Export Production in the Subarctic North Pacific over the Last 800 kyrs: No Evidence for Iron Fertilization?

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The subarctic North Pacific is a high nitrate-low chlorophyll (HNLC) region, where phytoplankton growth rates, especially those of diatoms, are enhanced when micronutrient Fe is added. Accordingly, it has been suggested that glacial Fe-laden dust might have increased primary production in this region. This paper reviews published palaeoceanographic records of export production over the last 800 kyrs from the open North Pacific (north of ~35°N). We find different patterns of export production change over time in the various domains of the North Pacific (NW and NE subarctic gyres, the marginal seas and the transition zone). However, there is no compelling evidence for an overall increase in productivity during glacials in the subarctic region, challenging the paradigm that dust-born Fe fertilization of this region has contributed to the glacial draw down of atmospheric CO_2. Potential reasons for the lack of increased glacial export production include the possibility that Fe-fertilization rapidly drives the ecosystem towards limitation by another nutrient. This effect would have been exacerbated by an even more stable mixed layer compared to today.

1. Introduction

Air bubbles trapped in Antarctic ice reveal that atmospheric CO_2 concentrations varied cyclically from low values (~180 ppm) during glacial periods to higher values (~280 ppm) during interglacials (Barnola *et al.*, 1987; Petit *et al.*, 1999). These changes were accompanied in lock step by changes in inferred air temperature and were followed by changes in global sea level (Petit *et al.*, 1999; Shackleton, 2000). There is a general consensus that changes in the ocean played a major role in controlling the variations in atmospheric CO_2. However, uncertainty remains regarding the process or the combination of processes that have led to the cyclical variations in atmospheric CO_2 concentrations. The ocean can influence atmospheric CO_2 on glacial-interglacial and millennial time-scales in various ways (see Sigman and Boyle, 2000 and Pedersen *et al.*, 2002 for recent reviews), one of which is a change in the strength of the ocean's biological pump.

The possibility that a stronger biological pump has contributed to lower glacial atmospheric CO_2 levels has long been debated (Broecker, 1982; Sarmiento and Toggweiler, 1984; Sarnthein and Winn, 1988; Sigman and Boyle, 2000 and others). In this scenario, the net carbon uptake by the marine biosphere is increased relative to upwelling fluxes during glacials and is subsequently sequestered into the deep ocean via particle flux.

The subarctic North Pacific is of particular interest in this context. Similar to the Southern Ocean and the Equatorial Pacific, this region is characterized by an excess pool of nitrate, phosphate and silicic acid in the euphotic zone, which is not fully utilized by marine phytoplankton under modern conditions. The present consensus is that the growth of large celled phytoplankton (diatoms) is limited chiefly because of the low ambient concentrations of the micronutrient iron (Martin and Fitzwater, 1988; Boyd *et al.*, 1996; Boyd and Harrison, 1999; Tsuda *et al.*, 2003). Observations and model results suggest that iron is delivered to the subarctic North Pacific mainly by atmospheric transport of mineral dust from central China (Duce and Tindale, 1991; Tegen and

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Fung, 1995; Fung et al., 2000; Kawahata et al., 2000). Marine, terrestrial and ice core records clearly indicate that the last glacial maximum (LGM) and previous glacial periods were characterized by a much more active dust cycle and globally enhanced rates of mineral dust deposition (see Kohfeld and Harrison, 2001, for a review). For example, according to numerical simulations by Mahowald et al. (1999) and Werner et al. (2002), dust deposition over the subarctic N. Pacific increased by factors of >20 and 2–5, respectively. The GISP-II ice core also records significantly higher dust accumulation during the LGM over Greenland compared to today, and the isotopic and mineralogical signature of this glacial dust suggest mainly an Asian source region, similar to today (Biscaye et al., 1997; Svensson et al., 2000). It was previously envisioned (Martin, 1990) that higher iron deposition over currently iron limited regions, such as the Southern Ocean, the Equatorial Pacific and the subarctic N. Pacific, during glacial periods led to more efficient nutrient utilization, a strengthening of the biological pump and a net draw down of atmospheric CO_2.

The purpose of this paper is to review palaeoceanographic records of export production in the subarctic N. Pacific over the late Quaternary (0–800 kyr) (see Fig. 1 and Table 1 for core locations). The focus is on records outside the influence of the eastern (California Current) and western (Kuroshio) boundary currents, which have their own oceanographic and biological processes. Over the last decade, considerable progress has been made in identifying suitable coring sites in the North Pacific that lie above the carbonate compensation depth (CCD) and are not influenced by turbidity currents. While there is still much room for improvement in terms of core density, temporal resolution, and proxy methods applied, we examine the palaeoceanographic records that are available from this region for evidence of past changes in the strength of the biological pump as recorded by changes in sedimentary fluxes of biogenic material (opal, organic carbon, brassicasterol) and a proxy of organic carbon flux (Ba). We find different patterns of export production change over time in the various domains of the North Pacific (NW and NE subarctic gyres, the marginal seas and the transition zone), but no compelling evidence for an overall increase in opal production, which would be a response to iron fertilization, in the glacial subarctic Pacific. Possible reasons for the lack of response of the biological pump to iron fertilization are discussed.

2. Modern Hydrography and Biology

The hydrographic and biological conditions of the subarctic Pacific are briefly reviewed here to provide the rationale for the discussion of the palaeo records. Harrison et al. (1999), drawing heavily on the results obtained during JGOFS process studies, and Harrison et al. (2004)

provide more detailed reviews of the biological oceanography of the open subarctic Pacific. The atmospheric pressure system over the region induces westerly winds, which are strongest during the winter season (Nov.–Feb.). The wind field causes divergent southward Ekman transport and associated Ekman pumping with upward velocities of about 30 m/yr over the entire subarctic North Pacific (north of ~35–40°N; Talley, 1985; Gargett, 1991). This slow upward movement of cold and nutrient-rich subsurface waters provides new nutrients to the upper ocean. However, surface buoyancy forcing and turbulent mixing also affect the net concentrations of nutrients in the euphotic zone of the North Pacific (Gargett, 1991; Glover et al., 1994; Whitney and Freeland, 1999). The surface layer is relatively fresh due to a combination of low evaporation rates and a small rate of through-flow of warmer and saltier surface waters from the south (Warren, 1983; Emile-Geay et al., 2003). Consequently, a strong halocline is present year round at around 120 m water depth, which is further reinforced by an even shallower seasonal thermocline that develops during the summer at approximately 50 m depth (Tabata, 1975; Warren, 1983; Denman and Gargett, 1988). The combined effect is a highly stratified surface ocean with mixed layer depths averaging ~50 m during the summer and ~120 m (in the NE) to 150 m (in the NW) during the windier winter season (Tabata, 1975; Glover et al., 1994; Whitney and Freeland, 1999; Tsurushima et al., 2002). With the onset of spring, as irradiance levels increase and the mixed layer shoals due to thermal heating, it becomes isolated from the nutrient reservoir in the subsurface waters and phytoplankton growth draws down surface nutrients to about 50% of their winter values (e.g. Whitney and Freeland, 1999; Wong et al., 2002). During the winter, stronger winds result in deeper mixing and replenishment of nutrients to the mixed layer. It follows that, at least on annual time scales, the availability of macronutrients in the euphotic zone is positively correlated with the depth of the winter mixed layer (e.g. Glover et al., 1994). Over the last four decades, trends towards warmer and fresher surface waters and lower winter nitrate and silicic acid levels have been observed in the NE subarctic Pacific, and it is speculated that these changes are reducing marine productivity in this area (Freeland et al., 1998; Whitney et al., 1998; Whitney and Freeland, 1999). Similarly, trends towards a fresher surface mixed layer, lower surface phosphate concentrations and reduced net community production were observed in the NW subarctic Pacific over the last three decades (Chiba et al., 2004).

