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A benthic Si mass balance on the Congo margin: Origin of the 4000 m DSi anomaly and implications for the transfer of Si from land to ocean

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Abstract:

To elucidate the origin of the silicic acid (DSi) anomaly observed along the 4000 isobath on the Congo margin, we have established a benthic Si mass balance and performed direct measurements of biogenic silica (bSiO₂) dissolution in the deep waters and in the sediments. Results strongly suggest that the anomaly originates from the sediments; the intensity of DSi recycling is consistent with the degradation of organic matter, as observed from Si:O₂ ratios in the benthic fluxes compared to that ratio observed in the anomalies. Strong imbalances, observed in both the Si and C mass balances, suggest that the biogenic matter that degrades and dissolves in these sediments near 4000 m does not come from pelagic sedimentation. It is probably not coming also from the deep channel, because observations were similar in the deep channel vicinity (site D) and further south, far from its influence (site C). The composition of the sediments, with an Si:C ratio close to that observed on continental shelves, suggests that this matter is coming from downslope transport. A first estimate of the magnitude of this flux at global scale, close to 12 T mol Si yr⁻¹, suggests that it may be an important path for transferring Si from land to ocean.

Keywords: Biogenic silica; Dissolution; Preservation; Continental margin; Congo

1. Introduction

Continental margins play a major role in the biogeochemical cycles of carbon and associated biogenic elements, in terms of sources and sinks, or in terms of filter towards carbon and nutrient inputs from land to ocean (Liu et al., 2000; 2009). They are also the site of the largest contribution to global new production, sustaining essential marine resources. But continental margins are also subject to very complex physical, biological and biogeochemical processes and prone to important anthropogenic perturbations; they display a dramatic heterogeneity, making it difficult to account for their importance in global budgets and global models. In this context, the LOICZ budgeting approach (Gordon et al., 1996) allows the comparison of simple mass balances established in some 200 study sites, focusing on C, N and P biogeochemical cycles (Smith et al., 2009), and a joint implementation plan is being prepared between LOICZ and IMBER to account for the strong interaction between biogeochemical cycles and food webs in these dynamic environments.

One key essential macronutrient has been neglected in this global approach, namely silicon (Si). This element is essential for diatoms, which play a key role in the export of carbon towards higher trophic levels (Cushing, 1989) and towards the ocean interior (Buesseler, 1998; Ragueneau et al., 2006a). For ecological, biogeochemical and paleoceanographic reasons, it is very important that more studies be devoted to the cycling of this element on continental margins, in close interaction with C and associated elements (Ragueneau et al., 2009). From a biogeochemical point of view, continental margins may well be the site where the missing Si sink could be located (DeMaster, 2002). In addition, anthropogenic perturbations of the Si cycle along the land-ocean continuum, due to eutrophication (Conley et al., 1993), river manipulations (Humborg et al., 1997) and invasive species (Ragueneau et al., 2005a), induce changes in the retention of terrigenous Si inputs on their way to the ocean with possible important implications for the ecology and biogeochemistry of the coastal zone on short time scales and the open ocean on longer time scales. From an ecological perspective, increased Si retention coupled to increasing inputs of N and P from human activities on the watersheds, often leads to drastic changes in phytoplankton dynamics in coastal waters (review in Ragueneau et al., 2006b, c) with important cascading effects on food webs (e.g. Turner et al., 1998). Finally, from a paleoceanographic point of view finally, it is very important to understand how Si delivery to the ocean may have changed in the past, for example on glacial/interglacial time scales. Changes in Si inventory in the ocean has been hypothesized to drive changes in the rain ratio, possibly accounting for a major fraction of

CO₂ atmospheric changes on these time scales. (Archer and Maier-Reimer, 1994; Archer et al., 2000; Heinze et al., 2003). However, as noted by Zabel and Hensen (2006), the natural driving forces behind changes in Si inputs to the ocean remain unknown, although hypotheses have been proposed in relation to changes in river (Froelich et al., 1993) or aeolian (Harrison, 2000) inputs.

In fact, compared to the 200 N and P budgets published on the LOICZ web site, there is a crucial lack of Si data, process studies and budgets on continental margins (Ragueneau et al., 2004). Existing studies have focused mostly on the shelf, such as in the Ross Sea (DeMaster et al., 1996; Nelson et al., 1995), off the coast of California (Berelson et al., 1987). Studies on the shelf have shown that the degree of coupling between Si and C cycles is much larger in this environment than in the open ocean (DeMaster, 2002). Even fewer studies have been performed at the mouth of large rivers, and the Amazon is an exception (DeMaster et al., 1996; DeMaster and Aller, 2001). In this context, the present study will contribute to increase the available data sets, by providing new data in the vicinity of the Congo river mouth. This is a very particular area, the second-largest flow in the world (Milliman, 1991), presently still connected to its submarine canyon (Babonneau et al., 2002).

The area off the Congo river is of particular interest in the perspective of understanding further the Si cycle on continental margins under the influence of such large rivers, be it in terms of Si mass balance on the margin or in terms of transfer of Si from land to ocean. Biogenic opal is well preserved in the Congo deep-sea fan, and it is in this area that the idea of an important role of aluminium in opal preservation was born (Van Bennekom et al., 1989). During hydrological surveys on the Guinea's gulf (Van Bennekom and Berger, 1984, Warren and Speer, 1991, Arhan et al., 1998, Oudot et al., 1998; Van Bennekom, 1996), a strong DSi positive anomaly has been observed along the 4,000 m isobath, associated with particularly low oxygen concentrations (see Vangriesheim et al., this issue, a). Elucidating the origin of these anomalies and their possible link is important, because this may provide important information on the mechanisms controlling (1) Si and C transfer from land to ocean, and (2) deep water replenishment with DSi along the path of the conveyor belt, two important processes controlling oceanic diatom productivity on long time scales (Ragueneau et al., 2000).

If high quantities of organic matter, with an important siliceous component, are degrading at the rise of the continental slope, it is important to know if the presence of this biogenic matter is linked to the deep channel, to surface productivity or to lateral transport of shelf

sedimentary material, three different modes of Si and C transfer from land to ocean. During the EQUALANT cruise (IRD) in 2000, Braga *et al.* (2004) showed that the strongest anomalies took place at the intersection between the Congo sub-marine channel and the 4,000 m depth), suggesting that this deep channel may well be the source of the anomalies. Alternatively, Van Bennekom (1996) suggested that these silica signals may be associated to enhanced surface waters diatom productivity in the vicinity of the Congo River plume. Finally, there exist no data in this area, about possible downslope transport of shelf sedimentary material, in a mechanism similar to that described off California by Jahnke *et al.* (1990). Elucidating the origin of such anomalies is also important, if we are to understand better the enrichment of bottom waters with DSi along the path of the conveyor belt (Ragueneau *et al.*, 2000) and such studies have been reported in the Weddell Sea (Van der Loeff and Van Bennekom, 1989) and more recently, in the Faeroe-Shetland Channel (Bonnin *et al.*, 2002).

What are the relative roles of the vertical flux and lateral transport (from deep channel or downslope), in the DSi anomaly observed at 4,000 m? Is this DSi anomaly linked to the degradation of organic matter, as suggested by the associated oxygen anomaly? Does this anomaly come from water column dissolution or sediment recycling?

