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Dear Erin,

Please find attached a revised version of our manuscript “Photic zone changes in the North West Pacific Ocean from MIS 4-5e” (ref: cp-2014-107). We welcome the positive and constructive comments made by both reviewers and have adjusted the manuscript accordingly as outlined below. At the end of this I have attached a marked-up copy of the manuscript highlighting the changes made within the text

Following these revisions I hope that you will consider this paper suitable for publication. Please do not hesitate to contact me if you have any queries.

Best wishes,

George

Reviewer 1 (responses in bold)

1) The reason why variations in pCO₂(aq) or d13C-DIC have negligible/minimal impacts on d13C-diatom is not clearly explained. **We have expanded this paragraph to explain this in more detail**

2) My complaint about the paper is that they treat biogenic opal as a better paleoproductivity proxy than biogenic barium (BioBa). **This issue was also raised by reviewer 2 and we have revised the text accordingly. We now provide a more balanced summary of the BioBa record in Section 4.2 and, in line with Jaccard et al. (2009), use BioBa to examine possible changes in organic carbon export in Section 4.2.2. In line with the suggestions of reviewer 2, however, we continue to focus most of our discussion on using the opal record as a proxy of siliceous productivity since this the diatom/siliceous fraction forms the basis of the interpretations made in the manuscript.**

3) Can we assume that the average value of seawater d30Si remained constant during the time interval considered in the study? **We have added some text explaining that we are assuming that modern day values are valid for the past. Whilst the $\delta^{30}\text{Si}$ of silicic acid may have changed over time, it is likely that such changes were small and do not significantly alter our interpretations. This is in light of evidence that the $\delta^{30}\text{Si}$ of silicic acid in the ocean (outside of seasonal biological fluxes) is fairly resilient to change over the timescales relevant to this study (De La Rocha and Bickle 2005 Marine Geology 271: 267-282), except in extreme circumstances linked to major reductions in riverine silicon flux.**

4) The absence of an increase of bioavailable iron supply in WSP can't be judged only from dust proxy. **We acknowledge that it is risky making inferences about the role of iron purely by looking at dust. At the end of this paragraph we have added a statement that due to the lack of records that will give us the necessary information we are unable to account for possible changing fluxes of bioavailable iron from the Okhotsk Sea, winter mixing and other sources already identified earlier in the same paragraph. Similar statements have been added elsewhere in the manuscript.**

5) A weakening of the thermocline must be important for the supply of nutrients and carbon. **Although the halocline is the most important control, changes in the thermocline may indeed be relevant. However, at this time there is no SST record for the region preventing us from speculating about this. We have added words to this effect at the end of the paragraph.**

Reviewer 2 (responses in bold)

We have made all the changes and suggestions made by the reviewer with the exception of the following points/issues that we wish to highlight below. The comments about the biogenic barium record are covered in our response to Reviewer 1 above.

1) I'm not sure I understand how Si(OH)_4 consumption can be above 100% (Fig. 3C). **This is already explained in the manuscript, but we have added to the figure caption to make it clear that changes in consumption/supply are relative to mean conditions in MIS 5e.**

2) Max et al., 2014 (Geology), which the authors may have been unaware of at the time of submission, show clear episodes of cooling (and sea-ice advance) concomitant with the short-term oscillations observed in Greenland ice-cores, in a sediment core from the Bering Sea. While one can certainly not directly compare the two North Pacific records at face value, would it be still be possible to better constrain a maximum upper limit for the volume of freshwater needed to explain the diatom- $\delta^{18}\text{O}$ excursions? **Existing work has shown that the Bering Sea and subarctic North Pacific Ocean display very different response/changes over the same time interval. Comparisons in this instances are further limited by the very different environments between the site of Max et al (sea-ice margin) and ODP Site 882 [this study] (significantly beyond the sea-ice margin). Max et al. does not provide us with an indication of what the freshwater isotope member for ODP Site 882 might be.... whilst we could "pick" a range of possible end-members to try and establish the volume of freshwater needed to explain the $\delta^{18}\text{O}_{\text{diatom}}$ excursions, this would be highly speculative and likely of little value given the guesswork that would be involved.**

3) The argumentation in this paragraph [Section 4.3] is too speculative and only randomly supported by the available data. I would suggest to remove it altogether as it does not provide critical new insights to the manuscript. **We are unsure what part of Section 4.3 the reviewer finds speculative. Paragraph 1 outlines what the results show in relation to existing work. Paragraph 2 does much the same. We can only assume the reviewer is concerned by our focus on changes that are much smaller than those discussed earlier in the manuscript. We believe that we have been cautious in interpreting these changes to avoid over-interpretation and do not feel that this section is too speculative.**

Additional editor comments (responses in bold)

The text within the green and red shading in Figure 3 does not print clearly. **We have altered the figure accordingly and thank the editor for pointing out this issues.**

Photic zone changes in the North West Pacific Ocean from MIS 4-5e

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10 **Abstract**

In comparison to other sectors of the marine system, the palaeoceanography of the subarctic North Pacific Ocean is poorly constrained. New diatom isotope records of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ ($\delta^{13}\text{C}_{\text{diatom}}$, $\delta^{18}\text{O}_{\text{diatom}}$, $\delta^{30}\text{Si}_{\text{diatom}}$), are presented alongside existing geochemical and isotope records to document changes in photic zone conditions, including nutrient supply and the efficiency of the soft-tissue biological pump, between Marine Isotope Stage (MIS) 4 and MIS 5e. Peaks in opal productivity in MIS 5b/c and MIS 5e are both associated with the breakdown of the regional halocline stratification and increased nutrient supply to the photic zone. Whereas the MIS 5e peak is associated with low rates of nutrient utilisation, the MIS 5b/c peak is associated with significantly higher rates of nutrient utilisation. Both peaks, together with other smaller increases in productivity in MIS 4 and 5a culminate with a significant increase in freshwater input which strengthens/re-establishes the halocline and limits further upwelling of sub-surface waters to the photic zone. Whilst $\delta^{30}\text{Si}_{\text{diatom}}$ and previously published records of diatom $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{diatom}}$) (Brunelle et al. 2007, 2010) show similar trends until the latter half of MIS 5a, the records become anti-correlated after this juncture and into MIS 4, suggesting a possible change in photic zone state such as may occur with a shift to iron or silicon limitation.

26 **Keywords:** diatom, freshwater; MIS 5e; nutrient; productivity; stratification

28 **1 Introduction**

The modern day subarctic North West Pacific Ocean represent a major component of the global oceanic system acting as the one of the terminuses of the deep water thermohaline circulation. Today high precipitation [and low evaporation](#) in the region maintains a year round halocline in the water column (water depth = 100-150 m), reinforced in the summer/early autumn months by the presence of a seasonal thermocline (water depth = 50 m) (Emile-Geay et al., 2003; Antonov et al., 2009; Locarnini et al., 2009). This stratification exerts a major impact on the regional ocean by limiting the mixing of surface waters with underlying nutrient and carbon rich deep water and by preventing convection and formation of North Pacific

36 Deep Water (Emile-Geay et al., 2003; Menviel et al., 2012).

38 The initial development of the halocline and stratified water column has been attributed to the onset of major
Northern Hemisphere Glaciation (NHG) at 2.73 Ma, which ~~reduced Sea Surface Temperatures (SST) and~~
40 increased the flux of freshwater to the region, via increased monsoonal rainfall and/or glacial meltwater, and
reduced Sea Surface Temperatures (SST) (Sigman et al., 2004; Haug et al., 2005; Swann et al., 2006; Nie et
42 al., 2008). The ~~decrease cessation~~ of abyssal water upwelling associated with this may have contributed to
the establishment of globally cooler conditions and the expansion of glaciers across the Northern
44 Hemisphere from 2.73 Ma (Haug et al., 2005). Whilst the halocline appears to have prevailed through the
late Pliocene and early Quaternary glacial-interglacial cycles (Swann, 2010), other studies have shown that
46 the stratification boundary may have broken down in the Late Quaternary at glacial terminations and during
the early part of interglacials (Sarnthein et al., 2004; Jaccard et al., 2005, 2009, 2010; Galbraith et al., 2007,
48 2008, Gebhardt et al., 2008; Brunelle et al., 2010; Kohfeld and Chase 2011).

50 Developing a complete understanding of the nature of regional stratification in the subarctic North Pacific
Ocean is important for a number of reasons. Firstly, the palaeoceanographic history of the region remains
52 poorly constrained relative to other sectors of the global ocean. Secondly, with evidence of a pervasive link
between the subarctic Pacific and Southern Oceans (Haug et al., 2005; Jaccard et al., 2005, 2010) records
54 from the former can be used to further investigate teleconnections between these regions (Haug and Sigman,
2009; Sigman et al., 2010). Thirdly, with subsurface waters in the ocean interior rich in carbon and nutrients
56 (Galbraith et al., 2007; Gebhardt et al., 2008; Menviel et al., 2012), any weakening/removal of the halocline
has potential implications for the regional soft-tissue biological pump and ocean-atmospheric exchanges of
58 CO₂.

