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GLACIAL-INTERGLACIAL CO₂ CHANGE:
THE IRON HYPOTHESIS

John H. Martin

Moss Landing Marine Laboratories
Moss Landing, California

Abstract. Several explanations for the 200 to 280 ppm glacial/interglacial change in atmospheric CO₂ concentrations deal with variations in southern ocean phytoplankton productivity and the related use or nonuse of major plant nutrients. An hypothesis is presented herein in which arguments are made that new productivity in today's southern ocean (7.4×10^{13} g yr⁻¹) is limited by iron deficiency, and hence the phytoplankton are unable to take advantage of the excess surface nitrate/phosphate that, if used, could result in total southern ocean new production of $2-3 \times 10^{15}$ g C yr⁻¹. As a consequence of Fe-limited new productivity, Holocene interglacial CO₂ levels (preindustrial) are as high as they were during the last interglacial (≈ 280 ppm). In contrast, atmospheric dust Fe supplies were 50 times higher during the last glacial maximum (LGM). Because of this Fe enrichment, phytoplankton growth may have been greatly enhanced, larger amounts of upwelled nutrients may have been used, and the resulting stimulation of new productivity may have contributed to the LGM drawdown of atmospheric CO₂ to levels of less than

200 ppm. Background information and arguments in support of this hypothesis are presented.

INTRODUCTION

One of the great advances of the 1980s was the development of the capability to measure the CO₂ content of ancient air trapped in ice [Berner et al., 1980; Delmas et al., 1980; Neftel et al., 1982; Barnola et al., 1987]. As a result, we now know that global atmospheric CO₂ levels were highest (≈ 280 ppm) during the present (preindustrial) and last interglacial periods and lowest during the glacials (e.g., ≈ 200 ppm during the last glacial maximum 18,000 years B.P. [Barnola et al., 1987]). This change in CO₂ concentration from 200 to 280 ppm represents about 170 Gt (gigatons) (billion tons) of C for the Earth's atmosphere. What factor or factors were responsible for these changes?

There is general agreement that oceanic processes were primarily involved, since the oceanic reservoir of CO₂ is about 60 times greater than that for the atmosphere [e.g., Berger and Keir, 1984; Duplessy, 1986]. Several ocean/atmosphere models have been developed. For example, Broecker [1981, 1982a, b] has observed that surface ocean CO₂ and atmospheric CO₂ amounts are lower than expected in comparison to alkalinity and oceanic CO₂ content. This disequilibrium is caused by

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the photosynthetic uptake of CO₂ and removal to the deep ocean when the remains of the phytoplankton sink away from the surface. This mechanism of CO₂ removal is referred to as the "biological pump." When it is functioning efficiently, atmospheric CO₂ levels are low, and vice versa.

Berger and Keir [1984] have summarized several models offered in explanation of CO₂ variation. These involve either phosphate extraction, denitrification, coral reef buildup, and/or changes in ratios of C:P and/or the organic/inorganic C ratio. Another group of models deals with changes in high-latitude circulation and/or productivity [Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984; Siegenthaler and Wenk, 1984; Toggweiler and Sarmiento, 1985; Keir, 1988]. Broecker and Peng [1990] recently presented an hypothesis which calls for CO₂ change in response to variations in polar surface water alkalinity.

In general, there appears to be agreement that changes in southern ocean phytoplankton productivity could very well have resulted in the observed rapid glacial-interglacial changes in atmospheric CO₂ content; however, why productivity rates changed, if they did, is unknown. For example, Keir [1988] poses the question of how a factor of 2-3 increase in Antarctic production could have occurred. Toggweiler and Sarmiento [1985] also wonder how high-latitude productivity could have changed and note that it is hard to imagine how a 500% increase in high-latitude glacial-period production could result from a 10-15% increase in insolation alone.

The iron hypothesis deals specifically with this issue. Arguments are presented herein that productivity in today's southern ocean is limited by iron deficiency, and hence the phytoplankton are unable to take advantage of the excess surface nitrate/phosphate (Table 1), the use of which could result in total southern ocean new production as high as 2-3 Gt C yr⁻¹. As a consequence of limited new productivity, Holocene interglacial CO₂ levels (preindustrial) are as high as they were during the last interglacial (≈ 280 ppm).

In contrast, atmospheric dust Fe supplies were 50 times higher during the last glacial maximum [De Angelis et al., 1987]. As a result of this Fe enrichment, phytoplankton growth may have been greatly enhanced, larger amounts of upwelled nutrients may have been used up, and this stimulation of new productivity may have contributed to the drawdown of atmospheric

CO₂ concentrations to less than 200 ppm during glacial periods. In the sections that follow, background information and arguments in support of this hypothesis are presented.

