Chapter 10

Biogeochemical Transformations of Silicon Along the Land–Ocean Continuum and Implications for the Global Carbon Cycle[1]

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10.1 Introduction

In the context of a changing Earth, one central interest is an improved understanding of the global carbon cycle and an improved prediction of its likely changes as consequence of global changes. Large-scale programs investigated the oceanic cycling of carbon (C) and associated biogenic elements, mainly nitrogen (N) and phosphorus (P), as limiting nutrients of the global production by marine phytoplankton (Falkowski 1997; Tyrrell 1999). However, continental margins play an essential role in the global C cycle, accounting for 14% of global primary production, 80–90% of new production, and 80% of global organic carbon (C_{org}) burial (Smith and Hollibaugh 1993; Rabouille et al. 2001). Continental margins also represent a filter that removes riverine dissolved and suspended constituents along their path from land to the open ocean (Billen et al. 1991). In order to characterize the C cycle on continental margins, their contribution to carbon dioxide (CO_2) sequestration and to determine horizontal C and associated biogenic element fluxes, some 200 N and P flux budgets have been constructed around the world (cf. Smith et al. 2003b, LOICZ 1998). One biogenic element, silicon (Si) has been largely ignored. Silicon is required by diatoms, (Guillard et al. 1973) which play a critical role in the marine C cycle (e.g., Smetacek 1999).

Our objectives in this paper are to demonstrate why Si is important in marine biogeochemical studies and to justify why we need to quantify Si fluxes on continental margins. We describe the importance of continental margins in the global Si cycle (DeMaster 2002), and the importance of Si in the export of carbon, toward both higher trophic levels (Cushing 1989) and toward the deep sea (Buesseler 1998; Boyd and Newton 1999; Ragueneau et al. 2006c). We suggest an approach that involves the extension of the LOICZ C, N, and P budgeting to Si. We present a mechanistic understanding and modeling of the processes that control the delivery of Si to the hydrosphere and the retention of Si along the Land–Ocean Continuum (LOC). We also briefly review our knowledge of these processes before finally examining the anthropogenic perturbations of the Si cycle along the land ocean continuum.

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10.2 Why Do We Need to Quantify Si Fluxes on Continental Margins?

The residence time of Si in the ocean relative to its supply from rivers, submarine weathering, hydrothermal vents, and atmospheric sources is on the order of 10,000–18,000 years (Tréguer et al. 1995). Thus, a near balance between Si supply and removal is not

unexpected during the present interglacial period (i.e., the Holocene) even if sources and sinks to and from the marine environment, as well as the standing crop of dissolved Si (DSi, Si(OH)$_4$) in the oceans may change somewhat on timescales of millennia. There are constraints on the marine DSi concentrations over the past several hundred million years (i.e., there is no evidence of oceanic DSi ever becoming so low that all siliceous biota die off, or so high that inorganic silica precipitates, respectively), but they allow for small differences between DSi supply and silica burial to occur. Nearly all marine silica budgets have attributed the preponderance of DSi removal to the formation and burial of biogenic silica (bSiO$_2$, opal), primarily by diatoms and radiolaria. Any attempt to balance the marine Si cycle should be predicated on this basic understanding.

10.2.1 Continental Margins and the Global Si Cycle

If the oceans are in steady-state balance, then must there be a Si burial flux similar to the rate of DSi supply? Several past marine Si budgets attributed most of the global oceanic bSiO$_2$ burial (6–7 Tmol Si yr^{-1}) to marine sediments surrounding Antarctica (4.1–4.8 Tmol Si yr^{-1}) and only 0.4–1.5 Tmol Si yr^{-1} to continental margin bSiO$_2$ accumulation rates (e.g., DeMaster 1981; Tréguer et al. 1995). These estimates in the Southern Ocean were based on bSiO$_2$ accumulation rates from some 50 sediment cores, but the strong effects of lateral sediment focusing on

accumulation rates were not considered. Employing [230]Th-normalized accumulation rates (cf. Bacon and Rosholt 1982; François et al. 1993; Frank et al. 1999), DeMaster (2002) compiled some 30 [230]Th-corrected accumulation rates from the literature and discovered that bSiO$_2$ accumulation rates in the Antarctic deep sea formerly were overestimated by as much as 35%. In order to bring the marine Si budget "back" into balance, an additional sink equivalent to approximately one quarter of the global bSiO$_2$ burial hence had to be identified.

Employing marine C$_{org}$ burial rates and typical bSiO$_2$/C$_{org}$ ratios in continental margin sediments, bSiO$_2$ accumulation on continental margins should account for most, if not all, of the "missing" bSiO$_2$ burial, i.e., 1–2 Tmol Si yr^{-1}, which corresponds to 30–50% of the global oceanic bSiO$_2$ accumulation (Heath et al. 1976; DeMaster 2002). Hedges and Keil (1995) estimate that 5.7 Tmol C$_{org}$ yr^{-1} are buried in continental margins. Correcting this value for terrigenous contribution ($\sim$0.7 wt% C$_{terr.}$ out of 1.5 wt C$_{tot.}$) yields a marine C$_{org}$ burial rate of $\sim$3 Tmol C$_{org}$ yr^{-1}. Assuming that the bSiO$_2$/C$_{org}$ weight ratio in North Carolina slope sediments and many continental margin upwelling areas (i.e., $\sim$3.1 weight-, or 0.6 mole ratio, Fig. 10.1.1) is indicative for dominant continental margins, the total bSiO$_2$ accumulation rate in continental margin sediments is estimated to be $\sim$1.8 Tmol Si yr^{-1} (DeMaster 2002). Since Berger et al. (1989) estimate the marine C$_{org}$ burial rate in continental margin sediments to be even 50% higher than Hedges and Keil (1995), this estimate should be considered a conservative value.

