

Relating the composition of continental margin surface sediments from the Ross Sea to the Amundsen Sea, West Antarctica, to modern environmental conditions

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Abstract Investigating the multiple proxies involving productivity, organic geochemistry, and trace element (TE) enrichment in surface sediments could be used as paleoenvironment archives to gain insights into past and future environmental conditions changes. We present redox-sensitive TEs (Mn, Ni, Cu, U, P, Mo, Co, V, Zn, and Cd), productivity-related proxies (total organic carbon and opal), and total nitrogen and CaCO₃ contents of bulk surface sediments of this area. The productivity proxies from the shelf and coastal regions of the Ross and the Amundsen seas showed that higher productivity was affiliated with an area of nutrient-rich deep water upwelling. The upwelling of weakly corrosive deep water may be beneficial for preserving CaCO₃, while highly corrosive dense water, if it forms on the shelf near the coastal region (coastal polynya), could limit the preservation of CaCO₃ in modern conditions. There were no oxic or anoxic conditions in the study area, as indicated by the enrichment factors of redox-sensitive TEs (Mn, Co, and U). The enrichment factor of Cd, which is redox-sensitive, indicated suboxic redox conditions in sediment environments because of high primary productivity and organic matter preservation/decomposition. The enrichment factors of other redox-sensitive TEs (P, Ni, Cu, V, and Zn) and the correlations between the element/Ti ratio with productivity and nutrient proxies indicated that the organic matter decomposed, and there was massive burial of phytoplankton biomass. There was variation in the enrichment, such that sediments were enriched in P, Mo, and Zn, but depleted in Ni, Cu, and V.

Keywords redox, nutrient, productivity, shelf and coastal region, offshore of Ruppert and Hobbs coasts, Ross Sea, Amundsen Sea

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1 Introduction

Multiple proxies, including indexes, concentrations, and

ratios of trace elements (TE) related to productivity and nutrients in shelf and coastal sediments, have been used to trace past relationships between sedimentary redox conditions, ocean circulation, and primary productivity (Calvert and Pedersen, 1993; Crusius et al., 1996; Morford et al., 2001; McKay et al., 2007). Changes in TEs accompanied

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by changes in productivity- and nutrient-related proxies at a single location are usually interpreted to indicate variations in ocean circulation and biogeochemical cycling during glacial/interglacial periods, and so provide insights into global climate dynamics (Wehausen and Brumsack, 2000; Paillet et al., 2002; Chang et al., 2015; Dou et al., 2015). Researchers have previously used multiple proxies to study the Mediterranean Sea and Cariaco Basin, and have reported that anoxic conditions are likely to occur within oxygen minimum zones, where there are massive burials of organic matter and bottom currents that have been relatively stagnant since ancient times (Thomson et al., 1995; Passier et al., 1999; Warning and Brumsack, 2000; Yarincik et al., 2000; Arnaboldi and Meyers, 2007). Additionally, there have been various studies of the eastern Pacific, where coastal upwelling zones drive high primary productivity (Nameroff et al., 2002; Nameroff et al., 2004; McManus et al., 2006; Chang et al., 2015). Researchers have also studied the redox chemistry of sediments, primary productivity, and nutrient levels of modern shelves and coastal regions of many parts of the South Pacific sector of the Southern Ocean (Abelmann and Gersonde, 1991; DeMaster et al., 1992; Isla et al., 2004; Baldi et al., 2010; Wagner et al., 2013; Wagner et al., 2015), but few researchers have reported information about the shelf and coastal areas of the Ross and Amundsen seas, apart from Kaiser et al. (2009), who studied shelf sediments from offshore of the Ruppert and Hobbs coasts and the Amundsen Sea. The unique oceanographic and geological setting of this region could mean that the concentrations of non-diagenetic TEs and the contents of productivity-related proxies in bulk sediments differ from those in other shelf and coastal regions. There are various reasons why the shelf and coastal sediments along Ross Sea and Amundsen Sea are different from those from other shelves and coastal regions worldwide, as follows. In this region, the sea ice and insolation vary considerably between seasons, which may affect the seasonal phytoplankton growth (Smith and Nelson, 1985; Smith and Gordon, 1997; Massom and Stammerjohn, 2010) and trigger rapid settling of biogenic organic particles on the seafloor. The nutrients in the water column could be depleted because of these seasonal variations in the primary productivity and regional variations in the nutrient pool (Smith et al., 2006), such that there would be limited export of nutrients with organic particles absorbed to the sediments. The organic matter recycling process in this region might be slow, because of the low temperature of the upper water mass (Gillooly et al., 2001), which would promote the settling of organic matter on the seafloor. This region is adjacent to a fast-changing marine-based ice sheet that includes the Ross Ice Shelf and the glaciers adjacent to the Amundsen Embayment. The detritus-laden glacier extends to the coastal region and so delivers terrigenous debris to the shelf and slope region (Mosola and Anderson, 2006), which obscures the enrichment signal of non-diagenetic TEs. The various well-ventilated water

masses present in this area, including Antarctic slope currents, Circumpolar Deep Water (CDW), Modified Circumpolar Deep Water (MCDW), and newly formed dense shelf water in coastal polynya and shelf-break regions (Budillon and Spezie, 2004; Assmann and Timmermann, 2005; Gordon et al., 2009; Padman et al., 2009), may inhibit the enrichment or remobilization of TEs under reducing conditions (Scholz et al., 2011).

Using multiple proxies to examine sediment paleo-redox conditions, nutrient levels, and productivity, researchers have explained variations in ventilation and productivity that were associated with past climate change (Chang et al., 2015; Wagner and Hendy, 2017). Therefore, investigations of past marine sediment records could help to predict future environmental change in the coastal and shelf region in the area from the Ross Sea to the Amundsen Sea. An earlier step involves investigating the TE concentrations in, and chemical characteristics of, surface sediments and then interpreting the TE enrichment of sediments with depth. Therefore, in this study, we measured the concentrations of a range of TEs, namely manganese (Mn), Nickel (Ni), Copper (Cu), uranium (U), phosphorus (P), molybdenum (Mo), cobalt (Co), cadmium (Cd), vanadium (V), zinc (Zn), barium (Ba), and titanium (Ti); the concentrations of total organic carbon (TOC) and nitrogen (TN), and the opal and CaCO₃ concentrations in surface sediments from 14 sediment cores extracted from 3 subregions along the Ross Sea and the Amundsen Sea, namely the Ross Sea Embayment, the Ruppert and Hobbs coasts, and the Amundsen Sea Embayment. We then analyzed the data to determine how the ventilation, and nutrient and organic carbon levels affected the surface sediment composition. The data reflect how the state of the high-latitude cryospheric environment has changed with change in climate in recent years, and could highlight the need to consider this region in global debates about climate change.

