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Phytoplankton community changes indicated by biomarker from sediment in Prydz Bay, Antarctica

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Abstract Biomarkers including brassicasterol, dinosterol and alkenone in sediments are used as indicators to reconstruct changes to the phytoplankton community in surface and sub-aerial sediments of Prydz Bay, Antarctica. The results indicate that the biomarker records in surface and core sediment samples changed with time and space. The total content of phytoplankton biomarkers ranges from 391.0—1 470.6 ng·g^{-1}. The phytoplankton biomass has increased in Prydz Bay over the past 100 years. This variation may be mainly related with climate change in the region. The total biomarker contents in surface sediments from 5 stations in Prydz Bay are in the range of 215.8—1 294.3 ng·g^{-1}. The phytoplankton biomass in Prydz Bay is higher than that outside of the bay. This is similar to the distributions of chlorophyll *a*, organic carbon and biogenic silica in surface waters determined through *in situ* investigation. Such consistency indicates a coupling between the bottom of the ocean and biogeochemical processes in the upper water.

Keywords **Prydz Bay, Antarctic, sediment, biomarker, phytoplankton biomass**

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0 Introduction

The base of the food chain in the Southern Ocean comprises phytoplankton, primarily diatoms, followed by dinoflagellates. Phytoplankton transform atmospheric CO_2 into organic carbon (OC) and "pump" the carbon into the deep ocean through direct and indirect means. This process regulates the atmospheric CO_2 concentration and the global carbon cycle[1-3]. Thus, the biological production of phytoplankton is closely related to the absorption of atmospheric CO_2. During austral summers, phytoplankton play a dominant role in absorbing atmospheric CO_2, thereby forming a strong CO_2 sink in the polar ocean[4]. However, the special geographic and climatic conditions in the Antarctic make large-scale and longstanding vessel surveys difficult to develop and undertake. Therefore, the Southern Ocean is lacking in data-intensive study of this kind in comparison with other oceans.

Previous studies on the biological production of marine phytoplankton and community structures have mostly adopted conventional means of measurement which cannot reflect the changes of the past. Currently, multi-parameter biomarker methods are being more widely used in the reconstruction of phytoplankton biomass and community structure. Some lipid biomarkers with special indication significance (such as phytoplankton markers) are highly stable and can be characterized with higher specificity than more generally used biogenic silica (BSi) and carbonate. There are a number of studies, both internationally[5-7] and domestically[8-11], which successfully demonstrate the restoration of marine phytoplankton community structures from the record in sediment.

This paper selects three specific phytoplankton markers, including brassicasterol, dinosterol, and alkenones, to mark the biomass of diatoms, dinoflagellates and coccolithophores, respectively, to demonstrate changes in the phytoplankton community structures. In combination with *in situ* survey data, this study adds to the current understanding of the spatial and temporal changes to the phyto-

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plankton community in the Southern Ocean.

1 Method

1.1 Sample collection

Sediment cores were collected at five stations in Prydz Bay during the twenty first Chinese National Antarctic Research Expedition (21st CHINARE, 30 January—2 February 2005) (Figure 1). Prydz Bay, located in the Indian Ocean sector of the Southern Ocean, is the 3rd largest bay along the Antarctic coast and is categorized as a marginal ice zone. As can be seen from Figure 1, the internal zone of Prydz Bay is south of 67°S, with water depths ranging from 400—600 m; whereas north of 66°S is a deep-water area, with water depths >3 000 m.

Sample collection at Site Ⅲ-12 involved using multi-tube, disturbance-free samplers (core Ⅲ-12 is 18 cm long), while at the other sites gravity columns were adopted for sample collection. Sample separation was carried out *in situ*, with intervals of 1 cm within 10 cm, and 2 cm below 10 cm. Freezing preservation was used for transportation of the samples back to the laboratory. In addition to organic experimental analysis of core Ⅲ-12, experimental analysis was also conducted on the uppermost (0—1 cm) sediment of other core samples.

