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Distribution of Biogenic Silica in Sediments of the Yellow River (Upper and Middle Reaches)

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An experiment is held to extract the biogenic silica from Yellow River sediments to explore how such four influencing factors as extraction time, the type and concentration of extracting agent, and solid-liquid ratio affect the content of biogenic silicon in the samples. Besides, the distribution characteristics of biogenic silica in sediments of the Yellow River (upper and middle reaches) are discussed based on the measured results. The experiment results demonstrate the optimal conditions for the extraction of biogenic silica in sediments of the Yellow River: weight 0.050g of sediment sample at 90°C and extract biogenic silica for 7 hours with 40mL 1.0mol/L Na_2CO_3 solution as the extracting agent. The biogenic silica content of the surface sediments in the upper and middle reaches of the Yellow River varies greatly from 0.07-3.06mg/g. In descending order, the samples are arranged as: MD1>XH2>BT9>WLT8>SSG7>SZS5>XG4>GD3>WH6. The highest content appears in Maduo segment at the source of the Yellow River, and the lowest content appears in Wuhai segment.

1. Introduction

Measured by abundance, silicon makes up 28.8% of the Earth's crust and is the second most abundant element in the crust, with only oxygen having a greater abundance. In natural water bodies, silicon is one of the major biological elements and a necessary nutrient element of aquatic plants. Biogenic silica mostly comes from diatoms, radiolarians, caltrops and other organisms. The accumulation of biogenic silica in river sediments can reflect the spatiotemporal variation of primary productivity in the upper layer of water, showcase the process of eutrophication, and demonstrate the productivity of the upper layer of water (Ahlem et al., 2016; Henry and Herley, 2015; Wang et al, 2008; Yan et al, 2010; Ran et al, 2013; Chen et al, 2011). Therefore, it is very important to study the determination of biogenic silica in sediments. According to literature, the determination methods of biogenic silica fall into the following categories (Li et al, 2013): X-ray diffraction, siliceous microfossil counting, infrared spectroscopy, elemental ratio calculation, and chemical extraction. Thanks to simple operation and high sensitivity, chemical extraction is the most widely used method around the world.

Chemical extraction is further divided into two categories: one is the continuous extraction method proposed by DE Master (De Master, 1981; De Master, 1979), the other is the single point extraction method proposed by Mortlock and Froehlich (Schlter and Ricker, 1998; Mortlock and Froehlich, 1989). The main principle is as follows: under high temperature and alkaline conditions, the biogenic silica component is dissolved more easily than the non-biogenic silica component; after sufficient dissolution, the silicon content is measured by the silicon-molybdenum blue method. The accuracy of chemical extraction is mainly influenced by the concentration of extracting agent, reaction temperature and dissolution time because the extraction efficiency of biogenic silica component varies with mineral composition and biologic source. Therefore, the most appropriate extraction conditions should be determined through experiment if the sediment samples come from different regions.

At present, Chinese researchers on biogenic silica in sediments mainly focus on coastal waters, the Yangtze River estuary and inner bays. Little research has been done on the testing and research of biogenic silica in

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the vast Yellow River basin. The Yellow River passes through regions with different landforms, vegetation and soils. There is also a big difference in terms of industrial and agricultural production and human activities. As a result, it is of great importance to explore the variation pattern of biogenic silica in the surface sediments along the Yellow River. It not only helps understand the geochemical cycle of silicon in the Yellow River basin, but also provides a new scientific basis for the study of biogeochemical cycle of silicon in watershed-ocean system.

2. Materials and methods

2.1 Sampling

The sediments are sampled from 2013 to 2014. By GPS positioning, the authors collect surface sediments from 9 sampling points, namely Maduo, Xinghai, Guide, Shizuishan, Wuhai, Sanshenggong, Urad Front Banner and Baotou. The samples are drained and placed in polyethylene bags. After air removal, the bags are sealed up and kept frozen. Prior to the experiment, the samples are naturally air-dried at room temperature. See Table 1 for specific locations of the sampling points.

