Cosmogenic Silicon – 32 reveals extensive authigenic clay formation in deltaic systems and constrains the marine silica budget

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Abstract of the Dissertation

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Silica is an essential nutrient and an important control on primary production, the biological pump, and carbon cycling in the ocean. In our current understanding of the marine silica cycle, the known sources outweigh the sinks, by as much as 35%. The quantity of biogenic silica stored in lithogenic sediments along continental margins is poorly constrained. Cosmogenic ^{32}Si ($t_{1/2}$ ~ 140 yrs) was used in a novel way to constrain the quantity of reactive Si storage and early diagenetic reactions of Si in the highly mobile deltaic sediments along the coast of French Guiana, representative of deposits along the ~1600 km Amazon – Guianas coastline downdrift of the Amazon delta. A sequential leach was developed to extract and purify SiO_2 from different operational pools in large samples of surface sediments (0 – 10cm). This methodology, a hot 1% Na_2CO_3 leach followed by a hot 4M NaOH leach, was adapted from the existing leaches widely used to estimate biogenic silica (bSi) content in marine sediments, and ultimately to constrain

the global oceanic Si budget. ^{32}Si activity was determined in each pool via its daughter product ^{32}P. Results from several sites in coastal mudbanks near Kourou and Sinnamary indicate no detectable ^{32}Si activity in the bSi fraction, whereas ^{32}Si was detected in the Si-NaOH fraction *after* removal of bSi. The lack of detectable activity in the 1% Na_2CO_3 leach and its detection in the NaOH fraction (0.4 – 2.5 dpm) indicate that the method widely used to determine bSi content recovers only a minor fraction of the originally deposited reactive bSi in these deposits. The results are consistent with rapid alteration of biogenic silica and clay authigenesis or reverse weathering. They also demonstrate that the current estimate of biogenic silica storage in tropical deltaic sediments is significantly underestimated by at least one order of magnitude. Assuming an initial diatom specific activity range of ~5 – 40 dpm/kg SiO_2, the ^{32}Si activity in the NaOH fraction corresponds to a reactive Si storage of ~150 – 18,000 μmol Si/g sediment. This magnitude is more consistent with estimates of reactive Si ($\sum Si_{hr}$) storage in the Amazon delta based on modified operational leach techniques (a 0.1N HCl pretreatment step followed by extraction with 1% Na_2CO_3) that target poorly crystalline clays and with diagenetic modeling of pore water K^+, F^-, and $Si(OH)_4$, though these modified leaches also appear to underestimate the amount of reactive Si stored along this system. To directly confirm whether these modified operational extractions underestimate reactive Si storage, a sequential extraction methodology was also developed to first isolate ^{32}Si activity in the $\sum Si_{hr}$ fraction (0.1N HCl followed by 1% Na_2CO_3) and then extract any remaining ^{32}Si from the residual fraction using 4M NaOH. ^{32}Si activity was detected in both these fractions in sediments collected from two sites at Sinnamary, demonstrating that reactive Si ($\sum Si_{hr}$) storage was 2 – 3x what previous operational leaches indicated. A simple transport – advection model, assuming an activity of 15dpm/kg SiO_2 in starting materials such as plankton, revealed a Si incorporation rate of 5 μmol Si/g/y along the Amazon – Guianas dispersal system and total Si burial of 0.3 Tmol Si/y. The combined Si storage in the Delta and along the coast to the Orinoco (0.4 Tmol/y) may account for 50% of the total dissolved Si delivery from the Amazon River to the global ocean.

In addition to sites in the Amazon – Guianas mudbelts, sediment from 2 stations in the Gulf of Papua, Papua New Guinea, 1 station in the northern Gulf of Mexico near the Southwest Pass, and 1 station in Long Island Sound (Smithtown Bay) were also extracted for ^{32}Si in the bSi fraction as well as the residual fraction after removal of bSi. Bulk ^{32}Si activities in the residual fractions in the Gulf of Papua (0.5 – 0.7 dpm/kg sediment) were used to extrapolate Si storage in the outer topset and forset of the clinoform delta. Initial estimates of Si burial in this region, as indicated from ^{32}Si activities, were ~0.10Tmol/y, or 74 – 99 % of the known total Si inputs to the Gulf. These results demonstrate that authigenic clay formation may be an important, and previously unnoticed/undetected?, sink of biogenic silica in this region.

Unlike the Amazon – Guianas mudwave system and the Gulf of Papua deposits, ^{32}Si activity was detected in the both the bSi (0.21 ± 0.04 dpm/kg sediment) *and* the residual fraction (0.44 ± 0.08 dpm/kg sediment) from the site in the Gulf of Mexico. A Si burial rate using the ^{32}Si activity in the bSi fraction (assuming an activity of 15dpm/kg in starting Si materials) of 0.004Tmol/y was calculated over approximately 5000 km^2 of the delta, whereas the burial rate calculated using the Si content in this same fraction from a classic bSi leach, was ~0.006Tmol/y. Adding the Si burial rate using the ^{32}Si activity in the residual fraction (0.008Tmol/y) yielded a total storage per year of 0.012Tmol Si, ~10% of the total Si inputs (dissolved and amorphous Si) from the Mississippi – Atchafalaya river system. ^{32}Si activity was also detected in the residual fraction (0.53 ± 0.08 dpm/kg sediment) after removal of $\sum Si_{hr}$ and using this activity yielded similar calculated rates of Si burial (~0.01 Tmol/y).

In Smithtown Bay, Long Island Sound, ^{32}Si activity was also detected in both the bSi (0.15 ± 0.05 dpm/kg sediment) and the residual (0.4 ± 0.2 dpm/kg sediment) fractions from the site in Smithtown Bay, Long Island Sound, yeilding a total Si storage estimate (assuming an activity of 15 dpm/kg in starting Si materials) of 1.6 x 10^{-3} Tmol/y over the entire Sound, comparable to estimates of Si storage calculated using the Si content in the classic bSi (1.1 x 10^{-3} Tmol/y) and the classic $\sum Si_{hr}$ (2.2 x 10^{-3} Tmol/y) leaches. It appears that reverse weathering is an important sink of Si in these deposits, and indeed may be in other temperate estuaries, and that classic bSi or $\sum Si_{hr}$ leaches can underestimate Si storage in these system by two to four - fold.

In summary, authigenic clay formation is a significant sink of biogenic silica in tropical deltaic systems. Cosmogenic ^{32}Si can be used to quantify the amount of reactive or biogenic Si buried in coastal sediment deposits more accurately than conventional operational leaches. Like tropical systems, initial findings suggest that reverse weathering plays a major role in Si burial in temperate estuaries and subtropical systems.

Dedication Page

This work is dedicated to my parents, Shamsad Ara and Habibur Rahman.

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Chapter 1: Introduction

Introduction and Importance

There is growing evidence that biogenic silica can undergo rapid reverse weathering and form authigenic clays effectively trapping Si in continental margins (Mackin and Aller, 1986; Michalopoulos and Aller, 1995; Michalopoulos et al., 2000; Ragueneau et al., 2000; DeMaster, 2002; Michalopoulos and Aller, 2004; Laruelle, et al., 2009), particularly in the tropics where the greatest sediment inputs to the ocean occur. This additional pathway of biogenic Si diagenesis is not yet widely accepted as a significant sink for Si. To date the general assumption is that the primary fate of sinking or deposited siliceous material includes dissolution, burial, or dissolution – recrystallization (Tréguer et al., 1995; Ragueneau et al., 2000; DeMaster, 2002; DeMaster, 2003). Marine Si budgets have also been calculated assuming the Si cycle in the oceans is in steady-state, with sinks of this essential nutrient mainly in the major upwelling zones and in polar and temperate regions.

Silicon is becoming an increasingly biolimiting nutrient in coastal systems with the anthropogenic enrichment of the nutrients N and P (Officer and Ryther, 1980; Conley and Malone, 1992; Justić et al., 1995; Rabalais et al., 1996; Wu and Chou, 2003; Gobler et al., 2006). Locally, in more pristine systems where diatoms are the dominant autotrophs and there is a large supply of Si from rivers, the element may also be a naturally biolimiting nutrient. Earlier budgets estimated that about 4 – 11% of the Amazon River Si input was deposited in the subaqueous delta, whereas more recent estimates, accounting for authigenic clay formation, suggests ~22% could be buried there (Michalopoulos and Aller, 2004). Recent re-evaluation of the Si cycle indicates biogenic silica accumulation in continental margins may be much higher than previously estimated: 2.4 – 3.1 x 10^{12} mol/y instead of 0.4 – 1.5 x 10^{12} mol/y (DeMaster, 2002), the majority of which may be the large deposition centers of the tropics. To constrain Si cycling and subsequently the carbon pump (Dugdale et al., 1995; Buesseler, 1998; Ragueneau et al., 2006; Bernard et al., 2011), it is crucial that the amount of biogenic Si buried in continental margins be quantified and confirmed, in particular in tropical systems which supply the vast majority of dissolved Si to the global ocean.

The main objectives of this thesis were to develop a methodology by which the cosmogenic radionuclide, ^{32}Si, could be used as an independent proxy to verify or refute authigenic clay formation and to quantify total biogenic Si burial. The only natural source of ^{32}Si is via production in the atmosphere by cosmic ray spallation of ^{40}Ar (Morgenstern et al., 1996). Once entering the ocean, ^{32}Si is taken up by siliceous organisms (Craig et al., 2000; Fifield and Morgenstern, 2009) and is delivered to the sea floor after these organisms die and sink. This radionuclide can serve as a tracer of Si of biogenic or opaline origin to more accurately determine the impact of authigenic clay formation on the global budgets of Si as well as trace elements from a variety of coastal regions.

Study sites in this thesis consisted of two tropical deltaic locations (the Gulf of Papua and the Amazon – Guianas mudbelts), one subtropical delta (the Mississippi Delta), and a western Atlantic Ocean steadily accreting temperate estuarine system (Long Island Sound). Given the intense physical and chemical weathering in tropical river systems, significant diatom abundances, and the extensive iron cycling that occurs in tropical deltas, the Amazon – Guianas mudbelts, and to a lesser extent, the Gulf of Papua, were given particular attention because these are environments where significant clay formation may occur.

Background

In addition to growing evidence of reverse weathering in tropical and subtropical deltas (Mackin and Aller, 1984; Mackin and Aller, 1986; Mackin, 1986; Michalopoulos and Aller, 1995; Michalopoulos et al., 2000; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008; Loucaides et al., 2010), authigenic clay formation has also been observed in other environments, including low sedimentation rate environments (Johnson, 1976; Heath and Dymond, 1977; Hein et al., 1979; Cole, 1985; Cuadros et al. 2011), though rates and quantities of formation here may have relatively minor impacts on the global oceanic Si budget as a whole. The formation of authigenic clays, or “reverse weathering” as first put forward by Mackenzie and Garrels (1966), is not yet widely accepted as an additional major pathway for Si sequestration in sediments.

The original concept that authigenic clay might be an important component of elemental cycling and alkalinity balances in the oceans was proposed in 1966 by MacKenzie and Garrels (1966), who hypothesized a general reaction of the form:

$$\text{X-ray amorphous-Al-silicate (reactive } Al(OH)_3) + HCO_3^- + SiO_2 + \text{cations} \rightarrow \text{cation Al silicate} + CO_2 + H_2O$$

These types of reactions, which encompass reconstitution and neoformation of clays, were termed “reverse weathering” reactions due to the net consumption of alkalinity and cations with concomitant release of CO_2. Such reactions contrast with weathering reactions on land or sea whereby CO_2 is consumed and alkalinity and cations produced (Mackenzie and Garrels, 1966). Mackenzie and Garrels further suggested that because illite, montmorillonite, and chlorite form the majority of clay mineral phases in ancient and present-day marine sediments, then K^+, Na^+, Mg^{++} , and other cations in seawater likely react to form similar cation-rich Al silicates. From their calculations, assuming steady – state conditions of delivery over a 100 million year time period, 30 – 90% of the total inputs of these cations to the ocean could be consumed and may be accounted for via the formation of authigenic clays. At the time, they had few data and field observations to support their hypothesis. Authigenic clay formation was assumed to occur slowly (e.g. >10,000yrs) and to be of insufficient magnitude to have a significant impact on the marine Si cycle (Sayles and Bischoff, 1973; Hurd, 1973; Kastner et al., 1977; Van Bennekom et al., 1989). Recent studies, however, revealed that clay formation can take place rapidly in tropical and subtropical deltas (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008; Loucaides et al., 2010), leading to a renewed interest in authigenic clay formation as an overlooked reaction pathway, one which can sequester significant quantities of dissolved Si on continental margins and proximal coastal regions (Laruelle et al., 2009; Tréguer and De La Rocha, 2013). The work discussed in this thesis demonstrates for the first time that natural ^{32}Si can provide critical constraints on the magnitude and generality of this process.

Marine Si budget

Marine silicon budgets have been calculated assuming the Si cycle in the oceans is in steady – state (mean residence time of ~10,000 years (Tréguer et al., 1995)), accounting for sources and sinks of this element from research conducted primarily in polar and temperate regions (DeMaster, 1979; DeMaster, 1981). Prior estimates of dissolved silica flux to the world ocean were about 6.7 x 10^{12} mol/yr (Tréguer et al., 1995; DeMaster, 2002) or 6.7 Tmol/y (Tmol = 10^{12} mol). Of the riverine dissolved silica supply, ~60%, or about 4 Tmol/y, was estimated to originate from tropical regions (Tréguer et al., 1995). This budget did not take into account groundwater discharge of dissolved Si, riverine biogenic silica supply, and higher estimates of riverine dissolved Si supply, inclusions of which revised total Si flux to the ocean upwards to 8.8 Tmol/yr (Laruelle et al., 2009; Dürr et al., 2011) to 9.4 Tmol/y (Tréguer and De La Rocha, 2013). Riverine biogenic Si includes amorphous silica associated with freshwater diatoms, phytoliths, as well as other non – crystalline forms of Si in soils (Conley, 1997; Clarke, 2003; Saccone et al., 2006; Saccone et al., 2007). Regolith bacteria which incorporate monomeric silica within their cells may also fall into this classification (Clarke, 2003). Estimates of some of these flux terms were based on limited datasets and remain highly uncertain. Since these tabulations the total riverine biogenic silica supply, also known as amorphous silica (ASi) or non – crystalline siliceous particulates which dissolve as they encounter the higher pH and salinity of estuaries (Loucaides et al., 2008; Carbonnel et al., 2013; Lehtimäki et al., 2013), has been revised up from 1.1 Tmol/y to 1.9 Tmol/y assuming that ASi is 0.6% of SPM and a total SPM flux of 19 trillion tons per year to the world's ocean (Conley, 1997; Frings et al. 2016).

There is also considerable uncertainty in the Si inputs from submarine groundwater discharge, both in the magnitude of volume discharged (Church, 1996; Taniguchi et al., 2002; Slomp and Van Cappellen, 2004, Frings et al., 2015) and in the Si concentration in groundwater, which is based on limited data (Laruelle et al., 2009; Tréguer and De La Rocha, 2013; Frings et al., 2016). Assuming an average [Si] of 380 ± 250 µM and groundwater inputs to the ocean with a volume of ~1850 km^3/y (5% of the global river freshwater discharge, 37 x 10^3 km^3/y), Frings et al. (2016) estimate a submarine groundwater discharge flux of 0.65 ± 0.54 Tmol dissolved Si/y. After adjusting for revisions in the inputs through chemical weathering of basalts, eolian inputs and hydrothermal inputs, this brings total Si input flux estimates to the ocean to 9.55 Tmol/y (Frings et al., 2016), with an uncertainty of approximately 50%.

During the 1980's, the single largest sink for biogenic silica was thought to be the siliceous ooze deposit of Antarctica, estimated to account for 4.1 – 4.8 Tmol/y (DeMaster, 1981; Tréguer et al., 1995). Since then, using ^{230}Th – normalized accumulation rates, DeMaster (2002) re – calculated the biogenic Si burial flux in the Southern Ocean as 3.1 ± 2.2 Tmol/y. More recently, using ~100 more samples covering the Atlantic Ocean sector, removal of biogenic Si to this repository has been re-estimated to 2.0 ± 1.2 Tmol/y, about 1/3 lower than prior calculations (DeMaster, 2002). Revised budgets, which are still poorly constrained, attribute greater Si burial, ~3.3 ± 2.1 Tmol/y, to continental margins (DeMaster, 2002; Tréguer and De La Rocha, 2013). In the open ocean, silica removal rates are estimated to be <1.04 ± 0.34 Tmol/y (DeMaster et al., 2002; Tréguer and De La Rocha, 2013). Current estimates of burial rates in the global ocean total ~6.3± 3.6 Tmol/y (Tréguer and De La Rocha, 2013), whereas net inputs of dissolved or labile Si total 9.4 – 9.55 Tmol/y ((Tréguer and De La Rocha, 2013; Frings et al., 2016), resulting in an imbalance of about 3 Tmol Si/y (Figure 1). Reverse weathering or authigenic clay formation in the marine environment may be a substantial sink for biogenic Si. Laruelle et al. (2009) estimate that in proximal coastal areas reverse weathering accounts for 1 Tmol/y of the coastal Si sink and may account for more, whereas Tréguer and De La Rocha (2013) estimated that reverse weathering may sequester up to 1.5 Tmol/y Si of the gross river flux of dissolved and biogenic Si (~7.3Tmol/y). It is essential, in order to constrain the global Si budget and that of other trace elements (e.g. Ge and Li) with strong associations to Si, that the amount of biogenic Si buried in continental margins be quantified and confirmed, particularly in tropical deltaic systems which supply the vast majority of dissolved Si to the global ocean.

Evidence of Silica Storage in Tropical Deltaic Systems

Evidence of the formation of authigenic clays arises from several types of data, such as incubation studies indicating rapid formation over the course of 12 – 36 months (Michalopoulos et al., 2000; Loucaides et al., 2010); direct SEM observations of authigenic clay flakes on diatom frustules (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008; Loucaides et al., 2010); X-ray diffraction spectra of clay structures on diatoms (Van Bennekom and Van der

Gaast; 1976;) porewater profiles indicating uptake of elements (e.g. Li, F, and K) with depth (Rude and Aller, 1994; Michalopoulos and Aller, 1995; Michalopoulos and Aller, 2004); the stoichiometry of elemental uptake (Mackin and Aller, 1986; Michalopoulos and Aller, 2004; Loucaides, 2009; Loucaides et al., 2010); significant storage of Si from reactive fractions which are not completely dissolved by traditional 1% Na_2CO_3 leaches used to quantify biogenic Si (Lewin, 1961; Hurd, 1973; Van Bennekom et al., 1989; Michalopoulos and Aller, 2004; Loucaides et al., 2010); and release patterns of K^+ and F^- from these reactive Si pools which are consistent with ratios of these ions to Si in clays (Rude and Aller, 1986; Michalopoulos and Aller, 1995; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). Some of these data and observations are discussed in more detail in the following section.

Porewater profiles of F^-, Mg^{2+} and K^+ indicating uptake at depth in the Amazon delta and Gulf of Papua, coupled with that of Si, suggest that authigenic clay formation is occurring, as was originally proposed by MacKenzie and Garrels (1966). These gradients are established despite frequent physical reworking, indicating that they form rapidly. Rude and Aller (1994) estimated that F^- uptake into authigenic clays on the Amazon Shelf may account for 7% of the global marine dissolved fluoride sink, whereas ~10% of the annual global K river flux is sequestered in the Amazon delta (Michalopoulos and Aller, 1995).

Diatom frustules and their fragments from various subsamples in Amazon cores were isolated and investigated using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Elemental Mapping (Energy – dispersive spectroscopy or EDS) (Michalopoulos and Aller, 2004). Authigenic aluminosilicate clays and metal – rich coatings were evident on the frustules. Some were in advanced stages of alteration. Valves of other diatoms showed pyrite filled interiors and enrichments of K, Al, and Fe. Frustules that contain little to no pyrite fill – ins show Fe enrichment in the aluminosilicate material (Michalopoulos et al., 2000, Michalopoulos and Aller, 2004) along with K and Mg.

Formation rates of authigenic clays were studied in laboratory incubation experiments using Amazon delta topset deposits (Michalopoulos and Aller, 1995; Michalopoulos et al., 2000). A variety of Si-bearing substrates including cultured diatoms were attached to acrylic slides, covered with membrane filters and inserted into containers of unaltered and unprocessed sediments from the Amazon delta, which were sealed and inserted into larger containers containing the same sediment, ensuring no exposure to oxygen. Suboxic conditions with a lack of sulfate reduction, prevalent throughout the Amazon – Guianas dispersal system, are essential for the neoformation of clays (Meunier and El Albani, 2006). Under these conditions metal oxides are remobilized and dissolved Fe, Mn, and Al are available for potential reverse weathering reactions, whereas under anoxic conditions Fe is precipitated as pyrite (Meunier and El Albani, 2006). After incubation periods ranging from 12 to 36 months, the slides were removed and imaged using TEM and SEM to confirm the transformation to clays: formation of flakes of authigenic clays, rich in Al and K, were evident on these frustules. These studies confirmed that reverse weathering can occur in the laboratory and that biogenic silica alters to aluminosilicate phases over short time spans. The rate at which biogenic silica is converted to these aluminosilicates in tropical deltaic systems and other depositional settings can be more accurately estimated using ^{32}Si as a tracer.

Cosmogenic ^{32}Si

The only natural source of ^{32}Si is via production in the atmosphere by cosmic ray spallation of ^{40}Ar (Morgenstern et al., 1996, Fifield and Morgenstern, 2009). The global atmospheric ^{32}Si production rate is based on global fallout curve generated by the only study which measured ^{32}Si concentrations in rainwater at different latitudes (Lal et al., 1979). Using those data, Craig et al. (2000) calculated the ^{32}Si production rate as 0.72atoms/m^2 s. Its half – life has been estimated as ~140 ± 10 years (Morgenstern et al., 1996; Fifield and Morgenstern, 2009). The number of atoms of ^{32}Si produced in the stratosphere (stratospheric production is the major component of the total production flux), has a strong dependence on latitude, whereas tropospheric ^{32}Si production rates are relatively constant. Geographic latitude determines atmospheric fallout patterns for ^{32}Si and other cosmogenic radionuclides, with greatest stratospheric dumping, or flux, into the troposphere occurring around 40° latitude (Machta et al., 1970; Craig et al., 2000) and lowest fluxes occurring at the equator and poles. Atmospheric production rates at the equator are ~0.4 atoms/cm^2/s, ~075 atoms/cm^2/s at 20° latitude, rising to over about 1.5 atoms/cm^2/s at 40°, and tapering off to ~0.25 atoms/cm^2/s at the poles (Figure 5 in Craig et al., 2000). Once in the troposphere, cosmogenic radionuclides are deposited on the Earth's surface by precipitation (Lal et al., 1958). Zonal atmospheric circulation uniformly mixes the activities of cosmogenic radionuclides, such that fallout activities at a particular latitudinal zone depend only on rates of precipitation (activity in precipitation appears to be inversely proportional to rainfall) (Lal et al., 1979; Craig et al., 2000; Fifield and Morgenstern, 2009). At steady state , the global production rate supports ~1kg of $^{32}SiO_2$ on the Earth's surface.

Like for many other key constituents, the Geochemical Ocean Sections Study (GEOSECS) provided the first profiles of ^{32}Si in the water column of the Atlantic, Indian, and Pacific Oceans (Somayajulu et al., 1987; Somayajulu et al., 1991). Whatever purported irregularities there may have been regarding that dataset, namely the ^{32}Si Paradox (Peng et al., 1993), were succinctly and carefully explained by Craig et al. (2000). Interpreting the GEOSECS ^{32}Si profiles as specific activities of dissolved Si only, Peng et al. (1993) contended that the ^{32}Si specific activities in the Indian and Pacific Oceans should be 3 -5 times lower than the activities in the Atlantic Ocean since dissolved silica concentrations in the Indian and Pacific Oceans are 3 – 5 times higher. Craig et al. (2000) demonstrated, however, that the ^{32}Si captured in the study came from a mixture of both particulate and dissolved Si, with particulate Si being the high activity end member. From that dataset, the average ^{32}Si activity in particulate Si in the surface Atlantic ocean was determined to be ~40dpm/kg SiO_2, ranging from 20 dpm/kg SiO_2 to 60 dpm/kg SiO_2, whereas those in the Pacific are approximately 11% lower (Somayajulu et al., 1987; Craig et al., 2000). Other more limited studies had estimated lower activities of ^{32}Si in biogenic silica: 5 – 15 dpm/kg SiO_2 (Lal et al., 1960; Kharkar et al., 1969; Lal et al., 1976). The average ^{32}Si specific activity of dissolved Si in the surface Atlantic Ocean was determined to be ~4.5 dpm/kg SiO_2 (dpm = disintegrations /minute), ranging from ~2.5 dpm/kg SiO_2 to 5 dpm/kg SiO_2, and dropping to essentially 0 dpm/kg SiO_2 in the surface Pacific Ocean (Craig et al., 2000).

The abundance of ^{32}Si in bulk natural silicon was first estimated in 1953 by irradiating quartz samples (Turkevich and Tompkins, 1953) and the radionuclide was first detected in marine sponge samples in 1960 by Lal et al. (1960) and was proposed as a dating tool to constrain processes that occur over a time scale not captured by ^{210}Pb or ^{14}C. Surveys of the activity of this radionuclide in natural samples are limited. Extending the data set for siliceous sponges, Lal et al. (1976) observed that the ^{32}Si specific activity in the animals varied inversely as a function of the dissolved Si concentration in the 0 – 500m layer of the water in which the sponges grew, where sponges from the Antarctic Ocean and Arctic were the low and high activity end members, respectively. The only study of ^{32}Si in rivers, Nijampurkar et al. (1966)

reported ^{32}Si activities in Indian rivers ranging from 0.15 dpm/m^3 near their source waters to 0.08 dpm/m^3 near river mouths. Absolute activities in meteoric waters ranged from 0.1 – 1 dpm/m^3 (Lal et al., 1979). Data from these studies are used in Chapters 3 and 4 to interpret the ^{32}Si activities obtained in this dissertation.

To date, given its low activity, the use of ^{32}Si as a tracer has been limited. It has been used to determine particle mixing rates in the deep sea (DeMaster and Cochran, 1982), sedimentation rates in deltas and lakes (Suckow et al., 2001; Morgenstern et al., 2001; Morgenstern et al. 2013) and ages of glacier ice (Nijampurkar et al. 1982; Nijampurkar et al. 1985; Morgenstern et al., 1996; Morgenstern et al., 2000). It has also been used as a tracer of stable silicon inputs into various water masses (Nijampurkar et al., 1966; Nijampurkar et al., 1983; Morgenstern et al., 1995) and to date groundwaters in aquifers (Nijampurkar et al., 1966; Morgenstern et al., 1995).   Biogenic silica production rates were first studied in the Weddell – Scotia Seas using artificially produced ^{32}Si, via spallation of Vanadium, by Tréguer et al. in 1991. Since then diatom growth rates, sponge ages, and silica production rates in different areas have been estimated using this radionuclide (Brzezinski and Phillips, 1997; Smith et al., 1999; Kristiansen et al. 2000; Kristiansen et al. 2001; Brzezinski et al., 2001; Ragueneau et al., 2002; Rousseau et al., 2002; Ellwood et al., 2007; Kemp and Villareal, 2013; Krause et al., 2013). This is the first study of its kind to use this cosmogenic radionuclide to determine silica storage in coastal sediments Figure 1 includes a representation of how cosmogenic ^{32}Si is incorporated into the marine Si cycle, whereas Figure 2 shows sites of prior ^{32}Si studies in sediment.

Objectives and Organization of Chapters

Earlier techniques quantifying biogenic silica phases in sediments may have significantly underestimated the amount of reactive silica. The dry sediment to volume ratio in these classic biogenic Si leaches (DeMaster, 1979; DeMaster, 1980) needed to be modified to quantify ^{32}Si for practical reasons. Given the low activity of ^{32}Si in opal – A, at least 1000 to 1500g dry sediment weight must be processed in order to acquire enough bulk silica to determine ^{32}Si activity, if present, which in turn would correspond to 1000 - 1500L of Na_2CO_3. The large quantity of leach required led us to determine experimentally the minimum leach volume required to obtain the same biogenic – Si released from a leach with excess Na_2CO_3. A significant portion of this thesis, as described in Chapter 2, was spent developing a sequential extraction protocol so that sufficient quantities of biogenic Si could be extracted in the modified version as in the classic version, while minimizing the Si extracted from background clays. This method can be applied to remove and quantify ^{32}Si activity from a variety of fractions and sources, and ultimately to assess the accuracy of the Si sink terms in the current global marine Si budget, as well as in local coastal systems.

The Amazon River alone supplies 6 – 7 percent (~1.1 – 1.3 x 10^9 tons/y) of the total global riverine input of suspended sediment to the wet tropics (~16 x 10^9 tons/y) and ~1Tmol/y of dissolved Si to the ocean (Mead et al., 1985; Nittrouer et al., 1995; Meybeck and Ragu, 1995). Another 2 -3% of this total sediment load to the wet tropics is supplied to the Gulf of Papua (Nittrouer et al., 1995; Milliman et al., 1999). Extensive Fe and metal cycling, influx of Al – rich materials, lack of net sulfate reduction, and a large supply of Si to sediments in these regions establish settings where significant formation of authigenic clays may occur. Analyses of samples from the Amazon – Guianas dispersal system, plus one from the mouth of the Amazon River constitute a large portion of this thesis. We also looked at the Mississippi River, a subtropical river, the 7th largest river in the world (Milliman and Mead, 1983), plus Long Island Sound, one of North America's largest temperate estuaries. Results from ^{32}Si sequential extractions from these four distinct depositional settings are discussed in Chapters 3 and 4. Chapter 3 presents the results from the seven sites in the Amazon – Guianas mudbank system and estimates the quantity of biogenic silica storage in that region. Chapter 3 has been written in manuscript form, a modified version of which is submitted for publication in *Geophysical Research Letters* with Robert C. Aller and J. Kirk Cochran as co – authors. Results and Si storage estimates from the remainder of the sites are discussed in Chapter 4, which will also be submitted for publication with Robert C. Aller and J. Kirk Cochran as co – authors. Finally, the impacts of these findings are discussed on a larger scale in Chapter 5.

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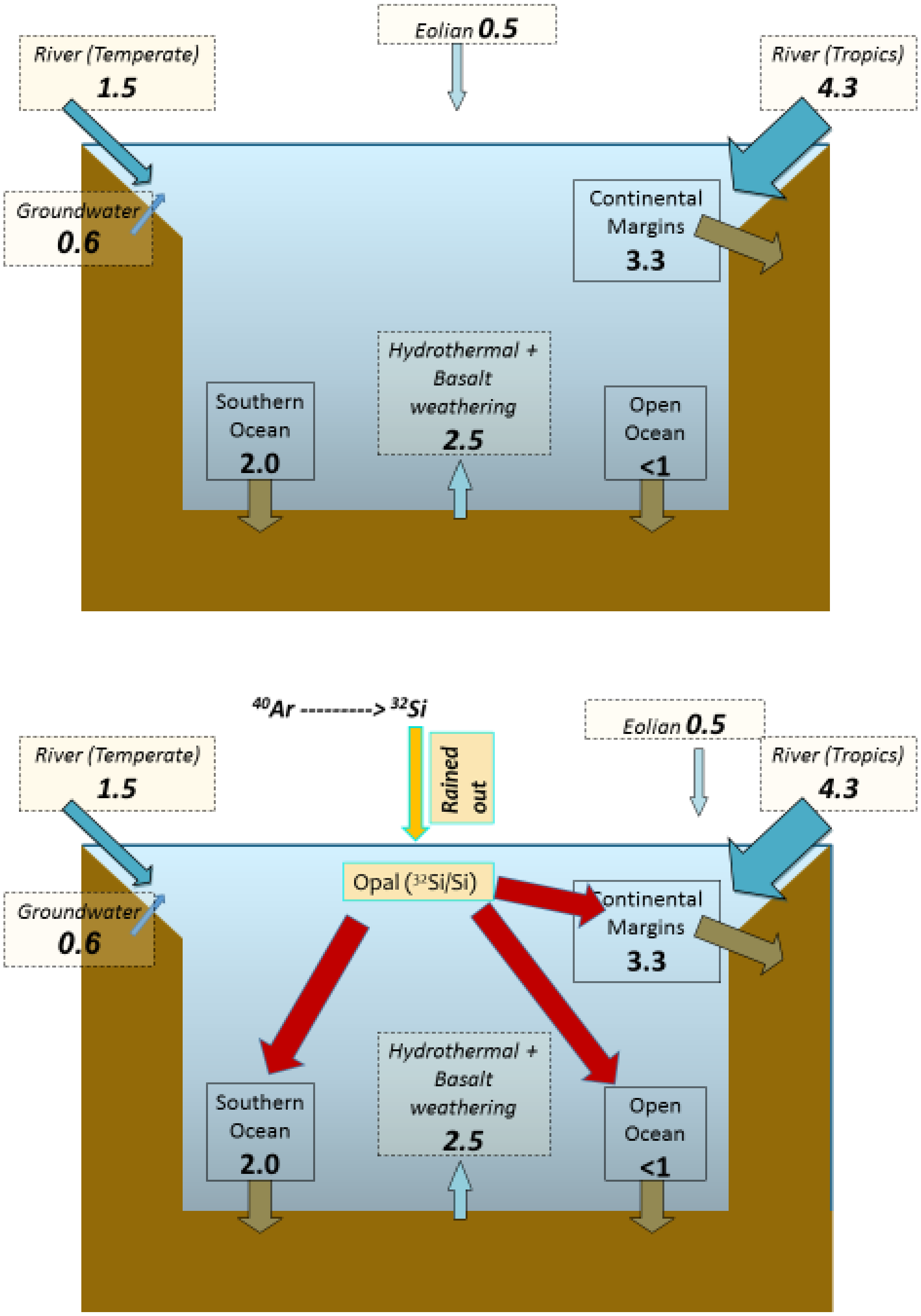

Figure 1. (A) Global marine Si budget, based primarily on Tréguer and De La Rocha (2013). All fluxes in Tmol/y (10^{12} mol/y). (B) Representation of the formation of ^{32}Si via cosmic ray spallation of ^{40}Ar and incorporation in the marine silica cycle following deposition via precipitation from the atmosphere. Uncertainties are typically 50 – 100%.

Figure 2. Map of study sites (Gulf of Papua, Amazon River mouth, French Guiana coast, Mississippi Delta, and Long Island Sound) indicated by filled circles (●). Approximate locations of prior ^{32}Si marine sediment studies (Bay of Bengal (Morgenstern et al., 2001), Gulf of California (DeMaster, 1980), Southern Ocean (DeMaster and Cochran, 1982), open Equatorial Pacific(DeMaster and Cochran, 1982)) indicated by open diamonds (◊).

Chapter 2: Methodology for ^{32}Si Extraction from Sediment

Introduction

^{32}Si has been proposed as a dating tool to constrain processes that occur over a time scale not captured by ^{210}Pb or ^{14}C (Fifield and Morgenstern, 2009). It has been used to determine sedimentation rates in the Ganges – Brahmaputra delta (Morgenstern et al., 2001) and glacier ice ages (Morgenstern et al., 2000). The only natural source of ^{32}Si is via production in the atmosphere by cosmic ray spallation of ^{40}Ar (Morgenstern et al., 1996, Fifield and Morgenstern, 2009). The ^{32}Si production rate, has been calculated as 0.72atoms/m^2 s (Craig et al., 2000) and its half – life has been estimated as 140 ± 10 years (Morgenstern et al., 1996, Fifield and Morgenstern, 2009). The atmospheric production and deposition rate of ^{32}Si is presumed to be constant. At steady state, this corresponds to a global inventory of <1 kg $^{32}SiO_2$.

For analysis of ^{32}Si in sedimentary biogenic silica by beta detection via gas flow proportional counters, the dry sediment to volume ratio in the classic biogenic Si (bSi) leach must be modified in order to keep liquid volumes within practical limits. Accelerator mass spectrometry (AMS) has also been used to detect ^{32}Si activity, but requires high ^{32}Si/Si ratios not achievable in sediment samples where background stable Si content is high. For bSi analyses in sediment, typically ~25 – 50mg of wet sediment is leached using 25 – 50ml of Na_2CO_3 solutions. Given the low activity of ^{32}Si in bSi and the small quantity of bSi in nearshore deposits, the primary target of the present study, at least 500g dry sediment weight must be processed in order to acquire enough bulk silica to determine ^{32}Si activity, if present, which corresponds to 500L of Na_2CO_3. In the present study, experiments were carried out to determine if the fluid / sediment ratio could be lowered while still extracting bSi at quantities equivalent to the traditional method. In these experiments, leach solution strengths, volumes and sequential extraction times were varied, to determine and optimize the minimum extraction volume required to obtain the same biogenic Si released from a leach with excess Na_2CO_3 (i.e. dry sediment weight:leach volume of ~1:1000 in classic leach). Sediment samples were never centrifuged, frozen, or ground and were otherwise left unaltered before beginning extraction.

Earlier techniques quantifying biogenic silica phases in sediments may have significantly underestimated the amount of bSi initially present because of alteration of bSi to less soluble forms such as authigenic clay. Extraction protocols have generally used a mild alkaline leach to dissolve and operationally define the biogenic silica phase (Eggimann et al., 1980; DeMaster, 1981; Mortlock and Froelich, 1989; Conley, 1998; Sauer, et al, 2006). The estimation of bSi is based on the enhanced reactivity of bSi relative to other, generally less hydrous silicate minerals such as lithogenic clays (Figure 3). Lewin (1961) noticed that diatoms cleaned with acid exhibited increased dissolution rates than untreated cells. The pretreatment step with mild acid removes coatings of metal oxides from the Si phases and activates them for dissolution and subsequent sampling by the mild alkaline phase (Mortlock and Froelich, 1989; Michalopoulos and Aller, 2004). The standard use of a mild alkaline leach step to quantify biogenic silica content is inaccurate to use in lithogenic marine environments where significant portions of opaline silica can become coated with metal oxides. In high deposition environments with extensive diagenetic metal cycling (i.e. Al, Fe, and Mn redox cycling), such as the Amazon – Guianas dispersal system (Sullivan and Aller, 1996; Aller et al., 2004), the likelihood that deposited biogenic silica will become coated with a metal oxide is high (Gibbs, 1977b; Eisma et al., 1978; Michalopoulos and Aller, 2004). Gibbs (1977) determined that metal oxide coatings existed on clay particles for a range of size fractions in the Amazon River and Delta (0.1 µm to 3.5 µm size fractions) with thicker coatings on larger particles. Based on this modification, biogenic silica phases were extracted from Amazon delta sediments using a combination of a mild 0.1N HCl acid leach (Si – HCl) followed by an alkaline 1% Na_2CO_3 leach (Si – Alk) to operationally define a closer approximation to the original total biogenic silica pool inclusive of its altered forms (defined here operationally as a highly reactive Si pool, $\sum Si_{hr}$ = Si – HCl + Si – Alk) in these sediments (Michalopoulus and Aller, 2004; Presti and Michalopoulos, 2008)). Without the removal of metal oxide coatings or metal doped surface Si, a significant portion of poorly crystalline biogenic silica goes undetected, as the metal oxide coatings prevent dissolution in alkaline solution. Coatings are likely discontinuous or their distrbutions unknown. Incorporation of Al into siliceous tests, substitution of Al for Si in frustules, or “aging” of frustules can also limit opal – Si solubility (Van Bennekom et al., 1989; Van Bennekom et al., 1991; Dixit et al., 2001; Dixit and Van Cappellen, 2002; Van Cappellen et al., 2002).

In the Amazon, prior studies estimated the biogenic silica (bSi) content of shelf sediments to be 0.2 – 0.4wt. %SiO_2 (DeMaster et al., 1983), whereas Michalopoulos and Aller (2004), using the two – step $\sum Si_{hr}$ leach on over 50 previously frozen samples from the river mouth and proximal delta (samples were never dried or ground), calculated the total pool of biogenic Si and its early diagenetically altered products to be 1.8 wt.% SiO_2 , an order of magnitude greater. The $\sum Si_{hr}$ leach extracted 300 – 400 µmol/g Si in the delta about 200km northwest of the river mouth, compared to 30 – 90 µmol/g Si that was extracted in the one – step bSi leach. Determining Si release from Mn, Fe, and Al – oxides versus biogenic Si phases, this study estimated <20 µmol/g Si in Amazon delta may be released by 0.1N HCl from metal oxides alone, whereas in deposits from the French Guiana coast <10 µmol/g Si may be released from the same phases. These estimates are significantly lower than the Si extracted in the 0.1N HCl leaches of Amazon delta and French Guiana sediments (Si – HCl fraction was 90 – 150 µmol/g in Amazon delta samples and 90 – 130 µmol/g in French Guiana samples in this study).

This two – step treatment may dissolve continental amorphous alumino – silicate materials, phytoliths or freshwater diatoms and was also tested on sediment from the Amazon river mouth. The classic bSi extraction dissolved ~50 µmol/g in the <63 µ fraction from a sediment sample from the Macapá channel near the river mouth (Michalopoulos and Aller, 2004) and 160 µmol/g, or ~1%, in Amazon suspended particulate matter (Conley, 1997). The two – step acid – alkaline leach dissolved ~100 µmol/g Si total in the same <63 µ fraction of the Macapá channel sample (~75% of total Si in the alkaline pool following acid – pretreatment). In our Amazon River mouth sample, Si in the classic bSi extraction was ~17 µmol/g whereas it was ~68 µmol/g in the 2 – step acid - alkaline treatment. This reactive particulate fraction, released in the two – step treatment, from rivers is not included in the dissolved Si and amorphous Si inputs to the global ocean. While not perfect, this acid – alkaline leach sequence comes closer to being consistent with other measures of diagenetic clay formation and compositional changes along the transit path than does the one – step alkaline leach alone.

