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The uptake and export of silicon and nitrogen in HNLC waters of the NE Pacific Ocean

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Abstract

The high-nitrate, low-chlorophyll (HNLC) waters of the Gulf of Alaska tend towards silicate rather than nitrate depletion as phytoplankton utilize nutrients during summer. This tendency is enhanced when iron supply is elevated through natural inputs such as from coastally generated mesoscale eddies or through artificial enrichment as was carried out in an in situ experiment in July 2002. However, ship-board incubations with iron enrichment demonstrate nitrate rather than silicate depletion for these waters. The difference between in situ and in vitro experiments occurs at least in part because deck incubations do not allow export of particulate Si and N. Due to the more efficient recycling of nitrogen and carbon, export favours the removal of silicon from the upper ocean (the Si pump). Previous measurements at Ocean Station Papa (50°N, 145°W) show that ~25% of the Si, but only ~7% of the C and ~4% of the N utilized during spring growth, is exported to a depth of 200 m. These results in the Gulf of Alaska agree with the present understanding of phytoplankton controls in other HNLC regions and show that any estimates of carbon export from iron enrichment should be based on Si- rather than N-limitation.

1. Introduction

Silicon is an important limiting element in the production and transport of organic material in high-nitrate-low-chlorophyll (HNLC) areas of world oceans (Dugdale et al., 1995; Ragueneau et al., 2000; Brzezinski et al., 2002; Ragueneau et al., 2002; Nelson et al., 2002; Francois et al., 2002). The export of Si from the upper ocean is dependant on dissolved silicate supply to the euphotic zone and its subsequent utilization by diatoms. Biogenic silica (BSi) can be effectively turned over in the upper ocean, especially in warm waters (Hurd, 1972). However, Si can be efficiently exported when diatoms flocculate or are packaged

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in fecal pellets (Ragueneau et al., 2000). Under low-temperature conditions such as seen in the Southern Ocean, bacterial degradation of organic materials coating diatom frustules is slowed enough to decrease Si solubilization, leading to increased Si deposition (Bidle et al., 2002). There is some suggestion that iron limitation may increase the silicification of diatoms (Ragueneau et al., 2000), and any enhancement of detrital sinking rates by grazers would also reduce silica dissolution in the upper ocean.

According to the Dugdale and Wilkerson (1998) model of the equatorial Pacific upwelling region, silicate limitation occurs in large part because, although the supply and uptake rates of nitrate and silicate are about equal, the more efficient recycling of N in the mixed layer by biota favours the export of Si. The Southern Ocean also experiences silicate limitation as a result of strong diatom growth and higher turnover rates of nitrogen than silicon (Boyd et al., 1999; Nelson et al., 2002).

The third great HNLC realm, the subarctic Pacific, occasionally experiences silicate depletion. Koike et al. (2001) sampled several North Pacific regions in the summer of 1999 and found silicate depletion in both the deep basin region of the Bering Sea and the Oyashio region of the western subarctic Pacific, but not in the Western Subarctic Gyre nor in the Gulf of Alaska (Alaska Gyre). These two gyres generally remain nitrate- and silicate-rich as a result of iron limitation of algal growth (Martin et al., 1989; Boyd et al., 1996). This is a typical condition in the subarctic NE Pacific (Whitney and Freeland, 1999), although silicate depletion has been observed sporadically. During the 1970s, when surface waters were frequently sampled at Ocean Station Papa (OSP; 50°N, 145°W), summer silicate levels declined to $\sim 1\,\mu M$ in 1972, 1976 and 1979 (Wong and Matear, 1999). On each of these occasions, nitrate remained abundant ($>2\,\mu M$). Also, Whitney and Welch (2002) found both oceanic and coastal areas of low silicate in 1998 and 1999, during and following the strong 1997–1998 El Niño. They show that source waters for winter mixing and summer upwelling changed dramatically during this El Niño due to strong northward advection of California Undercurrent waters (Freeland, 2002) and suggest that the resulting decrease of the Si/NO_3 ratio of these waters leads to silicate-limited conditions.

Iron supply and sunlight both control diatom growth in the Gulf of Alaska (Maldonado et al., 1999). Since iron levels usually decrease with distance from shore (Nishioka et al., 2001), any mechanism that increases iron supply to surface waters of the open ocean should increase Si drawdown. In this paper, Si drawdown and export from the upper ocean will be shown to be enhanced by iron additions from both mesoscale eddies that transport iron rich coastal waters into the Gulf of Alaska's HNLC region and an in situ enrichment experiment (Boyd et al., 2004) conducted near OSP in 2002.

