Dear Editor,

Please find below the detailed response of the authors to both reviewers, and the comments from Dr. K. Hendry. The authors would like to thank the reviewers for their comments and where possible they have tried to take them on board. Where changes have been made, new line numbers and Figure numbers have been provided in the responses below. Furthermore, where the authors feel that they have not been able to take comments on board, they describe in detail their response to the respective reviewers.

Please note that there is now a new Figure 2 on the suggestion of microscopy images of diatom isotope samples. Figure 3 is now therefore re-named Figure 4 and contains new total dry mass sediment flux (also added to Table 2) data and Figure 5 is new, displaying sequencing trap total dry mass sediment fluxes.

In principle, the authors have more fully outlined the main constraints of the data set (namely the absence of $\delta^{30}Si_{DSi}$ and $\delta^{30}Si_{diatom}$ monthly data), which was in particular picked up by Reviewer 2. These should now be clearer to the reader. As such, the authors argue that the data set provides a snapshot of modern day diatom fractionation factors (in particular ε_{uptake}), given the constraints of the data presented. More importantly, we argue that the data highlights the potential to apply stable isotope reconstructions in Lake Baikal, due to the findings that relate to the absence of diatom dissolution derived fractionation ($\varepsilon_{dissolution}$) down the water column and surface sediments.

In relation to reviewer 1, the authors have tried to address some of the more pertinent issues that they raise. However, in some instances the authors felt that some of the comments were already addressed in the existing manuscript and they did not feel further repetition would be a worthwhile addition as reference in many instances is made to existing review literature within a now well-established discipline. The authors hope that the Editor will accept this stance.

We would like to thank the reviewers for their time and considered comments and we hope that they, and the Editor, will accept our revised version of the manuscript.

Many thanks,
Virginia Panizzo and co-authors.

Author's reply to reviewers:

Reviewer 1

Comment 1, "the main objectives are not entirely clear"
Reviewer 1 raises a number of comments, which the authors feel have a common theme. Reviewer 1 suggests that the main objectives of the study are "not entirely clear". While the authors would like to thank the reviewer for their comments, they would argue that the main aims of the paper are clear we have now added a further section at the end of the Introduction (lines 91 to 111), which outlines in more detail the importance of this research (please also refer to comment 3). Furthermore, the main objectives of the manuscript are also detailed here in key bullet points, thereby addressing this comment.

Comment 2, "define the terms precisely".
With regards to defining terms, the authors feel that these terms are already well established and known within the scientific community and reference is made to the key literature where they are fully defined. Within the manuscript the authors refer to key leading papers (e.g. for ε_{uptake}: De La Rocha et al., 1997; Fripiat et al., 2011; Milligan et al., 2004; Varela et al., 2004; $\varepsilon_{dissolution}$; Demarest et al, 2009; Egan et al., 2012; Wetzel et al., 2014) (lines 60-68 and lines 72-81), which fully explore and define these terms.

However, some additional text has been added in the Introduction now to help clarify this further. ε_{uptake} has also been more fully defined in the discussion section (lines 332-364), picking up on comments by Reviewer 2 which discuss some of the limitations of the data set presented (e.g. absence of monthly DSi and BSi data). Where more full definition cannot be derived (e.g. detailed modeling via closed and open system approaches and respective equations provided) due to these limitations, the authors now describe which we hope will also address this comment of reviewer 1.

Comment 3, "provide more background information on $\delta^{30}Si_{diatom}$ as a palaeo proxy"
While the authors would like to thank the reviewer for their comments and while we understand this suggestion we do not feel that this would be a very valuable addition to the manuscript as the main aim (lines 105-111) here is to identify contemporary fundamentals of the proxy, rather than its application per se. Reference is made in the text to review papers that have touched at length upon the application of this method as a palaeo proxy (De La Rocha, 2006; Hendry and Brzezinski; Leng et al., 2009; Tréguer and De La Rocha, 2013).

Within the introduction (and as one of the main objectives of the manuscript) we discuss the main limitations of the proxy, namely being able to constrain fractionation factors associated with biomineralisation (ε_{uptake}) and dissolution ($\varepsilon_{dissolution}$). Of particular importance, reference has now been made to Sutton et al (2013) (lines 67-68), which highlights the importance these studies have in addressing these key limitations and addressing this comment. Some of these key limitations of the data set (and method) presented have also been added in the abstract (lines 33-41) and conclusion to make it clearer to the reader (lines 426-430) as well as in sections 5.1 and 5.2.

Comment 4, “be clear about their definitions”
As outlined in our response to comment 2, further text has now been added to address this, although we appreciate that full equations are not provided in the text (essentially as we argue a snapshot estimation of fractionation factors as we cannot fully constrain these processes via the closed or open system modeling e.g. Varela et al, 2004 and De La Rocha et al, 1997). For example, in Section 5.1. We would refer to Editor/reviewer to our response to comment 2 for further information.

Comment 5, “provide some context to why the data are relevant for the development of a paleoproxy”
Given the comments from reviewer 2, some additional text has been added to sections 5.1 and 5.2. In this text, we highlight more fully some of the limitations of the data set provided in enabling conclusive estimations (in situ) of $\varepsilon_{\mathrm{uptake}}$ and $\varepsilon_{\mathrm{dissolution}}$. The authors feel that this also addresses comment 5 of reviewer 1. In addition, further text was added to the end section of the Introduction (lines 91 to 111; see response to comment 1 also) which outline in more detail the importance of this research in addressing key principles in the development of $\delta^{30}\mathrm{Si}_{\mathrm{diatom}}$ as a palaeoproxy.

Reviewer 2 (Damien Cardinal).

P 9371, L23
This is a valid comment and the reference to Fripiat et al (2012) has now been in amended, in addition to the reference of Fripiat et al (2011) being removed. Please refer to new lines 82.

