# OXYGEN / CARBON ISOTOPES AND PALEOPRODUCTIVITY IN THE SOUTH CHINA SEA DURING THE PAST 110 000 YEARS

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#### ABSTRACT

Stable isotope measurements on both planktonic and benthic foraminifera in two deep sea sediment cores from the South China Sea allow a detailed stratigraphy for the past 110000 years. The isotope stratigraphy is based on the benthic foraminifera *Cibicidoides wuellerstorfi*, which reveals the more consistent and stable  $\delta^{18}$ O-profile. For the last Glacial and Holocene, ages were deriverd by comparison with AMS-<sup>14</sup>C-dated  $\delta^{18}$ O-curves of other cores, with appropriate U-Th-corrections applied to the conventional <sup>14</sup>C-dates. Sedimentation rates are generally higher in glacial than in interglacial time. The higher rates during Stages 4 and 5 in the deeper core are caused by turbidites.

The  $\delta^{13}$ C niveau < -22% of total organic carbon in the sediment indicates an increased terrignous supply during the Interglacials, while marine organic matter > -20% is dominating during the Glacial.

The estimated (marine carbon) paleoproductivity which is calculated by means of an empirical equation based on the organic carbon accumulation rates show a pronounced contrast between the last Glacial and the penultimate and present Interglacial, with the glacial productivity being higher by a factor of up to 4.

The  $\delta^{13}$ C values of the epibenthic *C. wuellerstorfi* in the South China Sea conforms with the regional decrease in the western Pacific observed from west of New Zealand to the Ontong Java Plateau. The Last Glacial  $\delta^{13}$ C levels are generally 0.3‰ lighter than in the Holocene and indicate bottom water renewal mainly through the deep Bashi Channel (threshold at ~ 2600 m) in the northeast.

### INTRODUCTION

The primary productivity of the surface ocean is estimated to have been more than 3 to 4 times the present level in the coastal and shelf regions and major upwelling areas of the oceans during the last Glacial (Reimers and Suess, 1983; Muller *et al.*, 1983; Sarnthein *et al.*, 1988; Sarnthein and Winn, 1990), leading to a drawdown of atmospheric  $CO_2$  as evidenced by ice core studies (Neftel *et al.*, 1982; Barnola *et al.*, 1987). The higher productivity was accompanied by higher nitrogen / carbon ratios during the glacials (Hartmann *et al.*, 1976; Muller *et al.*, 1983). This implies a reconsideration of the proportion of organic carbon to phosphate in the Redfield ratio, enabling a much higher productivity in the tropical oceans from a limited phosphate budget during the ice ages.

In order to estimate the extent of the fluctuations in the ocean carbon reservoir which constitutes about 98% of available total carbon, and to quantify the associated changes in atmospheric  $pCO_2$ , it is necessary to determine in detail the paleoproductivity of the different parts of the world's oceans. As part of an ongoing project within the framework of the German national climate programme, the nutrient budgets of various tropical and subtropical regions in glacial and interglacial periods were analysed (Sarnthein and Winn, 1990). Here, we present further results of detailed paleoproductivity studies supported by stable isotope stratigraphy in two deep sea sediment cores, Sonne 50–29KL (N18.4°, E115.7°, 3766 m) and Sonne 50–37KL (N18.9°, E115.8°, 2695 m). The cores were raised from the continental slope off South China in the northern part of the South China Sea.

#### METHODS

All cores were sampled at 10 cm intervals, and after determination of the water content, were wet-sieved through a 100  $\mu$ m mesh. The planktonic foraminifera *Globigerinotdes trilobus* sacculifer (Brady) and *G. ruber* (d'Orbigny) as well as the benthic foraminifera *Cibicidoides wuellerstorfi* (Schwager) were picked from the 315-400  $\mu$ m size fraction for oxygen and carbon stable isotope measurements. The runs were made with a Finnigan MAT-251 mass spectrometer coupled to the automated CARBO-KIEL sample preparation device. Samples were reacted by individual acid addition. The isotope results are given on the usual  $\delta$ -scale and have a standard deviation of  $\pm 0.07\%$  for oxygen and  $\pm 0.04\%$  for the carbon isotope ratio. Organic carbon contents (weight %) were determined with the LECO instrument (accuracy  $\pm 0.5\%$ ).

