Estuarine, Coastal and Shelf Science 149 (2014) 38–45

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

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

Shendong Xu [a], Guodong Jia [a, b, *], Wenfeng Deng [b], Gangjian Wei [a, b], Weifang Chen [c], Chih-An Huh [c]

[a] CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China
[c] Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan

ARTICLE INFO

Article history:
Received 4 December 2013
Accepted 14 July 2014
Available online 23 July 2014

Keywords:
carbon isotope ratio
carbon dioxide
foraminifera
coastal zone
sediments
Northern South China Sea

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

* Corresponding author. CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.
E-mail address: jiagd@gig.ac.cn (G. Jia).

http://dx.doi.org/10.1016/j.ecss.2014.07.008
0272-7714/

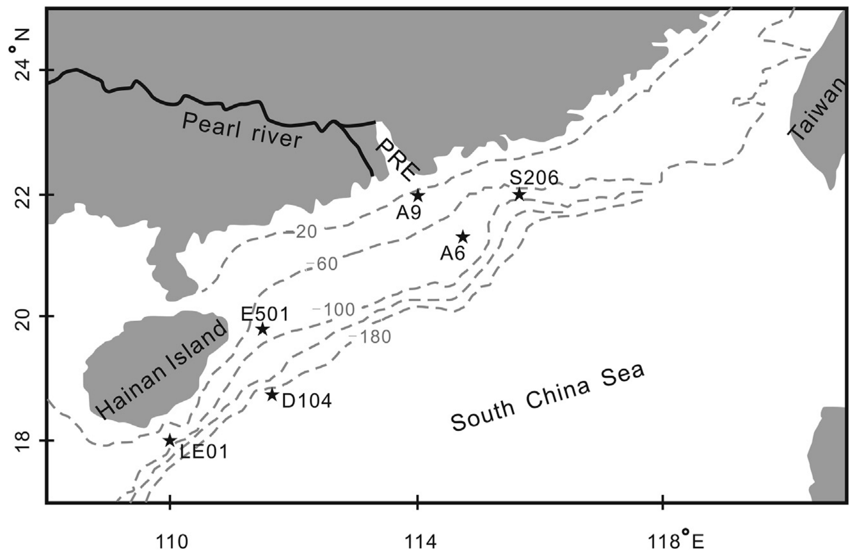

Fig. 1. Locations of sediment cores used in this study.

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