P.9373, L2
The authors have taken this comment on board (line 88).

P9375, L21
The authors agree that this is not very clear. The surface sediment weight is dry weight and reference to this has now been made in the text (line 192). However, there is a similar sample weight as the traps contained a high water content. As trap samples were not dried prior to diatom isotope preparation nor weighed after opal purification, an estimation of their dry mass flux isn’t possible. However, total mass dry weight fluxes are available from both the sequencing and open traps and these data have now been included in (Table 2/Figures 4 and 5, Results lines 297-302). Although the reviewer does raise an interesting point, with regards to estimations of BSi fluxes, the authors are unfortunately unable to calculate these. However, some existing literature from the years 1996 and 1997 (Ryves et al 2003), which contains estimations of this is now included in the discussion (lines 325-326).

P9379, 25 and P9380, Section 5.2.

As mentioned above, monthly and annual BSi fluxes are not available. However, data has now been included from Battarbee et al (2005) and Ryves et al (2003) (lines 325-326, 390-402), which demonstrates that *Synedra acus* var *radians* is (at least for the period 1996 and 1997) a spring/summer species (dominating phytoplankton between May to August). As such, with continued summer season diatom growth, the reviewer is correct to highlight the possibility of progressive enrichment in the surface layer DSi pool. The authors have therefore included more of a discussion on this in Section 5.2.

However, due to the absence of monthly DSi compositional data (synchronous with sequencing trap data) this cannot be fully explored. Nor can quantitative estimations be made (via closed or open system modelling) to the degree of DSi utilisation over the season (or indeed variations in ε_{uptake}). Therefore, while we now highlight this possibility (addressing the reviewer's comment) we feel we cannot fully constrain and quantify this due to the limitations of our data set.

P9380, Section 5.1

This is again a valid comment. The authors have added some more information to this section in order to comment on the reviewer's points and also more clearly define the terminology applied (refer to Reviewer 1's comments also). However, as mentioned in the above response, synchronous DSi and BSi signatures are not available for the surface layer over the course of the growing season. This would indeed have helped to constrain ε_{uptake} more comprehensively, particularly when addressing the above comment with regards to progressive enrichment of the DSi pool in the surface layer.

Instead, the authors detail the limitations of the data set (which we hope also addresses some of reviewer 1's comments). As such we propose to use the data set to estimate a mean spring/summer seasonal ε_{uptake} based on a snapshot $\delta^{30}Si_{DSi\ initial}$. While this is a constrained estimation, we feel it at least acts as the first application of the technique in Lake Baikal. Furthermore, it also highlights the importance of this estimation, as sediment archives of diatoms will themselves portray an amalgamation of diatoms that have bloomed throughout the dominant periods of the year (as with trap assemblages). This argument has also been added in the abstract (lines 33-41) and conclusion to make it clearer to the reader (426-430).

P9381, Line 10

The reviewer does raise an interesting discussion here with regards to the transfer of diatoms down the water column, into the sediment record and their preservation throughout. Unfortunately, diatom (BSi) fluxes are not available (see previous two comments) and the flux data presented here is only based on total dry mass fluxes (Table 2, Figures 4 and 5). However, diatom concentration data from the open traps are displayed (Figure 3) which does show a variation in the presence (and/or preservation) of diatoms through the water column. Of particular note are the values from the open trap at 1,350 m where concentrations sharply decline.

To further address this, the authors have included a few more lines that detail more fully the sensitivity of *Synedra acus var radians* to dissolution both during transportation through the water column and into the surface sediments of Lake Baikal (Battarbee et al, 2005; Ryves et al, 2003). This diatom is one of the more sensitive diatoms to dissolution with only 5% being incorporated into the sediment record (Ryves et al, 2003), so we feel confident that some dissolution has likely occurred. We hope that this discussion is clearer and that the conclusions are clear to this end, given the near constant composition of surface sediments and open traps (mean spring/summer compositional data).

Table 2:

1. The mistake has been corrected. Table headings now correctly refer to $\delta^{30}Si_{diatom}$, not $\delta^{30}Si_{DSi}$.
2. The 95% confidence interval is based on a weighted average of replicate samples when MBC and MEAS values were within analytical error as were multiple sample replicates. In this case, a 95% confidence of the weighted average sample value is given. This has been more fully explained (as per Table 1) in the Table 2 footer.
3. Unfortunately, BSi fluxes are not available. However, total dry mass fluxes are provided (Table 2, Figures 4 and 5; previous Figures 3 and 4). We are unable to quantify exactly the BSi flux however.

Figure 2.
Note, this is now Figure 3 after the addition of the two light microscopy images.

The authors acknowledge the comments of reviewer 2 in relation to the DSi concentration data. These are data that were collected 9 days apart from each other in March 2013. Concentrations were analysed via ICP-MS (data presented in this manuscript; Table 1) and via spectrophotometer methodology, both giving similar results (latter data not presented). However, the authors feel that they cannot fully explain the variation in the data. DSi concentration data is similar for the depths 10-50 m. Data below 50 m was not collected for BAIK13-1b and the main discrepancy appears to be in the surface sampling where concentrations are much lower for BAIK13-1b. We feel that we are unable to fully constrain why this discrepancy exists given the data we have. If anything, the authors feel that these data highlight the variability and therefore application of a surface water (1-180 m) weighted average composition for the purpose of providing a DSi initial for estimations (snap shot) of ε_{uptake}. As such, they unfortunately do not feel that they are able to discuss in much more detail these data in this instance.

Dr. Katherine Hendry Comments:

1. The authors also feel that reference should be made to the work by Sutton et al (2013). Particularly given its findings with regards to diatom species dependent fractionation effects. Please refer to lines 67-68.

