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Geochemical characteristics of biogenic barium in sediments of the Antarctica Ross Sea and their indication for paleoproductivity

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In this paper, the biogenic Ba of Column R11 in the Antarctic Ross Sea and its implications to the paleo oceanographic productivity since the late of Late Quaternary were discussed, combined with the organic carbon, opal and biogenic calcium carbonate. The biogenic Ba contents ranged from 51.8 to 508.4 µg/g overall, exhibiting a gradually rising trend from the bottom to the top. It highly correlated both with TOC and opal, revealing that on one hand biogenic Ba can be used to study the change of productivity in the Ross Sea; and on the other hand, the marine productivity gradually increased since the late Pleistocene. The new productivity based on Francois model varied from 0.40 to 233.90 gC/(m^2•a). The high values were mainly concentrated at the depth from 32 to 48 cm, but the new productivity values of the bottom were lower. It was inferred that the change in marine productivity in the Ross Sea was possibly affected by the ice cover since the late Pleistocene.

[**Keywords:** Biogenic barium; Geochemical characteristics; Paleoproductivity; The Antarctica Ross Sea]

Introduction

Marine primary productivity is the amount of organic carbon converted from inorganic carbon by planktons within unit time and unit area in the upper ocean[1,2]. Research on marine productivity contributes to further understand global carbon cycle, marine environment and atmospheric composition[3-6]. The direct determination of the marine paleoproductivity is unachievable, and therefore, exploring effective proxies has become the key. Abundant paleo oceanographic information is recorded in marine sediments, including the surface seawater productivity. Organic carbon, biogenic carbonate, biogenic silica, and paleontological fossils are usually used to invert the paleoproductivity[7-10], but these proxies are restricted by some factors to varying degrees, such as sedimentation and preservation[11-13]. With the development of analytical technology, more geochemical indices are used for the reconstruction of paleoproductivity, one of these is biogenic Barium[14,15]. Studies on the high productivity area in the Atlantic and the equatorial Pacific show that there is a positive correlation between marine productivity and biogenic Ba in sediments.

The Antarctic Ocean, the area with high productivity, plays an important role in global carbon cycle and climate regulation[16,17]. However, complex hydrological condition, sea ice distribution and climate change have increased the difficulty in studying the paleoceanographic productivity. Based on the biogenic silica, nutrients, and organic matters, biogeochemistry of the upper Antarctic waters are discussed[18-21], but the characteristics of the paleo oceanographic productivity in the Ross Sea are rarely involved. Hence, in this paper, by conducting the geochemical measurement for Column R11 in the Antarctica Ross Sea, the biogenic Ba and its implication to the paleoceanographic productivity since the late of Late Quaternary are discussed, combined with the organic carbon, opal and biogenic calcium carbonate.

Regional Setting

The Ross Sea, with the geographical coordinates of 72° S-85° S and 160° E-160° W, is located in the Pacific Ocean sector of the Antarctic Ocean, adjacent to the Marie Byrd Land by the east and the Victoria Land by the west. The Ross Ice Shelf in the south covers an area of 5×10^5 km^2, supplied by both of the East and West Antarctica Shelves[22]. The water depth ranges from 200 to 1000 m. On the continental shelf, there are troughs in north-south extention, possibly caused by the expansion of the ice sheet[23]. The circulation of this area flow along clockwise direction, slowly both in the east and center, but fast in the west[24].

Since the 1960s, several countries had conducted comprehensive geological survey for oil and gas resources in the Ross Sea. According to DSDP and geophysical data, sedimentary basins of the Ross Sea were divided into Vitoria Land Basin, Central Trough and Eastern Basin[25]. The glacial-marine sediments, about five kilometers thick, were accumulated in the Eastern Basin since the late Oligocene[26]. In the Vitoria Basin, a stratum over ten thousand meters thick was formed since the late Cretaceous or early Cenozoic[27], the bad sorted deposits since Miocene were related to the strengthening of glaciation[28].

Materials and Methods

Column R11 were collected in the Ross Sea, with coordinates of 167.8° E and 74.9° S, water depth of 448 m and column length of 86 cm. The column were separated at intervals of 2 cm, and the thickness of each sample was 2 cm. 22 samples were obtained.

