Evaluation and Correction of Spectrophotometric Determination of Alkali Extracted Biogenic Silica

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The solution of Na_2CO_3 was used as extraction liquid, silicon molybdenum blue method and two antipyrine methane method were adopted for the determination of silicon and titanium in reservoir sediments. The Si/Ti ratio was obtained through the formula: $W_{BSi} = W_{Si} - K(W_{Si}/W_{Ti}) \times W_{Ti}$ and adjusted by non-biologic silica correction. The optimum experimental conditions and data analysis methods for corrected biologic silica were acquired, which showed effectiveness in realizing the measurement of sheer biogenic silica overcoming the interference of abiotic silica.

Keywords: Biogenic silica, Non-biogenic silica, Titanium, Silica correction.

INTRODUCTION

Silicon is taking the second place after oxygen in the earth's crust[1] with the amount of 27.7 %. In aquatic ecosystems, biomes silicon constitutes an important element of siliceous shell slow dissolution rate, after the death of the organism, most directly sank and finally transformed into biogenic opal, collectively known as biogenic silica (biogenic silica, BSi). Spatial and temporal variations of BSi accumulation have been regarded as important proxys of paleoproductivity and paleoclimate reconstructions. It can also be a good index of primary productivity and nutrient status in inner bay surface waters[2]. Therefore, the precise determination of biogenic silica becomes very meaningful. Biogenic silica content of primary productivity and water are closely related and accurate determination of biogenic silica productivity is particularly important for both the reconstruction of ancient metamorphic and studies on diagenetic[3]. However at high extraction temperatures, non-biogenic silica (LSi) also occurs in extractant of biogenic silica, which interferes the determination of biogenic silica. Therefore, correction of non-biogenic silica content in biogenic silica is of particular importance. Ragueneau *et al.*[4] used Si:Al ratios to correct for the measurement of biogenic silica in suspended matter of coastal water. Using the SiO_2/ TiO_2 ratio[5], the detrital contribution to biogenic opal could be subtracted by the Ti contents in the alkali leachate. This is helpful to obtain precise results of those marine sediments in which biogenic opal content is low[6]. There have already been

several non-biogenic silica correction methods. Herein we discuss the method of using Si/Ti ratio correction to deduct the non-biogenic silica interference on biogenic silica.

Recent studies show little advancement regarding the enrichment of Ti in plankton, the producer of biogenic silica, while biogenic silica contains extremely low titanium. It is generally acknowledged that chemically extracted titanium is mainly contributed by clay; therefore, the measurement of Si/Ti ratio in extracting solution can be achieved by determining the contribution of abiotic silica to biogenic silica.

In this study, the alkali extraction method[7] is used to extract silicon in sediments, the two methane antipyrine spectrophotometric method to determine titanium[8] and the molybdenum blue method is employed to determine the two elements. The W_{Si}/W_{Ti} ratio is obtained for further calculation of W_{BSi} %. The experiment process of determination and calibration of biogenic silica in sediments is shown in Fig. 1.

EXPERIMENTAL

UV-visible spectrophotometer (Unico UV-2000), SHZ-88A-type reciprocating water bath oscillator (Taicang City Experimental Equipment Factory), DGG-9076A-type electric heated drying oven (on Hai Qixin Scientific Instrument Co.), Continuous BRAND pipette (Handy Step), PD suction head (5, 12.5 and 50 mL), centrifuge, polypropylene centrifuge tube (50 mL), colorimetric tubes (25 mL), pipette.

H_2O_2, HCl, Na_2CO_3, $(NH_4)_6Mo_7O_{24}$, $H_2C_2O_4$, $C_6H_8O_6$ and $C_{23}H_{26}N_4O_3$ are Sinopharm Chemical Reagent Co., AR.
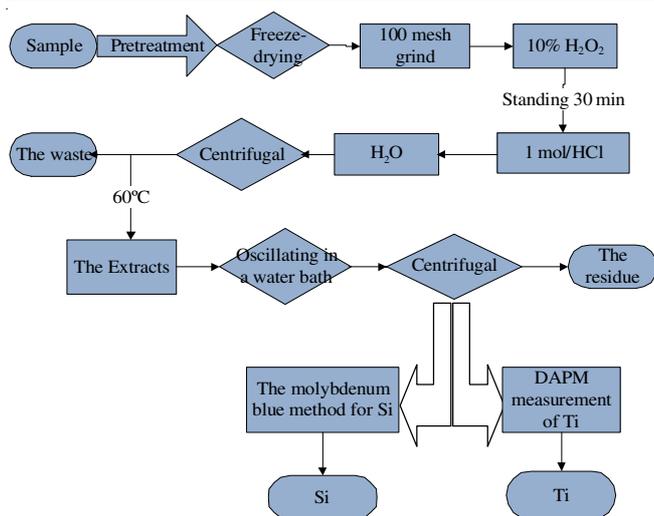
Fig. 1. Determination of BSi in sediments and calibration flow chart

Silicon single element standard solution (GSB 04-1752-2004) and titanium single element standard solution (GSB 04-1752-2004) bought from non-ferrous metals and electronic materials testing center.

