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Terrigenous Fe input and biogenic sedimentation in the glacial and interglacial equatorial Pacific Ocean

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Abstract. Many ocean regions important to the global carbon budget, including the equatorial **Pacific Ocean, have low chlorophyll concentrations despite high levels of conventional nutrients. Iron may instead be the limiting nutrient, and elevated input of terrigenous Fe during windy glacial episodes has been hypothesized to stimulate oceanic productivity through time and thus regulate the oceanic and atmospheric CO2 balance. To test whether particulate Fe input is related to the accumulation of biogenic matter in one important low chlorophyll-high nutrient area, that is, the equatorial Pacific Ocean, we present results from a suite of sediment cores that collectively record biogenic deposition through the last six glacial-interglacial cycles (~ 600,000 years). Our data set includes new chemical data on total Fe, terrigenous, and biogenic components in three cores as** well as previously published mineralogic records of eolian input to the region. Chemical, spectral, **and stratigraphic analysis indicates that (1) terrigenous input to the region shows no consistent pattern of either glacial or interglacial maxima, (2) the accumulation of particulate Fe is closely** related to the accumulation of terrigenous matter (linear $r^2 = 0.81 - 0.98$), (3) there are no coherent spectral relationships between Fe input and glacial periodicity (i.e., δ¹⁸O) in any of the orbital frequency bands, (4) the linear and cross-spectral correlations between Fe or eolian input and **CaCO3 concentration are most commonly the strongest observed relationships between Fe and any biogenic component, yet indicate a largely inverse pattern, with higher Fe being associated with** low CaCO₃, (5) there is no consistent linear r^2 correlation or spectral coherence between the accumulation of Fe and that of CaCO₃, C_{org}, or opal. Thus in total there is no relationship between terrigenous Fe input and sedimentary sequestering of carbon. Additionally, although we **cannot specifically address the potential for changes in solubility of the terrigenous fraction that may be driven by a terrigenous compositional change, the Fe/Ti ratio (which monitors first-order** mineralogic changes) records only slight variations that also are linearly and spectrally unrelated **to glacial periodicity, the bulk Fe flux, and the accumulation of any biogenic component. Finally, we find that the paleoceanographic flux of Fe is several order-of-magnitudes larger than modem** observations of eolian Fe input, suggesting that the long-term importance of Fe input by dust **storms (which deliver Fe on the order of the sedimentary burial) may be underestimated. The removal of particulate terrigenous Fe from the recently discovered source within the Equatorial Undercurrent, however, remains unquanfified and may also prove significant.**

Introduction

Three questions about the biogeochemical relationship between Fe and marine phytoplankton production have been highlighted for their potential importance to the oceanic and atmospheric CO₂ balance:

1. Does Fe limit modern-day production in regions like the equatorial Pacific and Southern Ocean, where low chlorophyll

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Paper number 95GB02833. 0886-6236/95/95GB-02833510.00 **concentrations are associated with high levels of conventional** nutrients (NO³, PO₄³, SiO₂) [*Martin et al.*, 1990, 1991; *Barber* **and Chavez, 1991; Bruland et al., 1991; Morel et aI., 199!; Price et al., 1991; Frost and Franzen, 1992; DiTullio et al., 1993; Kolber et al., 1994; Martin et al., 1994]?**

2. Would Fe fertilization stimulate production and thus be an effective strategy to sequester atmospheric CO₂ in sedimentary calcium carbonate (CaCO₃) and organic carbon (C_{org}) through **sedimentary burial (and thus final removal from the oceanatmosphere system) [Martin et al., 1990; Peng and Broecker, 1991; Martin, 1992; Watson et al., 1994]? and**

3. Did natural Fe fertilization via terrigenous input occur over glacial-interglacial timescales [e.g., Martin, 1990; Berger and Wefer, 1991]?

The equatorial Pacific plays an important role in the debate over Fe limitation of oceanic productivity because it has been specifically implicated in each of the three questions listed above and is critically important to global studies of ocean-atmosphere carbon cycling [e.g., Murray et al., 1994]. As such, although models predict the Fe-fertilized consumption of conventional nutrients in the Southern Ocean is more important to the

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atmospheric concentration of CO₂ [Sarmiento and Orr, 1991], **the equatorial Pacific was the location of a recently concluded experiment in which a large oceanic area was artificially fertilized with Fe and the biologic response was monitored [Kolber et ed., 1994; Martin et ed., 1994; Watson et ed., 1994]. Thus we focus on the equatorial Pacific Ocean to study the relationships between the input of terrigenous matter, total Fe, and biogenic sedimentation through time.**

In this paper, we test the hypothesis that long-term variation in terrigenous Fe flux has been associated with sequestering of carbon in the equatorial Pacific by examining the sedimentary record of the total Fe accumulation during the last six glacialinterglacial cycles (600,000 yr = 600 kyr). We report new chemical data that result from the chemical measurement of total Fe in three cores in the vicinity of 130^o - 140^o W, two of which **(GC51 and PC72) record Fe input for the past 600 kyr while the third (GC14) presents a shorter but higher resolution record (Figure 1; Table 1). We interpret these chemical data in the context of previously published mineralogic records of eolian input to the region, based on data from Core RC11-210 and Deep** Sea Drilling Project (DSDP) Hole 503B (Table 1) [Rea et al., **1986; Chuey et ed., 1987; Pisias and Rec, 1988; Reaet ed., 1991]. Although DSDP 503B is located well to the east of the other four cores located in the central equatorial Pacific (Figure 1), and thus in a different carbonate regime [Snoeckx and Rea, 1994], it is a particularly well-studied core in terms of the biogenic and eolian components (Table 1), and so it is appropriate to consider here. As we discuss below, our results address the first-order issue of the biogenic response to the total Fe input to the system, not the amount of reactive Fe. We will also address, however, the glacial-interglacial timing and extent of potential variations in reactive Fe input, and provide quantitative constraints on such potential variation.**