All measurements were completed at the State Key Laboratory of Marine Geology, Tongji University. The major and trace elements were analyzed by ICP-AES and ICP-MS, respectively. The samples were dissolved by mixing hydrofluoric acid and nitric acid, and then were diluted to certain concentrations for instrument analysis. Relative standard deviations (RSDs) of the results were below 1 % and 4 %, respectively.

Elementar Vario Cube was used for the determination of organic carbon content. The standard substance of GBW07314 and parallel samples were adopted to the precision control. RSDs of the measured values were less than 1 %.

The opal content was measured by the method of silicon-molybdenum blue colorimetry. Sodium carbonate solution was used to extract the biogenic opal in the samples, and the solution absorbance after the reaction was obtained by ultraviolet spectrophotometer. The opal content was calculated by the regression equation and the error was less than 3 %.

The calcium carbonate content was measured by the method of volume of carbon dioxide. According to the volume of carbon dioxide measured under the same temperature, the content of the standard sodium carbonate was found on the standard curve. The content of calcium carbonate was obtained by conversion and the error was below 3 %.

Moreover, four samples were selected for AMS ^{14}C of organic carbon. The test was completed at the Beta Laboratory, United States. The upper limit of AMS ^{14}C dating is 43 500 a.

Results and Discussion

Provenance and sedimentary rate

Chondrite-normalized REE partitioning patterns of Column R11 exhibited the right-leaning characteristics of the relative enrichment of LREE, the uniform content of HREE, the clear fractionations of LREE and HREE, and the negative anomaly of Eu, indicating that the sediments mainly derived from the weathering products of the upper continental crust[29]. Besides terrigenous materials, biogenic deposits were important sources of sediments in the Ross Sea. The results showed that content of $CaCO_3$ were detected in very few samples (Table 1), with the mean of 0.96 %, however, that of biogenic silica was high, with an average of 20.73 %, indicating that opal played an important role in the composition of biogenic materials in the Ross Sea.

The content of $CaCO_3$ in Column R11 was extremely low and no proper calcium carbonate shell was found, therefore, acid-insoluble components in organic carbon were selected for AMS ^{14}C. Because both of sampling position and water depth of Column R11 were similar with those of Huang et al.[30], 3045 a, the difference between the organic carbon age and the calcium carbonate age, was adopted as the recalcitrant carbon age for correction (Fig. 1). Calendar age

