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The changes of pigment contents and their environmental implications in the lake sediments of Ny-Ålesund, Svalbard, the Arctic

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Abstract According to palaeoclimatic and modern instrumental data, numerous studies have indicated that the Arctic climate has undergone a significant warming during the past 100 years, and this may lead to significant impact on the fragile lake ecosystem. In this study, we collected a lake sediment core from the Ny-Ålesund of Svalbard and determined the concentrations of four pigments including chlorophyll derivatives, total carotenoids, oscillaxanthin and myxoxanthophyll in the sediments. Combined with other physical and chemical proxies such as calcium carbonate, total organic carbon, biogenic silicon etc., we have reconstructed the historical changes of lacustrine primary productivity in Ny-Ålesund, especially for the past 100 years. The results showed that during the period of Little Ice Age (LIA), the climate was unfavorable for the growth of the lake algae, and thus the lacustrine productivity declined. This result was supported by the relatively low contents of pigment and biogenic silica in the sediments. In contrast, the contents of total organic carbon (TOC) and sediment pigments increased significantly in the upper 5 cm (~1890AD), reflecting the rapid growth of the lake algae, thus the great increase of lacustrine primary productivity, corresponding to the warming climate after LIA. However, the biogenic silica in the upper sediments still had a relatively low level, and this might be related to the growth competition with other algae species. Over the past 100 years, the ratio of Osc/Myx in the sediments decreased continuously, indicative of durative increase of myxoxanthophyll in blue-green algal pigments, and this might imply that the human activity had enhanced the nutrition level of the lake in the Arctic region.

Key words Arctic, Lake Sediments, Pigments, Primary Productivity, Climate Change.

1 Introduction

The Arctic is an important region for the atmosphere-ocean material energy exchange, and it play a significant role in the formation and evolution of global climate system. The climatic and environmental characteristics as well as the physical and chemical process in the Arctic are closely related to global changes, therefore, the Arctic region is an important composition of the international climatic research, such as Global Atmospheric Research Programme (GARP)、World Climate Research Programme (WCRP) and so on. Lake sediments are good materials to infer palaeoclimatic and palaeoenvironmental changes, which can fully record abundant information about the climate, vegetation and human activity. At present, the lake sediments have been widely used to study past global changes[1,2]. Studies on the varve thickness, diatoms fossil composition and ice cores have shown that the Arctic has undergone significant climatic changes during the recent 100 years [3]. Climatic change usually has significant impact on the freshwater ecosystem. Under the background of global warming, how can the Arctic fragile lake ecosystem respond to the warming climate? The spatial and temporal scales of such changes in the Arctic, however, are still poorly documented and understood, because long-term monitoring data are still scarce.

Lake algae contain a lot of pigments such as chlorophyll, carotenoids and so on, and they would be buried in lake sediments after their death. At present, the pigments in the sediments have been widely applied in past eco-environmental researches, such as the evolution of lake primary productivity[4,5], climate change[6], eutrophication history[7,8], acidification[9], historical ultraviolet radiation[10] and the influence of human activity[11]. In the palaeo-pigment studies, seven proxies including Chlorophyll derivatives (CD), Total Carotenoids (TC), Myxoxanthophyll (Myx), Oscillaxanthin (Osc), Native chlorophyll (NC), CD/TC and Osc/Myx are usually used[4]. It is well-known that the Arctic sediments are deposited under relatively cold climate conditions, in which the pigments should be preserved well. In this paper, we analyzed the pigment contents and other geochemical parameters in a lake sediment core from Ny-Ålesund, Svalbard, and focused on the lake ecosystem in response to climate warming over the past 100 years.

