

Problems with paleoproductivity proxies

Robert F. Anderson¹ and Gisela Winckler

Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, USA

Received 28 October 2004; revised 8 May 2005; accepted 13 June 2005; published 20 September 2005.

[1] Difficulties associated with reconstructing past changes in export production were highlighted recently by Averyt and Paytan (2004), who reported substantial disagreement among records developed using different paleoproductivity proxies extracted from two equatorial Pacific piston cores. Proxies included the accumulation rates of barite, excess Ba, and excess Al, as well as elemental ratios of Al/Ti and Ba/Ti. Here we build upon their work by presenting evidence for two factors that contributed to these discrepancies. First, elemental (Ba/Ti and Al/Ti) ratios are influenced by variability in space and time of the flux of Ti to equatorial Pacific sediments, so these proxies cannot be expected to hold a constant relationship to export production. Second, the late Holocene increase in CaCO₃ dissolution has caused concentrations of barite, excess Ba, and excess Al to be enriched in surface sediments relative to the depth interval over which sediment accumulation rates were evaluated in developing the algorithms used by Averyt and Paytan (2004). This produces an error in the accumulation rates of these proxies that varies from core to core, ranging from a few tens of percent to as much as a factor of 3. These errors would have been propagated into the export production algorithms on the basis of fluxes of barite, excess Ba, and excess Al. Furthermore, this bias created by the late Holocene increase in CaCO₃ dissolution will affect the development of any algorithm based on fluxes of sedimentary constituents. These factors must be taken into account in future paleoceanographic reconstructions.

Citation: Anderson, R. F., and G. Winckler (2005), Problems with paleoproductivity proxies, *Paleoceanography*, 20, PA3012, doi:10.1029/2004PA001107.

1. Introduction

[2] The ocean's biological pump [Volk and Hoffert, 1985] transfers carbon and nutrients from surface waters to the deep sea. Concentrations of carbon dioxide in the atmosphere are influenced by these processes through gas exchange at the air-sea interface. Paleoceanographic research on all aspects of the biological pump intensified following the discovery, nearly a quarter century ago, that concentrations of CO₂ in the atmosphere have changed systematically, and substantially, with changes in climate over recent glacial cycles (for a comprehensive review see Petit *et al.* [1999]). Identifying the processes responsible for past changes in atmospheric CO₂ concentration, and their sensitivity to climate variability, has been a high priority for paleoceanographers because of the likely role of the greenhouse properties of CO₂ in climate change and because ocean processes are generally believed to have regulated past changes in atmospheric CO₂ [Archer *et al.*, 2000; Sigman and Boyle, 2000].

[3] Much of the paleoceanographic research on the biological pump has focused on reconstructing past changes in biological productivity and the ensuing flux of particulate organic carbon to the deep sea, or export production. A

diverse array of biological and geochemical proxies has been exploited to reconstruct past changes in biological productivity [Lochte *et al.*, 2003]. However, none of these is a perfect paleoproductivity proxy. Although many parameters can be measured in marine sediments that are clearly influenced by past changes in biological productivity, each is affected by other factors as well, such as temperature, oxygen concentration, and ocean circulation, or by factors that regulate the composition and structure of pelagic ecosystems. Consequently, it is difficult to generate a unique and robust reconstruction of past changes in the ocean's biological pump, even when multiple proxies are used [e.g., Anderson *et al.*, 2002].

[4] Difficulties associated with reconstructing past changes in export production were highlighted recently by Averyt and Paytan [2004], who found substantial disagreement among records developed using different proxies extracted from a common core. The absolute magnitude of export flux, the peak-to-trough amplitude of relative change in export flux, and the timing of maximum and minimum fluxes with respect to glacial cycles differed between the proxies. As emphasized by Averyt and Paytan [2004], paleoceanographers must be cautious in making quantitative interpretations of paleoproductivity records. Errors can be introduced if assumptions inherent in a method are violated, as well as through problems in the calibration of a method and in the derivation of the record itself.

[5] Averyt and Paytan [2004] identified a number of factors that could have biased individual proxy records.

¹Also at Department of Earth and Environmental Science, Columbia University, New York, New York, USA.