To answer such questions and study in particular the influence of the deep channel, we have established benthic Si mass balances at two sites off the Congo margin. The first site (site D) is located near the deep channel whereas the second site (site C) is located further south, far from the influence of the channel (Fig. 1). Flux studies devoted to the comparison of sediment and water column fluxes (importance of vertical flux), which often exhibits strong discrepancies (Jahnke, 1996; Zabel and Hensen, 2006), included estimations of the opal rain rate by means of sediment traps, determination of benthic recycling by means of benthic chambers and calculation of diffusive fluxes from DSi gradients in interstitial waters, as well as direct determination of bSiO₂ accumulation rates. Process studies included direct measurements of bSiO₂ dissolution, both in the water column and in the sediments.

2. Methods

2.1. Sampling strategy

Within the framework of the BIOZAIRE programme (Sibuet *et al.*, this issue, introduction), we have studied a few sites sampled during the BIOZAIRE-3 cruise: Tête, D, C

and Lobe sites (Fig. 1). The Tête site receives direct continental inputs via the plume of the Congo's river. D site is located in the vicinity of the Congo submarine deep channel, and episodically subject to deep channel overflows. C site was considered as the reference site, located further south and out of the Congo's river influence. Finally, the Lobe site is located at the very end of the Congo deep channel, constituting a major depocenter (Table 1 and Fig. 1). It has been interesting to focus especially on the C and D sites, where sediment traps have been deployed and where we can compare the deep channel influence (site D) with a reference site (site C). For each site, we have evaluated the water column and the sediment stocks in bSiO₂, the bSiO₂ dissolution rates in the water column and at the sediment-water interface and measured the rain rate, the recycling fluxes and the sediment accumulation rates. Note that water column measurements (stocks and dissolution rates) have focused on the deep waters located around 4,000 m, to address the origin of the positive DSi anomaly.

The seawater has been sampled by Niskin bottles. One litre of seawater has been filtered onto polycarbonate Nucleopore filters (porosity 0,6 µm), with a Nalgène system. Filtrates (DSi measurements, see Vangriesheim *et al.*, this issue, a) and filters (bSiO₂ measurements) were preserved at 4°C and at ambient temperature, respectively. The sediment traps have been deployed at site C (400 m above the bottom) and site D (25 and 400 m above the bottom), to collect sinking particles (Rabouille *et al.*, this issue). Sediment traps were cone-shaped traps (Tecnicap) with 24 collection bottles. These traps had a sampling aperture of 1 m² covered with a honeycomb baffle of 1 cm diameter and 10 cm deep cells. Prior to deployment, the sampling bottles were filled with filtered seawater containing sodium borate buffered formalin to give a final concentration of 3% in order to prevent *in situ* microbial decomposition. The trap deployed at 400 m was not subject to sediment resuspension.

Sediment cores have been collected with a multicorer, which preserves the sediment-water interface remarkably well (Barnett *et al.*, 1984). Cores have been sliced in the cold room every 0,5 cm for the first five centimetres, every 1 cm down to 10 cm and every 2 cm below (down to 25-30 cm). Samples for the analysis of DSi concentrations immediately above the sediment-water interface were also collected by drawing water from 5 cm above the undisturbed interface. The separation of the porewater from the sediment slices has been performed by centrifugation (3,500 rpm for 20 minutes) at *in situ* temperature (2°C). The supernatant was then drawn into a Nalgène syringe, filtered onto pre-packed 0.45 µm Millipore filters and then stored in Teflon vials at 4°C for further DSi analysis. Sediment slices were stored frozen until bSiO₂ analysis.

2.2. Determination of bSiO₂ and DSi concentration in the water and in the sediment

The DSi concentrations in the water column and in the pore waters of the sediment were determined according to the molybdate blue spectrophotometric method (Mullin and Riley, 1965), adapted by Gordon *et al.* (1993). The Auto-analyser II technicon from Bran and Luebbe (0,5-1% analytical precision) was used. Repetability of DSi measurements in porewaters, based on replicate cores, is typically < 5% and closer to 2% (Ragueneau *et al.*, 2001). The bSiO₂ of the water column samples (filters) was determined by alkaline digestion according to Ragueneau *et al.* (2005b), i.e. 40 minutes of digestion in 0,2 M NaOH solution at 100°C. The correction for the mineral interference, inferred from the use of Si:Al ratios, proved to be useless in this environment where most of the study sites were beyond the Congo River plume. Precision is 5% based on replicate cores.

The opal content of the sediment traps and the sediment was determined according to the sequential extraction of DeMaster (1981) by alkaline digestion on dried sediment. The length and strength of the extractions have been adapted to the study sites following a few tests, including microscopic observations of diatom remains after each hour of extraction (Conley, 1998). 0,2 M NaOH has been used for sediment trap material (during one hour) and Na₂CO₃ 5%, has been used for the sediment, during 6 hours. Precision is also close to 5%.

2.3. Benthic flux measurements (chambers and the diffusive flux)

Benthic DSi fluxes have been estimated by means of benthic chambers (global fluxes, see the description of RAP2 chambers in Rabouille *et al.*, this issue) and from the DSi concentration gradient at the sediment-water interface, between the water column and sediment pore waters (diffusive fluxes). Fluxes of DSi across the sediment-water interface were calculated from the time-varying concentration of DSi in the overlying water of *in situ* incubation chambers. Precision is 2%, based on triplicates. For the diffusive fluxes, a first estimate can be obtained using Eq. (1) and a non-linear approximation for the first derivative of the gradient at the interface:

$$J_{\text{rec}} = -\phi_0 D_s [dC/dx]_{x=0} \quad (1)$$

J_{rec} is the diffusive flux, expressed in mmol Si m⁻² d⁻¹; ϕ_0 is the porosity measured at the interface (0.96); D_s is the whole sediment molecular diffusion coefficient for DSi.

Because the above approach depends strongly upon the vertical resolution of sampling (Zabel and Hensen, 2006), a more precise estimate can be obtained by fitting the full DSi profiles (see Sayles *et al.*, 1996), using Eq. (2) (McManus *et al.*, 1995):

$$C_x = C_d - (C_d - C_0)\exp(-\beta x) \quad (2)$$

Where C_x is the DSi concentration at the depth x , C_d is the asymptotic DSi concentration (assumed constant, i.e. steady state accumulation of a single bSiO₂ phase with a constant solubility), the first fitting parameter to be determined, C_0 is the bottom water DSi concentration and β is the second fitting parameter, the curvature of the profile. The flux is then determined using Eq. (3) which is the first derivative of Eq. (2) at the interface, substituted into Eq. (1) (McManus *et al.*, 1995):

$$J_{\text{rec}} = -\Phi_0^n D_m \beta (C_d - C_0) \quad (3)$$

As detailed in Ragueneau *et al.* (2001), typical uncertainties on benthic DSi fluxes estimated from whole core fitting procedures, based on several replicates, is close to 10-15%.

2.4. Determination of sedimentation flux through water column

The bSiO₂ flux in the water column, measured by means of sediment traps, is determined by the following equation (4):

$$J_{\text{bSiO}_2} = J_{\text{m tot}} \times \% \text{bSiO}_2 \quad (4)$$

Where J_{bSiO_2} is the bSiO₂ flux (mg bSiO₂.m⁻².d⁻¹), $J_{\text{m tot}}$ is the total mass flux of the traps (mg.m⁻².d⁻¹) and %bSiO₂ is the opal percentage in the traps, measured as described above (2.2), with a precision of 5%.

