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Silica burial enhanced by iron limitation in oceanic upwelling margins

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Models suggest that large swathes of ocean can be silica limiting for primary producers (diatoms) and this imposes a cap on the biological uptake of carbon dioxide into the ocean. Sedimentary burial of biogenic silica (opal) is the main oceanic silicon sink and is distributed equally between iron-limited open ocean provinces and upwelling margins. However, the margin silicon sink is mainly localised in the eastern Pacific while contributions from other upwelling systems are comparatively small. Such large inter-margin differences remain unexplained. Here we measure biogenic fluxes, diatom-bound iron concentrations and silicon isotope ratios in sedimentary material from the Gulf of California, an archetypal margin silicon sink. We suggest that transient iron limitation during intense upwelling periods dramatically increases silica relative to organic carbon export resulting in elevated silica burial -a view also supported by long sedimentary records from the same basin. Global compilations further show that hotspots of silicon burial in the ocean are all characterised by high silica to organic carbon export ratios, a diagnostic trait for diatoms growing under Fe stress. Therefore, we propose that prevailing conditions of silica limitation in the ocean is largely caused by Fe deficiency imposing an indirect constraint on oceanic carbon uptake. (199 words)

Diatoms, a group of phytoplankton with amorphous silica cell walls (opal), account for up to 40% of the marine primary production[1]. Because their frustules are siliceous and contain no calcium carbonate, they export carbon to the deep ocean as organic matter. Hence, their relative abundance determines the organic to calcium carbonate ratio of settling biogenic particles from the sea surface: the C rain-rate ratio[2]. This parameter regulates the efficiency of the biological pump of carbon by pushing the marine carbon cycle towards increased (high C rain-rate ratio) or decreased (low C rain-rate ratio) CO_2 drawdown from the atmosphere[3]. In ideal conditions, diatoms need biologically available silicic acid and nitrate with a ratio of 1:1 in the surface waters[4]. However, while silicic acid is generally above biological requirements in the deep ocean relative to other macronutrients such as nitrate and phosphate, thermocline waters fuelling biological productivity in most part of the ocean are depleted in silicic acid[5]. This lead to the yield limitation of diatom production by silicic acid in the surface ocean[6-8], restricting the amount of biogenic silica produced and hence the efficiency of the biological pump of carbon. Here we investigate the causes of this potentially widespread Si limitation in the ocean.

Silicon is introduced to the ocean via river runoff and is removed by sedimentary burial of mainly diatom opaline skeletal remains[2,9]. The ocean waters are undersaturated with respect to opal, and hence its burial efficiency is only 3% because of dissolution in the water column and superficial sediments. On an average Si is recycled ~25 times with in the ocean before permanent removal through sediment burial[9]. However, areas of high opal export also display higher sedimentary Si burial rates as pore waters become rapidly supersaturated in silicic acid, preventing further dissolution and increasing Si burial[10]. Shallow water column and high sedimentation rates in margins further aid the burial of biogenic Si by reducing its exposure to undersaturated seawater[2].

Concurrence of Marine Si sinks and Fe limitation

Marine Si sinks are highly localised with burial mostly occurring in the Southern Ocean (SO) and the North Pacific (NP) for the open ocean (3 Tmol $Si.yr^{-1}$)[11] and in continental margins (3.7 Tmol $Si.yr^{-1}$) influenced by upwelling (Supplementary Material section 2; Table 1). Despite covering a small surface area, coastal upwelling areas represent the main Si sink in ocean margins. However, not all comparably productive marginal environments are Si sinks. This is often overlooked and remains unexplained[12,13]. For instance, Si burial rates in the Eastern Pacific and Gulf of California (GoC) upwelling regions are one to two orders of magnitude higher than in the Arabian sea despite similar productivity levels[12-14]. Therefore, understanding why some oceanic margins are particularly efficient at removing Si is important in explaining silicic acid limitation in the surface ocean in view of the constraint it imposes on the biological C pump.

