

Published 2010 in Journal of Paleolimnology 44: 375-385 (<http://dx.doi.org/10.1007/s10933-009-9308-9>)

## A comparison of the Si/Al and Si/time wet-alkaline digestion methods for measurement of biogenic silica in lake sediments

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*Keywords:* Diatoms, Opal, Silicon, Aluminium, Productivity, Alkaline digestion

### Abstract

Existing techniques for measuring sediment Biogenic Silica (BSi) concentrations rely largely on conventional (Si-only) wet-alkaline digestion methods. Although results have provided detailed palaeoenvironmental information, potential errors can arise in accounting for sources of non-BSi. Here, I compare a conventional Si-only method to a Si/Al wet-alkaline digestion method, which in theory provides a more robust correction for concentrations of non-BSi. Late glacial/Holocene-aged sediment from Lake Baikal, Russia was used for the comparison. Results showed no significant difference between the two techniques, indicating that existing Si-only BSi methods are suitable for reconstructing environmental changes when levels of digested non-BSi are low to moderate.

### Introduction

Measurements of Biogenic Silica (BSi) concentrations in sediments provide a valuable tool for reconstructing past environmental changes at both marine and lacustrine sites. Given the strong relationship between BSi and primary productivity in the water column, measurements of BSi can often be interpreted as a record of surface water productivity (Nelson et al. 1995; Ragueneau et al. 2000). Measurements of BSi in sediment cores also often provide a more pragmatic approach to obtaining accurate estimates of oceanic and lacustrine palaeoproductivity, due to its order-of-magnitude better preservation than organic carbon (Berger et al. 1989). Analyses of BSi have enabled insights into large-scale palaeoclimatic and palaeoenvironmental events (e.g. Haug et al. 1999; Cortese et al. 2004), including the role of the biological pump in, for example, modulating oceanic draw-down of  $p\text{CO}_2$  (Broecker 1982; Harrison 2000; Ragueneau et al. 2000, 2006; Dugdale et al. 2004; Kemp and Dugdale 2006).

One problem with analysing concentrations of BSi in sediments is the absence of a standardised methodology for its determination in aquatic systems. Various techniques exist including diatom/microfossil counting (Leinen 1985; Pudsey 1992), normative calculation of mineral silicates (Leinen 1977), X-Ray Diffraction (XRD) (Goldberg 1958; Calvert 1966; Eisma and Van der Gaast 1971), infrared spectroscopy

(Vogel et al. 2008) and wet-alkaline digestion (Hurd 1972; De Master 1979 1981; Eggiman et al. 1980; Mortlock and Fröhlich 1989; Muller and Schneider 1993; Lyle and Lyle 2002). Of these methods, wet-alkaline digestions are most commonly used due to the method's simplicity and perceived robustness relative to other techniques (De Master 1981; Conley 1998; Conley and Schelske 2001; Sauer et al. 2006).

Although several variations of wet-alkaline digestion techniques exist (see review in Sauer et al. 2006), most studies follow either a timed sequential extraction (De Master 1979; 1981) or a single-step approach (Mortlock and Fröhlich 1989). A feature of all wet-alkaline digestions is the non-BSi simultaneously digested alongside sources of BSi. Whilst no statistical difference exists in the final BSi concentrations (Conley 1998), the process by which this pool of digested non-BSi is accounted for varies markedly between the timed sequential extraction and the single-step methods. Either all Si is assumed to originate from sources of BSi with no/negligible non-BSi contributions (single-step digestion) or concentrations of digested non-BSi are corrected for assuming a constant rate of non-BSi release throughout the alkaline digestion (timed sequential extraction) (Fig. 1a). An alternative and potentially more accurate method for performing non-BSi correction in wet-alkaline digestions may lie in an examination of the Al concentration within the digested solution (Eggimann et al. 1980). In alkaline digestions, strong linear relationships have been observed over time between the release of Si and Al from a range of clays including allophane, kaolinite, illite and montmorillonite ( $r = 0.988, 0.998, 0.994, 0.997$ , respectively) (Kamatani and Oku 2000). Higher-resolution, one-second measurements indicate that these relationships are established within the first 10 minutes of digestion (Koning et al. 2002). As such, by assuming that concentrations of Al in BSi are negligible, measurements of digested Al can be used to directly account for non-BSi leached during the alkaline digestion. This may be particularly important in accounting for the rapid parabolic release of non-BSi that occurs during the first two hours of an alkaline digestion (Schlüter and Rickert 1998; Kamatani and Oku 2000; Koning et al. 2002), which may lead to an over-estimation of the true amount of BSi, particularly in samples low in BSi in which the relative contributions from non-BSi may be high.

