Silicon fluxes and isotope composition of direct groundwater discharge into the Bay of Bengal and the effect on the global ocean silicon isotope budget

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ABSTRACT

This study presents silicon isotope data for rivers and groundwater from the Bengal Basin. Variations of Si isotope ratios were analyzed by means of high-resolution MC-ICP-MS using a NuPlasma HR. The rivers show typical positive δ^{30}Si values between 1.3 and 1.7‰, whereas the groundwater samples show decreasing δ^{30}Si values from 1.3‰ in shallow groundwater to − 0.2‰ in the deeper groundwater. Beside a very distinctive isotope composition, the concentration of dissolved Si in these groundwater samples is 2–3 times higher than in river samples taken during dry season. The resulting Si flux by groundwater (9.3×10^{10} mol yr^{-1}) is on the order of the combined Ganges–Brahmaputra Si fluxes, and equals 40% of the total (river + groundwater) annual Si flux into the Bay of Bengal. Given the significant large flux and distinctive isotope composition means that the overall isotopic input into the ocean is different from riverine values. However, a sound knowledge of all inputs into the ocean and of how these inputs might vary throughout time is mandatory, in order to correctly interpret palaeo-records of δ^{30}Si variations as recorded in sedimentary diatom opal from the last glacial maximum. We extrapolate our results from the Bengal Basin onto a global scale and assess the ocean's sensitivity to changes in inputs, as triggered by large-scale events, such as glaciation periods, where the hydrological cycle might be out of steady state due to the build-up of large continental ice-shields. In such a glaciation scenario, riverine vs. groundwater inputs can be shifted, favoring isotopically lighter groundwater over heavier river inputs into the ocean. The model proves impossible to change the biogenic output to a significant degree, on time scales of a few thousand years, by just changing the isotope inputs into the ocean.

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1. Introduction

The direct flux of groundwater into the ocean may contribute anything from a few percent to as much as 30% of the water flux from the continents to the oceans (Taniguchi et al., 2002). Groundwater is enriched in solutes and nutrients (Johannes, 1980), and this means that fluxes for some elements may be extremely significant for the oceanic budget. Silicon (Si) is one such key nutrient, and its isotopic ratio in marine diatom opal provides potential information about ocean biological productivity throughout time (De La Rocha et al., 1998; Varela et al., 2004). This requires that the oceanic isotope balance is well known however, but the direct groundwater contribution, its mass and isotopic inputs of Si to the ocean's budget, are unconstrained (Treguer et al., 1995). The direct groundwater flux of Si to the oceans may be on the order of surface riverine fluxes (Kim et al., 2005; Burnett et al., 2007; Niencheski, 2007), with Si isotope compositions in groundwater being potentially very distinct from riverine Si (Basile-Doelsch et al., 2005; Georg et al., 2009), which are usually isotopically positive (De La Rocha et al., 2000; Ding et al., 2004; Alleman et al., 2005; Ziegler et al., 2005; Georg et al., 2006a, 2007). Given the magnitude of Si fluxes from groundwater and its potentially distinctive isotope composition, means that changes in the balance of groundwater flux versus riverine fluxes could lead to variations in oceanic δ^{30}Si, normally ascribed to productivity, such as the shift in opal isotope records during the last glacial maximum (LGM) (De La Rocha et al., 1998; Brezinski et al., 2002; Beucher et al., 2007).

Here we report the concentration and isotopic composition of Si carried by rivers and groundwater within the Bengal Basin, one of the main river/groundwater systems providing nutrients to the oceans. The results are projected to a global scale and used to test the world's oceans sensitivity during large-scale events, such as the transition between glacial and interglacial periods, where the hydrological cycle might be out of steady state and relative changes of groundwater fluxes versus riverine fluxes might occur.

2. Sampling and analytical approaches

2.1. Sampling

Groundwater samples were taken from monitoring and domestic wells throughout the Bengal Basin in May 1999 and January

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2000 (Fig. 1). River samples from 6 sites within the Ganges–Brahmaputra system were collected during the dry season (between January and May 1999). Sampling procedures and analytical protocols can be found in more detail elsewhere (Basu et al., 2002; Dowling et al., 2002, 2003). Briefly, all samples were filtered (< 0.2 μm) and acidified with ultrapure HNO_3 at the sampling site and kept capped in pre-cleaned polypropylene bottles. Silicon concentrations were analysed colometrically by the molybdenum blue method using a spectrophotometer in Oxford prior to isotope analyses.

2.2. Mass spectrometry

Groundwater as well as river water samples were processed according to procedures described in more detail elsewhere (Georg et al., 2006a,b; 2007). Silicon isotope compositions were analysed by means of high-resolution multiple collector inductively coupled plasma mass-spectrometry using a *NuPlasma HR* (HR-MC-ICP-MS) at the Department of Earth Sciences in Oxford in mid 2007. This type of mass-spectrometer is capable of high mass resolution, and therefore enables the interference-free determination of all three stable Si isotope ion beams in medium pseudo high-resolution mode. The instrumental mass bias was corrected for by a standard-sample bracketing protocol. Samples were taken up via a self-aspirating 6 mm concentric micro-flow PFA nebuliser (Elemental Scientific Inc.) with typical uptake rates around 80 μl min^{-1} and aspirated into a DSN-100 (Nu Instruments) desolvation device. The dry sample aerosol was introduced into the plasma using a semi-demountable torch equipped with a sapphire injector (Elemental Scientific Inc.). The base sensitivity (low resolution mode) of this MC-ICP-MS was typically between ~50 and 60 V ppm^{-1} Si with an uptake rate of 0.1 ml min^{-1} when measured on Faraday cups with 10^{11} Ω resistors. However, setting the mass-spectrometer to medium resolution mode (source slit width decreases from 0.3 to 0.05 mm) reduces the transmission by approximately 80%. Further reduction is given by narrowing the alpha slits located in front of the electrostatic analyzer, so that the overall loss in transmission is around 85–90%. This substantial loss was compensated by running solutions with Si concentrations of ~1.5 ppm, resulting in ~12 V total beam intensities. Each sample was analysed at least 11 times, where each single δ-value represents one sample run and two bracketed standard runs. One run consists of 25 cycles, each integrated for 8 s. Silicon isotope data are reported as deviations of $^{30}Si/^{28}Si$ and $^{29}Si/^{28}Si$ from the international standard NBS-28 in parts per thousand (the standard delta notation $\delta^{30}Si$ and $\delta^{29}Si$, $x = 30$ or 29) as follows: $[(^{x}Si/^{28}Si_{sam}/{}^{x}Si/^{28}Si_{NBS-28}) - 1] \times 1000$.