The subarctic North Pacific is one of three high nutrient, low chlorophyll (HLNC) regions, where the major nutrients nitrate, silicic acid and phosphate are present year round, despite nutrient utilization during the summer months. Primary productivity measurements range
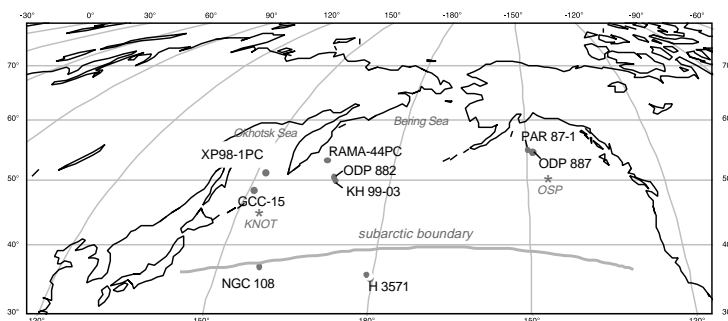
Fig. 1. Locations of core sites discussed in text. Ocean Station Papa (OSP) and KNOT are indicated by stars. The subarctic boundary (gray line) separates the subarctic region to the north from the subtropical region to the south (redrawn from Thomson, 1981).

from 300–600 mg C m^{-2}d^{-1} with little seasonal variation (2×) in the open NE Pacific (at Ocean Station Papa, OSP; Harrison *et al.*, 1999) to 50–530 mg C m^{-2}d^{-1} in the open NW Pacific, where the seasonal amplitude is significantly higher (10×; at Station KNOT; Imai *et al.*, 2002). The currently accepted view is that the growth of large phytoplankton cells (mainly diatoms) is limited by low Fe abundances (Martin and Fitzwater, 1988; Boyd *et al.*, 1996; Boyd and Harrison, 1999). In the NE subarctic Pacific, carbon biomass has been observed to increase significantly after a storm event bringing Gobi desert dust to the region (Bishop *et al.*, 2002), and recent open ocean Fe fertilization experiments in the NE and NW Pacific Gyres, SERIES (Boyd *et al.*, in prep.) and SEEDS (Tsuda *et al.*, 2003), respectively, have shown that diatom production increases after Fe stress is relieved. Smaller phytoplankton cells, however, which dominate the phytoplankton community and productivity, escape iron limitation by utilizing ammonium and urea as nitrogen substrates (Miller *et al.*, 1991; Varela and Harrison, 1999). Their abundance, in turn, appears to be controlled by micro zooplankton grazing (Miller *et al.*, 1991; Varela and Harrison, 1999). New production is 20–30% of total production at OSP (Varela and Harrison, 1999). These direct measurements are in good general agreement with estimates from a global biogeochemical modeling study that predicts f ratios of 0.3 in the open N. Pacific, and 0.5 along its margins (Laws *et al.*, 2000).

The Okhotsk and Bering Seas are characterized by subpolar conditions and extensive sea ice cover during at least 6–7 months every year (Nov.–April). Phytoplankton growth in these marginal seas is largely related to the seasonal retreat of sea ice, which enhances upper ocean stability, and the long duration (17–20 h) of daylight during the summer (e.g. Sorokin, 1999). Primary production rates are hence negligible in winter, but peak in May/June (2500–3000 mg C m^{-2}d^{-1}) and August/September (1000 mg C m^{-2}d^{-1}) with intermittently reduced primary pro-

ductivity (500 mg C m^{-2}d^{-1}) due to heterotrophic grazing during mid summer (Sorokin, 1999; Sorokin and Sorokin, 1999).

The transition zone between subarctic and subtropical water masses in the western Pacific extends from approximately 42–30°N and includes the eastwards extension of the Kuroshio Current. This region is characterized by steep gradients in temperature, salinity and nutrients (e.g. Levitus, 1994) and by a highly heterogeneous hydrography that includes cold fresh eddies south of the subarctic front (Yasuda *et al.*, 2001). Sediment trap experiments across the transition zone at ~175°E demonstrate that the mean annual fluxes of organic matter and opal increase towards the subarctic in this region (Kawahata *et al.*, 1998).

3. Strategy: Sedimentary Proxies to Reconstruct Export Production

Accumulation of biogenic opal, organic carbon (C_{org}), barium (Ba), and molecular biomarkers have been used in several studies to elucidate the history of export production in the North Pacific (Fig. 1, Table 1). Each proxy holds valuable information about the past carbon cycle, but has associated assumptions and problems. C_{org}: Numerous studies have shown an overall positive relationship between primary productivity, organic carbon export and burial (e.g. Müller and Suess, 1979; Sarnthein *et al.*, 1987; Calvert *et al.*, 1992, 1995), but the exact conditions under which organic carbon is preserved in the sediment are still subject to some debate (Hartnett *et al.*, 1998; Ganeshram *et al.*, 1999; Thunell *et al.*, 2000; Stott *et al.*, 2000; Hedges *et al.*, 2001). *Biogenic opal*: As the ocean is undersaturated with respect to silicic acid, biogenic opal dissolves on its way to the sea floor and at the sediment water interface. A small residual fraction of the settling opal escapes dissolution, however, and opal-rich sediments in the modern ocean are clearly linked to biogenic silica production and the tendency of a region to

Table 1. Sediment core records discussed in text.

