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Insights into the transfer of silicon isotopes into the sediment record

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Abstract. The first δ30Si\textsubscript{diatom} data from lacustrine sediment traps are presented from Lake Baikal, Siberia. Data are compared with March surface water (upper 180 m) δ30Si\textsubscript{DSi} compositions for which a mean value of +2.28‰ ± 0.09‰ (95% confidence) is derived. This value acts as the pre-diatom bloom baseline silicic acid isotopic composition of waters (δ30Si\textsubscript{DSi\textsubscript{initial}}). Open traps were deployed along the depth of the Lake Baikal south basin water column between 2012 and 2013. Diatom assemblages display a dominance (>85%) of the spring/summer bloom species Synedra acus var radians, so that δ30Si\textsubscript{diatom} compositions reflect predominantly spring/summer bloom utilisation. Diatoms were isolated from open traps and, in addition, from 3-monthly (sequencing) traps (May, July and August 2012) for δ30Si\textsubscript{diatom} analyses. Mean δ30Si\textsubscript{diatom} values for open traps are +1.23‰ ± 0.06‰ (95% confidence and MSWD of 2.9, n = 10). Total dry mass sediment fluxes are highest in June 2012, which we attribute to the initial export of the dominant spring diatom bloom. We therefore argue that May δ30Si\textsubscript{diatom} signatures (+0.67‰ ± 0.06‰, 2σ) when compared with mean upper water δ30Si\textsubscript{DSi} initial (e.g. pre-bloom) signatures can be used to provide a snapshot estimation of diatom uptake fractionation factors (ε\textsubscript{uptake}) in Lake Baikal. A ε\textsubscript{uptake} estimation of −1.61‰ is therefore derived, although we emphasise that synchronous monthly δ30Si\textsubscript{DSi} and δ30Si\textsubscript{diatom} data would be needed to provide more robust estimations and therefore more rigorously test this, particularly when taking into consideration any progressive enrichment of the DSi pool as blooms persist.

1 Introduction

Records of diatom silicon isotopes (δ30Si\textsubscript{diatom}) provide a key means to investigate changes in the global silicon cycle (De La Rocha, 2006; Hendry and Brzezinski, 2014; Leng et al., 2009; Tréguer and De La Rocha, 2013). Through measurements of δ30Si (including diatoms δ30Si\textsubscript{diatom} and the dissolved silicon (DSi) phase δ30Si\textsubscript{DSi}) it has been possible to elucidate a more comprehensive understanding of biogeo-
chemical cycling both on continents (e.g. Cockerton et al., 2013; Opfergelt et al., 2011) and in the ocean (Fripiat et al., 2012) allowing, for example, an assessment of the role of the marine biological pump in regulating past changes in atmospheric $pCO_2$ (aq) (e.g. Pichevin et al., 2009). These studies and their interpretations rely on work that has examined the mechanics of diatom silicon isotope fractionation, demonstrating an enrichment factor ($\epsilon_{\text{uptake}}$; resulting from the discrimination by diatoms against the heavier $^{30}\text{Si}$ isotope) of $-1.1\%e \pm 0.4$ to $-1.2\%e \pm 0.2$. In this case $\epsilon_{\text{uptake}}$ is the per mil enrichment between the resulting product and its substrate. Estimations of $\epsilon_{\text{uptake}}$ to be independent of temperature, $pCO_2$ (aq) and other vital effects (De La Rocha et al., 1997; Fripiat et al., 2011; Milligan et al., 2004; Varela et al., 2004), although more recent work on marine diatoms in laboratory cultures has argued for a species-dependent fractionation effect (Sutton et al., 2013). In this case, $\epsilon_{\text{uptake}}$ estimations were documented between $-0.53\%e \pm 0.11$ and $-0.56\%e \pm 0.07$ for the Fragilariopsis kerguelensis species (depending on the culturing strains used) and up to $-2.09\%e \pm 0.09$ for the Chaetoceros brevis species (Sutton et al., 2013).

A further assumption is that the isotopic signatures captured by diatoms in the photic zone are faithfully transported through the water column and into the sediment record, without alteration from dissolution or other processes. This has been questioned by evidence from diatom cultures which have revealed a diatom dissolution induced fractionation ($\epsilon_{\text{dissolution}}$) of $-0.55 \pm 0.05\%e$ from the preferential release of the heavier $^{30}\text{Si}$ isotope into the dissolved phase, over the lighter $^{28}\text{Si}$ during dissolution) that is independent of inter-species variations or temperature (Demarest et al., 2009), although the importance and indeed existence of an $\epsilon_{\text{dissolution}}$ has been questioned by studies in the natural environment (Egan et al., 2012) and the laboratory (Wetzel et al., 2014). Whilst measurements of $^{30}\text{Si}_{\text{diatom}}$ from sediment traps (Varela et al., 2004), core-tops (Egan et al., 2012) and in situ water column biogenic silica (BSi) (Fripiat et al., 2012) in marine systems have been used in isolation, an integrated record is needed to document the fate of $^{30}\text{Si}_{\text{diatom}}$ as diatoms sink through the water and become incorporated into the sediment record, particularly in a lacustrine system where hitherto no such work has taken place. Here, we present diatom bloom $^{30}\text{Si}_{\text{DSi,initial}}$ and $^{30}\text{Si}_{\text{diatom}}$ data from Lake Baikal, Siberia (Fig. 1). By analysing samples from sediment traps through the > 1600 m water column and a sediment core from the same site (Fig. 1), we document the good transfer of the photic zone $^{30}\text{Si}_{\text{DSi}}$ signature into diatoms and into the sediment record.