Due to the proximity of our core locations to land, the sediments may contain appreciable amounts of land derived organic matter. Therefore, we have also measured the stable isotope composition of the total organic matter in the sediment, a parameter which is dependent upon the terrigenous carbon input (Erlenkeuser, 1978). For organic carbon analysis  $CO_2$  gases were prepared from sediment samples by dry combustion after carbonates were gently removed by warm 2% HCl.

# **RESULTS AND DISCUSSION**

## **Oxygen** Isotopes

The oxygen isotope events have been identified by comparison with the standard reference section of the graphic correlation composite  $\delta^{18}$ O record for sediments of the Brunhes Chron. (Prell *et al.*, 1986). For the Holocene and the Last Glacial, we have converted to calendar dates following Bard *et al.* (1990) (Table 1). The older  $\delta^{18}$ O events were date by correlation with the high resolution chronostratigraphy of Martinson *et al.* (1987). The stage boundaries from the plankton oxygen isotope curves do not necessarily coincide with those from the benthic curve. This phenomenon has been observed in a large number of cores from other marine regions, and may be due to species–specific fractionation as well as

to the influence of different water masses and microhabitats ("vital effects"). In addition, carbonate dissolution has occurred in some horizons, with the thinner shelled planktonic foraminifera being more affected than the thinner shelled planktonic foraminifera being more affected than the thicker shelled benthos. For our chronostratigraphy, we have selected the more stable benthic  $\delta^{18}$ O-curve (Table 1, Figs.1 and 2).

$\delta^{18}$ O-event	Core 29KL	Core 37KL	Conventional <sup>14</sup> C-age	Corrected age *
Info annie ser ser	(depth, cm)		(in 1000 yrs)	
Present	0.0	0.0	0.0	0.0
End termination I	61.0	91.0	9.1	9.8*
Begin termination I	126.0	161.0	14.8	18.3*
$\delta^{18}$ O-event 3	321.0	316.0	26.0	29.3*
$\delta^{18}$ O-event 3.31	546.0	561.0	Section States	55.5**
$\delta^{18}$ O-event 4.24	631.0	641.0		71.1**
$\delta^{18}$ O-event 5.1	811.0	721.0		79.3**
$\delta^{18}$ O-event 5.2	861.0			90.9**
$\delta^{18}$ O-event 5.31	921.0			96.2**
$\delta^{18}$ O-event 5.33		831.0		103.3**
$\delta^{18}$ O-event 5.4	992.5		10m10403 (01010461.0	110.8 * *

**Table 1**  $\delta^{18}$ O stratigraphy and chronology of cores 29KL and 37KL.

\* Converted to  $^{238}$ U /  $^{230}$ Th age scale after Bard *et al.* (1990).

\* \* Chronology after Martinson et al. (1987).

For the upper part of the cores which represents the time interval from the Last Glacial maximum to the present, the AMS-stratigraphy of the South China Sea core V35-5 and the East Pacific core TR163-31 were used as guides (Broecker, 1988a, b). The chronology determined by Bard *et al.* (1990) applying the Uranium-Thorium method (calendar dates) shows significant offsets of the calendric time scale from the AMS <sup>14</sup>C-ages, especially during the Termination I and the Late Glacial. According to the new, but still tentative time scale, the  $\delta^{18}$ O Stage 2/3 boundary is dated at 29.3 ka, the beginning of Termination I at about 18.3 ka, the Younger Dryas event between 12.8 ka and 12.2 ka, and the end of Termination I at around 9.8 ka. The 2 cm thick volcanic ash layer encountered at 302-304 cm in core 29KL has an interpolated age of 28.3 ka.