IRON BACKGROUND INFORMATION

Iron is essential for all life on Earth and is especially important in oceanic plant nutrition because chlorophyll cannot be synthesized, nor can nitrate be reduced, nor atmospheric N fixed, without it [e.g., Rueter and Ades, 1987; Glover, 1977]. However, unlike major building block elements such as C, N, and P that have Redfield ratios of 6.6 C:N and 106 C:P, very small amounts of Fe are needed; that is, the molar ratios of C to Fe are of the order of 10,000 (Fe replete [Morel and Hudson, 1985]) to 100,000:1.0 (Fe deficient [Anderson and Morel, 1982]). In view of these small amounts, one would think that plant requirements would be easily met, especially since iron is the fourth most abundant element in the Earth's crust (5.63% [Taylor, 1964]). However, Fe is very insoluble in oxygenated seawater, since it is rapidly oxidized from the soluble Fe(II) to the highly insoluble Fe(III) state [e.g., Sung and Morgan, 1980].

In spite of the fact that the physiological importance of Fe in the ocean has been recognized at least since the 1920s [e.g., Hart, 1934], attempts to measure the concentration of this element in the water column have been frustrated by the horrendous contamination problems associated with collection and analytical procedures. Nevertheless, we are beginning to learn just how low open-ocean dissolved Fe levels really are (maximum = < 1 nmol kg⁻¹ [Martin and Gordon, 1988; Martin et al., 1989; Landing and Bruland, 1987]). Furthermore, Fe depth profiles are similar to those for other plant nutrients, that is, depleted at the surface and enriched at depth (Figure 1).

It also appears that the amounts of Fe are so low, at least in the Pacific, that the Fe mixed up into the euphotic zone via advective/diffusive processes would be exhausted long before the major nutrients that were mixed up along with it; for example, with 25 μmol of NO₃ carried up into the photic zone, the phytoplankton could produce 160 to 170 μmol of C, assuming the Redfield ratio of 6.6 C:1 N. The Fe transported along with the 25 μmol NO₃ (0.00028 μmol Fe; based on nmol Fe kg⁻¹ =

TABLE 1. Examples of Southern Ocean High-Surface Nutrient Concentrations From the Pacific, Atlantic, and Indian Ocean Sectors Poleward and Equatorward of 56°S

Station	Latitude °S	Longitude °W/E	Depth m	Temperature °C	Salinity	NO ₃ μmol kg ⁻¹	PO ₄
<u>South of 56°S</u>							
Pacific 285	61.48	169.97E	9	2.24	33.963	25.9	1.65
Atlantic 78	61.05	62.97W	6	1.35	33.833	25.1	1.69
Indian 430	59.98	60.97E	8	1.80	33.841	27.4	1.87
<u>North of 56°S</u>							
Pacific 322	43.0	129.56W	2	12.80	34.202	7.3	0.67
Atlantic 64	39.05	48.33W	12	14.11	34.374	3.7	0.49
92	46.11	14.36E	2	7.38	33.824	17.4	1.20
93	41.46	18.27E	11	13.67	34.853	4.2	0.47
Indian 429	47.40	57.51E	4	6.49	33.726	20.2	1.48
434	45.38	107.15E	4	11.76	34.641	8.6	0.76
435	39.57	109.58E	5	15.49	34.840	3.6	0.44

Data from GEOSECS (Pacific, Broecker et al. [1982]; Atlantic, Bainbridge [1981]; Indian, Weiss et al. [1983]).

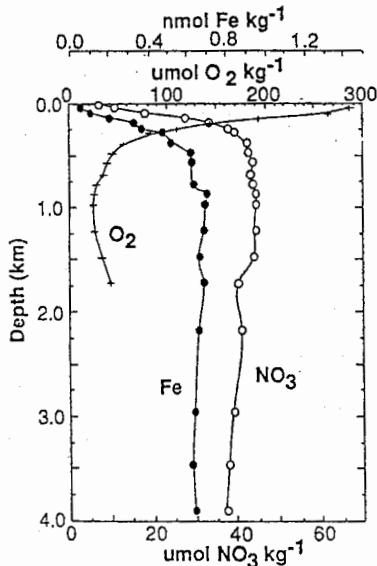


Fig. 1. Vertical distribution of dissolved iron, oxygen, and nitrate at Gulf of Alaska Ocean Station PAPA (50°N; 145°W). Figure from Martin et al. [1989].

