A comparison of multiple proxies for export production in the equatorial Pacific

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[1]   Several commonly used paleoproductivity proxies were compared to evaluate the validity of assumptions and limitations associated with each proxy. Export production fluxes (C_{export}) over glacial-interglacial timescales were calculated from previously developed, proxy-specific algorithms at TTN013-pc72 and TTN013-pc114, both located in the equatorial Pacific. Comparison of data from the same core intervals yields conflicting results despite calibrations based on the same core top samples. The periodicity of marine barite, excess Ba, and excess Al-based C_{export} records is similar. The relative magnitude of C_{export} when calculated using excess Ba and algorithms based on sediment trap data is significantly different than records based on core top calibrations, particularly during glacial intervals. At both sites, bulk sedimentary Al/Ti and Ba/Ti ratios covary; however, these ratios do not correspond with the downcore records of their respective excess concentrations (and their accumulation rates), or with contemporaneous records based on marine barite, excess Ba, and excess Al accumulation. Although downcore records based on sediment mass accumulation rates may be compromised by sediment focusing, this process cannot explain all the differences observed among the various data sets presented here. This implies that some or all of these proxies do not exclusively respond to changes in export production. The contradictions among these data highlight the importance of addressing inconsistencies among paleoproxies and re-examining assumptions imbedded in proxy fundamentals, prior to applying paleoproductivity proxies and interpreting paleoceanographic records.   *INDEX TERMS:* 1065 Geochemistry: Trace elements (3670); 4267 Oceanography: General: Paleoceanography; 4825 Oceanography: Biological and Chemical: Geochemistry; 9355 Information Related to Geographic Region: Pacific Ocean; *KEYWORDS:* marine barite, excess Ba, bulk ratios

1.   Introduction

[2]   A putative link exists between the cyclicity of Pleistocene atmospheric CO_2 concentrations and large-scale oceanographic changes; however, the mechanistic relationship of changes in atmospheric CO_2 with the marine chemical and biological components of the carbon cycle remains unclear [e.g., *Sigman and Boyle*, 2000]. There is no consensus whether glacial-interglacial CO_2 trends were driven by changes in nutrient distributions or the efficiency of nutrient uptake affecting C_{export} flux [*Knox and McElroy*, 1984; *McElroy*, 1983], carbonate ion balance and/or pH [*Anderson and Archer*, 2002; *Archer and Maier-Reimer*, 1994; *Broecker and Peng*, 1989; *Sanyal et al.*, 1995], partitioning of carbonate between the continental shelves and the deep sea [*Emerson and Archer*, 1992; *Opdyke and Walker*, 1992; *Walker and Opdyke*, 1995], or physical oceanographic processes [*Francois et al.*, 1997; *Keeling and Stephens*, 2001; *Stephens and Keeling*, 2000; *Toggweiler*, 1999]. In order to define the cause and effect relationship among these processes, better constraints on fluctuations in C_{export} must be established.

[3]   Several proxies have been used to infer how C_{export} has changed through time; these include accumulation of calcium carbonate [*Deuser et al.*, 1981; *Ruhlemann et al.*, 1996], opal [*Calvert*, 1966], and organic matter [*Finney et al.*, 1988; *Muller and Suess*, 1979; *Pedersen*, 1983], as well as changes in foraminiferal assemblage [*Berger et al.*, 1989; *Herguera*, 2000; *Herguera and Berger*, 1991; *Loubere*, 1999; *Loubere et al.*, 2003]. Accurate interpretation of these records is complex due to variable preservation and the response of organisms to environmental changes [e.g., *Farrell and Prell*, 1989; *Pedersen et al.*, 1988]. To overcome such limitations, additional geochemical paleoproductivity proxies have been proposed. These include (among others) accumulation rates of marine barite (BAR; *Paytan et al.* [1996]), excess Ba accumulation (BaAR; *Dymond et al.* [1992]; *Francois et al.* [1995]), and ratios of Ba/Ti and Al/Ti in bulk sediment [*Goldberg and Arrhenius*, 1958; *Murray et al.*, 2000; *Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993; *Schroeder et al.*, 1997].

[4]   Marine barite precipitates in the upper water column in microenvironments where supersaturation is achieved by the release of labile Ba from decaying organic matter [*Bernstein and Byrne*, 2004; *Bishop*, 1988; *Dehairs et al.*, 1992; *Ganeshram et al.*, 2003]. Empirical evidence from core top sediments shows that BAR corresponds with export production in the overlying water column [*Church*,

1970; *Eagle et al.*, 2003; *Gingele and Dahmke*, 1994; *Goldberg et al.*, 1969; *Paytan et al.*, 1993]. These observations are consistent with nutrient-type profiles of dissolved Ba [*Collier and Edmond*, 1984], and the correlation of suspended particulate Ba with dissolved oxygen [*Dehairs et al.*, 1992, 1980, 1990, 1987, 1997, 1991; *Stroobants et al.*, 1991]. Measurements of excess Ba (defined as the fraction of total Ba not associated with terrigenous material as determined from the total Al content; sometimes referred to as biogenic-Ba) in sediment traps and sinking particulate matter also correspond with the C_{export} flux [*Bishop*, 1988; *Dehairs et al.*, 1980, 2000, 1991; *Dymond et al.*, 1992; *Francois et al.*, 1995]. These associations have been applied to reconstruct C_{export} from sedimentary data after correction for preservation and sediment accumulation effects [e.g., *Dymond et al.*, 1992; *Francois et al.*, 1995]. If Ba_{excess} is related to export production, and one assumes that (1) the major source of elemental Ba to deep sea sediments is marine barite, and there is no significant contribution of Ba from other sources, or that components of Ba_{excess} other than barite are related to C_{export} in a predictable way, (2) terrigenous material has a known and constant Ba/Al ratio, and (3) the observed barite-C_{export} association in the present-day ocean was prevalent in the past, then excess Ba, like barite, should indeed correspond to C_{export}.

[5] Application of bulk Ba/Ti ratios has also been suggested as a productivity index [*Goldberg and Arrhenius*, 1958; *Murray et al.*, 2000; *Murray and Leinen*, 1993]. This proxy assumes that changes in the delivery of Ba in non-lithogenic material are implicit in the bulk ratio measurement, such that any increase in Ba/Ti through time may be interpreted as an accumulation of excess Ba, which may then be converted to productivity [*Murray et al.*, 2000; *Murray and Leinen*, 1993]. The advantage of a normalizing ratio (over accumulation rate-based proxies such as barite and excess Ba) is that it does not require conversion of concentrations to accumulation rates, such that errors associated with such conversions are not introduced [*Murray et al.*, 2000]. However, all the caveats mentioned above with respect to excess Ba also apply here. Similarly, Al/Ti ratios have been used to estimate C_{export} [*Murray and Leinen*, 1996; *Murray et al.*, 1993]; as with Ba/Ti ratios, there is no need to convert ratios to age model-dependent accumulation rates. The Al/Ti ratio proxy application assumes that in specific open ocean locations (with low terrigenous input) total particle flux is proportional to C_{export} [*Murray et al.*, 2000; *Murray and Leinen*, 1996; *Murray et al.*, 1993]. Since Al is particle reactive, the adsorbed fraction of Al should increase with increasing particle flux; therefore, the excess Al content of deep sea sediments (i.e., the fraction of Al not associated with aluminosilicate minerals) should covary with bulk particle flux, and thus C_{export} [*Murray et al.*, 2000; *Murray and Leinen*, 1996; *Murray et al.*, 1993]. Bulk ratio proxies (Ba/Ti and At/Ti) apply so long as (1) Ti is exclusively of terrigenous origin, (2) the fraction of Al or Ba associated with lithogenic Ti does not change significantly through time, and (3) the excess Al or Ba is related to C_{export} in a predictable and consistent manner.

[6] Barite accumulation, Ba/Ti, and Al/Ti have all been used in previous work to interpret the role of productivity in the carbon cycle through glacial-interglacial periods in cores from the equatorial Pacific collected during the EqPac JGOFS expedition [*Murray et al.*, 1995, 2000; *Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993; *Paytan et al.*, 1996; *Schroeder et al.*, 1997]. Although the data necessary for calculating excess Ba and computing export production for these cores using the *Dymond et al.* [1992] or *Francois et al.* [1995] algorithm are available (http://usjgofs.whoi.edu/), to our knowledge, changes in export production based on excess Ba through the Pleistocene in these equatorial Pacific cores have not been reported.