2 Study area

Svalbard Archipelago (74°-81°N, 10°-35°E), one of the northernmost land in the inhabited world, locates between the Barents Sea and the Greenland Sea, and it consists of Spitsbergen Island, Nordaustlandet Island, Edgeoya Island and other small islands. The total land area is about 61,200 km^2. About 60% of the land is permanently covered by ice and glaciers, and the permafrost is reaching to 500 meters thick, only 2～3 meters in depth can be unfrozen in summers. Because of the North Atlantic Ocean warm current flowing by the archipelago, the west part of the island has the polar-maritime climate characteristic. The island has abundant coal and apatite deposits. Ny-Ålesund (78°55′N, 11°56′E) is situated on the Brøggerhalvoya peninsula on the west coast of the Spitsbergen archipelago (Fig. 1), and it is an expedition base on Arctic. The bedrocks mainly consist of pit coal- Permian limestone and dolomite, and a small amount of neogene standstones can be found somewhere. The average summer temperature is around 5 ℃, while winter average is about −14 ℃. The mean annual temperature is about −5.8 ℃, 6-7 ℃ higher than east Greenland. The annual mean precipitation is about 400 mm along the west coast, and gradually drops to 200-300 mm toward the inland areas. Compared with Antarctica and other corresponding latitude Arctic areas, Ny-Ålesund is populated with much more plants, which predominantly grow in the inland fjords. The species of plants in Ny-Ålesund is relatively simple, and is mainly composed of Arctic tundra and polar desert communities[12].

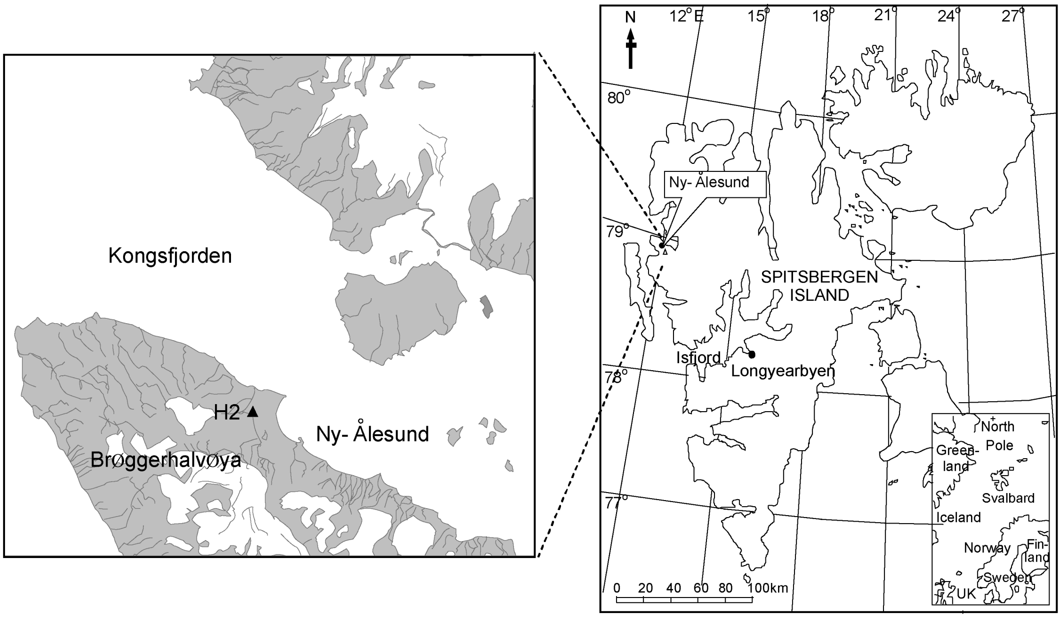

Fig. 1 The location of the Ny-Ålesund, Svalbard, Arctic and the sampling site.

3 Sampling and methods

Knudsenheia Lake (78°56′29″N, 11°49′16″E, elevation 35 m), ~3 km northwest to the Yellow River Station of China, is a relatively large lake located along the margin of the Brøgger Hill in Ny-Ålesund. A 58-cm long sediment core, named as H2, was retrieved from this lake with a water depth of 1.5 m in July 2006. The surface 20 cm of the core is black sapropel, and the further 20 cm of it is brown-yellow mud with a few gravels. The sediment core was sectioned at 1-cm intervals in the field. The divided samples were frozen and brought to the laboratory for analysis.

