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Research Paper

Paleoproductivity changes in the Southern South China Sea from the Last Glacial to the Holocene: Evidence from Stable Isotopes and Total Organic Carbon

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We reconstruct paleoproductivity changes during the past 37 kyr BP, from the southern South China Sea. We used productivity proxies such as planktonic and benthic foraminiferal stable isotope, total organic carbon, the relative abundance of *Globigerina bulloides*, and absolute abundance of planktonic foraminifera. The comparison between productivity proxies and previously published records suggest that $\delta^{13}C$ records of planktonic and benthic foraminifera responds better to surface water productivity changes and represent as a suitable proxy for paleoproductivity reconstructions. The faunal and geochemical proxies suggest that productivity in the South China Sea was higher during the Heinrich stadial. The planktonic and benthic $\delta^{13}C$ signals suggest overall low productivity, before the LGM (~24-22 kyr BP) and then increase subsequently. Furthermore, our records show that organic carbon content in the sediment has an oceanic origin and preservation of the organic matter depends on the sedimentation rates.

Keywords: Paleoproductivity, Stable isotopes, Total organic carbon, South China Sea

Introduction

The last glacial cycle which is categorized under the Quaternary period has been punctuated by a number of global climatic changes, including warmer and colder periods, because of the cyclic variations in the earth orbit parameters (Imbrie *et al*., 1989; Lisiecki and Raymo, 2005). These climatic oscillations control the fraction of available continental ice sheets, and it simultaneously led to changing the oceanic circulation and position of the oceanic front (Ruddiman, 2003; Kemp et al., 2010). These modifications of the ocean hydrology led to change the vertical outbreak of carbon and nutrient, and cause to limit the primary

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productivity (Sarnthein and Winn, 1990; Schneider and Schmittner, 2006; Piotrowski *et al*., 2009). The deep ocean is the largest reservoir for the CO_2, Variations in ocean circulation and the expecting primary productivity changes cause to imbalance atmospheric CO_2 concentration on the glacial/interglacial time scale (Sigman and Boyle, 2000; Eberwein and Mackensen, 2008).

The marine sediment cores, which have been used to reconstruct the paleoclimatic changes, become evident that the deep sea environment also strongly influence by the global climatic oscillations, including glacial-interglacial cycles. Deep marine sediments hold different types of paleoenvironmental proxies in lithology such as carbonates, organic and detrital materials, biogenic opals, and so on (Wei *et al*., 2003). To reconstruct the paleoenvironmental changes, several proxies such as foraminiferal abundance, pollen, radiolarian and stable isotopes on Carbon ($\delta^{13}C$) and Oxygen ($\delta^{18}O$) are liberally used in this field (Schmiedl and Mackensen, 2006; Xiang et al., 2007; Smart, 2008; Luo et al., 2018).