2.5. bSiO₂ dissolution rates in the water column and in the sediment

The bSiO₂ dissolution rate in the water column was quantified by the method of the isotopic dilution technique (Nelson and Goering, 1977) adapted by Corvaisier *et al.* (2005). Unfortunately, the unexpected low bSiO₂ concentrations, being three orders of magnitude lower than the DSi concentrations, didn't allow any accurate determination of the dissolution rates. Therefore, a value of 2.6 y⁻¹ has been chosen, as characteristic of water column silica dissolution at deep ocean temperature (Nelson *et al.*, 1995, Ragueneau *et al.*, 2000). Note that given the very low bSiO₂ concentrations in deep waters, multiplying or dividing this dissolution rate by a factor of two would not change our conclusions (see section 4.3) when the input of DSi to deep waters from sinking particles, obtained by multiplying this rate by the bSiO₂ inventory in the deep waters, will be compared to the benthic DSi efflux.

The dissolution kinetics of bSiO₂ in the sediment was measured using stirred flow-through reactors (Van Cappellen and Qiu, 1997a). The method consisted of placing in these reactors a known quantity of sediment in contact with an input DSi solution of known

composition (pH, ionic strength, and temperature controls) which was pumped through the reactor with a constant flow rate. The experiment is conducted until the DSi concentration in the reactor outflow exhibits a constant value. When steady-state conditions were reached, the DSi concentration in the output solution was compared with the input concentration. The difference, multiplied by the flow rate, allows the determination of bSiO₂ dissolution and precipitation rates. During the course of an experiment, the DSi concentration in the input solution is progressively increased to induce successively dissolution and precipitation. The value at which neither dissolution nor precipitation occurs is considered to be the apparent solubility (mixed system) of the bSiO₂. The experiment has been performed at pH 8, 25°C and an ionic strength of 0.7 M, i.e. conditions similar to those used by Van Cappellen and Qiu (1997a,b). For comparison with DSi concentrations in interstitial waters near 4000 m, all data have been recalculated at bottom temperature according to Rickert (2000). Solubility values were corrected for pressure, assuming that the relationship obtained by Willey (1974) with synthetic amorphous silica as a valid analog for biogenic silica (Dixit *et al.*, 2001). Uncertainty on solubility measurements vary between 10 and 18 % (Gallinari *et al.*, 2002).

3. Results

3.1. DSi and bSiO₂ concentrations in the water column and in the sediment

Figure 2 shows the vertical sections of dissolved oxygen and DSi concentrations, along the continental slope in the vicinity of the Congo river (see Vangriesheim *et al.*, this issue, a). DSi concentrations increase with depth, and at 4,000 m depth, a panache of low oxygen concentrations (220 $\mu\text{mol.l}^{-1}$) and high DSi concentrations (60 $\mu\text{mol.l}^{-1}$) is observed. The bSiO₂ concentrations (not shown) are very low, showing important fluctuations in surface waters (7– 125 nmol.l^{-1}), and a narrower range near 4,000 m, between 25 and 100 nmol.l^{-1} .

Two types of DSi profiles in the porewaters can be distinguished (Fig. 3a). The first one (Tête and Lobe sites) shows relatively stable concentrations down to 20 cm depth (100 - 200 $\mu\text{mol.l}^{-1}$). The second one (C and D sites) exhibits profiles more characteristic of deep-sea environments, with sharp gradients near the sediment-water interface and a stable asymptotic concentration (C_{asympt} , 400 $\mu\text{mol.l}^{-1}$).

Interestingly, the bSiO₂ profiles in the sediments (Fig. 3b) can also be classified in two groups, the same groups, with the Tête and Lobe sites that exhibit a strong decrease in the upper 5 cm while the other three sites display more stable concentrations downcore. This result is quite surprising, as this strong gradient near the interface observed at the Tête and

Lobe sites is not reflected in a sharp gradient in DSi concentration at these sites; this suggests that there, other processes than dissolution of bSiO₂ are controlling the DSi profiles.

3.2. Sediment trap fluxes

Fig. 4 shows the seasonal variations of bSiO₂ fluxes as recorded in sediment traps deployed at sites C and D. For the site C, the bSiO₂ fluxes varied more than 24-fold between the lowest fluxes of 0.02 mmol Si.m⁻².d⁻¹ recorded during winter (February 2003), and the highest fluxes, 0.48 mmol Si.m⁻².d⁻¹ recorded during summer (July 2003). For the site D, the bSiO₂ fluxes varied only 4.5-fold between the lowest fluxes of 0.13 mmol Si.m⁻².d⁻¹ recorded during the winter (November 2003), and the highest, 0.6 mmol Si.m⁻².d⁻¹ recorded during the beginning of summer (June 2003).

For the site C, J_{Bsi} was about 0.2 mmol Si.m⁻².d⁻¹ (or 0.073 mol Si.m⁻².y⁻¹), and for the site D, about 0.3 mmol Si.m⁻².d⁻¹ (or 0.11 mol Si.m⁻².y⁻¹). These fluxes are of similar magnitude as those encountered in the deep sea of the Atlantic (Lampitt *et al.*, 2001) and Pacific (Honjo *et al.*, 1995) oceans; they also fall in the range of bSiO₂ fluxes measured in several regions off NW, equatorial and SW Africa (Fischer *et al.*, 2004). They are much lower than fluxes measured in the Southern Ocean, or even on the continental slope off NE Africa, such as the Somali slope (Koning *et al.*, 1997).

3.3. DSi benthic fluxes

Benthic fluxes have been measured both using benthic chambers and the gradient of DSi concentrations in porewaters (Fick's law and whole core fitting). Results are presented in Table 2. For the diffusive fluxes, only the whole-core fitting procedure will be used because flux estimates based on a two-points gradient across the interface is too dependent upon sampling resolution (Zabel and Hensen, 2006). At C site, the total (benthic chambers) and diffusive (whole core fitting) estimates agree within 6%, with a value close to 0.8 mmol Si.m⁻².d⁻¹. At site D, the flux measured with the benthic chamber (0.47 mmol Si.m⁻².d⁻¹) is three times lower than the one obtained by fitting Eq. (2) (1.68 mmol Si.m⁻².d⁻¹). In general, when discrepancies between measured and calculated fluxes occur, the higher values are observed with benthic chambers because they account for processes that take place at the interface (Conley, 1987), or through other processes such as irrigation (Aller, 1982, Matisoff, 1995). Therefore, either the calculated or the measured flux is not correct. The fact that the bSiO₂ rain is higher at site D than at site C (Fig. 4, see below), while the sediment accumulation rate which is a very important control factor for bSiO₂ preservation in the sediments (Ragueneau

et al., 2000) is similar at both sites, suggests that the benthic fluxes should be higher at site D than at site C, and certainly not 3 times lower, all other factors being equal. Therefore, we have chosen to discard the low value measured at site D with benthic chambers.

Thus, in the following and for consistency between sites C and D, only the values determined from whole core fitting of Eq. (2) (Table 2) will be used in the establishment of the silica mass balance. Note that at site C, the value chosen ($0,75 \text{ mmol Si.m}^{-2}.\text{d}^{-1}$) is 12% lower than the mean value for the three methods ($0.86 \text{ mmol Si.m}^{-2}.\text{d}^{-1}$) and at site D, it is 10% higher than the mean ($1.53 \text{ mmol Si.m}^{-2}.\text{d}^{-1}$, after discarding the benthic chamber estimate, see above). As we shall see, this choice will not impact our conclusions because the imbalance discussed in section 4.1 is much larger than this uncertainty on benthic fluxes.