Within a single-step digestion, Si/Al ratios of catchment or clay standard material can be applied to digested concentrations of Si and Al to calculate BSi (e.g. Eggimann et al. 1980; Carter and Colman 1994; Ohlendorf and Sturm 2008). Alternatively, Si/Al ratios can be used to calculate non-BSi corrections through a double leachate procedure, following an initial four- or five-hour alkaline digestion (Eggimann et al. 1980; Ragueneau et al. 2005). Recent work has also focused on a single, sequential Si/Al extraction technique, in which a linear regression to the y-intercept is used to separate out the non-BSi phase on aliquots collected following complete BSi digestion (Fig. 1b) (Schlüter and Rickert 1998; Kamatani and Oku 2000; Koning et al. 2002). One advantage of this particular approach is the speed and ease with which samples can be analysed relative to other Si/Al methods. In addition, the sequential technique allows the Si/Al ratio of non-BSi to be calculated for every sample. Since this accounts for any variation in the clay matrix and non-BSi Si/Al ratios between different samples, the technique potentially provides more accurate

accountability for levels of digested non-BSi than a single step Si/Al approach. Although individual non-BSi Si/Al ratios are also derived with the double leachate procedure, the need to recover, dry and weigh the analysed material after each digestion increases the risk of an error in the BSi calculations.

To date, the sequential Si/Al method has been applied primarily to surface sediments (Kamatani and Oku 2000; Koning et al. 2002; Ragueneau et al. 2005), with comparisons failing to indicate a significant difference between conventional Si-only and sequential Si/Al measurements of BSi (Schlüter and Rickert 1998; Kamatani and Oku 2000). However, the sequential Si/Al method has yet to be applied and compared to conventional BSi techniques in a long core section. Here, records of Si only (Si/time) and sequential Si/Al BSi were measured on cores from two sites in Lake Baikal, Russia (Fig. 2). Sediment came from intervals covering the late glacial/Holocene, a period of variable but high diatom productivity and good diatom preservation (Morley 2005). Carrying out this study in Lake Baikal is significant given the role of BSi concentrations in elucidating the lake's palaeoclimate history (see below). By comparing the sequential Si/Al and Si-only datasets, the degree of similarity between the two techniques can be ascertained, enabling a discussion of the relative merits/disadvantages of each technique in documenting BSi changes in sediment cores.

## Methodology

### Site location

Lake Baikal, Russia, is a unique site for studying the palaeoclimate history of Central Asia, with an uninterrupted sediment record dating back to either the Middle Eocene (Hutchinson et al. 1992) or the Middle/Late Miocene (Williams et al. 2001; Sapota et al. 2004) (Fig. 2). One limitation of research in Lake Baikal is the very low amount of carbonate within the sediment record. However, with diatoms constituting c. 98% of all BSi within the sediment (Granina et al. 1992), conventional Si-only wet-alkaline measurements of BSi have been widely used to record variations in diatom productivity, and thereby palaeoenvironmental changes, over both glacial-interglacial (e.g. Colman et al. 1995, 1999; Williams et al. 1997) and shorter, millennial-interglacial timescales (e.g. Qui et al. 1993; Karabanov et al. 1998, 2004; Horiuchi et al. 2000; Prokopenko et al. 2001a,b).

In this study, two sites, one each from the north and south basins of Lake Baikal, were selected for analysis, both having been cored in July 2001 as part of the EU CONTINENT project. In July 2001, a 3.9-m core (CON01-603-5) was collected with a Kasten box corer. It was taken in the north basin from an elevated ridge along the eastern side of the lake (Latitude: 53°95'46"N, Longitude: 108°91'37"W; Fig. 2), a site subsequently referred to as Continent Ridge. Continent Ridge represents a site of continuous sedimentation connected, but morphologically isolated, from the Academician Ridge (see Charlet et al. 2005). In the south basin a 1.73-m trigger core (CON01-605-3a) and a 10.45-m piston core (CON01-605-3) were collected from Vydrino Shoulder (Latitude: 51°58'49"N, Longitude: 104°85'48"E) (Fig. 2), an elevated plateau which shows

no evidence of sediment reworking in the Holocene or late glacial (Morley 2005). Whilst the validity of BSi concentrations as a measure of diatom productivity has been questioned in glacial-age samples from MIS 3/2, when diatom dissolution was extremely high (Swann and Mackay 2006), results of laboratory experiments (Ryves et al. 2001) suggest that these issues should not apply to the samples analysed here where diatom dissolution is only low to moderate (Morley 2005; Rioual et al. in prep).

