Enhanced deepwater circulation and shift of sedimentary organic matter oxidation pathway in the Okinawa Trough since the Holocene

S. J. Kao,[1,2] C. S. Horng,[3] S. C. Hsu,[1] K. Y. Wei,[4] J. Chen,[1] and Y. S. Lin[4]

Received 4 April 2005; revised 11 July 2005; accepted 21 July 2005; published 12 August 2005.

[1] High-resolution biogeochemical and magnetic property analyses of a 20-kyr sediment core in the Okinawa Trough revealed a significant upward decrease in total sulfur content (TS) at around 10 cal ka BP, which coincides with a transformation from foliation to anomalous sedimentary magnetic fabric, which indicates an enhancement of deepwater circulation. Synchronous change in biogeochemical and magnetic properties in sediments was likely triggered by the intensified Kuroshio Current, which strengthened surface water productivity and the relative input of marine organics to the sediments. However, this event did not promote sedimentary sulfur burial; instead, the synchronously enhanced deepwater circulation switched the organic carbon oxidation pathway from sulfate reduction to aerobic respiration which resulted in TS-depleted sediments. **Citation:** Kao, S. J., C. S. Horng, S. C. Hsu, K. Y. Wei, J. Chen, and Y. S. Lin (2005), Enhanced deepwater circulation and shift of sedimentary organic matter oxidation pathway in the Okinawa Trough since the Holocene, *Geophys. Res. Lett.*, *32*, L15609, doi:10.1029/2005GL023139.

1. Introduction

[2] The Kuroshio Current (KC), which constitutes the Western Boundary Current of the western Pacific, carries abundant heat from equatorial to mid-latitudes and strongly influences climate over the northwestern Pacific region. The present KC enters the Okinawa Trough (OT) along the outer edge of the East China Sea continental shelf and flows to the northeast and bifurcates into the Ryukyu Arc through Tokara Strait and into the Yellow Sea and Japan Sea, respectively (Figure 1). However, during the last glacial maximum (LGM) the main route and strength of the KC probably differed from that at present due to a 120-m sea level drop and/or the hypothetical emergence of a Ryukyu-Taiwan land bridge [*Ujiié et al.*, 1991, 2003; *Ahagon et al.*, 1993; *Ijiri et al.*, 2005]. KC intensity and flow-path in the OT during the last glacial and Holocene periods have been documented, with most studies focusing on surface water hydrology by analyzing planktonic foraminiferal assemblages and their isotopic compositions [*Li et al.*, 1997, 2001; *Xu and Oda*, 1999; *Ujiié and Ujiié*, 1999; *Jian et al.*, 2000; *Ujiié et al.*, 2003]. These studies have paid little attention to sediment diagenesis and biogeochemistry related to deepwater hydrology. To decipher depositional conditions and diagenesis and their linkages to the surface KC dynamics and evolution of deepwater circulation, biogeochemical parameters coupled with paleomagnetic analyses were made on a sediment core from the southern OT.

2. Materials and Methods

[3] A giant piston core, MD012403 (total length 36 m), was taken by RV *Marion Dufresne* on May 28, 2001 at 123.28°E, 25.07°N (Figure 1) at a water depth of 1420 m during the IMAGES VII, WEPAMA cruise. Continuous paleomagnetic samples were obtained by pressing 7-cm^3 plastic cubes into the surface of the split core. Low-field magnetic susceptibility was measured with a Bartington Instruments MS2 system. An AGICO KLY-3S Kappabridge was used to measure the magnitude and direction of the anisotropy of magnetic susceptibility (AMS). The natural remanent magnetization (NRM) was measured with a 2G Enterprises cryogenic magnetometer. To examine the stability of the NRM, stepwise alternating field (AF) demagnetization was carried out on samples using an ASC D-2000 AF demagnetizer. Demagnetization was performed at 17 steps to 85 mT, with a 5 mT increment between steps. Characteristic remanent magnetization (ChRM) directions were determined by performing a linear regression through the data for multiple demagnetization steps [*Kirschvink*, 1980]. Maximum angular deviation values associated with the ChRM determinations are less than 10°.

