



Rapid transport and high accumulation of amorphous silica in the Congo deep-sea fan: A preliminary budget



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ARTICLE INFO

Article history:

Received 24 August 2013

Received in revised form 4 June 2014

Accepted 10 July 2014

Available online 16 July 2014

Keywords:

Continental margin

Land–sea export

Silica cycle

Congo canyon

Deep-sea fan

ABSTRACT

Mechanisms controlling the transfer and retention of silicon (Si) along continental margins are poorly understood, but play a major role in the functioning of coastal ecosystems and the oceanic biological pump of carbon. Deep-sea fans are well recognized as carbon sink spots, but we lack knowledge about the importance of the fans in the global Si cycle. Here, we provide a first estimate of the role played by the Congo deep-sea fan, one of the biggest in the world, in the Si cycle. Sediment cores sampled in the deep-sea fan were analyzed to build a Si mass balance. An exceptionally high accumulation rate of amorphous silica aSiO₂ ($2.29 \pm 0.58 \text{ mol Si m}^{-2} \text{ y}^{-1}$) was found, due to a high sedimentation rate and the presence of aluminum in the sediments. Although favored by bioirrigation, recycling fluxes remained low ($0.3 \text{ mol Si m}^{-2} \text{ y}^{-1}$) and reconstructed input fluxes could only be explained by lateral inputs coming from the canyon. Preliminary calculations show that the rapid transport of aSiO₂ through the canyon and the excellent preservation efficiency in the sediments imply that 50% of aSiO₂ river inputs from the Congo River accumulate annually in the deep-sea fan. Si:C ratios in deep-sea fan sediments were very low (0.2) and only three times as high as those measured in the river itself, which suggests that material from the river and the continental shelf was delivered directly through the canyon, with very little time for Si and C cycle decoupling to take place.

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1. Introduction

Better understanding of the fate of riverine silicon (Si) during its transit towards the ocean is essential, as Si is one of the limiting factors for diatom growth in aquatic systems. Diatoms are the main primary producers in coastal and oceanic waters (Nelson et al., 1995; Tréguer et al., 1995). In many coastal regions, in particular upwelling areas, diatoms constitute the basis of the most productive food chains (Cushing, 1989) and sustain intense fisheries. In the open ocean, diatoms contribute to up to 40% of global primary production (Nelson et al., 1995; Tréguer et al., 1995). They play a key role in the biological pump of carbon, thanks to the ballast role played by the diatom frustules, to the capacity of diatoms to form aggregates and to the fact that diatoms are food of choice for large zooplankton which expels the remains of the algae via fecal pellets. All these mechanisms produce in fact rapidly sinking particles that can escape degradation in surface waters (Moriceau et al., 2009; Ragueneau et al., 2006). Diatom dynamics are therefore pivotal to the functioning of continental margin ecosystems, but require Si. By limiting diatom blooms, the availability of Si affects

other biogeochemical cycles, including those of nitrogen and carbon (Chai et al., 2002; Froelich et al., 1992; Street-Perrott and Barker, 2008). Given the importance of Si in the functioning of coastal and oceanic ecosystems, quantifying Si inputs and understanding the processes that control the transfer of Si along continental margins, including retention in estuaries and continental shelves, are necessary to calculate a global Si budget (Dürr et al., 2011).

The majority of Si inputs to continental margins derive from land (Tréguer and De La Rocha, 2013; Tréguer et al., 1995). For a long time, it was thought that the only Si inputs into the ocean were in the form of dissolved Si (dSi), which is produced by the weathering of silicate rocks (Meybeck, 1982). Although this phenomenon remains a major contributor to the discharge of terrigenous Si, several complementary mechanisms have been discovered. It has been shown that 16–40% of the total Si export flux is in the particulate form (Conley, 1997; Smis et al., 2011; Dürr et al., 2011), in turn constituted mainly by amorphous silica (aSiO₂) derived from river diatoms, phytoliths or amorphous soils.

Moving from land to sea on continental margins, Si molecules undergo several cycles of production/dissolution and adsorption/desorption on suspended particles, both in surface waters and at the sediment–water interface (Ragueneau et al., 2010). On continental margins, abiotic reverse weathering converts dissolved to particulate Si (Mackenzie and Garrels,

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1966; Mackenzie and Kump, 1995; Michalopoulos and Aller, 1995, 2004), strongly impacting the C cycle due to CO₂ release (Mackenzie and Garrels, 1966). After revising the Antarctic Si budget, DeMaster (2002) showed that continental margins may become the missing Si sink to maintain Si biogeochemical cycle at steady state, implying that Si and C cycles were less decoupled than previously thought. In addition, it has been demonstrated that several anthropogenic perturbations such as eutrophication (Conley et al., 1993; Schelske and Stoermer, 1971) and damming (Humborg et al., 1997), as well as the proliferation of invasive species of bivalves (Ragueneau et al., 2002, 2005), may directly or indirectly alter Si transfer and retention, with important implications at short and long time scales for the functioning of coastal ecosystems and the input of Si to the global ocean.

If the transfer of Si from land to coastal waters is poorly understood, the exchange of Si between the margin and the open ocean is even less studied. Recently, Ragueneau et al. (2009) reported a direct input of Si from the margin to the deep sediments on the Congo system, suggesting that downslope sediment transport may be of global significance. No information however exists on the burial capacity of Si in deep sea fans or on the transfer of Si by active submarine canyons that fuel the fans.

Deep sea fans constitute the second largest global sink of atmospheric carbon (Covault, 2011; Galy et al., 2007) and the Congo deep-sea fan is one of the biggest in the world. This system is a major carbon burial region in the North Atlantic, with organic matter being directly discharged in the ocean by the associated canyon (Rabouille et al., 2009) and the Congo River being the second largest riverine source of Si to the ocean (Gaillardet et al., 1999). This suggests that the transfer of Si through the canyon could also be significant, leading to high global Si burial in the Congo deep-sea fan.