Table 1. Location of Equatorial Pacific Cores

Nominal Latitude	Barite			¹⁴ C Sed Rate ^b			Sed Rate, ^b cm/kyr
	Core ^a	Location	Depth Interval, cm	Core ^b	Location	Depth Interval, cm	
9°N	TT013-143MC	8.9250°N, 139.869°W	0–5	none	NA	NA	NA
5°N	TT013-104MC	5.0783°N, 139.636°W	0–5	TT013-108MC	5.0702°N, 139.636°W	13–27	1.27
4°N	TT013-113MC	4.0413°N, 139.850°W	0–5	none	NA	NA	NA
2°N	TT013-82MC	2.0633°N, 140.150°W	0–5	TT013-82MC	2.0633°N, 140.150°W	13–25	1.34
1°N	TT013-88MC	0.8150°N, 139.916°W	0–5	TT013-88MC	0.8150°N, 139.916°W	12–25	2.14
0°N	TT013-69MC	0.1117°N, 139.723°W	0–5	TT013-71MC	0.1144°N, 139.750°W	13–25	2.31
2°S	TT013-20SC	1.8665°S, 139.7178°W	0–5	TT013-19MC	1.8680°S, 139.7157°W	13–25	2.74
3°S	none	NA	0–5	TT013-27MC	2.8853°S, 139.8317°W	10–25	2.13
5°S	TT013-35SC	4.9725°S, 139.7367°W	0–5	TT013-41MC	4.9733°S, 139.7433°W	10–23	2.2
12°S	TT013-06SC	11.998°S, 134.954°W	0–5	none	NA	NA	NA

^aMulticores (MC) or spade cores (SC) from the Joint Global Ocean Flux Study (JGOFS) transect at approximately 140°W were used by *Averyt and Paytan* [2004] and by *Eagle et al.* [2003] to measure barite concentrations.

^bMC are from the JGOFS transect at approximately 140°W; MC ¹⁴C ages and sediment (Sed) accumulation rates are reported by *DeMaster and Pope* [1994] in the JGOFS database (<http://usjgofs.whoi.edu/jg/dir/jgofs/eqpac/tt013/>).

Here we build upon their work by presenting evidence for two specific factors that must have contributed to the inconsistencies among their export production records.

2. Proxies and Their Calibration

[6] *Averyt and Paytan* [2004] used several geochemical proxies to reconstruct records of export production from piston cores collected at the equator (TT013-72PC) and at 4°N (TT013-114PC) in the central equatorial Pacific Ocean (140°W). The original paper should be consulted for details of their approach. Briefly, the proxies included the accumulation rates of barite (BaSO₄), excess barium (Ba), and excess aluminum (Al), as well as elemental ratios of Al/Ti and Ba/Ti. Barite is formed in decomposing aggregates of biogenic detritus. Additional Ba, as well as dissolved Al, is scavenged by particulate biogenic material. Consequently, the fluxes to the seabed of barite, excess Ba, and excess Al, as well as their burial rates, are expected to increase with increasing export production.

[7] Accumulation rates of marine sediments are sensitive to the redistribution of particulate matter by deep-sea currents (sediment focusing [*Francois et al.*, 2004]). Furthermore, accumulation rates derived for any particular core are sensitive to errors in the age model applied to the core. Consequently, paleoceanographers have sought various methods to correct or to circumvent these problems. One strategy is to employ elemental ratios (e.g., Ba/Ti and Al/Ti), which has the advantage of being insensitive to sediment focusing and to errors in age models [*Murray et al.*, 2000].

[8] *Averyt and Paytan* [2004] developed export production algorithms by comparing the modern spatial relationship between export production and the values for each parameter (accumulation rates and elemental ratios) obtained from core top samples collected along a transect across the equator at 140°W. Cores used to develop the core top calibration, as well as piston cores used to generate down-core records, were collected during the U.S. Joint Global Ocean Flux Study (JGOFS) Equatorial Pacific

Process Study program. In addition, *Averyt and Paytan* applied to their down-core records the algorithm of *Dymond et al.* [1992] that derives new production (assumed to be equivalent to export production over appropriate timescales) from the flux of excess Ba.

3. Sources of Error

3.1. Dymond Algorithm

[9] Export fluxes derived by applying the algorithm of *Dymond et al.* [1992] to down-core records have a much greater peak-to-trough amplitude than do the records derived using other algorithms [*Averyt and Paytan*, 2004, Figures 2 and 3]. For example, over the past 500 kyr in core TT013-72PC the peak-to-trough range of export fluxes derived by applying the Dymond algorithm to excess Ba accumulation rates has an average amplitude of nearly a factor of 10, whereas the corresponding range for export production derived using barite accumulation rates has an average amplitude of less than a factor of 3 [*Averyt and Paytan*, 2004, Table 1]. Export fluxes derived using the two algorithms are similar during interglacial periods (minimum export), whereas the Dymond algorithm produces much larger export fluxes during glacial periods (maximum export).