For cores from each site 64 samples were selected for analysis at approximately constant intervals along the late glacial/Holocene section of the cores, with the exception of intervals for which no core material remained following previous diatom and geochemical analyses. Accordingly, no samples cover the last c. 0.8 ka at either site. Dates for the analysed interval at Continent Ridge are based on radiocarbon dating (Piotrowska et al. 2004; Rioual et al. in prep). Sample ages for Vydrino Shoulder are also based on a radiocarbon age model (Piotrowska et al. 2004; Morley 2005; Morley et al. 2005) with dates updated to use the INTCAL04 radiocarbon calibration curve (*pers. commun.* Rioual 2006) using OxCal version 3.10 (Bronk Ramsey 2005). To assess the potential for digested Al to originate from diatoms, an additional 22 pure diatom samples from Lake Baikal, previously extracted and cleaned for diatom isotope analysis at Continent Ridge, were dissolved and analysed for Si and Al using the same method outlined below. No pure diatom material was available or could be extracted in sufficient quantities for any late glacial or Holocene-age sample. Instead, all pure diatom samples came from the Kazantsevo, a warm period in Lake Baikal's history that is broadly synchronous with MIS 5e (Shackleton et al. 2003).

### BSi methods

Sediment samples were freeze-dried with 40 mg weighed into flat-bottomed, acid-washed bottles containing 40 ml of 5% Na<sub>2</sub>CO<sub>3</sub>, within the acceptable sample-solution ratios proposed by Gehlen and van Raaphorst (1993). A recent debate has arisen over the need to pre-treat samples with HCl and H<sub>2</sub>O<sub>2</sub> prior to digestion, to remove newly formed alumino-silicates and, consequently, improve the accuracy of BSi measurements. So far, however, the need for such pre-treatment has only been demonstrated in soil samples (Saccone et al. 2006). Since existing BSi techniques either use (Mortlock and Fröhlich 1989) or do not use (De Master 1979, 1981; Conley and Schelske 2001) pre-treatment, and because previous studies have demonstrated similar results between the two techniques (Conley 1998), there is unlikely to be a significant advantage in applying a pre-treatment stage here. Given the non-calcareous nature of sediments from Lake Baikal, such a conclusion is in agreement with results from Ohlendorf and Sturm (2008). It has also been established that errors and poor levels of reproducibility in wet-alkaline BSi measurements are most often caused by "human error", such as may occur during the weighing of samples and solutions (Conley and Schelske 2001). With any pre-treatment requiring several weighings and the recovery of small (<40 mg) samples without any loss of material, it is wise to avoid any pre-treatment whenever possible. Accordingly, no pre-treatment was used in this study.

The digestion procedure was the same for all samples, with measurements from a single sample digestion used to calculate both the Si-only and Si/Al measurements of BSi. Samples were immersed in a water bath heated to 85°C and periodically shaken throughout the digestion period to ensure full exposure of the sediment to the solution. For each core, sample replicates were analysed to check method reproducibility, and a set of blanks was run every ten samples. Following complete BSi dissolution (within first three hours of sample digestion), 2-ml sample aliquots were collected after 4, 5 and 6 hours of digestion and stored at c. 2°C prior to ICP-AES analysis. Concentrations of dissolved Si and Al were analysed using a Perkin Elmer Optima 3300RL ICP-AES at Royal Holloway, University of London. Whereas some laboratories employ a weak HCl solution to neutralise the alkaline solution following sample digestion (see Conley and Schelske 2001), here this stage was omitted to avoid diluting samples beyond ICP-AES detection limits. Instead, the cold storage of samples should have been sufficient to inhibit any further leaching within the aliquots. Prior to ICP-AES analysis, aliquots were removed from the refrigerator and allowed to warm to room temperature. Synthetic standards were produced and matrix-matched using the same alkaline concentrations as for the analysed samples. Solutions were spiked with concentrations similar to those expected in the digested samples. All results were corrected for analytical drift and elemental concentrations in procedural blanks. BSi was then calculated using both the timed Si-only sequential extraction (Si/time) (De Master 1979, 1981) (Fig. 1a) and the sequential Si/Al methods (Kamatani and Oku 2002) (Fig. 1b). Following Conley and Schelske (2001), the mean concentration of the three Si aliquots was used to calculate BSi concentrations for samples that produced negative slope regression coefficients.