Areas of high opal production usually support significant organic carbon (C_{org}) export[2] but there are notable exceptions to this[15] (Fig.1a & 1c). In the SO, parts of the NP and to a lesser extent the equatorial Pacific, C_{org} export is generally modest despite high biogenic silica fluxes. This results in very high biogenic silica to organic carbon ($Si:C_{org}$) ratios in the settling particles (up to 10), in contrast to the rest of the ocean where the $Si:C_{org}$ ratio is generally below 1 (Fig.1c, and Supplementary Material section 1 Fig.S1). The areas of high water column Si and Si/Corg export in Figure 1b are also regions that support relatively large sedimentary Si burial (Supplementary Material section 2; Fig.S3.) suggesting the close link between water column and sediment fluxes. These large open ocean regions with high Si exports are High Nitrate-Low Chlorophyll (HNLC) areas characterised by micronutrient limitation. In the ocean interior, dissolved iron concentration is generally below biological requirement relative to essential macronutrients leading to iron limitation in parts of the sea surface where additional continental supply of Fe is not sufficient[16,17]. The dearth of bioavailable Fe from continental sources limits primary production and nitrate utilisation in HNLC regions[18,19]. One direct consequence of this Fe deficiency is the depletion of silicic acid in these HNLC regions owing to the high uptake ratio of $Si(OH)_4$ relative to carbon and other macronutrients by diatoms growing under Fe stress[20,21]. This over consumption of silicic acid during diatom growth in turn leads to a high $Si:C_{org}$ ratio of the settling biogenic particles, thereby enhancing sedimentary Si burial. Similarly, in coastal areas the $Si:C_{org}$ ratio of settling particles varies greatly between margins. Continental margins that support high biogenic Si fluxes and burial such as the Eastern Pacific and the GoC show elevated $Si:C_{org}$ ratios (1-4.5), whereas biogenic fluxes in the Arabian Sea and the Benguela upwelling system display $Si:C_{org}$ ratios < 1 (Fig.1c). Such very large variations cannot be simply explained by differences in silicic acid to nitrate and phosphate ratios of thermocline waters that upwell and fuel biological production. Further analyses of sediment trap data[15] presented in Fig.1c indicate that such a large contrast between margins cannot be explained solely by variations in siliceous versus calcareous primary producers or the differences in the ability of these skeletal remains to ballast organic carbon. Instead, the high $Si:C_{org}$ fluxes (>1) are related to high elemental Si:C ratios of the siliceous producers themselves (see Supplementary Material section 1; Fig.S2). Notionally, unlike open ocean HNLC provinces, coastal upwelling areas receive additional iron inputs from the shelf and continental sources and are not expected to be iron-limited. However, recent evidence suggests that iron limitation can arise even in coastal systems during the course of intense upwelling when these additional terrestrial Fe inputs are not sufficient to meet consumption by biota[22-25]. Here, using a suit of diatom-bound geochemical tracers, we demonstrate that high $Si:C_{org}$ export ratios and biogenic silica burial in some upwelling margins can be attributed to iron limitation. We focus on the GoC which constitutes a large Si sink despite its small size and is widely regarded as the archetypal area for the formation of diatomaceous sediments[26] .

Opal exports in the Gulf of California

Biogenic silica fluxes and Si:C_{org} ratio of the settling particles recorded between 1990 and 1997 in a sediment trap from the GoC are shown in Figure 2a[14]. The Si:C_{org} ratio increases drastically during winters, when intense upwelling conditions prevail, leading to extremely high silica export to the sediment. Diatoms, the main siliceous producers, ideally need a silicic acid to nitrate ratio of about 1[4]. With a nutrient ratio of 1.8 in the subsurface water, silicic acid supplied to the biota is in excess relative to nitrate in the GoC[27]. Yet $Si(OH)_4$ becomes completely utilized by the phytoplankton at the sea surface over the course of the upwelling season during ‘normal’ years[27] (Supplementary Material 3). This apparent surfeit silicic acid consumption in the photic zone and the elevated Si:C_{org} rain-rate ratio, comparable to HNLC regions such as the SO, together point to increased $SiOH_4$ uptake by diatoms, greater export of biogenic silica relative to C_{org} during the productive season, and are diagnostic characteristics of the effect of iron limitation on diatoms[23].