Unlike in previous work using this method, samples were acidified with HNO_3. In order to achieve acid matrix matching between samples and standards we prepared NBS-28, IRMM-018, Diatomite and BigBatch Si standards according to the procedures described elsewhere (Georg et al., 2006b), but using HNO_3 with similar molarity instead of HCl. Different from the published method, the amount of acid used in each step was doubled. The reproducibility of IRMM-018 for a period of 6 months was ± 0.15‰ $\delta^{30}Si$ and ± 0.08‰ $\delta^{29}Si$ ($\pm 2\sigma_{SD}$, $n = 95$). The accuracy of IRMM-018 is given by $\delta^{30}Si - 1.63 \pm 0.15$‰ and $\delta^{29}Si - 0.84 \pm 0.08$‰, in agreement with the "calibrated" values for IRMM-018, of $\delta^{30}Si - 1.65 \pm 0.22$‰ and $\delta^{29}Si - 0.85 \pm 0.14$‰ (Reynolds et al., 2007). As for IRMM-018, silicon isotope values for BigBatch and Diatomite show consistency with values obtained from an inter-calibration exercise. Three full procedural repeats of the USGS basaltic rock standard BHVO-1 also reproduced to published values (Abraham et al., 2008) (Table 1). Based on the good reproducibility of these various Si isotope standards, we conclude that samples acidified with HNO_3 yield accurate Si isotope data.

3. Results

3.1. Silicon concentration

The average Si concentration of the rivers is 240 ± 30 μM ($\pm 1\sigma_{SD}$), groundwater samples have higher concentrations, averaging 620 ± 100 μM Si ($\pm 1\sigma_{SD}$), showing no relationship with depth (Table 1). The measured riverine Si concentration is similar to that reported for the Ganges and Brahmaputra in the GEMS-Water database (~275 μM) but is higher than the value observed during the monsoon by others (130–160 μM) (Galy and France-Lanord, 1999), probably because of dilution effects at high discharge.

3.2. Silicon isotope compositions

The isotope data are consistent with a single mass-dependent fractionation line with a slope of $\delta^{29}Si = 0.5178 \times \delta^{30}Si$, documenting the complete resolution of polyatomic mass interferences during analysis (Fig. 2 and Table 1). The $\delta^{30}Si$ isotope composition of the rivers varies between 1.3‰ and 1.7‰, with rivers from the Ganges basin varying between 1.45 and 1.71‰, averaging 1.63 ± 0.11‰ ($\pm 1\sigma_{SD}$, $n = 4$), and samples taken from the Brahmaputra show lower $\delta^{30}Si$ values of ~1.3‰. The groundwater $\delta^{30}Si$ is systematically lower than the rivers. Values vary with depth from 1.3‰ in shallow groundwater to − 0.15‰ for the deeper samples (Fig. 3).

4. Discussion

4.1. Groundwater Si fluxes

To date there is no estimate of the relative contributions of riverine inputs and direct groundwater discharge of Si to the Bay of Bengal. Taking the groundwater flux from the Bengal Basin (Dowling et al., 2003) of $1.5 \pm 0.5 \times 10^{11}$ m^3 yr^{-1} and multiplying by the average Si concentration (620 μM) yields a direct annual groundwater derived Si flux of ~9.3×10^{10} mol Si yr^{-1} into the Bay of Bengal. This groundwater Si flux equals 66% of the average annual riverine Ganges–Brahmaputra (G–B) Si flux into the Bay of Bengal (1.4×10^{11} mol yr^{-1}) (Galy and France-Lanord, 1999). The amount of Si delivered by groundwater appears to be high on first view, but it is consistent with Si fluxes found in other coastal settings (Kim et al., 2005). The total Si flux
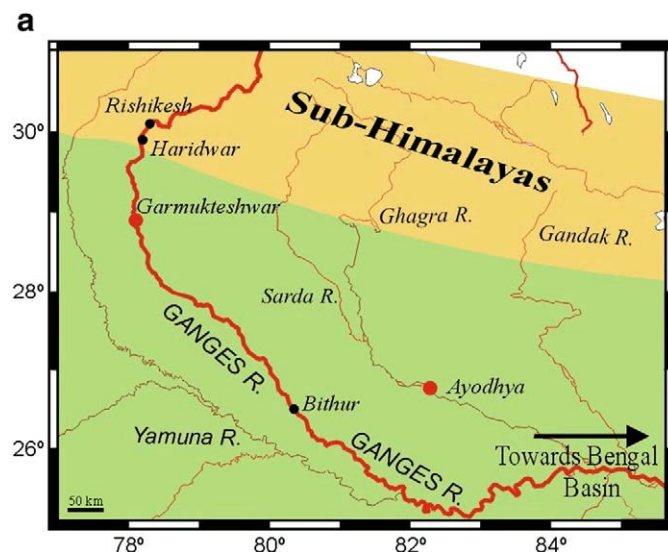