0.0137 [μmol NO₃ kg⁻¹] - 0.0619 [from Martin et al., 1989]) would support at most 30 μmol C of new growth (Figure 2). This means that about 80% of the NO₃ would be left unused following the cessation of new growth because of Fe depletion. This creates a classic marine example of Liebig's law of the minimum: growth stops

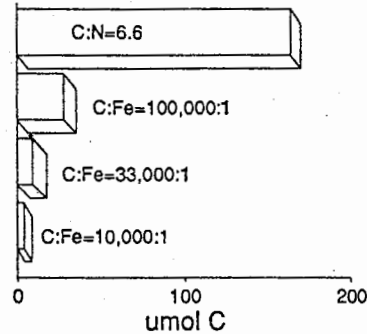


Fig. 2. Amounts of phytoplankton carbon that could be produced with 25 μmol NO₃ and the dissolved Fe that would mix up into the euphotic zone with the NO₃; that is, 0.00028 μmol Fe (from NO₃:Fe relationship of Martin et al. [1989]), assuming Redfield 6.6 C:N ratio and various C:Fe ratios (100,000:1 [Anderson and Morel, 1982], 33,000:1 [Martin et al., 1989], and 10,000:1 [Morel and Hudson, 1985]).

when the minimum requirements for an essential element are not met [Liebig, 1847]. Basically, then, offshore Pacific water is infertile and capable of supporting very little plant growth without supplemental Fe from sources other than conventional advective-diffusive input processes.

Meeting biological Fe requirements is relatively easy in neritic waters, where resuspended bottom sediments and associated Fe-rich oxides, colloids, etc., occur

together with elevated concentrations of dissolved Fe (e.g., see Figures 6 and 7 of Martin and Gordon [1988]). Hence excess NO₃ is never observed in coastal upwelling environments such as those off the west coasts of Africa and North and South America.

Although fulfilling the phytoplankton's offshore demand for this element is more of a problem, it appears that adequate Fe amounts are supplied to the oligotrophic gyres via long-range transport and fallout of Fe-rich atmospheric dust originally derived from terrestrial arid regions. Surprisingly, 95% of the North Pacific gyre phytoplankton's Fe requirement appears to be met via this mechanism [Duce, 1986; Martin and Gordon, 1988], an observation that is very important in the development of this hypothesis. Apparently, then, the problem of excess major plant nutrients occurs only in oceanic regions where the amounts of Fe falling down upon the surface are not sufficient to meet the demand created by the increased major nutrient input resulting from enhanced offshore upwelling (e.g., the Gulf of Alaska, the equatorial Pacific, and the southern ocean; see Figure 13 of Martin et al. [1989]).

THE POTENTIAL

The possibility of iron limitation is especially important in these environments because of the potential productivity the upwelling of major nutrients represents. For example, Chavez and Barber [1987] describe an area in the eastern equatorial Pacific of $1.1 \times 10^{13} \text{ m}^2$ with an upwelling rate of 0.39 m d^{-1} . Using their low NO₃ estimate of 10 mmol m^{-3} , the potential new (not total) productivity would be $\approx 26 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ($0.39 \text{ m d}^{-1} \times 10 \text{ mmol N m}^{-3} \times 6.6 \text{ C:N}$) or $9.5 \text{ mol C m}^{-2} \text{ yr}^{-1}$, or about 1.2 Gt C yr^{-1} for the entire area. This is a conservative estimate, since GEOSECS data [Broecker et al., 1982] show the equatorial high-nutrient region extending 5°-6° farther south than the 5°S bound used by Chavez and Barber [1987]. Evidence that this potential is not being realized is provided by the recent studies of Murray et al. [1989]. Estimates of new productivity via four different methods at two eastern equatorial Pacific stations with excess nutrients (surface NO₃ = 8.1, 10.8 $\mu\text{mol kg}^{-1}$) were in the range of 3-10 $\text{mmol C m}^{-2} \text{ d}^{-1}$; that is, 12-38% of the potential productivity based on the above

estimated ($26 \text{ mmol C m}^{-2} \text{ d}^{-1}$) upwelling of NO₃.

It is also apparent that the present biological working strength of the southern or Antarctic Ocean is very low, at least judging by the excess of unused major nutrients in seasonally well-lit surface waters (Table 1). Here, the potential maximum productivity is even greater than that for the equatorial Pacific; that is, the southern ocean upwelling rate is 60 Sv ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$) during the six summer months in the area from 56°S to the Antarctic continent ($2 \times 10^{13} \text{ m}^2$ [Gordon, 1971]). This represents an upwelling of $\approx 0.25 \text{ m d}^{-1}$. This rate times the NO₃ concentration times the Redfield ratio of 6.6 C:N results in a potential new productivity of $\approx 40 \text{ mmol C m}^{-2} \text{ d}^{-1}$ or an annual rate of $7.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (assuming production during 6 summer months only), or a total of 1.8 Gt C yr^{-1} for this area during the austral summer.

In addition, there is also excess NO₃ equatorward of 56°S to about 45°S (Table 1). This represents an additional high-nutrient area, between 45° and 56°S, of about $2.8 \times 10^{13} \text{ m}^2$. If these waters have an average of $15 \text{ mmol NO}_3 \text{ m}^{-3}$ and if a bloom removed all of this excess NO₃ to a depth of 30 m just once a year, the result would be an additional gigaton of new productivity C for this region. In summary, the equatorial Pacific and southern oceans, which represent only 18% of the global ocean area, have a potential new productivity of the order of 4 Gt C yr^{-1} . This equals 50-100% of the new productivity currently estimated for the entire ocean (e.g., Eppley and Peterson [1979] give 3.4-4.7, and Martin et al. [1987] give 7.4 Gt C yr^{-1} ; also see Table 7 of Sundquist [1985]).