For grain size analysis, the subsamples are dispersed fully by dispersant after treatment with carbonate, and determined by laser diffraction on a Winner-2116 laser particle size analyzer with an error less than 3%. Pigments were extracted from sediment samples by following the procedure of Swain with 90% acetone [4]. Based on the characteristic wavelength of different pigments, four pigment componenets including Chlorophyll derivatives (CD), Total Carotenoids (TC), Myxoxanthophyll (Myx) and Oscillaxanthin (Osc) were measured by ultraviolet spectrophotometer (UV-8500) and calculated the contents according to the formula prosposed by Swain (1985)[4]. The concentrations of Osc and Myx in the sediments were expressed as μg/g organic matter; CD and TC were expressed as absorbance per gram organic matter. Total nitrogen (TN) and total carbon are determined by a NCSH elemental analyzer (vario EL Ⅲ) with an error less than 1%. The water contents, $LOI_{550\,℃}$ and $LOI_{950\,℃}$ are determined by Heiri's methods[13]. The potassium dichromate oxidation-chemical volumetric methods are used to measure total organic carbon (TOC) with a duplication error of 5%[14]. Biogenic silica (BSi) concentration was determined using colorimetry method[15].

Sediment chronology was established using both ^{210}Pb and AMS^{14}C dating techniques. For ^{210}Pb analysis, the top 10 consecutive sediment samples (0—10 cm core depth) were processed to measure the activity of the excess ^{210}Pb. The mass depth will be calculated based on the determination of the net weight and dry density. The dry sediment subsamples and standard samples were put into the same shape of the tube, and the radioactivity was measured by the γ spectrometer. Unsupported ^{210}Pb activity per sample was calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity. The standard radionuclide samples were provided and calibrated by China Institute of Atomic Energy. The analytical instrument is the low background and high purity Germanium (HPGe) gamma ray spectrograph (GWL-DSPEC-PLUS) produced by AMETEK Company, America. All the measurement of radionuclide activities were performed in Institute of Polar Environment, University of Science and Technology of China. Four bulk sediment samples below 10 cm were selected for AMS^{14}C dating at Carbon Cycle Accelerator Mass Spectrometry Laboratory, University of California Irvine (KCCAMS UCI).

4 Results and Discussion

4.1 Chronology

As shown in Figure 2, significant levels of unsupported ^{210}Pb were detected in the top 5 cm sediment layer and the total ^{210}Pb activities were in equilibrium with the ^{226}Ra activity below 6 cm. As illustrated in Figure 2A, the excess ^{210}Pb activity of H2 sediment core shows a simple exponential correlation with depth, indicating that the chronology of this profile can be calculated using Constant Initial Concentration (CIC) model. The ages of top 5cm subsamples are given in Table 1, and the 5cm sediment depth corresponds to 117 yr BP.

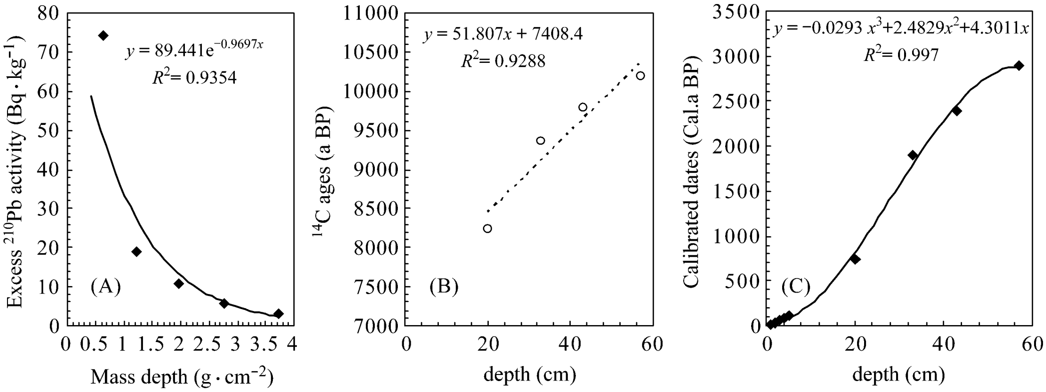

Fig. 2 Plots showing age-depth relationship in the sediment core H2. A: The change of excess ^{210}Pb activity against depth in the top 5 cm sediments; B: The determined AMS^{14}C dates as a function of depth; C: Both ^{210}Pb and AMS^{14}C calibrated ages versus depth.