Unlike in ocean systems, where $^{30}\text{Si}_{\text{diatom}}$ analyses have been used as a tracer for past surface water DSI utilisation and/or supply (De La Rocha, 2006; Pichevin et al., 2012; Panizzo et al., 2013), its application in lake systems has not been as fully explored. To date, only a handful of studies have aimed to validate the proxy in lacustrine systems via in situ measurements of seasonal DSI and BSI (Alleman et al., 2005; Opfergelt et al., 2011). Here we present a further validation of the proxy (e.g. estimations of $\epsilon_{\text{uptake}}$), which also aims to address more fully the preservation of the signal to the sediment record ($\epsilon_{\text{dissolution}}$), which is of great importance in Lake Baikal where dissolution of diatoms is prevalent. This is particularly important if measurements of $^{30}\text{Si}_{\text{diatom}}$ are to be used to reconstruct past DSI utilisation and/or supply in relation to climatic and/or environmental perturbations (Street-Perrott et al., 2008; Swann et al., 2010). Furthermore, with recent evidence highlighting the perturbation of the steady-state delivery of DSI to ocean systems as a result of lacustrine burial (Fringes et al., 2014), the application of $^{30}\text{Si}_{\text{diatom}}$ techniques may be of great value in the future.

The main objectives of this study are therefore

1. use annual sediment trap data as a means to document the good transfer of surface $^{30}\text{Si}_{\text{diatom}}$ compositions to the sediment record and validate the use of $^{30}\text{Si}_{\text{diatom}}$ methods in Lake Baikal as a proxy for DSI utilisation/supply, and

2. use sediment trap data, for the first time, to attempt to validate fundamental principles of $\epsilon_{\text{uptake}}$ and $\epsilon_{\text{dissolution}}$. 

Figure 1. Map of the Lake Baikal catchment, showing dominant inflowing rivers and the Angara River outflow. The three catchments are identified as well as the location of sites BAIK13-1 and BAIK13-4, where cores, sediment traps and water column profiles were collected.
in Lake Baikal, which to date have been more widely investigated in marine systems.

2 Lake Baikal

Lake Baikal (103°43′–109°58′ E and 51°28′–55°47′ N) is the world’s deepest and most voluminous lake (23 615 km³) containing one-fifth of global freshwater not stored in glaciers and ice caps (Atlas Baikalia, 1993; Gronskaya and Litova, 1991; Sherstyankin et al., 2006). Divided into three basins (south, central and north), the Academician Ridge separates the central (max depth 1642 m) and north (max depth 904 m) basins, while the Buguldeika ridge running north-easterly from the shallow waters of the Selenga delta divides the south (max depth 1460 m) and central basins (Sherstyankin et al., 2006) (Fig. 1). This study will focus on the southern basin (where sediment traps were deployed; Fig. 1), which has an estimated average depth of 853 m (Sherstyankin et al., 2006) and a long water residence time of 377–400 years (Gronskaya and Litova, 1991), although the residency time of silicon in the lake is estimated to be shorter at 170 years (Falkner et al., 1997).

Diatom dissolution in Lake Baikal occurs mainly at the bottom sediment–water interface as opposed to during down-column settling of diatoms (Ryves et al., 2003), with Müller et al. (2005) showing that remineralisation processes are an important constituent of surface water nutrient renewal. Lake Baikal may be thought of as having two differing water masses with the mesothermal maximum (MTM) separating them at a depth of ca. 200–300 m (Kipfer and Peeters, 2000; Ravens et al., 2000). In the upper waters (above ca. 200–300 m), both convective and wind forced mixing occurs twice a year (Shimaraev et al., 1994; Troitskaya et al., 2014) during spring and autumn overturn periods. These overturn periods follow (precede) ice-off (on) respectively and are separated by a period of summer surface water stratification (e.g. above the MTM). Diatom productivity in the lake is most notable during these overturn periods although spring diatom blooms tend to dominate annual productivity. Below ca. 300 m (e.g. below the MTM), waters are permanently stratified (Ravens et al., 2000; Shimaraev et al., 1994; Shimaraev and Granin, 1991), although despite this the water column of Lake Baikal is oxygenated throughout, and it is estimated that ca. 10% of its deeper water is renewed each year through downwelling episodes (Hohmann et al., 1997; Kipfer et al., 1996; Shimaraev and Granin, 1991; Weiss et al., 1991).

3 Methods

3.1 Sample locations

Upper water column (top 180 m) samples for DSi concentrations and δ30SiDSi analyses were collected on two occasions, when the lake was ice-covered, less than 2 weeks apart, in March 2013 at site BAIK13-1 (sampling a and b; Table 1) in the south basin of Lake Baikal (Fig. 1; 51.76778° N and 104.41611° E) using a 2 L Van Dorn sampler. This sampling coincided with the period when (1) riverine and precipitation inflows to the lake are minimal, and (2) photosynthetic activity in the lake was low (as demonstrated by negligible in situ chlorophyll a measurements). We argue that the average pre-bloom DSi and δ30SiDSi values represent the baseline nutrient conditions of the upper waters of the south basin. Samples were filtered on collection through 0.4 µm polycarbonate filters (Whatman) before storage in 125 mL acid-washed LDPE bottles, and acidified with Superpure HCl to a pH above 2.

At the same site, samples were collected from open sediment traps (n = 10) deployed by EAWAG and the Institute of Earth’s Crust/SB-RAS between March 2012 and March 2013 (from 100 to 1350 m water depth; Table 2) and from monthly sequencing traps (n = 3) on the same array at a water depth of 100 m. For all open traps and for three of the monthly traps (A4: 17 May to 7 June 2012, A6: 4 July to 31 July 2012 and A7: 31 July 2012 to 21 August 2012) it was possible to extract sufficient diatoms for isotope analysis (see below).

Sediment cores were collected from site BAIK13-1 (51.76778° E and 104.41611° N; Fig. 1) and from the nearby BAIK13-4 (51.69727° N and 104.30003° E; Fig. 1) using a UWITEC corer through ca. 78–90 cm of ice with on-site sub-sampling at 0.25 cm intervals. Both sediment cores were dated using 210Pb dating (at University College London) using the CRS (constant rate of supply) model (Appleby and Oldfield, 1978), which is in agreement with the individual 137Cs record for the two cores. Sub-samples corresponding to 0.6–0.8 cm at BAIK13-1 (core BAIK13-1C; age = 2007 AD ± 2 years) and 0.2–0.4 cm at BAIK13-4 (core BAIK13-4F; age = 2012 AD ± 7 years: the sampling period covered by the sediment traps) were processed to obtain diatoms for δ30SiDiatom analysis.