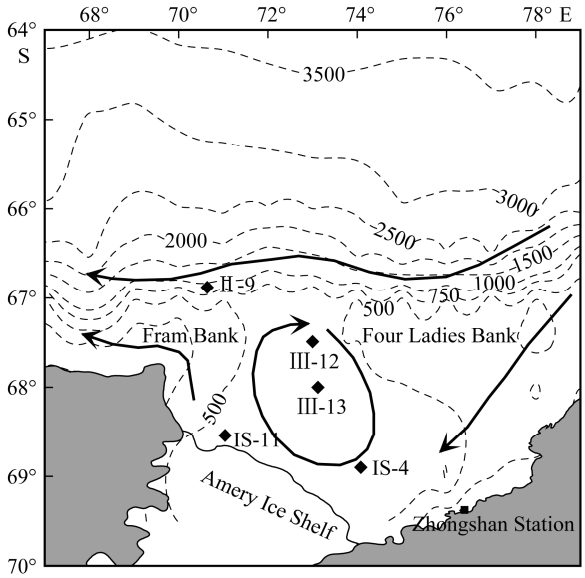

Figure 1 Bathymetric map of sediment sampling stations in the Southern Ocean of East Antarctica. Note the position of Zhongshan Station (arrows denote the schematic surface water current in this region).

1.2 Biomarker content analysis

1.2.1 Sample preparation

After freeze-drying and fine-grinding of the samples, mixed solvent of methylene chloride and methanol (with volume ratio at 3:1) is added, as well as 20 μL of internal standard isotriacontane (r-C_{30}) and nonadecyl alcohol ($C_{19}H_{39}OH$). Then, from Soxhlet extraction (the temperature of extract water was kept at 62℃ and backflow speed at 4—5 times per hour), the extractable organic matter can be obtained. Activated copper is added to this matter before being placed overnight for desulfurization. The extraction liquid, after being concentrated through rotary evaporation, and by addition of a methanol solution containing 6% KOH, has acidic components removed by alkaline water. After centrifugal separation, hexane is used for extracting (four times). The supernatant, after being concentrated through rotary evaporation, is dried by nitrogen. Then, hexane is used for chromatography and collection of alkane components, and methylene chloride is used for eluting and collection of alcohol and ketene components. The above two components are then dried by nitrogen and transferred separately into a 1 mL graduated tube, with alkanes thereof for gas chromatograph (GC) analysis directly. Alcohol and ketene components are transformed into trimethylsilyl ether derivatives (TMS-ether) by adding methylene chloride and N,O-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) before GC analysis.

1.2.2 Instrument conditions

Alcohol and ketene: gas chromatography (HP5890); fused silica capillary column (DB-5, 30 m×0.25 mm); temperature rising program: with initial temperature at 80℃ and heating rate of 25℃·min^{-1} up to 200℃, then 4℃·min^{-1} up to 250℃, 1.8℃·min^{-1} up to 300℃, and 5℃·min^{-1} up to 310℃, which is maintained for 5 min. Carrier gas: hydrogen, with flow rate of 1.2 mL·min^{-1}. The content of each component is calculated based on the ratio of peak area to internal standard area.

1.3 Other determinations

The ^{210}Pb dating method is used for dating sediment core samples and can be used to calculate sedimentation rates[12-13]. In this study an infrared carbon-sulfur analyzer (HCS-140G) was used to determine the amount of OC in the sediments. Standard samples were used as a reference during the measurement process, with parallel samples as controls with a standard deviation < 1%. The Na_2CO_3 extraction method was applied for the determination of BSi in sediments[14]. The concentration of chlorophyll *a* (Chl *a*) was determined by the extraction fluorescence method[15]. First 250 mL seawater sample was filtered by Whatman GF/F membrane (Φ 25 mm), which was then extracted by acetone for 18 h at -20℃. The extracting solution was determined using a Tuner Designs fluorometer (Model 10).