Amazon River clays are almost equal portions kaolinite, illite and montmorillinite, ~25 – 35%, near the river mouth (Gibbs, 1977a). Silica release from this two – step treatment on clay mineral structures were also investigated on three reference clays (kaolinite, illite, and montmorillonite, $\sum Si_{hr}$ from illite and kaolinite was ~ 20 – 55 µmol/g, and $\sum Si_{hr}$ from montmorillonite was 140 µmol/g) and compared to Si extracted from Amazon Delta samples in the same treatments (Michalopoulos et al., 2004). The magnitude of the subsequent of reactive Si release from the reference clays after acid – pretreatment was smaller than Si release from Amazon delta samples and similar to what was released from samples closer to the river mouth. Silica extracted from the one – step alkaline bSi leach was also comparable in magnitude to silica extracted from riverbed samples. The study also determined microscopically that this two – step $\sum Si_{hr}$ extraction protocol only dissolved "a very small portion" of fully altered diatoms (unknown absolute percentage) and other siliceous diagenetic alteration products, giving a conservative estimate of the biogenic silica pool (Michalopoulos and Aller, 2004). The question remains; however, as to how much biogenic silica is converted to authigenic clays along with how fast this clay fraction forms *in situ*. ^{32}Si may be used as a tracer, in these tropical sediment samples, to determine the rate and quantity of authigenic clay formation. It may also be used to trace the validity and accuracy of the classic biogenic Si leach.

Conventional Operational Leach Volumes and Sample Masses

In the fall of 2009 several liters of surface sediment gathered by Prof. John Mak (SoMAS) near Kourou during a cruise to French Guiana were used in a series of small scale leaches. Initially, classic leaches using 25 - 40mg dry weight of sediment and ~25ml of solution were extracted with 0.1M, 1M, and 2M Na_2CO_3 at 85°C and sampled serially over ~5 hours. Replicate leaches were also performed. Results of the sampling are presented in Figure 4 as silica content versus time, and summarized in Table 1. This scheme was also used with sediments that had been pretreated with a mild acid as outlined in Michalopoulos and Aller (2004), and the results from these leaches and replicate leaches are presented in Figure 5, and summarized in Table 1. Approximately 50 – 75 µmol Si/g dry sediment is extracted in the 0.1N HCl pre-treatment step in samples from French Guiana. DeMaster (1979; 1980) theorized that sediments were comprised of two pools of silica, one which is a fast dissolving biogenic Si fraction and the other which is a slow dissolving Si clay fraction. In excess mild alkaline solution heated to near boiling (i.e. 0.1M Na_2CO_3 at 85°C), the fast dissolving fraction should completely dissolve within one hour. According to DeMaster (1979; 1980), the biogenic silica fraction is calculated by fitting a line through the silica content in the leachate collected from ~1h to 5h and extrapolated to time zero. In the leaches with no acid pretreatment step, biogenic silica content was between 65µmol/g to 100 µmol/g, whereas it was between 175µmol/g and 250 µmol/g in the leaches with an acid pretreatment step. If using the data points collected from 2h to 5h for the mineral correction, the calculated biogenic silica content increases to 80 – 110 µmol/g, whereas in the two – step leach there was no appreciable change. In general, it appears that the concentration of Na_2CO_3 has little effect on the amount of silica extracted in this French Guiana sample.

In order to test the 2 – pool theory of Si in sediments outlined by DeMaster (1979, 1980, Figure 3), a homogenized mass of sediment was split into two 50ml centrifuge tubes. One sediment plug was pretreated with 25 – 30ml of 0.1M HCl overnight for 18 – 20 hours, after which the mixture was centrifuged and the overlying acid solution was decanted and saved for analysis. The pretreated sediment was washed with distilled water prior to addition of alkaline solution. Classic solid to leachate solution ratios, ~25 – 40mg to 25 – 30 ml 0.1 Na_2CO_3, were used in the following extractions. Both centrifuge tubes were placed in a hot water bath at 85°C for 1h increments, after which the slurry was centrifuged and the solution decanted and saved for analysis. After centrifugation, a fresh aliquot of ~20 – 30ml of 0.1M Na_2CO_3 was added to the sediment in each vial, sonicated, and re – introduced to the hot water bath for 1 hour and the procedure was repeated. This was done seven times and each aliquot of Na_2CO_3 which was isolated was analyzed for Si content. These results are presented in Table 2 and Figure 6. If the 2 – pool theory of Si solubility is accurate, all the biogenic silica should have been extracted in the first 1 hour – long extraction and the silica content in subsequent extractions 2 – 7 should be about equal. However, it appears the first 4 to 5 extractions continue to release Si until an asymptotic value of about 20 µmol/g is reached, suggesting that there are several Si phases of varying reactivity in the sample, not just two; similar to observations by other researchers (Shemesh et al., 1988; Dixit et al., 2001; Dixit and Van Cappellen, 2002; Van Cappellen et al., 2002; Loucaides et al., 2010).

In order to estimate its effects on background lithogenic material, this experimental setup was applied to four reference clays: halloysite, kaolinite, illite, and montmorillonite. The majority of the silty clay fraction (up to 30% of bulk sediment) in the surface mud flats along French Guiana is comprised of illite, kaolinite, smectite, and quartz (Allison et al., 1995). The majority of the suspended sediment load of the Amazon River itself is composed of illite, kaolinite, montmorillonite, quartz, and feldspar (Kuehl et al., 1996). If necessary, each dry clay was gently crushed into a powder and 40 – 50mg each put into two 50ml centrifuge tubes, one of which was pretreated with ~ 40 – 45ml 0.1N HCl. The HCl solution was isolated for analysis and the residual clay washed with distilled water prior to introduction of 0.1M Na_2CO_3. The clays were then leached six times for 1 – hour long extractions in an 85°C water bath with 40 – 45ml 0.1M Na_2CO_3. Each extraction used fresh aliquots of the alkaline solution. Results are presented in Table 3 and Figure 7. Both halloysite and montmorillonite appear to have some percentage of a more reactive Si phase present. This initial Si release may also be due to grinding effects. The Si content in the extractions of halloysite and montmorillonite appear to approach an asymptotic value, about 70 and 10 µmol/g respectively, after about five extractions in both the acid pretreated and untreated fractions. The Si content in extractions of illite and kaolinite remain relatively constant. The 0.1N HCl acid pretreatment step does not have a significant effect on the amount of Si extracted from any of the four clay standards studied.

The Si content extracted from these four clays was determined serially over 5 hours in excess 0.1M Na_2CO_3, in mass to solution ratios of ~50mg to 30ml, with and without acid pretreatment, according to DeMaster's procedure for determining biogenic silica content (1979, 1980). These results are presented in Table 4 and Figure 8. Linear trendlines were fit to the silica extracted between 1 and 5 hours to determine the biogenic silica content, or rather the "reactive" silica content (the intercept of the trendline), if present, in these clays. Pure reference clays should be composed of only one phase and the trendline should go through the origin. Instead, there appears to be a significant amount of a "reactive" or fast - dissolving Si phase present in the halloysite in both the acid pretreated and untreated sample, about 120 and 80 µmol/g respectively. There also appears to be some reactive Si release in the montmorillonite sample (~40µmol/g) following acid pretreatment versus the acid untreated sample (~8µmol/g). Acid pretreatment increases the amount of Si released from illite by about 10 µmol/g. The rates of release of Si in each clay were very similar between acid pretreated and untreated samples. There was most likely some internal conversion in the halloysite sample to a more reactive clay phase, perhaps a smectite or other amorphous or expandable clay.

Modifying Leach Volumes and Applying Sequential Extractions

A simple experiment was initially performed where a mass of wet sediment was homogenized and split between six tubes each with a final dry weight of ~0.4g solid. Tubes were paired based on the volume of 0.1N HCl or 0.1M Na_2CO_3, added which varied from 5ml, 10ml, or 15ml. One sample of each pair was pretreated with 0.1N HCl, either 5, 10 or 15ml, overnight for 18 – 20 hours. The tube was then centrifuged, the solution decanted and saved for analysis, and the sediment sample washed with distilled water. The corresponding volume of 0.1M Na_2CO_3 was then added to each pair of tubes. For example, to the tube which was pretreated with 5ml of 0.1N HCl was added 5ml of 0.1M Na_2CO_3. The tubes were placed in a 85°C hot water bath for 1 hour after which they were centrifuged and the solution decanted and saved for analysis. A fresh aliquot 0.1M Na_2CO_3 of the corresponding volume was then added to each tube and they were reintroduced to the hot water bath. This 1 – hour long extraction procedure was repeated for a total of seven extractions and the silica content in each extraction is presented in Table 5 and graphically in Figure 9. The amount of Si successively extracted using only 5ml at each step is significantly lower than what is extracted using 10 and 15 ml, whereas similar quantities are leached between the 10 and 15ml volumes. The first three extractions using 10ml and 15ml released the most Si from the acid pretreated samples, 50% or more of what was released using classic sediment to solution ratios of 25 – 50mg to 25 – 50ml. In the leaches using only 5ml, smaller quantities of Si were freed during each extractions. So, further optimization efforts were made with sediment to solution ratios of 0.4g to 10ml or 15ml.

Using sediment to solution ratios of 0.4g to 10ml or 15ml, multiple extractions were again performed but the time of each extraction step was increased from 1 hour to 2 hours. These results are presented in Table 6. A total of four 2 – hour long extractions were performed on homogenized sediments divided between two sets of two centrifuge tubes in hot water baths set at 85°C. In one set, 15ml of 0.1M Na_2CO_3 was used and one of the samples of the set was pretreated with 0.1N HCl (15ml volume) overnight for 18 – 20 hours. Only the volume in the other set was varied, from 15ml to 10ml of 0.1N HCl or 0.1M Na_2CO_3. Sediments were washed with distilled water prior to addition of the alkaline solution. After addition of the Na_2CO_3 solution, the tubes were placed in a hot water bath at 85°C for 2 hours apiece per extraction. After 2 hours the tubes were centrifuged, the solution decanted and saved for analysis, and a fresh aliquot of 10ml or 15ml 0.1M Na_2CO_3 was added prior to reintroduction to the hot water bath. The first two extractions release similar amounts of Si in the acid untreated samples, between 57 to 67 µmol/g, using either 10ml or 15ml Na_2CO_3. However, in the samples which had been pretreated with 0.1N HCl, the first two 10ml extraction release ~85 µmol/g versus ~140 µmol/g released in the first two 15ml volume extractions. In the 10ml extractions the Si release in acid pretreated samples is about 50% higher than in the untreated fraction in the first two extractions, whereas in the 15ml extractions it is ~100% higher. The 140 µmol/g Si leached using the higher volumes also falls within the range of Si extracted using the classic sediment to leachate ratios (i.e. 25 – 50mg to 25 – 50ml). Later optimization efforts focused on using sediment to solution ratios of 0.4g:15ml, or 1g:38ml.

To determine whether two or three 2 – hour long extractions, with and without acid pretreatment, should be used, the release of silica over time in 1% Na_2CO_3 in the residual sediment, at a solid to solution ratio of 0.4g:15ml, was studied after the sequential extractions and these results are presented in Table 7. The same experimental conditions were carried out using classic solid to solution ratios of 0.05g to 25 – 30ml 1% Na_2CO_3. Sediment from French Guiana was homogenized and divided between two sets of two centrifuge tubes; one set of two contained ~0.4g dry weight and the other set contained ~0.05g dry weight. One sample from each set was pretreated with 0.1N HCl overnight for 18 – 20hours. All four samples were then subjected to two or three 2 – hour long 0.1M Na_2CO_3 extractions in an 85°C hot water bath, after which a fresh aliquot of 15ml 0.1M Na_2CO_3 was added to the sample of 0.4g and 25 – 30ml 0.1M Na_2CO_3 was added to the samples of 0.05g. The tubes were reintroduced to the hot water bath at the same temperature and serially sampled over the next 4 hours for Si release. This release of Si after the 2 – hour long extractions is presented in Figure 9. The amount of bSi or $\sum Si_{hr}$ Si remaining in the sediment samples was determined from the y – intercepts of linear fits through the sample points. The difference in any remaining calculated reactive or biogenic Si in the treatments using 0.4g appears to be small; minor enough to constrain the extraction methodology to two 2 – hour long extractions instead of three as sufficient for extracting similar amounts of bSi as does the classic leaches.

To determine Si release in reference clays from two or three 2 – hour long extractions, this same experimental set – up was repeated with acid untreated and pretreated samples of halloysite, illite, kaolinite, and montmorillonite at solid to solution ratios of 0.4g:15ml. The Si content in each extraction were roughly the same between acid untreated and pretreated samples, whether two or three extractions were performed. After the 2 – hour long extractions, the release of silica from the clays was monitored over five hours and these results are presented in Tables 8 – 9 and Figures 11 – 12. When two extractions were performed, the remaining reactive Si pool appears to be somewhat higher in halloysite, (~20 µmol/g) versus the other three clays (0.5 - 5 µmol/g) in acid untreated samples. In acid pretreated samples, residual reactive Si pools in halloysite, illite, and kaolinite remain about the same, whereas in montmorillonite it increases to ~ 40 µmol/g. Increasing the number of extractions from two to three had little effect for illite or kaolinite in both the acid untreated and pretreated fractions.

Two sequential 2 – hour long extractions with and without acid pretreatment at sediment mass to solution volumes of 1g:38ml were chosen as the methodology for removing the majority of ^{32}Si associated with $\sum Si_{hr}$ or bSi pools from French Guiana mud samples. In the classic leaches with acid pretreatment, the range of reactive Si ($\sum Si_{hr}$) extracted ranges from about 120 – 200 µmol/g, whereas the range of biogenic Si (bSi) extracted without acid pretreatment is 40 – 80 µmol/g. About 70 – 100% of reactive and biogenic Si appears to be removed in two sequential 2 – hour long extractions at these modified sediment mass to solution ratios, when compared to what was removed in classic sediment to solution ratios. The Si fraction which may be removed in the third extraction was minor and, given the low activity of ^{32}Si in general, should not contribute significantly to ^{32}Si activity in the next sequence of extractions following the 0.1M Na_2CO_3. Also, all four reference clays released relatively small amounts (~10 – 40 µmol/g) of Si and the differences in the residual reactive Si content in the four clays between two and three 2 – hour long extractions was not great. Given these similarities between the two and three two – hour long extractions, fewer extractions will keep the amount of Si from lithogenic or more ordered older clay phases low while also keeping total solution volume low. The Si content in the distilled water wash following the bSi and the $\sum Si_{hr}$ extractions was low (~1 – 3 µmol Si/g) and this volume was discarded. The distilled water wash after the Si – NaOH leach contained ~10% of the Si extracted in the NaOH fraction and this wash was retained. The modified bSi and $\sum Si_{hr}$ leach schemes are given in Figures 13 and 14.

Separation of Si for ^{32}Si analysis

The two sequential 0.1M Na_2CO_3 leaches were combined and later neutralized with concentrated reagent grade HCl. A small excess of HCl was added, such that the pH of the solution was 2 or less, and the solution boiled down to near dryness to precipitate SiO_2. The silicon dioxide was purified according to DeMaster (1979). Briefly, the initially precipitated solid was rinsed several times with distilled water, dried at 200°C, and rinsed several times with distilled water. The solid was then baked in a furnace at 750 – 850°C. The SiO_2 was then redissolved in hot 4M NaOH and recrystallized. The sample, which was a mixture of SiO_2 and NaCl, was dried at 100 – 200°C and boiled in distilled water to remove the NaCl. The remaining SiO_2 was stored for 3 – 4 months to obtain secular equilibrium between ^{32}Si and ^{32}P, the daughter product of ^{32}Si.

To obtain the majority of the reactive and biogenic silica fractions from other sample sites, the sediment mass to 0.1M Na_2CO_3 solution ratios were varied. The bSi content in Long Island Sound at this station is about 7 - 8X higher than in French Guiana, whereas the $\sum Si_{hr}$ content in Long Island Sound is about 4 – 5X higher. Accordingly, the sediment mass to 0.1M Na_2CO_3 solution ratios were lowered when processing Long Island Sound samples. Approximately 1g:60ml was used for the bSi sequential leaches, whereas ~1g:145ml to extract reactive Si. The sediment obtained near the mouth of the Mississippi River had a bSi and $\sum Si_{hr}$ content of ~350µmol/g and ~410µmol/g, respectively. Biogenic Si contents of the Gulf of Papua sites are very similar to that of French Guiana sediments, whereas the Amazon River sediments show lower amounts of Si extracted in the bSi, 10 – 30 µmol/g fraction and the $\sum Si_{hr}$ fractions, 60 – 70 µmol/g.

Following the $\sum Si_{hr}$ and bSi extractions, the silicate phases with which any residual ^{32}Si is most likely associated, such as relatively reactive or poorly crystalline clay formed during early diagenesis, was extracted using near boiling 4M NaOH ("Si-NaOH(-bSi)" or "Si-NaOH(-$\sum Si_{hr}$)" pools, see Figures 12 and 13) at sediment mass to solution ratios of 1g to 10 – 12ml for 1.5 – 2h, according to DeMaster (1979). After the sediment was treated with the 4M NaOH, it was washed with distilled water at the same sediment mass to solution ratios and the distilled water was combined with the sodium hydroxide fraction. The same protocol was used to precipitate and purify the SiO_2 in this fraction as was used with the 0.1M Na_2CO_3 fractions. The silica content in the sodium hydroxide leach of French Guiana sediments can be upwards of 2500 µmol/g after the 0.1M Na_2CO_3 extractions. If the sediment were entirely composed of smectite, the Si content would be ~7300 µmol/g if all the SiO_2 was extracted. In Long Island Sound sediments, the silica content in the same leach was between 400 and 500 µmol/g after extraction with 0.1M Na_2CO_3, whereas in the Gulf of Mexico they were between 750 – 900 µmol/g. In the Gulf of Papua, the 4M NaOH fractions had Si contents between ~500 to ~800 µmol/g. The activities of ^{32}Si in the bSi, $\sum Si_{hr}$, Si-NaOH(-bSi), and Si-NaOH(-$\sum Si_{hr}$) fractions, if present, can then be compared to each other and amongst different sites to determine the relative accuracy of the classic biogenic Si leaches as well as the quantity and relative rates of opaline Si sequestration in continental margins in forms (e.g. authigenic clays) that are impervious to dissolution by Na_2CO_3.

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Figure 3. Time release pattern of alkaline extractable Si from a representative sediment sample. Highly reactive biogenic Si will dissolve rapidly, whereas more crystalline Si fractions such as lithogenic clays will dissolve slowly.

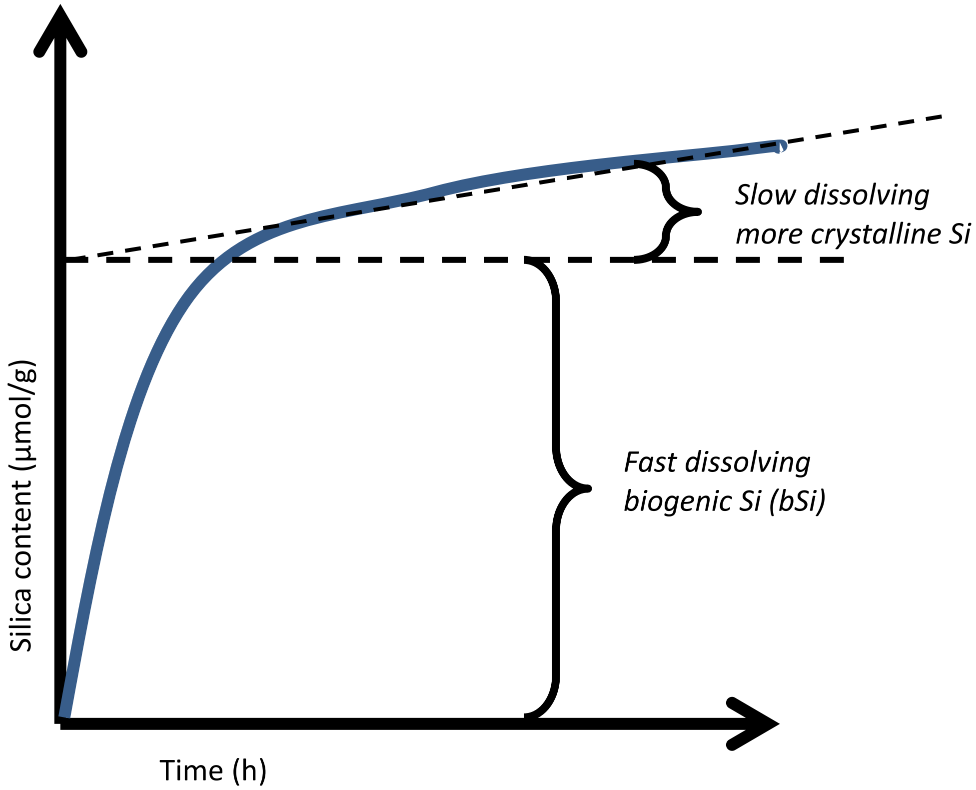


Figure 4. Si release over time during a classic biogenic Si leaches with no acid pretreatment using increasing concentrations of Na_2CO_3. Replicates of these leaches were performed and are also presented, except the 1% Na_2CO_3 leach which was not analyzed. Sediment sample was collected in 2009 from mudbank surface sediments (0-10 cm) off French Guiana. Sample mass was ~25g and leach volume was ~25ml.

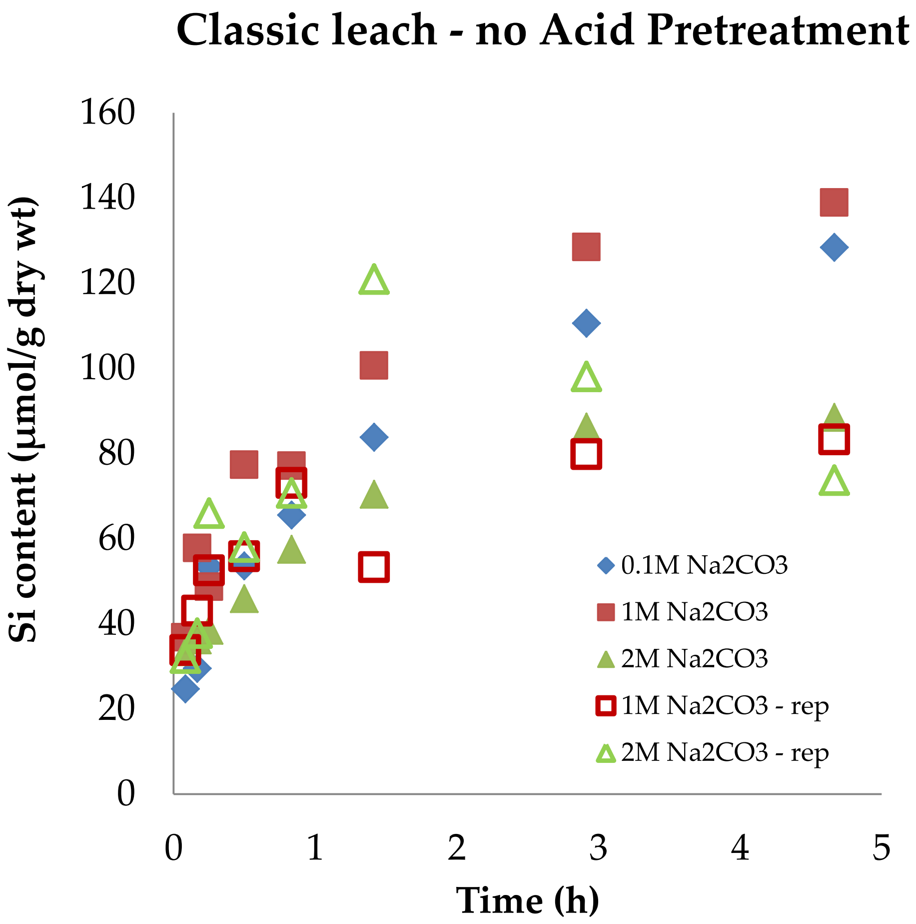


Figure 5. Si release over time during a classic biogenic Si leaches with acid pretreatment using increasing concentrations of Na_2CO_3. Replicates of these leaches were performed and are also presented. Sediment sample was collected in 2009 from mudbank surface sediments off French Guiana. Sample mass was ~25mg and leach volume was ~25ml.

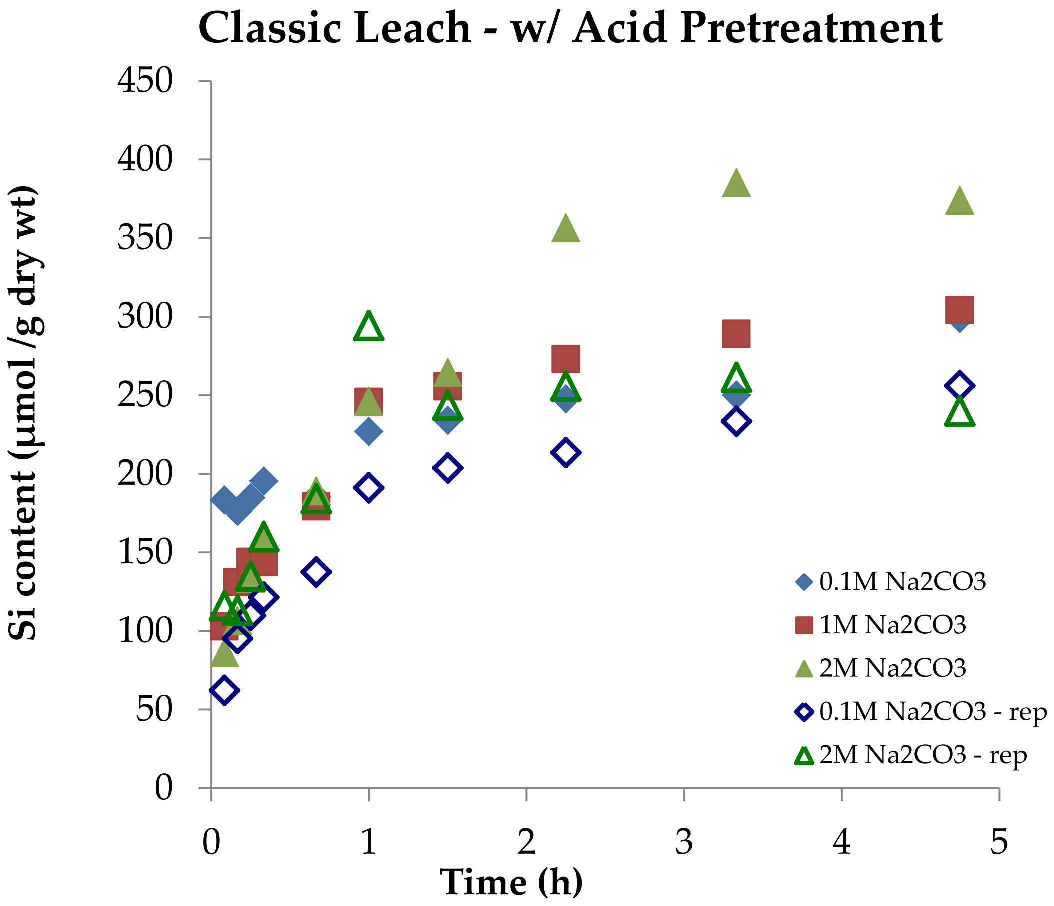


Table 1. Calculated biogenic silica content in French Guiana sediments from classic silica leaches with ($\sum Si_{hr}$) and without (bSi) an acid pretreatment step. Solid to solution ratios were ~25mg:25ml. The concentration of Na_2CO_3 was varied between 0.1M, 1M, and 2M. Silica content in the 0.1N HCl acid pretreatment was 105 – 150 µmol/g (sediment to solution ratio ~25mg:25ml).

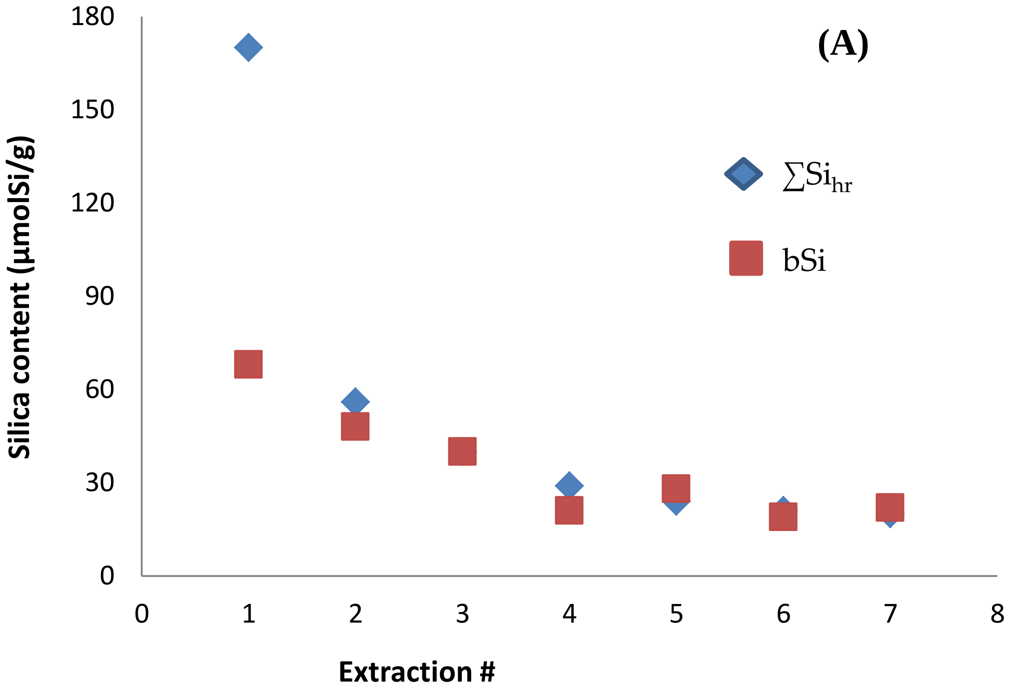
	Biogenic Silica Content (µmol/g dry wt)	
	bSi	$\sum Si_{hr}$
0.1M Na_2CO_3	65	206
1M Na_2CO_3	88	233
2M Na_2CO_3	67	183
0.1M Na_2CO_3 - replicate	---	176
1M Na_2CO_3 - replicate	59	443
2M Na_2CO_3 - replicate	100	281

Table 2. Silica released from homogenized sediment plugs in 1 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of sediment was homogenized and split into two 50 ml centrifuge tubes. Classic sediment to solution ratios or 25 – 40 mg to 25 – 30ml 0.1N HCl or 0.1M Na_2CO_3. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 25 – 30ml of 0.1M Na_2CO_3 was then added to the sediment plug and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Results are presented as µmol Si per g sediment.

	Extracted Si content (µmol Si/g dry wt)	
	$\sum Si_{hr}$	bSi
0.1M HCl pre – treatment	94	------
Extraction 1* (0.1M Na_2CO_3)	170	68
Extraction 2* (0.1M Na_2CO_3)	56	48
Extraction 3* (0.1M Na_2CO_3)	40	40
Extraction 4* (0.1M Na_2CO_3)	29	21
Extraction 5* (0.1M Na_2CO_3)	24	28
Extraction 6* (0.1M Na_2CO_3)	21	19
Extraction 7* (0.1M Na_2CO_3)	20	22
Total Si extracted	454	246

* extraction solution is 25 – 30ml of 0.1M Na_2CO_3

Figure 6. (A) Silica release in French Guiana sediments in 1 – h long extractions in 0.1M Na_2CO_3 at 85°C, with and without pretreatment with 0.1N HCl. Classic sediment to solution ratios or 25 – 40 mg to 25 – 30ml 0.1N HCl or 0.1M Na_2CO_3. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 25 – 30ml of 0.1M Na_2CO_3 was then added to the sediment plug and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Silica content in the 0.1N HCl pretreatment was 94 µmol/g. Total Si release in the two – step leach was 454 µmol/g, whereas it was 246 µmol/g in the one – step alkaline leach (B).



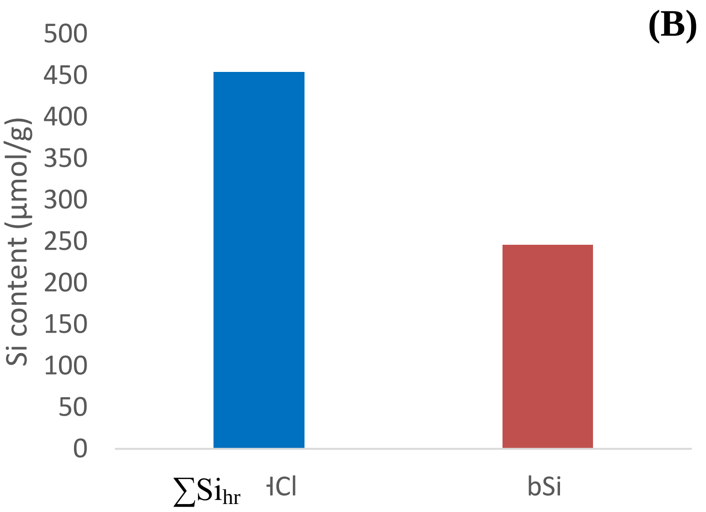
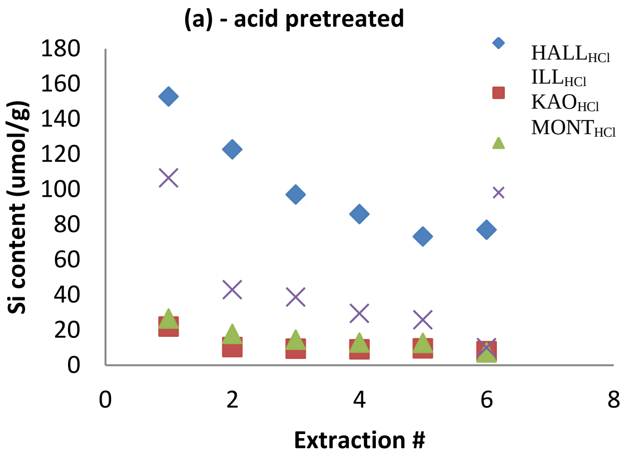


Table 3. Silica released from homogenized powdered clays in 1 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of clay was ground and split into two 50 ml centrifuge tubes. Classic sediment to solution ratios or 40 – 45 mg to 40 – 45ml 0.1N HCl or 0.1M Na_2CO_3. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 40 – 45ml of 0.1M Na_2CO_3 was then added to the clay sample and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Results are presented as µmol Si per g sediment.

	Silica release (µmo/g Si)							
	Halloysite		Illite		Kaolinite		Montmorillonite	
0.1M HCl pretreatment	n/a	21	----	19	----	-1	----	42
Extraction 1	135	153	14	22	33	26	67	106
Extraction 2	112	123	16	10	16	18	49	43
Extraction 3	101	97	15	9	12	14	31	39
Extraction 4	80	86	16	9	11	13	34	29
Extraction 5	68	73	6	10	12	13	28	26
Extraction 6	79	77	10	8	10	7	10	10

Figure 7. Silica release in four reference clays in 1 – h long extractions in 0.1M Na_2CO_3 at 85°C, (a) with and (b) without pretreatment with 0.1N HCl. Classic solid to solution ratios or 40 – 45 mg to 40 – 45ml 0.1N HCl or 0.1M Na_2CO_3. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 40 – 45ml of 0.1M Na_2CO_3 was then added to each clay and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Silica content in the 0.1N HCl pretreatment was 0 µmol/g (kaolinite), ~20 µmol/g (halloysite and illite), and ~40 µmol/g (montmorillonite).



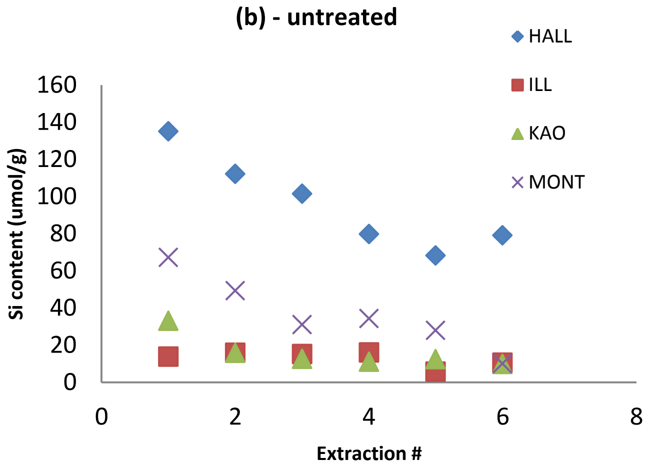
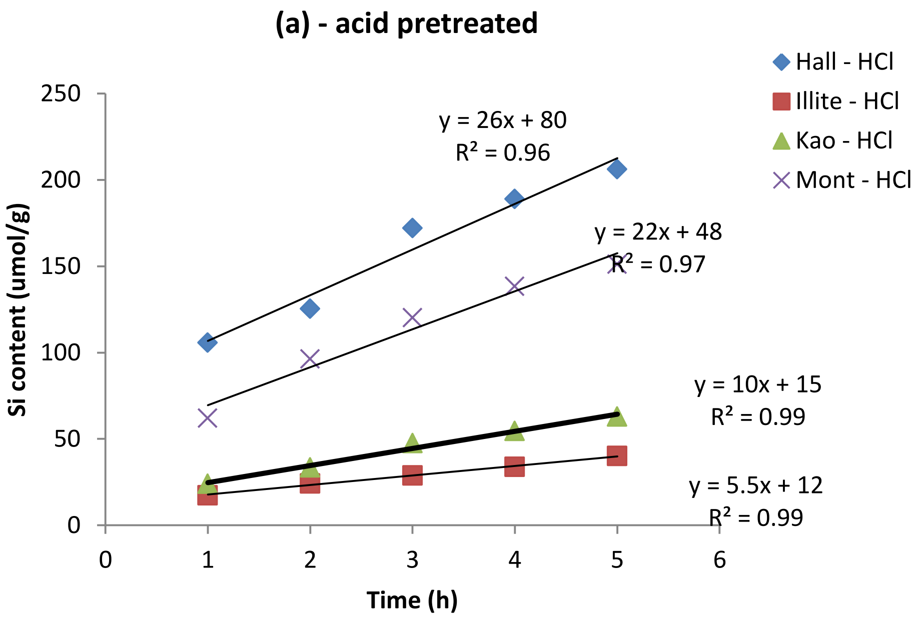


Table 4. Silica release over time from four reference clays in 0.1M Na_2CO_3, with and without acid pretreatment. Clay to solution ratios were ~50mg to ~30ml. Results presented as µmol Si released per gram of dry weight clay.

	Silica content (µmol/g)							
	Halloysite		Illite		Kaolinite		Montmorillonite	
0.1N HCl		37		16		1		41
1h	130	106	12	17	34	24	26	62
2h	177	125	18	24	51	34	49	96
3h	213	172	25	29	64	48	75	120
4h	229	189	31	34	75	55	96	138
5h	237	206	48	40	85	63	109	151

Figure 8. Si release over time in both (a) 0.1 N HCl pretreated and (b) untreated samples from four reference clays (Halloysite, Illite, Kaolinite, Montmorillonite) in solid to solution ratios of ~50mg to 30 ml 0.1M Na_2CO_3. At each sampling point, 0.500ml of the overlying solution was removed for total Si analysis.



