

A 400 kyr record of combustion oxygen demand in the western equatorial Pacific: Evidence for a precessionally forced climate response

Helen M. Perks and Ralph F. Keeling

Scripps Institution of Oceanography, University of California at San Diego, La Jolla

Abstract. We have developed a combustion analysis technique for sediments which measures the amount of O₂ consumed by the reduced species. We have measured this quantity, which we call "combustion oxygen demand (COD)," on a carbonate-rich sediment core from the Ontong-Java Plateau in the western equatorial Pacific back to marine oxygen isotope stage 11. The precision of the COD technique is $\pm 6.3 \mu\text{mol O}_2 \text{ g}^{-1}$, which corresponds to $\sim \pm 0.0076\%$ wt C_{org}, assuming oxidation of organic carbon dominates the signal. The COD time series is characterized by values which are about twice as high during glacial as during interglacials, the largest shift occurring from $401 \mu\text{mol O}_2 \text{ g}^{-1}$ in midstage 6 to $144 \mu\text{mol O}_2 \text{ g}^{-1}$ at 5e, and is coherent with the oxygen isotope curve of *Globigerinoides sacculifer* in the same core at the Milankovitch frequencies of 100 and 41 kyr. Pronounced variations in the 19-23 kyr band suggest that the climate of the western equatorial Pacific is sensitive to precessional forcing, a response not apparent from other records obtained in this region.

1. Introduction

In this paper we present a method for characterizing sediment chemistry based on measuring the total amount of oxygen consumed upon complete combustion of the sediment per unit mass of sample. This quantity, which we call combustion oxygen demand (COD), measures the amount of reduced materials in the sample which are oxidized under the conditions of combustion. This includes organic carbon as well as any other reduced components such as sulfides and reduced iron and manganese. We apply our technique to a high-carbonate sediment core from the Ontong-Java Plateau spanning the last ~400 kyr. The application of traditional organic carbon measurement techniques is problematic in high-carbonate cores because of the difficulty in distinguishing a small amount of organic carbon from the large inorganic carbon background [Hedges and Stern, 1984]. The COD method is advantageous because the separation of organic and inorganic carbon is unnecessary (the pyrolysis of carbonate does not consume O₂). We argue that in these sediments, organic carbon is the dominant contributor to oxygen demand.

The high-carbonate sediments on the Ontong-Java Plateau provide us with an ideal location in which to apply the combustion oxygen demand technique. Much of the seafloor beneath the tropical oceans consists of carbonate-rich (>80% wt CaCO₃) sediments, and many of these regions have been targeted by deep-sea drilling projects to retrieve samples which have been used to obtain detailed stratigraphic records of the isotopic content of benthic and planktonic foraminifera and to examine preservation and accumulation cycles in calcium carbonate [Shackleton and Opdyke, 1973; Berger et al., 1993a]. Notably lacking in many high-carbonate regions, however, are detailed records of sediment organic carbon content, which, although generally present in very

low amounts (<0.4% wt), may be an important indicator of the rates of productivity of surface waters [e.g., Pedersen, 1983; Sarnthein et al., 1988; Pedersen and Calvert, 1990; Lyle et al., 1992]. The stability of tropical climate is a leading issue in paleoclimate research because of the importance of the tropics to the energy and moisture budgets of the planet [Hastenrath, 1985].

The Ontong-Java Plateau, a mid-oceanic submarine plateau covered with >1000 m Mesozoic and Cenozoic carbonate deposits, straddles the equator to the north of the Solomon Islands in the western Pacific (Figure 1). The Plateau is located beneath the West Pacific Warm Pool (WPWP), which contains the warmest waters of the global oceans and is the Earth's major convective region with an important role in the dynamics of climate in the modern equatorial Pacific. However, despite well-studied cores from the Ontong-Java Plateau [e.g. Berger et al., 1993a], there has been little evidence for significant changes in the characteristics of the WPWP in the late Quaternary. This region of the equatorial Pacific lies near the boundaries of an extensive area extending across from SE Asia that is affected by a combination of monsoon-circulation- and trade-wind-influenced climate patterns. Just to the west of the WPWP lie the shallow shelf areas of the Indonesia-North Australia region, which are very sensitive to ice-volume-change-induced sea level fluctuations and became land during glacial periods. Milankovitch cyclicity at 41 and 100 kyr has been demonstrated by several data sets from the Ontong-Java Plateau [e.g., Berger et al., 1993b]. Sensitivity of low-latitude climatic and oceanographic signals to precessional forcing (19-23 kyr) has been demonstrated by data sets at several different locations and simulated by models [e.g., Prell and Kutzbach, 1987; Anderson and Prell, 1993; McIntyre and Molino, 1996; Beaufort, 1996]. However, a clear precession signal has not been detected in the western equatorial Pacific in the Quaternary. Evidence for precessional forcing here could provide a link between the responses of the Asian monsoon, trade wind dynamics, and the climate of the western equatorial Pacific to solar forcing in the past.

Copyright 1998 by the American Geophysical Union.