[10] Such a discrepancy could occur if glacial sediments (i.e., maximum discrepancy) contain a much larger amount of nonbarite excess Ba (e.g., Ba associated with oxides or adsorbed to biogenic phases) than do interglacial sediments. To test for this possibility, we compared concentrations of excess Ba with those of barite in TT013-72PC, one of the cores studied by *Averyt and Paytan* [2004]. In this core most of the excess Ba in sediments is associated with barite during both glacial and interglacial periods (Figure 1). Although the relationship in Figure 1 allows for about 290 ppm (on average) of nonbarite excess Ba, the concentration of nonbarite excess Ba does not vary systematically with climate or with barite concentration. These results are consistent with the recent findings of *Robin et al.* [2003], who reported that barite is the dominant form of excess Ba

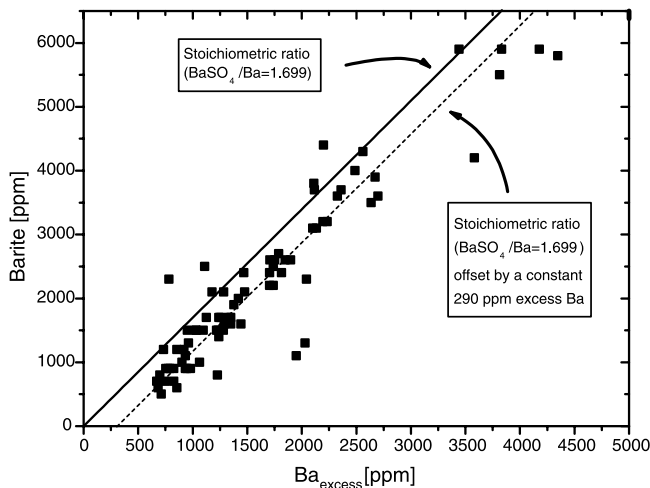


Figure 1. Concentrations of barite in core TT013-72PC are plotted against concentrations of excess Ba. Barite data are from *Paytan* [1995], while Ba data are from *Murray et al.* [2000] and are available from the World Data Center for Paleoclimatology (<http://www.ncdc.noaa.gov/paleo>). Excess Ba (Ba_{excess}) was calculated by subtracting the lithogenic Ba from the total Ba concentration using a $(Ba/Al)_{\text{terrigeneous}}$ ratio of 0.0075 [*Dymond et al.*, 1992]. Corrections for the terrigenous fraction are $<2\%$. Barite and Ba data were measured at slightly different depths in the core; therefore Ba results were interpolated onto the depths of the barite samples. The solid line shows the stoichiometric relationship (atomic weight ratio) between barite ($BaSO_4$) and Ba. The fit of the data about this stoichiometric relationship indicates that most Ba in these sediments exists as barite. The dashed line, representing an offset from the stoichiometric relationship by a constant 290 ppm excess Ba, provides a better fit to the data, suggesting that there may be a small amount of nonbarite excess Ba in these sediments.

in marine sediments. Consequently, the discrepancy in export production derived using the two proxies must reflect problems inherent in the calibration of one or both of the algorithms rather than variable amounts of nonbarite excess Ba. One probable calibration problem, related to variability of $CaCO_3$ preservation, is discussed in section 3.3.

3.2. Elemental Ratios

[11] Three assumptions are inherent in the use of elemental ratios (Ba/Ti and Al/Ti) to reconstruct past changes in export production: (1) The flux of Ti must be uniform among the sites used to calibrate the export production algorithm. (2) The flux of Ti must be constant throughout the time interval studied in the down-core records. (3) Where significant corrections must be made for Ba and Al contained in lithogenic phases, the Ba/Ti and Al/Ti ratios of these phases must be assumed to be constant, or they must be known so that appropriate corrections can be made.

[12] In the central equatorial Pacific region studied by *Averyt and Paytan* [2004], lithogenic Ba is a small part of the total Ba in sediments ($<2\%$ in TT013-72PC). Therefore

variability of the Ba/Ti ratio of the detrital end-member (assumption 3) is not expected to introduce significant error in the reconstruction of export production using Ba/Ti ratios of these sediments.

[13] Variability of the Ti flux is more likely to be a problem. Titanium is contained in lithogenic phases that are supplied to equatorial Pacific sediments primarily as mineral aerosols (dust). Dust fluxes vary in time and space in the equatorial Pacific region [*Rea*, 1994], so assumptions inherent both in the calibration (assumption 1) and in the application (assumption 2) of these elemental ratio proxies are violated.

