CO_2 partial pressures or ocean acidification. Our results showed that a decreasing pH value could trigger a high biomass of coccolithophore consistent with the conclusion of Iglesias-Rodriguez et al. (2008). The previous studies about change of coccolithophore species with CO_2 were mainly laboratory based experiments which had obvious differences with real oceanic conditions. In particular, coccolithophore species experienced more periods to adapt to ocean acidification or pH changes in real oceans, compared with short culture times and sharp ocean acidification conditions. Furthermore, experimental designs did not consider the adaptation to changing carbonate chemistry. In contrast, the experimental methods of Iglesias-Rodriguez et al. (2008) were close to real ocean structures of dissolved inorganic carbon reported in recent studies. Thus gradual ocean acidifications will possibly trigger increasing coccolithophore production according to our present data.

Langer et al. (2006) proved that coccolith morpholoyies did not present any evidence of significantly incomplete or malformed coccolith in the last glacial maximum and Holocene sediments according to analysis of sediment records samples before the lysocline in the Atlantic Ocean, suggesting adaptation of coccolithophore calcification to changing CO_2 concentrations in natural upper oceans. In other words, some species of coccolithophores have adapted their calcification mechanism to changes in carbonate chemistry which occurred since the last glacial maximum. The significant discrepancy of coccolith morphology between experimental and geological results (Langer et al., 2006) also indicated the experimental flaws can't reflect the adaptation of coccolithophore and possible products in real oceans. This indicated the importance of *in-situ* observations in the oceans. There were generally higher DIC concentrations during high CP periods. However, it was inconsistent in 1995 when there were low DIC and high CP. This is the reason that Haidar and Thierstein (2001) found there was a negative relation between DIC and CP at the same BATS using 3-years in-situ observations, opposite to our findings.

In highly calcifying cells of *E. huxleyi* HCO_3^- is the substrate for calcification (Nimer and Merrett, 1992) that can be schematically represented as follows:

