LETTERS
PUBLISHED ONLINE: 11 MARCH 2012 | DOI: 10.1038/NGEO1422
nature geoscience

Links between iron input and opal deposition in the Pleistocene equatorial Pacific Ocean

Richard W. Murray[1]*, Margaret Leinen[2] and Christopher W. Knowlton[3]

Increases in overall marine primary productivity and export production in high-nutrient, low-chlorophyll regions of the ocean have, particularly during dry and dusty glacial periods, been hypothesized to be linked to the enhanced delivery of iron[1]. In the modern ocean, iron availability limits production in high-nutrient, low-chlorophyll regions, and may be important in lower-nutrient settings as well[2]. Here, we assess the relationship between productivity and iron in sedimentary records from the high-nutrient, low-chlorophyll region of the equatorial Pacific Ocean over the past million years. We find strong links between iron input, the export and burial of biogenic silica (opal) and total export production. Our data demonstrate that iron accumulation was more closely tied to the accumulation of opal than any other biogenic component, with high iron input associated with substantially increased opal sedimentation. The strong links between iron and opal accumulation over the past one million years are in agreement with the modern biogeochemical behaviour of iron and silica, and the response of the diatom community to their mutual availablity[3,4]. Our data support earlier suggestions[1] of a biological response to iron delivery over geologic timescales.

Many studies in the modern ocean of naturally and experimentally iron (Fe)-stimulated regions have supported key aspects of the hypothesis that Fe addition to Fe-poor surface waters results in phytoplankton blooms and sometimes increases the flux of carbon to the deep sea[1,2,5]. Here, we address questions relating to Fe delivery and a putative biological response in the palaeo-oceanographic record in one important high-nutrient low-chlorophyll (HNLC) region of the global ocean, the equatorial Pacific.

We have previously shown that in this region the source of dissolved Fe—eolian dust, ash, or Equatorial Undercurrent transport from Papua New Guineau—does not influence biogenic sedimentation or climate during the Holocene, Pleistocene, or Miocene[6,7]. Here, we examine the relationship between Fe input flux and biogenic response through glacial–interglacial cycles in the region. As discussed in our earlier work[6], based on comparisons with modern observations we assume that the distribution of dissolved Fe in time and space follows to a first order the distribution of particulate Fe. We report here on the accumulation of Fe, biogenic silica (opal), calcium carbonate ($CaCO_3$), and total organic carbon (TOC) during the past one million years (Myr) in core TT013-PC72 (0° N, 140° W; hereinafter PC72; refs 8,9). This core lies beneath the present maxima in surface productivity and macronutrient concentrations[10], has been the focus of many palaeo-oceanographic studies[8,9,11–14] and exhibits the typical pattern of carbonate maxima with a 100,000-yr (100-kyr) period seen in other equatorial cores[15]. Studies of water-column (for example, primary productivity) and sedimentary (for example, seafloor phytodetritus) parameters demonstrate that the sediment here faithfully records upper-water-column processes[9,11,16,17] (Supplementary Information).

Biological productivity supported by divergence-driven upwelling in the region has led to a thick sequence comprising biogenic $CaCO_3$ (generally >90 wt%) and opal. Opal does not vary systematically with $CaCO_3$ (ref. 18). Dilution by $CaCO_3$ (Fig. 1), along with the great distance of this location from landmasses, causes the concentration of land-derived Fe to be extremely low, often significantly less than 1 wt%[6,8,9,12–14,17].

Fe and Ti concentrations are extremely well correlated ($r = 0.99, p < 0.001$) (Fig. 2), where r is Pearson's correlation coefficient, reflecting both dilution by carbonate and input from terrigenous sources mixed from Papua New Guineau, Chinese loess, oceanic island basalt and South America[6]. The somewhat weaker correlation between Fe and opal concentration ($r = 0.73, p < 0.001$) is consistent with a link between the processes responsible for Fe and opal delivery to the sea floor, in addition to common dilution by $CaCO_3$. It is impossible to differentiate the relative importance of those processes on the basis of concentration data alone. Fe and organic carbon are correlated ($r = 0.30, p < 0.001$), reflecting common dilution by $CaCO_3$, but the poorer relationship probably reflects diagenetic loss of organic carbon and a more weakly coupled pathway during sedimentation and burial.