## Results

### Analytical precision

Analytical precision of the ICP-AES was 0.50 ppm for Si and 0.03 ppm for Al. Replicate analyses of sediment samples from Lake Baikal indicated a final mean BSi reproducibility of 0.60 wt.% SiO<sub>2</sub> (1σ) under the Si/time method and 0.79 wt.% SiO<sub>2</sub> (1σ) under the sequential Si/Al method. BSi concentrations for both methods ranged from 0-34 wt.% SiO<sub>2</sub>.

### Method comparison

BSi results for both methods at Continent Ridge and Vydrino Shoulder show large changes through the late glacial/Holocene interval with concentrations peaking at 4.0 ka BP and at 1.5 ka BP (Fig. 3). Comparisons of the Si/time and sequential Si/Al methods at both sites indicate a strong 1:1 relationship between the two methods, which is significant at the 99.9% confidence level (Fig. 4).

## Discussion

Previous work on diatom species assemblages in the same samples analysed here led to detailed late glacial/Holocene palaeoenvironmental reconstructions (Morley 2005; Rioual et al. in prep; Oberhänsli and

Mackay 2005). Holocene reconstructions at other sites in Lake Baikal have also been derived from BSi concentrations (e.g. Qui et al. 1993; Carter and Colman 1994; Karabanov et al. 2004). No attempt is therefore made here to relate the observed temporal changes in BSi to palaeoenvironmental conditions. Instead, the discussion focuses on the possible advantages of using a sequential Si/Al method over a Si/time method.

### Diatom-bound Al

Use of the sequential Si/Al method to measure BSi assumes: 1) a constant linear relationship between the digestion of Si and Al from sources of non-BSi; 2) all Al digested during the alkaline extraction originates from non-BSi with negligible/no contributions from sources of BSi. Existing studies have demonstrated a linear relationship between the alkaline release of Si and Al from clay minerals, except during the first 5-10 minutes of digestion when Si release is greater than Al (Kamatani and Oku 2000; Koning et al. 2002). The extent to which this deviation occurs can vary spatially, according to the precise clay composition of each sample (Koning et al. 2002). Consequently, part of the non-BSi release during this initial period will remain under-accounted for when using sequential Si/Al corrections. The errors from this non-linear phase, however, will almost certainly be minimal relative to analytical and sample preparation errors, which are usually the largest source of error for BSi measurements (Conley and Schelske 2001).

The potential for digested Al to originate from diatoms, however, may introduce significant errors into any Si/Al BSi measurement unless such concentrations are either minimal or accounted for. Within the water column, levels of diatom-bound Al are minimal with Al/Si ratios of  $8.3 \times 10^{-3}$  to  $7.0 \times 10^{-5}$  (Lewin 1961; Martin and Knauer 1973; Kamatani 1974; van Bennekom et al. 1989; Schlüter and Rickert 1998; Beck et al. 2002; Gehlen et al. 2002). Although additional Al can become incorporated into the diatom frustule at the sediment-water interface (van Bennekom et al. 1988, 1991; Dixit et al. 2001; Dixit and van Cappellen 2002; van Cappellen et al. 2002; Gehlen et al. 2002; Rickert et al. 2002; Koning et al. 2007), the overall amount of Al originating from diatoms is likely to be negligible relative to contributions from non-BSi, particularly when sample BSi concentrations are low. Although van Bennekom et al. (1989) reported fossilised diatom Al concentrations of up to 6 wt.% in sediments from the Zaire/Congo deep-sea fan, a wealth of other data indicates that fossilised diatom Al concentrations actually peak at c. 1.0 wt.%, with typical concentrations <0.3 wt.% and many concentrations c. 0.01 wt.% (e.g. Shemesh et al. 1988; Schlüter and Rickert 1998; Ellwood and Hunter 1999; 2000; Dixit et al. 2001; Dixit and van Cappellen 2002; Lin and Chen 2002; Gehlen et al. 2002; van Cappellen et al. 2002; Kryc et al. 2003; Lal et al. 2006).