Paper number 97PA02892.
0883-8305/98/97PA-02892\$12.00

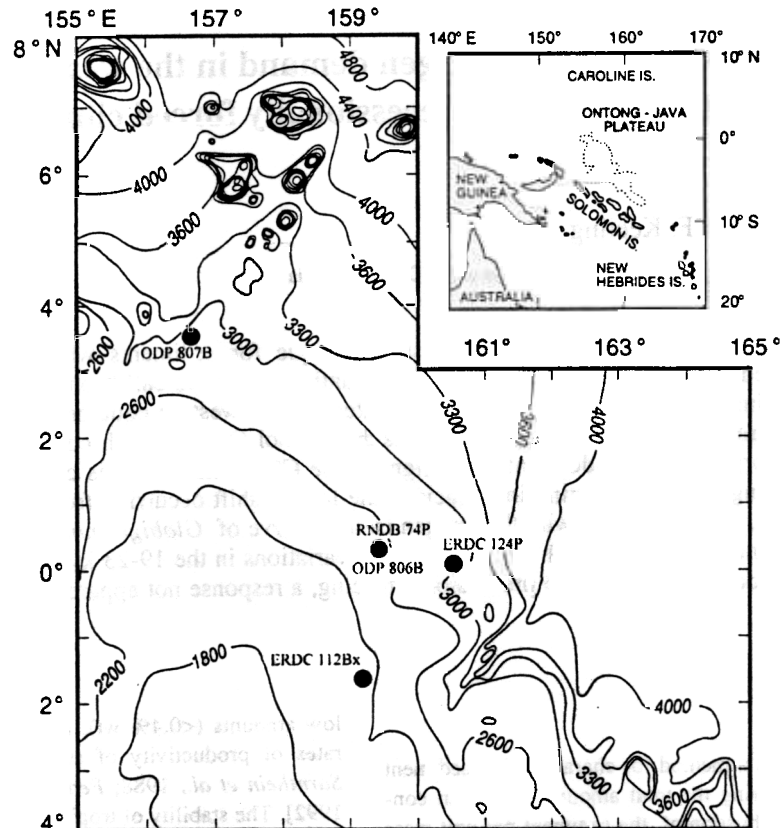


Figure 1. Map of the Ontong-Java Plateau showing the locations of the core sites referred to in the text: RNDB 74P (0°20.48'N, 159°22.49'E and 2547 m water depth); ERDC 112Bx (1°37'S, 159°14'E and 2169 m water depth); ERDC 124P (0°0'S, 160°24'E and 2946 m water depth); Ocean Drilling Program (ODP) 806B (0°19.11'N, 159°21.69'E and 2519.9 m water depth), and ODP 807B (3°36.39'N, 156°37.49'E and 2806.1 m water depth).

2. Methods and Samples

The COD method utilizes a paramagnetic oxygen analyzer connected downstream from an oven in which the sample is combusted. The experimental setup is shown in Figure 2. The sample is dried, weighed, and burned in an air stream flowing at a measured rate in a quartz tube heated to 950°C. The exhausted air is run through a liquid argon cold trap (87.5 K) to freeze out water vapor, CO₂, and other trace gases (but not O₂) and then passed through a Siemens Oxymat 5F O₂ analyzer which records the O₂ mole fraction. The "depletion peak" of the O₂ concentration caused by the combustion is integrated over the duration of the combustion and multiplied by the flow to yield the total moles of O₂ consumed because of the oxidation of the reduced material in the sample. The Oxymat analyzer is operated in a high-sensitivity mode in which the sample air stream is compared against a reference of slightly lower mole fraction (20.5% versus 21.0%). For carbonate-rich sediment types we typically use a sample size of 50-80 mg, on which the method achieves a precision on duplicate samples of $\pm 6.3 \mu\text{mol O}_2 \text{ g}^{-1}$ corresponding to $\pm 0.0076\%$ wt C_{org} (assuming only organic C consumes the O₂ and with an O₂:C ratio of 1 to 1). The signal-to-noise ratio of the oxygen demand values on a typical sediment sample containing the equivalent of $\sim 0.3\%$ wt C_{org} is $\sim 40:1$. The sensitivity of the instrument based upon combustion of a "pure" calcium carbonate "blank" is $\sim 1 \mu\text{mol O}_2$. The COD analyzer is calibrated by burning known

amounts of reference materials: for the Ontong-Java Plateau samples we generally used 100 μg aliquots of different concentrations of potassium hydrogen phthalate (KHP) solutions in water purified by a "milli-Q" system. The time required per sample measurement, including weighing and analysis, is ~ 10 mins.

Piston core RNDB 74P (0°20.48'N, 159°22.49'E) was taken during Roundabout Cruise 11 [Mayer *et al.*, 1991], the site survey cruise for Ocean Drilling Program (ODP) Leg 130 (Figure 1). The core is 805 cm in length extending back to ~ 400 ka and is from 2547 m water depth, which is above the present-day lysocline at 3400 m. The core was analyzed at 5 cm intervals corresponding to a time resolution of 2-3 kyr, close to the limits allowed by bioturbation. In order to better resolve trends through the Holocene, which is largely missing from the piston core, samples were also analyzed from box core ERDC 112Bx (1°37'S, 159°14'E and 2169 m water depth) at 1 cm intervals to a depth of 38 cm (which corresponds to an age of ~ 15 ¹⁴C ka). The box core was analyzed using solid benzoic acid standards for calibration of the COD instrument before the calibration was improved using KHP standard solutions, and the precision was estimated to be $\pm 21.6 \mu\text{mol O}_2 \text{ g}^{-1}$ corresponding to $\pm 0.026\%$ wt C_{org}.