Table 1: Overview of sampling sites

Sampling site and number	Location
Maduo, Qinghai MD1	34°53′7″N, 98°10′17″E, 4200.0 mH
Xinghai, Qinghai XH2	35°30′2″N, 100°01′1″E, 2671.0 mH
Guide, Xining GD3	36°02′28″N, 101°24′27″E, 2196.0 mH
Xigu, Lanzhou XG4	36°07′16″N, 103°39′27″E, 1522.0 mH
Shizuishan, Ningxia SZS5	39°14′27″N, 106°47′1″E, 1082.0 mH
Wuhai, Inner Mongolia WH6	39°42′31″N, 106°45′35″E, 1072.0mH
Sanshenggong, Inner Mongolia SSG7	40°44′13″N, 107°25′36″E, 1028.0 mH
Urad Front Banner, Inner Mongolia WLT8	40°43′17″N, 108°37′30″E, 1012.0mH
Baotou, Inner Mongolia BT9	40°31′51″N, 109°54′49″E, 999.8mH

2.2 Experiment methods

2.2.1 Sample handling

Weigh 50mg of dried sediment samples of the Yellow River, and put it into a 50mL polypropylene centrifuge tube. Add 5mL of 10% H_2O_2 and shake the tube for 30min. After that, add 5mL of 1.0mo1/L HCi, and shake again for 30min. After the centrifugation, wash the sediments twice with 10mL of double distilled water. After another round of centrifugal separation, place the sediment-containing centrifuge tube in a 60°C oven for 12 hours.

2.2.2 Extraction of biogenic silica from sediments

(1) The number of extraction and temperature

The chemical extraction of biological silicon has three branches: single extraction method, multiple extraction method and continuous extraction method. Featuring simplicity and rapidness, the single extraction method is the most widely used approach. Relevant research shows, the dissolved quantity of biogenic silica increases with the temperature when other conditions are constant. In particular, if the temperature exceeds 40°C, the dissolved quantity would increase exponentially. Most of the labs in the world set the extraction temperature between 85°C and 100°C. For reasons given above, the authors decide to adopt single extraction method and set the extraction temperature at 90 °C for the experiment.

(2) Extraction time

The shortest extraction time is 1h and the longest is 24h. To achieve complete extraction, it is generally recommended to control the extraction time is between 5h and 8h. In the experiment, the authors probe into the extraction time of biogenic silica in sediments of the Yellow River. See Table 2 for experiment data.

Table 2: The influence of different extraction times on the content of biogenic silica

The actual mass of the sample (g)	Extraction time (h)	Average absorbance	Silicon content (mg/g)
0.0512	5	0.272	1.615
	7	0.484	2.875
	8	0.490	2.910
	9	0.682	4.051

The experiment data indicates: when the extraction time is 5h, the content of biogenic silica is the lowest, indicating incomplete extraction; the silicon content of 7-hour extraction time is similar to that of 8-hour extraction time; when the extraction time is 9h, the silicon content is significantly increased, indicating that non-biogenic silica might be dissolved over time. Thus, the single extraction time is set as 7h.

(3) Selecting a proper type of extracting agent

The key to biogenic silica determination lies in selecting the proper type of extracting agent. As a strong alkali, NaOH can completely dissolve biogenic silica. It is more suitable for sediment samples with high biogenic silica content. For the samples with low biogenic silica content, extraction with NaOH would result in excessive dissolution of non-biogenic silica component, causing big errors in measurement. Hence, the extracting agent should be selected in accordance with the specific mineral composition and the content of biogenic silica. In the experiment, the authors investigate the effect of two extracting agents: NaOH and Na_2CO_3. See Table 3 for the experiment data.

(4) Determination of the concentration of extracting agent

Currently, there is no definite concentration of extracting agent that applies to all kinds of biogenic silica samples. Therefore, the authors carry out an experiment to compare the effect of 0.2mol/L NaOH, 0.5mol/L NaOH, 1.0mol/L NaOH, 0.2mol/LNa_2CO_3, 0.5mol/L Na_2CO_3, 1.0mol/L Na_2CO_3 and 2.0mol/L Na_2CO_3. See Table 3 for the experiment results.

Table 3: The influence of different extracting solutions and different solution concentrations on the content of biogenic silica

Type of extracting agent	Concentration of extracting agent ($mol•L^{-1}$)	The actual mass of the sample (g)	Average absorbance	Silicon content (mg/g)
NaOH	0.2	0.0305	0.018	0.179
NaOH	0.5	0.0292	0.043	0.448
NaOH	1.0	0.0308	0.272	2.685
Na_2CO_3	0.2	0.0310	0.026	0.255
Na_2CO_3	0.5	0.0352	0.035	0.302
Na_2CO_3	1.0	0.0291	0.265	2.766
Na_2CO_3	2.0	0.0308	0.234	1.925

The experiment data indicates: when the extracting agent is NaOH or Na_2CO_3 and the concentration is 0.2 or 0.5 mol/L, the measured content of biogenic silica stays at a low level, indicating that the concentration is too low to completely extract biogenic silica. The content of biogenic silica under 0.1mol/L NaOH is similar to that under 0.1mol/L Na_2CO_3, and the value is rather stable. When the extracting agent is 2.0mol/L Na_2CO_3, the content of biogenic silica in sediments does not increase. Taking into account the relatively large sand content of sediments in the Yellow River, the authors choose to use 1.0mol/LNa_2CO_3 solution as the extracting agent for the purpose of preventing excessive dissolution of the non-biogenic silica component from causing big errors of measurement.