Analysis of the Kazantsevo pure diatom frustules from Lake Baikal reveals a mean diatom Al concentration of 0.08 wt.% ( $1\sigma = 0.02$ ). One variable that may play a significant role in determining the amount of Al in diatoms is changes in the sediment clay composition (Koning et al. 2007). Late Quaternary sediments from Vydrino Shoulder, Continent Ridge and elsewhere in Lake Baikal are dominated by illite and

smectite (Fagel et al. 2003; 2007). While records show different relative abundances of these clays between Vydrino Shoulder and Continent Ridge, no significant change in the relative clay composition has occurred at either site over recent glacial/interglacial cycles (Fagel et al. 2007). Consequently, it is reasonable to presume that the Kazantsevo diatom-bound Al values are representative of concentrations within the analysed late glacial/Holocene sediment samples. By assuming this, BSi concentrations at both sites can be recalculated incorporating a mass balance correction for diatom Al concentration of 0.08 wt.%. Such calculations show that diatom-bound Al has only a negligible impact on the sequential Si/Al BSi results. For example, when using the Si and Al sample aliquot data at 0.8 ka BP at Continent Ridge (Si/Al-derived BSi concentration for this sample is 33.7 wt.% SiO<sub>2</sub>, the highest value observed in this study), a mass balance correction for a diatom Al concentration of 0.08 wt.% alters the final sequential Si/Al-BSi value by only 0.13 wt.% SiO<sub>2</sub>. When performing a similar correction for the Continent Ridge sample at 10.5 ka BP, which shows the highest Si/Al regression gradient, the BSi concentration was altered by only 0.23 wt.% SiO<sub>2</sub>. These “errors” are significantly less than the 0.79 wt.% SiO<sub>2</sub> precision associated with the sequential Si/Al technique, indicating that issues of diatom-bound Al can be ruled out as a factor in controlling the sequential Si/Al-BSi record for the samples analysed here.

#### Si/time vs. Si/Al

In line with existing comparisons (Schlüter and Rickert 1998; Kamatani and Oku 2000), results here indicate a strong 1:1 relationship at both Continent Ridge and Vydrino Shoulder between the Si-only (Si/time) and sequential Si/Al method for BSi values ranging from 0-34 wt.% SiO<sub>2</sub> (Fig. 4). Although for most samples BSi concentrations with the sequential Si/Al method are lower than the Si/time method, this difference is small (mean difference is 0.96 wt.% SiO<sub>2</sub> at Continent Ridge and 0.73 wt.% SiO<sub>2</sub> at Vydrino Shoulder) and within the combined Root Mean Square Error (RMSE) analytical reproducibility for the two methods (0.99 wt.% SiO<sub>2</sub>). This is reiterated via a Wilcoxon signed-rank test ( $p < 0.001$  for both sites). Although the relationship is reduced for samples containing less than 10 wt.% SiO<sub>2</sub> at Vydrino Shoulder, this change is not significant with  $p < 0.01$ . For comparison, at Continent Ridge  $p < 0.001$  for samples below 10 wt.% SiO<sub>2</sub>. Although more accurate measurements of BSi for both techniques may be obtainable with continuous/high-resolution measurements of Si and Al throughout the digestion period (Muller and Schneider 1993; Koning et al. 2002), the absence of such data here does not alter the strong relationship between the Si/time and Si/Al data. The most likely explanation for the similar results between the two methods, given that both techniques are dependent on the same initial ICP-AES data, is the absence of significant alumino-silicate digestion during the alkaline extraction. This is reflected in the low amounts of dissolved Al within the extracted sample aliquots, with concentrations at both sites typically ranging from 0.05-0.30 wt.% Al (mean = 0.21 wt.% Al). Such values contrast with significantly higher aliquot Al concentrations in sediments from Continent Ridge during MIS 3 (mean = 0.54 wt.% Al, max = 0.82 wt.% Al,  $n = 12$ ) (Swann 2007), although issues of diatom dissolution prevent a comparison of the Si/Al and Si/time methods with these samples (Swann and Mackay 2006). Consequently, although in this instance no

advantage exists in using a sequential Si/Al rather than a Si/time methodology, the Si/Al technique may still represent a more accurate measure of BSi for samples in which sources of non-BSi are more easily digested. To this end, further work is needed on both marine and lacustrine sediments from various locations to compare the sequential Si/Al technique to conventional BSi techniques, particularly where clay digestion is rapid and/or high. With virtually no additional work required to analyse Al concentrations when using ICP-AES, and given that the amount of non-BSi digestion is rarely known in advance, it is also suggested that future studies aim to obtain both Si-only and Si/Al measurements of BSi until the absolute accuracy of Si-only measurements is better understood.