3. Results and Discussion

Figure 3 shows values of combustion oxygen demand versus depth in RNDB 74P plotted with the $\delta^{18}\text{O}$ record (in the same

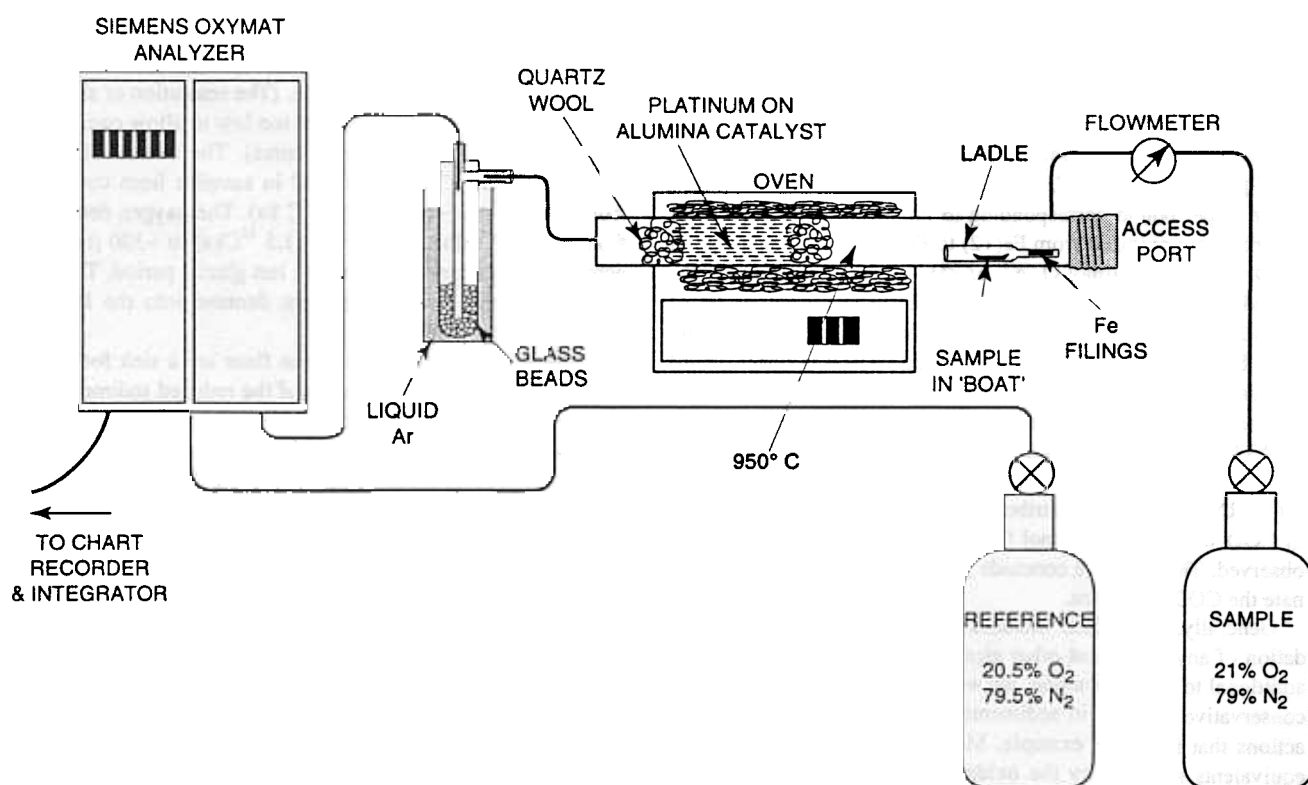


Figure 2. Experimental setup of the combustion oxygen demand (COD) apparatus.

core) from *Globigerinoides sacculifer*. The COD record displays a sawtooth pattern, similar to that of the $\delta^{18}\text{O}$, with higher values generally occurring during glacial periods and lower COD occurring during interglacial conditions. The oxygen demand is higher during glacials than during interglacials by at least a factor of 2

with the highest value of $401 \mu\text{mol O}_2 \text{ g}^{-1}$ in midstage 6 and the lowest value of $144 \mu\text{mol O}_2 \text{ g}^{-1}$ at stage 5e. The 400 kyr COD time series does not display any obvious overall down-core trend, indicating that any long-term losses due to oxidative degradation of organic matter in the sediment are small.