[4] Selected sediments were sampled for analysis of bulk geochemical parameters. Wet sediments were washed with deionized distilled water to remove porewater salt and were then freeze-dried [*Kao et al.*, 2004]. Aluminum (Al), total iron (Fe_T), acid extractable iron (Fe_A), barium (Ba), total sulfur (TS), total organic carbon (TOC) and total nitrogen (TN) were analyzed. A 0.2-g aliquot of each sample was digested as detailed elsewhere [*Hsu et al.*, 2003]. The digested solutions were analyzed for Al and Fe using an ICP-OES (Optima 3200DV, Perkin-Elmer™ Instruments, USA), and for Ba using an ICP-MS (Elan 6100, Perkin-Elmer™ Instruments, USA). TS and TOC contents were analyzed with a HORIBA model EMIA-220V C/S analyzer at 1350°C. For TOC analysis, bulk sediment was acidified with 1N HCl. Fe_A was defined as the extractable fraction of Fe using 1N cold HCl at room temperature. Sediments were extracted for 16 hours and centrifuged. The supernatants were measured for Fe_A; the residual carbonate-free sediments were measured for TOC/TN using a Carlo-Erba EA 2100 elemental analyzer.

[5] Specimens of planktic foraminifera (*Globigerinoides* and *Orbulina universa*) were picked from the >250 μm

[1]Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan.
[2]Institute of Hydrological Science, National Central University, Chung-Li, Taiwan.
[3]Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan.
[4]Department of Geosciences, National Taiwan University, Taipei, Taiwan.

0094-8276/05/2005GL023139$05.00

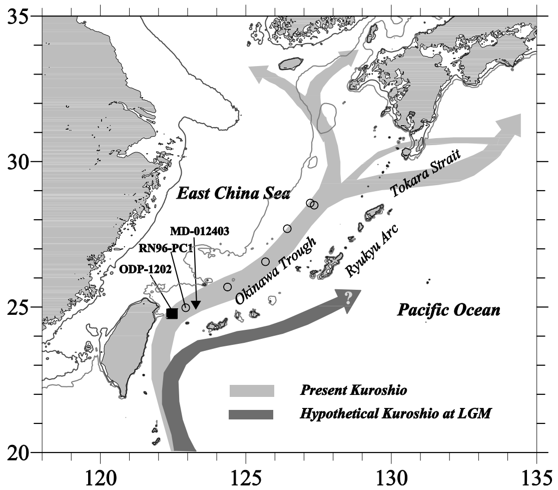

Figure 1. Location map for core MD012403 (▼), ODP1202 (■) and the core sites (○) reported by *Ujiié et al.* [2001]. The −40 and −120 m isobaths are shown.

sediment fraction at selected depths for ^{14}C-dating (Rafter Radiocarbon Laboratory, IGNS, NZ). The chronology was determined using eleven obtained ^{14}C ages. The reported ^{14}C ages were converted to "calendar ages" by employing the CALIB 5.0 program (http://radiocarbon.pa.qub.ac.uk/calib/calib.html) and a 400-year surface ocean reservoir correction [*Bard*, 1988].

3. Results and Discussion

[6] The oldest ^{14}C date of 20.7 cal ka BP marks the LGM at 19.9 m (Figure 2a). Calculated sedimentation rates for different time intervals range from 50 to 200 cm/kyr (with one exception), which indicates variable sediment supply (Figure 2a). An interval with extremely rapid sedimentation (2241 cm/kyr) occurred between 10.1 and 10.2 cal ka BP (gray shading). A hiatus was found at this time in nearby core RN96-PC1 (Figure 1) [*Ujiié and Ujiié*, 1999] and significant increases in the proportion of warm-water foraminiferal species, calcareous nannofossils and isotope-derived sea surface temperatures imply the intensification of the KC [*Li et al.*, 1997, 2001; *Xu and Oda*, 1999; *Ujiié and Ujiié*, 1999; *Ujiié et al.*, 2003]. Relatively rapid sedimentation (>100 cm/kyr) occurred between 8.7 and 12.8 cal ka BP when sea levels rose rapidly [*Siddall et al.*, 2003]. Similarly, increased offshore sediment transport during the early deglaciation occurred in association with rapid shelf submergence [*Oguri et al.*, 2000; *Wei et al.*, 2005].