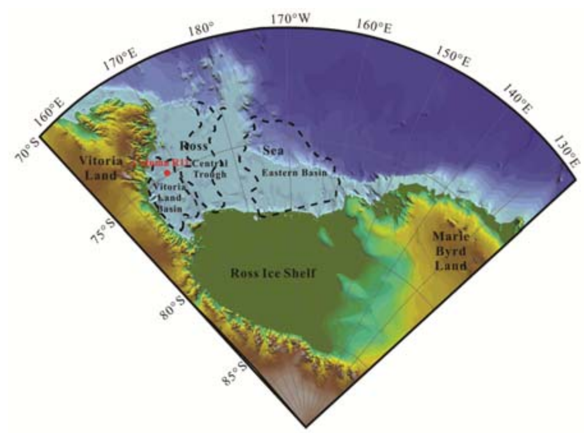

Fig. 1 — Regional unit and sampling location in the Antarctic Ross Sea

Table 1 — Results of Column R11 in the Antarctic Ross Sea

Depth /cm	Al /%	Fe /%	$CaCO_3$ /%	Organic carbon /%	Opal /%	Mn /μg·g^{-1}	V /μg·g^{-1}	U /μg·g^{-1}	Total Ba /μg·g^{-1}	Biogenic Ba[a] /μg·g^{-1}
0	4.767	2.478	N/A	1.009	26.853	390.6	81.11	5.70	832.6	508.4
4	4.397	2.223	N/A	1.035	26.674	317.6	79.02	10.00	695.0	396.0
8	4.439	2.260	N/A	1.071	27.765	318.0	77.94	6.29	681.8	380.0
12	4.368	2.238	N/A	1.097	24.196	313.4	76.54	5.26	672.6	375.5
16	4.546	2.427	N/A	1.036	26.038	321.9	80.90	6.80	667.8	358.6
20	4.299	2.220	N/A	1.090	26.323	297.9	81.89	6.69	694.7	402.3
24	4.259	2.362	N/A	1.045	26.212	308.5	79.77	6.19	678.2	388.5
28	4.264	2.449	N/A	1.072	26.745	310.8	85.01	6.78	696.5	406.5
32	4.230	2.438	N/A	1.062	27.196	298.7	87.40	6.11	720.9	433.2
36	4.616	2.234	N/A	0.910	23.082	327.6	82.16	5.17	689.7	375.7
40	4.481	2.477	N/A	0.953	26.923	328.6	87.62	5.21	721.1	416.3
44	4.559	2.376	N/A	0.859	22.835	341.1	85.41	4.60	663.1	353.0
48	4.487	2.398	N/A	0.867	23.900	320.4	87.43	5.25	668.0	362.8
52	4.495	2.491	N/A	0.916	23.900	326.5	91.23	5.55	621.2	315.5
56	4.549	2.413	N/A	0.933	20.700	333.1	89.48	4.96	619.3	309.9
60	4.734	2.471	N/A	0.865	20.254	356.4	91.25	4.72	674.5	352.5
64	5.006	2.564	2.030	0.963	15.652	433.6	92.16	4.44	603.3	262.9
68	4.747	2.339	0.300	0.581	12.070	388.3	64.77	3.28	445.5	122.7
72	10.787	2.787	0.460	0.425	7.162	470.8	71.35	2.39	447.6	59.3
76	10.210	2.464	0.670	0.389	3.099	447.7	63.96	2.58	458.5	91.0
80	10.096	2.832	1.020	0.345	4.960	576.8	65.49	2.04	415.2	51.8
84	10.566	2.879	0.910	0.334	5.653	494.3	66.53	2.49	476.0	95.7

[a]the difference between total Ba detected in sediments and terrigenous Ba calculated by formula (1).

Table 2 — AMS ^{14}C data of Column R11 in the Ross Sea

Depth / cm	Material	AMS ^{14}C age / a BP	Calendar age / cal a BP	Age range/ cal a BP, 1σ
8	organic carbon	4 670 ± 30	1 479	1 470 - 1 517
28	organic carbon	7 160 ± 30	4 556	4 521 - 4 579
48	organic carbon	7 470 ± 30	4 931	4 878 - 4 942
78	organic carbon	15 250 ± 50	14 055	14 003 - 14 103

was obtained using age calibration curve of SHC all 13 and software of Calib 7.0.4[31]. The dating results were listed in Table 2. Linear interpolation and extrapolation were used to calculate the ages of Column R11.

Figure 2 showed that the linear deposition rates were significantly different at various stages, and exceeded 50 cm/ka from 4.6 to 4.9 ka BP.

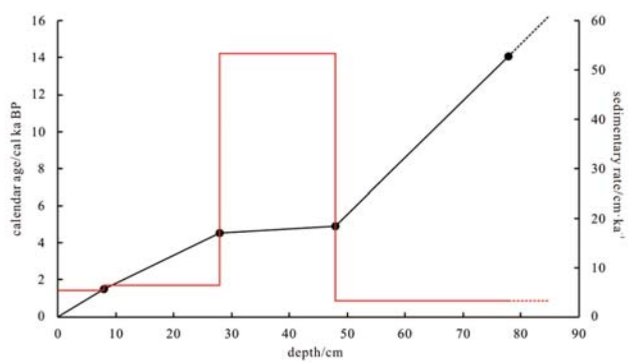

Fig. 2 — AMS ^{14}C age and sedimentation rate of Column R11

Estimation of biogenic Ba

Ba in marine sediments was mainly derived from terrigenous alumino silicates and barium sulfate crystals, a small portion was adsorbed in carbonate and iron-manganese oxides, and in addition, hydrothermal deposition was also an important source of Ba in some areas[32]. There were no reports of Quaternary seafloor hydrothermal activities in Ross Sea and nearby areas, so there was basically no hydrothermal Ba. Calcium carbonate was not detected in most samples of Column R11, and the contents of Fe and Mn were lower than those in the upper continental crust[33], indicating that no obvious iron-manganese oxide had no obvious enrichment. These all revealed that the content of Ba adsorbed in carbonate and iron-manganese oxide were remote. Therefore, Ba in column sediments was mainly derived from terrigenous and biogenic source.