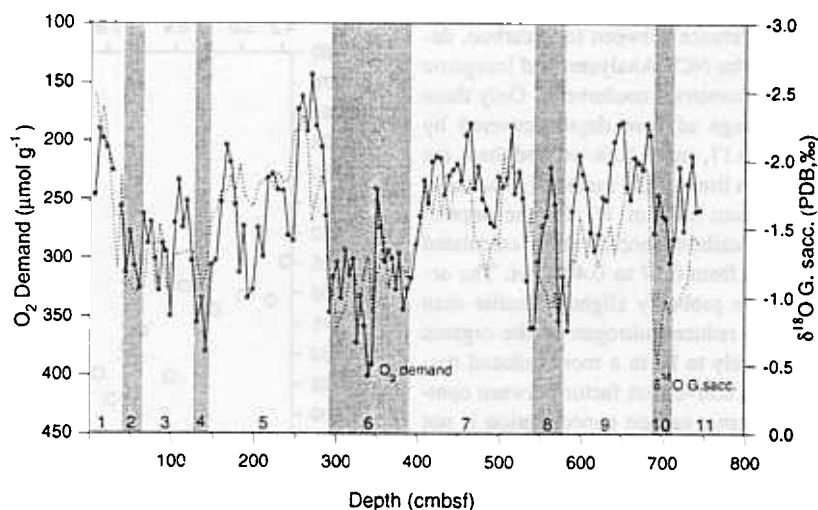


Figure 3. COD (solid line) in piston core RNDB 74P from the Ontong-Java Plateau plotted with $\delta^{18}\text{O}$ (*Globigerinoides sacculifer*) (dashed line) from the same core (M. Yasuda, personal communication, 1996) versus depth below sea floor. The shading indicates marine oxygen isotope stages for glacial periods [Shackleton and Opdyke, 1973]. The COD values are reported in $\mu\text{mol O}_2$ per g of (dry) sediment sample, and the COD axis is in descending magnitude for comparison with the $\delta^{18}\text{O}$ which are plotted according to the usual convention. The COD data show similar trends to the $\delta^{18}\text{O}$, with higher COD generally occurring during glacials (shaded areas) and lower COD occurring during interglacials. The largest transition in COD is from midstage 6 to 5e. In addition, COD exhibits proportionally larger higher-frequency fluctuations than the $\delta^{18}\text{O}$.

Organic carbon is clearly an important contributor to the oxygen demand observed, but how significant are the contributions from other elements? With respect to iron the total iron concentration measured in samples in the top 3 m of core ERDC 124P (0°0'S, 160°24'E and 2946 m water depth) ranges from 1356 to 3007 $\mu\text{g g}^{-1}$ (salt-free) (T. Fitts, personal communication, 1997). As an upper bound corresponding to this maximum range, if all the iron were oxidized from Fe(+2) to Fe(+3), then the change in COD would be $\sim 7 \mu\text{mol O}_2 \text{g}^{-1}$, or $<5\%$ of the COD changes observed across glacial-interglacial transitions. Concentrations of Mn(+2) mobilized in pore waters are negligible in neighboring ODP 806B (0°19.11'N, 159°21.69'E and 2519.9 m water depth) [Kroenke *et al.*, 1991]. Measurements of total sulfur concentration in late Quaternary samples from ODP 807B (3°36.39'N, 156°37.49'E and 2806.1 m water depth) vary by $\sim 0.02\%$ [Lind *et al.*, 1993]. In the extreme case, if the full range of sulfur variability in RNDB 74P were attributable to pyrite, the resulting range in COD would be $\sim 23 \mu\text{mol O}_2 \text{g}^{-1}$, which is $<10\%$ of the range observed. Therefore we conclude that organic carbon must dominate the COD variations.

Generally, since COD includes the oxygen consumed by oxidation of any pyrite and other electron acceptors in the sediment additional to organic carbon, we would expect COD to be a more conservative variable in sediments than organic carbon. The reactions that form, for example, Mn^{2+} , Fe^{2+} , and S^{2-} by reducing equivalents supplied by the oxidation of organic carbon, where the change in oxidation state is transferred from the organic carbon to the electron acceptors, simply trade off between the oxygen demand caused by organic carbon and that caused by the reduced ions. However, this situation may be complicated by the mobility of reduced species in the pore waters. Although we see no evidence for such processes in our samples from the Ontong-Java Plateau, the occurrence of concentrations of reduced precipitate, such as pyrite in carbonate-rich sediments, may be possible, and these would lead to large excursions in COD, which would then require further analysis.

Kroenke *et al.* [1991] report measurements of total organic carbon in ODP 806B by the difference between total carbon, determined by means of a Carlo Erba NCS Analyzer, and inorganic carbon, determined using a Coulometrics coulometer. Only three results which lie within the range of core depths covered by RNDB 74P are recorded, 0.13, 0.17, and 0.40% wt, and these are stated as being near the detection limit of the method [Kroenke *et al.*, 1991]. Assuming an oxidation ratio of 1:1 for the organic carbon, the values of organic carbon concentration calculated from COD in RNDB 74P range from 0.17 to 0.48% wt. The actual organic carbon contents are probably slightly smaller than this because of the presence of reduced nitrogen in the organic matter and because carbon is likely to be in a more reduced oxidation state than C(0). The exact conversion factor between combustion oxygen demand and organic carbon concentration is not well known and will be the subject of further study.