3.2 Analytical methods

3.2.1 Diatom counting

To assess the taxonomic composition of diatoms in the open sediment trap samples, diatom slides were prepared using a protocol that omits any chemical treatments or centrifugation in order to minimise further diatom dissolution and valve breakage (see Mackay et al., 1998, for full details). Slides were counted using a Zeiss light microscope with oil immersion and phase contrast at ×1000 magnification. Microspheres at a known concentration of 8.2 × 10⁶ spheres mL⁻¹ were added to all samples in order to calculate diatom concentrations.

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Table 1. δ$^{30}$Si$_{DSi}$, respective uncertainties (2σ, unless otherwise stated) and DSi concentrations for sampling in South Basin of Lake Baikal at site BAIK13-1 in March 2013. Bold values correspond to the weighted average mean values (with respective errors) of data presented. Data are plotted in Fig. 3.

| Depth (m) | DSi (ppm) | δ$^{30}$Si$_{DSi}$ | 2σ | δ$^{29}$Si$_{DSi}$ | 2σ |
|----------|-----------|-------------------|----|-------------------|----|
| BAIK13-1a | 0.4       | 1.22              | +2.34 | 0.15$^2$ | +1.22 | 0.10$^2$ |
| 3 Mar 2013 | 10        | 1.19              | +2.17 | 0.15$^2$ | +1.18 | 0.09$^2$ |
|          | 24        | 1.17              | +2.55 | 0.15$^2$ | +1.29 | 0.10$^2$ |
|          | 40        | 1.12              | +2.18 | 0.11    | +1.18 | 0.06    |
|          | 100       | 1.06              | +2.22$^1$ | 0.31    | +1.27$^1$ | 0.19    |
|          | 180       | 0.66              | +2.40 | 0.08    | +1.23 | 0.04    |

| BAIK13-1b | 1         | 0.74              | +2.16 | 0.09    | +1.14 | 0.04    |
| 12 Mar 2013 | 10        | 1.21              | +2.44 | 0.15$^2$ | +1.20 | 0.05$^2$ |
|          | 20        | 1.15              | +2.28 | 0.10$^2$ | +1.17 | 0.04$^2$ |
|          | 50        | 1.16              | +2.29 | 0.16$^2$ | +1.26 | 0.11$^2$ |

W.A MEAN +2.28$^2$ 0.09$^2$ +1.19$^2$ 0.03$^2$

MSDW 4.1 1.9

$^1$ This water sample was not pre-concentrated; refer to methods. $^2$ These water sample values are weighted averages for sample replicates that are analytically robust. These errors are at the 95 % confidence interval.

Table 2. Open and sequencing trap (sampling interval 2012–2013) δ$^{30}$Si$_{diatom}$ data and respective uncertainties (2σ, unless otherwise stated). Mean values for open trap δ$^{30}$Si$_{diatom}$ compositions are provided (in bold) along with 95 % confidence and the population MSWD value. Mean values for sequencing trap δ$^{30}$Si$_{diatom}$ are also displayed in bold, with respective 2 SD errors. Respective water column depths for open traps are presented along with the relative abundance of S. acus var radians (data not available for sequencing traps). All open trap data (Z2–Z11) are plotted in Fig. 4.

| Code | Depth (m) | δ$^{30}$Si$_{DSi}$ | 2σ | δ$^{29}$Si$_{DSi}$ | 2σ | Sediment flux (mg m$^{-2}$ d$^{-1}$) | S. acus var radians |
|------|-----------|-------------------|----|-------------------|----|----------------------------------|----------------------|
|      |           |                   |    |                   |    |                                  |                      |
| Open sediment traps                      |           |                   |    |                   |    |                                  |                      |
| Z2  | 100       | +1.19             | 0.12 | +0.62             | 0.07 | 1584 | 90 % |
| Z3  | 200       | +1.28             | 0.11 | +0.70             | 0.06 | 1503 | 90 % |
| Z4  | 300       | +1.11$^1$         | 0.15 | +0.61$^1$         | 0.08 | 1686 | 93 % |
| Z5  | 400       | +1.32$^1$         | 0.16 | +0.69$^1$         | 0.10 | 1772 | 93 % |
| Z6  | 600       | +1.38$^1$         | 0.15 | +0.71$^1$         | 0.10 | 1942 | 88 % |
| Z7  | 700       | +1.38             | 0.17 | +0.69             | 0.11 | 1997 | 94 % |
| Z8  | 900       | +1.26             | 0.14 | +0.66             | 0.10 | 1980 | 92 % |
| Z9  | 1100      | +1.21             | 0.13 | +0.60             | 0.10 | 1887 | 94 % |
| Z10 | 1300      | +1.17$^1$         | 0.12 | +0.61$^1$         | 0.07 | 1943 | 92 % |
| Z11 | 1350      | +1.25             | 0.11 | +0.62             | 0.10 | 1999 | 86 % |
| W.A Mean |       | +1.23$^1$         | 0.06$^1$ | +0.63$^1$        | 0.03$^1$ |          |                      |
| MSWD |           | 2.9               | 1.6 |                   |    |                                  |                      |
| Sequencing traps                         |           |                   |    |                   |    |                                  |                      |
| A4  | May       | +0.67             | 0.06 | +0.36             | 0.04 | 1650 |                   |
| A6  | Jul       | +1.22             | 0.08 | +0.53             | 0.09 | 175  |                   |
| A7  | Aug       | +1.37             | 0.07 | +0.69             | 0.03 | 169  |                   |
| Mean |           | +1.09$^2$         | 0.74 (2 SD) | +0.53$^2$       | 0.33 (2 SD) |          |                      |
| Sediment cores                           |           |                   |    |                   |    |                                  |                      |
| BAIK13-1C | 0.6–0.8 cm | +1.30             | 0.08 | +0.68             | 0.05 |          |                      |
| BAIK13-4F | 0.2–0.4 cm | +1.43             | 0.13 | +0.75             | 0.04 |          |                      |

