

## **Biogenic Sedimentation Patterns in the Northern South China Sea: An Ultrahigh-Resolution Record MD972148 of the Past 150,000 Years from the IMAGES III - IPHIS Cruise**

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### **ABSTRACT**

Ultrahigh resolution records of carbonate and organic carbon concentrations from core MD972148 (19°47.804'N 117°32.56'E; water depth 2830 m) provide information on glacial-interglacial as well as millennial to centennial scale variability in the production of biogenic sediments in the northern slope of the South China Sea (SCS) over the past 150,000 years. A preliminary age model of this record is estimated using a biostratigraphic datum of *Globigerinoides ruber* (pink) and the relationship of carbonate concentrations and  $\delta^{18}\text{O}$  of planktonic foraminifers shown in previous SCS records. The downcore patterns in this record show that the carbonate concentration maxima correspond to interglacial times and minima correspond to glacials, indicating effects of dilution of terrigenous clastic sediments from nearby continents. Exposure of extensive continental shelf and relatively dry climate during glacial periods are responsible for the enhanced input of terrigenous components into the SCS. Two long-term trends in which the organic carbon content was increased steadily from stage 5 to stage 2 and from the late stage 7 to stage 6 are clearly observed. High organic carbon concentrations seem to occur during the transition from major glacial to interglacial stages and are probably controlled by effects of preservation or rates of sedimentation, or biological productivity. We have also observed significant components of high-frequency variability in the carbonate and organic carbon concentration records. These rapid concentration changes can be attributed possibly to highly-unstable climatic conditions in the SCS during the late Quaternary.

(Key words: Paleoceanography, Late Quaternary, Carbonate sedimentology, South China Sea)

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## 1. INTRODUCTION

Analyses of air trapped in Antarctic polar ice cores (Barnola et al., 1987; Neftel et al., 1988) have shown that atmospheric carbon dioxide concentrations ( $p\text{CO}_2$ ) during the last ice age were significantly lower than during the preindustrial Holocene—about 200 ppm compared to 280 ppm. More recent studies on the oxygen isotope ratio ( $\delta^{18}\text{O}$ ) of the ice from Greenland and Antarctic ice core records (GRIP Project Members, 1993; Dansgaard et al., 1993; Jouzel et al., 1993) also indicate fluctuations of air temperatures at a higher frequency than orbital, Milankovitch time scales in the past 80,000 years. Attempts to explain the atmospheric  $p\text{CO}_2$  and the high-frequency climatic changes on this time scale focus on the factors of atmospheric circulation, iron supply, and marine nitrogen fixation rates in high-latitude oceans (Broecker and Henderson, 1998) as well as patterns of surface circulation in low-latitude oceans (Charles et al., 1996; Mix and Morey, 1996; Little et al., 1997).

Biogenic components in marine sediments are important proxy indicators for determining the past surface and deep circulation, and biological productivity patterns in paleoceanography. Most of these proxy indicators record more than one oceanic process, so two or more indices must be used to approach the question of the study. Among various indices, organic carbon and carbonate concentrations and fluxes are two most commonly-used. Carbonate and organic carbon accumulations in sediments depend on both surface water supply and seafloor preservation. A few long and high-quality records of the biogenic sediment components have up to now been available from the western tropical Pacific, one of the major controlling contributors of world climate (Wu and Berger, 1991; Thunell et al., 1992; Miao et al., 1994; Kawahata et al., 1998). In this study we present a detailed 150,000-year long (core length 48.72 m) and ultra-high resolution core record MD972148 of carbonate and organic carbon concentrations from the South China Sea (SCS), one of the major marginal seas in the western Pacific. MD972148 (19°47.804'N 117°32.56'E) is at a water depth of 2830 m on the northern slope of the SCS basin approximately 300 km off the mouth of Pearl River in the southeast coast of the mainland China. This core was taken during an IMAGES III cruise in 1997 (Chen, Beaufort, and the Ship-board Scientific Party, 1998). The location of this core receives sediments from both continental and oceanic sources and is consequently well-positioned to monitor the effects of glacial-interglacial sea-level changes on sediment delivery. The position of core MD972148 is also just at the "cold tongue" of a local water mass that is presently affected by cold winds and strong mixing during winter monsoon seasons (Ho et al., 1998; Chen et al., 1998). The sedimentary record from this position is therefore also responsive to changes in East Asian monsoon wind strength (Huang 1997a; b).