2. Light microscopy mages have now been added (x 1000) of the clean opal samples (Figures 2a and b).
3. The error in Table 2 (heading) has now been amended.
4. A more full explanation has now been made with regards to the 2SD errors in Table 2. Please refer to the footnote.

Insights into the transfer of silicon isotopes into the sediment record

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Abstract:

The first $\delta^{30}Si_{diatom}$ data from lacustrine sediment traps are presented from Lake Baikal, Siberia. Data are compared with March surface water (upper 180 m) $\delta^{30}Si_{DSi}$ 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 ($\delta^{30}Si_{DSi\ initial}$). Open traps were deployed along the depth of the Lake Baikal south basin water column between 2012-2013. Diatom assemblages display a dominance (> 85%) of the spring/summer bloom species *Synedra acus* var *radians,* so that $\delta^{30}Si_{diatom}$ compositions reflect spring/summer bloom utilisation. Diatoms were isolated from open traps and in addition, from 3 monthly (sequencing) traps (May, July and August 2012) for $\delta^{30}Si_{diatom}$ analyses. Mean $\delta^{30}Si_{diatom}$ values for open traps are +1.23‰ ±0.06 (at 95% confidence and MSWD of 2.9) and, when compared with mean upper water $\delta^{30}Si_{DSi}$ signatures, suggest a diatom fractionation factor (ε_{uptake}) of −1.05‰, which is in good agreement with published values from oceanic and other freshwater systems. Although synchronous monthly $\delta^{30}Si_{DSi}$ and $\delta^{30}Si_{diatom}$ data are not available to rigorously test this estimation of ε_{uptake}, nor to also document any alteration to the surface layer dissolved silica (DSi) pool via the progressive enrichment of DSi during diatom productivity the near constant $\delta^{30}Si_{diatom}$ compositions in open traps demonstrates the full preservation of the signal through the water column and thereby justifies the use and

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application of the technique in biogeochemical and palaeoenvironmental research. Data are finally compared with lake sediment core samples, collected from the south basin. Values of +1.30‰ ±0.08 (2σ) and +1.43‰ ± 0.13 (2σ) were derived for cores BAIK13_1C (0.6-0.8 cm core depth) and at BAIK13_4F (0.2-0.4 cm core depth) respectively. Trap data highlight the absence of a fractionation factor associated with diatom dissolution ($\varepsilon_{dissolution}$) (particularly as *Synedra acus* var *radians*, the dominant taxa in the traps, is very susceptible to dissolution) down the water column and in the lake surface sediments, thus validating the application of $\delta^{30}Si_{diatom}$ analyses in Lake Baikal and other freshwater systems, in palaeoreconstructions.

1. Introduction

Records of diatom silicon isotopes ($\delta^{30}Si_{diatom}$) 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 $\delta^{30}Si$ (including of diatoms; $\delta^{30}Si_{diatom}$ and the dissolved silicon (DSi) phase; $\delta^{30}Si_{DSi}$) it has been possible to elucidate a more comprehensive understanding of biogeochemical 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 (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 (ε_{uptake}; resulting from the discrimination by diatoms against the heavier ^{30}Si isotope) of −1.1 ± 0.4‰ to −1.2 ± 0.2‰. In this case ε_{uptake} is the per mil enrichment between the resulting product and its substrate. Estimations of ε_{uptake} (−1.1 ± 0.4‰ to −1.2 ± 0.2‰) have to date shown it to be independent of temperature, $pCO2_{(aq)}$ and other vital effects (De La Rocha et al., 1997; Fripiat et al., 2011; Milligan et al., 2004; Varela et al., 2004), although recent work on marine diatoms in laboratory cultures has argued for a species dependent fractionation effect (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 ($\varepsilon_{dissolution}$) of −0.55 ± 0.05‰ (from the preferential release of the heavier ^{30}Si isotope into the dissolved phase, over the lighter ^{28}Si during dissolution) that is independent of inter-species variations or temperature (Demarest et al., 2009), although the importance and indeed existence of an $\varepsilon_{dissolution}$ has been questioned by studies in the natural environment (Egan et al., 2012; Wetzel

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et al., 2014). Whilst measurements of $\delta^{30}Si_{diatom}$ 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 $\delta^{30}Si_{diatom}$ 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 pre-diatom bloom $\delta^{30}Si_{DSi\ initial}$ and $\delta^{30}Si_{diatom}$ data from Lake Baikal, Siberia (Fig. 1). By analysing samples from sediment traps through the >1,600 m water column and a sediment core from the same site (Figure 1), we document the good transfer of the photic zone $\delta^{30}Si_{DSi}$ signature into diatoms and into the sediment record.

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Unlike in ocean systems, where $\delta^{30}Si_{diatom}$ analyses have been used as a tracer for past surface water DSi utilisation and /or supply (De La Rocha, 2006; Panizzo et al. 2013; Pichevin et al., 2012), 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 ε_{uptake}), which also aims to address more fully the preservation of the signal to the sediment record ($\varepsilon_{dissolution}$), which is of great importance in Lake Baikal where dissolution of diatoms is prevalent. This is particularly important if measurements of $\delta^{30}Si_{diatom}$ 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 (Frings et al., 2014) the application of $\delta^{30}Si_{diatom}$ techniques may be of great value in the future.

The main objectives of this study are to therefore:

1. Use annual sediment trap data as a means to document the good transfer of surface $\delta^{30}Si_{diatom}$ compositions to the sediment record and validate the use of $\delta^{30}Si_{diatom}$ methods in Lake Baikal as a proxy for DSi utilisation/supply.
2. Use sediment trap data, for the first time, to attempt to validate fundamental principles of ε_{uptake} and $\varepsilon_{dissolution}$, in Lake Baikal, which to date have been more widely investigated in marine systems.

