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Silicon Isotopic Fractionation in Lake Tanganyika and Its Main Tributaries

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ABSTRACT. *Silicon isotopic measurements in Lake Tanganyika were performed using multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in dry plasma condition. Isotopic signatures are reported for dissolved ortho-silicic acid [Si(OH)*$_4$*] collected during a 1-year-long surface waters survey in the southern basin along with several of the major tributaries. Deep-water Si isotopic profiles from a north-south transect cruise conducted in July 2002 are also described. The nutrient-like shape dissolved Si profiles and the isotopic disequilibrium between surface (*$\delta^{29}Si = 0.87 \pm 0.08$ ‰*) and deep waters (0.61 ± 0.05 ‰) suggest the occurrence of biological isotopic discrimination induced by diatoms biomineralisation in a fresh water system. Short-term surface water Si isotopic and diatom biomass variations obtained during the 1-year bi-weekly monitoring (2002–2003) in the south confirms this biological effect. Five epilimnion biogenic opal samples also were analyzed. Their signature (*$\delta^{29}Si$ *of 0.28 ± 0.12‰) compared to those of surrounding waters are consistent with the diatom isotopic fractionation effect measured on marine tropical diatoms. This demonstrates the species and temperature independent character of the silicon isotope fractionations by diatoms. River signatures present variable dissolved Si concentrations which were positively correlated to *$\delta^{29}Si$ *values in the range of previously published world river data. Because of its fast response to climate variability, nutrient dynamics, and limnological changes,* $\delta^{29}Si$ *in siliceous organisms should be very useful in studying environmental changes and particularly the recent decline of diatom Si utilization in Lake Tanganyika.*

INDEX WORDS: *Lake Tanganyika, silicon isotopes, fractionation, diatoms.*

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INTRODUCTION

Silicon is biologically linked to aquatic (mostly diatoms, Yool and Tyrell 2003) and terrestrial life (phytoliths in vascular plants, Alexandre *et al.* 1997, Conley 2002). It is also affected by inorganic processes such as weathering (Gaillardet *et al.* 1999) and silcrete precipitations (Basile-Doelsch *et al.* 2005). Its oceanic biogeochemical cycle constitutes a difficult climate-related question owing to the close relationship with the carbon cycle (e.g., Tréguer *et al.* 1995, Harrison 2000, Dugdale *et al.* 2004). The preferential incorporation of lighter ^{28}Si isotope by diatoms to form opaline cell wall ($bSiO_2$) tends to gradually enrich the dissolved silicic acid pool ($Si(OH)_4$) in ^{29}Si and ^{30}Si. Such isotopic fractionation allows an estimation of the diatom relative assimilation of the dissolved silicon available. A constant enrichment factor $^{29}\varepsilon$ (= $[^{29}\alpha_{bSiO2-Si(OH)4)}-1]10^3$, with $^{29}\alpha_{bSiO2-Si(OH)4)}$ = $[^{29}Si/^{28}Si]_{bSiO2}$ / $[^{29}Si/^{28}Si]_{Si(OH)4}$) of silicon isotopes between the dissolved fraction and the opal were estimated in vitro ($^{29}\varepsilon$ = – 0.57‰ ± 0.2‰ per atomic mass unit) for various species of marine diatoms at different temperatures (12–22°C) (De La Rocha *et al.* 1997). Recent field studies have confirmed the link between the diatoms' silicon utilization and the Si isotopic compositions (De La Rocha *et al.* 2000, Varela *et al.* 2004, Cardinal *et al.* 2005). Consequently, well-preserved silicon isotopic information in the sediment has been used as a proxy to reconstruct the history of marine relative silicic acid use by diatoms (De La Rocha *et al.* 1998, Brzezinski *et al.* 2002).

In continental waters, the few silicon isotopic studies carried out to date were conducted on seven major rivers of the world including the Yangtze River (China) (De la Rocha *et al.* 2000, Ding *et al.* 2004). This later investigation considered both dissolved and particulate fraction, allowing interpreting silicon isotopic ratio variations in term of weathering or sedimentation processes and providing a large range of Si isotopic signature (0.35 to 1.7‰) than previous observations.

Applications of this new tracer in tropical lakes that contain important paleohydrology and diatom records (Barker *et al.* 2002) require development and validation. Lake Tanganyika is characterized by a rather constrained environment: distinct wet and dry seasons; a near optimum light intensity all year round; and a regular peak of diatom productivity, driven by the depth of the mixed layer and nutrient availability (Craig *et al.* 1974, Hecky *et al.* 1991) Moreover, the regional ecosystem is very sensitive to climate changes (O'Reilly *et al.* 2003, Verburg *et al.* 2003) and ENSO events (Plisnier *et al.* 2000, Pilskaln 2004). The objectives of this paper are to depict the Si isotopic behavior in a first attempt to describe the proxy in such a unique freshwater ecosystem. This work reports the first three complete deep water δ^{29}Si profiles of Lake Tanganyika (n = 37) and from some of its main tributaries (n = 8) along with the first freshwater surface biogenic Si isotopic signatures (n = 5). A 1-year-long survey of dissolved silicon isotopes (n = 42) is also described. We then discuss the main processes that are likely to be involved in controlling these silicon isotopic signatures.