For interpretation of the sedimentary carbonate and organic carbon records from marginal seas, additional factors such as the processes of terrigenous dilution, sediment advection and redistribution, as well as organic carbon preservation and remineralization must be evaluated as to their relative importance in contributing to the signals. Several previous studies have addressed some of these problems for SCS sediments (Thunell et al., 1992; Kuehl et al., 1993; Schönfeld and Kudrass, 1993; Miao et al., 1994; Chen et al., 1997). In these studies, changes in the position of sea-level were thought to be a primary control for the accumulation rate changes of terrigenous input, via a mechanism of shifting depocenters of fluvial deposits along

the outer shelf and continental slope (Schönfeld and Kudrass, 1993). Increased terrigenous input results in a dilution of carbonate composition in SCS sediments. Increased accumulation rates of organic carbon and carbonate are indicative of high surface water productivity in the glacial stages of the SCS (Thunell et al., 1992), and the glacial-interglacial accumulation changes reflect also a typical Indo-Pacific carbonate preservation pattern of better preservation in the glacial and less preservation in the interglacial stages (Chen et al., 1997).

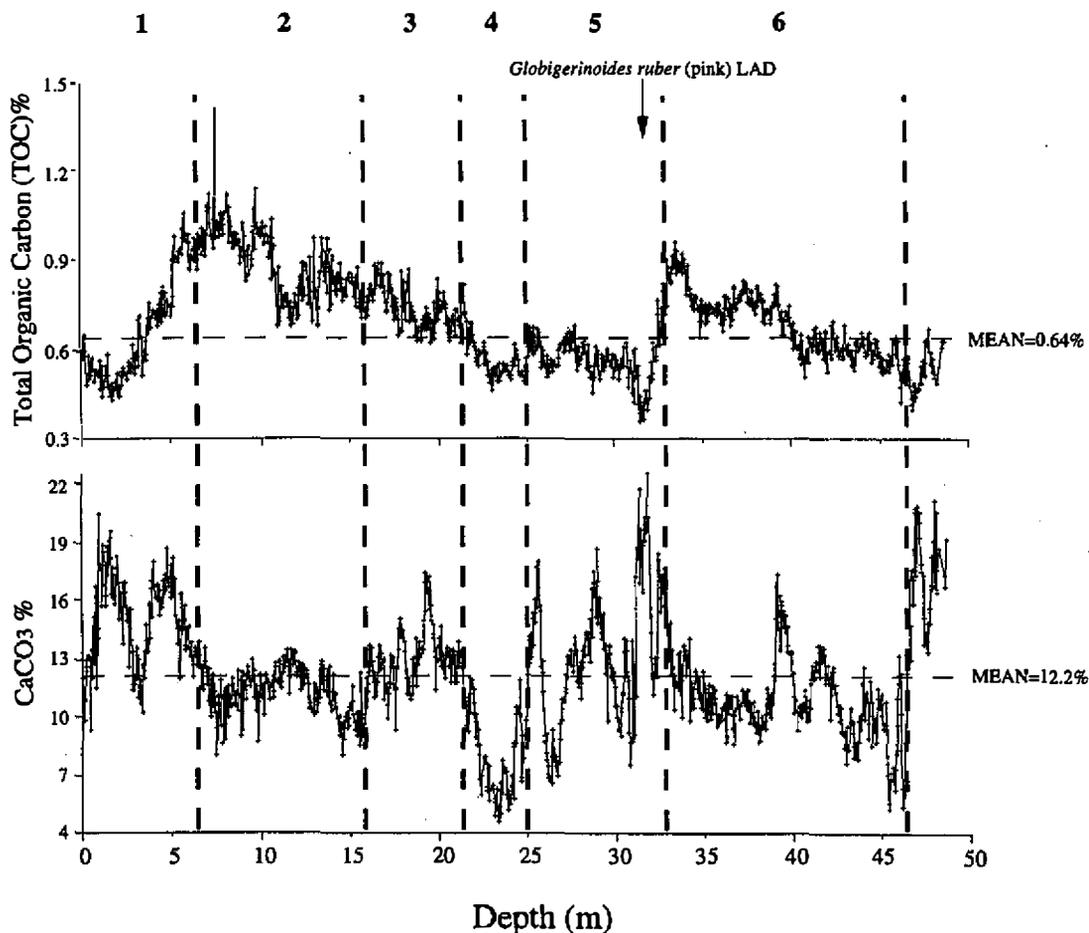
## 2. DATA AND METHODS

Downcore samples were collected at 4 cm intervals from core MD972148. The total length of the core 48.72 m allowed us to obtain approximately 1200 samples. In the preliminary stage of the study, our results are presented based on a qualitative age control in which the placement of oxygen isotope stage 1 through 7 is determined by the temporal pattern of carbonate concentrations and a biostratigraphic last appearance datum (LAD) of a planktonic foraminifer species *Globigerinoides ruber* (pink form) around 120,000 years ago (Thompson et al., 1979). The boundaries of major isotope stages coincide with major changes in carbonate concentrations (Figure 1) because the variations in the amount of dilution by terrigenous material in the SCS are associated with sea-level changes (Schönfeld and Kudrass, 1993). The first-order structures shown in Figure 1 indicate that three intervals of low carbonate concentrations (8-9 m, 23-24 m, and 38-39 m) can be correlated with oxygen isotope stage 2.2, 4.2, and 6.4; and three intervals of high carbonate concentrations (0-6 m, 24-34 m, and 46- m) are representative of stages 1, 5, and the latest part of stage 7. The success of this type of isotopic and sedimentological correlation in SCS records was demonstrated in many previous studies (Huang et al., 1997a; b; Chen and Huang, 1998). The LAD of *Globigerinoides ruber* (pink form) help to identify the boundary of stage 5 and 6. The location of this datum in this core is at 32 m, which is consistent with our preliminary age model estimates.