2 Regional setting

The study area stretches across the South Pacific sector of the Southern Ocean, from the Ross Sea to the Amundsen Sea (Figure 1). Because of its wide shelf region, polynya adjacent to the coastal region and ice shelf edge that trap sediment (DeMaster et al., 1992), and tendency for biomass blooms (Ditullio, 2000), the continental shelf adjacent to the South Pacific differs from other continental shelves worldwide. The topography of the seafloor in the study area changes rapidly from the continental shelf to the continental slope, and has several steep shelf breaks. The seafloor of the Ross Sea and the Amundsen Sea shelf region has been eroded by ice sheets that have advanced and retreated across the continental shelf, thereby removing sediments from many areas and carving numerous submarines through the basin, which has resulted in a bumpy bathymetry (Nitsche et al., 2007). Additionally, the isostatic depression

of Antarctica by the West Antarctic Ice Sheet may promote the deposition of debris from basal marine ice sheets and ice shelves close to their grounding line (i.e., the junction between the bedrock, water, and ice sheet) in the Ross and Amundsen seas (Anderson et al., 1980; Anderson et al.,

1992; Lowe and Anderson, 2002). This subglacial erosion, with the almost year-round cover of sea ice and massive icebergs in the Amundsen Sea, may lead to infrequent abundances of soft sediments and isopods (generally macrobenthic) (Kaiser et al., 2009).

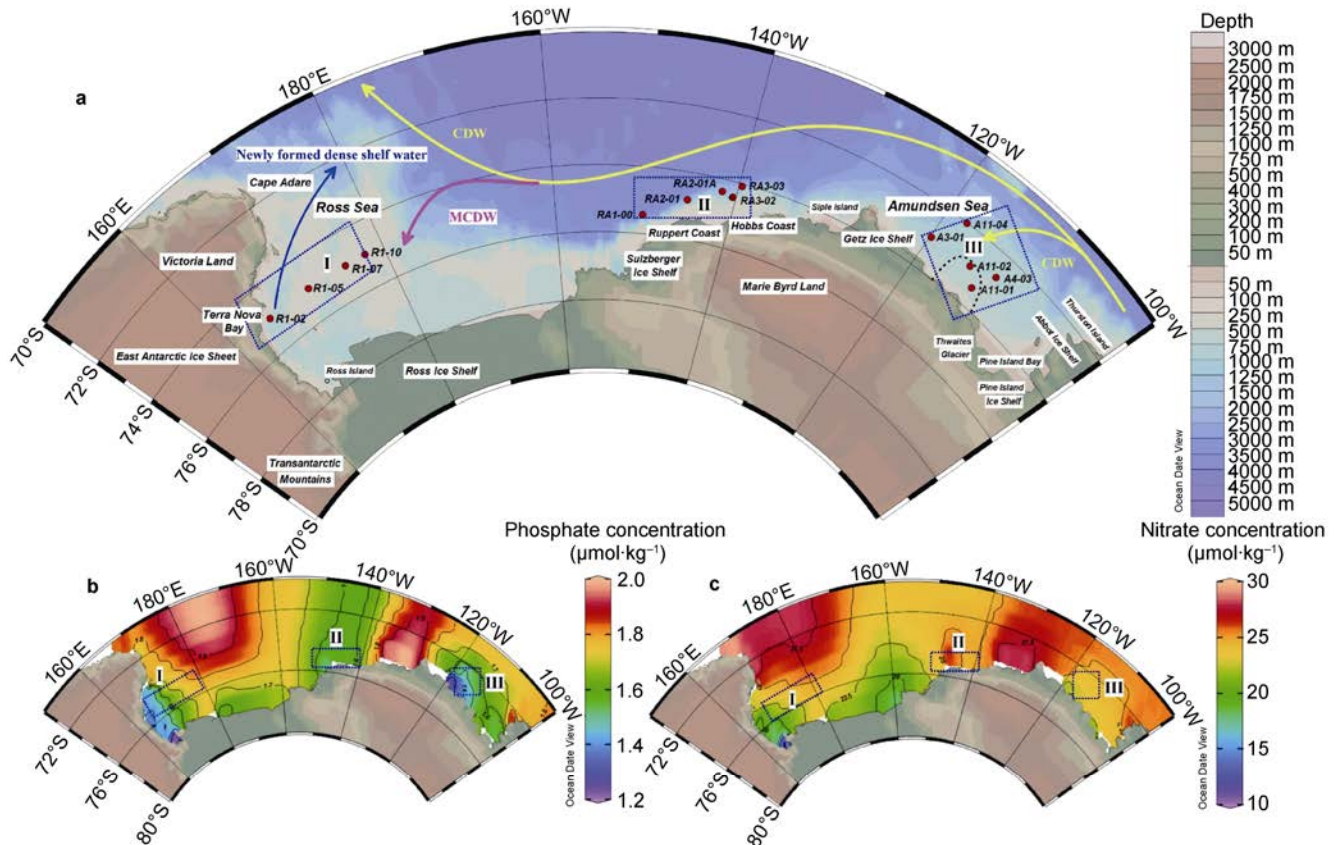


Figure 1 Locations of surface sediment sampling sites (see Table 1 for the longitude, latitude, and depth), and the phosphate and nitrate contents in the surface ocean in the study area. The blue dashed line boxes I, II, and III represent the Ross Sea, offshore of Ruppert and Hobbs coasts, and the Amundsen Sea sampling areas, respectively. The black dashed line indicates the Amundsen Sea polynya boundary (Kim et al., 2015). The phosphate and nitrate concentration data in the surface ocean are from the World Ocean Atlas 2018 (Boyer, 2018). MCDW represents modified Circumpolar Deep Water and CDW represents Circumpolar Deep Water.

Meltwater discharge and iceberg-rafting debris sediments to the shelf and coastal regions may be controlled or influenced by global climatic change (Bronselaeer et al., 2018). As the annual mean air temperature and/or precipitation increase, the deep water intrusion into the shelf region increases, leading to higher surface ablation, increases in basal melting and iceberg calving, and increases in meltwater and debris inputs (Jacobs and Comiso, 1997; Schmidtke et al., 2014; Dow et al., 2018). Furthermore, terrigenous detritus makes up a significant proportion of the sediment in the Ross and Amundsen embayments directly adjacent to the front of the ice sheet (including glaciers and ice shelves) (Sandroni and Talarico, 2006; Damiani and Giorgetti, 2008).

This study mainly considers the CDW and MCDW masses and the newly formed dense shelf water on the shelf region (Figure 1a). The warm, nutrient-rich, and

well-oxygenated CDW, the most prominent water mass that flows along the shelf break, influences the shelf region of the Ross Sea and the Amundsen Sea. The CDW is a relatively warm, salty, and nutrient-rich deep water mass (Jacobs et al., 1970; Jacobs, 1985) that can extend to a depth of about 4000 m (Budillon and Spezie, 2004). The MCDW, which is the primary source of nutrients, salt, and heat to the Ross Sea shelf region, forms when the incoming CDW is modified near the Ross Sea shelf region (Jacobs et al., 1970; Jacobs, 1985; Picco, 2000; Budillon and Spezie, 2004; Hiscock, 2004; Smith et al., 2006). The MCDW flows south onto the shelf along the western side of the Ross Sea and is modified further by cold and newly formed dense shelf water (Orsi and Wiederwohl, 2009) that forms in the coastal polynya and the edge of the ice shelf in the Ross Sea (Figure 1a) (Gordon et al., 2009; Padman et al., 2009; van Wijk and Rintoul, 2014; Gordon et al., 2015).

The phosphate and nitrate contents in the surface water in the Ross Sea and the Amundsen Sea area range from 1.4 to 1.8 $\mu\text{mol}\cdot\text{kg}^{-1}$ and from 20 to 25 $\mu\text{mol}\cdot\text{kg}^{-1}$, respectively (Figures 1b and 1c). The phosphate and nitrate contents generally follow a similar symmetrical distribution pattern, and are high near the shelf break and low in the coastal region of the Ross and Amundsen seas, apart from the nitrate content between the Ross and Amundsen seas (Figure 1c).