$$2HCO_3^- + Ca^{2+} \leftrightarrow H_2O + CaCO_3 + CO_2.$$

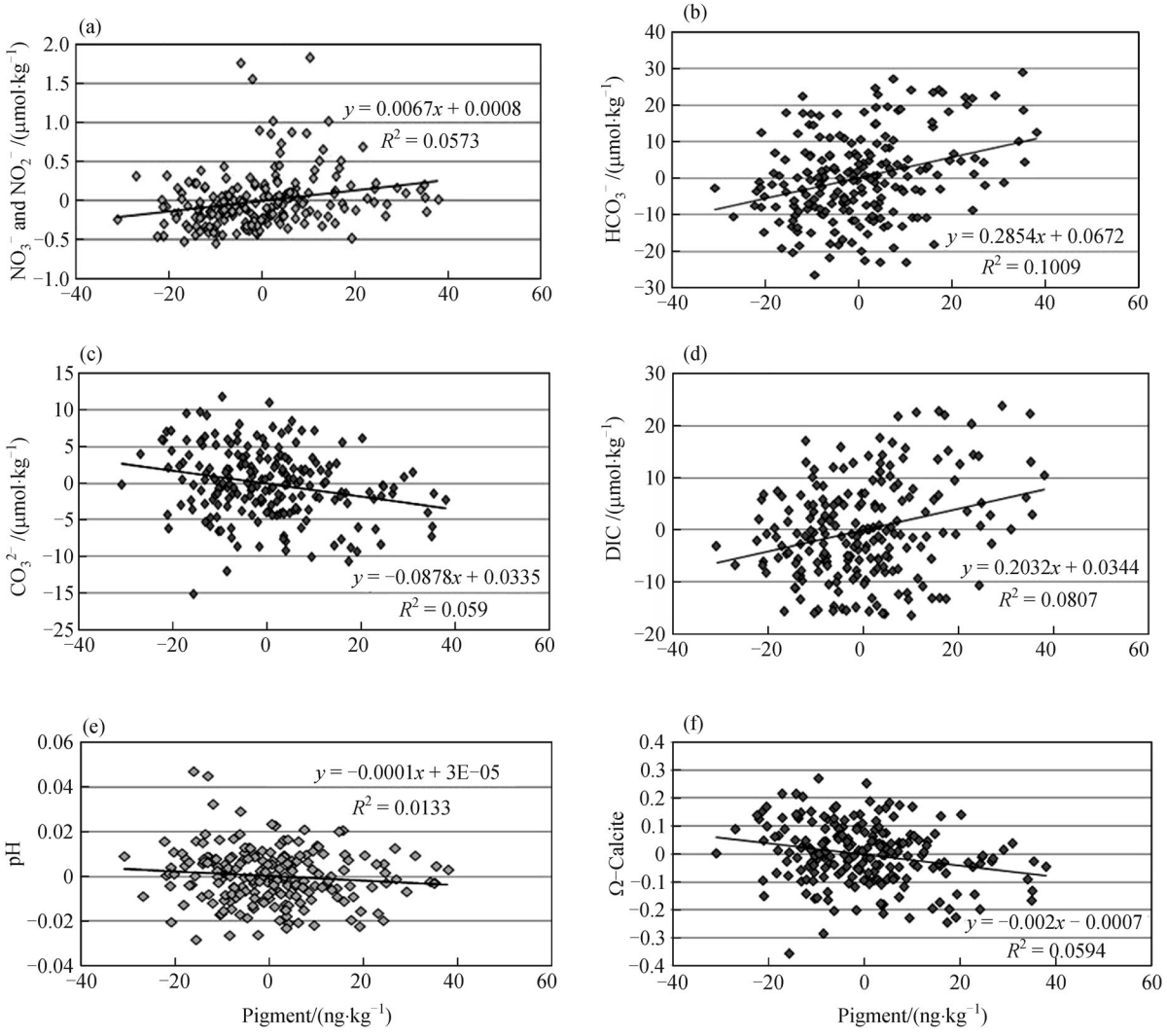

Fig. 6 Scatter diagrams between coccolithophore pigment and abiotic factors. Data used here are detrended. (a) CP *vs* NO_3^- and NO_2^-; (b) CP *vs* HCO_3^-; (c) CP *vs* CO_3^{2-}; (d) CP *vs* DIC; (e) CP *vs* pH; (f) CP *vs* Ω.

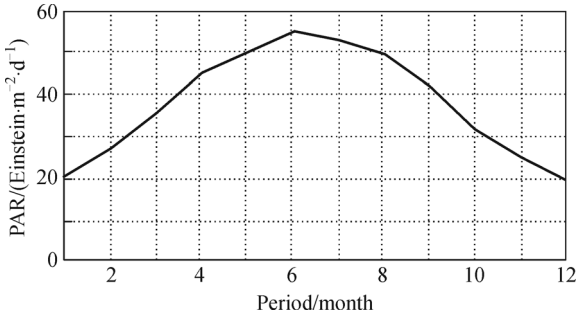

Fig. 7 Climatology of surface photosynthesis available radiance (PAR) (Einstein·m^{-2}·d^{-1}).

This reaction results in intracellular production of CO_2, which is closely coupled (i.e., ratio of C:P $\approx$ 1.0) to photosynthetic assimilation within the cell (Crawford and Purdie, 1997). The increase of [HCO_3^-] with ocean acidification induces possibly the above Chemical equilibrium moving the right side, producing more calcium carbonate, consistent with our preliminary results (Fig. 6 (b)). The speculation was also supported by the experimental results of Langer et al. (2006). Studies (Riebesell et al., 2000; Zondervan et al., 2001; Delille et al., 2005) from experimental results which demonstrated that different species of coccolithophores or species in different regions have different responses to changes in ocean acidifications. Thus, our study may only represent the characteristics of coccolithophore pigment change near BATS, not globally.