SOUTHERN OCEAN PRODUCTIVITY IN FE-RICH AND FE-POOR AREAS

There are no reliable water column Fe measurements for the Antarctic Ocean and hence no direct evidence that Fe deficiency is limiting phytoplankton growth. Nevertheless, there is abundant indirect evidence supporting an Fe limitation hypothesis. Suspicions of Fe deficiency are not new. For example, in discussing the extensive results of the 1925-27 Discovery expedition, Hardy [1967, p. 489] talks about Gran's observation that the greater abundance of phytoplankton " . . . often observed in proximity to land--in

what are technically known as neritic conditions--may be because of the presence of certain beneficial substances derived from land drainage." In reporting phytoplankton abundance, Hart [1934] noted that the neritic influence was very strong around South Georgia (52°-55°S; 33°-41°W) and that here phytoplankton concentrations were ten times higher than in other Antarctic oceanic regions. Hart [1934, p. 186] goes on to say that "Among the . . . chemical constituents of sea water . . . possibly limiting phytoplankton production, iron may be mentioned. . . . it may help to explain the observed richness of the neritic plankton . . . the land being regarded as a source of iron" Hart [1942, p. 339] says that "We are left with the hypothesis that extremely small amounts of organic compounds, iron, manganese . . . derived from the land, exert a strongly favourable influence on phytoplankton production. . . ." and [p. 330] "Only where these (neritic) influences are felt do the Antarctic seas retain their claim to be amongst the richest in the world."

Resuspended sediments with adsorbed oxides, etc., should provide an abundant source of Fe in the shallow waters around South Georgia. Resuspended Fe-rich sediments from the Antarctic peninsula may also be transported downstream to the Scotia Sea via the easterly flowing Antarctic Circumpolar Current [Whitworth, 1988]. Evidence of resuspended lithogenic material is provided by the Bransfield Strait sediment trap studies of Wefer et al. [1988]. They reported lithogenic fluxes of 471 and 777 mg m⁻² d⁻¹ for depths of 494 and 1588 m, respectively, during the month of January. In contrast, the total maximum particle flux in the Weddell Sea under ice-free conditions was ≈ 10 mg m⁻² d⁻¹ for a trap set at a depth of 863 m during the month of March [Fischer et al., 1988]. Fischer et al. [1988] also show that the annual lithogenic flux in the semienclosed Bransfield Strait (53.5 g m⁻² yr⁻¹) is more than 10,000 times greater than that in the open Weddell Sea (0.004 g m⁻² yr⁻¹).

In a recent discussion, El-Sayed [1988] notes that diatom blooms are rather common near the coastal regions and in the vicinity of islands. He goes on to say that productivity rates as high as 3.2 and 3.6 g C m⁻² d⁻¹ have been reported in the Gerlache Strait and near Deception Island, respectively, during the austral summer.

Such high rates ". . . have no doubt perpetuated the belief in the proverbial richness of the Antarctic waters" [El-Sayed, 1988, p. 491]. However, El-Sayed estimates the mean productivity rate for the open southern ocean at only 0.1 g C m⁻² d⁻¹, a value in agreement with the 0.1 g C m⁻² d⁻¹ rate of M. Tilzer and B. von Bodungen quoted by Wefer et al. [1982]. El-Sayed and Taguchi [1981] also report mean primary productivity rates of 0.104 g C m⁻² d⁻¹ for the deep northern central Weddell Sea area in comparison to the 0.41 g C m⁻² d⁻¹ rate measured in the shallow southern Weddell Sea shelf region.

Direct evidence that Fe is abundant in the highly productive Gerlache Strait was obtained in a particle trap study in cooperation with D. Karl of the University of Hawaii. A refractory Fe flux of 650 μmol Fe m⁻² d⁻¹ was measured at a depth of 100 m. This was an order of magnitude higher than the Fe flux measured in the Bransfield Strait and 2 orders of magnitude higher than a flux measured in the Drake Passage (Table 2). The latter serves as an example of the Fe-poor conditions in offshore southern ocean waters. Although it is located less than 50 km from the Antarctic peninsula, the Fe flux measured here is the same as that 1600 km offshore in the northeast Pacific (33°N; 139°W; 2.0 μmol Fe m⁻² d⁻¹ [Martin and Gordon, 1988]). In summary, southern ocean productivity rates are high in neritic areas, where it is logical to assume that resuspended sediment-associated dissolved and particulate Fe is abundant, and are low in deep, offshore waters, where Fe supplies are severely limited.