Biogenic Production: The Sedimentary Record

Considering the capability of the sedimentary paleochemical record to provide insight into the three biogeochemical questions

Figure 1. Map indicating locations of cores discussed in this study. See Table I for complete geographic information. Representative positions of sin'face ocean currents schematically shown as follows: NEC, North equatorial Current; NECC, North equatorial Countercurrent; SEC, South equatorial Current.

highlighted above, there are several critical issues that first must be addressed. We are unable to address question 1 through investigation of the palcochemical record because even the youngest sampled sediment in the region provides only a cumulative average signal of deposition over the past - 500 yr [e.g., Murray and Leinen, 1993; and references therein]. There is a rich literature that more appropriately addresses the topic of Fe limitation in the present-day equatorial Pacific (as cited above).

To investigate the second question quantitatively requires an understanding of the causes of the biogenic sedimentary cycles in **the equatorial Pacific. The literature provides much discussion of** whether Quaternary CaCO₃ and C_{org} maxima throughout the **equatorial Pacific predominantly reflect variations in productivity [e.g., Arrhenius, 1952; Pedersen, 1983; LyIe et al., 1988, 1992; Archer, 1991; Pedersen et ed., 1988, 1991; Murray et al., 1993; Herguera and Berger, 1994] or dissolution intensity [e.g., Berger, 1973; Emerson, 1985; Farrell and Prell, 1991]. Indeed, although the debate is often posed in a mutually exclusive** framework (i.e., production or dissolution), it is more appropriate **to consider the linkage between the two processes: As synthesized by Berger [1992], it is the large-scale glacialinterglacial changes in productivity that may also be responsible for varying dissolution intensity. While it is beyond the scope of this paper to settle or debate this issue, we believe that the biogenic cycles we discuss predominantly reflect productivity variations. There are many lines of evidence to support this,** including the broadly similar patterns of CaCO₃, C_{org}, and opal **accumulation [e.g., Lyle et ed., 1988; Reaet al., 1991] (each responding to different dissolution mechanisms; e.g., Martin et ed., [1991]), modeling considerations [e.g., Archer, 1991], a variety of trace metal proxies such as Ba, sedimentary I, scavenged A1, and redox sensitive metals [e.g., Pederson, 1983; Pederson et ed., 1988; Dymond etal., 1992; Murray et ed., 1993; R. W. Murray and M. Leinen, unpublished data, 1995], faunal abundances [e.g., Pederson et al., 1988; Herguera and Berger, 1991], as well as others. Most importantly, recall that question 2 concerns the relationship between Fe input and sequestration of** atmospheric CO₂ through final sedimentary burial. Thus **variations in dissolution that are superimposed upon the larger productivity signal [e.g., Wei et ed., 1994] will not compromise the sedimentary palcochemical record's capability to accurately document temporal changes in final carbon sequestration and terrigenous Fe input.**

Building on this discussion, the final question, which addresses the most important issue of this paper, will be addressed below by comparison of the terrigenous Fe input through time. By monitoring the input of terrigenous material, the input of Fe, and the accumulation of the biogenic components, we will examine the relationship between the potential for Fe fertilization and the biogenic response.

Sources of Eolian, Terrigenous, and Particulate Fe

The Fe hypothesis of phytoplankton limitation in the equatorial Pacific was originally phrased in the context of the Fe being delivered via eolian input [e.g., Martin, 1990; Martin et ed., 1994]. Recently, however, it was discovered that the Equatorial Undercurrent (EUC) carries a substantial dissolved and particulate load of Fe to the central equatorial Pacific, and that

| Core | Latitude, deg North | Longitude, deg West | Depth, m | Data Type | Data Source |
|---------------|------------------------|------------------------|-------------|---|---|
| WEC8803B-GC51 | 1.3 | 133.6 | 4410 | Fe, Ti, CaCO ₃ , C_{org} , opal | This work, and Murray et al. [1993] |
| WEC8402A-GC14 | 0.95 | 139 | 4287 | Fe, Ti, CaCO3, C_{org} , opal | This work, and Murray [1987] |
| TT013-PC72 | 0.1 | 139.4 | 4298 | Fe, Ti, CaCO3 | This work |
| RC11-210 | 1.8 | 140 | 4420 | Eolian, CaCO ₃ , C_{org} , opal | Chuey et al. [1987] Pisias and Rea [1988] Rea et al. [1991] |
| DSDP 503B | 4.0 | 95.6 | 3672 | Eolian, CaCO3, C_{org} , opal | Rea et al. [1986] |

Table 1. Core Locations and Data Type

this EUC input is a far more significant source to the euphotic zone than eolian input [Gordon et al., 1995]. Chemical analyses **of this EUC particulate matter suggest that it is similar in composition to upper continental crust [Gordon et al., 1995], and thus at this point we cannot distinguish in the sediment between particulate matter advected in the EUC and eolian particulate matter. Because of this, we refer to the total Fe in the sediment in the cores which we chemically analyzed as "terrigenous" (i.e., indistinguishable between advected and eolian sources). For RCll-210 and DSDP 503, however, the operationally defined eolian fraction was analyzed by previous workers (discussed below), and we indeed refer to this fraction as "eolian". The Fe analyses measure variation in the amount of total Fe supplied to the system via the combined sources of eolian input and the EUC, and we are thus examining in the sedimentary record the Fe fertilization hypothesis in the context of the relationship between the total Fe input and biogenic sedimentary response.**