The fluxes of organic carbon and biogenic silica (opal) produced in the surface water in the Ross Sea were estimated at about 142 and 121 $\text{g}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$, respectively (Nelson et al., 1996). However, because large amounts of biogenic silica are preserved in the Southern Ocean, organic carbon and biogenic silica accumulation in bottom sediment were estimated at only 0.25 and 6.97 $\text{g}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$, respectively (Nelson et al., 1996). The sinking fluxes of organic carbon and biogenic silica at a depth of 400 m in the sea ice region on the Amundsen Sea shelf region were estimated at about 2.2 and 9.4 $\text{g}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$, respectively (Kim et al., 2015).

3 Materials and methods

In this study, 14 surface samples were collected during the 36th Chinese National Antarctic Research Expedition (aboard R/V *Xuelong*) using a box corer at sampling stations between 72°S and 76°S, and 165°E and 110°W in the Ross Sea and the Amundsen Sea area. Information about the sampling positions is presented in Table 1 and Figure 1a.

Most of the samples were clayey silty sand with weak-medium plasticity and non-weak viscosity, and contained gravel grains between 2 and 10 mm. Biological disturbances were apparent in surface samples collected from the shelf and coastal region of the Ross and Amundsen seas but there were no apparent biological disturbances in the sediment samples collected between 150°W and 140°W offshore off the Ruppert and Hobbs coasts. All the experiments and measurements were performed at the Key Laboratory of Marine Sedimentology and Environmental Geology of the First Institute of Oceanography. The original samples were freeze-dried and ground into 200-mesh particles with an agate mortar. The samples were split and then were dried at 105°C and 60°C, in preparation for analyzing the element and total carbon concentrations, respectively.

In preparation for trace element analysis, about 0.05 g of dried sample was weighed into a polytetrafluoroethylene flask along with 3 mL hydrofluoric acid (HF) and 1 mL nitric acid (HNO₃). The flask was placed on an electric heating plate for sealing and was heated at 170°C for 48 h. After the flask had cooled, the lid was opened and 1 mL of perchloric acid (HClO₄) was added, and then the sample was steam dried on an electric heating plate at 170°C. Nitric acid (5 mL) with a concentration of 1:1 was added to the dried sample for extraction. The sample was then transferred to a colorimetric tube, made up to a constant volume of 25 mL, and tested on an inductively coupled plasma mass spectrometer (ICP-MS, X Series II, ThermoFisher, USA). The accuracy of repeated measurements was better than 2%.

Table 1 Surface sediment sampling sites and the water depths at these sites

Site	Sample ID	Latitude	Longitude	Water depth/m
Ross Sea	R1-02	74.98°S	164.98°E	893
	R1-05	74.98°S	170.40°E	331
	R1-07	75.00°S	175.27°E	286
	R1-10	74.98°S	177.77°E	471
Offshore of Ruppert and Hobbs coasts	RA1-00	75.45°S	149.95°W	3242
	RA2-01	74.83°S	145.13°W	1893
	RA2-01A	74.38°S	141.57°W	503
	RA3-02	74.47°S	140.30°W	482
	RA3-03	74.08°S	139.63°W	2561
Amundsen Sea	A3-01	73.00°S	119.83°W	406
	A11-04	72.02°S	117.83°W	502
	A11-02	72.97°S	115.05°W	660
	A11-01	73.43°S	113.52°W	623
	A4-03	72.70°S	112.40°W	438

In preparation for measuring the total carbon, TOC and TN, about 30 mg of dried ground sample was weighed and placed in a tin boat. A small amount (2 g) of the original sample was also weighed and placed in a 10 mL centrifuge tube with 0.2 mL of 1 mol·L⁻¹ hydrochloric acid and heated in a water bath for 1 h. A further 0.2 mL of hydrochloric acid was added and then the sample was heated for a further 12 h in a water bath. The acid was washed with 25 mL of ultrapure water three times until neutral, and then dried in a water bath at 60°C. Once dry, the sample was ground, and about 30 mg was placed in a tin boat. The total and organic carbon contents of the sample were measured on an element analyzer (Vario EL III, Elementar, Germany). The total inorganic carbon was calculated as the difference between the total carbon and the TOC, and the CaCO₃ concentrations were calculated by multiplying the total inorganic carbon concentrations by 8.33 (Kim et al., 2020, Kim et al., 2015). A CaCO₃ concentration expressed as 0% indicates that the measured value of the TOC was greater than the total carbon in these samples, and may reflect systematic errors during testing.

To determine the biogenic silica concentrations, the silica was extracted by alkaline, and the silica concentrations in the extract were determined by molybdate-blue spectrophotometry (ultraviolet and visible spectrophotometer, TU-1810PC, Beijing General Instrument Co. LTD). The biogenic opal concentration was calculated by multiplying the biogenic silica concentration by 2.4, and the biogenic opal (SiO₂+nH₂O)/Si ratio was determined by assuming that nH₂O accounted for 10% of biogenic SiO₂ (Mortlock and Froelich, 1989).

4 Results and discussion

4.1 Concentrations of productivity and nutrient-related proxies

The proxies from individual sites along the shelf and coastal region from the Ross Sea to the Amundsen Sea may be modified considerably by bottom current redistribution processes (Abelmann and Gersonde, 1991) that transport large quantities of biological/detrital particles to the deep channel or the low bathymetry shelf region (Isla et al., 2004), which act as the 'sediment trap'. This means that the correlation between the production of biological particles in surface water and the preservation concentration in the sediments directly below is much weaker than it otherwise might be. Additionally, the uncertainty in the provenance and the chemical composition of reflux detrital particles may lead to errors in estimating the enrichment of non-diagenetic components. Therefore, to obtain robust conclusions, the proxy data were divided to describe three different continental shelf and coastal areas, namely the Ross Sea, offshore from the Rupert and Hobbs coasts, and the Amundsen Sea.

The total contents of all the productivity and nutrition-related proxy indicators are shown in Table 2 and their distribution in surface sediments is shown in Figure 2. Our results show that the contents of the productivity-related proxies (Ba, TOC, and opal) were high in the Ross Sea and the Amundsen Sea, and the TOC and opal contents reached 0.62% and 15.30% at site R1-05 on the Ross Sea