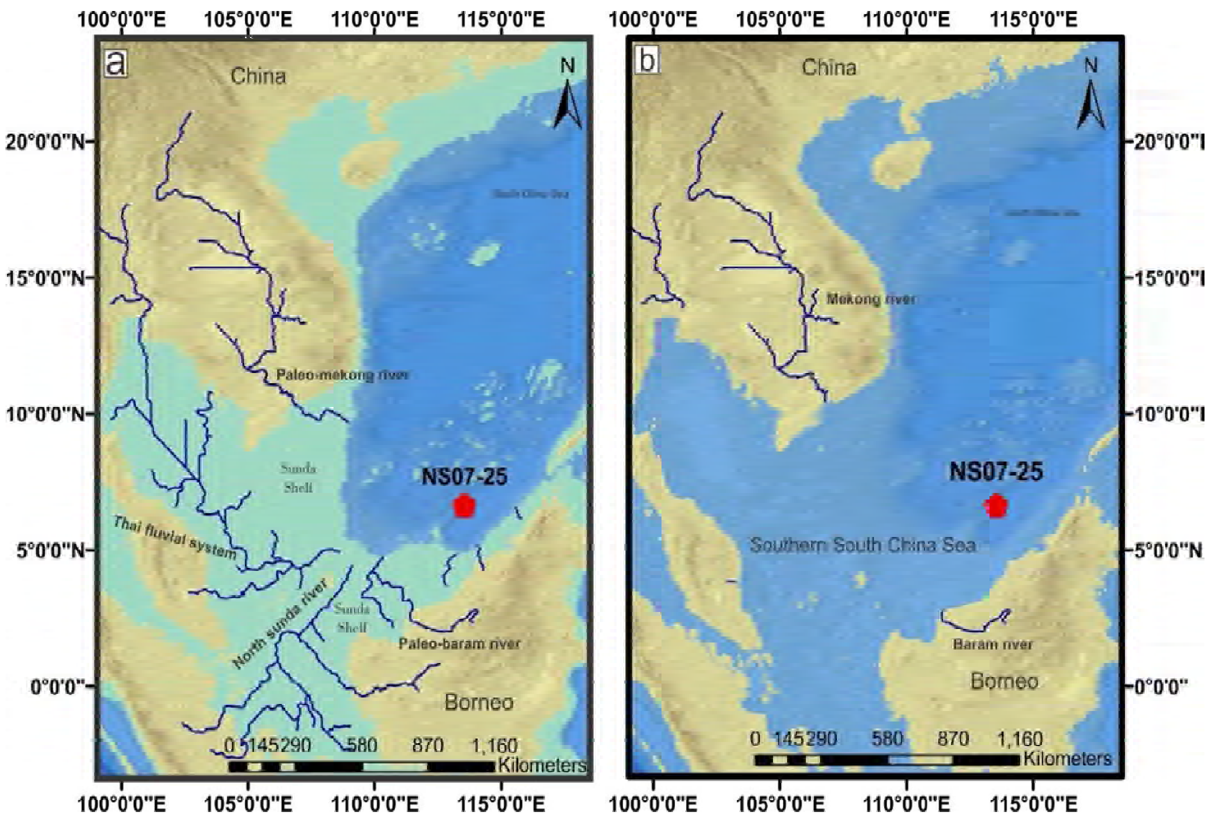
The primary productivity in surface water of modern ocean shows temporal and spatial fluctuations due to nutrient and light availability. This fluctuations in surface productivity affect the influx of organic carbon from the euphotic zone and are reflected in the deep ocean biology and chemistry (Corliss et al., 2006). These changes in water chemistry are meticulously recorded in the calcareous benthic foraminifera and serve as a reliable proxy to understand past productivity changes (Duplessy et al., 1988). Deep marine sediment off southern South China Sea have been studied by many authors to obtain information about the paleoceanography changes (Schönfeld and Kudrass, 1993; Pelejero et al., 1999; Pflaumann and Jian, 1999; Xiang et al., 2009). However, there are lack of studies regarding surface productivity of this region. Here, we use new planktonic stable isotopic records and benthic stable carbon isotopic records in comparison with previously published Total Organic Carbon (TOC) (Thilakanayaka et al., 2019) and planktonic foraminiferal abundance (Xiang et al., 2009) in the NS07-25 core to reconstruct the productivity changes in the southern South China Sea during the last 37 kyr BP. Our new records will provide further insight into the palaeoproductivity changes for the last glacial cycle.

Materials and Methods

Gravity core NS07-25 was collected from the southern South China Sea (6°39.945' N latitude and 113°32.936' E longitude), at a water depth of 2006 m (Figure 1). The 556 cm core was sub-sampled at 1 cm interval, and the chronology was established by Accelerator Mass Spectrometer (AMS) radiocarbon dates taken from Xiang et al. (2009). A total of 11 AMS radiocarbon dates on planktonic foraminifera, measured at the Xi-an Accelerator Mass Spectrometer center, China.

In order to pick foraminifera, about 10 g of the oven dried (60 °C) sediments weighted and soaked in de-ionized water for 24 h. Then wet-sieved through a 63 ìm fraction and dried again in the oven. Foraminifera was hand-picked from >150 μm size fraction. To calculate the relative abundance of *Globigerina bulloides*, an average of 904 specimens of planktonic foraminifera were picked from >150 μm size fraction (Xiang et al., 2009). For stable carbon and oxygen isotopic ratio ($\delta^{13}C$ and $\delta^{18}O$), samples were taken at 4 cm intervals for benthic foraminifera and 8 cm interval for planktonic foraminifera and a total of 138 and 72 samples were analyzed respectively. For