2 Results

2.1 Biomarker content in sediments

The total content of the three biomarkers in core Ⅲ-12 (brassicasterol, dinosterol, and alkenones) varies from 391.0—1 470.6 ng·g^{-1} (Table 1). Over the past ~100 years the content of single phytoplankton markers-brassicasterol,

dinosterol and alkenones-varies from 261.2—1 113.2 ng·g^{-1}, 101.6—352.9 ng·g^{-1} and 13.7—51.5 ng·g^{-1}, respectively. This shows that in phytoplankton community, diatom biomass indicated by brassicasterol was the highest. The vertical changes in the content of single phytoplankton markers in core Ⅲ-12 indicates significant change in the community structure, which is mainly reflected by changes in the relative content of diatoms or dinoflagellates. The relative content of diatoms is assessed to be in the range 60.9%—86.5%, dinoflagellates in the range 10.8%—36.4% and the content of coccolithophores in the range 1.5%—4.1%. The ratio of brassicasterol and dinosterol (diatom/dinoflagellate) fluctuates between 1.7 and 8.1, indicating that significant changes in the environment occurred in Prydz Bay.

Table 1 Relative percentage of biomarkers indicative of diatoms, dinoflagellates and coccolithophores in core III-12

III-12 Depth/cm	Total biomarkers /ng·g^{-1}	Brassicasterol /ng·g^{-1}	Dinosterol /ng·g^{-1}	Alkenones /ng·g^{-1}	Diatom /%	Dinoflagellate /%	Coccolithophore /%	Brassicasterol/ Dinosterol
surface	1 100.4	904.5	179.4	16.5	82.2	16.3	1.5	5.0
0.5~1	1 072.2	757.0	290.6	24.7	70.6	27.1	2.3	2.6
1~2	1 295.0	1 113.2	137.4	21.6	86.5	10.8	2.7	8.1
2~3	1 470.6	1 066.2	352.9	51.5	72.5	24.0	3.5	3.0
3~4	1 010.2	667.7	303.1	39.4	66.1	30.0	3.9	2.2
4~5	1 223.3	993.3	195.7	34.3	81.2	16.0	2.8	5.1
5~6	918.1	762.9	125.8	29.4	83.1	13.7	3.2	6.1
6~7	590.2	450.3	115.7	24.2	76.3	19.6	4.1	3.9
7~8	641.8	501.2	116.8	23.7	78.1	18.2	3.7	4.3
8~9	790.4	490.0	279.8	20.6	62.0	35.4	2.6	1.8
9~10	861.3	733.0	101.6	26.7	85.1	11.8	3.1	7.2
10~12	649.0	395.2	236.3	17.5	60.9	36.4	2.7	1.7
12~14	391.0	261.2	116.1	13.7	66.8	29.7	3.5	2.2
14~16	602.5	448.9	129.5	24.1	74.5	21.5	4.0	3.5
16~18	543.7	383.3	140.3	20.1	70.5	25.8	3.7	2.7

The total content of biomarkers in surface sediments from Prydz Bay varies from 215.8—1 294.3 ng·g^{-1} (Table 2). The content of diatoms in brassicasterol varies from 69.2%—80.0% (75.7% average), while the content of dinoflagellates in dinosterol varies from 17.9%—26.5% (21.7% average). The content of coccolithophore in alkenones varies from 1.9%—4.3% (2.6% average). All five sampling stations are dominated by diatoms and dinoflagellates. The ratio of brassicasterol to dinosterol in Prydz Bay is higher than that in the north (0.7 on average) and south (0.8 on average) of the East China Sea[9]. In the Southern Ocean, diatoms are dominant in the population of high productivity in the circumpolar coastal waters[16] and the Polar Front area[17]. Diatom blooms, which account for 75% of the primary productivity in the Antarctic, represent a large portion of export productivity in the region[18-19].

Table 2 Relative percentage of biomarkers indicative of diatoms, dinoflagellates and coccolithophores in surface sediments

Station	Total biomarkers /ng·g^{-1}	Brassicasterol /ng·g^{-1}	Dinosterol /ng·g^{-1}	Alkenone /ng·g^{-1}	Diatom /%	Dinoflagellates /%	Coccolithophore /%	Brassicasterol/ Dinosterol
IS-4	563.3	420.2	132.4	10.7	74.6	23.5	1.9	3.2
IS-11	257.0	201.2	50.1	5.6	78.3	19.5	2.2	4.0
II-9	215.8	149.3	57.2	9.3	69.2	26.5	4.3	2.6
III-12	1 294.3	1 035.4	231.7	27.2	80.0	17.9	2.1	4.7
III-13	976.6	745.1	205.1	26.4	76.3	21.0	2.7	3.5
Average	661.4	510.2	135.3	15.8	75.7	21.7	2.6	3.6

Note: The relative percentage of diatom, dinoflagellates and coccolithophore were calculated by brassicasterol, dinosterol and alkenone divided by total biomarkers, respectively.