Fig. 1. Map showing sampling locations. River samples (red dots) were taken from the Ganges basin (a) and from sites within the Brahmaputra catchment (b). Groundwater samples (green dots) were taken from domestic and monitoring wells from sites within the Brahmaputra catchment.
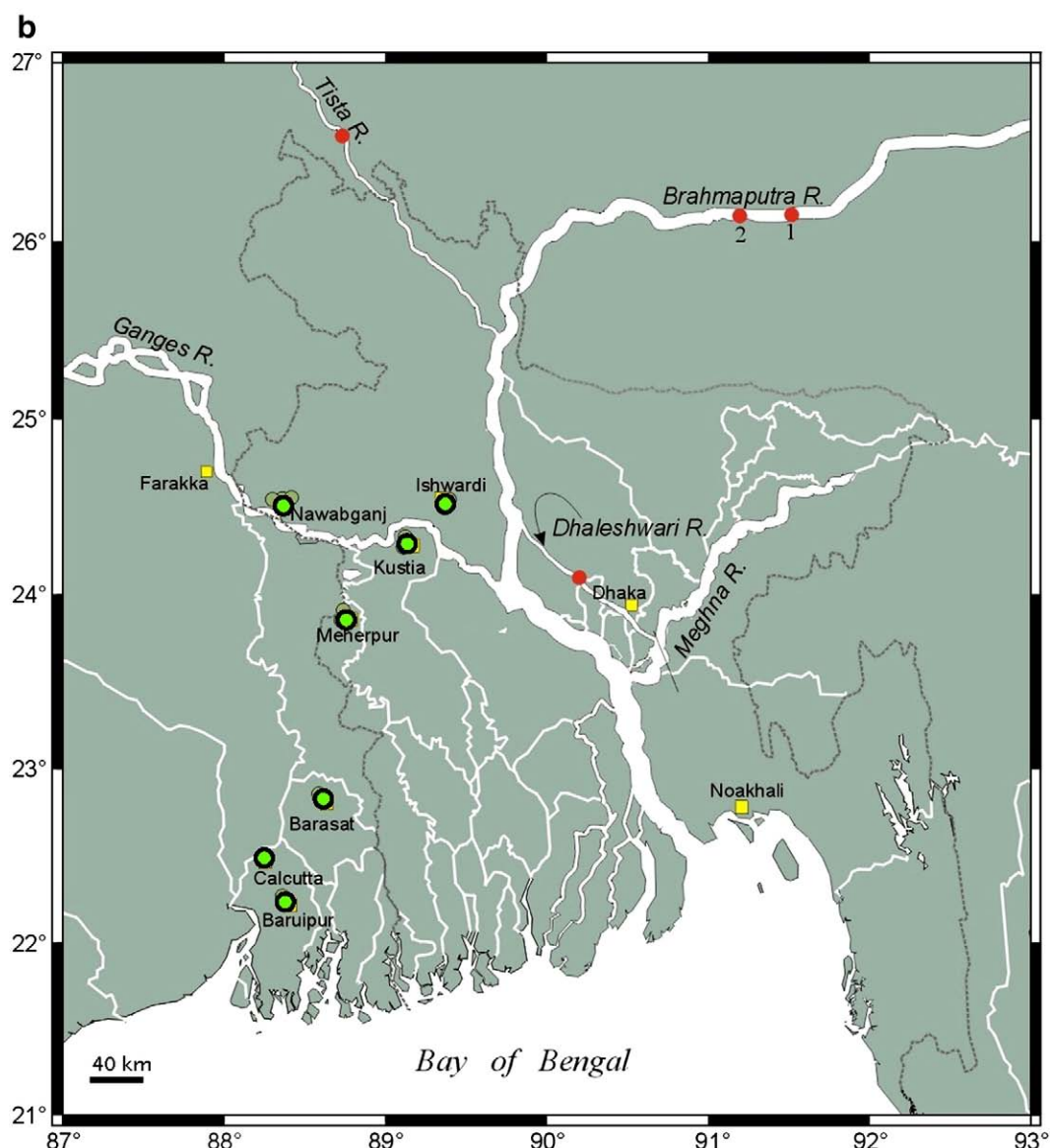
Fig. 1 (continued).

(riverine + groundwater) into the Bay of Bengal equates to approximately 2.3×10^{11} mol yr^{-1}, or 3.5% of the known global Si flux into the oceans (Tréguer et al., 1995). Though groundwater delivers approximately 40% of the total flux, the area-weighted contribution is even higher since the groundwater recharge area of the Bengal Basin (~250,000 km^2) is an order of magnitude smaller than the combined G–B catchments (~2.0×10^6 km^2). The high Si flux provided by the ~500×500 km large recharge area of the Bengal basin delivers around 1% of the known Si fluxes into the ocean.

4.2. Riverine Si isotope composition ($\delta^{30}Si_{River}$)

The positive riverine Si isotope composition is typical for $\delta^{30}Si$ values found in rivers (De La Rocha et al., 2000; Ding et al., 2004; Alleman et al., 2005; Ziegler et al., 2005; Georg et al., 2006a, 2007). There appears to be a slight difference of mean $\delta^{30}Si$ values between rivers from the Ganges basin and from the Brahmaputra basin. Given the few number of samples, this can either be coincidence, but could also potentially reflect differences in overall weathering intensity, where the lower average Si isotope composition of the Brahmaputra reflects higher chemical and physical weathering rates (Singh et al.,

2005), both of which appear to be inversely correlated with Si isotope compositions in rivers (Georg et al., 2006a, 2007).

4.3. Silicon isotope composition of groundwater ($\delta^{30}Si_{GW}$)

The Si isotope composition of the groundwater varies between 1.3 and − 0.2‰ with age and depth. Such evolutionary trend has been observed in other groundwater systems (Georg et al., 2009) and seems to reflect the change from primary to secondary Si sources (i.e., progressively greater input from the dissolution of isotopically lighter clays and silcretes (Basile-Doelsch et al., 2005; Georg et al., 2009). This evolutionary trend complicates the calculation of an average isotope composition of the groundwater Si flux to the Bay of Bengal. Simply weighting the isotopic flux by depth would assume only horizontal flow and would neglect the vertical component of groundwater flow that drives the observed isotopic gradient. Because groundwater flows beneath the surface by following a hydraulic gradient, usually consisting of a vertical and horizontal flow, we use a simplified hydraulic box model of flow through the basin aquifers, to calculate the weighted isotopic composition of the Si flux.

Table 1
Silicon isotope data, SiO$_2$ wt.% content, and Si concentration (μM) for analysed standards and water samples.

Sample	SiO$_2$ (wt.%)	$\delta^{30}Si$	$2\sigma_{SD}$	N in (‰)	$\delta^{29}Si$	$2\sigma_{SD}$	N
IRMM 018	99.2	− 1.63	0.15	95	− 0.84	0.08	95
IRMM-018[a]		− 1.65	0.22	563	− 0.85	0.14	740
Diatomite	99.3	1.23	0.16	60	0.62	0.11	60
Diatomite[a]		1.26	0.2	82	0.64	0.14	100
BigBatch	102.0	− 10.58	0.3	28	− 5.4	0.2	28
BigBatch[a]		− 10.48	0.54	158	− 5.35	0.3	198
BHVO-1a	50.0	− 0.27	0.1	24	− 0.16	0.1	24
BHVO-1b	49.7	− 0.29	0.17	38	− 0.16	0.12	38
BHVO-1c	50.5	− 0.31	0.18	25	− 0.18	0.12	25
BHVO-1mean	50.1	− 0.29	0.16	87	− 0.17	0.11	87
BHVO-1&2 mean[b]	n.a.	− 0.30	0.22	13	− 0.17	0.11	19