$^1$ These water sample values are weighted averages for sample replicates that are analytically robust. These errors are at the 95 % confidence interval.
3.2.2 Silicon isotope sample preparation

Prior to isotope analysis, 0.7–1.0 g of sediment core (dry weight) and trap material (wet weight) was digested of organic matter with analytical grade H₂O₂ (30 %) at 75 °C for ca. 12 h. This was followed by heavy density separation using sodium polytungstate (Sometu Europa) at 2500 rpm for 15 min, with centrifuge break off, at a specific gravity between 2.10 and 2.25 g mL⁻¹ (adjusted to suit sample contamination) to remove lithogenic particles and clays. Samples were washed (up to 10 times) with deionised water at 2500 rpm for 5 min before visual inspection for contaminants at ×−400 magnification on a Zeiss inverted light microscope. All samples showed no evidence of external contaminants that would impact the isotopic measurements (as displayed in light microscopy images; Fig. 2).

Silicon concentrations on all 25 samples (10 March lake water and 13 diatom opal trap samples (open Z and sequencing A traps) and 2 lake surface sediment samples) were measured on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Agilent Technologies 7500) at the British Geological Survey. Diatom samples were digested using the NaOH fusion method (Georg et al., 2006) with 1–3 mg of powdered material fused with a 200 mg NaOH (Quartz Merk) pellet in a silver crucible, covered within a Ni crucible of powdered material fused with a 200 mg NaOH (Quartz Merk) pellet in a silver crucible, covered within a Ni crucible.
exception of the surface sample at BAIK13-1b (0.74 ppm). As we are unable to fully account for this variability in DSI concentrations, we use a weighted mean of surface water (e.g. above the MTM) δ^{30}Si_{DSi} compositions, collected in March before the diatom bloom period, to act as the baseline isotopic composition (as will be discussed in Sect. 5.1). This is in order to compare with open trap data and estimate the fractionation effect of diatoms (ε_{dissolution}). In this case, δ^{30}Si_{DSi} means are +2.28‰ (± 0.09, 95 % confidence; Table 1), although some variability is highlighted between data (e.g. mean square weighted deviation (MSWD) = 4.1, n = 10; Table 1).

ICP-MS data of diatom opal show that ratios of Al:Si are all < 0.01 (data not shown), indicating that contamination in all sediment trap and core samples is negligible. This was confirmed by visual inspection of the diatom samples by light microscopy, prior to analysis (Fig. 2). Sediment trap diatoms are dominated (> 85 %) by the species *Synedra acus var radians*. Diatom concentrations show some variability, varying between ca. 3 × 10^5 and 7 × 10^4 valves g⁻¹ wet weight (Fig. 4), although lowest concentrations are seen in the open sediment trap at 1350 m depth (3 × 10^4 valves g⁻¹ wet weight Fig. 4). This is coincident with lowest diatom (*S. acus var radians*) valve abundances also (86 %; Table 2). δ^{30}Si_{diatom} data from the open sediment traps show little variability (within analytical uncertainty) down the water column profile in Lake Baikal (Table 2; Fig. 4) with values ranging from +1.11 to +1.38‰ (weighted mean +1.23‰ ± 0.06 at 95 % confidence, MSWD = 2.9, n = 10). Sequencing (A) traps from May, July and August following the onset of major diatom productivity in early spring show a degree of variability with July and August δ^{30}Si_{diatom} data similar to the open sediment traps but data from May lower at 0.67‰ ± 0.06 (Table 2). Surface sediment results from BAIK13-1C (0.6–0.8 cm core depth) and BAIK13-4F (0.2–0.4 cm core depth) are very similar to both open (Z) and July–August sequencing (A) traps with δ^{30}Si_{diatom} signatures of +1.30‰ ± 0.08 (2σ) and +1.43‰ ± 0.13 (2σ) respectively (Table 2). Open trap total dry mass fluxes show a near-constant value down the Lake Baikal water column (Table 2), with values ranging between 289.64 mg m⁻² d⁻¹ at 1300 m water depth and 327.32 mg m⁻² d⁻¹ at 900 m water depth. Sequencing traps show the highest peak in total dry mass fluxes for the month of June 1649.52 mg m⁻² d⁻¹ (although black particulate matter, of unknown origin, is also present) and remain higher (compared to winter months) from July to October (Fig. 5).
5 Discussion

The extreme continentality of the region around Lake Baikal generates cold, dry winters that create an extensive ice cover over the lake from October/November to May/June (north basin) and from January to April/May (south basin) (Atlas Baikalia, 1993). This ice cover plays a key role in regulating seasonal diatom productivity (as discussed in Sect. 2) with blooms developing following the (1) reductions in ice cover in spring and (2) after mixed-layer stratification in summer (Shimaraev et al., 1994; Popovskaya, 2000; Granin et al., 2000; Jewson et al., 2009; Troitskaya et al., 2014). These blooms are also coincident with periods of overturn in the upper waters of the lake (e.g. above the MTM; Sect. 2). The March $\delta^{30}$Si$_{DSi}$ data in this study were collected when there was no/negligible chlorophyll $a$ in the water column down to a depth of 200 m. Accordingly, we interpret March $\delta^{30}$Si$_{DSi}$ (+2.28% ± 0.09; 95 % confidence interval, $n = 10$; Table 1) as reflecting the pre-spring bloom isotopic composition of silicic acid in the mixed layer prior to its uptake and fractionation in subsequent weeks as the spring bloom develops. Whilst the open traps deployed from March 2012 to March 2013 may contain diatoms from both spring and autumnal blooms, we suggest that $\delta^{30}$Si$_{diatom}$ signatures from these traps are primarily derived from the first bloom in spring/summer due to the dominance of (1) spring diatom blooms in the annual record (Popovskaya, 2000), and (2) the dominance of spring/summer (May to August) blooming $\textit{S. acus var radians}$ (Ryves et al., 2003) in the traps ($> 85 \%$ relative abundance (Fig. 4). This is supported by total dry mass fluxes from the 100 m sequencing traps which peak in June to September (Fig. 5). We therefore argue that the open trap data should be primarily reflective of spring to summer silicic acid utilisation in the photic zone and so can be used to trace the fate of surface water signatures through the water column and into the sediment record.