The planktonic and benthic  $\delta^{18}$ O-records show last glacial to interglacial differences of 1.4–1.6‰. In general, the oxygen isotope stratigraphy of both planktonic and benthic species show comparable results down to the base of oxygen isotope Stage 4, which is remarkably well pronounced in both cores. Below Stage 4, the plankton oxygen isotope curve deviates considerably from the benthic profile in both cores. The  $\delta^{18}$ O minima are not identifiable as such but appear as rather broad plateaus. A detailed intercore comparison of the isotope curves of *G. ruber*, *G. sacculifer* and *C. wuellerstorfi*, however, suggests that only the upper parts of Stage 5 (5a, 5b) are identifiable in core 37KL, while the lowest horizon in core 29KL could be assigned to Stage 5c (5d?). The  $\delta^{18}$ O-values did not reach the typical light levels of Stage 5e, and this substage is certainly not cored. The comparatively heavy







Fig.2  $\delta^{13}$ C-records of *Globigerinoides trilobus sacculifer* (Brady), *G.ruber* (d'Orbigny) white and *Cibicidoides wuellerstorlf* (Schwager) in cores Sonne 50–29KL and 50–37 KL, northern part of the South China Sea. Refer to Table 1 for depth to age conversions.

 $\delta^{18}$ O values towards the base of core 37 would suggest a possible discontinuity with parts of Stage 6 at the bottom. This remains a paradox, as this feature is not reflected in the planktonic  $\delta^{18}$ O values.

The signal of the Younger Dryas cooling event which has been clearly identified in other sediment cores from the South China and the adjacent Sulu Sea (Broecker *et al.*, 1988 a & b, Kudrass *et al.*, 1991) is suppressed in both the planktonic and benthic records of our cores. On the other hand, the Bolling / Allerod climatic changes and the associated meltwater events (e.g., Sarnthein *et al.*, 1991) are fairly well recognised in the planktonic  $\delta^{18}$ O-records of the cores. A temporary halt or slight reversion of the deglacial  $\delta^{18}$ O trend may either be caused by a subsequent climatic deterioration or large fluctuations in the fluvial discharge. In the benthic  $\delta^{18}$ O profile, the Bolling / Allerod event is also recognisable, with the second phase of the termination (Termination Ib) as a well pro-

nounced feature. These records of rapid climatic changes at the end of the Last Glacial were also reflected in the foraminiferal abundances in the South China Sea Basin (Wang *et al.*, 1986; Broecker *et al.*, 1988 a & b).

The Cibicidoides wuellerstorfi oxygen isotope in both cores (shown on time axes for easy comparison, Figs. 1 & 2) reveal that the oxygen isotope profiles of the benthic C. wuellerstorfi are closely the same for the past 88 ka, signifying that both cores were in the same ambient water mass throughout this period.

Sedimentation rates calculated from benthic oxygen isotope stratigraphy of C. wuellerstorfi show that the interglacial stages 1 and 5 normally have lower sedimentation rates of 4.3-9.3 cm / ka while in the colder stages, the rates are up to twice as high (13.9-17.5 cm / ka). The high sedimentation rates during Stages 4 and 5 and in the upper part of Stage 2 in core 29KL are due to "turbidite" cycles (25-30 cm in thickness) with irregular bottom contacts observed in sediment radio-graphs. Core 37KL, on the other hand, does not show such silty episodes, and the good correlation between the two cores signifies that the turbidtes in our cores are of local importance only, and in general have not resulted in deep erosion of the sediment layers. Sediment physical and geotechnical properties measured during the course of this study did not show any indications of major and large-scale subaqueous sediment slumps, and the studied cores appear to lie outside the path of major turbidite movements (Kudrass *et al.*, this volume).