BSi vs C$_{org}$ for continental margin sediments

Fig. 10.1.1 Biogenic silica (bSiO$_2$) content plotted as a function of organic carbon (C$_{org}$) content from North Carolina slope sites (diamonds) as well as other continental margin environments (horizontal and vertical bars represent ranges in bSiO$_2$ and C$_{org}$ data, respectively). Redrawn from DeMaster (2002)
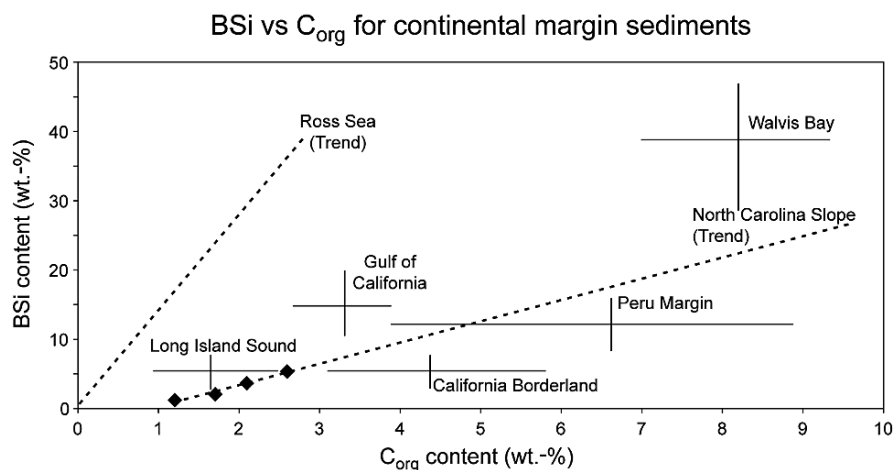
Continental margins, thus, may account for the missing sink in the global oceanic Si budget. Moreover, the mode of coupling the C_{org} and $bSiO_2$ cycles would change significantly if $bSiO_2$ burial is moving partly from the deep sea to the continental margins. When $bSiO_2$ is buried in the deep sea, almost no C_{org} is buried (mole ratio Si/C >1 outside the Southern Ocean, and >10 in the Southern Ocean, cf. Ragueneau et al. 2002b) due to an extensive regeneration in the overlying water column. On continental margins, however, C_{org} and $bSiO_2$ accumulate at nearly equal molar ratios (Si/C = 0.6, cf. DeMaster 2002). If 30–50% of the global oceanic $bSiO_2$ accumulates on continental margin sediments, the C_{org} and $bSiO_2$ cycles supposedly are coupled to a greater extent than previously thought.

10.2.2 Si and the C Cycle on Continental Margins

Diatoms form the basis of some of the most productive food chains and play a fundamental role in the export and transformation of C toward higher trophic levels (e.g., Ryther 1969; Cushing 1989) as well as toward the deep sea (Goldman 1988; Buesseler 1998; Smetacek 1999; Ragueneau et al. 2006c). Any factor changing the contribution of diatoms to the total primary production, therefore, will affect phytoplankton dynamics and, hence, the trophic transfer in marine ecosystems, as well as the efficiency of the biological pump of C_{org}.

The role of DSi as a limiting nutrient for diatom growth was suggested three decades ago, in both freshwaters (Kilham 1971) and marine waters (Officer and Ryther 1980). Since then, many case studies have been reported of DSi limitation, in both coastal waters (Conley and Malone 1992; Ragueneau et al. 1994; Turner et al. 1998) and marine waters (Dugdale and Wilkerson 1998; Pondaven et al. 1998; Wong and Matear 1999). DSi limitation causes shifts from diatoms to non-siliceous algae (Officer and Ryther 1980; Egge and Aksnes 1992) and is supposedly related to increasing harmful algae blooms in coastal waters (review in Smayda 1990) and decreasing export of C to the ocean's interior (e.g., Sieracki et al. 1993; Dugdale et al. 1995).

Thus, by controlling the contribution of diatoms to the total primary production, DSi can affect the C cycle on continental margins. Short-term consequences are expected with respect to the resource and the functioning of coastal ecosystems (review in Ragueneau et al. 2006a). Long-term consequences are also expected with respect to CO_2 sequestration on the shelf (Dugdale et al. 1995) and export to the ocean's interior, in particular via the auxiliary pump (Liu et al. 2000b).

Continental margins also play a filtering role with respect to Si inputs from land to the open ocean. Therefore, changing the Si cycle on continental margins may affect temporal variations in DSi inventories in the open ocean. Temporal variations in DSi availability play an important role in the relationship between C cycle and climate at glacial/interglacial time scales (Archer et al. 2000). Numerous hypotheses are proposed to explain atmospheric pCO_2 variations at glacial/interglacial timescales. Biological pump and rain ratio scenarios imply changes in the stripping of available nutrients or changes in the delivery of nutrients from the land–ocean interface. The effects of an altered delivery or use of N and P have been discussed abundantly (e.g., Falkowski 1997; Tyrrell 1999), as these nutrients have long been thought as the limiting or controlling factors of the biological pump. Iron (Fe) fertilization in these scenarios stimulates the export production in high latitudes (Anderson et al. 1998a), or enhances the nitrate (NO_3^-) inventory through increased N fixation in the tropics Gruber and Sarmiento 1997a). This works well if the ocean behaves as a box model. In a General Circulation Model that accounts for calcium carbonate ($CaCO_3$) compensation, however, neither Fe nor NO_3^- explain the observed decrease in pCO_2 during the Last Glacial Maximum (LGM) (Archer et al. 2000). Yet, Archer and Maier-Reimer (1994) and Heinze et al. (1999) make pCO_2 and $CaCO_3$ sensitive to the oceanic DSi concentration: increasing DSi would favor diatom production at the expense of $CaCO_3$ production and affect pCO_2 through the so-called rain ratio mechanism. Doubling the surface ocean DSi concentration via enhanced river input (Froehlich et al. 1992) and/or atmospheric deposition (Harrison 2000) may explain an important part of the glacial pCO_2 decrease. This hypothesis has been questioned by Ridgwell (2003), following the global analysis of sediment trap fluxes performed by Francois et al. (2002) and Klaas and

Archer (2002). Indeed, these meta-analysis studies suggested that $CaCO_3$ organisms would be more efficient at transporting carbon to the deep ocean than siliceous organisms. More recently, a re-analysis of sediment trap fluxes, sorting the data by basin (Ragueneau et al. 2006c), and a regional case study (Buesseler et al. 2007) have demonstrated that diatoms are an essential component of carbon export to the deep sea, bringing back the rain ratio hypothesis as one plausible mechanism controlling glacial/interglacial variations in atmospheric pCO_2 concentrations. Thus, reconstructing past delivery of DSi from the continents remains an important challenge.

10.3 How to Reconstruct Si Fluxes on Continental Margins

10.3.1 The Need to Extend the LOICZ N-P Budgeting Approach to Si

To better understand the major factors controlling the delivery of Si to the ocean, or its retention along the land–ocean continuum, and to be able to reconstruct past changes in this delivery or retention, we need to develop several approaches in parallel. The approach chosen needs to be adapted to the question raised. If the question is related to the influence of nutrient delivery on phytoplankton dynamics in the coastal zone, then most probably a detailed, mechanistic model needs to be developed that will, for example, resolve the seasonal variations in nutrient inputs (Ragueneau et al. 2005; Garnier et al. 2006). If the question is to evaluate the annual delivery of Si to the coastal zone and subsequently to the ocean, probably a simpler, more statistical approach, will be most appropriate (Sferratore et al. 2005). An important question is the extrapolation to global scale, because it is well recognized that the heterogeneity of continental margins dramatically complicates global estimates (Hofmann 1991). The estimated global $bSiO_2$ accumulation proposed by DeMaster (2002) has been obtained as the first, simplest possible, way of estimating the potential of continental margins as an important sink for Si. This approach needs to be refined now.