[14] Titanium accumulation rates in TT013-72PC varied by approximately a factor of 5 during the period studied by *Averyt and Paytan* [2004] (Figure 2). Part of this variability may be attributable to sediment focusing [*Marcantonio et al.*, 2001], although this remains controversial [*Lyle et al.*, 2005]. Even if part of the variability in Ti accumulation rate can be attributed to sediment focusing, there must have been some change in the supply of Ti associated with dust. Evidence for glacial-interglacial changes in dust flux comes both from models [*Mahowald et al.*, 1999] and from the sediment record [*Rea*, 1994]. Therefore export production reconstructed using Ba/Ti and Al/Ti ratios would be biased by failure to correct for past changes in the flux of Ti to the sediments.

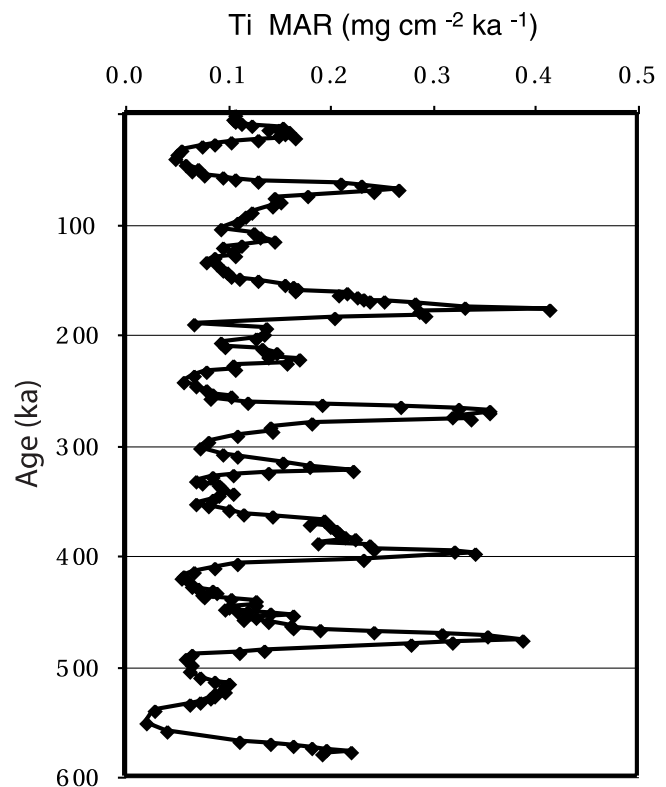


Figure 2. Titanium mass accumulation rates (MAR) over the past 600,000 years in core TT013-72PC ($0.1137^\circ N$, $139.4015^\circ W$) are plotted from data presented by *Murray et al.* [1995].

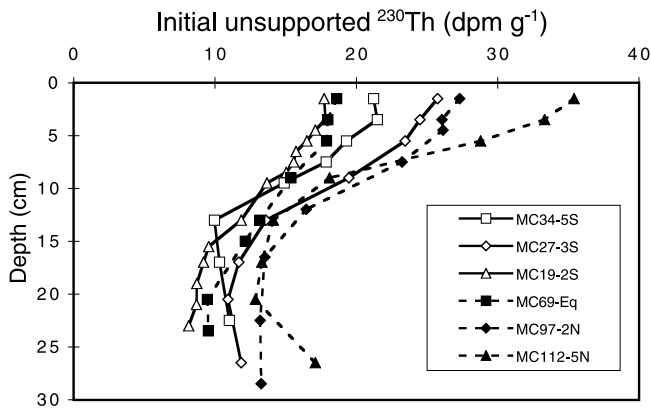


Figure 3. Concentration profiles of initial unsupported ^{230}Th in six multicores collected along the U. S. Joint Global Ocean Flux Study (JGOFS) Equatorial Pacific Process Study transect at 140°W are shown. Measured concentrations of ^{230}Th were corrected for radioactive decay and for lithogenic ^{230}Th , as described by *Berelson et al.* [1997], where these data were presented previously. Both corrections are small, given that the lithogenic content of these sediments is low (less than 5% except at 5°N , where it may be as high as 15%) and that the maximum age of these sediments (~ 38 ka at 5°N) is only about half of the 75 kyr half-life of ^{230}Th . Original thorium concentrations (without corrections) are available from the JGOFS database (<http://usjgofs.whoi.edu/jg/dir/jgofs/eqpac/tt013/>).

[15] Dust (Ti) fluxes decrease from north to south across the equator [*Murray and Leinen, 1993; Rea, 1994*]. Consequently, all other factors (e.g., concentrations of dissolved Ba and Al) being equal for a given level of export production, the Ba/Ti and Al/Ti ratios north of the equator should be lower than the corresponding elemental ratios south of the equator. Export production algorithms based on Ba/Ti and Al/Ti ratios are likely to have been biased by the modern meridional gradient in Ti flux.