In the box core (Figure 4) we observe a decrease, with some apparent oscillation, in COD from $\sim 210 \mu\text{mol O}_2 \text{g}^{-1}$ at the core top to $\sim 140 \mu\text{mol O}_2 \text{g}^{-1}$ at 26 cm ($\sim 11.5 \text{ }^{14}\text{C ka}$). This trend may be due to true variations caused by climatic changes in the region, but the measurements also place an upper bound on the possible extent of remineralization of organic matter in the core of $<70 \mu\text{mol O}_2 \text{g}^{-1}$. The average COD of $\sim 150 \mu\text{mol O}_2 \text{g}^{-1}$ from the top of the box core down to 24 cm ($\sim 11 \text{ }^{14}\text{C ka}$) compares with an av-

erage of $\sim 200 \mu\text{mol O}_2 \text{g}^{-1}$ for interglacial periods in the piston core and is similar to the lowest oxygen demand in the piston core which occurs during stage 5e. (The resolution of sampling in the Holocene in the piston core is too low to allow comparison of Holocene values between both cores). The lowest COD values ($\sim 125 \mu\text{mol O}_2 \text{g}^{-1}$) are observed in samples from the box core from 8 to 26 cm (~ 6.5 to $11.5 \text{ }^{14}\text{C ka}$). The oxygen demand rises from this low value at 26 cm ($\sim 11.5 \text{ }^{14}\text{C ka}$) to $\sim 300 \mu\text{mol O}_2 \text{g}^{-1}$ across the boundary back into the last glacial period. This is consistent with the measured oxygen demand into the last glacial transition in the piston core.

Surface sediments on the ocean floor are a sink for dissolved oxygen because of the oxidation of the reduced sediment components. Estimates of the proportion of these species not oxidized in the top layer of sediment can be derived by comparing COD with pore water O_2 flux measurements. Hales and Emerson [1996] observed a diffusive O_2 flux of $10\text{--}21 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ in waters from a few centimeters above the sediment-water interface down to a maximum depth of 9 cm at three sites between 2000 and 3000 m water depth on the Ontong-Java Plateau. A COD of $200 \mu\text{mol O}_2 \text{g}^{-1}$, typical of values in the top 8 cm of the box core, multiplied by the dry bulk sediment density (0.8 g cm^{-3}) and sedimentation rate (2.5 cm kyr^{-1}), yields a flux of reduced material into the sediment equivalent to an oxygen flux of $\sim 0.4 \mu\text{mol cm}^{-2} \text{yr}^{-1}$. Dividing this number by $10\text{--}21 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ [Hales and Emerson, 1996] yields a ratio of 0.02–0.04, implying that 96–98% of the reduced material is consumed above the depth range resolved by the box core. This evidence for very shallow oxidation of the majority of the reduced species, leaving a highly refractory component that is then conserved down core, is consistent with a lack of apparent down-core decrease in COD.

Figure 5 shows that the COD data contain information about the effects of astronomical forcing in the Ontong-Java Plateau region, which can be compared with the $\delta^{18}\text{O}$ time series controlled

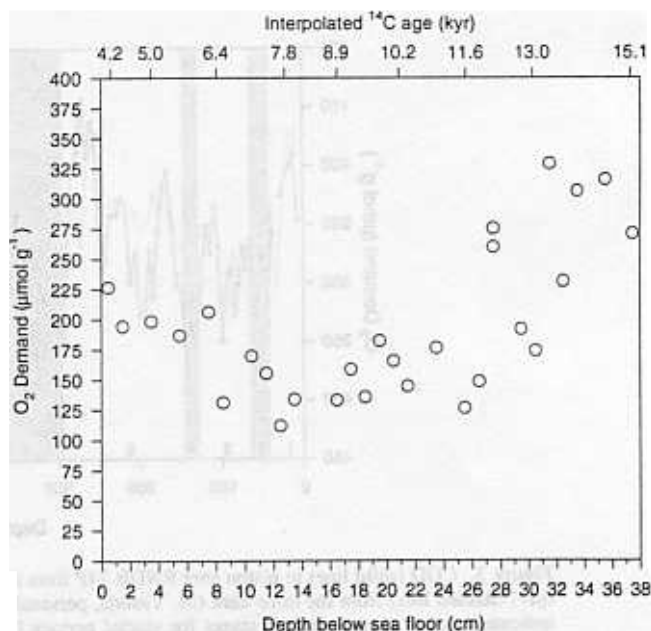


Figure 4. COD in box core ERDC 112Bx from the Ontong-Java Plateau versus depth below sea floor. Carbon 14 ages in uncorrected radiocarbon years are interpolated from data by Berger and Killingley [1982].