Rivers	Location	Depth (m)	Si (μM)	$\delta^{30}Si$	$2\sigma_{SD}$	N in (%)	$\delta^{29}Si$	$2\sigma_{SD}$	N
Brahmaputra-1			250	1.33	0.10	18	0.68	0.09	18
Brahmaputra-2			250	1.28	0.09	18	0.67	0.05	18
Dhaleshwari			280	1.63	0.11	17	0.85	0.07	17
Ghagra	Ayodhya		260	1.71	0.09	13	0.86	0.06	13
Ganges	Gormukteshwar		230	1.68	0.11	17	0.86	0.05	17
Tista			190	1.45	0.16	17	0.76	0.07	17
GW (0–30 m)									
IND-6	Barasat	18	540	0.98	0.04	17	0.5	0.06	17
BGD-38	Nawabganj	9	380	1.15	0.08	17	0.59	0.05	17
BGD-39	Nawabganj	19	550	1.34	0.10	17	0.69	0.07	17
GW (30–100)									
BGD-40	Nawabganj	34	490	1.05	0.12	17	0.54	0.06	17
BGD-41	Ishwardi	36	690	1.12	0.11	17	0.57	0.04	17
BGD-44	Ishwardi	35	620	1.14	0.07	17	0.59	0.07	17
BGD-47	Meherpur	32	530	1.17	0.12	17	0.61	0.09	17
BGD-49	Meherpur	36	520	0.98	0.10	17	0.5	0.08	17
IND-1	Moyna	50	573	1.16	0.10	17	0.61	0.05	17
IND-3	Moyna	47	668	1.13	0.11	17	0.57	0.06	17
BGD-55	Kustia	82	790	1.03	0.13	17	0.52	0.07	17
BGD-56	Kustia	90	770	0.82	0.07	17	0.41	0.05	17
GW (100–300 m)									
IND-7	Barasat	130	600	0.56	0.09	17	0.28	0.06	17
IND-8	Barasat	210	600	0.04	0.15	17	0.03	0.09	17
IND-9	Baruipur	300	510	− 0.15	0.13	17	− 0.07	0.08	17

Uncertainties for $\delta^{30/29}Si$ values are given as $\pm 2\sigma_{SD}$ in ‰ and ±2% for SiO$_2$ wt.% content and Si concentration. Sampling locations seen in Fig. 1a,b.
n.a. = not available.
[a] Calibrated" Si isotope values, Reynolds et al. (2007) − average isotope data are based on an inter-comparison, comparing data from numerous international laboratories.
[b] Data for BHVO-1&2 from Abraham et al. (2008).

In order to estimate an average river $\delta^{30}Si$ composition, we assume that the Si isotope composition of the rivers is modified by interaction with isotopically lighter shallow (0–30 m) groundwater before discharging into the ocean. Smaller tributaries and even side arms of the Brahmaputra, such as the Dhaleshwari, have $\delta^{30}Si$ as high as 1.7‰, this could be due to biological fractionation in smaller streams and catchment areas. However, the first 20–30 m of the aquifer is believed to be in hydraulic contact with the streams, influencing the chemistry before those rivers finally discharge into the Bay of Bengal (Dowling et al., 2003). This chemical alteration would also influence the Si isotope composition of those rivers, potentially lowering a higher riverine Si isotope composition towards a value closer to that of the shallow groundwater (0–30 m, mean $\delta^{30}Si$ 1.16 ± 0.18‰). Even though the $\delta^{30}Si$ average of all analysed rivers is around 1.5‰, groundwater input means the Brahmaputra's isotope composition (~1.3‰) is probably representative of the riverine Si isotope composition delivered into the Bay of Bengal.

4.4. Modeling the Si isotope composition of groundwater

The model (Fig. 4), a simplified hydraulic box, divides the aquifer into two sections: Section 1: shallow aquifer, 30–100 m depth and

Section 2: deep aquifer, 100–300 m depth. The 100 m division was chosen because it marks the depth below which the Si isotope composition gets significantly lighter. The following calculations are based on two groundwater packages: shallow GW ($\delta^{30}Si$ ~1.07 ± 0.11‰, ±1SD) and deep GW ($\delta^{30}Si$ ~0.15 ± 0.37‰), associated with aquifer Sections 1 and 2, respectively. Further parameters are shown in Table 2.

Dowling et al (2003) estimated an average vertical flow rate of 2.0 m yr^{-1}. The horizontal flow was calculated from the groundwater flux and seepage area of 500 × 0.27 km. (Note that the hydraulic box has a depth of 300 m, but the first 30 m depth will return to the river before reaching the coastline and will not be considered here.) In order to produce the calculated groundwater flux over the seepage area, the water body has to flow with a horizontal component of ~1100 m yr^{-1}, regardless of the vertical flow. This is an oversimplification as the real surface area may be significantly larger and the resulting flow rate lower. Having both the vertical and horizontal flow rates, we can calculate the flow time (in years) and horizontal distance (in km), which the water will need in order to recharge from the shallow aquifer into the deeper aquifer (below 100 m depth). The total horizontal flow distance will depend on the vertical flow component alone, as the horizontal flow rate is fixed. Simply speaking, assuming a high vertical flow rate, water will travel a
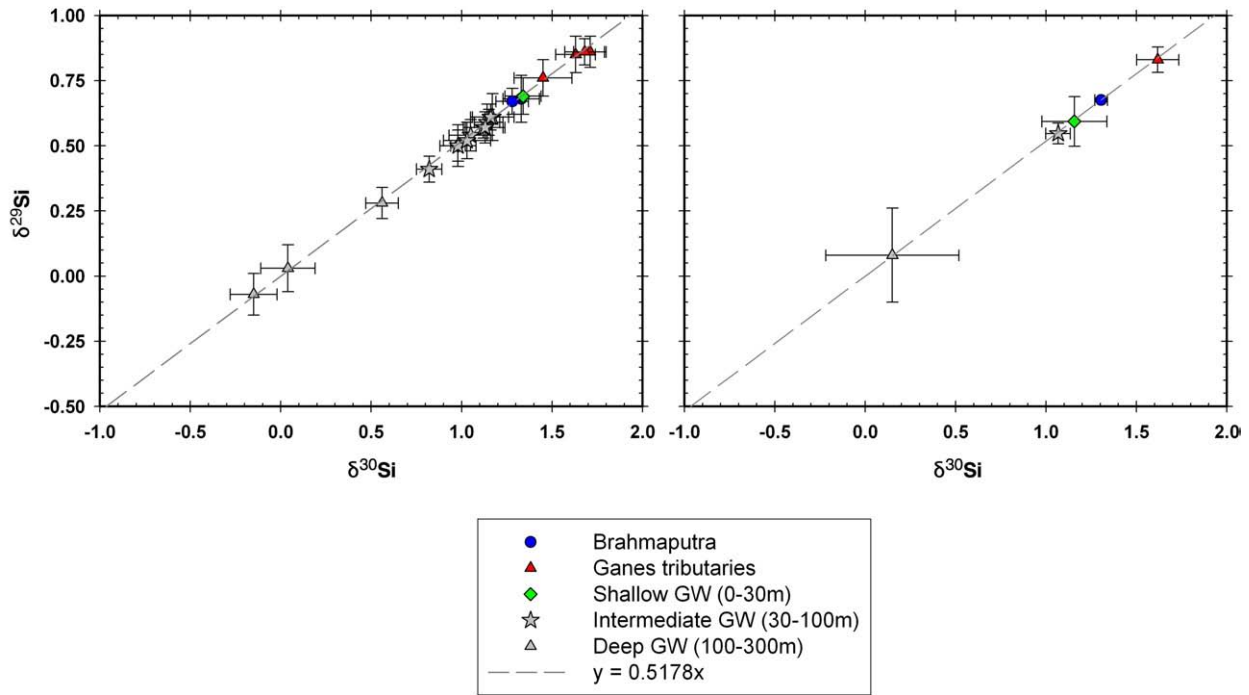
Fig. 2. Three isotope plot showing $\delta^{30}Si$ and $\delta^{29}Si$ isotope data (single A, and group means B) for analysed river and groundwater samples in ‰ relative to NBS-28. All samples plot onto a single mass-dependent fractionation line with a slope of 0.5178x. Uncertainties are given as $\pm 2\sigma_{SD}$.

shorter horizontal distance before recharging into the deeper groundwater. Performing a simple geometric calculation provides an estimate of the horizontal travel distance.