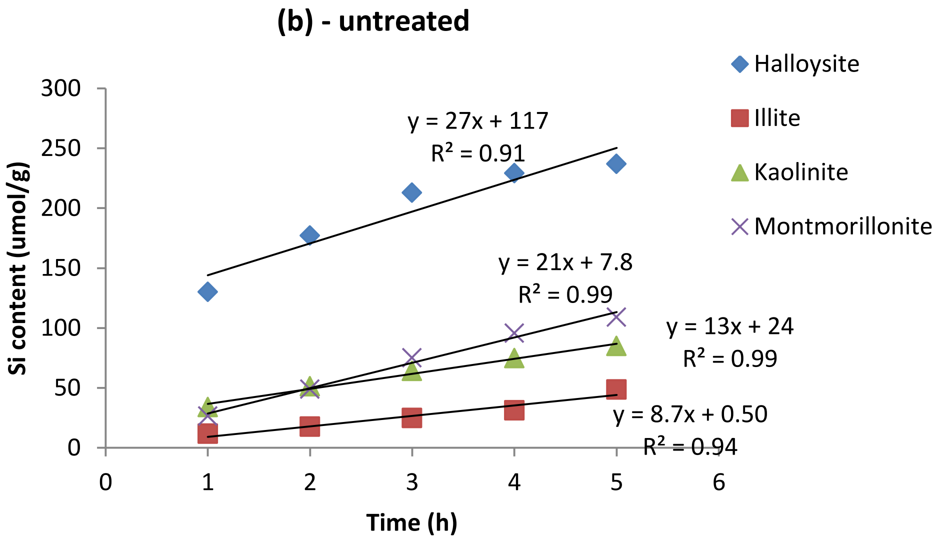
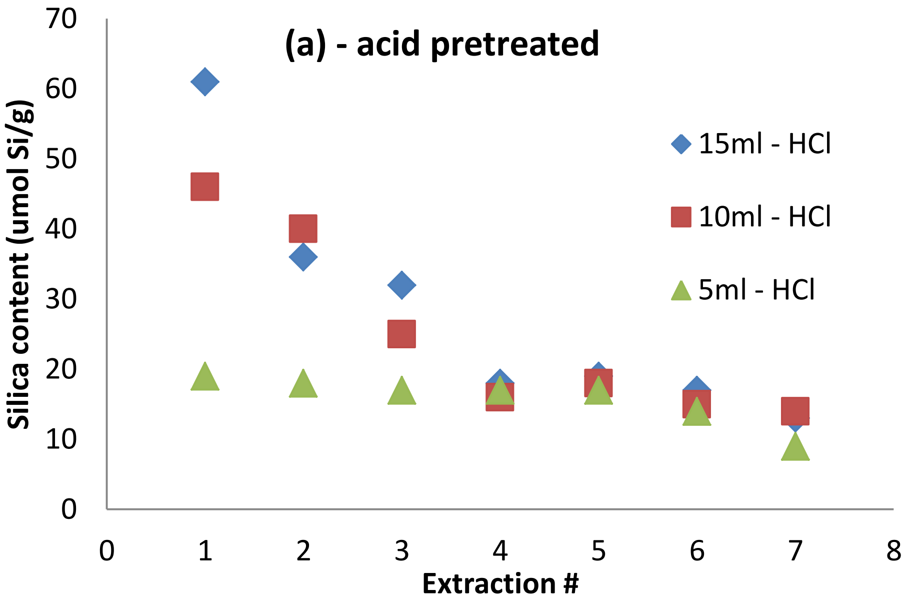
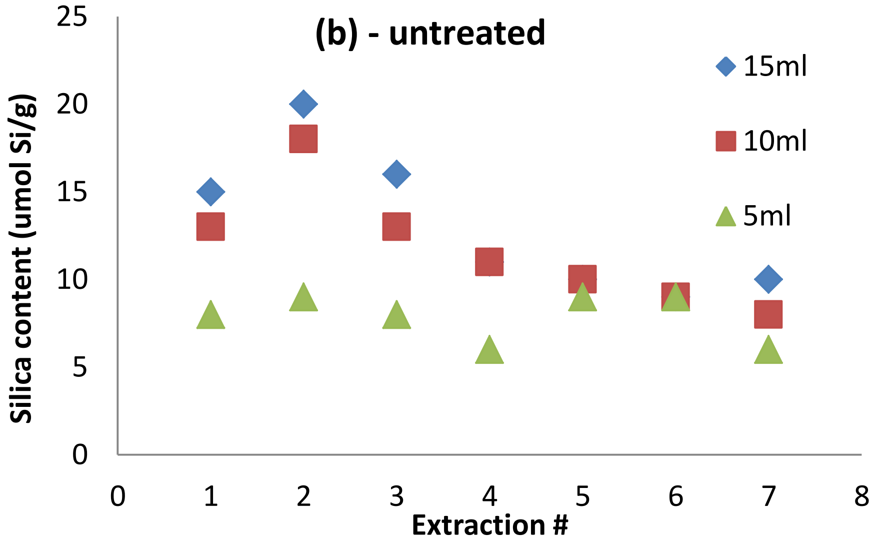


Table 5. Silica released from homogenized sediments from French Guiana in 1 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of wet sediment was homogenized and split into 6 centrifuge tubes. Sediment masses in each tube were about 0.4g dry weight, whereas solution volumes were varied between 5ml, 10ml, and 15ml 0.1N HCl (during the acid pretreatment step) or 0.1M Na_2CO_3. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of the corresponding 0.1M Na_2CO_3 (5ml, 10ml, or 15ml) was then added to each sample and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Results are presented as µmol Si per g sediment.

	Silica content (µmol/g)					
	15ml		10ml		5ml	
0.1N HCl	N/A	60	N/A	56	N/A	39
Extraction 1	15	61	13	46	8	19
Extraction 2	20	36	18	40	9	18
Extraction 3	16	32	13	25	8	17
Extraction 4	11	18	11	16	6	17
Extraction 5	10	19	10	18	9	17
Extraction 6	9	17	9	15	9	14
Extraction 7	10	13	8	14	6	9
Extraction 1 – 7 total	92	196	82	174	55	112
0.1N HCl + Extraction 1 – 7 total		256		230		151

Figure 9. Silica release in French Guiana sediments in 1 – h long extractions in 0.1M Na_2CO_3 at 85°C, (a) with, (b) without pretreatment with 0.1N HCl, and (c) cumulative release in bSi and $\sum Si_{hr}$ leaches. Modified sediment to solution ratios of ~40mg to either 5ml, 10ml, or 15ml 0.1N HCl or 0.1M Na_2CO_3 were used. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of either 5ml, 10ml, or 15ml 0.1M Na_2CO_3 was then added to each sample and the mixture was re – introduced to the 85°C water bath for the next 1 – hour long extraction. Silica content in the 0.1N HCl pretreatment was ~40 µmol/g (5ml extraction volume), ~55 µmol/g (10ml extraction volume), and ~60 µmol/g (15ml extraction volume).





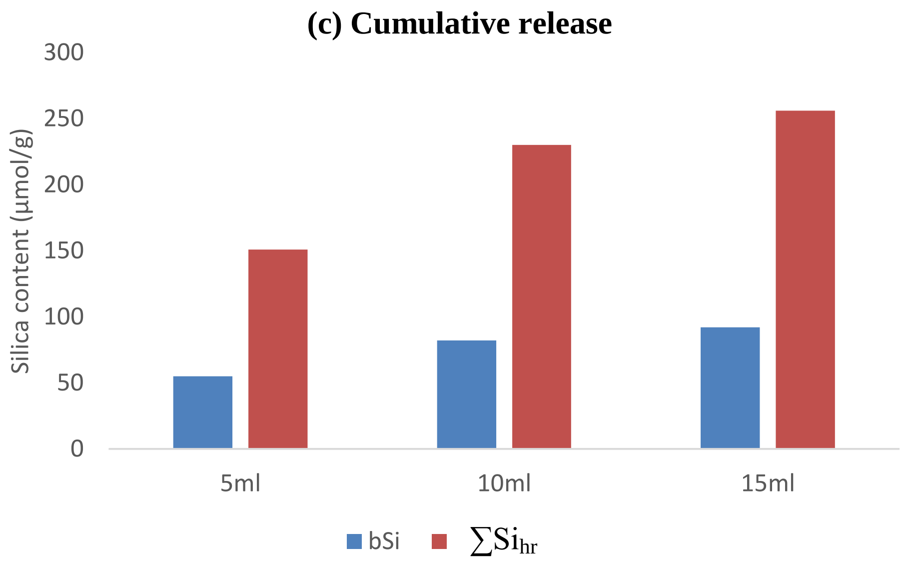

(c) Cumulative release
300
250
200
150
100
50
0
Silica content (µmol/g)
5ml
10ml
15ml
bSi
∑Si$_{hr}$

Table 6. Silica released from homogenized sediments from French Guiana in 2 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of wet sediment was homogenized and split into 6 centrifuge tubes. Sediment masses in each tube were about 0.4g dry weight, whereas solution volumes were varied between 10ml and 15ml 0.1N HCl (during the acid pretreatment step) or 0.1M Na_2CO_3 (during the 2 – hour extraction at 85°C). Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of the corresponding 0.1M Na_2CO_3, 10ml or 15ml, was then added to each sample and the mixture was re – introduced to the 85°C water bath for the next 2 – hour long extraction. Results are presented as µmol Si per g sediment.

	Silica content (µmol Si/g)			
	15 ml		10ml	
0.1 N HCl pretreatment	40	N/A	49	N/A
Extraction 1	62	35	53	27
Extraction 2	71	32	33	30
Extraction 3	27	16	26	18
Extraction 4	16	13	13	11

Table 7. Silica released from homogenized sediments from French Guiana in two or three sequential 2 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of wet sediment was homogenized and split into two sets of two centrifuge tubes; one set containing 0.4g dry weight and the other containing 0.05g dry weight. Solution volumes were either 15ml for the 0.4g or 25 – 30ml for the 0.05g sediment. Either 0.1N HCl was used during the acid pretreatment step or 0.1M Na_2CO_3 was used during the 2 – hour extraction at 85°C. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of the corresponding 0.1M Na_2CO_3, 15ml or 25-30ml, was then added to the corresponding samples and the mixture was re – introduced to the 85°C water bath for the next 2 – hour long extraction. Following the series of 2 – hour long extractions, another aliquot of the corresponding volume of 0.1M Na_2CO_3 was added to the residual sediment and Si release over time was measured to determine the remaining reactive Si pool, if still present. All results are presented as μmol Si per g sediment.

	Silica content (μmol/g Si)							
	Modified leaches				**Classic leaches**			
	$\sum \text{Si}_{hr}$		**bSi**		**$\sum \text{Si}_{hr}$**		**bSi**	
	2X-2h	**3X-2h**	**2X-2h**	**3X-2h**	**2X-2h**	**3X-2h**	**2X-2h**	**3X-2h**
0.1N HCl	77	71			97	96		
Extraction 1	79	71	22	24	200	197	77	89
Extraction 2	59	56	17	16	79	47	41	39
Extraction 3	----	39	----	11	----	43	----	41
TIME Series								
1h	8	14	17	6	27	31	14	14
2h	16	22	29	13	39	49	24	26
3h	21	30	37	15	53	61	35	34
4h	20	34	41	16	61	70	40	45

Figure 10. Silica release over time from French Guiana sediments, with and without acid pre-treatment, following two or three sequential two – hour long extractions in 0.1M Na_2CO_3 at 85°C. Results from the classic solution volumes to sediment masses (i.e. 25 – 30ml for 0.05g sediment), with and without acid pretreatment with 0.1N HCl, are presented in (a), whereas results from the modified solution to sediment mass ratios (e.g. 15ml to 0.4g dry mass), with and without acid pretreatment with 0.1N HCl, are presented in (b).

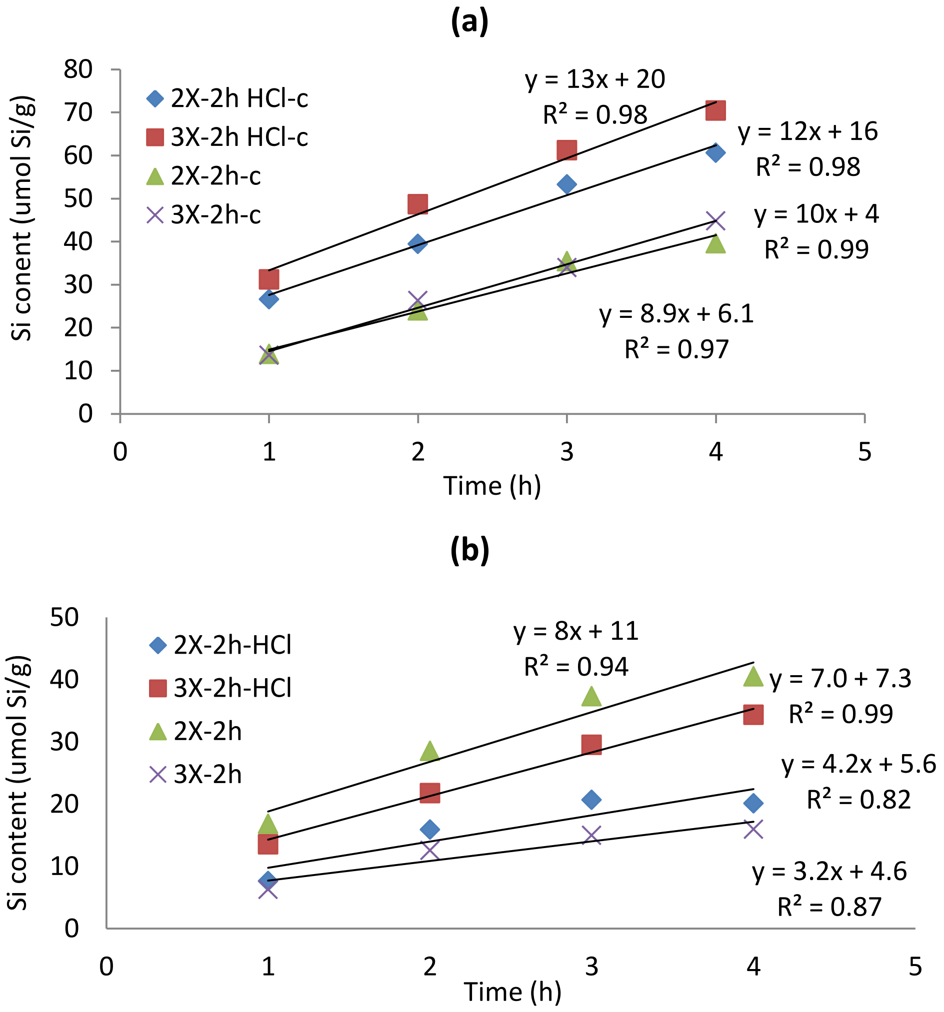


Table 8. Silica released from reference clays in two sequential 2 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of dry clay was ground and ~0.4g each was placed into two centrifuge tubes; one of which was pretreated overnight at room temperature with 0.1N HCl. Solution volumes were 15ml and either 0.1N HCl was used during the acid pretreatment step or 0.1M Na_2CO_3 was used during the 2 – hour extraction at 85°C. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 15ml 0.1M Na_2CO_3 was then added to the clay samples and the mixture was re – introduced to the 85°C water bath for the next 2 – hour long extraction. Following the series of 2 – hour long extractions, another 15ml aliquot of 0.1M Na_2CO_3 was added to the residual clay and Si release over time was measured to determine the remaining reactive Si pool, if present. All results are presented as µmol Si per g clay.

	Silica content (µmol/g)							
	Halloysite		Illite		Kaolinite		Montmorillonite	
0.1N HCl		19		12		4		39
Extraction 1	28	21	11	9	19	18	47	15
Extraction 2	26	21	9	7	13	11	48	28
Time Course								
1h	23	23	4	3	7	8	16	40
2h	30	26	7	7	12	12	51	54
3h	34	30	12	9	14	15	61	54
4h	36	32	15	12	17	17	80	57

Figure 11. Silica release over time from (a) untreated and, (b), acid pretreated standard reference clays halloysite, illite, kaolinite, and montmorillonite following two sequential 2 – hour long extractions in hot 1% Na_2CO_3. The mass of each clay was ~0.4g and the solution volume was 15ml.

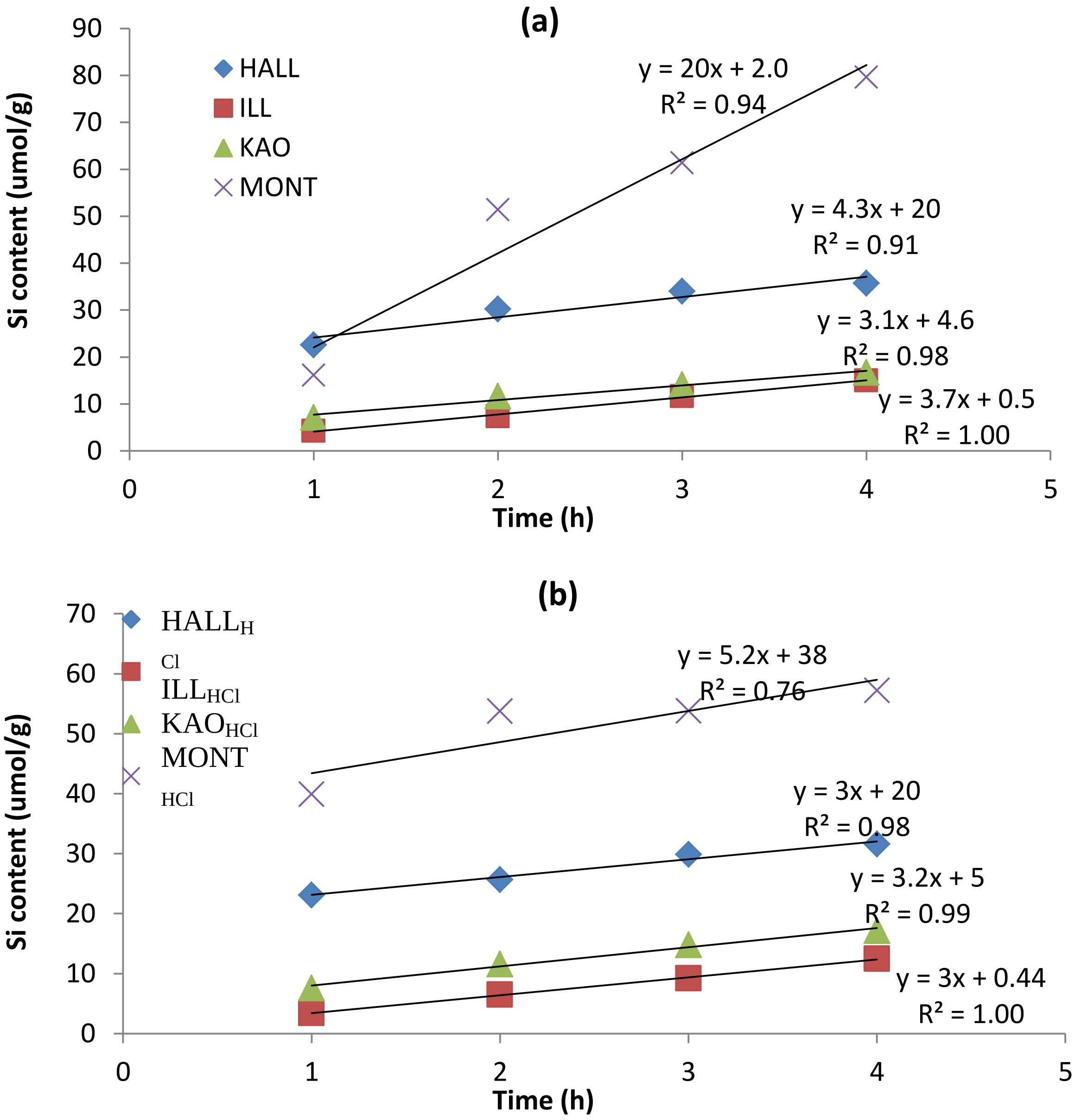


Table 9. Silica released from reference clays in three sequential 2 – hour long extractions in 0.1M Na_2CO_3 at 85°C with and without pretreatment with 0.1N HCl. A mass of dry clay was ground and ~0.4g each was placed into two centrifuge tubes; one of which was pretreated overnight at room temperature with 0.1N HCl. Solution volumes were 15ml and either 0.1N HCl was used during the acid pretreatment step or 0.1M Na_2CO_3 was used during the 2 – hour extraction at 85°C. Following each extraction, the slurries were centrifuged and the solution decanted and saved for analysis. A fresh aliquot of 15ml 0.1M Na_2CO_3 was then added to the clay samples and the mixture was re – introduced to the 85°C water bath for the next 2 – hour long extraction. Following the series of 2 – hour long extractions, another 15ml aliquot of 0.1M Na_2CO_3 was added to the residual clay and Si release over time was measured to determine the remaining reactive Si pool, if present. All results are presented as μmol Si per g clay.

Silica content (μmol/g)								
	Halloysite		Illite		Kaolinite		Montmorillonite	
0.1N HCl		21		12		4		41
Extraction 1	19	21	9	10	16	16	43	19
Extraction 2	30	26	7	8	12	13	48	35
Extraction 3	27	25	8	6	9	10	40	31
Time course								
1h	20	11	3	4	5	6	14	14
2h	32	15	7	8	10	11	26	29
3h	35	18	12	11	15	15	31	33
5h	40	19	17	16	18	18	42	40

Figure 12. Silica release over time from (a) untreated and (b) acid pretreated standard reference clays halloysite, illite, kaolinite, and montmorillonite following three sequential 2 – hour long extractions in hot 1% Na_2CO_3. The mass of each clay was ~0.4g and the solution volume was 15ml.

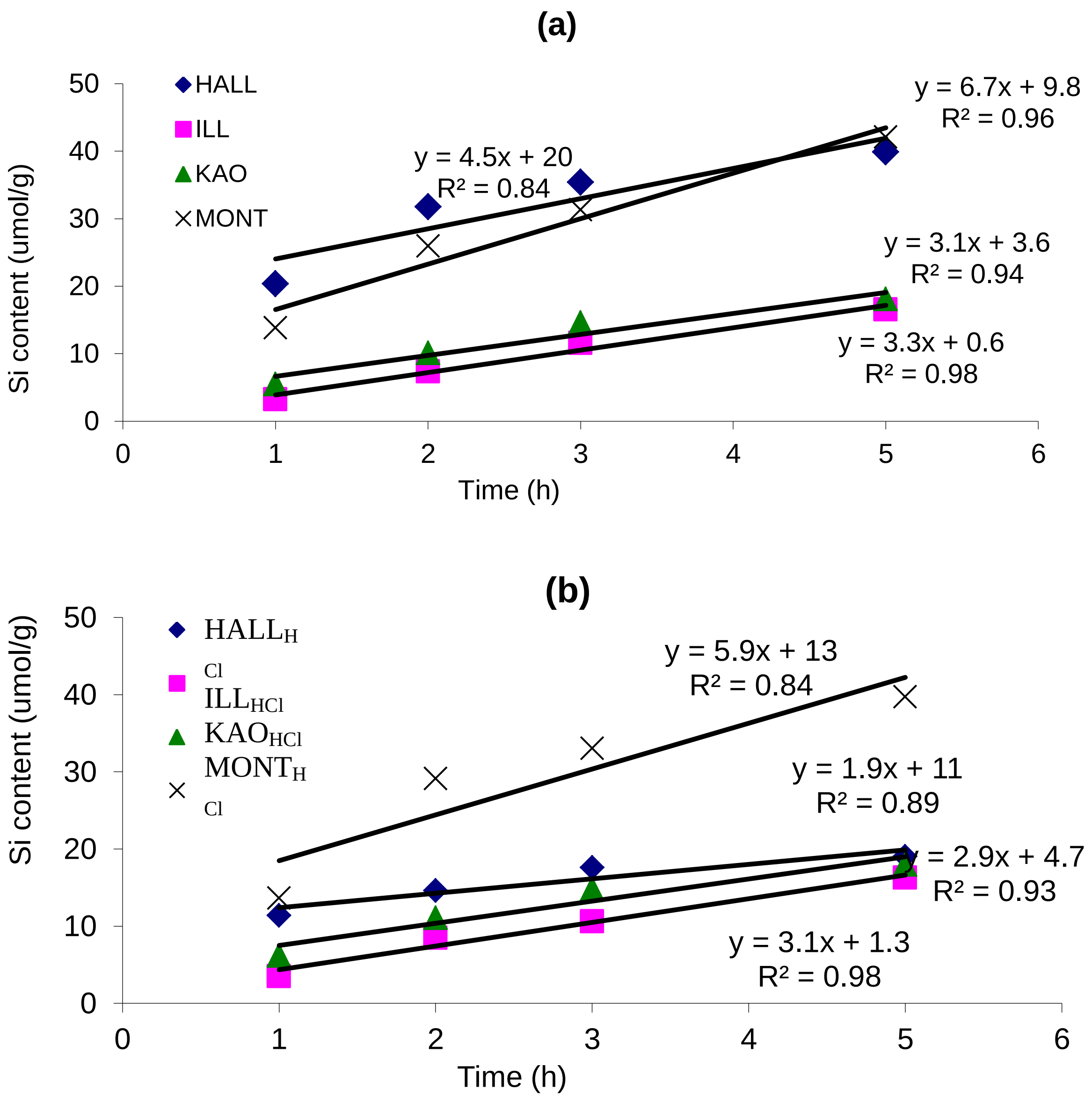


Figure 13. Leach scheme developed to extract ^{32}Si associated with different fractions of marine sediments, namely a biogenic (bSi) fraction and residual 4M NaOH fraction (Si-NaOH(-bSi) not removed with 0.1M Na_2CO_3.

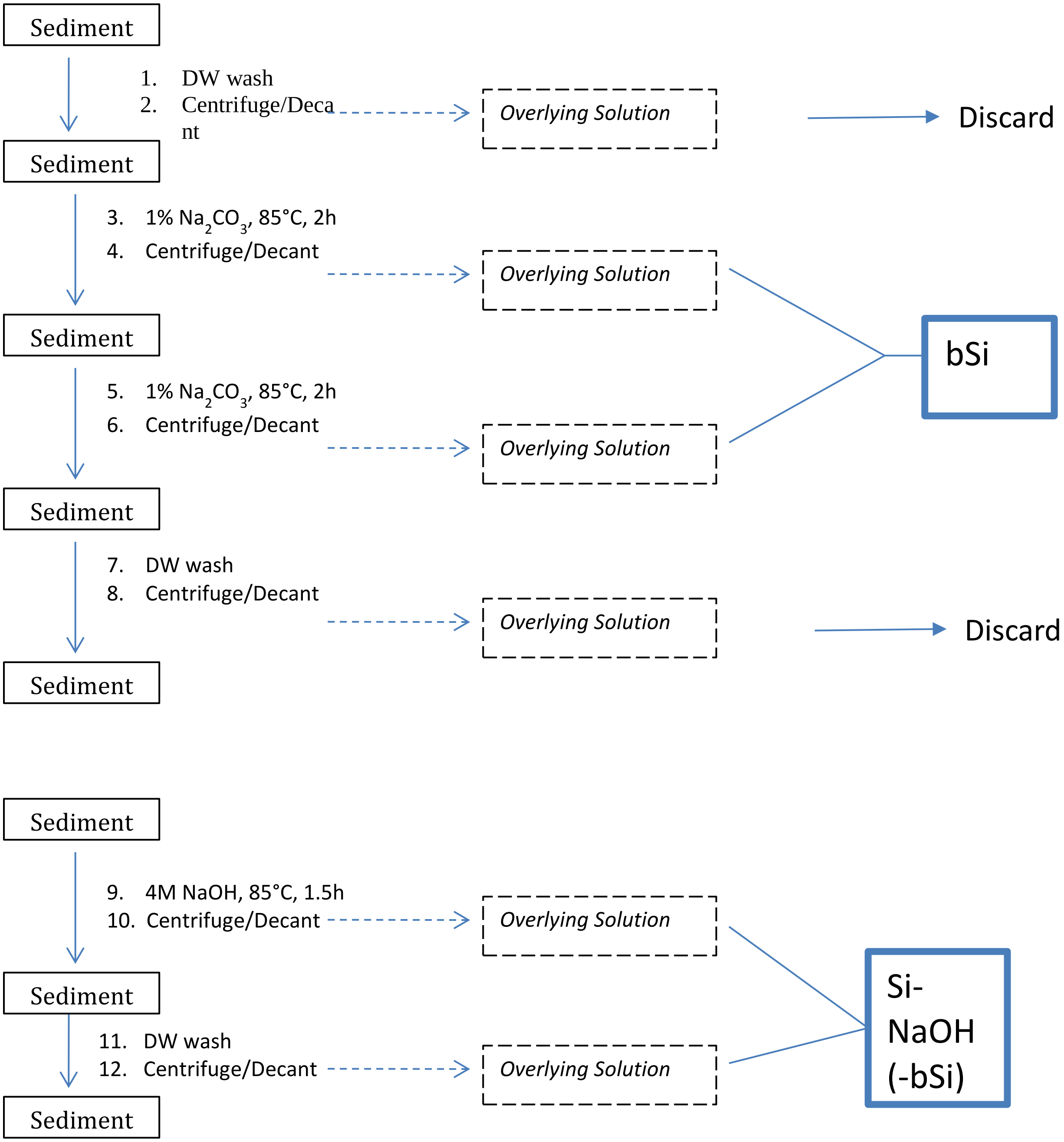


Figure 14. Leach scheme developed to extract ^{32}Si associated with different fractions of marine sediments, namely a biogenic and altered products ($\sum Si_{hr}$) fraction and residual 4M NaOH (Si-NaOH($-\sum Si_{hr}$)) not removed with 0.1N HCl or 0.1M Na_2CO_3(1% Na_2CO_3).

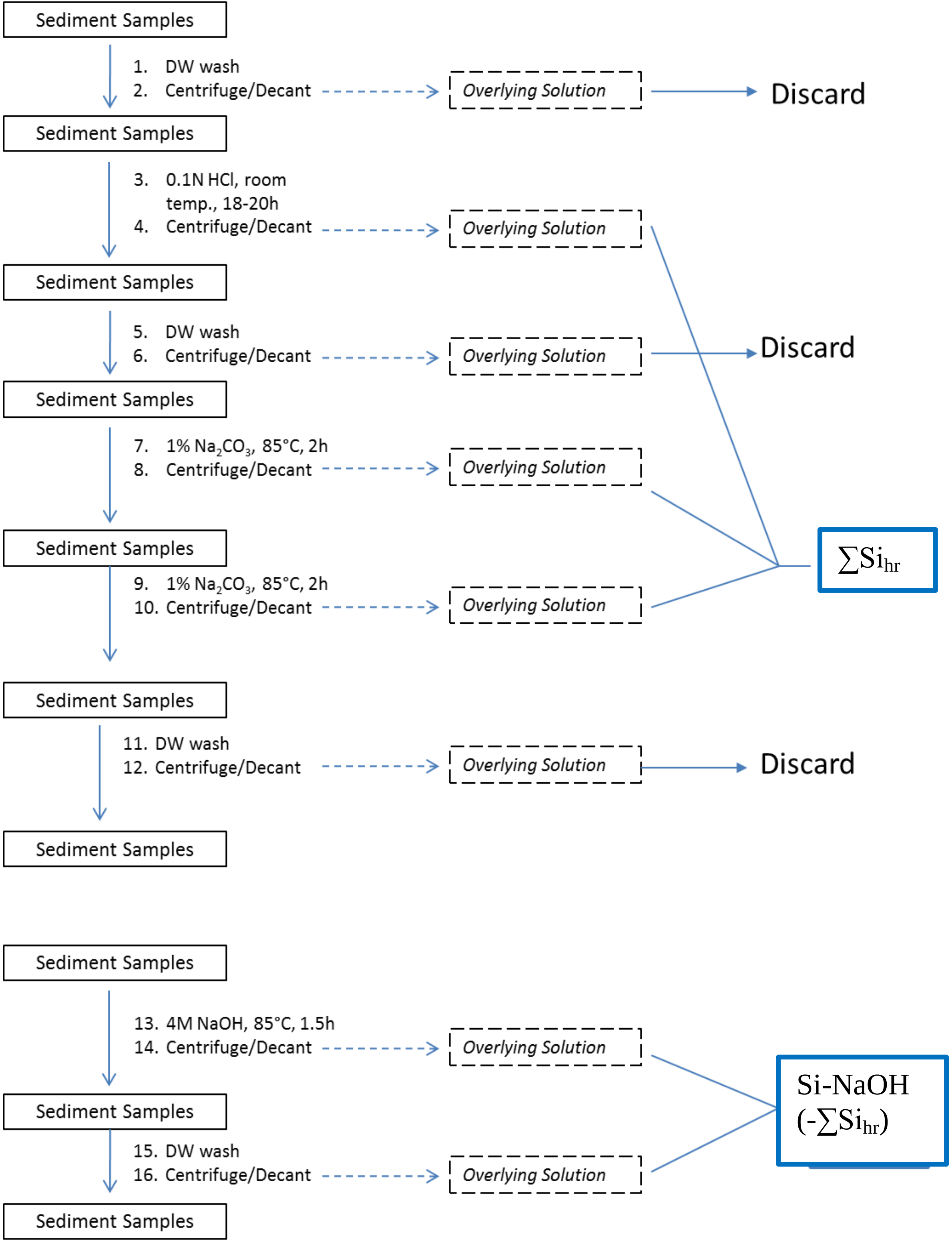


Table 10.: Biogenic (bSi) and $\sum Si_{hr}$ contents of sites in this study, and the corresponding modified sediment mass to 0.1N HCl or 0.1M Na_2CO_3 solution volumes used to extract ^{32}Si from these operational pools.

	bSi content (µmol/g)	$\sum Si_{hr}$ content* (µmol/g)	bSi sediment to solution ratios	$\sum Si_{hr}$ sediment to solution ratios
Amazon River Mouth	17 – 25	50 – 68	1:38	1:38
Sinnamary, French Guiana	8 – 35	200 – 350	1:38	1:38
Kourou, French Guiana	40 – 80	230 - 300	1:38	1:38
Macouria, French Guaina	35	200	1:38	1:38
Smithtown Bay, Long Island Sound	400	900	1:60	1:145
Louisiana Shelf, Gulf of Mexico	350	410	1:67	1:85
Gulf of Papua, Papua New Guinea	90	350	1:38	1:38

*$\sum Si_{hr}$ = Si-HCl + Si-Alk

Chapter 3: Amazon – Guianas Dispersal System

Abstract

Measurements of natural cosmogenic ^{32}Si ($t_{1/2}$ ~ 140 y) in tropical deltaic sediments demonstrate for the first time that most ^{32}Si is present in rapidly formed authigenic clays and not biogenic opaline silica (bSi). The burial of bSi in deltaic and continental margin sediments has likely been greatly underestimated because of diagenetic alteration of bSi to clay, little of which dissolves in the classically used operational bSi leach. Rapid reverse weathering reactions during early diagenesis must be considered as a significant pathway of reactive Si storage in deltaic deposits. Based on ^{32}Si, actual storage may be 2 – 3× the best recent estimates extrapolated from diagenetic models or attempts to modify bSi methods to include authigenic clay. Measurements of natural ^{32}Si inventories in sediments and initial specific activities in biogenic silica provide a means to independently constrain the marine Si cycle.

Introduction

Silica is an essential nutrient and an important control on primary production patterns, the biological pump, and C cycling in the oceans. Over the past few decades, one of the major changes in our understanding of the modern marine Si cycle has been the progressive recognition that continental shelves and margins are more significant global sinks for biogenic SiO_2 than previously believed, perhaps rivaling or exceeding the Southern Ocean diatomaceous sediment belt (DeMaster, 1981; DeMaster, 2002; Tréguer et al., 1995; Ragueneau et al., 2000; Laruelle et al., 2009; Tréguer and De La Rocha, 2013). There is growing evidence that a significant pathway by which biogenic silica is trapped along continental margins is through rapid reverse weathering reactions and storage of diagenetically altered biogenic Si in the form of authigenic clays, particularly in tropical regions where the greatest sediment inputs to the ocean occur (Ragueneau et al., 2000; Laruelle et al., 2009; Tréguer and De La Rocha, 2013; Mackin and

Aller, 1986; Rude and Aller, 1994; Michalopoulos and Aller, 1995; Michalopoulos and Aller, 2004). The magnitude of this additional pathway of biogenic Si burial is very difficult to quantify because of the large background of lithogenic clay debris supplied to the continental margins, and thus it is not yet widely accepted as a significant sink for Si. An independent characterization of possible Si sinks such as authigenic clay would be a critical constraint on Si budgets because these budgets traditionally have been calculated assuming the Si cycle is in steady-state in order to obtain balance. Here we utilize the natural cosmogenic radionuclide ^{32}Si in a novel application to confirm the extensive rapid formation of authigenic clay in tropical deltaic deposits, and also to demonstrate that ^{32}Si provides an independent means by which to quantify the global magnitude of biogenic silica burial in both altered and unaltered forms.

The total dissolved silica flux to the world ocean is believed to be ~10.9 Tmol/yr (Tmol = 10^{12} mol) the majority of which, ~57% (~ 6.2 Tmol/y) is supplied by rivers (DeMaster, 2002; Tréguer et al., 1995; Tréguer and De La Rocha, 2013). Groundwater discharge of dissolved Si, riverine biogenic silica supply (particulate), atmospheric inputs, basalt weathering, and hydrothermal sources comprise the remainder (Laruelle et al., 2009; Tréguer and De La Rocha, 2013; Dürr et al., 2011). Of the riverine dissolved silica supply, ~74% originates from tropical regions (Tréguer et al., 1995). In marine environments, most biologically precipitated Si is rapidly dissolved and recycled in both the water column and sediments, with only a few percent of the water column export flux in the open ocean eventually buried. The single largest sedimentary sink for biogenic silica has historically been recognized as the siliceous ooze deposits in the Southern Ocean surrounding Antarctica. Burial in the Southern Ocean was initially estimated to be ~ 4.1 – 4.8 Tmol/y (DeMaster, 2002) but more recent estimates have trended progressively downward to ~ 2 - 3.1 Tmol/y as sedimentation models have improved (DeMaster, 2002; Tréguer and De La Rocha, 2013; Chase et al., 2015). Revised global budgets, which are still poorly constrained, attribute greater Si burial to the continental margins. Authigenic clay burial in estuarine, shelf, and deltaic environments may account for ~1 – 1.5 Tmol/y of the coastal Si sink, perhaps comparable to the Southern Ocean, but these extrapolated estimates are derived from diagenetic models or bSi methods modified to include labile altered forms, and remain uncertain (Laruelle et al., 2009; Tréguer and De La Rocha, 2013).

The original concept that authigenic clay might be an important component of elemental cycling and alkalinity balances in the oceans was proposed in 1966 by F. MacKenzie and R. Garrels (1966), who hypothesized a general reaction of the form:

$$\text{X-ray amorphous-Al-silicate (reactive Al(OH)}_3\text{)} + HCO_3^- + SiO_2 + \text{cations} = \text{cation Al silicate} + CO_2 + H_2O$$

These types of reactions, which encompass reconstitution and neoformation of clays, were termed “reverse weathering” reactions due to the net consumption of alkalinity and cations, and concomitant release of CO_2. Such reactions contrast with weathering reactions on land or sea whereby CO_2 is consumed and alkalinity and cations produced (MacKenzie and Garrels, 1966) . Mackenzie and Garrels further suggested that because illite, montmorillonite, and chlorite form the majority of clay mineral phases in ancient and present-day marine sediments, then K^+, Na^+, Mg^{++} , and other cations in seawater likely react to form similar cation-rich Al silicates. At the time, they had few data and field observations to support their hypothesis. The subsequent discovery of hydrothermal vents demonstrated an even greater complexity of processes governing sources and sinks for a wide range of elements in the oceans, and low temperature reverse weathering reactions were deemed by most investigators as not only unsubstantiated but unnecessary for balancing elemental cycles and therefore unlikely. Although the widely recognized occurrence of authigenic clays such as the green glauconitic clays in shelf sands and deep-sea smectite deposits confirmed the potential process of reverse weathering, such minerals were assumed to be formed very slowly (e.g., > 10,000 yrs) and in insufficient magnitude to significantly impact marine elemental cycling relative to alternative reactions. The revelation that authigenic clay formation could take place very rapidly (< 1 yr) as disseminated phases in at least a subset of major marine deltaic depocenters (Mackin and Aller, 1986; Rude and Aller, 1994; Michalopoulos and Aller, 2004; Mackin and Aller, 1984) has refocused attention on reverse weathering as a possible significant reaction pathway in the ocean but, as noted previously, the magnitude and generality of the process remain to be accurately constrained globally. We demonstrate here, for the first time, that natural ^{32}Si can provide these constraints.

We focused our initial analytical efforts on deposits derived from the Amazon River delta where both diagenetic models of pore water and sediment composition, and experimental laboratory measures of clay formation have implied significant reverse weathering reactions (Michalopoulos and Aller, 2004). The Amazon River supplies ~6 – 7% of total global riverine input of suspended sediment, of which more than half is retained on the prograding subaqueous delta Kuehl et al., 1986; Milliman and Farnsworth, 2011). Table 11 summarizes key parameters of the rivers which contribute dissolved and amorphous Si to the study sites, as well as the major fluxes of dissolved and amorphous Si to the ocean. The Amazon River delivers 90% or more of the dissolved and amorphous Si load to our study region. About 15 – 20% of the Amazon outfall, comparable in magnitude to the annual sediment load delivered by the Mississippi River to the Gulf of Mexico, is initially trapped near Cabo Cassipore and Cabo Orange in Amapa, ~300km north of the Amazon River mouth, and moves northwestward towards the Orinoco River along the coast of Brazil and the Guianas as ~20 – 25 massive 5 – 10m thick mobile mud banks that migrate at a rate of 1 – 3 km/yr over relict mud deposits and typically extend 10’s of km along and offshore (Eisma et al., 1991; Allison et al., 1995; Allison et al., 2000; Anthony et al., 2010). Guyanese soils have different composition from these muds, which are effectively the same as Amazon River sediments (Eisma and van der Marel, 1971): ~20 – 40% expandable smectite, kaolinite, illite, quartz and small amounts of iron minerals, chlorite and feldspar (Mackin and Aller, 1986; Allison et al., 1995). Along Amapá during the late 1980s – mid 1990s, mudbank sediment were rapidly deposited from fluid mud suspensions between January and June (excess ^{234}Th activities were present past 25cm depth and X-radiographs indicated little biological mixing) and remobilized and advected to the northwest between July and December (Allison et al., 1995). The initial deposition formed a thick seasonal surface layer, as evidenced by uniform ^{210}Pb activities of 1.8 – 2.5 dpm/g down to 40 – 120cm. The mobile layer was absent during latter portions of the year as mud transited northward. In the mudbank deposits along Amapá, the activities of ^{7}Be and ^{137}Cs were too low to be used as independent proxies for sediment accumulation or mixing consistent with the large mass of remobilized material (Allison et al., 1995).