[7] Here, we compare trends in paleoproductivity calculated using the above set of paleoproxies for the same equatorial Pacific cores from sites TTN013-pc72 and TTN013-pc114 located at the equator and 4 degrees North along the 140°W longitudinal JGOFS transect [*Murray et al.*, 1995]. It must be emphasized that the major goal of this paper is to compare and critically evaluate the proxies. The same present-day productivity values were used for the core top calibration of each proxy (where applicable). The same sediment sections were used for downcore calculations, thus reducing any variability that may result from age correlations and changing accumulation rate. It is our intention in this comparison to use each proxy as it would be commonly applied by paleoceanographers, although we are aware that some proxies invoke assumptions that may be contradictory or incorrect. This intercomparison includes new marine barite and excess Ba-based C_{export} estimates records from TTN013-pc72 and TTN013-pc114, and existing Ba/Ti and Al/Ti data from *Murray et al.* [2000] which were converted to C_{export} rates. In addition, we show a new sedimentary core top-based calibration of excess Ba and excess Al accumulation rates for C_{export} calculations, and use this relationship to compare with the other proxies. Since all data shown here are from the same cores, this comparison provides a unique and important test to determine whether these proxies are consistent, and to evaluate the validity of their use by the paleoceanographic community at other sites and through varied time intervals.

2. Methodology
2.1. Data Acquisition

[8] Piston cores and multi cores were collected at the equator (pc72) and 4°N (pc114) along the 140°W latitudinal transect sampled during JGOFS cruise TTN013 (details are available in the work of *Murray et al.* [1995]). Marine barite was separated from piston cores pc72 (0 to 16 m) and pc114 (0 to 8 m) at approximately 10 cm intervals using the method described by *Paytan et al.* [1993] as revised by *Eagle et al.* [2003]. The weight% barite data for the upper part of the pc72 record are from *Paytan et al.* [1996]. All other geochemical and ancillary data, including bulk sediment elemental concentrations (i.e., Ba, Al, Ti concentrations), linear sedimentation rates, mass accumulation rates (MAR), weight percent (wt%) carbonate, $\delta^{18}O$, etc. were accessed from the JGOFS

database (http://usjgofs.whoi.edu/; *Murray et al.* [2000]). All analyses of bulk sediment chemistry are described in the work of *Murray et al.* [2000].

2.2. Export Production Algorithms and Major Assumptions

[9] The various paleoproxies used here have been applied on a wide range of timescales in varied oceanographic regimes [*Bains et al.*, 2000; *Bonn et al.*, 1998; *Ceccaroni et al.*, 1998; *Chase et al.*, 2003; *Dean et al.*, 1997; *Grant and Dickens*, 2002; *Latimer and Filippelli*, 2002; *Murray et al.*, 2000; *Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993; *Nilsen et al.*, 2003; *Nürnberg et al.*, 1997; *Pattan et al.*, 2003; *Paytan et al.*, 1996; *Pudsey and Howe*, 1998; *Rutsch et al.*, 1995; *Schmitz*, 1987; *Schroeder et al.*, 1997]. However, to our knowledge, paleoproductivity reconstructions using more than one of the proxies addressed here have not been compared at any given site. To compare results, geochemical data were converted to C_{export} using published algorithms (see below). As stated above, it is our intention in this comparison to use each proxy as it would be (and has previously been) applied by paleoceanographers.

2.2.1. Marine Barite

[10] Export production was determined from barite accumulation rates (BAR) using an empirical calibration based on a compilation of core top barite data [*Eagle et al.*, 2003]. The data for the JGOFS equatorial Pacific transect samples from *Paytan et al.* [1996] and *Eagle et al.* [2003] is shown in Figure 1a. The linear relationship between export production and core top BAR was used to calculate downcore fluctuations in export production.

2.2.2. Excess Barium

[11] Excess Ba accumulation rates (BaAR) were calculated from the total Ba and Al content of the sediment, and C_{export} was estimated using the *Dymond et al.* [1992] algorithm (referred to here as $BaAR_{Dymond}$). The elemental Ba not associated with terrigenous material (excess Ba) is calculated as in the work of *Dymond et al.* [1992]:

$$[Ba_{excess}] = [Ba_{total}] - \left\{ [Al_{total}] \times (Ba/Al)_{terrigenous} \right\}. \quad (1)$$

Values of $(Ba/Al)_{terrigenous}$ that have been used in previous work range from approximately 0.0045 to 0.0075 (as discussed in the work of *Eagle et al.* [2003]); the calculated excess Ba concentrations using these values do not vary by more than 0.2%. Results are reported here using $(Ba/Al)_{terrigenous} = 0.0075$ (as suggested by *Dymond et al.* [1992]). The algorithm defined by *Dymond et al.* [1992] calculates new production (P_{new}) as follows:

$$P_{new} = \left(\frac{F_{Ba} \times 0.171[Ba]_{1700} \times z^{0.476-0.00478[Ba]_{1700}}}{2056} \right)^{1.506} . \quad (2)$$

For paleoceanographic purposes, the new production (P_{new}) term is comparable to C_{export} (Figure 1b). F_{Ba} is the accumulation rate of excess Ba in the sediment (as calculated from MAR and excess Ba derived using equation 1), z is the water depth of the site from which the sediment sample was collected, and $[Ba]_{1700}$ is the Ba concentration at 1700 m depth in the water column overlying the site. Downcore C_{export} values were calculated according to equation (2) using Ba and Al concentrations and mass accumulation rates from the EqPac JGOFS online geochemical database (http://usjgofs.whoi.edu/). Although fluctuations in the concentration of $[Ba]_{SW}$ may have occurred through glacial-interglacial time [*Lea and Boyle*, 1989], no record of the temporal variation in the concentration of Ba at 1700 m depth over these sites exists. Therefore initially we use present-day values for both glacial and interglacial intervals. For $[Ba]_{1700}$ we used the data from the closest GEOSEC site as in the work of *Eagle et al.* [2003]. Once again, it must be kept in mind that we are trying to use the algorithm as it would be used by the oceanographic community, and choosing the correct Ba concentrations will remain a challenge (see discussion below).

2.2.3. Ba/Ti and Al/Ti Ratios

[12] Ba/Ti and Al/Ti were calculated from the total elemental concentrations in the cores. For comparison (see discussion below) excess Ba and excess Al were also calculated using Ti as the "normalizing" element. Normalizing to Ti has been suggested to account for the additional flux of Al to the sediments that is not of terrigenous origin [*Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993]. If all of the Ti in the sediment is of a source not related to productivity, this implies that Ba/Ti and Al/Ti ratios are equivalent to excess Ba and excess Al (as defined in equations (3) and (4)), respectively. These excess quantities (or their accumulation in the sediment), in turn, are expected to relate to C_{export}, as is suggested for the ratios themselves.

$$[Ba_{excess}] = [Ba_{total}] - \left\{ [Ti_{total}] \times (Ba/Ti)_{terrigenous} \right\} \quad (3)$$

$$[Al_{excess}] = [Al_{total}] - \left\{ [Ti_{total}] \times (Al/Ti)_{terrigenous} \right\} \quad (4)$$