The aims of this paper are to give a first estimation of silica accumulation in the Congo deep-sea fan, to discuss the role of biological processes on the benthic Si cycle, to establish a tentative budget of benthic Si cycling, especially sediment–water exchange of SiO₂, and to examine the role of the canyon in the rapid transport of riverine material to the deep ocean. The global role of submarine canyons and deep sea fans in Si delivery and storage in the deep ocean is also discussed.

2. Material and methods

2.1. Description of study area and sampling strategy

The Congo margin, and more specifically the terminal lobes of the Congo deep-sea fan, are a unique area in the world ocean. The lobes are fuelled quasi-continuously by turbidites containing a large proportion of labile organic matter delivered by the Congo River (the second largest river in the world by its freshwater discharge; Milliman, 1991). The annual sediment load from the Congo River is $48 \cdot 10^6 \text{ t yr}^{-1}$ (Covault et al., 2011) and its export of Si to the ocean is $2.23 \cdot 10^{11} \text{ mol dSi yr}^{-1}$ and $1.17 \cdot 10^{10} \text{ mol aSiO}_2 \text{ yr}^{-1}$ (Hughes et al., 2011). The existence of a connection between the Congo River and its submarine canyon is a unique feature (Babonneau et al., 2002), since all other large rivers (i.e. Amazon, Yangtze, Mississippi) are disconnected from their canyons due to the increase of sea level which followed the last interglacial periods. The absence of disconnection in spite of sea water rise in the Congo system must be explained by a sediment load overwhelming the capacity of sediment accumulation on the continental shelf (Covault, 2011), as well as longshore Northward drift, and canyon-flank instabilities caused by episodic hyperpycnal flow due to flooding (Savoye et al., 2009). High-energy turbidity currents ensure a massive transfer of particles through the canyon and channel system (Savoye et al., 2009) from the river mouth to the deep-sea fan, which displays the same features as a river delta, i.e. fresh terrestrial organic matter inputs and high burial rate (Burdige, 2005).

The sampling area is located on the lobe complex, which covers an area of about 3000 km² and expands between 4800 m and 5200 m

water depth at the outlet of the Congo submarine canyon, 750 km off the coast.

Samples were collected during the WACS 2011 cruise between February 20 and 25, 2011. Four sediment cores were sampled (Fig. 1) using the Remote Operated Vehicle (ROV) Victor 6000 (Ifremer). Their denomination and exact location are reported in Table 1. The core PL435 was sampled in the upper lobe (site A), PL436 and PL437 in the central part of the lobe (site C) and PL438 at the end of the lobe (site D). Three benthic chambers of the respirometer RAP were deployed to measure total benthic fluxes at site A (RAP3, close to PL435) and at site C (RAP4, close to PL436).

2.2. Sample processing

The cores were processed immediately after recovery in the cold room on board the ship at +5 °C. Overlying water of each core was sampled using a syringe. Cores were sliced at 0.5 cm intervals in the first 2 cm, at 1 cm intervals down to 10 cm and at 2 cm intervals between 10 and 20 cm. Sediment slices were placed in tubes and immediately centrifuged for 20 min at 3500 rpm. Sediments were then stored at –20 °C until aSiO₂ concentrations were analyzed in the laboratory. Overlying and pore waters were filtered through Millex filters (0.22 μm pore size) and stored at +4 °C until dSi analysis was performed. dSi flux through the sediment–water interface was measured in situ inside the benthic chambers carried by the respirometer RAP (an autonomous lander equipped with three cylindrical benthic chambers each 30-cm in diameter; for a detailed description, see Khrifpounoff et al., 2006). The functioning principle of the benthic chambers is to isolate and incubate a known volume of seawater in close contact with the enclosed sediment surface area. Three sampling cells, positioned within each chamber, enable water sample collection (100 ml) at predetermined time intervals for later calculation of fluxes. Water samples were taken at the beginning of the incubation (T0), after 7 h (T1), 13 h (T2) and 19 h (T3). Immediately after recovery, the sampling cells were removed from the chambers and the water samples collected by gravity flow in separate vials.

2.3. Analytical methods

Overlying and pore water dSi concentrations were measured using the colorimetric method of Tréguer and Le Corre (1975).

aSiO₂ concentrations in sediments have been calculated (see Section 2.4) using a modified version of the Si–Al method developed by Köning et al. (2002). This method consists of the simultaneous measurement of Si and Al concentrations during an alkaline digestion (90 min, NaOH, 0.5 M). The method was adapted to allow a larger amount of samples to be analyzed within a day, without losing its robustness. The continuous measurement of Si and Al concentrations was replaced by a multiple measurements done every minute during one hour of alkaline digestion. This required adaptation of the method of Aminot and Kerouel (2007) for the measurement of dSi concentrations during alkaline digestions, optimizing the sampling and rinsing time on the autoanalyzer. Accuracy was tested with standard solutions. Al concentrations were measured using the Lumogallion fluorescence method developed by Hydes and Liss (1976).

2.4. Calculation of benthic aSiO₂ concentrations, aSiO₂ burial and benthic dSi fluxes

Si and Al digestion curves were fitted in order to determine aSiO₂ concentrations in sediments, and distinguish aSiO₂ from lithogenic Si. Four models were applied to the Si and Al digestion curves, going from a single phase (model 1), two phases (model 2), three phases (model 3), and a continuum of phases (model 4) of aSiO₂ in the sediments (see Köning et al., 2002). One example of digestion curves and model application is shown in Fig. 2. Fig. 3 shows two vertical profiles

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