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Carbon isotopic disequilibrium between seawater and air in the coastal Northern South China Sea over the past century

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ABSTRACT

Six coastal sediment cores collected from the Northern South China Sea were dated by ^{210}Pb and analyzed for stable carbon and oxygen isotope composition of planktonic foraminifer *Globigerinoides ruber* ($\delta^{13}C_{Gr}$ and $\delta^{18}O_{Gr}$). Three of these cores were located east of Hainan Island and the other three off the Pearl River Estuary (PRE). Surface seawater $\delta^{18}O$ and dissolved inorganic carbon (DIC) $\delta^{13}C$ were identified as the dominant factors controlling downcore variations of $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$, respectively. Results of $\delta^{13}C_{Gr}$ were then used to study surface water $\delta^{13}C_{DIC}$ and its relation to $\delta^{13}C$ of atmospheric CO_2 ($\delta^{13}C_{atm}$) over the past century. Downcore records showed rather constant $\delta^{13}C_{Gr}$ in cores off Hainan Island, but moderate decreases of $\delta^{13}C_{Gr}$, at rates between −0.006‰ and −0.009‰ per year, in cores off the PRE. Isotopic disequilibrium between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{atm}$ was observed, with $\delta^{13}C_{DIC}$ apparently higher than expected at equilibrium with $\delta^{13}C_{atm}$ except at the site closest to the PRE. The relatively steady $\delta^{13}C_{Gr}$ values east of Hainan Island were explained by balanced vertical mixing and biological pump, whereas the moderate $\delta^{13}C_{Gr}$ decreases with time off the PRE were attributable to fluvial input of terrestrial carbon.

1. Introduction

Since the beginning of the industrial revolution, the $\delta^{13}C$ of the atmospheric CO_2 ($\delta^{13}C_{atm}$) has decreased by ~2‰ due to emission of ^{13}C-depleted CO_2 from human activities, such as fossil fuel burning and land clearing (Druffel and Benavides, 1986). The so-called "^{13}C Suess effect" (Keeling, 1979) also occurs in surface oceans through air–sea exchange (Broecker and Maier-Reimer, 1992; Quay et al., 1992; Lynch-Stieglitz et al., 1995; Bacastow et al., 1996), which has implications for the estimation of uptake of anthropogenic CO_2 by the oceans. The rate of $\delta^{13}C$ change in seawater dissolved inorganic carbon (DIC) has been determined since the 1970s (Kroopnick, 1974; Quay et al., 1992; Bacastow et al., 1996), and longer-term variations were estimated from shallow-dwelling corals (e.g., Swart et al., 2010). Both direct measurements of $\delta^{13}C_{DIC}$ and coral $\delta^{13}C$ records display significant inter-ocean variability in the changing rate, which is associated with several factors, such as the time for surface ocean $\delta^{13}C$ air-sea equilibration, subsurface upwelling, and terrestrial carbon input (Böhm et al., 1996; Körtzinger et al., 2003; Swart et al., 2010). However, in the Northern South China Sea (NSCS), where these factors may interact, little is known about how much surface seawater $\delta^{13}C$ has changed during the past century.

The coastal area in the NSCS is ideally suited for deciphering the occurrence or not of the Suess effect by reading from sediment records due to the relatively stable and high sedimentation rates there. The NSCS is under the influence of monsoon climate. During summer the coastal circulation in the NSCS is characterized by upwelling due to the combined effect of southwesterly alongshore current and bottom topography, resulting in numerous upwelling patches distributed from SE off Hainan Island to the NE off the Mainland China (Su and Pohlmann, 2009; Jing et al., 2009; Gan et al., 2010). During winter strong northeasterly winds may cause intensive vertical mixing in the coastal environment. The continental shelf east of Hainan Island is narrow (Fig. 1) and is affected little by river discharge, and thus reflects mainly the interactions between shelf and open ocean. In contrast, the shelf south of the mainland China is wider and receives huge discharges from the Pearl River (PR), the third largest river in China. Therefore, the coastal areas east of Hainan Island and

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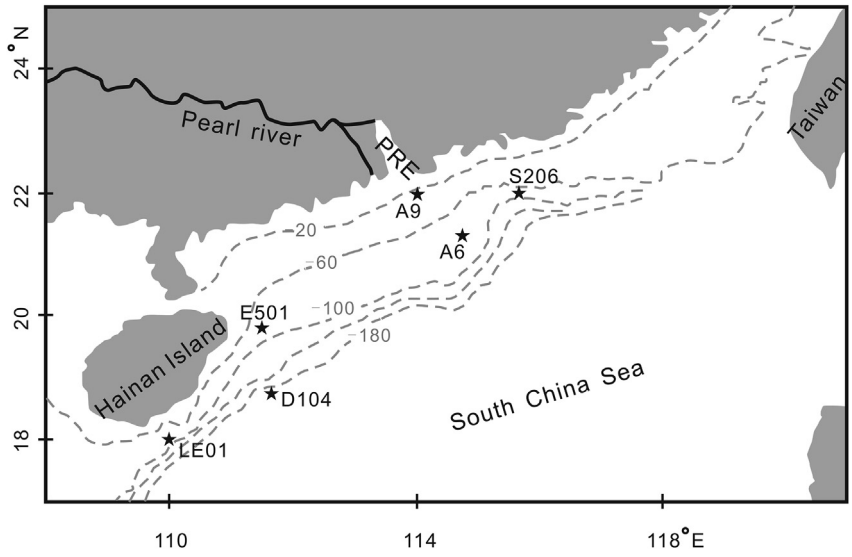