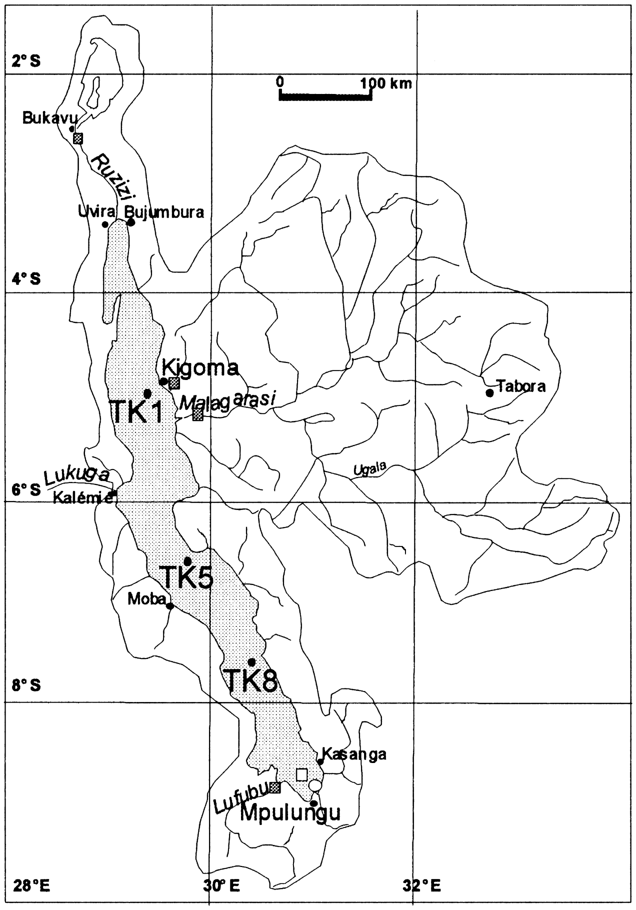

FIG. 1. Map of Lake Tanganyika and its watershed showing the transect sampling stations (black dots), the monitoring stations (Coastal 0 m CLIMC-M, white circle and Pelagic 20 m CLIMP-M, white square) and rivers stations (gray squares) dealt with in this study.

SAMPLING LOCATION, MATERIALS, AND METHODS

In the East African Rift, Lake Tanganyika (3°20′; 8°45′ S. and 29° 05′; 31°15′ E.) is surrounded by Burundi, Tanzania, Zambia, and the Democratic Republic of Congo (Fig. 1). This 10 to 20 million years old lake (Coulter 1991) is 680 km long and 72 km at the widest point and covers about 32,900 km^2. It is divided in two main basins separated by the Kalemie ridge. With a volume of 18,880 km^3 (max. depth: 1,470 m), it is the second largest fresh water lake in the world. The Tanganyika region is under a semi-humid tropical climate with a main rainy season from October to April. Precipitation is abundant (1,654 mm in 2002 in Mpulungu, the southernmost end of the lake) but variable (from 800 to 2,000 mm yr^{-1}). High rainfall is counterbalanced by strong evaporation processes (Bergonzini 1998). In addition, three main permanent rivers (Rusizi, Malagarasi, and Lufubu), representing 55% of the total riverine input (Langenberg *et al.* 2003a), contribute to the lake recharge with a marked seasonal variability highlighted by a maximum water discharge in April–May. Water exits via the Lukuga River and the lake is in quasi equilibrium through water loss by evaporation (Bergonzini 1998). In 2002, average temperature and pH from the water column ranged from 23.4 to 28.3°C and 8.4 to 9.2 respectively, in accordance with previous observations. A well-defined thermal stratification varies seasonally on top of a permanent anoxic hypolimnion located below 50 to 100 m in the North and 250 m in the South (Coulter 1991). This stratification controls the mixing with nutrient-rich deep waters. During the dry and windy season (May to September), phytoplankton productivity in the south increases due to upwelling of deep cold waters (e.g., Hecky and Fee 1981, Sarvala *et al.* 1999), favoring a characteristic increase of diatom abundance, which may become the dominant algae group (Descy *et al.* 2005). The diatom assemblage is dominated by pennate, needle-like colonial taxa, *Nitzschia asterionelloides* and *N. fonticola* representing 45 to 95% of the diatom biomass in 2002 near Mpulungu (Cocquyt and Vyverman, submitted). The dissolved Si residence time of 611 years (Branchu 2001) is in the same order of magnitude as the one of the whole lake water (290 to 440 years: e.g., Coulter 1991, Cohen *et al.* 1997). The relative importance of internal and external Si sources has been previously estimated based on literature and measurement data (Hecky *et al.* 1991, Branchu 2001). They concluded that the surface Si budget was mainly influenced by vertical mixing while Si loading from tributaries was at most representing 2 to 3% of it.