Table 2 Element concentration data for the bulk surface samples

Sample ID	Productivity					Nutrient	Redox									
	Ti/ %	CaCO ₃ / %	Ba/ (μg·g ⁻¹)	TOC %	Opal/ %		TN/ %	Mn/ %	Ni/ (μg·g ⁻¹)	Cu/ (μg·g ⁻¹)	U/ (μg·g ⁻¹)	Co/ (μg·g ⁻¹)	Cr/ (μg·g ⁻¹)	V/ (μg·g ⁻¹)	P/ %	Mo/ (μg·g ⁻¹)
R1-02	0.33	0.00	607.87	0.39	9.73	0.05	0.04	13.06	11.91	1.66	8.29	37.91	55.45	0.07	0.58	58.07
R1-05	0.24	0.00	426.72	0.62	15.30	0.07	0.03	14.81	12.40	1.36	6.49	60.59	47.17	0.05	0.49	49.35
R1-07	0.25	1.38	382.38	0.18	7.75	0.04	0.04	15.82	7.98	1.00	7.68	57.47	52.05	0.05	0.36	40.56
R1-10	0.22	9.53	451.67	0.23	12.49	0.04	0.04	14.18	14.17	1.25	7.68	41.75	56.49	0.05	0.22	51.21
RA1-00	0.41	0.11	625.66	0.09	3.55	0.03	0.07	24.84	19.33	2.36	12.79	47.25	72.30	0.09	0.51	90.21
RA2-01	0.47	0.00	637.89	0.10	5.71	0.02	0.08	23.17	23.96	1.85	13.74	36.21	80.43	0.10	0.49	99.01
RA2-01A	0.49	0.55	637.89	0.11	5.73	0.03	0.08	18.68	38.05	2.05	14.00	35.36	94.40	0.12	0.69	100.02
RA3-02	0.57	0.07	567.90	0.12	8.24	0.03	0.09	25.39	32.15	2.05	17.05	47.21	100.97	0.12	0.62	106.65
RA3-03	0.49	0.37	713.05	0.10	5.11	0.02	0.08	21.42	20.15	1.93	11.99	40.23	90.28	0.08	0.82	84.27
A3-01	0.40	0.61	637.69	0.15	3.64	0.03	0.05	15.54	11.97	1.54	11.37	31.77	76.54	0.09	0.41	88.33
A11-04	0.46	4.58	961.37	0.49	2.40	0.08	0.12	31.71	30.11	2.04	17.00	46.01	92.14	0.09	1.00	112.85
A11-02	0.53	0.00	822.22	0.73	11.17	0.12	0.07	32.87	32.75	2.99	16.65	50.60	113.59	0.08	0.96	188.06
A11-01	0.54	0.03	796.97	0.71	9.16	0.13	0.14	33.76	32.68	2.77	20.39	49.33	111.81	0.09	1.78	175.82
A4-03	0.51	0.59	747.92	0.69	7.20	0.12	0.16	41.04	29.17	2.52	16.59	49.43	100.16	0.09	2.39	159.88

Note: Productivity, nutrient, and redox show in subtitle represent the productivity-related proxies, nutrient-related proxy, and redox-related proxies

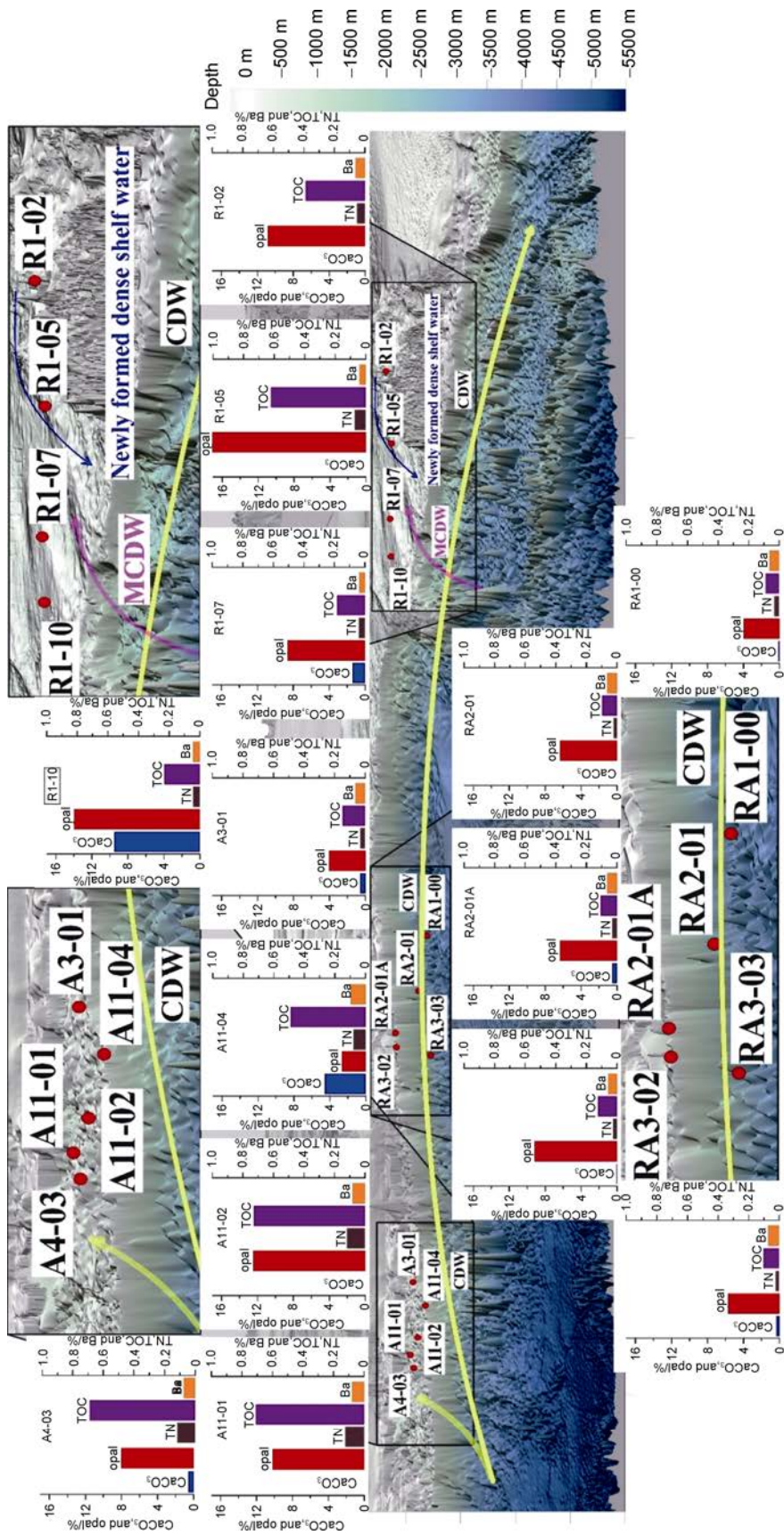


Figure 2 Spatial distribution of the productivity and nutrient-related proxy concentrations in bulk surface sediments.

shelf region, respectively. The contents of the productivity-related proxies were lowest in the sediment from the region offshore from the Ruppert and Hobbs coasts, and had minimum TOC and opal contents of 0.09% and 3.55% at site RA1-00 on the bottom continental slope, respectively. This distribution is consistent with the results of a previous study (Arrigo and van Dijken, 2003), who also found that the primary productivity was highest in the shelf and coastal region along the Ross Sea to the Amundsen Sea, and suggested that it was affiliated with phytoplankton blooms in the coastal polynya.

A trace element, Ba mainly occurs as the mineral barite (BaSO_4) in the marine environment. Previous studies suggested a potential relationship between the Ba flux and the TOC/opal flux into the seafloor (Bishop, 1988; Dymond, 1992; Francois et al., 1995; Bonn et al., 1998). Our results showed that the Ba concentration distribution in the bulk sediments was different from the TOC/opal and other productivity proxies. The Spearman Rank correlation coefficients (ρ) between the Ba and opal and TOC contents were -0.387 and 0.306 , respectively, and the Spearman Rank correlation coefficients (ρ) for the relationship between the Ba/Ti and the opal and TOC contents were 0.178 and 0.424 , respectively. This decoupling between Ba or Ba/Ti and other productivity proxies may reflect the different degrees to which opal and TOC are preserved in these three sub-regions, and will be discussed later. Moreover, all the Spearman Rank correlation coefficients for Ba/Ti and the opal and TOC contents were higher than those for the Ba concentration and the opal and TOC contents, which may indicate that the detrital dilution effect contributes to the decoupling of the Ba content and the productivity in bulk sediments around the Antarctic.