## Conclusions

Conventional Si-only BSi measurements have been widely used to estimate siliceous microfossil productivity in both lacustrine and marine sequences. Although corrections for non-BSi in existing techniques may appear overly simplistic (Si/time) or non-existent (Si single step), samples here from Lake Baikal indicate no significant difference between conventional Si/time or sequential Si/Al calculations of BSi. This is attributed to the low concentrations of Al, and consequently low amounts of non-BSi, that were digested from the analysed late glacial/Holocene samples. However, because the magnitude of digested non-BSi is rarely known in advance, it is recommended that the sequential Si/Al method be used in conjunction with Si-only measurements of BSi when using ICP-AES given the minimal amount of additional work involved.

## Acknowledgments

This paper is submitted as part of the EU CONTINENT research project (<http://continent.gfz-potsdam.de/>) (Contract no. EVK2-2000-00057). The study was carried out during a NERC PhD studentship award at UCL (NER/S/A/2004/12193) and CASE studentship award at NIGL (IP/812/0504). Funding for the ICP-AES analyses at Royal Holloway were supported by a NERC ICP facility grant to Mark Maslin (OSS/314/0906) with analytical support provided by Emma Tomlinson. Thanks are owed to two anonymous reviewers for their comments, Mark Brenner for his editorial support, Rick Murray and Christa Ziegler for assisting with earlier work on the Si/Al technique, and David Morley, Patrick Rioual and Anson Mackay for providing age model data and commenting on an earlier version of this manuscript.

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## Figures

Figure 1: A) Theoretical dissolution curve (solid line) of Si (or SiO<sub>2</sub>) from a sediment sample containing a mixture of diatoms and clays/alumino-silicates during the first five hours of digestion. Following c. 1-2 hours, BSi digestion is complete. Short dashed line indicates a least-squares linear regression of the analysed samples to the y-intercept, enabling the separation of BSi from sources of non-BSi (De Master 1979; 1981). Figure adapted from De Master (1979) and Conley and Schelske (2001). B) Assuming a linear relationship in the release of Si and Al from non-BSi, BSi concentrations can be calculated using a linear regression to the y-intercept between dissolved concentrations of Si (or SiO<sub>2</sub>) and Al (or Al<sub>2</sub>O<sub>3</sub>) following complete BSi dissolution (Kamatani and Oku 2000).

Figure 2: Location of Continent Ridge (north basin) and Vydrino Shoulder (south basin) in Lake Baikal, Russia.

Figure 3: Lake Baikal Si/time and sequential Si/Al late glacial/Holocene changes in BSi.

Figure 4: Comparison of the Si/time and sequential Si/Al methods.