[7] Sediment magnetic properties provide paleocurrent and paleoenvironmental information. Usually, gravitational settling dominates when sedimentation is not affected by strong currents. Without further flow-driven realignment, the magnetic fabric is dominantly a foliation, and the inclination of the maximum AMS axis (iK_{max}) will be parallel to the depositional surface (i.e., 0°), whereas high values may reveal an intensification of bottom currents [*Rees and Woodall*, 1975; *Park et al.*, 2000, and references therein]. In Figure 2b, consistently low iK_{max} values (<10°) in the lower part of the core indicate stable depositional conditions. Following KC intensification event and massive increase in sediment supply, the iK_{max} values increase abruptly and reach a maximum (∼80°) at 8.7–6.6 cal ka BP. Bioturbation, magnetic grain size, mineralogy, or coring disturbances can cause changes in magnetic fabric patterns [*Rees et al.*, 1982; *Thouveny et al.*, 2000]. The ChRM inclinations (Inc_{ChRM}; Figure 2c) have a mean of 33 ± 14°, which is close to but shallower than the expected value (43°) at ∼25°N. Inclination shallowing is commonly observed in compacted terrigenous sediments. Result suggests sediment core has not been severely disturbed except for 3 thin intervals in the topmost 3 m, where iK_{max} minima coincide with anomalous Inc_{ChRM} values. The bulk susceptibility (Figure 2d) is significantly higher in the iK_{max} transition zone that suggests an increase in magnetic mineral concentration. However, the down-core pattern of bulk susceptibility differs significantly from that of iK_{max} (and also TS content, see below) indicating that diagenetic alteration does not account for the shift in magnetic fabric. Elevated iK_{max} values suggest a higher energy depositional environment during the Holocene [*Ellwood*, 1980; *Park et al.*, 2000].

[8] During burial of sedimentary organic matter, oxygen is rapidly consumed to low levels. Sulfate reduction and thus iron sulfidation become important processes in sediment diagenesis. In Figure 2e, TS contents vary by over an order of magnitude from ∼0.01 to ∼0.5%. Variable but persistently higher TS contents (mostly >0.1%) occur below 8 m, where framboidal pyrite was frequently identified. By contrast, a progressive decrease in TS contents started since ∼10 cal ka BP. The timing of the TS and magnetic fabric transitions coincides with KC intensification event suggesting that the intensified KC might have triggered deepwater circulation and affected sediment biogeochemistry.

[9] The relative abundances of organic carbon (quantity and quality) and available iron are the main controls on iron sulfidation in marine sediments [*Morse and Berner*, 1995]. TOC contents (Figure 3a) vary within a narrow range from 0.5 to 0.8% (average 0.65 ± 0.05%), which is consistent with those of southern OT surface sediments [*Kao et al.*, 2003]. However, TOC contents reveal a different pattern to the TS contents indicating that the TS trend is not controlled