Diagenetic conditions in mudbank sediments are comparable to those in the proximal Amazon delta. Extensive Fe and metal cycling during suboxic remineralization of C, influx of Al oxide – rich materials, lack of net sulfate reduction, and a large supply of biogenic Si to sediments from enhanced primary production in this region establish conditions in both the delta and mudbank deposits where significant formation of Fe-rich authigenic clays may occur (Aller et al., 2004). Despite high primary productivity by diatoms and mangroves along this entire coastal system, only small quantities of biogenic Si (~0.2 wt % SiO_2; ~33 µmol Si/g dry wt) have been observed throughout the Amazon – Guianas mudbelt (Michalopoulos and Aller, 2004; DeMaster et al., 1983) based on classic mild alkaline biogenic silica operational leaches. When using a 2 – step leach designed to remove metal oxide coatings which commonly form on diatom frustules in Amazon Delta deposits and activate frustule surfaces for dissolution, (a 0.1N HCl pre – treatment leach followed by a mild alkaline leach), highly reactive Si contents were estimated in >50 topset sediment samples and were on average 8 – fold higher (~1.8 wt % SiO_2) than biogenic Si estimates (Michalopoulos and Aller, 2004). Aluminum and Fe – oxyhydroxide coatings also form on particles in the Orinoco delta (Eisma et al., 1978). Diatom frustules can rapidly, in 12 – 36 months, become highly altered (e.g. loss of microarchitecture, fragmented frustules) in these sediments and replaced with aluminosilicate materials or filled with framboidal pyrite (Michalopoulos et al., 2000; Michalopoulos and Aller, 2004). A portion of the highly altered diatoms or reconstituted biogenic silica do not dissolve in the two – step acid – alkaline leach or the one – step alkaline leach , so that estimates of reactive Si content are thought to be conservative estimates of total buried bSi (bSi + altered bSi) (Michalopoulos and Aller, 2004). Reactive Si contents retrieved in the acid – alkaline combination leach increases steadily, up to ~4 – 5X, laterally from the river mouth across the deltaic dispersal system. The concentration of K^+ in leachates also increases in direct proportion with the quantity of reactive Si. Solute fluxes of K, F, and Al in porewaters of mobile mud zones indicate progressive neoformation of K – and Fe – rich aluminosilicates (Michalopoulos and Aller, 1995; Michalopoulos and Aller, 2004).

Site Description

In the present study, we utilized for analysis sediment samples from the upper 10 cm of migrating coastal mudbank deposits, which at the time of sampling (2012, 2013) were located near the towns of Macouria and Sinnamary along the coast of French Guiana (Figure 15, (Anthony et al., 2014)). The samples were collected from different facies of the mudbank deposits, including highly mobile mud and mangrove fringe mud flats. A sample from Kourou, collected in 2009, and a sample from the Amazon River mouth, collected in 2014, were also analyzed to characterize initial input to the dispersal system.

The majority of the samples (Kourou, Macouria, Sinnamary 1 and 2) were from subtidal mobile mudbanks 2 – 4km offshore on the inner shelf (<5m isobath). Fluid mud suspensions (10 – 400 g/l) and mobile muds overlie relict deposits at these sites. Surface waters rapidly turn green upon exposure to sunlight, indicative of high primary productivity. Three samples (stations Sinnamary 3 – 5, MI AA, MI E, and MI H) were taken from different facies on the westward flank of an intertidal accreting mangrove island approximately 1 km long and 0.5km wide, located ~1.5km northwest of the mouth of the Sinnamary river and ~1 – 2 km offshore. Site "MI H" was located on the shoreward facing side of the island in a grove of the tallest young mangroves (~3 – 5m height). Sediment from this site rapidly becomes desiccated and covered with dark green algal mats upon aerial exposure, and was the most consolidated of all the sites. Mangrove rhizosheres likely impact diagenetic processes. Site "MI E" was located in the approximate center of the island, where juvenile pioneering mangroves a few centimeters tall were colonizing the facies. A thin layer of brown mud (mm – thick) immediately overlay sediment which was dark.brown or black. Within 1 – 6 hours of exposure, the surface of this site became more consolidated and covered with green algae, some forming mats a few millimeters thick. The shore facie base of the island, site "MI AA", had the least consolidated mud and showed no signs of mangrove growth the year the samples were collected. Within one year of sample collection, this island was unreachable by small craft due to net upwards sediment accretion on the island and the main channel that gave access to the island. Representative sites which are comparable to our study sites, but are not the actual sample sites, are depicted in Figure 15.

Cosmogenic ^{32}Si

The only natural source of ^{32}Si is via production in the atmosphere by cosmic ray spallation of ^{40}Ar (Lal et al., 1960; Fifield and Morgenstern, 2009). The ^{32}Si production rate, has been calculated as 0.72 atoms/m^2 s (Craig et al., 2000), and its half – life has been estimated as 144 ± 11 years (Fifield and Morgenstern, 2009). The atmospheric production and global deposition rate of ^{32}Si are presumed to be constant. On entering the ocean, ^{32}Si is taken up by siliceous organisms, largely diatoms (DeMaster, 1980; Fifield and Morgenstern, 2009), a portion is recycled in nutrient mode and a portion is eventually delivered to the seabed as biogenic opaline debris. The average ^{32}Si specific activity of dissolved Si in the surface Atlantic Ocean was determined to be ~4.5 dpm/kg SiO_2 (dpm = disintegrations /minute) (Craig et al., 2000), ranging from ~2.5 dpm/kg SiO_2 to 5 dpm/kg SiO_2. The average ^{32}Si specific activity of particulate Si in the surface Atlantic ocean was determined to be 40 dpm/kg SiO_2 (Craig et al., 2000; Somayajulu et al., 1987), ranging from 20 dpm/kg SiO_2 to 60 dpm/kg SiO_2. Other studies estimate the range of activities of ^{32}Si in biogenic silica to be ~5 – 15 dpm/kg SiO_2 (Lal et al., 1960; Kharkar et al., 1969; Lal et al., 1976; Somayajulu et al., 1991). Natural ^{32}Si has been proposed as a dating tool to constrain processes that occur over a time scale not captured by ^{210}Pb or ^{14}C (Lal et al., 1960; Fifield and Morgenstern, 2009). It has been used to determine sedimentation rates in the Ganges – Brahmaputra delta (Morgenstern et al., 2001) and glacier ice ages (Nijampurkar et al., 1985; Morgenstern et al., 2000). ^{32}Si generated from proton spallation of Vanadium was utilized as a tracer in studies of biogenic silica production in the Weddell – Scotia Seas (Tréguer et al., 1991).

The first major studies of natural ^{32}Si in sediments were carried out in laminated diatom-rich deposits of the Gulf of California by DeMaster (1980), and in the Southern Ocean by DeMaster and Cochran (1982), with a primary goal of constraining its half-life and utilizing it in conjunction with excess ^{210}Pb profiles to determine particle mixing rates. A significant assumption was that all sedimentary ^{32}Si was incorporated into biogenic silica, and a substantial effort was made to develop an analytical scheme to exclude contaminating lithogenic clays from any estimates of reactive opaline Si and thus ^{32}Si carrier budgets. ^{32}Si activities measured in large bulk sediment samples (> kg) were assigned entirely to quantities of biogenic silica independently measured on small subsamples (25 – 100 mg). This assumption and analytical scheme, which do not compromise application of ^{32}Si as a method to determine sediment accumulation, were continued in later studies by Morgenstern et al. (2001); Suckow et al. (2001); and Morgenstern et al. (2013). Since DeMaster’s pioneering studies of ^{32}Si in sediments, it has become clear that authigenic clay formation can be a significant pathway of biogenic Si diagenesis in both deep-sea deposits (Sayles and Bischoff, 1973; Hurd, 1973; Hein et al., 1979; Cole, 1985; Cuadros et al., 2011) and, most importantly, high accumulation rate deltaic systems, which are the dominant sediment depocenters on Earth (Mackin and Aller, 1986; Michalopoulos et al., 2000; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). We decided to directly test the assumption that ^{32}Si was associated entirely with biogenic Si and by doing so; to evaluate previous estimates of authigenic clay formation derived from diagenetic models and laboratory experiments. We reasoned that if conversion of biogenic Si to authigenic clay were rapid and significant in magnitude, then a substantial portion of natural ^{32}Si activity should be found not only in residual biogenic Si but also in clays. Furthermore, if it were found in clays or other diagenetically altered products of siliceous debris, the distribution of natural ^{32}Si inventories would provide a means to better constrain the global burial of biogenic Si and thus the global marine Si cycle.

Methods

A major difficulty in analyzing sediments for natural ^{32}Si within different mineral pools such as biogenic Si, is to scale operational analytical techniques up from small (25 -50 mg) to large samples (> kg) required for radiochemical detection (AMS analysis of ^{32}Si is not possible because of the large Si background in sediments (Fifield and Morgenstern, 2009). Solution – sediment ratios must be adjusted to maintain solution volumes within practical laboratory limits while reproducing the same fractional mass proportions of biogenic Si obtained across all analytical modifications. We developed an optimal procedure for large samples that minimizes solution volume and reproduces operational pool fractions obtained from traditional methods for small samples. A series of sequential extractions were performed on 0.5 - 2 kg mudbank samples. These extractions were modified from existing methods to, first, remove the biogenic silica (bSi) fraction using 0.1 M (1%) Na_2CO_3 (the method most commonly used to estimate biogenic Si content) and, second, to remove any remaining crystalline Si phases with which ^{32}Si might be associated using a hot 4M NaOH solution (DeMaster, 1979; DeMaster, 1980). The latter treatment extracts reactive clays and to some extent, lithogenic clays.

Sediment samples from French Guiana mudbanks typically have a bSi fraction of 40 - 60 μmol/g, as defined by the classic biogenic silica leach developed by DeMaster (1979, 1980). It is critical to recognize that the global sedimentary Si budget is largely based on this widely used classic operational leach. Given the low activity of ^{32}Si in biogenic Si (opal), large masses of sediment (0.5 - 2kg dry weight) must be processed in order to extract sufficient SiO_2 and yield detectable ^{32}Si activities. The sediment to solution ratios in the classic bSi leach are 1g to 1 - 2L 0.1 M Na_2CO_3. Using this same ratio for 0.5 - 2kg of sediment would yield a minimum of 500 - 2000L of solution. Instead, the volume of 0.1 M Na_2CO_3 was reduced such that the sediment to volume ratios were 1g : 40ml for sediments from the Amazon - Guianas mudbelts (further details can be found in Chapter 2). Briefly, sediment samples at dry weight to solution volumes of 1g to ~40ml were leached two times with 1g:40ml of 1% Na_2CO_3 for 2 hours apiece in water baths set at 85-90°C to remove the bSi phase ("bSi" fraction). The sum of the Si fractions in these leaches total 40 - 60 µmol/g . The leaches were combined, acidified, and evaporated (boiled) to yield SiO_2, which was then purified and stored according to DeMaster (1979). Following the two, 2h-long extractions with 1% Na_2CO_3, the residual sediment was rinsed with distilled water. The rinse was discarded. The sample was then leached with 4M NaOH for 1.5 - 2h in a water bath set at 85 - 90°C at a sediment to solution ratio of 1g:12ml to remove the residual poorly crystalline Si phases ("Si-NaOH(-bSi)" fraction). The NaOH leachate was collected and the sediment was given a final rinse with distilled water, which was also collected and combined with the 4M NaOH solution. This strong alkaline leach and distilled water wash were also acidified and boiled down to yield SiO_2, which was purified and stored (DeMaster, 1979). Please note that these sediment to solution ratios were optimized for samples from French Guiana and will need to be modified for sediments from different sites with different bSi contents and characteristics. The amounts of Si extracted from four standard clays (kaolinite, illite, montmorillonite, halloysite) were also investigated at these modified sediment to solution ratios (1g:40ml) to approximate extractable silica from background lithogenic clays at our study sites. Relatively small amounts of Si were removed from the pure clay phases.

In the two – step $\sum Si_{hr}$ leach (Si – HCl → Si – Alk), sediment samples are first extracted with mild 0.1N HCl over ~20h to remove metal coatings and Si associated with these coatings which may form on frustules and then extracted with 1% Na_2CO_3 using the same sediment mass to solution volume ratios as in the classic bSi leach (hereby referred to as the classic $\sum Si_{hr}$ leach). This leach was modified to extract ^{32}Si, detailed in Chapter 2. Briefly, sediment samples were pretreated overnight (~18 – 22h) at room temperature with 0.1N HCl at dry weight to solution volume ratios of 1g to ~40ml. The mixture was centrifuged and the solution decanted before addition of 1% Na_2CO_3. The sediment sample was then leached sequentially two times at 2 hours apiece in hot water baths set at 85-90°C at the same dry weight to solution volumes. The two aliquots of 1% Na_2CO_3 were isolated and combined with the 0.1N HCl fraction to give an estimate of $\sum Si_{hr}$. The leaches were combined, acidified, and evaporated (boiled) to yield SiO_2, which was then purified and stored. The sum of these combined fractions yield at least 70% of the Si as would be removed if classic sediment mass to solution volumes were used. Following the two 2h-long extractions with 1% Na_2CO_3, the residual sediment was rinsed with distilled water and the rinse was discarded. The sediment was retained for further extraction using 4M NaOH for 1.5 – 2h in a water bath set at 85 - 90°C at a sediment to solution ratio of 1g:12ml to remove the residual poorly crystalline Si phases ("Si-NaOH(-$\sum Si_{hr}$)" fraction). Please note that these sediment to solution ratios were optimized for samples from French Guiana and may need to be modified for sediments from different sites with different $\sum Si_{hr}$ contents and characteristics. The amounts of Si extracted from four standard clays (kaolinite, illite, montmorillonite, halloysite) were also investigated at these modified sediment to solution ratios (1g:40ml) in this two – step leach process. Relatively small amounts of Si were extracted from the pure clay phases.

Purified SiO_2 samples were stored for 3 - 4 months after which they were milked for ^{32}P, the daughter product of ^{32}Si. During storage, ^{32}P, which has a half - life of 14.3 days, reaches secular equilibrium with ^{32}Si and once isolated, its decay can be tracked via beta counting. Following multiple purification steps, samples were β-counted on low background counters over the course of 3 - 6 weeks to confirm the decay of ^{32}P and estimate the initial activity of ^{32}Si in each sample. The counting efficiency of ^{32}P in this particular geometry was 25% (Chapter 2). After activities of the samples had decayed to background, the solid precipitates were weighed to determine percent yields. The initial activities of ^{32}Si ranged from 1 dpm to 2 dpm, and decay patterns were those expected for daughter ^{32}P (Figs. 2 – 7).

Counting Efficiency

The counting efficiency of P-32 on the gas – flow RiSO counters that were used to count our samples was determined using a 1mCi stock standard of P-32 as disodium phosphate obtained from Perkin – Elmer. Ten microliters of the diluted stock ^{32}P standard was added to two 0.700ml aliquots of a 0.4M stable phosphorus carrier solution, such that the activity of ^{32}P in solution was 2.775 dpm. Then 20ml of magnesia reagent and 25ml of concentration ammonium hydroxide was added to each ^{32}P spiked aliquots of stable phosphorus carrier to precipitate magnesium ammonium phosphate. The magnesium ammonium phosphate was collected on a filter and dried at ~40 – 50 °C before being mounted and put on the beta counters. These two spiked standard replicates wee in the sample geometry as our actual samples. The counting efficiency was calculated as follows:

$$\mathrm{EFF}_{32P} = (\mathrm{CPM}_{32P}/(\%\ \mathrm{yield}))\ /\ \mathrm{DPM}_{32P} \qquad (1)$$

where EFF_{32P} is the calculated counting efficiency, CPM_{32P} is the detected initial activity of the spiked matrix – matched standards as determined by the decay curve shown in Figure 22, *% yield* is the percent yield of the precipitated spiked standard (average % yield of the 2 replicates was 97 ± 2%), and DPM_{32P} is the actual ^{32}P activity that was added to the stable P carrier, in this case 2.775 dpm. Taking into account the detected initial activity of ^{32}P spiked standards and the % yields, the calculated counting efficiency was 24.8 ± 0.4%.

Results

Results were obtained from samples at 7 mudbank sites off French Guiana and at a river bank deposit near the mouth of the Amazon River (Figure 19). ^{32}Si activities in the bSi fractions were in three cases indistinguishable from background, which was stable at 0.19 ± 0.01 CPM (cpm = counts / minute) and the ^{32}Si activities in the bSi pools at all other stations were assumed to also be at or below background. In contrast, following the removal of bSi, there was detectable ^{32}Si activity in the residual Si-NaOH(-bSi) pools (bSi $\rightarrow$ Si-NaOH) extracted by 4M NaOH (Figures 16 – 19), consistent with essentially all ^{32}Si having been transferred to the operationally defined reactive clay fraction. The estimated ^{32}Si specific activities for these sites are presented in Table 13. Further, at two sites on the transient mangrove island off the coast of Sinnamary, there was detectable activity in both the $\sum\mathrm{Si}_{hr}$ and Si-NaOH(-$\sum\mathrm{Si}_{hr}$) fractions (Figures 20 – 21). There was also detectable activity in the residual Si-NaOH(-$\sum\mathrm{Si}_{hr}$) fraction in the Amazon River mouth sample (Figure 19). The low activity at Sinnamary 5 (MI H) may be due to an analytical error, namely that enough sediment may not have been processed to extract adequate SiO_2 to return activities much above background count rates.

Discussion

Estimating ^{32}Si specific activity

One perspective for interpretation is to assume that all measured ^{32}Si in the Si-NaOH(-bSi) fraction is attributable entirely to the silica extracted in the classic biogenic silica leach, that is, ~20 – 40 µmol Si/g sediment (Tables 2 and 3). The required ^{32}Si activity of starting material (e.g. diatom SiO_2) would then range from 300 – 2200 dpm/kg SiO_2, far greater (~5 – 100x) than any Atlantic Ocean measurements reported for dissolved or planktonic SiO_2 in the Atlantic Ocean (Somayajulu et al., 1987; Craig et al., 2000) or typical planktonic values of 5 – 15 dpm/kg SiO_2 (0.3 – 0.9 dpm/mol Si) summarized by Fifield and Morgenstern (2009). If, however, it is assumed that the ^{32}Si activity is derived from the operational reactive Si, or ∑Si, pool extracted in a 2 – step leach designed to approximate combined bSi and poorly crystalline or labile authigenic clay, as outlined in Michalopoulos and Aller (2004), then the estimate of ^{32}Si activity in a precursor bSi source ranges between 15 – 300 dpm/kg SiO_2 (average 110 dpm/kg SiO_2) which is more in line with, but still substantially higher than reported specific activities of Atlantic Ocean SiO_2.

At two sites, Sinnamary3 and Sinnamary 5 (Table 12), on a transient mangrove island, the $\sum Si_{hr}$ sequential extraction was utilized. Unlike the bSi extractions, there was detectable ^{32}Si activity in the $\sum Si_{hr}$ fraction, 0.17 ± 0.04 dpm/kg and 0.25 ± 0.03 dpm/kg, (Figures 20 – 21). At these same sites, the activities in the Si-NaOH(-$\sum Si_{hr}$) fractions were 0.22 ± 0.08 dpm/kg and 0.34 ± 0.07 dpm/kg, respectively (the maximum SiO_2 extracted in the bSi fractions was <5g, which was too small a mass to show any detectable activity). These results suggest that the $\sum Si_{hr}$ removes about 40 – 45% of the total ^{32}Si in these sequential extractions, unlike the bSi leach which appears to miss virtually all of the ^{32}Si, indicating that the Si storage in this area is at least two times higher than prior estimates.

If the initial specific activity of source bSi were known, the measured ^{32}Si activities in the Si-NaOH(-bSi) fractions could be used to calculate the total reactive Si content of these deposits and also to infer the quantity of authigenic clay. The Kourou site has a high bulk activity and is not included in the following calculations, which in turn may be considered conservative estimates. We estimate the likely range of initial activities of source SiO_2 in three ways (Table 14). The first assumes that particulate biogenic SiO_2 in the Amazon delta has the specific activity measured in plankton throughout the surface Atlantic Ocean: 40 dpm/kg (Craig et al., 2000; Somayajulu et al., 1987). In this case, not accounting for decay of ^{32}Si, total reactive Si incorporated into French Guiana deposits, must be at least 120 – 700 µmol Si/g sediment (average 340 µmol Si/g), or 1 – 4 wt % SiO_2 (average 2 wt %). A second approach is to use measurements of ^{32}Si activities in low latitude rivers and oceanic end- members presumed comparable to our study region. Nijampurkar et al. (1966) report ^{32}Si activities in Indian rivers of 0.08 dpm/m^3 near river mouths, leading to an estimated particulate ^{32}Si activity of ~9 dpm/kg SiO_2 in the Amazon (assuming a dissolved Si concentration of ~144 µmol/L (DeMaster and Pope, 1996), whereas, measured particulate activities in the open *equatorial* Atlantic Ocean range from 9 to 18 dpm/kg SiO_2 (Somayajulu et al., 1987). Therefore, assuming an average specific activity of starting material of 15 dpm/kg SiO_2, estimated total reactive Si is ~300 – 2000 µmol Si/g (average 900 µmol Si/g, or ~ 5 wt% SiO_2). The third approach is based on the observation that the ^{32}Si specific activity of siliceous sponges varies inversely as a function of the dissolved Si concentration of the water in which the sponges grew (Lal et al., 1976; Figure 23), where sponges from the Antarctic Ocean were the low activity end member with average ^{32}Si activities ~6 dpm/kg SiO_2, and the highest dissolved Si concentrations, ~ 30 – 70 µmol/L. On the basis of Amazon River dissolved [Si] concentrations (~144 µmol/L (DeMaster and Pope, 1996)), Amazon shelf waters could have a sediment ^{32}Si/Si activity lower than the Antarctic sponges, and up to ~10X lower than particulate matter in the open Atlantic, in the range of ~ 5 dpm/kg (similar to the estimated initial activity of sediment deposited in the Bay of Bengal (Morgenstern et al., 2001). In this case, the estimated reactive Si storage in mudbank deposits mudbelts would increase to 900 – 5700µmol Si/g sediment (average 2700 µmol Si/g sediment, or 16 wt % SiO_2). The lowest of these various estimates of Si content of biogenic origin in this region (2%) is comparable to estimates of Si associated with the authigenic clay content (~ 1.8% SiO_2) inferred from diagenetic models and operational extractions of Amazon Delta topset deposits, the source of French Guiana mudbank sediment (Michalopoulos and Aller, 2004), whereas the highest is 8 times greater. A comparison of silica storage estimates using the classic bSi and ∑Si operational leaches compared to using 32Si activities is presented in Figure 24.

The activities in the $\sum Si_{hr}$ extractions at sites Sinnamary 3 and 5 range from 70 – 800 µmol Si/g in the $\sum Si_{hr}$ fraction and 90 – 1100 µmol Si/g in the Si-NaOH(-$\sum Si_{hr}$) fractions. The estimates of Si storage from the bSi sequential extractions are higher than those from the $\sum Si_{hr}$

extractions (Si – HCl → Si – Alk → Si – NaOH) at site Sinnamary 3. At this site, collected near pioneering mangroves on the transient island, enough sediment mass may not have been processed for the $\sum Si_{hr}$ sequential extractions.

These various estimates are most likely conservative lower limit estimates of total silica storage in the system, because, as noted, they assume no decay of ^{32}Si from initial specific activity values. For example, if the ^{32}Si in the Guiana mudbank sediment represents a mixture of neoformed clays from fresh material as well as reworked older material, then the estimates of Si storage would be greater. On the other hand, estimates of marine-derived Si storage could be overestimates if the material delivered by the Amazon River has substantial soil generated authigenic clay and is transported to the Guianas in less than ~ 100 – 200 years. Given the half – life of ^{32}Si and the likely residence times of sediment in the delta topset plus estimated transit times of this material (1 – 3 km/y) from the mouth of the Amazon River to French Guiana (Kuehl et al., 1986; Anthony et al., 2010), to attribute the detected ^{32}Si activity mostly to pedogenic authigenic clays would imply fresh starting material with activities much higher than has been reported in regions with high concentrations of background stable Si (Lal et al., 1976) or than we measured near the mouth (Table 3). At migration rates of 1 – 3km/y, the transit time of delta topset material from Cabo Cassipore, near the southern Amapá coast, the start of the mudbanks, to the sites in this study ~300km away is between 100 to 300y, and any initial activity in this material would decay by 50 – 88% by the time it reaches Kourou or Sinnamary., or alternatively, activity at Kourou or Sinnamary would be 12 – 50% of initial activity at the Amazon River mouth. Froidefond et al. (1988) determined mudbank migration rates along French Guiana to be ~0.3 – 1.2 km/y, average 0.9 km/y, whereas Allison and Lee (2004) determined average velocities to be ~1.4km/y along this coastline, therefore a 50% decay in activity is most likely a conservative estimate. This estimate also does not take into account the transit time of the sediment from the Amazon River mouth to Cabo Cassipore. There are no significant inputs of sediment from small rivers along the transit path (Eisma and van der Marel, 1971; Anthony et al, 2010).

Sediment transport and Si storage

Of the 1200 million tons of sediment that is discharged annually by the Amazon River, about 20% moves northeastwards along the Guianas coastline towards the Orinocos River via tides, the North Brazil Current and waves generated by Trade Winds (Froidefond et al., 1988; Eisma et al., 1991). Of this 20% (~250 x 10^6 tons/y), anywhere from 100 to 200 million tons is transported in suspension, whereas the remainder is advected in the form of shore – attached mudwaves (Kineke et al., 1996). These mudbanks migrate up the coast at an average velocity of 1 – 1.5 km/y and have average lengths of 20 – 35km (Augustinus, 2004). Allison and Lee (2004) determined that the cycling of sediment between the outer mudbanks and the mangrove fringe, between sediments in suspension and in the mudbanks, is greater than or equal to ~250 x 10^6 tons/y, the average annual input of sediment from the Amazon to the Amazon – Guianas dispersal system.

Particles can also be transported to the study site via the Amazon River freshwater plume. The freshwater outflow of the Amazon River water flows northwestward along the Guianas coastline 20 – 50km offshore towards the Caribbean Sea between the months of February and May as a low – salinity lens that is 5 – 10m thick and anywhere from 80 – >200km wide (Muller – Karger et al., 1988; Lentz and Limeburner, 1995; Limeburner et al., 1995; Kineke et al., 1996). This near – surface Amazon plume is retroflected between the months of June to January into the North Equatorial countercurrent and moves eastwards into the North Atlantic (Muller – Karger et al., 1988; Limeburner et al., 1995). Kineke et al. (1996) estimated the mass of sediment transported by this freshwater plume was approximately 50 – 60 x 10^6 tons/y (~5% of the annual Amazon River sediment delivery) by assuming an average thickness of 5m, a width of 100km, an average along – plume velocity of 0.36m/s, and an average suspended sediment concentration of 0.01 g/l. These parameters were measured near Cabo Cassipore (Lentz, 1995; Kineke et al., 1996). During periods of high freshwater discharge (month of May), Kineke and Sternberg (1995) estimated less than 1% (~ 12 x 10^6 tons/y) of the total Amazon suspended load (1.2 x 10^9 tons/y) is within the low – salinity plume.

The ^{32}Si detected along the French Guiana coast could have been transported there in a matter of days in suspension by the low – salinity Amazon River plume, in which case the activity would not reflect biogenic silica storage but rather pedogenic clay content from the Amazon River. The freshwater plume would contribute sediment to the French Guiana region between the months of February and May when the flow is towards the Caribbean sea, resulting in a flux of ~ 5 x 10^6 tons/y up to ~20 – 25 x 10^6 tons/y (~40% of the total annual flux in the Amazon Plume, 12 – 60 x 10^6 tons/y, over 4 – 5 months). If sediment contribution from the low – salinity plume is the only fraction which contains any ^{32}Si activity and is ~5 – 25 x 10^6 tons/y during the months of February to May when the plume flows towards the Caribbean Sea, this would make up ~2 – 10% of the total annual flux from the Amazon River that moves up the Guyanas coastline (~250 x 10^6 tons/y), indicating that the ^{32}Si initial activity in the plume particles would need to be at 12 - 60X greater than the activity at the Amazon River mouth to account for the average ^{32}Si activity found at the study sites (~0.84 dpm/kg sediment). In other words, the bulk activity of the suspended sediment in the plume would need to be ~ 8 – 40 dpm/kg sediment (this would also imply that another ~8 – 40 dpm/kg sediment is advected into the North Atlantic during the months of June to January). Using the Ganges – Brahmaputra deltaic system as an analogue for the Amazon (Nijampurkar et al., 1966), currently the best estimate of ^{32}Si specific activity at the Amazon River mouth is ~8dpm/kg SiO_2, which would imply an unlikely Si content of particulate matter in the plume of ~100 – 500 wt % SiO_2. Furthermore, suspended matter concentrations decrease within the plume with increasing salinity and distance from the Amazon River mouth (Milliman and Boyle, 1975; Edmonds et al., 1981). Off the coast of French Guiana, these concentrations can range from 0.008 – 0.00005 g/L. Froidefond et al. (2002) also observed this low – salinity (salinity ~ 22) lens off the coast of French Guiana, which at the time was 5 – 8m thick and had average mineral particle concentrations of 0.002 – 0.004 g/l, parameters which would lead to lower average estimates of total annual sediment transported to the study region directly by this plume. Additionally, with its high nutrient concentrations, significant diatom blooms occur within this low – salinity plume after suspended detrital material settles out of the plume and transparency increases (Edmonds et al., 1981; Sholkovitz and Price, 1980). This marine biogenic debris gets transported in the brackish plume and further dilutes suspended matter of continental origin.

Using excess ^{210}Pb (range 400 – 3300 dpm/kg) , ^{7}Be (present only in some sites with activities of 10 – 660 dpm/kg), and ^{137}Cs (10 – 410 dpm/kg) profiles in sediment cores from several inner mudbank stations off the coast of Sinnamary, French Guiana, Allison and Lee (2004) determined sediment particles most likely take anywhere from several days to several thousand years to reach the French Guiana coast from the Amazon River mouth. They also determined that at least 250 x 10^6 tons of sediment is exchanged annually between the mangrove fringe (inner shore) and outer mudbanks and fluid muds in suspension, with the magnitude of exchange increasing with increasing distance from the Amazon river mouth.

In a detailed study of carbon remineralization (Aller and Blair, 2006), natural abundances of ^{13}C and ^{14}C in bulk sediment and net $\sum CO_2$ from the Amazon River mouth to French Guiana coupled with excess ^{210}Pb and ^{234}Th profiles in surface deposits, revealed that small quantities of fresh marine plankton are continuously entrained along the Amazon – Guianas dispersal system to ~1km from shore. Marine C_{org} in this region has a $\delta^{13}C$ isotopic composition of ~ – 19.5‰ (Showers and Angle, 1986), whereas Amazon River terrestrial C_{org} has a $\delta^{13}C$ isotopic composition of approximately – 28‰ (Hedges et al., 1986; Showers and Angle, 1986; Keil et al., 1997). Approximately 85 – 90% of terrestrial sedimentary Co_{rg} loading is lost ~600 – 700 km downdrift of the Amazon River mouth (Aller and Blair, 2006): initial terrestrial C_{org} load of 0.6 – 0.7 mg C m^{-2} decreases to ~0.07 – 0.09 mg C m^{-2} near Kourou and Sinnamary, French Guiana. Bulk sedimentary C_{org} in French Guiana mudbanks has average $\delta^{13}C$ and $\Delta^{14}C$ of – 24.7‰ and – 197‰ (bulk age ~ 1700 years), respectively, whereas the $\delta^{13}C$ isotopic composition of $\sum CO_2$ released during carbon remineralization is ~ – 19‰, net $\Delta^{14}C$ is ~ + 80‰ (Figure 9 in Aller and Blair, 2006). Isotopic mixing models of terrestrial and marine endmember $\delta^{13}C$ and $\Delta^{14}C$ compositions demonstrate that marine substrate contribution to remineralized $\sum CO_2$ of pore water increases from 55% in the proximal delta topset (~100km off river mouth) to 100% off the coast of Amapá and further to French Guiana, 400 km and 600 km downdrift of Amazon River mouth, respectively (Zhu et al. 2002; Aller and Blair, 2006). Other studies indicate that marine debris is incorporated throughout the Amazon – Guianas dispersal system. Showers and Angle (1986) observed marine organic carbon dominates composition in Amazon delta bottomset surface sediments and surface sediments >400km north of the Amazon River mouth and during periods of lowest Amazon river flow, marine derived POC comprised a significant portion, ~20%, of the particulate organic carbon pool near the river mouth (Druffel et al., 2005). In sediments off the coast of Macouria, French Guiana, total nitrogen (TN) content and total organic carbon (TOC) content, atomic TN:TOC ratios, as well as $\delta^{13}C$ and $\delta^{15}N$ of TOC, indicated that organic matter was composed primarily of suspended particulate matter ($\delta^{13}C$ ~ – 23.6‰), marine microphytobenthos, and C_3 terrestrial plants, with marine phytoplankton making up a significant portion of the suspended particulate matter (Gontharet et al., 2014). In the Kaw estuary, marine diatom species (*Coscinodiscus centralis*, *Cyclotella stylorum*, *Thalassionema nitzschioides*) dominated plankton assemblages in the fluid mudflats and estuarine channel of the Kaw River, as well as bordering mangrove swamps (Sylvestre et al., 2004).

The ^{32}Si activities likely trace the cumulative formation of marine authigenic clays and diagenesis along the coastal dispersal system from the Amazon Delta to the sampled region in French Guiana and not simply local processes. Given the highly dynamic and non – steady state nature of sediment accretion and erosion in this dispersal system over 100 year timescales (Anthony et al., 2014; Moore et al., 1996), we approximated the movement of sediment as a continuous stream of mobile mud moving from the Amazon to the Orinoco. A simple advection-reaction model (Figure 25) can be utilized to calculate Si incorporation rates along the mud stream using the ^{32}Si activities in the bulk sediment. Ignoring transient migrating mudbank facies along the system, which are exchanged on a timescale short with respect to shore perpendicular or vertical homogenization and lateral transport, if sediment is advecting at a velocity υ, and a constant Si alteration – incorporation rate, *R*, is maintained along the entire dispersal path, then the ^{32}Si activities can be described by the equations:

$$\frac{\partial C}{\partial t} = 0 = -\upsilon\frac{\partial C}{\partial x} - \lambda C + R$$

$$C = \left(C_0 - \frac{R}{\lambda}\right)e^{-\frac{\lambda x}{\upsilon}} + \frac{R}{\lambda}$$

where *C* is the ^{32}Si bulk activity, λ is the decay ^{32}Si decay constant, *R* is a constant ^{32}Si incorporation rate, and *x* is the distance along the system from a source concentration at $x = 0$, in this case the Amazon River. This model assumes that lateral migration and homogenization of sediment is rapid relative to shore perpendicular or local vertical gradients of ^{32}Si, consistent with ^{210}Pb and ^{234}Th distributions within mud banks and across the Amazon delta (Kuehl et al., 1986; Moore et al., 1996; Allison et al., 1995; Allison et al., 2000, Allison and Lee, 2004). The starting ^{32}Si bulk activity at $x = 0$ is $C_0 = 0.65$ dpm/kg sediment, determined from the sediment sample taken close to the mouth of the Amazon River near the base of mature mangroves (Table 3). The average ^{32}Si bulk activity of the Sinnamary and Macouria samples, 0.83 dpm/kg sediment (median 0.85 dpm/kg, standard deviation, 0.5 dpm/kg) was used to determine average R along a distance ~700 km from the source. An average mudwave velocity, *v*, of 1.5 km/yr was used, leading to an average incorporation rate, R, of ~0.004 dpm/kg/yr, or a constant addition rate of ~5 µmol Si/g/yr (assuming a 15 dpm/kg SiO_2 ^{32}Si activity of starting material, approximately the average of measured particulate activities of 9 to 18 dpm/kg SiO_2 in the open *equatorial* Atlantic Ocean (Somayajulu et al., 1987)). This incorporation rate would be higher if the Kourou sample was also included in the model. This addition rate implies a total accumulated authigenic clay content of ~2200 µmol Si/g (~13 wt % SiO_2)at 700 km from the Amazon River mouth (Figure 26, Table 15). A Si incorporation rate of 16 of µmol/g/yr was determined for the mobile mud layer in the Amazon delta, giving a total storage estimate of ~300 µmol/g (Michalopoulos and Aller, 2004). The Amazon delta rate applies to material buried in the proximal delta below the surface mobile layer. Our estimate is ~ 7× greater and applies to the ~15% of the Amazon load that moves along the coast to the Orinoco. We assume that by the time sediment arrives at the Orinoco delta, another 900 km downstream, the accumulated authigenic clay must roughly double from that present along French Guiana (e.g. 4400 µmol Si/g or ~26 wt % SiO_2). This interpretation of continuous accumulation of authigenic clay along the dispersal path is consistent with the progressive increase of K^+ and F^- contents of clay from the Amazon River to the Orinoco (Eisma et al., 1971; Rude and Aller, 1984; Michalopoulos and Aller, 2004). Assuming that the mean accumulation along the dispersal system is ~2000 µmol Si/g (0 at x = 0; 4000 at x = 1600 km) and that the flux of sediment in mudbanks along the coast is ~150 x 10^{12} g / yr (Allison et al., 1995), then the Amazon – Guianas mud stream consumes ~ 0.3 Tmol Si / yr. This quantity represents a ~20 -30% increase above the present best estimates of coastal Si sinks (Tréguer and De La Rocha, 2013). Taken together, the Si burial in the proximal Amazon Delta and diagenetic consumption along the Guianas coastline accounts for ~50%, or 0.4 Tmol/y, of the annual dissolved Si delivered to the global ocean by the Amazon River (~0.8 Tmol/y, Table 2). Other major coastal dispersal systems such as the Changjiang – East China Sea system, which supplies ~0.1 Tmol/y dissolved Si to the global ocean (Zhang et al., 2003; Ran et al., 2013), likely behave similarly (Yao et al., 2014). Taken together, ~0.4 – 0.5 Tmol/y of Si may be buried in these two dispersal systems alone, accounting for 30 – 50% of the coastal Si sink attributed to authigenic clay burial in estuarine, shelf and deltaic environments extrapolated from diagenetic models (Laruelle et al., 2009; Tréguer and De La Rocha, 2013).

Conclusions

The fundamental conclusions from these measurements are: (1) In Amazon – Guianas sediments, natural ^{32}Si is found predominantly in mineral pools other than the operational biogenic Si pool commonly used to constrain the sedimentary Si cycle. (2) The extraction of ^{32}Si and its activities relative to operational analyses of reactive Si pool are consistent with its dominant incorporation into rapidly formed authigenic clay. (3) Without correction for decay or dispersal system transport, the estimates of reactive Si storage based on ^{32}Si are in the general range of those made previously using local diagenetic models of authigenic clay formation and operational leaching methods designed to target authigenic clays ($\sum Si_{hr}$), but tend to be at least 2 – 3× higher. When utilized in more general coastal mud transport – reaction models, biogenic Si incorporation rates suggest that coastal bSi burial rates are likely 20 – 30% higher globally than presently estimated. (4) ^{32}Si further validates the inference that reverse weathering is a major pathway affecting the Si cycle in high sedimentation rate continental margin environments, and perhaps most importantly it provides a means of independently constraining diagenetic processes controlling Si and biogenic Si storage. The present data indicate that deltaic and associated dispersal systems may rival the Southern Ocean in importance as sites of reactive Si (bSi + altered products of bSi) storage and that the marine Si cycle remains to be accurately constrained.

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Figure 15. (A) Map of coastal study site locations along French Guiana and Amazon River mouth (adapted from Anthony et al., 2015). A = Amazon River site; M = Macouria; S = Sinnamary. Arrows indicate general path of sediment along the Amazon – Guianas dispersal system (~15 – 20% of the Amazon load moves NW; the remainder forms the proximal Amazon delta (Kuehl et al., 1986; Eisma et al. 1991; Allison et al., 1995). (B) Representative facies on mangrove island and mobile mudbanks that are comparable to our study sties (adapted from Anthony et al., 2010).

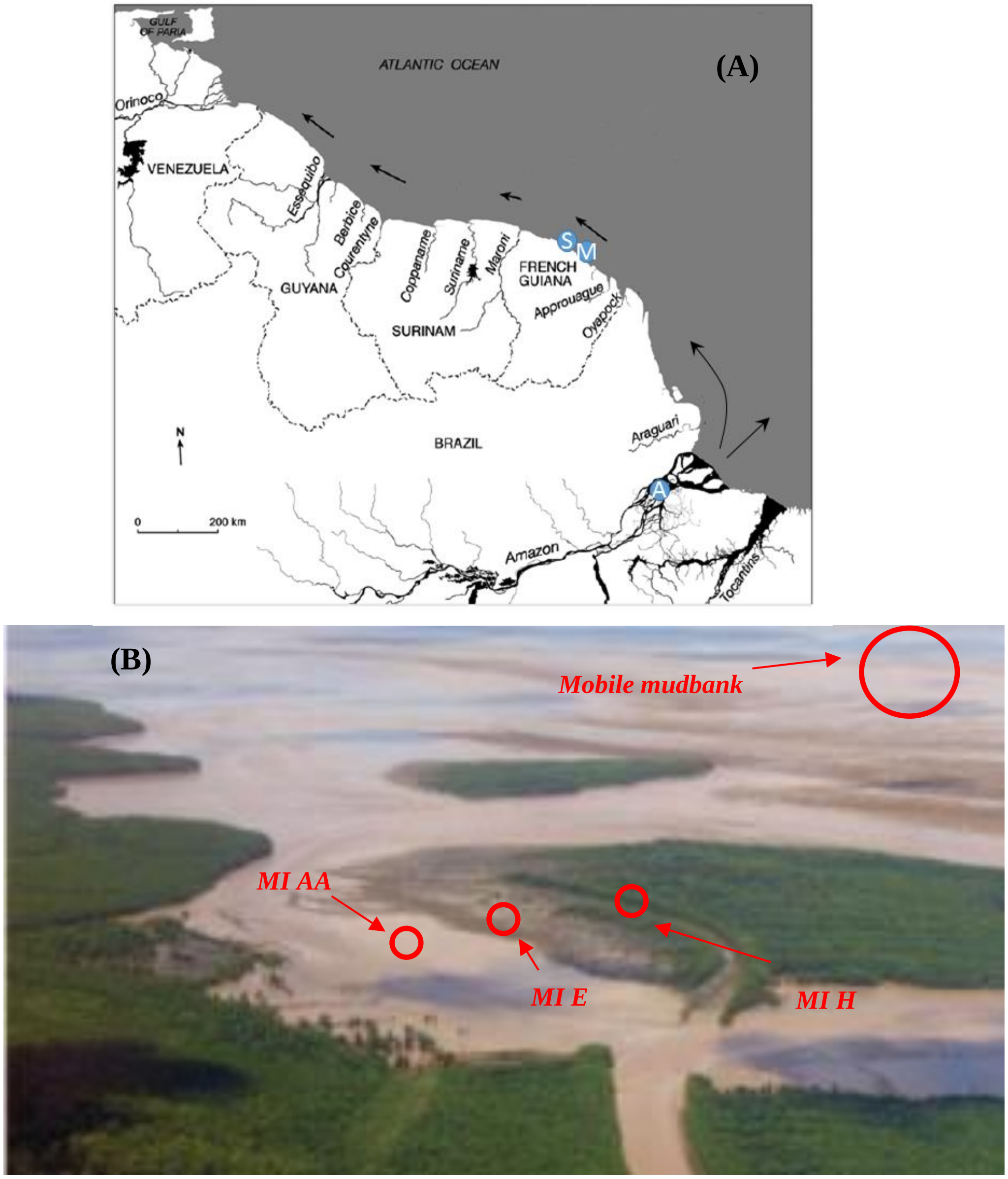


Figure 16. Decay profiles of ^{32}P in the residual Si-NaOH(-bSi) pool after the removal of bSi at (A) Sinnamary1 (mobile mud site), (B) Sinnamary2 (mobile mud site), and (C) Macouria (mobile mud site). Counts per minute are plotted verus e$^{(-\lambda t)}$ where λ is the decay constant of ^{32}P and t is the time elapsed from unsupported ^{32}P activity. The slope of the line is the initial activity of ^{32}P and consequently, ^{32}Si, in the sample. A counting efficiency of 24.8 ±0.004% was determined for these samples (see Figure S1). Taking into account the percent yield of the final ^{32}P precipitate, 30% at (A), 42% at (B), and 43% at (C) the initial activity of ^{32}Si (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]) is 1.0 ± 0.2 dpm, 1.2 ± 0.3dpm, and 1.7 ± 0.3dpm respectively, in the residual pool after removal of the bSi fraction. The background counting rate of the gas proportional counters was 0.19 ± 0.01 CPM (dashed horizontal line).