Analysis and calculation methods

Analysis method: Silicon-molybdenum blue method and two antipyrine methane in sediments was used to determine the content of titanium and silicon in sediments.

Calculation method: Weigh a set of samples in weight-ascending order and pre-treat with alkali extraction method. $A_{(Si)}$ and $A_{(Ti)}$ in the extractant for silicon and titanium are measured for a standard curve. $m_{(Si)}$ and $m_{(Ti)}$ are calculated through linear regression equation to obtain Si, Ti and Ti-Si % curve and slope $k_{(Si/Ti)}$. BSi % is calculated *via* following formula as:

$$m_{(Si)}/ug = \frac{A_{(Si)} - K_{(Si)}}{S_{(Si)}} \cdot \frac{25}{0.2} ; \quad W_{si}(\%) = \frac{m_{(Si)}/ug}{m/g \cdot 100000}$$

$$m_{(Ti)}/ug = \frac{A_{(Ti)} - K_{(Ti)}}{S_{(Ti)}} \cdot \frac{25}{10} ; \quad W_{Ti}(\%) = \frac{m_{(Ti)}/ug}{m/g \cdot 100000}$$

$$W_{BSi}(\%) = W_{Si} - K_{(Si/Ti)} \cdot W_{Ti}(\%)$$

Sample preparation: (1) Weigh a set of samples in weight-ascending order (40-90 mg) and remove into 50 mL polypropylene centrifuge tubes; (2) Add 5 mL 10 % H_2O_2 to every tube and stand the tubes for 0.5 h. Add another 5 mL 1 mol/L HCl solution relatively and shake for 0.5 h; (3) Add 25 mL ultrapure water to each tube and centrifuge the tubes at 4000 rpm for 5 min the centrifugation was placed in a drying oven at 50 °C for one night.

Determination of silicon samples

Optimization of extraction conditions[9]: 2 mol/LNa$_2$CO$_3$, 1 mol/L Na$_2$CO$_3$, 0.5 mol/L Na$_2$CO$_3$, 0.1 mol/L Na$_2$CO$_3$ and 0.5 mol/L NaOH as the extraction, the comparison of BSi extraction efficiencies by using different extracting solutions are shown by Fig. 2.
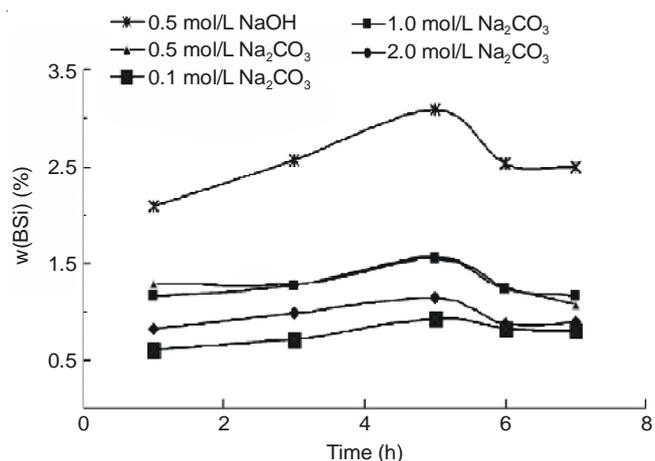

Fig. 2. Comparison of BSi extraction efficiency by using different extracting solutions

It is obtained that the best optimization condition are the extract of 0.5 mol/L Na$_2$CO$_3$ and extracting time for 5 h while temperature is 85 °C.

Alkaline extraction method: Centrifuge tubes were pretreated by adding 25 mL 0.5 mol/L Na$_2$CO$_3$ solution, respectively, heated in water bath at 85 °C after being shaken and oscillated for 5 h to ensure adequate dispersion. The tubes were removed immediately from the oscillator and centrifuge at 4000 rpm for 5 min.

The content of dissolved silica in sediments was measured. 0.20 mL supernatant were accurately pipetted into a 25 mL colorimetric tube and dilute with ultrapure water to the mark.

The solution in tubes were mixed with 0.5 mL 1:1 HCl solution and 1 mL 10 % ammonium molybdate solution and stand for 10 min. The solution was mixed with 1 mL 7.5 % oxalic acid solution and stand for 2-15 min. 1 mL 1 % ascorbic acid was added into each tube and shake well for 15 min. The absorbance of the solution was measured at 812 nm, using ultrapure water as reference solution.