# Paleo Productivity and the $\delta^{13}C$ Record

The new (or export) productivity of the euphotic zone, which characterizes the organic matter that leaves the surface layer, sinks into the deep sea and is preserved as organic carbon in sediment (as opposed to the total primary productivity which includes reutilized organic matter), has been estimated using the equation of Sarnthein *et al.* (1988).

$$P_{\rm exp} = 0.0238 \times C^{0.6429} \times S_{\rm B}^{0.8575} \times DBD^{0.5364} \times Z^{0.8292} \times S_{\rm B-c}^{-0.2392}$$
(1)

where

 $C = \text{organic carbon content} \quad (\text{weight \%}) \text{ of the sample} \\ DBD = \text{dry bulk density} \quad (g/\text{ ccm}) \quad (\text{solid particle density} \times (1-\text{porosity}/100)) \\ S_{\text{B}} = \text{bulk sedimentation rate} \quad (\text{cm}/\text{ka}) \\ S_{\text{B-C}} = \text{carbon free sedimentation rate} \quad (\text{cm}/\text{ka}) \\ Z = \text{water depth} \quad (\text{m}) \\ \end{cases}$ 

The results reveal that total export productivities were generally about 2.5 times higher during the glacial than during the interglacials. However, these estimates incorporate not only the marine production, but also a possible fraction of terrigenous organic carbon. The primary  $\delta^{13}$ C signatures of these two organic fractions are usually well distinguished, amounting to about - 19.5‰ (vs. PDB) for marine organic matter from equatorial oceans, and to about -26.5‰ for the terrigenous component (Erlenkeuser, 1978; Muller *et al.*, 1983; Westerhausen *et al.*, 1991). Within the bounds of these source isotope compositions, a simple two source mixing model has been applied to differentiate between the contributions of these organic fractions. The  $\delta^{13}$ C-profile and the distribution of the organic carbon content down the core run closely in parallel and clearly show that the relative proportion as well as the absolute amount of the total marine organic matter culminates in the glacial  $\delta^{18}$ O Stage 2, while in the interglacial Stages 1 and 5, the relative abundance of marine matter is on a pronouncedly lower level (Tables 2 and 3). The sample at 940–942 cm in core 29KL possibly indicates that an even higher supply of terrigenous organic matter occurs in the older interglacial deposits. It thus appears that the glacial climates are not conductive for large belts of vegetation as found today in the neighbouring continental area. These results are in harmony with the findings of Adams *et al.* (1990) showing extended desert terresded deserts and decreased vegetation , and hence reduced terrestrial organic carbon production on the Chinese mainland during the Last Glacial Maximum, 18000 year ago.

Core No. SO50-29KL		Core No. SO50-37KL	
Interval measured	$\delta^{13}\mathrm{C}$	Interval measured	$\delta^{13}C$
(cm)	‰vs. PDB	(cm)	‰vs. PDB
20-22	$-21.23 \pm 0.02$	20-22	$-21.21 \pm 0.04$
30-32	$-21.33 \pm 0.04$	40-42	$-21.24 \pm 0.02$
50-52	$-21.54 \pm 0.02$	60-62	$-21.21 \pm 0.04$
150-152	$-20.76 \pm 0.03$	80-82	$-21.39 \pm 0.04$
180-182	$-20.41 \pm 0.03$	200-202	$-20.34 \pm 0.04$
200-202	$-20.28\pm0.02$	210-212	$-21.48\pm0.03$
220-222	$-20.24 \pm 0.03$	230-232	$-24.42 \pm 0.02$
250-252	$-20.02 \pm 0.02$	250-252	$-20.29 \pm 0.06$
350-352	$-20.25 \pm 0.02$	307-309	$-19.82 \pm 0.02$
400-402	$-20.31 \pm 0.02$	347-349	$-19.72 \pm 0.02$
500-502	$-21.12 \pm 0.03$	397-399	$-20.14\pm0.02$
620-622	$-21.16 \pm 0.04$	447-449	$-19.92 \pm 0.01$
710-712	$-22.90 \pm 0.03$	500-502	$-20.64 \pm 0.02$
760-762	$-21.89 \pm 0.03$	550-552	$-20.74 \pm 0.01$
850-852	$-21.79 \pm 0.03$	600-602	$-20.85\pm0.01$
880-882	$-22.49 \pm 0.03$	650-652	$-21.46 \pm 0.03$
920-922	$-22.09\pm0.02$	710-712	$-21.53 \pm 0.03$
940-942	$-23.54 \pm 0.02$	750-752	$22.93\pm0.03$
960-962	$-22.19 \pm 0.01$	800-802	$-21.87 \pm 0.04$