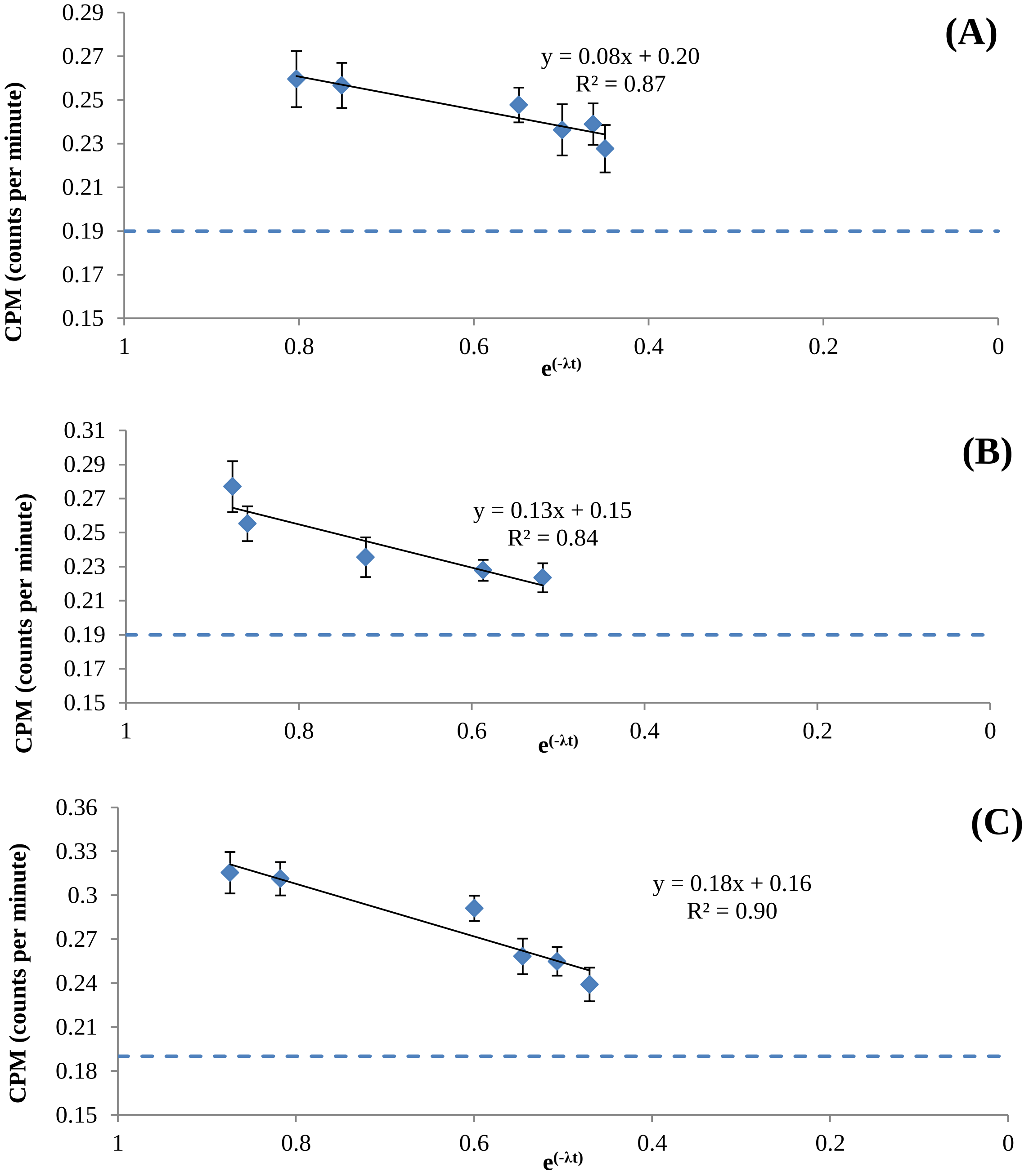


Figure 17. Decay plots of ^{32}P in the residual Si-NaOH(-bSi) pools <u>after</u> the removal of bSi at (A) Sinnamary (transient mangrove island site, Sinnamary 3), (B) Sinnamary mudbank (shoreface of transient mangrove island, Sinnamary 4), and (C) Sinnamary mangrove island (Sinnamary 5). The slope of the line gives the initial activity of ^{32}P and consequently, ^{32}Si, in the sample (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]; percent yields in Table 2, counting efficiency of 24.8%). Activities of ^{32}Si (dpm) were calculated from these data (Table 1) taking into account the counting efficiency and chemical yield. Dashed horizontal line indicates detector background.

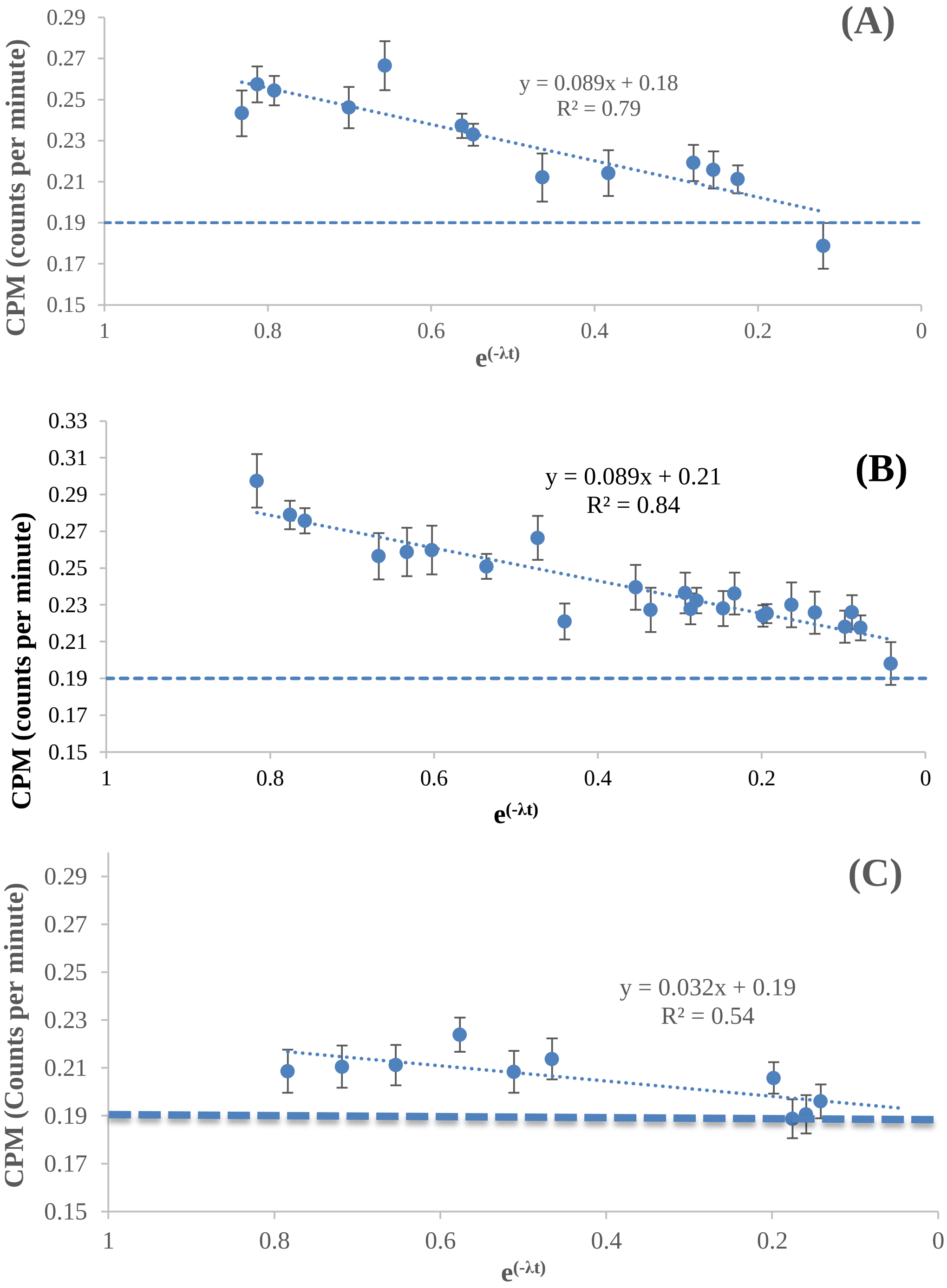


Figure 18. Decay plots of ^{32}P in the residual Si-NaOH(-bSi) pool after removal of the bSi fraction at a mobile mudwave off the coast of Kourou. (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]; percent yields in Table 2, counting efficiency of 24.8%).

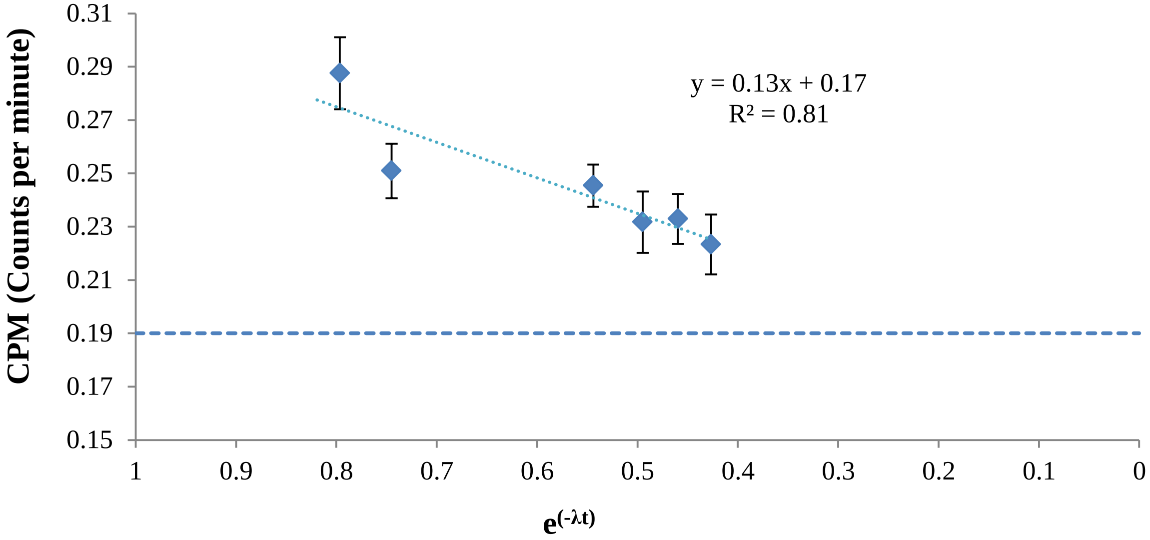
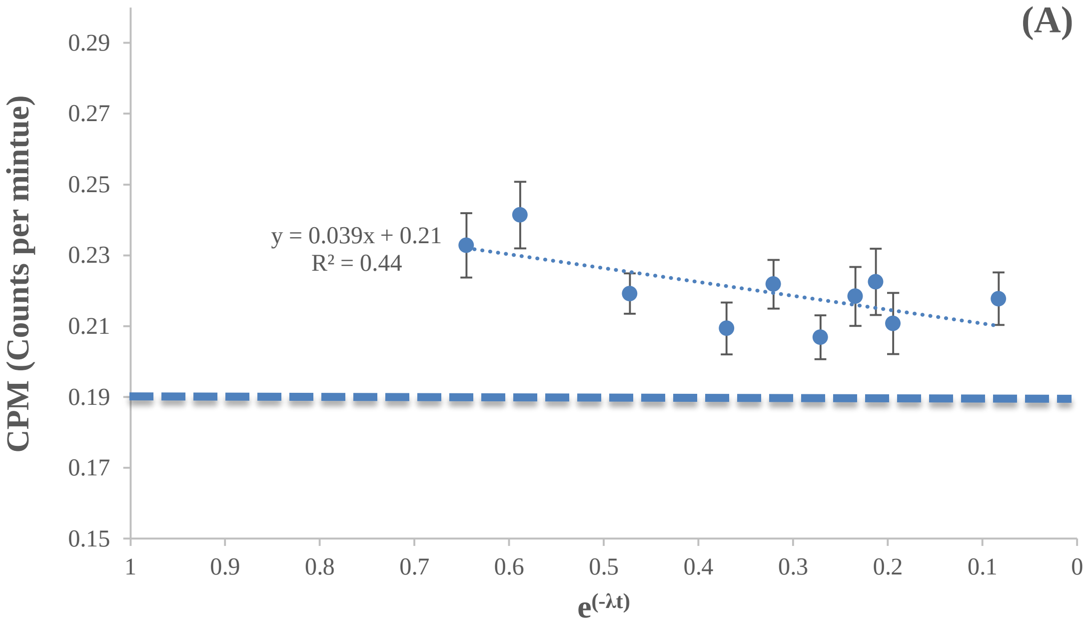


Figure 19. Decay plots of ^{32}P at the Amazon River mouth in (A) the residual (Si-NaOH(-bSi) pool after removal of the bSi fraction, and (B) the residual (Si-NaOH(-$\sum$Si$_{hr}$) after removal of the $\sum$Si$_{hr}$ fraction. (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]; percent yields in Table 2, counting efficiency of 24.8%).



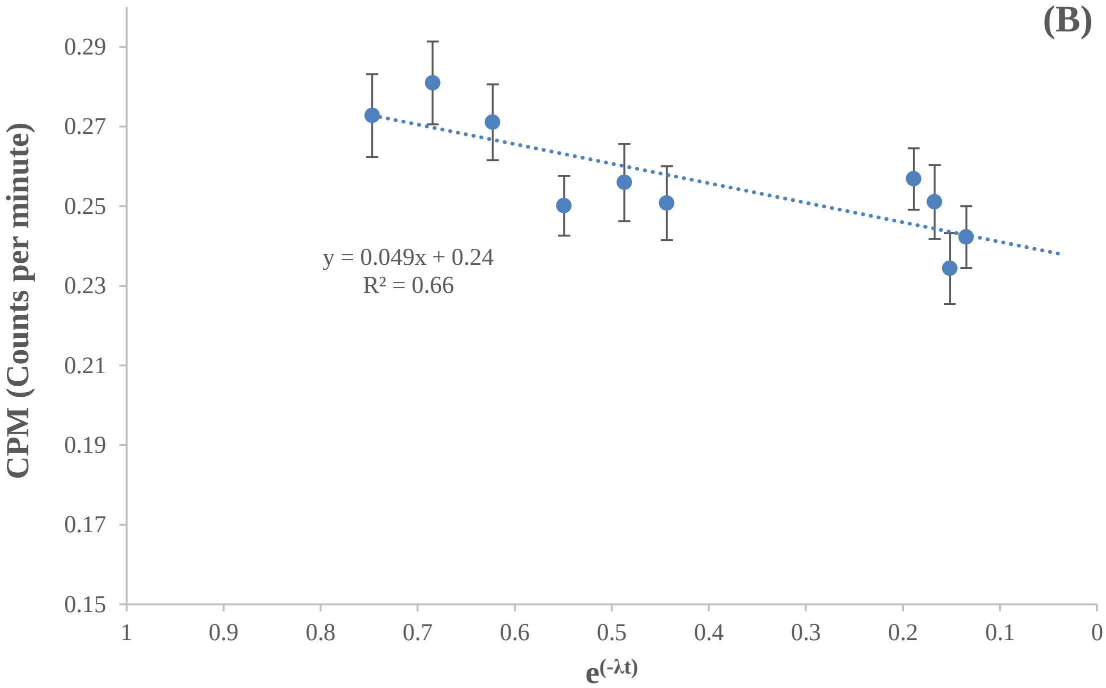


Figure 20. ^{32}P decay plots in (A) the $\sum\mathrm{Si}_{hr}$ and (B) the residual Si-NaOH(-$\sum\mathrm{Si}_{hr}$) pool at transient mangrove island off the coast of Sinnamary (Sinnamary3 site). This combined $\sum\mathrm{Si}_{hr}$ treatment corresponds to one operational definition of reactive Si designed to be inclusive of authigenic clay (Michalopoulos and Aller, 2004). (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]; percent yields in Table 2, counting efficiency of 24.8%).

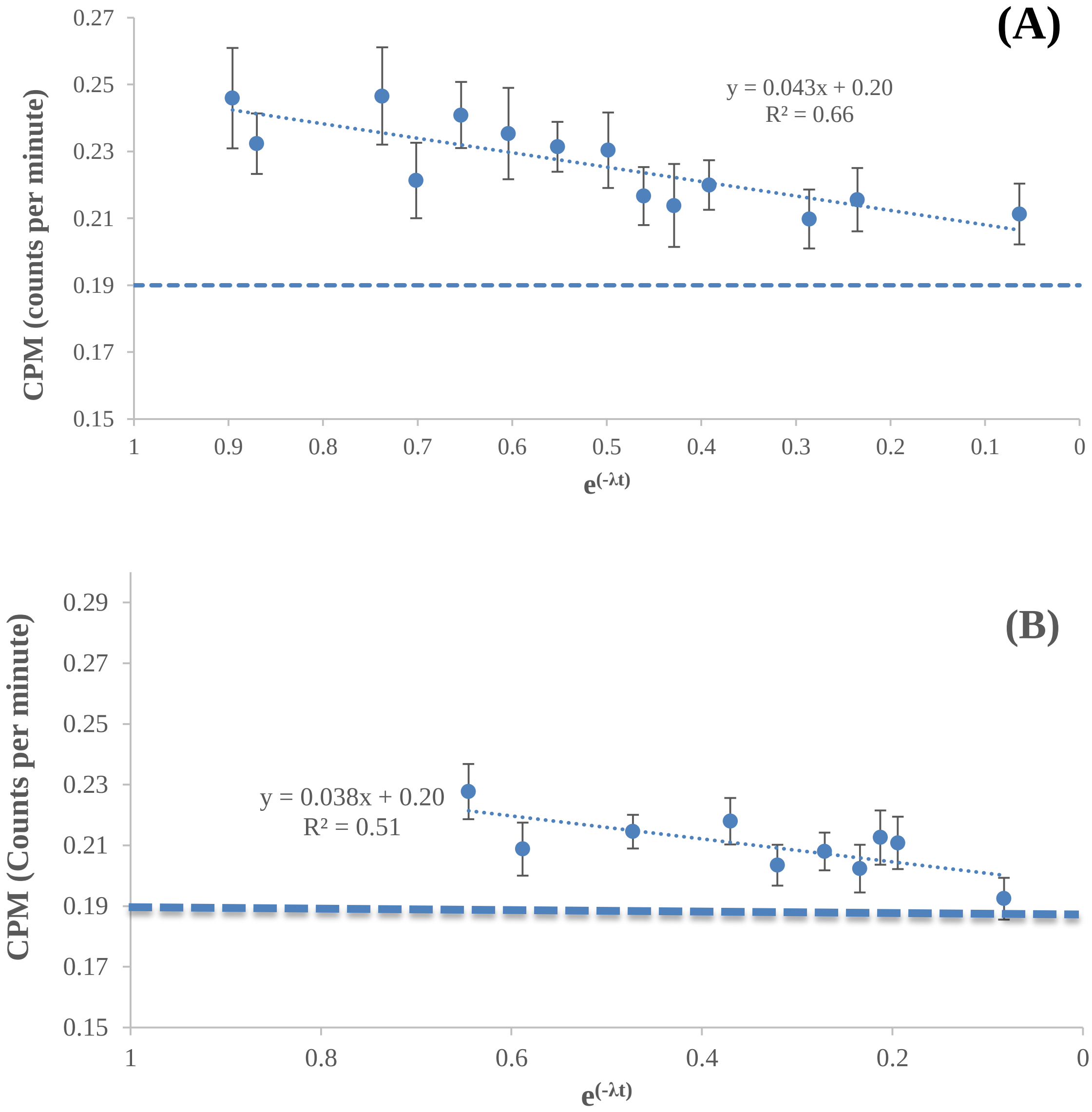


Figure 21. ^{32}P decay plot for the (A) $\sum Si_{hr}$ fraction and, (B), the residual Si-NaOH($-\sum Si_{hr}$) fraction at transient mangrove island site off the coast of Sinnamary (site Sinnamary5). (^{32}Si initial activity = [(^{32}P initial activity) * (percent yield)$^{-1}$ * (counting efficiency)$^{-1}$]; percent yields in Table 2, counting efficiency of 24.8%).

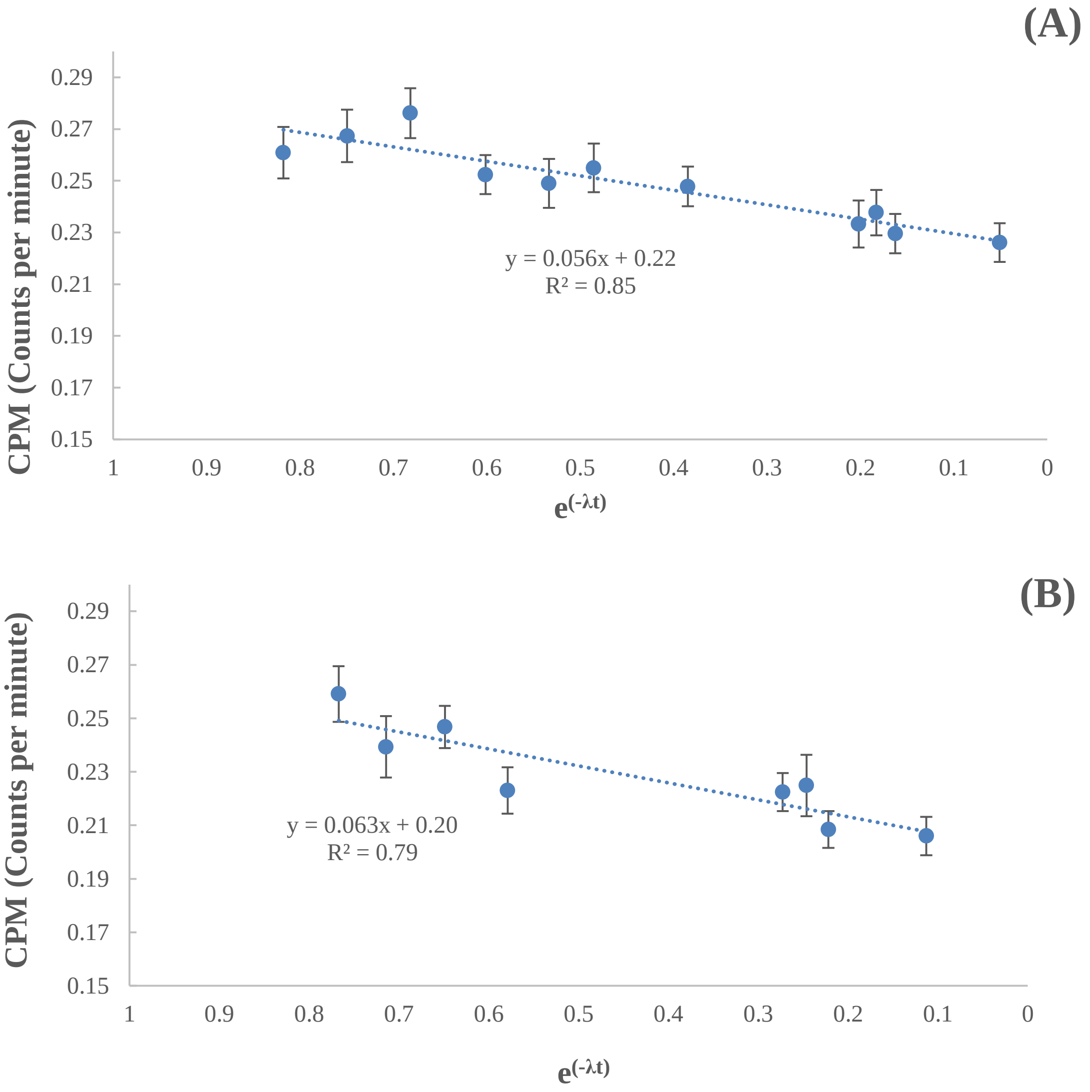


Figure 22. Decay curve of the ^{32}P spiked precipitated standards. The average of the two replicates along with the standard deviation is plotted. Counts per minute are plotted verus $e^{(-\lambda t)}$ where λ is the decay constant of ^{32}P and *t* is the time elapsed from unsupported ^{32}P activity. The slope of the line is the detected initial activity of ^{32}P in the sample. The actual activity of the ^{32}P spike was 2.775 DPM. After accounting for the percent yield of the precipitated standards, the resulting counting efficiency is 24.8 ± 0.4%. The background count rate of the detectors was 0.19 ± 0.1 CPM.

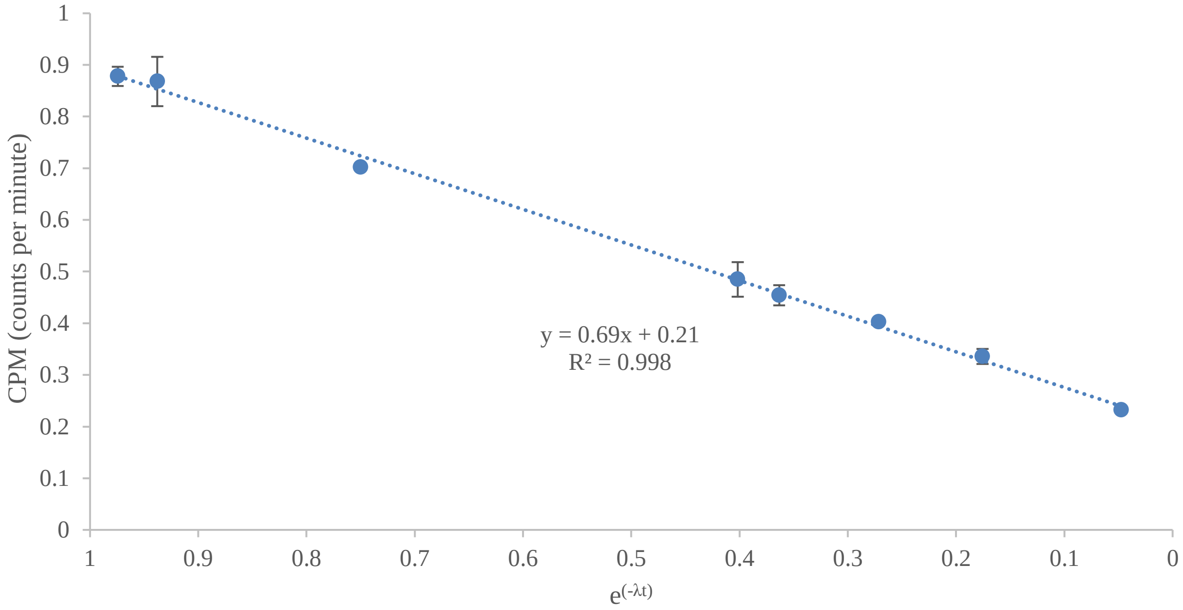


Figure 23. The ^{32}Si specific activity of sponges as a function of average dissolved stable silica concentrations in the surface 0 – 500m layer of different oceans from the areas in which they were collected (adapted from Fig. 2, Lal et al. (1976)).

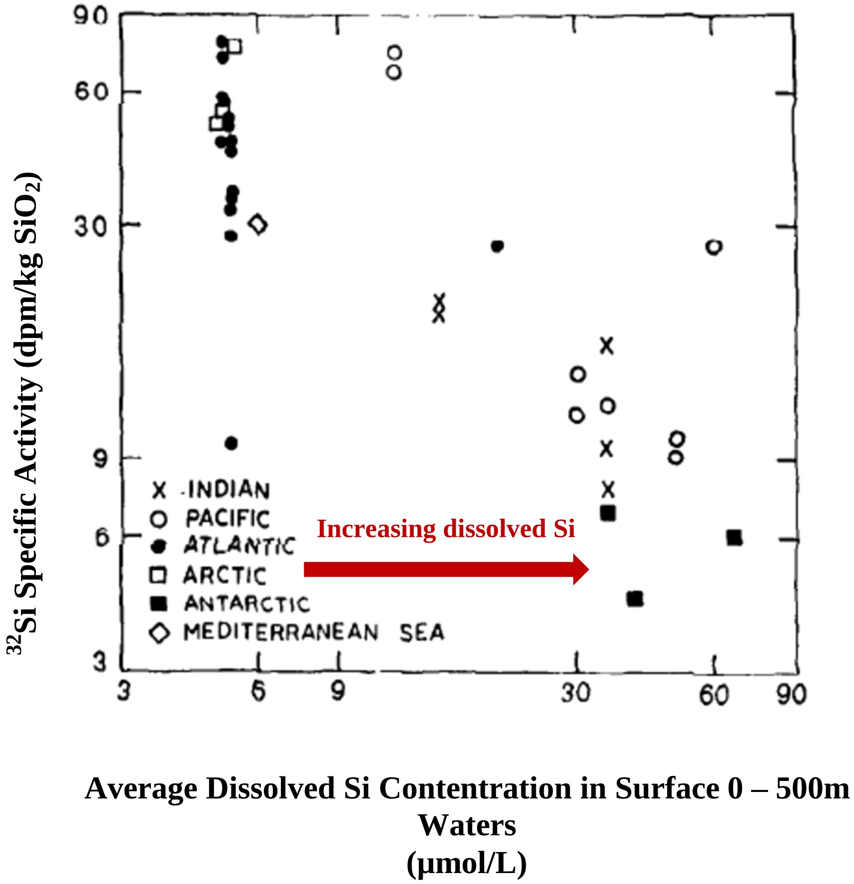


Figure 24. Average silica content estimates of Amazon River mouth sediment and French Guiana sediments using silica extracted from classic bSi and ∑Si_{hr} operational leaches compared to estimates using measured ^{32}Si activity and a range of source specific acitivities. Silica content estimates using ^{32}Si calculated using two different specific activities of initial biogenic material, 15 dpm/kg SiO_2 ("32Si-15") and 5 dpm/kg SiO_2 ("32Si-5").

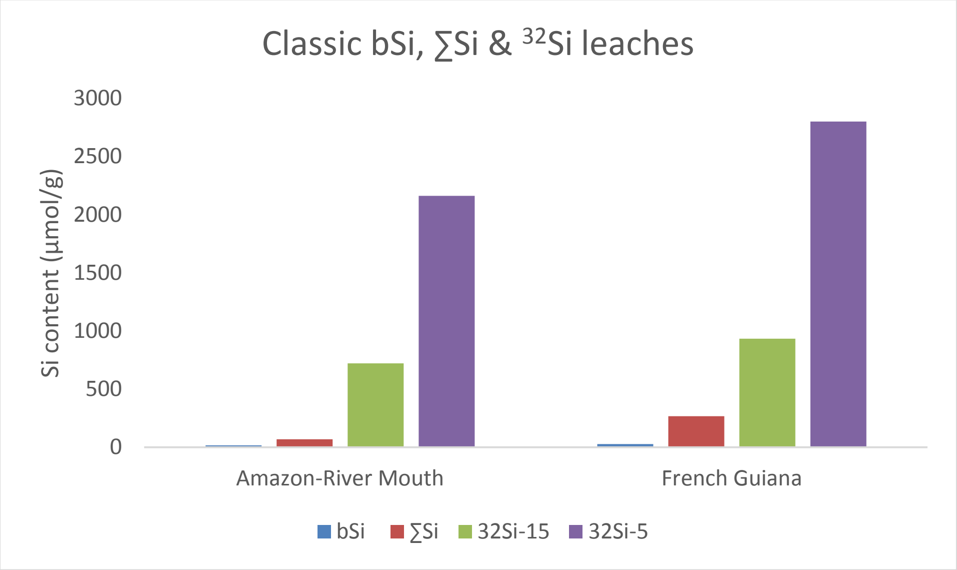


Figure 25. Model conceptualization of lateral sediment transport and progressive clay authigenesis along the Amazon – Guianas dispersal system, extending from the Amazon Delta to the Orinoco Delta.

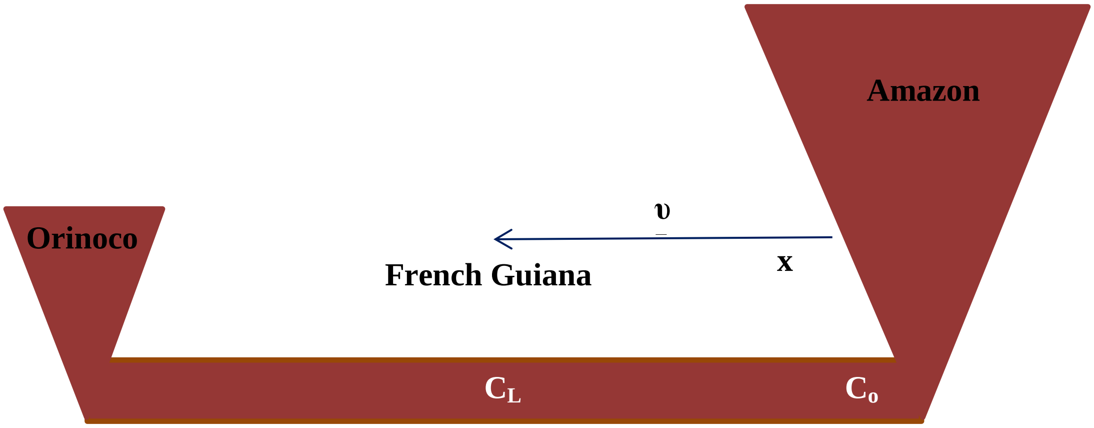


Figure 26. Example model distributions of ^{32}Si activity along coast as a function of mudbank advection velocity. A scenario with no incorporation of fresh material with 32Si activity is represented by the dashed line (incorporation rate R = 0, average mudbank velocity of 1.5km/y).

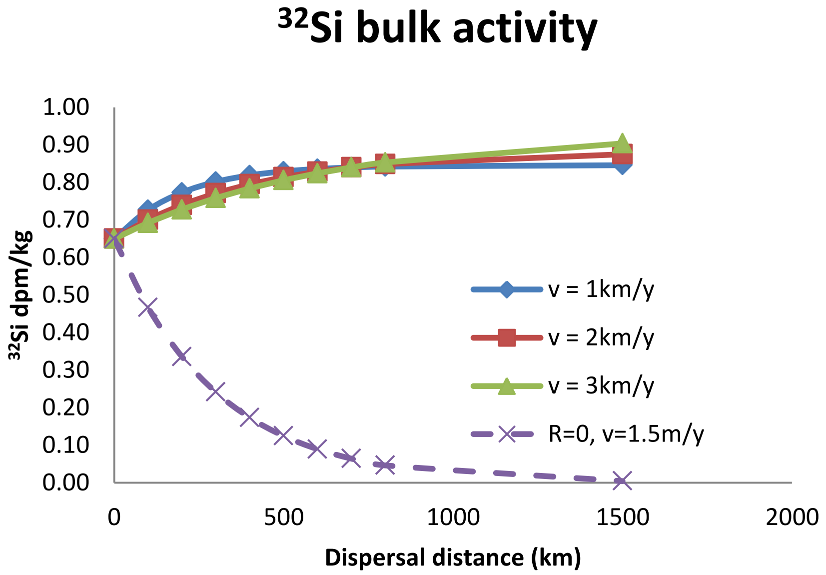


Table 11. Select characteristics/parameters of the rivers supplying the majority of reactive Si to study sites. The majority of this information is replicated from the data base created by Meybeck and Ragu (1995). When multiple values are found from different references for the same parameter, the more recent estimate was used in this study.

Study Site	River	Drainage Area (10^6 km^2)	Riverine freshwater Discharge (km^3/y)	Annual Suspended Load (10^6 tons/y)	TSS* (mg/L)	TDS** (mg/L)	DSi (µmol/ L)	DSi Riverine Flux[1] (Tmol/y)	ASi Flux[2] (Tmol/y)	SGD DSi Flux[3] (Tmol/y)	Total Flux (Tmol/y)
French Guiana											
	Amazon	6.112	6590	1200	182	44	115	0.76	0.12	0.13	1.0
	Tocantins	0.7570	372	75	202	40.8	193	0.072	0.0075	7.1×10^{-3}	0.086
	Suriname	0.0160	11.00	0.30	27.3	30.2	145	0.0016	3.0×10^{-5}	2.1×10^{-4}	0.0018
	Approuague	0.0102	11.60	0.20	17.2	35.8	250	0.0029	2.0×10^{-5}	2.2×10^{-4}	0.0031
	REGION TOTAL	6.90	6985	1276				0.83	0.13	0.13	1.1

[*] TSS = Total suspended solids

[**] TDS = Total dissolved solids

[1] Riverine DSi flux = (river freshwater discharge (L/y)) x (riverine dissolved Si concentration (µM)

[2] ASi Flux = (river freshwater discharge (L/y)) x (TSS(g/L)) x (0.006)/ (60 g/mol SiO_2)

[3] SGD DSi = (river freshwater discharge (L/y)) x (0.05) x (380 (µM))

Table 12. Bulk ^{32}Si activities and other parameters for the bSi and $\sum Si_{hr}$ classic and sequential extractions.

	^{32}Si Bulk Activity (dpm/kg dry wt)	% yield[a]	Bulk Sediment Mass (g)	Classic leach Si contents (µmol/g)[b]	bSi/$\sum Si_{hr}$ %	% total activity (^{32}Si extractions)
Amazon – Guianas						
Amazon River Mouth						
bSi	N.D.		1712	17	25%	0%
Si-NaOH(-bSi)	0.65 ± 0.26	14	1712	613		100%
$\sum Si_{hr}$	N.D.		3271	68		
Si-NaOH(-$\sum Si_{hr}$)	0.22 ± 0.05	28	3271	613*		
Sta 1 (Sinnamary 1)						
bSi	Bkgd		1291	35	17.5%	0%
Si-NaOH(-bSi)	0.78 ± 0.15	30	1291	916		100%
$\sum Si_{hr}$	N.D.			200		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			916*		
Sta 2 (Sinnamary 2)						
bSi	Bkgd		1333	35	17.5%	0%
Si-NaOH(-bSi)	0.92 ± 0.25	43	1333	1347		100%
$\sum Si_{hr}$	N.D.			200		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			1347*		
Sta 3 (Macouria)						
bSi	Bkgd		968	35	17.5%	0%
Si-NaOH(-bSi)	1.72 ± 0.29	43	968	944		100%
$\sum Si_{hr}$	N.D.			200		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			944*		
Kourou						
bSi	N.D.		466	40	13.3%	0%
Si-NaOH(-bSi)	5.4 ± 1.3	21	466	2100		100%
$\sum Si_{hr}$	N.D.			300		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			2100*		
MI AA (Sinnamary 4)						
bSi	N.D.		2262	20	6.8%	0%

Si-NaOH(-bSi)	0.37 ± 0.03	43	2262	985		100%
$\sum Si_{hr}$	N.D.			294		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			908		
MI E (Sinnamary 3)						
bSi	N.D.		959	20	5.6%	0%
Si-NaOH(-bSi)	1.0 ± 0.2	38	959	931		100%
$\sum Si_{hr}$	0.17 ± 0.04	56	1766	355		44%
Si-NaOH(-$\sum Si_{hr}$)	0.22 ± 0.08	38	1766	792		56%
MI H (Sinnamary 5)						
bSi	N.D.		1239	8	2.6%	0%
Si-NaOH(-bSi)	0.28 ± 0.09	36	1239	650		100%
$\sum Si_{hr}$	0.25 ± 0.03	40	2290	309		42%
Si-NaOH(-$\sum Si_{hr}$)	0.34 ± 0.07	33	2290	546		58%

[a] Actual yield of final product)/(100% theoretical yield of final product). Final product was magnesium ammonium phosphate – hexahydrate (100% yield = 0.0981g).