Determination of titanium in the sample: Curves of titanium in sediments acquired under optimum experimental conditions are shown in Figs. 3 to 6.
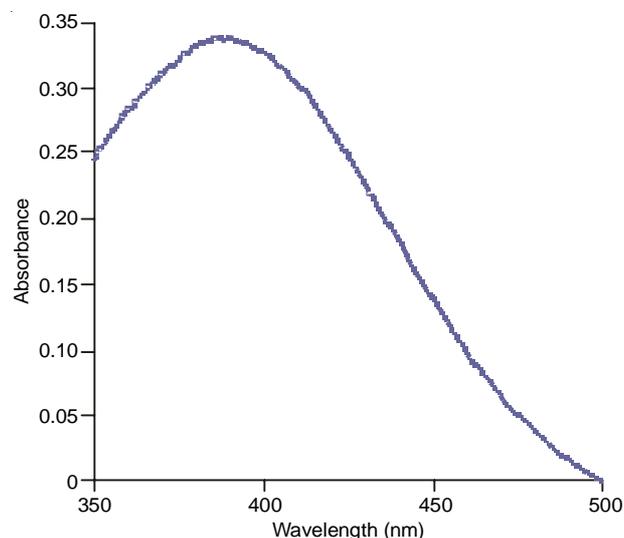

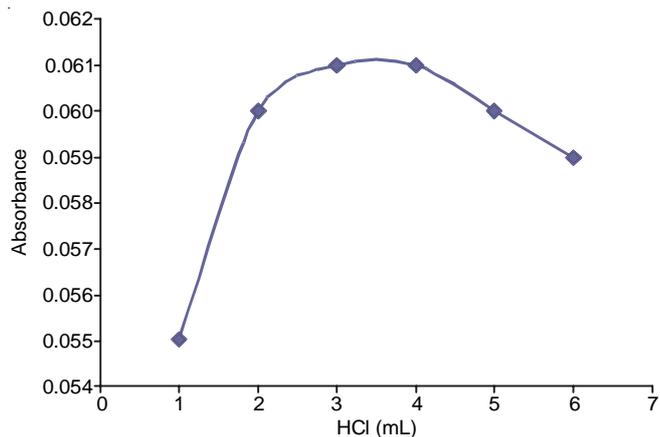Fig. 3. Wavelength-absorbance curves
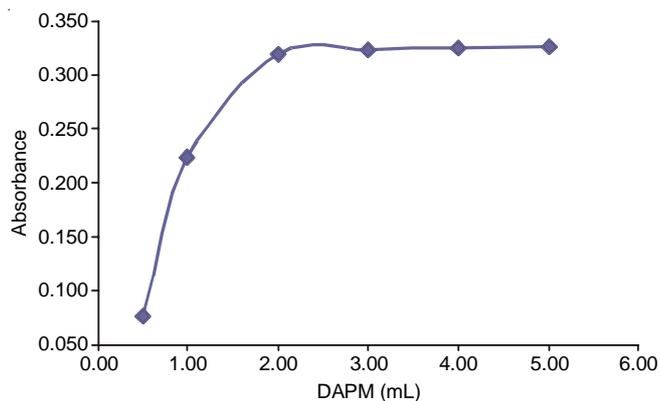
Fig. 4. Acidity-absorbance curves

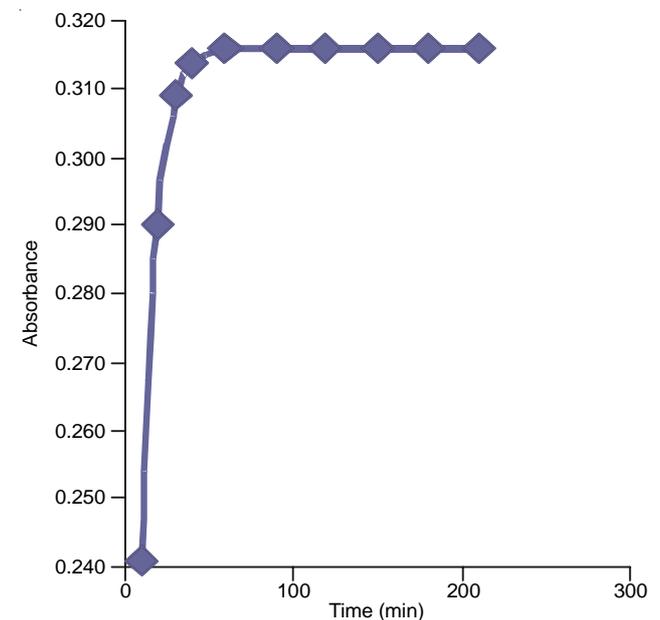Fig. 5. Titanium complex chromogenic reagent time