Samples were crushed to a fine powder after drying at 50°C, and split into several sub-samples for analyses. The total carbon content (TC) of the samples was determined by a HORIBA EMIA-8200 Carbon Analyzer. The procedure involves heating the sub-samples at ~1300°C and measuring the combustion product CO<sub>2</sub> gases by gas chromatography. The resulting precision was ±3% of the values being measured. The carbonate content of the samples was determined by a fuming method. HCl acid was used to remove the carbonate content (TIC) of separate sub-samples. The sub-samples after the acid reaction were repeatedly determined for remaining carbon content by the combustion method using the Carbon Analyzer. The carbonate content can thus be calculated by subtraction of TOC from TIC values. The TOC and carbonate concentration data of MD972148 tabulated vs. depth are available electronically at Paleooceanographic Data Center of Core Laboratory-Center for Ocean Research, NSC, at the Institute of Applied Geophysics, National Taiwan Ocean University, Keelung, Taiwan, R.O.C. (Internet:<http://140.121.175.114>).

## 3. RESULTS

Carbonate content makes up ~ 5 - 23 wt.% of the MD972148 sediments (Figure 1). The



*Fig. 1.* Total organic carbon (TOC) and carbonate ( $\text{CaCO}_3$ ) concentrations of sediments from oxygen isotope stages 1 through the late stage 7 in MD972148. The placement of the oxygen isotope stages 1 through 7 in the record is assigned on the basis of carbonate -  $\delta^{18}\text{O}$  relationship recognized in many previous South China Sea studies (Thunell et al., 1992; Wang et al., 1995; Chen et al., 1997). Major changes in concentrations of  $\text{CaCO}_3$  occur at stage boundaries in response to differences in glacial-interglacial / sea-level conditions in the South China Sea.

mean value is ~12.2 wt.%. The general downcore pattern of the maxima and minima is that carbonate abundance maxima correspond to interglacial times and minima correspond to glacials, the well-known pattern for the SCS cores above regional lysocline (Thunell et al., 1992; Wang et al., 1995; Chen et al., 1997). High abundances are observed in downcore depths of around 1.5 m, 5 m, 19.5 m, 25.5 m, 29 m, 31.5 m, 32.5 m, 39.5 m, 47 m, and 48 m.

The quantitative age controls of these high abundances peaks are awaiting for high-resolution oxygen isotope and AMS C<sup>14</sup> dating stratigraphies. But preliminary age estimates can be determined by the isotopic and sedimentological correlation on the basis of previous SCS cores as following: 1.5 m and 5 m (stage 1); 19.5 m (stage 3); 25.5 m, 29 m, 31.5 m, and 32.5 m (stage 5); 39.5 m (stage 6); 47 m and 48 m (stage 7). Low abundances are observed in downcore depths of around 0 m (coretop), 3 m, 7.5 m, 15 m, 23.5 m, 26.5 m, 30.5 m, 37 m, 41 m, 43 m, and 43.5 m. The age estimates for these carbonate lows are as following: 0 m and 3 m (stage 1); 7.5 m and 15 m (stage 2); 23.5 m, 26.5 m, and 30.5 m (stage 5); 37 m, 41 m, 43 m, and 43.5 m (stage 6). Although most of the high carbonate abundances are associated with interglacial stages (excluding a small peak around 39.5 m), some carbonate low abundances seem to occur during interglacial stages. These interglacial low carbonate events are clearly amplified in oxygen isotope stage 1 and 5. Besides the most recent one in the coretop, one event at around 3 m seems to have occurred during the middle Holocene, and three pronounced events at around 23.5 m, 26.5 m, and 30.5 m seem to be associated with stage 5.0, 5.2, and 5.4. These interglacial low carbonate abundances values show comparable, or even more lower values, than the values in the glacial stages.