There were two ways to achieve measurement of biogenic Ba, i.e., deduction and extraction. Because of the uncertainty in the selection of reagent and the process of extraction, deduction was also used to directly calculate the content of biogenic Ba. Biogenic Ba is the difference between the total Ba in the sediment and the terrigenous Ba in the silicate, the formula is as follows[15].

$$Ba_{bio} = Ba_{total} - Al_{sed} \times (Ba/Al)_{terr} \quad \dots (1)$$

Where, Ba_{bio} is the biogenic Ba, Ba_{total} is the total Ba in the sediments, Al_{sed} is the total Al in the sediments$(Ba/Al)_{terr}$ is the ratio of Ba/Al in the terrigenous clastics. Some scholars also used Ti to carry out the deduction of terrigenous Ba[34], but considering a certain amount of ilmenites in the surface sediments of the Antarctic Prydz Bay, this could lead to the abnormal enrichment of Ti. Study showed that "excess aluminum", the part more than the Al/Ti ratio in PAAS, existed in the areas where the deposits were dominated by biogenic materials. Dymond et al.[35] proposed that "excess aluminum" had a significant positive correlation with the opal in the equatorial Pacific. The ratio of Al/Ti of Column R11 ranged from 12.95 to 16.07, with the mean of 13.93, less than 16.77 of PAAS[33], and there was no positive correlation between Al and opal in column sediments (Figure 3), but negative correlation. These indicated that Al was mainly derived from terrigenous materials, and not adsorbed on opals. In this paper, it was appropriate to select Al as background element.

Because the geochemical characteristics of sediments in the Ross Sea were similar to those of upper continental crust[29], this paper adopted 0.0068 of UCC as the ratio of Ba/Al in the terrigenous materials[30], which was very close to 0.0067 of sediments in the southern Weddell Sea[19]. The content of biogenic Ba ranged from 51.8 to 508.4 μg/g, with an average of 309.9 μg/g. The biogenic Ba showed a gradually rising trend overall from the bottom to the top (Figure 4), specially, increased significantly at the depth of 68 cm, corresponding to the interpolation age of about 11 ka BP. This revealed that the marine productivity in Ross Sea gradually increased since the late Pleistocene.

Correlation analysis

Although preservation rates varied, TOC and opal were still effective proxies for marine productivity[19,36]. Figures 3 and 4 showed that there were similar vertical variation of content and a higher positive correlation (R^2=0.91) between TOC and opal, indicating that both of them revealed the change of marine productivity in the Ross Sea. The study showed that diatom was the dominant species of phytoplankton around the Antarctica coastal area, accounting for about 75 % of the primary productivity[37]. The biogenic Ba and TOC both had high correlation with opal (Fig. 3), proving that, on