2. Methods

The Line P Program surveys the southern Gulf of Alaska typically three times each year. The survey line extends from the coast of British Columbia (BC) to Ocean Station Papa (OSP at 50°N, 145°W), some 1500 km to the west (Whitney and Freeland, 1999). Data from 1998, 2000 and 2002 surveys were used in this paper, and are available through the Line P web site (http://www-sci.pac.dfo-mpo.gc.ca/osap/data/linep/linepselectdata_e.htm). Often, other research programs participate in these surveys, so that surveys frequently cover a broader area of the Gulf of Alaska. In 2000 and 2001, surveys of anticyclonic Haida eddies (Crawford and Whitney, 1999) were sequential with Line P cruises. In September 2002, the Line P survey returned along a northern section into Hecate Strait (north coast of British Columbia, Fig. 1).

Temperature and salinity data were routinely collected by Seabird 911+ CTD on ocean surveys. "Surface" water samples were collected from ~ 5 m (within the mixed layer) at stations along survey lines. Samples were analysed onboard ship for dissolved nutrients using a Technicon AAII Autoanalyzer and modified Technicon procedures (Barwell-Clarke and Whitney, 1996; analytical precision quoted as $0.1\,\mu M$ nitrate or NO_3^-, $0.4\,\mu M$ silicate or H_4SiO_4 (silicic acid) and

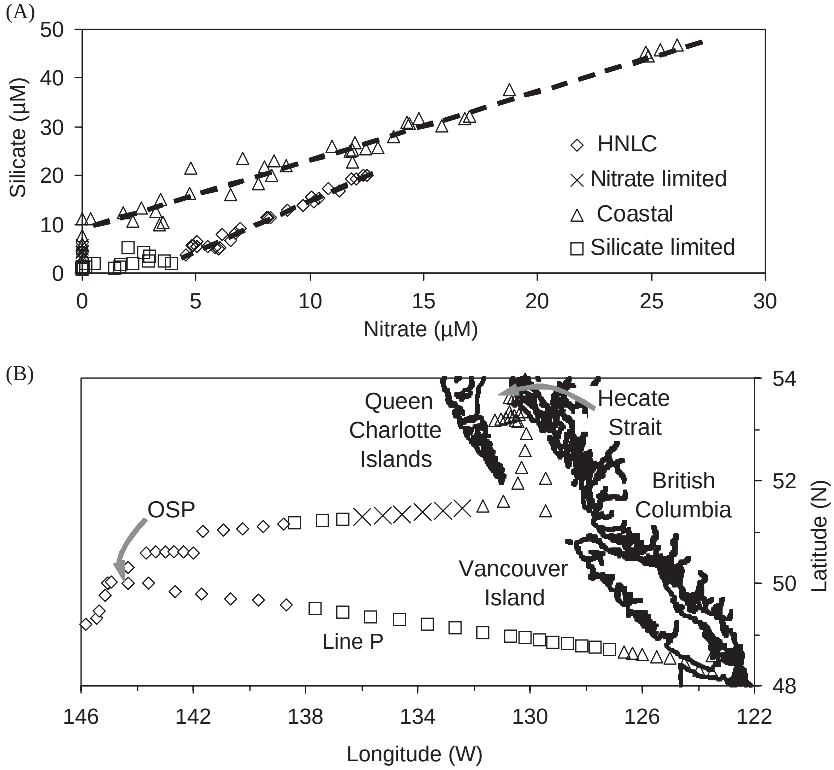

Fig. 1. Silicate vs. nitrate plot (A) for surface waters (~5 m depth) of the Gulf of Alaska in September 2002. Several distinct water masses are identified by their nutrient properties and the distribution of these is shown geographically in the bottom panel (B). Linear regression lines are shown for HNLC (slope = 2.03, $r^2 = 0.98$) and for coastal (slope = 1.46, $r^2 = 0.94$) waters. Ocean Station Papa (OSP), the terminal station of Line P at 50°N, 145°W, is indicated.

0.02 µM phosphate or PO_4^{-3}), and for chlorophyll-*a* following the fluorometric procedure of Strickland and Parsons (1972).

On-deck incubations of iron-enriched seawater (1–2 nM Fe added) collected at OSP from a depth of ~10 m (within the mixed layer) were carried out onboard Line P cruises in both the June 2001 and September 2002. Incubators were temperature regulated with surface seawater and screened to ~30% ambient light (neutral density screening). All incubation containers were carefully acid-washed to eliminate trace metal contamination (e.g., Crawford et al., 2003). In both experiments, iron analyses showed that dissolved Fe levels were ~0.1 nM in control containers (Crawford et al., 2003), typical of mixed-layer values at OSP (Nishioka et al., 2001; Johnson et al., 2005). As a result, control containers experienced little or no increase in chlorophyll over the experiments. Nutrients were sampled each 1–2 days and analysed onboard ship.

An in situ iron-enrichment experiment called SERIES (Subarctic Ecosystem Response to Iron Enrichment Study), the initial experiment of the Canadian Surface Ocean Lower Atmosphere Study (C-SOLAS), was hosted by the Line P Program between July 9 and August 4, 2002 near OSP. Ferrous sulphate was dissolved in acidified seawater and added to a patch of ocean 8 km × 8 km to enrich the mixed layer with ~4 nM Fe (W.K. Johnson, pers. comm.). A second smaller Fe addition took place July 16 following a deepening of the mixed layer. These iron enrichments stimulated phytoplankton growth that resulted in a diatom bloom and silicate depletion (Boyd et al., 2004).