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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 km^3) containing one fifth of global freshwater not stored in glaciers and ice caps (Gronskaya and Litova, 1991; Sherstyankin et al., 2006). Divided into three basins (south, central and north) the Academician Ridge separates the central (max depth 1,642 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 1,460 m) and central basins (Sherstyankin et al., 2006)(Figure 1). This study will focus on the southern basin (where sediment traps were deployed; Figure 1), which has an estimated average depth of 853 m (Sherstyankin et al., 2006) and a long water residency 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 c. 200-300 m (Kipfer and Peeters, 2000; Ravens et al., 2000). In the upper waters (above c. 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 proceed (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 c. 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 c. 10% of its deeper water is renewed each year through down-welling episodes (Hohmann et al., 1997; Kipfer et al., 1996; Shimaraev et al., 1993; Weiss et al., 1991).

3. Methods:

3.1. Sample locations

Upper water column (top 180 m) samples for DSi concentrations and $\delta^{30}Si_{DSi}$ analyses were collected on two occasions, when the lake was ice-covered, less than two weeks apart, in March 2013 at site BAIK13_1 (sampling a and b; Table 1) in the south basin of Lake Baikal (Figure 1; 51.76778ºN and 104.41611ºE) using a 2 litre 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 Chl *a* measurements). We argue that the average of these captured, pre-bloom, DSi and $\delta^{30}Si_{DSi}$

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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: 17th May 2012 to 7th June 2012, A6: 4th July 2012 to 31st July 2012 and A7: 31st July 2012 to 21st August 2012) it was possible to extract sufficient diatoms for isotope analysis (see below).

Sediment cores were collected from site BAIK13_1 (51.76778ºE and 104.41611ºN; Fig. 1) and from the nearby BAIK13_4 (51.69272°N and 104.30003°E; Fig. 1) using a UWITEC corer through c. 78–90cm of ice with on site sub-sampling at 0.25 cm intervals. Both sediment cores were dated using ^{210}Pb dating (at University College London) using the CRS (constant rate of supply) model (Appleby and Oldfield, 1978), which is in agreement with the individual ^{137}Cs 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_4F (core BAIK13_4F; age = 2012 AD ± 7 years: the sampling period covered by the sediment traps) were processed to obtain diatoms for $\delta^{30}Si_{diatom}$ analysis.

3.2. Analytical methods

3.2.1. Diatom counting

To assess the taxonomic composition of diatoms in the 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 x1000 magnification. Microspheres at a known concentration of 8.2 x 10^6, were added to all samples in order to calculate diatom concentrations.

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 H_2O_2 (30%) at 75°C for c. 12 hours. This was followed by heavy density separation using sodium polytungstate (Sometu Europa) at x 2,500 rpm for fifteen minutes, with centrifuge break off, at a specific gravity between 2.10-

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 x 2,500 rpm for five minutes before visual inspection for contaminants at x 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; Figure 2a and b).

Silicon concentrations on all 25 samples (10 March lake water and 13 diatom opal trap samples (Z and 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 with lid, for 10 minutes in a muffle furnace at 730°C. Following fusion, silver crucibles were placed in a 30 ml Teflon Savillex beaker and rinsed with Milli Q water before adding Ultra Purity Acid (UPA) HCl (Romil) to reach a pH above 2. Samples were sonicated to ensure they were fully dissolved and mixed before leaving overnight in the dark.

Water samples with DSi concentrations <1.5 ppm were pre-concentrated prior to column chemistry by evaporating 30 ml of sample to 5 ml at 70°C on a hotplate in a Teflon Savillex beaker in a laminar flow hood. This follows Hughes et al (2011) who showed no evaporative alteration of Si in samples and reference materials, provided samples are not evaporated to dryness. This was not conducted for sample BAIK1a_100 m as there was insufficient sample to do so (Table 1). Following pre-concentration, samples were purified by passing a known volume (between 1 and 2.5 ml depending on Si concentration) through a 1.8 ml cationic resin bed (BioRad AG50W-X12) (Georg et al., 2006) and eluted with 3 ml of Milli Q water in order to obtain an optimal Si concentration of between 3-10 ppm.

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3.2.3. Silicon isotope analysis

All isotope analyses were carried out on a ThermoScientific Neptune Plus MC-ICP-MS (multi collector inductively coupled plasma mass spectrometer), operated in wet-plasma mode using the method/settings outlined in Cockerton et al (2013). To overcome any analytical bias due to differing matrices, samples and reference materials were acidified using HCl (to a concentration of 0.05 M, using Romil UPA) and sulphuric acid (to a concentration of 0.003 M, using Romil UPA) following the recommendations of Hughes et al (2011) the principle being that doping samples and standards alike, above and beyond the natural abundance of Cl^- and SO_4^{2-}, will evoke a similar mass bias response in each. All samples were doped with ~300 ppb magnesium (Mg, Alfa Aesar SpectraPure) to allow the data to be corrected for the effects of instrument induced mass bias (Cardinal et al., 2003; Hughes et al., 2011). In order to do this Mg concentrations were the same in both standard and samples.

Background signal contributions on ^{28}Si were typically between 50 and 100mV. Total procedural blanks for water samples were 15 ng compared to typical sample amounts of 4000 ng. Procedural blank compositions are difficult to accurately measure (due to exceedingly low Si signals), but as a worse-case scenario may have deviated from sample compositions by ca. 0.38%, contributing up to a ca. 0.02‰ shift in typical sample compositions. This increases to c. 0.20‰ compositional shift in exceptional cases i.e. for one sample replicate (BAIK13_1, 0m), which has a Si concentration of much less than 1ppm. Fusion procedural blanks were c. 42 ng compared to typical fusion sample amounts of 4900 ng. Again Procedural blank compositions are difficult to accurately measure, but may have deviated from sample compositions by c. 0.04%, contributing up to a less than 0.01‰ shift in the sample compositions.