A first possible approach would be to benefit from the LOICZ budgeting approach (Gordon et al. 1996).
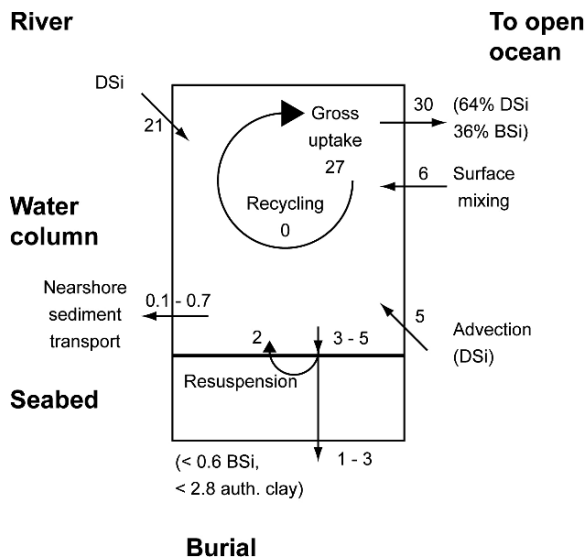
Fig. 10.3.2 Biogeochemical Si fluxes on the Amazon Shelf (modified after DeMaster and Aller 2001). Si fluxes are given in 10^8 mol Si d^{-1}

The idea is to extend the C–N–P approach (see Smith et al. 2003b) to the element Si; although Si data probably are not available for the 200 study sites, several tens of budgets (see for example, Fig. 10.3.2, a budget for the Amazon river) could hopefully be derived, which would dramatically increase the number of Si budgets, which are very rare at present (Ragueneau 2004). The comparison of these budgets, established in areas contrasting in their morphological and/or hydrodynamical characteristics, their climate, and/or their anthropogenic influence, would provide important information, crucial to our understanding of the major mechanisms controlling Si delivery. As one example, Chou and Wollast (2006) contrast the weak biological uptake of DSi in large, stratified estuaries, with the more efficient DSi uptake by diatoms in smaller estuaries that are tidally well mixed.

10.3.2 Construction of a Global Box Model of Si Transformations Along the Land–Ocean Continuum

A second approach has been undertaken by the Si-WEBS project with the development of a global box model describing the Si cycle from land to ocean
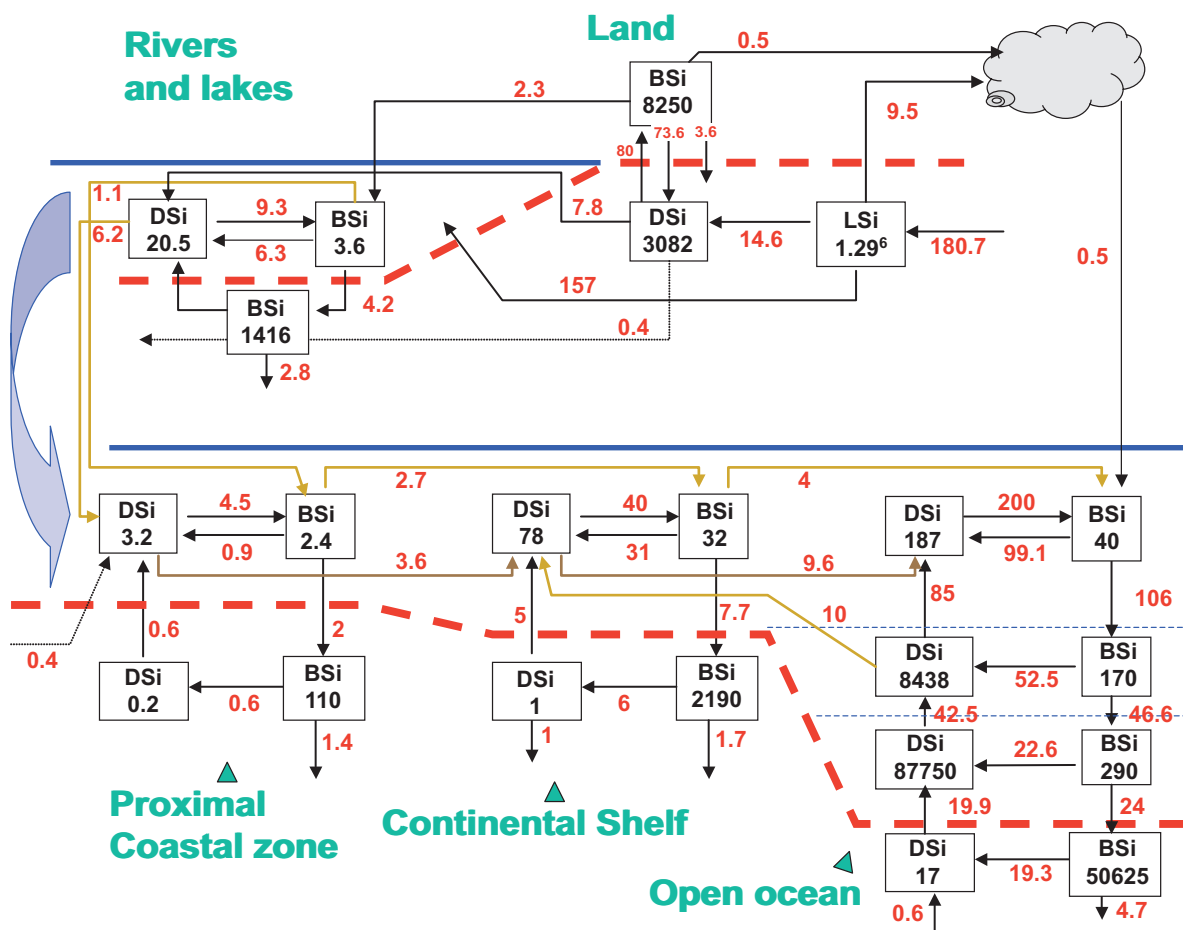
Fig. 10.3.3 Steady state global biogeochemical cycle of silicon from the land to the ocean, going through rivers and lakes, the proximal coastal zone and continental shelves (redrawn from Laruelle et al. in review). Reservoirs are in Tmol Si and fluxes in Tmol Si yr^{-1} (1 Tmol = 10^{12} mol). Squares represent DSi and bSiO$_2$ stocks and black arrows, fluxes between these stocks (DSi uptake, bSiO$_2$ dissolution). Colored arrows represent DSi and bSiO$_2$ fluxes from one compartment of the continuum to another. Stocks have been estimated using the best possible estimates we have of mean concentrations in each reservoir and the volume of these reservoirs. Fluxes between these reservoirs are based on water fluxes (Rabouille et al. 2001) and associated DSi and bSiO$_2$ concentrations. See Laruelle et al. (in review) for detailed calculations