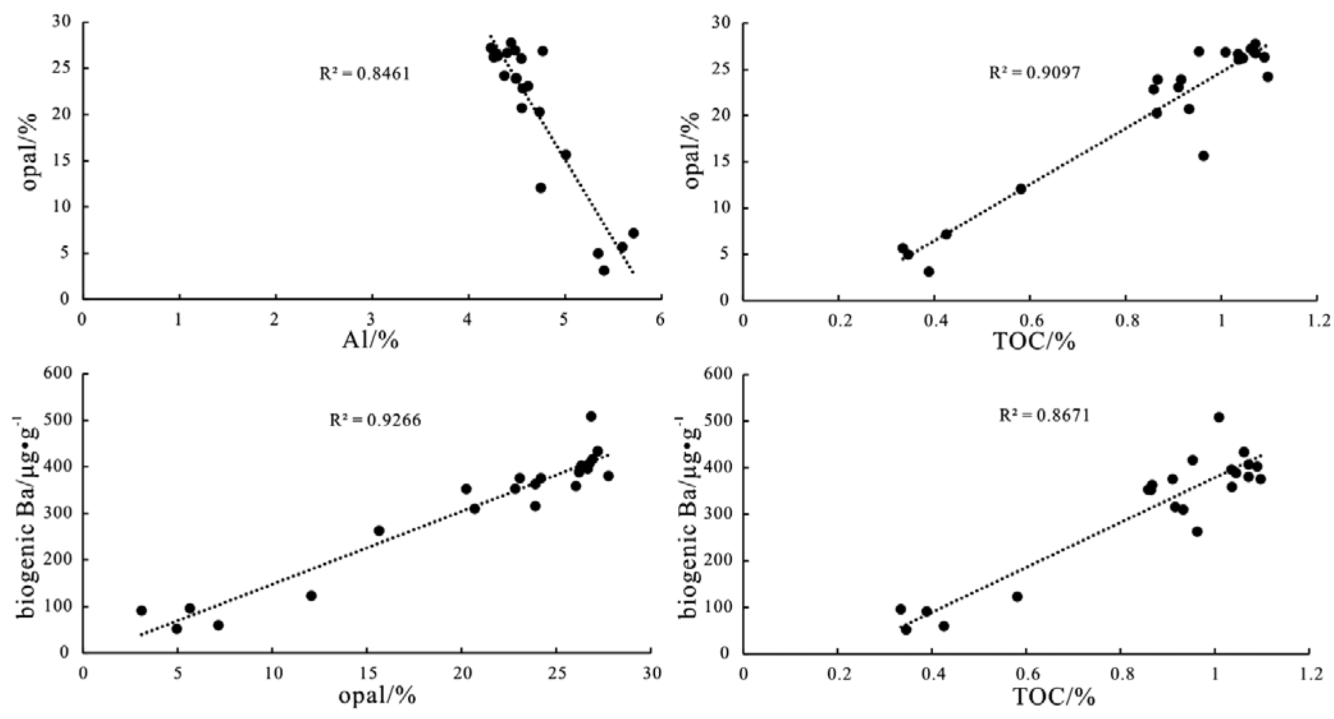

Fig. 3 — Correlation of several elements of Column R11

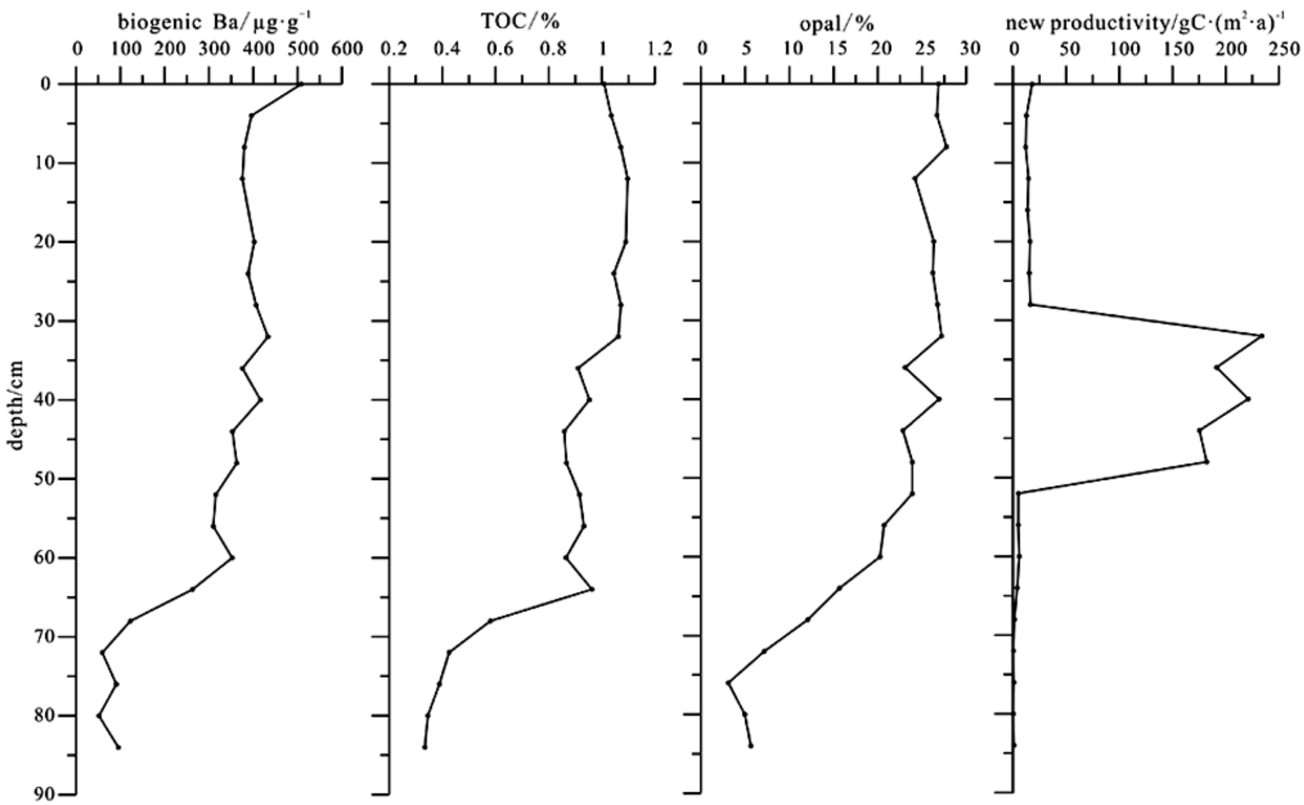

Fig. 4 — Vertical variation of components in Column R11

the one hand, the biogenic Ba could reflect the changes of marine productivity; on the other hand, it was feasible to use the Al element as the background element for deducting the terrigenous Ba. The correlation between biogenic Ba and TOC was lower than that between biogenic Ba and opal, probably because the preservation rate of TOC in sediments was lower than that of opal. In addition, TOC and biogenic Ba did not have a negative correlation, indicating that the degradation of organic matter in sediments did not excessively cause the decomposition of sulfate. Studies suggested that some substances secreted by siliceous organisms contributed to a suitable microenvironment for the formation of opal[38], which might be an important reason for the higher correlation between biogenic Ba and opal.

The content of biogenic Ba in the sediments was directly related to the productivity of upper water, and also influenced by the oxidation and reduction environment[39]. Generally, the oxidative environment was more conducive to the preservation of barite. Each trace element had distinctive redox sensitivity and exhibited unique occurrence in different oxidation-reduction intervals[40]. V and U were typical oxidation-reduction sensitive elements, significantly enriched in anoxic marine sediments and insufficient in oxidizing marine sediments. The contents of V and U in Column R11 were generally low (Table 1), close to those (V = 130 μg/g, U = 3μg/g) in oxidized marine sediments[41]. This indicated that the sedimentary environment was oxidizing, and barite was hard to decompose under this environment. Moreover, in the oxidizing environment, the preservation of barite was not affected by the diagenesis[42].

Indication for paleo productivity

The calculation models of marine paleo-productivity based on biogenic Ba were proposed by Dymond et al.[15] and Francois et al.[43], respectively. In fact, the latter was the simplification of the former. Bonn et al.[19]selected both of the models to estimate the paleo productivity in the Antarctic continental margin sea and achieved satisfactory results. In this paper, the Francois model was used to estimate the paleo productivity of Column R11. The dry density of sediment was 1 g/cm^3, proposed by Atkins and