Palaeo-oceanographers commonly convert concentrations into accumulation rates, which are mass-based sedimentation rates with units of $mg\,cm^{-2}\,kyr^{-1}$ (Supplementary Information). One component of the accumulation-rate calculation is linear sedimentation rate ($cm\,kyr^{-1}$), which has historically been determined by interpolation between $\delta^{18}O$-determined ages. Recent discussion of deep-sea deposition rates, using a newer method that assesses the amount of ^{230}Th produced as part of the U-decay series, highlights the potential for bottom-water circulation to physically focus sedimentation[12,13,19]. Thus, there is lengthy discussion about the best method to quantify the sedimentation-rate term in the accumulation calculation[19–24].

We do not preferentially endorse either the $\delta^{18}O$-based or ^{230}Th-based approach here or elsewhere, and have evaluated both in the Supplementary Information. Our conclusions are not dependent on calculation technique. Here, we emphasize the $\delta^{18}O$-based approach because the 1-Myr $\delta^{18}O$-based data set is significantly longer (owing to U-series decay, the ^{230}Th method is restricted to sediment younger than ~500 kyr). Although between-parameter correlations resulting from the techniques are different, the Fe–opal relationship is statistically stronger than that between Fe and any other biogenic component regardless of the technique used to calculate sedimentation rate. As the opal data are low resolution (10 kyr) and intermittently spaced through time we cannot carry

---

[1]Department of Earth Sciences, Boston University, Boston, Massachusetts 02215, USA, [2]Harbor Branch Oceanographic Institute, Associate Provost for Marine and Environmental Initiatives, Florida Atlantic University, 5600 US 1 North, Fort Pierce, Florida 34946, USA, [3]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882, USA. *e-mail: rickm@bu.edu.

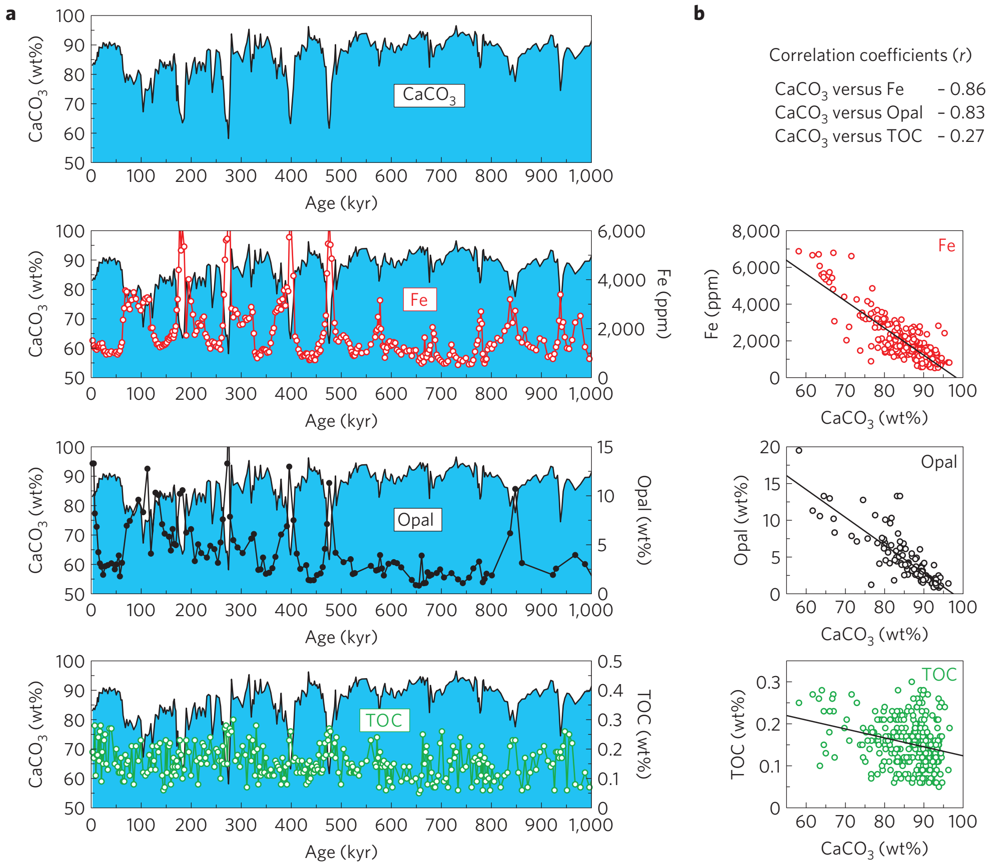

Figure 1 | Concentrations of the biogenic components and Fe in core PC72. **a**, Time series of CaCO3 (wt%), Fe (ppm), biogenic opal (wt%) and TOC (wt%), plotted versus age (in kyr). **b**, Correlations between CaCO3and the components shown in **a**, with (*r*) as shown. All $p < 0.001$.