(Fig. 10.3.3). On land, in rivers, estuaries, shelves, and in the ocean, from the surface to the sediment, the Si standing stocks as DSi and bSiO$_2$ and the fluxes (DSi uptake, bSiO$_2$ dissolution) between the boxes have been quantified (Laruelle et al. in review). Figure 10.3.4 presents a synthetic view of production and preservation (accumulation/production), as a percentage of the global estimates, along the land—ocean continuum (data in Fig. 10.3.3). The land and the shelves preserve about 4.5% of their bSiO$_2$ production, and contribute a similar proportion of the global production and accumulation, ca. 25% for the land and 12% for the shelves. The situation is radically different in rivers and in the proximal coastal zone. There, the contribution to the global production is small (<3%) due to a small surface area. A preservation efficiency close to 30% leads to a contribution to global accumulation close to 20% for rivers and 10% for the proximal zone. Due to its surface area, the open ocean contributes to 60% of the global production but its contribution to the global accumulation is twice as low, due to a preservation efficiency of only 2%. The model suggests that the proximal + distal accumulation is 3 Tmol Si yr^{-1}, even more bSiO$_2$ accumulation than suggested by DeMaster (2002). Altogether, 25% of the global bSiO$_2$ accumulation (333 Tmol Si yr^{-1},

Fig. 10.3.4 Percent of global production (*white bars*) and accumulation (*black bars*) in each compartment of the land–ocean continuum (derived from Fig. 10.3). Numbers indicate the preservation efficiency (accumulation/production) in each compartment
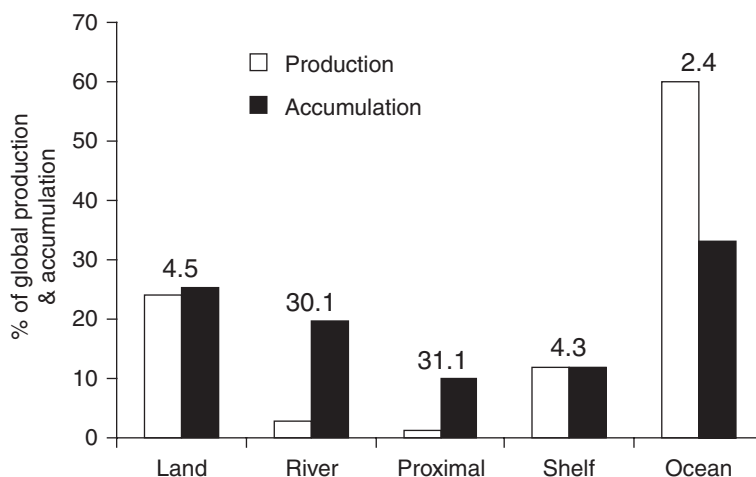
Fig. 10.3.3) takes place on land, 42% along the river-proximal–distal coastal continuum, and 33% only in the open ocean. Figure 10.3.3 presents a reasonable Si cycle along the land–ocean continuum, established with the data presently available. Obviously, these numbers will be refined as more Si budgets are established and more data become available, especiallys we move landward.

10.3.3 A Typology of Si Delivery to the Open Ocean

A third approach toward global extrapolation of intermediate complexity, would be to establish a typology of DSi delivery at the global scale by combining the coastal segmentation of Meybeck et al. (2006) and a typology of land–ocean continuums in which we would be able to quantify the major controls of Si retention. A typology of DSi delivery by rivers to the coast is on its way (Dürr et al. 2006). The budget is based on a segmentation scheme of the coastal zone and includes a characterization of Regional and Marginal Seas as mega-filters of land to ocean riverine fluxes.

Coastal segmentation, as established by Meybeck et al. (2006), is used to calculate natural silica fluxes from river to coastal segments. DSi concentration is multiplied with discharge of rivers for each segment for documented basins and segments. In total, about 200 rivers are documented (GEMS-GLORI and GEMS-PRISRI databases), representing 57% of exorheic area and 57% of total exorheic discharge. Segments with no documentation available are estimated using expert judgment based mainly on considerations of local climate, lithology, and lake retention. Results have been established for silica fluxes, concentrations, and yield for drainage basins of the different oceans' basins as well as coastal segment basins (Fig. 10.3.5). For the continental surfaces actually draining into the oceans (exorheic regions, representing $114.7 \, M \, km^2$), $375 \, Mt \, yr^{-1}$ of DSi are transported, corresponding to a mean concentration of $9.3 \, mg \, l^{-1}$ and to a mean yield of $3.3 \, t \, km^{-2} \, yr^{-1}$. Yields exceeding $6.6 \, t \, km^{-2} \, yr^{-1}$, i.e., $> 2 \times$ the global average, represent 17.4% of the global continental ice-free exorheic area but correspond to 56.0% of DSi fluxes. The variation of DSi yields between coastal segments is about 2 orders of magnitude.

The coastal segmentation does not account for the subsequent transformations seaward of the river mouth or the influence of upwelling which can be very important in some coastal areas (Meybeck et al. 2006; Wollast 2002). Thus, this approach needs to be coupled with an estimate of Si retention within a typology of land–ocean continuums. While an assessment of the cycling/retention effects or a typology of the proximal coastal zone itself is not yet possible for DSi because of a dramatic lack of data, an estimation has been achieved for regional and marginal seas (Meybeck et al. 2007). Three types of regional seas (quasi-enclosed, semi-enclosed, and open) as well as archipelagic coasts and extended platforms have
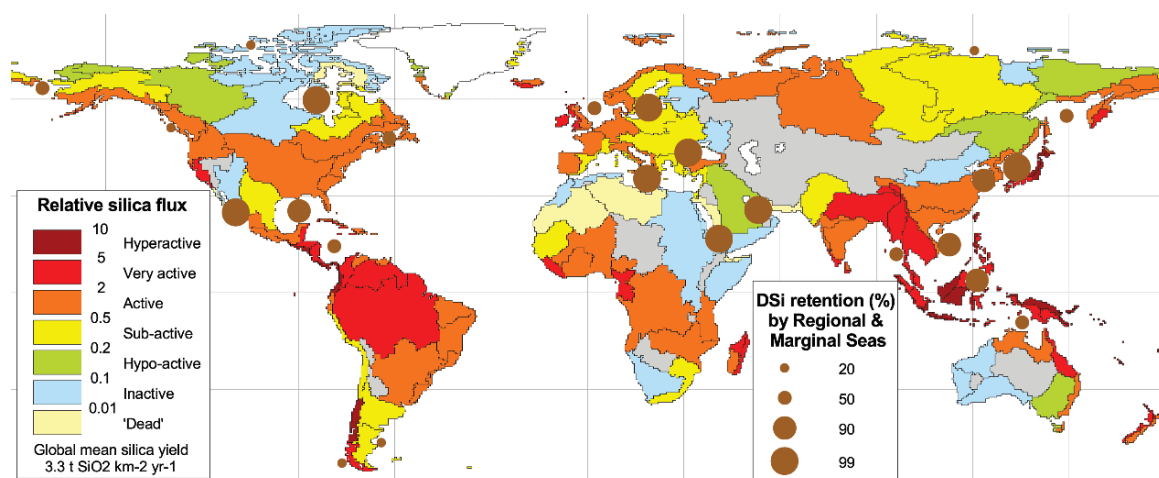
Fig. 10.3.5 Relative (normalized to global mean) natural silica yield for catchment basins related to exorheic coastal segments (*colors*) and retention by regional and marginal seas basins (*circles*). Redrawn from Meybeck et al. (2007) and Dürr et al. (2006)