Organic carbon content constitutes ~0.2 - 1.4 wt.% of the sediments (Figure 1). The mean value is ~0.64 wt.%. The general downcore pattern of the organic carbon maxima and minima exhibits more low-frequency variability than that shown in carbonate abundances. Over the broad, low-frequency curve of the organic carbon concentration variations, high values are observed in downcore depths of around 7.5 m and 33.5 m; and low values are observed around 2 m and 31.5 m. Two long-term trends in which the organic carbon content was increased steadily are clearly observed: one from the core bottom to around 33.5 m and another from around 31.5 m to 7.5 m. High organic carbon concentrations seem to occur during the transition from major glacial to interglacial stages. For example, at 7.5 m depth of the core, the organic carbon concentrations are increased during the transition of stage 2 to stage 1; and at 33.5 m depth, the organic carbon concentrations are increased during the transition of stage 6 to stage 5. Two minimum organic carbon concentration values seem to occur during interglacial stages: the low values of 2 m in the Holocene and of 31.5 m in the stage 5.5. We want to emphasize here that because of the lack of a quantitative, high-resolution age model at this preliminary stage of analysis, calculation of mass accumulation rates (MAR: g/cm<sup>2</sup>/kyr) is impossible. To avoid the forced apparent anticorrelation in percentage data, we need to quantify the true variability of each component by calculating MAR in future studies.

#### 4. DISCUSSION

Cyclical fluctuations in carbonate concentrations are common features of pelagic and hemipelagic marine sediments deposited during the late Neogene and Quaternary. The variations in concentrations of carbonate in the samples we examined from core MD972148 are identical to the patterns reported by many previous studies (Thunell *et al.*, 1992; Wang *et al.*, 1995; Chen *et al.*, 1997; Chen and Huang, 1998), while the results presented here represent so far the most high-resolution and longest record (stage 1 to late stage 7) from the SCS. We

therefore use these carbonate fluctuations to compare organic matter delivery in the SCS for the past 150,000 years, with a possible resolution up to millennial to centennial time scales. In general, sediments deposited during glacial periods have low abundances of carbonate, whereas those deposited during interglacial periods have elevated abundances. The carbonate abundance can be affected by three main processes: carbonate dissolution, dilution of non-biogenic material such as terrigenous, eolian, and volcanic particles, or of biogenic siliceous particles, and carbonate productivity (Volat et al., 1980).

Carbonate dissolution in depths above the regional lysocline (~ 3000 m, Rottman, 1979), as at core location of MD972148, appears to be caused principally by microbial degradation of marine organic matter and consequent production of interstitial dissolved carbon dioxide (Berger, 1970; Berger et al., 1982; Emerson and Bender, 1982). This dissolution is controlled by the availability of readily metabolized marine organic matter in sediments. A particularly important factor that usually modifies delivery of marine organic matter to slope sediments is glacial-interglacial variations in sea level. Supply of organic matter from the continental shelf increases during regressions and decreases during transgressions (Thunell, 1976; Broecker, 1982; Diester-Haass et al., 1986). In addition, wind strength evidently intensifies and enhances surface water productivity during glacial periods. In the SCS, many previous studies (Duplessy, 1982; Huang et al., 1997a; b; Chen and Huang, 1998) suggest that glacial periods are characterized by strong winter monsoon winds. The resulting increased productivity further magnifies delivery of marine organic matter to the sea bottom during glacial intervals. Dissolution does not, however, appear to have been important in determining the carbonate abundance fluctuations in core MD972148. In contrast, dissolution seems to be increased during interglacial periods, inasmuch as the fragmentation rate of planktonic foraminifers (M.-T. Chen, unpublished data) is relatively high in interglacial sediments.

