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# Enhanced Carbon Pump Inferred from Relaxation of Nutrient Limitation in the Glacial Ocean

Authors: Pichevin L.E., Reynolds B.C., Ganeshram R.S., Cacho I., Pena L., Keefe K., Ellam R.M.

Address for correspondence:

Laetitia Pichevin  
School of Geosciences,  
Grant Institute,  
University of Edinburgh,  
The King's Buildings  
West Mains Road,  
Edinburgh, UK  
EH9 3JW

Email: laetitia.pichevin@ed.ac.uk

## **Enhanced Carbon Pump Inferred from Relaxation of Nutrient Limitation in the Glacial Ocean**

Pichevin L. E.<sup>1</sup>, Reynolds B. C.<sup>2</sup>, Ganeshram R. S.<sup>1</sup>, Cacho I.<sup>3</sup>, Pena L.<sup>3</sup>, Keefe K.<sup>4</sup>,  
Ellam R. M.<sup>4</sup>

1. School of Geosciences, Grant Institute, University of Edinburgh, West Main Road, EH10 3JW, Edinburgh, UK, [laetitia.pichevin@ed.ac.uk](mailto:laetitia.pichevin@ed.ac.uk), Tel +44 131 650 8547, Fax +44 131 668 3184

2. IGMR, ETH Zürich, Clausiusstrasse 25, CH-8092 Zürich, Switzerland

3. GRC Geociències Marines, Facultat de Geologia, Universitat de Barcelona C/ Martí Franques s/n 08028 Barcelona, Spain

4. Scottish Universities Environment Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, UK

**The modern Eastern Equatorial Pacific (EEP) is a major oceanic source of carbon to the atmosphere<sup>1</sup>. During glacial periods, increased deep-sea carbon export in this region supported by additional input of dust-born iron<sup>2, 3</sup> could have contributed towards lower atmospheric CO<sub>2</sub> levels. Such a role for the EEP is supported by higher organic carbon burial rates<sup>4, 5</sup> documented in underlying glacial sediments but the lower opal accumulation rates had cast doubts<sup>6, 7</sup>. Here we present a new silicon isotope record that suggests the paradoxical decline in opal accumulation rate in the glacial EEP resulted from a decrease in Si:C uptake ratio of diatoms under conditions of increased Fe availability from enhanced dust inputs. Consequently, our study provides support for an invigorated biological pump in this region during the last glacial period that**

**could have contributed to glacial CO<sub>2</sub> drawdown. Additionally, using evidence from silicon and nitrogen isotope changes we infer that, in contrast to modern situation, the biological productivity in this region is not constrained by the availability of Fe, Si and N during the glacial period. Therefore, we hypothesise that an invigorated biological CO<sub>2</sub> pump constrained perhaps only by P limitation was a more common occurrence in low-latitude areas of the glacial ocean.**

The Eastern Equatorial Pacific (EEP), an important area of biogenic opal production and burial in the ocean<sup>8</sup>, accounts for more than two third of the marine CO<sub>2</sub> efflux to the atmosphere today<sup>1</sup>. This situation arises because primary productivity in the EEP is co-limited by silicic acid and iron availability<sup>9</sup> and therefore the biological CO<sub>2</sub> pump is unable to compensate for the CO<sub>2</sub> out-gassing that occurs through upwelling of deep waters<sup>10</sup> (Fig.1).

In figure 2, we present glacial-interglacial records of biogenic accumulation as well as stable N and Si isotope records spanning the last 35 ka from a EEP marine sediment Core ODP 1240 (Fig. 1). Organic carbon concentrations in the sediment were double during the Last Glacial Maximum (LGM) compared to the Holocene and peak during the deglacial. The <sup>230</sup>Th-normalised organic carbon accumulation rates also retain the same trend (Fig. 2). The doubling of organic carbon accumulation during the LGM is in agreement with previous studies showing that organic carbon export in the EEP was higher during the LGM<sup>4, 5</sup>, and may imply an invigorated biological CO<sub>2</sub> pump during this period (see supplementary material). Contradicting such an assertion, opal concentration in Core 1240 was reduced roughly by a factor of 2 during the LGM, consistent with existing opal accumulation records in the region<sup>7</sup>,

<sup>6</sup>. Such differences in biogenic accumulation records cannot be explained by local changes in upwelling alone.