IRON IN ICE

In addition to high rates of primary productivity in neritic areas, there are numerous reports of enhanced phytoplankton productivity along retreating ice edges [e.g., Hart, 1934, 1942; Marra and Boardman, 1984; Smith and Nelson, 1985a, b]. For example, Hart [1942, p. 339] states "One important feature of the work . . . is the great importance of the pack-ice in maintaining the flora within the Antarctic zone and in giving rise to . . . pseudo-coastal conditions at vast distances from land" The greater productivity is related to the increased stability of the water column; that is, as the ice melts, the warmer, less salty water forms a stable layer in which phy-

TABLE 2. Refractory (RE) and Leachable (LE; 25% Acetic Acid) Fe Fluxes Measured in Inshore (Gerlache Strait), Nearshore (Bransfield Strait), and Semioffshore (Drake Passage) Waters Using VERTEX-Type Particle Traps Set at 100 m for 24 Hours in January 1987

Location	Fluxes, m ⁻² d ⁻¹				Ratios ^a C:Fe	Ef Fe/Al
	Organic C mmol	RE Fe μmol	LE Fe μmol			
Gerlache Strait (64°17'S;61°17'W)	31	650	4.0		450	0.61
Bransfield Strait (63°14'S;60°55'W)	21	65	0.16		3,200	0.91
Drake Passage (61°55'S;62°00'W)	8.1	2.4	0.046		28,000	0.85

Carbon data courtesy of David Karl, University of Hawaii. Enrichment factors (Ef) were calculated using crustal abundance data of Taylor [1964].

^a Fe = LE + 10% of RE.

toplankton can maintain themselves in the light and grow. The melting ice also facilitates growth by contributing a "seed" population of diatoms. Nevertheless, other factors are involved. Nelson et al. [1989] report phytoplankton biomass distributions with little correlation with the meltwater field. In considering various reasons for the lack of growth in stable, well-lit, major-nutrient-rich waters, they mention the possibility of Fe deficiency. The low chlorophyll levels they observed in relation to high carbon biomass also suggest "chlorosis," a condition resulting from Fe deficiency.

It has been suggested that atmospheric dust iron that accumulates over the winter is released with the summer ice meltback, and this may also stimulate growth [Martin et al., 1989; Martin and Gordon, 1988]. Although there are no Fe estimates for modern annual sea ice, it is assumed that there is about as much as that in present-day dome C snow (≈ 0.02 nmol Fe g⁻¹ [Petit et al., 1981]) or as much as that contained in Holocene ice from the Vostok ice cores; that is, about 0.03 nmol Fe g⁻¹ [De Angelis et al., 1987]. The amount of sea ice melting and freezing each year has been estimated by Munk [1966] at 2.3×10^{19} g. Assuming that each gram of ice has ≈ 0.03 total nmol of Fe and that 10% becomes available to the phytoplankton [see Duce, 1986], the annual release would be about 7×10^{16} nmol or 7×10^7 mol of Fe. Assuming a 33,000 C:1.0 Fe

ratio [Martin et al., 1989], the total new phytoplankton production from annual ice-meltback-released Fe would be 2.3×10^{12} mol C. Dividing by the winter-summer sea ice area estimate of Cooke and Hays [1982] (1.5×10^{13} m²) results in a new productivity rate of 150 mmol C m⁻² yr⁻¹.

This is a very low rate when expressed on an annual basis; however, it occurs over a period of a few days as the ice melts back. For example, if all of the productivity takes place in a week, the daily rate would be around 20 mmol C m⁻². In the oligotrophic north Pacific, estimated daily new primary productivities are of the order of 4 mmol m⁻² d⁻¹ [Martin et al., 1987]; this occurs over a whole year, for a total of 1.5 mol C m⁻² yr⁻¹ instead of the 0.13 mol C m⁻² yr⁻¹ estimated here.

CURRENT SOUTHERN OCEAN NEW PRODUCTIVITY

In addition to the new productivity resulting from ice meltback, Fe would also be provided via upwelling and summer dust fallout on open water. Based on the NO₃-Fe relationship of Martin et al. [1989], the amount of Fe supplied via upwelling would be 6.25 mmol NO₃ m⁻² d⁻¹ $\times 0.0137$ (NO₃) - $0.0619 = 0.024$ μmol Fe m⁻² d⁻¹. This would be enough Fe ($\times 33,000$) to produce 800 μmol C m⁻² d⁻¹, or 2% of the potential capacity based on the upwelling of NO₃ (see above). Although estimates for summer dust Fe input are not available, it

is assumed that the Fe input would be about the same as that estimated for ice meltback. Thus, if, indeed, the Antarctic is Fe limited, the total new productivity today may be as low as $1.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 3). This is about 4% of the estimated potential productivity based on NO₃ upwelling. Using the average total productivity rate of El-Sayed [1985] ($\approx 11 \text{ mmol C m}^{-2} \text{ d}^{-1}$) for the 120- to 150-day austral light regime or M. Tilzer and B. von Bodungen (as cited by Wefer et al. [1982]) ($\approx 8.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$), the ratio of new/total productivity (the f value) would be 0.14-0.19. These values are similar to those for the oligotrophic ocean [Eppley and Peterson, 1979].