Within this hydraulic setting, whether groundwater discharges to the oceans from a shallow or deep source (i.e. above or below the 100 m mark), depends on where the water initially recharges into the aquifer system, relative to the coastline. Water that recharges into the subsurface at a sufficient distance from the coastline, will seep below the 100 m line before discharging into the ocean, and thus contributes to the deep GW. Water that recharges closer to the coastline and does not have time to reach the 100 m depth contributes to the shallow groundwater discharge. The travel distance required for water to reach 100 m depth for a given vertical flow rate can be used to calculate the

proportion of the basin area that will contribute to either deep or shallow GW. These proportions can then be used to weigh the isotope and Si flux balances. A range of hydraulic scenarios can be explored by keeping the horizontal flow constant while varying the vertical component. Applying the model to the calculation of total Si fluxes makes little difference to the final estimate of contributions from groundwater (resulting in a groundwater contribution from 39 to 40% of total Si flux, depending on vertical flow rate), because Si concentration is relatively constant with depth within the groundwater. However the model is important for calculating the average isotopic composition of the groundwater flux, because of the significant isotopic variation with depth.
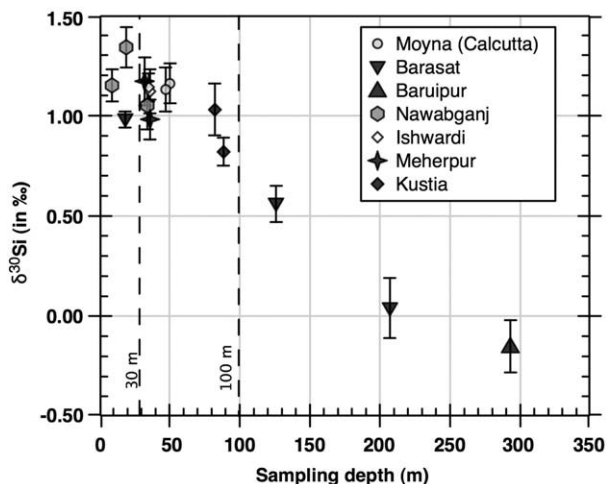

Fig. 3. Isotopic evolution of dissolved Si in groundwater with depth ($\delta^{30}Si \pm 2\sigma_{SD}$). Sampling locations are given in diagram legend.
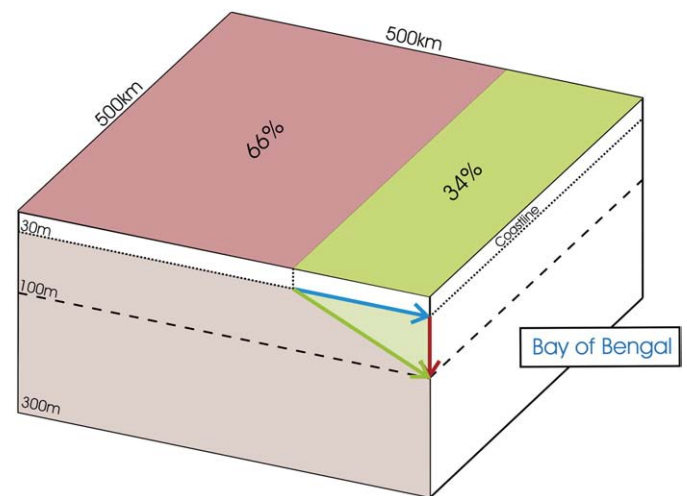

Fig. 4. The Si isotope composition is weighted based on surface recharge areas. Vertical flow F_v (blue arrow) as well as horizontal flow F_h (red arrow) rates are assumed and flow velocities are used to calculate associated recharge areas. Depending on the vertical flow, groundwater will either contribute to shallow GW (above 100 m mark) or deeper and isotopically evolved GW (below 100 m mark) before discharging into the ocean. Extrapolated areas are used to weigh the isotope balance of the outgoing groundwater flux.

Table 2
Parameters used for the hydraulic box model.

Bengal Basin hydrological box	$500 \times 500 \times 0.27$ km
Groundwater flux (Dowling et al., 2003)	1.5×10^{11} m³/yr
Vertical flow F_V	0.1–5.0 m/yr
Average horizontal flow F_H	1100 m/yr

The recharge area of the Bengal Basin is ~250,000 km² and for convenience, the box was set up to represent the area as a square of 500×500 km.

Scenario 1, vertical flow of 0.5 m yr^{-1}: The horizontal flow distance, before the water contributes to deep groundwater (100 m depth), is around 222 km. All the water recharging within a 222 km zone from the coastline will not make it below the 100 m depth, thus discharging as shallow groundwater. The associated area (222×500 km) represents 44% ($f = 0.44$) of the Bengal basin surface area. The isotope balance is:

$$\delta^{30}Si_{GW} = \left(\delta^{30}Si_{deep} \times (1-f) \right) + \left(\delta^{30}Si_{shallow} \times f \right)$$

$$\delta^{30}Si_{GW} = (0.15‰ \times 0.56) + (1.07‰ + 0.44) = 0.56‰$$

Scenario 2, vertical flow of 2 m yr^{-1}: Horizontal flow distance equals around 56 km. The associated area (56×500 km) represents 11%, and the isotope balance is:

$$\delta^{30}Si_{GW} = \left(\delta^{30}Si_{deep} \times (1-f) \right) + \left(\delta^{30}Si_{shallow} \times f \right)$$

$$\delta^{30}Si_{GW} = (0.15‰ \times 0.89) + (1.07‰ + 0.11) = 0.25‰$$

According to Dowling et al (2003) the vertical flow rate averages 2 m yr^{-1}, so that scenario 2, although highly simplified, is most likely. Combining this Si isotope composition for the groundwater discharge with the riverine isotope composition (1.31‰ for the river mainstream) gives the isotope balance for the total Si flux into the Bay of Bengal:

$$\delta^{30}Si_{total} = (0.25‰_{Gw} \times 0.4) + (1.31‰_{River} \times 0.6) = 0.88‰$$

Giving an isotope difference of $\approx 0.4‰$ when comparing the riverine runoff with the total Si flux, including the groundwater.