60 To further understand the subarctic North West Pacific Ocean, diatom isotope measurements of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$
and $\delta^{30}\text{Si}$ ($\delta^{13}\text{C}_{\text{diatom}}$, $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{30}\text{Si}_{\text{diatom}}$) are presented here from the open waters of ODP Site 882 between
62 MIS 4 and MIS 5e (Fig. 1). Existing research from the region has revealed two periods of elevated opal
concentration in this interval alongside large changes in proxies relating to nutrient supply and utilisation
64 (Jaccard et al., 2005, 2009; Brunelle et al., 2007, 2010). The new diatom isotope data presented here will
allow the changes in photic zone conditions and the response of the soft-tissue biological pump to be further
66 constrained. Diatoms, unicellular siliceous algae, are ideally suited for this purpose as they: 1) occupy the
uppermost sections of the water column above the halocline; 2) dominate export production in high latitude
68 and upwelling zones (Nelson et al., 1995); 3) represent a key component of the soft-tissue biological pump in
transferring carbon into the ocean interior by incorporating c. 23.5% of all carbon produced by net primary
70 production into their cellular organic matter (Mann, 1999).

72 2 Methods

ODP Site 882 is located on the western section of the Detroit Seamounts at a water depth of 3,244 m (50°22'N, 167°36'E) (Fig. 1). The age model used in this study is derived from the astronomical calibration of high resolution GRAPE density and magnetic susceptibility measurements with linear interpolation between selected tie-points (Jaccard et al., 2009). Ages are constrained by two radiocarbon dates and verified by correlating magnetic susceptibility and benthic foraminifera $\delta^{18}\text{O}$ records from ODP Sites 882 and 883. Samples were prepared for diatom isotope analysis using techniques previously employed at this site (Swann et al., 2006; 2008) with the 75-150 μm fraction analysed. Diatom biovolumes, calculated following Hillebrand et al. (1999) and Swann et al. (2008), show that samples in this fraction are dominated by a single taxa *Coscinodiscus radiatus* (Ehrenb.) (Fig. 2) which blooms throughout the year with elevated fluxes often occurring in autumn/early winter (Takahashi, 1986; Takahashi et al., 1996; Onodera et al., 2005). Consequently, the diatom isotope measurements obtained here are interpreted as primarily reflecting annually averaged conditions with a slight bias towards autumn/early winter months. Smaller size fractions which contain a greater diversity of taxa were not analysed due to the potential for vital effects in $\delta^{18}\text{O}_{\text{diatom}}$ (Swann et al., 2008). Sample purity was assessed for all samples using light microscopy and SEM with unclean samples disregarded for isotope analysis. Both techniques show the excellent preservation of diatoms in the sediment record and suggest that issues of dissolution/diagenesis are not relevant to this study.

$\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{30}\text{Si}_{\text{diatom}}$ were analysed following a combined step-wise fluorination procedure at the NERC Isotope Geoscience Laboratory (UK) (Leng and Sloane, 2008) with measurements made on a Finnigan MAT 253 and values converted to the VSMOW and NBS28 scale respectively using the NIGL within-run laboratory diatom standard BFC_{mod} which has been calibrated against NBS28. A small subset of the $\delta^{18}\text{O}_{\text{diatom}}$ data was previously published as part of an investigation in $\delta^{18}\text{O}_{\text{diatom}}$ vital effects in Swann et al., (2008) (see Supplementary Table 1). Where sufficient material remained following $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{30}\text{Si}_{\text{diatom}}$ analysis, samples were analysed for $\delta^{13}\text{C}_{\text{diatom}}$ using a Costech elemental analyser linked to an Optima mass spectrometer via cold trapping (Hurrell et al., 2011). Replicate analysis of sample material across the analysed interval indicate an analytical reproducibility (1σ) of 0.4‰, 0.06‰ and 0.3‰ for $\delta^{18}\text{O}_{\text{diatom}}$, $\delta^{30}\text{Si}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ respectively.

100

3 Results

Through the analysed interval $\delta^{13}\text{C}_{\text{diatom}}$ largely follows previously published siliceous productivity (opal) records from the region in indicating two intervals of higher productivity from 130-114 ka BP (MIS 5e) and 101-86 ka BP (MIS 5b/c) (Jaccard et al., 2005, 2009) (Fig. 3). Before/after each of these intervals $\delta^{13}\text{C}_{\text{diatom}}$ is lower at $<-18\text{‰}$. These trends are also largely mirrored by the $\delta^{30}\text{Si}_{\text{diatom}}$ and $\delta^{15}\text{N}$ records of diatom bound nitrogen ($\delta^{15}\text{N}_{\text{diatom}}$) (Brunelle et al., 2007, 2010) records of nutrient supply/utilisation, except during MIS 5e when values for both remain low and comparable to those in MIS 5d (Fig. 3). Following a return to lower values in MIS 5a, all productivity/nutrient proxies show a series of abrupt oscillations that continue into MIS 4 with values in this interval equivalent to the peaks and minima documented in MIS 5b-e.

110

Measurements of $\delta^{18}\text{O}_{\text{diatom}}$ can be classified into three stages: 1) periods of relative stability in MIS 5e and
112 MIS 5b-c (124-114 and 102-87 ka BP); 2) periods of significant decreases ($\geq 4\%$) in MIS 5d and MIS 5a
(113-100 and 85-76 ka BP); 3) periods of increase variability in MIS 5a-4 (75-57 ka BP) (Fig. 3). Intervals of
114 high and stable $\delta^{18}\text{O}_{\text{diatom}}$ values in MIS 5e and MIS 5b-c coincide with peaks in $\delta^{13}\text{C}_{\text{diatom}}$ and opal
concentrations. The termination of both productivity phases, as indicated by changes in $\delta^{13}\text{C}_{\text{diatom}}$, $\delta^{15}\text{N}_{\text{diatom}}$,
116 $\delta^{30}\text{Si}_{\text{diatom}}$ and opal concentrations, are then concordant with the large reductions in $\delta^{18}\text{O}_{\text{diatom}}$ during MIS 5d
and MIS 5a, suggesting a link between the processes controlling $\delta^{18}\text{O}_{\text{diatom}}$ and photic zone
118 productivity/nutrient utilisation. This is reinforced by the often synchronous changes between $\delta^{18}\text{O}_{\text{diatom}}$,
 $\delta^{30}\text{Si}_{\text{diatom}}$ and opal concentrations during MIS 5a and into MIS 4.

120

4 Discussion

122 *4.1 Environmental controls on diatom isotopes*

Given the limited number of published diatom isotope records in palaeoceanography, the section below
124 summarises the main controls on $\delta^{18}\text{O}_{\text{diatom}}$, $\delta^{30}\text{Si}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{diatom}}$. Diatom isotopes act as an alternative
proxy to records from planktonic foraminifera at sites, such as ODP Site 882, depleted in carbonates.
126 Measurements of $\delta^{18}\text{O}_{\text{diatom}}$ can be interpreted in the same way as those of planktonic foraminifera ($\delta^{18}\text{O}_{\text{foram}}$)
(Swann and Leng, 2009) with variations linked to changes in temperature ($-0.2\text{‰}/^{\circ}\text{C}$) (Brandriss et al., 1998;
128 Moschen et al., 2005; Dodd and Sharp, 2009; Crespin et al. 2010) and surface water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{water}}$). During
biomineralisation diatoms uptake silicon, in the form of silicic acid (H_4SiO_4), with the lighter ^{28}Si
130 preferentially used over ^{29}Si and ^{30}Si . With an enrichment factor independent of temperature, the
concentrations of CO_2 in the water ($p\text{CO}_{2(\text{aq})}$) and other vital effects (De La Rocha et al., 1997; Milligan et al.,
132 2004), $\delta^{30}\text{Si}_{\text{diatom}}$ reflects changes in photic zone silicic acid utilisation which is regulated by the biological
demand for silicic acid, the rate at which nutrients are supplied to the photic zone and the $\delta^{30}\text{Si}$ composition
134 of the silicic acid substrate ($\delta^{30}\text{Si}_{\text{DSi}}$) (De La Rocha, 2006; Reynolds et al., 2006).

136 A number of studies have examined the controls on $\delta^{13}\text{C}_{\text{diatom}}$ on carbon from bulk cellular diatom organic
material including the cytoplasm. Whilst palaeoenvironmental reconstructions solely analyse the cell wall,
138 which is preserved in the sediment and protected from dissolution by the diatom frustule (Abramson et al.,
2009), it is assumed that the controls on cell wall $\delta^{13}\text{C}_{\text{diatom}}$ are similar to those for bulk $\delta^{13}\text{C}_{\text{diatom}}$ as the cell-
140 wall organic matter forms a key template for diatom biomineralisation (Hecky et al., 1973; Swift and
Wheeler, 1992; Kröger et al., 1999; Sumper and Kröger, 2004). During photosynthesis, organic carbon
142 matter is formed from both HCO_3^- and $\text{CO}_{2(\text{aq})}$ (Tortell et al., 1997) using both active and indirect
transportation mechanisms (Sültemeyer et al., 1993) and C_3 and C_4 photosynthetic pathways (Reinfelder et
144 al., 2000). Marine studies including those from the Bering Sea and North Pacific Ocean have demonstrated
that the majority of diatom carbon originates from HCO_3^- via direct transportation (Tortell and Morel, 2002;

146 Cassar et al., 2004; Martin and Tortell, 2006, Tortell et al., 2006, 2008). Although $\text{HCO}_3^-:\text{CO}_{2(\text{aq})}$ uptake ratios
may alter with inter-species variations in cell morphologies (Martin and Tortell, 2008), no link exists with
148 changes in $p\text{CO}_{2(\text{aq})}$, Fe availability, growth rates, primary productivity or frustule area:volume ratios (Cassar
et al., 2004; Martin and Tortell, 2006, Tortell et al., 2006, 2008).