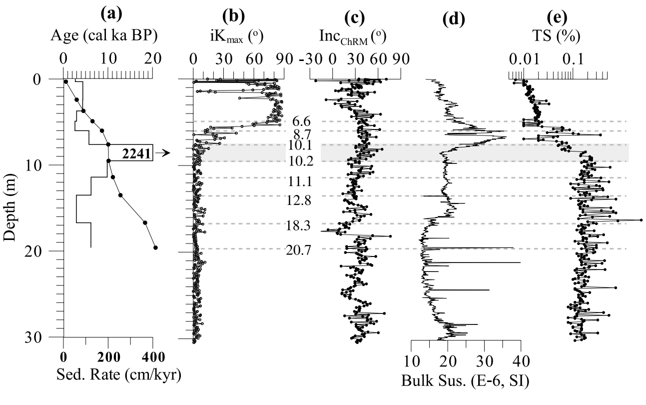

Figure 2. Chronology and down-core profiles for: (a) dates (upper x-axis) and sedimentation rate (lower x-axis), (b) inclination of maximum AMS axis, (c) inclination of ChRM, (d) bulk susceptibility, and (e) total sulfur (logarithmic scale). The gray dashed lines and gray area mark, respectively, synchronous ages and the time period of the inferred Kuroshio Current intensification (see text).

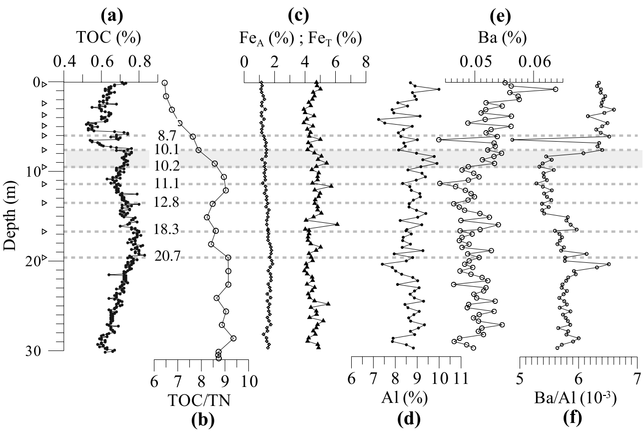

Figure 3. Down-core profiles for: (a) total organic carbon content, (b) TOC/TN ratio, (c) contents of acid extractable and total iron, (d) aluminum content, (e) barium content, and (f) the bulk Ba/Al ratio.

by organic quantity. On the other hand, TOC/TN ratios, which are representative of organic sources [*Stein*, 1991], range from 6.5 to ~9.5 and tend to decrease since ~10 ka BP (Figure 3b). This upward decrease resembles those in six sediment cores (indicated by circles in Figure 1) from the OT [*Ujiié et al.*, 2001]. This decreasing trend was basin-wide. Preferential removal of nitrogen in organics might cause such a down-core profile, however, based on a co-varying lignin phenol concentration, *Ujiié et al.* [2001] concluded that terrestrial vascular plant inputs decreased gradually during the post-glacial period, responding to landward retreat of the shoreline with progressive sea level rise. Enhanced lateral transport of marine organics from the productive shelf may also have contribution to lower TOC/TN [*Oguri et al.*, 2003]. Thus the upward decrease of TOC/TN illustrates that the enhanced KC and sea level rise elevated burial of marine organics over the entire OT. Meanwhile, increased input of marine organics eliminated the organic quality control.

[10] Insufficient iron supply might limit TS formation in sediments. However, TS contents appear to be low relative to consistently high iron contents (4.5 ± 0.2% for Fe_T and 1.3 ± 0.1% for Fe_A), implying an excess of reactive iron available for sulfidation over the last 20 ka.

[11] TOC contents in marine sediments primarily represent the residual organics that have been oxidized to varying degrees through a variety of pathways (i.e., oxygen, iron, sulfate). Insignificant down-core variation in measured TOC indicates that the residual organics were preserved by similar amounts; in contrast, the mineralized fraction, which has been oxidized, cannot be measured. However, the amount of metabolized organic carbon decomposed via sulfate reduction can be derived stoichiometrically from the measured total sulfur by assuming that all the reduced sulfur produced through sulfate reduction was fixed without re-oxidation [*Morse and Berner*, 1995; *Kao et al.*, 2004]. Thus, low TS in the upper part of the core suggests that less abundant organics were mineralized via sulfate reduction. The most plausible cause for the reduction of sedimentary TS is the water column processes. The enhanced deepwater circulation provided additional oxygen to maintain a higher redox potential at the sediment-water interface, thereby diminishing sulfate reduction (or oxidizing reduced sulfur like H_2S), and resulting in low TS burial. Mediterranean sapropels are an obvious example of similar processes, where the carbon-iron-sulfur relationship and redox-sensitive elements provide evidence of periodically changing environmental conditions with varying bottom-water ventilation and productivity [e.g., *Passier et al.*, 1999; *Larrasoana et al.*, 2003].