Spatial and vertical distributions of silicon concentrations and isotopic compositions have been determined in Lake Tanganyika at three deep stations during a north-south transect on board of the M.V. *Maman Benita* in July 2002. Samples were collected in the northern (Station TK1—Kigoma basin: 5°05′S 29°31′E) and southern parts of the lake (Station TK5—Kalemie basin: 6°33′S 29°49′E and Station TK8—Kipili basin: 7°24.6′S 30°28.2′E) from 0 to 1,200 m (Fig. 1). The Southern basin, exhibiting a strong biological activity due to intense seasonal mixing, was monitored from January 2002 to February 2003 near Mpulungu (Zambia) on a pelagic site (CLIMP-M) at 20 m depth (8°43.98′S 31°02.43′E) and a coastal site (CLIMC-M) just below the surface (thereinafter referred to 0 m) (8°45.226′S 31°05.15′E), only a few kilometers apart from each other (Fig. 1). Diatoms were collected simultaneously at these two locations using a 10 µm mesh phytoplankton net, hauled from 100 m depth, then filtered onto polycarbonate membranes and dried. The water sampling bottles (Go-Flo™ or Hydrobios™) were sub-sampled for silicon isotope analyses into 100-mL acid cleaned high-density polyethylene (HDPE) bottles. After filtration on 0.4 µm polycarbonates membranes, the samples were kept cold or frozen until precipitation and analysis in the laboratory in Belgium. Samples from tributaries of Lake Tanganyika (Rusizi, Malagarasi, and Lufubu) (Fig. 1) were collected on several occasions and analyzed similarly in order to estimate the external Si sources signatures on a regional scale.

Silicate analyses were completed on site within 24 hours on samples preserved at 4°C and filtered through 0.7 µm glass-fiber filters by spectrophotometry using the molybdenum blue standard method (Greenberg *et al.* 1992).

Diatom biomass was assessed independently from counts under an inverted microscope. Biomass estimations, expressed as mg m^{-3} fresh weight, were calculated from biovolumes, using mean linear dimensions, assuming a density of 1 (Hillebrand *et al.* 1999).

For isotopic analyses, silicic acid was extracted and purified through its quantitative reaction with triethylamine molybdate, precipitation as triethylamine silicomolybdate, and combustion to form SiO_2 (De La Rocha *et al.* 1996). Diatoms (> 10 µm) deposited on filters ($bSiO_2$) were leached with a NaOH (0.2M) solution at 100°C during 45 mn in order to reduce residual contamination from clay material (Ragueneau *et al.* 2005). The solution was then neutralized with suprapur HCl and the supernatant was precipitated following the same procedure as for silicic acid.

The Si isotopic measurements were carried out under dry plasma conditions (Aridus desolvator) using a Nu Plasma MC-ICP-MS, with a Mg external standard. This procedure ensures high sensitivity as well as good repeatability and accuracy to the acquisition of relative natural silicon isotope abundances (see Cardinal *et al.* 2003, Carignan *et al.* 2004 for details). $\delta^{29}Si$ values express the deviations in ‰ of $^{29}Si/^{28}Si$ ratios, from the same ratio of the NBS28 standard reference material.

$$\delta^{29}Si = \left[\frac{\left(^{29}Si/^{28}Si\right)_{sample}}{\left(^{29}Si/^{28}Si\right)_{NBS28}}\right] \times 1000$$

We have measured and used exclusively the $\delta^{29}Si$ notation as the ^{30}Si signal is disturbed by isobaric interference on the low resolution Nu Plasma instrument. Because this prevents us from detecting any analytically induced mass dependent fractionation processes between Si isotopes through a $\delta^{30}Si$ vs $\delta^{29}Si$ graph, we checked such bias daily (for independent analytical sessions) using Mg vs. Si isotopes ratios on every NBS 28 standards analyzed between each sample. Based on this standard bracketing technique, few atypical results (less than 10% of the whole dataset) presenting an instable analytical fractionation line have been discarded as they generally reflected unsteadiness of the plasma or the dissolvating system. The $\delta^{30}Si$ notation, often used in previous silicon isotopic works, can be attained assuming a mass dependent fractionation between ^{30}Si, ^{29}Si and ^{28}Si ($\delta^{30}Si = 1.934 \times \delta^{29}Si$), analytically verified by De La Rocha (2002). A reproducibility test that included molybdate coprecipitation and isotopic analyses of 10 individual aliquots from a single sea water sample gave a standard deviation on the $\delta^{29}Si$ of 0.035‰ (1 σ) (Cardinal *et al.* 2005). Several replicates performed on particulate and dissolved Lake Tanganyika samples produced a similar reproducibility.