Fig. 1. Locations of sediment cores used in this study.

off the PR estuary (PRE) may be conceived as ocean-dominated and river-dominated settings, respectively. We thus hypothesized that surface seawater $\delta^{13}C$ may exhibit distinct temporal patterns between the two marine settings in the NSCS under the backdrop of increasing anthropogenic CO_2 in the atmosphere.

In addition to corals, planktonic foraminifera have also been used to trace the recent marine $\delta^{13}C$ changes via either the comparison of the planktonic foraminiferal $\delta^{13}C$ in surface water with that in surface sediment samples (Beveridge and Shackleton, 1994; Bauch et al., 2000; King and Howard, 2004) or the downcore secular sedimentary records (Al-Rousan et al., 2004; Black et al., 2011). Similar to these works, planktonic foraminiferal $\delta^{13}C$ from 6 short sediment cores, three each from the two settings mentioned above (Fig. 1), are reported in this study. We will show that marine DIC was in isotopic disequilibrium with atmospheric CO_2 in both the settings, but changes of marine $\delta^{13}C$ during the past century were distinct between them, with relatively constant values off Hainan Island, but moderate decreases off the PRE.

2. Material and methods

2.1. Sample collection

Six box cores collected in August 2009 in the coastal shelf of NSCS, i.e., LE01, D104 and E501 in the east of Hainan Island, and A6, A9 and S206 off the PRE, were studied in this work (Fig. 1). Water depths for these cores were in the range of 33–198 m, with A9 being the shallowest and D104 the deepest. The core tops were well preserved upon collection as evidenced by fairly clear water above the sediment in the box corer. After the overlying water was siphoned out, core barrels (11.4 cm i.d.; 60 cm in length) were pushed into the box to take subcores. Sediments in the subcores were then extruded onboard with a hydraulic jack and sectioned at 2-cm intervals. The sectioned samples were sealed in plastic jars (i.d., 8.5 cm; height, 7.5 cm) or bags and kept frozen until freeze-drying in the home laboratory.

2.2. ^{210}Pb dating

The study cores were dated using ^{210}Pb methods. Measurements were performed using ORTEC HPGe detectors (GEM, Lo-Ax and GMX) at the Institute of Earth Sciences, Academia Sinica, Taiwan (e.g., Huh et al., 2006). The international standard reference materials (IAEA-133A, 327, 375) were used for energy, efficiency and mass calibration for every detector. Constant ^{210}Pb activities in the lower portions of the cores were assumed to represent supported ^{210}Pb, and this value was subtracted from total activity to yield excess ^{210}Pb activity ($^{210}Pb_{ex}$). Based on the decay (hence, decrease) of $^{210}Pb_{ex}$ with depth in core, sedimentation rates were calculated.

2.3. C and N elemental analysis

After removal of carbonate with dilute HCl from bulk sediments, carbon and nitrogen content were analyzed using an elemental analyzer (Vario Pyro Cube). Then the content of total organic carbon (TOC) and total nitrogen (TN) in raw sediments were calculated. The average standard deviations of these measurements were ±0.05% for TOC and ±0.01% TN.

2.4. Foraminiferal $\delta^{18}O$ and $\delta^{13}C$ analysis

The planktonic foraminifer, *Globigerinoides ruber*, was picked out from >150 μm fraction in sediments. Around 10–20 shells were pooled, sonicated for 5–20 s in dilute H_2O_2 until clean, and then reacted in supersaturated H_3PO_4 at 90 °C. The resulting CO_2 was analyzed by an Isoprime isotope ratio mass spectrometer for $\delta^{18}O$ and $\delta^{13}C$ whose values were reported in ‰ notation relative to the Vienna Pee Dee Belemnite (VPDB) standard. The long-term reproducibility for $\delta^{18}O$ and $\delta^{13}C$ based on measurements of a reference standard was 0.08‰ and 0.05‰, respectively.

3. Results and discussion

3.1. Dating results

^{210}Pb dating results of cores A6 and A9 have been published (Jia et al., 2013) and are shown here for comparison. Generally, each core displayed log-linear $^{210}Pb_{ex}$ profiles when plotted against cumulative mass downcore (Fig. 2), thus the constant initial concentration (CIC) model was used for the calculation of mass accumulation rate (MAR) and age of sediment deposition (Krishnaswami et al., 1971). Relatively uniform $^{210}Pb_{ex}$ activities

occurred in near surface layers of cores LE01 and A9, indicating a zone of bioturbation and mixing of sediments (Nittrouer et al., 1979). These anomalies could have a significant effect on chronologies only when the thickness of the disturbed zone exceeds about 15% of the depth of the $^{210}Pb_{ex}$ profile (Oldfield and Appleby, 1984). In our cores, as the coverage of the surficial anomalous layer was within the limits of this assumption, we assumed that mixing exerted a negligible effect. The specific reason for the "jumps" in the lower part of $^{210}Pb_{ex}$ profiles of core S206 and A6 are not clear at present, but they might result from a hiatus in deposition.