				Reference
NE Pacific	ODP 887B	54°21.92′ N	148°26.78′ W	McDonald *et al.*, 1999
NW Pacific	ODP 882	50°22′ N	167°36′ E	Haug *et al.*, 1995, 1999
	KH99-03 Sta. ES	49°44.7′ N	168°18.9′ E	Narita *et al.*, 2002
	RAMA 44PC	53°00′ N	164°39′ E	Keigwin *et al.*, 1992
Okhotsk	XP98 1PC	51°00.9′ N	152°00.5′ E	Narita *et al.*, 2002
	GCC-15	48°10.1′ N	151°20.2′ E	Ternois *et al.*, 2001
Transition zone	NGC 108	36°36.85′ N	158°20.9′ E	Maeda *et al.*, 2002
	H3571	34°54.25′ N	179°42.18′ E	Kawahata *et al.*, 2000

support diatom blooms, especially those dominated by large or heavily silicified species (e.g. Calvert and Price, 1983; Nelson *et al.*, 1995; Ragueneau *et al.*, 2000; Pondaven *et al.*, 2000). In one sediment record discussed here (ODP 887B), downcore changes in the Si/Al ratio (wt.%/wt.%) are considered to reflect changes in biogenic opal content (McDonald *et al.*, 1999), since normalization to Al corrects for potential variations in detrital aluminosilicate input. Direct measurements of biogenic opal agree well with the Si/Al ratio in this core (Galbraith and Calvert, unpub. data, 2003). As opal is the most widely used proxy in studies carried out in the North Pacific, we mainly focus on this proxy here, but we refer to additional export production proxy data if they exist from the same core. In all cases the different proxies give a coherent picture of past changes in export production. *Biomarkers*: Brassicasterol (24-methylcholesta-5,22-dien-3β-ol) represents over 90% of the sterols in most species of diatoms (Volkman, 1986) and has been used as an organic diatom marker in the Okhotsk Sea (GCC-15, Ternois *et al.*, 2001). *Barium (Ba)*: Biogenic Ba precipitation (as barite, $BaSO_4$) in the water column is linked to downward carbon flux (e.g. François *et al.*, 1995; Dymond and Collier, 1996; Gingele *et al.*, 1999). Although barite is relatively inert, it dissolves in pore waters of suboxic and sulphate reducing sediments (Von Breymann *et al.*, 1992; McManus *et al.*, 1998).

For both C_{org} and Ba, quantitative algorithms have been proposed to relate the sedimentary contents of these components to past primary and export production in terms of g C m^{-2}y^{-1} (Sarnthein and Winn, 1988; Dymond *et al.*, 1992; François *et al.*, 1995). However, the C_{org} based algorithm is problematic because linear sedimentation rates (LSR) in marine sediment cores often vary much more than the C_{org} content (Middelburg *et al.*, 1997), so that the estimated C_{org} accumulation rate of a given sediment core mainly reflects LSR. Thus, we treat all of

the available proxy data in a qualitative manner, and attempt to assess whether export production and/or the tendency of the pelagic ecosystem to support diatom blooms increased or decreased over time.

The sedimentary concentration of each proxy reflects some balance between downward (export) flux from the euphotic zone, lateral flux, preservation efficiency, and dilution by other sedimentary components. In order to correct for variable dilution, fluxes of the material of interest to the sea floor are often estimated from mass accumulation rates (MARs, where MAR = dbd × LSR × [i], where dbd is the dry bulk density of the sediment in g/cm^3, LSR is the linear sedimentation rate in cm/kyr between dated horizons, and [i] is the concentration of the compound of interest in wt.%). This approach, in turn, is hampered by the resolution and accuracy of the stratigraphy, the error associated with dry bulk density measurements, and, as pointed out above, the dominant control of large changes in sedimentation rates (Middelburg *et al.*, 1997). We plot mainly percentage values here, but point out that for all but one core, percentages and MARs give the same general picture (see original references). In the case of core GCC-15 from the Okhotsk Sea, percentages and MARs imply a slightly different pattern during the last deglaciation and we present both proxies in this case (see Fig. 5). The potentially most serious problem with most records presented here (% and MAR) is their inability to distinguish between downward and lateral fluxes. Lateral fluxes of material to (or from) the core site by bottom currents can greatly affect sediment accumulation (e.g. Marcantonio *et al.*, 2001). Flux normalization to the particle reactive radio nuclide ^{230}Th holds great promise for reconstructing true vertical fluxes of biogenic constituents and thereby for obtaining a more accurate estimate of palaeo export (e.g. Bacon, 1984; François *et al.*, 2003). Briefly, this approach relies on the assumption that the flux of ^{230}Th reaching the sea floor is

equal to its known production rate by ^{234}U decay in the overlying water column. In contrast to U, ^{230}Th is strongly particle reactive. In settings where particles settle through the water column without lateral redistribution, the ^{230}Th inventory in a sediment interval should match its production in the overlying water column integrated over the time period represented by the sediment section (François et al., 2003). This approach was applied in this study using a core from the Alaskan Gyre region (PAR 87-1) (see Fig. 3). At this site, good agreement between corrected fluxes of Si and C and the Si/Al ratio is observed. At a site in the NW subarctic Pacific (RAMA 44PC), new ^{230}Th measurements also confirm previous findings based on MAR and percentages (Crusius, unpub. data). However, ^{230}Th measurements are still lacking from all other sites presented here, so that the conclusions we reach may well be overturned when ^{230}Th-normalized accumulation rates become available for other sites.

The age models of the cores discussed here are adopted from the original publications and are described in the figure captions.

4. Palaeoceanographic Results: Overview by Regions

4.1 Open Pacific

We first examine available long time-scale records from the open North Pacific, that is the region minimally influenced by coastal processes, such as upwelling and/or strong tidal mixing.