2.2 Vertical distribution of ^{210}Pb and sedimentation rate

The radioactivity of ^{210}Pb decreases as the sediment depth increases in core Ⅲ-12 (Figure 2). Such a trend reflects a centennial-scale sedimentation rate in this core. The sedimentation rate of core Ⅲ-12 from Prydz Bay was calculated by the least squares method. As shown in Figure 2,

there are two sections of decay throughout core Ⅲ-12. The upper section of decay is from 0—7 cm with a sedimentation rate of 1.29 mm·a^{-1}. The amount of ^{210}Pb increases slightly between 7 and 12 cm, indicating some mixing. The lower section of decay, from 10—15 cm, has a sedimentation rate of 1.10 mm·a^{-1}. The amount of ^{210}Pb below 15 cm decreases and eventually reaches background values. The sedimentation span of core Ⅲ-12 is calculated to be about 100 a based on the dating of core samples from different depths, and the surface layer sampling completed in 2005.

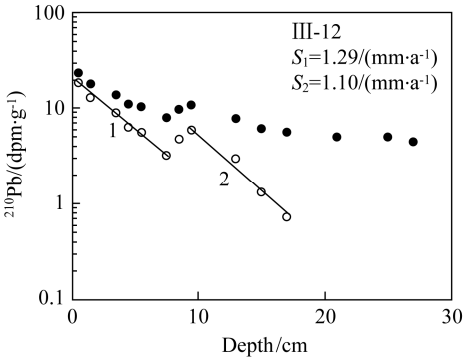

Figure 2 Distribution of ^{210}Pb in core Ⅲ-12 (note: X-axis is depth along core). The solid symbols (●) represent the specific radioactivity of ^{210}Pb and the open symbols (○) represent the excess specific radioactivity of ^{210}Pb (unit of decay is disintegrations per min per gram).

3 Discussion

3.1 Changes of phytoplankton biomass

The phytoplankton biomass estimated by biomarkers in the last ~100 years shows a generally upward trend (Figure 3), most likely as a result of regional climatic change. For example, the air temperature in the Antarctic has risen by nearly 0.6℃ in the latest 40 years, although differences exist for different regions. This is mainly because of the enlargement of oceanic areas of the Antarctic and the number of independent subsystems with varied functions.

The warming trend that appears in modern Antarctic areas occurs mainly in the Antarctic Peninsula region. In contrast, temperatures in the East Antarctic as well as that in the Prydz Bay region appear to have decreased[20]. For example, there are studies indicating that temperatures near the Zhongshan Station of Prydz Bay tend to fall in spring and winter, while they rise in autumn and summer[21]. Because Prydz Bay is located marginally to the cold and high-pressure climate of the Antarctic continent, it is commonly affected by warm and humid air flow from the north and cold air from the continental interior. This results in frequent abnormal climatic conditions, with temperatures having decreased by 0.066℃·a^{-1} in the last 10 years[22]. The above indicates that there is no significant warming trend in the area of Zhongshan Station but there are complex annual temperature changes. Therefore, further studies of changes in marine productivity and correspondence to climatic changes on an inter-annual scale are needed.

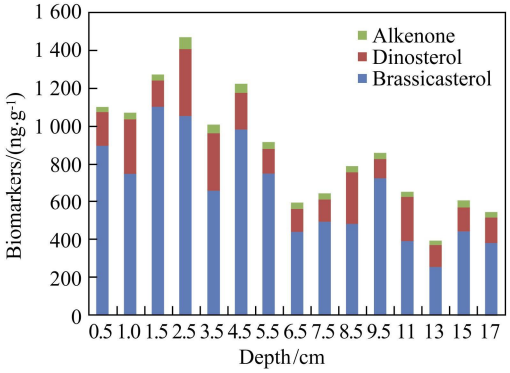

Figure 3 Changes in phytoplankton biomarker abundance in core Ⅲ-12.