Fig. 6. DAPM-absorbance curves

The content of dissolved titanium in sediments was measured as below: 10 mL supernatant of silicon solution of each sample was dissolved with ultrapure water to the marks in 25 mL volumetric flasks. 2 mL of 1 % ascorbic acid and 5 mL of 1:1 HCl were added slowly to the tube and place for 5 min. 3 mL of DAPM solutions was added into the tube, dilute to marks and shake for 1 h. The absorbance of the solution was measured at 410 nm, using ultrapure water as reference solution.

RESULTS AND DISCUSSION

Data processing and calculation method: The experimental data and calculations of parallel samples are shown in Figs. 7 and 8.
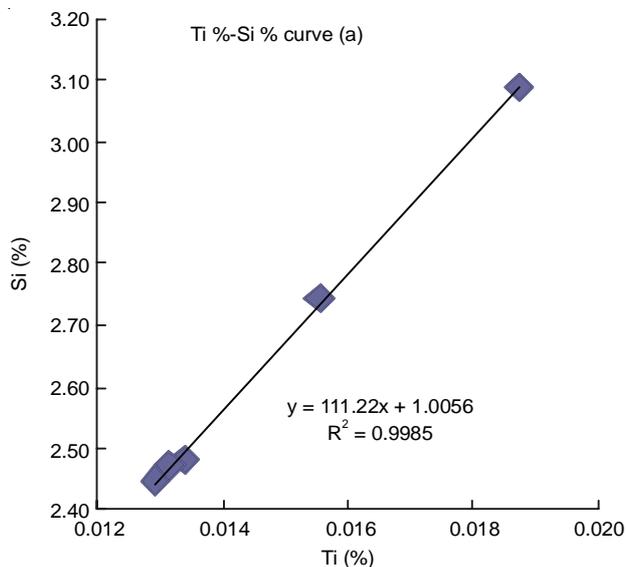

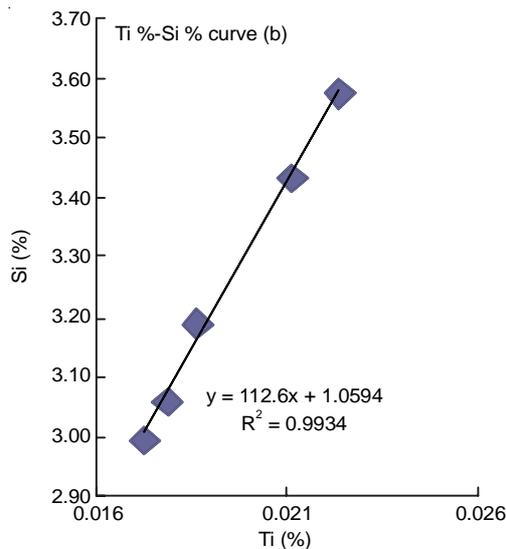Fig. 7. w_{Ti}- w_{Si} % curve (a)

Fig. 8. W_{Ti}-W_{Si} % curve (b)

Under the most reasonable solid-liquid ratio condition, the contents of BSi were measured in samples of different weight and obtained similar results with errors range of ± 3 %. W_{Si}/W_{Ti} results of parallel samples under the same conditions are compared in Table-1.

TABLE-1
COMPARISON OF PARALLEL SAMPLES

Sample	R^2	W_{Si}/W_{Ti} (%)	Average W_{Bsi} (%)	Relative error (%)
(a)	0.9985	111.22	1.00	2.91
(b)	0.9934	112.60	1.06	

It can be concluded from Table-1 that Ti-Si % of two repeated experiments satisfy a linear curve and data acquired, *i.e.*, (W_{Si}/W_{Ti} %) a =111.22 and (W_{Si}/W_{Ti} %) b = 112.60, are

close. The average of W_{BSi} % in two sets of samples are BSi a =1, BSi b = 1.06 and the relative error of parallel samples is 2.91 %.

Conclusion

It is ideal to obtain the abiogenic silica corrected Si/Ti ratio in reservoir sediments by slope method and to acquire BSi % through formula $W_{BSi} (\%) = W_{Si} - K_{(Si/Ti)} \cdot W_{Ti} (\%)$. The results can provide the determination of biogenic silica in Cameroon region with effective methods, promote the study in characteristic of biogenic silica distribution in reservoirs, facilitate the study in mechanism of the influence of river cascades on transformation of silicon and offer insights into the impact of dam interception on geochemical cycle of biogenic silica reliable basis.

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