Figure 1

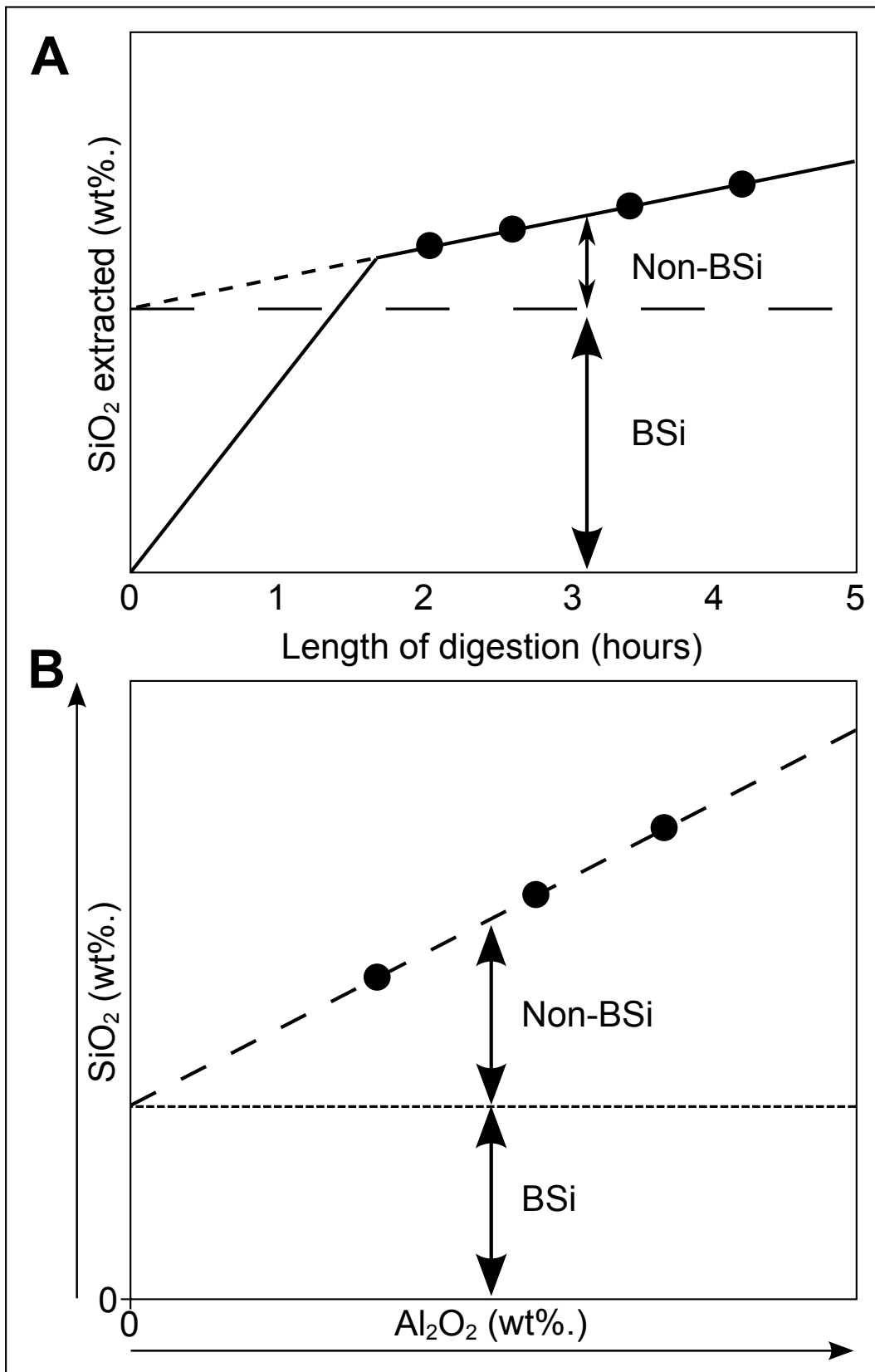


Figure 2

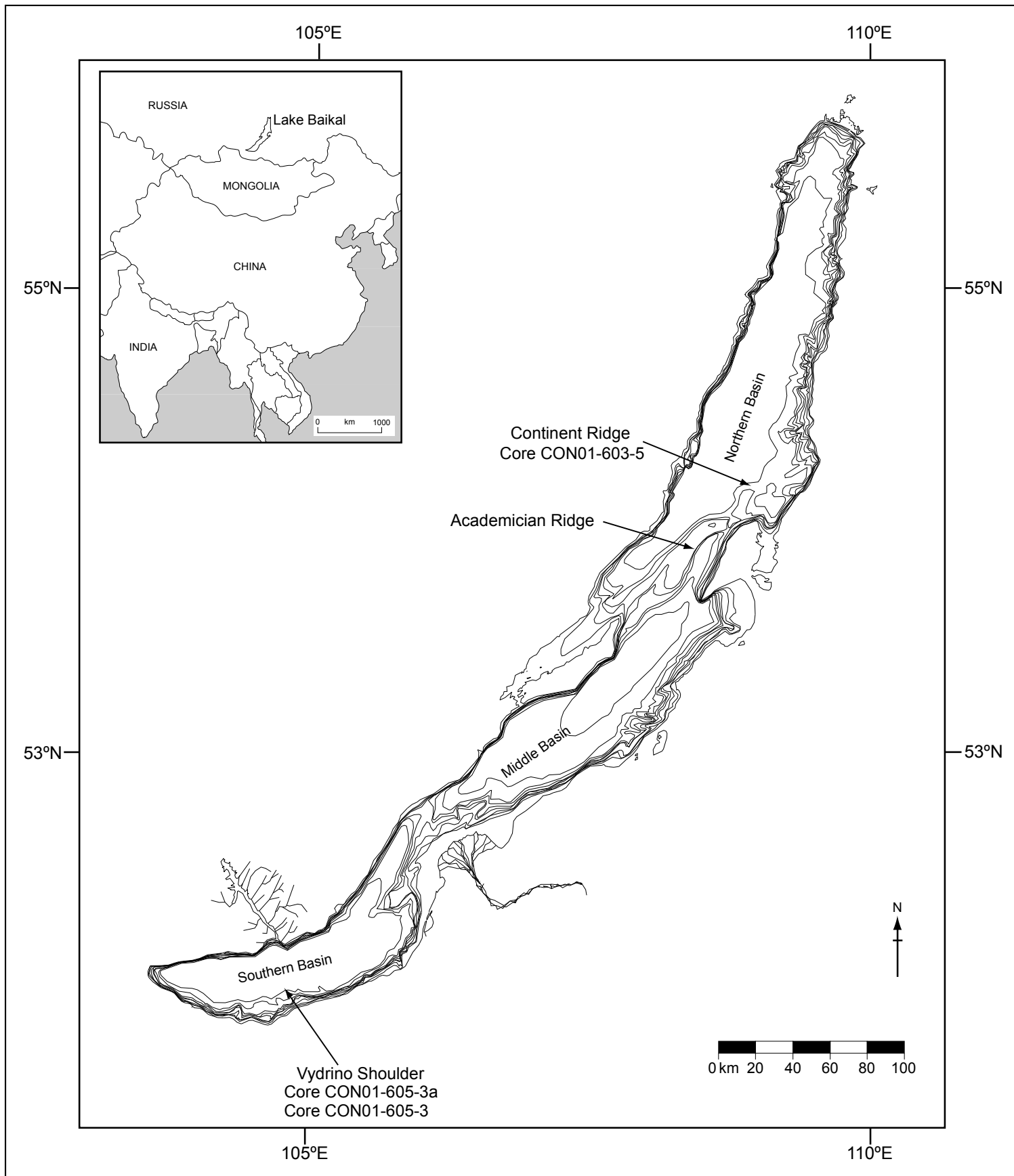


