**Germanium-silicon fractionation in a river-influenced continental margin:
The Northern Gulf of Mexico**

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ABSTRACT

In this study we have sampled the water column and sediments of the Gulf of Mexico to investigate the effects of high riverine terrigenous load and sediment redox conditions on the cycling of Ge and Si. Water column Ge/Si ratios across the Gulf of Mexico continental shelf range from 1.9 to 25 $\mu\text{mol/mol}$, which is elevated compared to the global ocean value of 0.7 $\mu\text{mol/mol}$. The Ge enrichment in the Gulf of Mexico seawater is primarily due to anthropogenic contamination of the Mississippi river, which is the main Ge and Si source to the area, and to a smaller extent due to discrimination against Ge during biogenic silica (bSi) production ($\text{Ge/Si} = 1.2 - 1.8 \mu\text{mol/mol}$), especially by radiolarians and siliceous sponges ($\text{Ge/Si} = 0.6 - 1.1 \mu\text{mol/mol}$). Most sediment pore waters ($\text{Ge/Si} = 0.3 - 4.5 \mu\text{mol/mol}$) and sediment incubation experiments (benthic flux $\text{Ge/Si} = 0.9 - 1.2 \mu\text{mol/mol}$) indicate precipitation of authigenic phases that sequester Ge from pore waters (non-opal sink). This process appears to be independent of oxidation-reduction reactions and suggests that authigenic aluminosilicate formation (reverse weathering) may be the dominant Ge sink in marine sediments. Compilation of previously published data shows that in continental margins, non-opal Ge burial flux is controlled by bSi supply, while in open ocean sediments it is 10 – 100 times lower and most likely limited by the supply of lithogenic material. We provide a measurement-based estimate of the global non-opal Ge burial flux as $4 - 32 \text{ Mmol yr}^{-1}$, encompassing the $2 - 16 \text{ Mmol yr}^{-1}$ needed to keep the global marine Ge cycle at steady state.

1. Introduction

Germanium (Ge) is a trace element whose chemical behavior in the natural environment closely mimics that of silicon (Si). These elements are supplied to the ocean predominantly as dissolved species in river water and hydrothermal fluid discharge (Froelich et al., 1985). These two sources have distinct Ge/Si signatures and together account for ~70% of total Ge input. Dust delivery, seafloor basalt weathering, terrestrial biogenic silica, and groundwater inputs are believed to account for the balance of the inputs (Hammond, McManus, et al., 2004; Wheat and McManus, 2008; Tréguer and De La Rocha, 2013). Diatoms in surface seawater and sponges in the benthos remove the majority of dissolved Ge and Si from the ocean through uptake, with other biosilicifiers playing a smaller role. Most of the biogenic silica (opal, termed here bSi) re-dissolves in the water column and in surficial sediments, but a small fraction is buried (Tréguer and De La Rocha, 2013). The sedimentary record of $\text{Ge/Si}_{\text{opal}}$ therefore holds information on past changes in the Si cycle.

The $\text{Ge/Si}_{\text{opal}}$ recorded in opal-rich marine sediments has varied significantly over time (Kolodny and Halicz, 1988; Murnane and Stallard, 1988; Froelich et al., 1989; Shemesh et al., 1989; Mortlock et al., 1991; Froelich et al., 1992; Bareille et al., 1998; Lin and Chen, 2002). Both Si and Ge exhibit oceanic residence times of approximately 10 ky or less (Hammond et al., 2000; Tréguer and De La Rocha, 2013), allowing changes in their cycles on these timescales to be examined. Indeed, the $\text{Ge/Si}_{\text{diatom}}$ signature records a clear glacial-interglacial signal over the last 500 ky (Mortlock et al., 1991; Froelich et al., 1992), in addition to a long-term trend from the Oligocene to the present (Shemesh et al., 1989). Recent field measurements have shown that diatom Ge/Si deviates from that of the surrounding seawater only when Si is depleted below ~5 μM (Sutton et al., 2010). This finding suggests that bulk $\text{Ge/Si}_{\text{diatom}}$ is unlikely to reflect biological fractionation, since it only occurs when Si is depleted and diatom productivity is low, e.g., at the end of a seasonal bloom. An absence of a biological signal in the paleorecord is showcased by very similar $\text{Ge/Si}_{\text{diatom}}$ recorded over the last 20 ky at Southern Ocean sites

located both north and south of the Antarctic Polar Front, i.e. across a strong surface Si concentration gradient (Froelich et al., 1992; Ellwood et al., 2010). These diatom records must therefore reflect whole ocean seawater Ge/Si (Ge/Si_{sw}) changes as opposed to local changes in biological fractionation. Other biosilicifiers, such as radiolarians and siliceous sponges, are known to fractionate Ge/Si more strongly, even at deep water Si concentrations (Froelich et al., 1992; Ellwood et al., 2006). Their importance in the global Si budget, however, is still highly uncertain (Tréguer and De La Rocha, 2013).

Whole ocean glacial-interglacial Ge/Si variations imply a rapid (<10 ky) change in either the input or the output fluxes of Ge or Si. Oceanic spreading rate and the resulting hydrothermal flux of solutes is driven by plate tectonics and is likely to be mostly independent of glacial-interglacial climate changes. If the removal rate is constant, glacial-interglacial variability of whole ocean Ge/Si should be driven by a change in either the magnitude of the riverine input flux or its Ge/Si. With this in mind, several efforts have been made to interpret $\text{Ge/Si}_{\text{diatom}}$ as a proxy for chemical weathering intensity on the continents (Murnane and Stallard, 1990; Froelich et al., 1992; Lin and Chen, 2002). However, the interpretation of the $\text{Ge/Si}_{\text{diatom}}$ as a paleo-weathering proxy has been complicated by the identification of a non-opal Ge sink in Fe-rich reducing marine sediments (Murnane et al., 1989; Hammond et al., 2000; King et al., 2000; McManus et al., 2003). During sediment diagenesis Ge and Si are congruently released from bSi dissolution into the pore waters, as observed in oxygenated deep ocean sediments. However, in reducing sediments the precipitation of authigenic minerals scavenges Ge from pore waters preferentially relative to Si (Murnane et al., 1989; Hammond et al., 2000; King et al., 2000). During glacial periods, a drop in seawater temperature could slow down the dissolution of sinking bSi, and in turn increase the amount of Ge delivered to the sediments and removed into the non-opal sink. Modeling by (Hammond, McManus, et al., 2004) has shown that this mechanism could cause a whole ocean Ge/Si_{sw} shift of the same magnitude as that observed in the paleorecord by Mortlock et al. (1991). However, it is unclear which mineral phase (or phases) is responsible for Ge sequestration and what factors enable this process. For example, sediment accumulation rate, opal rain rate, and Fe redox chemistry might all play a role. Finally, the global spatial extent of this non-opal Ge sink in the modern ocean is poorly constrained.

Diatom productivity is responsible for a large fraction of carbon export from the surface ocean (e.g. Buesseler, 1998; Ragueneau et al., 2006). Continental margin environments in particular experience high rates of biogenic and lithogenic particle sedimentation, thus accounting for 50 – 80% of global C and Si burial, while comprising only 15 – 20% of the seafloor area (Aller, 2014). The high delivery rate of both biogenic and terrestrial particles is conducive to the formation of reducing sediments and potential diagenetic Ge sequestration. Motivation for studying river plume environments comes from the fact that these settings serve as the entry zone and filter for riverine Si and Ge entering the ocean. Much of this Si and Ge is taken up by diatom blooms in the river plume, deposited to the coastal sediments, redissolved in the top few centimeters of sediment, and refluxed back into the water column, possibly going through several such cycles before being exported into the open ocean. Therefore, any diagenetic processes in the sediments can have an impact on the flux of elements into the open ocean. For example, the most recent review of the Si cycle (Tréguer and De La Rocha, 2013) estimates that 11 – 38% of river-delivered Si is buried during diagenetic secondary aluminosilicate formation (i.e. reverse weathering) in coastal margin sediments, indicating that such environments might play a key role in the Si cycle, despite comprising only a small fraction of the global ocean floor.