Figure 1: a) During Low Sea Level Periods (~120 m Lower Than Present Day), Sunda Shelf Exposed With a Large Riverine Network Including North Sunda River, Thai Fluvial System, Paleo Mekong and Paleo Baram Rivers, Supplying Higher Sediment Amount to the Southern SCS, to the Study Area; b) During Higher Sea Level Periods, Entire Sunda Shelf Submered with the River Systems Reducing the Higher Sediment Inputs to the Core Location



benthic foraminiferal stable carbon isotope analyses, about 3-5 specimens of the *Uvigerina peregrina* or *Cibicidoides wuellerstorfi* picked from the >150 μm size fraction and analyzed by using a Finnigan MAT252 mass spectrometer at the Marine Geology laboratory of Tongji University, Shanghai. Measurement precision was better than ±0.06‰ for oxygen isotope and the carbon isotope. The obtained stable isotope data are given in the usual d notation, which is referred to as Peedee Belemnite (PDB) standard. Following the method of Shackleton and Hall (1983), 0.77‰ was added from the δ^{13}C values of *U. peregrina* to make them comparable to the δ^{13}C in *C. wuellerstorfi*.

Results

Age Model

Eleven ^{14}C AMS ages (Table 1) were used as the basis of the age model for core NS07-25 (Figure 2). According to the age model, the sedimentation rate of the core shows three major stages such as a very low sedimentation rate (2.8 cm/kyr) since 15 kyr BP, moderate sedimentation rate (14 cm/kyr) between 31 and 15 kyr BP and a high sedimentation rate (~60 cm/kyr) between 37

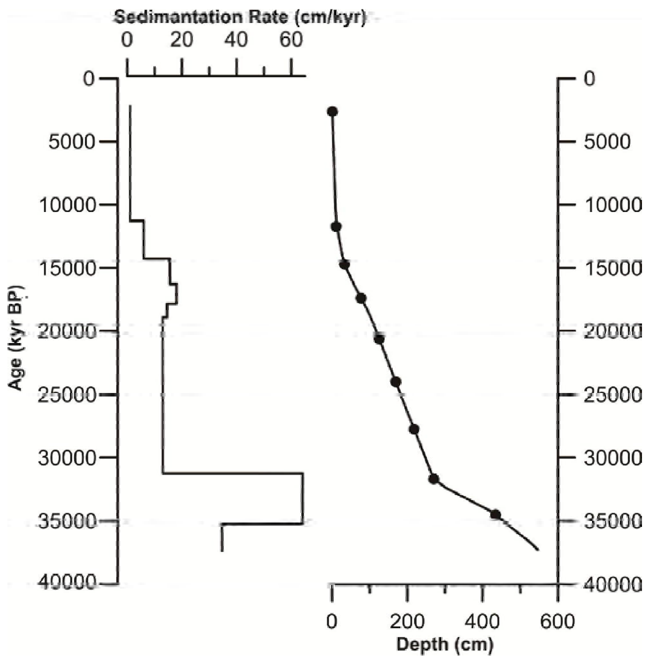
Table 1: AMS14C Age Data for Core NS07-25

Sample No.	Depth (cm)	Dating Material	AMS^{14}C Age, (yrs BP)	Calendar Years BP	1σ Error Bars, (yrs)
XA2831	4-5	*G.sacc*	5165±34	5480	40
XA2832	10-11	*P.obli + N. dut*	10282±29	11200	40
XA2833	29-32	*P.obli + N. dut*	12890±38	14520	200
XA2834	57-60	*G.sacc + P.obli + G.mena*	14153±46	16320	120
XA2835	98-102	*P.obli + N. dut + G.mena + G.sacc*	15680±49	18620	70
XA2836	197-202	Most planktonic foraminifera	22175±195	26310	210
XA2837	271-276	Most planktonic foraminifera	27290±93	31920	70
XA2838	309-312	Most planktonic foraminifera	27649±83	32120*	90
XA2839	343-345	*P.obli + N. dut + G.sacc*	33229±128	37470*	740
XA2840	463-467	*P.obli + N. dut + G.sacc*	30953±118	34940	200
XA2841	549-553	*P.obli + N. dut + G.sacc*	33142±183	37390	710

Note: *indicates data point not adopted in the age-model reconstruction; a *G.sacc=G. sacculifer*; *P.obli=P. obliquiloculata*; *N. dut=N. dutertrei*; *G.mena=G. menardii*; b All ages were converted to calendar years using the CALPAL 2007-Hulu software (Jöris and Weninger, 1997).

Xiang et al., 2009

Figure 2: Age Versus Depth Diagram for Core NS07-25 with Sedimentation Rate



Xiang et al., 2009

and 31 kyr BP. The age of the oldest sediments in core YDY05 is about 37.39 kyr BP.

