Quaternary Science Reviews 30 (2011) 1112–1121

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

High-resolution opal records from the eastern tropical Pacific provide evidence for silicic acid leakage from HNLC regions during glacial periods

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ARTICLE INFO

Article history:
Received 8 April 2010
Received in revised form
3 February 2011
Accepted 7 February 2011
Available online 8 April 2011

Keywords:
Opal
Silicic acid
Eastern tropical Pacific
Productivity
Last glacial
Carbon dioxide

ABSTRACT

A shift from carbonate- to silica-dominated primary production could significantly affect the oceanic carbon cycle via changes in the particulate carbon rain-rate ratio ($C_{organic}$:$C_{inorganic}$ fluxes). An increase in C rain rate ratio has been invoked to explain lower glacial pCO_2; however, firm evidence of an ecological shift towards silica-dominated productivity during the last glacial period is lacking. Here, we present new high-resolution reconstructions of biogenic silica and total production over the past 40,000 yr BP in 3 cores from the eastern tropical North Pacific (ETNP) off Mexico and Nicaragua. These records reveal a clear regional pattern of higher siliceous productivity with higher opal accumulation during the last glacial period compared to interglacial times. Higher Si:C and Si:N ratios of glacial sediments in these records suggest a net increase in siliceous production over total production. We attribute this to the additional supply of silicic acid to the ETNP margins favouring diatoms over other non-siliceous algae. This suggestion for increased supply of Si during glacial periods is consistent with the proposed large-scale redistribution of excess silicic acid from High Nitrate Low Chlorophyll (HNLC) regions like the eastern equatorial Pacific (EEP) and the Southern Ocean by the Silicic Acid Leakage Hypothesis (SALH). In these HNLC regions, the Si-isotope composition of diatom frustules ($\delta^{30}Si$) has provided evidence for the generation of surplus of silicic acid during diatom growth under conditions of higher Fe availability during glacial periods. We suggest that silicic acid leakage from the HNLC regions to the adjoining oceans may have increased the carbon rain rate ratio and ultimately, contributed to the decrease in glacial atmospheric pCO_2.

1. Introduction

Increase in the magnitude and changes in the nature of the marine productivity may have caused glacial declines in atmospheric CO_2 (pCO_2) (Berger and Wefer, 1991; Broecker et al., 1992; Archer et al., 2000a, 2000b). Model results suggest that a 40% increase in the *rain-rate ratio* (the flux of POC:$CaCO_3$ to the ocean interior) could explain the ~80 ppmv decrease in pCO_2 during the Last Glacial Maximum (LGM) relative to pre-industrial levels (Archer and Maierreimer, 1994; Ridgwell et al., 2002). However, such a severe change requires a drastic ecological shift in favour of non-calcareous phytoplankton like diatoms (Archer et al., 2000a). Such a shift could be caused by increasing the availability of silicic acid ($Si(OH)_4$) during glacial periods, permitting siliceous diatoms to out-compete smaller non-siliceous species such as calcareous coccolithophorids for limiting nutrients like nitrate (NO_3) and iron (Fe) (Ridgwell et al., 2002). The resulting enhancement in rain-rate ratios would in turn, decrease the alkalinity gradient between surface and deep-ocean lowering pCO_2 levels (Dymond and Lyle, 1985; Sigman and Boyle, 2000). Models of silica-dominated primary production causing lower glacial pCO_2 are also attractive because diatom frustules can transfer carbon to the deep-ocean more efficiently than pico- and nanoplankton, which are more prone to grazing pressure (Brzezinski et al., 2002; Ganeshram, 2002; Matsumoto et al., 2002).