We have investigated Ge and Si systematics in the northern Gulf of Mexico (GoMex) – a continental margin setting heavily influenced by the Mississippi-Atchafalaya river plume. Our initial hypothesis was that the high input of dissolved and particulate Si and Fe by the rivers, combined with strongly reducing sediment character, may enhance the diagenetic processes that sequester Ge in the sediments (the non-opal sink). The aim of this study is to assess how the river-delivered Ge/Si signature is transformed over the continental shelf by processes occurring in the water column, as well as the sediments. To achieve this, we have combined field observations with experimental sediment core and in situ benthic chamber incubations. Finally, we compared GoMex data with previously studied regions to identify the primary controls on Ge non-opal burial and to provide the first empirical global estimate of this flux that is based on field measurements rather than calculations that assume a steady-state Ge cycle.

2. Study site

The northern Gulf of Mexico is characterized by the large shallow Louisiana-Texas continental shelf, onto which the Mississippi-Atchafalaya river system delivers a large amount of terrigenous sediment, as well as a high dissolved nutrient load (Turner et al., 2007). These conditions typically cause extensive diatom blooms and bottom water hypoxia over the shelf, especially during the summer months (Rabalais et al., 2002). Due to prevailing east winds, the plume frequently gets trapped on the shelf and transported westwards (Walker et al., 2005). Indeed, surface water salinity data indicate some plume influence as far as Station 2 (Fig. 1). The hypoxic bottom water zone extended across most of the Louisiana shelf, as mapped by Rabalais and Turner (2011) the week before our cruise. We collected water and sediment samples from 13 sites in the northern GoMex continental margin during summer 2011. Sites were selected to range from the shallow near-shore regions to deeper offshore waters, including shelf stations near major river plumes and spanning a range of bottom water oxygen concentrations (Table 1 and Fig. 1).

3. Methods

Detailed methods are given in the Supplementary Material. Below is a brief summary.

3.1 Water and sediment sampling

All samples were collected on research cruise EN-497 aboard R/V Endeavor during July 30, 2011 – August 19, 2011, except for Mississippi River water which was collected using an acid-rinsed plastic bucket a few days later off a pier in New Orleans (Table 1). Water column samples were collected using a CTD rosette equipped with Niskin bottles and filtered immediately on board. Sediment cores were collected using a multicorer, and pore waters were sampled using either Rhizons or centrifugation.

Core incubations were done as previously described by Hammond, Cummins, et al. (2004). At the end of the incubations, sediments were collected and refrigerated until bSi analysis. Benthic chamber incubations were carried out as described previously (Berelson and Hammond, 1986). Grain size was determined using a Beckman Coulter LS 13 320 Particle Size Analyzer, with Aqueous Liquid Module for sample introduction on parallel cores.

3.2 Biogenic silica analysis using timed alkaline extraction

Classic method. The biogenic silica fraction in the surface sediments (0 – 2 cm depth) of Sta. 1 and Sta. G was determined using a sequential chemical extraction technique adapted from DeMaster (1981) and Mortlock and Froelich (1989), described in detail by Collins et al. (2011).

Briefly, ~100 mg of dried and crushed sediment was leached using 5% Na₂CO₃, sampling after 3, 4, and 5h. Si concentration in the aliquots was analyzed colorimetrically and plotted versus leach time. The y-axis intercept (time = 0) in excess of that in the starting Na₂CO₃ was taken as the amount of Si (and Ge) released from bSi dissolution, giving the weight percent fraction of bSi (as %bSiO₂) and bulk Ge/Si_{opal}.

Modified method. A split of Sta. G surface sediment sample was pre-treated with H₂O₂ and HCl to remove organic and carbonaceous material, as well as the majority of non- and poorly crystalline phases, such as authigenic aluminosilicates and ferrihydrite (Gehlen and van Raaphorst, 1993; Raiswell et al., 1994; Presti and Michalopoulos, 2008). Both pretreated and untreated splits were then subjected to the same alkaline leach procedure at 60 °C for 24 hours. This gentler approach results in reduced dissolution of lithogenic clays, as evidenced by slower increase of Si concentration at the end of the leach relative to the “classic” method. The %bSi determined for the internal reference standard was within 10% of previously measured values (Collins et al., 2011) and agreed within 1% between the classic and the modified methods. Using the modified method we measured Ge/Si_{opal} = 0.7 μmol/mol, which is in excellent agreement with San Pedro basin Ge/Si_{SW} (Murnane et al., 1989) as well as the global ocean Ge/Si_{SW} (Sutton et al., 2010).

3.3 Biogenic silica analysis using physical separation and cleaning

For direct determination of Ge/Si in the bSi fraction, siliceous microfossils were isolated from bulk sediments of Stations M and G (0 – 4 cm depth) and cleaned following a procedure adapted from Shemesh et al. (1988), Morley et al. (2004), and Andersen et al. (2011). Briefly, bulk sediment was treated with hot HCl, H₂O₂, and sodium hexametaphosphate. The >20 μm size fraction was collected and treated again. Opal was separated using sodium polytungstate heavy liquid (~2.15 g/cm³ density) to remove the remaining clastic particles and boiled in H₂O₂ to remove any remaining organic coating. SEM imaging showed that this “regular” cleaned fraction contained bSi with few to no clastic particles (see Section 4.4). A split of the purified bSi from Sta. M 2 – 4 cm depth was then wet-sieved into 20 – 63 μm and >63 μm fractions and treated with 0.25% NH₂OH-HCl in glacial acetic acid to solubilize any adsorbed metal oxyhydroxide particles, etched in 0.1% NaF to remove any diagenetic alteration on the surface of microfossils, and treated with Teflon-distilled 7 N HNO₃ + 1.5 N HCl solution to dissolve any remaining detrital particles (“reductive” cleaning). The purified bSi was dissolved in trace-clean NaOH, pre-spiked with ⁷⁰Ge for Ge concentration analysis (see Section 3.5). Ge and Si blanks in the reagents were negligible and Ge/Si_{opal} obtained from replicate dissolutions of the same bSi sample agreed within 1%.

3.4 Nutrient, major element, and trace metal analysis

Silicic acid and NH₄⁺ concentrations were measured using either standard colorimetric techniques (Mullin and Riley, 1955; Bower and Holm-Hansen, 1980, for Si and NH₄⁺ respectively) onboard during the cruise; or segmented flow analyzer back at Oregon State University (Armstrong et al., 1967; Atlas et al., 1971; Gordon et al., 1994). Iron and manganese concentrations were analyzed by ICP-MS on a Thermo Scientific X-Series II at Oregon State University. Detection limits for the final undiluted samples within our data set were dependent on sample dilution and conditions specific to an individual run and ranged from 0.26 to 3.2 μM for Mn and 0.32 to 3.9 μM for Fe. Pore water sulfate concentrations (measured as total sulfur) were analyzed on a Teledyne Leeman Prodigy ICP-OES at Oregon State University.

3.5 Germanium analysis

Inorganic Ge concentration was measured using isotope dilution-hydride generation-inductively coupled plasma-mass spectrometry (ID-HG-ICP-MS) as described in detail in Mortlock and Froelich (1996) and Hammond et al. (2000), on a Thermo Element 2 mass spectrometer at the University of Southern California. Briefly, the samples were spiked with ^{70}Ge solution and converted to gaseous germane (GeH_4), which was then collected and separated from organic Ge hydride species in a liquid N_2 trap. Germane peaks at $m/z = 70$ and $m/z = 74$, respectively, were integrated to obtain the total signal for the respective Ge isotopes. Ge concentration was calculated using the known amount of sample and ^{70}Ge spike added. The reproducibility of ^{70}Ge spike concentration was checked using internal standards and was better than 3% (1σ S.D., $n = 39$). The reproducibility of several internal seawater standards, as well as a NIST 3120a Ge standard, was in the 1 – 3 % range (1σ , $n = 34$ total). The reproducibility of a surface seawater sample with Ge concentration < 2 pM was 0.5 pM (1σ , $n = 7$). We thus adopt the conservative uncertainty of 3% or 0.5 pM, whichever is higher.

4. Results

4.1 Water column

The Mississippi river dissolved Si and Ge concentrations were measured as 169 μM and 264 pM, respectively, with a Ge/Si of 1.56 ± 0.07 $\mu\text{mol/mol}$. Shelf and offshore water column concentrations of these elements were much lower (Fig. 2, data are tabulated in Electronic Annex Table EA1). Vertical profiles generally show depletion in surface water and enrichment in bottom water for both elements, indicating diatom productivity in the photic zone and biogenic silica remineralization below. However, there are significant differences between Ge and Si concentration variations with depth, especially in the Si-depleted surface waters (concentrations below 5 μM Si; Fig. 3a).