150

With ^{12}C preferentially fractionated over ^{13}C (Laws et al., 1995), $\delta^{13}\text{C}_{\text{diatom}}$ predominantly reflect changes in
152 photosynthetic carbon demand driven by variations in biological productivity or carbon cellular
concentrations. Smaller magnitude variations in $\delta^{13}\text{C}_{\text{diatom}}$ may then arise with changes in the composition of
154 the dissolved inorganic carbon substrate ($\delta^{13}\text{C}_{\text{DIC}}$) and through the intracellular and extra-cellular balance of
 CO_2 with an increase in photic zone $p\text{CO}_{2(\text{aq})}$ reducing $\delta^{13}\text{C}_{\text{diatom}}$ (Laws et al., 1995; Rau et al., 1996, 1997).

156 Whilst questions remain over the potential for $\delta^{13}\text{C}_{\text{diatom}}$ to be impacted by changes in $\text{HCO}_3^-:\text{CO}_2$ uptake,
growth rates, amino acid composition, cell morphology as well as the diffusion of carbon into the cell by the
158 enzyme RuBisCO (Laws et al., 1995, 1997, 2002; Rau et al., 1996, 1997, 2001; Popp et al., 1998; Cassar et
al., 2006), many of these physiological processes as well as the impact of inter-species vital effects (Jacot
160 Des Combes et al., 2008) can be partially circumvented by analysing samples comprised of a single taxa.

Consequently, with samples in this studies overwhelmingly dominated by *C. radiatus*, changes in $\delta^{13}\text{C}_{\text{diatom}}$
162 are primarily interpreted as reflecting changes in photic zone productivity (Fig. 2). We argue that the impact
of a changes in $\delta^{13}\text{C}_{\text{DIC}}$ –with negligible/minimal influence arising from variations in $p\text{CO}_{2(\text{aq})}$ – or $\delta^{13}\text{C}_{\text{DIC}}$ is
164 negligible due to the aforementioned evidence that $\delta^{13}\text{C}_{\text{DIC}}$ exerts only a minimal impact on $\delta^{13}\text{C}_{\text{diatom}}$, likely
within analytical error, although the lack of carbonates in the sediments prevents an independent $\delta^{13}\text{C}$ record
166 being established to prove this beyond doubt. (Fig. 2). Similarly we argue that higher $\delta^{13}\text{C}_{\text{diatom}}$ values in MIS
5e, when higher $p\text{CO}_{2(\text{aq})}$ should have acted to reduce $\delta^{13}\text{C}_{\text{diatom}}$, points towards $p\text{CO}_{2(\text{aq})}$ not exerting a
168 significant control on $\delta^{13}\text{C}_{\text{diatom}}$, although we are aware of the circular reasoning with this argument.

170 4.2 Changes in the regional biological pump (MIS 5e to MIS 5b)

Previously published opal concentration data (Jaccard et al. 2009) together with $\delta^{13}\text{C}_{\text{diatom}}$ data from this study
172 indicates two intervals of high siliceous productivity at ODP Site 882 through the analysed interval, the first
from 130-114 ka BP corresponding to the last interglacial (MIS 5e: 130-116 ka BP), the second from 101-86
174 ka BP covering the latter half of MIS 5c (105-93 ka BP) and most of MIS 5b (93-86 ka BP) (Jaccard et al.,
2009) (Fig. 3, green shading). Whilst records of Biogenic Barium (BioBa) capture the MIS 5e peak (Jaccard
176 et al., 2009), they fail to do so with the second flux event. Assessing the accuracy of BioBa as a measure of

export production is beyond the scope of this study. However Modern day calibrations others have noted the
178 lack of a relationship between BioBa and export production in the region (Serno et al. 2014) and speculated
that the mismatch can be attributed to early diagenetic remobilization of barium following a change in redox
180 state (Gebhardt et al., 2008). On the other hand all evidence points against an actual preservation/dissolution
issue in this BioBa record (see Jaccard et al., 2009) and so, in line with Jaccard et al. (2009), we interpret
182 BioBa as a measure of organic carbon export rather than siliceous productivity. With the isotope records

184 reported here derived from diatoms and the siliceous fraction of the sediment record, we focus our discussion
on the opal siliceous productivity record and only used BioBa as proxy of organic carbon export.

186 Similar to the Southern Ocean, the modern day subarctic North West Pacific Ocean photic zone is largely
188 limited by iron availability (Harrison et al., 1999; Tsuda et al., 2003). Accordingly, increases in bioavailable
190 iron represent a plausible mechanism for explaining the two main (opal inferred) productivity peaks during
192 MIS 5. Today iron supply is thought to primarily occur via aeolian dust deposition originating from East Asia
194 and the Badain Juran desert (Yuan and Zhang, 2006) and other global regions (Hsu et al., 2012). Additional
196 iron is then derived from volcanic activity (Banse and English, 1999), continental margins (Lam and Bishop,
198 2008), advection of waters from the Okhotsk Sea (Nishioka et al. 2007) and winter mixing of surface/sub-
200 surface water (Shigemitsu et al. 2012). Both productivity peaks occur without a corresponding increase in
202 aeolian dust at “Station 3” (close to ODP Site 882 at 50°00'N, 164°59'E) (Shigemitsu et al., 2007) or in East
204 Asian winter monsoon records from the Chinese Loess Plateau and other marine sites (Sun et al., 2006;
Zhang et al., 2009). Whilst a doubling in aeolian dust does occur at “Station 3” during the early stages of
MIS 5c, this ceases before any increase in $\delta^{13}\text{C}_{\text{diatom}}$, opal or other proxy at ODP Site 882 (Shigemitsu et al.,
2007). The absence of a significant increase in bioavailable iron would appear to rule out a major role for
iron in driving the two productivity peaks in MIS 5e and MIS 5b/c. This would be in line with evidence
indicating that productivity peaks during the last deglaciation across the North Pacific Ocean also occur
without a corresponding increase in aeolian dust or other iron source input (Kohfeld and Chase, 2011).
Others have also argued that iron only exerts a secondary or minor control on regional water column
productivity in the palaeo record (Kienast et al., 2004; Lam et al., 2013) whilst we are unable to account for
possible changing fluxes of bioavailable iron from the Okhotsk Sea, winter mixing and other sources
identified above.

206 4.2.1 Nutrient utilisation and supply

208 The deep and intermediate waters of the subarctic North Pacific Ocean contain some of the highest nutrient
210 levels in the world (Whitney et al. 2013). Accordingly productivity peaks over glacial-interglacial cycles,
212 including those covered in this study, have been linked to changes in the regional halocline and water column
214 stratification which would alter the advection of nutrient and carbon rich sub-surface waters into the photic
216 zone (Jaccard et al., 2005; Gebhardt et al., 2008). A key difference between the two productivity events in
MIS 5e and MIS 5b/c is the response of the biological community to raised photic zone nutrient availability.
Although productivity is high during MIS 5e, values are low for $\delta^{30}\text{Si}_{\text{diatom}}$ at ODP Site 882 (<1.0‰, n=3) and
for $\delta^{15}\text{N}_{\text{diatom}}$ (<6‰) at a nearby site (49°72'N, 168°30'E) (Brunelle et al., 2010) (Fig. 3). In contrast during
MIS 5b-c the productivity peak is concordant with an increase in $\delta^{30}\text{Si}_{\text{diatom}}$ and $\delta^{15}\text{N}_{\text{diatom}}$ to c. 1.2-1.3‰ and
>6‰ respectively (Fig. 3).

218 Changes in $\delta^{30}\text{Si}_{\text{diatom}}$ may reflect either increased biological uptake of silicic acid (consumption) and/or

220 changes in the supply of silicic acid to the photic zone. The modern day regional stratified water column is
 221 best represented by a closed system model in which a finite amount of silicic acid exists for
 222 biomineralisation (Reynolds et al. 2006). In contrast an unstratified water column would be reflected by an
 223 open system model with continual supply of silicic acid. By assuming that the two productivity peaks reflect
 224 a weakening in the stratification, an open system model can be used to investigate the controls on $\delta^{30}\text{Si}_{\text{diatom}}$:

$$226 \quad \delta^{30}\text{Si}_{\text{diatom}} = \delta^{30}\text{Si}(\text{OH})_4 + \varepsilon * f \quad (\text{Eq. 1})$$

228
 229 where $\delta^{30}\text{Si}(\text{OH})_4$ is the isotopic composition of dissolved silicic acid supplied to the photic zone, ε is the
 230 enrichment factor between diatoms and dissolved silicic acid and f is the fraction of utilised $\text{Si}(\text{OH})_4$
 231 remaining in the water. Existing work from the North Pacific Ocean has estimated $\delta^{30}\text{Si}(\text{OH})_4$ at 1.23‰ and ε
 232 as 1.0 (Reynolds et al. 2006). Using changes in $\text{Si}(\text{OH})_4$ consumption (Equation 1), ~~and~~ siliceous
 233 productivity (opal) and assuming modern day estimates of $\delta^{30}\text{Si}(\text{OH})_4$ are valid for the past, the supply of
 234 $\text{Si}(\text{OH})_4$ in the photic zone can be constrained relative to mean conditions during MIS 5e as:

$$236 \quad \text{Si}(\text{OH})_{4 \text{ supply}} = \frac{\text{Opal}_{\text{sample}} / \text{Opal}_{\text{MIS 5e}}}{(1 - f_{\text{consumed}}^{\text{sample}}) / (1 - f_{\text{consumed}}^{\text{MIS 5e}})} \quad (\text{Eq. 2})$$