In order to further investigate the influence of oceanic acidification, we compared the pigments concentration in the same period. The results also showed that higher [HCO_3^-] corresponded with higher coccolithophore pigments. Furthermore, the fact that seasonal changes of DIC

(Fig. 3(a)) were stronger than the inter-annual signal can also suggest that phytoplankton may probably adapt to the environment of ocean acidifications and changes of anthropogenic CO_2 at the present rate due to relative slow inter-annual changes compared with seasonal changes in this region.

19'-Hexanoyloxyfucoxanthin exists widely in pelagophyceae and prymnesiophyceae including coccolithophore, which may lead to wrong results if 19'-Hexanoyloxyfucoxanthin is used as an indicator of coccolithophore. However, phytoplankton from pelagophyceae (Lochhead et al., 2001; Silva et al., 2013) is not dominant in our study area; the influence of the phytoplankton pigment out of coccolithophore can be neglected in our study. Moreover, the good correlation ($r = 0.65$, $p < 0.05$) presented between the MODIS-derived particulate inorganic carbon data and Hexfuco (Fig. 8) suggested that Hexfuco can be used as a good indicator of coccolithophore in our region. In addition, we calculated the $CaCO_3$ flux using 200-m fluxes of mass, particulate organic carbon (POC), and particulate organic nitrogen (PON) according to the Redfield ratio of C:N:P (106:16:1) and the ratio of C:O:H (12:16:2), given negligible contribution of other elements than the above to the total mass fluxes. This is reasonable because diatom algae are not a dominant species in the region. The results calculated

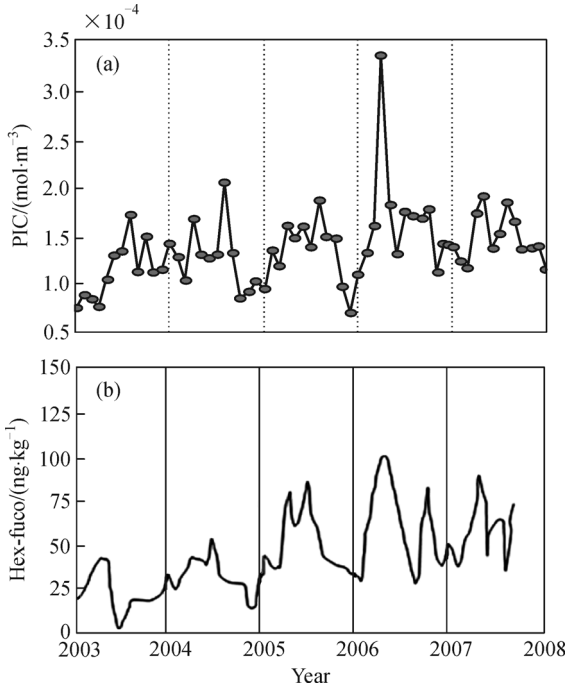

Fig. 8 (a) Satellite-derived particulate inorganic carbon (PIC) and (b) 19'-Hexanoyloxyfucoxanthin (Hex-fuco).