Stable Isotopes

The $\delta^{13}C$ values in *G. ruber* vary between 0.55‰ and 1.65‰, with an average of 1.12‰ (Figure 3). The distinct enrichment in $\delta^{13}C$ observed during the Heinrich Event (HE). The $\delta^{18}O$ records of *G. ruber* vary between -3.38‰ and -1.52‰, with an average $\delta^{18}O$ of -2.27‰ (Figure 3). Higher proportions of negative $\delta^{18}O$ records occur during the period between 37 and 15 kyr BP, and higher proportions of positive $\delta^{18}O$ records occur after 15 kyr BP.

The $\delta^{13}C$ values obtained from *C. wuellerstorfi* specimens are shown in Figure 3. Glacial $d^{13}C$ values of *C. wuellerstorfi* in core NS07-25 shows minor fluctuations. The values obtained with $\delta^{13}C$ analysis of *C. wuellerstorfi* range between 0.60‰ and -0.69‰. Maximum and minimum $\delta^{13}C$ values for *C. wuellerstorfi* are referred to as 10.2 and 17.6 kyr BP.

Faunal Variation

The relative abundance of *G. bulloides* in the core NS07-25 range from 0.88% to 19.26% (Figure 3). The peaks of the *G. bulloides* abundance observed during the period between 15 to 18 (HE1), 24 to 27 (HE2) and 30 to 32 kyr BP. The relative abundance of *G. bulloides* decreases throughout the deglaciation until 13 kyr BP. The abundance of *G. bulloides* is uniform throughout the period between 13 to 6 kyr BP. The high planktonic foraminiferal abundance observed during the period between 36 to 31 kyr BP (Figure 3). A gradual increase in planktonic foraminiferal abundance is observed during the deglaciation and early Holocene. The relative abundance of warm water species including *G. ruber, G. mernadii* and *G. sacculifer* was higher after the 17.5 kyr BP and lower during the glacial (Figure 3).

Total Organic Carbon (TOC) and C/N

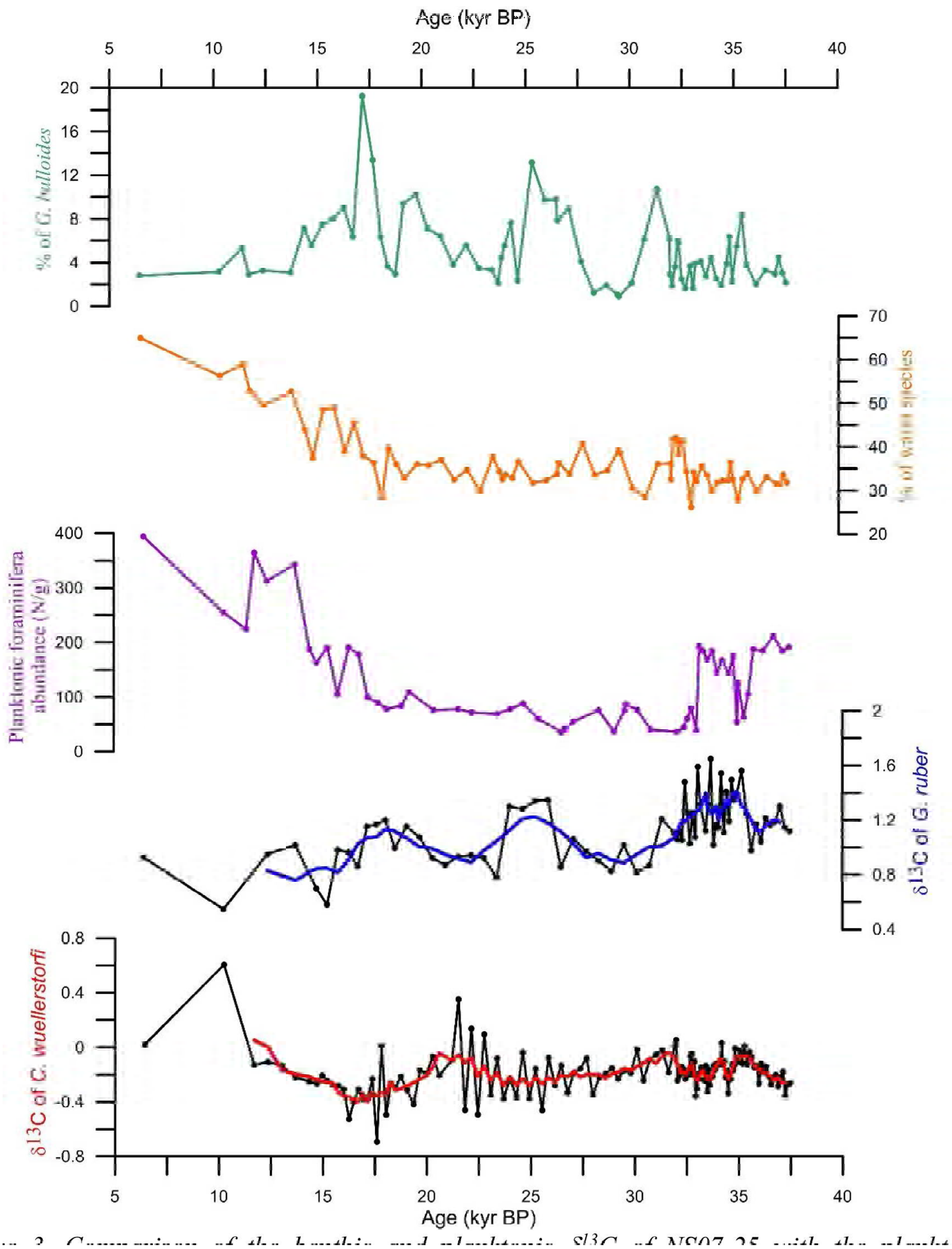
The range of values in the core NS07-25 is from 2.16% to 0.87% for TOC with 1.51% average value (Figure 4). A relatively low values in TOC is observed during the period between 37 to 31 kyr BP, followed by a gradual decrease during the period between 30 to 27 kyr BP. A distinct increase in TOC is observed during the HE2 and HE1. The C/N fluctuations in our study range from 14 to 7 (Figure 4).