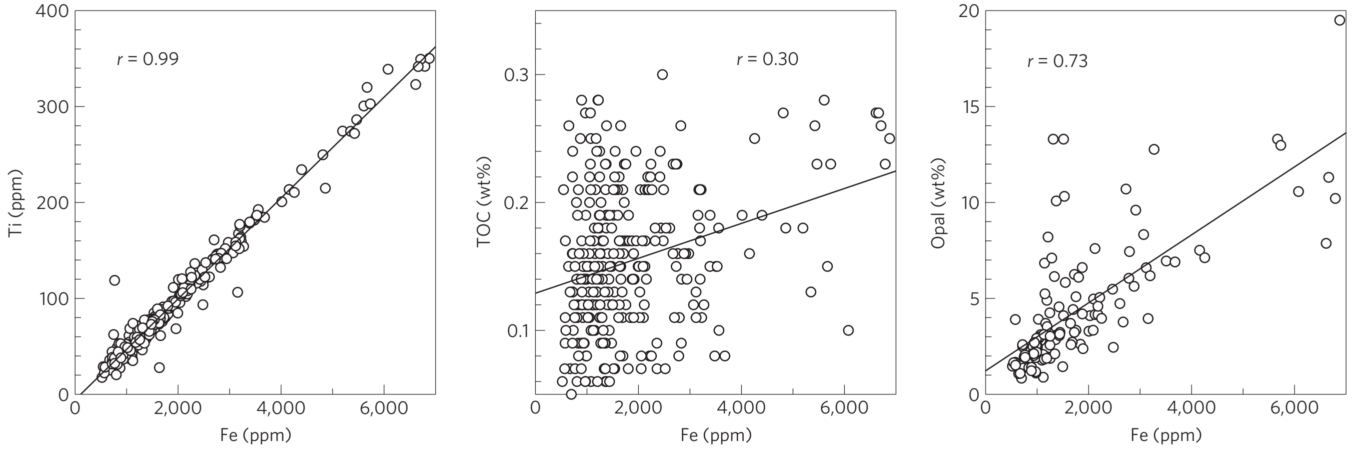

Figure 2 | Concentrations of Fe versus biogenic components and Ti in core PC72. Fe concentration (ppm) versus concentrations of Ti (ppm), TOC (wt%) and opal (wt%), with (*r*) as shown. All $p < 0.001$. See Fig. 1b for relationship between CaCO3 and Fe.

out time-series analyses with it, but the correlations are clear both visually and statistically (*r*-values).

Considering the entire 1-Myr record (Fig. 3), the δ^{18}O-based accumulations of Fe and opal are strongly correlated ($r = 0.61, p < 0.001$). Correlations between Fe accumulation and that of TOC and CaCO$_3$ are successively weaker. There seem to be age-related differences in these relationships. For example, in addition to the strong Fe–opal relationship in sediment older than ∼550 kyr, the correlation between the accumulation of Fe, CaCO$_3$ and TOC through this interval is stronger than between these parameters in the younger record. The Fe–opal link also breaks down younger than ∼180 kyr. This includes the Last Glacial Maximum, which may behave differently from other glacials with regard to palaeo-export production[9]. Nonetheless, through the great majority of the 1-Myr record, even subtle increases and decreases in Fe accumulation are closely matched by changes in opal accumulation, and the correlation between Fe and opal accumulation through the lengthy 180–1-Myr interval is even stronger ($r = 0.83, p < 0.001$) than the overall correlation. The correlation between Fe and opal is also strongest when using ^{230}Th-based accumulations through the shorter record. Thus, Fe is most closely related to biogenic