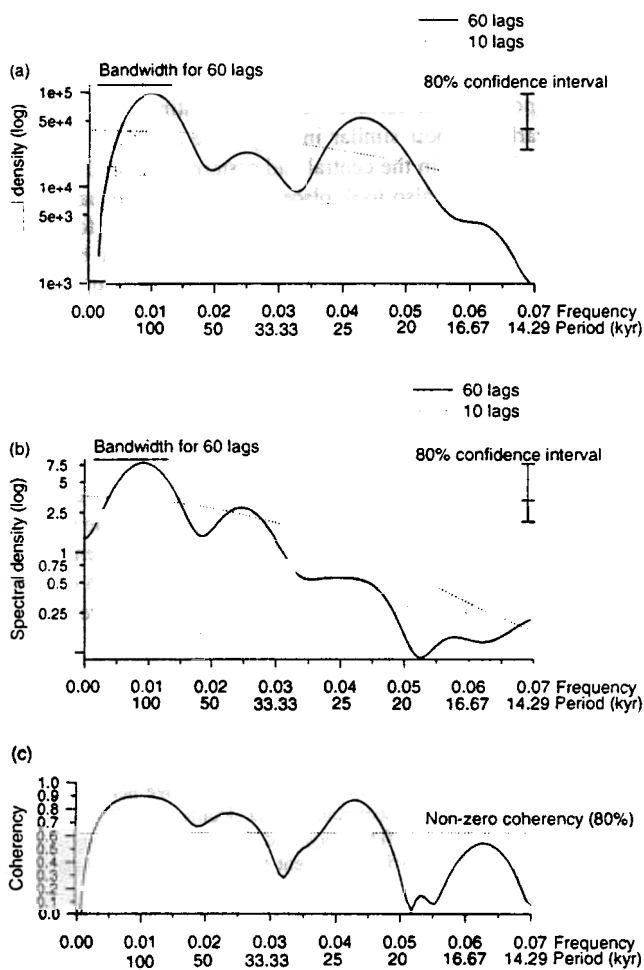


Figure 5. Power spectral analysis of (a) COD and (b) $\delta^{18}\text{O}$ (*Globigerinoides sacculifer*) in piston core RNDB 74P from the Ontong-Java Plateau presented in Figure 3. The analysis was performed with unfiltered data sets. Ages were assigned for both data sets by fitting them to the age model for ODP Hole 806B [Berger, 1996] and interpolation. 195 data points were used in each analysis with a sampling interval of 4 kyr. Graphs show variance spectra as spectral density ($\sigma^2 f^{-1}$, where σ^2 is variance and frequency f is 1 per period) against frequency (not plotted to the Nyquist frequency as spectral densities at frequencies higher than those plotted were very low) and period at 60 lags (solid line) and 10 lags (dotted line). Spectral density is plotted on a logarithmic scale. The 80% confidence limit and bandwidth for the variance spectra are given in the upper right and left of the graphs, respectively. The low-lag spectra provide a baseline against which the significance of peaks in the high-lag spectra can be assessed. Significant peaks occur at 100 kyr for both data sets and 23 kyr in the COD time series. The 23 kyr peak is not significant at the 80% confidence limit in the $\delta^{18}\text{O}$ time series and could be placed over the range 21–26 kyr, and is markedly stronger and narrower in COD. Figure 5c shows the coherence output from a cross-spectral analysis (Blackman-Tukey method) of Figures 5a and 5b (60 lags). The 80% coherence significance level is indicated by the horizontal line. Coherency between two time series can be assigned when both series exhibit significant spectral peaks that are coherent with a significant peak in the coherence function.

by global ice volume and, to a lesser extent, with local sea surface temperatures (SST). In the COD time series there is a pronounced signal at the precessional period of 23 kyr, which was found to be significant at the 95% confidence limit. In the $\delta^{18}\text{O}$ a small signal can be detected at this period, but it is not significant even at the

80% limit. (Both multitaper and Blackman-Tukey methods [Yiou *et al.*, 1996] were applied to the two data sets).

The variations in COD we detect could either be driven by changes in the amounts or types of organic material delivered to the seafloor from the surface waters or by changes in the deep water environment that affect preservation. One possible deep water mechanism that may cause changes in the sediment organic matter content is changes in the amount of CaCO_3 preserved in the sediment driven by changes in deep water CO_3^{2-} concentration. Carbonate dissolution is higher during interglacials [Wu and Berger, 1991] which, by concentrating the residual sediment constituents, would tend to increase the oxygen demand signal and organic carbon weight percentage during interglacial conditions. In fact, we see the opposite. In addition, the constancy of the sedimentation rate (see below) does not allow for great enough fluctuations in calcium carbonate weight percentages to cause the factor of 2 changes in COD values that we observe. It is also possible that changes in deep water temperature or dissolved O_2 could produce changes in deep water metabolic activity, although it is hard to imagine how the changes could have been large enough to cause the observed variations in oxygen demand without producing pronounced features in other paleoceanographic records in the western equatorial Pacific. We conclude therefore that the observed variation in COD cannot be driven by changes in bottom water environment.

Considering possible changes in surface water export, a mechanism which could be driving the COD signal is variations in nonorganic particle fluxes from the surface waters (dilution). The calculated sedimentation rates for the Ontong-Java Plateau are remarkably constant over the last 400 kyr, varying between 1.85 and 2.1 cm kyr^{-1} [Berger, 1994]. This represents a maximum variation of a factor of just 1.16 over the course of the presented COD record and indicates that variations in COD are not primarily controlled by variations in the dilution of organic matter.

Another possible surface water mechanism is changes in the export of organic matter from the surface waters to the seafloor affecting the amount of organic matter ultimately preserved in the sediment column. Organic matter export rates could change in association with changes in population abundances or changes in the amount or type of organic matter associated with a particular species. Although conclusive proof is lacking, we believe this the most likely mechanism. Additional support for this mechanism is provided by similarities in COD data with benthic foraminiferal abundance from the Ontong-Java Plateau (S. Burke, personal communication, 1996), which has been correlated to the organic carbon flux arriving at the seafloor [Herguera and Berger, 1991, 1994]. Ohkouchi *et al.* [1997] analyzed lipid class compounds and measured $\delta^{13}\text{C}_{\text{org}}$ in a core from the Caroline Basin in the western tropical Pacific. They conclude that there was a decrease during the last deglaciation in the export of organic matter from the surface waters, from both marine organisms and terrestrial sources, and that the terrestrial component of this organic matter was very small.

