Deep-Sea Research II 58 (2011) 462–476

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Net biogenic silica production and nitrate regeneration determine the strength of the silica pump in the Eastern Equatorial Pacific

Mark S. Demarest [a,b,*], Mark A. Brzezinski [a,b], David M. Nelson [c,1], Jeffrey W. Krause [c,2], Janice L. Jones [b], Charlotte P. Beucher [b]

[a] Department of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, CA 93106, USA
[b] Marine Science Institute, University of California, Santa Barbara, CA 93106, USA
[c] College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA

ARTICLE INFO

Article history:
Received 9 August 2010
Accepted 9 August 2010
Available online 18 August 2010

Keywords:
Equatorial Pacific
Biogenic silica
Silica production
Silicon cycling
HNLC
Nitrification
Tropical instability wave

ABSTRACT

The high-nitrate, low-silicic acid character of the eastern equatorial Pacific (EEP) has been attributed to the preferential export of diatom biogenic silica ($bSiO_2$) over particulate organic nitrogen due to less efficient recycling of Si in surface waters. To gain insight into the strength of this silica pump, we examined [$Si(OH)_4$] and [$bSiO_2$] distributions and net $bSiO_2$ production rates in two regions of the EEP, one spanning the equator from 4°N to 3.25°S at 140°W and the other along a tropical instability wave (TIW) at 0.5°N between 132.5 and 123.4°W, ending within a cold vortex at 1.75°N by 125°W. Large uncertainty in the net $bSiO_2$ production rate measurement precluded a detailed examination of trends at high spatial resolution, but averaged data revealed clear differences in Si cycling between these two sampling areas. Surface [$Si(OH)_4$] generally remained at levels <4 μM across both, but [$bSiO_2$] nearly doubled to values as high as 226 nmol Si L^{-1} along the TIW. The mean integrated net rate of $bSiO_2$ production along the meridional transect was no more than 0.29 mmol Si m^{-2} d^{-1} to the 0.1% light level depth and -0.31 mmol Si m^{-2} d^{-1} to a depth of 300 m, implying net loss of $bSiO_2$ to dissolution in the upper 300 m in this area. In contrast, integrated net $bSiO_2$ production rates were five times higher on average in the zonal sampling area, exhibiting a mean of 1.45 mmol Si m^{-2} d^{-1} within the euphotic zone that declined by only ~15% to a depth of 300 m, suggesting a significant potential for silica export to deeper waters along the TIW. In total, the fraction of $bSiO_2$ produced in the euphotic zone that was supported by new inputs of $Si(OH)_4$ was at least 3.7 times greater on average than the fraction of inorganic nitrogen taken up as NO_3^-, consistent with expectations for a silica pump. However, the mean integrated rate of NO_3^- uptake exceeded that of new $Si(OH)_4$ uptake by at least five times, implying preferential nitrate depletion in contradiction to nutrient distributions that indicated preferential $Si(OH)_4$ drawdown. This discrepancy can be resolved if, on average, ~70% of the nitrate taken up was regenerated in the euphotic zone rather than being supplied by 'new' upwelled sources. These results suggest that the silica pump in the EEP arises only in part from the less efficient recycling of biogenic silica compared to organic matter, but also requires efficient recycling of nitrate in surface waters to reduce the rate of new nitrogen production well below the rate of gross nitrate uptake. Additional work will be necessary to confirm this apparent dependency and its relationship to variations in the physical and biological processes driving new production in this system. A relationship between bacterial protease activity and rates of silica recycling was also identified, but, unlike in coastal systems, the contribution of particle-associated bacteria was relatively unimportant in effecting $bSiO_2$ dissolution in the EEP.