Fluctuations in carbonate productivity is another possible cause for the changes in carbonate abundances recorded in core MD972148. In the SCS, the surface water productivity was estimated as approximately 2 times higher during the last glacial maximum (Thunell et al., 1992). Sediments in core MD972148 contain evidence of higher marine productivity during glacial periods. The evidence includes the higher abundance of alkenones, biosynthesized by a restricted group of prymnesiophyte algae, with most from the coccolithophorid *Emiliania huxleyi* (Volkman et al., 1980; Brassell et al., 1986) during glacial times (C.-Y. Huang, unpublished data). Therefore, productivity appears to be insignificant in controlling the carbonate abundance fluctuations in core MD972148.

On the basis of the preliminary observation, we infer that the dominant factor for controlling the carbonate concentration cycles in SCS sediments is variation in the amount of dilution by non-biogenic material. Clastic continental sediments are apparently increased at this location during glacial periods due to more closer depocenters of fluvial deposits along the outer shelf and continental slope associated with the sea-level changes (Schönfeld and Kudrass, 1993). More terrigenous input during glacial times are also attributable to dryer / less vegetation cover conditions over the nearby continents. The dilution by biogenic siliceous particles during glacial periods is also possible, but no firm evidence exists to document the variability of this component at this stage. Some short periods of low carbonate concentrations may be caused by high downward fluxes of biogenic siliceous particles, in response to high productiv-

ity, or increased silica input into the oceans by volcanic activities.

Organic carbon concentrations of core MD972148 are increased during glacial periods. Intensification of East Asian winter monsoon winds is postulated to have increased mixing in surface waters and consequently increased primary productivity (Huang *et al.*, 1997a; b). Increased glacial abundances of alkenones in this core (C.-Y. Huang, unpublished data) may support that the productivity increased over the northern slope of the SCS during glacial times. The greater inputs of clastic sediments during periods of glacial climate may have been also accompanied by high fluxes of continental organic matter into the SCS. Moreover, the higher glacial sedimentation rates may have preserved a large fraction of downward fluxes of organic matter into the sediments. Further measurements of organic matter C/N ratios and  $\delta^{13}\text{C}$  values will help to distinguish among these possibilities. We have noticed that high organic carbon concentrations in this record seem to occur during the transition from major glacial to interglacial stages, at 7.5 m and 33.5 m depths (Figure 1). If this pattern is attributed to preservation, it implies the presence of more nutrient-depleted deep waters with lower  $\text{CO}_2$  content during these two intervals. Previous analyses of carbonate preservation patterns in the Indo-Pacific Ocean (Peterson and Prell, 1985; Farrell and Prell, 1989) and in the SCS (Chen *et al.*, 1997) indicated that during the glacial to interglacial transitions, carbonate preservation levels are increased than that in the other intervals. On the basis of these we conclude that corrosiveness with respect to carbonate in deep water masses seems to be a factor controlling the organic carbon concentration pattern in core MD972148.

Considerable variability exists in the organic carbon concentrations, especially in the interval of 5 - 25 m depth of core MD972148. Several extraordinarily high concentration values seem to occur during the oxygen isotope stage 2-4. Concentrations in closely spaced samples differ by a factor of two, indicating significant changes. The rapid organic carbon concentration changes can be attributed to either dilution effects or productivity fluctuations, or a combination of both factors. No matter which factor plays a role, the variability suggests that the climate condition in this core location was highly-unstable during the latest glacial stage.

## 5. CONCLUSIONS

The results of measurements of TOC and carbonate concentrations for the ultra-high resolution core record MD972148 provide information about glacial-interglacial, as well as millennial to centennial scale variability in the delivery or production of organic matter and carbonate in the northern slope of the SCS. The following conclusions can be drawn from the presentation of this study:

(1) Over a glacial-interglacial time scale, the carbonate concentration maxima correspond to interglacial times and minima correspond to glacials in this core. This downcore carbonate fluctuation exhibits the well-known pattern for the SCS cores above regional lysocline and is driven by dilution of terrigenous clastic sediments;

(2) The general downcore pattern of the organic carbon maxima and minima exhibits more low-frequency variability than that shown in carbonate abundances. Two long-term trends in which the organic carbon content was increased steadily from stage 5 to stage 2 and

from the late stage 7 to stage 6 are clearly observed. High organic carbon concentrations seem to occur during the transition from major glacial to interglacial stages. The temporal patterns of organic carbon seem to reflect changing levels in biological productivity, preservation, and/or sedimentation rates;

(3) Considerable variability exists in the carbonate and organic carbon concentrations. These rapid concentration changes can be attributed to possibly highly-unstable climatic conditions in the SCS during the late Quaternary.

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