Discussion

Sedimentation Rate

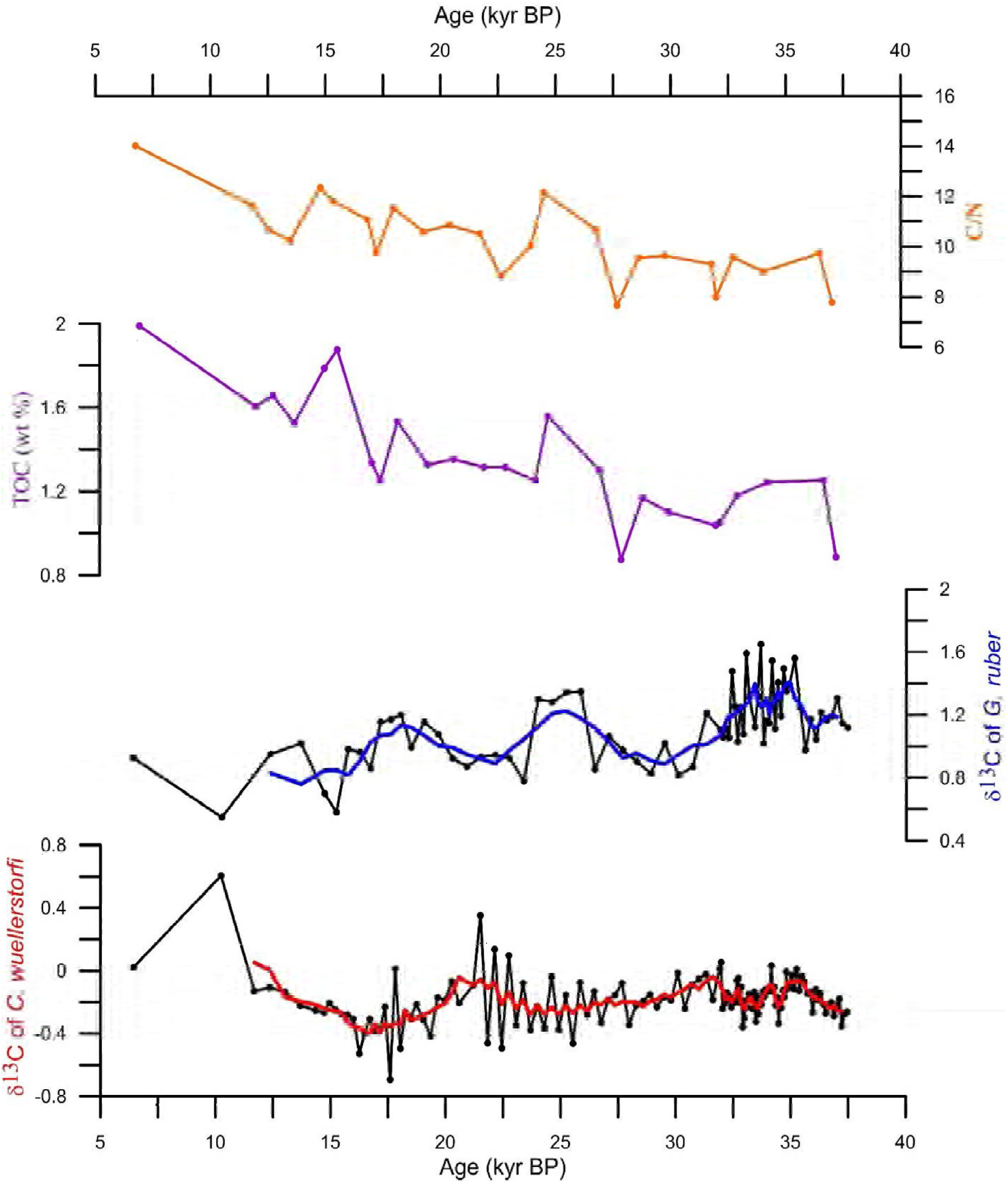
The total sedimentation rate (or sediment accumulation rate) control the proportion of organic matter preservation in the marine sediment (Müller and Suess, 1979). The high sedimentation rates indicate high organic carbon burial rate. In this study, the most prominent increase in sedimentation rates is shown during the glacial than Holocene (Figure 2). The changes of sedimentation rate patterns reflect the impact of climate change to colder and drier condition during the period between ~36 to 31 kyr BP, tentatively assigned to Heinrich event 4 (Fang et al., 1998). The highest sedimentation rate may have occurred due to a higher aeolian flux (Thilakanayaka et al., 2019). This significantly higher sediment input may increase marine productivity by providing more nutrient to the ocean. Very low sedimentation rate during the interglacial could be due to the higher sea level, which reduced the terrigenous input to the core location.