Spatially, mass accumulation rates were higher at sites off the PRE (0.33–0.58 g cm^{-2} yr^{-1}) than those in the east of Hainan Island (0.21–0.35 g cm^{-2} yr^{-1}), which should be associated with more terrestrial input from the Pearl River.

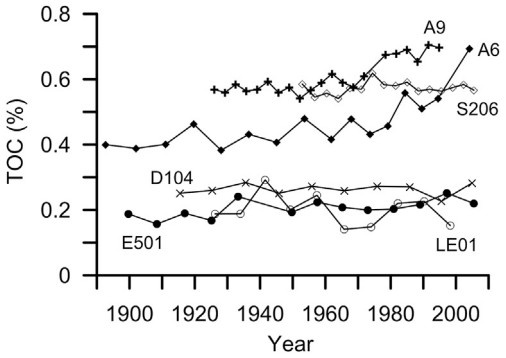

Fig. 3. Downcore records of TOC.

3.2. Bulk organic matter

TOC values, ranging from 0.14% to 0.29%, in the three cores east of Hainan Island were relatively constant through time and consistently lower than those (0.38%–0.71%) in the cores off the PRE (Fig. 3). Values of TOC/TN weight ratio in these six cores fell between 3.5 and 7.7, indicating predominant marine origin for the sedimentary organic matter (OM). $\delta^{13}C_{OM}$ values downcore A9 and A6 off the PRE were reported to be −21.51 ± 0.12‰ and −21.36 ± 0.10‰, respectively, also indicating typical marine OM (Jia et al., 2013). Nevertheless, TOC/TN ratio exhibited slightly higher values in the three cores off the PRE (6.8 ± 0.2, 6.2 ± 0.2 and 6.7 ± 0.1 in cores A9, A6 and S206, respectively) than those in the East of Hainan Island (6.5 ± 0.2, 5.6 ± 1.0 and 4.8 ± 0.5 in cores D104, E501 and LE01, respectively), which may suggest a weak influence of trace amount of terrestrial OM off the PRE. By using the branched and isoprenoid tetraether (BIT) index, a proxy for estimating the relative contribution of soil OM to marine sediments, the contribution of soil OC to TOC has been estimated to be 16 ± 4% in A9 and 9 ± 2% in A6 (Jia et al., 2013). As to the other four cores, since they were farther away from the PRE and had similar or lower TOC/TN ratios, we are confident that the contribution of terrestrial OC would be also insignificant.

In our study cores, the linear sedimentation rates were much higher than 35 cm ka^{-1}, a threshold above which the preservation of autochthonous OM is largely independent of whether the bottom water is oxic or anoxic (Tyson, 2001). So the sedimentary TOC%