Although an average vertical flow rate is given with 2 m yr^{-1} (Dowling et al., 2003), it is important to assume that the permeability of the aquifer is not isotropic and can vary with depth and lithology, and to assess the sensitivity of the model to variation in vertical flow rates. The sensitivity of the isotope balance was tested for a range of vertical flow rates from 0.1 to 5.0 m yr^{-1} taking the 1SD uncertainty of each average estimate into account (Fig. 5). The weighted $\delta^{30}Si_{GW}$ is not sensitive to changes in vertical flow rates greater than 1.0 m yr^{-1}, and contributions from the deep groundwater to $\delta^{30}Si_{GW}$ decrease significantly only if the vertical flow rate drops below 1.0 m yr^{-1}. The calculated Si isotope composition of the total Si flux delivered to the oceans (groundwater + river) is even less sensitive (responding only to vertical flow below 0.5 m yr^{-1}) because of the larger fluxes involved. Even if vertical flow is heterogeneous, as a result of variability within the aquifer, the low sensitivity of the model means the results would not differ significantly from a scenario with a vertical flow of 2 m yr^{-1}, which implies an average $\delta^{30}Si_{GW}$ composition of ~0.25‰.

As mentioned above, the real discharge surface area might be significantly larger and the resulting horizontal flow would be accordingly lower. The consequences for the model would be that the deeper groundwater would gain more relative importance and the Si isotope composition of the groundwater as well as the total Si flux would be torn towards lighter Si isotope compositions. However, these effects are small and decreasing the horizontal flow by a factor of 10 would shift the groundwater as well as the total $\delta^{30}Si$ isotope composition by only $-0.02‰$, and even a 100-fold decrease would result in a difference of maximal $-0.05‰$. Although lowering the horizontal flow means the proportions of deep to intermediate groundwater shift towards the deep end-member, the overall impact on the total $\delta^{30}Si$ isotope composition delivered into the Bay on Bengal is rather minute thus negligible.

4.5. Modeling the global perspective

The groundwater data presented here suggest that the total continental inputs to the oceans are altered by groundwater discharge towards lower $\delta^{30}Si$ values. Groundwater discharge from the Bengal Basin, with average $\delta^{30}Si_{GW}$ of ~0.25‰, contributes around 40% of the total Si delivered into the Bay of Bengal. More important, high Si fluxes from groundwater contribution appear to be a global phenomena (Kim et al., 2005; Burnett et al., 2007; Niencheski, 2007). While the Si isotope composition and mass contribution from different groundwater systems is likely to vary somewhat, projecting the results of this study to a global scale suggests that these inputs will inevitably modify ocean isotopic budgets. Assessing the impact on the global oceans of isotopically distinct groundwater input, such as that observed in the Bengal Basin, is important for being able to accurately interpret palaeo-records of ocean Si isotopes.

Moderate changes in the magnitude of the riverine Si flux have been shown to have relatively little impact on the Si isotopic composition of the oceans. For a fixed $\delta^{30}Si$ of 1‰, riverine Si fluxes would have to increase 2.5 times or decrease by more than 50% in order to significantly change the ocean's Si isotope composition (De La Rocha and Bickle, 2005). However previous models have not taken into account isotopically distinct groundwater inputs, which may vary in relative importance with time. Major changes in the hydrological cycle might occur during large-scale events, such as the formation or retreat of major ice sheets. The proportions of river versus groundwater inputs into the ocean might shift significantly over glacial–
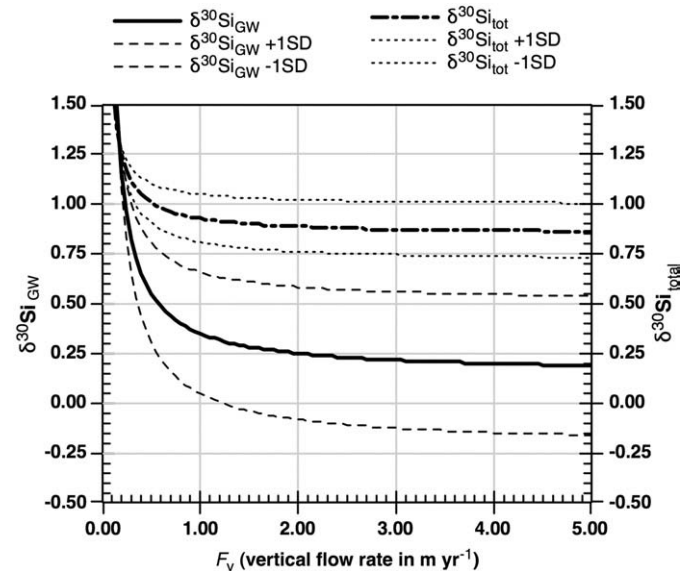

Fig. 5. Sensitivity analyses of $\delta^{30}Si_{GW}$ and $\delta^{30}Si_{tot}$ for various vertical flow rates (F_v). The isotope composition of groundwater (red curve) is insensitive to changes of the vertical flow above 1.0 m yr^{-1}. Because of the higher fluxes involved, the isotope composition of the total Si flux (blue curve) is less sensitive to changes in hydraulic flows. The low sensitivity means that anisotropic hydraulic flow will not significantly alter the resulting Si isotope composition of the groundwater. Dashed and dotted lines give the uncertainty of the model based on the $1\sigma_{SD}$ of each average estimate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

interglacial transitions, especially when the ice sheets are at full extent, so that groundwater fluxes are enhanced by recharge of subglacial meltwater, while surface runoff is suppressed (Boulton et al., 1996).

The isotopic distinction between river and groundwater means that such hydrologic shifts might systematically change the input into the ocean. In a scenario where the riverine input into the oceans is restricted by the growth of ice sheets, while the groundwater still discharges into the ocean, the average inputs into the oceans would be severely offset towards an isotopically lighter composition. Changes of such global scale might be recorded in palaeo-records (De La Rocha et al., 1998; Brezinski et al., 2002; Beucher et al., 2007) and are consistent with the observation that diatom δ^{30}Si values were lowest during the LGM and rise towards heavier compositions with transition to the interglacial. These data have previously been interpreted as the result of decreased biological Si utilization, reflecting lower biological productivity within the ocean during the LGM. The faithfulness of Si isotope records as a productivity proxy would be undermined by a quantitatively important role for global hydrologic variability in forcing changes to oceanic Si isotope ratios.