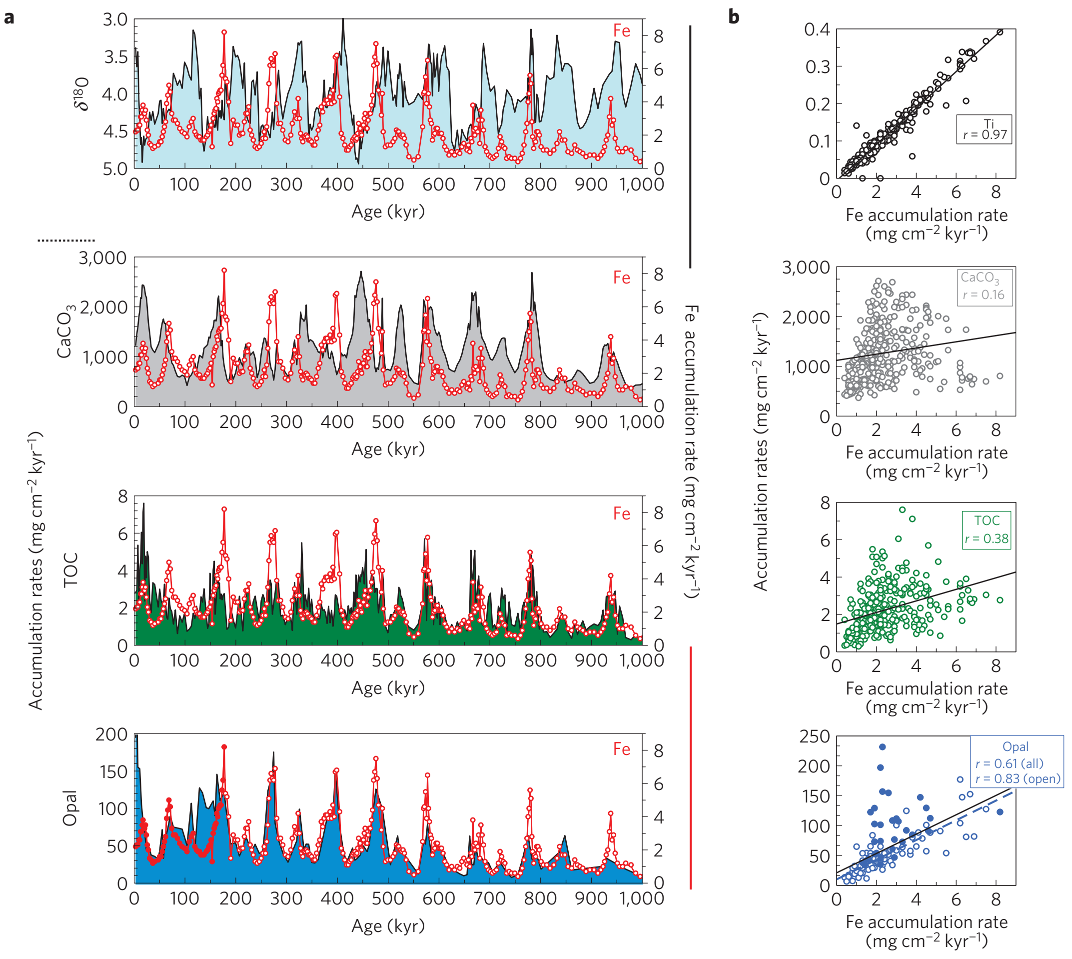

Figure 3 | Accumulation rates of the biogenic components and Fe in core PC72. a, $\delta^{18}O$ and accumulation rates of $CaCO_3$ (grey), TOC (green), opal (blue) and Fe (red), plotted versus age (kyr). Filled symbols in the bottom panel identify samples younger than ~180 kyr, where the Fe–opal relationship is weaker. **b**, Correlations between Fe accumulation rate and parameters shown in **a**, as well as between Fe accumulation and Ti accumulation. All $p < 0.001$. Filled symbols in the bottom panel identify samples younger than ~180 kyr, where the Fe–opal relationship is weaker. Correlation coefficient of $r = 0.61$ (solid line) is for the entire data set, the $r = 0.83$ applies to data older than ~180 kyr (dashed line).

opal whether as measured concentration (Fig. 2) or as calculated accumulation rate (Fig. 3).

The accumulation of elemental Ba, long used as a proxy of total export production (along with its main carrying phase, barite ($BaSO_4$); refs 9, 11), is well correlated with the accumulation both of Fe and of opal (Fig. 4), indicating strong links between Fe input, opal export and total export. Fe accumulation is also most strongly correlated with Ba and opal accumulation using the ^{230}Th-based approach.