238
 239 Estimates of $\text{Si}(\text{OH})_4$ consumption and supply from Equations 1 and 2 are only applicable for intervals when
 240 the water column represents an open system (e.g., the productivity peaks in MIS 5e and MIS 5b/c) and are
 241 dependant on modern day estimates of $\delta^{30}\text{Si}(\text{OH})_4$ being representative of past conditions. The results show
 242 that the productivity peaks in MIS 5e and MIS 5b/c are both closely correlated with elevated levels of
 243 $\text{Si}(\text{OH})_4$ being supplied to the photic zone (Fig. 3), supporting the suggesting that these intervals are linked to
 244 a reduction in water column stratification and an increase in the vertical flux of nutrients bearing sub-surface
 245 waters into the photic zone (Jaccard et al., 2005; Gebhardt et al., 2008). However, whilst the increase in
 246 $\text{Si}(\text{OH})_4$ supply in MIS 5b/c is matched by a corresponding increase in biological consumption of $\text{Si}(\text{OH})_4$,
 247 increasing the ratio of regenerated to preformed nutrients in the ocean interior, the opposite occurs during
 248 MIS 5e when the rates of $\text{Si}(\text{OH})_4$ consumption are at their lowest over the analysed interval. (Fig. 3). Whilst
 249 reduced $\text{Si}(\text{OH})_4$ consumption during MIS 5e could be linked to iron limitation, records indicate that aeolian
 250 dust deposition was equally low during both the MIS 5e and the MIS 5b/c productivity peaks. However, as
 before we are unable to account for changing in iron arising from non-aeolian sources.

252 4.2.2 Implications for $p\text{CO}_2$

254 Understanding the mechanisms that regulate changes in atmospheric concentrations of CO_2 ($p\text{CO}_2$) remains a
 255 key objective in palaeoclimatology. Previous research has demonstrated that the Southern and low-latitude
 256 Oceans act as the dominant source/sink of atmospheric CO_2 over glacial-interglacial cycles (Pichevin et al.,

2009; Fischer et al., 2010; Sigman et al., 2010). Whilst the North Pacific Ocean does not need to be invoked
258 to explain the full amplitude of glacial-interglacial changes, recent work has advocated a potential role for
the region in regulating atmospheric $p\text{CO}_2$ over the last termination (Rae et al. 2014).

260

Today the net annual ocean-atmosphere exchange of CO_2 in the subarctic North West Pacific Ocean is close
262 to zero, but alters from being a sink of atmosphere CO_2 in spring to a source in winter (Takahashi et al.,
2006; Ayers and Lozier, 2012) (Fig. 4a). This seasonal variability can be attributed to changes in the
264 biological pump and in SST which affects the solubility of CO_2 (Honda et al., 2002; Chierici et al., 2006;
Ayers and Lozier, 2012). A weakening of the halocline stratification in MIS 5e and MIS 5b/c would have
266 increased the advection of nutrient and carbon rich waters from the ocean interior, raising photic zone
 $p\text{CO}_{2(\text{aq})}$ and the potential for CO_2 to be ventilated into the atmosphere due to an air-sea disequilibrium in
268 CO_2 . This, however, is dependant on the response and relative efficiency of the biological pump in taking
advantage of the increased nutrient supply and altering the ratio of regenerated:performed nutrients to re-
270 export carbon into the deep ocean (Sigman et al., 2004, 2010; Marinov et al., 2008). Whilst changes in
temperature/thermocline may also have been important, similar to the modern day, no SST record currently
272 exists for the region.

274 During MIS 5e a scenario of both higher $p\text{CO}_{2(\text{aq})}$ and incomplete/low rates of nutrient utilisation suggests the
regional ocean could have ventilated CO_2 into the atmosphere faster than the soft-tissue biological pump
276 reabsorbed and sequestered CO_2 into the deep ocean (Fig. 4b) despite evidence for higher organic carbon
export (BioBa) in this period (Fig. 3). The culmination of this interval at the end of MIS 5e would have
278 resulted in the system returning to a stratified state, perhaps similar to the modern day water column (Fig. 4a)
with minimal air-sea fluxes of CO_2 . In contrast the opal productivity peak in MIS 5b/c is marked by similar
280 levels of photic zone $\text{Si}(\text{OH})_4$ supply as in MIS 5e but with c. 20% higher rates of $\text{Si}(\text{OH})_4$ consumption (Fig.
3, 4c). The combination of high siliceous productivity ($\text{opal}/\delta^{13}\text{C}_{\text{diatom}}$) and a highly efficient biological pump
282 ($\delta^{30}\text{Si}_{\text{diatom}}/\delta^{15}\text{N}_{\text{diatom}}$) during this interval suggests that the net flux of ocean-atmosphere CO_2 exchanges arising
from the sea-air disequilibrium could have remained close to zero if photosynthetic carbon demand was
284 similar to the rate of sub-surface carbon flux to the photic zone. Whilst a highly efficient soft-tissue
biological pump raises the possibility for the region to have acted as a net sink of atmospheric CO_2 , the
286 potential and significance for this is limited by the relatively low proportion of surface waters which reach
the deep ocean interior (Gebbie and Huybers, 2011) and low BioBa in this interval (Fig. 3).

288

Whilst Although the data suggests that changes in the regional photic zone may have contributed to variations
290 in atmospheric $p\text{CO}_2$ during MIS 5, both via the soft-tissue biological pump and associated changes in ocean
alkalinity, it is not possible to quantify the magnitude of any fluxes or assess whether they were
292 accompanied by a change in diatom silicification and cellular Si:C ratios. Firstly, insufficient purified diatom
material remains to measure diatom silicon concentrations. Secondly, although diatom elemental carbon

294 measurements obtained during the analysis of $\delta^{13}\text{C}_{\text{diatom}}$ increase from <0.3 wt.% in MIS 5e to c. 0.4 wt.% in
MIS 5b-d (see Supplementary Information) the analytical reproducibility for C_{diatom} is relatively high at 0.1%
296 (1σ) (Hurrell et al 2011) and measurements are derived from the cell wall material and not the bulk cellular
matter formed during photosynthesis. Furthermore, whilst other cores from the region show a similar double
298 peak in opal productivity during MIS 5 (Narita et al., 2002) records at other sites suggest that the second
peak is restricted to MIS 5b with no increase in MIS 5c (Shigemitsu et al., 2007). Such discrepancies either
300 suggest poor stratigraphic controls on the age-model for either core, or suggests the potential for significant
spatial variability across the region and reiterates that the magnitude of any ocean-atmosphere fluxes of CO_2
302 would be low compared to those occurring elsewhere in the marine system such as the Southern and low-
latitude oceans.

304

4.2.3 Freshwater controls on siliceous productivity

306 Records show that the decline in siliceous productivity for both intervals culminates with large decreases in
 $\delta^{18}\text{O}_{\text{diatom}}$ of c. 3-5‰ from c. 113 ka BP and 85 ka BP (Fig. 3, red shading). The magnitude of change is too
308 large to be driven by reductions in deep water upwelling or shifts in ocean water masses from both higher
and lower latitudes, which would only alter $\delta^{18}\text{O}_{\text{water}}$ by c. 1‰ (LeGrande et al., 2006). Instead the drop in
310 $\delta^{18}\text{O}_{\text{diatom}}$ suggests an input of isotopically depleted freshwater that may be similar in origin to events
documented at the same site during the Late Pliocene/early Quaternary (Swann, 2010).

312

Although the modern day regional halocline is maintained by high precipitation and low evaporation in the
314 region (Emile-Geay et al., 2003), it is difficult to envisage a sufficient increase in precipitation to initiate a 3-
5‰ decrease in $\delta^{18}\text{O}_{\text{diatom}}$. This is reiterated by evidence that monsoonal activity was largely stable during
316 MIS 5b-e (Sun et al., 2006; Zhang et al., 2009). At the same time the potential for a glacial source is
questioned by evidence indicating a restricted glaciation in North East Russia, closest to ODP Site 882, at the
318 Last Glacial Maximum (LGM) (Barr and Clark 2011, 2012), although other work suggests these ice-sheets
may have been considerably larger prior to the LGM (Bigg et al., 2008; Barr and Solomina, 2014). Recent
320 work has shown that both of the major decreases in $\delta^{18}\text{O}_{\text{diatom}}$ coincide with increases in IRD accumulation in
some, but not all, cores from the Okhotsk Sea (Nürnberg et al. 2011). It has also been argued that the
322 regional water column was regulated by significant inputs of meltwater from the northern American ice
sheets during the last deglaciation (Lam et al., 2013). In either case, the decrease in $\delta^{18}\text{O}_{\text{diatom}}$ at the end of
324 each siliceous productivity peak suggests that inputs of freshwater helped re-establish/strengthen the
halocline, limiting the upwelling of nutrient/ CO_2 rich sub-surface waters and biological activity. However,
326 with the decrease in $\delta^{18}\text{O}_{\text{diatom}}$ only occurring after the initial decline in productivity, freshwater can only be
acting as a secondary control in re-establishing the halocline.