This inference is supported by the near-complete depletion of dissolved Fe (dFe) in the surface waters of the central region of the GoC and the low dFe:PO_4 ratios (generally $<10^{-3}$) in subsurface waters[28] falling well below the lower limit of the optimum subsistence ratio for coastal diatoms and close to the limit for other phytoplankton groups (Supplementary Material 4)[17,29]. This suggests that the GoC can be iron-limited during upwelling seasons when diatom production and biological consumption of both macro- and micro-nutrients increases[23,24].

In addition to Si:C_{org} rain-rate ratio, we track seasonal changes in the biological availability of dissolved Fe in the GoC using trace metal composition of isolated and cleaned diatom frustules from the sediment trap samples collected between March 1996 and February 1997[14] (Fig.2a). In the Supplementary Material (Section 3.3; Fig.S5), we show that Fe concentrations in diatom frustules track iron availability in natural seawater. In the GoC, Fe:SiO_2 ratios are elevated during the summer months (July and August) when the water column is stratified due to weak, southerly winds and productivity is at its lowest[14,27]. Iron measurements in the surface water of GoC corroborate this finding and reveal high dFe concentrations and dFe:macronutrient ratio in excess relative to biological requirement under stratified conditions due to terrestrial Fe inputs[28]. After stratification breaks down, Fe concentrations in the diatom frustules decrease by a factor of 5 on average (Fig.2b). The lowest Fe:SiO_2 ratios are generally associated with the highest Si:C_{org} ratio in settling particles and elevated biogenic silica fluxes, typically >1500 $mmole.m^{-2}.yr^{-1}$. The initial decrease in Fe availability (October) occurs in conjunction with increased biogenic carbon fluxes (carbonate and C_{org}) at the beginning of the upwelling season but prior to the biogenic silica peak, further documenting the sequence of events in the basin: increased biological consumption of iron in the surface and upwelling of Fe deficient water from the subsurface trigger Fe limitation, which in turn causes a dramatic increase in Si export as a result of increased Si:C uptake ratio by diatoms. Fe availability remains low during late winter-early spring and is only replenished in the summer when the water column becomes stratified and biological production reaches a minimum. Therefore, we suggest that conditions of transient iron limitation in the GoC fostered by high biological productivity following intense upwelling events result in high biogenic Si and Si:C_{org} fluxes[17,20] causing the GoC to operate as an enhanced Si sink[27].

It is important to recognize that in this scenario, Fe limitation is caused by intense upwelling of waters that are deficient in Fe relative to other macronutrients such that the supply of Fe from continental sources are insufficient to raise Fe levels to meet biological uptake. Thus, dampened upwelling should reduce the amount of micro-nutrient required from terrestrial sources to consume upwelled macronutrients. This in turn could lift Fe limitation. Such conditions occur during El Niño episodes, such as the 1991 event, in the Gulf of California (Fig.2a). As seen in Figure 2 (a & c), biogenic Si fluxes and the seasonal sharp increase in the Si:Corg ratio of settling particles are much less pronounced during El Niño than during intense upwelling years. In addition, excess silicic acid has been reported in the GoC during El Niño events, once again reflecting reduced Si uptake relative to other macronutrients[27]. As a corollary, one can envision that climatic periods characterised by dampened winter upwelling conditions will see the relaxation of Fe limitation in the basin, a significant reduction in Si burial and the build up of unutilised silicic acid at the sea surface.