The maximum content of total biomarkers in core Ⅲ-12 occurs at 2—3 cm , as well as that of brassicasterol, dinosterol and alkenones (Figure 3, Table 1). Based on the ^{210}Pb dating result, the 2—3 cm depth corresponds to deposition during the 1980s. During this decade there were two well-documented occurrences of the El Niño phenomenon[23]. This includes an event that lasted from 1982—1983 and another from 1986—1988. Similar, sudden warming phenomena occurred from 1972—1973[23], a time that corresponds to the 4—5 cm depth of the core. At this depth, biomarker contents in the sediments reach their higher value. However, striking cooling events occurred during periods that correspond to depths of 3—4 cm and 6—7 cm (1973—1976 and 1954—1957, respectively)[23]. At these depths the biomarkers in the sediments are at their minimum value. Occurrences of both warming and cooling events may have affected the Prydz Bay area of Antarctica, as demonstrated by the record of changes to the biomarker content of sediments from the upper ocean in the Prydz Bay area.

3.2 Change in biomarkers at different stations

The total content of phytoplankton biomarkers was found to be at its maximum at station Ⅲ-12 (1 294.3 ng·g^{-1}), followed by station Ⅲ-13 (Figure 4); while the minimum value, 215.8 ng·g^{-1}, occurred at station Ⅱ-9 (Figure 4). The OC contents of the surface sediment at station Ⅲ-12 and Ⅲ-13 reach values of 1.05% and 0.99%, respectively, with BSi contents of 85.41% and 68.20%, respectively. The Chl *a* content in the surface seawater reaches values of 5.22 μg·L^{-1} and 5.05 μg·L^{-1}, respectively. Significant positive correlation exists among the above parameters, indicating that the content of organic matter in sediments is closely associated with changes of primary productivity in the upper water column. The phytoplankton community of Prydz Bay is dominated by large cells and chain-like diatoms. The growth rate of phytoplankton is strongly related to the type of environment, as is evident from the densest area of phytoplankton growth, which is located within

Prydz Bay south of 67°S[24]. Within this central region of Prydz Bay, the upper water column is relatively stable, and thus favorable for reproduction within the phytoplankton population. Therefore, phytoplankton cell abundance, primary productivity and new productivity are comparatively high.