328

Previous work has suggested a link between changes in the subarctic North West Pacific Ocean and the
330 Southern Ocean (Jaccard et al., 2005, 2010; Brunelle et al., 2007; Shigemitsu et al., 2007; Galbraith et al.,

2008; Sigman et al., 2010). The most viable mechanism for synchronous changes between polar regions are
332 temperature and salinity driven variations in water column density (Brunelle et al., 2007). For example a
cooling of polar SST would reduce the rate of sub-surface upwelling into the photic zone (de Boer et al.,
334 2007), lowering nutrient availability and potentially triggering the initial decline in *siliceous* productivity. At
the same time, a decrease in SST would increase the sensitivity of the water column to subsequent changes in
336 salinity, making the region highly vulnerable to inputs of freshwater which would strengthen the water
column and inhibit productivity (Sigman et al., 2004). Additional reductions in *siliceous* productivity may
338 then arise from lower North Atlantic overturning and associated deep-water incursions and upwelling in the
North Pacific (Schmittner, 2005). Support for a series of events similar to this at ODP Site 882 lies with the
340 concordant decreases at ODP Site 882 between supplied $\text{Si(OH)}_4/\delta^{30}\text{Si}_{\text{diatom}}/\text{opal}$ and Antarctic (δD)/NGRIP
($\delta^{18}\text{O}_{\text{ice}}$) ice-core records (NGRIP, 2004; Jouzel et al., 2007) at the start of each productivity decline from c.
342 118 and 89 ka BP respectively (Fig. 3). The final switch to a low productivity system then coincides with the
later decreases in $\delta^{18}\text{O}_{\text{diatom}}$ at 113 and 85 ka BP, suggesting that the climatic deterioration associated with
344 lower $\delta D/\delta^{18}\text{O}_{\text{ice}}$ may have fuelled the increase in precipitation and/or an advancement of regional glaciers
around the North Pacific Basin that triggered the increase in freshwater input. Whilst it remains unclear what
346 initiated either *siliceous* productivity peak, it can be speculated that reductions in freshwater after 100 ka BP
could have weakened the halocline and created the conditions for the second productivity bloom to
348 eventually develop later in MIS 5b-c.

350 *4.3 Photic zone changes from MIS 4-5a*

Previous research has documented reduced levels of productivity in the North West Pacific Ocean during the
352 last glacial in response to surface water stratification (Narita et al., 2002; Jaccard et al., 2005, 2010; Brunelle
et al., 2007; 2010; Shigemitsu et al., 2007; Galbraith et al., 2008; Gebhardt et al., 2008). From the latter half
354 of MIS 5a onwards records of $\delta^{15}\text{N}_{\text{diatom}}$ and $\delta^{30}\text{Si}_{\text{diatom}}/\text{Si(OH)}_4$ consumption become anti-correlated (Fig. 3).
Combined with a long-term shift to lower rates of Si(OH)_4 supply and higher rates of Si(OH)_4 consumption,
356 this supports suggestions that changes in dust/iron inputs in the last glacial may have helped regulate the
biological pump by altering the biological demand for individual nutrients (Brunelle et al., 2007, 2010;
358 Galbraith et al., 2008; Shigemitsu et al., 2008), in this case by increasing biological uptake of silicon over
nitrogen to the extent that Si(OH)_4 consumption in MIS 4 was up to 40% higher than during MIS 5e.
360 Elevated Si(OH)_4 consumption may also indicate that the availability of Si(OH)_4 rather than iron may
have ultimately limited *siliceous* productivity over this interval, in line with a previous suggestion by Kienast
362 et al (2004).

364 Superimposed on a trend of low *siliceous* productivity during MIS 5a and MIS 4 are two small-moderate
increase in opal at c. 76-74 ka BP and c. 70 ka BP (Fig. 3, green shading). The increase at 70 ka BP does not
366 coincide with any samples analysed in this study, but the increase at 76-74 ka BP coincides with higher
 $\delta^{13}\text{C}_{\text{diatom}}$, $\delta^{30}\text{Si}_{\text{diatom}}$ and Si(OH)_4 supply/consumption (open model). Similar to before, both opal peaks

368 culminate with a 2-3‰ reduction in $\delta^{18}\text{O}_{\text{diatom}}$ (Fig. 3, red shading), reiterating the role of freshwater in
controlling photic zone dynamics in an era that coincides with increased monsoonal and thus precipitation
370 variability (Sun et al., 2006; Shigemitsu et al., 2007; Zhang et al., 2009). However, whereas the earlier
declines in siliceous productivity during MIS 5e and MIS 5b/c are accompanied by reductions in both
372 $\text{Si}(\text{OH})_4$ supply and consumption, here the declines initially occur with reduced $\text{Si}(\text{OH})_4$ supply and higher
rates of $\text{Si}(\text{OH})_4$ consumption. This advocates the aforementioned suggestion that the photic zone shifted to a
374 new state from the end of MIS 5a, highlighted by further large changes in $\text{Si}(\text{OH})_4$ consumption in MIS 4
that do not coincide with a changes in siliceous productivity or $\delta^{18}\text{O}_{\text{diatom}}$ (Fig. 3).

376

5 Conclusions

378 Results here provide evidence for significant temporal changes in the strength and efficiency of the regional
soft-tissue biological pump from MIS 4-5e, altering the ratio of regenerated to preformed nutrients in the
380 water column. In particular the results show evidence of an inefficient soft-tissue biological pump from 124-
114 ka BP, creating the potential for the region to have played a role in maintaining the warm climate of the
382 last interglacial through the ventilation of oceanic CO_2 to the atmosphere. In addition to highlighting
temporal changes in the biological pump, the data also reveals that the end of both these and other siliceous
384 productivity fluxes over the analysed interval are linked to significant increases in freshwater input to the
region, re-establishing/strengthening the halocline and limiting the sub-surface supply of nutrient and carbon
386 rich waters to the photic zone. However, further work is needed to resolve the source of these freshwater
inputs and the mechanisms responsible for initiating the ~~initial~~ increase in siliceous productivity and $\text{Si}(\text{OH})_4$
388 supply to the photic zone. Finally, whilst these findings reiterate earlier work in indicating a highly dynamic
and changing water column in the subarctic North Pacific Ocean during the last glacial-interglacial cycle,
390 further work is needed to assess the spatial representativeness of these results in other sectors of the subarctic
North Pacific Ocean.

392

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398

References

- 400 Abramson, L., Wirrick, S., Lee, C., Jacobsen, C., and Brandes, J. A.: The use of soft x-ray spectromicroscopy to investigate the
distribution and composition of organic matter in a diatom frustule and a biomimetic analog, *Deep-Sea Res Pt II*, 56, 1369-1380,
402 2009.
- Adams, J. M., Faure, H., Faure-Denard, L., McGlade, J. M., and Woodward, F. I.: Increases in terrestrial carbon storage from the Last
404 Glacial Maximum to the present, *Nature*, 348, 711-714, 1990.