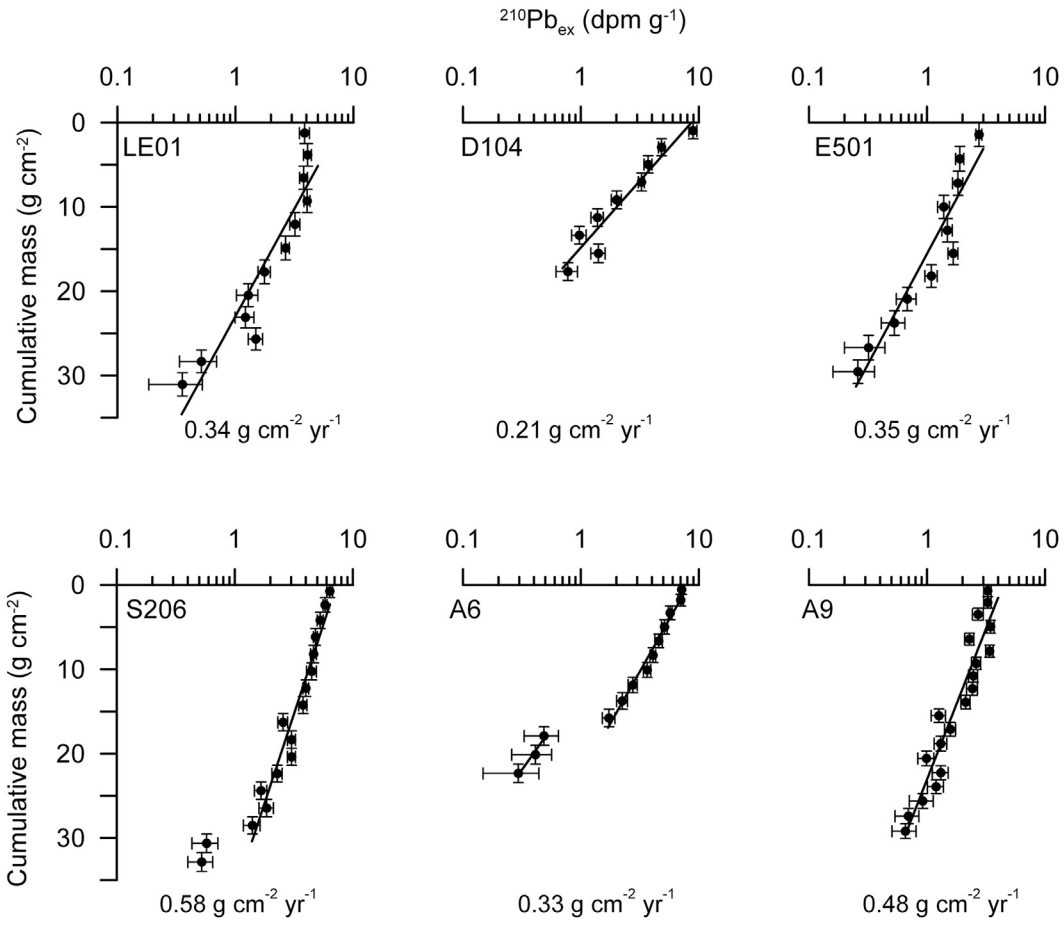

Fig. 2. Activity-cumulative mass profiles of $^{210}Pb_{ex}$ in the six sediment cores. Data of core A6 and A9 are from Jia et al. (2013).

in this work is a function of OM input and MAR. As stated above, we assumed that MAR, being predominantly determined by terrestrial materials, was constant based on the ^{210}Pb profiles for the study cores. So downcore profiles of TOC MAR, being associated mainly with paleo-productivity, would be parallel with those of TOC%. A significant TOC% increase occurred circa 1970 in cores A6 and A9 directly off the PRE has been attributed to the increase of anthropogenic nutrient input and resultant eutrophication over the last several decades (Jia et al., 2013). By contrast, the relatively constant TOC% downcore S206, D104, E501 and LE01 may suggest less human-disturbed, steady aquatic productivity at these sites.

3.3. Seasonality of Globigerinoides ruber isotope signals

Globigerinoides ruber has been known as an upper mixed layer species and its shell $\delta^{18}O$ suggested to be controlled mainly by sea surface temperature (SST) in the SCS from plankton tow and sediment trap data (Lin and Hsieh, 2007; Lin et al., 2011). *G. ruber* $\delta^{18}O$ value ($\delta^{18}O_{Gr}$) is determined by ambient temperature and seawater $\delta^{18}O$, following the equation:

$$T = 14.9 - 4.8*\left(\delta^{18}O_{Gr} - \delta^{18}O_{sw}\right) \quad (1)$$

where T is ambient temperature (°C), $\delta^{18}O_{sw}$ is the $\delta^{18}O$ values of seawater (converted from the VSMOW scale to VPDB by subtracting 0.27‰). This equation was developed for *Orbulina universa* under "high-light" culture conditions by Bemis et al. (1998) and has been determined to be applicable for *G. ruber* (Thunell et al., 1999; Spero et al., 2003). Details of water column $\delta^{18}O_{sw}$ are lacking in the study area, but we collected surface water samples at some sites in January and August 2009 and measured $\delta^{18}O_{sw}$ values. By simply assuming that these $\delta^{18}O_{sw}$ values represent seasonal mixed layer ones and remain constant in recent years, we tried to predict temperatures using the core top $\delta^{18}O_{Gr}$ values and compare them with actual temperatures. As shown in Table 1, the application of August $\delta^{18}O_{sw}$ values gave unreasonably low temperatures, whereas the practice using January $\delta^{18}O_{sw}$ values produced acceptable temperatures matching the in situ measurements. The differences between the predicted and the measured winter temperatures are <2.1 °C. The slightly large differences are reasonable because sedimentary $\delta^{18}O_{Gr}$ integrated multi-year variations while $\delta^{18}O_{sw}$ and in situ temperatures were only a snapshot. As many planktonic species have seasonality in flux, sediment records of these species are strongly skewed toward the season of peak production and sedimentation (e.g. Mohiuddin et al., 2004; King and Howard, 2005; Kuroyanagi et al., 2008; Mohtadi et al., 2009). So based on above temperature estimation and comparison, we tentatively thought that *G. ruber* records in our study area may be biased towards wintertime. Of course, this conclusion should be validated by future time-series water column investigations.

Table 1
Comparison of measured surface water temperatures with calculated temperatures from *G. ruber* and surface water $\delta^{18}O$.