The Canadian Coast Guard Ship *John P. Tully* supported eddy, Line P, and SERIES surveys. Data are shown from a September 5 to October 3, 2000 survey of Line P and Haida eddies, and an August 24 to September 12, 2002 Line P and Hecate Strait survey. Surface measurements from eddy cruises in February and June 2000 are used to estimate nutrient utilization. SERIES data are shown only for the period during which the Tully was sampling the iron-enriched patch. Further measurements were taken from R/V *El Puma* (Mexico) and R/V *Kaiyo Maru* (Japan), and are described in Boyd et al. (2004).

3. Results

3.1. Nutrient distribution

Throughout this paper a distinction will be made between nutrient "uptake" by phytoplankton in culture and "drawdown" that is observed in situ from seasonal surveys. Drawdown is the net result of processes that include uptake by plankton, recycling within the upper ocean, and export either by grazing or vertical transport to the intermediate ocean.

In summer 2002, near the seasonal nutrient minimum in the Gulf of Alaska (Whitney and Freeland, 1999), surface nutrient concentrations defined several distinct water masses (Fig. 1). Coastal waters tended to nitrate exhaustion, containing about 9 μM Si when nitrate was depleted. The linear regression of these data has a slope of 1.5 μM Si/μM NO_3. Since these waters are in large part produced by upwelling and mixing in tidal channels, then exported onto the shelf by estuarine circulation (e.g., Crawford and Dewey, 1989), this regression might be considered an estimate of the nutrient drawdown ratio and is the same as that calculated by Whitney and Freeland (1999) for OSP. HNLC waters, on the other hand, tended towards Si depletion, with surface nutrient values lying along a regression line with a Si/N slope of 2.0 and an intercept of 3 μM NO_3. Si levels decline to ~2 μM in the coastal extreme of these waters (Fig. 1), a level which is thought to limit diatom growth (Ragueneau et al., 2000; Peterson et al., 2005).

Between coastal and HNLC regions in summer 2002 existed a broad transitional area, extending seaward of the continental shelf to almost 600 km offshore, in which silicate was low to the south and nitrate depletion occurred to the north. Along Line P, the data show a slight decrease in Si towards the coast, reaching a low value of 0.8 μM Si in nitrate-depleted waters. Northern transitional waters show broad NO_3 depletion and a range of Si concentrations depending on their proximity to the Si- and Fe-rich coastal waters.

3.2. Nutrient drawdown in Haida eddies

The Haida eddy that formed in winter 2000 (Haida-2000) was sampled during its formation in February and after it had left the coast, in June and September of its natal year. The winter survey found that mixed-layer nutrient levels were slightly higher in the eddy than in surrounding waters, exceeding 25 μM silicate and 15 μM nitrate at the eddy centre (Fig. 2). The variability of the mixed-layer depth and nutrient dynamics within this layer is discussed in detail by others (Chierici et al., 2005; Peterson et al., 2005). In April, satellite imagery shows that this eddy experienced a spring bloom with chlorophyll levels exceeding 3 μg/L (Crawford et al., 2005).

The next sampling of Haida-2000 was in June, 2 months after its spring bloom and ~150 km to the west of its winter position. At this time, silicate was less than 3 μM in the eddy-mixed layer, distinctly less than in surrounding waters (Fig. 2). Nitrate levels were ~4 μM, similar to neighbouring waters. The nutrient drawdown through spring (February minus June) equalled 11 μM nitrate and 22 μM silicate, a Si/N ratio of 2.0. Although it will not be discussed further, phosphate drawdown over this period was 0.67 μM, resulting in an N/P of 16 (the Redfield ratio). This rate of nutrient drawdown is considerably more than has been observed seasonally at OSP (6.9 μM NO_3 and 11.1 μM Si, Whitney and Freeland, 1999).

The survey of surface waters in June 2000 (Fig. 3) found somewhat different nutrient levels