- 406 Antonov, J. I., Seidov, D., Boyer, T. P., Locarnini, R. A., Mishonov, A. V., Garcia, H. E., Baranova, O. K., Zweng, M. M., and Johnson, D. R.: World Ocean Atlas 2009, Volume 2: Salinity, in: Levitus, S. (Ed.), NOAA Atlas NESDIS 69, U.S. Government Printing Office, Washington, D.C., 184 pp, 2010.
- 408 Ayers, J. M. and Lozier, M. S.: Unraveling dynamical controls on the North Pacific carbon sink, *Journal of Geophys Res.*, 117, C01017, 2012.
- 410 Banse, K. and English, D. C.: Comparing phytoplankton seasonality in the eastern and western subarctic Pacific and the western Bering sea, *Prog Oceanogr.*, 43, 235-288, 1999.
- 412 Barr, I. D. and Clark, C. D.: Glaciers and climate in Pacific Far NE Russia during the Last Glacial Maximum, *J Quaternary Sci.*, 26, 227-237, 2011
- 414 Barr, I. D. and Clark, C. D.: Late Quaternary glaciations in Far NE Russia; combining moraines, topography and chronology to assess regional and global glaciation synchrony, *Quaternary Sci Rev.*, 53, 72-87, 2012.
- 416 Barr, I. D. and Solomina, O.: Pleistocene and Holocene glacier fluctuations upon the Kamchatka Peninsula, *Global Planet Change.*, 113, 110-120, 2014
- 418 Bigg, G. R., Clark, C. D., and Hughes, A. L. C.: A last glacial ice sheet on the Pacific Russian coast and catastrophic change arising from coupled ice–volcanic interaction, *Earth Planet Sc Lett.*, 265, 559-570, 2008.
- 420 Brandriss, M. E., O’Neil, J. R., Edlund, M. B., and Stoermer, E. F.: Oxygen isotope fractionation between diatomaceous silica and water. *Geochim Cosmochim Ac.*, 62, 1119-1125, 1998
- 422 Brunelle, B. G., Sigman, D. M., Cook, M. S., Keigwin, L. D., Haug, G. H., Plessen, B., Schettler, G., and Jaccard, S. L.: Evidence from diatom-bound nitrogen isotopes for subarctic Pacific stratification during the last ice age and a link to North Pacific denitrification changes, *Paleoceanography*, 22, PA1215, doi:10.1029/2005PA001205, 2007
- 424 Brunelle, B. G., Sigman, D. M., Jaccard, S. L., Keigwin, L. D., Plessen, B., Schettler, G., Cook, M. S., and Haug, G. H.; Glacial/interglacial changes in nutrient supply and stratification in the western subarctic North Pacific since the penultimate glacial maximum, *Quaternary Sci Rev.*, 29, 2579-2590, 2010.
- 428 Cassar, N., Laws, E. A., Bidigare, R. R., and Popp, B. N.: Bicarbonate uptake by Southern Ocean phytoplankton, *Global Biogeochem Cy.*, 18, GB2003, doi:10.1029/2003GB002116, 2004.
- 430 Cassar, N., Laws, E. A., and Popp, B. N.: Carbon isotopic fractionation by the marine diatom *Phaeodactylum tricorutum* under nutrient- and light-limited growth condition, *Geochim Cosmochim Ac.*, 70, 5323-5335, 2006.
- 432 Chierici, M., Fransson, A., and Nojiri, Y.: Biogeochemical processes as drivers of surface $f\text{CO}_2$ in contrasting provinces in the subarctic North Pacific Ocean, *Global Biogeochem Cy.*, 20, GB1009, doi:10.1029/2004GB002356, 2006
- 434 Crespin, J., Sylvestre, F., Alexandre, A., Sonzogni, C., Pailles, C., and Perga, M-E.: Re-examination of the temperature-dependent relationship between $\delta^{18}\text{O}_{\text{diatoms}}$ and $\delta^{18}\text{O}_{\text{lake water}}$ and implications for paleoclimate inferences, *J Paleolimnol.*, 44, 547-557, 2010.
- 436 de Boer, A. M., Sigman, D. M., Toggweiler, J. R. and Russell, J. L.: Effect of global ocean temperature change on deep ocean ventilation, *Paleoceanography*, 22, PA2210, doi:10.1029/2005pa001242, 2007.
- 438 De La Rocha, C. L.: Opal-based isotopic proxies of paleoenvironmental conditions, *Global Biogeochem Cy.*, 20, GB4S09. doi:10.1029/2005GB002664, 2006.
- 440 De La Rocha, C. L., Brzezinski, M. A., and DeNiro, M. J.: Fractionation of silicon isotopes by marine diatoms during biogenic silica formation, *Geochim Cosmochim Ac.*, 61, 5051-5056, 1997.
- 442 De Pol-Holz, R., Keigwin, L., Southon, J., Hebbeln D., and Mohtadi, M.: No signature of abyssal carbon in intermediate waters off Chile during deglaciation, *Nat Geosci.*, 3, 192-195, 2010.
- 444 Dodd, J. P., and Sharp, Z. D.: A laser fluorination method for oxygen isotope analysis of biogenic silica and a new oxygen isotope calibration of modern diatoms in freshwater environments, *Geochim Cosmochim Ac.*, 74, 1381-1390, 2010.

- 446 Emile-Geay, J., Cane, M. A., Naik, N., Seager, R., Clement, A. C., and van Green, A.: Warren revisited: atmospheric freshwater
448 fluxes and “Why is no deep water formed in the North Pacific”, *J Geophys Res.*, 108, C6, 3178, doi:10.1029/2001JC001058,
2003.
- Fischer, H. Schmitt, J., Lüthi, D., Stocker, T. F., Tschumi, T., Parekh, P., Joos, F., Köhler, P., Völker, C., Gersonde, R., Barbante, C.,
450 Le Floch, M., Raynaud, D., Wolff, E.: The role of Southern Ocean processes in orbital and millennial CO₂ variations - a
synthesis, *Quaternary Sci Rev.*, 29, 193-205, 2010.
- 452 Galbraith, E. D., Jaccard, S. L., Pedersen, T. F., Sigman, D. M., Haug, G. H., Cook, M., Southon, J. R., and Francois, R.: Carbon
dioxide release from the North Pacific abyss during the last deglaciation, *Nature*, 449, 890-894, 2007.
- 454 Galbraith, E. D., Kienast, M., Jaccard, S. L., Pedersen, T. F., Brunelle, B. G., Sigman, D. M., and Kiefer, T.: Consistent relationship
456 between global climate and surface nitrate utilization in the western subarctic Pacific throughout the last 500 ka.
Paleoceanography, 23, PA2212, doi:10.1029/2007PA001518, 2008.
- Gebhardt, H., Sarnthein, M., Grootes, P. M., Kiefer, T., Kuehn, H., Schmieder, F., and Rohl, U.: Paleonutrient and productivity
458 records from the subarctic North Pacific for Pleistocene glacial terminations I to V, *Paleoceanography*, 23, PA4212,
doi:10.1029/2007PA001513, 2008
- 460 Gebbie, G. and Huybers, P.: How is the ocean filled? *Geophys Res Lett.*, 38, L06604, 2008.
- Harrison, P. J., Boyd, P. W., Varela, D. E., Takeda, S., Shiimoto, A., and Odate, T.: Comparison of factors controlling phytoplankton
462 productivity in the NE and NW subarctic Pacific gyres, *Prog Oceanogr.*, 43, 205-234, 1999.
- Haug, G. H. and Sigman D. M.: Polar twins, *Nat Geosci.*, 2, 91-92, 2009.
- 464 Haug, G. H., Ganopolski, A., Sigman, D. M., Rosell-Mele, A., Swann, G. E. A., Tiedemann, R., Jaccard, S., Bollmann, J., Maslin, M.
A., Leng, M. J., and Eglinton, G.: North Pacific seasonality and the glaciation of North America 2.7 million years ago, *Nature*,
466 433, 821-825, 2005.
- Hecky, R. E., Mopper K., Kilham, P., and Degens, E. T.: The amino acid and sugar composition of diatom cell-walls, *Mar Biol.*, 19,
468 323-331, 1973.
- Hillebrand, H., Dürselen, C-D., Kirschtel, D., Pollinger, U., and Zohary, T.: Biovolume calculation for pelagic and benthic
470 microalgae, *J Phycol.*, 35, 403-424, 1999.
- Honda, M. C., Imai, K., Nojiri, Y., Hoshi, F., Sugawara, T., Kusakabe, M.: The biological pump in the northwestern North Pacific
472 based on fluxes and major components of particulate matter obtained by sediment-trap experiments (1997–2000), *Deep-Sea Res*
Pt II., 49, 5595-5625, 2002.
- 474 Hsu, S-C., Huh, C-A., Lin, C-Y., Chen, W-N., Mahowald, N. M., Liu, S-C., Chou, C. C. K., Liang, M-C., Tsai, C-J., Lin, F-J., Chen,
J-P., and Huang, Y-T.: Dust transport from non-East Asian sources to the North Pacific, *Geophys Res Lett.*, 39, L12804,
476 doi:10.1029/2012GL051962, 2012.
- Hurrell, E. R., Barker, P. A., Leng, M. J., Vane, C. H., Wynn, P., Kendrick, C. P., Verschuren, D., and Street-Perrott, F.: Developing a
478 methodology for carbon isotope analysis of lacustrine diatoms, *Rapid Commun Mass Sp.*, 25, 1567-1574, 2011.
- Jaccard, S. L., Haug, G. H., Sigman, D. M., Pedersen, T. F., Thierstein, H. R., and Röhl, U.: Glacial/interglacial changes in subarctic
480 North Pacific stratification. *Science*, 308, 1003-1006, 2005
- Jaccard, S. L., Galbraith, E. D., Sigman, D. M., Haug, G. H., Francois, R., Pedersen, T. F., Dulski, P., and Thierstein, H. R.:
482 Subarctic Pacific evidence for a glacial deepening of the oceanic respired carbon pool, *Earth Planet Sc Lett.*, 277, 156-165, 2009.
- Jaccard, S. L., Galbraith, E. D., Sigman, D. M., and Haug G. H.: A pervasive link between Antarctic ice core and subarctic Pacific
484 sediment records over the past 800 kyrs, *Quaternary Sci Rev.*, 29, 206-212, 2010
- Jacot des Combes, H., Esper, O., De La Rocha, C. L., Abelmann A., Gersonde R., Yam R., and Shemesh A. Diatom $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and
486 C/N since the Last Glacial Maximum in the Southern Ocean: Potential Impact of Species Composition, *Paleoceanography*, 23,
PA4209, doi:10.1029/2008PA001589, 2008.