Although correlations of core top Ba/Ti and Al/Ti ratios with primary production along the 140°W EqPac JGOFS transect have been published along with downcore Ba/Ti and Al/Ti ratio data [*Murray et al.*, 2000], the core top calibration was not converted to quantitative export production values (i.e., g C m^{-2} yr^{-1}). We use the relationship between core top sediment Ba/Ti and Al/Ti with water column primary productivity (shown in the work of *Murray et al.* [2000] from equatorial Pacific core top samples (Figures 1c and 1d) to calculate export production based on downcore Ba/Ti and Al/Ti values. For consistency and a simple comparison of all data, we convert the core top primary productivity data to C_{export} using an f ratio of 0.15, as was done for the barite accumulation calibration [*Eagle et al.*, 2003]. We emphasize that the export production values used in all the calibrations shown in Figure 1 are
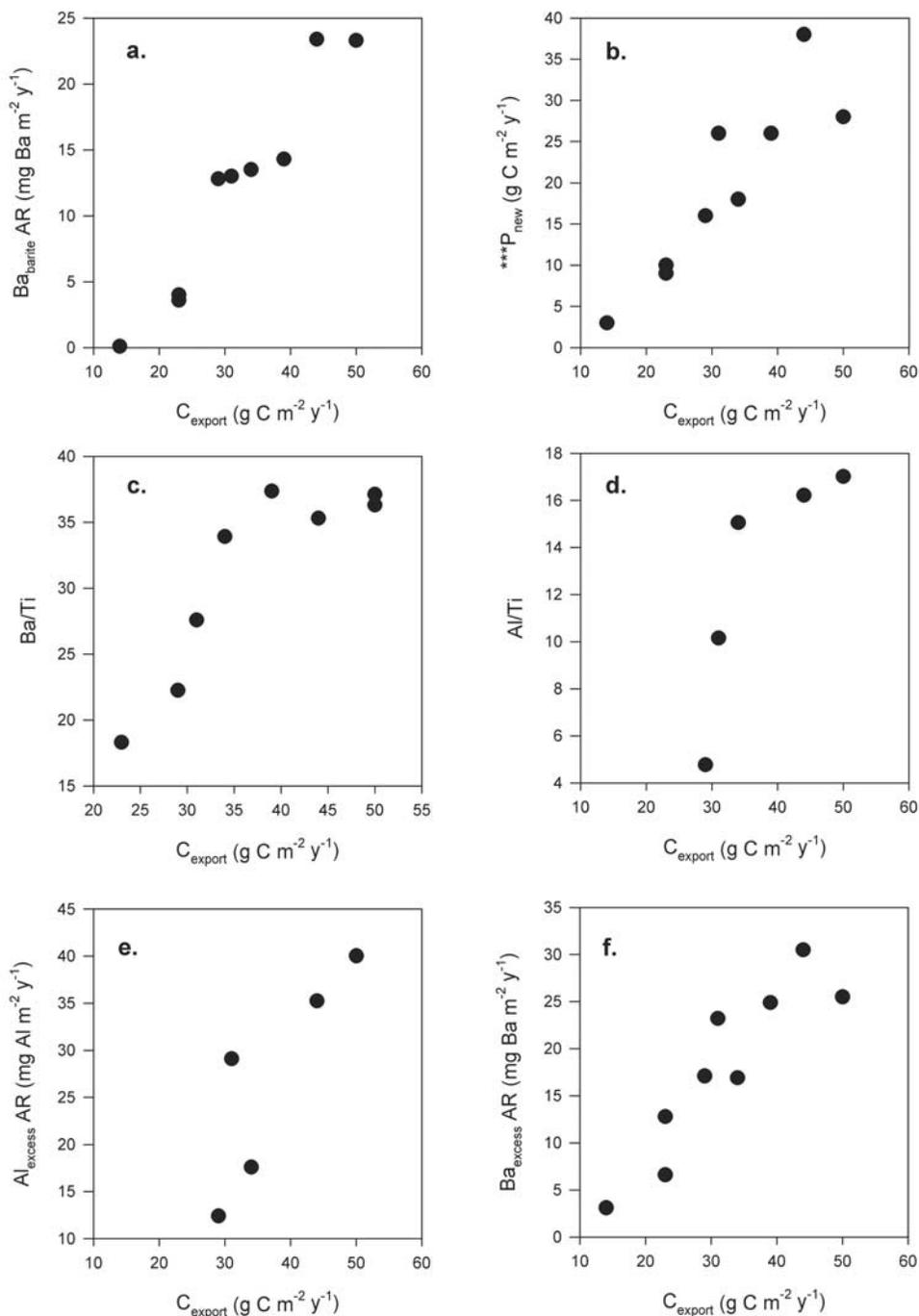
Figure 1. Core top geochemical proxy relationships with C_{export} in the equatorial Pacific. All C_{export} values are from sources in the work of *Paytan et al.* [1996] and *Eagle et al.* [2003]. The same productivity values are used for each site. Data shown here do not include samples sites in the equatorial Pacific other than those located along the TTN013 transect. (a) Accumulation rate of Ba from marine barite versus C_{export}. All data are from *Eagle et al.* [2003]. The calibration used to construct downcore C_{export} values is reported in the work of *Eagle et al.* [2003]. (b) P_{new} as calculated from *Dymond et al.* [1992] versus C_{export} of the overlying water column as reported in the work of *Eagle et al.* [2003]. (c) Ba/Ti ratios and (d) Al/Ti ratios versus C_{export}. Ratio data are from *Murray et al.* [2000] and *Murray and Leinen* [1996]. (e) Accumulation rate of excess Al versus C_{export}. Excess Al was calculated as discussed in the text using data from *Murray and Leinen* [1996] and *Murray et al.* [2000]. (f) Accumulation rate of excess Ba versus C_{export}. Ba data are from *Eagle et al.* [2003]. This is not a geochemical measurement; P_{new} is calculated from excess Ba in the core tops and the *Dymond et al.* [1992] algorithm.

based on the same primary productivity data used by *Paytan et al.* [1996] and the f ratio applied here is the same as in the *Eagle et al.* [2003] relationship. Although it is unlikely that the f ratio at both locations is constant in the modern ocean, much less that it has remained constant through time, it is C_{export}, not primary productivity, that all of the above proxies are theorized to represent. Consequently, although the temporal history of variations in the f ratio is unknown, it is convention to report paleoproductivity data in terms of estimates of C_{export}. Moreover, at least for BAR, the core top calibration reported in the work of *Eagle et al.* [2003] is based on C_{export} data for core tops spanning a wide range of productivity and f ratios, yet the data still show a significant, linear relationship.

2.2.4. Excess Al and Excess Ba Accumulation Rates

[13] To our knowledge, there is no published core top relationship between excess Al accumulation rates and productivity, although it has been hypothesized that excess Al is related to particle flux [*Murray and Leinen*, 1996; *Murray et al.*, 1993] or opal flux [*Dymond et al.*, 1997]. Using bulk Al and Ti data published in the work of *Murray et al.* [2000], *Murray and Leinen* [1996], and *Schroeder et al.* [1997], we have calculated excess AlAR (using equation (4) and MAR) and compared it with productivity in the overlying water column at the JGOFS EqPac sites (MAR and productivity values from *Paytan et al.* [1996]; Figure 1e). As with the other core top calibrations, we converted primary production to export production using an f ratio of 0.15 [*Eagle et al.*, 2003]. Figure 1e shows a linear relationship between excess Al accumulation rates and C_{export} ($R^2 = 0.9$).

[14] For comparison with the sediment trap-based excess Ba calibrations ($BaAR_{Dymond}$), we constructed a core top calibration based on sedimentary excess Ba accumulation rates at the JGOFS EqPac sites from *Eagle et al.* [2003], and the C_{export} in the overlying water column (referred to here as $BaAR_{ct}$; Figure 1f). Using these calibrations, we have estimated C_{export} at pc72 and pc114 based on the accumulation rates of excess Al (AlAR) and excess Ba ($BaAR_{ct}$) in downcore sediments at both locations.

[15] It is important to note that the major goal of this paper is to compare the data obtained by the various proxies and not to accurately reconstruct past productivity. Accordingly, as long as the primary production values and f ratio used for calibration of proxies (where applicable) are consistent, the comparison is valid.

2.3. Age Models and Mass Accumulation Rates

[16] All age model data (and mass accumulation rates) are from *Murray et al.* [2000]. Glacial-interglacial intervals were assigned using a comparison of the $\delta^{18}O$ of foraminifera in the cores to the SPECMAP record, and stage boundaries are according to those listed by *Prell et al.* [1986] and *Imbrie et al.* [1984]. All data from each site are plotted using the same age model, thus there is no age/depth bias when comparing proxy records from the same location.

[17] Mass accumulation rates (MARs) reported by *Murray et al.* [2000] were used to calculate the accumulation rates of barite, excess Ba, and excess Al. It is common

practice to apply accumulation rates to paleoproxies to account for dilution effects of minor sedimentary components. For comparison with MARs, the weight percent (wt%) barite and excess Ba and Al concentrations were also determined on a calcium carbonate free basis. Since the equatorial Pacific sediments recovered at these sites are predominantly carbonate (>80%; *Murray et al.* [2000]), this correction accounts for dilution effects by this major phase. However, this type of conversion does not necessarily imply that the accumulated sediment was delivered only from sinking particles; laterally transported material from sediments of other locations or the water column, which may not be related to local C_{export}, may be deposited after burial (e.g., sediment focusing; *Marcantonio et al.* [1996]).