RESULTS

Water Column Si Profiles

Dissolved Si vertical profiles at pelagic stations TK1, TK5, and TK8 present a typical nutrient-like shape, i.e., a large depletion in the mixed layer (0–100 m: 44 ± 10 µmol L^{-1} (n = 17)) relatively to the deep water (Fig. 2; data are available upon request from first author). Below the 100–250 m silicicline (sharp increase of silicic acid contents), the higher dissolved Si content (up to 385 µmol L^{-1}) (Fig. 2) stays much below the maximum solubility of $bSiO_2$ (1,600–1,900 µmol L^{-1}, Rickert *et al.* 2002). These Si profiles fit with previous Tan-

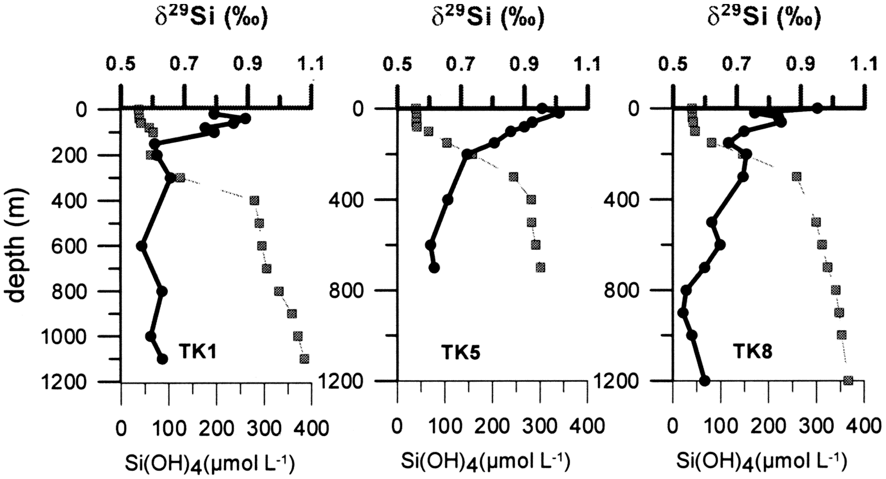

FIG. 2. Dissolved Si concentration (dashed line) and δ29Si (bold line) profiles at station TK1 (northern basin), TK5 and TK8 (southern basin) collected in July 2002.

TABLE 1. Dissolved Si concentrations and δ^{29}Si from Lake Tanganyika tributaries.

Rivers	Dates	δ^{29}Si (‰)	Si(OH)$_4$ (μM)
Malagarasi	10-Aug-01	0.90	231
	04-Jul-02		20
	16-Feb-03	0.75	173
	17-Jul-03	0.96	274
	27-Jan-04	0.60	100
Lufubu	16-Jul-02	0.92	218
	14-Jul-03	0.36	74
	06-Feb-04		89
Ruzizi	17-Mar-03	0.88	145
	25-Aug-03	1.30	92
mean river		0.82	142
std dev.		0.28	81

ganyika results (Craig *et al.* 1974, Edmond *et al.* 1993) and are within the range of those found in the large lakes such as the Laurentian Great Lakes (e.g., Johnson and Eisenreich 1979).

The heaviest Si isotopic compositions (Fig. 2) are observed in the mixed layer (mean δ^{29}Si = 0.86 ± 0.08 ‰ (n = 15)) where diatoms are mainly present. The silicicline displays a lighter signal (mean δ^{29}Si = 0.69 ± 0.07‰ (n = 6)). The deep waters from both basins exhibit equivalent homogeneous isotopic profiles below 300 m (mean δ^{29}Si = 0.61 ± 0.05‰ (n = 16)). Station TK1 shows a well-stratified profile while TK5 and TK8 present more gradual Si concentrations and δ^{29}Si variations with depth attributed to the occurrence of an effective water-mixing in the southern basin in July 2002.

River Signature Characterization

During our survey, the rivers Rusizi, Malagarasi, and Lufubu had a much higher dissolved Si concentration than the lake surface waters. Although variable over time and between watercourses (mean: 142 ± 81 μmol L^{-1}; Table 1), these concentrations span the range of data obtained by Craig *et al.* (1974) for various rivers collected in spring 1973 and 1974 around the lake (mean: 145 ± 63 μmol L^{-1}). However, higher and more variable values have been sometimes obtained (Van Meel 1987, Vandelannoote *et al.* 1999). Beauchamp (Van Meel 1987) presented Si concentrations for the Rusizi (275 μmol L^{-1}), the Luiche (675 μmol L^{-1}), and the Malagarasi (630 μmol L^{-1}) during a cruise in July 1937. Vandelannoote *et al.* (1999) recently published a larger range for the Rusizi (197 to 1,180 μmol L^{-1}).