GoMex shelf water column Ge/Si_{SW} ratios vary with depth at each station and among stations, with values ranging from 1.87 ± 0.18 to 25.1 ± 5.5 $\mu\text{mol/mol}$. Individual deep water (below 500 m) samples at Station G exhibit relatively constant Ge/Si_{SW} ratios in the range of 0.60 – 0.84 $\mu\text{mol/mol}$, with an average of 0.79 ± 0.11 $\mu\text{mol/mol}$ (excluding a single uncharacteristically low value of 0.23 ± 0.06 $\mu\text{mol/mol}$; Figs. 2 and 3a). A linear regression of Ge vs Si concentrations at this station produces a slope of $\text{Ge/Si}_{\text{SW}} = 0.70 \pm 0.05$ $\mu\text{mol/mol}$ (Fig. 3b). Both of these values are analytically indistinguishable from the global ocean regression value of 0.76 $\mu\text{mol/mol}$ (Sutton et al., 2010). In contrast, all stations on the shelf show Ge/Si_{SW} ratios that are significantly higher than the global ocean, throughout the entire water column. The highest ratios are observed in the most Si-depleted surface waters at the shallowest stations (Sta. 1 and 2), similar to those reported in extremely Si-depleted surface waters previously (Ellwood and Maher, 2003). Linear regression of all the shelf station data yields a Ge/Si slope of 2.16 ± 0.08 $\mu\text{mol/mol}$, which is much higher than the global ocean value (Fig. 3b).

4.2 Pore waters

Based on their Si and NH_4^+ pore water profiles, all the stations can be divided into four categories:

Type A. Continental shelf (15 – 30 m water depth) in the vicinity of either the Mississippi or Atchafalaya river plumes (Sta. 1, 4, and A);

Type B. Continental shelf closer to the coast and generally further away from river plumes (Sta. 2, 3, 9, and 10);

Type C. Continental slope (50 – 500 m water depth; Sta. 5, 7, and M); and
Type D. Continental rise (1500 – 2200 m water depth; Sta. 6 and G).

Pore water profiles of Ge, Si, NH_4^+ , Fe^{2+} , and Mn^{2+} for a representative station of each type are shown in Fig. 4. Profiles of Si, NH_4^+ , Fe^{2+} , and Mn^{2+} for several additional stations are shown in Figure 5. All the pore water data is tabulated in Table EA2 of the Electronic Annex. The oxidants used to remineralize organic matter and the resulting pore water profiles at each station are governed by a combination of factors, the primary being the rate of biogenic matter rain to the seafloor and sediment accumulation, bottom water O_2 concentration, and benthic activity (bioturbation and bioirrigation). In terms of the sequence of electron acceptors involved in organic matter (OM) remineralization ($\text{O}_2 > \text{NO}_3^- > \text{Mn}^{3+} > \text{Fe}^{3+} > \text{SO}_4^{2-}$), Type D stations show typical deep-water profiles with very low NH_4^+ concentrations, Mn^{2+} appearing only below 15 cm depth, and no detectable Fe^{2+} within our sampling depth. Type C sediments become reducing within the first few centimeters, as indicated by the appearance of Mn^{2+} followed by Fe^{2+} and NH_4^+ . Type A and B sediments are completely Mn-reducing and become Fe-reducing within the first centimeter. Pore water Fe^{2+} and Mn^{2+} concentrations decrease to $\sim 20 \mu\text{M}$ at almost all the shelf stations below 20 – 30 cm depth (Figs. 4 and 5). The silicic acid pore water concentration trend among the stations (Type B > A > C ~ D) is similar to the other solutes (Figs. 4 and 5). Except for Type A stations, the Si concentrations are on the low end of observations in the marine environment (McManus et al., 1995; Gallinari et al., 2002), ranging from 70 to 700 μM (Fig. 4, Electronic Annex Table EA2). The pore water profiles of several shelf stations do not reach a constant asymptotic concentration; instead they often decrease after reaching a shallow maximum (especially pronounced at Type B stations). Type A stations have generally lower and less variable Si concentrations (150 – 300 μM), while Type B exhibit higher and more irregular Si concentrations in the range of 200 – 700 μM . Type C and D (continental slope and rise) stations have the lowest pore water Si concentrations (60 – 200 μM).

Germanium was measured in pore waters from 4 stations (Fig. 4). Similar to Si, Ge concentration profiles exhibit a near-surface maximum at each station followed by a decrease at similar depths. However, the variations in Ge concentration are relatively larger than those in Si concentration, as indicated by a variable pore water (Ge/Si_{PW}) ratio (Fig. 4).

4.3 Benthic fluxes

Core and benthic chamber incubations utilize the pore water Si and Ge concentration gradients in quantifying the fluxes of these species across the sediment-water interface (Fig. 6). The positive fluxes (release of Si and Ge into the overlying water over time) reflect the net result of various diagenetic reactions, most notably the dissolution of bSi. To quantify the diffusive (and possibly advective) Si and Ge fluxes, two to three cores per station were incubated, with good agreement among measured fluxes for the different cores at each station (Fig. 6). The linear slopes suggest that the diagenetic reactions controlling the flux are influenced by the same phase (or phases) during the course of the experiment. Only the first two time points (0 – 15 h) were used to calculate the Si and Ge fluxes at Sta. M since cold room temperature could not be kept at a constant value close to *in situ* for the remainder of the experiment.

Additional Si flux estimates were obtained from *in situ* benthic chamber incubations (Table 2). Variability in Si flux as measured by the standard deviation of the fluxes determined ranged from 1 – 33% for chambers and from 2 – 42% for incubated cores. This variability is most likely caused by variations in macrofauna mixing and sediment irrigation, which results in spatial variability of various solute fluxes. Both *ex situ* core incubations and *in situ* benthic lander

incubations were carried out at Sta. 1 allowing for comparison between the two methods. Core incubation seems to underestimate the Si flux by ~40% at this station (Table 2) – possibly an effect of benthic fauna dying off as the overlying water becomes O₂-depleted over the course of the incubation or perhaps due to imperfect temperature correction. However, the *in situ* and *ex situ* measured Si fluxes are indistinguishable within 1σ S.D. of their replicates. The benthic chamber data were used in the modeling of Ge and Si cycling at Sta. 1 (Section 5.2), as we suspect it to be more accurate.

The Ge vs Si concentration slope at each station represents the Ge/Si ratio of the flux (Ge/Si_{flux}) into the overlying bottom water (Fig. 6), which reflects Ge/Si of dissolving opal, as well as any diagenetic overprint. Another way to estimate this value is from separately calculated fluxes for each element (Table 2). This latter approach results in slightly higher uncertainties, but the values obtained are within uncertainty of the slopes in Figure 6.

4.4 Sediments

Sediments in our study area are primarily composed of clastic material, with the silt size fraction (4 – 63 μm) typically comprising 50 – 70%, sand (>63 μm) 20 – 30% and clay (<4 μm) 10 – 20% of total sediments. Stations closer to the river plumes have generally higher and more variable sand content: ~40% within the top 5 cm at Sta. 4 and ~70% at 8 cm at Sta. 9. Sta. 10 is on average 50% sand, reaching up to 94% at 12 cm depth. The continental shelf sediments (Sta. 2, 3, 4, 8, 9, 10, and A) contain 0.03 – 1.8% total organic carbon (TOC) with a mean of 0.7%.

The weight fractions of biogenic silica in the 0 – 2 cm of sediments at Sta. 1 and Sta. G are 0.53 ± 0.06% and 1.3 ± 0.1% respectively, within the previously reported range of 0.15 – 1.3% for Mississippi delta sediments (Turner and Rabalais, 1994; Presti and Michalopoulos, 2008). Alkaline leaching without pre-treatment (“classic” method) of Sta. 1 sediments yielded Ge/Si_{opal} of 4.5 μmol/mol, while a leach with HCl and H₂O₂ pre-treatment (“modified” method) at Sta. G yielded Ge/Si_{opal} of 1.17 μmol/mol (Table 3). The Ge/Si_{opal} signature of physically separated and cleaned bSi is typically lower than bulk Ge/Si_{opal} and differs slightly between various size fractions (Table 3). Scanning electron micrographs of this purified material show that it is heavily dominated by radiolarian tests and their fragments, as well as some large sponge spicules, with only a few diatom frustules or frustule fragments spotted (Fig. 7).