The AMS ^{14}C dating results are also listed in Table 1. Those obtained radiocarbon ages are stratigraphically consistent, perhaps indicating good preservation of sediments after deposition. Assuming that the surface date could be used to estimate the lake reservoir effect, the reservoir-corrected date can be built up by subtracting this age from the measured date. Following the conventional processing method, the regression line between depth and ^{14}C age shows that the age of uppermost surface sediments could be 7408 years (Fig. 2B), quite different from the results of ^{210}Pb dating (Table 1). Here, we suggest that the unmatched results are probably caused by lake reservoir effects because there are large distributions of carbonate from the bedrock as well as the exposed coal-bearing strata in this region. Therefore, we subtracted this value from all determined radiocarbon dates and then converted these corrected-radiocarbon ages to calendar year ages using the Calib program version 4.4 (Table 1). Combined with ^{210}Pb and calibrated AMS ^{14}C ages, a third order polynomial curve was fitted to the age depth data, and the age-depth model is described by the equation: Ages (a B.P) $= -0.0293 \times \text{depth(cm)}^3 + 2.4829 \times \text{depth(cm)}^2 + 4.3011 \times \text{depth(cm)}$ (Fig. 2C).

Table. 1 Results of AMS^{14}C and ^{210}Pb calibration ages for the H2 sediment samples

Method	Dated material	Sediment No.	Depth /cm	Age		
				Corrected age/a B.P	Calibrated age/a B.P	Uncertainty (1σ)/a
^{210}Pb dating	Bulk sediments	H2-57	0-1	20	20	±7
		H2-56	1-2	39	39	±6
		H2-55	2-3	61	61	±5
		H2-54	3-4	87	87	±5
		H2-53	4-5	117	117	±5
AMS^{14}C dating	Bulk sediments	H2-38	19-20	827	737	±20
		H2-25	32-33	1952	1907	±20
		H2-15	42-43	2367	2387	±20
		H2-1	56-57	2782	2890	±25

4.2 Changes of physical and chemical proxies

The grain size distributions can directly reflect the environmental change during the deposition. According to the results of grain size compositions, the sediments predominantly consist of clay and silt; the portion of clay size material (<2 um) varies from 10.5 to 22.7%, and silt (2-63 um) from 68.6 to 89.5%, indicating the relative stable sedimentary environment. The dry density is about 2~2.5 g/cm^3. The significant decreases of dry density are observed in the top 6 cm sediments, corresponding to increases of water content and organic matter.

Percentage loss on ignition has been widely used to represent the relative contents of organic matter and inorganic carbon[13]. $LOI_{550℃}$ and TOC are plotted in Figure 3 versus depth. As shown in this figure, $LOI_{550℃}$ and TOC display very similar change patterns with the depth, and the result of correlation analysis shows that they have strongly positive relationship with a correlation coefficient of 0.81. The $LOI_{550℃}$ values in the sediments are present at low level (~9%) below 15 cm depth, and rise to ～14% at 5 cm and then remain relatively high level in the upper 5 cm sediment layer (Fig. 3). TOC reflects the balance between organic matter production and decomposition, and can partially tracks aquatic

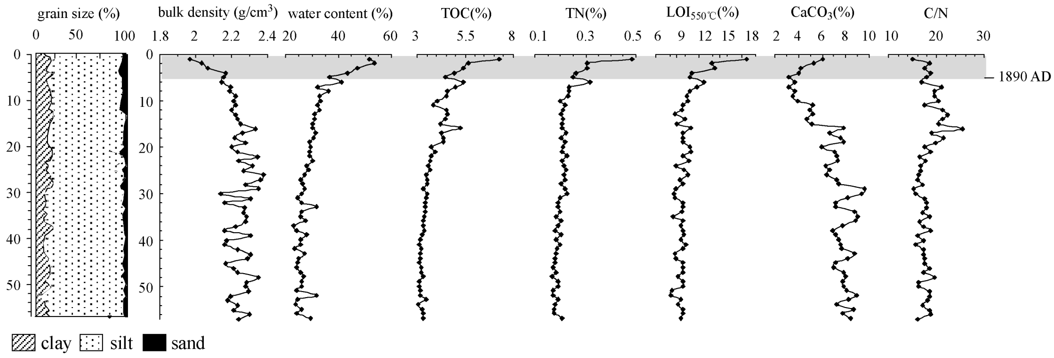

Fig. 3 Changes of physical and chemical proxies in the H2 sediment core versus depth.