Analytical Methodology and Stratigraphy

Complete core and geographic information is provided in Table 1, as is a summary of the available data discussed in this paper. Calcium carbonate in gravity core WEC8803B-GC51 (subsequently abbreviated as "GC51") and piston core TT013- PC72 (abbreviated as "PC72") was determined by standard coulometric techniques, as was C_{org} in GC51 (see Murray et al. **[1993] for determinations of precision and accuracy). Opal in GC51 was determined using a normative calculation that was calibrated to opal measured by a timed-dissolution technique on similar samples from the equatorial region [Murray and Leinen, 1993]. Biogenic components in WEC8402A-GC14 (abbreviated as "GC14") were determined as described in Murray [1987]. Data for the biogenic components in RC11-210 and DSDP 503B (abbreviated as "503B") were taken from the literature [Reaet al., 1986; Chuey et al., 1987; Pisias and Rea, 1988; Rea et al., 1991].**

For GC51, total Fe and Ti were determined by Xray fluorescence spectrometry (XRF) (XRay Assay Laboratories, Toronto, Canada); precision, determined by blind analysis of ~

10 replicate powders submitted over three different analytical runs several months apart, is 7% of the measured value for Fe and 2% of the measured value for Ti. Accuracy was assessed by blind analysis of reference sediment NBS-1C (argillaceous limestone, Fe = 0.38 wt. %; Ti = 0.04 wt. %); values agree within **precision. To verify Fe data in GC51, 21 samples selected to represent the entire Fe concentration range were also analyzed by inductively coupled plasma-emission spectrometry (ICP-ES) at Boston University, using sample preparation methods described by Murray and Leinen [1993]. Agreement between XRF and ICP-ES data was excellent even for the lowest Fe concentrations, and because the ICP-ES data are preferred for reasons of quality control the original XRF data were slightly corrected by a linear regression generated from the comparative data (** $r^2 = 0.984$ **). These corrections do not affect the temporal pattern of Fe abundance or accumulation in any way, and the dual measurements serve to verify and confirm the analytical results.** Owing to the extremely high CaCO₃ concentrations in some **samples (up to 91 wt. %), some Ti values are below the XRF detection limit. For PC72, Fe and Ti were determined by ICP-ES at Boston University. Precision was assessed by repeated preparation and analysis of sediment from the 432- to 433-cm interval of PC72, and is 4% of the measured value for both Fe and Ti. Accuracy was assessed by analysis of reference sediment NBS-1C (described above), values agree within precision. Because the amounts of Fe and Ti in NBS-1C are somewhat greater than are found in equatorial Pacific samples, however, we also analyzed an aliquot of NBS-1C that had been diluted as a powder by ultrapure CaCO3 powder (ULTREX, J. T. Baker, Inc.)** to Fe and Ti concentrations (Fe \sim 300 ppm, Ti \sim 30 ppm) more **representative of or lower than those found naturally. The analyzed concentrations of both Fe and Ti in this modified reference, as well as the Fe/Ti ratio, also agreed within precision to the expected values. For GC14, Fe and Ti were determined using a wavelength dispersive Philips PW1600 simultaneous XRF spectrometer at Oregon State University [Murray, 1987]. Values presented here have been slightly adjusted from the original data in Murray [1987], based on comparative atomic absorption spectrometry (AA) analyses of a suite of samples from GC14 and a nearby box core. Although the trends are similar,**

XRF values were subsequently linearly corrected to the preferred **AA results; again, these corrections do not affect the temporal pattern of Fe abundance or accumulation in any way and the dual** measurements serve to verify and confirm the analytical results. **Precision of the GC14 analyses remains better than 3% and accuracy is better than 7% of the measured value.**

The age model for GC51 ties together the δ^{18} O-based age model using Globorotalia tumida from 0 to 412 kyr **[LaMontagne, 1993] and the carbonate-based age model from 412 to 619 kyr [Murray et al., 1993] that is based on correlation** of CaCO₃ concentration in GC51 to that in RC11-210 which is in **turn isotopically calibrated to the SPECMAP stack [Pisias and Rea, 1988]. The age model for GC14 is based on a correlation to** the SPECMAP stack [*Imbrie et al.*, 1984] of the δ^{18} O record **measured on G. turnida using the signal correlation technique of Martinson et al. [1982] and eight coefficients to define the mapping function. Accumulation rates for GC14 presented here are slightly different from those presented graphically by Lyle et a/. [1988], due to small revisions of the age model. The age** model for PC72 was determined by δ^{18} O analysis of Cibicides **wuellerstorfi and correlation to the SPECMAP stack [Irnbrie e t al., 1984]. The age models for RCll-210 and 503B are taken from the literature [Rea et a!.,.1986; Pisias and Rea, 1988]. Only the 0 to 600 kyr portion of the published record from RCll-210 is reproduced here because it is only this interval that we can compare to the 0 to 600 kyr records of GC51 and PC72. As will be shown below, slight differences in the age models between the various cores discussed here will not affect the main points of this paper. We instead emphasize variations within each core and further note that these variations are internally consistent between the cores.**