Dunbar[44]. The new productivity of Column R11 ranged from 0.40 to 233.90 gC/ (m^2•a), with an average of 52.13 gC/ (m^2•a). The high values of new productivity were mainly concentrated at the depth from 32 to 48 cm, with an average of 200.75 gC/ (m^2•a), determined by the higher deposition rate (Fig. 2). Generally, the greater the mass accumulation rate is, the higher the preservation of biogenic Ba is[15]. The new productivity values at the bottom were low, corresponding to the last stage of late Pleistocene. According to the quantitative analysis for the productivity of the Antarctic continental margin sea, it was found that the expansion and contraction of the glacier were important factors causing changes of marine productivity in different periods, because the coverage of glacier severely restricted the acquisition and utilization of light by marine organisms[19]. It was inferred that the change of marine productivity in the Ross Sea was possibly affected by ice cover since the late Pleistocene.

It was noted that the productivity model was based on the data of the equatorial India and the Atlantic, whether these models were applicable to the Antarctic Ocean remained to be further studied and verified. In addition, the quantification of the biogenic Ba based on deduction calculation could result to certain deviations. Therefore, how to extract biogenic Ba more easily and accurately was still an important direction for future study.

Conclusion

The content of biogenic Ba based deduction method ranged from 51.8 to 508.4 μg/g. The biogenic Ba exhibited a gradually rising trend overall from the bottom to the top, revealing that the marine productivity in Ross Sea gradually increased since the late Pleistocene.

Biogenic Ba was highly correlated with both TOC and opal, and could be used to study the change of productivity in the Ross Sea. The degradation of organic matter in sediments did not excessively cause the decomposition of sulfate, and the oxidation environment was more conducive to the preservation of barite.

The new productivity of Column R11 based on Francois model varied from 0.40 to 233.90 gC/ (m^2•a). The high values were mainly concentrated at the depth from 32 to 48 cm, but new productivity values of the bottom were lower. It was inferred that ice cover possibly affected the change of marine productivity in the Ross Sea since the late Pleistocene.

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