[12] It might be argued that TS-depleted sediments were resulted from insufficient delivery of labile organics to the sea floor due to low surface productivity. Here, we use Ba/Al ratios to indicate productivity [*Bishop*, 1988]. We assume that changes in the delivery of Ba in non-lithogenic material are implicit in bulk ratio measurements, such that any increase in normalized Ba/Al through time may be interpreted as an accumulation of excess Ba, which may then be converted to surface productivity [*Murray et al.*, 2000; *Weedon and Hall*, 2004]. Aluminum contents vary from 6.5 to 10% with most values falling within a narrow range of 8.2–9.2% (Figure 3d), indicating relatively steady contributions of terrigenous particles in response to sea-level changes. Bulk Ba concentration ranges from 0.043 to 0.064%, displaying an upward increase that started at ~10 cal ka BP (Figure 3e). Normalized Ba/Al ratios have higher ratios ($\sim 6.5*10^{-3}$) in the upper part of the core (Figure 3f) suggesting enhanced Holocene surface production. This conclusion is supported by modern observations that the intensified KC induced upwelling around the shelf break between the ECS and the southern OT and brought intermediate water with abundant nutrients into the shallow shelf to be the most important nutrient source to the ECS [*Chen*, 1996; *Liu et al.*, 2000]. Enhanced production also explains the low TOC/TN ratios in the upper part of the core.

[13] A semi-closed basin during a sea level low stand will certainly have lower rates of vertical and horizontal water mass exchange, thus one can expect lower export production in the surface ocean without external nutrient supply. However, this low export production still resulted in high TS burial as a result of poor ventilation. Oppositely, the KC-induced new production (positive) and concurrently enhanced deepwater circulation (negative) may have compensation effects on the delivery flux of organics. Therefore, the export production may have rapidly decomposed in the water column or after deposition under oxic conditions [*Wong et al.*, 1991]. The strength and initiating mechanism of the deepwater circulation change remains unknown, yet this multiple proxy research offers new insights into linkages among surface current, deepwater hydrodynamics and sediment diagenesis in the OT. In summary, the strength of the KC governed not only the surface water properties but also the deepwater hydrology, and consequently shifted the carbon oxidation pathway from sulfate reduction to aerobic respiration.

[14] **Acknowledgments.** This study was supported by grants from the National Science Council of Taiwan. We acknowledge the crew and scientists on board RV *Marion Dufrense* for retrieving IMAGES core MD 012403. The journal reviewers are gratefully acknowledged.

References

Ahagon, N., Y. Tanaka, and H. Ujiié (1993), *Florisphaera profunda*, a possible nannoplankton indicator of late Quaternary changes in sea water turbidity at the northwestern margin of the Pacific, *Mar. Micropaleontol.*, *22*, 255–273.