ODP Site 887 from the Alaskan Gyre shows periods of markedly increased Si/Al ratios (Fig. 2) throughout the last 760 kyrs (McDonald et al., 1999). The changes in the Si/Al ratio at this site correspond well to biogenic opal values, which vary from 10% (Si/Al = 5) to over 70% (Si/Al = 30; Galbraith and Calvert, unpub data, 2003). Maxima in the Si/Al ratio are accompanied by relatively high Ba/Al ratios (not shown) and are interpreted to represent sporadic periods of intense export production in this region (McDonald et al., 1999). No consistent glacial-interglacial cyclicity is apparent in these productivity events, but the Si/Al maxima occur predominantly during cooler interglacial substages such as 5.2 (87 kyrs), 5.4 (109 kyrs), 9.2 (320 kyrs) and 11.2 (375 kyrs) and during climate transitions such as from oxygen isotope stage (OIS) 5 to 4 at 75 kyrs (McDonald et al., 1999). The intervals with high Si/Al ratios are characterized by high abundances of large (>150 μm) diatom frustules (McDonald et al., 1999). Measurements of ^{230}Th in the nearby site survey core PAR 87-1 indicate that the intervals with high Si/Al ratio accumulated 2–5 times faster than adjacent sediment intervals (McDonald et al., 1999). Moreover, the ^{230}Th measurements allow for flux-corrected estimates of vertical C_{org}, Si, and Ba rain (Fig. 3). These results imply that the increase in Si export was
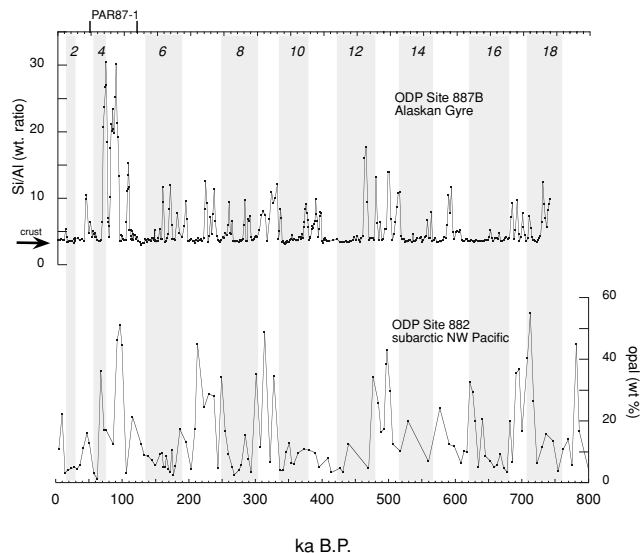

Fig. 2. The Si/Al ratio, a proxy for biogenic opal, from the Alaskan Gyre in the NE Pacific (McDonald et al., 1999) and biogenic opal (%) from the subarctic NW Pacific (Haug et al., 1995). Arrow on Y-axis in top panel indicates Si/Al ratio in average crust (3.48; Krauskopf, 1979). The age models are based on orbital tuning and magnetic reversals (ODP Site 882; Tiedeman and Haug, 1995) and ^{14}C measurements (0–40 kyrs) and δ^{18}O stratigraphy (ODP Site 887; McDonald et al., 1999), respectively. Grey shadings indicate glacial marine oxygen isotope stages. Vertical bars over top panel indicates the time interval for which ^{230}Th measurements are available from site survey core PAR 87-1, close to ODP Site 887 (see Fig. 3).

accompanied by an increase in organic carbon export. Large differences in δ^{18}O between coeval benthic and planktonic foraminifera species suggest that the episodes of high surface productivity were often associated with low surface salinities, and carbon isotope ratios of bulk organic matter are interpreted to suggest that they were also associated with a decrease in surface water PCO_2 (McDonald et al., 1999). The authors proposed that regional influences such as dust-born iron inputs, possibly from Asian and/or Alaskan sources and iron injections from melt water, might have triggered these productivity events. Alternatively, eddies spinning of off the western continental margin of North America might have supplied Fe and other nutrients from the coastal zone to the Gulf (Whitney and Robert, 2002).

Irrespective of the cause of these intense but sporadic productivity events in the NE Pacific, they do not appear to be tightly coupled with periods of high opal accumulation in the western subarctic Pacific. At ODP Site 882 opal percentages (Fig. 2) and opal MARS (not shown) are generally higher during interglacials, suggest-
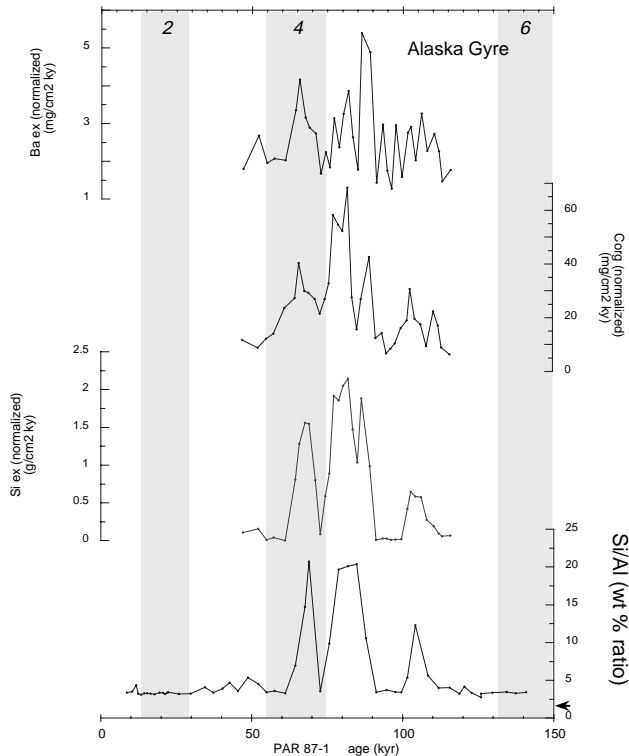
Fig. 3. ^{230}Th normalized fluxes of excess Ba, C_{org} and excess Si compared to the Si/Al ratio of site survey core PAR-87-1 in the Alaskan Gyre from 50 to 120 kyrs BP. ^{230}Th data (corrected for detrital input and in situ decay), Si and Ba data (corrected for detrital input) and C_{org} data are from McDonald *et al.* (1999) and McDonald and Pedersen (unpub.). ^{230}Th data were used here to calculate vertical fluxes according to Bacon (1984) and François *et al.* (2003). Note the good correspondence between maxima in Si and C_{org} flux. Arrow on Y-axis in bottom panel indicates Si/Al ratio in average crust (Krauskopf, 1979). No ^{230}Th data are available for the time intervals from 0–40 kyrs and 120–150 kyrs BP.
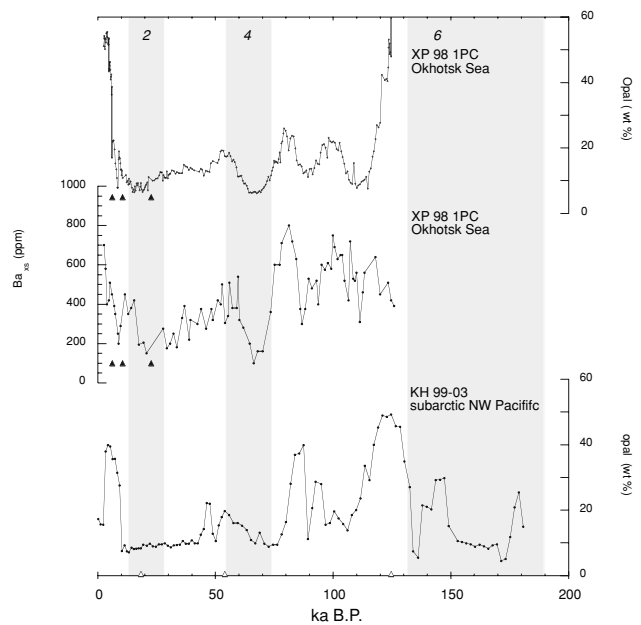