PRODUCTIVITY DURING THE LAST GLACIAL MAXIMUM

There is evidence that paleoproductivity rates may have been higher during glacial periods than in previous and present interglacial stages, perhaps by a factor of three [Sarnthein et al., 1987]. With the onset of the present interglacial, Sarnthein et al. [1988] estimate, new productivity rates in low- and mid-latitude upwelling regions decreased by 2-4 Gt C yr⁻¹. Sarnthein et al. [1988] attribute these decreases in productivity to decreased meridional wind strength and the lowering of upwelling rates. Sarnthein et al. [1987, p. 311] also note that eastern Atlantic productivity began ". . . to decrease slightly prior to or simultaneously with global ice melting, synchronously with a drastic increase in atmospheric CO₂"

As noted above, the equatorial Pacific has excess nutrients that are not used up

by the resident phytoplankton. Pedersen et al. [1988] present evidence that eastern equatorial Pacific productivity rates were markedly higher during the LGM than at present. These higher rates may have resulted not only from intensified upwelling of major nutrients but also from greater availability of Fe. In addition to the wind strength studies of Sarnthein et al. [1987], Petit et al. [1981] also note that in general, glacial period tropical arid areas were 5 times greater, wind speeds 1.3-1.6 times higher, and Fe-rich atmospheric dust loads 10-20 times greater. Dramatic evidence of these increased winds and arid conditions is provided by the dune studies of Sarnthein [1978]. In comparison to present conditions and those during the climatic optimum (6000 years B.P.), active dune fields were plentiful in the southern as well as the northern hemisphere 18,000 years B.P. during the LGM. It is obvious that these climatic conditions also resulted in the transport of large amounts of dust down into the Antarctic. For example, the dust load in the Vostok ice core was 50 times higher during the LGM (Figure 3). If the Fe-limited new productivity estimates based on ice meltback and summer atmospheric dust input ($0.16 \text{ mol C m}^{-2} \text{ yr}^{-1}$; Table 2) are multiplied by this factor of 50, an estimated glacial southern ocean new productivity of $8 \text{ mol C m}^{-2} \text{ yr}^{-1}$ results. This value is about equal to the potential productivity based on the upwelling of nitrate ($7.2 \text{ mol m}^{-2} \text{ yr}^{-1}$; see above) and indicates that surface nutrients could have been used up instead of sinking away unused as preformed nutrients, as is the case in the present-day ocean.

TABLE 3. Summary of Estimated Fe-Limited New Productivity Rates in Southern Ocean

Process	Daily Rate $\text{mmol m}^{-2} \text{ d}^{-1}$	Annual Rate $\text{mol m}^{-2} \text{ yr}^{-1}$	Total Grams of C
Upwelling	0.78	0.14	3.4×10^{13}
Ice meltback	12.0 ^a	0.082	2.0×10^{13}
Summer atmospheric fallout	0.45	0.082	2.0×10^{13}
Total new production	1.6 ^b	0.30	7.4×10^{13}
Potential new production	40.0 ^c	7.2	1.7×10^{15}

^a For a few days while ice is melting back.

^b El-Sayed [1985] average total primary production = $11 \text{ mmol C m}^{-2} \text{ d}^{-1}$ for 120- to 150-day austral light regime; new/total = f = 0.15.

^c Six summer months only.

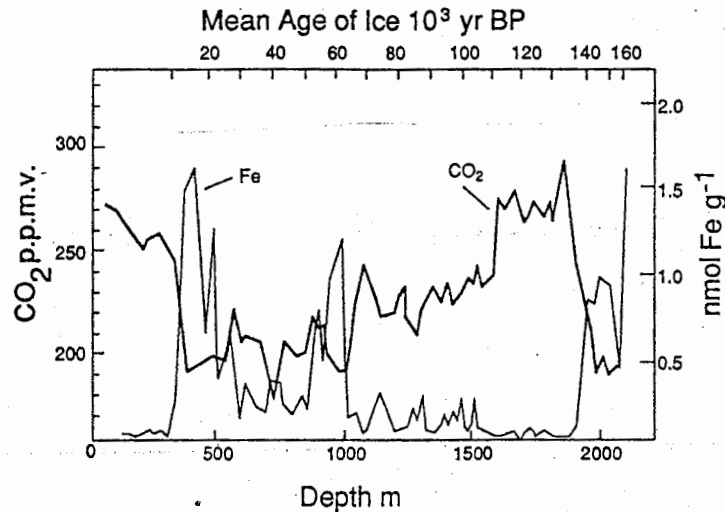


Fig. 3. Fe concentration as a function of real depth in Antarctic Vostok ice core, together with mean CO₂ concentrations in air trapped in ice, versus mean age of air. Original figure taken from De Angelis et al. [1987]. Their Al data were converted to Fe estimates using Taylor's [1964] crustal abundance values. Age data are from Lorius et al. [1985]; CO₂ concentrations are from Barnola et al. [1987]. Air age was used for the CO₂ plot because of the 2000- to 4000-year difference between ice and air ages [see Barnola et al., 1987].