Bard, E. (1988), Correction of accelerator mass spectrometry ^{14}C ages measured in planktonic foraminifera: Paleoceanographic implications, *Paleoceanography*, *3*, 635–645.
Bishop, J. K. B. (1988), The barite-opal-organic carbon association in oceanic particulate matter, *Science*, *332*, 341–343.
Chen, C. T. A. (1996), The Kuroshio intermediate water is the major source of nutrients on the East China Sea continental shelf, *Oceanol. Acta*, *19*, 523–527.
Ellwood, B. B. (1980), Application of the anisotropy of magnetic susceptibility method as an indicator of bottom-water flow direction, *Mar. Geol.*, *38*, 83–90.
Hsu, S. C., F. J. Lin, W. L. Jeng, Y. C. Chung, and L. M. Shaw (2003), Hydrothermal signatures in the southern Okinawa Trough detected by the sequential extraction of settling particles, *Mar. Chem.*, *84*, 49–66.
Ijiri, A., L. Wang, T. Oba, H. Kawahata, C. Y. Huang, and C. Y. Huang (2005), Paleoenvironmental changes in the northern area of the East China Sea during the past 42,000 years, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *219*, 239–261.
Jian, Z., P. Wang, Y. Saito, J. Wang, U. Pflaumann, T. Oba, and X. Cheng (2000), Holocene variability of the Kuroshio Current in the Okinawa Trough, northwestern Pacific Ocean, *Earth Planet. Sci. Lett.*, *184*, 305–319.
Kao, S. J., F. J. Lin, and K. K. Liu (2003), Organic carbon and nitrogen contents and their isotopic compositions in surficial sediments from the East China Sea shelf and the Okinawa Trough, *Deep Sea Res., Part II*, *50*, 1203–1217.
Kao, S. J., S. C. Hsu, C. S. Horng, and K. K. Liu (2004), Carbon-sulfur-iron relationships in the rapidly accumulating marine sediments off southwestern Taiwan, in *Geochemical Investigations in Earth and Space Science*, edited by R. J. Hill et al., *Spec. Publ. Geochem. Soc.*, *6*, 441–457.
Kirschvink, J. L. (1980), The least-squares line and plane and the analysis of palaeomagnetic data, *Geophys. J. R. Astron. Soc.*, *62*, 699–718.
Larrasoana, J. C., A. P. Roberts, J. S. Stoner, C. Richter, and R. Wehausen (2003), A new proxy for bottom-water ventilation in the eastern Mediterranean based on diagenetically controlled magnetic properties of sapropel-bearing sediments, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *190*, 221–242.
Li, B., Z. Jian, and P. Wang (1997), *Pulleniatina obliquiloculata* as a paleoceanographic indicator in the southern Okinawa Trough during the last 20,000 years, *Mar. Micropaleontol.*, *32*, 59–69.
Li, T., Z. Liu, M. A. Hall, S. Berne, Y. Saito, S. Cang, and Z. Cheng (2001), Heinrich event imprints in the Okinawa Trough: Evidence from oxygen isotope and planktonic foraminifera, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *176*, 133–146.
Liu, K. K., T. Y. Tang, G. C. Gong, L. Y. Chen, and F. K. Shiah (2000), Cross-shelf and along-shelf nutrient fluxes derived from flow fields and chemical hydrography observed in the southern East China Sea off northern Taiwan, *Cont. Shelf Res.*, *20*, 493–523.
Morse, J. W., and R. A. Berner (1995), What determines sedimentary C/S ratio?, *Geochim. Cosmochim. Acta*, *59*, 1073–1077.
Murray, R. W., C. Knowlton, M. Leinen, A. C. Mix, and C. H. Polsky (2000), Export production and carbonate dissolution in the central equatorial Pacific Ocean over the past 1 Ma, *Paleoceanography*, *15*, 570–592.
Oguri, K., E. Matsumoto, Y. Saito, M. C. Honda, N. Harada, and M. Kusakabe (2000), Evidence of the offshore transport of terrestrial organic matter due to the rise of sea level: The case of the East China Sea continental shelf, *Geophys. Res. Lett.*, *27*, 3893–3896.