[b] Si content in classic bSi, Si--NaOH(---bSi), $\sum Si_{hr}$, or Si--NaOH(---$\sum Si_{hr}$)

[1] 891 μmol/g extracted from the combined 0.1N HCl and 1% Na_2CO_3 leaches, whereas 822μmol/g extracted in the 1% Na_2CO_3 leach alone. The Si in the 0.1N HCl pool was lost in the large – scale ^{32}Si extractions.

Table 13. ^{32}Si bulk activity in various fractions (*bSi*, *Si-NaOH(-bSi)*, $\sum Si_{hr}$, or *Si-NaOH(-*$\sum Si_{hr}$*)*) of modified sequential extractions, Si contents in classic bSi and $\sum Si_{hr}$ leaches, and calculated ^{32}Si specific activities. All ^{32}Si activity assigned to either the SiO_2 extracted in the classic bSi (1% Na_2CO_3 leach) or the classic $\sum Si_{hr}$ (0.1N HCl and 0.1M Na_2CO_3 leaches) leaches in calculations of specific activity.

Study Site	Fraction	^{32}Si bulk activity (dpm/kg sed)	Bulk Sediment Mass (g)[*]	Classic bSi[**] (µmol Si/g sed)	Classic $\sum$Si[***] (µmol Si/g sed)	^{32}Si specific activity (dpm/kg bSi)[a]	^{32}Si specific activity (dpm/kg $\sum$Si)[b]
French Guiana							
Amazon RM	*Si-NaOH(-bSi)*	0.65 ± 0.26	1712	17	68	650 ± 260	160 ± 60
	Si-NaOH(-$\sum Si_{hr}$*)*	0.22 ± 0.08	3271	17	68	220 ± 50	50 ± 10
Sta 1 (Sinnamary 1)	*Si-NaOH(-bSi)*	0.78 ± 0.15	1291	35	200	370 ± 70	65 ± 12
Sta 2 (Sinnamary 2)	*Si-NaOH(-bSi)*	0.92 ± 0.25	1333	35	200	400 ± 100	77 ± 21
Sta 3 (Macouria)	*Si-NaOH(-bSi)*	1.7 ± 0.3	968	35	200	800 ± 100	143 ± 24
Kourou	*Si-NaOH(-bSi)*	5.4 ± 1.3	466	40	300	2200 ± 500	300 ± 70
MI AA (Sinnamary 4)	*Si-NaOH(-bSi)*	0.37 ± 0.03	2262	20	294	300 ± 30	21 ± 2
MI E (Sinnamary 3)	*Si-NaOH(-bSi)*	0.96 ± 0.15	959	20	355	800 ± 100	45 ± 7
	$\sum Si_{hr}$	*0.17 ± 0.04*	1766	20	355	140 ± 30	8 ± 2
	Si-NaOH(-$\sum Si_{hr}$*)*	*0.22 ± 0.08*	1766	20	355	190 ± 60	11 ± 4
MI H (Sinnamary 5)	*Si-NaOH(-bSi)*	0.28 ± 0.09	1239	8	309	600 ± 200	15 ± 5
	$\sum Si_{hr}$	*0.25 ± 0.03*	2290	8	309	510 ± 70	13 ± 2
	Si-NaOH(-$\sum Si_{hr}$*)*	*0.34 ± 0.07*	2290	8	309	700 ± 100	18 ± 4

[**] Sample mass used in ^{32}Si bSi sequential extractions (bSi followed by 4M NaOH) given in parentheses.

[**] Si extracted in the classic 0.1 M Na_2CO_3 bSi leach (DeMaster, 1979) using classic sediment mass to solution volumes. Si content in hot 4M NaOH leach using ~1g:10ml solution volumes given in parentheses.

[***] Si extracted in the combined 0.1N HCl and 0.1 M Na_2CO_3 leach fractions using classic sediment mass to solution volumes as outlined in Michalopoulos and Aller (2004). When available, the Si content in hot 4M NaOH leach following the $\sum$Si sequential extraction is given in parentheses.

[a] Specific activity of initial bSi calculated assigning all ^{32}Si activity to the SiO_2 extracted in the operationally defined bSi fraction (classic 0.1M Na_2CO_3 leach)

[b] Specific activity of initial bSi calculated assigning all ^{32}Si activity to the SiO_2 extracted in the operationally defined $\sum$Si fraction (classic 0.1N HCl followed by 0.1M Na_2CO_3 leach).

Table 14. ^{32}Si activity in residual 4M NaOH pool after removal of bSi and $\sum Si_{hr}$ fractions and reactive Si storage estimates.

Study Site	Fraction	^{32}Si bulk activity (dpm/kg sed)	Calculated Biogenic Si (mmol Si/g)	Calculated Biogenic Si (mmol Si/g)	Calculated Biogenic Si (mmol Si/g)
			SM = 5 dpm/kg SiO_2[a]	*SM = 15 dpm/kg* SiO_2[b]	*SM = 40 dpm/kg* SiO_2[c]
FRENCH GUIANA					
Amazon RM	*Si-NaOH(-bSi)*	0.65 ± 0.26	2.2 ± 0.9	0.7 ± 0.3	0.3 ± 0.1
	Si-NaOH(-$\sum Si_{hr}$*)*	0.22 ± 0.08	0.7 ± 0.2	0.24 ± 0.06	0.09 ± 0.02
Sta 1 (Sinnamary 1)	*Si-NaOH(-bSi)*	0.78 ± 0.15	2.6 ± 0.5	0.9 ± 0.2	0.32 ± 0.06
Sta 2 (Sinnamary 2)	*Si-NaOH(-bSi)*	0.92 ± 0.25	3.1 ± 0.8	1.0 ± 0.3	0.4 ± 0.1
Sta 3 (Macouria)	*Si-NaOH(-bSi)*	1.7 ± 0.3	6 ± 1	1.9 ± 0.3	0.7 ± 0.1
Kourou	*Si-NaOH(-bSi)*	5.4 ± 1.3	18 ± 4	6 ± 1	2.2 ± 0.5
MI AA (Sinnamary 4)	*Si-NaOH(-bSi)*	0.37 ± 0.03	1.2 ± 0.1	0.41 ± 0.03	0.15 ± 0.01
MI E (Sinnamary 3)	*Si-NaOH(-bSi)*	0.96 ± 0.15	3.2 ± 0.5	1.1 ± 0.2	0.40 ± 0.06
	$\sum Si_{hr}$	0.17 ± 0.04	0.6 ± 0.1	0.19 ± 0.04	0.07 ± 0.02
	Si-NaOH(-$\sum Si_{hr}$*)*	0.22 ± 0.08	0.7 ± 0.3	0.25 ± 0.09	0.09 ± 0.03
MI H (Sinnamary 5)	*Si-NaOH(-bSi)*	0.28 ± 0.09	0.9 ± 0.3	0.3 ± 0.1	0.12 ± 0.04
	$\sum Si$	0.25 ± 0.03	0.8 ± 0.1	0.27 ± 0.04	0.10 ± 0.01
	Si-NaOH(-$\sum Si_{hr}$*)*	0.34 ± 0.07	1.1 ± 0.2	0.37 ± 0.08	0.14 ± 0.03

[a] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is lower estimate of particulate Si in the Atlantic Ocean of 5 dpm/kg SiO_2 (Lal et al., 1976; DeMaster and Pope, 1996).

[b] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is the average of activities (15 dpm/kg SiO_2) in low latitude tropical rivers and particulate Si in Equatorial Atlantic Ocean waters of 10 – 20 dpm/kg SiO_2 (Nijampurkar et al., 1966; Somayajulu et al., 1987; DeMaster and Pope, 1996).

[c] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is average estimate of particulate Si in the surface Atlantic Ocean of 40 dpm/kg SiO_2 (Craig et al., 2000; Somayajulu et al., 1987).

Table 15. Calculated ^{32}Si bulk activities using various estimates of R, determined for different values of υ, the average velocity at which sediment is advecting along the Amazon – Guianas dispersal system, at increasing distance from the origin, the Amazon River mouth, to the Orinoco, 1600 km away.

x (km)	^{32}Si bulk activity (dpm/kg) (R = 0.0042 dpm/kg/y)[1]	^{32}Si bulk activity (dpm/kg) (R = 0.0044 dpm/kg/y)[2]	^{32}Si bulk activity (dpm/kg) (R = 0.0046 dpm/kg/y)[3]
0	0.65	0.65	0.65
100	0.73	0.70	0.69
200	0.77	0.74	0.73
300	0.80	0.77	0.76
400	0.82	0.80	0.78
500	0.83	0.81	0.81
600	0.84	0.83	0.82
700	0.84	0.84	0.84
800	0.84	0.85	0.85
1500	0.85	0.88	0.90

[1] R calculated assuming $\upsilon = 1$ *km/y*
[2] R calculated assuming $\upsilon = 2$ *km/y*
[3] R calculated assuming $\upsilon = 3$ *km/y*

Chapter 4 – Gulf of Papua, Mississippi Delta, and Long Island Sound

Abstract

In order to determine the magnitude of biogenic silica storage in coastal sediments, a new application of the cosmogenic radionuclide ^{32}Si ($t_{1/2}$ ~ 140y) was developed. The common operational leaches that target biogenic Si (bSi) were modified for large scale samples necessary for measurement of ^{32}Si. Two sequential extractions were developed to target reactive silica including bSi and authigenic silicates: one, a hot 1% Na_2CO_3 solution followed by a hot 4M NaOH leach (bSi sequential extraction: bSi → Si – NaOH); and, two, a 0.1N HCl pretreatment step prior to hot 1% Na_2CO_3 and 4M NaOH ($\sum Si_{hr}$ sequential extraction: Si – HCl → Si – Alk → Si – NaOH). Three disparate depositional settings were sampled. Sediment from 2 stations in the Gulf of Papua, Papua New Guinea, 1 station in the northern Gulf of Mexico near the Southwest Pass, and 1 station in Long Island Sound (Smithtown Bay) were extracted for ^{32}Si in the bSi fraction as well as the residual fraction after removal of bSi. Only enough sediment was available at the Gulf of Mexico and Long Island Sound sites for the $\sum Si_{hr}$ sequential extraction.

Bulk ^{32}Si activities in the Gulf of Papua (0.5 – 0.7 dpm/kg sediment) were used to extrapolate total opaline Si storage in the outer topset and forset of the clinoform delta. Initial estimates of Si burial in this region, as indicated from ^{32}Si activities, were ~0.10Tmol/y, or 74 – 99% of the total Si inputs by rivers to the Gulf. These results are consistent with authigenic clay formation as a major process controlling the fate of biogenic silica in this region. The almost total conversion of biogenic Si to clay in the Gulf of Papua is similar to that found in the Amazon – Guianas deltaic system (Chapter 3).

^{32}Si activity was detected in both the bSi (0.24 ± 0.06 dpm/kg sediment) *and* the residual fraction (0.4 ± 0.1 dpm/kg sediment) from the site in the Gulf of Mexico. A Si burial rate using the ^{32}Si activity in these two fractions (assuming an initial ^{32}Si/Si activity of 15dpm/kg) of 0.012 Tmol/y was calculated over approximately 5000 km^2 of the delta. This amount corresponds to ~10% of the total Si inputs from the Mississippi – Atchafalaya river system. ^{32}Si activity was also detected in the $\sum Si_{hr}$ (0.27 ± 0.05) and the residual Si – NaOH pools (0.59 ± 0.08 dpm/kg sediment) and using these activities yielded similar calculated rates of Si burial (~0.016Tmol/y). Si burial calculated using operational bSi leaches alone are 50 – 60% lower. Initial results imply ~60 - 70% conversion of biogenic silica to authigenic clay at this particular site.

In Smithtown Bay, Long Island Sound, ^{32}Si activity was also detected in both the bSi (0.15 ± 0.05 dpm/kg sediment) and following Si – NaOH (0.48 ± 0.09 dpm/kg sediment) fractions in surface sediment (0 – 10 cm), yeilding a total Si storage estimate of 1.2 – 3.5 x 10^{-3} Tmol/y, when extrapolated over the entire Sound (depending on the initial ^{32}Si/Si activity). ^{32}Si activity was also detected in both fractions of the large – scale $\sum Si_{hr}$ sequential extractions, leading to similar estimates of Si storage (1.2 – 3 x 10^{-3} Tmol/y). The Si content in the classic bSi and $\sum Si_{hr}$ leaches indicate Si burial of 7.4 x 10^{-4} and 1.4 x 10^{-3} Tmol/y, respectively. The $\sum Si_{hr}$ procedure extracts a portion of the altered bSi but still underestimates total storage of bSi and its alteration products.

In summary, results indicate that ^{32}Si activity can be used successfully to estimate reactive (~biogenic) Si burial in a variety of depositional settings. In tropical deltas, the radionuclide activity demonstrates rapid and almost complete alteration of biogenic Si to an altered phase, most likely as authigenic clay. Classic bSi leaches consistently underestimate the magnitude of Si burial in temperate estuaries and subtropical deltas by 2 – 4 fold.

Introduction

The extent of reactive Si burial in the form of primary and diagenetically altered biogenic silica in three disparate depositional settings was investigated using cosmogenic ^{32}Si. In addition to sites in the Amazon – Guianas mudbelt (Chapter 3), sediment from 2 stations in the Gulf of Papua, Papua New Guinea, 1 station in the northern Gulf of Mexico near the Southwest Pass of the Mississippi River, and 1 station in central Long Island Sound (Smithtown Bay) were also extracted for ^{32}Si using the modified large – scale bSi and total reactive Si sequential extractions. Only sediments from the Gulf of Mexico and Long Island Sound were subjected to the large – scale $\sum Si_{hr}$ sequential extractions. Limited masses of sediment were available from the Gulf of Papua, enough for one sequential extraction.

Like the Amazon subaqeous clinoform delta, deltaic topset muds in the Gulf of Papua, Papua New Guinea (PNG) are comprised of two layers: an upper mobile layer overlying thicker older anoxic deposits. In a region of the Earth where small mountainous islands of the Indo – Pacific supply over 4 billion tons of sediment annually to the global ocean, sediment loads from PNG rivers account for 1.7 x 10^9 t/y alone, representing 8 – 10% of total estimated sediment discharge to the ocean (Milliman et al., 1999; Walsh et al., 2004). Of this amount, 0.38 x 10^9 t/y is delivered to the Gulf of Papua (Milliman et al., 1999) on the southern coast of Papua New Guinea. This amount is approximately ~1/3 of the delivery from the Amazon River, but with <10% of the corresponding freshwater discharge (Table 16). Unlike the Amazon – Guianas system which forms a series of mobile mud banks, the majority of the sediment delivered to the Gulf remains in the Gulf, with less than 5% discharging to the adjoining shelf region (Walsh et al, 2004). Half of this sediment discharge may remain sequestered on the inner shelf in the Gulf of Papua or the Arafura Shelf. Diagenetic silica cycling in this major tropical deltaic system has not been extensively studied.

Background Information

The delivery of total dissolved and reactive Si to the Gulf of Papua was approximated using available monitoring data (Table 16), and totals ranged from 0.072 to 0.14 Tmol/y depending on the inclusion of sources other than the three major rivers of the Gulf. The total annual freshwater discharge to the Gulf of Papua is 15,000 m^3/y (Wolanski et al., 1995) or about 473 km^3/y. Of this amount, about 260 km^3/y can be attributed to the Fly, Puraru and Kikori Rivers (Meybeck and Ragu, 1995). Other rivers that discharge into Gulf of Papua are the Bamu and Turama Rivers. As summarized in Table 16, the Fly, Kikori, and Purari Rivers have average freshwater discharge volumes of 141, 40, and 84 km^3/y respectively and average dissolved Si concentrations of 150, 133, and 230 µM, respectively (Meybeck and Ragu, 1995; Gaillardet et al., 1999). In the absence of additional data, it was assumed that the dissolved Si concentration in the remainder of the freshwater discharge, 213 km^3/y, was an average of that in these three rivers (~171 µM) and a total DSi flux to the Gulf was approximated to be 0.08 Tmol/y (Table 16). Applying the same relationship that Frings et al. (2016) determined to extrapolate the global delivery of amorphous Si (ASi) to the world's ocean, an estimate of ASi delivery using a total sediment load of 0.384 x 10^9 tons/y to the Gulf of Papua was calculated (ASi = 0.04 Tmol/y). An input of a further 0.009 Tmol/y of dissolved Si via submarine groundwater discharge was calculated using 5% of the total freshwater input to the Gulf, 473km^3/y, and an average [Si] of 380 µM (Frings et al., 2015, see Chapter 1). Therefore, the combined average flux of DSi and ASi to the Gulf of Papua used in this study was 0.14 Tmol/y.

The Mississippi and Atchafalaya Rivers to the Gulf of Mexico delivers the 7th largest sediment load in the world's ocean, approximately 210 x 10^9 kg/y (Milliman and Meade, 1983). A more recent estimate of the sediment load delivery from the Mississippi River is 500 x 10^9 kg/y (Meybeck and Ragu, 1995). About 130 – 150 x 10^9 kg/y, is delivered through the Mississippi River's birdsfoot delta of which, recent studies indicate, only ~40% accumulates in the delta. The remainder moves off and along shore during the winter due to high velocity winds and wave action (Corbett et al. 2004, Corbett et al., 2006). The river has an annual water discharge rate of ~620 km^3/y (long – term average over the years 1950 – 1996) or 19, 920 m^3/s (Goolsby et al., 1999). The combined mean annual flux of dissolved Si to the Gulf of Mexico from the Mississippi – Atchafalaya River Basin, representing the flux calculated over a period of 17 years from 1980 – 1996, is ~2.3 x 10^6 (± 0.3 x 10^6) metric tons, or ~0.08 Tmol (Goolsby et al., 1999). Silicate concentrations in the Mississippi River have declined since the 1960s from ~155 µM to ~110 µM, whereas both phosphorus and nitrogen have increased two to three – fold (Turner and Rabalais, 1991; Justić et al., 1995(a); Justić et al., 1995(b); Rabalais et al., 1996), resulting in Si:N ratios that have dropped from 4:1 to closer to 1:1. Silica to nitrogen ratios that are closer to 1:1 may lead to eutrophication or shifts in composition of phytoplankton species in this region (Turner and Rabalais, 1994; Rabalais et al., 1996). Reported bSi concentrations on the adjacent shelf west of the Southwest Pass range from 0.15 – 1.3 % (Turner and Rabalais, 1994). Regions of seasonal hypoxia develop in the upper/northern Gulf of Mexico during late – spring to late – summer (Turner and Rabalais, 1994; Justić et al., 1993; Rabalais et al., 1996; Rabalais et al., 1999; Rabalais et al., 2001; Rabalais et al., 2002; Scavia et al., 2003). The total range of reactive and dissolved Si inputs to the Mississippi from these various discharge and sediment load parameters was 0.097 – 0.14 Tmol/y.

One sample was obtained from a temperate coastal system, Long Island Sound, an estuarine environment approximately 150 km long and 30km wide. The Connecticut River supplies the majority of the freshwater and suspended sediment to the Sound. The freshwater input from the East River to western Long Island Sound was <10% of the total freshwater input to the estuary (Kim and Bokuniewicz; 1991). Long Island Sound is connected at its western end to the East River and New York Harbor, to the Atlantic Ocean on its eastern end, and within its watershed over 8 million people are housed (Knebel et al.; 1999; Knebel et al; 2000). It receives numerous inputs of anthropogenic wastes from sewage from the New York City – Connecticut area as well as cropland and urban runoff. The Sound consists of 3 major basins, and the site sampled in this study comes from Smithtown Bay, located in the Central Basin and representative of silty/clay sediments which cover ~60% of the total area of the Sound (Sun et al., 1994). Modelling of fluvial inputs to the Sound suggest that about 45% of the total sediment supply has a source in the neighboring coastal ocean (Kim and Bokuniewicz; 1991), with the majority of muddy sediment accumulating in the western and central sound (Kim and Bokuniewicz; 1991; Aller, 1994). The top few centimeters of sediment in the Sound are rapidly reworked by bioturbation, and are underlain by a slower reworked layer down to 1 – 2 m (Aller and Cochran, 1976; Goldhaber et al., 1977; Benninger et al., 1979). The total dissolved and reactive silica inputs to the Sound approximated in this study, 0.0018 Tmol/y, are summarized in Table 16.

Sampling

Two archived samples collected between 2003 – 2004 from the Gulf of Papua, Papua New Guinea, one from the inner topset and one from the foreset, were used in this dissertation. Samples from the Gulf of Papua, Papua New Guinea were obtained during several expeditions to the region (Aller et al., 2008). Samples were collected aboard the R/V *Cape Ferguson* in February and November 2003, and the R/V *Melville* was used in August – September 2003, January 2004, and May 2004 (see Aller et al. (2008) and Aller et al. (2008) for complete sampling information). One sample, collected June 2014, from the Mississippi Delta was obtained from an area of relatively low to intermediate sediment accumulation west of the Southwest Pass for this study (based on Corbett, et al, 2004). The sample was collected during a research cruise aboard the R/V *Gadawall* (Louisiana Universities Marine Consortium) in June 2014. The top 10cm from grab samples were retained for ^{32}Si extractions. The sample from Smithtown Bay was gathered using an Ocean Instruments Mark IVbox corer (0.25 m^2) aboard the R/V *Seawolf* in 2012. The top 5 – 10cm of the core was retained for this study. Locations of the study areas are presented in Figure 27.

Methods

The two samples from the Gulf of Papua were each processed using the bSi sequential extraction: 1% Na_2CO_3 leach (the "bSi" fraction) followed by a 4M NaOH leach (the "Si-NaOH(-bSi)" fraction), as detailed in Chapter 2. This operational sequential extraction may be referred to as "bSi$\rightarrow$Si-NaOH" in the text. A little over 1100g was processed from each site using sediment mass to solution volumes of ~1g:37ml, similar to what was used in French Guiana. The bSi leaches yielded sufficiently little SiO_2 (e.g. ~10g) that the ^{32}Si activity was assumed to be below the detection limit of the beta detectors, and only the ^{32}Si activities in the 4M NaOH leaches were determined (see Table 17 and Figure 28). The extracted SiO_2 was stored for several months prior to the milking of ^{32}P which had grown in during that time (complete details of this procedure can be found in DeMaster (1979)). Percent yields of the final phosphate salt which is put on the counter to determine ^{32}P decay can be found in Table 17 for each sample.

In the Gulf of Mexico, several kilograms of surface sediment (0 – 10cm) were gathered from grab samples just west of the Southwest Pass (29° 08.564' N, 89° 46.462' W) in June 2014. Enough sample mass was present to perform not only the bSi sequential extraction, but also the $\sum Si_{hr}$ sequential extraction. The $\sum Si_{hr}$ sequential extraction is first comprised of a 0.1N HCl pretreatment prior to a 1% Na_2CO_3 leach (0.1N HCl + 1% Na_2CO_3 = "$\sum Si_{hr}$" fraction, the sequence also indicated by "Si-HCl $\rightarrow$Si-Alk") followed by 4M NaOH (the "Si-NaOH(-$\sum Si_{hr}$)" fraction). This entire sequence is referred to as "Si-HCl$\rightarrow$Si-Alk$\rightarrow$Si-NaOH" in the text. Given the biogenic and reactive Si contents at this site, sediment mass to solution volume ratios for the bSi extractions (1% Na_2CO_3) were ~1g:70ml, whereas for the $\sum Si_{hr}$ extractions (0.1N HCl and

1% Na_2CO_3) were ~1g:90ml. The extracted silica in each fraction was purified according to DeMaster (1979) and stored for 2 months, after which the sample was milked for ^{32}P.

Enough sediment from a site in Smithtown Bay, Long Island Sound was collected from the upper 5 – 10cm layer to also perform both the bSi (bSi $\rightarrow$ Si – NaOH) and $\sum Si_{hr}$ (Si – HCl $\rightarrow$ Si – Alk $\rightarrow$ Si – NaOH) sequential extractions. Sediment mass to solution volume ratios for the bSi fraction was 1g:60ml for a total of 1730g, and for the $\sum Si_{hr}$ fraction was 1g:120ml for a total of 741g. The SiO_2 extracted and purified in the ^{32}Si large scale $\sum Si_{hr}$ leaches did not include the fraction in the 0.1N HCl pretreatment step, which was lost during the purification of SiO_2 prior to storage.

Results

Gulf of Papua

The ^{32}Si activities in the total bulk sediment at sites GS48 (foreset) and GH 14 (inner topset) in the residual NaOH fraction after removal of bSi (bSi $\rightarrow$Si-NaOH)were 0.65 ± 0.07 dpm/kg sediment and 0.5 ± 0.2 dpm/kg sediment, respectively. Decay profiles of ^{32}P from these sites are presented in Figure 28 and activities are summarized in Table 17, which includes results from the Amazon – Guianas dispersal system (Chapter 3) for comparison. The bSi content, determined using the single step classic biogenic silica operational leaches (DeMaster, 1979; DeMaster, 1981), in these two cores were <90 µmol Si/g sediment, whereas the content in the Si-NaOH after removal of bSi (or: bSi $\rightarrow$Si-NaOH) fractions ranged from 500 – 800 µmol/g (see Table 17). The 90 µmol/g retrieved after 1.75h in the hot 1% Na_2CO_3 bSi leaches at these two PNG sites was likely an overestimate of the biogenic silica content in these deposits; a 1h leach would extract less Si and give a more accurate approximation.(a 1 hr leach closely approximates the bSi value derived from an extrapolation to t = 0 from a serial 5 hr leach). Given the low Si content in the bSi extractions, it was assumed the ^{32}Si activity in this fraction would be below the background count rate of the beta counters.

Mississippi Delta

At the station in the northern Gulf of Mexico, ^{32}Si activity was detected in all fractions of the bSi (bSi → Si – NaOH) and $\sum Si_{hr}$ (Si – HCl → Si – Alk → Si – NaOH) sequential extractions. The bulk ^{32}Si activity in the bSi fraction was 0.24 ± 0.06 dpm/kg sediment and was 0.4 ± 0.1 dpm/kg sediment in the Si-NaOH(-bSi) fraction. In the $\sum Si_{hr}$ fraction (Si – HCl → Si – Alk) the activity was 0.27 ± 0.05 dpm/kg sediment, whereas it was 0.59 ± 0.08 dpm/kg sediment in the Si – NaOH(-$\sum Si_{hr}$) fraction (NaOH after removal of highly reactive $\sum Si_{hr}$ pool). The ^{32}P decay profiles in the two fractions of the bSi sequential extraction are presented in Figure 29, whereas those in the $\sum Si_{hr}$ sequential extractions are presented in Figure 30. The Si content retrieved in the classic mild alkaline bSi and acid – alkaline $\sum Si_{hr}$ leaches were ~350 µmol/g and ~410 µmol/g, respectively, whereas in the residual 4M NaOH fractions it is was 750 – 800 µmol/g (Table 17).

Long Island Sound

In Smithtown Bay, ^{32}Si activity was detected in both fractions of the bSi (bSi → Si – NaOH) and $\sum Si_{hr}$ (Si – HCl → Si – Alk → Si – NaOH) sequential extractions. The Si in the 0.1N HCl pretreatment step (~70 µmol/g) was lost and could not be combined with the subsequent mild alkaline leach. The ^{32}Si activities in the bSi and Si – NaOH(-bSi) fractions were 0.15 ± 0.05 dpm/kg sediment and 0.48 ± 0.09 dpm/kg sediment, respectively (Figure 31). In the $\sum Si_{hr}$ and Si – NaOH(-$\sum Si_{hr}$) fractions, ^{32}Si activities were 0.3 ± 0.1 dpm/kg sediment and 0.4 ± 0.4 dpm/kg sediment (Figure 32), respectively. The silica contents retrieved in the classic bSi and $\sum Si_{hr}$ leaches were ~460 µmol/g and ~890 µmol/g, respectively, and were 450 – 490 µmol/g in the 4M NaOH extractions that followed (see Table 17).

Discussion

Operational opaline Si leaches and estimating specific activities

Several approaches were taken in order to interpret the ^{32}Si activities and ultimately estimate reactive Si content (bSi + diagenetically altered bSi) in these three contrasting depositional regimes. First, specific activities attributing all the ^{32}Si activity in the various fractions to the silica extracted in the small scale classic bSi and modified $\sum Si_{hr}$ leaches, were calculated, replicating the protocol that DeMaster (1979, 1981) used to determine the half –life of ^{32}Si. These calculated specific activities are summarized in Table 18. This scenario is one in which it is assumed that the conventional one – step mild alkaline bSi leach accurately targets the majority of the biologically derived reactive silica buried in these deposits. For example, at station GS 48 the ^{32}Si activity was 0.73 dpm and with a biogenic Si content of 90 µmol/g, a total of 6.09g of biogenic SiO_2 would be extracted from 1128g of sediment, leading to a calculated specific activity of 120 dpm/kg SiO_2 (i.e. 120 dpm/kg SiO_2 = 0.73 dpm/0.00609 kg biogenic SiO_2). No water column biogenic silica source with such a high activity has ever been found.

In the Gulf of Papua ^{32}Si specific activities calculated in this manner ranged from 100 – 120 dpm/kg SiO_2, implying that the classic bSi leaches significantly underestimates, by at least one order of magnitude, the reactive Si buried in these sediments. At these two sites, the classic bSi leach retrieves only 20 – 25% of the reactive Si (bSi + poorly crystalline diagenetically altered products of bSi) from the $\sum Si_{hr}$ extractions (Table 17). Estimated specific activites from the Amazon – Guianas dispersal system (Chapter 3), included in Tables 17 and 18 as points of comparison, were 3 – 20x higher. Like the Amazon – Guianas results, attributing all the ^{32}Si activity from the residual fraction to the mass of Si extracted in a classic $\sum Si_{hr}$ leach (~400 µmol/g sediment) also leads to unusually high, albeit more reasonable, calculated specific activities (22 – 27 dpm/kg SiO_2), indicating that the reactive Si content in the Gulf of Papua is greater than 400 µmol/g. Using data from the only study on ^{32}Si activities in rivers,(Nijampurkar et al., 1966), and the dissolved Si concentrations in the Fly, Kikori, and Pururi rivers (Table 16) the expected ^{32}Si specific activity in these Papua New Guinea rivers can be estimated, in the same manner the expected specific activity in the Amazon River mouth was calculated (Chapter 3). Nijampurkar et al. (1966) report ^{32}Si activities in Indian rivers of 0.08 dpm/m^3 near river mouths of both the Ganges and Godavari, leading to an estimated particulate ^{32}Si activity of ~9, 10, and 6 dpm/kg SiO_2 in the Fly, Kikori, and Purari rivers, respectively.

Unlike the Gulf of Papua, ^{32}Si was detected in both fractions of the bSi (bSi → Si – NaOH) and $\sum Si_{hr}$ (Si – HCl + Si – Alk → Si – NaOH) sequential extractions in the Mississippi Delta (Figures 29 and 30), indicating that some degree of alteration of the initial biogenic Si phase is probably occurring, and that conversion to clay, although occurring, may not be as rapid as in tropical deltas. The ^{32}Si bulk activities in the first operational pools of both of these sequential extractions, the bSi and $\sum Si_{hr}$ fractions, are very similar (i.e. 0.26 dpm/kg versus 0.27 dpm/kg sediment). These activities reflect the similarity between Si contents retrieved from the conventional bSi and $\sum Si_{hr}$ leaches, ~350 µmol/g and ~410 µmol/g respectively. The activities in the bSi and $\sum Si_{hr}$ fractions account for ~34 – 38% of the total ^{32}Si activity at this site (Tables 17 and 18), whereas the ratio of classic bSi to $\sum Si_{hr}$ is over 80%, and may indicate freshly deposited biogenic material. This percentage also indicates that the classic $\sum Si_{hr}$ extraction underestimates the amount of extractable Si of opaline origin present in sediments. Relative ^{32}Si activities in these various operational pools downcore at the same site would clarify whether the surface layer that was sampled at this site represents freshly deposited biogenic material, specifically if the relative activities in the $\sum Si_{hr}$ pools increase. Observations by Presti and Michalopoulos (2008) are consistent with downcore increases in the $\sum Si_{hr}$ pool (Si – HCl → Si – Alk). Attributing all of the ^{32}Si activity to the Si extracted in the classic bSi or $\sum Si_{hr}$ leaches yields specific activities between 10 and 13 dpm/kg SiO_2, comparable to those found in the open ocean (Fifield and Morgenstern, 2009), though likely too high for a site close to the mouth of the Mississippi River, a high source of stable dissolved silicate. Assuming all the biogenic ^{32}Si delivered to the area is homogenized and represented by one specific activity, the higher calculated specific activities in the residual Si – NaOH fractions imply that the Si content in these pools, at a minimum, is about twice that in the classic bSi (350 µmol/g) and $\sum Si_{hr}$ (409 µmol/g) fractions (Table 17). These calculated specific activities not only highlight the differences in the fate of deposited reactive Si between tropical deltaic systems and subtropical systems, they also reveal the inadequacy of the widely – accepted biogenic Si leach in extracting diagenetic alteration products of biogenic Si in these regions.

Like the site in the Mississippi Delta, ^{32}Si activity was detected in both fractions of the bSi (bSi → Si – NaOH) and $\sum Si_{hr}$ (Si – HCl → Si – Alk → Si – NaOH) sequential extractions in LIS sediments (Figures 31 and 32), demonstrating not only that the classic bSi leach underestimates Si burial, but also that alteration of biogenic silica phases is occurring, though at a slower rate than in the tropical dispersal systems in this study. Note that samples from Smithtown were used at least twice previously to test the ^{32}P milking protocol outlined in DeMaster (1979) and activities presented here, taking into consideration sample loss during manipulations, are likely slightly lower than what was in the original samples. The Si extracted in the classic bSi accounts for 52% of that in the $\sum Si_{hr}$ leach. The ^{32}Si activities in these same fractions, bSi and $\sum Si_{hr}$ (Si – HCl → Si – Alk) are 24% and 43% of the total activities. The sum of the bulk activities in the bSi sequential extraction (bSi → Si – NaOH) is 0.6 ± 1 dpm/kg sediment. In the $\sum Si_{hr}$ sequential extractions (Si – HCl → Si – Alk → Si – NaOH) the sum of the bulk activities is 0.6 ± 0.4 dpm/kg SiO_2. The range of specific activities calculated when attributing the ^{32}Si activity in all four fractions of the large – scale sequential extractions to the Si extracted in the classic bSi leach (462 µmol/g) is 5 – 13 dpm/kg SiO_2, whereas attributing it all to the Si in the $\sum Si_{hr}$ fraction yields a range ~3 – 9 dpm/kg SiO_2. These values appear to be reasonable for the North Atlantic. One aspect of the calculations stands out, namely that attributing the ^{32}Si activity in the bSi pool to the classic bSi content and the activity in the $\sum Si_{hr}$ pool to the classic $\sum Si_{hr}$ content yields similar specific activities, implying that 5 dpm/kg SiO_2 may be a close approximation of the actual initial ^{32}Si/Si activity of deposited biogenic Si in this region. Given that higher ^{32}Si activity is detected in the residual Si-NaOH(-bSi) pool after removal of bSi (bSi → Si – NaOH), the 5dpm/kg SiO_2 would be a conservative estimate of the initial activity of biogenic Si. If valid, this further implies that the Si content in the Si-NaOH(-bSi) fraction should be 3X that in the classic bSi leach, or ~1400 µmol/g, leading to a total Si burial of ~1900 µmol/g in the Central Basin of the Sound. A similar estimate is reached when using the activities in the $\sum Si_{hr}$ sequential extractions (Si – HCl → Si – Alk → Si – NaOH) and 5 dpm/kg SiO_2 as the initial ^{32}Si/Si activity. As in the Mississippi Delta, comparing the relative ^{32}Si activities in the various operational pools downcore at this site would reveal degree of alteration or authigenic clay formation. Interpreting such results in the context of downcore ^{210}Pb profiles also could constrain the rate at which initially deposited biogenic Si is altered. Relative activities would also reveal whether authigenic clay formation is limited by reactive Fe and Al at this site, possibly underscoring the importance of suboxic conditions necessary to steadily supply these reactants. At a minimum, it appears that the classic bSi leach underestimates Si storage in this region by 2 to 4 fold.

Estimating Biogenic Silica Storage

Because the specific activity of the initially deposited biogenic silica is unknown, another approach to treating the ^{32}Si activities is to use specific activities of SiO_2 from representative data to infer the biogenic or reactive silica content at the three study sites (Table 19). GEOSECS data from the top 1000m of Indian Ocean Station 452 and Pacific Ocean Stations 263 and 306 (Somayajulu et al., 1991) were used to approximate ^{32}Si/Si ratios in oceanic starting material particulate matter in the Gulf of Papua region. These three stations appear closest in proximity to the Gulf of Papua. At station 452, the average ^{32}Si/Si activity was ~15dpm/kg SiO_2 in the top 1000m, whereas it was ~7 and 39 dpm/kg SiO_2 at stations 263 and 306 respectively. These values are similar to what was used to calculate the range of biogenic Si storage in the Amazon River Mouth and French Guiana, and the same values will be used for the Mississippi Delta and Long Island Sound (e.g. 5dpm/kg SiO_2, 15 dpm/kg SiO_2, and 40 dpm/kg SiO_2). Further, Craig et al. (2000) contend that the specific activities of particulate matter in the Atlantic Ocean are about 11% higher than in the Pacific for the same particulate mass. The inferred reactive silica contents from the various fractions in the sequential extractions are given in Table 19. Results from the Amazon – Guianas dispersal system (Chapter 3) are included in Table 19 for comparison.

In the Gulf of Papua, reactive or extractable Si storage estimates ranged from 220 µmol Si/g to 2100 µmol Si/g (Figure 33), or 1.3 – 12.8 wt. % SiO_2, using the ^{32}Si activity in the Si-NaOH(-bSi) pool (bSi $\rightarrow$ Si – NaOH), similar to what was found in the Amazon – Guianas dispersal system. Note that even the lowest silica storage estimates using the highest $^{32}Si/SiO_2$ initial specific activity of 40 dpm/ kg SiO_2 (unlikely to be so high given the proximity of the major rivers and the high end – member sources of stable silica in the Gulf of Papua to GH14 and GS48) is twice as high as what was found in the classic bSi leach at these two sites, indicating that the classic bSi leach significantly underestimates the reactive Si buried in these deposits. Even using initial activities of 15 dpm/kg SiO_2, as a conservative estimate, 7 – 8X more Si is predicted to be buried in these sediments than is from the classic bSi leaches.

In the Mississippi Delta, silica contents in the same residual pool, Si-NaOH(-bSi), were lower, ranging from 160 – 1300 µmol/g, or 0.9 to 8.6 wt % SiO_2. When adding the storage estimates from the activity in the bSi pool, totals ranged from 260 to 2100 µmol Si/g (Figure 33), or 1.5 – 12.8 wt. % SiO_2. In the modified $\sum Si_{hr}$ sequential extraction (Si – HCl $\rightarrow$ Si – Alk $\rightarrow$ Si – NaOH), the sum of the inferred Si contents in the $\sum Si_{hr}$ and the residual Si – NaOH(-$\sum Si_{hr}$) pools ranged from 360 to 2900 µmol Si/g 2.1 – 17 wt.% SiO_2, depending on the initial $^{32}Si/SiO_2$ activity. Previous estimates of biogenic Si storage using the conventional bSi leach near the

Mississippi Delta sampling site were between 0.5 and 1 wt. % silica (Turner and Rabalais, 1994; Rabalais et al., 1996). Presti and Michalopoulos (2008) extracted 557 µmol Si/g and 682 µmol Si/g in the conventional bSi and $\sum Si_{hr}$ (Si – HCl $\rightarrow$ Si – Alk) leaches, respectively. It appears that initial specific activities of ≤15dpm/kg SiO_2 yield Si contents similar to what was measured from the classic bSi (350 µmol/g) and $\sum Si_{hr}$ (409 µmol/g) leaches in sediments from this study's site in the Gulf of Mexico (Table 17). Estimates of total reactive Si using the same initial ^{32}Si activity in the top 10cm at this site are ~ 650 µmol/g (bSi + Si-NaOH(-bSi)) and ~950 µmol/g ($\sum Si_{hr}$ + NaOH(-$\sum Si_{hr}$)).

Presti and Michalopoulos (2008) performed classic bSi and $\sum Si_{hr}$ leaches from cores taken at ~10 stations in the Mississippi Delta and found similar Si contents in the two pools in the surface 0 - 10cm layer at their station MSS10. That station appears to be the closest in proximity to the site in this study. The Si retrieved in the classic bSi leaches in the kasten core at MSS10 decreases from about 200 µmol/g at the surface to approximately 50 – 60 µmol/g below 20cm (sediment accumulation rates <0.5 cm/y), whereas the $\sum Si_{hr}$ remains between 300 – 400 µmol/g downcore, which these authors interpreted as formation of glauconitic clays in suboxic areas of the core. Similar values of bSi and $\sum Si_{hr}$ may indicate the material in the surface layer is recently deposited reactive Si, which has undergone limited alteration, or that the alteration rates are slower at this site, when compared to the Gulf of Papua. Underlying sediment layers would need to be extracted and measured for ^{32}Si to clarify these issues.