The ratio of the annual export flux of solid opal to organic carbon in the euphotic zone of the Southern Ocean is generally about 2.5 (Jennings et al., 1984; DeMaster et al., 1992). However, researchers have reported that this ratio can be more than 30 in deep sediments (DeMaster et al., 1992, Nelson et al., 1996). This difference between the organic carbon and silicon ratios and the absence of a relationship between biogenic silica-rich sediment and high primary productivity areas mean that opals are not a reliable indicator of productivity (Pondaven et al., 2000). Our results showed that there was a significant correlation between the bulk sediment TOC content and the opal concentration in the study region, with a Spearman Rank correlation coefficient (ρ) of 0.568 (Table 3), and may be related to the productivity in the study area. However, it is noteworthy that the value of ρ for the relationship between the TOC and opal contents (ρ was close to 0.5) was lower than that between TOC and TN ($\rho=0.949$), and may indicate that the conditions for preserving organic matter are relatively poor in the Ross and the Amundsen seas shelf region, where the higher oxygen-rich water ventilation is not conducive to preserving organic matter (Kim et al., 2020). Moreover, the slight increase in the TOC content that corresponded to the significant increase in the opal concentrations in sediments from offshore of the Ruppert and Hobbs coasts (Figures 2 and 3a) may reflect the ‘opal paradox’ (Pondaven et al., 2000), which indicates higher preservation of opal than organic carbon in this region. This index should therefore be used with caution and should be combined with other bulk sedimentary proxies to make a holistic judgment about the region’s productivity, especially the sedimentary environment offshore from the Ruppert and Hobbs coasts.

Table 3 Spearman Rank Correlation Coefficients of Ti normalized trace elements, productivity, and concentrations of nutrient-related proxies

	Mn	P	V	Co	Ni	Cu	Zn	Mo	Cd	U	opal	TN	TOC	CaCO ₃
Mn	1.000	-0.138	0.095	0.556	0.508	0.345	0.358	0.323	-0.200	0.081	-0.486	0.103	-0.075	0.393
P		1.000	-0.451	-0.169	-0.481	-0.064	-0.314	-0.710	-0.481	-0.231	-0.301	-0.582	-0.671	0.162
V			1.000	0.609	0.626	0.477	0.451	0.240	0.771	0.349	0.402	0.595	0.625	0.418
Co				1.000	0.705	0.582	0.754	0.266	0.305	0.332	0.015	0.602	0.462	0.356
Ni					1.000	0.323	0.468	0.451	0.618	0.424	0.191	0.618	0.539	0.338
Cu						1.000	0.552	0.253	0.279	0.292	0.169	0.395	0.354	0.147
Zn							1.000	0.332	0.292	0.459	0.051	0.627	0.576	0.016
Mo								1.000	0.292	0.327	0.130	0.760	0.691	-0.209
Cd									1.000	0.451	0.613	0.651	0.739	0.187
U										1.000	0.415	0.533	0.396	-0.162
opal											1.000	0.450	0.568	-0.376
TN												1.000	0.949	-0.052
TOC													1.000	-0.117
CaCO ₃														1.000

Notes: (1) The correlation was significant at the 0.01 level (double-tailed) in bold;

(2) The correlation was significant at the 0.05 level (double-tailed) in bold and in italic.

Similar to the productivity-related proxies, nutrient-related proxies (TN) were also significantly correlated with the TOC content, with a ρ value of 0.949, but were less strongly correlated with the opal concentration, with a ρ value of 0.450. Moreover, the significant increase in the opal concentration in sediment offshore from the Ruppert and Hobbs coasts was not accompanied by a corresponding increase in the TN concentration (Figure 3c). This suggests that the size of the nutrient pool may control the primary productivity in the Ross Sea and Amundsen Sea shelf and coastal region. However, there were minor variations in the TOC and TN contents in the sediments from offshore from the Ruppert and Hobbs coasts that were not present in the shelf and coastal sediment in the Ross and Amundsen seas (Figures 3b and 3c). These variations may reflect a shrinking of the nutrient pool caused by (1) the lower effective use of nutrients, which meant that less nutrients were absorbed from the surface water by the sediment, or (2) the relative stability of the nutrient pool in the water mass offshore from the Ruppert and Hobbs coasts caused by a lack of nutrients from other nutrient pools. These interpretations are preliminary hypotheses, which need to be

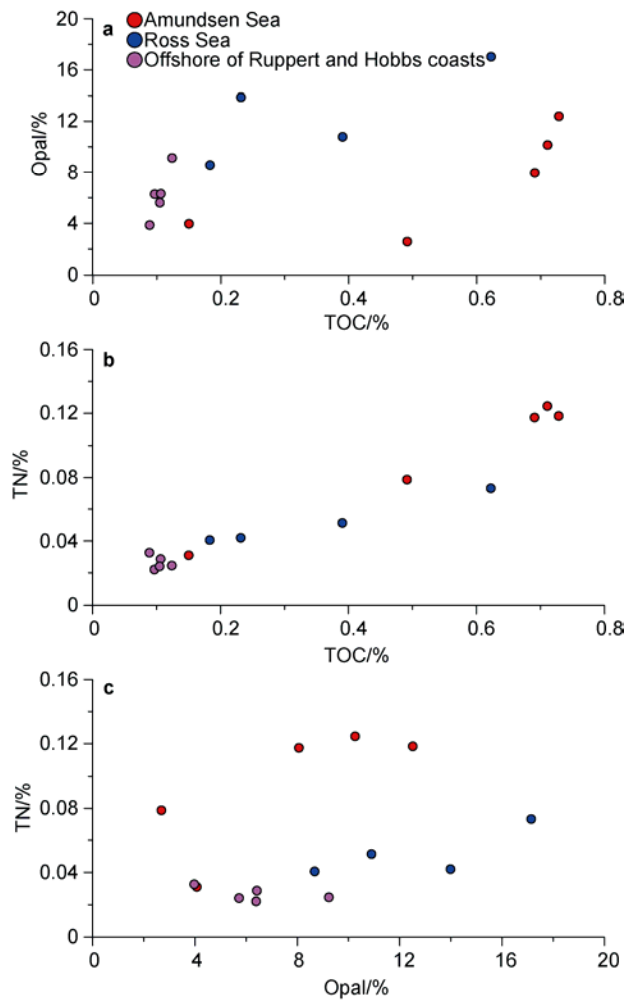


Figure 3 Scatter distribution of the TOC, TN, and opal contents in bulk surface sediments.

tested further against data for the $\delta^{15}\text{N}$ in different components of surface sediments (bulk surface sediment, diatom shells, acid-insoluble organic carbon, or apatite).

4.2 Distribution of CaCO_3

Studies have shown that CaCO_3 content peaks observed in the past in the sediments from the South Pacific sector of Southern Ocean usually corresponded to an enriched layer of foraminifera (mainly sinistral *Neogloboquadrina pachyderma*) in Antarctic continental sediment and represented higher paleo-productivity (Hillenbrand et al., 2002; Hillenbrand et al., 2009). However, the premise for this suggestion is that the CaCO_3 content in the bulk surface sediments of the Southern Ocean is influenced by carbonate (including coccolith and foraminifer) productivity, opal dilution, and its preservation efficiency (Howard and Prell, 1994). Kim et al. (2020) suggested that the CaCO_3 was preserved in the Southern Ocean shelf and coastal sediment because (1) there was limited intrusion of a corrosive bottom water mass, (2) high-energy bottom currents restricted the fine material deposition, and (3) reduced formation of corrosive dense water mass. The infrequent preservation, or absence, of CaCO_3 in surface sediment may also reflect a decrease in organic carbon preservation of deep sea sediment and $[\text{CO}_3^{2-}]$ in deep water, leading to the further potential dissolution of CaCO_3 (Yu et al., 2014). In contrast, a large supply of organic matter may lead to the preservation of large amounts of CaCO_3 (Sayles et al., 2001). Additionally, CaCO_3 was not preserved in surface sediment below the calcium carbonate compensation depth (CCD).