Oguri, K., E. Matsumoto, M. Yamada, Y. Saito, and K. Iseki (2003), Sediment accumulation rates and budgets of depositing particles of the East China Sea, *Deep Sea Res., Part II*, *50*, 513–528.
Park, C. K., S. J. Doh, and K. H. Kim (2000), Sedimentary fabric in deep sea sediments from KODOS area in the eastern Pacific, *Mar. Geol.*, *171*, 115–126.
Passier, H. F., J. J. Middelberg, G. J. de Lange, and M. E. Bottcher (1999), Models of sapropel formation in the eastern Mediterranean: Some constraints based on pyrite properties, *Mar. Geol.*, *153*, 199–219.
Rees, A. I., and W. A. Woodall (1975), The magnetic fabric of some laboratory deposited sediments, *Earth Planet. Sci. Lett.*, *25*, 121–130.
Rees, A. I., C. M. Brown, E. A. Hailwood, and P. J. Riddy (1982), Magnetic fabric of bioturbated sediment from the northern Rockall Trough: Comparison with modern currents, *Mar. Geol.*, *46*, 161–173.
Siddall, M., E. J. Rohling, A. Almogi-Labin, Ch. Hemleben, D. Meischner, I. Schmelzer, and D. A. Smeed (2003), Sea-level fluctuations during the last glacial cycle, *Nature*, *423*, 853–858.
Stein, R. (1991), *Accumulation of Organic Carbon in Marine Sediments*, 217 pp., Springer, New York.
Thouveny, N., E. Moreno, D. Delanghe, L. Candon, Y. Lancelot, and N. J. Shackleton (2000), Rock magnetic detection of distal ice-rafted debris: Clue for the identification of Heinrich layers on the Portuguese margin, *Earth Planet. Sci. Lett.*, *180*, 61–75.
Ujiié, H., and Y. Ujiié (1999), Late Quaternary course changes of the Kuroshio Current in the Ryukyu Arc region, northwestern Pacific Ocean, *Mar. Micropaleontol.*, *37*, 23–40.
Ujiié, H., Y. Tanaka, and T. Ono (1991), Late Quaternary paleoceanographic record from the middle Ryukyu Trench slope, northwest Pacific, *Mar. Micropaleontol.*, *18*, 115–128.
Ujiié, H., Y. Hatakeyama, X. X. Gu, S. Tamamoto, R. Ishiwatari, and L. Maeda (2001), Upward decrease of organic C/N ratios in the Okinawa Trough cores: Proxy for tracing the post-glacial retreat of the continental shore line, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *165*, 129–140.
Ujiié, Y., H. Hjiie, A. Taira, T. Nakamura, and K. Oguri (2003), Spatial and temporal variability of surface water in the Kuroshio source region, Pacific Ocean, over the past 21,000 years: Evidence from planktonic foraminifera, *Mar. Micropaleontol.*, *49*, 335–364.
Weedon, G. P., and I. R. Hall (2004), Neogene palaeoceanography of Chatham Rise (southwest Pacific) based on sediment geochemistry, *Mar. Geol.*, *205*, 207–225.
Wei, K. Y., H. S. Mii, and C. Y. Huang (2005), Age model and oxygen isotope stratigraphy of site ODP 1202 in the southern Okinawa Trough, northwestern Pacific, *Terr. Atmos. Ocean. Sci.*, *16*, 1–18.
Wong, G. T. F., S. C. Pai, K. K. Liu, C. T. Liu, and C. T. A. Chen (1991), Variability of the chemical hydrography at the frontal region between the East China Sea and the Kuroshio northeast of Taiwan, *Estuarine Coastal Shelf Sci.*, *33*, 105–120.
Xu, X., and M. Oda (1999), Surface-water evolution of the eastern East China Sea during the last 36,000 years, *Mar. Geol.*, *156*, 258–304.

J. Chen, S. C. Hsu, and S. J. Kao, Research Center for Environmental Changes, Academia Sinica, P.O. Box 1-55, Nangang, Taipei 11529, Taiwan. (sjkao@rcec.sinica.edu.tw)

C. S. Horng, Institute of Earth Sciences, Academia Sinica, P.O. Box 1-55, Nangang, Taipei 11529, Taiwan.

Y. S. Lin and K. Y. Wei, Department of Geosciences, National Taiwan University, Taipei 106, Taiwan.