**Table 2**  $\delta^{13}$ C measurements on total organic carbon in sediment

Correcting for the allochthonous contribution of organic matter from land, the dissimilarities between the paleoproductivities during the cold and the warm periods become even more accentuated. The glacial / interglacial difference for both cores increaes to a factor of up to 4, compared to a factor of 2.5 before correcting for the terrigenous fraction. Correcting for the terrigenous contribution could has far reaching implications for the global paleoproductivity and reconstructed carbon budgets, as our previous estimates (Sarnthein and Winn, 1990) did not adequately correct for terrestrial carbon because appropriate supporting data is lacking. The role of the oceans as a reservoir for carbon may have to be

further upgraded. The difference between the paleoproductivity during the last Interglacial and from Stage 4 to the lower part of Stage 3 in core 37KL is small, but is appreciable in the deeper water core 29KL (Fig. 3). This is probably an artifact of the very high sedimentation rates during Stage 4 in the latter core, and is due to the higher clastic flux and to the possibly associated amounts of allochthonous organic material. In both cores the paleoproductivities are high in Stage 2, and declined during the Holocene to present day levels. This decrease of productivity towards the end of the Last Glacial preceded the  $\delta^{18}$ O signals of both plankton and benthos in both cores by 800–1000 years.

Time period	$\delta^{13}$ C (‰ vs. PDB)	Terrigenous material (%)*
Holocene	-21.2 to -20.5	20-25
$\delta^{18}$ O Stage 2	-19.8 to -20.5	0-8
$\delta^{18}$ O Stage 3	-19.7 to -21.1	0-18
$\delta^{18}$ O Stage 4	-20.9 to -21.2	15-20
$\delta^{18}$ O Stage 4–5.1	-21.5 to -22.9	25-48
$\delta^{18}$ O Stage 5.1–5.2	-21.8 to -21.9	30-48
$\delta^{18}$ O Stage 5.3	-20.0	0-2
$\delta^{18}$ O Stage 5.4	-22.2 to -23.5	37-58

Table 3	Terrigenous fraction of	total organic carbon from	the carbon isotope levels
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\* Calculated using the end values of -19.5% for full marine and -26% for terrestrial organic material.

The  $\delta^{13}$ C records plotted vs. age (Fig.2) of the benthic foraminifera *C. Wuellerstorfi* in cores 29KL and 37KL, are almost identical for the past 88 ka. The response of  $\delta^{13}$ C of this species to the surface productivity—with the higher productivity being reflected by the lighter  $\delta^{13}$ C values—is clearly seen from a glacial-interglacial difference in  $\delta^{13}$ C of 0.45–0.5‰

(Figs. 2 and 3). The  $\delta^{13}$ C record of the planktonic species *G. ruber* in core 37KL reveals a similar response to the higher glacial productivity, corresponing with findings in other oceanic regions (Sarnthein and Winn, 1990). On the other hand, the  $\delta^{13}$ C record of *G. trilobus sacculifer* in core 29 KL shows only a general gradual trend towards heavier  $\delta^{13}$ C levels during the past 60 ka, without any distinct response to the higher glacial productivity. Since both cores lie in similar oceanographic and geographic settings, this phenomenon might be attributed to a species—specific characteristic.