Accumulation rates were calculated using the standard protocol of the accumulation rate of a given element (or component) equaling the product of linear sedimentation rate (derived from the age model), dry bulk density, and concentration of the element or component in question. For GC51 mid PC72, dry bulk density was calculated from a relationship between CaCO₃ and dry bulk density specific to this region [Murray and **Leinen, 1993]. For GC14, dry bulk density was determined using methods described by Murray [1987]. The accumulation of the biogenic and eolian components in RCll-210 and 503B are taken from Rea et al. [1986], Chuey et al. [1987], and Pisias and Rea [1988], in which the operationally defined eolian component was** determined by a series of chemical extractions. **accumulation rates in RC11-210 for samples younger than 50 kyr are not presented because they are referred to by the original authors as "anomalous"; there also is an ash layer at 75 kyr [Chuey eta/., 1987]. In 503B, the eolian and opal accumulation rates were measured on slightly different intervals than were the** accumulations of CaCO₃ and C_{org}. For purposes of calculating **correlation coefficients (see below), the accumulations of eolian and opal were linearly interpolated onto the depths for which CaCO3 and Corg were measured.**

Spectral analyses of the cores for which we have chemical data was performed using standard menu-driven software from Brown University that is based on the Blackman-Tukey method **[Jenkins and Watts, 1968]. For GC51, spectral analyses were performed only on the portion of the core with ages that are isotopically defined (0 to 412 kyr). Interpretation of the 100 kyr period in GC14 (a 240 kyr record) must be made with caution because only two 100 kyr cycles are recorded.**

Results

Data for GC51, GC14, and PC72 are given in the appendices (Tables A1 - A3). Linear correlation coefficients (r^2) between **the accumulation of the biogenic components, the accumulation** of the respective eolian component, the Fe/Ti ratio (g/g) , and the concentration of CaCO₃ (wt. %) are given in Table 2. Results of cross-spectral analyses are given in Table 3. Downcore profiles **of the various components for each core are presented in Figures** 2 - 6. The concentration of CaCO₃ is plotted only for the cores **for which the new Fe data is given (GC51, GC14, and PC72); similarly, spectral analyses were only performed on these cores.**

Downcore profiles of CaCO₃ concentration and accumulation **in all cores display the well-known increases and decreases that broadly follow glacial-interglacial cyclicity (as cited above). In GC51, GC14, and PC72, the accumulation of Ti, which we use to track terrigenous input [Taylor and McLennan, 1985; Murray et aL, 1993], records maxima during both glacial and interglacial periods, with no consistent pattern. In all cores, the accumulation of Fe closely follows that of the terrigenous component, as measured by Ti (Tables 2 and 3). Most significantly, in these cores the accumulation of Fe is not related to the accumulation of** CaCO₃, C_{org}, or opal, neither in terms of the linear r^2 values **(Table 2) nor in terms of spectral coherence (Table 3). In four of** the five cores, the strongest linear r^2 correlation between Fe or **terrigenous accumulation and any biogenic variable is with** CaCO₃ wt. %, and this correlation is negative. (The relatively strong r^2 between Fe and opal accumulation in GC51 results essentially solely from the paired maximum at \sim 330 kyr.) In the **one core for which the correlation is not negative (RCll-210),** the correlation between eolian input and CaCO₃ wt. % is exactly **zero and the correlation between eolian input and the accumulation of CaCO 3, Corg, and opal also are essentially zero (respectively, 0.01, 0.02, and 0.04; Table 2). Spectral analyses confirm the lack of consistent relationship between the accumulation of Fe and the accumulation of any biogenic component at any orbital frequency, as well as the much stronger** and essentially inversely related (~ 180° out-of-phase) relationship between Fe accumulation and CaCO₃ abundance **(Table 3).**

In GC51 and PC72, the Fe/Ti ratio records a long-term decrease from 600 kyr to ~ 350 kyr, after which it either slightly increases or maintains a relatively constant median value to modern-day levels (Figures 2 and 4). There are also higher frequency variations superimposed on these long-term trends, such as found in GC14 (Figure 3). Neither the long-term trend nor the short-term variability in Fe/Ti is related to glacial periodicity, nor are they significantly related to the accumulation of any biogenic component (Tables 2 and 3).

In RCll-210, the accumulation of the eolian component records both glacial and interglacial maxima (Figure 5). In 503B, eolian accumulation appears to be predominantly interglacial accumulation of any of the biogenic components.

Discussion

For the following reasons, we interpret the Fe profiles in GC51, GC14, and PC72 as records of the terrigenous input of Fe

| | Fe | Tì | CaCO ₃ | \mathbf{C}_{org} | Opal | Fe/Ti | CaCO ₃ , % | Eolian | | | |
|--|---|--|---|---------------------------------|-------------------------|-----------------|-----------------------|--|--|--|--|
| GC51 (0 - 600 kyr) | | | | | | | | | | | |
| Fe Ti CaCO ₃ C_{org} Fe/Ti CaCO ₃ (%) | 1.00 0.93 0.09 0.16 0.53 -0.08 -0.17 | 1.00 0.05 0.14 0.50 -0.20 -0.24 | 1.00 0.24 0.46 0.00 0.30 | 1.00 0.41 -0.03 0.00 | 1.00 -0.06 0.00 | 1.00 0.26 | 1.00 | | | | |
| | | | | GC14 (0 - 240 kyr) | | | | | | | |
| Fe Ti CaCO ₃ C_{org} Opal Fe/Ti CaCO ₃ (%) | 1.00 0.81 -0.01 0.00 -0.07 0.23 -0.11 | 1.00 0.04 0.03 -0.01 0.00 0.00 | 1.00 0.48 0.04 -0.27 0.73 | 1.00 0.18 -0.17 0.30 | 1.00 -0.14 0.00 | 1.00 -0.26 | 1.00 | | | | |
| | | | | $PC72 (0 - 600 kyr)$ | | | | | | | |
| Fe Ti CaCO ₃ Fe/Ti CaCO ₃ (%) | 1.00 0.97 -0.01 -0.05 -0.46 | 1.00 -0.03 -0.15 -0.52 | 1.00 0.12 0.35 | 0.16 | | 1.00 | 1.00 | | | | |
| | | | | RC11-210 (0 - 600 kyr) | | | | | | | |
| Eolian CaCO ₃ C _{org} CaCO ₃ (%) | | | 1.00 0.54 0.05 0.55 | 1.00 0.05 0.20 | 1.00 -0.03 | | 1.00 | 1.00 0.01 0.02 0.04 0.00 | | | |
| | | | | DSDP 503B (0 - 420 kyr) | | | | | | | |
| Eolian CaCO ₃ C_{org} Opal CaCO ₃ (%) | | | 1.00 0.00 -0.45 0.79 | 1.00 0.21 -0.10 | 1.00 -0.72 | | 1.00 | 1.00 -0.15 0.15 0.37 -0.39 | | | |