The validation material (Diatomite) was analysed repeatedly during each analytical session and a secondary reference material (an in-house river water sample, RMR4) was also periodically analysed. Data were corrected on-line for mass bias using an exponential function, assuming $^{24}\text{Mg}/^{25}\text{Mg} = 0.126633$. All uncertainties are reported at 2σ absolute, and incorporate an excess variance derived from the Diatomite validation material, which was quadratically added to the analytical uncertainty of each measurement. $\delta^{30}\text{Si}:\delta^{29}\text{Si}$ ratios of all data were compared with the mass dependent fractionation line (1.93), with which all data comply (Johnson et al., 2004). Long term (~ 2 years) variance for the method is: Diatomite = +1.23‰ ± 0.16‰ (2σ, n=210) (consensus value of +1.26‰ ± 0.2‰, 2σ; Reynolds et al., 2007) and RMR4 = +0.88‰ ± 0.20‰ (2σ, n=42).

4. Results

Below ice $\delta^{30}\text{Si}_{\text{DSi}}$ and DSi values in March 2013 from the top 1 m of the water column, collected within 2 weeks of each other, are +2.34‰ ± 0.15 (2σ), 1.22 ppm and +2.16‰ ± 0.09 (2σ), 0.74 ppm for BAIK13_1a and BAIK13_1b respectively (Figure 3; Table 1). DSi compositions show some variability with depth at both sites, with overall trends showing decreasing concentrations with depth (Figure 3), with the 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 surface water (e.g. above the MTM) $\delta^{30}\text{Si}_{\text{DSi}}$ compositions collected in March before the diatom bloom period, to act as the baseline isotopic composition (as will be discussed in Section 5.1). This is in order to compare with

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open trap data and estimate the fractionation effect of diatoms (ε_{uptake}). In this case, $\delta^{30}Si_{DSi}$ 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; 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 (Figures 2a and b), prior to analysis. Sediment trap diatoms are dominated (> 85%) by the species *Synedra acus* var *radians*. Diatom concentrations show some variability, varying between c. 3 x 10^4 and 7 x 10^4 valves/g wet weight (Figure 4), although lowest concentrations are seen in the open sediment trap at 1,350 m depth (3 x 10^4 valves/g wet weight Figure 4). This is coincident with lowest diatom (*Synedra acus* var *radians*) valve abundances also (86%; Table 2). $\delta^{30}Si_{diatom}$ data from the open sediment traps show little variability (within analytical uncertainty) down the water column profile in Lake Baikal (Table 2; Figure 4) with values ranging from +1.11‰ and +1.38‰ (weighted mean +1.23‰; 0.06 at 95% confidence). 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 $\delta^{30}Si_{diatom}$ data similar to the open sediment traps but data from May lower at 0.67‰ (Table 1). 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 the both open (Z) and July, August sequencing (A) traps with $\delta^{30}Si_{diatom}$ 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 (Figure 5).

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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-May/June (north basin) and January-April/May (south basin). This ice-cover plays a key role in regulating seasonal diatom productivity (as discussed in Section 2) with blooms developing following the: 1) reductions in ice-cover in spring; and 2) mixed layer stratification in summer (Granin et al., 2000; Jewson et al., 2009; Popovskaya, 2000; Shimaraev et al., 1994; 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; Section 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 $\delta^{30}Si_{DSi}$ 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-March 2013 may contain diatoms from both spring and autumnal blooms, we suggest that $\delta^{30}Si_{diatom}$ signature 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 *S. acus* var *radians* (Ryves et al., 2003) in the traps (>85% relative abundance; Figure 4). This is supported by dry mass fluxes from the 100 m sequencing traps which peak in June to September (Figure 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. Diatom $\delta^{30}Si$ fractionation (ε)

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 ε (the per mil enrichment factor between dissolved (DSi) and solid (diatom) phases) during biomineralisation (ε_{uptake}) of −1.1 ± 0.4‰ to −1.2 ± 0.2‰ (De La Rocha et al., 1997; Fripiat et al., 2011; Milligan et al., 2004; Varela et al., 2004). Such estimations of ε_{uptake} have been applied within both closed system (De La Rocha et al., 1997) and open system (Varela et al., 2004) modeling as a means to estimate variations in $\delta^{30}Si$ compositions. Although, as discussed in Section 1, some recent evidence from cultured marine diatoms does suggest species dependent fractionation effects (Sutton et al., 2013).

Monthly data for both $\delta^{30}Si_{DSi}$ and $\delta^{30}Si_{diatom}$ are not available in order to fully constrain ε_{uptake} over the course of the diatom growing season (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 ε_{uptake}, when a comparison is made between $\delta^{30}Si_{DSi}$ initial and annual open trap compositions (e.g. the resulting $\delta^{30}Si_{diatom}$ product). Our work, therefore extends this estimation of ε_{uptake} into lacustrine systems by suggesting a diatom fractionation effect (ε_{uptake}) of −1.05‰ (within uncertainty of previous estimates) based on a comparison of the mean pre-bloom spring top water (incorporating 0 to 180 m) $\delta^{30}Si_{DSi}$ compositions of +2.28‰ (± 0.09, 95% confidence interval, n = 10) (Table 1) and the mean open sediment trap $\delta^{30}Si_{diatom}$ of +1.23‰ ± 0.06 (95% confidence interval, n = 10) (Table 2). Evidence for a similar (within

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analytical uncertainty) ε_{uptake} between marine and lacustrine systems both validates existing studies on freshwater systems (Alleman et al., 2005; Chapligin et al., 2012; Street-Perrott et al., 2008; Swann et al., 2010) and opens future applications of $\delta^{30}Si_{diatom}$ analyses in these environments. We propose that this fractionation factor of −1.05‰, based on data derived from open sediment traps, can be used to interpret changes in $\delta^{30}Si_{diatom}$ within the sediment record. However, to fully constrain silicon cycling in Lake Baikal and highlight any possible seasonal variations in ε_{uptake}, monthly $\delta^{30}Si_{diatom}$ and $\delta^{30}Si_{DSi}$ data are needed across the year. Here we are only able to present $\delta^{30}Si_{diatom}$ data from sequencing traps in May, July and August, due to the limited amount of material in the traps, and the absence of corresponding monthly $\delta^{30}Si_{DSi}$.