3.4. Spatial differences of the dissolution rates of opal in the water and in the sediment

bSiO_2 dissolution rates in sediments have been quantified by means of flow-through reactors. Calculated reaction rates for sediment samples are plotted vs. DSi concentrations inside the reactors (Fig. 5). Apparent solubilities are calculated by linearly interpolating negative and positive rates observed close to equilibrium (Van Cappellen and Qiu, 1997a-b). At both sites, the function is nearly linear and the apparent solubilities (recalculated at bottom water temperature) are respectively $195 \pm 35 \mu\text{mol l}^{-1}$ and $263 \pm 162 \mu\text{mol l}^{-1}$ for the D and C sites. The dissolution rate constants are 0.31 year^{-1} for the site D ($0.16 \text{ nmol.s}^{-1}.\text{g}_{\text{bSiO}_2}^{-1}$) and 0.42 year^{-1} for the site C ($0.22 \text{ nmol.s}^{-1}.\text{g}_{\text{bSiO}_2}^{-1}$). The dissolution rate of the opal in the sediment is therefore about 10-fold lower than typical values encountered in the water column near 2°C .

It is interesting to note that the solubilities measured at the two sites (around $200 \mu\text{mol.l}^{-1}$) are very low, especially compared to the solubility of fresh diatoms, close to $1000 \mu\text{mol.l}^{-1}$ at 2°C (review in Dixit *et al.*, 2001). It has been shown that the solubility decreases with increasing Al concentrations (Van Cappellen and Qiu, 1997a-b). Our study site is the site where the role of Al on bSiO_2 early diagenesis has been first evidenced (Van Bennekom *et al.*, 1989) so the low solubilities measured with flow-through reactors are not surprising. Solubilities have been measured only near the sediment-water interface; they must increase downcore up to values close (or higher) to the asymptotic DSi concentration measured at $400 \mu\text{M}$ (Fig. 3a), i.e. with a profile similar to that encountered by Gallinari *et al.* (2002) in the equatorial Pacific.

4. Discussion

4.1. Origin of the DSi anomaly

The excess DSi present at the isobath 4,000 m (Fig. 2, see also Vangriesheim *et al.*, this issue, a) could originate from (1) the dissolution of bSiO₂ in the water column, (2) the desorption of DSi from resuspended particles or (3) the refuelling from benthic fluxes.

Resuspension of bottom particles can enrich the DSi concentration in bottom waters following desorption processes (Gehlen and Van Raaphorst, 2002). Van der Loeff and Boudreau (1997) have shown that for resuspension to enhance bSiO₂ dissolution, near-bottom conditions should be highly turbulent. Indeed, this process has been shown to be a potentially important mechanism to account for the DSi anomaly observed in the Faeroe-Shetland Channel (Bonnin *et al.*, 2002) where currents up to 65 cm.s⁻¹ have been measured (Hosegood and Van Haren, 2003). In the BIOZAIRE study area, currents never reached such high values (Vangriesheim *et al.*, this issue, b) and it is unlikely that resuspension could contribute an important fraction of the DSi anomaly observed permanently at 4,000 m. Additionally, the fact that there also exists an anomaly in O₂ concentration at that depth strongly suggests that the origin of both anomalies are common and linked to the concomitant degradation of biogenic matter and the dissolution of bSiO₂. Two major reasons suggest that dissolution and degradation take place in the sediments

In the deep waters, the bSiO₂ concentration ranges from 25 to 100 nmol Si l⁻¹. With a dissolution rate of 2.6 y⁻¹, the dissolution flux from suspended particles in the deep waters falls in the range 0.065 to 0.26 mmol Si m⁻³ y⁻¹. This flux is to be compared with the benthic flux, ranging from 0.5 to 1.7 mmol m⁻² d⁻¹ (Table 2). Calculated over a year and distributed over the depth of the DSi anomaly (300 meters above the seafloor, see Fig. 2), the enrichment of bottom waters with DSi from the sediment should range between 0.61 and 2.07 mmol m⁻³ y⁻¹. From this calculation, it is obvious that the enrichment potential is one order of magnitude higher in the sediment than in the water column, despite a dissolution rate that is one order of magnitude lower in the sediments. This is clearly due to the stock of bSiO₂ dissolving, which is 4-5 orders of magnitude higher in the sediments compared to the deep waters.

The second reason deals with the remarkable consistency between the DSi and O₂ gradients in the deep waters which make up the anomalies in the 300 meters above the seafloor (Fig. 2). At site C, between 3,500 m and the seafloor, the slope of the O₂ consumption gradient is -0.05 mmol O₂ m⁻⁴ (Vangriesheim *et al.*, this issue, a) while the slope of the DSi enrichment gradient is 0.02 mmol Si m⁻⁴, yielding a Si/O₂ ratio of -0.38. At that station, the DSi benthic diffusive flux is 0.75 mmol Si m⁻² d⁻¹ (Table 2) while the O₂ benthic

flux is $-2.4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Rabouille *et al.*, this issue), so the Si/O₂ ratio is -0.31 , a value very close to that estimated from the water column gradients. A similar calculation performed at station 32 (near site D) shows a similar consistency, with a Si/O₂ ratio close to -0.6 for both estimates. It is interesting to note that these ratios fit remarkably well the global algorithm proposed by Holstein and his collaborators, cited in Zabel and Hensen (2006): benthic Si and O₂ fluxes seem to be tightly related at global scale, with $F_{\text{Si}} = 0.54.F_{\text{O}_2}$.

Thus, the DSi anomaly is most probably coming from the sediment, and seems to be clearly associated with the degradation of organic debris. Why does this degradation generate such an anomaly?

4.2. Establishment of a benthic Si mass balance

To answer this question and discuss whether the benthic degradation is proportional to the vertical flux or subject to lateral inputs, we have established a mass balance of Si fluxes at the sediment-water interface, at the rise of the continental slope (Table 3). A mass balance of Si fluxes can be built at the sediment-water interface at sites C and D, by comparing the measured bSiO₂ rain rate (Fig. 4) to the sum of the benthic recycling flux (Table 2) and the opal mass accumulation rate (MAR). Opal MAR has been estimated at sites C and D using the following equation:

$$J_{\text{acc}} = (1 - \Phi).w.S.b\text{SiO}_2 \quad (4)$$

Where w is the sediment density (g.cm^{-3}) and S is the sediment accumulation rate (cm.y^{-1}). With a sediment density close to 2.5 g.cm^{-3} , a porosity close to 0.9 and a sedimentation rate of 1 mm y^{-1} (Rabouille *et al.*, this issue), the opal MAR (estimated using a mean value of % bSiO₂ between 15 and 25 cm , of 4.5% , see Fig. 3b), at site C and D is $0.17 \text{ mol Si.m}^{-2} \text{ .y}^{-1}$ and $0.31 \text{ mol Si.m}^{-2} \text{ .y}^{-1}$, respectively. Note that accumulation rates have been determined using the downcore linear decrease of ^{210}Pb below the bioturbated zone; they are well constrained and, excluding the particular REGAB site which displays a higher accumulation rate (2 mm y^{-1}) yield a mean value at $1.04 \pm 0.11 \text{ cm y}^{-1}$.

With these values of bSiO₂ MAR, a mass balance of Si fluxes at sites C and D can be constructed (Fig. 6). Assuming steady state, and that the benthic flux of DSi comes from the dissolution of bSiO₂ with no or negligible contribution from silicate minerals, the mean rain rate of bSiO₂ measured at 400 m above the seafloor by sediment traps can be compared to the rain reconstructed by summing the benthic flux and the accumulation flux. This method highlighted a major imbalance as the reconstructed opal rain at site C is $0.45 \text{ mol Si.m}^{-2} \text{ .y}^{-1}$, i.e. 6.1 times higher than the measured value of $0.07 \text{ mol Si.m}^{-2} \text{ .y}^{-1}$. A similar result was

observed at site D where the reconstructed bSiO_2 rain ($0.92 \text{ mol Si}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$) was 8.4 times greater than the measured value ($0.11 \text{ mol Si}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$). It should be noted that similar differences were observed for organic carbon fluxes, with reconstructed values being 6.5 and 8.2 greater than measured values at sites C and D, respectively (Rabouille *et al.*, this issue).