1.1. Silicic acid availability and opal burial

Production of siliceous phytoplankton in large parts of the modern ocean is limited by the availability of silicic acid ($Si(OH)_4$) (Brzezinski and Nelson, 1996). The *Silicic Acid Leakage Hypothesis* (SALH) (Brzezinski et al., 2002; Matsumoto et al., 2002; Matsumoto and Sarmiento, 2008) postulates that a meridional redistribution of nutrients -rather than a whole-ocean increase in $Si(OH)_4$- could have promoted diatom production and increased the C rain rate

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0277-3791/$ – see front matter
doi:10.1016/j.quascirev.2011.02.002

ratios in low latitudes. This hypothesis stems from modern observations that High Nitrate Low Chlorophyll (HNLC) regions, where biological production is subject to severe Fe-limitation (e.g. the equatorial Pacific and the Southern Ocean), are also important areas of opal burial accounting for as much as two thirds of the Si sink in the modern ocean (DeMaster, 2002). The high opal burial in these HNLC regions is at least partly attributed to the production of heavily silicified diatom frustules under conditions of persistent Fe-limitation (Leynaert et al., 2004; Takeda et al., 2006). Thus, an increase in iron fluxes to HNLC regions during LGM might have relaxed Fe-limitation leading to a decrease in the relative utilisation of $Si(OH)_4$ compared to NO_3^- by diatoms. This conservation of $Si(OH)_4$ during diatom growth under Fe-replete conditions is supported by laboratory and shipboard bottle experiments (Martin et al., 1990; Takeda, 1998; Frank et al., 2000a; Marchetti et al., 2010), by artificial and natural Fe-fertilization (Nelson et al., 2001; Wong et al., 2006; Brzezinski et al., 2008; Mosseri et al., 2008), and by modelling studies in these areas (Takeda et al., 2006). In the Southern Ocean and equatorial Pacific, Fe-addition can account for a large decline in the Si:N uptake ratio, from ratios of ~4 to 1 to 1:1 (Takeda, 1998; Brzezinski et al., 2003; Marchetti and Cassar, 2009). The exact cause for this change in Si:N uptake ratios is currently being debated. The factors responsible may include reduced silicification of diatom frustules (Boyle, 1998; Takeda, 1998; Franck et al., 2000), differences in growth conditions, shifts in diatoms species composition and genetic variability or morphological changes (Marchetti and Cassar, 2009). Nevertheless, an important point to note is that a generally consistent outcome of iron fertilisation experiments in HNLC regions is the relative depletion of NO_3, leaving a surplus of $Si(OH)_4$. This surplus could be then transported out of these regions increasing diatom production in areas outside the HNLC region where $Si(OH)_4$ is limiting (Matsumoto et al., 2002; Pichevin et al., 2009).

Si-isotope composition ($\delta^{30}Si$) of diatom frustules has provided evidence for the presence of surplus $Si(OH)_4$ during the LGM in the Southern Ocean (Brzezinski et al., 2002) and the eastern equatorial Pacific (EEP) (Pichevin et al., 2009). However, glacial–interglacial trends in opal accumulation over large region such as the Southern Ocean could be variable, perhaps responding to additional local factors such as sea ice cover, stratification and wind mixing, or sediment redistribution (Francois et al., 1997; Dezileau et al., 2003; Bradtmiller et al., 2009). Therefore, it is critical to evaluate further the evidences for the conservation and redistribution of silicic acid during diatom growth in the glacial ocean under increased Fe-availability. An important aspect of this evaluation is to assess whether the excess silicic acid exported out of the HNLC regions acted as a net additional source of $Si(OH)_4$ for adjoining areas. Importantly, this additional $Si(OH)_4$ source could have drastically increased diatom growth in the glacial ocean in areas where Si is in short supply allowing diatoms to out-compete calcareous algae and leading to a net increase in the C rain rate ratio (Matsumoto and Sarmiento, 2008).

In this study, we investigate the evidence for increased $Si(OH)_4$ supply to the eastern tropical North Pacific (ETNP) margins (Fig. 1). We present 3 high-resolution records of opal contents (wt %), Si:C and Si:N ratios, spanning the last 40,000 yrs. The ETNP margins are well suited to evaluate the export of excess silicic acid from HNLC regions during glacial periods for the following reasons. First, productivity in these upwelling margins is limited by availability of Si and N, but not generally constrained by persistent Fe limitation (Fig. 1). Second, the generation of excess $Si(OH)_4$ in the glacial Southern Ocean and the EEP should augment Si supply to the ETNP margins due to regional surface and subsurface circulation of the eastern Pacific. Therefore, diatom production in ETNP margins is expected to respond sensitively to the excess silicic acid supply from HNLC regions during glacial periods.