been identified based on morphological characteristics. Filter coefficients have been derived for the different types for dissolved material such as DSi. As such, regional and marginal seas intercept 33% of the total DSi fluxes, and river inputs of DSi to the open ocean decrease by 26% (Fig. 10.3.5). A major effort needs to be undertaken to quantify Si retention in other types of continuums such as in fjords, mangroves, and deltas, so this filter can be applied to all the coastal segments defined by Meybeck et al. (2006) and the retention along the land–ocean continuum, as shown in Fig. 10.3.4, can be refined and regionalized.

10.3.4 The Need for a More Mechanistic Understanding of Si Transformations

To be able to move from simple quantification (of various complexity, 10.3.1–10.3.3) and perform retrospective or prospective estimates of Si delivery to the ocean, we need to achieve a basic understanding of the mechanisms that control the fate of Si along the land–ocean continuum and develop integrated models describing this fate. Reconstructing Si delivery and retention for past periods when climate was different and/or human influence was less significant is extremely difficult – yet crucial – since $bSiO_2$ accumulated on continental slopes and rises dur-

ing glacial times rather than on continental margins due to a reduced shelf area resulting from low sea-level conditions. Proxies of continental weathering are difficult to develop due to long residence times (cf. $^{87}Sr/^{86}Sr$), large glacial to interglacial water-mass circulation changes affecting their local distributions (cf. Ba, Cd), and large uncertainties in their oceanic budgets (cf. V, U, Ge). For example, the idea that glacial Si fluxes were two times higher during the last glacial has been inferred from the use of Ge/Si ratios (Froehlich et al. 1992), an approach that has been questioned later in reducing continental margin sediments (Hammond et al. 2000). It is important to develop such proxies though, because of the importance of reconstructing past changes in nutrient delivery to the ocean. In parallel to the on-going effort in developing reliable proxies of continental weathering, we need to better understand and model the processes that control Si delivery to the hydrosphere and retention along the LOC.

10.4 What Do We Know About Processes Controlling Si Delivery/Retention Along the LOC?

10.4.1 Si Inputs to the Hydrosphere

Most of the DSi supply to the oceans originates from rivers (84%). Ultimately, DSi arises from weathering of Si-containing minerals or geological deposits

(Meybeck 1996; Millot et al. 2002). However, input of particulate amorphous silica (i.e., $bSiO_2$) must also be considered as it potentially dissolves in the coastal zone and participates in the biogeochemical Si cycle. Early estimates suggested the $bSiO_2$ flux to at least $1.1\,Tmol\,Si\,yr^{-1}$ (Conley 1997, see also Fig. 10.3.3), but recent data on $bSiO_2$ concentrations in rivers suggest a significant upward revision of this number (Humborg et al. 2006; Conley unpub. data).

DSi inputs through submarine groundwater discharge (SGD) are poorly quantified because they are highly variable, both spatially and temporally (Slomp and Van Cappellen 2004). DSi concentrations in groundwaters are of the same magnitude as in rivers (Table 10.4.1 in Ragueneau et al. 2006a) and in areas with elevated N inputs, Si:N ratios in SGD are well below the Redfield ratio. This means that in coastal areas where SGD may represent an important proportion of the water flux, such as in regions where coastal aquifers consist of permeable sand and limestone (Slomp and Van Cappellen 2004 and references therein), SGD of nutrients may also contribute to modifying the nutrient balance and affect phytoplankton dynamics.

Table 10.4.1 The marine Si budget (after DeMaster 2002)

| Si Sources and sinks	Flux ($Tmol\,Si\,yr^{-1}$)
DSi sources	
Rivers	5.6
Hydrothermal emanations and submarine weathering	0.6
Eolian dust	0.5
Total supply rate	6.7
$bSiO_2$ burial rates	
Deep sea	4.1–4.3
Antarctic Deep Sea	3.1
North Pacific + adjacent seas	1
Si poor deep-sea sediments	<0.2
Continental margins	2.3–3.1
Estuaries	<0.6
Upwelling areas (Gulf of California, Walvis Bay, Peru/Chile coast)	0.3–0.5
Antarctic margin	0.2
All other margins	1.8
Total burial rate	6.4–7.4

10.4.2 Si Transformations Along the Land–Ocean Continuum

A variety of processes influence the transport of Si to the continental margin and the amount of Si reaching the ocean is intimately tied to events occurring on land. On the continents, DSi is incorporated into the living tissues of growing plants as amorphous Si bodies ("phytoliths", Kaufmann et al. 1981). The incorporation of Si in terrestrial plants is a significant process within the terrestrial Si cycle (60–$200\,Tmol\,yr^{-1}$, Conley 2002) rivaling that of the oceanic cycle at $240\,Tmol\,yr^{-1}$ (Tréguer et al. 1995). In addition, large stores of amorphous silica accumulate in soils primarily in upper soil horizons (Saccone et al. 2007) and can be 500–1000 times larger than found in plant biomass (Bartoli 1983). Internal recycling of the phytolith pool is intense with riverine fluxes of DSi to the oceans strongly buffered by the terrestrial biogeochemical Si cycle (Conley 2002; Derry et al. 2005). In addition, DSi export from marshes, both freshwater and saltwater, contributes significantly to estuarine Si availability (Struyf et al. 2006).

In the riverine part of the continuum, a significant factor is the growth of diatoms which leads to the conversion of DSi to $bSiO_2$ (e.g., Conley 1997; Ragueneau et al. 2002c). Moreover, DSi concentrations in rivers are influenced by watershed characteristics as the number of lakes causing retention of Si, other nutrients, and suspended matter (Fig. 10.4.6, Conley et al. 2000), or the plant community composition (Bartoli 1983). Biological uptake, generally, takes place where the combination of light and nutrient availability is optimal. If rivers are too turbid, this occurs in ponds or quiescent areas in the river, or offshore. In a delta or in an estuary, this occurs, for example, in the Amazon river, as soon as the total suspended matter decreases below $10\,mg\,l^{-1}$ (DeMaster et al. 1983). Obviously, this area of high biological uptake moves along the estuary and displays seasonal and interannual variability, as evidenced in the Danube delta (Humborg et al. 1997; Ragueneau et al. 2002c). We have seen that at global scale, riverine production accounts for a very small proportion of the global DSi uptake (Fig. 10.3.4). However, it is very important at local scale as $bSiO_2$ inputs may account for a similar proportion as DSi inputs in some rivers and during bloom