5. Discussion

5.1 Water column Ge/Si enrichment

The elevated Ge/Si_{SW} in GoMex shelf water is primarily a result of the anthropogenic Ge contamination in the Mississippi River basin, which is the major source of Ge and Si to the continental shelf. Germanium is found in high concentrations in coal and especially coal burning products, such as fly ash, which are stored in waste ponds located along river banks (Froelich and Lesley, 2001). Over time, leakage or leaching releases Ge into from waste ponds into the rivers, including the Mississippi and its various tributaries (Froelich et al., 1985). Indeed, the Mississippi River Ge/Si of 1.56 μmol/mol presented here is relatively low compared to previous measurements that have indicated Ge/Si in the range of 3 – 4 μmol/mol, with one sample reaching up to 6.5 μmol/mol (Froelich et al., 1985).

Another possibility is that shelf water Ge/Si_{SW} is further enriched due to biological fractionation by biosilicifiers. It is known that sponges (Ellwood et al., 2006) and, under Si limitation, diatoms (Sutton et al., 2010) discriminate against Ge during growth, resulting in lower Ge/Si_{opal}, and depending on the degree of Si uptake, higher Ge/Si_{SW}. Indeed, Ge/Si_{opal} of purified

bSi (Table 3) is significantly lower than surface Ge/Si_{sw} (Fig. 3, Electronic Annex Table EA1) across the GoMex continental shelf. We have built a steady-state box model to assess whether biological Ge/Si fractionation needs to be invoked to explain water column Ge/Si data at Sta. 1. The full description of the box model is given in the Supplementary Material and the full set of input parameters and results is given in Electronic Annex Tables EA4 and EA5. Briefly, the model is composed of three boxes: the surface water, the bottom water, and the sediments at Sta. 1. The water boxes exchange solutes with an offshore member (either Sta. 5 or Sta. G) and the model is mass-balanced for water, salt, Si, and Ge. We initially used river input values with Ge/Si ranging from 1.56 to 6.5 $\mu\text{mol/mol}$ (Supp. Material Table S1) to test which scenario would produce the most realistic sedimentary Ge/Si output. Model runs with riverine Ge/Si of 1.56 $\mu\text{mol/mol}$ resulted in negative sedimentary Ge burial, indicating an underestimation of river-borne Ge input. In contrast, model runs with riverine Ge/Si ≥ 4 $\mu\text{mol/mol}$ often resulted in Ge/Si enrichment in opal relative to seawater. Field and culture studies to date have only indicated the opposite phenomenon, i.e. Ge/Si depletion in opal (Froelich et al., 1992; Ellwood et al., 2006; Sutton et al., 2010), suggesting that model runs with such high Ge/Si are unrealistic as well. We therefore selected model runs with riverine Ge/Si of 2.2 – 3.5 $\mu\text{mol/mol}$ as the most robust scenario. Indeed, the majority of Mississippi River samples measured by Froelich et al. (1985) fall within this range.

One way that biological Ge/Si fractionation can be quantitatively assessed is a simple Rayleigh distillation framework, where Ge is assumed to behave as a “pseudo-isotope” of Si (Froelich et al., 1992). This approach assumes that fractionation is independent of the Si or Ge concentrations of the water that diatoms grow in and can be described using a constant fractionation factor:

$$K_D = \frac{Ge/Si_{opal}}{Ge/Si_{sw}} \quad (\text{Eq. 1})$$

Box model results indicate that even with riverine Ge/Si set between 2.2 – 3.5 $\mu\text{mol/mol}$, Ge/Si_{opal} at Sta. 1 must be $1.54^{+0.25}_{-0.27}$ $\mu\text{mol/mol}$ (Supp. Material Table S1). Ge/Si_{opal} was measured to be slightly lower (1.17 $\mu\text{mol/mol}$) at the offshore Sta. G (Table 3), most likely due to waning influence of the Ge-contaminated Mississippi-Atchafalaya river system. Nevertheless, box model results imply that $K_D < 1$ at Sta. 1, which means that some biological Ge/Si fractionation is needed to balance the mass fluxes (Supp. Material Table S1).

Alternatively, biological Ge/Si fractionation can be described within the Michaelis-Menten uptake kinetics framework, where the degree of fractionation depends on the Si concentration in the water column. This approach has been previously applied to both sponges (Ellwood et al., 2006) and diatoms (Sutton et al., 2010). The application of this framework to the box model results is consistent with a possible (small) diatom Ge/Si fractionation in the surface waters. In contrast, a larger degree of Ge/Si fractionation is predicted in the bottom waters, which can only be explained by invoking some Si uptake by other non-diatom biosilicifiers, such as siliceous sponges or radiolarians (see Supp. Material). These results are supported by the analysis of bSi purified from GoMex shelf sediments. First, visual inspection of scanning electron micrographs reveal that the >20 μm bSi size fraction is dominated by radiolarians, silicoflagellates, and sponge spicules, with very few diatom frustules preserved (Fig. 7). Second, Ge/Si_{opal} of these samples range from 0.63 – 1.08 $\mu\text{mol/mol}$ (Table 3), significantly lower than bulk bSi (total

Ge/Si_{opal} range of 1.17 – 1.79 $\mu\text{mol/mol}$, combining measurements at Sta. G and box model results at Sta. 1).

It must be noted that the elevated Ge/Si_{SW} in GoMex shelf waters could also be the result of Ge desorption from coal ash particles delivered by the rivers (Froelich and Lesley, 2001). However, the strongest Ge/Si_{SW} enrichment is observed at Sta. 2 (Fig. 3), which is located far away from river estuaries and salinity gradients (Fig. 1), where desorption is most likely to take place. In addition, the strongest Ge/Si_{SW} enrichment is observed at the lowest Si concentrations (Fig. 3a), consistent with Michaelis-Menten type biological fractionation. Finally, the degree of Ge/Si_{SW} enrichment here is similar to previous observations in pristine ocean waters unaffected by anthropogenic contamination (Ellwood and Maher, 2003; Sutton et al., 2010). Nevertheless, we note that the degree of Ge desorption from particulate contaminants in northern GoMex is unconstrained and could provide an alternative hypothesis to biological Ge/Si fractionation.

5.2 Sediment diagenesis

5.2.1 Sediment bioirrigation

Physical disturbance of sediments can have a strong impact on the pore water chemistry and benthic fluxes of solutes. Mixing and resuspension of sediments can occur either through bottom currents, or through bioturbation and bioirrigation by benthic macrofauna (e.g. Allison et al., 2000; Corbett et al., 2006). These processes act to dilute the pore waters with overlying bottom water, enhance and redistribute remineralization by mixing down fresh biogenic matter, and affect redox-sensitive elements through injection of more oxidizing species. At most of our study sites, pore water solute profiles are irregular (Fig. 5), indicating either bioirrigation or non-steady state behavior, perhaps due to seasonal dynamics in particulate rain to the seafloor, storm events, or large chemical changes brought on by changes in the extent of the hypoxic zone (Fig. 1). While we observed multiple worm burrows at various depths, it is hard to estimate their impact on pore water solutes. However, Si and NH_4^+ profiles are very different from either Fe^{2+} or Mn^{2+} at any given station (Fig. 5), suggesting that diagenetic reactions, rather than advective mixing, have a dominant control over pore water solute concentrations.