Thus, Fe concentration and accumulation rates are most closely related to opal concentration and accumulation rates. Furthermore, Fe and opal accumulation are closely related to Ba accumulation and thus, by proxy, both to total palaeo-export. Even though it has long been established that surface productivity is decoupled from export production[25], studies of opal in sediment traps[26] and on the sea floor[17] confirm that sedimentary opal is essentially controlled by its flux to the sea floor[27]. Indeed, in PC72 opal accumulation seems to be regulated by variable production by diatoms in the overlying water[14]. Thus, the accumulation of opal and Fe co-vary, are independent of the carbonate flux, and their relationship is not a result of dilution or mathematical forcing by the sedimentation rate. There is a first-order link between Fe input, export production and opal burial.

How do these results based on sediments compare with modern water-column studies of Fe input and diatom response? In general, areas of present-day natural Fe enrichment have higher productivity and higher export than adjacent unfertilized areas[2]. Virtually all induced Fe-enrichment experiments resulted in increased primary productivity. Those with substantial silicate availability in surface waters indicate stronger export as well, dominantly by siliceous phytoplankton. Fe addition requires pre-existing silicate and new production is dominated by diatoms[16,28]. The largest increase of silicate uptake in modern equatorial Pacific waters occurs when Fe is added, either naturally or artificially, leading to the concept of co-regulation with varying effects on diatom growth rate and cellular silicification[3,4]. Thus, there clearly are relationships between Fe and diatom opal in the modern, and we further discuss below several representative studies that demonstrate coherence between modern processes and the palaeo-oceanographic record.

Diatom and non-diatom chlorophyll distributions were studied during the IronEx fertilization experiments in the equatorial Pacific[16]. During higher growth periods, the large, order-of-magnitude increase in diatoms outpaced the non-diatom assemblages, which showed only a modest biomass increase[16]. Furthermore, in a microcosm nutrient-amendment experiment using mixed-layer water gathered at the same location as core PC72, Marchetti *et al.*[4] documented phytoplankton ecosystem responses under various conditions of Fe and Si availability. Fe- and Si-replete conditions preferentially led to large, heavily

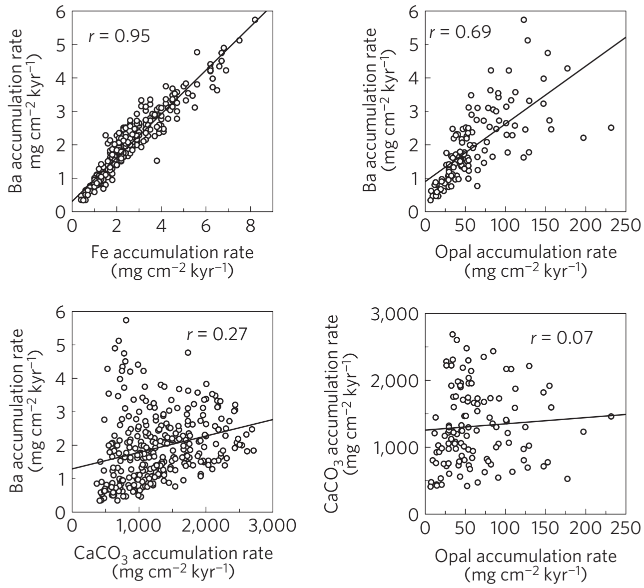

Figure 4 | Comparisons of the δ^{18}O-based accumulation rates of Ba, Fe, opal and CaCO$_3$. Values of (r) as shown. All $p < 0.001$, except for the lower right, where $p = 0.449$, confirming the poor correlation. All rates in mg cm^{-2} kyr^{-1}.

silicified diatoms that contained less organic matter than diatoms in Fe-replete/Si-limited conditions. Such a system was postulated to produce a high ratio of biogenic silica to particulate organic carbon that could be exported into deep water[4]. Diatom cell division may become decoupled from organic-matter accumulation depending on whether the environment is Fe-limited alone or also limited by silicate and nitrate. These mesocosm observations[4] are further supported by more recent studies of nine microcosm experiments in the equatorial Pacific[3]. Collectively, these representative studies[3,4,16] demonstrate modern ecological responses in the uppermost water column that are well suited for preservation in the sediment, consistent with previous observations linking water-column processes to seafloor distributions of the biogenic components, and with the records of Fe and opal in PC72.