Table 3 presents a compilation of similar benthic mass balances established at about ten sites in the world ocean, including the two sites described herein. For about half of these sites, the measured and reconstructed opal rain rates agree within 30%, which provides confidence in the measurements and allows a reasonable estimate of the Si preservation efficiency at the sediment-water interface to be calculated. At those sites, the preservation efficiency of the bSiO_2 reaching the seafloor varies between 5 and 15%, meaning that 85-95% of the bSiO_2 rain rate returns to the deep waters on an annual basis (see review in Ragueneau *et al.*, 2000; 2001). For the other sites, mostly located in the Southern Ocean, and C and D sites of our study area, the discrepancy is large between measured and calculated fluxes so no reasonable estimate of the opal preservation efficiency can be established.

Several reasons may explain such discrepancies. First, the different time scale of the three fluxes used for reconstruction: sediment traps operate from days to one year while the benthic fluxes integrates dissolution in the upper sediment column that took place in the past several years or decades, and accumulation integrates over millennia. The examination of the PAP site in the NE Atlantic clearly illustrated this problem (Ragueneau *et al.*, 2001). There, the reconstructed rain rate was $0.065 \text{ mol Si}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ which is 50% higher than the value of $0.043 \text{ mol Si}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$ measured with sediment traps over two years (1997-1998, Lampitt *et al.*, 2001). Knowing that benthic fluxes integrate over several years, an estimate of the rain was measured over a 10-year period thanks to the long-time series of sediment trap data existing at that site. In that case, the mean bSiO_2 flux reaching the seabed over ten years was $0.045 \text{ mol Si}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$, which was remarkably consistent with the reconstructed rain rate using the mean value of the benthic fluxes estimated from 29 cores obtained during two years (Ragueneau *et al.*, 2001, Table 2). At sites C and D, we have seen that the mean fluxes measured from the sediment traps are reasonably consistent with fluxes measured in other regions off Africa in the Atlantic Ocean. It is important to note that no correction has been performed for silica dissolution in the cups of the sediment traps, so real fluxes may well be higher. For fluxes in the range $0.1 - 0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ though (see Fig. 4), Ragueneau *et al.* (2001) suggest that the extent of the correction should not exceed 20%. It is therefore unlikely that fluxes would have been underestimated by at least, a factor of 6 as that required to account for the imbalance shown in Fig. 6. The most likely hypothesis concerns the lateral transport of sediments.

In general, the silica accumulation is about one order of magnitude lower than the benthic flux (Table 3, see also Ragueneau *et al.*, 2000). At sites C and D, the accumulation represents one half of the benthic flux, which is extremely unusual and suggests that sediment lateral transport might be involved to explain the difference between the measured and calculated opal rain rates. The sites where an imbalance has already been observed are located in the Southern Ocean (Table 3) where it has been demonstrated that both burial and diffusive fluxes have been overestimated as a result of sediment focusing induced by strong bottom currents (Pondaven *et al.*, 2000; DeMaster, 2002). Given the fact that similar imbalances are observed for carbon and silica (see Rabouille *et al.*, this issue), it is reasonable to suggest that these sites are subject to accumulation rates resulting from lateral transport and that the simple 1D mass balance presented Fig. 6 can not be discussed in terms of preservation efficiency of the downward opal flux.

4.2. The source of sediments at sites C and D

Would the imbalance have taken place only at site D, located directly under the influence of the Congo deep sea fan, we could have hypothesized that the excess sediment is coming from the deep channel itself, in agreement with the hypothesis of Braga *et al.* (2004). The fact that the imbalance has also been observed at site C which is far from the valley influence suggests that the sediment, instead, may come from the continental shelf, through downward transport along the slope. A confirmation of this hypothesis comes from the combination of Si and C-org accumulation rates (see Rabouille *et al.*, this issue). The two estimates yield a Si:C molar ratio of 0.55 and 0.57 at sites C and D, respectively. This ratio is remarkably similar to the mean Si:C ratios compiled by DeMaster (2002) for different continental shelves around the world (0.6). It suggests that the origin of the sediments encountered at sites C and D indeed is the shelf and that this material has not been greatly modified during the down slope transport. This is consistent with the idea that a large portion of the off-shelf transport of biogenic matter may be old terrestrial or relic matter (Chen, 2009; Kao and Liu, 2000; Bauer *et al.*, 2001), so it has already been degraded before off-shelf transport actually starts. Interestingly, the Si:C ratio in the accumulation flux is similar to that measured in the trap deployed at site C (0.52 in the traps, 0.55 in the sediments), and even lower for site D (0.79 in the traps and 0.57 in the sediments). This strongly confirms that the material found in C and D sites sediments has almost nothing to do with pelagic sedimentation. Indeed, it has been shown that typically, the Si:C ratio increases between the

rain and the accumulation by a mean factor of ca. 4 at global scale (Ragueneau *et al.*, 2002), an increase that is not observed at C and D sites.

There exist very few data concerning the mechanism of down slope transport, at least for Si, as a means of exchanging matter between the shelf and the open ocean. In fact, in the most recent Si budget constructed at global scale, from the land to the sea (Laruelle *et al.*, in revision), this flux could not be estimated. The observations from BIOZAIRE-3 provide the first possibility to estimate such a flux. According to Chen (2009), the downslope transport of modern particulate carbon at global scale is 0.5 Pg C.y^{-1} , half of which is organic. Therefore, the shelf-ocean export of organic carbon at global scale amounts to 21 Tmol C.y^{-1} . The results from the BIOZAIRE study area suggest that the Si:C molar ratio did not change between its value on the shelf and its value we measured at the foot of the slope. Applying this value of 0.56 for the molar Si:C ratio (which seems conservative, see DeMaster, 2002) to the global estimate of POC off-shelf transport, yields a first estimate of bSiO_2 down slope transport close to $12 \text{ Tmol Si.y}^{-1}$. This is a huge number, to be compared to the $5\text{-}6 \text{ Tmol Si.y}^{-1}$ brought by rivers (Tréguer *et al.*, 1995; Laruelle *et al.*, in revision). It is interesting to note that this flux is largely compensated by an influx of DSi from intermediate waters upwelling onto the shelf, estimated at $10 \text{ Tmol Si.y}^{-1}$ by Laruelle *et al.* (in revision). Truly, this is a first estimate of the magnitude of this flux for the Si cycle and this magnitude implies that this hypothesis needs to be tested in various regions. In particular, what is crucially needed is to test the assumption that the Si:C ratio is not so much modified during downslope transport of shelf sedimentary material, as observed in the Congo margin environment. Data bases of Si and C concentrations in shelf, slope and rise sediments of various margins need to be scrutinized carefully in this perspective.