The CaCO_3 contents of sediments varied considerably through the region. Sediment from coastal polynya of the Ross Sea (Terra Nova polynya, 0% in both sites R1-02 and R1-05) and Amundsen Sea (Amundsen Sea polynya, 0.03% and 0% in sites A11-01 and A11-02, respectively), and offshore of the Ruppert and Hobbs coasts (0.07%, 0.37%, 0.55%, and 0.11% in sites RA3-02, RA3-03, RA2-01, RA2-01A, and RA1-00, respectively), had extremely low concentrations of CaCO_3 or no CaCO_3 . Sediments from the Amundsen shelf region (0.59%, 0.61% in sites A4-03 and A3-01, respectively) have higher CaCO_3 content than those above. The CaCO_3 contents were the highest near the shelf break of all study sites (1.38%, 9.53%, and 4.58% in sites R1-07, R1-10, and A11-04, respectively). Except for the Ross Sea shelf region, low CaCO_3 concentrations were generally accompanied by high opal concentrations (Figure 2). An earlier study showed significant fluxes of CaCO_3 moving towards the seafloor in the modern Ross Sea (Collier et al., 2000) but low fluxes of CaCO_3 settling in the modern Amundsen Sea shelf region (sea ice region) (Kim et al., 2015). However, because of intensive biogeochemical processes in the modern Southern Ocean south of the polar front, the coastal waters are closer to becoming corrosive than elsewhere in the ocean (Orr et al., 2005; McNeil and

Matear, 2008; McNeil et al., 2010). Moreover, Tamura et al. (2008) reported that the annual sea-ice production was highest in the Ross Sea (Terra Nova polynya), and high in the Amundsen Sea coastal polynya, and these areas were associated with dense water formation (Massom and Stammerjohn, 2010). Additionally, the CaCO_3 contents in the three sub-regions were not correlated with the other productivity proxies in our study (Table 2). Therefore, we suggest that the distribution of CaCO_3 may be related to (1) the newly formed dense corrosive shelf water, which limits the preservation of CaCO_3 in the coastal polynya region of the Ross Sea and the Amundsen Sea; (2) the low CaCO_3 production in surface water of the modern Amundsen Sea sea-ice zone and offshore from the Ruppert and Hobbs coasts; (3) sediment located below the local modern CCD and/or a decrease in the preservation of organic carbon in deep sediments (Figure 2); (4) the intrusion of weakly corrosive CDW/MCDW along the shelf break region in the Ross Sea and the Amundsen Sea; or (5) a dilution effect related to the high opal preservation.

4.3 Biochemical behavior of TEs and redox sensitive variations in TEs

The total concentrations of all the proxies are presented in Table 2. The TE enrichment was determined by normalizing the bulk sediment TE concentrations to Ti and then comparing with the detritus background. Here, to compare the enrichment of the TEs, the TE concentrations are given in the form of enrichment factors (EFs), calculated as follows:

$$X_{\text{EF}} = (X/\text{Ti})_{\text{sample}} / (X/\text{Ti})_{\text{PAAS}},$$

where X and Ti represent the weight concentrations of the elements X and Ti , respectively, and the PAAS value was from McLennan (2001). *EFs* are useful for rapid estimates if the TEs are from authigenic or detrital sources. *EF* values larger than 1.0 suggest TE enrichment relative to the detrital background value (Xiong et al., 2012). Similar results may be obtained by normalizing with Al, as the excess Al may be captured by sink organic-sourced particles, leading to a possible excess of Al (Murray and Leinen, 1993, 1996). This method should be used with caution because it may lead to false normalization of sediment that receives large quantities of detrital material and organic-sourced particles. Thus, the discussion and data presentation here are based on data normalized with Ti. The distribution of the EFs in surface sediment is shown in Figure 4.

The Southern Ocean has long been considered an unlikely environment for TE accumulation because the seafloor is well ventilated and the sedimentation rates are low (Crusius and Thomson, 2000). In line with this earlier finding, the sediments in the three subregions were weakly enriched by Mn, Ni, Cu, Co, U, and V. However, sediments confined to specific areas were highly enriched by TEs, reflecting the high primary productivity. This limited enrichment was obvious in areas such as the shelf break and

coastal polynya region where elements including P, Zn, Mo, and Cd may be associated with organic matter complexes or decomposition (Tribovillard et al., 2006). Manganese has a limited role as a redox substitute (Calvert and Pedersen, 1993). However, its unique geochemical behavior means it plays a prominent role in the enrichment of TEs (Ni, Cu, and Co) from oxic water to sediments, resulting in co-authigenic sedimentation processes (Tribovillard et al., 2006). Ni, Co, and Cu enrichment may occur in anoxic to euxinic conditions, by reducing the low state ion and combining with S to precipitate at the water-sediment interface (Tribovillard et al., 2006). There may also be U and V enrichment in sediment under anoxic conditions, through reduction reactions and adsorption or precipitation as UO_2 (uraninite, the most frequent form), U_3O_7 , or U_3O_8 (Morford et al., 2001; McManus et al., 2005), with insoluble matter forming when reduced ion V(III) complexes with hydroxyl (Breit and Wanty, 1991). Thus, there was no enrichment of Mn, Ni, Cu, Co, U, and V (Figure 4), and significant enrichment of Cd, in the three subregions, which suggests the sedimentary environment in the modern Southern Ocean was neither oxic nor anoxic (Tribovillard et al., 2006) and that there were mild or strong suboxic conditions in the shelf and coastal environments (Calvert and Pedersen, 1993; Rosenthal et al., 1995; Morford et al., 2001; Chaillou et al., 2002), respectively.

The preservation of organic matter did not seem to be important for the enrichment of Mn, Cu, U, and Co, as these TEs were not significantly correlated with the TOC content (Figure 5, Table 3). However, the distribution pattern of the enrichment factors of TEs such as Mn, Ni, Cu, U, Co, V, and Cd indicates that there was widespread preservation of TOC, as also discussed in section 4.1. We suggest that the sedimentary redox chemistry may be strongly influenced by the flux of organic matter into the sediments and the decomposition/remineralization of this organic matter, which then affects the accumulation of TEs by driving the consumption of oxidants and maintaining the suboxic conditions in the shelf and coastal sediment. Moreover, we suggest that the difference in the degree of decay of organic matter between the shelf and coastal sediments in the Ross Sea, Amundsen Sea, and offshore from the Ruppert and Hobbs coasts may mean that the TE enrichment differs among the subregions. For example, the Cd concentration was correlated with the TOC content, with a ρ value of 0.739. However, the high TOC content may reflect relatively well preserved organic carbon in the Ross Sea and the Amundsen Sea shelf, and coastal sediment may drive the Cd enrichment.