3. Results and Discussion

[18] The downcore changes in export production determined using marine barite, excess Ba, excess Al, Ba/Ti, and Al/Ti ratios are inconsistent (Table 1, Figures 2 and 3). The records differ in the magnitude and timing of productivity maxima, the relative latitudinal trends, and the range of changes in export flux (difference between maximum and minimum). These differences occur despite the common productivity values used in calibrating most of these indices, and the use of samples from the same cores. The major relationships among these data are:

[19] 1. Barite-based export estimates correlate in shape (timing of fluctuations) with export fluxes calculated using the *Dymond et al.* [1992] algorithm, but the magnitudes of C_{export} are significantly different (Figures 2a, 2b, 3a, and 3b). Glacial time C_{export} fluxes calculated using $BaAR_{Dymond}$ are at least 5 times greater than estimates based on BAR, yet interglacial C_{export} is similar (Table 1).

[20] 2. Export productivity based on Ba/Ti ratios correspond to those derived from Al/Ti ratio-based trends in timing and magnitude, (particularly during maxima); the latitudinal variations in these ratios are also similar (Figures 2c, 2d, 3c, and 3d).

[21] 3. Records of excess Al and excess Ba ($BaAR_{ct}$) accumulation rates based on core top data vary similarly with records based on barite accumulation rate (Figures 2e, 2f, 3e, and 3f).

[22] 4. Barite, excess Al, $BaAR_{ct}$ and $BaAR_{Dymond}$-based C_{export} calculations do not correspond with the magnitudes of, or spatial or temporal trends in, C_{export} calculated using Ba/Ti and Al/Ti records (Figures 2 and 3).

[23] The correlation among C_{export} estimates based on marine barite, excess Ba, and excess Al accumulation, (similar fluctuations in time although of different magnitude at times) implies that these geochemical indices are responding to some common processes. The correspondence between Al/Ti and Ba/Ti, and the disagreement between the ratios and the respective proxies based on accumulation rates, suggests that these are responding to a different set of mechanisms. Although the arguments for the application of marine barite accumulation, excess Ba, and elemental ratios (Ba/Ti, Al/Ti) as productivity proxies are all supported by empirical data and oceanographic observations, the extent to which the observed trends directly and

Table 1. Downcore Maxima and Minima in C_{export} at pc72 and pc114 According to Different Proxies[a]

Age Interval, kyr	Average Export During Maxima, g C m^{-2} yr^{-1}		Average Export During Minima, g C m^{-2} yr^{-1}		Decrease From Maximum to Minimum, %	
Site	pc 72	pc 114	pc 72	pc 114	pc 72	pc 114
Barite: Eagle et al. [2003]						
0–500	57	50	21	14	62	72
500–800	42	41	13	12	69	71
800+	51	25	14	13	72	49
Excess Ba: Dymond et al. [1992]						
0–500	259	158	27	12	89	92
500–800	159	243	15	9	91	96
800+	124	373	12	10	91	97
Ba/Ti: Murray et al. [2000]						
0–500	51	35	40	31	22	12
500–800	53	39	40	34	25	12
800+	50	34	38	30	23	11
Al/Ti: Murray et al. [2000]						
0–500	52	31	37	24	29	23
500–800	55	34	41	27	25	20
800+	51	27	33	23	34	15
Excess Ba: Francois et al. [1995]						
0–500	430	242	63	29	85	88
500–800	336	543	36	17	89	97
800+	191	134	34	34	82	75
Excess Al: This Work						
0–500	55	43	27	23	51	47
500–800	41	63	22	22	46	65
800+	50	44	23	24	54	46

[a]To account for baseline shifts in downcore fluctuations, data are reported in intervals between approximately 0–500, 500–800, and 800+ kyr. Maxima and minima were determined visually, and the mean is reported. The percent change between intervals is reported as the decrease from the average max to the average min. The ratio data show the smallest amplitude of change, and estimates based on *Dymond et al.* [1992] and *Francois et al.* [1995] show large excursions. In general, each proxy suggests different trends in C_{export}.

consistently represent export production is uncertain. To assess the range of processes (in addition to productivity) to which these proxies may respond, we compare the data sets and examine the assumptions imbedded in the application of these paleo-C_{export} proxies and address the above mentioned relationships among the data.

3.1. Marine Barite, Excess Ba and Excess Al

[24] BAR-based C_{export} estimates are approximately 60% greater during glacial intervals than during interglacials at both pc72 and pc114 (Table 1, Figures 2a and 3a). C_{export} fluxes during glacial times (maxima) are similar at both sites; however, through interglacial periods between the present and 500 kyr ago, C_{export} is higher at the equatorial site (pc72) than at the more northerly locale (pc114). Prior to the mid-Pleistocene transition (~500 kyr), the glacial-interglacial fluctuations are significantly less pronounced at both sites. This is similar to what is observed in the excess Ba accumulation rate ($BaAR_{Dymond}$) record as calculated from the *Dymond et al.* [1992] algorithm. At both sites, $BaAR_{Dymond}$ and BAR track glacial-interglacial cycles, with

maxima occurring during glacials (Figures 2a, 2b, 3a, 3b). Through interglacial intervals, C_{export} estimates using $BaAR_{Dymond}$ are slightly lower than the BAR based estimates. During glacial periods, however, C_{export} calculated using $BaAR_{Dymond}$ exceeds 150 g C m^{-2} yr^{-1}, which is ~8 times greater than interglacial values (Table 1). These values are significantly greater than the barite-based C_{export} estimates for the same samples, and are much higher than present-day C_{export} fluxes in this oceanic region. Using excess Al accumulation rates (AlAR) and excess Ba ($BaAR_{ct}$) accumulation rates, based on the core top calibration of EqPac sites (Figures 1e and 1f), to calculate C_{export}, yields at both sites fluctuations consistent in timing with the BAR records (Figures 2e, 2f, 3e, and 3f). The magnitude of these fluctuations is also very similar to the BAR records. It is surprising how consistent the accumulation rates of barite and excess Ba are with excess Al, considering the independent mechanisms by which each proxy is related to C_{export}. This may be coincidental, but, if indeed these proxies represent export production over time, it is encouraging to see similarities among these records, at least at these locations.

[25] The similar interglacial magnitude of C_{export} indicated by BAR and $BaAR_{Dymond}$ (Figures 2a, 2b, 3a, and 3b) are consistent with *Eagle et al.* [2003]. *Eagle et al.* [2003] show that in the modern ocean (interglacial), calculations of carbon export in equatorial Pacific core top sediments using the Dymond algorithm (equation (2)) only slightly underestimate export production in the overlying water column. In contrast, our data indicate that during glacial times the magnitude of C_{export} calculated using these two proxies significantly diverges. A two-fold increase in C_{export} (as suggested by the barite records; Figures 2a and 3a) is a large oceanographic change, but a fivefold increase (or more) calculated using $BaAR_{Dymond}$ (Figures 2b and 3b) is most likely unrealistic since C_{export} of hundreds of g C m^{-2} yr^{-1} is large and not common in the present-day open ocean.

[26] These extremely high glacial C_{export} values determined using $BaAR_{Dymond}$ may be because the relationships depicted by the algorithm do not accurately describe the interaction between excess Ba and C_{export} in the glacial equatorial Pacific. In other words the excess Ba and C_{export} calibration is not valid for the presumed high biological productivity or other water column conditions prevailing during glacial times (as compared with the modern ocean). Indeed it has been shown that at high C_{export} fluxes, the excess Ba flux observed in sediment traps approaches a maximum, and does not increase linearly with C_{export} [*Dymond and Collier*, 1996]. If this were the case, however, then one would expect relatively low accumulation of excess Ba during periods of high C_{export}. Thus we would not expect the large glacial increases in C_{export} observed in the $BaAR_{Dymond}$ record (Figures 2b and 3b).