## Deep Water Distribution

The Geosecs sections illustrating the distribution of total  $CO_2$  in the western Pacific (Craig *et al.*, 1981) show a water mass spreading northward between 2000 m and 3000 m water depth (Fig. 4). A transect of the Holocene  $\delta^{13}C$  levels of the benthic species *C. wuellerstorfi* which measures the carbon isotope composition of the deep water mass show a gradual trend towards lighter values from New Zealand (cores DSDP 594 and Q208,  $\delta^{13}C$  between 0.94‰ and 0.47‰) through the Fiji Islands (0.54‰ to 0.32‰, Winn *et al.*, 1990) to  $\delta^{13}C$  of 0.32‰ to 0.25‰ on the Ontong Java Plateau (Vincent *et al.*, 1981) and  $\delta^{13}C$  levels between 0.27‰ and 0.22‰ in the South China Sea (this study). The glacial

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**Fig.3** Estimates of total export productivity and net export productivity of marine provenance (dark hatched area) in the South China Sea cores Sonne 50–29 KL and 50–37 KL. Note that the apparent high productivity around 75 ka in core SO50–29 KL is an artifact of high sedimentation rates due to turbidites.

ransect shows a similar trend towards lighter  $\delta^{13}$ C levels with values between 0.34‰ and 0.19‰ off New Zealand to figures of 0.21‰ to -0.05% in the Fiji–Lau basins, to-0.24% in the Ontong Java region, to values of -0.19% to -0.23% in the South China Sea. For both time slices, however, core V35–05 from the southern part of the basin (Broecker *et al.*, 1988 a and b) reveals much lighter values (by 0.2‰) (Fig.4). In general, glacial  $\delta^{13}$ C values are about 0.3‰ lighter than in the Holocene. During the glacial, the South China Sea is an enclosed inland sea of limited extent having its main connection to the West Pacific through the Bashi Channel with a threshold depth of around 2500 m, and through the

Balabac and Mindoro Straits to the Sulu Sea (Wang, 1990). The regional  $\delta^{13}$ C trends are thus in accordance with this paleogeographical setting, with major deep water renewal / ventilation only through the north-east sector of the basin.



Fig.4  $\delta^{13}$ C transects across the western Pacific contours show total carbon dioxide in sea water after Craig *et al.* (1981). (a) Holocene; (b) Last Glacial.

# CONCL USIONS

High resolution oxygen isotope stratigraphy based on planktonic and benthic foraminifera in two deep sea sediment cores from the northern flank of the South China basin show that the major global isotope signature is also well documented in this area. Both cores penetrated down to isotope Stage 5. The glacial-interglacial  $\delta^{18}$ O shift amounts to about 1.6‰ for the planktonic species G. trilobus sacculifer and G. ruber, and is about 1.4‰ for the

benthic C. wuellerstorfi. Sedimentation rates were up to twice as high during the glacial stages than during the interglacials. Coarse turbidites were not encountered. The silty "turbidite" cycles below Stage 3 in core 29KL have only local significance. The volcanic ash layer in core 29 KL has an interpolated age of 28.4 ka.

 $\delta^{13}$ C values of total organic fraction indicate that the glacial sediments have organic carbon of dominantly marine provenance. On the other hand, the interglacial deposits reveal a higher supply of terrigenous organic matter, thus enhancing the relative glacial / interglacial contrast in marine productivity.

Export productivities were up to 400% higher during the last glacial compared to the penultimate and present interglacials. The carbon isotope signature of the benthic foraminifera *C. wuellerstorfi* are similar in both cores for the past 88 ka and reflect this productivity effect—the glacial-interglacial difference in  $\delta^{13}$ C being -0.45% to -0.50%. The  $\delta^{13}$ C response of the planktonic foraminifera *G. ruber* to the higher glacial productivity is observed in core 37KL.

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