An approximate doubling in organic carbon mass accumulation rate (MAR) [Pedersen, 1983; Pedersen *et al.*, 1991], calcium carbonate MAR [Isern, 1991; Snoeckx, 1995] and barite MAR [Paytan, 1995; Paytan *et al.*, 1996] has been recorded for glacial conditions in the Quaternary in the eastern and central equatorial Pacific. Increases in biogenic sedimentation rates in these regions during glacials are also described by Lyle *et al.* [1988] and Rea *et*

al. [1991]. Although on the basis of an independent method, our results suggest that similar changes in organic matter content (and because of the low variation in sedimentation rate, organic matter MAR) occurred in the western equatorial Pacific. The eastern and central Pacific data sets have been interpreted as reflecting changes in organic carbon export from surface waters, and if this interpretation is valid, our results suggest that similar changes also occurred in the western equatorial Pacific. The increases in organic carbon export from the waters above the Ontong-Java Plateau during glacial periods may have been caused by increased trade wind strength resulting in enhanced equatorial upwelling and thus supply of nutrients to surface waters [Pedersen *et al.*, 1991; Sarnthein *et al.*, 1988] and may indicate changes in the structure of the WPWP over the last 400 kyr.

4. Summary

We have described a chemical analysis technique for the study of deep-sea sediments, which records the total amount of oxidizable species in the sediment sample, and applied it to carbonate-rich sediments on the Ontong-Java Plateau in the western equatorial Pacific. This variable, combustion oxygen demand (COD), is dominated by the organic carbon content in such sediment types, precise measurement of which is difficult with conventional techniques. The COD method provides a better signal-to-noise ratio than most other lithological measurements that have been made in these sediments. We have demonstrated large changes in COD over the last 400 kyr on the Ontong-Java Plateau, with at least a doubling of oxygen demand during glacials as compared to inter-

glacials. We conclude that such variations in COD in these sediments are caused by changes in the amount or types of organic matter exported from surface waters, suggesting that changes in organic carbon export similar in magnitude and timing to those previously inferred in the central and eastern equatorial Pacific in the late Quaternary also took place in the western equatorial Pacific. The COD record displays strong Milankovitch forcing, including marked forcing in the precessional frequency band. This is the first data set from the region to show such precessional structure in the late Quaternary, indicating that the organic carbon signal here may be controlled by the responses of low-latitude climate processes to astronomical forcing. The COD measurements imply that the West Pacific Warm Pool may not have been a stable feature during the late Quaternary.

We have demonstrated here the usefulness of the COD method in carbonate-rich sediments; the method may also be useful for characterizing more organic carbon-rich sediments. The COD apparatus could be employed as a shipboard instrument, which might allow analysis prior to any oxidative degradation of highly reduced sediments since it is quick and fairly insensitive to vibration.

Acknowledgments. We wish to thank M. Yasuda for many helpful discussions. The original manuscript was improved by comments and reviews from C. Charles, M. Delaney, J. Gieskes, J. C. Herguera, R. Jahnke, T. Pedersen, N. Pisias, and N. Shackleton. We are grateful to R. Weiss and the staff of Scripps Analytical Facility. We acknowledge W. Paplawsky and also U. Ninnemann and D. Hunter. Finally, we are indebted to T. Herbert, who first suggested the potential of applying the new method to carbonate-rich sediment types, specifically those of the Ontong-Java Plateau.