production. The increase of TOC in the surface sediments may indicate the development of lake algae associated with the warming climate. Furthermore, TN is significantly correlated with the TOC: TN(%)=0.0507×TOC(%)+0.0185(r=0.866). Compared with the TN values (TN=0.169%～0.484%, averaging 0.213%), the small intercept of 0.0185% indicates a negligible fraction of inorganic nitrogen in the sediments. Thus, the measured nitrogen is associated with organic matter, and the TOC/TN ratios, or C/N values, can be employed to determine the origin of organic matter[16]. Generally speaking, C/N ratios of aquatic organic matter are significant lower than the terrestrial organic matter[17]. In the H2 lake sediments, the C: N ratios range from 15.0～25.5, with a mean of 18.2. The catchment of H2 lake is predominantly covered by moss with C/N values of 40-50[18], much higher than H2 lake sediments. Therefore, the terrestrial moss input can not be the main source of organic matter in the H2 sediments, and the organic matter in the H2 core may be mainly produced in the lake. As shown in Figure 4, the C/N ratios display a notable peak in the sediments between 5 and 16 cm. Based on our age-depth model mentioned above, these sediments were deposited at 1420-1850AD, corresponding well to the onset of Little Ice Age. The cold climate might cause a reduction in the lake production, but an increase in the input percentage of terrestrial organic matter later on, and thus relatively high C/N ratios occurred. After that, the C/N ratios gradually declined, and reached the lowest level in the upper 5 cm sediments (about 1890 AD), indicating enhanced contributions of organic matter derived from lake aquatic sources, and probably reflecting the increase of lake algae production. As illustrated in Figure 3, $CaCO_3$ shows negative correlation with TOC below 5 cm sediments, but positive correlation occurs apparently in the top sediment layer, this may be caused by the fact that recent prosperous growth of lake algae has promoted the precipitation of calcium carbonate due to the numerous absorbtion of CO_2 in the water[8].

4.3 Pigments

CD and TC are used to infer changes in lake primary productivity. In lakes with high water temperature and flourish algae growth, high CD and TC contents should appear in the sediments [19]. Osc is only found in *Oscillaria* and *Arthrospira* species, and *Oscillaria* is considered to be one of dominant algaes firstly present in phytoplankton during the period of lake eutrophication, thus the Osc can be used to reveal the change of historical eutrophication[11]. Myx can indicate the contents of the blue-green algal in plankton, and thus this proxy can provide the important sedimentation evidence for the change of blue-green algae population[20].

The changes of pigment contents and biogenic silica (BSi) in the H2 sediment core are plotted in Figure 4. As shown in this figure, all the pigment concentrations display notable fluctuations versus depth. The continuous low pigment concentrations between 5～17 cm were probably associated with the presence of glacier in the catchment during the LIA. During cold and dry climate conditions [21], BSi content also exhibited decreasing trend at the beginning of 17 cm, reflecting decreased diatom population in the lakes. From 5 cm depth, the contents of four pigments including CD, TC, OSC, Myx and BSi began to rise rapidly. According to ^{210}Pb result, the 5cm sediment depth corresponded to 1890AD, in consistent with the end time of LIA. In the top 5 cm sediment layer, all the pigment contents show rapid increase, especially for the myxoxanthophyll (Myx), its average level is 35 μg/g org in the uppermost 4 cm sediments, about 3 times higher than that in the lower part of the core, this agrees well with the change of organic matter content. The notably increasing pigment contents in the uppermost sediments may be attributed to two possible reasons: an increase in the lake productivity and a better preservation effect.