5.1 Estimations of diatom fractionation factors ($\epsilon$)

During biomineralisation, diatoms discriminate against the heavier $^{30}$Si isotope, preferentially incorporating $^{28}$Si into their frustules and leaving ambient waters enriched in $^{30}$Si. Existing work from culture experiments and marine environments has suggested an $\epsilon$ (the per mil enrichment factor...
between dissolved (DSi) and solid (diatom) phases) during biomineralisation ($\epsilon_{\text{uptake}}$) of $-1.1 \pm 0.4$ to $-1.2 \pm 0.2\%_c$ (De La Rocha et al., 1997; Milligan et al., 2004; Varela et al., 2004; Fripiat et al., 2011). Such estimations of $\epsilon_{\text{uptake}}$ have been applied within both closed system (De La Rocha et al., 1997) and open system (Varela et al., 2004) modelling as a means of estimating variations in $\delta^{30}\text{Si}$ compositions, although, as discussed in Sect. 1, more recent evidence from cultured marine diatoms does point to a species-dependent fractionation effect, which could range anywhere between $-0.53\%_c \pm 0.11$ (Fragilariopsis kerguelensis species) and $-2.09\%_c \pm 0.09$ (Chaetoceros brevis species) (Sutton et al., 2013).

Monthly data for both $\delta^{30}\text{Si}_{\text{DSi}}$ and $\delta^{30}\text{Si}_{\text{diatom}}$ are not available in order to fully constrain $\epsilon_{\text{uptake}}$ over the course of the diatom growing season in Lake Baikal (e.g. estimating variations between the open and closed system models, where the import/export of DSi and BSi can be more fully estimated from surface waters). Nevertheless, we can apply the data in this context to provide a snapshot of $\epsilon_{\text{uptake}}$, when a comparison is made between $\delta^{30}\text{Si}_{\text{DSi}}$ initial and the first monthly sequencing trap $\delta^{30}\text{Si}_{\text{diatom}}$ compositions. We select the May $\delta^{30}\text{Si}_{\text{diatom}}$ signatures as we propose it reflects the initiation of the diatom bloom and therefore captures theopal exported (based on total dry mass sediment flux data; Fig. 5) from surface waters at this time. These compositions will therefore most likely derive from DSi initial compositions (March surface waters) before any (or minimal) progressive DSi enrichment occurs. We propose these data for discursive reasons in order to extend the estimations of $\epsilon_{\text{uptake}}$ from lacustrine systems and argue that they act as a snapshot estimation in this instance.

When examining sequencing trap total dry mass sediment fluxes for the year 2012–2013, numbers are greatest for the month of June (Fig. 5). This directly follows the period when $\delta^{30}\text{Si}_{\text{diatom}}$ isotopic compositions are the lowest of the three sequencing traps presented (May 2012 = $+0.67\%_e \pm 0.06, 2\sigma$). Although diatom concentrations are not available for the sequencing traps, we propose that these higher total dry mass sediment fluxes (Fig. 5) capture the exported May 2012 diatom bloom (e.g. the spring bloom) following ice-off and, based on flux data, most likely represent the event more closely associated with pre-bloom surface water (e.g. March) $\delta^{30}\text{Si}_{\text{DSi}}$ compositions ($+2.28\%_e \pm 0.09; 95\%$ confidence interval, $n = 10$; Table 1). Although later monthly $\delta^{30}\text{Si}_{\text{DSi}}$ data are not available, it is probable that the heavier isotopic $\delta^{30}\text{Si}_{\text{diatom}}$ compositions of July and August sequencing traps (Table 2) reflect the progressive enrichment of the DSi surface pool as the bloom develops. On the contrary, open trap data (Table 2) constitute the mean annual $\delta^{30}\text{Si}_{\text{diatom}}$ composition of diatoms, incorporating signatures derived from throughout the year (a mean $\delta^{30}\text{Si}_{\text{diatom}}$ composition of $+1.23\%_e \pm 0.06; 95\%$ confidence interval, $n = 10$; Table 2).

Although diatom uptake fractionation factors cannot be fully constrained in this study (particularly when addressing open trap $\delta^{30}\text{Si}_{\text{diatom}}$ signatures), due to the absence of comprehensive monthly DSi and BSi data, we can still provide an estimation of $\epsilon_{\text{uptake}}$ for Lake Baikal. However, we emphasise that this is for discussion purposes alone and that in order for this to be a more robust estimation, there is a need for more seasonal investigations. Nevertheless, if we argue that May $\delta^{30}\text{Si}_{\text{diatom}}$ act as the dominant spring bloom composition ($+0.67\%_e \pm 0.06, 2\sigma$; Table 2) exported from the surface zone and we compare this with our March 2013 mean pre-bloom spring top water (incorporating 0 to 180 m) $\delta^{30}\text{Si}_{\text{DSi}}$ composition (e.g. a DSi initial) of $+2.28\%_e$ ($\pm 0.09, 95\%$ confidence interval, $n = 10$) (Table 1), we can derive an estimation of $\epsilon_{\text{uptake}}$ of $-1.61\%_e$ (ranging between $-1.46$ and $-1.70\%_e$ when taking account of respective analytical uncertainty). We propose that this reflects more fully the initial uptake of DSi by diatoms, following ice-off and turnover, while later sequential trap data (of July and August; $+1.22\%_e \pm 0.08$ and $+1.37\%_e \pm 0.07$ respectively; Table 2) quite possibly reflect the progressive enrichment of the surface DSi pool which cannot be constrained here. Although this $\epsilon_{\text{uptake}}$ estimation of $-1.61\%_e$ falls within (or just outside of, e.g. $-1.2\%_e \pm 0.2$ from Fripiat et al., 2011) analytical uncertainty of existing estimations of $\epsilon_{\text{uptake}}$ (e.g. from temperate/sub-polar marine diatoms, $-1.1\%_e \pm 0.4$; De La Rocha et al., 1997), we propose that they highlight the need for further estimations within the literature. This is particularly important within the context of freshwater Si palaeoconstructions where there is a paucity of laboratory culture experiments, as the handful of in situ measurements derived from lacustrine studies have calculated $\epsilon_{\text{uptake}}$ values closer to $-1.1\%_e$ (e.g. Allemann et al., 2005; Opfergelt et al., 2011). What is more, these estimations of $\epsilon_{\text{uptake}}$ are further compounded by the more recent evidence which has thrown into question the role that species-dependent fractionation factors may take during diatom biomineralisation (e.g. Sutton et al., 2013), although investigations of this in lacustrine environments are still to be conducted.