In contrast, the strengthened decomposition/remineralization of organic matter (lower TOC content) accompanied by the EF_{Cd} value below 1 in sediment from offshore of the Ruppert and Hobbs coasts may indicate the release of TEs complexed with organic carbon into pore water (Figures 2, 4). This process has been observed in various continental margin sediments in the South Pacific

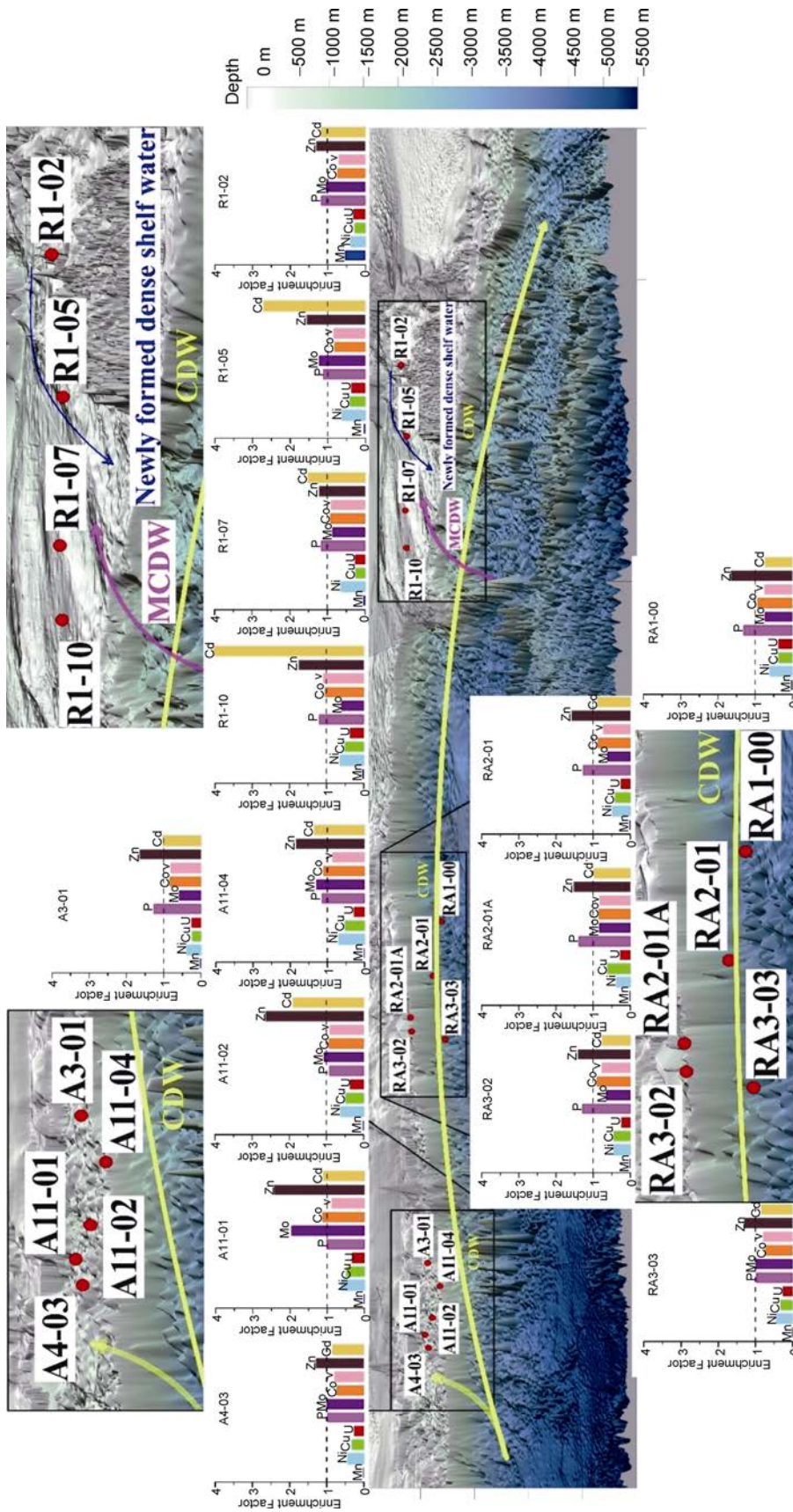


Figure 4 Spatial distribution of the TE enrichment factor in bulk surface sediments.

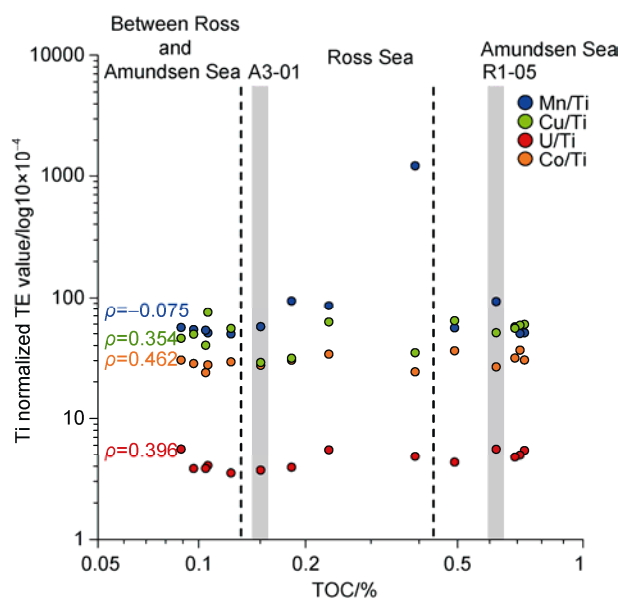


Figure 5 Scatter distribution of the TOC content with Mn/Ti, Cu/Ti, U/Ti, and Co/Ti in bulk surface sediments. The data points of sites A3-01 and R1-05 are shaded gray.

sector of the Southern Ocean (Wagner et al., 2013, 2015). Notably, although the EFs of Mn were less than 1 in all three subregions, the EF_{Mn} was higher in the sediment from the Ross Sea coastal polynya (Terra Nova Bay) than at other sites, which may reflect the formation of oxygen-rich dense water that flushing the adjacent shelf region, led to the penetration of oxygen to the sediment porewater and the oxidation of Mn^{2+} in pore water. Moreover, since Holocene, the sediment preserving the last deglacial and/or early Holocene relict manganese oxide during near modern subsequent sediment and then burial in the sub-surface sediments under relative oxic porewater conditions (Pavia et al., 2021), which may help to explain the high value (close to 1) for the EF_{Mn} in the surface sediment from the Ross Sea polynya.

Phosphorus plays a vital role in many metabolic processes (Tribovillard et al., 2006). Usually, P is released from decaying organic matter below the sediment-water interface, and P could be trapped within the sediment during this process of P remineralization (Span et al., 1992). Previous studies have reported that some TEs (including Cd, Mo, U, and Zn) were significantly enriched in phosphorites relative to their average shale background value (Prévôt and Lucas, 1980, 1986; Jarvis, 1995; Nathan et al., 1997). Middelburg and Comans (1991) reported that Cd and U were strongly enriched in phosphorites. However, these TEs may not necessarily be located in the apatite structure itself and may be associated with other minerals (mainly sulfides) and organic matter (Tribovillard et al., 2006). Overall, the P/Ti was negatively correlated with productivity and nutrient-related proxies, with ρ values of 0.582 and 0.671 for TN and P/Ti, and for TOC and P/Ti, respectively. The ρ

values between P and the other TEs were also low (Table 3). Therefore, the P enrichment may reflect the high degree of organic decomposition in deep sediment from off the Ruppert and Hobbs coasts and it may not be in the form of apatite.