The Crozet Islands of the open Southern Ocean provide natural Fe input downstream of an otherwise HNLC regime[29]. This natural Fe fertilization results in a two- to three-fold increase in carbon flux out of the surface[29]. These increases in flux were observed in deep sediment traps ~3,000 m below the ocean surface, and organic carbon delivery to the sediment was approximately twice as great inside the Fe-fertilized region as outside. That a response was recorded in the sediments indicates that our conclusions, based in the equatorial Pacific, may also be applicable to other HNLC regions.

Glacial cycles in PC72 are characterized by higher inferred dust input when the ^{230}Th accumulation method is used[12]. If this method of calculating rates is correct, our results would further link the Fe content of dust to higher opal export during glacials, as noted in the discussion of Fe and silica co-limitation[3]. Time-series analysis of the Fe flux and δ^{18}O record in PC72 over the past 1 Myr (Fig. 3) indicates that Fe input leads ice volume by ~25 kyr in the 100-kyr period[8]. However, relating opal flux specifically to climate remains complex[14]. Through the shorter, ^{230}Th-based record it seems that although several glacial terminations coincide with maxima in opal accumulation, there are important inconsistencies[14]. Some of these disparities occur during similar time intervals that show the greatest divergence between the δ^{18}O and the ^{230}Th stratigraphies. Regardless, the very close relationship between Fe and opal accumulation in sediment older than ~180 kyr indicates that Fe may have been a more unitary driver of opal productivity before then, and that other factors (for example, ocean circulation, other nutrients) may have provided additional forcings since 180 kyr ago. Such potential processes[3,14] deserve focus by future studies.

The 1-Myr record documents that variation in natural Fe flux (regardless of Fe source[6,7]) is related to changes in opal burial. Increases and decreases in Fe input are most strongly correlated with increases and decreases in opal accumulation. We propose that Fe input during most of the past ~1 Myr controlled the long-term variability in surface diatom production and the subsequent flux of opal to the sea floor. Although much remains unclear about the relationships between Fe input and ecosystem response in both the modern system and the palaeo-oceanographic past, and the relationship to climate through different time periods, our results indicate a first-order link between Fe input and opal production, transfer to the sea floor and removal from the biogeochemical system by sedimentation and burial.

Received 13 January 2011; accepted 14 February 2012; published online 11 March 2012

References

1. Martin, J. H. Glacial–interglacial CO$_2$ change: The iron hypothesis. *Paleoceanography* **5,** 1–13 (1990).
2. Boyd, P. W. *et al.* Mesoscale iron enrichment experiments 1993–2005: Synthesis and future directions. *Science* **315,** 612–617 (2007).
3. Brzezinski, M. A. *et al.* Co-limitation of diatoms by iron and silicic acid in the equatorial Pacific. *Deep-Sea Res.* **58,** 493–511 (2011).
4. Marchetti, A. *et al.* Iron and silicic acid effects on phytoplankton productivity, diversity, and chemical composition in the central equatorial Pacific Ocean. *Limnol. Oceanogr.* **55,** 11–29 (2010).
5. de Baar, H. J. W. *et al.* Synthesis of iron fertilization experiments: From the iron age in the age of enlightenment. *J. Geophys. Res.* **110,** C09S16 (2005).
6. Ziegler, C. L., Murray, R. W., Plank, T. & Hemming, S. R. Sources of Fe to the equatorial Pacific Ocean from the Holocene to Miocene. *Earth Planet. Sci. Lett.* **270,** 258–270 (2008).
7. Lyle, M. Bloom without fertilizer. *Nature Geosci.* **1,** 576–578 (2008).
8. Murray, R. W., Leinen, M., Murray, D. W., Mix, A. C. & Knowlton, C. W. Terrigenous Fe input and biogenic sedimentation in the glacial and interglacial equatorial Pacific Ocean. *Glob. Biogeochem. Cycles* **9,** 667–684 (1995).
9. Murray, R. W., Knowlton, C., Leinen, M., Mix, A. C. & Polsky, C. H. Export production and carbonate dissolution in the central equatorial Pacific Ocean over the past 1 Ma. *Paleoceanography* **15,** 570–592 (2000).
10. Murray, J. W., Barber, R. T., Roman, M. R., Bacon, M. P. & Feely, R. A. Physical and biological controls on carbon cycling in the equatorial Pacific. *Science* **266,** 58–65 (1994).
11. Paytan, A., Kastner, M. & Chavez, F. P. Glacial to interglacial fluctuations in productivity in the equatorial Pacific as indicated by marine barite. *Science* **74,** 1355–1357 (1996).
12. Winckler, G., Anderson, R. F., Fleisher, M. Q., McGee, D. & Mahowald, N. Covariant glacial–interglacial dust fluxes in the equatorial Pacific and Antarctica. *Science* **320,** 93–96 (2008).
13. Anderson, R. F., Fleisher, M. Q., Lao, Y. & Winckler, G. Modern CaCO$_3$ preservation in equatorial Pacific sediments in the context of late-Pleistocene glacial cycles. *Mar. Chem.* **111,** 30–46 (2008).
14. Hayes, C.T., Anderson, R.F. & Fleisher, M.Q. Opal accumulation rates in the equatorial Pacific and mechanisms of deglaciation. *Paleoceanography* **26,** PA1207 (2011).
15. Farrell, J. W. & Prell, W. L. Climatic change and CaCO$_3$ preservation: An 800,000 year bathymetric reconstruction from the central equatorial Pacific Ocean. *Paleoceanography* **4,** 447–466 (1989).
16. Barber, R. T. & Hiscock, M. R. A rising tide lifts all phytoplankton: Growth response of other phytoplankton taxa in diatom-dominated blooms. *Glob. Biogeochem. Cycles* **20,** GB4S03 (2006).
17. Murray, R. W. & Leinen, M. Chemical transport to the seafloor of the equatorial Pacific across a latitudinal transect at 135W; Tracking sedimentary major, trace, and rare earth element fluxes at the Equator and the Intertropical Convergence Zone. *Geochim. Cosmochim. Acta* **57,** 4141–4163 (1993).
18. Lyle, M. *et al.* The record of late Pleistocene biogenic sedimentation in the eastern tropical Pacific Ocean. *Paleoceanography* **3,** 39–59 (1988).
19. Marcantonio, F. *et al.* Sediment focusing in the central equatorial Pacific ocean. *Paleoceanography* **16,** 260–267 (2001).
20. Thomas, E., Turekian, K. K. & Wei, K-Y. Productivity control of fine particle transport to equatorial Pacific sediment. *Glob. Biogeochem. Cycles* **14,** 945–955 (2000).