showed a similar tendency (Fig. 9) ($r = 0.21$, $p < 0.001$) to

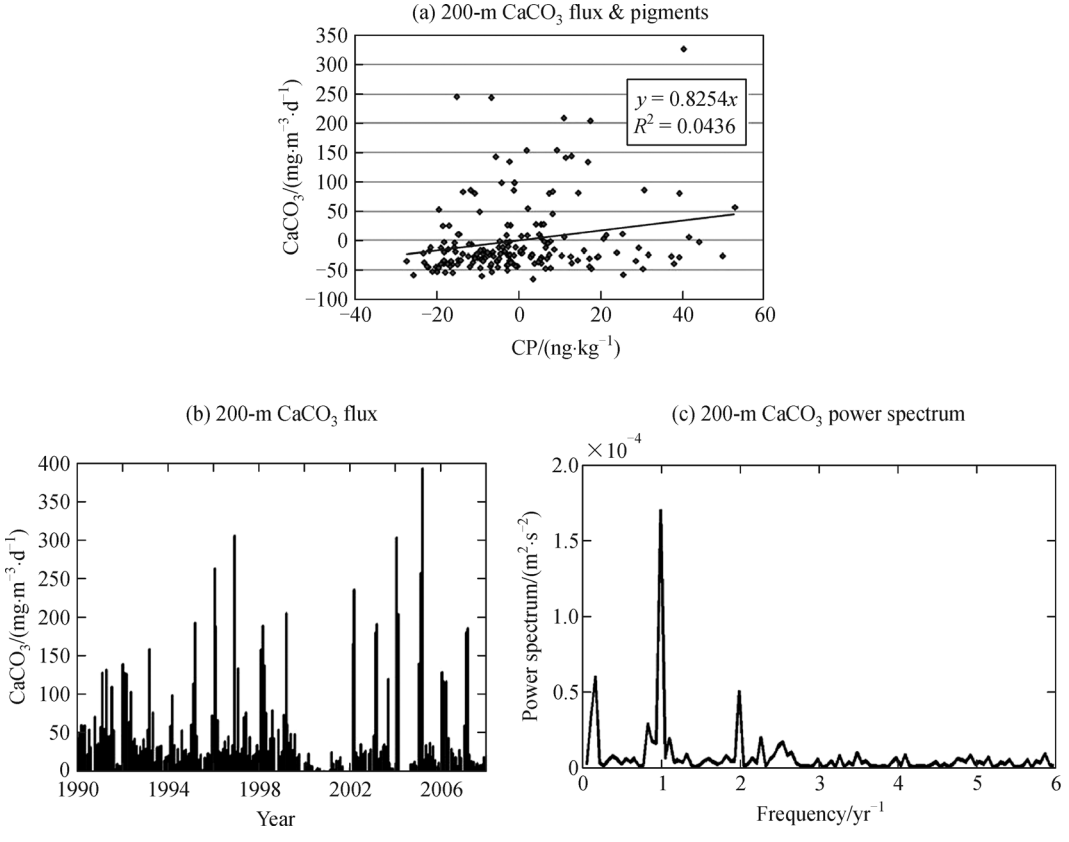

Fig. 9 (a) Scatter diagram of $CaCO_3$ flux at the 200-m depth and CP; (b) $CaCO_3$ flux at 200-m depth; (c) the power spectra of $CaCO_3$ flux at 200-m depth.

19'-Hexanoyloxyfucoxanthin pigment, implying that it as the indicator of coccolithophore is acceptable. Considering the complexity of seawater chemistry and factors influencing oceans, our speculation needs to be investigated further in the future.

5 Summary

Coccolithophore pigment presented evident seasonal and inter-annual cycles with the highest concentrations in early spring and the lowest concentrations in early autumn. Overall, an increasing trend of coccolithophore pigments was observed over 1990−2008. The variation of coccolithophore pigments was closely associated with DIC and nutrients. [HCO_3^-] of DIC species showed the most significant correlation with coccolithophore pigments, implying that [HCO_3^-] regulated the coccolithophore pigments more efficiently and significantly. Due to an increase in [HCO_3^-] triggered by ocean acidification or increasing anthropogenic CO_2, ocean acidification will probably enhance the calcification or coccolithore production in the study area.

Acknowledgements Hui ZHAO would like to thank the Nippon foundation, the Programme for Observation of the Global Ocean, Bermuda Institute of Ocean Science, Dr. Tony Knap, Dr. Gerald Plumley, and Jerome Aucan. The success of the BATS program to date is the result of the hard work and dedication of many scientists and technicians. We acknowledge them for providing support and scientific guidance, and for carrying out the initial analyses or processing of some of the core measurements. The study would not have been finished without the outstanding support of the captains, crews, and marine technicians of the research vessels.

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