Site	$\delta^{18}O_{Gr}$ (‰, VPDB)*	Surface water $\delta^{18}O$ (‰, VSMOW)		Jan. water temperature (°C)		Aug. water temperature (°C)	
		Jan.	Aug.	Calc.†	Meas.	Calc.†	Meas.
A9	−1.87	−0.93	−1.97	18.12	16.84	13.12	28.50
A6	−2.38	−0.35	−1.75	23.35	21.26	16.63	28.80
S206	−2.27	−0.54	−1.70	21.91	22.06	16.34	30.02
E501	−2.47	−0.71	−1.54	22.05	24.10	18.07	29.75
D104	−1.93	–‡	−1.82	–‡	–‡	14.13	29.59
LE01	−2.32	–‡	−1.44	–‡	–‡	17.83	29.98

* Core top values.
† Based on Equation (1) in the text.
‡ No data.

3.4. Factors controlling downcore isotopic records

Values of $\delta^{18}O_{Gr}$ were similar in the study cores except in core A9, specifically, −2.14 ± 0.27‰ in A6, −2.19 ± 0.18‰ in S206, −2.28 ± 0.23‰ in D104, −2.42 ± 0.15‰ in LE01, −2.47 ± 0.21‰ in E501 and −1.42 ± 0.28‰ in A9. The apparent higher $\delta^{18}O_{Gr}$ values in A9 are attributable to lower temperatures at the site in wintertime. $\delta^{18}O_{Gr}$ record exhibited a significant decreasing trend in A9, whereas it remained roughly constant over time scales in other cores (Fig. 4). Values of $\delta^{13}C_{Gr}$ ranged between 1.6‰ and 2.5‰ and exhibited no significant temporal trend in the three cores east of Hainan Island, but clear decreases can be seen in cores off the PRE (Fig. 4). $\delta^{13}C_{Gr}$ in cores S206 and A6 off the PRE were between 1.0‰ and 2.3‰, slightly lower than those in the cores east of Hainan Island. However, $\delta^{13}C_{Gr}$ displayed significant lower values between −0.8‰ and 0 in core A9. Correlation analyses showed different relationships between $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$, i.e., positive correlation in A9, negative correlation in LE01, and no correlation in D104, E501, A6 and S206 (Fig. 5).

Culture experiments have suggested that calcifying temperature and carbonate chemistry of seawater, in addition to $\delta^{18}O_{sw}$ and $\delta^{13}C_{DIC}$, may affect the $\delta^{18}O$ and $\delta^{13}C$ of foraminiferal shells (Spero et al., 1997; Bemis et al., 2000). For *Globigerinoides ruber*, the isotopic differences between shell and ambient water, i.e., $\Delta\delta^{13}C_{shell-DIC}$ and $\Delta\delta^{18}O_{shell-sw}$, decrease with increasing carbonate ion concentration ($[CO_3^{2-}]$) at rates of −0.0089‰ μmol^{-1} kg^{-1} and −0.0022‰ μmol^{-1} kg^{-1}, respectively (Spero et al., 1997; Bijma et al., 1998); whereas with increasing temperature, $\Delta\delta^{13}C_{shell-DIC}$ increase at +0.05‰ °C^{-1} but $\Delta\delta^{18}O_{shell-sw}$ decrease at −0.21‰ °C^{-1} (Bemis et al., 1998, 2000). The effect of $[CO_3^{2-}]$ was confirmed by later field investigations (Russell and Spero, 2000). Temperature effect on temporal trends of $\delta^{13}C_{Gr}$ and $\delta^{18}O_{Gr}$ is unlikely significant in our results, because the warming trend found in the SCS over the past century (Bao and Ren, 2014) was not reflected in our less changed $\delta^{18}O_{Gr}$ records except at site A9 and even opposed the decreasing trends in some $\delta^{13}C_{Gr}$ records including at A9. Similarly, the different temporal patterns between $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$ records except in core A9, as well as no or negative correlation between them, do not support $[CO_3^{2-}]$ as the dominant controlling factor either. Changes in seawater $\delta^{18}O$ and $\delta^{13}C_{DIC}$, therefore, are preferred here as the determinants for the downcore $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$ variations, respectively.

The similar decreases of $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$ values with time and their positive correlation shown in core A9 likely imply different controlling factors from other cores. Increase in $[CO_3^{2-}]$ at the site might be a cause, because enhanced algal photosynthesis and slowdown of $CaCO_3$ production in the surface water due to human-induced eutrophication, which could help to decline aquoues pCO_2 but raise $[CO_3^{2-}]$, have been suggested from downcore sediment record (Jia et al., 2013). However, thus inferred rise of $[CO_3^{2-}]$ would be discounted or balanced by the rise in atmospheric CO_2. In addition, human-induced eutrophication was also suggested to occur at site A6 (Jia et al., 2013), where no concurrent decreases of $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$ was observed. As an alternative, we suggest that increase in freshwater input, which is characterized by lighter $\delta^{18}O$ and $\delta^{13}C_{DIC}$ values, might have governed the observed decreasing trends and positive correlation between $\delta^{18}O_{Gr}$ and $\delta^{13}C_{Gr}$ at this site closest to the PRE. The assumed increase of freshwater input is consistent with the 10% increase in the PR runoff over the past 50 years (Xu et al., 2010).