Figure 3: Comparison of the Benthic and Planktonic D[13]c Of Ns07-25 With the Planktonic Foraminiferal Abundance, Percentage of Warm Species



Xiang et al., 2009

Figure 4: Comparison of Benthic and Planktonic D[13]c Of Ns07-25 With the Total Organic Carbon (TOC) and C/N Ratio



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Carbon and Nitrogen Ratio (C/N)

The ratio of sedimentary C/N is extensively used to distinguish the terrestrial and marine organic carbon. It has been revealed that terrigenous C/N ratios are typically higher than 20, whereas marine C/N ratios range between 5 to 10 (Tyson, 2012). In this study, ratios of C/N range between 14 and 7 suggest an organic matter in the marine sediments originates within the marine environment (Figure 4).

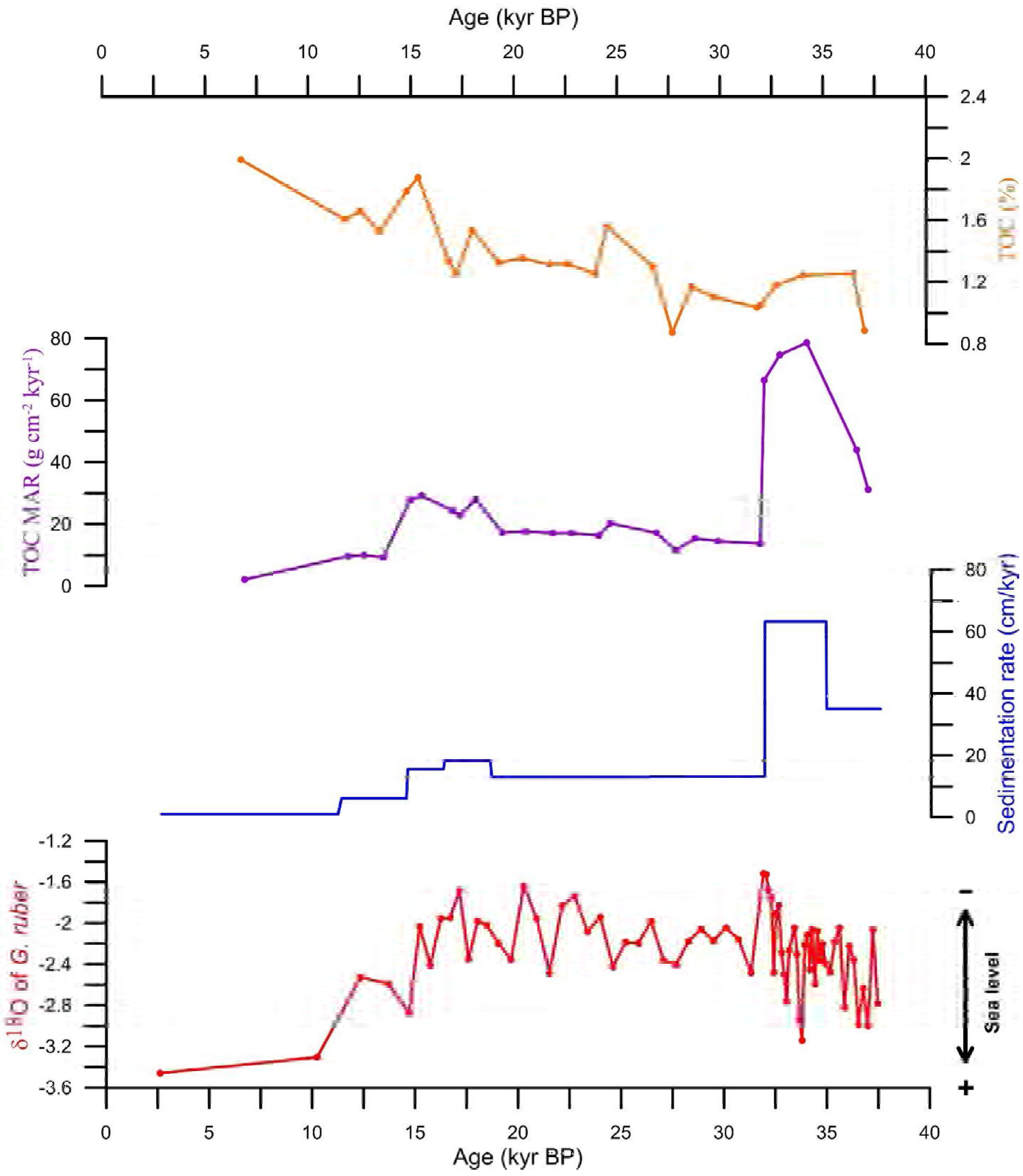
Foraminiferal $\delta^{13}C$ and Paleoproductivity

The $\delta^{13}C$ recorded by epibenthic *C. wuellerstorfi* and planktonic *G. ruber* in core NS07-25 reflects the millennial climate and productivity changes during the last 37 kyr BP. The accurate information about the environmental changes is faithfully recorded in the stable isotope composition of benthic foraminifera. Benthic foraminiferal carbon isotopic composition is considered as a faithful recorder of the $\delta^{13}C_{DIC}$ of the bottom water mass and is widely used in the paleoenvironmental reconstructions (Mackensen et al., 1994; Thomas et al., 1995; Loubere, 1999; Wollenburg et al., 2001; Waddell et al., 2009). On the other hand, the planktonic foraminiferal $\delta^{13}C$ is widely used as surface water paleoproductivity indicating proxy in the ocean (Berger et al., 1978; Penaud et al., 2010; El Frihmat et al., 2015). Increasing $\delta^{13}C$ values in planktonic foraminifera reflect enriched surface water productivity, as the enrichment in ^{13}C in the sea surface due to rapid use of ^{12}C through the photosynthesis (Penaud et al., 2010).