(5) Selecting the solid-liquid ratio

During the extraction process, the solid-liquid ratio has a great influence on the complete dissolution of biogenic silica. An excessively low solid-liquid ratio causes over-extraction, and an excessively high solid-liquid ratio hinders complete extraction of samples. It is of great importance to find a suitable solid-liquid ratio for the accuracy and precision of the experiment results. In the experiment, the authors use 40mL of 1.0mol/L Na_2CO_3 as the extracting agent, set the extraction time as 7h, and study samples which weigh 0.030g, 0.050g, and 0.070g respectively. See Table 4 for the experiment data.

Table 4: The influence of different solid-liquid ratios on the content of biogenic silica

The actual mass of the sample (g)	Average absorbance	Silicon content (mg/g)
0.0301	0.376	3.799
0.0495	0.443	2.718
0.0605	0.494	2.483
0.0701	0.353	1.531

The experiment data indicates: when the solid- liquid ratio is 0.75g/L, the silicon content is significantly increased; when the solid-liquid ratio is between 1.25g/L and 1.5g/L, the content of extracted biogenic silica remains stable, indicating minimum dissolution of non-biogenic silica. However, when the solid-liquid ratio is 1.75g/L, the content of dissolved biogenic silica is significantly reduced, indicating incomplete extraction.

2.2.3 Determination of the content of biogenic silica

The silicon content is determined by silicon molybdenum blue spectrophotometric method: Take 2mL of liquid supernatant from the centrifuge tube into a 25mL colorimetric tube, and adjust the pH value to 1.0 with 6mol/L HCl. Add 1.0mL of 5% ammonium molybdate solution, shake it well, and let it stand for 15min. Add 5.0mL of 4% oxalic acid solution and 2.0mL of ascorbic acid - oxalic acid solution, shake it well, and dilute it to 25mL. After 25min of developing, use a 1cm cuvette to measure the absorbance at the wavelength of 810nm.

3. Results and discussion

3.1 Distribution of biogenic silica in the surface sediments in the upper and middle reaches of the Yellow River

See Table 5 for the measured results of biogenic silica in the surface sediments in the upper and middle reaches of the Yellow River.

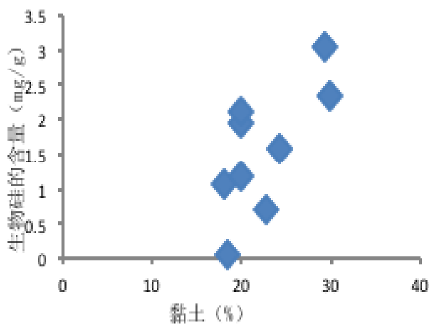
Table 5: Physical and chemical properties and biogenic silica content of surface sediments in the upper and middle reaches of the Yellow River

Sample No.	Grain size (μm)	Clay (%)	Silt (%)	Sand (%)	Organic matter (%)	BSi(mg/g)
MD1	36.18	29.20	55.57	15.23	1.96	3.06
XH2	42.08	29.90	51.34	18.76	1.07	2.34
GD3	55.14	22.70	63.74	13.56	0.14	0.73
XG4	55.51	18.00	66.62	15.38	0.30	1.08
SZS5	25.90	19.91	67.31	12.78	0.52	1.19
WH6	33.25	18.32	61.53	20.15	0.42	0.07
SSG7	26.40	24.30	63.93	11.77	0.61	1.58
WLT8	27.90	19.90	63.27	16.83	0.56	1.94
BT9	40.13	20.00	62.83	17.17	0.54	2.12

According to Table 5, the biogenic silica content of the surface sediments in the upper and middle reaches of the Yellow River varies greatly from 0.07-3.06mg/g. In descending order, the samples are arranged as: MD1>XH2>BT9>WLT8>SSG7>SZS5>XG4>GD3>WH6. The highest content appears in Maduo segment at the source of the Yellow River, and the lowest content appears in Wuhai segment.