The sedimentary ratio of  $\text{Si}_{\text{opal}}$  to organic carbon (Si:C) in Core 1240 increases drastically during the glacial to interglacial transition with values almost 3 times higher during the early Holocene compared to the LGM (Fig. 2). This change in the relative accumulation of opal and carbon is seen across the entire EEP and therefore cannot be simply explained by factors such as differential distribution and preservation of these biogenic components (supp. mat.).

The contrast between opal and organic carbon accumulation trends during the LGM in the EEP could be reconciled by invoking a shift in the phytoplankton communities from diatomaceous to coccolithophorid production. This would have reduced the C rain-rate ratios (the relative contributions of organic carbon and  $\text{CaCO}_3$  to total export production) in the glacial EEP and hence the capacity of the marine C reservoir to sequester carbon<sup>11</sup>. However,  $\text{CaCO}_3$  contents and accumulation rates in Core 1240 do not show a clear glacial-interglacial pattern to support such a shift in the rain-rate ratio of particulate export (Fig. 2). The estimates of carbonate accumulation rates in the EEP either based on the  $^{230}\text{Th}$  normalisation technique or high resolution  $^{14}\text{C}$  stratigraphy unequivocally document reduced carbonate fluxes and production during the LGM<sup>12</sup>. Moreover, a recent study<sup>13</sup> of carbonate accumulation corrected for sedimentary dissolution has even suggested that primary production in the EEP shifted from  $\text{CaCO}_3$  to opal production during the LGM compared to the Holocene. Thus, sedimentary opal records from the EEP, which show halved accumulation rates during the LGM compared to the Holocene epoch<sup>7</sup>, implying a less efficient biological  $\text{CO}_2$  pump, are in contradiction to the inferences based on enhanced organic carbon production and has until now remained a paradox. Resolving this

paradox has important implications in understanding the role of EEP in glacial CO<sub>2</sub> drawdown and the impact of enhanced Fe delivery on nutrient limitation and biological CO<sub>2</sub> pump during the glacial periods.

Availability of silicic acid in the surface water of the EEP is considered as the major control on opal production<sup>10</sup> - a view that stems from modern observations of Si-limitation in this region (Fig. 1). However, LGM conditions could have been drastically different for diatom growth when dust-borne iron delivery to the surface EEP was twice as much as today, as recorded by sediment cores in this area<sup>2, 3</sup> (Fig.2). The impact of this increased iron delivery on opal production in the Fe-limited low latitude Pacific ocean<sup>2, 3</sup> has never been fully explored. Results from *in situ* Fe-fertilisation experiments<sup>14, 15</sup> reveal that the alleviation of Fe limitation in the EEP causes a 2 to 3 fold decrease in Si:C uptake ratios of siliceous producers due to decreased cell silicification<sup>14, 15</sup>. If this were to happen during the Fe-replete LGM this may have resulted in lower Si uptake during diatom growth and consequently reduced opal accumulation. In addition, given the large decline in Si:C uptake ratios documented in these experiments, silicic acid may have been available in surplus during diatom production. Thus, the reconstruction of glacial silicic acid utilisation in the EEP could be the missing link to unravel the opal accumulation “paradox” and to address carbon mass balance during the LGM.

We evaluate the possibility of lowered Si utilisation during diatom growth under Fe-replete glacial periods using a record of  $\delta^{30}\text{Si}$  of opal (Fig.2). During the Holocene  $\delta^{30}\text{Si}$  values are  $\sim+1.3\text{‰}$ , a value close to the isotopic composition of silicic acid in intermediate water masses of the tropical Pacific<sup>16, 17</sup>. This indicates near complete utilisation of the available silicic acid, consistent with modern observations of its limitation in the EEP. In contrast, the LGM values were much lower ( $<0.9\text{‰}$ ). This

lower  $\delta^{30}\text{Si}$  signature may reflect a decrease in the relative utilisation of silicic acid in the EEP during glacial period provided this shift is not affected by glacial change in the nutrient source.