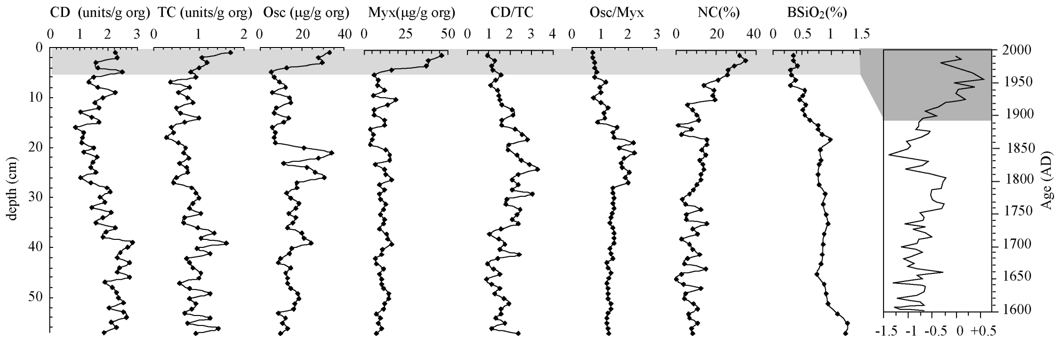

Fig. 4 Changes of sediment pigments and their relative ratios, biogenic silica content The summer temperature change in the Arctic on the right redrew from reference[22].

The native chlorophyll (NC) represents the content of the chlorophyll which was undecomposed, thereby providing an index for pigment preservation level. Higher NC content indicates better preservation conditions for pigments[4]. The change of NC content is plotted in Figure 4. As depicted in this figure, on the whole the native chlorophyll (NC) exhibit increasing trend, indicating that the preservation condition of pigments in the H2 sediment core became better from the bottom to top. The results of correlation analysis showed that the NC had no significant correlation with CD, TC or Osc, and a weak positive correlation with Myx, indicating that the preservation condition is not the main control factor on the pigment variations in the H2 sediment sequence. According to the field investigation, H2 Lake is a closed lake, so the effect of catchment should be neglected. In addition, there are only some mosses growing around the lake catchment, and the disturbance of animals is unlikely. Therefore, the enhanced lake primary production should be the main cause for the rapid increases in pigment contents over the past 100 years.

According to paleoclimatic and modern instrumental data, the global climate has undergone a significant warming since the 20th century, and the Arctic regions have been subject to larger extent of warming relative to other global areas. A compilation of paleoclimate records from lake sediments, trees, glaciers, and marine sediments has shown that the Arctic has undergone a marked warming from 1840 to the mid-20th century[22]. A 800-year ice core record showed that the cold climate on Svalbard occurred from about AD 1500 to 1900s[23], and the coldest local temperatures took place between about 1760 and 1900AD, and then the climate became warm gradually. With a warming climate, there is a general tendency for lake water to become warmer and the ice-free season become longer. This increased buffering releases more nutrients and dissolved solids into the lake, together with the increased solar radiation energy for the aquatic plants growing in lake, resulting in the increase of primary productivity and pigments. However, the content of biogenic silica did not increase significantly, indicating that the diatom biomass remained constant, and this might be owing to the competition between the growth of algae, that is to say, the large number of blue-green algae growth restrained the bloom of diatom.