[16] Taking into account the spatial and temporal variability in the supply of Ti to central equatorial Pacific sediments, it is not surprising that down-core records of export production derived using algorithms based on elemental ratios are inconsistent with those derived using other approaches. With fluxes of Ti varying in time and space, down-core records of Al/Ti and Ba/Ti ratios can hardly be expected to have a constant relationship to export production.

3.3. Calibration of Algorithms Based on Accumulation Rates

[17] An insidious source of error in accumulation-based algorithms is introduced by the late Holocene increase in CaCO_3 dissolution that has affected equatorial Pacific sediments [*Keir and Berger, 1985; Keir and Michel, 1993*]. This source of error has not been recognized previously in the development of paleoproductivity algorithms for this region, so we explain in some detail the nature and origin of the problem.

[18] For each core used in the development of the export production algorithms, accumulation rates of barite, excess Ba, and excess Al were determined by multiplying the concentration of each proxy in surface sediment by a sediment accumulation rate calculated from down-core ^{14}C ages [*Averyt and Paytan, 2004; Eagle et al., 2003*]. However, as a consequence of the late Holocene increase in CaCO_3 dissolution, proxy concentrations in surface sediments are enriched relative to those deeper in the core, where the ^{14}C ages were determined, thereby causing proxy accumulation rates to be overestimated.

[19] Near-surface enrichment of the concentrations of many noncarbonate species is evident in multicores collected throughout the JGOFS transect at 140°W , and this effect is strongest within the uppermost 10 cm of sediment [*Berelson et al., 1997; Stephens and Kadko, 1997*]. Profiles of ^{230}Th provide a good illustration of this point (Figure 3). The flux of ^{230}Th to the sediments is nearly constant through time, so the concentration of ^{230}Th in sediments (corrected for radioactive decay and for ^{230}Th contained within lithogenic phases) varies inversely with sediment mass accumulation rate [*Francois et al., 2004*]. Steep ^{230}Th concentration gradients in surface sediments of the equatorial Pacific Ocean reflect the recent increase in CaCO_3 dissolution [*Berelson et al., 1997*]. That is, the concentration of ^{230}Th increases toward the surface because the bulk sediment mass accumulation rate is decreasing with time (less CaCO_3 , the dominant component of the sediments, is

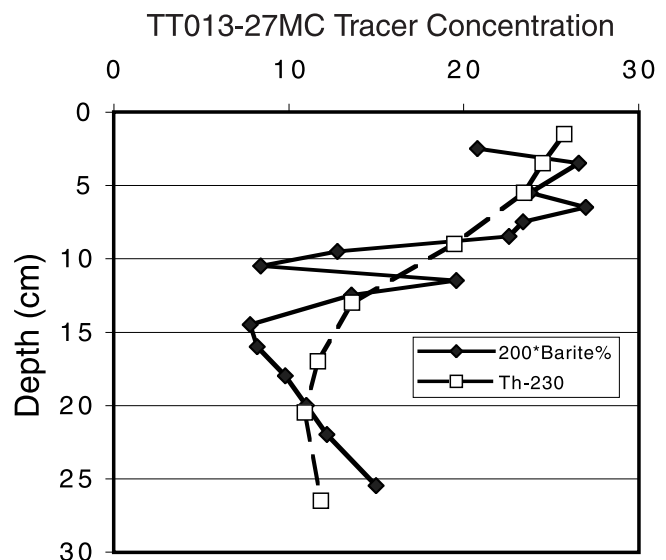


Figure 4. Concentration profiles of initial unsupported ^{230}Th (dpm/g) and of barite (percent by weight multiplied by 200 to put values on the same scale as ^{230}Th) in multicore TT013-27MC (3°S , 140°W) are shown. Concentrations of ^{230}Th are from Figure 3, while barite concentrations are from *van Beek et al.* [2004]. Barite and thorium concentrations were measured in samples from different multicore tubes. No adjustment of depth has been made to align the profiles.