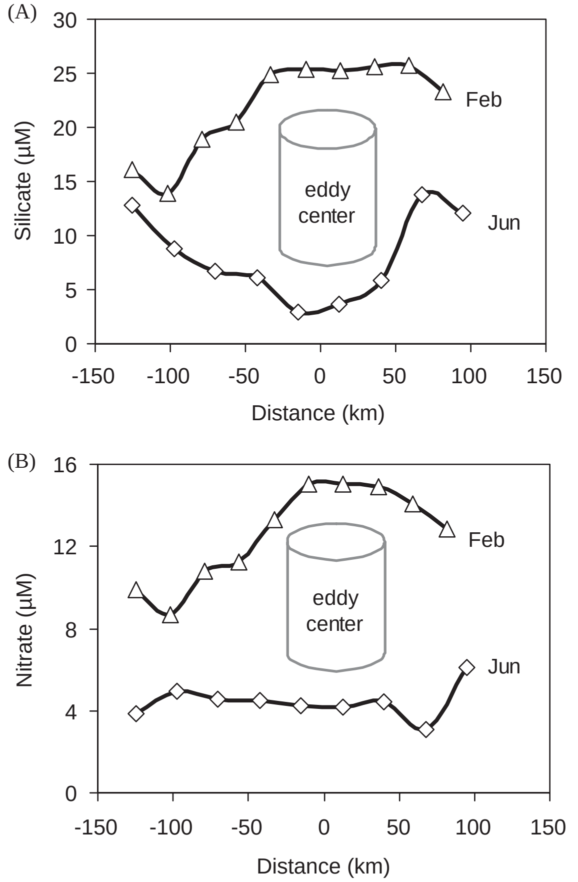

Fig. 2. Silicate (A) and nitrate (B) concentrations at a depth of 5 m across the anticyclonic eddy, Haida-2000, in February and June 2000. Locations of the eddy sections are shown in Fig. 3. Distance scales for February are from east (negative) to west (positive), and for June are from south (negative) to north (positive).

than observed in September of 2002. Because this was a spring cruise, silicate limitation had not yet developed in transition waters, although nitrate depletion was observed offshore from the shelf. Coastal waters with high Si abundance are still evident in Juan de Fuca Strait, but do not extend onto the shelf. At this time of year, there is no indication of coastal upwelling, which supplies nutrient-rich waters onto the shelf in summer (Freeland and Denman, 1982). However, the Haida-2000 eddy has nutrient properties resembling summer HNLC waters (Figs. 1 and 3) because it has already experienced a spring bloom (Peterson et al., 2005). These waters are relatively rich in nitrate compared with silicate, the eddy centre having as little as 3.0 µM silicate and 4.2 µM nitrate.

A feature of Figs. 1 and 3 is that nutrient data from three dominant water masses (coastal, transition and HNLC) tend to cluster along linear regression lines. Nutrient concentrations in surface waters are determined by physical (winter mixing, characteristics of source waters, advection) and biological (uptake by plankton, remineralization) processes, which makes interpretation of these regressions complex. The slopes of the regressions are noted, but not discussed further.

Another patch of low-Si water was sampled by chance on the June survey. About 50 km to the NE of OSP, Si levels were less than 2 µM, nitrate exceeded 7 µM (Fig. 3), and chlorophyll *a* was ~1.5 µg/L, compared with 0.1 to 0.3 µg/L in surrounding waters. A 3-year-old Haida eddy has been tracked to this location (Whitney and Robert, 2002) and was faintly evident in satellite altimetry images of June 2000.

Iron and silicate profiles from Line P station P16 (49.28°N, 134.67°W) in June and September 1998 show the influence of Haida-1998 on these waters (Fig. 4). Iron data were presented in Nishioka et al. (2001) and are reproduced here on an expanded scale to show the importance of eddies in transporting iron. In June 1998, iron levels at P16 were typical of open ocean.

However, when Haida-1998 arrived at this site, dissolved iron (0.45 µM filtrate) levels increased to an almost uniform 0.6 nM below the mixed layer. This water mass does not have the typical oceanic correlation between Fe and Si (0.0047 nM Fe/µM Si, Martin et al., 1989; 0.0043 nM Fe/µM Si from Nishioka et al., 2001). Rather, the Fe/Si ratio at 100 m depth was 0.071, more than an order of magnitude higher than normal for these waters. At 200 m in the eddy, this ratio was 0.018, still much higher than is typical for oceanic waters. Haida-2000 also transported waters that were relatively rich in iron compared with silicate and nitrate (Johnson et al., 2005; Peterson et al., 2005; Chierici et al., 2005).