A 2-box model (De La Rocha and Bickle, 2005) was adopted and modified in order to assess how isotopically light groundwater fluxes, such as those reported here for the Bengal Basin, might impact the ocean isotopic composition during glacial–interglacial transitions, and if such events could be recorded in biogenic opal. The model was validated by using identical starting parameters to those used for the Quaternary ocean by De La Rocha and Bickle (2005) (including input fluxes of 7.0 Tmol Si with an δ^{30}Si of 0.8‰). Initial steady state was reached in less than 100 yr and results for ocean Si concentrations and isotope values exactly replicate reported values (De La Rocha and Bickle, 2005).

In order to explore the role of isotopically distinct groundwater, a triple-input system, comprising a groundwater component as well as igneous and riverine inputs, was implemented. Parameter values were set by extrapolating the results from the Bengal Basin to a global scale, where groundwater contributes ~60% of the riverine Si flux into the ocean, with a δ^{30}Si value of 0.25‰, in contrast to a riverine δ^{30}Si value of 1.3‰. The absolute flux of other sources (denoted igneous sources) with a δ^{30}Si$_{ign}$ value of − 0.3‰ was kept constant at values reported in De La Rocha and Bickle (2005). Under these conditions the inputs yield Si fluxes of ~10.6 Tmol with a δ^{30}Si value of 0.8‰, representing an isotope balance between the three different input components

$$\delta^{30}\text{Si}_{\text{Fin}} : \left(\delta^{30}\text{Si}_{\text{riv}} \times 0.56\right) + \left(\delta^{30}\text{Si}_{\text{GW}} \times 0.34\right) + \left(\delta^{30}\text{Si}_{\text{ign}} \times 0.1\right) = 0.8‰.$$

Different from the model by De La Rocha and Bickle (2005), each of the three input components can be independently varied in magnitude as well as isotope ratio, with the isotope composition of the total input to the oceans being consequently adjusted. The residence time of Si would be around 9 kyr, given an oceanic Si inventory of approximately 95 Pmol and an input of 10.6 Tmol.

To test whether the accumulation of large ice-shields can change the Si isotope composition of the ocean and of biogenic opal output, riverine and groundwater fluxes were altered after the model reached steady state. Total runtime was set as 32,000 yr and changes in input fluxes were introduced into a steady-state system 1500 yr after initialization. In order to simulate interruptions of the hydrological cycle due to storing fresh water in ice-shields, riverine fluxes were decreased by 50%, whilst groundwater fluxes were kept constant. The isotopic input into the oceans changes accordingly by 0.2‰ towards lighter δ^{30}Si values. Despite this change in inputs, the characteristics of the ocean Si pool did not significantly change. Concentrations of dissolved Si remained at 72 μM and 6 μM, in the deep and surface ocean, respectively, and δ^{30}Si values in both reservoirs dropped by ~0.2‰ until the end of the run (Fig. 6). However, changes in the
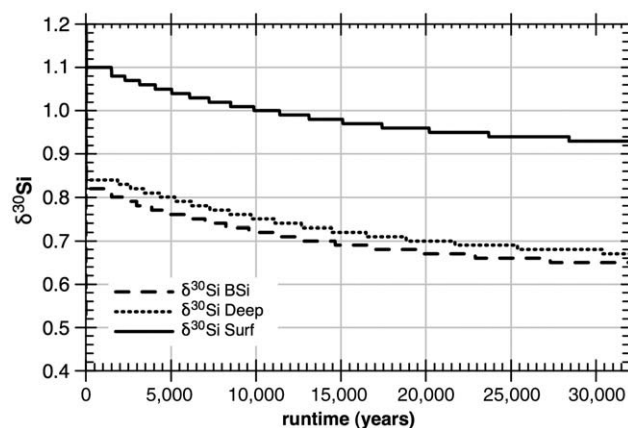

Fig. 6. The sensitivity of the world's oceans to changes in Si inputs. Changes of Si inputs were introduced at 1500 yr into a model running at steady state. Riverine fluxes were decreased by 50%, whereas groundwater and 'igneous' fluxes were kept constant. Despite this dramatic change in inputs towards lighter Si isotope compositions, the d^{30}Si of each pool required approximately 30,000 yr to adapt to these changes. This slow response cannot explain observed shifts in palaeo-opal records from the LGM.

biogenic output are not significant and rapid enough to explain the excursion observed in diatom records from the LGM (De La Rocha et al., 1998; Brezinski et al., 2002; Beucher et al., 2007), as the biogenic output required about 30,000 yr for adaptation of varying inputs. A range of different input scenarios was simulated, e.g. river fluxes decreased by 50% and groundwater fluxes elevated by 30%, with none able to change the sedimentary opal δ^{30}Si output to a significant (>0.2‰) degree within a few thousand years of a glacial–interglacial time scale. The actual magnitude of the observed shift is not the most important observation, and although being able to shift the isotope composition of the oceanic reservoirs by changing the input conditions, the timescale on which these changes occur is imperative. The ocean is a sufficiently large reservoir of Si, relative to the input fluxes, and even extreme changes in inputs cannot sufficiently alter the Si isotope composition of any oceanic reservoir on a time scale of ~10,000 yr. Variations in palaeo-diatom data show that the δ^{30}Si changes relatively quick on time scales of only a few 1000 yr (De La Rocha et al., 1998; Brezinski et al., 2002; Beucher et al., 2007), the only parameter in our model that was directly able to cause significant shifts in opal δ^{30}Si of more than 0.3‰ on time scales of a few hundred to a few thousand years, was the bio-productivity. The results of our model are in good agreement with those made by De La Rocha and Bickle (2005), even though large and isotopically lighter groundwater inputs were not taken into account in previous models.

5. Conclusions

The data presented here show that groundwater from the Bengal Basin is isotopically distinct from riverine values of the Ganges and Brahmaputra system, and that Si fluxes by groundwater into the Bay of Bengal rival in magnitude to riverine fluxes. Our new data indicate the importance of groundwater derived Si fluxes when estimating the continental input into the ocean. So far being only estimated from riverine values, future studies have to take the groundwater derived continental input into the ocean into account. Whilst being an important component of the overall ocean Si budget, the isotope composition of groundwater fluxes cannot explain glacial–interglacial variability in δ^{30}Si. Even extreme changes in inputs, e.g. shifting isotopically heavier river vs. isotopically lighter groundwater inputs, are unable to reproduce Si isotope pattern observed in biogenic opal (De La Rocha et al., 1998). The only plausible mechanism that can account for significant changes in the sedimentary opal δ^{30}Si record on such short time scales, is introducing changes in the rate of biological Si utilization, as proposed by De La Rocha et al. (1998).

Records of marine opaline δ^{30}Si consequently remain a faithful and robust record of biological productivity on glacial time scales, despite possible variations in isotopic inputs into the ocean, as caused by disruptions of the hydrological cycle.