Figure 3

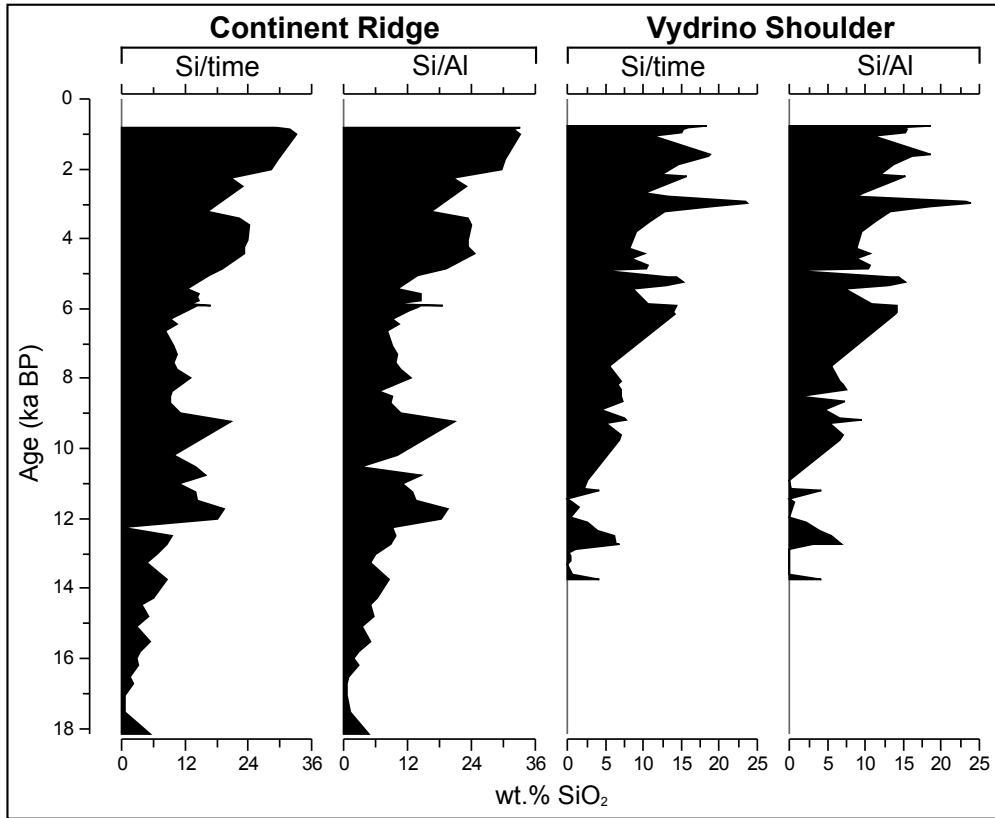


Figure 4