5.2. *The fate of diatom utilisation and $\delta^{30}Si_{diatom}$ in Lake Baikal*

$\delta^{30}Si_{diatom}$ signatures through the open traps show minimal variation (mean of +1.23‰ ±0.06 at 95% confidence and MSWD of 2.9; Table 2). Similar values are also seen in the sequencing traps, except in May when values are considerably lower at +0.67‰ (±0.06‰; 2σ). When applying the calculated mean annual ε_{uptake} of −1.05‰ to the May (2012) data, a $\delta^{30}Si_{DSi}$ of between +1.66 to +1.78‰ (when taking into account the $\delta^{30}Si_{diatom}$ analytical variability of 2σ) is estimated. These values fall outside of the uncertainty of weighted mean March surface (namely depths above the MTM) water data (+2.28‰ ± 0.09, 95% confidence interval; Table 1).

One option is that the May $\delta^{30}Si_{DSi}$ is lower than (below ice) March $\delta^{30}Si_{DSi}$ (+2.28‰ ± 0.09, 95% confidence interval). Although deep water compositional data are not available, one possible explanation for a lower May $\delta^{30}Si_{DSi}$ (based on the assumption that ε_{uptake} does not change) is the mixing of surface and deeper waters (which typically have a higher DSi concentration and lower $\delta^{30}Si_{DSi}$ signature, if an analogue from the deep Lake Tanganyika is applied; e.g. Alleman et al., 2005). Without corresponding monthly DSi endmembers for May and the other monthly sequencing traps, we are unable to fully constrain this or quantify the seasonal utilisation of DSi using either open or closed system mass balance modelling.

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 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 ($\varepsilon_{dissolution}$) or other processes. This is particularly important for the species *Synedra acus* var *radians* (which dominates open trap compositions for the year 2012-2013; Table 2) as

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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 c. 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 (Battarbee et al., 2005; Ryves et al., 2003), $\delta^{30}Si_{diatom}$ 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 (Figure 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 $\varepsilon_{dissolution}$ or at least no other alteration of the $\delta^{30}Si_{diatom}$ 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 $\delta^{30}Si_{diatom}$ can be used in lacustrine sediment cores to constrain biogeochemical cycling (building on work by Egan et al., 2012).

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6. Conclusions:

The first $\delta^{30}Si_{diatom}$ data from lacustrine sediment traps are presented from Lake Baikal, Siberia and their use in interpreting the fate of $\delta^{30}Si_{diatom}$ in the sediment record is shown. Mean values for open traps (+1.23‰ ±0.06 at 95% confidence and MSWD of 2.9), when compared with mean surface water March $\delta^{30}Si_{DSi}$ compositions (+2.28‰ ±0.09 at 95% confidence) suggest a ε_{uptake} of −1.05‰, which is in good agreement with published values from marine and other lacustrine systems of between −1.1 and −1.2‰. Although monthly synchronous $\delta^{30}Si_{DSi}$ and $\delta^{30}Si_{diatom}$ 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 $\delta^{30}Si_{diatom}$ 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 ($\varepsilon_{dissolution}$) down the water column, of particular importance as the diatom species *Synedra acus* 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 $\varepsilon_{dissolution}$

due to the similar compositions (within uncertainty) of surface sediment $\delta^{30}Si_{diatom}$ when compared to trap data.

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Tables and Figures:

Table 1. $\delta^{30}Si_{DSi}$, respective uncertainties (2σ) and DSi concentrations for sampling in South Basin of Lake Baikal at site BAIK13_1 in March 2013. Data are plotted in Figure 3.

Table 2. Open, sequencing trap and sediment core $\delta^{30}Si_{diatom}$ data and respective uncertainties (2σ). Mean values for open and sequencing trap $\delta^{30}Si_{diatom}$ compositions are provided along with 95% confidence and the population MSWD value (in bold). Respective water column depths are presented along with the relative abundance of *Synedra acus* var *radians* (data not available for sequencing traps). Total dry mass sediment fluxes are also shown for open trap data (mg m^{-2} d^{-1}). All open trap data are plotted in Figure 4.

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.

Figure 2. Light microscopy images of open trap diatom species from Lake Baikal (x 1000). Images show the purity of samples used for $\delta^{30}Si_{diatom}$ analyses.

Figure 3. Depicting water column sampling from Lake Baikal (180 m below surface) of DSi concentrations (ppm) shown in green and $\delta^{30}Si_{DSi}$ (‰) signatures. The two sampling intervals (BAIK13_1a and 1b) from March 2013 are both displayed. Note the different sampling depths for these two data sets. All analytical errors of uncertainty are shown in grey (2σ). All data correspond to Table 1.