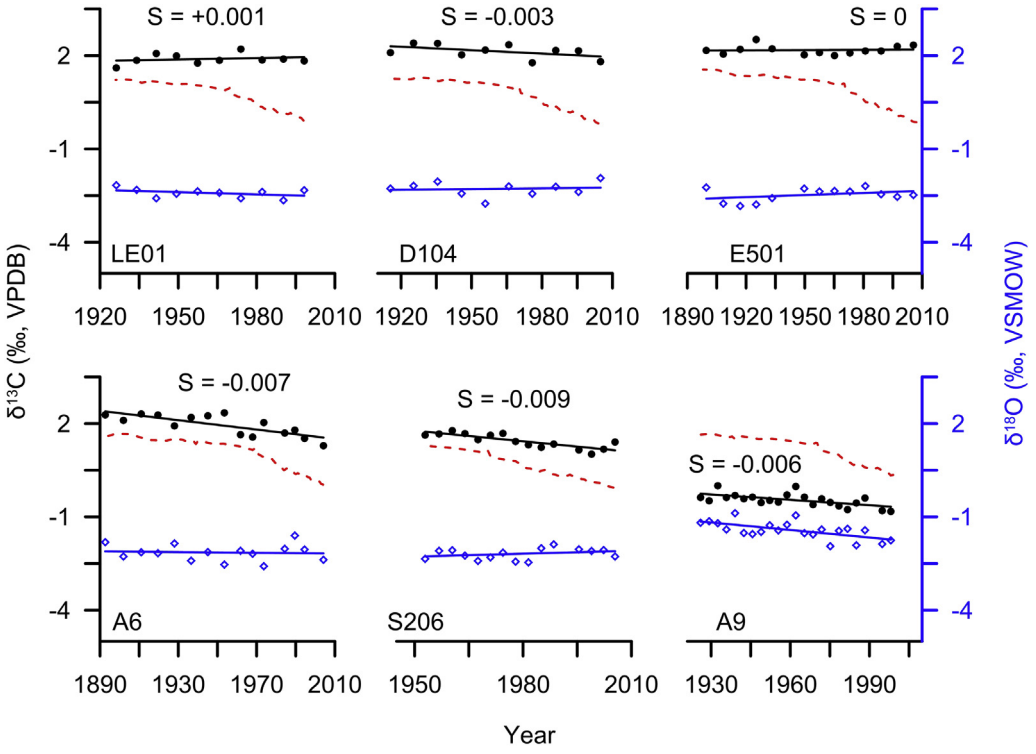

Fig. 4. Downcore carbon and oxygen isotope records. Black: $\delta^{13}C_{Gr}$; Blue: $\delta^{18}O_{Gr}$; Red dash: surface water $\delta^{13}C_{DIC}$ assumed to be in isotopic equilibrium with $\delta^{13}C_{atm}$ using the isotopic fractionation between DIC and gaseous CO_2: $\varepsilon = -0.105^{*}T\,(^{\circ}C) + 10.51$ (Zhang et al., 1995), in which T was winter (DJF) temperature at each site according to the World Ocean Atlas (WOA) 2001 in the National Oceanographic Data Center (NODC). Data for $\delta^{13}C_{atm}$ before 1978 were from Francey et al. (1999), and those after 1980 were taken from http://cdiac.ornl.gov/trends/co2/iso-sio/iso-sio.htm. S denotes the slope of linear trend of $\delta^{13}C_{Gr}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.5. Down $\delta^{13}C_{Gr}$ records

The above discussion suggests that $\delta^{13}C_{Gr}$ records in this study may predominantly reflect seawater $\delta^{13}C_{DIC}$ over the past. However, by comparison of $\delta^{13}C_{Gr}$ records with $\delta^{13}C_{DIC}$ curves assumed to be in isotopic equilibrium with $\delta^{13}C_{atm}$, we found that values of $\delta^{13}C_{Gr}$ were apparently higher than the assumed $\delta^{13}C_{DIC}$ values except at site A9 where $\delta^{13}C_{Gr}$ were lower (Fig. 4). Many studies have shown that $\delta^{13}C$ of foraminifer shells often deviates from the ambient $\delta^{13}C_{DIC}$ with offset being attributed to so called "vital effects", a collective noun for a suite of biologically, physically and chemically controlled processes (e.g. Oppo and Fairbanks, 1989; Kroon and Ganssen, 1989; Spero, 1992; Mulitza et al., 1999). For *Globigerinoides ruber*, the offset is generally negative and a values of −0.94‰ has been suggested from plankton tow data from foraminifera collected in the tropical Atlantic and northern Caribbean (Spero et al., 2003). In our study area, the vital effect is unclear due to the lack of relevant studies. However, at the SEATS site (18°N, 115.5°E) in the open SCS, mixed layer seawater $\delta^{13}C_{DIC}$ averaged 0.74‰ (0.66–0.83‰ range) during 2002–2003 (Chou, 2004), whereas sediment trap $\delta^{13}C_{Gr}$ averaged 0.46‰ (−0.02–0.79‰ range) during 2004–2005 (Lin et al., 2011), also suggesting negative values for the vital effect. Therefore, the apparently higher $\delta^{13}C_{Gr}$ records observed here may mean that the actual $\delta^{13}C_{DIC}$ values would be even higher than those expected to be in equilibrium with $\delta^{13}C_{atm}$.