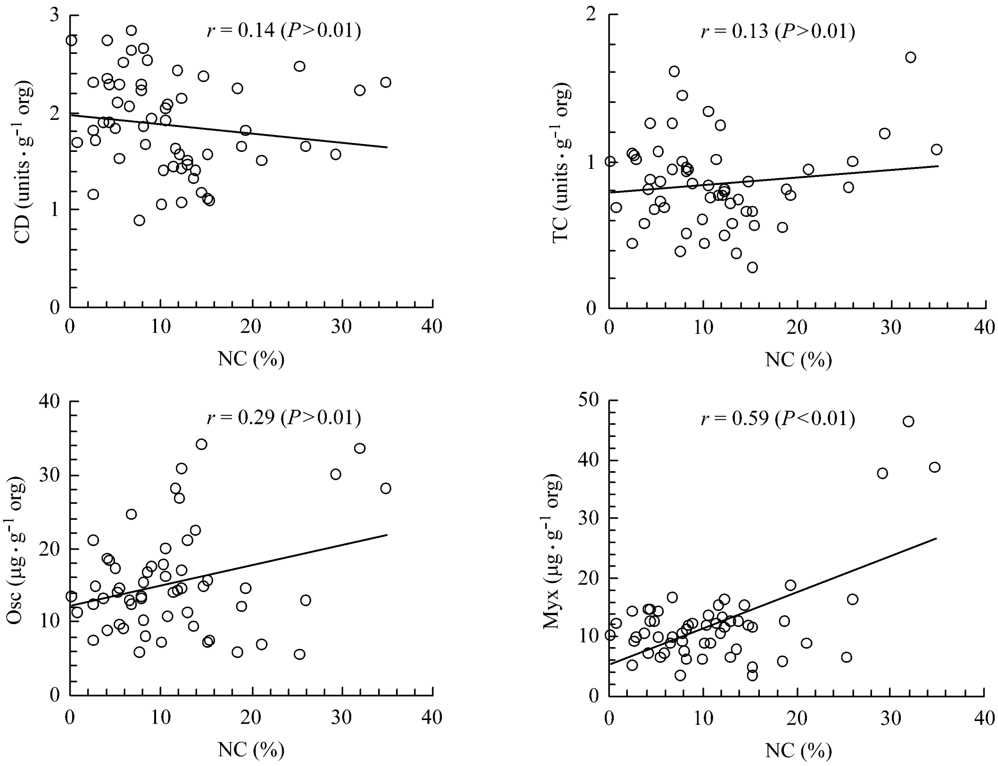

Fig. 5 Correlations of the CD, TC, Osc and Myx with the NC.

Carotenoids degrade faster than chlorophyll under oxidizing conditions and the ratio of chlorophyll derivatives to total carotenoids (CD/TC) is lower in lake sediments than that in soils[24]. The high CD/TC ratios indicate the large input of exogenous organic matter, whereas the low values suggest the well preserved condition and/or the increase of lake primary productivity[4]. The continuous decline of CD/TC between 16～5 cm might be related to the better preservation of total carotenoids under reducing conditions during the LIA. In contrast, the continue decline of CD/TC in the upper 6 cm might be attributed to the increase growth of the algal and high primary production, which would result in the high proportion input of autogenous organic matter into the lake sediments. The contents of Osc and Myx are variable because of the different preservation conditions, however, their decomposition rates are similar in nature, so the ratio of oscillaxanthin to myxoxanthophyll (Osc: Myx) can be used to measure the relative production of the oscillatoria and blue-green algae in the lake[4]. The higher ratios (usually >1.0) indicate the dominance of Oscillatoria and its relatively high production, and vice versa. The dominance of myxoxanthophyll possibly corresponds to the increase of lake eutrophication. Under the condition of Little Ice Age, the decline of lake productivity and the continued decrease of Osc/Myx, probably reflecting the more rapid drop of oscillatoria algae biomass relative to the blue-green algae. In the uppermost 5 cm sediments, the ratios of Osc/Myx are lower than 1, indicating a durative increase of myxoxanthophyll in blue-green algal pigments, and this may imply that the human activity has enhanced the nutrition level of the lake[25].

5 Conclusions

(1) The higher content of organic matter and the decreased C/N values in the top 5cm sediments of H2 core from Ny-Ålesund, Svalbard, the Arctic, indicated the increased contributions of organic matter derived from lake aquatic sources. Combined with the pigments results, it was revealed that the lake production had been subject to strong enhancement over the past 100 years.

(2) The contents of four pigments (CD, TC, Myx, Osc) and their ratios in the H2 sediments were closely associated with Arctic climate change. During the deteriorative Little Ice Age (LIA), sedimentary pigment contents were relatively low as a whole, reflecting the decreased primary productivity. In contrast, after LIA, the sediment pigments increased significantly, in consistent with the rapid growth of lake algae, indicating the great increase of lacustrine primary productivity. This was likely related to the prolonged Arctic warming climate in the past 100 years.

(3) The blue-green algaes were predominant in the upper sediments, whereas the diatom species was still scare, indicating that the climate warming over the past 100 years not only caused the increase in the lake productivity, but also resulted in the changes of lake ecosystem composition and function. Climate models projected that the Arctic would experience prolonged large-scale warming in the future, so it was necessary to pay more attention to study the Arctic lake ecosystem in response to the global warming.

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