5. Conclusion

The establishment of a Si mass balance at the sediment-water interface on the continental margin in the vicinity of the Congo deep sea fan allowed us to derive important conclusions regarding the origin of the DSi anomaly observed at 4,000 m in this area, and opens important perspectives concerning the transfer of Si from the margin to the open ocean. Due to a much larger standing stock of bSiO_2 in the sediments compared to the bottom waters, the DSi anomaly is coming mostly from benthic recycling, although dissolution rates are one order of magnitude lower in the sediment compared to the water column. The richness

of sediments in bSiO_2 , at the origin of this anomaly, is not due to pelagic sedimentation so that it is difficult to relate this anomaly to an intense productivity in surface waters as proposed by Van Bennekom (1996). In fact, a major imbalance has been observed when comparing the measured bSiO_2 rain rate, based on particle traps deployed at 400 m above the seafloor, and the rain rate reconstructed by summing the recycling and accumulation fluxes. Reconstructed fluxes are 6-8 times higher than measured fluxes, an observation which has also been made for organic matter (Rabouille *et al.*, this issue). Biogenic matter, that does not come from above, must be accumulating in this area, strongly associating Si and organic matter as the Si and C imbalances match pretty well and the bottom water DSi enrichment is very consistent with the O_2 consumption rate needed to degrade this organic matter. Because these observations were made at the foot of the slope, at both sites D and C, they are probably not associated to the deep channel as proposed by Braga *et al.* (2004); it is rather suggested that this biogenic matter is derived from downslope transport. Because the composition of the sediments, as seen from Si:C ratios, is very similar at the foot of the slope compared to values typically encountered on continental shelves (ca. 0.6, DeMaster, 2002), it is suggested that this biogenic matter is not so much altered during this downslope transport. This needs to be verified in other margin environments, as it may have important implications for the transfer of Si, and C_{org} , from the shelf to the open ocean, an area where many unknowns remain (Chen, 2009).

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Table 1. Sites sampled during the BIOZAIRE 3 cruise and their corresponding CTD, MTB and MLP numbers. See Vangriesheim et al. (this issue, a) for detailed positions and characteristics. See also Fig. 1.

Site	n°CTD (bathyprobe)	n°MTB (multicores)	n°MLP (sediment traps)
Tête	23	23	
D	11	20	18
D	32	32	
C	20	21	15
Lobe	36	33	

Table 2. Estimation of the DSi benthic fluxes ($\text{mmol Si m}^{-2} \text{ d}^{-1}$) with the three calculation methods (see text), for the C (MTB 21) and D (MTB 20) sites.

MTB	From benthic chambers	From Fick's law	From whole-core fitting
21 (C)	0.85	0.99	0.75
20 (D)	0.47	1.37	1.68

Table 3. Benthic mass balance of Si fluxes at the PAP site during 1997, compared to other deep sea environments where such an exercise can be performed. All data in $\text{mol Si.m}^{-2}.\text{y}^{-1}$. The reconstructed bSiO_2 input flux corresponds to the sum of the DSi benthic flux and the bSiO_2 accumulation flux, assuming steady-state. The value is compared to the bSiO_2 flux measured by means of sediment traps deployed at 3,000 m (Calculated/Measured*100). Also given are the sedimentation rates and the sediment preservation efficiencies calculated by dividing the accumulation flux by the reconstructed rain rate. Data are from Sayles *et al.* (1996) for the BATS site, Koning *et al.* (1997) for the Indian Ocean, Berelson *et al.* (1997) for the Equatorial Pacific, DeMaster *et al.* (1996) for the Ross Sea, Rabouille *et al.* (1997) and Pondaven *et al.* (2000) for the Indian sector of the Permanently Open Ocean Zone (POOZ) and the Polar Front Zone (PFZ) of the Southern Ocean. Note that the accumulation rate at the BATS site is a recalculation from data in Sayles *et al.* (1996) and those from the Indian Ocean have been kindly provided by E. Koning. Two values are given for the measured bSiO_2 flux at the PAP site, the first is the one obtained during the 2 years of the BENGAL project and the second one given in parenthesis is a mean over the last decade.

Ocean basin Study site	Atlantic Ocean				Indian Ocean	Pacific Ocean	Southern Ocean			
	North east (PAP/NABE)	North west (BATS)	Equatorial East		North west (Somali)	Equatorial (EqPac)	PO OZ (Ind. Sec.)	PFZ (Ind. Sec.)	Inner Ross Sea	Outer Ross Sea
			BIOZAIRE/C	BIOZAIRE/D						
Measured input flux ($\text{mol.m}^{-2}.\text{y}^{-1}$)	0.043 (0.062)	0.019	0.073	0.11	0.32	0.109	0.51	0.40	1.30	0.400
Reconstructed input flux ($\text{mol.m}^{-2}.\text{y}^{-1}$)	0.065	0.018	0.446	0.921	0.28	0.140	2.45	1.09	2.13	0.374
Recycling flux ($\text{mol.m}^{-2}.\text{y}^{-1}$)	0.057	0.017	0.274	0.614	0.26	0.131	2.03	0.73	0.89	0.367
Accumulation flux ($\text{mol.m}^{-2}.\text{y}^{-1}$)	0.008	0.001	0.172	0.307	0.018	0.009	0.42	0.36	1.24	0.007
Preservation efficiency (%)	12.3	5.6	38.6	33.3	6.4	6.4	17.1	33.0	58.1	1.9
Calculated/Measured * 100 (%)	151.2	94.7	610.9	837.3	87.5	128.4	480.4	272.5	163.8	93.5
Sedimentation rate (cm.ky^{-1})	7.5	0.7	100.0	120.0	4.0	1.7	10.0	10.0	16.0	1.2

Figure captions

Figure 1. Bathymetric map of the Gulf of Guinea with the CTD stations investigated during the BIOZAIRE-3 cruise (December 2003 to January 2004). Among the different sites where process studies have been performed (e.g. Tête located on the shelf, Lobe, located at the end of the deep channel), the main focus of this study is placed on site D under the influence of the deep channel and on site C located further south.

Figure 2. East-West (a) and (b) and North-South (c) and (d) sections of dissolved silicate and oxygen concentrations ($\mu\text{mol.kg}^{-1}$), respectively, on the continental slope off the Congo river. Evidence for the co-occurrence of the DSi and O_2 anomalies. Colour scale, not linear, chosen to highlight the deep layer anomaly. Drawn with ODV software Schlitzer, R., 2008 <http://odv.awi.de>. See Vangriesheim et al., this issue, a.

Figure 3. Downcore profiles of DSi (μM) (a) and bSiO_2 (weight %) (b) concentrations. (MTB-23, Tête site; MTB-33, Lobe site; MTB-21, C site; MTB-32, D site; MTB-20, D site).

Figure 4. Seasonal evolution of the bSiO_2 rain fluxes ($\text{mmol Si m}^{-2} \text{d}^{-1}$) for the C and D sites, during the year 2003, as measured by means of sediment traps deployed 400 m above the seafloor (i.e. 3,600 m depth). See Rabouille et al., this issue.

Figure 5. Dissolution and precipitation rates of surface sediment silica (R, y^{-1}) as a function of the outflow DSi concentrations measured at equilibrium in the flow-through reactors for sites C (squares) and D (triangles). Reaction rates have been recalculated at 2°C , the *in situ* temperature at 4000 m.

Figure 6. Benthic Si mass balance at site C (a) and site D (b). Stocks in boxes are in mmol Si m^{-3} of water (measured at 4000 m) or porewater (measured at 15 cm downcore). Downward grey arrows show the bSiO_2 measured rain rate and accumulation rate (in $\text{mol Si m}^{-2} \text{y}^{-1}$) while the upward black arrow shows the benthic flux (in $\text{mol Si m}^{-2} \text{y}^{-1}$). These flux values are highlighted in bold, to show the major imbalance discussed in the text, at both sites (adding the benthic and accumulation fluxes largely exceeds the measured rain). The horizontal grey,

dashed arrow shows the dissolution rate (in y^{-1}) in the water column and that measured in the sediments using flow-through reactors.