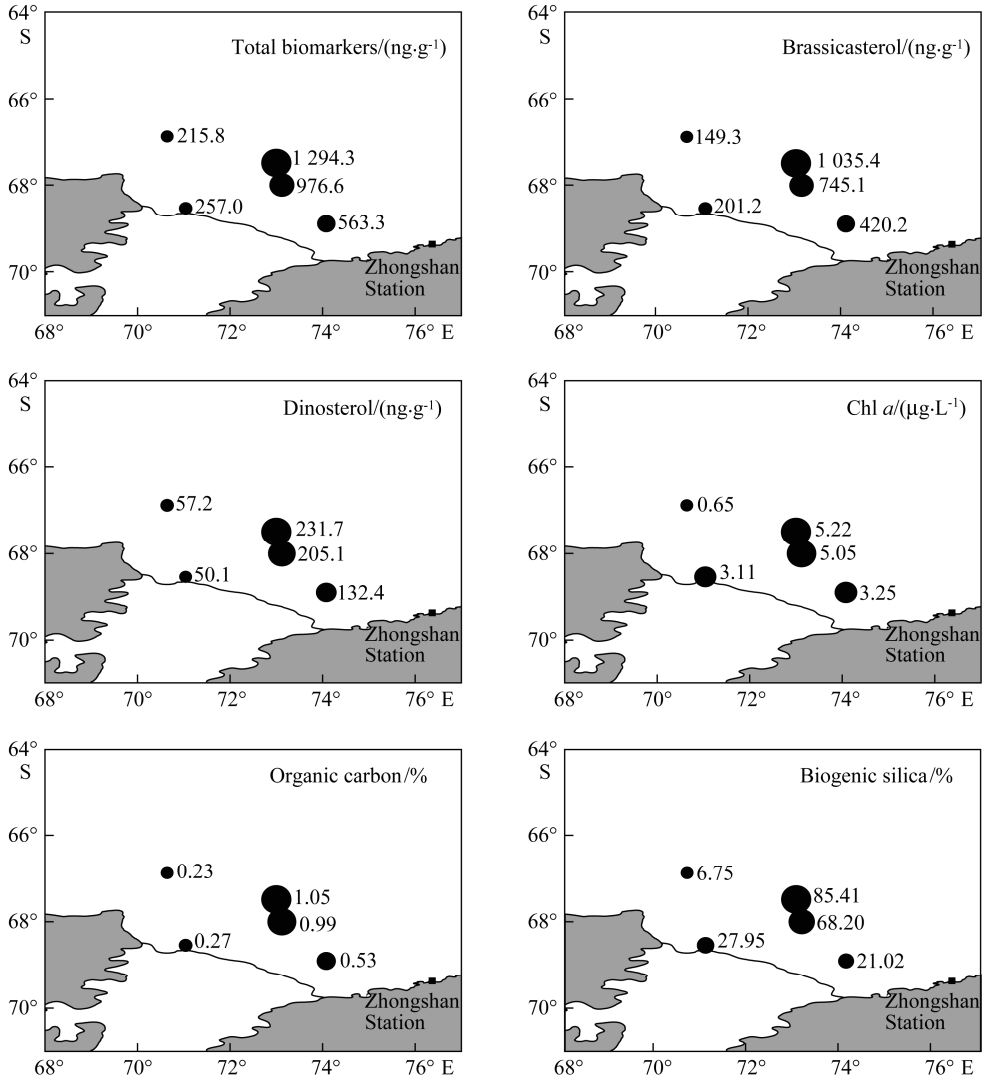

Figure 4 Distributions of biomarkers, OC and BSi in surface sediments and Chl *a* in the surface water of Prydz Bay.

The total content of biomarkers and OC in surface sediments at Station IS-4 and IS-11 are 563.3 ng·g^{-1} and 257.0 ng·g^{-1}, and 0.53% and 0.27%, respectively, with comparatively high content of Chl *a*. However, because these two stations are adjacent to the ice shelf and continental margin, the period of open waters formation is short and the ice coverage rate is relatively high[25]. As a result, the production period is short, with low productivity output. At station Ⅱ-9 (located on the Fram Bank), the content of biomarkers, OC, BSi, and Chl *a* are comparatively low. Water depth at this station is shallow, with the continental shelf of Prydz Bay forming the ocean bottom in the south, while north of 66°S is the continental slope. Importantly, the continental slope is located near the boundary of Antarctic Divergence, where a marked salinity boundary occurs in the Southern Ocean. Owing to the impact of perennial westerly wind drifts and the storm effect of the westerlies, the upper water column mixes intensely here. Such poor vertical stability of the water column is unfavorable for phytoplankton production.

4 Conclusions

(1) This study has focused on the phytoplankton community structures in the Prydz Bay region of East Antarctica. Using brassicasterol, dinosterol and alkenones as biomarkers to reconstruct phytoplankton biomass, it has been shown that in the past ~100 years, the total amount of phytoplankton markers varied from 391.0—1 470.6 ng·g^{-1}. The phytoplankton biomass in the study area has thus increased during this time, most likely as a result of climatic changes in the Prydz Bay region. The biomarkers in sediments also

reflect recorded changes in productivity in the upper water column.

(2) The total content of biomarkers, OC and BSi in surface sediments from Prydz Bay is closely related to the Chl *a* content and primary productivity in the upper water column. Maximum values occur in the central region of circulation in Prydz Bay, which indicates that the content of phytoplankton markers buried in the sediments is consistent with the diatom community. The seafloor sediment record thus corresponds to processes in the upper water column, indicating that phytoplankton markers in sediments of Prydz Bay are sensitive indicators of the phytoplankton biomass within the upper water column.

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