Fig. 4. Biogenic opal and Ba (excess) records of Okhotsk Sea core XP98-1 PC (from Narita *et al.*, 2002; Sato *et al.*, 2002, respectively) and biogenic opal of core KH99-03 from the subarctic NW Pacific (Narita *et al.*, 2002) for the last 200 kyrs. Age models are from original authors. The age model of core XP98 1PC is based on ^{14}C dates for the period 0–22 kyrs BP (solid triangles) and on correlating the opal record to the normalized oxygen-isotope profile of Martinson *et al.* (1987), assuming that periods of high opal values correspond to interglacials, as suggested by the ^{14}C ages covering the last glacial-interglacial transition. For core KH99-03, approximate age fix points (open triangles) were assigned by correlating its opal record to the opal record of core XP98 1PC. Grey shadings indicate glacial marine oxygen isotope stages.

ing that diatom production in this region was more intense during warm periods of the climate system (Haug *et al.*, 1995). This pattern is consistent with the shorter core record KH99-03 from the vicinity of ODP site 882 (Fig. 4) where opal percentages increase from <10% during the glacial to 20–40% during the Holocene (Narita *et al.*, 2002).

Piston core RAMA 44 PC in the NW Pacific provides a high resolution record of the last 20 kyrs, which includes the later part of the LGM, the deglaciation and the Holocene (Keigwin *et al.*, 1992). A marked increase in export production during the deglaciation is evident in this high resolution record (Fig. 5). Opal percentages increase from low glacial values (<10%) to over 35% at 14.6 kyrs and reach intermediate values during the

Holocene (10–15%). The deglacial productivity event is also evident in C_{org} percentages and opal and C_{org} MARs from the same core (Keigwin *et al.*, 1992). δ^{18}O data of the planktonic foraminifera *N. pachyderma* are interpreted to reflect reduced sea surface salinity during the event, similar to the observation of low salinity during the sporadic productivity events in the Alaskan Gyre (McDonald *et al.*, 1999). Prior to the productivity event, high concentrations of ice rafted debris in this core suggest the frequent occurrence of ice berg drifts over the site.

4.2 Marginal Seas
4.2.1 Sea of Okhotsk

Similar to the open NW Pacific, core record XP98 1PC from the Okhotsk Sea shows high opal percentages (~50%) in the Holocene and the previous interglacial (OIS 5), and lower opal percentages (~10%) during the LGM
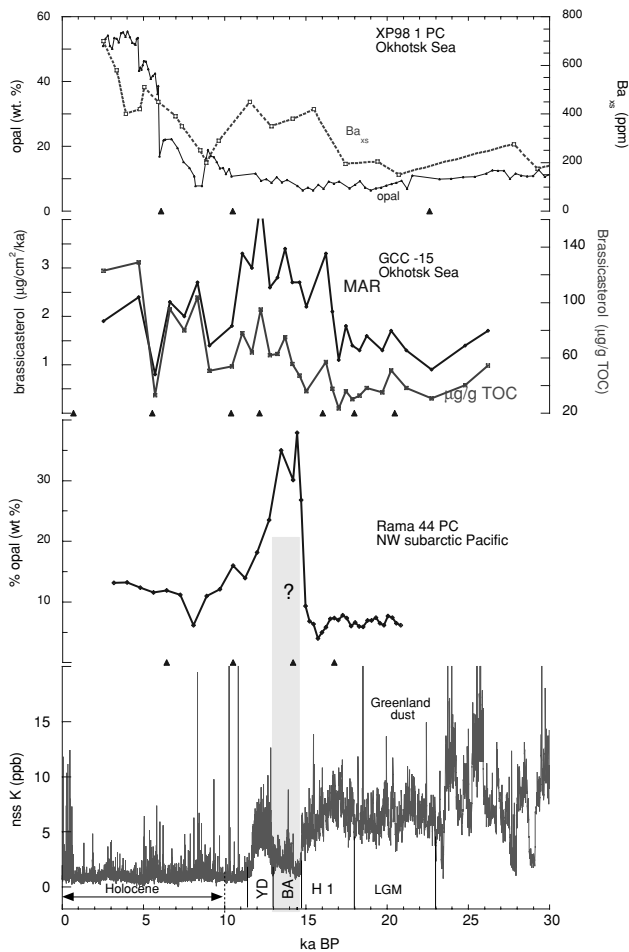
Fig. 5. Biogenic opal and Ba records of Okhotsk Sea core XP98-1 PC (Narita *et al.*, 2002; Sato *et al.*, 2002), Brassicasterol (MAR and μg/g C$_{org}$ total) of Okhotsk Sea core GCC-15 (Ternois *et al.*, 2001), and biogenic opal of RAMA 44 PC from the NW Pacific Gyre (Keigwin *et al.*, 1992) over the last 30 kyrs. Solid triangles in top three panels indicate ^{14}C dates. Age model of core XP98-1 PC is from Narita *et al.* (2002), age model of GCC-15 is from Ternois *et al.* (2001), based on ^{14}C dates by Keigwin (1998). Age model of Rama-44PC is based on ^{14}C dates published by Keigwin *et al.* (1992), which have been converted to calendar ages using a –700 (±200) reservoir correction and the radiocarbon calibration database and software (CALIB 4.3) of Stuiver *et al.* (1998) for this study. Bottom panel shows non-sea salt potassium (K^{+}, in ppb), part of the total dust flux with a dominant Asian provenance, as recorded in Greenland core GISP-II (Rohling *et al.*, 2003 and references therein). The present interglacial (Holocene) and the last glacial maximum (LGM) are indicated. The Younger Dryas (YD) cold period, Bølling-Allerød (BA) warm period, and Heinrich event 1 (H 1) are well recognized North Atlantic climate events.

and cold stage 4 (Fig. 4; Narita *et al.*, 2002). These findings are in agreement with Ba measurements on the same core (Fig. 4; Sato *et al.*, 2002), earlier Okhotsk Sea opal records (Gorbarenko, 1996), and with biomarker changes in Okhotsk Sea core GCC-15 (Ternois *et al.*, 2001). In LGM sediments at this latter site, brassicasterol (Fig. 5) and phytol (not shown) are present at minute concentrations only and alkenones (not shown) are close to the limit of detection. These findings suggest that algal production, including diatoms and haptophytes, was severely limited during the LGM. At the same time, the remaining diatom assemblage was dominated by members of the sea ice flora (*Niztschia grunowii* and *Niztschia cylindra*), suggesting that perennial sea ice covered large parts of the Okhotsk Sea during the LGM (Shiga and Koizumi, 2000).