Pliestocene opal burial in the Gulf of California

We examine this scenario using high-resolution sedimentary records from the GoC (Fig.3). Drastic declines in Si burials rates have been reported during Heinrich events-cold climatic periods in the Northern Hemisphere when eastern Pacific margins including the GoC experience reduced upwelling[30]. In particular, we explore whether such reduction in biogenic Si burial is matched by increased Fe biological availability and excess photic zone silicic acid by combining estimates of diatom-bound Fe and Si isotope ratios in Core MD02-2515. These long-term records suggest that the GoC has been operating in two modes with respect to iron status (replete vs. limited) during the last 26 kyrs. Periods of high Si burial and Si/Corg ratios at the core site correspond to periods of low diatom Fe/SiO_2 ratios and elevated δ^{30}Si (~1.2‰) On the other hand, the onsets of Heinrich events at 17 and 12.5 kys BP are characterised by decrease in Si burial and Si:Corg ratios, low δ^{30}Si and high Fe/SiO_2. The δ^{30}Si of dissolved silicic acid supplied to the GoC are estimated to be around 1.2‰[31,32]. Using a Raleigh fractionation model in a closed system (Supplementary Material section 4.2), we calculate that episodes of high opal burial correspond with periods of complete silicic acid utilisation in the GoC by biota[27]. Given that silicic acid to nitrate ratio is about 1.8 in the

GoC[27], complete silicic acid utilisation in upwelled waters requires diatom uptake of these nutrients in proportions >1 which is typical of iron limited conditions[20,22,33]. This is evident from the low Fe:SiO_2 recorded by diatoms during these periods. In contrast, Heinrich events were matched by 2- to 3-fold higher diatom-bound Fe/SiO_2 than the rest of the record, suggesting that Fe biological availability increased during diatom growth in these intervals. Assuming silicate to nitrate ratio of upwelling waters remained at 1.8, to achieve ~50% silicic acid relative utilisation diatoms should have consumed silicic acid and nitrate at a ratio close to 1. This uptake ratio of 1 suggests diatom growth under Fe replete conditions and diatom opal yield only limited by N. Therefore, the δ^{30}Si values measured during Heinrich events are consistent with the absence of Fe limitation. Importantly, these results suggest that the declines in Si burial during Heinrich events resulted from reduced Si uptake relative to other macronutrients by diatoms growing under Fe replete conditions, leaving surplus silicic acid at the surface of GoC. These conditions are similar to observations during modern El Niño episodes in the GoC[27]. This case study illustrates the switch from N limitation during dampened upwelling (El Niño) to Si limitation during intense upwelling periods (eg. La Niña) due to increased diatom $Si(OH)_4$:NO_3^- uptake ratios under Fe stress. Additionally, our sedimentary records suggests that intense upwelling conditions increase the biological consumption of Fe and the resultant transient Fe limitation is the key factor that enhances biogenic silica burial rates in the GoC.

Implications for the Marine Silicon Budget

The episodic nature of the upwelling process and the strong biological requirement for dFe imposed on restricted time and spatial scales make upwelling margins prone to transient Fe limitation, although at variable frequency and intensity subject to local conditions causing large differences in Si burial between upwelling margins. Upwelling margins such as the eastern Pacific with high opal burial also show high Si/Corg export in the water column (Fig.1a and also see Supplementary Material section 2; Fig.S3). This suggests Fe limitation is a key factor enhancing opal burial in these margins as our case study in the GoC illustrates. Eastern Pacific margins, where previous studies have reported transient Fe limitation, are an important contributor to the marine Si sink and could possibly account for the burial of 1.5 Tmol Si /year or ~25% of the marine Si sink. This is comparable to the largest open ocean Si sinks in the North Pacific and the SO (table 1, Supplementary Material section 2). We estimate from our global compilation that between 60 to 75% of the total Si sink may occur in open ocean and margins where Fe limitation is prevalent. Without these Si burial hotspots, oceanic Si limitation[5,6] would be much diminished. Thus our study reveals the intrinsic link between Fe stress and Si removal from the ocean and the indirect constraint imposed by Fe on the C rain-rate ratio and oceanic CO_2 uptake by fostering Si deficiency in the ocean.