Fig. 10.4.6 Mean flow weighted DSi concentration as a percentage of lakes and reservoirs in a watershed from 61 sites located throughout Sweden (*black dots*) for the period 1971–1994 and from 30 watersheds located throughout Finland (*white dots*) for the period 1971–1993. Conley et al. (2000)
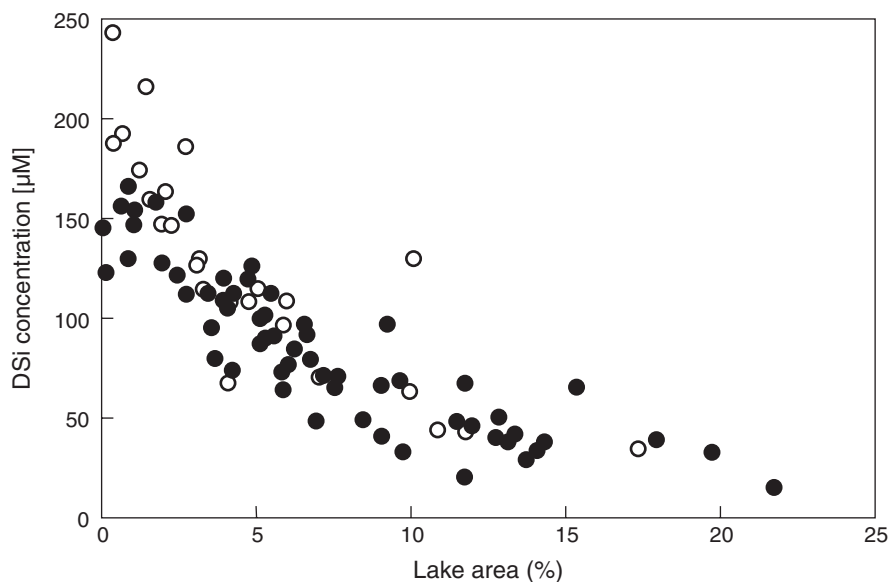
periods (Conley 1997). It is essential to account for this form of Si delivery, i.e., particulate, and study its fate in the mixing zone as well as in coastal waters, because its remineralization can provide an additional source of DSi for diatoms (Ragueneau et al. 2006a).

In the mixing zone, removal of Si varies between 0 and 100% of the river Si inputs, with an average close to 20% (DeMaster 1981) and a very low influence of abiotic processes (review in Chou and Wollast 2006). However, most estimates of Si retention along the LOC are based on DSi–salinity relationships (e.g., Liss 1976; Billen et al. 1985; Shiller 1996) that are subject to several caveats. First, they assume that river water and surface ocean water are the only two end members, with no additional source of nutrients. Actually, nutrient fluxes in the coastal ocean depend not only on river discharge and exchange with the surface ocean but also on groundwater discharge, atmospheric input, benthic fluxes resulting from diagenetic processes in sediments, and transfer of deep ocean water across the shelf break by upwelling or vertical mixing (Wollast 2002; Ragueneau et al. 2006a). Second, it has been demonstrated that linear property–salinity plots can be obtained in a system characterized by transient conditions; such limits have been pointed out over two decades ago (Officer and Lynch 1981) and have been demonstrated with a one-dimensional, time-dependent transport model which includes tidal fluctuations (Regnier et al. 1998). These authors in

particular have shown that in systems in which time dependencies of the hydrodynamic forcing are significant, flux estimates based on mixing curves produce meaningless results. Third, uptake mechanisms can be compensated by dissolution mechanisms, so that the behavior of a given property appears conservative, despite important biological processes taking place. This implies that if we are to understand the processes during mixing, we should not focus only on nutrient delivery in the dissolved form, but also take into account that an important fraction of these nutrients may be delivered in the form of particulate matter (Mayer et al. 1998; Conley 1997). In the Danube delta, for example, a diatom bloom took place at salinities between 2 and 5 PSU during spring, as seen from direct DSi uptake measurements (Ragueneau et al. 2002c) but was not visible on the DSi mixing diagram because of DSi replenishment coming from the dissolution of freshwater diatoms as they were entering the salinity gradient. Relying only on these mixing diagrams of DSi may also have compromised our understanding of the C cycle along the salinity gradient. Indeed, these diatoms, being produced in the river system and in the upper reaches of salinity gradients, fuel bacterial activity further downstream (Becquevort et al. 2002). Thus, quantifying nutrient fluxes across the land–ocean interface require that we explore, far beyond the use of property–salinity plots, the form under which nutrients are being delivered and that

we perform direct measurements of nutrient uptake and particulate matter degradation along salinity gradients.

The fate of the $bSiO_2$ produced in the river system or within the estuary is difficult to establish either due to hydrosedimentary processes transporting particles both upstream and downstream, poorly known, or due to the lack of studies devoted to dissolution of freshwater diatoms entering a salinity gradient. Many freshwater diatoms species do not survive in saline waters (Roubeix et al. 2008b). As salinity increases, the osmotic stress leads to cell lysis and through the combined effect of increasing salinity and bacterial activity, dissolution of diatom frustules increases rapidly, as seen in vitro by Roubeix et al. (2008a) and in situ, in the Danube delta, by Ragueneau et al. (2002c). Massive sedimentation may also occur, in which case $bSiO_2$ dissolution will take place at the sediment–water interface (D'Elia et al. 1983; Anderson 1986). Figure 10.3.4 is suggesting that in rivers and in the proximal coastal zone, conditions are optimal for an efficient preservation efficiency of the $bSiO_2$ produced, at close to 30%.

It is very important to understand the fate of this Si brought by rivers in the form of particulate matter because $bSiO_2$ dissolution (1) refuels the water with DSi which can be taken up by diatoms further downstream with potentially important ecological consequences, especially in coastal waters subject to DSi limitation and (2) helps in closing the budgets of Si fluxes because Si removal along the LOC cannot be taken simply as the difference between river inputs and uptake by diatoms (DeMaster et al. 1983). In addition, the riverine $bSiO_2$ that does not get dissolved may be buried in the form of $bSiO_2$ and participate in the retention of Si along the land–ocean continuum; it is also a possible source of authigenic clay formation in continental margin sediments (Michalopoulos and Aller 1995).

In coastal areas and on continental shelves, the combined processes of DSi uptake, diatom growth, degradation, frustule dissolution, will continue. Interestingly, the overall preservation efficiency in this area is close to 4.3%, as on land (Fig. 10.3.4). This is twice as high as in the open ocean, but 1 order of magnitude below the preservation estimated in the river and proximal zone. Additionally, an important component is entering the game, in intertidal areas and as turbidity decreases, in subtidal areas: the microphytoben-

thic compartment. Benthic diatoms constitute a biofilm which may compete with pelagic diatoms for available DSi and which may modulate benthic DSi fluxes on several time scales (Ni Longphuirt et al. 2009). Benthic diatom dynamics have been well studied in intertidal areas and more recently, evidence has been provided for migration of benthic diatoms in subtidal areas, in relation to the diel cycle and the tidal cycle (Ni Longphuirt et al. 2007). Direct measurement of Si uptake by benthic diatoms and dissolution of benthic diatoms, however, is missing but deserves study, as benthic C primary production supposedly can be as high as pelagic C production (e.g., Guarini 1998; Clavier and Guarrigue 1999).