During the glacial, silicic acid leakage from the Southern Ocean, whereby enhanced dust-borne iron input to the Southern Ocean resulted in the conservation of silicic acid over other nutrients leading to its export to the low latitude<sup>18, 19</sup>, is one mechanism that could have potentially altered silicic acid supply to the EEP and its isotopic signature. It has been estimated that during the glacial, low latitude Pacific could have received 3 times more silicic acid through the sub-Antarctic mode waters, with a  $\delta^{30}\text{Si}$  signature as high as +3‰<sup>20</sup>. Complete diatom utilisation of this additional supply of heavy  $\text{Si}(\text{OH})_4$  in the EEP should have increased glacial opal burial accompanied by heavier shift in  $\delta^{30}\text{Si}$ . To the contrary, Core 1240 records a glacial decline in opal accumulation with lighter isotopic values (Fig.2).

The reason for the apparent contrast becomes clear if one considers how glacial increase in dust-borne Fe inputs would have impacted silicic acid utilisation locally within the EEP. The increased Fe input and the resultant decline in Si:C uptake ratios, as was proposed for the Southern Ocean, should have also operated in the glacial EEP leading to the conservation of silicic acid<sup>14, 18</sup>. This would explain the decline in opal accumulation and the lighter  $\delta^{30}\text{Si}$  values in the glacial intervals of Core 1240. Paradoxically, the increased silicic acid supply from the Southern Ocean appears to have occurred at the time the demand for this nutrient declined locally within the EEP -a contention that is supported by the similar glacial-interglacial histories of dust input in these two regions<sup>3</sup>. Thus, this new result documenting excess silicic acid in the glacial EEP strongly implies that the decline in opal accumulation in LGM sediments is not controlled by the availability of silicic acid and therefore could

be attributed to the consequence of Fe-fertilisation and lowered Si:C uptake ratios during diatom growth. Importantly, the glacial decrease in opal accumulation observed across the EEP<sup>6, 7</sup> does not reflect a decline in C rain-rate ratio and the biological CO<sub>2</sub> pump as previously suggested<sup>6</sup>.

Our results suggest that the glacial scenario of nutrient limitation and the constraints on biological production in the EEP were drastically different from the modern situation depicted in Figure 1. In contrast to modern conditions, enhanced Fe delivery and the resultant switch to lower Si:C uptake ratio by diatoms led to conditions where Fe and Si are no longer limiting factors for biological productivity. Based on glacial  $\delta^{30}\text{Si}$  values in Core 1240 and applying a steady state model<sup>17</sup> we estimate relative silicic acid utilisation during the LGM declined by about 25% from a near complete utilisation during the Holocene. This calculation assumes a constant Si(OH)<sub>4</sub> source of around +1.2‰ in agreement with low latitude Pacific intermediate water values<sup>16, 17</sup>. This estimate of decreased Si(OH)<sub>4</sub> utilisation would be even greater if the leakage of isotopically heavy silicic acid from the sub-Antarctic is taken into account<sup>20</sup>. Similarly, the N-isotope record allows us to assess the potential for glacial nitrate limitation. The lack of Fe and Si co-limitation during the glacial should have led to increased nitrate utilisation and heavier glacial  $\delta^{15}\text{N}$ . In contrast, the N-isotope profile (Fig. 2) trends towards lower  $\delta^{15}\text{N}$  values during the LGM relative to the Holocene, consistent with other similar studies in this region<sup>21</sup>. However, given that nitrate utilisation is incomplete in the modern EEP a further  $\delta^{15}\text{N}$  decrease (>3‰) during the glacial period cannot be simply explained by changes in nitrate uptake by biota alone as it would entail a very large reduction in utilisation during this period. Therefore, we suggest that the low LGM  $\delta^{15}\text{N}$  values relative to the Holocene reflect additional