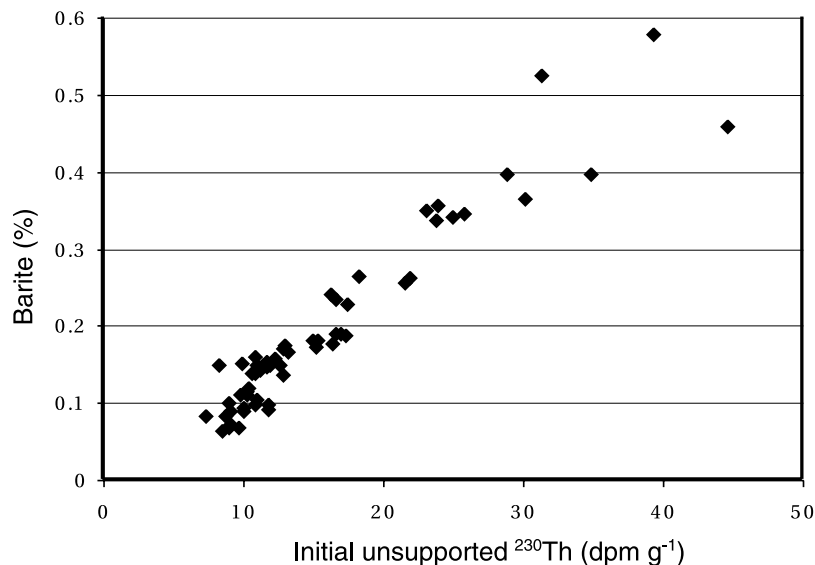


Figure 5. Concentrations of barite in core TTO13-72PC are well correlated with the initial concentration (decay corrected) of unsupported ^{230}Th . Concentrations of barite are from *Paytan* [1995], while the ^{230}Th results are from *Marcantonio et al.* [2001] and this study. Original thorium concentrations (without corrections) are available from the JGOFS database (<http://usjgofs.whoi.edu/jg/dir/jgofs/eqpac/tt013/>). Barite samples were offset in depth from ^{230}Th samples by between 1 and 5 cm, so barite concentrations were interpolated onto the depths of the Th samples to generate this plot.

preserved and buried), whereas the flux of ^{230}Th remains constant.

[20] Although high-resolution concentration profiles for barite, excess Ba, and excess Al were not reported for the cores used to calibrate the export production algorithms, surface enrichment similar to the ^{230}Th profiles is expected for two reasons. First, the concentration profiles of barite [*van Beek et al.*, 2004] and of ^{230}Th in TT013-27MC from the JGOFS transect exhibit strong first-order similarities (Figure 4). More structure is evident in the barite profile, but, as for ^{230}Th , the average barite concentration in the upper 8 cm is about a factor of 2 greater than below 10 cm. Second, over longer timescales the concentrations in these sediments of unsupported ^{230}Th and of barite are well correlated (Figure 5). The principal factor creating the correlation in Figure 5 is the common effect of variable dilution of noncarbonate species by CaCO_3 . Therefore it is reasonable to expect surface enrichment of barite, excess Ba, and excess Al among all of the JGOFS multicores, similar to the gradients in ^{230}Th (Figure 3).

[21] The late Holocene increase in CaCO_3 dissolution severely decouples the concentrations of the productivity proxies in surface sediments from the calculated sediment accumulation rate. This is best illustrated for barite, for which the most information exists. Barite results used by *Averyt and Paytan* [2004] were presented originally by *Eagle et al.* [2003]. Concentrations of barite were determined in the upper 5 cm of sediments in each core [*Eagle et al.*, 2003], whereas sediment accumulation rates were derived using ^{14}C ages measured at depths from and below 10 cm (Table 1), where the effect of the late Holocene

increase in CaCO_3 dissolution is small or negligible, i.e., below the depth at which ^{230}Th concentration profiles exhibit the largest change in slope (Figure 3). Therefore, in each core the sediment accumulation rate derived from ^{14}C ages is much greater than the accumulation rate that would be appropriate for the upper 5 cm, which is most affected by the recent increase in CaCO_3 dissolution. Consequently, by neglecting this surface enrichment of barite (as well as excess Ba and excess Al) the accumulation rate of barite is overestimated for each core.

[22] Unfortunately, the degree to which the accumulation rate of barite and other proxies is overestimated by this calibration method varies from core to core, so there is no simple way to correct this problem. Surface enrichment of proxy concentrations will increase with increasing values of the modern ratio of CaCO_3 dissolution to CaCO_3 supply or rain rate. Dissolution of CaCO_3 is driven largely by the undersaturation of bottom waters, so the rate of CaCO_3 dissolution is nearly constant for all of the JGOFS multicores [*Berelson et al.*, 1997]. In contrast, the rain rate of CaCO_3 is much greater near the equator than at the sites located several degrees to the north and south of the equator. Consequently, the ratio of CaCO_3 dissolution to CaCO_3 supply increases with increasing latitude. In the extreme case, at the northernmost sites along the JGOFS transect, it appears that the dissolution rate of CaCO_3 currently exceeds the rain rate, and chemical erosion is occurring [*Berelson et al.*, 1997; *Stephens and Kadko*, 1997]. Thorium 230 profiles provide a qualitative illustration of this effect, in that the largest enrichment in surface sediment occurs at the sites away from the equator (Figure 3). In the most extreme case,

at 5°N, the error in proxy accumulation rate, estimated as the ratio of ²³⁰Th concentration in the upper 5 cm to the concentration below 10 cm, is about a factor of 3.