21. Paytan, A., Lyle, M., Mix, A. & Chase, Z. Climatically driven changes in oceanic processes throughout the equatorial Pacific. *Paleoceanography* **19,** PA4017 (2004).
22. Lyle, M. *et al.* Do geochemical estimates of sediment focusing pass the sediment test in the equatorial Pacific? *Paleoceanography* **20,** PA1005 (2005).
23. Siddall, M. *et al.* Modeling the particle flux effect on distribution of ^{230}Th in the equatorial Pacific. *Paleoceanography* **23,** PA2208 (2008).
24. Broecker, W. Excess sediment ^{230}Th: Transport along the sea floor or enhanced water column scavenging? *Glob. Biogeochem. Cycles* **22,** GB1006 (2008).
25. Eppley, R. W. & Peterson, B. J. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* **282,** 677–680 (1979).
26. Honjo, S., Dymond, J., Collier, R. & Manganini, S. J. Export production of particles to the interior of the equatorial Pacific Ocean during the 1992 EqPac experiment. *Deep-Sea Res.* **42,** 831–870 (1995).
27. Archer, D., Lyle, M., Rodgers, K. & Froelich, P. What controls opal preservation in tropical deep-sea sediments? *Paleoceanography* **8,** 7–21 (1993).
28. Dugdale, R. *et al.* The regulation of equatorial Pacific new production and $p\mathrm{CO}_2$ by silicate-limited diatoms. *Deep-Sea Res.* **58,** 477–492 (2011).
29. Pollard, R. T. *et al.* Southern Ocean deep-water carbon export enhanced by natural iron fertilization. *Nature* **457,** 577–581 (2009).

Acknowledgements

We thank R. F. Anderson (Lamont–Doherty Earth Observatory) for many discussions over the past years. Research initially supported by US NSF grant OCE9301097 to R.W.M. and M.L.

Author contributions

R.W.M. carried out the original Fe analyses[8], led and contributed to the writing of the manuscript and made essential and substantive contributions to the intellectual discussions. M.L. made essential and substantive contributions to the writing of the manuscript and the associated intellectual discussions, and supervised the master's thesis research of C.W.K. C.W.K. carried out the original biogenic opal, $CaCO_3$ and TOC analyses, and made essential and substantive contributions to the intellectual content of the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.W.M.