supply of isotopically lighter N due to reduced denitrification in the oxygen minimum zones (OMZ) off Peru and Mexico<sup>22, 23</sup>. Today the prevalence of denitrification in these margins bordering the EEP makes the source waters supplied to the EEP thermocline depleted in nitrate relative to phosphate (sub-redfieldian N:P) and with a relatively heavy N-isotope signature (+6.5‰ as opposed to the +4.8‰ ocean average) due to mixing with partially-denitrified heavy nitrate<sup>24</sup>. Thus, reduced denitrification during glacial periods would enhance the nitrate inputs into the EEP by increasing the N/P ratio of upwelling waters and provide nitrate that is isotopically lighter. In combination both these factors would lead to a shift to lighter sedimentary N-isotope signatures irrespective of any glacial change in local upwelling<sup>25, 26</sup>. Thus, the lighter N-isotope values provide evidence that nitrate is also not a limiting nutrient in the glacial EEP- a condition comparable to the modern situation. Therefore the data strongly suggest simultaneous removal of constraints imposed by Fe, Si and N limitation on biological production in the EEP during the LGM. This argues for a more invigorated biological CO<sub>2</sub> pump in the glacial EEP perhaps ultimately constrained by the availability of dissolved phosphate. The resulting increase in carbon export and rain-rate ratio as documented in the glacial sediments of the EEP (supp. mat.) should have reduced CO<sub>2</sub> evasion. Such an assertion is also consistent with the timing of the first phase of the atmospheric CO<sub>2</sub> rise during the last glacial termination (~18 ka) which is contemporaneous, within dating uncertainties, to the decline in dust delivery and the increases in sedimentary Si:C and  $\delta^{30}\text{Si}$  in EEP records.

Finally, we suggest that our results have much wider ramifications because the EEP provides an illustration of the constraints imposed on the biological CO<sub>2</sub> pump in

low-latitude oceans of the glacial periods. In currently Fe limited open ocean High Nitrate Low Chlorophyll regions, such as the EEP and Southern Ocean, the switch to Fe-replete LGM conditions led to the generation of excess silicic acid during diatom growth, which in turn is subject to dispersal through surface and subsurface ocean circulation increasing the availability of silicic acid over much wider area of the glacial ocean<sup>18, 19</sup>. This additional silicic acid supply occurs at a time when its demand by biota is already reduced due to Fe-fertilisation, which should have caused drastic reductions in Si limitation over large areas of the glacial ocean.

Also, the documented glacial decline in denitrification in the world's OMZ is expected to have increased the availability of nitrate<sup>27, 23</sup>. For instance, NO<sub>3</sub>:PO<sub>4</sub> ratio at the surface of the modern EEP is about 12.5, i.e. lower than N:P Redfield ratio of 16. In contrast, a 30% increase in nitrate inventory during the last glacial period compared to today as suggested by modelling work<sup>28</sup> could have been sufficient to cause the N:P ratio in the EEP to exceed the Redfield ratio. Such changes occurring more widely would have resulted in an invigorated CO<sub>2</sub> pump in low latitude oceans ultimately constrained by the availability of dissolved phosphate as suggested by the case study reported here and predicted by recent model results<sup>29</sup>. Therefore, we hypothesise that P limitation was much more widespread during the glacial periods - a situation fundamentally different to that of the modern ocean.

### **Method Summary**

Core ODP 202 1240 was retrieved from Cocos ridge (00°01.31N; 86°27.76W, 2,921 m depth) in the EEP. The age model is based on 13 AMS<sup>14</sup>C dates on planktonic foraminifers<sup>25</sup>. Determination of the opal content (%) was performed by molybdate-blue spectrophotometry on alkaline extracts. Organic C (%), total N (%) and δ<sup>15</sup>N (‰)

were determined on bulk sediments using a Carlo Erba elemental analyzer coupled to a VG Prism III mass spectrometer at the University of Edinburgh.  $^{230}\text{Th}$  normalization was performed using acid digestion on bulk samples and column chemistry followed by MC-ICPMS analyses.

Purification of the diatom samples for silicon isotope measurement has been performed by chemical leaching of the carbonate and organic fractions, sieving and differential settling. Silicon isotope determination has been conducted in ETH Zürich on the Nu1700 high-resolution MC-ICPMS<sup>30</sup>.

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Supplementary Information is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature)

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### **Author Contributions:**

L.E.P. and R.S.G. initiated the project. L.E.P. and B.C.R. measured silicon isotopes in ETH Zurich, L.E.P. measured elemental composition and nitrogen isotopes, L.E.P., K.K. and R.E. made the <sup>230</sup>Thorium measurements. I.C. and L.P. provided the age model. L.E.P. and R.S.G. wrote the paper with the participation of B.R.C. All authors participated to the discussions on the results and commented on the manuscript.