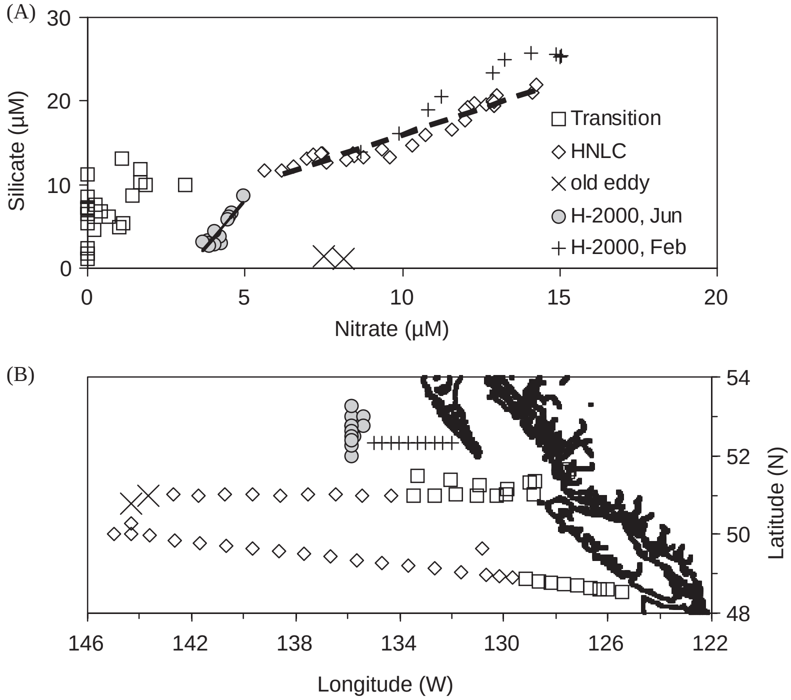

Fig. 3. Silicate vs. nitrate plot (A) for surface waters (~5 m depth) west of British Columbia in February and June 2000. Nutrient distributions in June identify several water types (B) in the Gulf of Alaska, including coastal, transition, HNLC and Haida Eddy. A mesoscale eddy was tracked to a position north of OSP and two samples collected in it are identified. Linear regressions are shown for June Haida-2000 (slope = 4.56, $r^2 = 0.81$) and HNLC waters (slope = 1.20, $r^2 = 0.91$).

3.3. Nutrient drawdown in response to iron enrichment experiments

On-deck incubations repeatedly show that nitrate is depleted when Gulf of Alaska HNLC waters are iron enriched (Martin et al., 1989; Boyd et al., 1996; Crawford et al., 2003). Recent experiments reproduce these results. By enriching water from OSP with 1–2 nM Fe, nitrate was completely used within 8 d both in June 2001 (Fig. 5A) and September 2002 (Fig. 5B) deck incubations, whereas Si remained replete. As has been previously observed in situ at OSP (Whitney and Freeland, 1999), nitrate uptake precedes silicate utilization in spring. Through the period of diatom growth (silicate utilization), Fe-rich oceanic waters behave much like diatom cultures (Brzezinski, 1985) in that the uptake ratio of Si and NO_3 is close to 1. This is observed over the last 2 days in June 2001 and over the last 4 days of the September 2002 incubations.

However, nutrient dynamics during the recent SERIES experiment in July 2002 were much different. Following an initial period of entrainment, nutrients in the mixed layer (~20 m) were drawn down at a Si/NO_3 ratio of 2.8 over a 1-week period (Fig. 5). Since initial nutrient concentrations were on the order of 10 µM NO_3 and 15 µM Si, the high drawdown ratios lead to silicate-rather than nitrate-depletion (Boyd et al., 2004). Haida-2000 also saw high silicate drawdown compared to nitrate (Peterson et al., 2005).

4. Discussion

In the past few years, the importance of Si in controlling primary productivity in HNLC waters

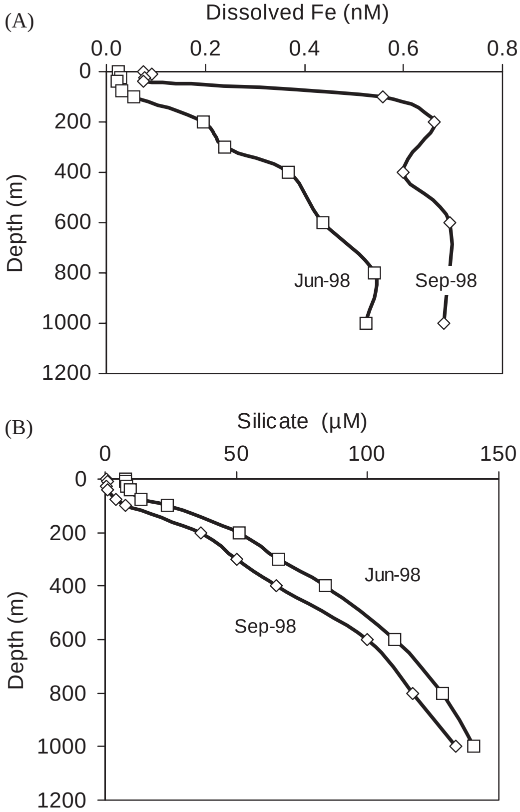

Fig. 4. Dissolved iron (A) and silicate (B) profiles at Line P station 16 (49°17′N, 134°40′W) in June and September 1998. The mesoscale eddy, Haida-1998, was located at this station in September.