Table 2. Linear Correlation Coefficients Between Fe, Ti, and Biogenic Accumulation, as well as Fe/Ti and CaCO₃ Abundance

Linear correlation coefficients are r^2 . Missing values are for data not gathered for that particular core. CaCO₃ % is CaCO₃ abundance.

to the central equatorial Pacific: (1) This region is not affected by the largescale hydrothermal inputs that are located well to the **east [Leinen and Stakes, 1979; Dymond, 1981; Murray and Leinen, 1993]; (2) although the Fe/Ti ratios in these cores** (ranging from ~ 10 to 25) are often somewhat greater than that of **average pelagic clay (= 14) [Taylor and McLennan, 1985] and** Mesozoic/Cenozoic andesite (= 11) [Condie, 1993] (and thus **could be interpreted as reflecting variation in the abundance of diagenetic oxides), iron oxides, however, m'e themselves known** to be common components of eolian dust [*Duce and Tindale*, **1991; and references therein]; (3) the fact that the Fe and Ti accumulation profiles record identical downcore patterns in each of the three cores indicates that the Fe and Ti share a primary and common terrigenous source; and (4) Fe accumulation varies by up to a factor of 4, which is greater than can be explained by the maximum potential variation (between 30 and 45%; Murray** [1987]) in the diagenetic and eolian oxide component, indicating **that oxides are not the primary Fe-bearing phase in these sediments. Thus we conclude that our measurements of total Fe reflects terrigenous Fe in these sediments.**

Glacial and Interglacial Input of Fe

The temporal patterns of Fe input in these cores do not support the hypothesis that long-term variation in total Fe input controls glacial-interglacial biogenic cyclicity [Martin, 1990; Berger and Wefer, 1991]. First, the terrigenous and eolian accumulation **patterns (based on Ti in GC14, GC51, and PC72, and the eolian measurements in RCll-210 and 503B) show no consistent increase during glacial episodes. Second, linear and spectral** analysis show that there is no evidence that $CaCO₃$, C_{org} , or opal **accumulation was related to the flux of Fe during the past six** glacial-interglacial cycles. Third, the linear r^2 and spectral correlations between Fe or eolian input and CaCO₃ concentration is either negative or zero (for the r^2) or essentially 180^o out-of**phase (for the cross-spectral analysis, and only where there is any relationship at all). Thus there is no evidence that the input of Fe influenced the final sedimentary sequestering of biogenically produced carbon in the equatorial Pacific.**

Comparing these chemical records to the mineralogic studies of eolian accumulation in RC11-210 and 503B confirms the lack

| | | Phase Difference ± Phase Error / Coherency 2 | | | | | | | | |
|---------------------------|-----------------------------|--|--|--|--|--|--|--|--|--|
| Variables | Core | $100 \,\mathrm{kyr}$ | 41 kyr | 23 kyr | | | | | | |
| Fe acc. $/ \delta^{18}$ O | GC14 GC51 PC72 | $-261 \pm 12/0.84$ $±$ 10/0.81 92 | $97 \pm 20/0.60$ | | | | | | | |
| Fe acc. / Carb. % | GC14 GC51 PC72 | ± 14/0.81 131 $160 \pm 12/0.76$ | 177 ± 17/0.69 $±$ 13/0.71 - 178 | $169 \pm$ 18/0.65 $-164 \pm 11/0.79$ | | | | | | |
| Fe acc. / Carb. acc. | GC14 GC51 PC72 | ± 17/0.72 122 $119 \pm 21/0.50$ | | | | | | | | |
| Fe acc. / C_{org} acc. | GC14 GC51 | | | | | | | | | |
| Fe acc. / Opal acc. | GC14 GC51 | $192 \pm 25/0.54$ | | | | | | | | |
| Fe acc. / Ti acc. | GC14 PC72 | $5 \pm 4/0.98$ ± 2/0.99 1 | ±7/0.95 17 $1 \pm 2/0.99$ | $21 \pm 11/0.86$ 5 ± 3/0.98 | | | | | | |
| Fe/Ti / $\delta^{18}O$ | GC14 GC51 PC72 | $116 \pm 13/0.84$ | | $±$ 19/0.64 40. | | | | | | |