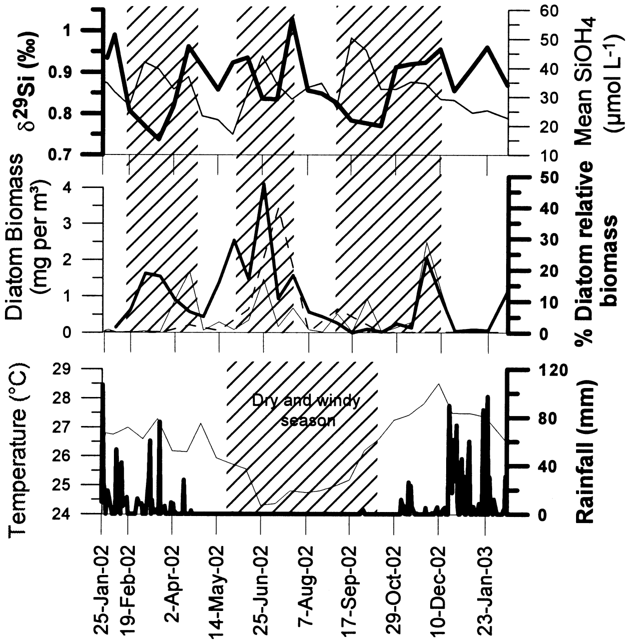

FIG. 3. (A) Mean dissolved Si concentrations (solid line) and δ^{29}Si (bold line) from measurements at CLIMC-M (0 m) and CLIMP-M (20 m) stations from February 2002 to January 2003. (B) Surface water diatom biomass at CLIMC-M (~0 m) (dashed line) and CLIMP-M (20 m) (solid line) in mg per m^3 and percentage (%) of diatom relative biomass at CLIMP-M, as inferred from marker pigments (see details in Descy* et al. *2005) (bold line)(C) Surface water temperature monitoring (solid line) and rainfall (bold line) in 2002 in Mpulungu.

The Si isotopic signature of Lake Tanganyika tributaries range from δ^{29}Si = +0.36‰ for the Lufubu and up to δ^{29}Si = +1.30‰ for the Rusizi. They tend to vary seasonally and between rivers along with silicic acid contents (Table 1).

Mixed Layer Monitoring (January 2002–February 2003)

During the 1 year monitoring, Si concentrations displayed substantial variations (15 to 51 μmol L^{-1}, Fig. 3A, Table 2) in surface water collected at the coastal (near surface—0 m) and pelagic sites (20 m) with a good correlation at all times between these two locations (r^2 = 0.92). The mean annual Si content at 32 ± 8 μmol L^{-1} for both sites is con-

TABLE 2. Dissolved Si concentrations, δ²⁹Si, diatom biomass, and average water temperatures, from Lake Tanganyika monitoring in Mpulungu (Zambia) at the coastal-CLIMC-M (0 m) and pelagic-CLIMP-M (20 m) stations.

Date	CLIMC-M (0 m) $Si(OH)_4$ (µM)	$\delta^{29}Si$ (‰)	Diatom biomass (mg/m^3)	CLIMP-M (20 m) $Si(OH)_4$ (µM)	$\delta^{29}Si$ (‰)	Diatom biomass (mg/m^3)	Average temperature (°C)
25-Jan-02	35.4		0.42	35.0		0.66	26.03
29-Jan-02	33.7	0.94		35.9	0.93	1.04	26.79
05-Feb-02	30.5	0.99		32.9		0.25	26.74
19-Feb-02	23.1	0.81	0.11	30.9	0.81	0.19	26.99
05-Mar-02	41.7	0.66		42.4	0.89	0.46	26.59
19-Mar-02	40.9	0.79	0.00	38.3	0.68	0.31	27.29
02-Apr-02	31.3	0.84		34.0	0.8	9.32	26.17
16-Apr-02	38.4	0.96	7.67	35.6		18.66	26.14
29-Apr-02	23.2			23.7		0.94	27.13
14-May-02	22.3	0.89	1.54	22.0	0.83	3.03	25.93
28-May-02	15.0			19.1	0.92	1.09	25.73
11-Jun-02	31.0	0.96	8.68	32.0	0.91	4.77	25.55
25-Jun-02	45.5			43.0	0.84	19.17	24.3
09-Jul-02	33.6	0.85	46.05	35.0	0.82	2.27	24.36
23-Jul-02	33.5			25.1	1.03	8.14	24.8
07-Aug-02	32.9	0.94	0.13	33.7	0.77	0.9	24.74
20-Aug-02	34.7			34.9	0.85	0.21	24.8
03-Sep-02	26.2	0.84	8.49	26.4	0.81	6.82	24.96
17-Sep-02	50.9			49.9	0.78	0.45	25.17
01-Oct-02	46.8			45.5		11.89	26.19
15-Oct-02	33.0	0.86	0.03	32.3	0.68	0.09	26.6
29-Oct-02	33.5	0.97		31.9	0.86		27.25
12-Nov-02	36.6	0.88	0.12	33.9	0.96	3.93	27.42
26-Nov-02	35.4	0.9		34.0	0.95	32.23	27.81
10-Dec-02	31.0			27.5	0.96	14.54	28.51
23-Dec-02	28.9	0.83		28.9	0.88	0.0	27.49
09-Jan-03	24.3	0.91	0.34	24.8		0.4	27.48
23-Jan-03	25.2			25.6	0.96	0.25	27.36
11-Feb-03	23.1	0.85	0.05	22.3	0.89		26.52
mean	32.5	0.88		32.3	0.86		26.3
std dev.	8.0	0.08		7.2	0.09		1.12

firmed by the monitoring performed over a 2-year period in 2002 and 2003 (31.5 µmol L^{-1}) at the same stations (Descy *et al.* 2005). Si isotopic compositions varied substantially from 0.66‰ to 1.03‰ at both southern stations (Fig. 3A, Table 2) and present comparable averaged values (0.88 ± 0.08‰ (n = 19) at 0 m and 0.86 ± 0.09‰ (n = 23) at 20 m. It must be noted that surface data at TK1, 5, and 8 during the cruise (Fig. 2) are similar to the ones measured during the same period (July 2002) at the monitoring sites. Small $\delta^{29}Si$ differences between the coastal and pelagic sites also observed with diatom biomass estimations (calculated from biovolumes or marker pigments, Descy *et al.* 2005), may suggest some local influences, although presenting generally comparable variations on a seasonal scale (Fig. 3B).