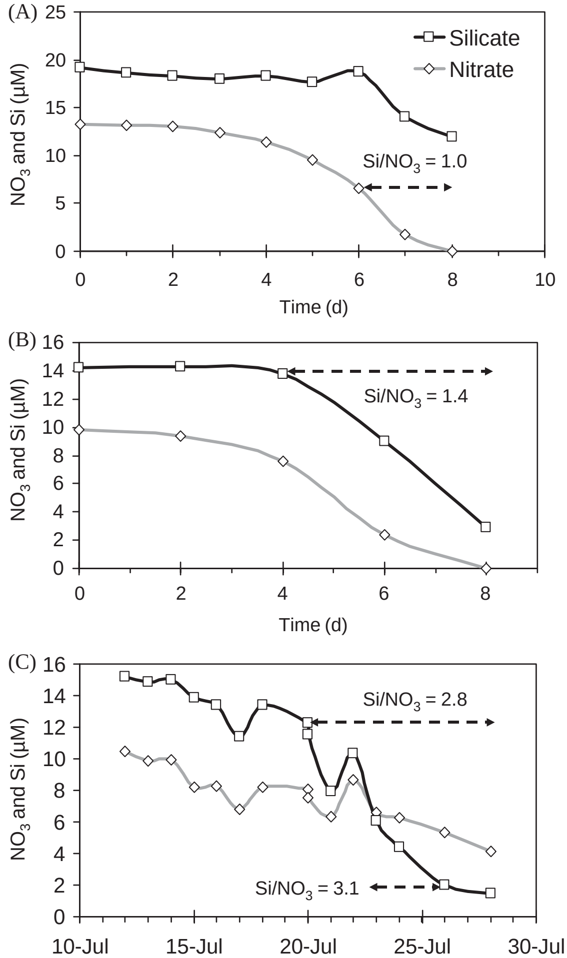

Fig. 5. Time course experiments of nutrient uptake following iron enrichment. The upper panel (A) tracks nitrate and silicate uptake in a deck incubation study from June 2001. A similar experiment was carried out in September 2002 (B). The bottom panel (C) shows nitrate and silicate in the mixed layer during the SERIES experiment in July 2002. The uptake ratio of Si/NO_3 is noted for periods of diatom growth in each study.

and in contributing to the transport of C into the interior ocean has been reassessed. Si appears to be part of a complex nutritional control of diatom growth in HNLC waters that, in addition, includes at least iron, nitrate and light. In the equatorial Pacific, Dugdale and Wilkerson (1998) suggest that Si supply limits new production. Their model of this system exports all biogenic Si that is grazed, but only 30% of the N. Since source waters supply Si and NO_3 to the euphotic zone at a ratio near 1, such export fractionation runs waters towards Si rather than N depletion, a process that has been termed the Si pump (Dugdale et al., 1995). In the Southern Ocean, Franck et al. (2000) found that iron limited primary productivity to the south of the polar front, whereas Si was limiting north of the front. In the same HNLC region, south of New Zealand, Boyd et al. (1999) found seasonal phytoplankton growth dependencies on iron, silicate and/or light. In the subarctic NE Pacific, a co-limitation of iron and light has been described (Maldonado et al., 1999).

Transporting phytoplankton carbon effectively to the intermediate or deep ocean requires that sinking particles contain ballast beyond what the organic constituents of cells supply (Francois et al., 2002). The primary high-density materials produced by plankton are opal (hydrated SiO_2) and calcium carbonate. Of these two materials, carbonate is the more effective ballast material for organic carbon transport to the deep ocean (Francois et al., 2002), although opal is important at high latitudes in removing organic carbon and nitrogen out of the mixed layer. In most deep ocean regions, little opaline material is deposited in sediments. The major exception to this is in the polar region of the Southern Ocean where a substantial percentage of the world's Si deposition occurs (DeMaster, 2002; Nelson et al., 2002). It appears this occurs because silicon fixation rates by diatoms are very high (Nelson et al., 2002) and perhaps because the digestion rate of the organic film which protects the opal surface of diatom frustules is slowed in cold waters (Bidle et al., 2002), thus decreasing the dissolution rate of opal. Iron-limited growth in the Southern Ocean leads to the preferential export of Si compared with C and N, due to the faster turnover of nitrogen and carbon (Brzezinski et al., 2003). In general, the transport of Si from the surface to the deep ocean is decoupled from fluxes of C and N due to processes which occur largely in the upper ocean (Ragueneau et al., 2002).

4.1. Si supply and drawdown in the Gulf of Alaska

Silicate drawdown to concentrations potentially limiting to phytoplankton (~1–2 μM, since this amount of Si is commonly residual in surface waters; Whitney and Welch, 2002), is not common in the HNLC waters of the Gulf of Alaska. However this low concentration was observed three times during the 1970s at OSP (Wong and Matear, 1999) and was measured near OSP in June 2000 at the location of an old Haida eddy (Fig. 3). The June 2000 measurements found a high level of unused nitrate (~8 μM), similar to results of Koike et al. (2001) in the Bering Sea Basin in the summer of 1999. Following the 1997–1998 El Niño, Whitney and Welch (2002) observed areas of low (<2 μM) Si off the B.C. coast and suggested this resulted from an enhanced northward flow of California Undercurrent waters. These waters are the source of coastal upwelling (Mackas et al., 1987) and are relatively low in silicate compared with nitrate, the Si/N ratio varying between 1.0 and 1.4 at a depth of 100 m in the past 15 years (Whitney and Welch, 2002).