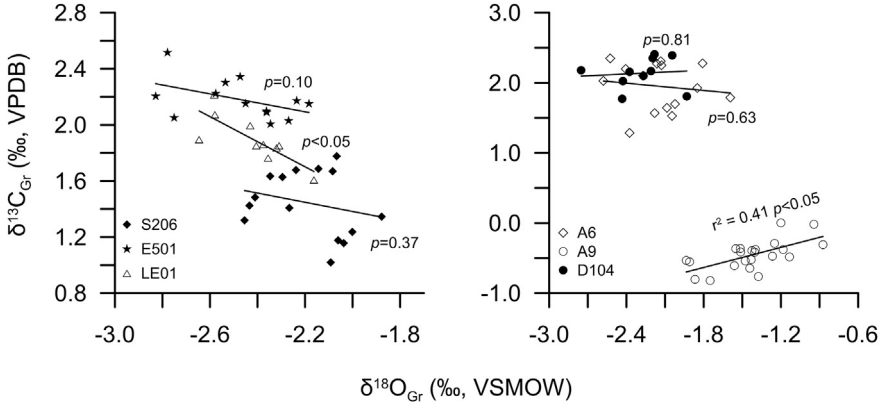

Fig. 5. Scatter plot showing relationships between $\delta^{13}C_{Gr}$ and $\delta^{18}O_{Gr}$ in the study cores.

Downcore records of $\delta^{13}C_{Gr}$ showed different patterns in our results: those located east of Hainan Island displayed no or insignificant decreases at rates from −0.003 to +0.001‰ yr^{-1}, whereas those off the PRE showed decreases at rates from −0.006 to −0.009‰ yr^{-1} (Fig. 4). The decreasing rates off the PRE are comparable to the rate of −0.007 ± 0.013‰ yr^{-1} over the past century in the Pacific and Indian Oceans recorded by coral skeleton $\delta^{13}C$ (Swart et al., 2010) and slightly higher than a −0.63‰ change over the last two centuries, i.e. −0.003‰ yr^{-1}, in the Red Sea estimated from planktonic foraminiferal $\delta^{13}C$ records (Al-Rousan et al., 2004). Faster and greater changes have been observed in the Caribbean Sea, with a rate of < −0.01‰ yr^{-1} occurring prior to 1950 and increasing to almost −0.025‰ yr^{-1} by 2008 (Black et al., 2011).

Several processes have been proposed to explain the surface ocean $\delta^{13}C$ change in the recent centuries. One is the time history of $\delta^{13}C_{atm}$ and the air-sea isotopic exchange state of equilibration, with the latter depending on the exposure time of the surface water relative to the air-sea isotopic equilibration time (~10 years) for the DIC pool (Lynch-Stieglitz et al., 1995). The second is water supplied from depth where it has been isolated from the atmosphere for a long period of time. This subsurface water could carry with it lighter $\delta^{13}C$ carbon and higher nutrient level than the ambient surface water, the influence of which is complicated because ^{12}C could be preferentially fixed during the stimulated biological photosynthesis due to the rise of nutrient levels, and then could be exported to the depth again (Nozaki et al., 1978; Böhm et al., 1996; Körtzinger et al., 2003). The third is the freshwater input for river-dominated shelf areas, which also could bring to the surface ocean lighter $\delta^{13}C$ carbon, higher nutrient level and, especially, the terrigenous OM that can be oxidized to release ^{13}C-depleted CO_2 (Baker et al., 2010; Swart et al., 2010). In the following we try to explain our observed patterns of $\delta^{13}C_{Gr}$ in the coastal NSCS.

Surface ocean $\delta^{13}C$ higher than expected at atmospheric equilibrium, as observed in this study, has also been observed in the subtropical and tropical oceans, the reason for which is the ~10 year air-sea isotopic equilibration time for the DIC pool that allows vertical upwelling/mixing and biological productivity to keep the surface ocean $\delta^{13}C$ out of atmospheric equilibrium (Nozaki et al., 1978; Böhm et al., 1996; Quay et al., 2003). We believe that this scenario would also be true in our study area, because water residence time is about 1–2 yrs in the surface SCS (Cai et al., 2004), suggesting that the surface waters would not have a sufficient chance to isotopically equilibrate with the atmosphere. Therefore, the persistent isotopic disequilibrium between oceanic DIC and atmospheric CO_2 over the past century in the NSCS may be caused by vertical upwelling/mixing and associated biogeochemical processes.