Five large diatom samples ($bSiO_2$ larger than 10 µm) collected simultaneously with the dissolved fraction during this survey have been analyzed in duplicates (Table 3). They display relatively lighter $\delta^{29}Si$ (mean of 0.28 ± 0.12‰, n = 5) compared to the dissolved Si signature of the surrounding water (mean of 0.85 ± 0.05‰, n = 5).

DISCUSSION

Si Isotopes in Tributaries

The range of $\delta^{29}Si_{Si(OH)4)}$ in world rivers (0.2 to 1.7‰, De La Rocha *et al.* 2000, Ding *et al.* 2004) is

TABLE 3. Δ^{29}Si calculated values based on mean δ^{29}Si in the dissolved fraction and in biogenic opal from Lake Tanganyika particles.

Date	Average δ^{29}Si $Si(OH)_4$ (‰)	Average δ^{29}Si BSi (‰)	Δ^{29}Si (‰)
19-Feb-02	0.81	0.16	–0.65
02-Apr-02	0.82	0.14	–0.68
14-May-02	0.86	0.37	–0.49
03-Sep-02	0.83	0.38	–0.45
12-Nov-02	0.92	0.37	–0.55
mean	0.85	0.28	–0.56
std dev.	0.04	0.12	0.10

much heavier than those of mafic (–0.33 ± 0.10‰) and felsic (–0.04 ± 0.09‰) igneous rocks (Douthitt 1982, Ding *et al.* 1996) or felsic metamorphic rocks (–0.05 ± 0.13‰, Ding *et al.* 1996). This implies a large isotopic fractionation process. Because Si uptake by river diatoms is unlikely to account for such a huge fractionation, De La Rocha *et al.* (2000) suggested that phytoliths and low temperature clay formation could play a role. Previous phytoliths studies have evidenced lighter phytolith isotopic composition compared to their water source, symptomatic of a biological fractionation effect (Douthitt 1982, Ziegler *et al.* 2002, Opfergelt *et al.* 2004). Likewise, Ding *et al.* 2004 evoked as well a biological uptake through vegetation of riverine dissolved Si to partly explain its negative relationship with the silicon isotopic signatures (dissolved Si increase while δ^{30}Si decrease). The rather good positive correlation between δ^{29}Si and dissolved Si concentrations in Lake Tanganyika tributaries is very similar to the one published for other world rivers (De La Rocha *et al.* 2000) (Fig 4). It may reflect some mixing processes between two extreme components. The low Si, ^{29}Si-depleted end member might reflect the crustal rocks or crustal-derived clays, because weathering of insoluble quartz-rich felsic rocks and clays would liberate a solution characterized by low Si contents and δ^{29}Si either undifferentiated (for a pure crustal component: –0.05‰) or relatively depleted (for Kaolinite: –0.80 ± 0.25‰, De La Rocha *et al.* 2000). The high Si, ^{29}Si-enriched end member might correspond to the dissolution of phytoliths, that would produce a solution with high $Si(OH)_4$ concentrations and positive δ^{29}Si (+ 0.6 to + 1.2‰), according to the small database presently available for phytoliths (Ding *et al.* 1996). Consequently, we may consider dissolved Si in tributaries of Lake Tanganyika to be mostly driven by changes in the mineralogical components involved in the weathering processes, with little influence from the fresh water diatom activity.

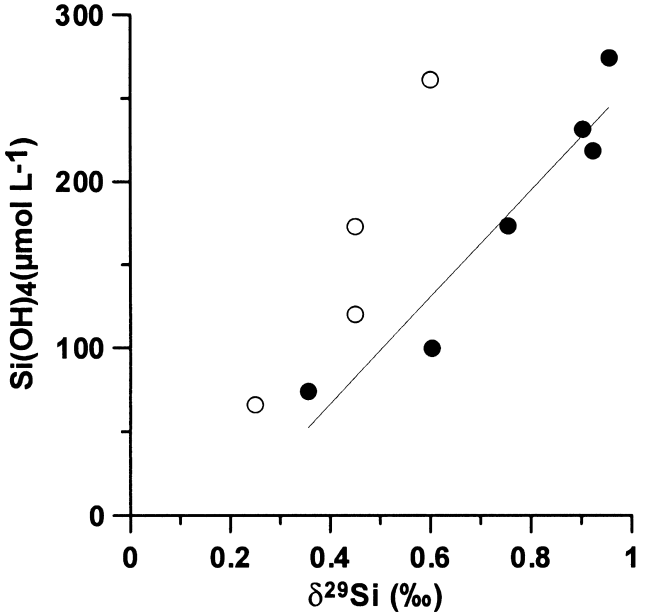

FIG. 4. Tanganyika tributaries δ^{29}Si values plotted against dissolved Si (black circles). (Rusizi values have not been plotted as they are influenced by diatom activity and hydrothermalism from Lake Kivu). World river data are also reported for comparison purpose (white circles) (De La Rocha **et al.** ***2000).***