Although the Vostok ice core clearly shows that Fe was readily available, were LGM southern ocean productivity rates really 50 times higher? Keir [1988] points out that there is little direct evidence of increased Antarctic productivity during the LGM other than the $\delta^{13}\text{C}$ findings of Curry et al. [1988]; that is, the isotopic records from two cores demonstrate that the glacial-interglacial change in $\delta^{13}\text{C}$ of the southern ocean is the largest observed, 0.8‰ . More significantly, the southern ocean cores have the lowest $\delta^{13}\text{C}$ observed in the glacial ocean: -0.46 . Curry et al. [1988, p. 328] also note that late Holocene $\delta^{13}\text{C}$ values for the southern ocean fall between the values of the North Atlantic Deep Water (NADW) and recirculated Pacific deep water, showing the effects of mixing ^{13}C -enriched NADW into the southern ocean. They argue that the lowest observed glacial $\delta^{13}\text{C}$ values from the southern ocean demonstrate the reduced glacial production of NADW.

Obviously, it is argued here that these very low glacial $\delta^{13}\text{C}$ values may also have resulted from the remineralization of organic C that was originally produced at the surface when enhanced Fe

input facilitated the greater utilization of major nutrients upwelling to the surface in the southern ocean during the summer months.

Evidence of increased productivity is also provided by the non-seasalt sulphate data of Legrand et al. [1988]; that is, sulphate amounts in the Vostok core from phytoplankton production during the LGM are approximately 3 times higher than those in the present interglacial. Nonetheless, evidence of increased southern ocean productivity in the way of ocean sediment skeletal remains is difficult to find. The situation is complicated by the nonpreservation of CaCO₃ phases in these waters and the shifts in annual sea ice coverage during the glacials [e.g., Cooke and Hays, 1982]. On the other hand, favorable conditions for diatom growth do exist in the Antarctic, and siliceous frustules are found in the sedimentary record. Indeed, Holocene siliceous oozes do occur of such purity that, when dried, they give the appearance of glass wool [e.g., Cooke and Hays, 1982].

One of the more abundant species in the southern ocean is *Phaeocystis pouchetti* [El-Sayed, 1985], a plant that has no CaCO₃ or siliceous hard parts. If it were

the dominant species during the ice ages, no skeletal remains would have been left behind for paleoceanographers to ponder over. It is also observed that diatoms, when growing rapidly, may not lay down thick frustules. For example, in Fe limitation experiments at Ocean Station PAPA, the diatom *Nitzschia* sp. took up scarcely any SiO₃ in a 6-day experiment [Martin et al., 1989]. Hart [1934, p. 186] also observed that although the diatom *Coscinodiscus* sp. was dominant in Antarctic bottom sediments, it rarely exceeded 1-2% of the surface phytoplankton species composition. Furthermore, dominant surface forms such as *Chaetoceros*, *Corethron*, and *Rhizosolenia* ". . . are but rarely represented in the bottom samples." Hence it is very possible that the phytoplankton that were growing during the LGM left little evidence of high productivity in the way of skeletal remains. Nevertheless, in spite of these arguments, the lack of clear evidence for increased glacial Antarctic productivity is a weak point of this hypothesis.

Another argument against high productivity during glacial periods is that widespread anoxia would have resulted, and no evidence of low oxygen conditions can be found. Again, it must be remembered that conditions in the southern ocean are different; that is, assuming that krill were the dominant grazers, as they are today, the large fecal pellets produced by these euphausiids would sink at a rate of the order of hundreds of meters each day [Small and Fowler, 1972]. Perhaps, then, these rapidly sinking packages, falling through very cold water, would use up relatively little oxygen in the upper water column; most would be consumed in the more oxygen-rich deep water. This would also provide the mechanism whereby intermediate-depth nutrients would be transferred to deeper waters [Boyle, 1988]. Pedersen et al. [1988] also present several strong arguments that eastern equatorial deep water remained oxygen replete in spite of the higher productivity occurring in this region during the LGM. Rapid sinking of particulate matter could also be facilitated if Fe-stimulated blooms occurred sporadically, as is the case with the northeast Atlantic spring bloom [Billett et al., 1983; Lampitt, 1985].