Table 3. Results of Cross-Spectral Analysis, Cores GC14, GC51, PC72

Cross-spectral analysis based on the Blackman-Tukey method [Jenkins and Watts, 1968]. Positive phase angles indicate the first variable leads the second. No phase angle is given if records are not coherent at the 80% confidence level, or if one variable shows no increase in variance at the period of interest. Values of coherency² at 80% confidence are as follows: Core GC14 = $\frac{1}{2}$ **0.52; GC51 = 0.42; PC72 = 0.29, with respective bandwidths of 0.0133, 0.0095, and 0.0095 and lags of 25, 35, and 35. All records** interpolated at $\Delta t = 2$ kyr with cross-spectral analysis performed at $\Delta t = 4$ kyr. For Core GC51, only the 0 - 412 ky was analyzed **(the portion of the core for which ages are isotopically defined; see text); PC72 was analyzed from 0 - 600 kyr. Note that GC14 records only 240 kyr of deposition and thus the 100 kyr period is defined only by two cycles. Ti accumulation not included for GC51 due to many values being below XRF detection limit (Table A1).**

of relationship between eolian input and biogenic accumulation. In RC11-210, eolian accumulation exhibits both interglacial and **glacial maxima and does not correspond tothe accumulation of any biogenic component. Similarly, in the shorter record at DSDP 503B, eolian accumulation does not correspond to either CaCO3 accumulation maxima or minima.**

In addition to addressing the Fe fertilization hypothesis, these collected chemical and mineralogic data further document that **the equatorial Pacific does not exhibit the same "glacially dusty" patterns found in Antarctic ice [Petit et al., 1990] and northwest Pacific sediment [Hovan et al., 1991]. This discrepancy emphasizes the importance of the temporal and spatial patchiness of terrigenous input to the surface and near-surface ocean. Indeed, as noted by Boyle [1983] in a study of a core located in the far eastern equatorial Pacific, the collected data sets indicate that such inputs not only respond to global aridity and wind strength, but to other factors as well.**

Solubility Variation of the Terrigenous Component?

The sedimentary Fe data cannot resolve differences in the soluble fraction of terrigenous input (~ 10 % of the total Fe input) [Duce and Tindale, 1991] through time and we therefore cannot explicitly rule out potential changes in Fe solubilization (and thus

bioavailability of dissolved Fe) that may result from variation in weathering or mineralogy of the terrigenous source over the **glacial-interglacial timescale. Any hypothesis ofFe fertilization that requires temporal variation of Fe solubility, however, must invoke the solubility being unrelated to both Fe input and the total terrigenous input. Indeed, our data indicate that there is no increase in biogenic burial during those time periods where the terrigenous Fe input in fact increases by up to a factor of 5 (Figures 2- 4). Thus if an Fe fertilized system were operating, the solubility of the terrigenous fraction would have to decrease during those periods of high particulate input. Recall, however, that neither the long-term decrease nor the higher frequency** variations in Fe/Ti in GC51, GC14, or PC72 correspond to glacial-interglacial cyclicity in biogenic burial, which implies that **neither the Fe source terrain nor the solubility of the Fe** component is varying in concert with biogenic production. This variation in Fe/Ti is nonetheless intriguing; future studies of the terrigenous sediment fraction and potential source terrains should **address this variation in order to constrain these observations.**

Terrigenous Input of Fe to the Equatorial Pacific

The results of this study also address the input budget of Fe to equatorial Pacific waters. Modern estimates of the total average

Figure 2. Downcore age profiles of the concentration of CaCO₃ (wt. %) in GC51 (with numbered and shaded isotopic glacial stages from *Imbrie et al.* [1984]), the accumulation rates of CaCO₃, C_{org}, opal, Fe, and Ti (x 10), as **well as the age profile of Fe/Ti. Missing values in Ti accumulation and Fe/Ti reflect Ti concentrations below analytical detection limit (see text).**

eolian flux of Fe to the ocean in the equatorial Pacific are on the order of 0.1 nag cm '2 kyr '1 [Duce andTindale, 1991]. This value is at least an order of magnitude smaller than that recorded in sediment over the longer timescale (Figures 2 - 4) as well as substantially smaller than values calculated from the eolian **accumulation record at RCll-210 and 503B (based on a** representative Fe concentration in terrigenous matter [Taylor and **McLennan, 1985] and the abundance of eolian matter in the cores [Rea et al., 1986; Chuey et al., 1987]). This data indicates that**

the importance of dust storms, which can deposit Fe at a rate on the order of 3 mg cm^{-2} kyr⁻¹ [*Young et al.*, 1991], may be **underestimated by modern observations and that the average eolian estimates may not be representative ofthe longer scale input. With the recent observation that the EUC is an additional and important source of particulate Fe to the region [Gordon et al., 1995], however, future research needs to quantify the amount of Fe from the EUC that is removed to the sediment (i.e., how much of the EUC Fe is indeed removed by particles settling**

Figure 3. Downcore age profiles of the concentration of $CaCO₃(wt. %)$ in GC14 (with numbered and shaded **isotopic glacial stages from Imbrie et al. [1984], note that glacial Stage 8 extends off the bottom of the figure), the** accumulation rates of $CaCO₃, C_{org}$, opal, Fe, and Ti (x 10), as well as the age profile of Fe/Ti.

Figure 4. Downcore age profiles of the concentration of CaCO₃ (wt. %) in PC72 (with numbered and shaded isotopic glacial stages from *Imbrie et al.* [1984]), the accumulation rates of CaCO₃, C_{org}, opal, Fe, and Ti (x 10), as well as the age profile of Fe/Ti.

through the EUC). For example, previous studies of Fe and ten'igenous deposition across the equatorial productivity gradient indicate that the flux of Fe and terrigenous material at $\sim 4^{\circ}$ N **(located beneath the Intertropical Convergence Zone and intepreted as eolian in origin) is 3 to 5 times as large as the flux at the Equator [Murray and Leinen, 1993; Murray et al., 1993]. This is also consistent with the fact that eolian fluxes are known to be larger in the northern hemisphere [Duce and Tindale, 1991]. Thus several issues relating to the particulate Fe cycle in the Central equatorial Pacific remain unresolved.**

Conclusion

Chemical and mineralogic data from the equatorial Pacific indicate that there is no relationship between terrigenous input of Fe and burial of carbon on the glacial-interglacial timescale. We reiterate the following points:

1. The accumulation of terrigenous material in general, and terrigenous Fe in specific, shows no consistent glacial or interglacial maxima or minima.