[27] The high glacial C_{export} values calculated from $BaAR_{Dymond}$ could result from violation of one or more of the assumptions embedded in the use of this proxy. Calculations of $BaAR_{Dymond}$ (equation (1)) assume that all Ba containing phases (other than terrigenous material) are predictably and consistently (in space and time) related to
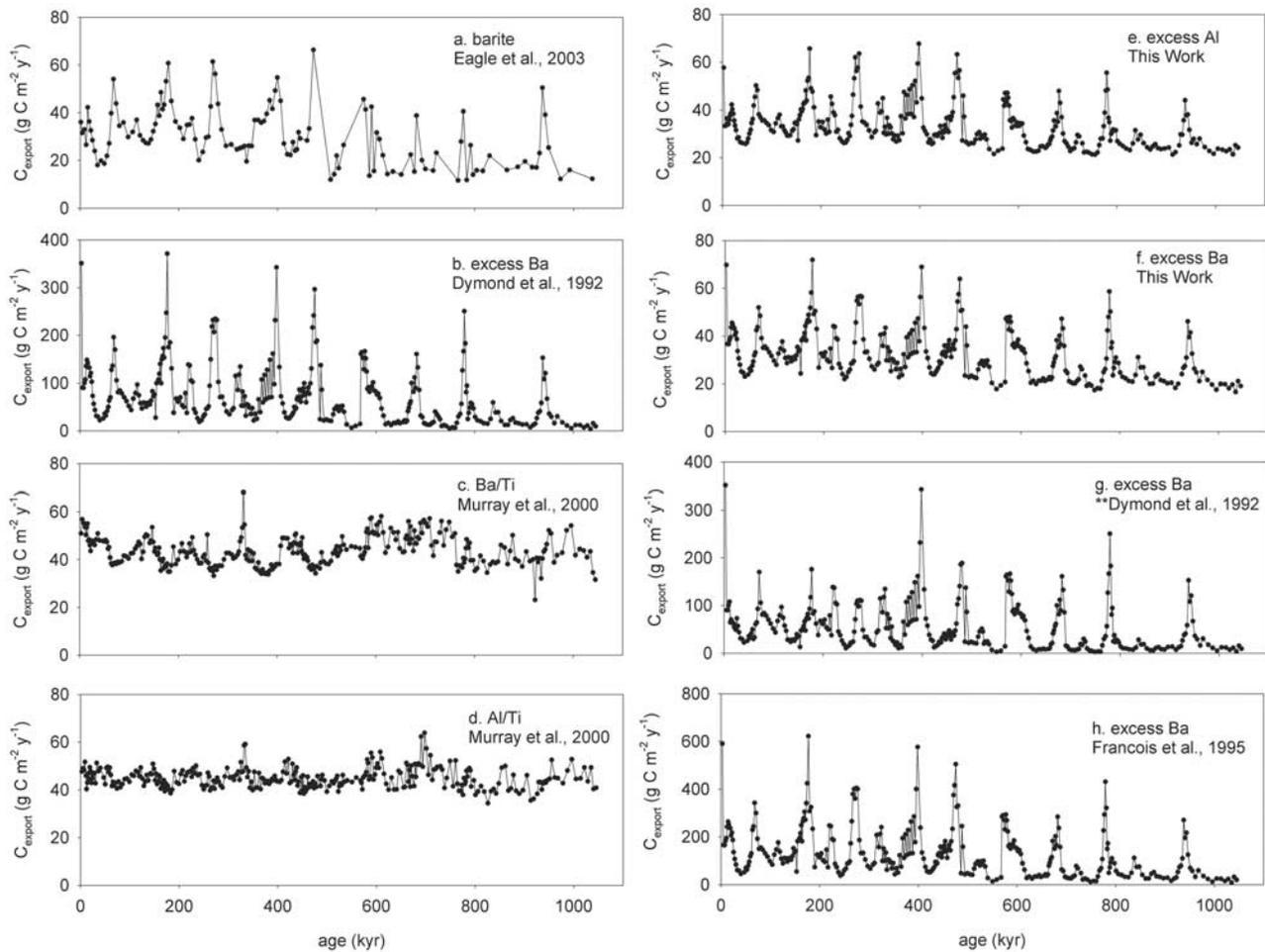
Figure 2. Downcore variations in C_{export} at TTN013-pc72 as estimated using (a) marine barite [*Eagle et al.*, 2003], (b) excess Ba [*Dymond et al.*, 1992], (c) Ba/Ti ratios [*Murray et al.*, 2000], (d) Al/Ti ratios [*Murray et al.*, 2000], (e) excess Al (calibration from Figure 1f), (f) excess Ba (calibration from Figure 1e), (g) excess Ba [*Dymond et al.*, 1992] (this calculation accounts for a 25% reduction in $[Ba]_{1700}$ during glacial intervals as reported in the work of *Lea and Boyle* [1990]), and (h) excess Ba [*Francois et al.*, 1995]. When $[Ba]_{1700}$ is decreased by 25%, the value of P_{new} calculated from equation (2) decreases by approximately 50%. Prior to about 500,000 years BP in the downcore record, the peaks in C_{export} calculated without the correction (Figure 2b) are not coincident with glacial cycles, so Figures 2g and 2b are the same. However, between 500 kyr and present, the peaks in C_{export} (Figure 2b) occur during glacial cycles, so decreasing the value of $[Ba]_{1700}$ results in depressed peaks (Figure 2g).

the C_{export} flux. This requires that (1) the Ba/Al or Ba/Ti ratio (depending if Al or Ti is used for normalization) of the terrigenous fraction delivered to the sediment be reliably known, (2) that Al (Ti) be exclusively of terrigenous origin, (3) that the fraction of Ba associated with Al (Ti) remains relatively constant and (4) that all Ba carrying particulate matter other than terrigenous material be consistently and predictably related to C_{export}. For example, the accumulation of a component in the excess Ba flux other than barite [*Dymond et al.*, 1992; *Eagle et al.*, 2003; *Kryc et al.*, 2003; *Schroeder et al.*, 1997], that is possibly unrelated to C_{export}, may systematically vary over glacial-interglacial cycles. Both Al and Ti have been instigated as having a significant component that is not terrigenous but may be scavenged, violating requirement number 2 above. However, the presumed high particulate flux during glacials would result in

increased Al or Ti scavenging, decreasing the bulk Ba/Al or Ba/Ti ratio, thus resulting in lower, not higher, C_{export} during such times. If cyclic changes occurred in Ba/Al or Ba/Ti in the detrital sedimentary fraction between glacial and interglacial intervals, then amplified or mitigated excess Ba records that are not directly related to C_{export} could result. However, using a wide range of possible terrigenous Ba/Al ratios, *Eagle et al.* [2003] have shown that this cannot change the C_{export} flux calculated using equation (2) by more than a few percent in oceanic areas with low terrigenous input, such as the equatorial Pacific. Indeed, our own calculations using different Ba/Al ratios for these samples confirm this (data not shown).

