Chapter 10

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

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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.

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 Rossholt 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 (~0.7 wt% C\(_{terr}\) out of 1.5 wt C\(_{tot}\)) yields a marine C\(_{org}\) burial rate of ~3 Tmol C\(_{org}\) yr\(^{-1}\) for continental margins. Assuming that the bSiO_2/C\(_{org}\) weight ratio in North Carolina slope sediments and many continental margin upwelling areas (i.e., ~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 ~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.

![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)](image-url)