References

- Anderson, D. M., and W. L. Prell, A 300 kyr record of upwelling off Oman during the late Quaternary: Evidence of the Asian Southwest Monsoon, *Paleoceanography*, 8, 193-208, 1993.
- Beaufort, L., Dynamics of the monsoon in the equatorial Indian Ocean over the last 260,000 years, *Quat. Int.*, 31, 13-18, 1996.
- Berger, W. H., and J. S. Killingley, Box cores from the equatorial Pacific: ^{14}C sedimentation rates and benthic mixing, *Mar. Geol.*, 45, 93-125, 1982.
- Berger, W. H., *et al.*, *Proceedings of the Ocean Drilling Program Scientific Results vol.*, 130, 867 pp., Ocean Drill. Program, College Station, Texas, 1993a.
- Berger, W. H., T. Bickert, H. Schmidt, G. Wefer, and M. Yasuda, Quaternary oxygen isotope record of pelagic foraminifers: Site 805, Ontong Java Plateau, *Proc. Ocean Drill. Prog. Sci. Results*, 130, 363-379, 1993b.
- Berger, W. H., Quaternary time scale for the Ontong Java Plateau: Milankovitch template for Ocean Drilling Program Site 806, *Geology*, 22, 463-467, 1994.
- Berger, W. H., Reconstruction of atmospheric CO_2 from ice-core data and the deep-sea record of Ontong Java Plateau - The Milankovitch Chron, *Geologische Rundsch.*, 85, 466-495, 1996.
- Hales, B., and S. Emerson, Calcite dissolution in sediments of the Ontong Java Plateau: In situ measurements of pore water O_2 and pH, *Global Biogeochem. Cycles*, 10, 527-541, 1996.
- Hastenrath, S., *Climate and Circulation of the Tropics*, 455 pp., Kluwer Acad., Norwell, Mass., 1985.
- Hedges, J. I., and J. H. Stern, Carbon and nitrogen determinations of carbonate-containing solids, *Limnol. Oceanogr.*, 29, 657-663, 1984.
- Herguera, J. C., and W. H. Berger, Paleoproductivity from benthic foraminifera abundance: Glacial to postglacial change in the west-equatorial Pacific, *Geology*, 19, 1173-1176, 1991.
- Herguera, J. C., and W. H. Berger, Glacial to postglacial drop in productivity in the western equatorial Pacific: Mixing rate vs. nutrient concentrations, *Geology*, 22, 629-632, 1994.
- Isern, A. R., Calcium carbonate and organic carbon accumulation in the central equatorial Pacific, M.S. thesis, 200 pp., Univ. of R. I., Providence, 1991.
- Kroenke, L. W., *et al.*, *Proceedings of the Ocean Drilling Program Initial Report vol.*, 130, 867 pp., Ocean Drill. Program, College Station, Texas, 1991.
- Lind, J. L., T. R. Janecek, L. A. Krissek, M. L. Prentice, and R. Stax, Color bands in Ontong Java Plateau carbonate oozes and chalks, *Proc. Ocean Drill. Prog. Sci. Results*, 130, 453-470, 1993.
- Lyle, M., D. W. Murray, B. P. Finney, J. Dymond, J. M. Robbins, and K. Brooksforce, The record of late Pleistocene biogenic sedimentation in the eastern tropical Pacific Ocean, *Paleoceanography*, 3, 39-59, 1988.
- Lyle, M., R. Zahn, F. Prah, J. Dymond, R. Collier, N. Pisias, and E. Suess, Paleoproductivity and carbon burial across the California current: The multitracers transect, 42°N, *Paleoceanography*, 7, 251-272, 1992.
- Mayer, L. A., T. H. Shipley, E. L. Winterer, D. Mosher, and R. A. Hagen, Seabeam and seismic reflection surveys on the Ontong Java Plateau, edited by L. W. Kroenke *et al.*, *Proc. Ocean Drill. Program Initial Rep.*, 130, 45-75, 1991.
- McIntyre, A., and B. Molino, Forcing of Atlantic equatorial and subpolar millennial cycles by precession, *Science*, 274, 1867-1870, 1996.
- Ohkouchi, N., K. Kawamura, and A. Taira, Fluctuations of terrestrial and marine biomarkers in the western tropical Pacific during the last 23,300 years, *Paleoceanography*, 12, 623-630, 1997.
- Paytan, A., Marine barite, a recorder of oceanic chemistry, productivity and circulation, Ph.D. thesis, 111 pp., Univ. of Calif. at San Diego, 1995.
- Paytan, A., M. Kastner, and F. P. Chavez, Glacial to interglacial fluctuations in productivity in the equatorial Pacific as indicated by marine barite, *Science*, 274, 1355-1357, 1996.
- Pedersen, T. F., Increased productivity in the eastern equatorial Pacific during the last glacial maximum (19,000 to 14,000 yr B.P.), *Geology*, 11, 16-19, 1983.
- Pedersen, T. F., and S. E. Calvert, Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? *Am. Assoc. Petr. Geol. Bull.*, 74, 454-466, 1990.
- Pedersen, T. F., B. Nielsen, and M. Pickering, Timing of late Quaternary productivity pulses in the Panama Basin and implications for atmospheric CO_2 , *Paleoceanography*, 6, 657-677, 1991.
- Prell, W. L., and J. E. Kutzbach, Monsoon variability over the past 150,000 years, *J. Geophys. Res.*, 92, 8411-8425, 1987.
- Rea, D. K., N. G. Pisias, and T. Newberry, Late

- Pleistocene paleoclimatology of the central equatorial Pacific: Flux patterns of biogenic sediments. *Paleoceanography*, 6, 227-244, 1991.
- Sarnthein, M., K. Winn, J.-C. Duplessy, and M. R. Fontugne. Global variations of surface ocean productivity in low and mid latitudes: Influence on CO₂ reservoirs of the deep ocean and atmosphere during the last 21,000 years. *Paleoceanography*, 3, 361-399, 1988.
- Shackleton, N. J., and N. D. Opdyke, Oxygen isotope and paleomagnetic stratigraphy of equatorial Pacific core V28-238: Oxygen isotope temperatures and ice volumes on a 10³ year and 10⁶ year scale. *Quat. Res.*, 3, 39-55, 1973.
- Snoeckx, H., Late Pleistocene history of ocean-atmosphere interaction in the eastern equatorial Pacific, Ph.D. thesis, 199 pp., Univ. of Mich., Ann Arbor, 1995.
- Wu, G., and W. H. Berger, Pleistocene $\delta^{18}\text{O}$ records from Ontong-Java Plateau: Effects of winnowing and dissolution. *Mar. Geol.*, 96, 19, 209, 1991.
- Yiou, P., E. Baert, and M. F. Loutre, Spectral analysis of climate data. *Surv. Geophys.*, 17, 619-663, 1996.

R. F. Keeling and H. M. Perks, Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093-0236. (e-mail: hperks@ucsd.edu)

(Received June 15, 1997; revised October 8, 1997; accepted October 14, 1997.)