Figure 1.

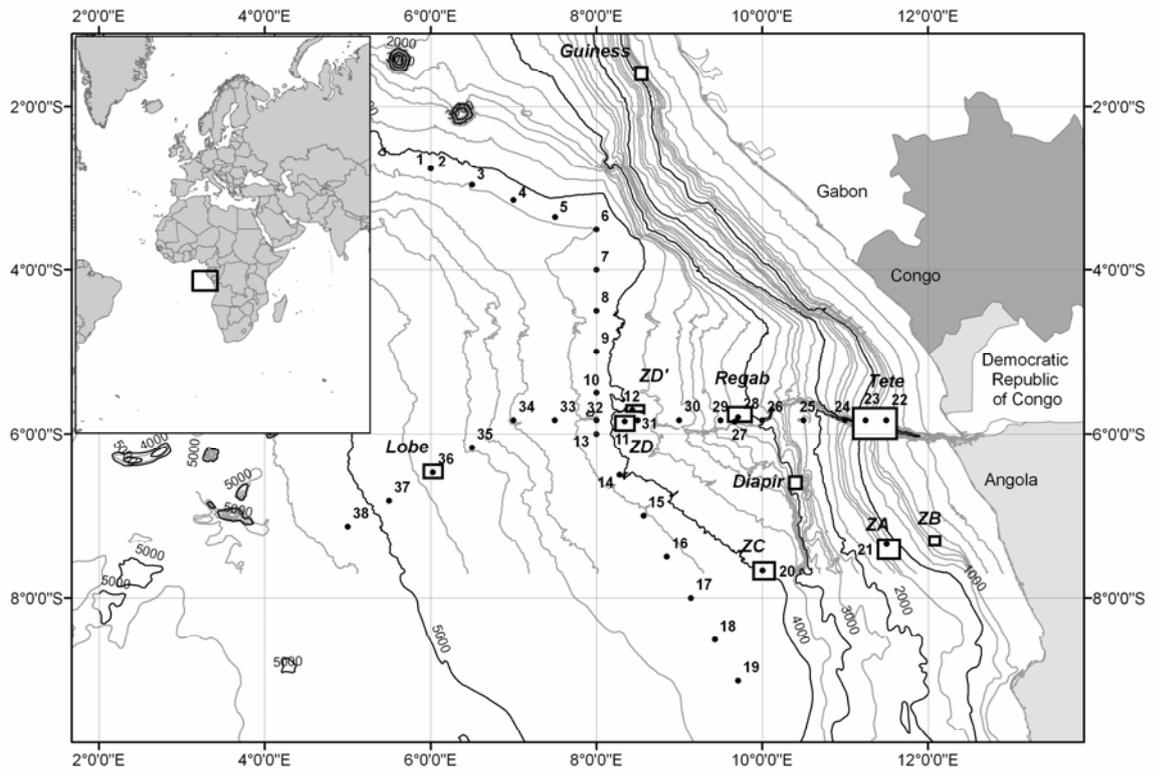
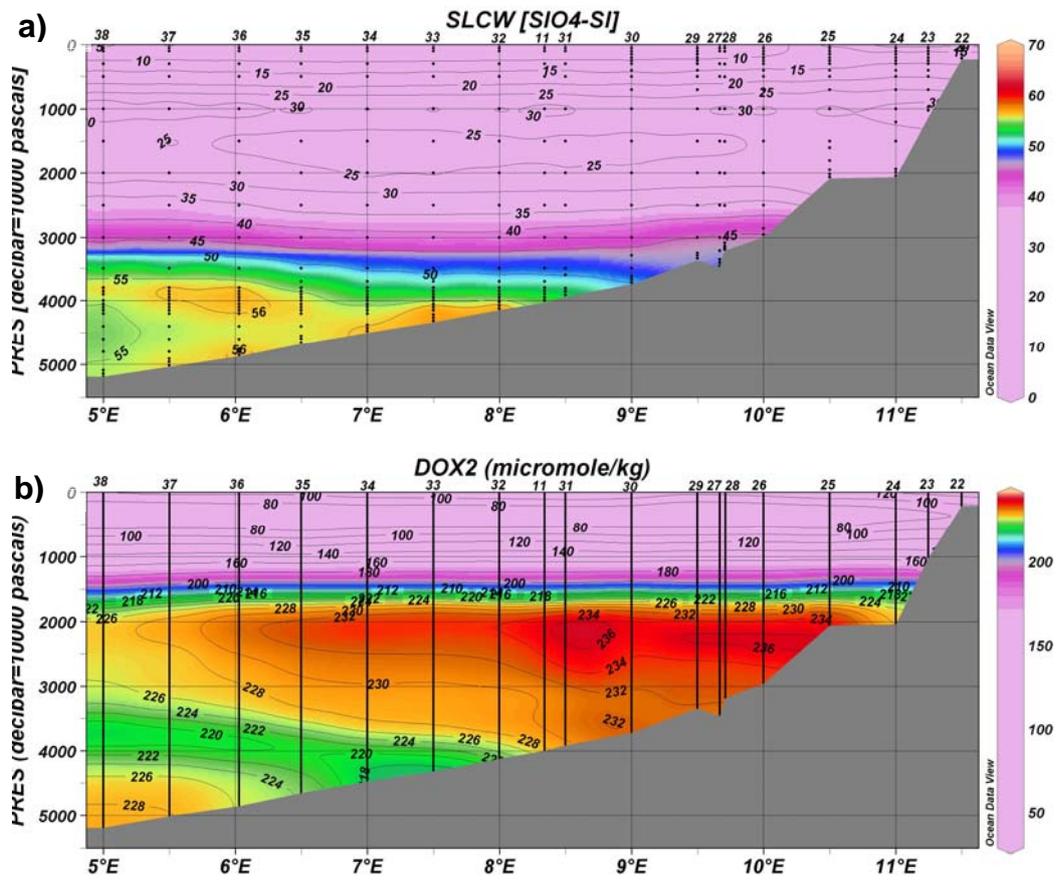