Figure 5. Downcore age profiles of the concentration of CaCO₃ (wt. %) in RC11-210 (with numbered and shaded isotopic glacial stages from *Imbrie et al.* [1984]), and of the accumulation rates of CaCO₃, C_{org}, and opal.

Table A1. Data for Core GC51

 \mathcal{A}

| | | | weight % | | | mg cm ⁻² kyr ⁻¹ | | | | | |
|----------------|-------------|------|----------|-----------|------------|---------------------------------------|------|---------------------------|------|-------|--|
| Depth, cm | Age, kyr | Fe | Opal | C_{org} | BAR | CaCO ₃ | Opal | \mathbf{C}_{org} | Fe | Ti | |
| 290 | 365 | 0.64 | 13.0 | 0.12 | 264 | 185 | 34 | 0.32 | 2.64 | 0.098 | |
| 295 | 377 | 0.62 | 13.0 | 0.12 | 267 | 198 | 35 | 0.32 | 2.40 | 0.088 | |
| 300 | 389 | 0.79 | 15.5 | 0.09 | 234 | 147 | 36 | 0.21 | 2.29 | 0.101 | |
| 305 | 400 | 0.81 | 17.2 | 0.15 | 248 | 151 | 43 | 0.37 | 2.16 | 0.110 | |
| 310 | 410 | 0.82 | 18.4 | 0.11 | 256 | 155 | 47 | 0.28 | 2.15 | 0.115 | |
| 315 | 420 | 0.14 | 6.9 | 0.04 | 704 | 606 | 48 | 0.28 | 1.01 | 0.038 | |
| 320 | 424 | 0.17 | 6.8 | 0.04 | 910 | 786 | 62 | 0.36 | 1.32 | 0.044 | |
| 325 | 429 | 0.07 | 4.3 | 0.04 | 974 | 879 | 42 | 0.39 | 0.65 | 0.047 | |
| 330 | 433 | 0.15 | 3.5 | 0.03 | 975 | 880 | 34 | 0.29 | 1.35 | | |
| 335 | 438 | 0.17 | 4.4 | 0.05 | 945 | 837 | 42 | 0.47 | 1,61 | | |
| 340 | 442 | 0.07 | 3.5 | 0.05 | 1077 | 968 | 38 | 0.54 | 0.77 | | |
| 345 | 446 | 0.12 | 3.3 | 0.04 | 952 | 846 | 32 | 0.38 | 1.15 | 0.040 | |
| 350 | 451 | 0.14 | 4.6 | 0.04 | 937 | 825 | 43 | 0.37 | 1.40 | 0.051 | |
| 355 | 455 | 0.19 | 4.9 | 0.04 | 1029 | 899 | 51 | 0.41 | 1.92 | 0.080 | |
| 360 | 459 | 0.21 | 5.6 | 0.05 | 906 | 780 | 51 | 0.45 | 1.87 | 0.076 | |
| 365 | 464 | 0.38 | 8.2 | 0.08 | 525 | 419 | 43 | 0.42 | 2.12 | 0.104 | |
| 370 | 475 | 0.84 | 15.4 | 0.13 | 256 | 169 | 39 | 0.33 | 2.94 | 0.109 | |
| 375 | 486 | 0.60 | 14.3 | 0.07 | 357 | 252 | 51 | 0.25 | 2.44 | 0.092 | |
| 380 | 493 | 0.29 | 8.4 | 0.04 | 393 | 324 | 33 | 0.16 | 1.09 | 0.045 | |
| 385 | 508 | 0.20 | 8.7 | 0.04 | 287 | 238 | 25 | 0.11 | 0.70 | 0.028 | |
| 390 | 520 | 0.17 | 9.0 | 0.03 | 339 | 288 | 31 | 0.10 | 0.59 | 0.022 | |
| 395 | 532 | 0.10 | 6.8 | 0.03 | 628 | 553 | 42 | 0.19 | 0.63 | 0.023 | |
| 400 | 536 | 0.09 | 5.3 | 0.03 | 901 | 796 | 48 | 0.27 | 0.67 | 0.049 | |
| 405 | 541 | 0.17 | 8.0 | 0.04 | 834 | 704 | 67 | 0.33 | 1.29 | 0.045 | |
| 410 | 546 | 0.17 | 5.6 | 0.03 | 718 | 633 | 40 | 0.22 | 1.15 | 0.039 | |
| 415 | 553 | 0.14 | 5.0 | 0.03 | 540 | 470 | 27 | 0.16 | 0.83 | 0.029 | |
| 420 | 561 | 0.33 | 6.7 | 0.05 | 509 | 425 | 34 | 0.25 | 1.77 | 0.067 | |
| 425 | 568 | 0.50 | 12.3 | 0.06 | 360 | 272 | 44 | 0.22 | 1.87 | 0.078 | |
| 430 | 580 | 0.28 | 9.8 | 0.05 | 310 | 252 | 30 | 0.16 | 1.03 | 0.037 | |
| 435 | 592 | 0.30 | 10.0 | 0.05 | 364 | 296 | 36 | 0.18 | 1.16 | 0.046 | |
| 440 | 601 | 0.30 | 10.6 | 0.06 | 400 | 316 | 42 | 0.24 | 1.15 | 0.060 | |
| 445 | 610 | 0.30 | 11.8 | 0.04 | 581 | 452 | 69 | 0.23 | 1.70 | 0.056 | |
| 450 | 615 | 0.20 | 9.7 | 0.07 | 868 | 732 | 84 | 0.61 | 1.50 | 0.047 | |
| 455 | 619 | 0.14 | 5.6 | 0.03 | 703 | 607 | 39 | 0.21 | 0.92 | | |