1. Introduction

The eastern equatorial Pacific Ocean (EEP) is a high-nutrient, low-chlorophyll (HNLC) upwelling area characterized by persistently low concentrations of dissolved Si relative to those of nitrate (Peña et al., 1992; Dunne et al., 1999; Raimbault et al., 1999; Fiedler and Talley, 2006). It has been suggested that this depressed silicon status is maintained by preferential export of siliceous material over organic matter, dubbed the silica pump (Dugdale et al., 1995; Dugdale and Wilkerson, 1998). Unlike

* Corresponding author at: Department of Biological Sciences, University of North Texas, Denton, TX 76203, USA.
Tel.: +1 940 369 7989.
E-mail addresses: Mark.Demarest@unt.edu (M.S. Demarest), brzezins@lifesci.ucsb.edu (M.A. Brzezinski), david.nelson@univ-brest.fr (D.M. Nelson), krause@lifesci.ucsb.edu (J.W. Krause), ja_jones@lifesci.ucsb.edu (J.L. Jones), beucher@lifesci.ucsb.edu (C.P. Beucher).
[1] Present address: Institut Universitaire Européen de la Mer, Technopôle Brest-Iroise, Place Nicolas Copernic, Plouzané 29280, France.
[2] Present address: Marine Science Institute, University of California, Santa Barbara, CA 93106, USA.

0967-0645/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dsr2.2010.08.007

nitrogen, which is utilized by all organisms, dissolved Si is taken up as silicic acid, $Si(OH)_4$, predominantly by diatoms, for the purpose of producing the amorphous biogenic silica, $bSiO_2$, of their cell walls. $Si(OH)_4$ is primarily regenerated by the physico-chemical dissolution of $bSiO_2$, rather than through biological remineralization. According to the silica pump model, this results in less efficient recycling of silicon relative to nitrogen, leading to more efficient export of Si from surface waters (e.g. Thunell et al., 2008; reviewed in Ragueneau et al., 2006) and, potentially, Si limitation of $bSiO_2$ production (Brzezinski et al., 2008) and/or diatom growth (Dugdale and Wilkerson, 1998).

Si limitation is likely to be of particular significance in the EEP, where diatoms are probably responsible for a disproportionately large portion of nitrate uptake (Jin et al., 2006; Krause et al., 2011). Indeed, despite their relatively low biomass and contribution to the total primary production of the region (e.g. Chavez et al., 1991; Price et al., 1994; Martin et al., 1994; Blain et al., 1997; Dugdale and Wilkerson, 1998), some analyses of N uptake patterns suggest that diatoms may account for virtually all of the nitrate-based production in the equatorial Pacific, with the primary production contributed by other taxonomic groups being based almost entirely on the recycled N pool (Blain et al., 1997; Dugdale and Wilkerson, 1998; Leynaert et al., 2001). Any limitation of diatom growth may therefore equate to limitation of new and export production in this important region of ocean-atmosphere CO_2 exchange (e.g. Tans et al., 1990; Takahashi et al., 2002; Mikaloff Fletcher et al., 2007; Takahashi et al., 2009).

While the silica pump mechanism provides an elegant explanation for the persistently low dissolved $Si(OH)_4$:NO_3^- character of the EEP, the hypothesis remains unconfirmed due to a lack of direct Si cycling rate data for the area. In particular, the relative contributions of new and recycled $Si(OH)_4$ to the production of $bSiO_2$ have remained little investigated, in large part because both new and regenerated Si are present as chemically identical $Si(OH)_4$, making it difficult to distinguish uptake between them. In the absence of sufficient direct measurements, known general trends have been applied to infer a relatively low level of $bSiO_2$ recycling compared to that of PON in the equatorial Pacific (Jiang et al., 2003). These include the tendency for diatoms to take up greater amounts of Si relative to N under iron-limited conditions (e.g. Martin and Fitzwater, 1988; Boyle, 1998; Hutchins and Bruland, 1998; Takeda, 1998; Brzezinski et al., 2001) and the likelihood that they will exhibit relatively high rates of sinking, due to their larger average size and density, tendency to form aggregates, consumption by larger grazers, and ballasting by biogenic silica (e.g. Bogoyavlenskiy, 1967; Alldredge and Gotschalk, 1989; Smetacek, 2000; Armstrong et al., 2002; Goutx et al., 2007).