5.2 The fate of diatom utilisation and $\delta^{30}\text{Si}_{\text{diatom}}$ in Lake Baikal

Asides from the discussions surrounding the biological uptake of DSi by diatoms and the seasonal relationship between DSi compositions, the isotopic composition of trap data (Table 2) from down the water column (except for the May sequencing trap) (Table 2) highlights the fact that the isotopic signature incorporated into diatoms in the photic zone during biomineralisation is safely transferred through the water column without alteration, either from dissolution ($\epsilon_{\text{dissolution}}$) or other processes. Indeed, $\delta^{30}\text{Si}_{\text{diatom}}$ signatures through the open traps show minimal variation (mean of $+1.23\%_e \pm 0.06$ at 95% confidence and MSWD of 2.9, $n = 10$; Table 2).
The role of dissolution is particularly important for the species *Synedra acus var radians* (which dominates open trap compositions for the year 2012–2013; Table 2) as the literature has demonstrated the fragility of this valve, particularly its sensitivity to water column and surface sediment interface dissolution (Battarbee et al., 2005; Ryves et al., 2003). While this species is sensitive to dissolution, Mackay et al. (1998) have nevertheless documented an increased percentage presence in south basin Lake Baikal sediments over the past ca. 60 years (to between 10 and 20 % relative abundance), thought to represent a biological response to late 20th century warming in this region. Although the majority of dissolution in Lake Baikal occurs at the surface–sediment interface, with only 1 % of phytoplanktonic diatoms becoming incorporated into the sediment record (Ryves et al., 2003; Battarbee et al., 2005), δ_{30}Si_{diatom} in sediment core surface samples (i.e. post burial) at BAIK13-1C (0.6–0.8 cm core depth) and at BAIK13-4F (0.2–0.4 cm core depth) of +1.30‰±0.08 (2σ) and +1.43‰±0.13 (2σ) respectively (Fig. 4), are also similar (within uncertainty) to the sediment trap data of +1.23‰±0.06 (95 % confidence). These data confirm that in contrast to previous work (Demarest et al., 2009) there is no ε_{dissolution} or at least no other alteration of the δ_{30}Si_{diatom} signature from diatoms sinking through the water column and during burial in the sediment record. This in agreement with previous studies on marine diatoms (Wetzel et al., 2014) and validates that δ_{30}Si_{diatom} can be used in lacustrine sediment cores to constrain biogeochemical cycling (building on work by Egan et al., 2012).

6 Conclusions

The first δ_{30}Si_{diatom} data from lacustrine sediment traps are presented from Lake Baikal, Siberia, and their use in interpreting the fate of δ_{30}Si_{diatom} in the sediment record is shown. Mean values for open traps (+1.23‰±0.06 at 95 % confidence and MSWD of 2.9, n = 10) suggest no alteration to the signal through the water column. Sequencing traps (May, July and August) do show variation in their δ_{30}Si_{diatom} signatures, with May the lowest at +0.67‰ (±0.06). With total dry mass sediment fluxes highest in June 2012, we argue that May represents the initial diatom bloom export from surface waters. As such, we provide a snapshot estimation of ε_{uptake} in Lake Baikal of −1.61‰, when comparing May δ_{30}Si_{diatom} compositions and mean surface water March δ_{30}Si_{DSI} compositions (+2.28‰±0.09 at 95 % confidence). Although monthly synchronous δ_{30}Si_{DSI} and δ_{30}Si_{diatom} are not available to fully constrain ε_{uptake} (nor indeed any seasonal progressive enrichment of DSI in surface waters) in Lake Baikal surface waters, the data provide a snapshot into stable isotope processes in freshwater systems which to date have not been fully explored. The near-constant δ_{30}Si_{diatom} compositions in open traps demonstrates the full preservation of the signal through the water column and thereby justifies the use and application of the technique in biogeochemical and palaeoenvironmental research. In particular, data highlight the absence of a fractionation factor associated with diatom dissolution (ε_{dissolution}) down the water column, of particular importance as the diatom species *Synedra acus var. radians* is known to be sensitive to dissolution with estimations of only up to 5 % making it to the sediment interface (Ryves et al., 2003). This is further reinforced by lake surface sediment data from south basin cores, which also demonstrate the absence of ε_{dissolution} due to the similar compositions (within uncertainty) of surface sediment δ_{30}Si_{diatom} when compared to open trap data.

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References

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

Appleby, P. G. and Oldfield, F.: The calculation of 210Pb dates assuming a constant rate of supply of unsupported 210Pb to the sediment, Catena, 5, 1–8, 1978.

Atlas Baikalia: “Siberia” Program Interdepartmental Scientific Committee of the SB RAS, Federal’naya Sluzhba Geodezii i Kartografii Rossii, Moscow, 1993 (in Russian).