5.2.2 Non-opal Ge sources and sinks

Excluding bioirrigation, pore water Ge and Si concentrations are chiefly controlled by the competition between the rates of bSi deposition, dissolution, and re-precipitation of authigenic secondary phases. If congruent dissolution of bSi were the sole process controlling the buildup of dissolved Ge and Si in pore fluids, then Ge/Si_{PW} should approach Ge/Si_{opal}, which ranges from 1.17 $\mu\text{mol/mol}$ (Table 3) to $1.54^{+0.25}_{-0.27}$ $\mu\text{mol/mol}$ (Supp. Material Table S1). However, most GoMex sediment Ge/Si_{PW} values fall outside of the range expected from congruent opal dissolution or mixing with overlying bottom waters (hatched areas in Fig. 4). This variability therefore cannot be explained by bioirrigation and must reflect diagenetic processes that fractionate Ge/Si through dissolution and precipitation of phases other than opal. Germanium is most strongly scavenged with depth at the continental slope Stations M and G, and much less pronounced at continental shelf Stations 1 and 2. In fact, supply of non-opal Ge is apparent at Sta. 1, as Ge/Si_{PW} exceeds Ge/Si_{opal} and Ge/Si_{OLW} at certain depths. Most primary silicate minerals have Ge/Si ratios higher than 2 $\mu\text{mol/mol}$ (Mortlock and Froelich, 1987; Kurtz et al., 2002), while secondary weathering products such as aluminosilicates and Fe-Al sesquioxides can display Ge/Si in excess of 1000 $\mu\text{mol/mol}$ (Kurtz et al., 2002). It is therefore likely that additional Ge is supplied to the pore waters through leaching of river-delivered lithogenic

material, or perhaps Ge-enriched coal ash in the continental shelf sediments (Sta. 1 and 2). Another possibility is that storm mixing or seasonal blooms and bottom water oxygen dynamics have resulted in dissolution of previously formed authigenic Ge-enriched phases during our sampling period. The decrease of NH_4^+ concentration with depth at these stations (Figs. 4 and 5) is indicative of some type of non-steady state process. Regardless of the driver of non-steady state diagenesis, dissolution of phases other than bSi makes it difficult to estimate the actual degree of non-opal sequestration in shelf sediments, as exemplified by the high uncertainty of box model calculated non-opal Ge burial flux (FGe_{NOB}) at Sta. 1 (Supp. Material Table S1). However, offshore sediments (Sta. M and G) are much less affected by either river-delivered material or non-steady state processes and exhibit clear Ge sequestration throughout our sampled pore water horizons (Fig. 4).

A non-opal Ge sink has been first proposed as necessary to balance the modern ocean Ge budget (Elderfield and Schultz, 1996) and subsequently identified in some Fe-rich sediments, where the precipitation of iron (oxy)hydroxides (FeOx), pyrite, and/or Fe-rich aluminosilicates have all been speculated to scavenge Ge from marine sediment pore waters (Murnane et al., 1989; Hammond et al., 2000; King et al., 2000; McManus et al., 2003). Sulfate reduction and some pyrite precipitation likely occur at Type B stations, based on pore water Fe^{2+} (Fig. 5) and SO_4^{2-} (Supp. Material Fig. S2) depletion. Station G (Type D) sediments are too oxic for sulfate reduction within our sampling depth, ruling out pyrite precipitation as a Ge scavenging mechanism in continental rise sediments. Further, the Fe redox zone does not correlate with Ge/Si minima at any of the sampling sites, perhaps with the exception of the surface horizon at Sta. 1 (Fig. 4). However, even a small amount of FeOx precipitation could significantly influence the dissolved Ge concentration. Alternatively, the dynamic nature of GoMex shelf bottom water hypoxia could conceivably result in a temporary decoupling of Fe redox and Ge/Si minima in the pore waters. Fe oxides therefore cannot be ruled out as a potential non-opal Ge sink.

Nevertheless, the strong Ge/Si depletion in the relatively oxidized surficial Sta. G sediments (Fig. 4) suggests that Fe redox may not be necessary to sequester Ge from marine pore waters.

Germanium is known to be preferentially incorporated into secondary clays during silicate weathering on land (Murnane and Stallard, 1990; Froelich et al., 1992; Kurtz et al., 2002), pointing to the possibility that similar partitioning may take place during authigenic aluminosilicate formation in the marine environment. A high rate of such clay formation has been shown to occur in Mississippi and Amazon delta sediments (Michalopoulos and Aller, 1995; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). Besides Si and Al, authigenic clays are known to incorporate various trace elements, including Fe and Mn (Loucaides et al., 2010). We therefore speculate that reverse weathering may be occurring throughout the GoMex continental shelf and slope sediments, and that it may be responsible for some or all of the observed decrease in Si, Fe^{2+} , Mn^{2+} , and Ge concentrations with depth at most stations (Figs. 4 and 5).

In agreement with the pore water results, the benthic flux signatures ($\text{Ge/Si}_{\text{flux}} = 0.88 - 1.24$; Table 2) were lower than bulk $\text{Ge/Si}_{\text{opal}} (= 1.17 - 1.79 \mu\text{mol/mol})$ (Table 3), indicating Ge retention in the sediments across GoMex continental shelf and slope. Using the contrast between $\text{Ge/Si}_{\text{flux}}$ and $\text{Ge/Si}_{\text{opal}}$ we calculate that at Sta. 1, Sta. M, and Sta. G, around 10 – 20% of pore water Ge is removed into the solid phase and about half of all Ge is buried in this non-opal sink (Table 4). However, the actual non-opal burial flux (FGe_{NOB}) is elevated due to the supply of anthropogenic Ge to the area by the coal ash contaminated Mississippi-Atchafalaya river system (Froelich and Lesley, 2001). This effect can be corrected for by assigning $\text{Ge/Si}_{\text{opal}} = 0.7$

$\mu\text{mol/mol}$ (the value diatoms would be expected to have if Mississippi River was not delivering Ge-enriched waters into the shelf) and using the fraction of Ge removed from pore waters by diagenesis (f-ratio in Table 4). Applying this correction reduces FGe_{NOB} by about half at each of these sites (Table 4).

5.3 Global extent of the non-opal Ge sink

The data presented above shows that non-opal Ge sequestration can occur in different sedimentary environments. A better sense of the factors that control the non-opal Ge flux, as well as its importance to the marine Ge cycle, can be obtained by summarizing previous studies that have investigated Ge cycling in different sedimentary environments (Table 4). FGe_{NOB} values for GoMex continental slope (Sta. M) and rise (Sta. G) sediments agree well with those previously estimated for open ocean sediments in the Equatorial Pacific ($2 - 12^\circ\text{S}$) (Hammond et al., 2000) and Subantarctic Southern Atlantic ($41 - 53^\circ\text{S}$) (King et al., 2000), while the continental shelf (Sta. 1) is similar to other continental margin sediments in the Pacific. Importantly, pooling all the data published to date reveals that FGe_{NOB} appears to correlate strongly with benthic Si flux in continental margins but not in open ocean sediments (Fig. 8). This duality suggests that the low supply of detrital material to open ocean sediments imposes a first order limitation on FGe_{NOB} , as observed in the Southern Ocean (King et al., 2000). Once that limitation is lifted, such as in continental margin sediments receiving large detrital particle inputs, FGe_{NOB} scales with bSi delivery to the sediments, for which the benthic Si flux is a good proxy. Coincidentally, such a dual limitation mechanism has already been proposed for authigenic aluminosilicate formation, where it is limited by detrital Fe- and Al-oxide supply in the open ocean and by opal supply in continental margins (Aller, 2014). As such, it appears likely that significant or perhaps even the majority of non-opal Ge sequestration in marine sediments may be occurring during reverse weathering. This hypothesis is also supported by preliminary laboratory experiments that showed significant uptake of Ge during authigenic Fe-rich clay formation (Tosca et al., 2014).