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Figure 4. Open sediment trap (2012-2013) data from site BAIK13_1, south basin Lake Baikal. Samples are displayed along a y-axis of water column depth. $\delta^{30}Si_{diatom}$ data (‰) are expressed with respective analytical errors (2σ) and surface sediment samples from cores BAIK13_1C and BAIK13_4F are also displayed (in green) along with mean March surface water compositions (in blue). As estimation of ε_{uptake} is also presented. Percentage abundance of the dominant diatom *Synedra acus* var *radians*, diatom concentrations (valves/g wet weight) and total dry mass sediment fluxes (mg m^{-2} d^{-1}) are also provided. All data are presented in Table 2.

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Figure 5. Total dry mass sediment fluxes (mg m^{-2} d^{-1}) for monthly sequencing traps, positioned at 100 m water depth in the south basin of Lake Baikal (2012-2013).

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Table 1.

	Water depth (m)	**DSi (ppm)**	**$\delta^{30}Si_{DSi}$ (‰)**	**Prop' 2s abs**	**$\delta^{29}Si_{DSi}$ (‰)**	**Prop' 2s abs**
BAIK13_1a	0.4	1.22	**+2.34**	0.15[1]	**+1.22**	0.10[1]
03/03/2013	10	1.19	**+2.17**	0.15[1]	**+1.18**	0.09[1]
	24	1.17	**+2.55**	0.15[1]	**+1.29**	0.10[1]
	40	1.12	**+2.18**	0.11	**+1.18**	0.06
	100	1.06	**+2.22***	0.31	**+1.27***	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
12/03/2013	10	1.21	**+2.44**	0.15[1]	**+1.20**	0.05[1]
	20	1.15	**+2.28**	0.10[1]	**+1.17**	0.04[1]
	50	1.16	**+2.29**	0.16[1]	**+1.26**	0.11[1]
W.A MEAN			**+2.28**	**0.09**[1]	**+1.19**	**0.03**[1]
MSDW			**4.1**		**1.9**	

**This water sample was not pre-concentrated, refer to methods.*

[1] These water sample values are weighted averages for sample replicates that are analytically robust. These errors are at the 95% confidence interval.

Table 2.

Code name	**Water column depth (m)**	**$\delta^{30}Si_{diatom}$ (‰)**	**Prop' 2s abs**	**$\delta^{29}Si_{diatom}$ (‰)**	**Prop' 2s abs**	**Sediment Flux (mg m^{-2} d^{-1})**	***Synedra acus* var *radians* (% abundance)**
Z1	100	**+1.19**	0.12	**+0.62**	0.07	1584	90
Z2	200	**+1.28**	0.11	**+0.70**	0.06	1503	90
Z3*	300	**+1.11**[1]	0.15	**+0.61**[1]	0.08	1686	93
Z4	400	**+1.32**[1]	0.16	**+0.69**[1]	0.10	1772	93
Z5	600	**+1.38**[1]	0.15	**+0.71**[1]	0.10	1942	88
Z6	700	**+1.38**	0.17	**+0.69**	0.11	1997	94
Z7	900	**+1.26**	0.14	**+0.66**	0.10	1980	92
Z8	1100	**+1.21**	0.13	**+0.60**	0.10	1887	94
Z9	1300	**+1.17**[1]	0.12	**+0.61**[1]	0.07	1943	92
Z10	1350	**+1.25**	0.11	**+0.62**	0.10	1999	86
W.A Mean		**+1.23**	0.06[1]	**+0.63**	0.03[1]		
MSWD		**2.9**		**1.6**			
	Sequencing traps						
A4	May	**+0.67**	0.06	**+0.36**	0.04	1650	
A6	July	**+1.22**	0.08	**+0.53**	0.09	175	
A7	August	**+1.37**	0.07	**+0.69**	0.03	169	
Mean		**+1.09**	0.74 (2SD)	**+0.53**	0.33 (2SD)		
	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.*

Figure 1.

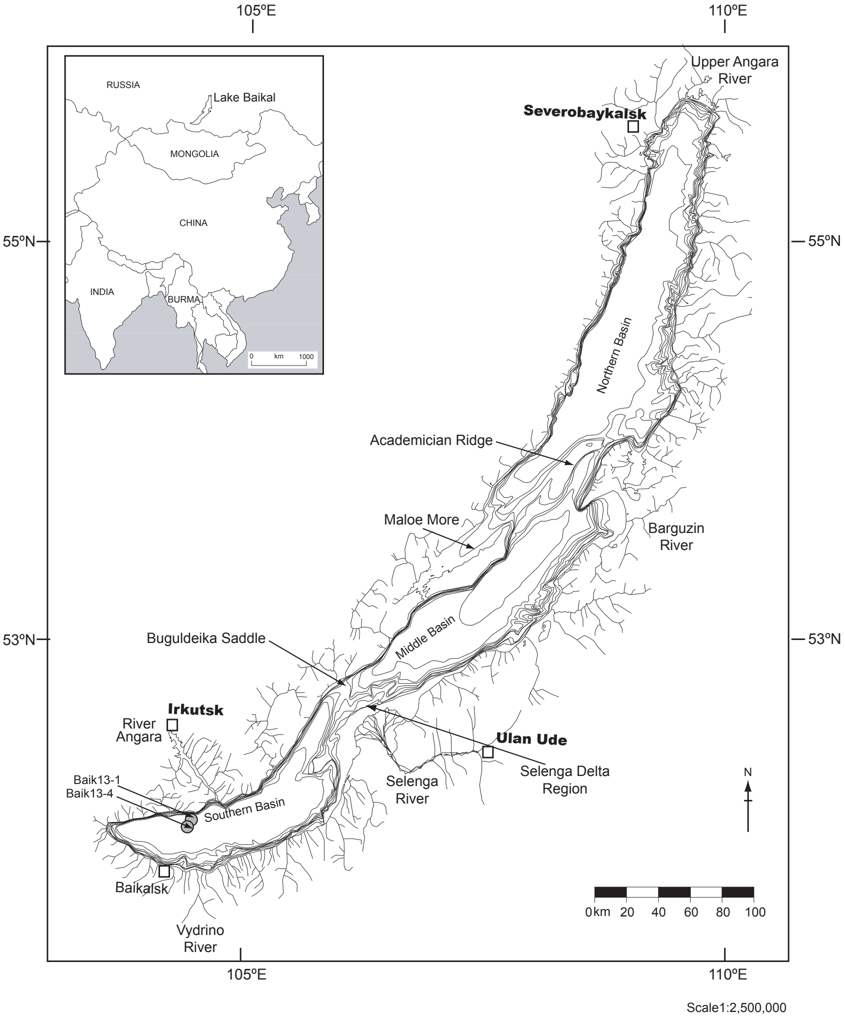
105ºE
110ºE
RUSSIA
Lake Baikal
MONGOLIA
CHINA
INDIA
BURMA
0 km 1000
Upper Angara River
Severobaykalsk
55ºN
55ºN
Northern Basin
Academician Ridge
Maloe More
Barguzin River
Middle Basin
53ºN
53ºN
Buguldeika Saddle
Irkutsk
River Angara
Ulan Ude
Selenga Delta Region
Selenga River
Baik13-1
Baik13-4
Southern Basin
N
Baikalsk
Vydrino River
0km 20 40 60 80 100
105ºE
110ºE
Scale1:2,500,000