Still, phytoplankton production in the Gulf of Alaska is thought to be controlled by nitrate, iron or light (Boyd et al., 1999; Maldonado et al., 1999; Denman and Peña, 2002). Perhaps this is understandable since areas that typically become nutrient-depleted each summer are nearer shore, where Si input from rivers is high. The Columbia River discharges on the order of 50×10^9 mol Si into the ocean annually (Hooper et al., 2001; United States Geological Survey) and the Fraser River adds about 10×10^9 mol Si yr^{-1} to the BC coast (Environment Canada). Other minor rivers and coastal runoff increase this input. Columbia and Fraser discharges are sufficient to enrich a coastal band of water 100 km wide by 40 m deep between latitudes of 40° and 55°N (Northern California to the BC–Alaska border) by 10 μM Si annually. This input is approximately the level of excess Si found in coastal waters during the September 2002 survey (Fig. 1) and ensures that the shelf/slope region off the coast of BC will become nitrate-rather than silicate-depleted each summer (Whitney et al., 1998). The coastal view of nutrient limitation has been injudiciously applied to HNLC waters where Si supply is much more tentative. For example, the seasonal drawdown of Si/NO_3 at OSP is ~1.5, which is similar to the supply ratio found in the winter mixed layer (Whitney and Freeland, 1999). With supply and drawdown ratios so close, either nitrate or silicate could become limiting if iron limitation were removed.

4.2. Role of Fe in regulating nutrient uptake

Iron limitation is well documented in the HNLC waters of the Gulf of Alaska, starting with the early studies of Martin et al. (1989). Consistently, onboard-ship iron-enrichment experiments result in nitrate rather than silicate depletion (e.g. Figs. 5A and B). However, silicate demand is higher in iron replete Haida eddies (Fig. 3; Whitney and Robert, 2002; Peterson et al., 2005).

In an extreme case, waters near OSP contained $>7\,\mu M$ nitrate when silicate was limiting to diatoms ($<2\,\mu M$; Fig. 3). The SERIES iron enrichment experiment in July 2002 (Boyd et al., 2004) permitted biogenic export with the result that Si became the limiting nutrient. SERIES confirms that low silicate in the HNLC North Pacific results from Fe enrichment, as was the contention of Wong and Matear (1999) in explaining three periods of low Si at OSP in the 1970s.

Dust transport events from Gobi Desert storms or Alaskan volcanoes have been perceived as iron sources capable of producing episodic bursts of primary production (Boyd et al., 1998). In addition, there is now evidence of iron transport by Haida eddies from continental margins into the Gulf of Alaska and enhanced productivity within these eddies (Fig. 4; Johnson et al., 2005; Chierici et al., 2005; Peterson et al., 2005). These eddies were larger and more numerous during the 1982 and 1998 El Niño events (Crawford, 2002). A large eddy can transport $5000\,km^3$ of coastal waters, rich in nutrients, into the Gulf of Alaska (Whitney and Robert, 2002). If enriched in iron by 1 nM, the eddy would carry 5×10^6 mol Fe offshore (see Johnson et al., 2005, for details of iron transport in Haida eddies). At a cellular quotient of $\sim2.4\,\mu M$ Fe/mol C for $>3\,\mu m$ phytoplankton (Maldonado and Price, 1999), this is sufficient iron to support the production of $\sim2\times10^{12}$ mol C, equal to the average annual new production of OSP (~3 mol $C\,m^{-2}\,yr^{-1}$, Wong et al., 1995), over an area of close to $10^6\,km^2$, although eddy iron would largely be added to pycnocline waters (100–400 m depth) where it could be slowly entrained into the mixed layer over several years. Such iron enrichment is particularly important in stimulating diatom growth, which increases Si demand. Observations in eddies and SERIES suggest that iron enrichment increases the drawdown ratio of Si/N from the typical seasonal level of 1.5 (Whitney and Freeland, 1999) to ratios between 2 (Haida-2000 seasonal) and 2.8 (diatom bloom in SERIES). Takeda (1998) found that the Si/NO_3 uptake ratio increased to 2.0 for two diatom species during iron deficiency, although Brzezinski et al. (2003) observe that diatoms rely more on regenerated nitrogen under such conditions with the result that Si/total N uptake ratio does not change appreciably from Brzezinski ratio of ~1 (Brzezinski, 1985).

4.3. Export fractionation

The prime tenet of the Si pump mechanism is that there is a preferential retention of N in the upper ocean, compared with Si (Dugdale et al., 1995). That we see Si/NO_3 drawdown ratios during SERIES and in eddies of 2–3, yet measure ratios closer to 1 in deck incubations, demonstrates export fractionation is occurring. Data from OSP can be used to estimate the efficiency of the Si pump in this region. Seasonal drawdown of Si and NO_3 from May through June, when silicate utilization is evident, occurs at a ratio of 1.5 (Whitney and Freeland, 1999). Annual particulate fluxes to sediment traps at 200 m (Wong et al., 1999) occur at a Si/N ratio of 5.3, and at a ratio of 6.8 in May/June. The preferential recycling of N and C, compared with Si, is enhanced with depth (Table 1). These spring data show the efficiency of the Si pump at OSP, with molar C:Si:N ratios reaching 8.4:24:1 in particulate materials at 3800 m rather than the more typical 6.6:1.2:1 in diatoms (Brzezinski, 1985).