As previously mentioned, we clearly lack direct estimates of Si retention on continental shelves. This needs to be quantified in the form of $bSiO_2$ but not only. Recently, the transformation of diatom $bSiO_2$ to authigenic clay minerals in continental margin sediments was observed (cf. Michalopoulos and Aller 1995; Michalopoulos et al. 2000; Michalopoulos and Aller 2004), based on pore water stoichiometry, scanning electron microscope (SEM) studies, and acid/base selective leaches in order to resolve whether or not clay minerals originate from $bSiO_2$ or terrestrial sources. SEM studies confirm that the transformation of diatom $bSiO_2$ to authigenic clays is occurring, but not known to which extent. Clay mineral formation on the Amazon shelf (≤ 0.17 Tmol Si yr^{-1}) corresponds to 20% of the riverine Si discharge; other estimates for other deltas have been obtained recently, such as off the Mississippi (Presti and Michalopoulos 2008), but similar estimates need to be obtained for other continental margins so that a reasonable estimate of the importance of this mechanism and form of Si retention can be assessed on a global scale.

In this overview of the processes that take place along the land ocean continuum, it is important to stress that perhaps the major unknown lies in the exchange between the margin and the open ocean. First, coastal upwelling is an essential source of nutrients for many coastal waters (Wollast 2002). Ignoring this source can lead to substantial misunderstanding of phytoplankton dynamics on the shelf and in the establishment of Si budgets at river mouths. For example, upwelling and relaxation events have been shown to select for different phytoplankton assemblages in a Spanish ria and induce either export to the shelf or retention within the ria of the species selected

(Tilstone et al. 2000). Distinguishing land-derived from upwelling-derived Si is essential for estimating Si retention along the LOC in general and for understanding whether increased productivity on continental margins during the LGM in particular is due to increased upwelling or increased supply of river-borne nutrients (e.g., Abrantes 2000; Peterson et al. 2000). Conversely, the export of Si from the shelves to the open ocean is poorly known. For example, an important pathway may be through downslope sediment transport. Refueling of deep waters on continental slope and rise has been studied in the north Atlantic (Bonnin 2004), the equatorial Atlantic (Ragueneau et al. 2009), or in the Weddell Sea (Rutgers van der Loeff and Van Bennekom 1989). These studies suggest that an excess of $bSiO_2$ is accumulating in some areas, leading to the observed deep water DSi anomalies, and that it must come from downslope transport. There exists no estimates of this process at the global scale, but a back-of-the-envelope calculation suggests that this flux may be very important. Earlier, we have seen that the global accumulation of $bSiO_2$ has been obtained from a global estimate of C_{org} accumulation on shelves multiplied by the Si:C ratio typical of these shelves. The most recent estimate of the global C_{org} export through downslope transport is 0.25 Gt C yr^{-1} (Chen, Chap. 13). Multiplying this value by the Si:C ratio of 0.6 (DeMaster 2002) yields an Si export through this mechanism, as high as 10 Tmol Si yr^{-1}, almost twice as high as the DSi input from rivers (Tréguer et al. 1995). Obviously, such an estimate needs to be refined but this large value suggests that it should be quantified properly. Interestingly, this flux almost balances the most recent estimate of the DSi upwelling flux on continental margins, as estimated from a global box model of Si transformations along the land–ocean continuum (Fig. 10.3.3, Laruelle et al. in review).

10.5 Anthropogenic Perturbations of Si cycle

For many decades the input of Si to the coastal zone and the open ocean was believed to be mostly a natural phenomenon from simple weathering of rocks. The reason was because Si inputs were seen only in the form of DSi and because DSi inputs to the hydrosphere originate from the weathering of silicate minerals (Meybeck 1996; Millot et al. 2002), a natural, physico-chemical process with important implications on atmospheric CO_2 concentrations in geological timescales (Berner et al. 1983; Blum and Erel 1995; Gaillardet et al. 1999). With the realization that Si is an essential nutrient for many organisms living on land and in the ocean, life cycles have emerged as an important control on the Si cycle along the entire land–ocean continuum. Several hypotheses have emerged linking the dramatic increase in DSi inventory to the widespread development of diatoms during the early Miocene (Kidder and Gierlowski-Kordesch 2005). Others have linked the massive development of diatoms in the ocean to the evolution of C_4 plants on land, which are hypothesized to have had major implications for the weathering of silicate rocks (Falkowski et al. 2004).

It is through the role of diatoms that the first anthropogenic perturbations of the Si cycle have emerged in the literature over three decades ago. With increasing eutrophication (Howarth et al. 1996; Nixon et al. 1996), such as the one that has accompanied human settlement on the watersheds of the Great Lakes in North America, diatom growth has been stimulated, leading to enhanced Si retention in the sediments along its path to the ocean (Schelske and Stoermer 1971). The conditions leading to reduced inputs of DSi to the coastal zones and the consequences for coastal food webs have been reviewed in a number of ecosystems around the world by Conley et al. (1993). The second human-induced mechanism altering Si delivery to the coastal zone is the so-called "artificial lake effect", as described by Van Bennekom and Salomons (1981). Several major illustrations of this effect include rivers such as the Nile (Wahbi and Bishara 1980), the Mississippi (Turner and Rabalais 1991), the Danube (Humborg et al. 1997) and more recently, the Changjiang where the Si:N ratio of waters discharging to the East China Sea has decreased by a factor of almost four with the first filling phase of the Three-Gorges dam (Gong et al. 2006). The mechanism was long thought to be relatively similar to the first perturbation, with enhanced diatom production (due to the construction of a reservoir instead of eutrophication), increased Si sedimentation, and decreased DSi inputs downstream (Humborg et al. 2000). But diatoms are probably not the only main players in this process. Recently, other mechanisms have been shown to play an important role in this dam-induced

retention, including the trapping of phytoliths (Conley 2002), changes in vegetation associated with the construction of the reservoirs (Humborg et al. 2004), or much lower exchanges with the riparian zone that reduce the connectivity with aquifers typically rich in DSi (Teodoru et al. 2006b). As noted by the latter for the Danube–Black Sea case study, it is not necessarily the construction of the Iron Gates dam that has led to the observed drastic decrease of DSi inputs to the Black Sea observed by Cocciasu et al. (1996). Friedl et al. (2004) constructed a Si mass balance in this large reservoir, suggesting a reduction of DSi by only 5%, which is confirmed by studying $bSiO_2$ accumulation in sediment cores taken from the reservoir (Teodoru et al. 2006a). In fact, it is not necessarily the largest reservoirs that cause the major biogeochemical changes, but rather the effect of all dams, the presence of side bays as nutrient sinks (McGinnis et al. 2006) and hydraulic alterations (lowering the natural water level that control the silicon weathering rates) need to be considered all along the river stretch (Teodoru et al. 2006b).