Previous estimates of FGe_{NOB} range from $4 - 5 \text{ Mmol yr}^{-1}$ (King et al., 2000; Hammond, McManus, et al., 2004) and were calculated by assuming that the modern ocean Ge cycle is at steady state. Adjusting for recent revisions of the global Si cycle (Tréguer and De La Rocha, 2013), the best current estimate is 6.9 Mmol yr^{-1} with a range of $2 - 16 \text{ Mmol yr}^{-1}$. The relationship in Fig. 8 can be used to provide an empirical estimate of FGe_{NOB} that is independent of other fluxes in global Ge cycle. Using area of $197 \times 10^6 \text{ km}^2$ for the open ocean (deeper than 1km) that receives opal rain (Tréguer and De La Rocha, 2013) and FGe_{NOB} ranging between 6 and $68 \text{ pmol m}^{-2} \text{ d}^{-1}$ (Table 4, Fig. 8) with an average of $30 \text{ pmol m}^{-2} \text{ d}^{-1}$, we calculate the total open ocean FGe_{NOB} as $2.1_{-1.6}^{+2.8} \text{ Mmol yr}^{-1}$. Estimates of continental margin (30 – 1000 m water depth) global mean benthic Si flux vary between 1 and $5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ or $16 - 87 \text{ Tmol yr}^{-1}$, assuming an area of $43.3 \times 10^6 \text{ km}^2$ (Berelson et al., 2003; Tréguer and De La Rocha, 2013). Using the relationship in Fig. 8, we obtain FGe_{NOB} of $200 - 1700 \text{ pmol m}^{-2} \text{ d}^{-1}$ or $3.4 - 27 \text{ Mmol yr}^{-1}$ in continental margin sediments. The total global ocean FGe_{NOB} is therefore estimated to be in the $4 - 32 \text{ Mmol yr}^{-1}$ range. It is encouraging that the lower half of the independent empirical (i.e., measurement-based) FGe_{NOB} estimate presented here matches the value required to keep the global marine Ge budget at steady state ($2 - 16 \text{ Mmol yr}^{-1}$). However, the fact that the empirically estimated FGe_{NOB} range is on average twice as high could be indicative of current underestimation of marine Ge inputs or overestimation of the outputs. As discussed above, we observed significant burial of bSi with biologically fractionated, relatively low $\text{Ge/Si}_{\text{opal}}$ (Table 3), as opposed to unfractionated $\text{Ge/Si}_{\text{diatom}}$ in GoMex shelf sediments. If this applies to other continental margin environments, it could mean that the global Ge opal burial is lower than

previously estimated, while non-opal Ge burial is higher. Nevertheless, the robustness of the relationship in Fig. 8 and the possibility that the global Ge and Si cycles are not in steady state require further studies of various marine sedimentary environments.

5.4 Implications for Ge/Si_{opal} paleoproxy

The observed relationship between the benthic Si flux and the non-opal Ge burial flux in continental margins supports the hypothesis that glacial-interglacial Ge/Si_{diatom} variations (Shemesh et al., 1989; Mortlock et al., 1991) are caused by changes in FGe_{NOB}. As argued previously, lower seawater temperature during glacial periods should have resulted in a higher fraction of opal rain reaching the seafloor and therefore more non-opal Ge sequestration in the sediments (Hammond, McManus, et al., 2004). Several other factors may have increased the FGe_{NOB} during glacial periods. First, the aeolian supply of lithogenic material was higher (de Angelis et al., 1987), possibly enhancing reverse weathering throughout the global ocean. Alternatively, or in addition, lower bottom water O₂ (e.g., Jaccard and Galbraith, 2011) should have shoaled the sedimentary Fe redox zone closer to where the majority of bSi dissolves, allowing FeOx precipitation to scavenge more Ge from the pore waters. Finally, diatom productivity in the Southern Ocean was shifted north (e.g. Beucher et al., 2007) and enhanced by continental dust input (Anderson et al., 2014; Martinez-Garcia et al., 2014), once again shifting a large portion of global opal rain to sediments with a generally higher detrital fraction.

The combined effects of higher opal rain to the seafloor (especially in continental margins) and higher detrital rain (especially in the open ocean) should have resulted in higher benthic Si flux and FGe_{NOB}, reducing the global ocean Ge/Si_{SW} during glacial periods, as indicated by diatom paleorecords (Shemesh et al., 1989; Mortlock et al., 1991). Although it is unclear how much the riverine Ge and Si inputs have varied over glacial-interglacial cycles, the high sensitivity of the Ge cycle to marine bSi dynamics demonstrated here provides a simple and realistic mechanism to vary global ocean Ge/Si_{SW} over such geologically short timescales, without the need to invoke large scale changes in the continental weathering Si flux, such as those previously proposed (Froelich et al., 1992).

6. Conclusions

Water column Ge/Si ratios over the northern Gulf of Mexico continental shelf are significantly higher than the global ocean average due to 1) the supply of Ge-enriched Mississippi-Atchafalaya river water into the area and 2) some degree of discrimination against Ge by biosilicifiers.

Analysis of different bSi size fractions supports previous data showing that radiolarians and sponges (i.e. non-diatoms) fractionate Ge/Si more strongly than diatoms. Although difficult to quantify, the importance of sponge and radiolarian bSi burial in continental margin sediments is apparent from visual analysis and is also reflected in the bulk opal Ge/Si signature. These observations might support the recent hypothesis that sponges are disproportionately important to bSi burial in continental margin environments and may help balance the modern ocean Si budget (Tréguer and De La Rocha, 2013).

Germanium sequestration from the pore waters (“non-opal Ge sink”) occurs in GoMex continental shelf, slope, and rise sediments. The observed Ge depletion does not strongly correspond to Fe or sulfate redox zones, suggesting that authigenic silicate formation (reverse weathering) may be the dominant non-opal sink, although a contribution from Fe oxide cycling cannot be ruled out.

The non-opal Ge burial flux in northern Gulf of Mexico sediments is consistent with other similar sedimentary environments. A summary of published data indicates that continental margin environments display non-opal Ge burial fluxes 10 – 100 times higher than open ocean sediments – more than enough to balance the modern ocean Ge budget. To achieve a high rate of non-opal Ge burial a high supply of both opal and lithogenic material is required. This correlation supports a previous hypothesis (Hammond et al., 2000; Hammond, McManus, et al., 2004) that variations in the non-opal Ge burial flux could explain the glacial-interglacial Ge/Si_{diatom} paleorecord (Mortlock et al., 1991; Froelich et al., 1992).

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Figure captions

Figure 1. Map of sampling stations of cruise EN-497 that are discussed in this study. Bathymetry lines of 50 m and 500 m are given as operational definitions of continental shelf and continental slope, respectively. The inset shows the location of the study area on a continental scale. Station details are given in Table 1. Surface water salinity and bottom water O₂ concentration grids are for July 24 – 30th from Rabalais and Turner (2011).

Figure 2. Water column profiles of dissolved Ge and Si concentrations and Ge/Si over the continental shelf (Sta. 1 and 2), continental slope (Sta. 5), and offshore (Sta. G). Where not

visible, the error bars are smaller than the symbols. All water column data are given in Electronic Annex Table EA1.

Figure 3. Ge as a function of Si in the water column of the Northern Gulf of Mexico: A) Ge/Si plotted as a function of Si concentration at all stations. Inset shows a magnified region of the same data; B) Ge plotted as a function of Si, with linear regression slopes for offshore Sta. G (solid line) and all shelf station samples (dashed line). Symbols are the same as in panel A. Slope uncertainties are reported as $\pm 2\sigma$ S.D. Value in brackets was not included in slope calculation. Where not visible, the error bars are smaller than the symbols. All water column data are given in Electronic Annex Table EA1.

Figure 4. Pore water profiles of dissolved Si, Ge, Fe^{2+} , Mn^{2+} , and NH_4^+ at Sta. 1 (Type A: cont. shelf close to river plumes), Sta. 2 (Type B: cont. shelf far from river plumes), Sta. M (Type C: cont. slope), and Sta. G (Type D: cont. rise). Pore water Ge/Si profiles are plotted in the middle panel. Note the scale changes for Si and Ge among different stations. Horizontal dashed lines mark the sediment-water interface, and the sample above the line is the overlying bottom water. The hatched area encloses the range of Ge/Si_{PW} expected from mixing of dissolving opal and overlying water. Vertical error bars represent the range of sampling depth for composite aliquots and horizontal error bars represent analytical uncertainty (where not visible, error bars are smaller than symbols). Fe^{2+} , Mn^{2+} , and NH_4^+ data for Sta. 1 and Sta. 2 were obtained from different cores than Si and Ge data. All pore water data are given in Electronic Annex Table EA2.

Figure 5. Pore water profiles of dissolved Si, Fe^{2+} , Mn^{2+} , and NH_4^+ at several stations. Stations are color coded according to different pore water profile types (see Section 4.2). All pore water data are given in Electronic Annex Table EA2.

Figure 6. Core incubation experiment data. Left panels: Ge and Si concentration increase over time in each core at a given station. Right panels: Ge concentration plotted as a function of Si concentration. Each core is fit with a linear slope, accounting for both Ge and Si analytical uncertainties. The Ge/Si values given are the mean ± 1 S.D. of all the slopes at each given station.