3.2 Analysis of correlation between biogenic silica content and sediment composition

There is no obvious correlation between biogenic silica content and the volume fraction of components of different grain sizes in the sediments. As shown in Figure 1, the composition of sediments in the upper and middle reaches of the Yellow River is dominated by silt, and the grain size distribution does not change much. Being the main component, the volume fraction of silt is about 51.34% -67.31%. The stable grain size distribution has little influence on the absorption of biogenic silica. This means the difference in mechanical composition of the silt-dominated sediments has little to do with on the accumulation of biogenic silica. That is possibly why the accumulation of biogenic silica is not much affected by the composition of sediments in the upper and middle reaches of the Yellow River.



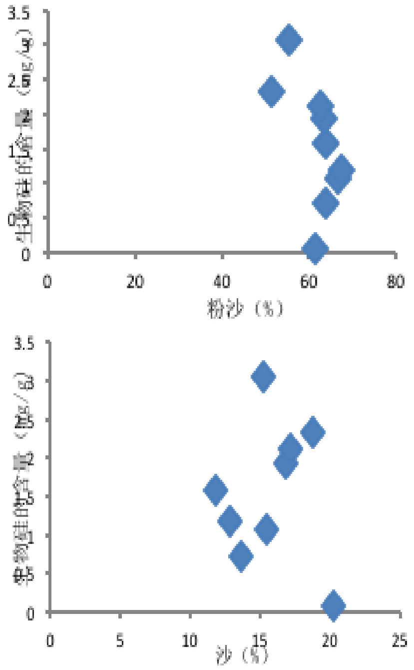


Figure 1: Correlation between biogenic silica content in sediments of the Yellow River and the sediment composition

3.3 Analysis of correlation between biogenic silica content and organic matter

Biogenic silica is an effective indicator of productivity because the generation and preservation of biogenic silica in the sediments are closely related to organic matter. As shown in Figure 2, there is a significant positive correlation between the biogenic silica content and the mass fraction of organic matter in the sediments in the upper and middle reaches of the Yellow River, indicating that the accumulation of biogenic silica in the sediments is highly dependent on the organic matter. Thus, the organic matter in the sediments has a protective effect on biogenic silica. Capable of slowing down the dissolution rate of biogenic silica in the sediments, the organic matter is an important factor of controlling the enrichment of biogenic silica in the sediments. According to Table 5, at the source of the Yellow River, Maduo segment boasts much higher biogenic silica content than other regions. The high content may be attributable to the high organic matter content in the sediments thanks to the large stretches of grassland and forests, lush vegetation, and rich wild plant resources in Maduo.

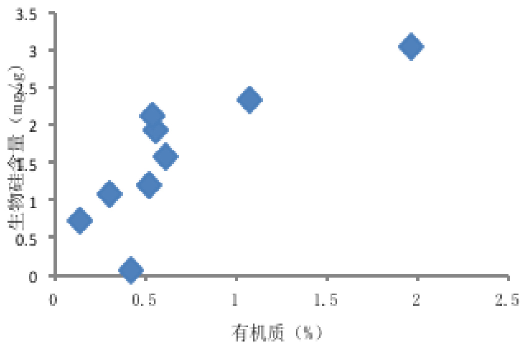


Figure 2: Correlation between biogenic silica content and organic matter in sediments of the Yellow River

4. Conclusion

(1) The results of the contrast experiments indicate: the temperature for extracting biogenic silica from the sediments of the Yellow River should be set at below 90°C, the single extraction method should be adopted, and the extraction time should be set as 7h. Taking into account the relatively large sand content of sediments

in the Yellow River, the authors choose to use 1.0mol/LNa_2CO_3 solution as the extracting agent for the purpose of preventing excessive dissolution of the non-biogenic silica component from causing big errors of measurement. when the solid-liquid ratio is between 1.25g/L and 1.5g/L, the content of extracted biogenic silica remains stable, indicating minimum dissolution of non-biogenic silica.

(2) The biogenic silica content of the surface sediments in the upper and middle reaches of the Yellow River varies greatly from 0.07-3.06mg/g. In descending order, the samples are arranged as: MD1>XH2>BT9>WLT8>SSG7>SZS5>XG4>GD3>WH6. The highest content appears in Maduo segment at the source of the Yellow River, and the lowest content appears in Wuhai segment.

(3) The composition of sediments in the upper and middle reaches of the Yellow River is dominated by silt, and there is no obvious correlation between biogenic silica content and the volume fraction of components of different grain sizes in the sediments, but a significant positive correlation between the biogenic silica content and the mass fraction of organic matter.

The deposition and preservation of biogenic silica are affected by various factors, such as sedimentary environment, hydrodynamic environment, organic nitrogen and phosphorus distribution. Therefore, further research is needed to reveal the distribution characteristics and influencing factors of biogenic silicon in the sediments of the Yellow River.

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