In Long Island Sound, calculated biogenic Si contents from the large – scale bSi fractions were 60 – 500 µmol/g, whereas contents in the Si-NaOH(-bSi) fractions ranged from 200 to 1600 µmol/g, for a total of 260 to 2100 µmol/g (1.5 – 13 wt. % SiO_2), depending on the initial selected $^{32}Si/SiO_2$ specific activity. The bSi fraction accounts for only ~1/3 of the sum total ^{32}Si activity in this sequential extraction (bSi $\rightarrow$ Si – NaOH). In the $\sum Si_{hr}$ sequential extraction (Si – HCl $\rightarrow$ Si – Alk $\rightarrow$ Si – NaOH), detected ^{32}Si activity lead to an estimated total Si storage of 310 – 1900 µmol/g, with the first $\sum Si_{hr}$ fraction accounting for ~50% of the total. Interestingly, it appears that in Smithtown Bay initial specific activities of 5dpm/kg SiO_2 return Si content values very similar to what was extracted in the classic bSi (462 µmol/g) and $\sum Si_{hr}$ (822 µmol/g) extractions. In the previous section, approximately 5 – 6 dpm/kg SiO_2 was the specific activity calculated when attributing all the activity in the large – scale bSi fraction (0.15 dpm/kg sediment) to the Si extracted in the classic bSi leach, and the activity in the large – scale $\sum Si_{hr}$ fraction (0.3 dpm/kg sediment) to the Si extracted in the classic $\sum Si_{hr}$ leach. Applying this activity to the residual fractions yields Si storage estimates of ~2000 µmol/g (~13 wt.% SiO_2, Figure 33). DeMaster (1979, 1981) estimated an average biogenic Si content in Long Island Sound sediments of 4 wt. % SiO_2. Using ^{32}Si activity to calculate Si storage therefore returns estimates which are 2 – 3X higher than using extracted Si alone.

Calculating total Si flux and the global marine Si budget

Sediment accumulation rates over the generalized areas represented by the sites in this study can be used to approximate the total regional Si burial flux. These fluxes were calculated assuming that most ^{32}Si enters deposits in the form of opaline bSi. This opaline bSi is assumed to either dissolve in the water column or near the sediment water interface, be buried as unaltered biogenic Si, or undergo diagenetic alteration. These fluxes, along with the parameters (^{32}Si activity versus classic bSi or $\sum Si_{hr}$ silica contents) used to calculate them, are summarized in Table 20. Silica contents calculated assuming initial $^{32}Si/SiO_2$ activities of 15 dpm/kg SiO_2 and the activities in the modified bSi sequential extraction were used from all three study sites to give a conservative estimate of the burial flux (Figure 34). At the Long Island Sound site, an initial activity of 5 dpm/kg SiO_2 was also used to calculate Si storage, since this initial activity appears to approximate the Si contents retrieved from the classic leaches. Using this end – member, 5dpm/kg SiO_2, for the other two sites would increase silica content estimates by three – fold.

Sediment accumulation rates in the mid – topset of the Gulf of Papua, represented by site GH14, areal extent of 15.5 x 10^9 m^2, ranged from 0.6 to more than 1.5 $g/cm^2/y$ (site G19, Walsh et al., 2004) at the site closest to GH14. Brunskill et al. (2003) estimated mass accumulation rates in this region of 1.1 $kg/m^2/y$ (core 224, 15m water depth). The average accumulate rate, ~0.8$g/cm^2/y$, of these two sites (G19 and core 224) was used to calculate burial of 0.07 ± 0.03 Tmol Si per year using ^{32}Si activity in the Si-NaOH(-bSi) pool, almost 6X higher than what is estimated using Si content in the classic bSi extraction (~90 µmol/g). For the foreset deposits, average accumulation rates were 0.96 $g/cm^2/y$ over an area of 3.97 x 10^9 m^2 (Aller et al., 2008), and the Si burial flux from ^{32}Si activity was 0.027 ± 0.003 Tmol Si/y, ~8X higher than fluxes calculated using classic bSi contents. Taken together, a total Si burial of 0.10 ± 0.03 Tmol Si per year was estimated over the inner – topset and foreset of the Gulf of Papua using ^{32}Si, versus 0.015 Tmol/y using classic bSi leaches. As a conservative estimate, classic bSi leaches appear to account for, at most, 15% of the total diagenetically altered products in these deposits

The site sampled in the Gulf of Mexico appeared to be on the border between two areas with two different accumulation rates, determined from surface ^{210}Pb activities, both of which were the two lowest rates determined for the shelf west of the Southwest Pass (Corbett et al., 2006). Corbett et al. (2004) found that mobile mud distribution off the Southwest Pass varied a great deal seasonally, so it was presumed the ^{32}Si activities in the extracted operational pools, from a sample collected in a different year than the Corbett et al. study, could be representative of both regions, and the burial flux was calculated over the sum of the two areas. The lowest accumulation rate, average 0.16 g/cm^2/y, was over an area of 3.44 x 10^9 m^2, and the second lowest rate, 0.72 g/cm^2/y, was over an area of 1.55 x 10^9 m^2. A Si burial flux calculated from the ^{32}Si activity in the bSi fraction was 0.0045 Tmol/y, whereas a flux calculated from the Si-NaOH(-bSi) pool (bSi → Si – NaOH) was 0.0078 Tmol/y, leading to a total of 0.012 ± 0.002 Tmol/y, or about 10% of the total known reactive Si inputs to the region. When using classic bSi contents, a Si burial flux of 0.0058 Tmol/y was calculated, or ~48% of the flux using ^{32}Si acitivities. The total Si burial calculated using ^{32}Si activities in the operational pools of the $\sum Si_{hr}$ sequential extraction (Si – HCl → Si – Alk → Si – NaOH) and the above parameters was 0.016 ± 0.001 Tmol/y, as compared to 0.0069 Tmol/y, the flux calculated using Si contents in classic $\sum Si_{hr}$ leaches. Presti and Michalopoulos (2008) calculated a similar total Si burial of 0.0145 Tmol/y in the Delta using classic bSi and $\sum Si_{hr}$ leaches, though their estimates were over a greater area (5990 km^2 versus 4990 km^2) and included regions of high accumulation rates (e.g. 1.5 – 9.5 g/cm^2/y) as determined by Corbett et al. (2006). Presti and Michalopoulos (2008) contended that greater alteration of biogenic silica occurred primarily in areas of higher deposited reactive silica and hypoxic regions, areas which are not represented by the site sampled in this study. Preliminary sediment budgets show that of the total sediment delivered annually west of the Southwest Pass, about 40 to 50% of it is moved across the shelf via resuspension and slides and mass wasting (Corbett et al., 2006). Sampling sites for ^{32}Si analysis in the high – accumulation areas, along the mobile muds that are transported along the Louisiana coast (Corbett et al., 2004), and in sediment layers downcore at these sites, would provide a more complete picture of the Si burial flux in the shelf adjacent to the Mississippi outfall.

A total annual Si burial rate of 1.2 ± 0.2 x 10^{-3} Tmol (assuming initial $^{32}Si/Si$ = 15 dpm/kg SiO_2) was estimated for Long Island Sound, using the ^{32}Si activities in the bSi sequential extractions (bSi $\rightarrow$ Si – NaOH) from Smithtown Bay, for an area comprised mainly of clay and silt covering ~60% (Sun et al., 1994) of the Sound, and the long – term average sediment accumulation rate of 0.08 $g/cm^2/y$ (Kim and Bokuniewicz; 1991). The combined ^{32}Si activities in the $\sum Si_{hr}$ sequential extraction (Si – HCl $\rightarrow$ Si – Alk $\rightarrow$ Si – NaOH) also leads to a burial rate of 1.2 ± 0.7 x 10^{-3} Tmol/y. Using only the classic bSi and $\sum Si_{hr}$ leaches Si contents and the above sediment accumulation rate leads to calculated Si burial fluxes of 7.4 x 10^{-4} Tmol/y and 1.4 x 10^{-3} Tmol/y, which are 62% and 119%, respectively, of the fluxes calculated by the ^{32}Si activities. Assuming an initial activity of 5 dpm/kg SiO_2 in the deposited reactive siliceous material, a reasonable assumption which approximates the Si contents in the classic bSi (462 µmol/g) and $\sum Si_{hr}$ (891 µmol/g), leads to Si burial fluxes which are about 3 – 3.5 x 10^{-3} Tmol/y, and indicates that classic leaches retrieve only ~40 – 50% of the total Si of biogenic origin sequestered in these deposits. The higher burial flux, 3 – 3.5 x 10^{-3} Tmol/y, also implies that the sources of Si to this area are greater than what was approximated in this study (0.0018 Tmol/y, see Table 16).

Determining terrestrial sources of ^{32}Si activity

The ^{32}Si activity in the samples from Papua New Guinea or Mississippi Delta could conceivably reflect a predominantly continental source of ^{32}Si, in the form of pedogenic clays or freshwater diatoms or phytoliths, rather than a marine source. The ^{32}Si activity in sediments from rivers discharging into these areas was not determined in this study. The transit time of riverine material from highlands to the study sites in the Gulf of Papua in particular can be significantly shorter than the transit time of fluvial material from the Amazon to reach French Guiana (Goni et al., 2008; Alin et al., 2008; Anthony et al., 2010). The rivers draining into the Gulf of Papua have a total catchment area of 142 x 10^3 km^2 (1.42 x 10^{11} m^2), delivering ~100 – 200 x 10^6 tons of sediment (100 – 200 x 10^9 kg/y) and 330 – 400 km^3 of freshwater per year (Brunskill et al., 2009). Using annual ^{32}Si and ^{210}Pb fallout rates in this area, the relative contribution of continental ^{32}Si delivery to the topset and foreset regions of the Gulf of Papua sediments may be examined.

According to Craig et al. (2000), the average annual fallout rate of ^{32}Si around 10° latitude is ~0.11 dpm/m^2 y and the average ^{32}Si concentration in precipitation should be ~0.07dpm/m^3. However, the measured ^{32}Si concentration at Kodaikanal, India (10.23° latitude) was 0.20 dpm/m^3 which had annual rainfall of 170cm (Lal et al., 1979; Craig et al., 2000) and may indicate a small stratospheric dump into the troposphere characteristic of this latitudinal zone (5 - 10°). The total annual ^{32}Si delivery from the atmosphere to the catchment area, 1.42 x 10^{11} m^2, is 1.6 x 10^{10} dpm, with an inventory or ~23 dpm/m^2. In a study of the use of ^{32}Si for dating the ages of groundwater, the activity of this nuclide in soils was investigated (Franke et al., 1988). In a ~4m soil profile, the depth integrated soil inventory was 0.4Bq/m^2, which was 67% of the 0.6Bq/m^2 total ^{32}Si inventory in that region (Franke et al., 1988; Fröhlich et al., 1987). ^{32}Si was preferentially found in horizons containing humics, iron and manganese oxyhydroxides, and clays. The rest of the ^{32}Si will remain in the aqueous phase in groundwater, where a significant portion may be taken up into plants. Fröhlich et al. (1987) determined ^{32}Si activities of 0.64 Bq (38dpm) and 1.07Bq (64dpm) per kilogram of extracted SiO_2 from conifer needles and horsetail, respectively. With an above ground living biomass of 210.7 Mg/ha in trees with >1cm DBH (diameter at breast height), as well as a further 25.29 Mg/ha in roots, this may host a sizeable portion of the total ^{32}Si inventory.

The fraction of the continental ^{32}Si inventory that is delivered to the Gulf in the suspended sediment load can be approximated using the fractional delivery of excess ^{210}Pb as an analogue. The production of excess ^{210}Pb in the atmosphere in that region, determined at North Queensland, Australia, is 50 Bq/m^2/y (Brunskill et al., 2009). This supports a soil inventory of 1.59 x 10^3 Bq/m^2 and a total annual ^{210}Pb flux of 7.1 x 10^{12} Bq/y to the region. The activity of excess ^{210}Pb measured in at the Fly River mouth (Purutu 5 station, Aller et al., 2008) was ≤10 Bq/kg sediment. Given a suspended sediment delivery of 1.5 – 2 x 10^{11} kg/y, ≤1.5 – 2 x 10^{12} Bq/y of excess ^{210}Pb reaches the Gulf of Papua via rivers. This represents 21 – 28% of the total annual ^{210}Pb flux to the catchment area. Applying this fractional riverine ^{210}Pb delivery and assuming 67% of the total ^{32}Si annual inventory is associated with soils, leads to a maximum ^{32}Si activity of 0.015 – 0.02 dpm/kg from continental sources. Continental ^{32}Si can only account for a maximum of 3 – 4% of the activity recovered in the Si – NaOH(-bSi) pools at sites GH14 and

GS48 (0.52 – 0.65 dpm/kg sediment). This is a maximum estimate because it assumes the ^{32}Si is in the form of pedogenic clays, versus phytoliths or diatoms which would subsequently be dissolved in a mild alkaline leach (bSi).

A similar analysis can be done for the Mississippi River and Connecticut River drainage basins, using average annual fallout rates at representative latitudinal zones (Lal et al., 1979; Craig et al., 2000) and drainage basin area. ^{32}Si fallout fluxes at Pathankot (32.23° latitude) and Ludhiana (30.93°) were 0.334 dpm/m^2/y and 0.264 dpm/m^2/y, respectively. The drainage basin area of the Mississippi river is 2,980 km^2 and which leads to annual ^{32}Si fallout of 7.9 – 10 x 10^{11} dpm. The mean soil inventory of ^{210}Pb at lowland sites along the eastern and mid-western United States is 27.7 dpm/cm^2(Graustein and Turekian, 1986), which indicates an atmospheric flux of 8727 dpm/m^2/y. Over the catchment area of the Mississippi drainage basin, the annual atmospheric deposition rate of ^{210}Pb is 2.6 x 10^{16} dpm. The excess ^{210}Pb concentration near the river mouth was ~1100 – 1200 dpm/kg (Allison et al., 2000), which leads to a total flux of 5.5 – 6 x 10^{14} dpm/y transported on 5 x 10^{14} g/y of suspended sediment. This flux is ~2 – 3% of the total ^{210}Pb soil inventory in the Mississippi River catchment area. Applying the likely percentage of ^{32}Si retained on soils, ~67%, from Franke et al. (1988), leads to an approximation of the continental supply of ^{32}Si to the Mississippi Delta of 0.02 – 0.03 dpm/kg.

The catchment area of the Connecticut River is 2.5 x 10^{10} m^2, which leads to ^{32}Si fallout flux of 6.6 – 8.4 x 10^9 dpm/y when using the same zonal fallout fluxes for the Mississippi. The atmospheric flux and soil inventory of ^{210}Pb in the Connecticut River catchment area is 1 dpm/cm^2/y (Benninger, 1978), which leads to a total inventory of 2.5 x 10^{14} dpm/y. The excess ^{210}Pb activity in river suspended sediments is 6 dpm/g (Benninger, 1978). The annual delivery of suspended sediment to Long Island Sound is 9.9 x 10^{11}g/y (Table 16), which leads to an excess ^{210}Pb riverine delivery of 5.9 x 10^{12} dpm/y, or ~2.4% of the total annual atmospheric ^{210}Pb flux to the catchment area. Applying this fractional ^{210}Pb erosion rate and a ^{32}Si soil retention rate of 67% (Franke et al., 1988) in Connecticut River suspended sediments leads to a maximum estimate of continental ^{32}Si delivery of 0.11 – 0.13 dpm/kg.

All of these environments import water, and marine biogenic Si, from offshore due to estuarine flow (Shiller and Boyle, 1991; Turner and Rabalais, 1994; Wolanski et al., 1995; Aller et al., 2008). From these calculations, it is evident that the majority of the ^{32}Si bulk activity in the Gulf of Papua must have a marine biogenic Si source rather than a continental one. A study of organic carbon remineralization also indicates significant marine carbon sources in this region (Aller et al., 2008). It also seems likely that the ^{32}Si activities in the Si – NaOH operational pools at the Mississippi Delta site have a significant marine contribution. δ^{13}C signatures of sedimentary organic carbon at this particular study site indicates a mix of terrestrial and marine sources (Turner and Rabalais, 1994), and marine carbon inputs appear to dominate 40 – 60 km west of the study site. Approximately half of the sediment which accumulates in Long Island Sound is of marine origin (Bokuniewicz et al., 1976). Sedimentary organic carbon also appears to be primarily of marine origin in Long Island Sound (Sun et al., 1994). The ^{32}Si activities in Smithtown Bay may reflect regional authigenic clay formation.

In summary, ^{32}Si activities reveal that both conventional bSi and $\sum Si_{hr}$ operational leaches consistently underestimate e the amount of biogenic and reactive Si that is buried in a variety of different depositional settings from tropical to temperate regions. Some of this reactive silica may have a continental origin (e.g. phytoliths or diatoms) and may reflect rapidly formed pedogenic silicates. In tropical settings, the classic leaches fail to extract the vast majority of biogenic and reactive Si. In subtropical and temperate settings anywhere from 57 – 75% of reactive Si may remain in sediments as an altered form, presumably authigenic clay. In tropical and subtropical deltaic systems, ^{32}Si activities indicate that the extractable Si in sediment has gone through a marine biogenic phase. Relative ^{32}Si activities also confirm that almost complete alteration of biogenic Si, most likely to an authigenic clay, occurs very rapidly in tropical deltas where Al- and Fe-oxide supplies are high due to intense drainage basin weathering. In subtropical deltas and temperate estuaries Si contents are 2 – 4X higher than those derived using classic biogenic Si leaches alone.

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Table 16. Select characteristics/parameters of the rivers supplying the majority of reactive Si to study sites. The majority of this information is replicated from the data base created by Meybeck and Ragu (1995). When multiple values are found from different references for the same parameter, the more recent estimate was used in this study.

Study Site	River	Drainage Area (10^6 km^2)	Riverine freshwater Discharge (km^3/y)	Annual Suspended Load (10^6 tons/y)	TSS* (mg/L)	TDS** (mg/L)	DSi (µmol/L)	DSi Riverine Flux[1] (Tmol/y)	ASi Flux[2] (Tmol/y)	SGD DSi Flux[3] (Tmol/y)	Total Flux (Tmol/y)[1]
French Guiana											
	Amazon	6.112	6590	1200	182	44	115	0.76	0.12	0.13	1.0
	Tocantins	0.7570	372	75	202	40.8	193	0.072	0.0075	7.1 x 10^{-3}	0.086
	Suriname	0.0160	11.00	0.30	27.3	30.2	145	0.0016	3.0 x 10^{-5}	2.1 x 10^{-4}	0.0018
	Approuague	0.0102	11.60	0.20	17.2	35.8	250	0.0029	2.0 x 10^{-5}	2.2 x 10^{-4}	0.0031
	REGION TOTAL	6.90	6985	1276				0.83	0.13	0.13	1.1
Gulf of Papua											
	Fly	0.061	141	16.33	816	116	150	0.021	0.012	2.7 x 10^{-3}	0.035
	Kikori	0.0132	47.30			177	133	0.0063		9 x 10^{-4}	0.0072
	Purari	0.0306	84.13	80	951	126	230	0.019	0.008	1.6 x 10^{-3}	0.029
	REGION TOTAL	0.105	272.4 (473[a])	96.33 (384[b])				0.047 (0.081)[e]	0.02 (0.04)[f]	5.2 x 10^{-3} (9 x 10^{-3})[g]	0.072–0.14
Northern Gulf of Mexico											
	Mississippi	2.98	580 (628[c])	500 (210[d])	862	216	112	0.065 (0.082)[h]	0.0 (0.021)[i]	0.011 (0.012)[j]	0.097–0.14
Long											

Island Sound											
	Connecticut	0.025	17	0.99		70	84	0.0014	3.6×10^{-6}	3.2×10^{-4}	0.0018

[*] TSS = Total suspended solids

[**] TDS = Total dissolved solids

[1] Riverine DSi flux = (river freshwater discharge (L/y)) x (riverine dissolved Si concentration (μM)

[2] ASi Flux = (river freshwater discharge (L/y)) x (TSS(g/L)) x (0.006)/ (60 g/mol SiO_2)

[3] SGD DSi = (river freshwater discharge (L/y)) x (0.05) x (380 (μM))

[a] Ref – Wolanski et al. (1995) estimated the combined freshwater discharge to the Gulf of Papua as ~15, 000 m^3/s

[b] from Milliman et al. (1999)

[c] Goolsby (1999) estimated a long – term average discharge rate of 19, 920 m^3/s (~628 km^3/y) of the Atchafalaya and Mississippi Rivers to the Gulf of Mexico from 1950 – 1996.

[d] Milliman and Meade (1983) Mississippi River sediment load estimate was 210 x 10^6 tons/y.

[e] 0.081 Tmol/y riverine DSi flux calculated using freshwater discharge rate of 15, 000 m^3/s (Wolanski et al., 1995) and average [Si] of the Fly, Kikori, and Purari rivers (e.g. 171 μM).

[f] 0.04 Tmol/y ASi flux calculated using TSS load of 384 x 10^6 tons/y (Milliman et al., 1999) delivered to the Gulf of Papua

[g] 0.009 Tmol/y SGD DSi Flux calculated using freshwater discharge rate of 15, 000 m^3/s (Wolanski et al., 1995)

[h] Goolsby (1999) estimated an average dissolved Si flux of 2, 316, 800 ± 289, 700 tons/y from 1980 – 1996.

[i] 0.021 Tmol/y ASi flux calculated using the suspended load estimate in Milliman and Meade (1983) of 210 x 10^6 tons/y.

[j] 0.012 Tmol/y SGD DSi Flux calculated using freshwater discharge rate of 628 km^3/y.

Table 17. Bulk ^{32}Si activities and other parameters for the bSi and $\sum$Si$_{hr}$ classic and sequential extractions.

	^{32}Si Bulk Activity (dpm/kg dry wt)	% yield[a]	Bulk Sediment Mass (g)	Classic leach Si contents (µmol/g)[b]	bSi/$\sum$Si$_{hr}$ %	% total activity (^{32}Si extractions)[c]
Amazon – Guianas						
Amazon River Mouth						
bSi	N.D.		1712	17	25%	0%
Si-NaOH(-bSi)	0.65 ± 0.26	14	1712	613		100%
$\sum$Si$_{hr}$	Bkgd		3271	68		
Si-NaOH(-$\sum$Si$_{hr}$)	0.22 ± 0.05	28	3271	613*		
Sta 1						
bSi	Bkgd		1291	35	17.5%	0%
Si-NaOH(-bSi)	0.78 ± 0.15	30	1291	916		100%
$\sum$Si$_{hr}$	N.D.			200		
Si-NaOH(-$\sum$Si$_{hr}$)	N.D.			916*		
Sta 2						
bSi	Bkgd		1333	35	17.5%	0%
Si-NaOH(-bSi)	0.92 ± 0.25	43	1333	1347		100%
$\sum$Si$_{hr}$	N.D.			200		
Si-NaOH(-$\sum$Si$_{hr}$)	N.D.			1347*		
Sta 3						
bSi	Bkgd		968	35	17.5%	0%
Si-NaOH(-bSi)	1.72 ± 0.29	43	968	944		100%
$\sum$Si$_{hr}$	N.D.			200		
Si-NaOH(-$\sum$Si$_{hr}$)	N.D.			944*		
Kourou						
bSi	N.D.		466	40	13.3%	0%
Si-NaOH(-bSi)	5.4 ± 1.3	21	466	2100		100%
$\sum$Si$_{hr}$	N.D.			300		
Si-NaOH(-$\sum$Si$_{hr}$)	N.D.			2100*		
Sinnamary – MI AA						

bSi	N.D.		2262	20	6.8%	0%
Si-NaOH(-bSi)	0.37 ± 0.03	43	2262	985		100%
$\sum \mathrm{Si}_{\mathrm{hr}}$	N.D.			294		
Si-NaOH(-$\sum Si_{hr}$)	N.D.			908		
Sinnamary – MI E						
bSi	N.D.		959	20	5.6%	0%
Si-NaOH(-bSi)	1.0 ± 0.2	38	959	931		100%
$\sum \mathrm{Si}_{\mathrm{hr}}$	0.17 ± 0.04	56	1766	355		44%
Si-NaOH(-$\sum Si_{hr}$)	0.22 ± 0.08	38	1766	792		56%
Sinnamary – MI H						
bSi	N.D.		1239	8	2.6%	0%
Si-NaOH(-bSi)	0.28 ± 0.09	36	1239	650		100%
$\sum \mathrm{Si}_{\mathrm{hr}}$	0.25 ± 0.03	40	2290	309		42%
Si-NaOH(-$\sum Si_{hr}$)	0.34 ± 0.07	33	2290	546		58%
Gulf of Papua						
GH14						
bSi	N.D.		1132	90	23%	0%
Si-NaOH(-bSi)	0.52 ± 0.21	22	1132	525		100%
$\sum \mathrm{Si}_{\mathrm{hr}}$	N.D.	N.D	N.D.	385		
Si-NaOH(-$\sum Si_{hr}$)	N.D.	N.D	N.D.	525*		
GS48						
bSi	N.D.		1128	90	22%	0%
Si-NaOH(-bSi)	0.65 ± 0.07	41	1128	823		100%
$\sum \mathrm{Si}_{\mathrm{hr}}$	N.D.	N.D.	N.D.	401		
Si-NaOH(-$\sum Si_{hr}$)	N.D.	N.D.	N.D.	823*		
Gulf of Mexico						
Mississippi						
bSi	0.24 ± 0.06	29	1970	350	86%	38%
Si-NaOH(-bSi)	0.4 ± 0.1	23	1970	880		62%
$\sum \mathrm{Si}_{\mathrm{hr}}$	0.27 ± 0.05	27	2724	409		34%
Si-NaOH(-$\sum Si_{hr}$)	0.59 ± 0.08	22	2724	753		66%
Long Island Sound						

Smithtown Bay						
bSi	0.15 ± 0.05	54	1730	462	52%	24%
Si-NaOH(-bSi)	0.48 ± 0.09	27	1730	448		76%
$\sum Si_{hr}$	0.3 ± 0.1	51	741	822 (891)[1]		43%
Si-NaOH(-$\sum Si_{hr}$)	0.4 ± 0.4	25	741	486		57%

[a] Actual yield of final product)/(100% theoretical yield of final product)

[b] Si content in classic bSi, Si-NaOH(-bSi), $\sum Si_{hr}$, or NaOH(-$\sum Si_{hr}$)

[1] 891 μmol/g extracted from the combined 0.1N HCl and 1% Na_2CO_3 leaches, whereas 822μmol/g extracted in the 1% Na_2CO_3 leach alone. The Si in the 0.1N HCl pool was lost in the large – scale ^{32}Si extractions.

Table 18. ^{32}Si bulk activity in various fractions (bSi, Si-NaOH(-bSi), ∑Si$_{hr}$, or NaOH(-∑Si$_{hr}$)) of modified sequential extractions, Si contents in classic bSi and ∑Si$_{hr}$ leaches, and calculated ^{32}Si specific activities. All ^{32}Si activity assigned to either the SiO$_2$ extracted in the classic bSi (1% Na$_2$CO$_3$ leach) or the classic ∑Si$_{hr}$ (0.1N HCl and 0.1M Na$_2$CO$_3$ extraction) leaches in calculations of specific activity.

Study Site	Sequential Extraction Fraction[1]	^{32}Si bulk activity (dpm/kg dry wt)	Bulk Sediment Mass (g)[*]	Classic bSi[**] (µmol Si/g sed)	Classic ∑Si$_{hr}$[***] (µmol Si/g sed)	^{32}Si specific activity (dpm/kg bSi)[a]	^{32}Si specific activity (dpm/kg ∑Si$_{hr}$)[b]
French Guiana							
Amazon RM	*Si-NaOH(-bSi)*	0.65 ± 0.26	1712	17	68	650 ± 260	160 ± 60
	Si-NaOH(-∑Si$_{hr}$*)*	0.22 ± 0.08	3271	17	68	220 ± 50	50 ± 10
Sta 1	*Si-NaOH(-bSi)*	0.78 ± 0.15	1291	35	200	370 ± 70	65 ± 12
Sta 2	*Si-NaOH(-bSi)*	0.92 ± 0.25	1333	35	200	400 ± 100	77 ± 21
Sta 3	*Si-NaOH(-bSi)*	1.7 ± 0.3	968	35	200	800 ± 100	143 ± 24
Kourou	*Si-NaOH(-bSi)*	5.4 ± 1.3	466	40	300	2200 ± 500	300 ± 70
Sinnamary – MI AA	*Si-NaOH(-bSi)*	0.37 ± 0.03	2262	20	294	300 ± 30	21 ± 2
Sinnamary – MI E	*Si-NaOH(-bSi)*	0.96 ± 0.15	959	20	355	800 ± 100	45 ± 7
	∑Si$_{hr}$	*0.17 ± 0.04*	1766	20	355	140 ± 30	8 ± 2
	NaOH(-∑Si$_{hr}$*)*	*0.22 ± 0.08*	1766	20	355	190 ± 60	11 ± 4
Sinnamary – MI H	*Si-NaOH(-bSi)*	0.28 ± 0.09	1239	8	309	600 ± 200	15 ± 5
	∑Si$_{hr}$	*0.25 ± 0.03*	2290	8	309	510 ± 70	13 ± 2
	Si-NaOH(-∑Si$_{hr}$*)*	*0.34 ± 0.07*	2290	8	309	700 ± 100	18 ± 4
Gulf of Papua							
GS48	*Si-NaOH(-bSi)*	0.65 ± 0.07	1128	90[1]	401	120 ± 13	27 ± 3
GH14	*Si-NaOH(-bSi)*	0.52 ± 0.21	1132	90[1]	385	96 ± 40	22 ± 9
Northern Gulf of Mexico							
Mississippi	*bSi*	0.24 ± 0.06	1970	350	409	11 ± 4	10 ± 3
	Si-NaOH(-bSi)	0.4 ± 0.1	1970	350	409	18 ± 5	16 ± 4

	$\sum Si_{\mathrm{hr}}$	0.27 ± 0.05	2725	350	409	13 ± 2	11 ± 2
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$)	0.59 ± 0.08	2725	350	409	28 ± 4	24 ± 3
Long Island Sound							
Connecticut	*bSi*	0.15 ± 0.05	1730	462	822^{2}	5 ± 2	2.8 ± 0.9
	Si-NaOH(-bSi)	0.48 ± 0.09	1730	462	822^{2}	17 ± 3	9 ± 2
	$\sum Si_{\mathrm{hr}}$	0.3 ± 0.1	741	462	822^{2}	10 ± 5	6 ± 3
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$)	0.4 ± 0.4	741	462	822^{2}	13 ± 14	7 ± 8

**Sample mass used in ^{32}Si bSi sequential extractions (bSi followed by 4M NaOH) given in parentheses.

**Si extracted in the classic 0.1 M Na_2CO_3 bSi leach (DeMaster, 1979) using classic sediment mass to solution volumes. Si content in hot 4M NaOH leach using ~1g:10ml solution volumes given in parentheses.

***Si extracted in the combined 0.1N HCl and 0.1 M Na_2CO_3 leach fractions using classic sediment mass to solution volumes as outlined in Michalopoulos and Aller (2004). When available, the Si content in hot 4M NaOH leach following the $\sum Si_{\mathrm{hr}}$ sequential extraction is given in parentheses.

[a] Specific activity of initial bSi calculated assigning all ^{32}Si activity to the SiO_2 extracted in the operationally defined bSi fraction (classic 0.1M Na_2CO_3 leach)

[b] Specific activity of initial bSi calculated assigning all ^{32}Si activity to the SiO_2 extracted in the operationally defined $\sum Si_{\mathrm{hr}}$ fraction (classic 0.1N HCl followed by 0.1M Na_2CO_3 leach).

[1] Si content after 1.75h long extraction in hot 0.1M Na_2CO_3

[2] 891 µmol/g extracted from the combined 0.1N HCl and 1% Na_2CO_3 leaches, whereas 822µmol/g extracted in the 1% Na_2CO_3 leach alone. The Si in the 0.1N HCl pool was lost in the large – scale ^{32}Si extractions, so the 822 µmol/g Si content was used to calculate specific activity attributed to $\sum Si_{\mathrm{hr}}$ pool in these samples.

Table 19. ^{32}Si activity in residual 4M NaOH pool after removal of bSi and $\sum Si_{\mathrm{hr}}$ fractions and reactive Si storage estimates.

Study Site	Fraction[1]	^{32}Si bulk activity (dpm/kg sed)	Calculated Biogenic Si (mmol Si/g)	Calculated Biogenic Si (mmol Si/g)	Calculated Biogenic Si (mmol Si/g)
			SM = 5 dpm/kg SiO_2^{a}	*SM = 15 dpm/kg* SiO_2^{b}	*SM = 40 dpm/kg* SiO_2^{c}
FRENCH GUIANA					
Amazon RM	*Si-NaOH(-bSi)*	0.65 ± 0.26	2.2 ± 0.9	0.7 ± 0.3	0.3 ± 0.1
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$*)*	0.22 ± 0.08	0.7 ± 0.2	0.24 ± 0.06	0.09 ± 0.02
Sta 1	*Si-NaOH(-bSi)*	0.78 ± 0.15	2.6 ± 0.5	0.9 ± 0.2	0.32 ± 0.06
Sta 2	*Si-NaOH(-bSi)*	0.92 ± 0.25	3.1 ± 0.8	1.0 ± 0.3	0.4 ± 0.1
Sta 3	*Si-NaOH(-bSi)*	1.7 ± 0.3	6 ± 1	1.9 ± 0.3	0.7 ± 0.1
Kourou	*Si-NaOH(-bSi)*	5.4 ± 1.3	18 ± 4	6 ± 1	2.2 ± 0.5
Sinnamary – MI AA	*Si-NaOH(-bSi)*	0.37 ± 0.03	1.2 ± 0.1	0.41 ± 0.03	0.15 ± 0.01
Sinnamary – MI E	*Si-NaOH(-bSi)*	0.96 ± 0.15	3.2 ± 0.5	1.1 ± 0.2	0.40 ± 0.06
	$\sum Si_{\mathrm{hr}}$	0.17 ± 0.04	0.6 ± 0.1	0.19 ± 0.04	0.07 ± 0.02
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$*)*	0.22 ± 0.08	0.7 ± 0.3	0.25 ± 0.09	0.09 ± 0.03
Sinnamary MI H	*Si-NaOH(-bSi)*	0.28 ± 0.09	0.9 ± 0.3	0.3 ± 0.1	0.12 ± 0.04
	$\sum Si_{\mathrm{hr}}$	0.25 ± 0.03	0.8 ± 0.1	0.27 ± 0.04	0.10 ± 0.01
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$*)*	0.34 ± 0.07	1.1 ± 0.2	0.37 ± 0.08	0.14 ± 0.03
GULF OF PAPUA					
GS48	*Si-NaOH(-bSi)*	0.65 ± 0.07	2.1 ± 0.2	0.72 ± 0.08	0.27 ± 0.03
GH14	*Si-NaOH(-bSi)*	0.52 ± 0.21	1.7 ± 0.7	0.6 ± 0.2	0.22 ± 0.09
GULF OF MEXICO					
Mississippi	*bSi*	0.24 ± 0.06	0.8 ± 0.2	0.27 ± 0.07	0.10 ± 0.03
	Si-NaOH(-bSi)	0.4 ± 0.1	1.3 ± 0.4	0.4 ± 0.1	0.16 ± 0.04
	$\sum Si_{\mathrm{hr}}$	0.27 ± 0.05	0.9 ± 0.2	0.30 ± 0.06	0.11 ± 0.02
	Si-NaOH(-$\sum Si_{\mathrm{hr}}$*)*	0.59 ± 0.08	2.0 ± 0.3	0.66 ± 0.09	0.25 ± 0.03
LONG ISLAND SOUND					
Smithtown	*bSi*	0.15 ± 0.05	0.5 ± 0.2	0.2 ± 0.05	0.06 ± 0.02

Bay					
	Si-NaOH(-bSi)	0.48 ± 0.09	1.6 ± 0.3	0.5 ± 0.1	0.20 ± 0.04
	$\sum Si_{\text{hr}}$	0.3 ± 0.1	0.9 ± 0.4	0.3 ± 0.1	0.11 ± 0.06
	Si-NaOH(-$\sum Si_{\text{hr}}$*)*	0.4 ± 0.4	1 ± 1	0.4 ± 0.4	0.2 ± 0.2

[1] Final product was magnesium ammonium phosphate – hexahydrate (100% yield = 0.0981g).

[a] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is the lower end of the average range given by Fifield and Morgenstern (2009) (5 dpm/kg SiO_2) and the average ^{32}Si/SiO_2 activity in the top 1000m at GEOSECS Pacific Ocean Station 263 (Somayajulu et al., 1991).

[b] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is the average of activities (15 dpm/kg SiO_2) in low latitude tropical rivers and particulate Si in Equatorial Atlantic Ocean waters of 10 – 20 dpm/kg SiO_2 (Nijampurkar et al., 1966; Somayajulu et al., 1987), and the average ^{32}Si/SiO_2 activity in the top 1000m at GEOSECS Indian Ocean Station 452 (Somayajulu et al., 1991).

[c] Biogenic Si storage calculated assuming initial ^{32}Si activity of starting material is average estimate of particulate Si in the surface Atlantic Ocean of 40 dpm/kg SiO_2 (Somayajulu et al., 1987; Craig et al., 2000), and the average ^{32}Si/SiO_2 activity in the top 1000m at GEOSECS Pacific Ocean Staion 306 (Somayajulu et al., 1991). Specific activities in particulate matter in the Atlantic Ocean are ~11% higher than in the Pacific for the same mass (Craig et al., 2000).

Table 20. ^{32}Si activities in the operational pools of the modified bSi sequential extraction (1% M Na_2CO_3 leach followed by 4M NaOH) and regional Si burial flux using an initial ^{32}Si/SiO_2 activity of 15 dpm/kg SiO_2.

Study Site	Operational Pool*	^{32}Si bulk activity (dpm/kg sed)	Assumed Biogenic Si (mmol Si/g)	Accumulation Rate (g/cm^2/y)	Area (cm^2)	Classic Si burial flux (Tmol/y)[1]	Si burial flux from ^{32}Si (Tmol/y)	$bSi_{classic}$ /bSi_{32Si} (%)
Gulf of Papua								
GH14	*Si-NaOH(-bSi)*	0.5 ± 0.2	0.570 ± 0.23	0.80[a]	1.55 x 10^{14} (a)	0.0112	0.07 ± 0.03	17
GS 48	*Si-NaOH(-bSi)*	0.65 ± 0.07	0.718 ± 0.078	0.96[b]	3.97 x 10^{13} (b)	0.0034	0.027 ± 0.003	13
					TOTAL =	**0.015**	**0.10 ± 0.03**	**15**
Gulf of Mexico								
Mississippi	*bSi*	0.24 ± 0.06	0.267 ± 0.070	0.72[c] 0.16[c]	1.55 x 10^{13} (c) 3.44 x 10^{13} (c)	3.9 x 10^{-3} 1.9 x 10^{-3}	3.0 ± 0.8 x 10^{-3} 1.5 ± 0.4 x 10^{-3}	130 130
	Si-NaOH(-bSi)	0.4 ± 0.1	0.42 ± 0.12	0.72[c] 0.16[c]	1.55 x 10^{13} (c) 3.44 x 10^{13} (c)		5 ± 1 x 10^{-3} 2.3 ± 0.7 x 10^{-3}	0 0
					TOTAL =	**0.0058**	**0.012 ± 0.002**	**48**
	$\sum Si_{hr}$	0.27 ± 0.05	0.303 ± 0.058	0.72[c] 0.16[c]	1.55 x 10^{13} (c) 3.44 x 10^{13} (c)	4.6 x 10^{-3} 2.3 x 10^{-3}	3.4 ± 0.6 x 10^{-3} 1.7 ± 0.3 x 10^{-3}	135 135
	Si-NaOH(-$\sum Si_{hr}$)	0.59 ± 0.08	0.657 ± 0.090	0.72[c] 0.16[c]	1.55 x 10^{13} (c) 3.44 x 10^{13} (c)		7 ± 1 x 10^{-3} 3.6 ± 0.5 x 10^{-3}	0 0
					TOTAL =	**0.0069**	**0.016 ± 0.001**	**43**
LIS								
Smithtown Bay	*bSi*	0.15 ± 0.05	0.166 ± 0.052 (0.50 ± 0.16)[d]	0.08[e]	2.0 x 10^{13} (f)	7.4 x 10^{-4}	2.7 ± 0.8 x 10^{-4} (8 ± 2 x10^{-4})[d]	274 (93)[d]
	Si-NaOH(-bSi)	0.48 ± 0.09	0.56 ± 0.11 (1.67 ± 0.32)[d]	0.08[e]	2.0 x 10^{13} (f)		9 ± 2 x 10^{-4} (2.6 ± 0.5 x 10^{-3})[d]	0 0
					TOTAL =	**7.4 x 10^{-4}**	**1.2 ± 0.2 x 10^{-3}**	**62**

							(3.5 ± 0.6 x 10^{-3})^d	**(42)^d**
	∑Si$_{hr}$	0.3 ± 0.1	0.31 ± 0.15 (0.92 ± 0.44)^d	0.08^e	2.0 x $10^{13\ (f)}$	1.4 x 10^{-3}	5 ± 2 x 10^{-4} (1.5 ± 0.7 x 10^{-3})^d	260 (87)
	Si-NaOH(-∑Si$_{hr}$*)*	0.4 ± 0.4	0.41 ± 0.44 (1.2 ± 1.3)^d	0.08^e	2.0 x $10^{13\ (f)}$		7 ± 7 x 10^{-4} (2 ± 2 x 10^{-3})^d	0 0
						1.4 x 10^{-3}	**1.2 ± 0.7 x 10^{-3}** **(3 ± 2 x10^{-3})^d**	**119** **47^d**

*Operational pool which contains the ^{32}Si activity given in parentheses for each site

[1] Flux calculated using extracted Si from the classic bSi alkaline leach or the two – step acid – alkaline ∑Si$_{hr}$ leach (Table 3).