Figure 7. Scanning electron micrographs of bSi purified from Sta. M sediments at 2 – 4 cm depth. The majority of bSi in the >20 and $>63 \mu\text{m}$ size fractions is composed of radiolarian tests, sponge spicules, silicoflagellates, and their fragments.

Figure 8. Ge non-opal burial (FGe_{NOB}) as a function of benthic Si flux ($\text{JSi}_{\text{sedflux}}$) in global ocean sediments (data sources given in Table 4). For GoMex stations, FGe_{NOB} was corrected for the influence of the Ge-enriched Mississippi River (Table 4) to estimate an uncontaminated signal. At two of the California margin sites (Tanner Basin and Cascadia Basin, dashed symbols) a large range of $\text{Ge/Si}_{\text{sedflux}}$ values has been observed and the data are too scarce to confidently estimate the long-term average FGe_{NOB} (Table 4), therefore the maximum observed flux was used. The black solid line shows a power-law fit to all the continental margin sites plotted. The gray dashed lines enclose the range of FGe_{NOB} observed in deep ocean sediments.

Table 1

Table 1. Sampling station details.

Station	Casts	Data ^a	Sampling date	Latitude, °	Longitude, °	Bottom depth, m	Surface salinity, psu	Surface [Si], $\mu\text{mol/L}$	Surface [NO ₃], $\mu\text{mol/L}$	Bottom O ₂ , $\mu\text{mol/kg}$
1	CTD- 5/6, MC-2/3	WC, PW, CI, BC, S	2011-08-01	28.591	-90.541	30 – 38	26.10	3.2	n/m ^c	31 – 51
A	CTD-8, MC-4	PW	2011-08-02	28.759	-92.184	40	32.93	n/m	n/m	155
2	CTD-10, MC-5/6/7	WC, PW, CI	2011-08-03	29.198	-92.919	22 – 24	31.32	2.1	0.01	27
3	CTD-18, MC-9	PW, BC	2011-08-04	29.115	-93.224	23	32.02	3.1	0.05	153
4	CTD-20, MC-10	PW, BC	2011-08-05	29.147	-91.942	17	28.96	17.1	0.05	4
5	CTD-23, MC-11/13	WC, PW, CI	2011-08-06	28.199	-92.081	90	34.90	1.4	BDL ^d	143
6	MC-14	PW, BC	2011-08-08	26.963	-92.285	1547	36.20	1.5	0.01	174
G	CTD-32/33, MC-15	WC, PW, CI, S	2011-08-09	26.372	-92.141	2141	36.32	0.3	n/m	209
7	CTD-36, MC-17	WC, PW, BC	2011-08-12	27.952	-92.128	145	35.20	1.2	0.05	116
M	CTD-41, MC-18	PW, CI, S	2011-08-13	27.911	-91.797	438	35.00	1.7	0.04	115
8	CTD-42	WC	2011-08-14	28.830	-91.065	15	27.25	n/m	n/m	2
9	CTD-43/45, MC-22	WC, PW, BC	2011-08-15	28.971	-90.402	22	25.10	12.1	0.03	11
10	CTD-46, MC-26	PW, BC	2011-08-17	30.189	-88.629	23	31.00	n/m	n/m	128
MR ^b	bucket	WC	2011-08-20	29.934	-90.050	–	0	169.3	n/m	n/m

^a WC = water column (referring to Ge and Si conc.); PW = pore waters; CI = core incubations; BC = benthic chamber incubations; S = sediments.

^b Mississippi River, New Orleans.

^c n/m = not measured

^d BDL = Below detection limit.

Table 2. Benthic Si and Ge fluxes

Station	Benthic chambers	Core incubations		
	Si flux, mmol m ⁻² d ⁻¹	Si flux, mmol m ⁻² d ⁻¹	Ge flux, nmol m ⁻² d ⁻¹	Ge/Si _{flux} [*] , μmol/mol
Sta. 1	4.11 ± 1.37 (n = 3)	2.43 ± 0.67 (n = 4)	2.22 ± 0.67 (n = 2)	1.19 ± 0.41
Sta. 2	–	1.86 ± 0.19 (n = 4)	–	–
Sta. 3	5.29 ± 0.76 (n = 2)	–	–	–
Sta. 4	8.16 ± 3.02 (n = 3)	–	–	–
Sta. 5	–	0.64 ± 0.27 (n = 4)	–	–
Sta. 6	1.56 (n = 1)	–	–	–
Sta. 7	0.80 (n = 1)	–	–	–
Sta. 9	11.45 ± 2.72 (n = 3)	–	–	–
Sta. 10	8.57 ± 0.86 (n = 5)	–	–	–
Sta. M	–	0.59 ± 0.01 (n = 3)	0.64 ± 0.15 (n = 3)	1.09 ± 0.24
Sta. G	–	0.18 ± 0.04 (n = 3)	0.15 ± 0.05 (n = 3)	0.87 ± 0.38

Uncertainty of station averages given as ± 1σ S.D., where multiple cores or chambers were used. Where not given, fluxes have not been measured.

* Calculated as the ratio of average fluxes only from cores where both Si and Ge data are available. Uncertainty propagated from the corresponding flux uncertainties.

Table 3. Ge/Si_{opal} ratios of biogenic silica from Gulf of Mexico sediments

Method	Depth	Size fraction	Ge/Si _{opal} , $\mu\text{mol/mol}$		
			Sta. 1	Sta. M	Sta. G
Model calculation ^a	n/a	Bulk	1.27 – 1.79	–	–
Classic leaching ^b (no pre-treatment)	0 – 2 cm	Bulk	(4.5) ^f	–	–
Modified leaching ^c (pre-treatment)	0 – 2 cm	Bulk	–	–	1.17
Separation ^d (regular cleaning)	0 – 2 cm	>20 μm	–	0.86	0.90
Separation (regular cleaning)	2 – 4 cm	>20 μm	–	0.83	0.68
Separation ^e (reductive cleaning)	2 – 4 cm	20 – 63 μm	–	0.63	–
Separation (reductive cleaning)	2 – 4 cm	> 63 μm	–	1.08	–

^a See Supplementary Material, Table S1.

^b Bulk sediment leached with 5% Na₂CO₃ at 85 °C for 5h (see Supp Material for full procedure).

^c Bulk sediment pre-treated with HCl and H₂O₂, then leached with 5% Na₂CO₃ at 60 °C for 24h (see Supp Material for full procedure).

^d bSi purified by treatment of bulk sediment with hot HCl, H₂O₂, Na-hexametaphosphate, and heavy liquid separation (see Supp Material for full procedure).

^e bSi further purified as above and in addition treated with NH₂OH-HCl, NaF, and HNO₃ + HCl solution to remove any potential authigenic coatings and stuck lithogenic particles (see Supp Material for full procedure).

^f Value typical of silicate minerals (e.g., Mortlock and Froelich, 1987), indicating some dissolution of crustal material, authigenic aluminosilicates, or possibly Ge-enriched anthropogenic coal ash contaminants.