Mo can be removed by organic detritus or trapped by pyrite from the water column. It is abundant relative to the biological requirements of its distribution and contrasts sharply with the nutrient-like distribution characteristics of many other TEs that are essential for organisms (Collier, 1985). Additionally, Ni behaves as a nutrient-like TE, and, as Ni complexes with organic matter, Ni will be scavenged in the water column (Tribovillard et al., 2006). Previous experiments in the Southern Ocean have suggested that Zn is a co-limiting nutrient, primarily through the regulation of silicic acid uptake by diatoms in the South Pacific sector of the Southern Ocean (Franck et al., 2000, Cochlan et al., 2002). Thus, Zn may to be added to the sediment in association with planktonic materials (Francois, 1988) and it may also exhibit the behavior of a nutrient-like TE.

Moreover, under moderate reducing conditions, V(V) will transfer to V(IV) and form insoluble hydroxides $VO(OH)_2$ when organic acids are present (Tribovillard et al., 2006). Sayles et al. (2001) interpreted pore water data and suggested that the enrichment of Mo in the Pacific sector did not imply that the surface sediment environment was fully anoxic, which is consistent with our interpretation about no anoxic conditions in the study area. Therefore, this enrichment pattern of Mo may be related to organic carbon export and decomposition associated with nutrient use by phytoplankton rather than the sediment redox conditions. Furthermore, we also suggest that, through the decomposition of organic matter, TEs (Zn, Ni, and V) could be transferred into the pore water and thereby contribute to the distribution pattern of Zn, Ni, and V. This may help explain (1) the ρ values of 0.576, 0.539, and 0.625 between TOC and Zn/Ti, Ni/Ti, and V/Ti, respectively; (2) the ρ values of 0.627, 0.618, and 0.595 between TN and Zn/Ti, Ni/Ti, and V/Ti, respectively (Figure 6, Table 3); and (3) the absence of any enrichment of Ni and V. Moreover, there was significant enrichment of Zn (Figure 4), which may relate to the massive burial of planktonic materials in these three subregions (Francois, 1988).

5 Summary and conclusions

In this study, we reported the TE concentrations in continental margin surface sediments from three subregions, namely the Ross Sea, offshore from the Ruppert and Hobbs coasts, and the Amundsen Sea. The main findings of this study are as follows:

(1) Regardless of the potential differences in the degree of preservation of TOC/opal, our data suggest that of these three sub-regions, the primary productivity should be highest in the Amundsen Sea. Productivity proxies,

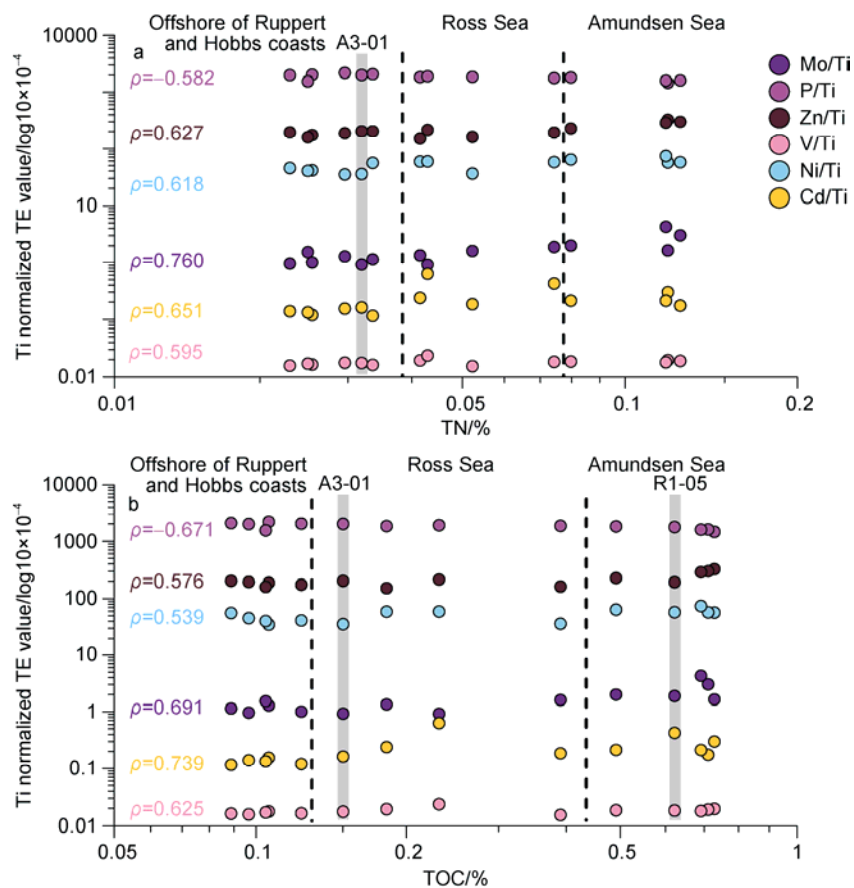


Figure 6 Scatter distribution of the TN and TOC contents with Mo/Ti, P/Ti, Zn/Ti, V/Ti, Ni/Ti, and Cd/Ti in bulk surface sediments. The data points for sites A3-01 and R1-05 are shaded gray.

including opal, TOC, and TN, could indicate the spatial variation in primary productivity in the seas around the margins of the Antarctic. We reduced the potential bias from the opal by coupling the opal concentration with the TOC and TN concentrations, even though the opal preservation may be much higher than the TOC preservation in these subregions.

(2) The CaCO₃ content in the three subregions represents the degree of preservation and mainly reflects the occupation of newly formed dense shelf water and the upwelling of CDW/MCDW in the shelf region of the Ross Sea and the Amundsen Sea and the decomposition of organic carbon in sediment from the area offshore of the Ruppert and Hobbs coasts.

(3) The EF values for Mn, Ni, Cu, U, Co, and V were lower than 1 in all the subregions, meaning that they were not significantly enriched. This indicates that the conditions in these subregions were neither oxic nor anoxic. The EF values of P, Mo, and Zn were either greater than or approximately equal to 1 in the subregions. These values may reflect the decomposition/preservation of organic carbon and settling of biogenic particles and the nutrient supply status. There was significant enrichment of Cd in the shelf and coastal region of the Ross Sea and the

Amundsen Sea, which may reflect the high organic carbon flux and/or that the conditions were conducive to preservation.

(4) Overall, the TOC, opal, and CaCO₃ concentrations in the sediments were moderately elevated, which, along with the TE concentrations, suggests that the sedimentary redox conditions are mainly controlled by the organic carbon flux or preservation and that the TE enrichment was not blurred by the ventilation of oxygen-rich newly formed water or upwelling of deep water. Our results suggest that the remineralization of sedimentary organic matter may promote stable redox conditions in the sediments across the study area, and may also control the sedimentary redox chemistry in other sectors of the Southern Ocean (Wagner et al., 2013, 2015).

Notably, the surface sediments examined in this study were mainly from the continental shelf and coastal areas, and the chemical composition of sediments from the central and inner shelf might be different from the composition of sediments from the top and bottom of the continental slope. Sediments from these other areas should be surveyed in the future to facilitate further investigations of the relationships between multiple proxies and the environmental conditions, thereby improving our understanding of paleoceanographic environments.

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