(2499 words)

Methods

Silicon isotope determination has been conducted in ETH Zürich. A small amount of biogenic opal (0.5 mg) was dried down with concentrated perchloric acid at ~180°C in Teflon© vials, and then dissolved in 100 µl of 1 M NaOH, before being diluted to 5 ml with 0.01 M HCl after 24 hours. Equivalent to 10 µg of opal was loaded onto a pre-cleaned 1.8ml DOWEX 50W-X12 cation exchange resin bed (in H^+ form) and eluted with 5 ml of purified water (Milli-Q element 18.2 $M\Omega.cm^{-1}$). 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[34,35]. All results in this study were calculated using the $\delta^{30}Si$ notation for deviations of the measured $^{30}Si/^{28}Si$ from the international Si standard NBS28 in parts per thousand (‰). The long-term reproducibility was better than 0.07‰ δ^{30}Si (1 s.d.). Samples were measured at least 5 times, which resulted in a 95 % confidence level below 0.08‰.

The trace metal measurements on cleaned diatom frustules[36,37] were performed on an Ion Microprobe Cameca ims-4f at the NERC (National Environment Research Council) Microprobe Facility located at the School of Geosciences, University of Edinburgh. The clean diatom samples (2 mg) were pressed into an indium foil and analysed several (10-12) times for up to 10 cycles with the ion microprobe. We used a 10nA primary beam, 25 micron image field and energy filtering (75eV). The metal:SiO_2 values represent the average of the 10-12 measurements made for each sample. (253 words)

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Author Contributions L.E.P. and R.S.G. initiated the project. L.E.P. and R.H. measured diatom-bound trace metals, L.E.P. measured elemental composition and silicon isotopes, W.G and R.T. provided samples for diatom-bound trace metal measurements, L.E.P. and R.S.G. wrote the paper with the participation of W.G. All authors were involved in the discussions of the results and commented on the manuscript.

References

1 Nelson, D. M., Treguer, P., Brzezinski, M. A., Leynaert, A. & Queguiner, B. Production and Dissolution of Biogenic Silica in the Ocean - Revised Global Estimates, Comparison with Regional Data and Relationship to Biogenic Sedimentation. *Global Biogeochemical Cycles* **9**, 359-372 (1995).

2 Ragueneau, O. *et al.* A review of the Si cycle in the modem ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. *Global and Planetary Change* **26**, 317-365 (2000).

3 Archer, D. & Maier-reimer, E. Effect of Deep-Sea Sedimentary Calcite Preservation on Atmospheric Co2 Concentration. *Nature* **367**, 260-263 (1994).

4 Brzezinski, M. A. The Si-C-N Ratio of Marine Diatoms - Interspecific Variability and the Effect of Some Environmental Variables. *Journal of Phycology* **21**, 347-357 (1985).

5 Sarmiento, J. L., Gruber, N., Brzezinski, M. A. & Dunne, J. P. High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature* **427**, 56-60 (2004).

6 Moore, J. K., Doney, S. C. & Lindsay, K. Upper ocean ecosystem dynamics and iron cycling in a global three-dimensional model. *Global Biogeochemical Cycles* **18** (2004).

7 Dugdale, R. C., Wilkerson, F. P. & Minas, H. J. The Role of a Silicate Pump in Driving New Production. *Deep-Sea Research Part I-Oceanographic Research Papers* **42**, 697-719 (1995).

8 Dugdale, R. C. & Wilkerson, F. P. Silicate regulation of new production in the equatorial Pacific upwelling. *Nature* **391**, 270-273 (1998).

9 Tréguer, P. *et al.* The silica balance in the world ocean: a reestimate. *Science (New York, N.Y.)* **268**, 375-379, doi:10.1126/science.268.5209.375 (1995).

10 Broecker, W. S. & Peng, T. H. *Tracers in the Sea*. (Eldigio Press, 1984).

11 Tréguer, P. & De La Rocha, C. The world ocean silica cycle. *Annual Review of Marine Science* **5**, 477-501, doi:10.1146/annurev-marine-121211-172346 (2013).