Although external Si inflows (rivers) are potentially important in some freshwater systems (Conley 2002), within large lakes, the Si cycle is generally dominated by biological activity and regeneration (e.g., Rickert *et al.* 2002). In Lake Tanganyika, rivers/run-off as well as internal recycling through upwelling, vertical mixing or internal waves are the main sources of Si that have been estimated in previous studies (Hecky *et al.* 1991, Branchu 2001 and reference therein). The surface waters present a mean δ^{29}Si of 0.87 ± 0.08‰ less variable but comparable to riverine values (0.83 ± 0.28‰) which could suggest that tributaries of the Tanganyika control the Si isotopic signature. However, external Si sources (5.84 Gmol/yr; Branchu 2001) are reported to represent annually at most 6 % of the surface water (0–100 m) estimated stock of dissolved Si (95 Gmol Si in 2002). Moreover, neither the high Si concentration in rivers nor the negative precipitation-evaporation budget could explain the Si depleted surface water of the lake, neglecting any significant influence from external Si sources on a more global lake scale.

Testing the Si Isotopes as a Freshwater Diatom Proxy of Relative Si Uptake

Given the overall low impact of the external Si sources on the Si internal reservoir, one cannot consider them as a major driving force of the lake silicon cycle. Yet, due to a marked rainy season (November to April/May), rivers/run-off and rainfall may locally have some impact during stratified periods, while vertical mixing is most pronounced during the dry and windy season (May–June to October) (Langenberg *et al.* 2003a, b). Internal recycling and mixing is the major source of fresh dissolved silicic acid to the mixed layer (Hecky *et al.* 1991, Branchu 2001). Water mass upward advection tends to enrich the epilimnion with a high Si content and low δ^{29}Si signatures. The vertical profiles in the northern and southern basins have a heavier isotopic signature in surface waters (δ^{29}Si = 0.86±0.08 ‰) associated to low Si concentrations and inversely in deep waters (δ^{29}Si = 0.61±0.05 ‰). The differences in isotopic signatures are consistent with a preferential ^{28}Si biological uptake by diatoms in surface waters, which is regenerated by their dissolution in deep waters in a way similar to the one encountered in marine environment. Moreover, observations made during the year long survey contribute to that hypothesis. Three distinct episodes of high Si concentrations (highlighted on Fig. 3A, B, C) echo a lighter δ^{29}Si signatures, characteristic of nutrient replenishments. These episodes are rapidly followed by a phytoplankton bloom materialized by a diatom biomass increase, lower dissolved Si and heavier δ^{29}Si values (Fig. 3A, B), a sign of a biological control.

To give additional support on such a mechanism, we have determined Si isotopic composition of the biogenic silica from size fraction > 10 µm at various seasons which can be assumed to mainly represent the diatom signature (Table 3). Indeed, the choice of this size fraction and the NaOH leaching during the biogenic silicon extraction avoid significant bias from clay minerals. Moreover, while contributions from phytoliths present in riverine particles (Conley 2002) could represent a potentially a large fraction of biogenic Si as in Lake Malawi tributaries (Bootsma *et al.* 2003), phytoliths are limited in the Lake Tanganyika samples. Indeed, phytoliths and sponge spicules counted in the five phytoplankton samples collected in this study represented only 0.5 to 2.5% of the total number of opal particles. The difference between the surrounding dissolved Si and biogenic silica fractions ($\Delta^{29}Si = \delta^{29}Si_{Si(OH)4} - \delta^{29}Si_{\,bSiO2}$) is –0.56 ± 0.1‰. This result is similar to the mean value obtained for the ^{29}Si enrichment factor ($^{29}\varepsilon$) on tropical marine diatoms – 0.57 ± 0.2‰ (recalculated from De La Rocha *et al.* 1997 using a $\delta^{29}Si = \delta^{30}Si/1.934$, De La Rocha 2002). For small levels of Si isotope fractionations, Δ^{29}Si offers an excellent approximation to $^{29}\varepsilon$ if an isotopic equilibrium has been reached between the dissolved and particulate phases. Therefore, our Δ^{29}Si provides the first evidence that silicon isotopes are a relevant proxy to diatom relative silicon utilization in fresh water environments under high temperature conditions (24–28°C). This enlargement of the non-species dependent character of this proxy underlines its general worldwide applicability for monitoring past changes in diatom activity in both marine and fresh water palaeoenvironments.