Our stable carbon isotopic data comparison shows that late glacial productivity relatively higher than the Holocene. These productivity changes between late glacial and Holocene is in line with other published records from nearby locations (Pelejero et al., 1999). The $\delta^{13}C$ variation of the *C. wuellerstorfi* during the period between 37 to 22.5 kyr BP shows minor fluctuation compared to the planktonic $\delta^{13}C$ variations. The planktonic $\delta^{13}C$ records combined with a high *G. bulloides* abundance indicates increased surface productivity during the Heinrich Event (HE) 1 and 2 (Figure 3). These higher surface water productivity during the HE 1 and HE 2 was recorded by different studies in different oceans (Zarriess and Mackensen, 2010, 2011). Relatively low epibenthic $\delta^{13}C$ during the HE1 further corroborate high organic matter input from surface productivity. The prominent and apparent increase in productivity signal marked in the period between 36 to 31 kyr BP by a decreasing trend to low epibenthic $\delta^{13}C$ values, increasing values of planktonic $\delta^{13}C$ records combined with similar higher planktonic foraminifera absolute abundance and *G. bulloides* abundance (Figure 3). The Holocene planktonic and epibenthic $\delta^{13}C$ records in this study is restricted to a few data points (n=5). However, the $\delta^{13}C$ fluctuations between the planktonic and epibenthic indicate relatively low sea surface productivity during the early Holocene. It is further supported by the very low abundance of *G. bulloides*.