12 Sirocko, F. DEEP-SEA SEDIMENTS OF THE ARABIAN SEA - A PALEOCLIMATIC RECORD OF THE SOUTHWEST-ASIAN SUMMER MONSOON. *Geologische Rundschau* **80**, 557-566, doi:10.1007/bf01803686 (1991).

13 Demaster, D. J. THE SUPPLY AND ACCUMULATION OF SILICA IN THE MARINE-ENVIRONMENT. *Geochimica Et Cosmochimica Acta* **45**, 1715-1732, doi:10.1016/0016-7037(81)90006-5 (1981).

14 Thunell, R. C. Seasonal and annual variability in particle fluxes in the Gulf of California: A response to climate forcing. *Deep-Sea Research Part I-Oceanographic Research Papers* **45**, 2059-2083 (1998a).

15 Honjo, S., Steven, J. M., Richard, A. K. & Roger, F. Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983. *Progress in Oceanography* **76**, doi:10.1016/j.pocean.2007.11.003 (2008).

16 Jickells, T. D. *et al.* Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **308**, 67-71, doi:10.1126/science.1105959 (2005).

17 Brand, L. E. Minimum Iron Requirements of Marine-Phytoplankton and the Implications for the Biogeochemical Control of New Production. *Limnology and Oceanography* **36**, 1756-1771 (1991).

18 Martin, J. H. *et al.* Testing the Iron Hypothesis in Ecosystems of the Equatorial Pacific-Ocean. *Nature* **371**, 123-129 (1994).

19 Falkowski, P. G. Evolution of the nitrogen cycle and its influence on the biological sequestration of CO2 in the ocean. *Nature* **387**, 272-275 (1997).

20 Takeda, S. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. *Nature* **393**, 774-777 (1998).

21 Brzezinski, M. A. *et al.* A switch from Si(OH)(4) to NO3- depletion in the glacial Southern Ocean. *Geophysical Research Letters* **29** (2002).

22 Hutchins, D. A. & Bruland, K. W. Iron-limited diatom growth and Si : N uptake ratios in a coastal upwelling regime. *Nature* **393**, 561-564 (1998).

23 Firme, G. F., Rue, E. L., Weeks, D. A., Bruland, K. W. & Hutchins, D. A. Spatial and temporal variability in phytoplankton iron limitation along the California coast and consequences for Si, N, and C biogeochemistry. *Global Biogeochemical Cycles* **17** (2003).

24 Fitzwater, S. E. *et al.* Iron, nutrient and phytoplankton biomass relationships in upwelled waters of the California coastal system. *Continental Shelf Research* **23**, 1523-1544, doi:10.1016/j.csr.2003.08.004 (2003).

25 Chase, Z. *et al.* Manganese and iron distributions off central California influenced by upwelling and shelf width. *Marine Chemistry* **95**, 235-254, doi:10.1016/j.marchem.2004.09.006 (2005).

26 Calvert, S. E. Accumulation of diatomaceous silica in the sediments of Gulf of California. *Geological Society of America Bulletin* **77**, 569-596 (1966).

27 Pichevin, L. *et al.* Silicic acid biogeochemistry in the Gulf of California: Insights from sedimentary Si isotopes. *Paleoceanography* **27**, doi:Pa220110.1029/2011pa002237 (2012).

28 Segovia-Zavala, J. A., Lares, M. L., Delgadillo-Hinojosa, F., Tovar-Sanchez, A. & Sanudo-Wilhelmy, S. A. Dissolved iron distributions in the central region of the Gulf of California, Mexico. *Deep-Sea Research Part I-Oceanographic Research Papers* **57**, 53-64, doi:10.1016/j.dsr.2009.10.007 (2010).

29 Twining, B. S. *et al.* Metal quotas of plankton in the equatorial Pacific Ocean. *Deep-Sea Research Part Ii-Topical Studies in Oceanography* **58**, 325-341, doi:10.1016/j.dsr2.2010.08.018 (2011).