Others point out [e.g., Roger and Wilson, 1988] that glacial-interglacial changes in nutrients ($\approx 20\%$ [Boyle, 1986a, b]) were not large enough to account for

the observed CO₂ change. The record laid down via analog-Cd in benthic foraminifera shells fails to distinguish between preformed and regenerated Cd/nutrients. If southern-ocean-krill-rapid-sinking-fecal-pellet regeneration was largely in deep waters, not near the surface as it is in today's low-latitude ocean [e.g., Martin et al., 1987], the deep-water regenerated nutrients could be of similar concentration to the preformed nutrients occurring in modern deep water. For example, using depth-dependent elemental -O₂:C:N:P ratios, Martin et al. [1987] estimate that about three-fourths of the NO₃ and PO₄ at GEOSECS 246 (0°0';178°59'E [Broecker et al., 1982]) is preformed and only one-fourth regenerated at depths of ≈ 5000 m. If all southern ocean surface major nutrients were used up during the austral summer (that is, half of the preformed nutrients annually), the deep Pacific (GEOSECS 246) proportions would change to 63% regenerated, 37% preformed (e.g., 0.82 preformed; 1.39 regenerated; total = 2.21 $\mu\text{mol PO}_4 \text{ kg}^{-1}$ at 5497 m). The increase in regenerated PO₄ would have an accompanying C increase of 134 $\mu\text{mol kg}^{-1}$ using the VERTEX depth-dependent C:P ratio of 164 C:1 P for a depth of 5000 m. It is also apparent that the use of the VERTEX O₂:P ratio for 5000 m (-259 O₂:1 P) would result in the complete utilization of the available oxygen (5497 m = 196 $\mu\text{mol kg}^{-1}$; 259 X 0.82 $\mu\text{mol PO}_4 \text{ kg}^{-1}$ = 212 $\mu\text{mol O}_2$). On the other hand, the use of the -183 O₂:1 P ratio of Broecker et al. [1985] would result in leftover deep oxygen of 46 $\mu\text{mol O}_2$. Be that as it may, the point here is that the forams recording these events via Cd would be showing 2.12 $\mu\text{mol PO}_4$ in spite of large changes in amounts of CO₂, oxygen, and portions of regenerated versus preformed nutrients.

CONCLUSION

This hypothesis, concerned with glacial-interglacial CO₂ change, deals with ". . . the concentration of preformed nutrients as the master variable controlling both atmospheric pCO₂ and deep-sea oxygen" [Ennever and McElroy, 1985, p. 157]. In accordance with ice core records, it provides a mechanism whereby changes in atmospheric CO₂ could have taken place rapidly, in hundreds, not thousands, of years [Keir, 1988; Sarnthein et al., 1987, 1988]. It also supports the suggested sequence of primary productivity

TABLE 4. Glacial-Interglacial Atmospheric C Rates of Change

Description	Mean Age of Air Years B.P.	CO ₂ Concentration ppm	Total Gt C	Average Rates of Change Gt C yr ⁻¹
End of penultimate glacial to beginning of last interglacial	146,340 to 134,170	191.0 to 296.5	222	+0.018
End of last interglacial to beginning of last glacial	115,290 to 112,700	276.0 to 240.0	76	-0.030
Beginning of last glacial to end of last glacial	112,700 to 16,250	240.0 to 193.0	99	-0.001
End of glacial to beginning of present interglacial	16,250 to 12,930	193.0 to 245.0	110	+0.033

Data from Barnola et al. [1987].

change --> CO₂ change --> climate change [Shafter, 1989]. Potential Fe-stimulated changes in new productivity rates are large (2-4 Gt C yr⁻¹) in relation to changes in the Vostok record (e.g., 0.03 Gt C yr⁻¹; Table 4). The Vostok record (Figure 3) clearly shows that atmospheric dust Fe was abundant when CO₂ was low, and vice versa.

This hypothesis can be tested in two ways. In addition to looking for evidence of increased glacial southern ocean productivity, we can seek proof that, indeed, productivity is limited by Fe deficiency in the present southern ocean and equatorial Pacific. Assuming we find evidence, as was the case in the Gulf of Alaska [Martin and Fitzwater, 1988; Martin et al., 1989], it then becomes feasible to perform realistic large-scale Fe enrichment experiments in which phytoplankton species composition, elemental ratios of C:N:P and Si, δ¹³C ratios, etc., can be determined, as well as the effects of grazing and associated fecal pellet production, sinking rate, and oxygen consumption processes. One can even contemplate the ultimate enrichment experiment: the fertilization of the whole southern ocean with 430,000 tons of Fe, the amount required to support the removal of 3 Gt C yr⁻¹. Clearly, the reasons for glacial-interglacial CO₂ change are complex. Iron availability appears to have been a player; however, whether it had a lead role or a bit part remains to be determined.

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- J. H. Martin, Moss Landing Marine Laboratories, Moss Landing, CA 95039.
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