[28] The calculation of C_{export} using the Dymond algorithm may not accurately account for postburial processes that affect excess Ba accumulation and preservation
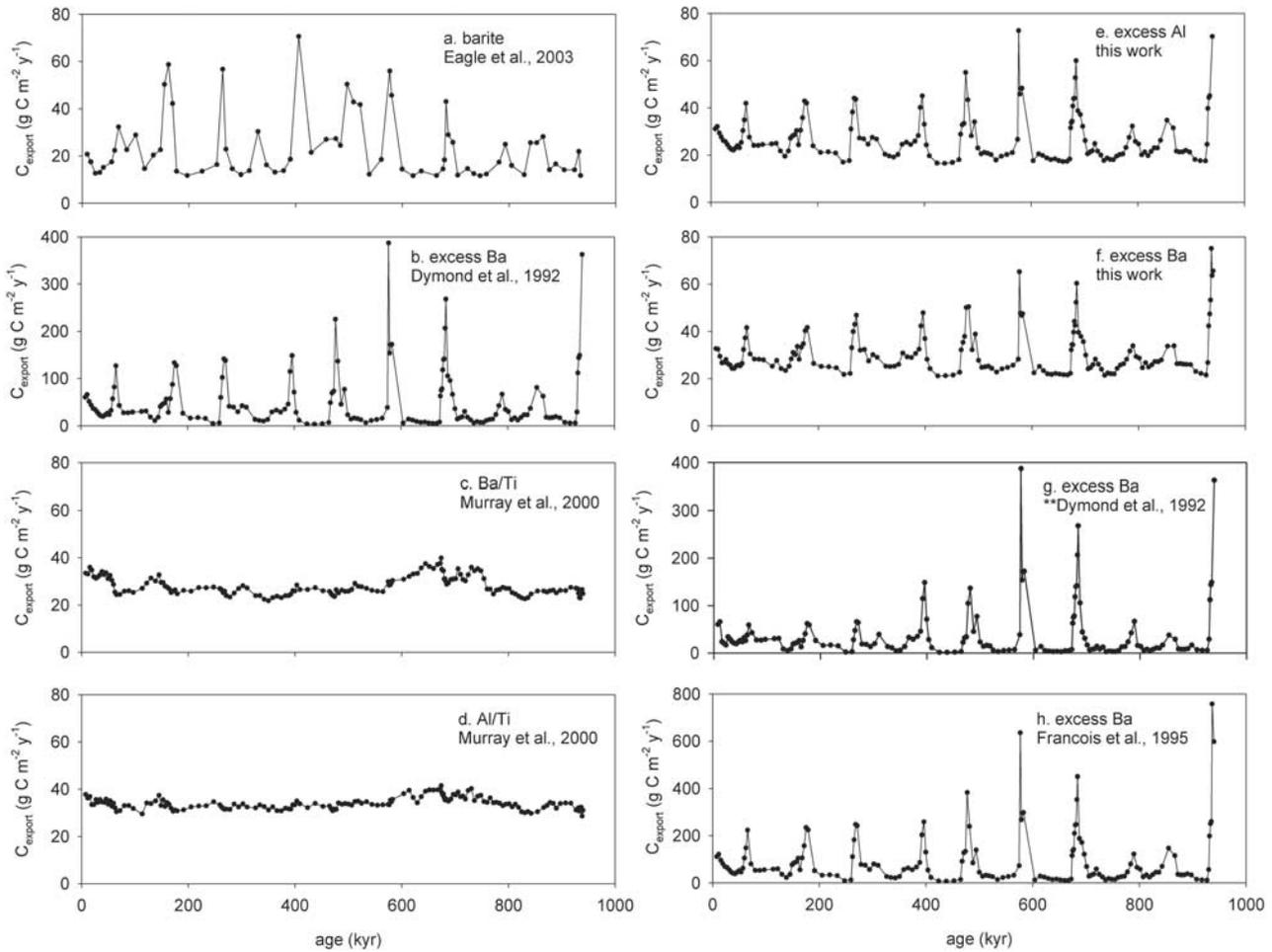
Figure 3. Downcore variations in C_{export} at TTN013-pc114 as estimated using (a) marine barite [*Eagle et al.*, 2003], (b) excess Ba [*Dymond et al.*, 1992], (c) Ba/Ti ratios [*Murray et al.*, 2000], (d) Al/Ti ratios [*Murray et al.*, 2000], (e) excess Al (calibration from Figure 1f), (f) excess Ba (calibration from Figure 1e), (g) excess Ba [*Dymond et al.*, 1992] (this calculation accounts for a 25% reduction in $[Ba]_{1700}$ during glacial intervals as reported in the work of *Lea and Boyle* [1990]), and (h) excess Ba [*Francois et al.*, 1995]. When $[Ba]_{1700}$ is decreased by 25%, the value of P_{new} calculated from equation (2) decreases by approximately 50%. The time period prior to about 500,000 years BP in the downcore record, the peaks in C_{export} calculated without the correction (Figure 3b) are not coincident with glacial cycles, so Figures 3g and 3b are the same. However, between 500 kyr and present, the peaks in C_{export} (Figure 3b) occur during glacial cycles, so decreasing the value of $[Ba]_{1700}$ results in depressed peaks (Figure 3g).

[*Dymond et al.*, 1992; *Fagel et al.*, 2002] since the algorithm in equation (2) is based on Holocene sediment traps and not deep sea sediments. Thus the calibration process may exclude postdepositional effects on the excess Ba signal. A related complication is that to calculate C_{export} from equation (2), excess Ba concentrations are converted to a rain rate, after mathematically accounting for processes affecting the accumulation and preservation of excess Ba (mass accumulation rates, water depth, seawater Ba concentrations; *Dymond et al.* [1992]). One questionable relation in the algorithm is the degree of preservation of barite in the water column, which according to *Dymond et al.* [1992] is related to the $[Ba]_{1700}$ term (equation (2)). It is not clear that this value ($[Ba]_{1700}$) is consistently related to barite preservation [see also *Francois et al.*, 1995]. Regardless, even if $[Ba]_{1700}$ is a good representation, as previously

mentioned there is no record of variations in $[Ba]_{SW}$ at these locations, much less at a depth of 1700 m.

[29] Available data [*Lea and Boyle*, 1990] indicate a possible 25% decrease in dissolved Ba concentrations of Pacific deep waters during the glacial periods. If we assume that $[Ba]_{SW}$ decreased by 25% through every glacial interval in the record (as defined by *Prell et al.* [1986] and *Imbrie et al.* [1984]), and calculate C_{export} from equation (2) accordingly, cyclic changes are still evident (Figures 2g and 3g). For the time period prior to ~500 kyr BP in the downcore record, the peaks in C_{export} calculated without the $[Ba]_{1700}$ correction (Figures 2b and 3b) are not coincident with glacial cycles, so before 500 kyr, Figures 2b and 3b and Figures 2g and 3g appear similar. Between 500 kyr and present, the peaks in C_{export} (Figures 2b and 3b) occur during glacial cycles, therefore using the 25% lower value

for $[Ba]_{1700}$ results in depression of the peak signals (Figures 2g and 3g).When $[Ba]_{1700}$ is reduced by 25% (during glacial cycles) the value of P_{new} calculated from equation (2) decreases by approximately 50%, however this correction does not fully resolve the conflicting results between the magnitude of change in C_{export} using this proxy compared to the other proxies; C_{export} is still higher that expected. This shows that the C_{export} term in the *Dymond et al.* [1992] equation is sensitive to changes in $[Ba]_{1700}$ and seawater Ba concentrations. *Francois et al.* [1995] concluded that seawater Ba concentrations are unimportant to the excess Ba-C_{org} relationship, and thus that the $[Ba]_{1700}$ term in equation (2) is unnecessary. *Francois et al.* [1995] provided a revised algorithm for determination of P_{new}

$$P_{new} = 1.95 \times F_{BA}^{1.41}, \qquad (5)$$

where F_{Ba} is the flux of excess Ba to the sediments (as in equation (2)). Figures 2b, 2h, 3b, and 3h show that there is a systematic offset between P_{new} calculated using equations (2) and (5); the *Francois et al.* [1995] algorithm values are approximately 48% greater than those calculated using *Dymond et al.* [1992] throughout the records at both sites (Table 1). However, if indeed variations in seawater Ba are important in preservation of the excess Ba signal, and the estimate of a 25% decrease in $[Ba]_{SW}$ is valid [*Lea and Boyle*, 1990], then the *Dymond et al.* [1992] equation gives more realistic although still very high (five-fold higher during maxima than during minima) values for organic C flux to the seafloor during glacials. The strong dependence of C_{export} calculated from $BaAR_{Dymond}$ on $[Ba]_{1700}$, and the lack of a reliable $[Ba]_{1700}$ record, complicates the application of the Dymond equation as large errors are introduced.

[30] Equations (2) [*Dymond et al.*, 1992] and (5) [*Francois et al.*, 1995] are based on Ba collected in sediment traps, as opposed to those derived directly from sediments, which would take into account water column processes and early diagenetic alteration. For example, the marine barite calibration is based directly on core top sediment analyses of >50 samples from a range of oceanographic settings and should therefore include the influence of early diagenetic processes on barite preservation (Figure 1a; *Eagle et al.* [2003]). However, the Dymond and Francois algorithms are based predominantly on sediment trap data, and in particular traps from continental margins. The C_{export}-excess Ba relation observed may vary regionally and in response to ecosystem structure in addition to early diagenetic parameters that may not be represented in equation (2) or (5) [*Dymond and Collier*, 1996; *Francois et al.*, 1995].

[31] Indeed, downcore $BaAR_{ct}$ values at both sites (Figures 2f and 3f) do not show the huge C_{export} maxima evident in the records derived from *Dymond et al.* [1992] and *Francois et al.* [1995]. The sediment-based (accumulations of marine barite, excess Ba, excess Al) C_{export} trends are more logical than those derived from *Dymond et al.* [1992] and *Francois et al.* [1995] in terms of absolute C_{export} values.

[32] The barite proxy also has its limitations; it is possible that changes in barite preservation not represented by the wide range of conditions in the present-day ocean may have occurred over glacial-interglacial cycles and influenced the record. In addition, barite is not preserved in sulfate reducing sediments or in low productivity areas [*Eagle et al.*, 2003; *McManus et al.*, 2002; *Paytan and Kastner*, 1996; *Paytan et al.*, 1996], limiting the locations from which reliable barite records can be derived to open ocean sites with relatively high productivity and pore water sulfate concentrations of >15 mM. The sites used in this study are consistent with these requirements; however, if pore water sulfate concentrations do not accurately represent episodic dissolution/ preservation events, then it is possible that variable preservation may account for the cyclic changes observed in Figures 2a and 3a. If this is the case, the similar cyclicity among all the records based on BaAR and AlAR would suggest that Al preservation is also affected by dissolution associated with sulfate reduction, which is highly unlikely.