Acknowledgements

References

Abraham, K., Opfergelt, S., Fripiat, F., Cavagna, A.-J., de Jong, J.T.M., Foley, S., Andre, L., Cardinal, D., 2008. δ^{30}Si and δ^{29}Si determination on BHVO-1 and BHVO-2 reference materials with a new configuration on a Nu Plasma Multi Collector ICP-MS. Geostand. Geoanal. Res. 32, 193–202.

Alleman, L.Y., Cardinal, D., Cocquyt, C., Plisnier, P.D., Descy, J.P., Kimirei, I., Sinyinza, D., Andre, L., 2005. Silicon isotopic fractionation in Lake Tanganyika and its main tributaries. J. Great Lakes Res. 31, 509–519.

Basile-Doelsch, I., Meunier, J.D., Parron, C., 2005. Another continental pool in the terrestrial silicon cycle. Nature 433, 399–402.

Basu, A.R., Jacobsen, S.B., Poreda, R.J., Dowling, C.B., Aggarwal, P.K., 2002. Large groundwater strontium flux to the ocean from the Bengal Basin and the marine strontium isotope record. Science 293, 1470–1473.

Beucher, C.P., Brzezinski, M.A., Crosta, X., 2007. Silicic acid dynamics in the glacial sub-Antarctic: implications for the silicic acid leakage hypothesis. Glob. Biogeochem. Cycles 21, GB3015.

Boulton, G.S., Caban, P.E., van Gijssel, K., Leijnse, A., Punkari, M., van Weert, F.H.A., 1996. The impact of glaciation on the groundwater regime in Northwest Europe. Glob. Planet. Change 12, 397–413.

Brezinski, M.A., Pride, C.J., Franck, V.M., Sigman, D.M., Sarmiento, J.L., Matsumoto, K., Gruber, N., Rau, G.H., Coale, K.H., 2002. A switch from Si(OH)$_4$ to NO$_3^-$ depletion in the glacial Southern Ocean. Geophys. Res. Lett. 29, 1564.

Burnett, W.C., Gullaya, W., Taniguchi, M., Dulaiova, H., Sojisuporn, P., Rungsupa, S., Ishitobi, T., 2007. Groundwater-derived nutrient inputs to the Upper Gulf of Thailand. Continental Shelf Res. 27, 176–190.

De La Rocha, C.L., Bickle, M.J., 2005. Sensitivity of silicon isotopes to whole-ocean changes in the silica cycle. Mar. Geol. 217, 267–282.

De La Rocha, C.L., Brzezinski, M.A., DeNiro, M.J., 2000. A first look at the distribution of the stable isotopes of silicon in natural waters. Geochim. Cosmochim. Acta 64, 2467–2477.

De La Rocha, C.L., Brzezinski, M.A., DeNiro, M.J., Shemesh, A., 1998. Silicon-isotope composition of diatoms as an indicator of past oceanic change. Nature 395, 680–683.

Ding, T., Wan, D., Wang, C., Zhang, F., 2004. Silicon isotope compositions of dissolved silicon and suspended matter in the Yangtze River, China. Geochim. Cosmochim. Acta 68, 205–216.

Dowling, C.B., Poreda, R.J., Basu, A.R., Peters, S.L., 2002. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. Water Resour. Res. 38, 1173.

Dowling, C.B., Poreda, R.J., Basu, A.R., 2003. The groundwater geochemistry of the Bengal Basin: weathering, chemsorption, and trace metal flux to the oceans. Geochim. Cosmochim. Acta 67, 2117–2136.

Galy, A., France-Lanord, C., 1999. Weathering processes in the Ganges–Brahmaputra basin and the riverine alkalinity budget. Chem. Geol. 159, 31–60.

Georg, R.B., Reynolds, B.C., Frank, M., Halliday, A.N., 2006a. Mechanisms controlling the silicon isotopic compositions of river waters. Earth Planet. Sci. Lett. 249, 290–306.

Georg, R.B., Reynolds, B.C., Frank, M., Halliday, A.N., 2006b. New sample preparation techniques for the precise determination of the Si isotope composition of natural samples using MC-ICP-MS. Chem. Geol. 235, 95–104.

Georg, R.B., Reynolds, B.C., Burton, K.W., Halliday, A.N., 2007. Silicon isotope variations accompanying basalt weathering on Iceland. Earth Planet. Sci. Lett. 261, 476–490.

Georg, R.B., Zhu, C., Reynolds, B.C., Halliday, A.N., 2009. Stable silicon isotopes of groundwater, feldspars, and clay coatings in the Navajo Sandstone aquifer, Black Mesa, Arizona, USA. Geochim. Cosmochim. Acta. 73, 2229–2241.

Johannes, R.E., 1980. The ecological significance of the submarine discharge of groundwater. Mar. Ecol., Prog. Ser. 3, 365–373.

Kim, G., Ryu, J.W., Yang, H.S., Yun, S.T., 2005. Submarine groundwater discharge (SGD) into the Yellow Sea revealed by ^{228}Ra and ^{226}Ra isotopes: implications for global silicate fluxes. Earth Planet. Sci. Lett. 237, 156–166.

Niencheski, L.F.H., 2007. Submarine groundwater discharge of nutrients to the ocean along a coastal lagoon barrier, Southern Brazil. Mar. Chem. 106, 546–561.

Reynolds, B.C., Aggarwal, J., Brzezinski, M.A., Cardinal, D., Engström, E., Georg, R.B., Land, M., Leng, M., Opfergelt, S., Vroon, P.Z., 2007. An inter-laboratory calibration of Si isotope reference materials. J. Anal. At. Spectrosc. 22, 561–568.

Singh, S.K., Sarin, M.M., France-Lanord, C., 2005. Chemical erosion in the eastern Himalaya: major ion composition of the Brahmaputra and δ^{13}C of dissolved inorganic carbon. Geochim. Cosmochim. Acta 69, 3573–3588.

Taniguchi, M., Burnett, W.C., Cable, J.E., Turner, J.V., 2002. Investigation of submarine groundwater discharge. Hydrol. Process. 16, 2115–2129.

Tréguer, P., Nelson, D.M., Van Bennekom, A.J., DeMaster, D.J., Leynaert, A., Quéguiner, B., 1995. The silica balance in the world ocean: a reestimate. Science 268, 375–379.

Varela, D.E., Pride, C.J., Brzezinski, M.A., 2004. Biological fractionation of silicon isotopes in Southern Ocean surface waters. Glob. Biochem. Cycl. 18 (GB1047), 1–8.

Ziegler, K., Chadwick, O.A., Brzezinski, M.A., Kelly, E.F., 2005. Natural variations of δ^{30}Si ratios during progressive basalt weathering, Hawaiian Islands. Geochim. Cosmochim. Acta 69, 4597–4610.