However, other factors controvert a low relative rate of $bSiO_2$ recycling in the region. For example, $bSiO_2$ dissolution rates increase considerably with temperature, such that $bSiO_2$ particles in equatorial waters may be expected to dissolve at specific rates more than ten times those of particles found in the coldest marine waters (e.g. Lewin, 1961; Kamatani, 1982; Bidle et al., 2002; Natori et al., 2006). This shift may decrease the Si:C preservation ratio from values of ~6-13 at cold temperatures to values of only ~1-3 in warm conditions (Bidle et al., 2002). Similarly, the mostly small, pennate forms that dominate the diatom community of the EEP (Chavez et al., 1991; Blain et al., 1997; Kobayashi and Takahashi, 2002) are likely to exhibit high loss to dissolution in surface waters (Alexander, 1957; Nelson et al., 1991) as a consequence of their relatively large surface area to volume ratios and low rates of settling (Smetacek, 2000). Relative increases in silicification due to environmental iron deficiency may be offset by the low-$Si(OH)_4$ condition of the EEP, as some diatoms grown under silicon deficiency exhibit lower relative Si incorporation (Paasche, 1973a,b; Conway and Harrison, 1977; Martin-Jézéquel et al., 2000). Baines et al. (pers. comm.) measured a Si:N ratio of 0.95 for pennate diatoms in the region, which is slightly lower than the culture-based average of 1.1 for a variety of species grown under nutrient-replete conditions (Brzezinski, 1985). These various factors would seem to reduce silicon export efficiency in the EEP relative to other systems. Indeed, Blain et al. (1999) compared gross silica production rates to the $bSiO_2$ flux captured by sediment traps at 165°W longitude in the equatorial Pacific and estimated that >90% of the $bSiO_2$ produced in the region dissolved within the upper 125 m of the water column, compared to a global average of only ~50% (Nelson et al., 1995).

Furthermore, the low abundance of diatoms compared to non-siliceous phytoplankton in the EEP may diminish the significance of any differences in recycling efficiency between Si and N in determining relative bulk export of organic matter. During a cruise in August of 1991, Price et al. (1994) estimated that phytoplankton sized smaller than 3 μm – thus excluding essentially all diatoms – were responsible for greater than 85% of the nitrate uptake along a transect spanning from 20°S to 10.5°N in the vicinity of 140°-150°W. This finding implies a relatively high level of new production by non-siliceous phytoplankton in the broader system, although the extent to which this general finding applies to the narrower HNLC upwelling zone along the equator is unclear. Such contributions of nitrate-based production by non-diatoms would be expected to favor nitrogen export due to the uncoupling of nitrate from silicic acid utilization (Dunne et al., 1999).

Because the export of $bSiO_2$ is a function of the balance between its production and dissolution in the surface ocean, insight into Si recycling can be gained by measuring the net rate of $bSiO_2$ production in the water column. Using this approach, Adjou et al. (2011) found that $bSiO_2$ production was generally offset by dissolution within the upper 100-150 m at nine stations in the EEP between 110°W and 140°W in December 2004, suggesting little potential for $bSiO_2$ export to the ocean interior. Thus, little evidence for the existence of a silica pump was seen at the time of that study. Here we continue the investigation of Si recycling in surface waters of the EEP by evaluating net $bSiO_2$ production patterns nearly a year later, during the second cruise of the Equatorial Biocomplexity Project (this volume). Bacterial protease activities were also examined to investigate the role of bacterial activity in facilitating $bSiO_2$ recycling and, potentially, weakening of the silica pump (Bidle and Azam, 1999, 2001; Bidle et al., 2002, 2003; Natori et al., 2006) in this system.

2. Methods

2.1. Sample collection

Seawater samples were collected from the EEP from Sept. 9-24, 2005 using a CTD rosette assembly. All sample bottles utilized closure mechanisms of silicone tubing with Teflon-coated springs to avoid trace-metal contamination. Vertical profiles were obtained at 22 stations: 16 along a transect spanning the equator from 4.0°N to 3.25°S at 140.0°W, 5 along a westward-propagating tropical instability wave (TIW) from 132.5°W to 123.4°W at 0.5°N, and 1 within a TIW-induced cold vortex further north at 1.75°N by 125.0°W (Table 1, Fig. 1; see also Strutton et al., 2011). The meridional transect along 140°W was likely situated at the leading edge of two weak TIW vortices that were distributed nearly symmetrically across the equator, resulting in moderate upwelling plumes near 2°N and 2°S possibly as a result of poleward displacement of equatorial upwelling, with the northern of these being slightly stronger (Strutton et al., 2011).