Figure 2a and b.

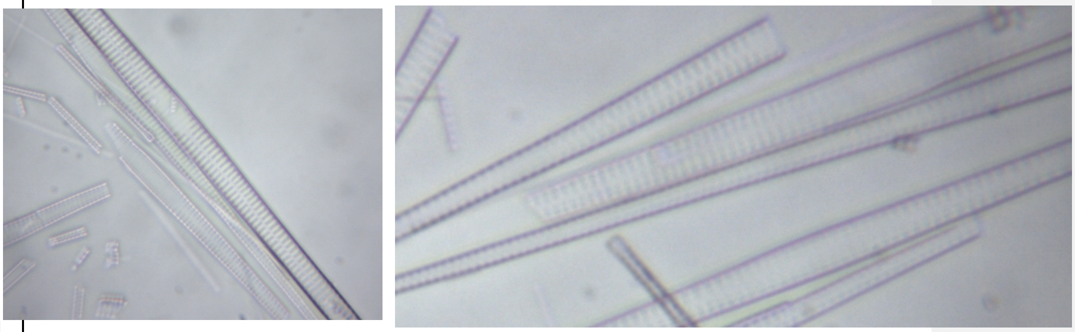

Figure 3.

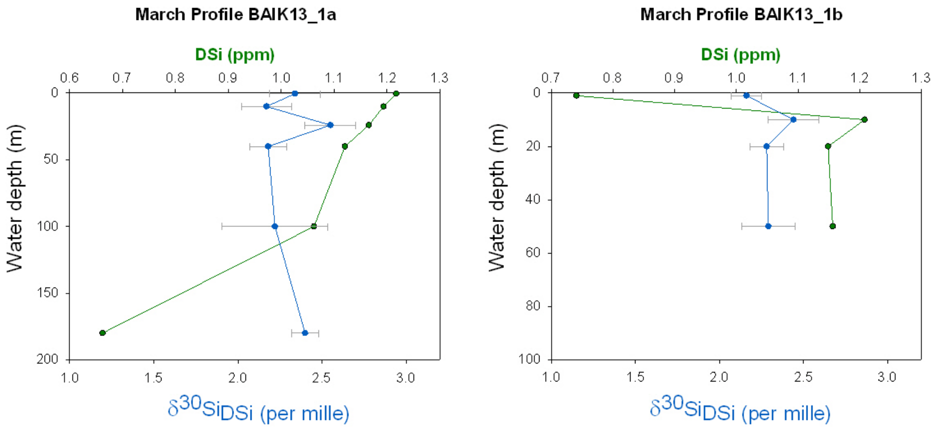

Figure 4.

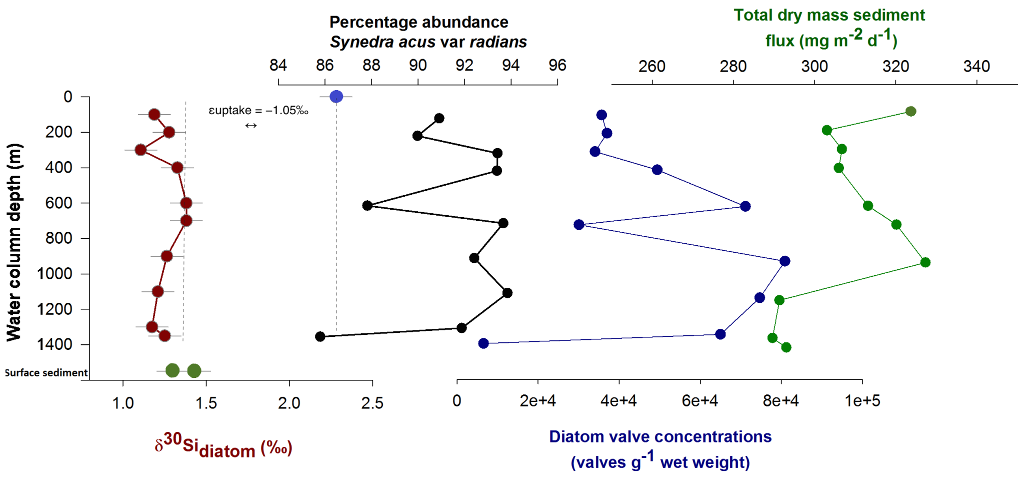

Figure 5