- 488 Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J., Barnola, J. M.,
Chappellaz, J., Fischer, H., Gallet, J. C., Johnsen, S., Leuenberger, M., Loulergue, L., Luethi, D., Oerter, H., Parrenin, F.,
490 Raisbeck, G., Raynaud, D., Schilt, A., Schwander, J., Selmo, E., Souchez, R., Spahni, R., Stauffer, B., Steffensen, J.P., Stenni, B.,
Stocker, T. F., Tison, J. L., Werner, M., and Wolff, E. W.: Orbital and millennial Antarctic climate variability over the past
492 800,000 years, *Science*, 371, 793-796, 2007.
- Kienast, S. S., Hendy, I. L., Crusius, J., Pedersen, T. F., and Calvert, S. E.: Export production in the subarctic North Pacific over the
494 last 800 kyrs: no evidence for iron fertilization?, *J Oceanogr.*, 60, 189-203, 2004.
- Kohfeld, K. E. and Chase, Z.: Controls on deglacial changes in biogenic fluxes in the North Pacific Ocean, *Quaternary Sci Rev.*, 30,
496 3350-3363, 2011
- Kröger, N., Deutzmann, R. and Sumper, M.: Polycationic peptides from diatom biosilica that direct silica nanosphere formation,
498 *Science*, 286, 1129-1132, 1999.
- Lam, P. J. and Bishop, J. K. B.: The paleoclimatic record provided by eolian deposition in the deep-sea: the geologic history of wind,
500 *Geophys Res Lett.*, 35, L07608, doi:10.1029/2008GL033294, 2008.
- Lam, P. J., Robinson, L. F., Blusztajn, J., Li, C., Cook, M. S., McManus, J. F., Keigwin, L. D.: Transient stratification as the cause of
502 the North Pacific productivity spike during deglaciation, *Nat Geosci.*, 6, 622-626, 2013.
- Laws, E. A., Popp, B. N., Bidigare, R. R., Kennicutt, M. C., and Macko, S. A.: Dependence of phytoplankton carbon isotopic
504 composition on growth rate and $(\text{CO}_2)_{\text{aq}}$: theoretical considerations and experimental results, *Geochim Cosmochim Acta.*, 59, 1131-
1138, 1995.
- 506 Laws, E. A., Bidigare, R. R., and Popp, N. B.: Effect of growth rate and CO_2 concentration on carbon isotope fractionation by the
marine diatom *Phaeodactylum tricornutum*, *Limnol Oceanogr.*, 42, 1552-1560, 1997.
- 508 Laws, E. A., Popp, B. N., Cassar, N., and Tanimoto, J.: ^{13}C discrimination patterns in oceanic phytoplankton: likely influence of CO_2
concentrating mechanisms, and implications for palaeoreconstructions, *Funct Planet Biol.*, 29, 323-333, 2002.
- 510 LeGrande, A. N. and Schmidt, G.A.: Global gridded data set of the oxygen isotopic composition in seawater, *Geophys Res Lett.*, 33,
L12604, doi: 10.1029/2006GL026011, 2006.
- 512 Leng, M. J. and Sloane H.J.: Combined oxygen and silicon isotope analysis of biogenic silica, *J Quaternary Sci.*, 23, 313-319, 2008.
- Locarnini, R. A., Mishonov, A. V., Antonov, J. I., Boyer, T. P., Garcia, H. E., Baranova, O. K., Zweng, M. M., and Johnson, D. R.:
514 *World Ocean Atlas 2009, Volume 1: Temperature*, in: Levitus, S. (Ed.), NOAA Atlas NESDIS 68, U.S. Government Printing
Office, Washington, D.C., 184 pp, 2010.
- 516 Mann D.G.: The species concept in diatoms., *Phycologia*, 38, 437-495, 1999.
- Marinov, I., Follows, M., Gnanadesikan, A., Sarmiento, J. L., and Slater, R. D.: How does ocean biology affect atmospheric $p\text{CO}_2$?
518 *Theory and models*, *J Geophys Res.*, 113, C07032, doi:10.1029/2007JC004598, 2008
- Martin, C. L. and Tortell, P. D., Bicarbonate transport and extracellular carbonic anhydrase activity in Bering Sea phytoplankton
520 assemblages: results from isotope disequilibrium experiments, *Limnol Oceanogr.*, 51, 2111-2121, 2006
- Martin, C. L. and Tortell, P.D.: Bicarbonate transport and extracellular carbonic anhydrase in marine diatoms, *Physiol Plantarum.*,
522 133, 106-116, 2008.
- Menviel, L., Timmermann, A., Timm, O., Mouchet, A., Abe-Ouchi, A., Chikamoto, M. O., Harada, N., Ohgaito, R., and Okazaki,
524 Y.: Removing the North Pacific halocline: Effects on global climate, ocean circulation and the carbon cycle, *Deep-Sea Res Pt II.*,
61-64, 106-113, 2012.
- 526 Milligan, A. J., Varela, D. E., Brzezinski, M. A., and Morel, F. M. M.: Dynamics of silicon metabolism and silicon isotopic
discrimination in a marine diatom as a function of $p\text{CO}_2$, *Limnol Oceanogr.*, 49, 322-329, 2004.
- 528 Moschen, R., Lücke, A., and Schleser, G.: Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and
palaeoclimatology, *Geophys Res Lett.*, 32, L07708, doi:10.1029/2004GL022167, 2005.

- 530 Narita, H., Sato, M., Tsunogai, S., Murayama, M., Ikehara, M., Nakatsuka, T., Wakatsuchi, M., Harada, N., and Ujiie, Y.: Biogenic
opal indicating less productive northwestern North Pacific during the glacial ages, *Geophys Res Lett.*, 29, 1732,
532 doi:10.1029/2001GL014320, 2002.
- Nelson, D. M., Tréguer, P., Brzezinski, M. A., Leynaert, A., and Quéguiner, B.: Production and dissolution of biogenic silica in the
534 ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation, *Global Biogeochem
Cy.*, 9, 359-372, 1995.
- 536 North Greenland Ice Core Project members: High-resolution record of Northern Hemisphere climate extending into the last
interglacial period, *Nature*, 431, 147-151, 2004.
- 538 Nie, J., King, J., Liu, Z., Clemens, S., Prell, W., and Fang, X.: Surface-water freshening: a cause for the onset of North Pacific
stratification from 2.75 Ma onward?, *Global Planet Change.*, 64, 49-52, 2008.
- 540 Nishioka, J., Ono, T., Saito, H., Nakatsuka, T., Takeda, S., Yoshimura, T., Suzuki, K., Kuma, K., Nakabayashi, S., Tsumune, D.,
Mitsudera, H., Johnson, W.K., and Tsuda, A.: Iron supply to the western subarctic Pacific: Importance of iron export from the Sea
542 of Okhotsk, *J Geophys Res.*, 112, C10012, doi:10.1029/2006JC004055, 2007.
- Nürnberg, D., Dethleff, D., Tiedemann, R., Kaiser, A., and Gorbarenko, S. A.: Okhotsk Sea ice coverage and Kamchatka glaciation
544 over the last 350 ka — Evidence from ice-rafted debris and planktonic $\delta^{18}\text{O}$, *Palaeogeogr Palaeoclimatol.*, 310, 191-205, 2011.
- Nishioka, J., Ono, T., Saito, H., Nakatsuka, T., Takeda, S., Yoshimura, T., Suzuki, K., Kuma, K., Nakabayashi, S., Tsumune, D.,
546 Mitsudera, H., Johnson, W. K., and Tsuda, A.: Iron supply to the western subarctic Pacific: Importance of iron export from the
Sea of Okhotsk, *J Geophys Res*, 112, C10012, doi:10.1029/2006JC004055, 2007.
- 548 Onodera, J., Takahashi, K., Honda, M. C.: Pelagic and coastal diatom fluxes and the environmental changes in the northwestern
North Pacific during 1997-2000, *Deep-Sea Res Pt II.*, 52, 2218-2239, 2005.
- 550 Pichevin, L. E., Reynolds, B. C., Ganeshram, R. S., Cacho, I., Pena, L., Keefe, K., Ellam, R.M.: Enhanced carbon pump inferred
from relaxation of nutrient limitation in the glacial ocean, *Nature*, 459, 1114-1118, 2009.
- 552 Popp, B. N., Laws, E. A., Bidigare, R. R., Dore, J. E., Hanson, K. L., and Wakeham, S. G.: Effect of phytoplankton cell geometry on
carbon isotopic fractionation, *Geochim Cosmochim Acta.*, 62, 69-77, 1998.
- 554 Rau, G. H., Riebesell, U., and Wolf-Gladrow, D.: A model of photosynthetic ^{13}C fractionation by marine phytoplankton based on
diffusive molecular CO_2 uptake, *Mar Ecol-Prog Ser.*, 133, 275-285, 1996.
- 556 Rau, G. H., Riebesell, U., and Wolf-Gladrow, D.: $\text{CO}_{2\text{aq}}$ -dependent photosynthetic ^{13}C fractionation in the ocean: a model versus
measurements, *Global Biogeochem Cy.*, 11, 267-278, 1997.
- 558 Rau, G. H., Chavez, F. P., and Friederich, G. E.: Plankton $^{13}\text{C}/^{12}\text{C}$ variations in Monterey Bay, California: evidence of non-diffusive
inorganic carbon uptake by phytoplankton in an upwelling environment, *Deep-Sea Res Pt I.*, 48, 79-94, 2001.
- 560 Rae, J. W. B., Sarnthein, M., Foster, G. L., Ridgwell, A., Grootes, P. M., and Elliott, T.: Deep water formation in the North Pacific
and deglacial CO_2 rise, *Paleoceanography*, 29, 645-667, 2014.
- 562 Reinfelder, J. R., Kraepiel, A. M. L., and Morel, F. M. M.: Unicellular C_4 photosynthesis in a marine diatom, *Nature*, 407, 996-999,
2000.
- 564 Reynolds, B. C., Frank, M., and Halliday, A. N.: Silicon isotope fractionation during nutrient utilization in the North Pacific, *Earth
Planet Sc Lett.*, 244, 431-443, 2006.
- 566 Sarnthein, M., Gebhardt, H., Kiefer, T., Kucera, M., Cook, M., and Erlenkeuser, H.: Mid Holocene origin of the sea-surface salinity
low in the subarctic North Pacific, *Quaternary Sci Rev.*, 23, 2089-2099, 2004.
- 568 Schmittner, A.: Decline of the marine ecosystem caused by a reduction in the Atlantic overturning circulation, *Nature*, 434, 628-633,
2005.
- 570 Serno, S., Winckler, G., Anderson, R. F., Hayes, C. T., Ren, H., Gersonde, R., and Haug, G. H.: Using the natural spatial pattern of
marine productivity in the Subarctic North Pacific to evaluate paleoproductivity proxies. *Paleoceanography*, 29, 438-453, 2014.