These results, as well as those from the equatorial Pacific (Dugdale and Wilkerson, 1998) and Southern Ocean (Boyd et al., 1999; Nelson et al., 2002), suggest that HNLC waters will head into Si-limited conditions when iron supply increases. Recent work on silica transport in the Southern Ocean (Ragueneau et al., 2000; Nelson et al., 2002; DeMaster, 2002) has resulted in models that are including silicon as a control on phytoplankton (Pondaven et al., 1999; Moore et al., 2002). This seems to be an important step, especially as models are developed to look at the effects of climate change (e.g., Denman and Peña, 2002) and agencies consider the effectiveness of oceanic iron enrichment in removing carbon dioxide from the atmosphere.

In their model of Si and N in HNLC waters, Pondaven et al. (1999) select a higher rate of particulate N remineralization ($0.10\,d^{-1}$) than biogenic Si dissolution ($0.05\,d^{-1}$) in detritus in

Table 1
Estimates of C, N and Si fixed by primary production in the mixed layer and elemental fluxes from mixed layer to deep ocean during the May–July period at Ocean Station Papa. Surface nitrate and silicate data are assumed to be representative of a mixed layer which is 40 m deep (Whitney et al., 1998). The percent of primary production or nutrient drawdown that is exported from the mixed layer is shown in brackets for each sediment trap depth

	Carbon (mmol $m^{-2} d^{-1}$)	Nitrogen (mmol $m^{-2} d^{-1}$)	Silicon (mmol $m^{-2} d^{-1}$)
Mixed layer	40[a]	2.2[b]	6.9[b]
200 m trap[c]	2.9 (7.3%)	0.25 (4.2%)	1.7 (25%)
1000 m trap	0.75 (1.9%)	0.097 (2.4%)	1.5 (22%)
3800 m trap	0.31 (0.8%)	0.037 (1.2%)	0.90 (13%)

[a]Primary productivity data from Wong et al. (1995).
[b]Surface nutrient data from Whitney and Freeland (1999).
[c]Sediment trap data from Wong et al. (1999).

the North Pacific to generate the substantial Si fluxes that are observed. They suggest that export production from HNLC waters is based almost entirely on diatom growth (as do Dugdale and Wilkerson, 1998). Results presented here suggest that such models may need to use an even stronger Si/N fractionation ratio to reproduce nutrient removal from the upper ocean.

4.4. Implications on CO_2 sequestration by iron enrichment

For two reasons, iron fertilization of HNLC regions of the world's oceans may be inefficient in sequestering carbon from the atmosphere into the deep ocean. Firstly, transport of carbon to the deep ocean by particles ballasted with BSi appears to be an ineffective process (Francois et al., 2002; Ragueneau et al., 2002). Since HNLC regions base C export largely on diatom growth and opal ballast, C exported from the upper ocean will be efficiently remineralized before reaching great depth. The shallower remineralization occurs, the less effectively C is removed from the atmosphere. Chierici et al. (2005) found no evidence of increased carbon export in the Haida-2000 eddy, even though there was a substantial drawdown of CO_2 and silicate by phytoplankton in spring. Their conclusion was that this mesoscale eddy was a recycling system, not one that exported carbon to the deep ocean.

The second problem with iron enrichment of HNLC waters, according to early results from the SERIES experiment, is that iron-stimulated phytoplankton growth increases the effectiveness of the Si pump as diatoms become the dominant species. For example, at OSP winter nitrate of 15 μM typically decreases to 7.5 μM in summer (Whitney and Freeland, 1999) as 11 μM of Si are utilized. Increased iron supply may increase the Si/NO_3 drawdown ratio during a diatom bloom to 3. At a ratio of 3, the 25 μM of Si available in winter would result in the drawdown of 8 μM NO_3, leaving 7 μM nitrate unused. Examples of this occurred during periods of Si depletion at OSP in the 1970s, when residual nitrate levels of 3–8 μM were measured (Wong and Matear, 1999; Stephens, 1977). Therefore, iron enrichment would not increase nitrate drawdown or carbon fixation from what currently occurs with iron limitation. These trends are counter to the results of incubation experiments by Takeda (1998) and Hutchins and Bruland (1998), which show that iron enrichment decreases the uptake ratio of Si/NO_3. Recent results of Brzezinski et al. (2003) suggest however, that when estimating Si/N uptake ratios in phytoplankton, all forms of available nitrogen must be considered. One of the primary points in this paper is that incubation experiments are not an adequate means of describing the transport of biogenic materials in open ocean. Without considering the role of nutrient recycling and export fractionation, it is not possible to predict which nutrient will limit productivity of a marine ecosystem.

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