Beyond eutrophication and river damming, there are other ways by which humankind may alter the biogeochemical Si cycle, which deserve special attention and quantification. The proliferation of invasive species is potentially one of them (Ragueneau et al. 2005). Some alien species, especially benthic suspension feeders, through their filtering and biodeposition activities, create the conditions for an enhanced retention of biogenic elements accompanying their proliferation. This is particularly the case for the element Si because these organisms produce feces that are enriched in Si which is not used for their metabolism (Ragueneau et al. 2005). Some plants may also play a similar role, such as *Phragmites* sp. and *Spartina* sp., a siliceous organism that is trapping sediment and nutrients and which invades many wetlands in temperate regions (Struyf et al. 2006).

The actual impact of invasive species on Si retention along the land–ocean continuum is not known. It has been demonstrated in the Bay of Brest, France, but needs to be tested in other places subject to such invasions, for example, through sediment cores analyses and/or revisiting monitoring stations, searching long-term nutrient data for evidence of decreasing DSi concentrations coinciding with the start of the proliferation of alien species.

Anthropogenic alterations of the Si cycle do not always lead to DSi reductions. Soluble silicates used in both industrial and household activities (Van Dokkum et al. 2004) as well as commercial fertilizers (Datnoff et al. 2001) provide additional quantities of DSi which are poorly constrained at global scale. Little is known also about changes in the production and weathering of Si with changes in land use. The scant information available has shown higher DSi concentrations in streams during the first several years after logging, and decreasing DSi concentrations several years after disturbance (Likens et al. 1977). However, the mechanisms for these changes are uncertain. The long-term effects of disturbance with agriculture and the more recent effect of acid rain on weathering, and thus the production of DSi, are also not known. Taking into account human impact as an effective geological force (Hooke 1994, 2000), plowing fields (among others) will generate stronger soil disturbance than natural river or glacier or wind forces can cause (Haff 2002).

10.6 Conclusions

The Si cycle plays an important role in continental margin ecology and biogeochemistry. Conversely continental margins play an important role in the global Si cycle. Although major progress has been accomplished over the past three decades in our understanding of this interdependency, much remains to be done. This is true, concerning both detailed studies that need to be performed on a site by site basis, if we study more the functioning of coastal ecosystems, as well as other approaches devoted to obtaining a global picture of the role of margins in the global Si cycle.

Understanding better the response of coastal ecosystems to temporal changes in nutrient inputs from the watersheds implies that we take into account the nutrient balance between silicon and other elements, as one controlling process among others (see Ragueneau et al. 2006b). As we have seen, this requires that we not only focus on silicon inputs in the dissolved form (and Si:N and Si:P nutrient ratios) but also study the delivery of particulate silica (river diatoms, phytoliths) and its fate (relative to that of other elements) during estuarine mixing and in coastal waters and sediments. Because in diatoms, the fate of Si and

C are strongly coupled (Moriceau et al. 2009), we suggest that dissolution of diatom frustules and degradation of organic matter coming down rivers and entering estuaries, be conducted simultaneously, along with studies of the fate of other elements (N, P). If such direct measurements of Si regeneration in rivers and estuaries are crucially missing, it should be noted that even direct uptake measurements are also very scarce. These, together with determination of DSi uptake kinetic parameters, need to be performed along the land–ocean continuum to better understand the relation between Si content of diatoms, their metabolism, and the role of environmental factors such as salinity, pH, and osmotic pressure (Claquin et al. 2006). Finally, because benthic diatoms can represent an important component of primary production in many ecosystems (Heip et al. 1995; Guarini et al. 2000), we suggest that a major effort should be directed to understand better the dynamics of benthic diatoms and their influence on the Si cycle which has been shown to take place at several temporal scales, from hourly to seasonal (Ni Longphuirt et al. 2007).

Beyond these efforts to improve our understanding of the transformations of Si all along the land–ocean continuum, we also need to work toward the development of an approach at regional and even global scale. We have seen that presently, data are crucially missing and a major effort should be directed toward collecting all the Si data on continental margins, for example, at the 200 LOICZ sites, where Si budgets could be built (Ragueneau 2004). We have also noted that these data are becoming more and more scarce as we move from the ocean to the land, so this effort of data collection would also need to combine terrestrial and aquatic data sets. With this data collection, the comparison of Si budgets and an improved understanding of Si transformations along the land–ocean continuum in contrasted settings, we hope that the major controls on Si retention versus delivery to the ocean will be better constrained. This way, a typology of Si delivery to the ocean could be established, combining a basic understanding of Si transformations in typical continuums (deltas, stratified estuaries, fjords, etc.) and the coastal segmentation proposed by Meybeck et al. (2006).

The approaches undertaken at local and/or global scales, obviously of various complexity, will benefit one from each other. They can be used to better understand the linkages between terrestrial ecosystems and the functioning of the coastal zone, or between the land, the margins, and the functioning of the oceanic biological pump. This can be done under the present situation as well as for past periods, such as during the last glacial. In such approaches, accounting for the role of anthropogenic alterations of the Si cycle will be of major importance. As the retention of Si along the continuum is modified by eutrophication, the construction of dams or the increasing biodeposition of invasive species, traces of these human-induced perturbations can be found in the sediments through enhanced diatom production and accumulation (Schelske et al. 1983; Teodoru et al. 2006a) or through enhanced preservation conditions (Ragueneau et al. 2005). Therefore, it is important to recognize these influences so as to differentiate between the natural spatial and temporal variability of retention and anthropogenic influences. The impact of the human influence on the Si cycle and the functioning of coastal ecosystems can be very high at the local scale. The impact at the global scale of increasing temperature and damming has been explored by the Si-WEBS project, in a prospective way, using a global box model (Laruelle et al. in review). Such an approach could be used to explore the potential impact of a process such as increasing biodeposition. Indeed, the proliferation of invasive species is being recognized as a major threat to biodiversity, the functioning of ecosystems and biogeochemical cycles (Mack et al. 2000), but its potential impact at global scale on the Si cycle is completely unknown.

As noted by Ragueneau et al. (2006b), a hotspot for future studies devoted to the impact of anthropogenic perturbations of the Si cycle may well be Southeast Asia, where damming, eutrophication, deforestation, and the proliferation of invasive species are flourishing. This region is playing a critical role in land–ocean fluxes in general and in Si inputs in particular (Ittekkot et al. 2000), constituting an important source of DSi fueling equatorial pacific production (Dugdale et al. 2002).