Table AI. (continued)

Data for CaCO₃ wt. % and Ti wt. % are in *Murray et al.* [1993]. Ages from 0 to 412 kyr from **the state of the state isotopic model in LaMontagne [1993]; from 412 to 619 kyr from carbonate model in Murray et al. [1993]. BAR is bulk accumulation rate. Missing values in Ti accumulation are where Ti < detection limit.**

Table A2. Data for Core GC14

| | | weight % | | | | | $mg \, \text{cm}^{-2} \, \text{kyr}^{-1}$ | | | | | | |
|--------------|-------------|-------------------|------|-----------|------|-------|---|-------------------|------|-----------|------|------|--|
| Depth, cm | Age, kyr | CaCO ₃ | Opal | C_{org} | Fe | Ti | BAR | CaCO ₃ | Opal | C_{org} | Fe | Tì | |
| 0.5 | 0 | 82 | 10.8 | 0.30 | 0.27 | 0.019 | 618 | 504 | 66 | 1.88 | 1.67 | 0.12 | |
| 3.5 | 2.48 | 83 | 11.1 | 0.25 | 0.24 | 0.016 | 679 | 560 | 75 | 1.71 | 1.65 | 0.11 | |
| 6.5 | 4.81 | 83 | 11.1 | 0.23 | 0.23 | 0.016 | 813 | 674 | 91 | 1.88 | 1.83 | 0.13 | |
| 9.5 | 6.79 | 83 | 12.0 | 0.23 | 0.19 | 0.014 | 990 | 826 | 118 | 2.24 | 1.90 | 0.14 | |
| 12.5 | 8.17 | 85 | 11.5 | 0.18 | 0.16 | 0.016 | 1441 | 1228 | 166 | 2.62 | 2.36 | 0.23 | |
| 15.5 | 9.22 | 86 | 10.8 | 0.18 | 0.16 | 0.012 | 1601 | 1384 | 172 | 2.91 | 2.59 | 0.19 | |
| 18.5 | 10.40 | 89 | 7.5 | 0.15 | 0.16 | 0.013 | 1326 | 1182 | 99 | 2.02 | 2.13 | 0.17 | |
| 21.5 | 12.07 | 89 | 6.7 | 0.15 | 0.14 | 0.012 | 1203 | 1067 | 81 | 1.83 | 1.69 | 0.14 | |
| 24.5 | 13.59 | 91 | 6.8 | 0.21 | 0.14 | 0.012 | 1480 | 1340 | 100 | 3.03 | 2.13 | 0.18 | |
| 27.5 | 14.67 | 90 | 7.3 | 0.18 | 0.16 | 0.012 | 1791 | 1611 | 131 | 3.22 | 2.86 | 0.21 | |
| 30.5 | 15.74 | 91 | 6,4 | 0.35 | 0.17 | 0.013 | 1579 | 1434 | 101 | 5.45 | 2.73 | 0.21 | |
| 33.5 | 17.10 | 93 | 3.9 | 0.29 | 0.17 | 0.013 | 1213 | 1129 | 48 | 3.50 | 2.07 | 0.16 | |
| 36.5 | 18.97 | 93 | 3.8 | 0.25 | 0.17 | 0.011 | 1075 | 995 | 41 | 2.64 | 1.83 | 0.12 | |
| 39.5 | 20.90 | 93 | 3.6 | 0.21 | 0.16 | 0.013 | 1093 | 1020 | 40 | 2.34 | 1.80 | 0.14 | |

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BAR is bulk accumulation rate.

Table A2. (continued)

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Table A3. Data for Core PC72

Table A3. (continued)

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1023

579.3 2251

88.0

1993

84.7

Figure 6. Downcore age profiles of the concentration of CaCO₃ (wt. %) in 503B (with numbered and shaded isotopic glacial stages from *Imbrie et al.* [1984]), and of the accumulation rates of CaCO₃, C_{org}, and opal.

2. The accumulation of the biogenic components $CaCO₃$, C_{org} , and opal show no linear r^2 or spectral relationship to that of **terrigenous matter and Fe.**

3. The linear r^2 and spectral correlations between Fe or eolian input and CaCO₃ concentration are either negative or zero and essentially 180° out-of-phase.

4. Collectively, therefore, there is no evidence that the input of Fe influenced the final sedimentary sequestering of biogenically produced carbon in the equatorial Pacific.

Thus while much biological and chemical oceanographic research has indicated that Fe may indeed serve as a micronutrient in surface waters (as cited above), the sedimentary **record indicates that the terrigenous input of Fe is not implicated in glacial/interglacial cycles in productivity and biogenic accumulation. These combined data sets, in concert with** **previously published records from elsewhere around the globe !e.g., from ice cores), indicate that input of Fe and bulk particulate matter to surface waters is patchy both spatially and temporally. Future work should address the spatial and temporal** scales of the patchiness, further target the potential for solubility **variations in terrigenous source terrain, and focus on the** importance of factors other than wind strength and aridity to the **bulk transport of terrigenous material.**

Appendix

Data for Core GC51 (Table A1), Core GC14 (Table A2), and Core PC72 (Table A3).

BAR is bulk accumulation rate

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