[a] Average estimate of sediment accumulation rate for the mid – topset in the Gulf of Papua was used to calculate Si burial flux (Brunskill et al., 2003; Walsh et al., 2004) over an area of 15,500km^2. See text for details.

[b] Average sediment accumulation rate and areal extent of the foreset in the Gulf of Papua taken from Aller et al. (2008).

[c] Sediment accumulation rate of 0.16 g/cm^2/y was over an area of 3.44 x 10^{13} cm^2 and an accumulation rate of 0.72 g/cm^2/y spanned an area of 1.55 x 10^{13} cm^2. Areal extent and accumulation rates taken from Corbett et al. (2006).

[d] Calculated Si content and total Si burial flux assuming and initial ^{32}Si/Si activity of 5dpm/kg SiO$_2$, which is consistent with Si contents in classic bSi and ∑Si$_{hr}$ leaches.

[e] Average long – term sediment accumulation rate from Kim and Bokuniewicz (1991).

[f] 60% of total area of Long Island Sound (~3300 km^2) covered by clay/silty sediments (Sun et al., 1994).

Figure 27. Field areas investigated in this study: (A) Mississippi Delta (adapted from Corbett et al., 2006), (B), Gulf of Papua (adapted from Aller et al., 2008), and (C) Long Island Sound (adapted from DeMaster, 1981).

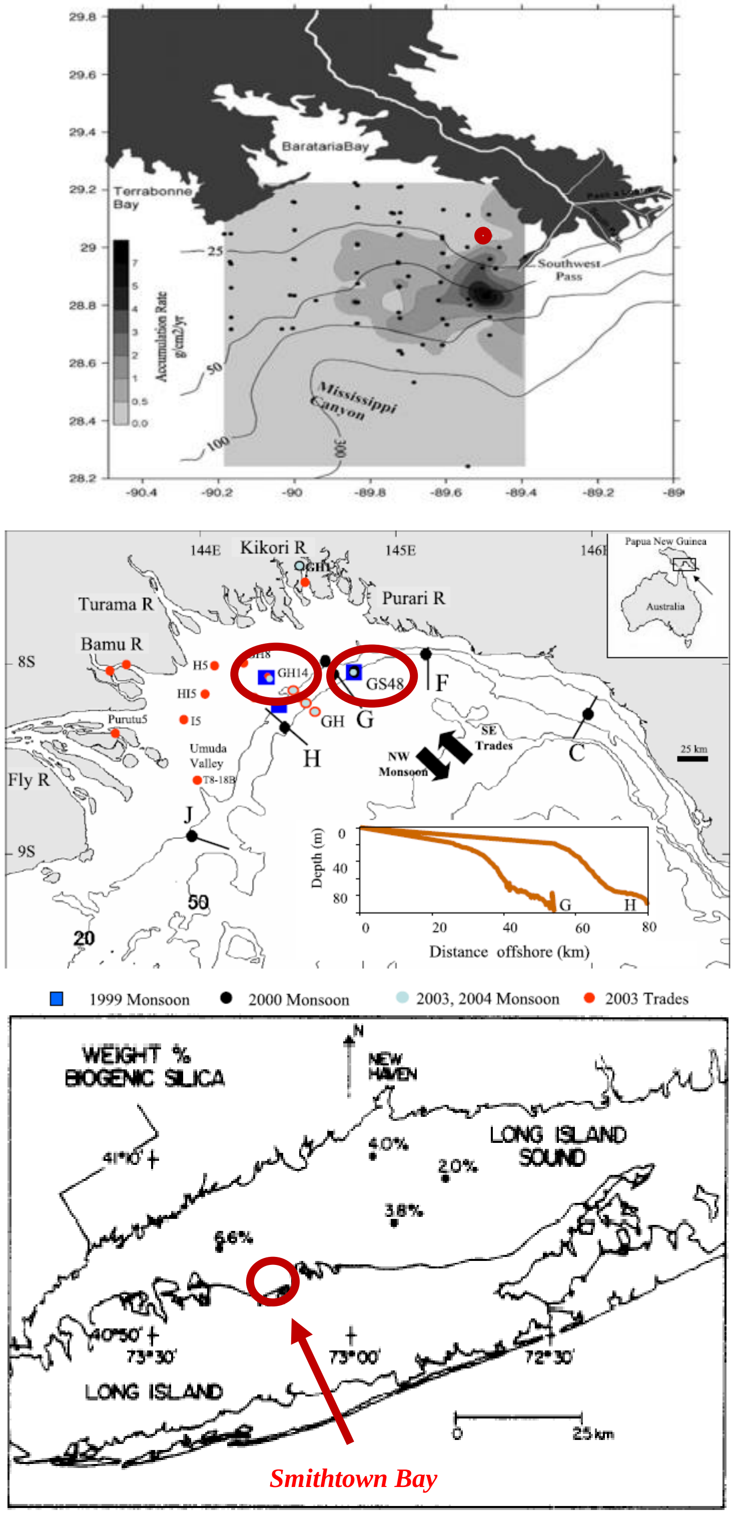


Figure 28. Decay profiles of ^{32}P milked from ^{32}Si in the Si-NaOH(-bSi) fraction (residual pool after removal of bSi; bSi → Si – NaOH) at site (A) GH14 and (B) GS48 in the Gulf of Papua, Papua New Guinea.

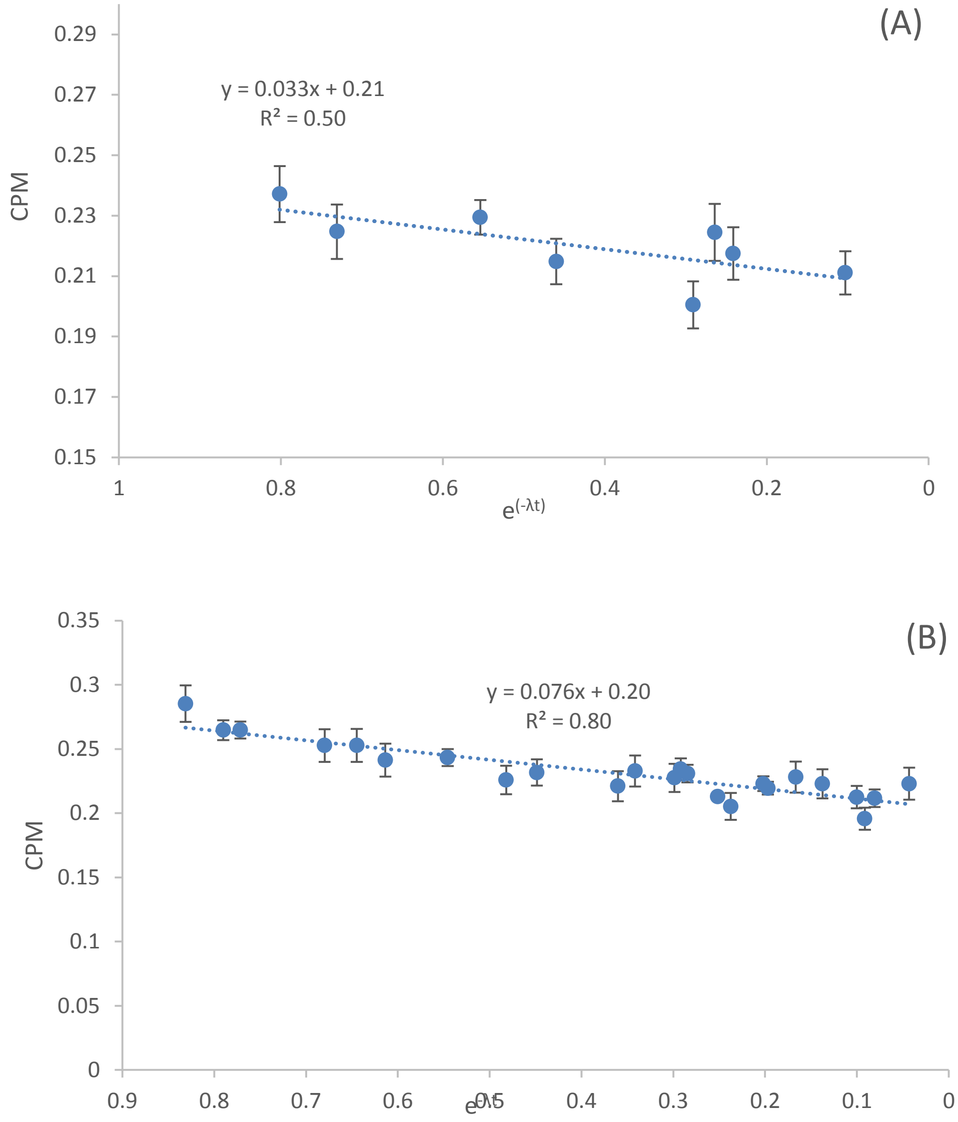


Figure 29. Decay plots of ^{32}P milked from ^{32}Si in (A) the bSi and (B) the residual Si-NaOH(-bSi) fraction at the northern Gulf of Mexico site.

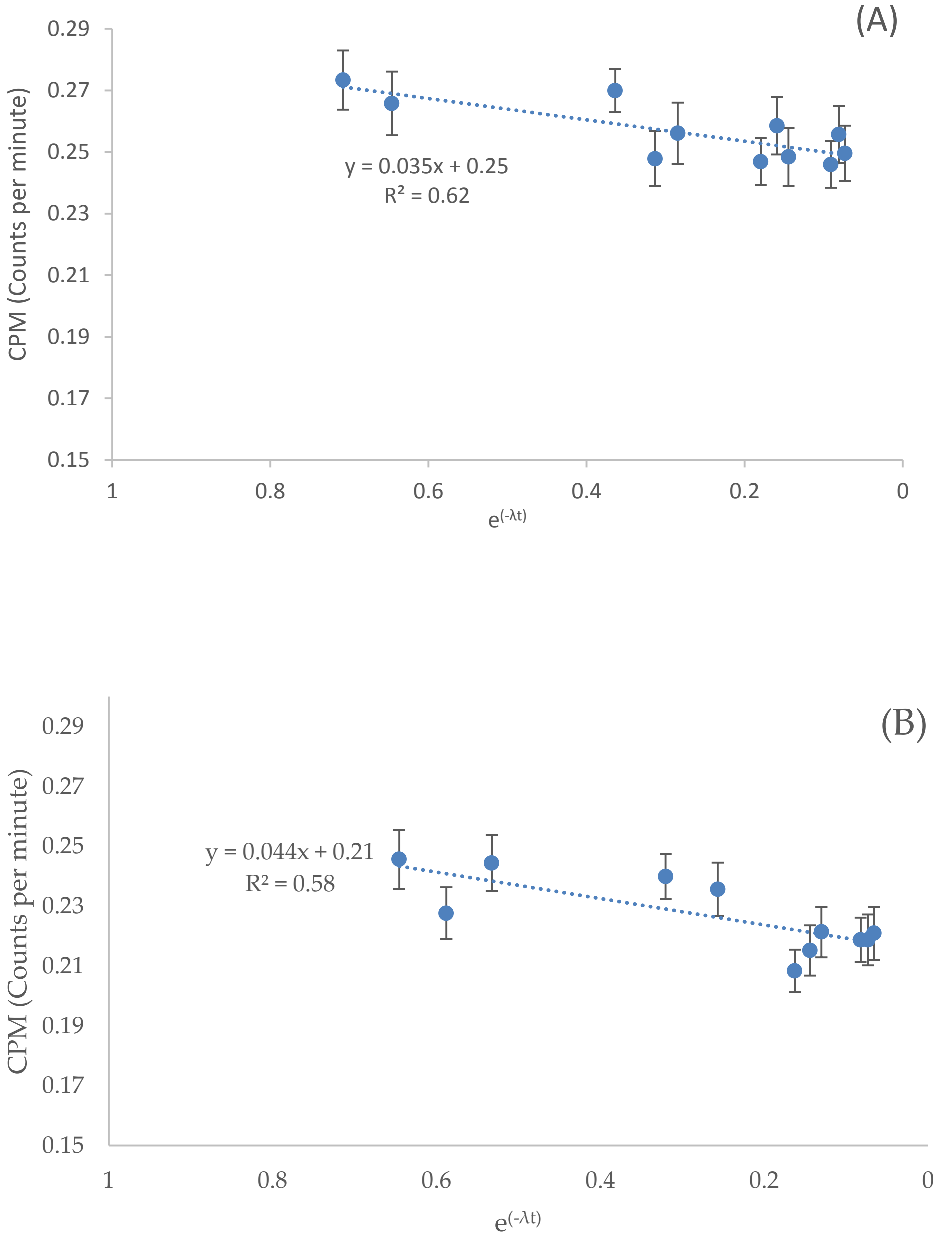
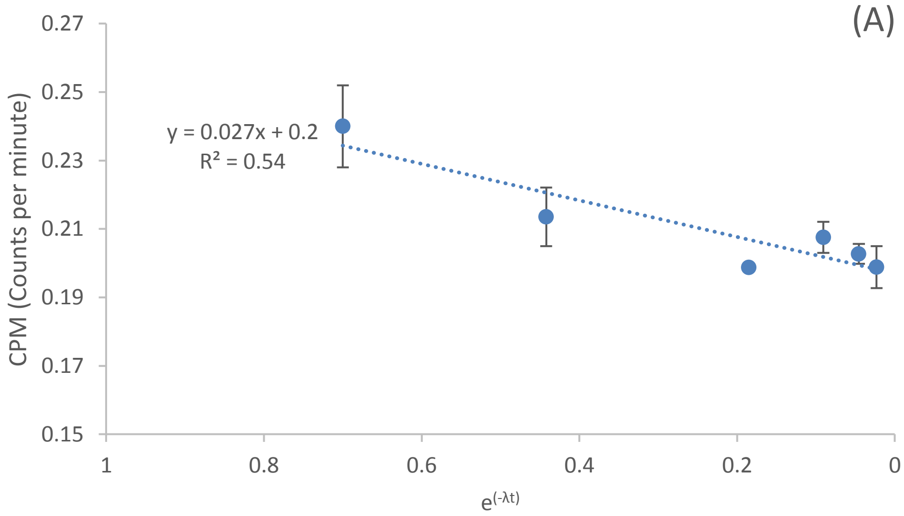


Figure 30. Decay plots of ^{32}P milked from ^{32}Si in (A) the $\sum Si_{hr}$ fraction and (B) the residual NaOH(-$\sum Si_{hr}$) fraction at the northern Gulf of Mexico site.



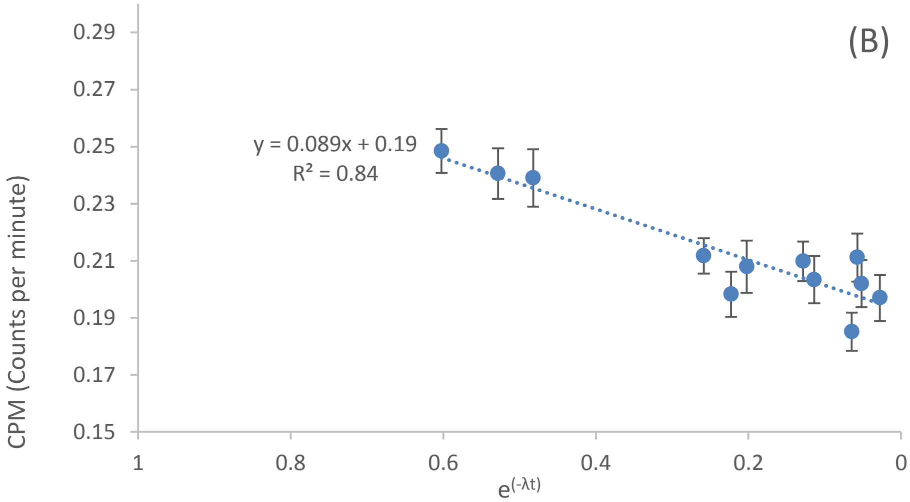


Figure 31. Decay plots of ^{32}P milked from ^{32}Si in (A) the bSi fraction and (B) the residual Si-NaOH(-bSi) fraction at the Smithtown Bay, Long Island Sound.

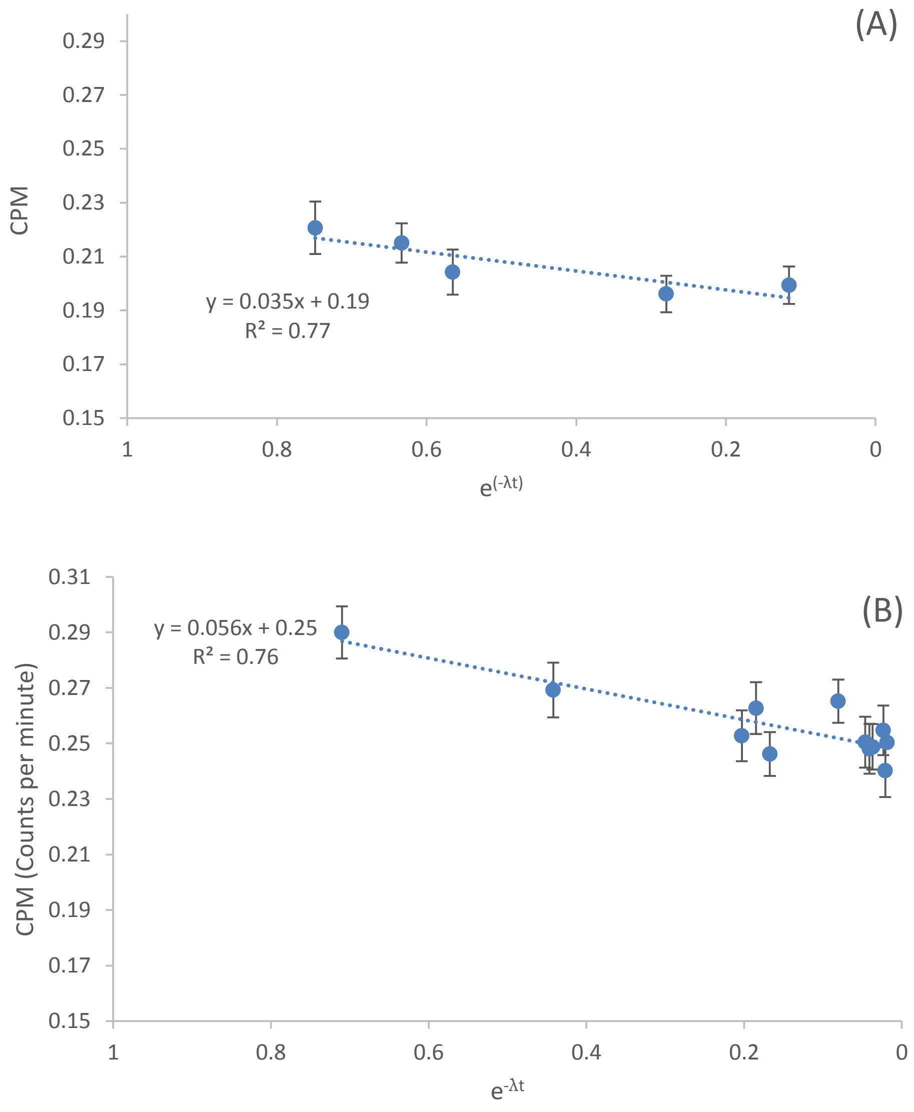


Figure 32. Decay profiles of ^{32}P milked from ^{32}Si in the (A) $\sum Si_{hr}$ and (B) residual Si – NaOH(-$\sum Si_{hr}$) fractions in Smithtown Bay, Long Island Sound.

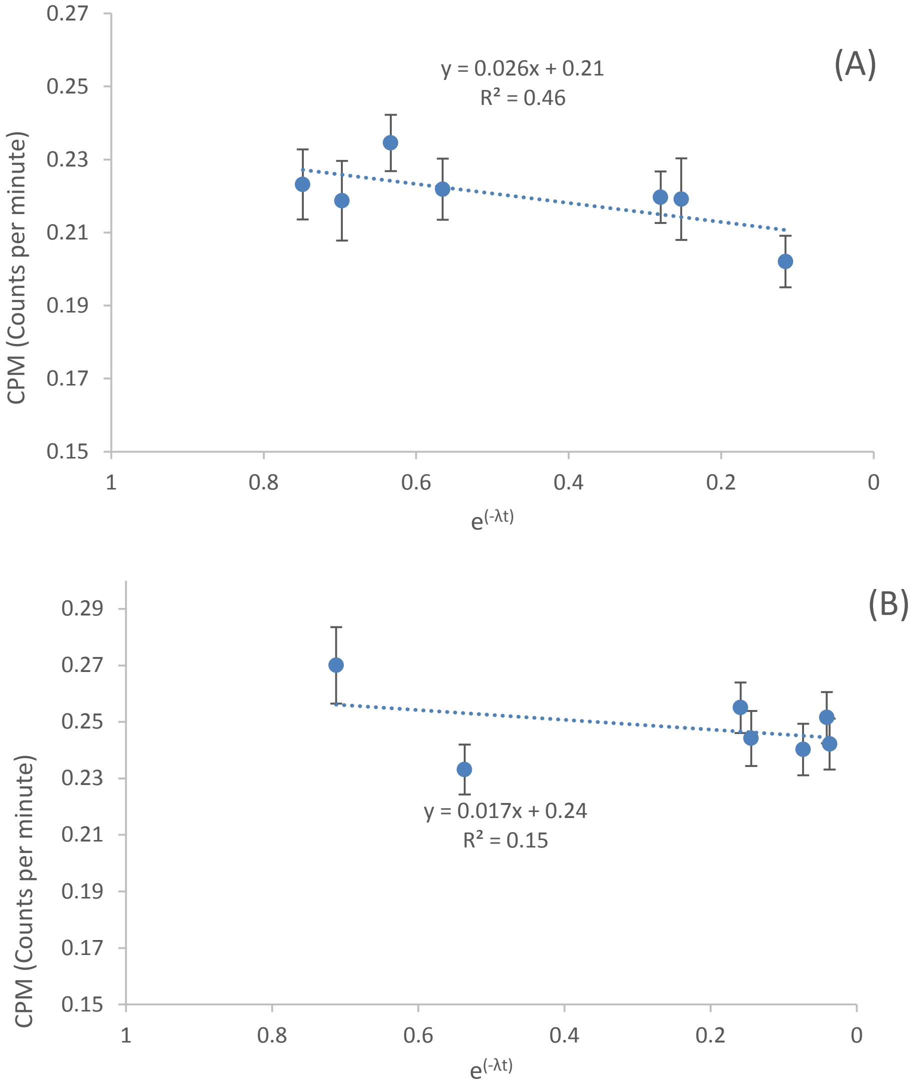


Figure 33. Estimates of original biogenic Si contents using Si extracted from conventional bSi (Table 18), conventional $\sum Si_{hr}$ (Table 18), and ^{32}Si extractions (Table 4). Estimates using ^{32}Si calculated assuming two different initial specific activities of starting biogenic Si materials, namely 5dpm/kg SiO_2 ("32Si-5") and 15 dpm/kg SiO_2 ("32Si-15"). For the Gulf of Papua, estimates are the averages of sites GH14 and GS48. For the Mississippi Delta and Long Island Sound, estimates are the averages of the sum of the operational pools in the two sequential extractions (in other words the average of total ^{32}Si in [bSi + Si-NaOH(-bSi)] and [$\sum Si_{hr}$ + Si-NaOH(-$\sum Si_{hr}$]).

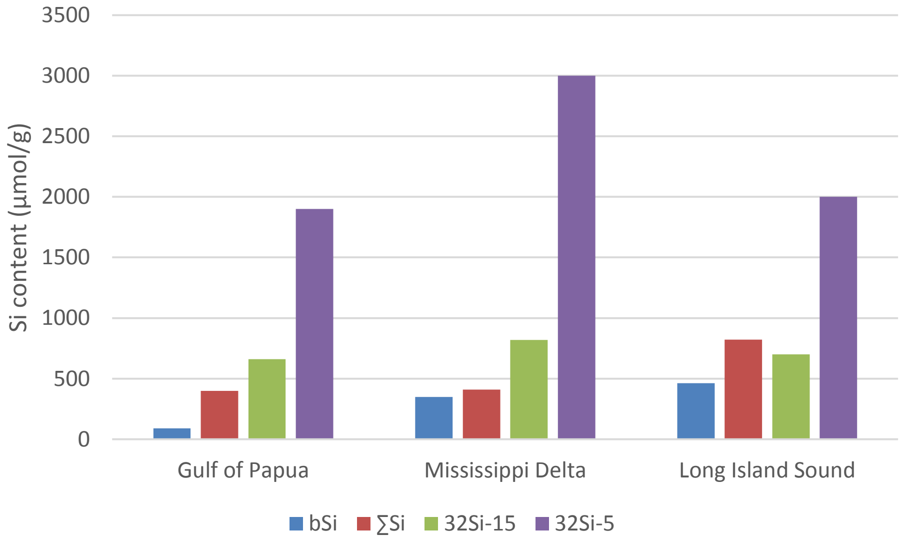
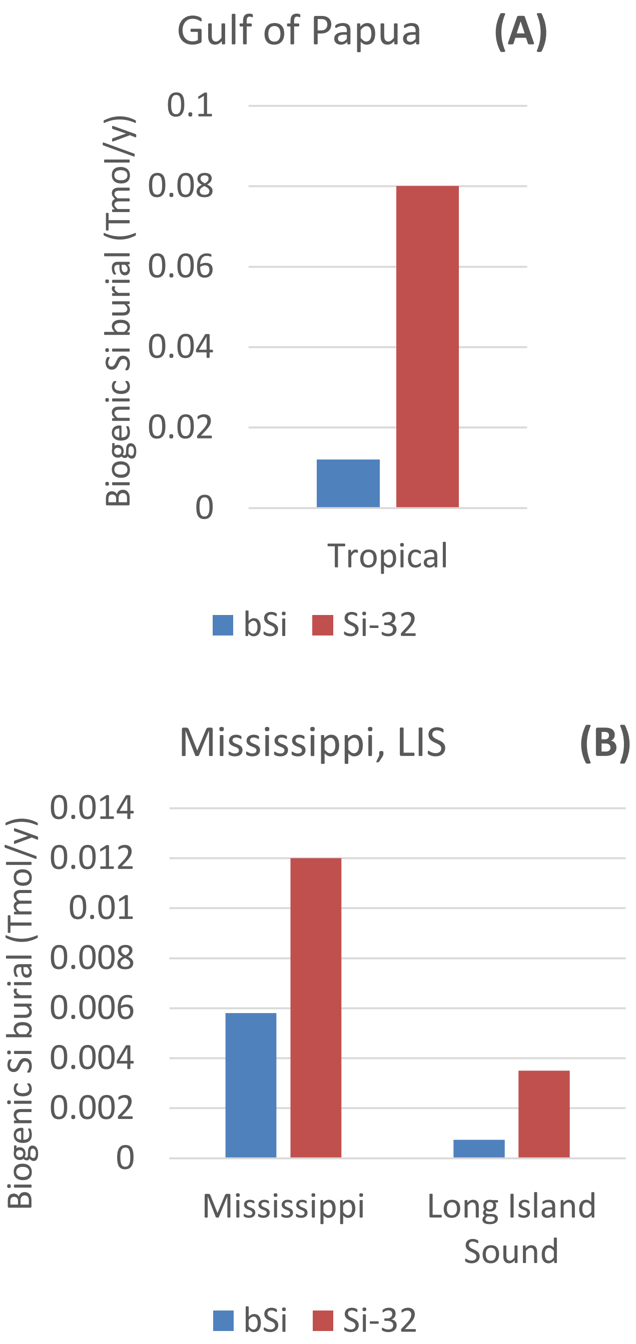


Figure 34. Total storage estimates of original biogenic Si in (A) the Gulf of Papua and (B) Mississippi Delta and Long Island Sound (LIS) using average sediment accumulation rates and Si extracted from the classic bSi leach compared to estimates using ^{32}Si activity (Table 5). Units are in Tmol/y or 10^{12} mol/y.



Chapter 5: Conclusions and Future work

Summary

The objectives of this thesis were several – fold and centered on using cosmogenic ^{32}Si to trace biogenic Si storage in coastal marine sediments in order to decrease the uncertainty of the magnitude of some of the sinks of the global marine Si budget. To that end, a methodology was developed to isolate ^{32}Si in various operational pools and successfully used on deltaic and estuarine sediments. The relative ^{32}Si activities in these various pools revealed that Si sequestration along continental margin sediments has been consistently underestimated by anywhere from 2 up to 20 – fold, and possibly higher. The classic operational leaches designed to extract biogenic silica, on which the marine silica budget is based, cannot be used ubiquitously in all sedimentary environments, and indeed, for most depositional environments will give a significantly lower estimate of reactive or extractable Si storage than actually occurs. Using the ^{32}Si data, some preliminary correction factors may be applied to the marine silica budget, which is done in the following section.

This thesis indicates that cosmogenic ^{32}Si can be used effectively to trace biogenic Si and can now be used, along with other tracers such as stable Si isotopes, to further constrain the Si cycle. More information, some site specific, is needed to validate or revise the initial findings of Si burial using this radionuclide. The major piece that is missing from this work is an accurate estimate of the initial ^{32}Si/Si specific activity of fresh siliceous materials in the study sites of this thesis. Plankton tows should be undertaken in these areas to retrieve adequate sample masses for ^{32}Si analysis in order to define this end – member more accurately. Also, characteristic sediment samples from river mouths, along with measurements of SPM or TSS, should be taken to define the ^{32}Si activity in this source material. Downcore measurements of relative ^{32}Si activity in the various defined operational pools at particular sites would demonstrate the degree of authigenic clay formation or bSi alteration, and the rates of conversion. Degree of Si sequestration in soils and in riverbeds could also be traced using ^{32}Si to obtain a more complete source – to – sink perspective of the Si cycle.

Revisiting the marine Si budget

The Si burial rates calculated in this study based on cosmogenic ^{32}Si activities in sediments can be used to revise some of the sinks in the global marine Si budget (Table 21). The ^{32}Si – based rates of burial relative to those based on classic bSi leaches lead to an increased magnitude of Si removal in continental margins (Table 21 and 22). An initial estimate of Si in tropical and subtropical deltas was added as a specific burial term in the continental margins in Table 21 and expanded in Table 22.

First, in temperate estuarine systems, relative ^{32}Si bulk activities suggest that Si sequestration in sediments is 2 – 4X that predicted using the classic bSi leach. This is in good agreement with the relative increases of bSi estimated in this thesis for Long Island Sound. Second, the total Si burial fluxes, likely through authigenic clay formation, from the two tropical and one subtropical dispersal systems were summed and added as a discrete burial term in continental margins. The Amazon – Guianas dispersal system sequesters ~0.5Tmol/y, the Gulf of Papua sequesters 0.08Tmol/y, and the Mississippi, 0.012 – 0.016Tmol/y, for a total of ~0.6Tmol/y in these three regions alone. Assuming the Orinoco systems behaves similarly to the Amazon Delta, then applying the 1.8 wt. % Si content of Amazon deltaic sediments (Michalopoulos and Aller, 2004) to the Orinoco leads to further burial of 0.097Tmol Si per y. If the the Changjiang – East China Sea dispersal system with its regions of mobile muds behaves similarly to the Amazon – Guianas system, then a further 0.05Tmol/y Si, 50% of the ~0.1Tmol Si per year supplied by the river, may be buried there (Zhang et al., 2003; Ran et al., 2013; Yao et al., 2014).

The estimate in the Mississippi Delta covers a region of relatively low sediment accumulation. Presti and Michalopoulos (2008) using the classic bSi and $\sum Si_{hr}$ leaches came up with a similar burial term for the Delta, but their study included regions of high sediment accumulation rates. It is worth noting that using cosmogenic ^{32}Si, even after removal of the $\sum Si_{hr}$ fraction, which had comparable amounts of Si as Presti and Michalopoulos (2008), twice as much ^{32}Si activity remained in the residual NaOH(-$\sum Si_{hr}$) fraction. So, conservatively based on relative ^{32}Si activities, the Mississippi Delta may entrain 2X as much Si as was estimated by those researchers (i.e. ~700 – 900 µmol/g), for a total burial rate of ~0.03Tmol/y, ~20% of the total reactive Si inputs to the area. If a similar Si content is applied to the 43 x 10^6 tons/y sediment flux from the Zaire, which also features a submarine canyon (Nittrouer et al., 1995), a further 0.03Tmol/y Si may be buried there.

About 2200 x 10^6 tons/y of sediment flux from the Indo – Pacific islands discharges onto broad continental shelves, like the 384 x 10^6 tons/y that discharges onto the Gulf of Papua (Walsh et al., 2004). The other 1950 x 10^6 tons/y discharges onto narrow shelves from the Archipelago. Using the calculated biogenic Si storage estimates, 570 µmol Si/g and 718 µmol/g, from the Gulf of Papua presented in Chapter 4 (Table 20) and applying it to the ~2 x 10^{15} g/y sediment flux onto broad continental shelves in Oceania leads to a total Si burial of 1.3 – 1.6 Tmol/y.

There is ^{32}Si activity data available from a core taken in the foreset of the subaqeous delta in the Bay of Bengal, where researchers used ^{32}Si to determine sedimentation rates (Morgenstern et al., 2001). After the initial extraction of SiO_2 using 4M NaOH, their methods deviated from that outlined in DeMaster (1979), which was the basis for SiO_2 purification in this work. They estimated an initial specific activity of ~6dpm/kg SiO_2. However, it is not clear how much sediment was processed for each sample, and from the brevity of information regarding their methods and calculations, Si storage using ^{32}Si activities in this subaqeous delta was not be calculated using their ^{32}Si data. They did estimate a bSi content of ~1% from their sediment extractions. Milliman and Meade (1983) estimated a sediment flux of 1670 x 106 tons/y from the Ganges/Brahmaputra river system, and applying a bSi content of 1% SiO_2, leads to Si storage of 0.3Tmol/y in the Bay of Bengal. Adding the Si storage from this region to the projections to the ones above lead a total Si burial of 2.3 – 2.6 Tmol/y in tropical/subtropical systems similar to our study sites.

Sources or sinks of reactive and dissolved Si

Submarine groundwater discharge may be a source of dissolved and reactive Si to the global ocean on par with riverine discharge. This source term in the marine budget is quite uncertain and is estimated based on freshwater or meteoric water discharge through aquifers, and does not consider recirculated brackish waters. In a study of SGD in a highly permeable coastal zone and the influence on nutrient exports to the coast, researchers found significant seasonal variation, with SGD accounting for 0 to 76% of the total dissolved Si flux to the area (Kim et al., 2008). Preliminary estimates of SGD to Smithtown Bay indicate rates which vary over two orders of magnitude depending on the season (J.J. Tamborski, unpublished data, personal communication) and can be equal to the freshwater discharge from the Nissequogue River, a local river (freshwater discharge ~ 0.02km^3/y) which drains directly into Smithtown Bay. Indeed, Garcia – Orellana et al. (2014) calculated the SGD to the Long Island Sound, consisting almost entirely of recirculated groundwater, was 1 – 3x the freshwater discharge from the Connecticut River. Submarine groundwater Si fluxes to the Bay of Bengal, 0.093Tmol/y, were estimated to be almost equal to the total riverine dissolved Si flux from the Ganges – Brahmanputra drainage basin of 0.14 Tmol/y (Georg et al., 2009). This input alone accounts for 15% of the 0.6 ± 0.6 Tmol/y Si source via SGD by Treguer and De La Rocha (2013). Given this data, revisions upwards of Si flux via SGD to the global ocean seem likely.

Another source of reactive silica which may warrant upwards revision is amorphous Si supplied by rivers. This source was estimated at ~1.1 ± 0.2 Tmol/y as part of the riverine Si flux, based primarily on classic bSi extractions of river SPM. The bSi content of SPM in the Amazon River is 160 µmol/g, or 0.96 wt% bSi (Conley, 1997). The bSi and $\sum Si_{hr}$ derived Si contents of channel sediments were 37 µmol/g and 56 µmol/g, respectively, whereas they were 51 µmol/g and 102 µmol/g in the <63 µm fraction of the same sediment. If the Amazon River mouth sample in this study is representative of SPM in this river, the ^{32}Si activity in the residual NaOH(-bSi) fraction indicates that there is significantly more biogenic or reactive Si (and Si-32) stored in the Amazon riverbed than these prior studies had estimated, by anywhere from 3 - to 20 – fold more, depending on the initial ^{32}Si/Si specific activity (see Chapter 4, Table 17). These activities also indicate that Si moves rapidly (on the order of a couple hundred years) through tropical ecosystems and into riverine suspended sediments. Using stable Si or Li isotopes, along with ^{32}Si, may help deconvolve whether the Si is in an opaline form (i.e. diatoms or phytoliths) or an amorphous aluminosilicate. This fraction may be an indication of the reverse weathering sink which may sequester 20% (1.5 Tmol/y) of the riverine DSi and ASi sources (7.3 Tmol/y) to the global ocean (De La Rocha, 2013). This fraction, most likely, also acts as a source of DSi to the delta as it encounters the increased ionic strength of seawater and a portion of it dissolves, as was observed in dissolution experiments involving a variety of different siliceous substrates (Loucaides et al., 2008). Extracting riverbed sediments from headwaters to the river mouth for ^{32}Si activity in different operational pools could quantify the amount of DSi that becomes trapped in river channels. Coring along transects of the topset could also help clarify how much Si is released. The portion that is trapped may vary between rivers that are more chemically weathered to ones which are more physically weathered. Some of the study sites in Sinnamary, French Guiana were on a transient mangrove island, and these plants may at times, like siliceous sponges, act as a net sink or source of dissolved silicate. In general phytoliths have been overlooked in the global ocean Si budget.

In brief, over 100 – 500 yr timescales, cosmogenic ^{32}Si can provide a means to constrain the marine Si burial budget. However, it is critical that the specific activities of source siliceous materials be determined for regions under investigation to derive accurate budgets. Additionally, down core measurements of relative ^{32}Si activities in various operational pools need to be measured in order to determine different modes of storage (i.e. burial of opaline Si versus alteration to an authigenic clay). Relative ^{32}Si activities compared to sediment chronology, determined for example by excess ^{210}Pb, may further constrain Si storage budgets by providing rates of burial or conversion to early diagenetic Si products.

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Table 21. Marine Si Budget. All values given are in 10^{12} mol Si per year (Tmol/y Si).

	DeMaster (1981); Treguer et al. (1995)	DeMaster (2002)	Revised estimate[*]
Sources of silicate			
Rivers	5.6	5.6	3.3 – 8.3[a]
Hydrothermal emanations + Basalt weathering	0.6	0.6	1.4 – 3.6
Eolian	0.5	0.5	0 – 1
SGD			0 – 1.2
Total supply rate	**6.7**	**6.7**	**4.7 – 14.1**
Sedimentary repositories for biogenic silica			
Deep sea total	**5.1 – 6.0**	**4.1 – 4.3**	**1.5 – 4.58[b]**
Antarctic	4.1 – 4.8	3.1	<2.0 ± 1.2
Polar Front	2.7 – 3.4	0.3	
Non – Polar Front	1.4	2.8	
Bering Sea	0.5	0.5	0.5
North Pacific	0.3	0.3	0.3
Sea of Okhotsk	0.2	0.2	0.2
Low Si sediments	<0.2	<0.2	<0.2
Eq. Pacific	0.02	0.02	0.02
Continental margins total	**0.4 – 1.5**	**2.4 – 3.1**	**1.2[**] – 5.4[c]**
Estuaries	0.2 – 0.6	<0.6	<1.2[**]
Gulf of California	0.2	0.2	0.2
Walvis Bay	<0.2	0.2	0.2
Peru/Chile	<0.1	<0.1	<0.1
Antarctic margin	0.2	0.2	0.2
Other margins	<0.2	1.8	0.6 – 4.2[d]
Tropical/subtropical			2.3 – 2.6
Total removal rates	**5.5 – 7.5**	**6.5 – 7.4**	**2.7 –10**

[*] Most estimates from Treguer and De La Rocha (2013).

[a] Treguer and De La Rocha (2013) estimate riverine dissolved Si (DSi) flux of 6.2±1.8 Tmol/y, riverine amorphous Si (ASi) flux of 1.1±0.2Tmol/y, and a reverse weathering sink in estuaries and plumes of 1.5 ± 0.5, leading to a total net Si supply by rivers of 3.3 – 8.3 Tmol/y.

[b] Deep ocean sink of <1.04 ± 0.34Tmol/y plus Southern Ocean sink of >2.0 ± 1.2 Tmol/y, leading to total estimate of 1.5 – 4.52Tmol/y. This doesn't make sense that the So, Ocean value is greater than the total deep ocean

[c] Maximum of Si burial estimate in margins of 3.3 ± 2.1 Tmol/y based solely on organic C burial rate of 4.6 x 10^{12} mol organic C/y and a molar Si:C_{org} of ~0.7 (Tréguer and De La Rocha, 2013).

[d] maximum 4.2Tmol/y burial in "other margins" calculated by subtracting minimum burial in estuaries from a total of 5.4Tmol/y burial in continental margins.

[**] Revised estimate from this study. For temperate margins, estimates were doubled from DeMaster (2002). Itropical margins: sum of fluxes from Amazon – Guianas dispersal system, Gulf of Papua, and Mississippi Delta = 0.5Tmol/y + 0.08 Tmol/y + 0.012 Tmol/y = 0.59 Tmol/y. Other estimates are expanded in Table 2 and the text.

Table 22. Si storage in tropical/subtropical continental margins estimated using ^{32}Si.

Continental Margins		Si Storage (Tmol/y)
Other Margins		
	Amazon – Guianas	0.5
	Orinoco	0.097
	Mississippi	0.03
	Zaire	0.03
	Indo – Pacific Archipelego* Gulf of Papua	1.3 – 1.6 0.10
	Bay of Bengal	0.3
	East China Sea	0.05
TOTAL		**2.3 – 2.6**

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