30 Arellano-Torres, E., Pichevin, L. E. & Ganeshram, R. S. High-resolution opal records from the eastern tropical Pacific provide evidence for silicic acid leakage from HNLC regions during glacial periods. *Quaternary Science Reviews* **30**, 1112-1121, doi:10.1016/j.quascirev.2011.02.002 (2011).

31 De la Rocha, C. L., Brzezinski, M. A. & DeNiro, M. J. A first look at the distribution of the stable isotopes of silicon in natural waters. *Geochimica Et Cosmochimica Acta* **64**, 2467-2477 (2000).

32 Reynolds, B. C., Frank, M. & Halliday, A. N. Silicon isotope fractionation during nutrient utilization in the North Pacific. *Earth and Planetary Science Letters* **244**, 431-443 (2006).

33 Franck, V. M., Brzezinski, M. A., Coale, K. H. & Nelson, D. M. Iron and silicic acid concentrations regulate Si uptake north and south of the Polar Frontal Zone in the Pacific Sector of the Southern Ocean. *Deep-Sea Research Part Ii-Topical Studies in Oceanography* **47**, 3315-3338 (2000).

34 Georg, R. B., Reynolds, B. C., Frank, M. & Halliday, A. N. New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. *Chemical Geology* **235**, 95-104 (2006).

35 Reynolds, B. C., Georg, R. B., Oberli, F., Wiechert, U. H. & Halliday, A. N. Re-assessment of silicon isotope reference materials using high-resolution multi-collector ICP-MS. *Journal of Analytical Atomic Spectrometry* **21**, 266-269 (2006).

36 Morley, D. W. *et al.* Cleaning of lake sediment samples for diatom oxygen isotope analysis. *Journal of Paleolimnology* **31**, 391-401 (2004).

37 Ellwood, M. J. & Hunter, K. A. Determination of the Zn/Si ratio in diatom opal: a method for the separation, cleaning and dissolution of diatoms. *Marine Chemistry* **66**, 149-160 (1999).

Figure 1: **The distribution of biogenic silica fluxes and molar biogenic silica (Si) to organic carbon (Si:Corg) ratios shows the variability in Si:Corg ratio amongst a wide range of oceanic provinces (a & b):** ODV maps and shading are derived from JGOFS[15] (black dots) and the Guaymas basin, Gulf of California[14] (GoC, black star) sediment trap data. High-Nitrate, Low Chlorophyll regions (dotted white ellipses) and North East Pacific margin display higher Si:Corg export ratio than the surrounding open ocean. **(c)** Corg normalised biogenic Si and inorganic carbon (Cinorg) ratios in JGOFS sediment traps.

Figure 2: **Biogenic fluxes, Si:Corg ratio and diatom-bound Fe in the GoC sediment trap** **(a)** Si fluxes and Si:Corg ratios drastically increase during winter upwelling (blue stripes). **(b)** A close up on year 1996-1997 shows that Fe:SiO_2 (ppm, grey bars) is high during the stratified period and decreases during the upwelling season when inorganic (green) and organic carbon (black) fluxes increase. **(c)** 1990-1997 average biogenic flux changes in the GoC. Winter and upwelling conditions show elevated Si fluxes and Si:Corg ratios relative to summers and El Niño winter. Relatively constant inorganic carbon (Cinorg) suggests Si:Corg variations are not related to calcareous production.

Figure 3: **Multiproxy reconstruction of silica cycling and iron biological availability in the GoC over the last climatic cycle in core MD 02-2515** (27°53'N, 111°40'W) **illustrates the long-term impact of Fe limitation on Si burial.** Diatom-bound Fe **(a)** increases at the onset of Heinrich event 1 and the Younger Dryas period (yellow stripes), in conjunction with decreasing silicic acid relative utilisation (δ^{30}Si, **(b)**)[27], biogenic silica concentration (weight %) **(c),** Si:Corg molar ratio **(d).**