During the last deglaciation, however, perennial sea ice cover retreated significantly in the Okhotsk Sea (Shiga and Koizumi, 2000). Maximal MARs of brassicasterol (Fig. 5), C37 alkenones as well as phytol (not shown) and % C$_{org}$ (not shown) at site GCC-15 suggest that there was a high productivity pulse in the Okhotsk Sea during the deglaciation, similar to the western subarctic gyre. The diatom flora during that interval (11–17 kyrs) is dominated by *Thalassionema nitzschioides*, a species indicative of productive waters (Shiga and Kuizumi, 2000). Although there is good overall agreement between Ba and opal concentrations in core XP98-1 PC (Fig. 4), Ba concentrations are also moderately elevated in this core during the deglaciation where as opal concentrations are not (Fig. 5). This could suggest that phytoplankton other than diatoms might have proliferated after the cessation of full glacial conditions (Sato *et al.*, 2002), however, this interpretation would be inconsistent with the high MAR of brassicasterol during the deglaciation at site GCC-15 (Fig. 5). The Holocene in the Sea of Okhotsk is characterized by high sedimentary opal contents (~50 wt.%, Gorbarenko, 1996; Narita *et al.*, 2002). Together with a maximal ratio of brassicasterol/total organic carbon (Fig. 5), this implies a predominance of diatoms in the phytoplankton community and high overall export productivity during the last 10 000 years.

4.2.2 Bering Sea

Sancetta (1983) and Sancetta *et al.* (1985) used diatom assemblages to reconstruct glacial conditions in the Bering Sea. *Nitzschia* species that are common in sea ice (*N. grunowii* and *N. cylindra*) are found in the modern sediments only along the northern part of the Bering shelf, consistent with the distribution of sea ice today. However, these species are found in large numbers in glacial sediments in the southern and western parts of the Bering Sea, implying that sea ice covered most of the Bering Sea under glacial conditions (Sancetta, 1983; Sancetta *et al.*, 1985). In addition, *Thalassiosira trifulata*, a diatom
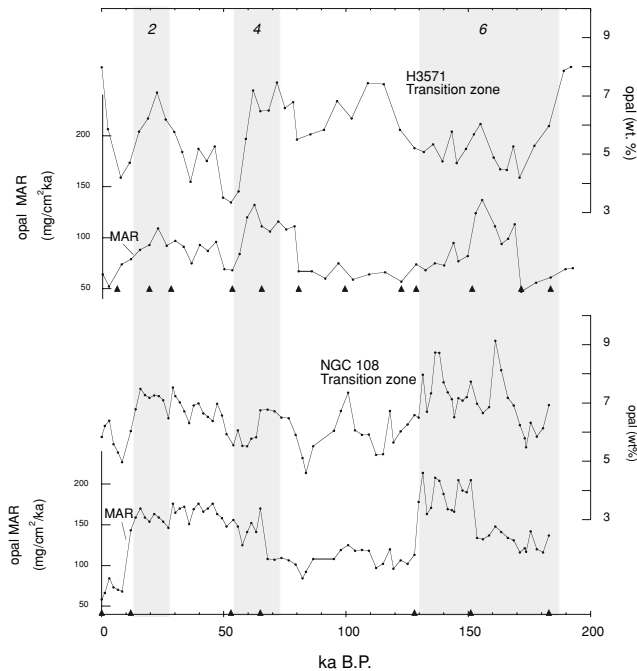
Fig. 6. Biogenic opal (% and MAR) of cores H3571 (Kawahata *et al.*, 2000) and NGC 108 (Maeda *et al.*, 2002) from the transition zone between subarctic and subtropical waters over the last 200 kyrs. Age models are based on correlating the $\delta^{18}O$ stratigraphies of NGC 108 and H3571 to the global SPECMAP $\delta^{18}O$ time scale (Imbrie *et al.*, 1984; solid triangles are assigned control points). Grey shadings indicate glacial marine oxygen isotope stages.

typical of the modern Okhotsk Sea, where winter sea ice and strong summer vertical stratification prevail, is abundant in glacial sediment sections from the Bering Sea and the northernmost parts of the NE and NW subarctic Pacific (Sancetta, 1983). These findings imply that ice melting in summer resulted in low surface salinities in these regions during the glacial. Organic carbon percentages are higher in Holocene sediment sections, which are also more diatomaceous, suggesting higher export production today compared to the last glacial (Gorbarenko, 1996). Low glacial export production was probably caused by the intensive sea ice cover and related light limitation during much of the year, together with the strong stratification and reduced vertical mixing rates when the sea ice melted during the summer (Sancetta, 1985; Gorbarenko, 1996). During the last deglaciation, C_{org} values show intermittent maxima in Bering Sea cores (Gorbarenko, 1996). Sedimentary nitrogen isotope data from the Bering Sea during the deglaciation suggest that nitrate utilization was enhanced, which is interpreted to reflect higher biological production during that time (Nakatsuka *et al.*, 1995). New palaeo records from the Bering Sea (Cook

and Keigwin, in prep.) are consistent with this interpretation, and suggest a strong productivity event in the Bering Sea during the last deglaciation similar to the deglacial productivity pulse recorded in the open NW Pacific (RAMA-44PC) and possibly the Sea of Okhotsk (GCC-15).

4.3 Transition zone between the subarctic and subtropical Pacific

The pattern of change in export production inferred from the transition zone between the subarctic and subtropical regimes is opposite to that in the western subarctic Pacific. Thus, cores NGC 108 and H3571 generally show higher opal percentages and MARs (Fig. 6) during glacial stages OIS 2, 4 and 6, similar to C_{org} percentages and MARs (not shown), suggesting that export production was generally higher in glacial periods (Kawahata *et al.*, 2000; Maeda *et al.*, 2002). Note, however, that this pattern is more pronounced in the MAR estimates and that the MAR estimates can be seriously compromised by the effects of lateral sediment redistribution, as noted earlier. Pollen are more abundant in glacial sediments in this region, similar to Al and rounded quartz grains, implying that aerosol accumulation was generally higher during glacial periods (Kawahata *et al.*, 2000, 2002). These cores south of the modern subarctic boundary provide the only evidence so far for a possible increase in export fluxes during glacial periods in the North Pacific.

5. Discussion

Taken together, the sedimentary records currently available from the subarctic Pacific suggest that export production, especially that of opal producing phytoplankton, did not increase during glacial stages. Specifically, there is no correlation between downcore changes in biogenic opal and the dust records from Antarctica or Greenland. In fact, opal records from the subarctic NW Pacific imply lower opal export during the last several glacial cycles and significantly higher opal accumulation during interglacials, similar to records from the Okhotsk and Bering Seas. Only in the transition zone between subarctic and subtropical water masses is there evidence for an increase in export production during glacials. We are not aware of any record from the subtropical Pacific that would extend this pattern of production change into the subtropical gyre on the time-scale of interest here. Taken at face value, the absence of increased opal or carbon contents in glacial sediments in the subarctic region implies that increased particle export due to iron fertilization did not occur. This is not consistent with the overwhelming evidence of increased dust accumulation during glacials (e.g. Kohfeld and Harrison, 2001) and the well documented effect of iron fertilization on phytoplankton growth rates in this region today (e.g.