[23] Calibration of export production algorithms will be affected by this error, both because the proxy accumulation rates are overestimated and because the degree to which they are overestimated varies among the sites used in the calibration. Future calibration efforts involving proxy accumulation rates should aim to evaluate average proxy concentrations over the depth interval for which sediment accumulation rates are determined.

[24] Furthermore, with two exceptions, it appears that core top barite concentrations were measured in different multicores than those used for ¹⁴C age determinations (Table 1). *Eagle et al.* [2003] do not present the ¹⁴C data used to derive the barite accumulation rates, but they cite a conference presentation by *DeMaster and Pope* [1994] as the source of the ¹⁴C ages. *DeMaster and Pope's* data are provided in the JGOFS database, which was consulted in preparing Table 1. If these are the ¹⁴C data used by *Eagle et al.* [2003], then for most of the sites used to derive the export production algorithm, barite concentrations and ¹⁴C-based accumulation rates were measured in different cores (Table 1). It is difficult to estimate the error in the barite accumulation rate associated with extrapolating ¹⁴C-derived sediment accumulation rates from one core to another, but results from two cores collected at the equator site illustrate the potential magnitude of the error. In TT013-71MC the ¹⁴C ages of *DeMaster and Pope* [1994] produce a linear sedimentation rate of 2.31 cm/kyr (Table 1). However, in TT013-69MC, the core used to measure the barite concentration, the ¹⁴C-based linear sedimentation rate was reported to be 3.4 cm/kyr [*Murray and Leinen*, 1996], nearly 50% greater than the sedimentation rate used by *Eagle et al.*

[2003]. Thus the extrapolation of sediment accumulation rates from one core to another must have introduced an additional error into the accumulation-rate-based export production algorithms.

4. Conclusions

[25] Quantitative reconstruction of past changes in primary production or export production is fraught with difficulties as illustrated by the recent analysis of *Averyt and Paytan* [2004], which shows that different proxy methods produce quantitatively different export production records when applied to a common core. Although some of the factors that contributed to the inconsistencies noted by *Averyt and Paytan* [2004] can be identified, correction for these factors alone will not be sufficient to generate quantitative reconstruction of paleoproductivity. Every proxy is influenced by multiple factors, and the sensitivity of each proxy to these factors will likely change in space and time. Consequently, rather than endeavoring to reconstruct productivity quantitatively, a more achievable objective is to generate multiple proxy records that are internally consistent in a qualitative sense. Doing so would represent an important contribution toward understanding the sensitivity to climate change of marine ecosystems and their impact on the ocean carbon cycle. As such, this represents a worthwhile goal for paleoceanographers.

[26] **Acknowledgments.** Support for this work was provided by the U.S. NSF and from a grant/cooperative agreement from the National Oceanic and Atmospheric Administration. The views expressed herein are those of the authors and do not necessarily reflect the views of NOAA or any of its subagencies. The ²³⁰Th data shown in this paper were generated at LDEO by Yong Lao and Martin Fleisher. Comments by Mary-Elena Carr and two anonymous referees are much appreciated. This is LDEO contribution 6810.