- 572 Shigemitsu, M., Narita, H., Watanabe, Y. W., Harada, N., and Tsunogai, S.: Ba, Si, U, Al, Sc, La, Th, C and $^{13}\text{C}/^{12}\text{C}$ in a sediment core
in the western subarctic Pacific as proxies of past biological production, *Mar Chem.*, 106, 442-455, 2007.
- 574 Shigemitsu, M., Watanabe, Y. W., and Narita, H.: Time variations of $\delta^{15}\text{N}$ of organic nitrogen in deep western subarctic Pacific
sediment over the last 145 ka, *Geochem Geophys Geosy.*, 9, Q10012, doi:10.1029/2008GC001999, 2008.
- 576 Shigemitsu, M., Okunishi, T., Nishioka, J., Sumata, H., Hashioka, T., Aita, M. N., Smith, S. L., Yoshie, N., Okada, N., and Yamanaka,
Y.: Development of a one-dimensional ecosystem model including the iron cycle applied to the Oyashio region, western subarctic
578 Pacific, *J Geophys Res.*, 117, C06021, doi:10.1029/2011JC007689, 2012.
- Sigman, D. M., Jaccard, S. L., and Haug, G. H.: Polar ocean stratification in a cold climate, *Nature*, 428, 59-63, 2004.
- 580 Sigman, D. M., Hain, M. P., and Haug, G. H.: The polar ocean and glacial cycles in atmospheric CO_2 concentration, *Nature*, 47-55,
2010.
- 582 Sültemeyer, D., Schmidt, C., and Fock, H. P.: Carbonic anhydrases in higher plants and aquatic microorganisms, *Physiol Plantarum.*,
88, 179-190, 1993.
- 584 Sumper, M. and Kröger, N.: Silica formation in diatoms: the function of long-chain polyamines and silaffins, *J Mater Chem.*, 14,
2059-2065, 2004.
- 586 Sun, Y., Clemens, S. C., An, Z., and Yu, Z.: Astronomical timescale and palaeoclimatic implication of stacked 3.6-Myr monsoon
records from the Chinese Loess Plateau, *Quaternary Sci Rev.*, 25, 33-48, 2006.
- 588 Swann, G. E. A.: Salinity changes in the North West Pacific Ocean during the late Pliocene/early Quaternary from 2.73 Ma to 2.53
Ma, *Earth Planet Sc Lett*, 297, 332-338, 2010.
- 590 Swann, G. E. A. and Leng M. J.: A review of diatom $\delta^{18}\text{O}$ in palaeoceanography. *Quaternary Sci Rev.*, 28, 384-398, 2009.
- Swann, G. E. A., Maslin, M. A., Leng, M. J., Sloane, H. J., and Haug, G. H.: Diatom $\delta^{18}\text{O}$ evidence for the development of the
592 modern halocline system in the subarctic northwest Pacific at the onset of major Northern Hemisphere glaciation,
Paleoceanography, 21, PA1009, doi:10.1029/2005PA001147, 2006.
- 594 Swann, G. E. A., Leng, M. J., Sloane, H. J., and Maslin, M. A.: Isotope offsets in marine diatom $\delta^{18}\text{O}$ over the last 200 ka, *J*
Quaternary Sci., 23, 389-400, 2008.
- 596 Swift, D. M. and Wheeler, A. P.: Evidence of an organic matrix from diatom biosilica, *J Phycol.*, 28, 202 -290, 1992.
- Takahashi, K.: Seasonal fluxes of pelagic diatoms in the subarctic Pacific, 1982-1983, *Deep-Sea Res.*, 33, 1225-1251, 1986.
- 598 Takahashi, K., Hisamichi, K., Yanada, M., and Maita, Y.: Seasonal changes of marine phytoplankton productivity: A sediment trap
study. *Kaiyo Monthly* 10, 109-115, 1996.
- 600 Takahashi, T., Sutherland, S. C., Feely, R. A., and Wanninkhof, R.: Decadal change of the surface water $p\text{CO}_2$ in the North Pacific: a
synthesis of 35 years of observations, *J Geophys Res.*, 111, C07S05, doi:10.1029/2005JC003074, 2006.
- 602 Tortell, P. D. and Morel, F. M. M.: Sources of inorganic carbon for phytoplankton in the eastern Subtropical and equatorial Pacific
Ocean, *Limnology and Oceanography*, 47, 1012-1022, 2002.
- 604 Tortell, P. D., Reinfelder, J. R., and Morel, F. M. M.: Active uptake of bicarbonate by diatoms, *Nature*, 390, 243-244, 1997.
- Tortell, P. D. Martin, C. L., and Corkum, M. E.: Inorganic carbon uptake and intracellular assimilation by subarctic Pacific
606 phytoplankton assemblages, *Limnol Oceanogr.*, 51, 2102-2110, 2006.
- Tortell, P. D., Payne, C., Gueguen, C., Strzepek, R. F., Boyd, P. W., and Rost, B.: Inorganic carbon uptake by Southern Ocean
608 phytoplankton, *Limnol Oceanogr.*, 45, 1485-500, 2008.
- Tsuda, A., Takeda, S., Saito, H., Nishioka, J., Nojiri, Y., Kudo, I., Kiyosawa, H., Shiimoto, A., Imai, K., Ono, T., Shimamoto, A.,
610 Tsumune, D., Yoshimura, T., Aono, T., Hinuma, A., Kinugasa, M., Suzuki, K., Sohrin, Y., Noiri, Y., Tani, H., Deguchi, Y.,
Tsurushima, N., Ogawa, H., Fukami, K., Kuma, K., and Saino, T.: A Mesoscale Iron Enrichment in the Western Subarctic Pacific
612 Induces a Large Centric Diatom Bloom, *Science*, 300, 958-961, 2003.

Whitney, F. A., Bograd, S. J., and Ono, T.: Nutrient enrichment of the subarctic Pacific Ocean pycnocline, *Geophys Res Lett.*, 40, 2200-2205, 2013.

Yuan, W. and Zhang, J.: High correlations between Asian dust events and biological productivity in the western North Pacific, *Geophys Res Lett.*, 33, L07603, doi:10.1029/2005GL025174, 2006.

Zhang, Y. G., Ji, J., Balsam, W., Liu, L., Chen, J.: Mid-Pliocene Asian monsoon intensification and the onset of Northern Hemisphere glaciation, *Geology*, 37, 599-602, 2009.

620 **Supplementary material**

Supplementary Table 1: ODP Site 882 $\delta^{13}\text{C}_{\text{diatom}}$, $\delta^{18}\text{O}_{\text{diatom}}$ and $\delta^{30}\text{Si}_{\text{diatom}}$ data together with C_{diatom} and relative species biovolume composition in the analysed samples.

624 **Figure legends**

Figure 1: Location of ODP Site 882 in the subarctic North West Pacific Ocean.

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Figure 2: Relative diatom species biovolumes in samples analysed for $\delta^{18}\text{O}_{\text{diatom}}$.

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Figure 3: Data from ODP Site 882 showing changes in: 1) productivity [$\delta^{13}\text{C}_{\text{diatom}}$, BioBa (Jaccard et al., 2005) and opal concentrations (Jaccard et al., 2009)]; 2) nutrient dynamics [$\delta^{30}\text{Si}_{\text{diatom}}$ and $\delta^{15}\text{N}_{\text{diatom}}$ (Brunelle et al., 2010)]; 3) modelled $\text{Si}(\text{OH})_4$ supply/consumption in an open system model; and 4) freshwater input ($\delta^{18}\text{O}_{\text{diatom}}$) together with EPICA Antarctic δD (Jouzel et al., 2007) and NGRIP Greenland $\delta^{18}\text{O}_{\text{ice}}$ (NGRIP, 2004). [Changes in the supply/consumption of \$\text{Si}\(\text{OH}\)_4\$ are relative to mean conditions in MIS 5e.](#) Green/red shading indicate the increases in productivity and decreases in $\delta^{18}\text{O}_{\text{diatom}}$ respectively that are discussed in the text.

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Figure 4: Schematic models showing subarctic North West Pacific Ocean conditions for: A) Modern day: halocline water column with nutrient poor surface waters limiting biological export; B) MIS 5e: no halocline and enhanced upwelling of nutrient and carbon rich sub-surface waters leading to increased productivity. Low rates of nutrient utilisation suggest a possible increase in $p\text{CO}_2$ and release of CO_2 to the atmosphere; C) MIS 5b-c: conditions similar to MIS 5e but with higher rates of nutrient consumption and a more efficient soft-tissue biological pump limiting/preventing ventilation of CO_2 .