Battarbee, R. W., Anderson, N. J., Jeppesen, E., and Leavitt, P. R.: Assessing lake ecosystem response to nutrient reduction, Freshwater Biol., 50, 1772–1780, 2005.

Cardinal, D., Alleman, L. Y., de Jong, J., Ziegler, K., and Andre, L.: Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode, J. Anal. Atom. Spectrom., 18, 213–218, 2003.

Cockerton, H. E., Street-Perrott, F. A., Leng, M. J., Barker, P. A., Horstwood, M. S. A., and Pashley, V.: Stable-isotope (H, O, and...
Si) evidence for seasonal variations in hydrology and Si cycling from modern waters in the Nile Basin: implications for interpreting the Quaternary record, Quaternary Sci. Rev., 66, 4–21, 2013.

De La Rocha, C. L.: Opal-based isotopic proxies of palaeoenvironmental conditions, Global Biogeoc. Chem., 20, GB4S09, doi:10.1029/2005GB002664, 2006.

De La Rocha, C. L., Brzezinski, M. A., and DeNiro, M. J.: Fractionation of silicon isotopes by marine diatoms during biogenic silica formation, Geochim. Cosmochim. Ac., 61, 5051–5056, 1997.

Demarest, M. S., Brzezinski, M. A., and Beucher, C. P.: Fractionation of silicon isotopes during biogenic silica dissolution, Geochim. Cosmochim. Ac., 73, 5572–5583, 2009.

Egan, K. E., Rickaby, R. E. M., Leng, M. J., Hendry, K. R., Hermoso, M., Sloane, H. J., Bostock, H., and Halliday, A. N.: Diatom silicon isotopes as a proxy for silicic acid utilisation: A Southern Ocean core top calibration, Geochim. Cosmochim. Ac., 96, 174–192, 2014.

Falkner, K. K., Church, M., Measures, C., LeBaron, G., Tournon, D., Jeandel, C., Stordal, M. C., Gill, G. A., Mortlock, R. A., and Froelich, P.: Minor and major element chemistry of Lake Baikal, its tributaries, and surrounding hot springs, Limnol. Oceanogr., 42, 329–345, 1997.

Frings, P. J., Clymans, W., Jeppesen, T. L., Struyf, E., and Conley, D. J.: Lack of steady-state in the global biogeochemical Si cycle: emerging evidence from lake Si sequestration, Biogeochemistry, 117, 255–277, doi:10.1007/s11001-013-9444-z, 2014.

Fripiat, F., Cavagna, A.-J., Dehairs, F., Speich, S., André, L., and Cardinal, D.: Silicon pool dynamics and biogenic silica export in the Southern Ocean inferred from Si-isotopes, Ocean Sci., 7, 533–547, doi:10.5194/os-7-533-2011, 2011.

Fripiat, F., Cavagna, A.-J., Dehairs, F., de Brauwere, A., André, L., and Cardinal, D.: Processes controlling the Si-isotopic composition in the Southern Ocean and application for paleoceanography, Biogeoosciences, 9, 2443–2457, doi:10.5194/bg-9-2443-2012, 2012.

Georg, R. B., Reynolds, B. C., Frank, M., and Halliday, A. N.: New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS, Chem. Geol., 235, 95–104, 2006.

Grani, N. G., Jewson, D. H., Gnatovsky, R. Y., Levin, L. A., Zhdanov, A. A., Gorbunova, L. A., Tsekhansky, V. V., Doroschenko, L. M., and Mogilev, N. Y.: Turbulent mixing under ice and the growth of diatoms in Lake Baikal, Verh. Lomonoll. 27, 1–3, 2000.

Granskaya, T. P. and Litova, T. E.: Kratkaya Harakteristika Vodnogo Balansa Ozera Baikal za Period 1962–1988 (Short characteristics of the water balance of Lake Baikal during 1962–1988), Gidrometeoizdsat, Leningrad, 1991.

Hendy, K. R. and Brzezinski, M. A.: Using silicon isotopes to understand the role of the Southern Ocean in modern and ancient biogeochemistry and climate, Quaternary Sci. Rev., 89, 13–26, 2014.

Hohmann, R., Kipfer, R., Peeters, F., Piepke, G., Imboden, D. M., and Shimaraev, M. N.: Deep-water renewal in Lake Baikal, Limnol. Oceanogr., 42, 841–855, 1997.

Hughes, H. J., Delvigne, C., Korntheuer, M., de Jong, J., Andre, L., and Cardinal, D.: Controlling the mass bias introduced by an-ionic and organic matrices in silicon isotopic measurements by MC-ICP-MS, J. Anal. Atom. Spectrom., 26, 1892–1896, 2011.

Jewson, D. H., Grani, N. G., Zhdanov, A. A., and Gnatovsky, R. Y.: Effect of snow depth on under-ice irradiance and growth of Aulacoseira baicalensis in Lake Baikal, Aquat. Ecol., 43, 673–679, 2009.

Johnson, C. M., Beard, B. L., and Albarède, F.: Overview and general concepts, in: Geochemistry of Nontraditional Stable Isotopes, Reviews in Mineralogy and Geochemistry, edited by: Johnson, C. M., Beard, B. L., and Albarède, F., 1–24, 2004.

Kipfer, R. and Peeters, F.: Some speculations on the possibility of changes in deep-water renewal in Lake Baikal and their consequences, in: Lake Baikal: A Mirror in Time and Space for Understanding Global Change Processes, edited by: Minoura, K., Elsevier, Chapter 24, ISBN: 978-0-444-50434-0, 273–280, 2000.

Kipfer, R., AeschbachHertig, W., Hofer, M., Hohmann, R., Imboden, D. M., Baur, H., Golubev, V., and Klerkx, J.: Bottomwater formation due to hydrothermal activity in Frolikha Bay, Lake Baikal, eastern Siberia, Geochim. Cosmochim. Ac., 60, 961–971, 1996.