Lake Tanganyika Secular Si Trend: the Isotopic Constraint

Edmond *et al.* (1993) estimated that productivity in Lake Tanganyika should be very sensitive to climate changes due to a quasi equilibrium of processes such as input-output and uptake-mineralization involved in the biological loop. The recently demonstrated warming trend of Tanganyika surface waters (Plisnier 2000, O'Reilly *et al.* 2003) has clearly influenced the Si cycle as evidenced by the historical increase in the lake surface water Si concentrations recently published (Verburg *et al.* 2003). The present study tends to confirm this evolution with mean surface dissolved Si of 32 ± 8 µmol L^{-1} in the northern and southern basins, among the highest ever reported values. Although historical data from Verburg *et al.* (2003) may underestimate some regional and seasonal variability, they clearly show a significant (threefold) increasing trend between the 1938–1975 period (9.5 ± 4.6 µmol L^{-1}) and the year 2000 (27.3 ± 2 µmol L^{-1}) (99% confidence level on a t-test). Adding our values collected in 2002–2003 increases the mean 2000–2003 dissolved Si to 31 ± 11 µmol L^{-1}, and corresponds to a Si rise in the mixed layer of about 70 mmol m^{-2} yr^{-1} during the last 28 years (1975–2003), in the order of magnitude of the whole external input estimated for the lake (179 mmol m^{-2} yr^{-1}; Branchu 2001).

There has been no evidence of a dramatic change in silica loading by tributaries in recent years (Van Meel 1987, Craig *et al.* 1974, Kimbadi *et al.* 1999, Vandelannoote *et al.* 1999, this study). Consequently, Verburg and colleagues (2003) considered this Si trend to mainly reflect a lower diatom activity due to a decreasing phosphorus and nitrate availability. This lower productivity follows a 30-year period of diminishing exchange rate between shallow and deep water (higher density gradient and stratification) triggered by a warming trend and less wind (O'Reilly *et al.* 2003). This could be constrained with Si isotopes in two ways. First, a declining nutrient-bearing deep water exposure in the mixed layer is translated into an increase of the dissolved silicon and a probable decrease in average δ^{29}Si signatures of both surface waters and sedimenting diatom frustules. Therefore, silicon isotopes may be used to describe a temporal trend, by comparing the δ^{29}Si signatures of present-day diatoms to their counterparts from the last two centuries preserved in the uppermost part of the lake sedimentary column. That should be an objective for future works. Second, the impact of this long-term trend should be also recorded in the deep water Si isotopic compositions. Indeed, the high Si content of deep waters is generally explained by a gradual dissolution of biogenic opal settling along the water column, favored by microbial activity, high pH, and temperature and Si under-saturated waters. Therefore, the silicic acid isotopic signatures of deep water must record the dissolution-integrated signal of past diatom cells over a time scale corresponding to the residence time of dissolved Si (i.e., a few hundred years, Branchu 2001). The large silicon isotopic differences between the 2002 surface diatoms (0.28 ± 0.12‰) and both silicicline (0.69 ± 0.07‰) and deep water (0.61 ± 0.05‰) may therefore point to a modern lowering of diatom Si utilization compared to the recent past. This discrepancy can also be assessed by correlating the dissolved δ^{29}Si with $\ln[\mathrm{Si(OH)_4}]$ measured in deep waters below 200 m ($y = -0.14\,x + 1.42$ ($n = 19$)), displaying a fair r^2 value (0.63). The slope (–0.14) estimates the mean offset between the sinking biogenic opal and the dissolved Si in surrounding waters (De La Rocha *et al.* 2000). Subtracting this offset from the upwelled waters signature in the silicicline (0.69 ± 0.07‰) should be representative of the biogenic opal δ^{29}Si produced in the past (0.55 ± 0.07‰), which strongly contrasts with the modern ones (0.28 ± 0.12‰). This difference underlines the non steady state Si cycle of the lake, and is therefore well in accordance with diminishing trend of diatom relative Si consumption in recent years, supporting the Verburg *et al.* (2003) hypothesis. This should be conclusively confirmed by looking at δ^{29}Si signature variations in the upper top sedimentary record.

CONCLUSIONS

Our Si isotopic data on Lake Tanganyika tributaries are consistent with the data measured on a worldwide scale by De La Rocha *et al.* (2000). The rather good positive correlation between δ^{29}Si and dissolved Si concentrations is tentatively explained as a mixing curve resulting from contrasted weathering of two major soil components: crustal-derived rocks or clays and phytoliths. On-going studies on silicon isotope fractionations by phytoliths and clays (e.g., Opfergelt *et al.* 2004) should better constrain this hypothesis.

These first silicon isotopic determinations in fresh water and biogenic opal of Lake Tanganyika confirm the fractionation process previously evidenced on marine diatoms. It gives further support to the non species-specific, non-temperature dependent character of the silicon isotope fractionation by diatoms. Because of the fast response of δ^{29}Si in siliceous organisms to climate variability, nutrient dynamics, and limnological changes, this isotopic tool may be very useful in the prospect of corroborating the recent decline of diatom Si utilization in Lake Tanganyika.

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