The planktonic foraminiferal abundance during the late glacial is comparatively lower than Holocene (Figure 3). This distinct difference may be attributed to the difference in terrigenous inputs. The glacial sea level was about 115 m lower than the present (Siddall et al., 2003; Romahn et al., 2015), which may have reduced the distance between the river mouth and the core site (Figure 1a). This reduction in the distance might have directly increased the input of the terrigenous materials and lead to dilute planktonic foraminifera during the glacial. Higher $\delta^{18}O$ values of *G. ruber* confirmed a lower sea level during glacial and high sea level during the Holocene period (Figure. 5). Apart from that, the relative abundance of warm water species gradually

Figure 5: Comparison of the Planktonic d18O of NS07-25 With the Sedimentation Rate, Total Organic Carbon (TOC) and TOC Mass Accumulation rate (TOC MAR)



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increases after 17.5 kyr BP may responsible for the higher planktonic foraminiferal abundance during the interglacial (Xiang et al., 2009) (Figure 3).

Total Organic Carbon (TOC) and Paleoproductivity

High surface water primary production increases the organic matter flux to the seafloor enhanced preservation of organic carbon in the sediment (El Frihmat et al., 2015). Thus, the presence of organic carbon content in the marine sediments reflect the surface water productivity (Sarnthein et al., 1988; Jahn et al., 2003). The comparison of the TOC and mass accumulation rates of TOC (TOC MAR) of core NS07-25 shows the discernible difference during the period between 36 and 31 kyr BP. During this period, TOC MAR shows significant higher values correlating with the sedimentation rate while TOC shows relatively low value (Figure 5). Thus, we reveal that organic carbon variation in the marine sediments might be attributed to variations in surface water productivity or organic matter preservation by higher sedimentation rates. However, there is a no well-known correlation between sedimentation rate and surface productivity. Therefore, during the low productivity periods, we can have a difference in terrestrial inputs giving different organic carbon content and accumulation rates.

During the period between 15 and 2 kyr BP, TOC shows enriched values; in contrast, TOC MAR reveals low values indicating the inverse (Figure 5). The high TOC content during the period between 36 and 31 kyr BP may vary due to the excellent preservation of organic carbon due to high sedimentation rate. Therefore, we infer that organic carbon content in the marine sediments affected by both productivity and sedimentation rate. Furthermore, fluctuations in TOC and TOC MAR do not correlate with planktonic $\delta^{18}O$ records (Figure 5). The maxima of planktonic $\delta^{18}O$ reflect the periods of low sea level resulting in high nutrient influx to the study area, thus high surface productivity. Therefore, as a proxy for surface paleoproductivity, TOC is not robust for this study due to the influence of terrestrial organic matter, while the TOC MAR can be used to understand the depositional environments of organic carbon.

Conclusion

Several proxies are widely used to reconstruct the paleoproductivity changes. In addition to previously used proxies from different studies, the tracing of our productivity proxies variations (Benthic and planktonic stable carbon isotope, Total organic carbon) suggested that the stable carbon isotope constitutes of planktonic and benthic foraminifera as a reliable proxy that can be used to reconstruct the past marine productivity variations. The core NS07-25 used in this paper showed complete sedimentary records of the last 37 kyr BP.

The late glacial productivity is relatively higher than the Holocene. Enhanced surface water productivity associated with high terrigenous nutrient input during the HE1 and HE2 suggested by faunal and geochemical proxies. The planktonic and benthic $\delta^{13}C$ signals suggest low productivity, before the LGM (~24-22 kyr BP) and then increase afterward. In addition, our records show that organic carbon content in the sediment has an oceanic origin and preservation of the organic matter depends on the sedimentation rates. The buried organic matter shows a clear trend to the marine origin.

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