[33] Another complication that is relevant to marine barite, excess Al, and excess Ba is the conversion to accumulation rates. Marine barite comprises less then 1% of deep sea sediment ($\sim$0.2%) and excess Ba and Al concentrations in these sediments are also minimal ($\sim$700 to 4000 ppm, and $\sim$2000 to 20000 ppm, respectively), such that dilution effects may be significant. To avoid complications related to dilution effects, it is common practice to convert weight% data (in this case wt% barite, excess Al or excess Ba) to an accumulation rate [e.g., *Lyle and Dymond*, 1976]. Accordingly, any errors in mass accumulation rate estimates that stem from inaccurate age models, or mass accumulation that differs from vertical particle flux (sediment redistribution, focusing, etc.), will be propagated to the BAR, BaAR, and AlAR calculation. To partially eliminate this problem and evaluate the potential control of systematic MAR changes on the record, we compare the accumulation rates of these proxies to their carbonate free weight percents. Figure 4 shows that the AR of marine barite, excess Al and excess Ba vary similarly with their respective concentrations in the sediment (wt% calculated on a carbonate free basis), indicating that the mass accumulation rate is not exclusively controlling the fluctuations in the record. However, there is still variance among the data, implying that there are processes affecting the conversion to accumulation rates. One possibility is that dilution by the noncarbonate fraction, such as opal, is not accounted for. It is known that the delivery of this phase has changed in the Pacific through time [*Lyle*, 1988], so it is possible that dilution by opal may be affecting these trends as well. However, high opal content during glacials will tend lower the wt% barite (and excess Ba and Al), while the records show maximum content of these elements during glacials.

[34] It has been argued, based on [230]Th and [3]He data applied as constant flux proxies, that sediment redistribution and focusing have affected the sedimentary records in this area, and that any record based on sediment mass accumulation rates calculated from linear sedimentation
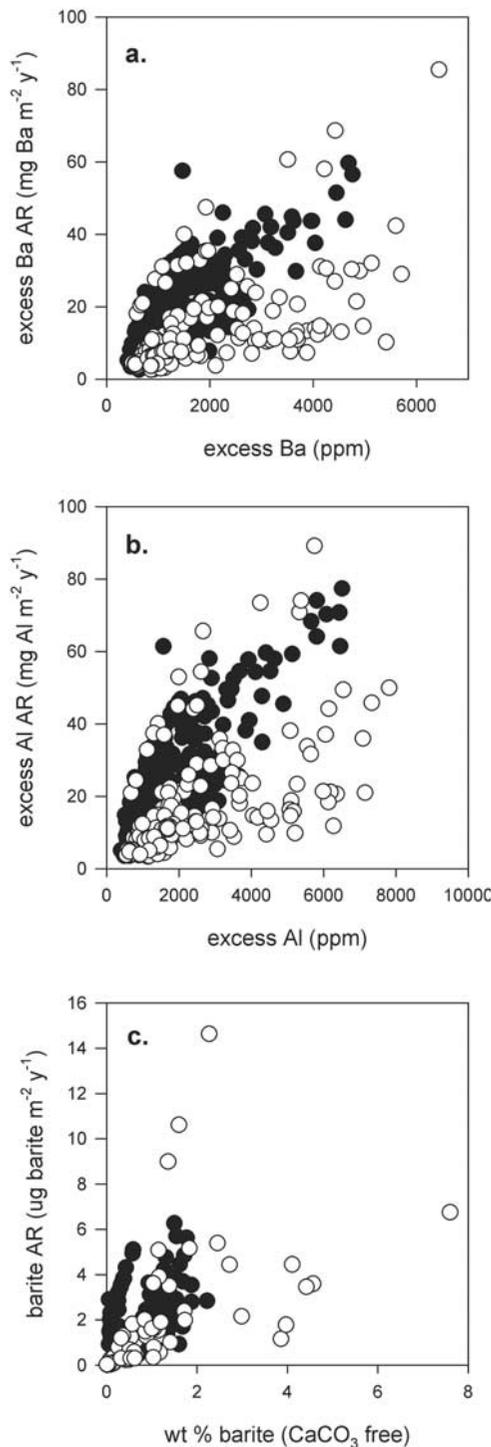
Figure 4. Accumulation rate compared with sediment concentration data. Solid circles are samples from pc72; open circles are from pc114. (a) Excess Ba versus excess Ba AR, (b) excess Al versus excess Al AR, and (c) wt % barite (calculated on a calcium carbonate free basis) versus barite AR. Accumulation rates are all based on data from *Murray et al.* [2000] and references therein.

rates and dry bulk density may not respond exclusively to water column processes [*Marcantonio et al.*, 2001, 1996, 1998, 1995]. However, the use of ^{230}Th- or ^{3}He-based accumulation rates also has implicit assumptions and limitations. It is beyond the scope of this paper to discuss the advantages and disadvantages of the use of ^{230}Th and ^{3}He to calculate vertical MAR (for further discussion, see *Bacon and Anderson* [1982], *Farley and Eltgroth* [2003], *Farley and Patterson* [1995], *Francois et al.* [2004], *Marcantonio et al.* [1996], and *Thomas et al.* [2000]. Using ^{230}Th- or ^{3}He-based MAR may indeed change the observed patterns in our records, as shown in the work of *Paytan et al.* [1996], where Th-corrected barite data from pc72 (0 to 500 kyr) show mitigated productivity cycles. However, at this stage ^{3}He data are not available to us for both sites for comparison between these two approaches. Moreover, although using ^{230}Th or ^{3}He may change the absolute values of the C_{export} reported here using the various proxies, it will not reconcile the observed discrepancies in magnitude among the MAR proxies.

[35] Regardless of the mechanism causing the absolute dissimilarities in C_{export} estimates based on marine barite, excess Ba, and excess Al, the systematic covariation of all these records (whether using conventional MAR calculations or ^{230}Th- or ^{3}He-based MAR) implies that deposition of marine barite, excess Al and excess Ba are responding to common forcing and are dominating trends in the long-term record.

3.2. Al/Ti and Ba/Ti Ratios

[36] At all locations along the 140°W transect, records of Ba/Ti correspond with Al/Ti, and BaAR correspond with AlAR (Figures 5a and 5b). On the basis of assumptions associated with the ratio proxies, Ba/Ti and Al/Ti trends should correspond with contemporaneous records of excess Ba and excess Al, respectively. It is clear in Figures 5c and 5d that this does not occur.

[37] Delivery of excess Al and excess Ba to the seafloor has been linked to particle, opal, or organic carbon flux [*Choi et al.*, 2001; *Dehairs et al.*, 1987, 1991; *Dymond et al.*, 1992; *Francois et al.*, 1995; *Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993], yet it is not obvious whether Ba/Ti and Al/Ti ratios specifically represent C_{export} since the empirical relationship between sedimentary ratios and primary productivity is based on a small data set (*Murray et al.* [2000] and Figures 1c and 1d). The downcore concentrations of Ba, Al, and Ti may be affected by differences in the fractional solubility of Al and Ba carried in dust [*Sato et al.*, 2002], changes in the sediment provenance from which terrestrial dust originated [*Klump et al.*, 2000], and/or scouring of and subsequent delivery of material of different Al/Ba/Ti ratios [*Mackey et al.*, 2002; *Wells et al.*, 1999]. Any of these processes may have resulted in variable deposition of a component with different Ba/Al/Ti, possibly over glacial-interglacial cycles as a result of systematic, climatically driven changes in ocean-atmosphere circulation.