References

- Anderson, R. F., Z. Chase, M. Q. Fleisher, and J. Sachs (2002), The Southern Ocean's biological pump during the last glacial maximum, *Deep Sea Res., Part II*, 49, 1909–1938.
- Archer, D., A. Winguth, D. Lea, and N. Mahowald (2000), What caused the glacial/interglacial atmospheric pCO₂ cycles?, *Rev. Geophys.*, 38(2), 159–189.
- Averyt, K. B., and A. Paytan (2004), A comparison of multiple proxies for export production in the equatorial Pacific, *Paleoceanography*, 19, PA4003, doi:10.1029/2004PA001005.
- Berelson, W. M., et al. (1997), Biogenic budgets of particle rain, benthic remineralization and sediment accumulation in the equatorial Pacific, *Deep Sea Res., Part II*, 44, 2251–2282.
- DeMaster, D. J., and R. H. Pope (1994), C-14 chronologies, biogenic accumulation rates and sediment mixing coefficients along the equatorial Pacific JGOFS transect, paper presented at the 4th Annual Meeting, Oceanogr. Soc., Honolulu, Hawaii.
- Dymond, J., E. Suess, and M. Lyle (1992), Barium in deep-sea sediment: A geochemical indicator of paleoproductivity, *Paleoceanography*, 7, 163–181.
- Eagle, M., A. Paytan, K. R. Arrigo, G. van Dijken, and R. W. Murray (2003), A comparison between excess barium and barite as indicators of carbon export, *Paleoceanography*, 18(1), 1021, doi:10.1029/2002PA000793.
- Francois, R., M. Frank, M. M. R. van der Loeff, and M. P. Bacon (2004), ²³⁰Th normalization: An essential tool for interpreting sedimentary fluxes during the late Quaternary, *Paleoceanography*, 19, PA1018, doi:10.1029/2003PA000939.
- Keir, R. S., and W. H. Berger (1985), Late Holocene carbonate dissolution in the equatorial Pacific: Reef growth or neoglaciation?, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, *Geophys. Monogr. Ser.*, vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 208–219, AGU, Washington, D. C.
- Keir, R. S., and R. L. Michel (1993), Interface dissolution control of the ¹⁴C profile in marine sediment, *Geochim. Cosmochim. Acta*, 57(15), 3563–3573.
- Lochte, K., R. F. Anderson, R. Francois, R. A. Jahnke, G. Shimmield, and A. Vetrov (2003), Benthic processes and the burial of carbon, in *Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change*, edited by M. J. R. Fasham, pp. 196–216, Springer, New York.
- Lyle, M., N. Mitchell, N. Piasias, A. Mix, J. I. Martinez, and A. Paytan (2005), Do geochemical estimates of sediment focusing pass the sediment test in the equatorial Pacific?, *Paleoceanography*, 20, PA1005, doi:10.1029/2004PA001019.
- Mahowald, N., K. Kohfeld, M. Hansson, Y. Balkanski, S. P. Harrison, I. C. Prentice, M. Schulz, and H. Rodhe (1999), Dust sources and deposition during the last glacial maximum and current climate: A comparison of model results with paleodata from ice cores and marine sediments, *J. Geophys. Res.*, 104(D13), 15,895–15,916.
- Marcantonio, F., R. F. Anderson, S. Higgins, M. Stute, P. Schlosser, and P. Kubik (2001), Sediment focusing in the central equatorial Pacific Ocean, *Paleoceanography*, 16, 260–267.
- Murray, R. W., and M. Leinen (1993), Chemical transport to the seafloor of the equatorial Pacific Ocean across a latitudinal transect at 135°W: Tracking sedimentary major, trace, and rare earth element fluxes at the equator and the Intertropical Convergence Zone, *Geochim. Cosmochim. Acta*, 57(17), 4141–4163.
- Murray, R. W., and M. Leinen (1996), Scavenged excess aluminum and its relationship to bulk titanium in biogenic sediment from the central equatorial Pacific Ocean, *Geochim. Cosmochim. Acta*, 60(20), 3869–3878.
- Murray, R. W., M. Leinen, D. W. Murray, A. C. Mix, and C. W. Knowlton (1995), Terrigenous

- Fe input and biogenic sedimentation in the glacial and interglacial equatorial Pacific Ocean, *Global Biogeochem. Cycles*, 9(4), 667–684.
- 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 Myr, *Paleoceanography*, 15, 570–592.
- Paytan, A. (1995), Marine barite, a recorder of ocean chemistry, productivity, and circulation, Ph.D. thesis, Univ. of Calif., San Diego, La Jolla.
- Petit, J. R., et al. (1999), Climate and atmospheric history of the past 42,000 years from the Vostok ice core, Antarctica, *Nature*, 399(6735), 429–436.
- Rea, D. K. (1994), The paleoclimatic record provided by eolian deposition in the deep sea: The geologic history of wind, *Rev. Geophys.*, 32(2), 159–195.
- Robin, E., C. Rabouille, G. Martinez, I. Lefevre, J. L. Reyss, P. van Beek, and C. Jeandel (2003), Direct barite determination using SEM/EDS-ACC system: Implication for constraining barium carriers and barite preservation in marine sediments, *Mar. Chem.*, 82(3–4), 289–306.
- Sigman, D. M., and E. A. Boyle (2000), Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, 407(6806), 859–869.
- Stephens, M. P., and D. C. Kadko (1997), Glacial-Holocene calcium carbonate dissolution at the central equatorial Pacific seafloor, *Paleoceanography*, 12, 797–804.
- van Beek, P., J.-L. Reyss, D. DeMaster, and M. Paterne (2004), ^{226}Ra -in marine barite: Relationship with carbonate dissolution and sediment focusing in the equatorial Pacific, *Deep Sea Res., Part I*, 51, 235–261.
- Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO_2 changes, in *The Carbon Cycle and Atmospheric CO_2 : Natural Variations Archean to Present*, *Geophys. Monogr. Ser.*, vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 99–110, AGU, Washington, D. C.

R. F. Anderson and G. Winckler, Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA. (boba@ldeo.columbia.edu)