Bishop *et al.*, 2002; Tsuda *et al.*, 2003; Boyd *et al.*, in prep.). In the first part of the discussion, we assume that the palaeo proxies provide an accurate picture of water column fluxes and discuss possible causes for the absence of higher export production during glacials in the subarctic Pacific. The findings from the transition are discussed next, and possible biases of the sedimentary record of export production are addressed in the third part of the discussion.

The first question is whether enhanced dust deposition rates during the glacial were sufficient to relieve iron stress in the subarctic N. Pacific. Bopp *et al.* (2003) examine this question for the LGM using the ocean biogeochemistry model of Aumont *et al.* (2003), which includes an explicit representation of diatoms and nannoplankton and co-limitation by iron, silicic acid and phosphate. Changes in marine biota are simulated using the dust deposition maps of Mahowald *et al.* (1999; suggesting an >20 fold increase in dust deposition over the subarctic Pacific), sea surface temperatures and sea ice cover from CLIMAP (1981) and Crosta *et al.* (1998) and ocean circulation patterns reconstructed for the LGM (Fleury and Marti, pers. com. in Bopp *et al.*, 2003). Forced with these boundary conditions, the Bopp *et al.* (2003) model shows an ecosystem shift in the subarctic N. Pacific towards diatoms at the expense of nannoplankton and an overall increase in export production of 10–20 g C/m²y⁻¹. This increase is significant compared to a present day export production rate of roughly 33–66 g C/m^{-2}y^{-1} (based on 110–220 g C m^{-2}y^{-1} or 300–600 mg C m^{-2}d^{-1} of primary production and an f-ratio of 0.3). However, as shown here, and as noted by Bopp *et al.* (2003), the predicted increase in export flux conflicts with the opal palaeoproductivity records from this region.

A number of factors can be proposed to reconcile this apparent contrast. While the positive relationship between iron supply and phytoplankton growth rates is well documented (Boyd *et al.*, 1996; Coale *et al.*, 1996; Boyd and Harrison, 1999; Tsuda *et al.*, 2003, and others), it is still undetermined whether or not an increase in iron supply leads to increased export of particulate carbon (Charette and Buesseler, 2000; Buesseler and Boyd, 2003). Furthermore, even if future mesoscale Fe fertilization experiments do show sustained export increases following mixed-layer Fe fertilization, it is still unclear whether prolonged iron supply during glacial periods can lead to a strengthening of the biological pump over long timescales and over large areas. While iron might be the proximal limiting nutrient in the subarctic North Pacific today, stimulating production by adding iron might have rapidly driven the system towards limitation of another nutrient such as silicic acid or nitrate. This is especially true if iron is delivered to the North Pacific predominately through the atmosphere, as suggested by present day ob-

servations and modeling (Duce and Tindale, 1991; Tegen and Fung, 1995). Dust storms at the beginning of a glacial period might well have led to a rapid growth of diatoms. However, the growing stock of diatoms might have simply used up all the silicic acid and/or nitrate, eventually sinking out, and leaving a macronutrient-depleted euphotic zone behind which was only capable of sustaining small cell phytoplankton production. This community would then rely on regenerated nutrients and not contribute to any significant export of carbon and opal. Miller *et al.* (1991) predicted a similar scenario as a consequence of a hypothetical large scale iron addition experiment in the subarctic North Pacific based on observations during the SUPER ecosystem research program. Until the euphotic zone is resupplied with macronutrients from below the mixed layer during the next winter, additional iron will have no effect. In principle, one could argue that higher overall wind speeds should increase the depth of the mixed layer as well as the vertical velocity of Ekman pumping during the glacials, thereby supplying more macronutrients to the euphotic zone. However, palaeo records of upper ocean density are inconsistent with this idea. Stable oxygen isotope ratios in planktonic foraminifera in the NW and the NE subarctic Pacific imply that the glacial surface ocean was even *less* dense and more stratified than today (Zahn *et al.*, 1991; Keigwin *et al.*, 1992). The δ^{18}O data are consistent with independent evidence for lower sea surface salinities based on fossil dinocyst (DeVernal and Pedersen, 1997) and diatom assemblages (Sancetta, 1983). By analogy with today, the increase in surface stratification is likely to have led to a reduction in macronutrient supply to the euphotic zone, precluding significant rates of new primary production.

Additional factors most likely played a role in keeping glacial productivity low in this region. Fossil diatom and dinocyst assemblages indicate that large parts of the Bering and Okhotsk Seas were covered with perennial sea ice (Sancetta, 1983; Sancetta *et al.*, 1985; Shiga and Koizumi, 2000) and that sea ice might also have been present during parts of the year in the Alaskan Gyre (DeVernal and Pedersen, 1997). The presence of sea ice most likely caused significant light limitation and a shorter growing season, especially in the higher latitudes.

After the glacial period of low export production, a strong productivity pulse apparently occurred during the last deglaciation in the NW Pacific Gyre, the Bering Sea and the Okhotsk Sea. Keigwin *et al.* (1992) suggested that this pulse was related to the northward withdrawal of a seasonally oscillating sea ice margin, by analogy with the occurrence of phytoplankton blooms triggered by the summer melt of marginal ice zones in the Bering Sea (McRoy and Goering, 1974; Sorokin, 1999) and the Southern Ocean (Smith and Nelson, 1985; Buesseler *et al.*, 2003). The ice melt reduces sea surface salinity (as

reflected in the $\delta^{18}O$ anomalies observed by Keigwin *et al.*, 1992) thereby possibly promoting a level of upper water column stability that fosters phytoplankton growth but does not prevent the resupply of nutrients from below. Furthermore, the ice melt is likely to release accumulated iron and other nutrients. Summer insolation increased during the last deglaciation (Laskar, 1990), possibly combining with the retreating sea ice to create ideal conditions for maximal export production. The exact timing of the productivity pulse in the subarctic Pacific and the Bering Sea is currently being investigated (Cook and Keigwin, in prep.). In the open subarctic NW Pacific (RAMA 44 PC, Fig. 5) the productivity pulse starts at 14.6 kyrs B.P., coeval with the onset of the Bølling-Allerød warm period.