Leng, M. J., Swann, G. E. A., Hodson, M. J., Tyler, J. J., Patwardhan, S. V., and Sloane, H. J.: The potential use of silicon isotope composition of biogenic silica as a proxy for environmental change, Silicon, 1, 65–77, 2009.

Mackay, A., Flower, R., Kuzmina, A., Grania, L., Rose, N., Appleby, P., Boyle, J., and Battarbee, R.: Diatom succession trends in recent sediments from Lake Baikal and their relation to atmospheric pollution and to climate change, Philos. T. Roy. Soc. B, 353, 1011–1055, 1998.

Milligan, A. J., Varela, D. E., Brzezinski, M. A., and Morel, F. O. M. M.: Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO2, Limnol. Oceanogr., 49, 322–329, 2004.

Müller, B., Maerki, M., Schmid, M., Vologina, E. G., Wehrli, B., Wuest, A., and Sturm, M.: Internal carbon and nutrient cycling in Lake Baikal: sedimentation, upwelling, and early diagenesis, Global Planet. Change, 46, 101–124, 2005.

Opfergelt, S., Hertwig, E. S., Burton, K. W., Einarsson, A., Siebert, C., Gislason, S. R., and Halliday, A. N.: Quantifying the impact of freshwater diatom productivity on silicon isotopes and silicon fluxes: Lake Myvatn, Iceland, Earth. Planet. Sci. Lett., 305, 73–82, 2011.

Panizzo, V., Crespin, J., Crosta, X., Shemesh, A., Masse, G., Yan, M., Mattielli, N., and Cardinal, D.: Sea ice diatom contributions to Holocene nutrient utilization in East Antarctica, Paleooceanography, 29, 328–342, 2013.

Pichevin, L. E., Reynolds, B. C., Ganeshram, A. R., Carco, I., Penna, L., Keefe, K., and Ellam, R. M.: Enhanced carbon pump inferred from relaxation of nutrient limitation in the glacial ocean, Nature, 459, 1114–1198, 2009.

Pichevin, L., Ganeshram, S. R., Reynolds, B. C., Prabl, F., Pedersen, T. F., Thunell, R., and McClenny, E. L.: Silicic acid biogeochemistry in the Gulf of California: Insights from sedimentary Si isotopes, Paleooceanography, 27, PA2201, doi:10.1029/2011PA002377, 2012.

Popovskaya, G. I.: Ecological monitoring of phytoplankton in Lake Baikal, Aquat. Ecosyst. Health, 3, 215–225, 2000.
Ravens, T. M., Kocsis, O., Wuest, A., and Granin, N.: Small-scale turbulence and vertical mixing in Lake Baikal, Limnol. Oceanogr., 45, 159–173, 2000.

Reynolds, B. C., Aggarwal, J., André, L., Baxter, D., Beucher, C., Brzezinski, M. A., Engström, E., Georg, R.B., Land, M., Leng, M. J., Opfergelt, S., Rodushkin, I., Sloane, H. S., van den Boorn, S. H. J. M., Vroon, P. Z., and Cardinal, D.: An inter-laboratory comparison of Si isotope reference materials. J. Anal. Atom. Spectrom., 22, 561–568, 2007.

Ryves, D. B., Jewson, D. H., Sturm, M., Battarbee, R. W., Flower, R. J., Mackay, A. W., and Granin, N. G.: Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Baikal, Siberia, Limnol. Oceanogr., 48, 1643–1661, 2003.

Sherstyankin, P. P., Alekseev, S. P., Abramov, A. M., Stavrov, K. G., De Batist, M., Hus, R., Canals, M., and Casamor, J. L.: Computer-based bathymetric map of Lake Baikal, Dokl. Akad. Nauk, 408, 102–107, 2006.

Shimaraev, M. N. and Granin, N. G.: Temperature stratification and the mechanisms of convection in Lake Baikal, Dokl. Akad. Nauk, 321, 1991.

Shimaraev, M., Verbolov, V., Granin, N., and Sherstyankin, P.: Physical limnology of Lake Baikal: A Review, Baikal International Centre for Ecological Research, Irkutsk & Okayama, 81 pp., 1994.

Street-Perrott, F. A., Barker, P. A., Leng, M. J., Sloane, H. J., Wooller, M. J., Ficken, K. J., and Swain, D. L.: Towards an understanding of late Quaternary variations in the continental biogeochemical cycle of silicon: multi-isotope and sediment-flux data for Lake Rutundu, Mt Kenya, East Africa, since 38 ka BP, J. Quaternary Sci., 23, 375–387, 2008.

Sutton, J. N., Varela, D. E., Brzezinski, M. A., and Beucher, C. P.: Species-dependent silicon isotope fractionation by marine diatoms, Geochim. Cosmochim. Ac., 104, 300–309, 2013.

Swann, G. E. A., Leng, M. J., Juschus, O., Melles, M., Brigham-Grette, J., and Sloane, H. J.: A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El’gygytgyn, North East Siberia, Quaternary Sci. Rev., 29, 774–786, 2010.

Tréguer, P. J. and De La Rocha, C. L.: The world ocean silica cycle, Ann. Rev. Mar. Sci., 5, 477–501, 2013.

Troitskaya, E., Blinov, V., Ivanov, V., Zhdanov, A., Gnatovsky, R., Sutyrina, E., and Shimaraev, M.: Cyclonic circulation and upwelling in Lake Baikal, Aquat. Sci., 77, 171–182, doi:10.1007/s00027-014-0361-8, 2014.

Varela, D. E., Pride, C. J., and Brzezinski, M. A.: Biological fractionation of silicon isotopes in Southern Ocean surface waters, Global Biogeochem. Cy., 18, doi:10.1029/2003GB002140, 2004.

Weiss, R. F., Carmack, E. C., and Koropalov, V. M.: Deep-water renewal and biological production in Lake Baikal, Nature, 349, 665–669, 1991.

Wetzel, F., de Souza, G. F., and Reynolds, B. C.: What controls silicon isotope fractionation during dissolution of diatom opal?, Geochim. Cosmochim. Ac., 131, 128–137, 2014.