Table 4

Table 4. Comparison of Si and Ge fluxes at different locations

Location	References	Water depth, m	bSi rain flux ^a , mmol m ⁻² d ⁻¹	Benthic Si flux ^b , mmol m ⁻² d ⁻¹	bSi burial flux ^c , mmol m ⁻² d ⁻¹	%bSi in surface sediments	Fraction of bSi rain buried	Benthic flux Ge/Si ^d , μmol/mol	Fraction of dissolved Ge sequestered (f-ratio) ^e	Ge nonopal burial flux ^f , pmol m ⁻² d ⁻¹	Fraction of Ge burial as non-opal ^g
Gulf of Mexico margin											
Sta. 1 (actual) (contam. corr.) ^h	1, 23	30	4.55 (3.07 – 6.36)	4.11 ± 1.37	0.44	0.5%	10% (10 – 14%)	1.24 ± 0.13	19% (2 – 35%)	1240 (128 – 2259) 562 ^h (37 – 1458)	65% (19 – 78%)
Sta. M (actual) (contam. corr.) ^h	1, 23	438	0.66 (0.61 – 0.72)	0.59 (0.57 – 0.60)	0.08	–	12% (6 – 16%)	1.04 ± 0.04	11 ± 7%	76 (-131 – 246) 47 ^h (14 – 82)	46% (-101 – 84%)
Sta. G (actual) (contam. corr.) ^h	1, 24	2141	0.23 (0.18 – 0.27)	0.18 (0.15 – 0.22)	0.044	1.2%	20% (18 – 20%)	0.88 ± 0.11	25 ± 12%	51 (37 – 75) 31 ^h (12 – 62)	50% (40 – 64%)
N. American margin basins											
Santa Monica Basin	2, 3, 4, 8, 9, 10, 11	910	1.12 (0.25 – 2.5)	1.10 (1.1 – 2.3)	0.020 ± 0.002	0.3%	1.8 ± 0.2%	0.28 (0.2 – 1.8)	61% (-165% – 74%)	483 (-607 – 1034)	97% (-4200% – 99%)
San Pedro Basin	2, 5, 6, 7, 11	890	1.70 (0.6 – 5.1)	1.62 (0.7 – 2.9)	0.08 ± 0.03	0.2%	4.7 ± 1.8%	0.33 (0.15 – 0.78)	55% (-15% – 80%)	640 (350 – 1232)	92% (82% – 97%)
San Nicolas Basin	5, 7, 11	1800	0.76 ± 0.12	0.7 ± 0.1	0.06 ± 0.02	0.4%	7.9 ± 2.6%	0.5 ± 0.3	31% (-18% – 74%)	154 (128 – 285)	78% (70% – 90%)
Catalina Basin	2, 7, 10, 11, 18	1300	0.80	0.77 (0.56, 0.97)	0.03	0.6%	4.3%	0.61 (0.05 – 0.68)	15% (0% – 93%)	84 (0 – 398)	77% (0% – 94%)
Tanner Basin	2, 11, 18	1514	1.90	1.87 (0.98 – 2.38)	~0.03 ⁱ	–	1.6%	1.02 (0.62 – 1.14)	0%? (-68% – 18%)	0? (-918 – 333)	0%? (-4400% – 93%)
Cascadia Basin	12, 13, 15, 26	2798	1.07	1.03 (0.48, 1.57)	0.04	9.5%	3.8%	0.99 (0.62, 1.35)	0%? (-99% – 18%)	0? (-322 – 220)	0%? (-1200% – 88%)
Peru-Chile margin											
MC22, MC24 (40°S)	2, 19, 21	246, 430	0.78	0.70	0.08	3.2%	10%	0.39 (0.34, 0.43)	47% (37% – 55%)	235 (175 – 294)	81% (76% – 84%)
MC34, MC39, MC42 (36°S)	2, 19, 21	133 – 1028	3.41	3.30	0.11	5.6%	3%	0.33 (0.25 – 0.39)	54% (43% – 67%)	1276 (638 – 1734)	94% (89% – 96%)
MC82 (14°S)	2, 20, 22	264	22.3	7.0	15.3	~10%	69%	0.28	61 ± 2%	3080 ± 280	22% (20% – 23%)
Equatorial Pacific											
JGOFS 19 (2°S)	11, 14, 16, 17	4376	0.35	0.46	0.04	7%	11%	0.68	6%	18	39%
JGOFS 10 (12°S)	11, 14	4280	0.09	0.08	0.01	3%	9%	0.64	11%	6	54%
Subantarctic South Atlantic											
21GGC (41°S)	8	4978	0.24	0.019	0.22	17%	92%	0.03	96%	13	8%
22GGC (43°S)	8	4647	0.15	0.063	0.08	20%	57%	0.03	95%	44	43%
10GC (47°S)	8	4399	0.57	0.074	0.49	35%	87%	0.08	89%	38	10%
17GGC (50°S)	8	3664	4.44	2.49	1.95	45%	44%	0.71	1%	18	1%
13MC (53°S)	8	2851	2.93	1.48	1.45	65%	50%	0.69	5%	68	6%

References: (1) This study; (2) McManus et al. (2003); (3) Baronas (2014); (4) Landry et al. (1992); (5) Murnane et al. (1989); (6) Collins et al. (2011); (7) Berelson et al. (1987); (8) King et al. (2000); (9) Christensen et al. (1994); (10) Boucher (1984); (11) Hammond et al. (2000); (12) Esther et al. (2010); (13) Gallagher (2007); (14) McManus et al. (1995); (15) Hedges et al. (1999); (16) Hammond et al. (1996); (17) Berelson et al. (1997); (18) Schwalbach and Gorsline (1985); (19) Romero and Hebbeln (2003); (20) Böning et al. (2004); (21) Muñoz et al. (2004); (22) Koide and Goldberg (1982; McCaffrey et al. (1990); (23) Gordon and Goñi (2004); (24) Allison et al. (2000); Corbett et al. (2006); (25) Jahnke (1990); (26) Johnson et al. (2006)

^a Sediment trap data for San Pedro basin, San Nicolas basin, and JGOFS 19; calculated as the sum of benthic and burial fluxes for the other sites.

^b For Santa Monica and San Pedro basins, calculated as the difference between average bSi_{rain} and burial fluxes. For GoMex Sta. 1, benthic chamber data was used (Table 2). For other sites, taken as a simple average of all measurements (the range given in brackets).

^c San Pedro, San Nicolas, JGOFS 19, and South Atlantic values from the literature. All others calculated from sediment accumulation rate and %bSi, assuming 2.5 g/cm³ sediment density (see Electronic Annex Table EA4). %bSi not measured at Sta. M but assumed 1 ± 0.5% based on the other two stations.

^d GoMex values obtained from slopes in Fig. 6. For Santa Monica, San Pedro, Catalina, and Tanner basins the average of benthic chamber measurements taken as the main value. For all other sites, simple average of all measurements taken as the main value. Range of all measurements, including benthic chamber incubations, core incubations, and pore water gradient modeling is given in brackets.

^e As previously defined in Ref. 8, the fraction of the “potential” benthic Ge flux that is sequestered by the non-opal phase, or $(\text{Ge/Si}_{\text{opal}} - \text{Ge/Si}_{\text{sedflux}}) / (\text{Ge/Si}_{\text{opal}})$.

^f Model-calculated for Sta. 1; calculated as $(\text{Ge/Si}_{\text{opal}} - \text{Ge/Si}_{\text{sedflux}}) * \text{Si}_{\text{sedflux}}$, taking $\text{Ge/Si}_{\text{opal}} = 1.17 \pm 0.05 \mu\text{mol/mol}$ for GoMex Sta. M and Sta. G, $\text{Ge/Si}_{\text{opal}} = 0.72 \pm 0.04 \mu\text{mol/mol}$ for California, Cascadia, and Eq. Pacific sites, and $\text{Ge/Si}_{\text{opal}} = 0.72$ for the South Atlantic sites (King et al., 2000). For Tanner and Catalina basins, the average value was $<0 \text{ pmol m}^{-2} \text{ d}^{-1}$. Since this is not a sustainable situation over long term, $0 \text{ pmol m}^{-2} \text{ d}^{-1}$ was taken as the long term value instead.

^g Defined as $(\text{non-opal Ge burial flux}) / (\text{total Ge burial flux})$.

^h The “actual” FGe_{NOB} at GoMex stations (measured at Sta. M and G, model-calculated at Sta. 1) reflects the influence of anthropogenically contaminated Mississippi-Atchafalaya river system delivering a large amount of Ge to the shelf. To correct for this contamination, the FGe_{NOB} here was calculated by assigning $\text{Ge/Si}_{\text{opal}} = 0.72 \pm 0.04 \mu\text{mol/mol}$ (the typical opal value in uncontaminated regions) and using the actual f-ratio (fraction of Ge sequestered after opal dissolves in the sediments), since the latter should only be dependent on diagenetic characteristics of the sediments. This contamination corrected FGe_{NOB} value is plotted in Fig. 8 and included in the power-law fit of benthic Si flux vs. FGe_{NOB} in continental margin regions.

ⁱ Calculated using sediment accumulation rate from Ref. 18 and assuming %bSi = 0.6%, same as in Catalina Basin.

Figure 1

FIGURES

Figure 3

Figure 6

>63 μm size fraction

D3.2 x120 500 μm

>20 μm size fraction

D6.4 x150 500 μm

Figure 8