The SCS is a completely isolated basin at depth below 2400 m, where the water comes from the adjacent intermediate North Pacific water through the Luzon Strait (Dai et al., 2013, and references therein). The short residence time of the deep water, i.e., <30 yrs (Qu et al., 2006), suggests that it must rise to the upper layer through strong diapycnal mixing (Dai et al., 2013). According to Dai et al. (2013), when being transported into the euphotic zones, the deep water-sourced DIC in SCS is surplus relative to nutrients for biological uptake, which eventually lead to CO_2 degassing. Since biological uptake preferentially removes ^{12}C relative to ^{13}C on a shorter time scale than the atmospheric equilibration time of ~10 years, it is likely that this biogeochemically altered and isotopically enriched DIC, despite it is lighter in $\delta^{13}C$ at depth (Chou et al., 2007), is responsible for maintaining a persistent isotopic disequilibrium between seawater and atmosphere observed here. This is plausible because surface water in the coastal NSCS could be readily replenished or renewed by waters from depth via intensive vertical mixing caused by strong northerly wind in winter. Therefore, a well-balanced upward DIC transport into and downward OC export out of the euphotic zone, as partly reflected by little changes in downcore TOC%, may be adequate to explain the relatively constant $\delta^{13}C_{Gr}$, hence irrelevant with $\delta^{13}C_{atm}$, over the past century east of Hainan Island.

However, for coastal areas off the PRE, the huge PR discharge should not be neglected. Freshwater DIC may be readily imprinted with $\delta^{13}C_{atm}$ signals, because a great part of freshwater DIC originates from soil CO_2 that is derived from soil OM oxidation during weathering (e.g., Wachniew, 2006). The freshwater DIC influence on coastal waters could be demonstrated by the apparently lower $\delta^{13}C_{Gr}$ values at site A9 closest to the PRE. So the moderate $\delta^{13}C_{Gr}$ decreases off the PRE may reflect partly changes of the terrestrial C isotope and/or freshwater input. However, the freshwater influence at sites S206 and A6 seems insignificant because $\delta^{13}C_{Gr}$ values therein were only slightly lower than those from east of Hainan Island. We suppose this might be associated with higher OC production in coastal waters off the PRE, as inferred from the clearly higher downcore TOC% values and sedimentation rates there (Figs. 2 and 3). The higher OC production may be induced by terrestrial nutrients input in addition to those supplied from depth. In others words, $\delta^{13}C_{Gr}$ values would have been lower than recorded values off the PRE if the PR-induced OC production were not relatively high.

Nevertheless, we noticed that the prominent TOC% increases after ~1970 at sites A6 and A9, caused by the growth of primary productivity due to enhanced anthropogenic nutrient input (Jia et al., 2013), were not followed by any increases in $\delta^{13}C_{Gr}$. Thus, an additional process is required to balance, or even exceed, the presumed aqueous $\delta^{13}C$ increase induced by the marked growth of marine OC production. Here, we hypothesize that increased terrestrial C inputs as a result of river basin-wide deforestation and development, especially in the PR delta (Jia et al., 2013), over the last several decades could have contributed additional ^{13}C-depleted sources to the coastal ocean, as has been noted for the Caribbean Sea and Florida Bay (Baker et al., 2010; Swart et al., 2010). We believe that this increased terrestrial C input, together with its $\delta^{13}C$ signature that could have been partly imprinted with the $\delta^{13}C_{atm}$ decrease, should have played a part in maintaining the observed $\delta^{13}C_{Gr}$ decreases off the PRE in spite of the prominent growth of OC production after ~1970.

Therefore, the different performances of surface water $\delta^{13}C$ change during the past century between areas east of Hainan Island and off the PRE likely resulted from their different oceanic settings, i.e., a river-dominated setting for the area off the PRE, and an ocean-dominated setting for the area east of Hainan Island. This observation is compatible with the recently proposed concepts of River-dominated Ocean Margin (RiOMar) (McKee et al., 2004) and Ocean-dominated Margin (OceMar) (Dai et al., 2013), which have different physical–biogeochemical processes and different implications for the carbon mass balance and flux estimation.

4. Conclusions

Surface water in the SCS has a residence time of ca. 1–2 years, which is far shorter than the air-sea isotopic equilibration time (~10 years) for the DIC pool. This provides an opportunity to understand carbon dynamics by comparing the isotopic relationship between surface water DIC and atmospheric CO_2; the latter shows Suess effect due to emission of ^{13}C-depleted CO_2 from human activities. In this study, downcore records of foraminifera *Globigerinoides ruber* $\delta^{13}C$ in the northern coastal SCS were used to infer $\delta^{13}C_{DIC}$ in coastal areas east of Hainan Island and off the PRE, and air-sea isotopic disequilibrium was observed. The two areas are different in oceanic settings influenced predominantly by open

ocean and large fluvial input, respectively. The different settings likely led to different $\delta^{13}C_{DIC}$ changing patterns over the past century, with relatively constant values east of Hainan Island and moderate decreasing trend off the PRE. The relatively stable $\delta^{13}C$ values east of Hainan Island may have been caused by a well-balanced upward DIC transport into and downward OC export out of the euphotic zone, whereas the moderate $\delta^{13}C$ decreases with time off the PRE should have been associated with the fluvial input of terrestrial carbon. This work thus confirms the occurrence of different carbon processes in the river-dominated and ocean-dominated areas in the SCS.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ecss.2014.07.008.

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