Figure 2



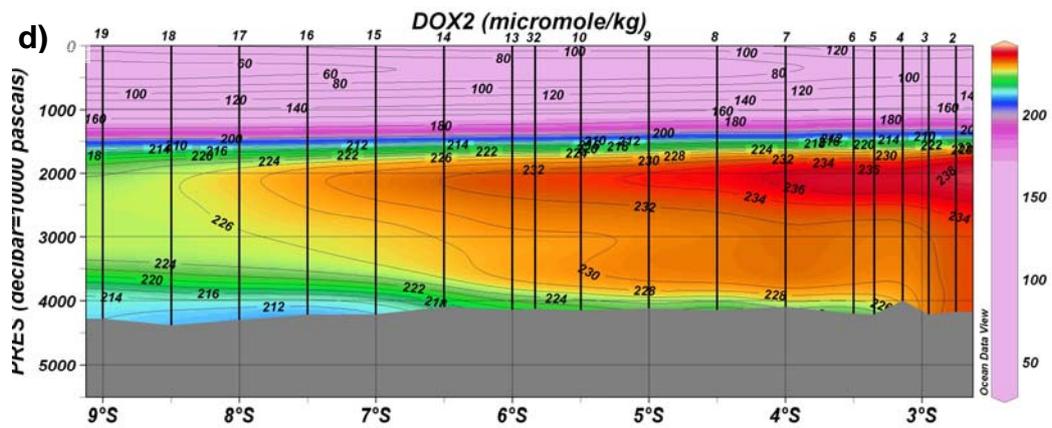
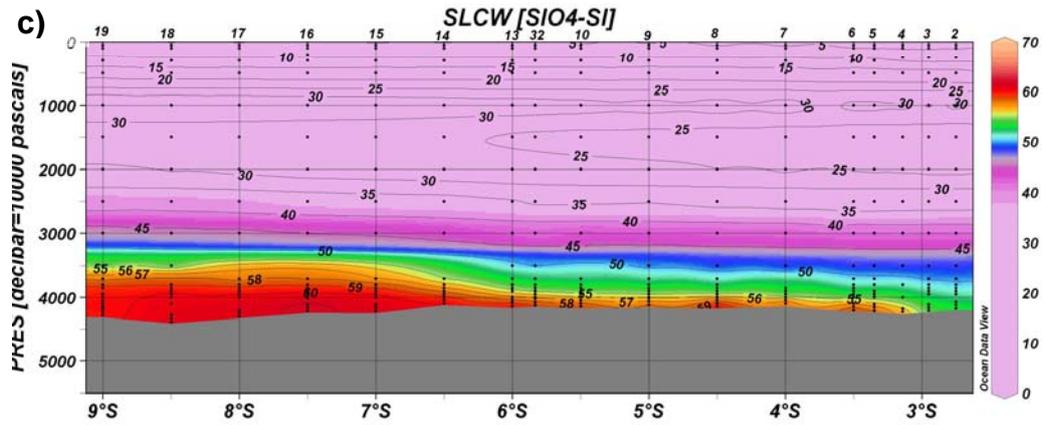


Figure 3.

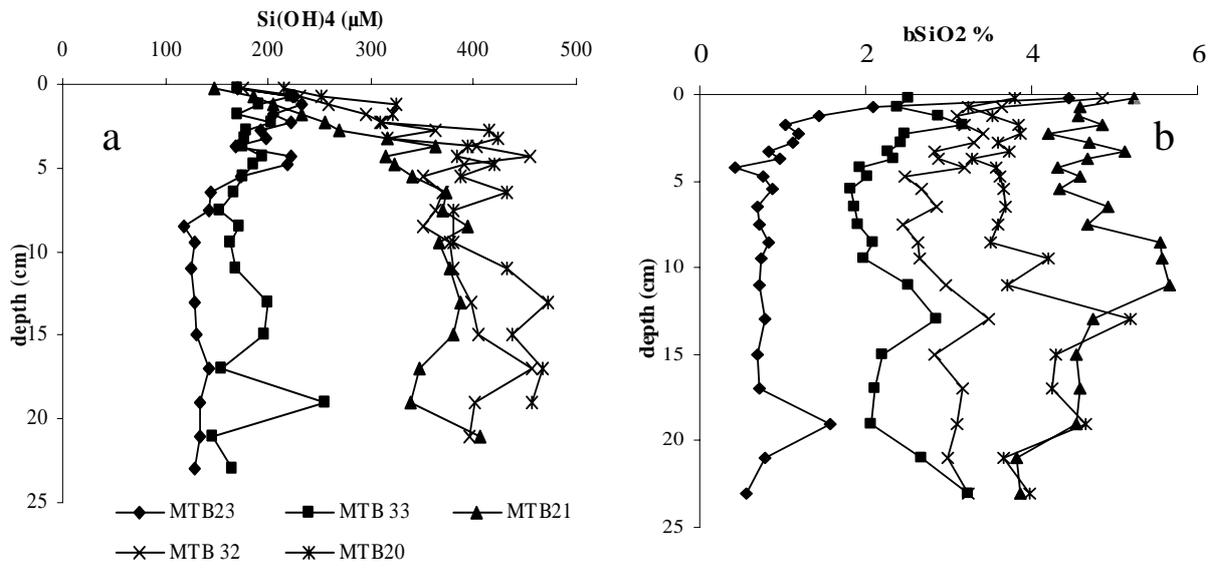
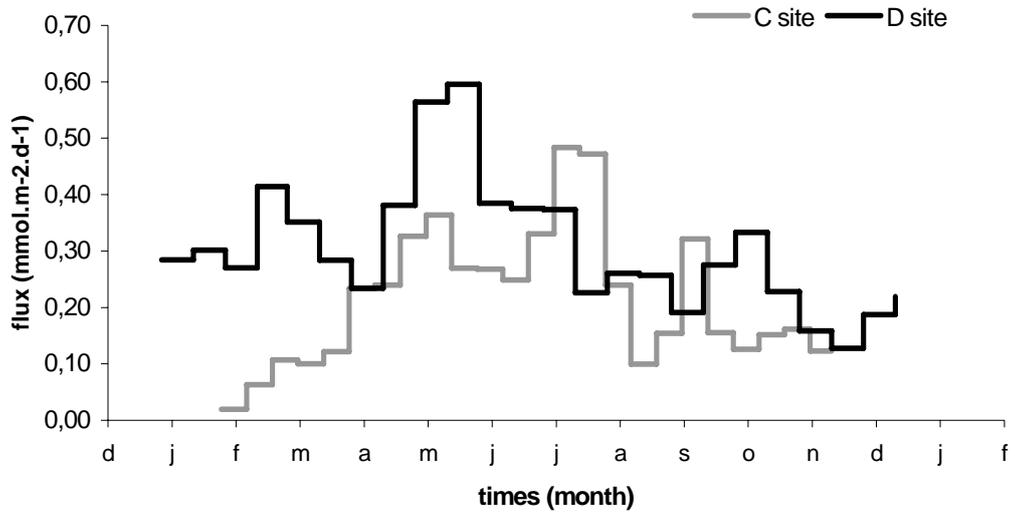


Figure 4.



2°C, pH8

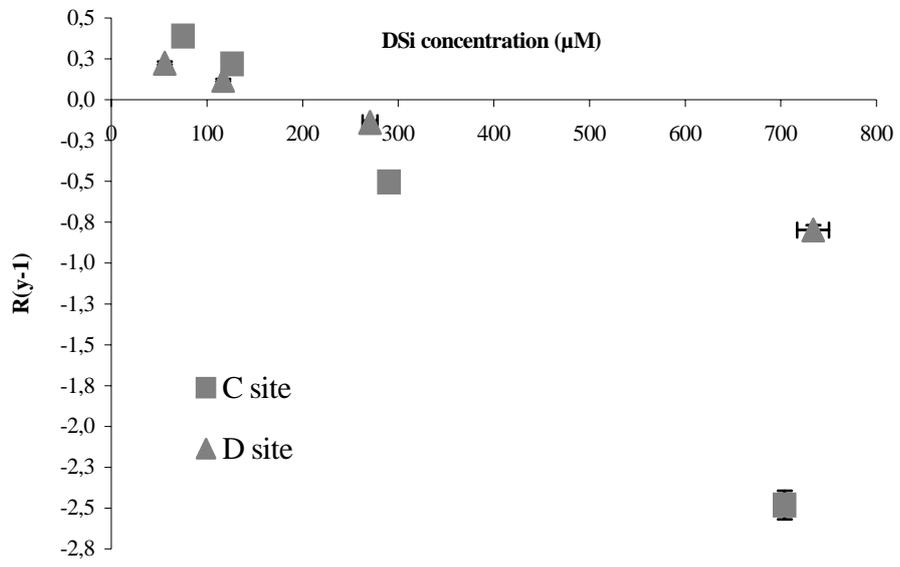


Figure 6.