2. Study site and methods

Three marine sediment cores were retrieved from the eastern tropical North Pacific (ETNP) with a Calypso piston corer during the MONA Cruise (IMAGES VIII-Internal Marine Global Changes, Jun-2002) (Fig. 1). The Core MD02-2519 was collected off Mazatlan, NW Mexico (lat. 22°30.89'N; long. 106° 39.00'W; 955 m water depth); the Core MD02-2520 from the Gulf of Tehuantepec, Mexico (lat. 15°40.14'N; long. 95°18.00'W; 712 m water depth); and the Core MD02-2524 from the Nicaragua Margin (lat. 12°00.55'N; long. 87°54.83'W; 863 m water depth). The ETNP is a region of high-productivity and elevated chlorophyll-*a* concentrations (Fig. 1-A) fuelled by active seasonal upwelling of subsurface waters of equatorial origin (Kessler, 2006). The ETNP margins are generally characterised by low silicic acid concentrations (Fig. 1-B) where $Si(OH)_4$

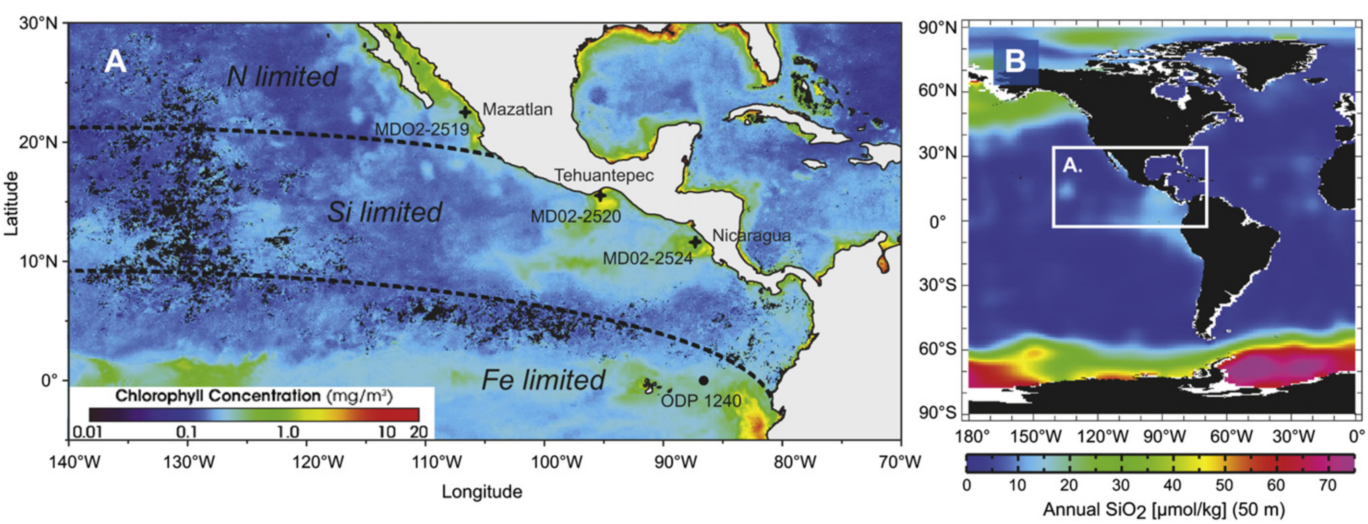

Fig. 1. Study area. (A) Location of cores collected off Mazatlan (MD02-2519), the Gulf of Tehuantepec (MD02-2520) and Nicaragua (MD02-2524). Core ODP 1240 collected north of the Carnegie Ridge in the Panama basin (0°01.31 N; 86°27.76 W; 2.921 m water depth) (Pichevin et al., 2009). Colours show the average Chlorophyll-*a* concentrations (mg/m^3) during winter derived from SeaWIFS satellite imagery. Dotted lines show areas of N, Si and Fe limitation in the eastern tropical Pacific (*from* Moore et al., 2004). (B) [SiO_2] at 50 m depth (Levitus et al., 1994).