[38] The differences observed in the ratio and excess data of Ba and Al (Figures 5c and 5d) challenges the assump-
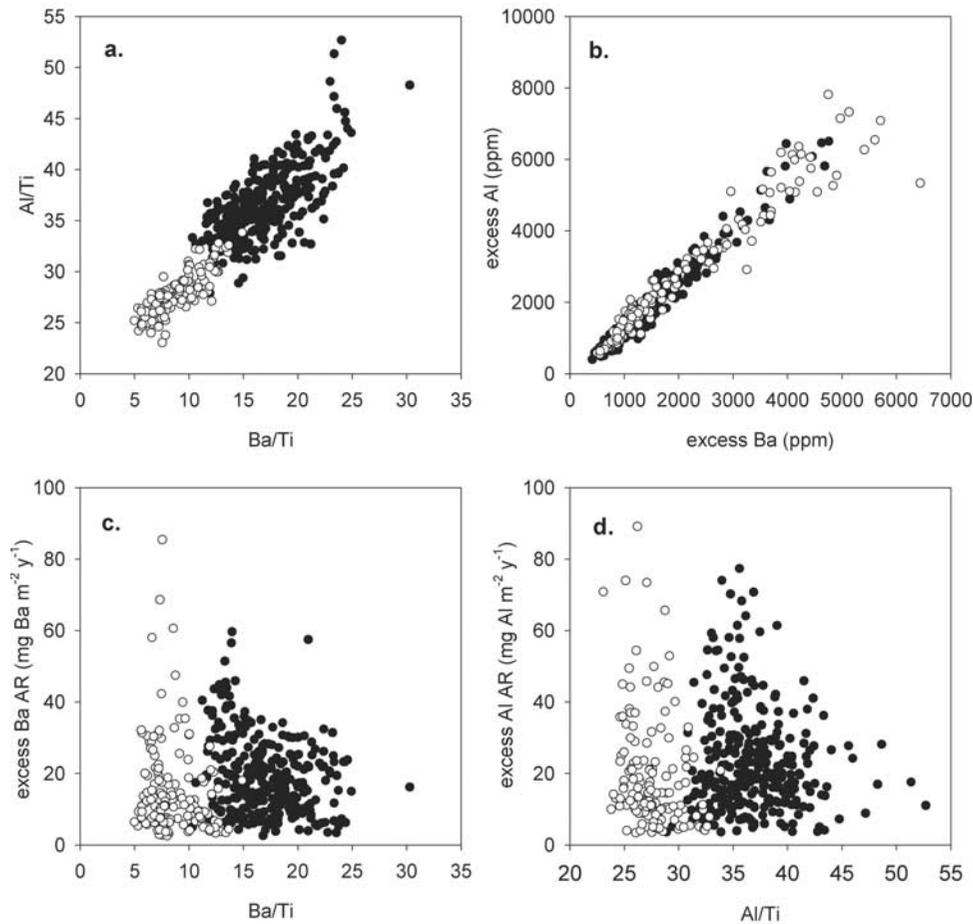
Figure 5. Direct comparison of downcore Ba, Al, and Ti data. Solid circles are samples from pc72, open circles are from pc114. (a) Ba/Ti versus Al/Ti. (b) Excess Ba versus excess Al. Since the MAR are the same for these samples, the same linear relationship is observed when accumulation rates are applied to these data. (c) Ba/Ti versus excess Ba AR. (d) Al/Ti versus excess Al AR. Note that when the ratio data (Ba/Ti and Al/Ti) are compared with their respective excess concentrations (not the accumulation rate), there is still no significant relationship among the data at either site.

tions that Ba/Al/Ti ratios of the terrigenous/detrital fraction did not vary significantly through time and/or that all of the sedimentary Ti is of lithogenic origin. Indeed, recent work by *Kryc et al.* [2003] suggests a possible link between sedimentary Ti and organic matter. *Timothy and Calvert* [1998] have also suggested that bulk ratio trends from *Murray and Leinen* [1993] are an artifact of authigenic clay mineral formation or another process altering the aluminosilicate content of the sediment. Using the regression methods described in the work of *Timothy and Calvert* [1998], the records from two other cores from the EqPac transect, pc32 and pc18 (data not shown), show the presence of sedimentary components within these cores with at least two distinct Ba/Al/Ti ratios. Indeed, *Murray et al.* [2000] discuss a Ti-rich mafic component at one of these southerly sites (5°S, TTN013-pc32), likely originating from the Marquesas Island. If the presence of additional Ti from the Marquesas is evident at sites as close to the equator as 2°S (TTN013-pc18), as our calculations suggest, it is possible that oceanographic changes might also affect delivery of

Ti to the pc72 or pc114, thus altering downcore trends in Ba/Ti and Al/Ti. *Murray et al.* [2000] have documented changes in sediment provenance, but argue that this is insignificant relative to changes in the Ba and Al associated with particulate fluxes [*Murray et al.*, 2000; *Murray and Leinen*, 1993, 1996; *Murray et al.*, 1993]. The lack of consistency between ratios and excess accumulation rates shown in Figure 5 suggests that this assumption should be re-evaluated.

[39] The advantage of ratio (normalization)-based proxies over accumulation rate-based indices is that they are not dependent on conversion to accumulation rates, and thus are less sensitive to errors associated with mass accumulation estimates and sediment focusing. Thus another potential explanation for the differences in the ratio-based records with excess Ba and excess Al (Figures 5c and 5d) might be bias introduced by applying accumulation rates. Although Figure 4 shows that there is a strong correlation between the concentrations of excess quantities and their respective accumulation rates, as discussed in section 3.2, there are complicating factors.

Until the influence of winnowing and focusing processes can be constrained, the specific mechanism accounting for the differences in the ratio and excess records will remain unclear.

3.3. All Data

[40] The downcore C_{export} trends derived from Ba/Ti and Al/Ti covary and show significantly smaller amplitude variations relative to C_{export} values from barite or excess Al and excess Ba accumulation (Figures 2c, 2d, 3c, and 3d). At pc72 (Figure 2), the average export during maxima in barite accumulation (Figure 2a), Ba/Ti (Figure 2c), Al/Ti (Figure 2d), AlAR (Figure 2e) and BaAR$_{ct}$ (Figure 2f) records are similar, although the timing of the ratio-based and accumulation-based proxies is not. The average C_{export} value during minima of the Ba/Ti and Al/Ti records are, however, at least 50% greater than the C_{export} minima values calculated using the other proxies, resulting in G-I changes on the order of 20–30%, as compared with ~60% for the barite, BaAR, and AlAR records. At pc114 there is little similarity in the magnitude of the maxima, minima, and relative changes in C_{export}, in addition to differences in the timing of the peaks between the ratio and accumulation based proxies (Figure 3). The average change in productivity between maximum and minimum is approximately 12% based on Ba/Ti and Al/Ti, but is 50–70% according to the other proxies. In general, the ratio-based calculations show a more significant latitudinal change in export compared to the accumulation rate-based records, with highest C_{export} flux at the equator [*Murray et al.*, 2000]. This latitudinal trend occurs in the barite, AlAR, and BaAR based records only during interglacial periods between 0 and 500 kyr. The timing of peak C_{export} flux also differs. The maxima in the ratio-based records are coincident with glacial-interglacial transitions and occur several thousands of years after the barite, AlAR and BaAR peaks, at least for the past 500 kyr, before which there is a baseline shift in the ratio-based productivity records (Table 1).

[41] Unless accumulation rate bias is forcing the observed trends in barite, excess Ba, and excess Al, at least one of the groups of proxies discussed here (barite, BaAR and AlAR, or Ba/Ti and Al/Ti) is not exclusively tracking C_{export} to the seafloor (directly or through particle flux). Considering that the same productivity data, core tops and downcore samples were used to empirically calculate C_{export}, it is surprising that there is little agreement among the data sets (Figures 2 and 3).

4. Conclusions

[42] Although Figures 2 and 3 show a response by all indices to some cyclic (glacial-interglacial) climatic forcing, it is clear that these proxies are not responding similarly. The discrepancies among the magnitude of C_{export} calculated from marine barite, and the excess Ba and excess Al accumulation rate calibrations, and the *Dymond et al.* [1992] and *Francois et al.* [1995] algorithms, and the differences in timing and magnitude of C_{export} derived from Ba/Ti and Al/Ti ratios and their respective excess elemental accumulation in bulk sediments, might result from numerous processes. These include sediment redistribution, changes in the relative contribution of lithogenic material with significantly different Ba/Al/Ti ratios, modification of scavenging processes in the water column, regeneration processes in the sediment, variable delivery of elemental Ti to the equatorial Pacific, insufficient calibration of proxies, or other undefined processes. Regardless of the mechanism(s) responsible, it is clear that none of these proxies alone is the "silver bullet" that can be used to determine paleo C_{export}.

[43] Given that several of the proxies shown here were developed based on data collected from the equatorial Pacific, and that applying these indices downcore (at the same sites) yields conflicting results, this comparison illustrates that caution must be taken in making interpretations based on these proxies.

[44] The assumptions involved and limitations associated with using any paleoceanographic index must be evaluated and acknowledged when interpreting data for C_{export} reconstruction. The similar cyclicity of excess Ba, excess Al, and barite and their respective accumulation rates, and the lack of a relationship between C_{export} estimates based on the accumulation rate based proxies and bulk ratios proxies, imply that there are ill-defined processes, possibly unrelated to productivity, affecting sedimentary Ba, Al, and/or Ti.

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