In the northwestern subarctic Pacific (ODP Site 882), opal export appears to have been consistently higher during previous interglacial periods, similar to the Bering and Okhotsk Seas, were opal and Ba records are highest during warm OIS 1 and 5. It has previously been suggested that the strength of North Atlantic Deep Water (NADW) formation controls the nutrient supply to the northwestern subarctic Pacific (Haug *et al.*, 1995), assuming this is the region where abyssal deep waters ultimately well up to the surface. In this scenario, vigorous NADW formation and abyssal circulation cause high nutrient contents, high productivity, and cool sea surface temperatures in the NW Pacific during interglacials and interstadials (Haug *et al.*, 1995; Kiefer *et al.*, 2001). However, the present oceanographic understanding of the region does not necessarily support this concept. The balance between wind driven upwelling and surface stratification determines the supply of nutrients to the euphotic zone (Gargett, 1991), and the deep water overturn of the North Pacific is usually shown as upwelling of northward flowing bottom water from the South Pacific into the overlying Pacific Deep water layer, which then returns southwards at middepths (~2000–4000 m; Roemmich and McCallister, 1989; Talley, 1995, 2003; Ganachaud, 2003). In contrast to the control by NADW, and similar to the controls on export production proposed here for glacial-interglacial time-scales, Haug *et al.* (1999) suggested that the onset of permanent stratification in the subarctic Pacific was responsible for the large reduction in opal MARs recorded at 2.73 million years B.P. at OPD site 882. Before 2.73 million years, opal MAR at this site was significantly higher than the values recorded during the late Pleistocene, which are discussed here.

5.1 Transition zone

In contrast to the subarctic Pacific, there is an apparent increase in export production during glacial periods (OIS 2, 4, and 6) in the transition zone between subartic and subtropical water masses. Based on their sediment core findings, Maeda *et al.* (2002) and Kawahata *et al.* (2000) suggest that a southward shift in the position of the subantarctic front and an increase in aerosol accumulation during glacial stages might have been responsible for increased export fluxes of biogenic materials. For this region, the sediment core results are qualitatively consistent with the ocean biochemistry model of Bopp *et al.* (2003), which predicts an increase in export production of 0–10 g C/m^2y^{-1} during the LGM in response to higher dust accumulation, cooler SSTs and ocean circulation changes (see above). The high degree of upper ocean stratification inferred for the subarctic region, which we assume prevented nutrient re-supply from below, might not have characterized the transition zone during the glacials. Thus, one could speculate that macro nutrient supply from below was sufficient and that iron fertilization indeed stimulated export production in this region. However, more and tighter proxy data are needed before this can be accepted with any degree of confidence.

On the basis of the available evidence, therefore, the palaeo records imply that although export production in the transition zone might have been higher during glacial periods of increased dust inputs, such evidence is lacking from the subarctic Pacific, where Fe additions have been shown to stimulate production, as well as from the Bering and Okhotsk Seas. Hence, these latter regions do not appear to qualify as areas of additional CO_2 sinks during glacial periods.

5.2 Possible biases in the sedimentary records

Taking the sedimentary opal records discussed here at face value, however, might be misleading for three reasons. First, species that do not build opal frustules, such as phaeocystes, might have proliferated under glacial conditions. However, a systematic increase in export rain of any phytoplankton species during glacials should ideally be reflected in higher organic carbon or Ba contents in glacial sediment sections. None of the records from the subarctic Pacific examined here shows a clear pattern of higher sedimentary C_{org} or Ba values during glacials (see figure 2 in Haug *et al.*, 1995; figure 4 in McDonald *et al.*, 1999).

Second, there is a growing body of evidence that syndepositional redistribution of sediments by bottom currents occurs on a variety of spatial scales. In areas of dynamic bottom currents, the accumulation of laterally redistributed sediments is often several fold larger than the flux of material initially sinking from the euphotic zone (e.g. Marcantonio *et al.*, 2001). Failing to take lateral fluxes and winnowing and their potential changes over time into account can result in serious errors in estimating actual palaeo fluxes from the surface. Flux normalization to the particle reactive radio nuclide ^{230}Th, such as done here for site PAR 87-1, offers a means of

correcting for lateral flux and for assessing palaeo export fluxes with greater confidence (François *et al.*, 2003). However, apart from site PAR 87-1 and also RAMA-44PC, where new ^{230}Th measurements (Crusius, unpub. data) confirm the previous results based on percentages and MARs, these measurements are still lacking from all other sites in the North Pacific.

The third complicating factor in our interpretation is the potential change in the Si:C uptake ratio of phytoplankton over glacial-interglacial time scales. Diatoms under iron stress take up more silicic acid relative to carbon and nitrogen than diatoms under Fe replete conditions (Hutchins and Bruland, 1998; Takeda, 1998; Firme *et al.*, 2003), which leads to the production of more heavily silicified diatoms that have higher sinking rates (Muggli *et al.*, 1996). Release from iron stress during glacials might thus have permitted diatoms to grow with lower Si:C uptake ratios, and hence carbon export might have been higher without a concomitant increase in opal export. However, as mentioned above, there is no clear pattern of higher sedimentary C_{org} or Ba values during glacials. Moreover, flux-corrected organic carbon values at the Alaskan Gyre survey site (PAR87-1) correspond well to flux-corrected Si values (Fig. 3), suggesting that Si and C export increased at the same time during the sporadic export production events.

6. Conclusions

We reviewed existing sedimentary records from the North Pacific for evidence of past changes in the strength of the biological pump by compiling downcore records of biogenic opal, C_{org}, biomarkers, and Ba. We focused on the last 8 full glacial-interglacial cycles (0–800 kyrs). Based on this review, the following conclusions can be drawn:

• In the transition zone between subarctic and subtropical water masses, export production has apparently increased during glacial stages 2, 4, and 6, contemporaneously with higher pollen and aerosol inputs.

• In the western subarctic Pacific, opal export decreased during glacial periods compared to interglacials. Similarly, opal export was higher during the Holocene compared to the last glacial period in the Bering and Okhotsk Seas. A high level of upper ocean stratification, inhibiting the resupply of nutrients from below, extensive sea ice and light limitation are suggested as possible causes for reducing export production during glacials and for counteracting any possible Fe-fertilization in these domains.

• In the Alaskan Gyre region, export production does not appear to show a strong glacial-interglacial cyclicity. Instead, export production has increased during sporadic events throughout the last 800 kyrs. The trigger of these events remains elusive, but might be related to regional effects such Fe delivery by dust storms, melt water inputs, or eddies originating from the Alaskan and British Columbian coastlines.

The results presented here are based on a limited number of core sites, and the development of new and tighter palaeo data constraints (such as ^{230}Th, δ^{15}N and δ^{32}Si, as well a measurement of frustule silicification) might well lead to a different and perhaps more complex picture of past variations in the biological pump than that described here. However, based on the currently available records, no case can be made for consistently increased export production during glacials in response to iron fertilization in the subarctic Pacific.

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