### **Figure captions**

Figure 1: Annually averaged CO<sub>2</sub> partial pressure difference between the atmosphere and the ocean for year 1995 (modified from<sup>1</sup>; <http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/>). Also depicted is the hierarchy of nutrient limitation for diatom growth across the low latitude Pacific Ocean. Black lines delimit the area where the most severe limitation is imposed by iron, dotted lines delimit the area of silicic acid limitation. Beyond these lines the ocean is firstly nitrate limiting (modified from<sup>9</sup>). Note the geographical correspondence between CO<sub>2</sub> efflux maxima (warm colours) and iron and silicic acid limitation areas. Core site ODP 202 1240 is shown with a white dot.

Figure 2: Sedimentary records from Core 1240 plotted versus calendar ages B.P; (a)  $\delta^{15}\text{N}$  signal of bulk material (bold line = 2 points average), (b) the  $\delta^{30}\text{Si}$  signal of diatoms (errors bars are 1 sigma error of the mean), (c) Si:C ratio (bold line = 2 points average), elemental concentrations (solid line) and <sup>230</sup>thorium normalized accumulation rates (dotted lines) of (d) organic carbon (wt.%), (e) opal (wt.%), (f) carbonate (wt.%), (g) dust fluxes in Core ODP 138-849A and 138-850A<sup>2</sup>, and (h) atmospheric PCO<sub>2</sub> record from EPICA dome C ice core<sup>31</sup>. T1 and LGM stand for Termination 1 and Last Glacial Maximum, respectively.

## **Methods**

Core ODP 202 1240 (00°01.31N; 86°27.76W, 2,921 m depth) was retrieved on Cocos ridge (see ODP report [http://www-odp.tamu.edu/publications/202\\_IR/chap\\_11/chap\\_11.htm](http://www-odp.tamu.edu/publications/202_IR/chap_11/chap_11.htm)).

The age model is based on 13 AMS<sup>14</sup>C dates on planktonic foraminifers. Determination of the opal content (%) was performed by molybdate-blue

spectrophotometry on alkaline extracts according to the method published in<sup>32</sup>. Organic Carbon (%) and N (%) contents were determined by using a Carlo-Erba elemental analyser on 10 mg of freeze-dried and powdered bulk sediment. The isotopic composition of sedimentary nitrogen ( $\delta^{15}\text{N}$ ) was measured with a VG Prism III mass spectrometer on freeze-dried and powdered bulk sediments. Thorium 230 normalization was used to account for the effect of sediment focusing<sup>33</sup> and performed using acid digestion on bulk samples and column chemistry followed by multi collector ICP-MS analyses at the Scottish Universities Environment Research Centre <sup>34</sup>(supp. mat.).

Purification of the diatom samples for silicon isotope measurement has been performed by chemical leaching of the carbonate and organic fractions, sieving and differential settling following a cleaning method published recently<sup>35</sup>. Silicon isotope determination has been conducted in ETH Zürich on the Nu1700 high-resolution MC-ICPMS<sup>6</sup>. A small amount of biogenic opal (0.5 mg) was dried down with concentrated perchloric acid at  $\sim 180^\circ\text{C}$  in Teflon<sup>©</sup> vials, and then dissolved in 100  $\mu\text{l}$  of 1 M NaOH, before being diluted to 5 ml with 0.01 M HCl after 24 hours. Equivalent to 10  $\mu\text{g}$  of opal was loaded onto a pre-cleaned 1.8ml DOWEX 50W-X12 cation exchange resin bed (in  $\text{H}^+$  form) and eluted with 5 ml of purified water (Milli-Q element 18.2  $\text{M}\Omega\cdot\text{cm}^{-1}$ ). The Si isotope composition was determined on the diluted solution (0.6ppm Si) on the Nu1700 high-resolution MC-ICPMS at ETH Zürich, using a standard-sample-standard bracketing protocol. All results in this study were calculated using the  $\delta^{30}\text{Si}$  notation for deviations of the measured  $^{30}\text{Si}/^{28}\text{Si}$  from the international Si standard NBS28 in parts per thousand (‰). The long-term reproducibility was better than 0.07‰  $\delta^{30}\text{Si}$  (1 s.d.)<sup>36</sup>. Samples were measured at

least 5 times, which resulted in a 95 % confidence level below 0.08%. Error bars on the  $\delta^{30}\text{Si}$  plot are calculated as 1 sigma error of the mean (Fig. 2).

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Sea-Air  $\text{PCO}_2$  difference ( $\mu\text{atm}$ )



