

Toxicological & Environmental Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gtec20>

Temporal variability and environmental availability of inorganic constituents in an Antarctic marine sediment core from a polynya area in the Ross Sea

Mery Malandrino^a, Edoardo Mentasti^a, Agnese Giacomino^a, Ornella Abollino^a, Enrico Dinelli^b, Silvia Sandrini^c & Laura Tositti^c

^a Department of Analytical Chemistry, University of Torino, Via Giuria 5, 10125 Torino, Italy

^b CIRSA (Interdepartmental Research Centre for Environmental Sciences), University of Bologna, Via Sant'Alberto 163, 48100 Ravenna, Italy

^c Department of Chemistry "G. Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy

Published online: 12 Mar 2010.

To cite this article: Mery Malandrino, Edoardo Mentasti, Agnese Giacomino, Ornella Abollino, Enrico Dinelli, Silvia Sandrini & Laura Tositti (2010) Temporal variability and environmental availability of inorganic constituents in an Antarctic marine sediment core from a polynya area in the Ross Sea, *Toxicological & Environmental Chemistry*, 92:3, 453-475, DOI: [10.1080/02772240903300147](http://dx.doi.org/10.1080/02772240903300147)

To link to this article: <http://dx.doi.org/10.1080/02772240903300147>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims,

proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Temporal variability and environmental availability of inorganic constituents in an Antarctic marine sediment core from a polynya area in the Ross Sea

Mery Malandrino^{a*}, Edoardo Mentasti^a, Agnese Giacomino^a, Ornella Abollino^a, Enrico Dinelli^b, Silvia Sandrini^c and Laura Tositti^c

^aDepartment of Analytical Chemistry, University of Torino, Via Giuria 5, 10125 Torino, Italy; ^bCIRSA (Interdepartmental Research Centre for Environmental Sciences), University of Bologna, Via Sant'Alberto 163, 48100 Ravenna, Italy; ^cDepartment of Chemistry "G. Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy

(Received 31 October 2008; final version received 13 August 2009)

Marine sediments are sinks and repositories of matter recirculated in the environment by a number of different processes. They behave as environmental archives, providing a key to the understanding of the processes occurring in a given region in the course of time. In this work, we characterized the inorganic composition of a surface sediment core collected in the polynya of Terra Nova Bay (TNB) in the Ross Sea, an area of major environmental interest as it hosts a number of crucial processes connecting atmospheric transport with the Southern Ocean system. The total concentrations of major, minor, and trace elements were determined. The results were treated with chemometric techniques. In order to investigate the environmental mobility of several elements, the modified Bureau of Community Reference (BCR) three-step sequential extraction procedure was applied and the partitioning of eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) into different fractions was determined. The knowledge of the metal distribution across this Antarctic sediment core allowed us to assess long-term climatic changes and possible natural background values in this specific environment. Furthermore, the results showed a separation between higher and lower sections of the core that suggests a stronger fingerprint from biogenic and geological processes, respectively.

Keywords: Antarctic marine sediments; metal; polynya area; pattern recognition; fractionation

Introduction

The Southern Ocean plays a pivotal role in the contemporary global cycle of matter (Bathmann et al. 1999; Schlitzer 2002; Takahashi et al. 2002) and in the control of climate changes (Sarmiento et al. 1998; Tréguer and Pondaven 2002). Within the Southern Ocean, the Ross Sea has been shown to support high levels of new production (Nelson et al. 1996; Smith and Dunbar 1998) and holds an important function in the removal of carbon (Ditullio et al. 2000; Sweeney et al. 2000).

*Corresponding author. Email: mery.malandrino@unito.it

The Ross Sea is the site of the most widely extended planktonic bloom in the entire Southern Ocean (Sullivan et al. 1993) that starts in the Ross Sea polynya and spreads northward with the receding ice edge.

In polar seas, polynyas are the ice-free areas of increased productivity (Smith and Gordon 1997; Saggiomo et al. 1998; Arrigo et al. 2000), which can be considered as biological “hot spots” as compared to the surrounding waters. In the western Ross Sea, Terra Nova Bay (TNB) is the site of a stable, annually recurring coastal polynya, which is maintained by the combined action of katabatic winds and of the Drygalski Ice Tongue (Kurtz and Bromwich 1985) which borders TNB to the south and acts as a physical barrier, preventing the northward drift of ice pack. Katabatic winds originate over the Antarctic continental plateau and persistently blow offshore, shifting the formation of sea ice eastward. The polynya of TNB is known to play a crucial role in the formation of the high salinity shelf water (HSSW) (Jacobs, Fairbanks, and Horibe 1985; Budillon and Spezie 2000), the densest water mass in the Southern Ocean that directly contributes to the bottom water formation. At the same time it allows the diffusion of atmospheric CO₂ into seawater, thereby supporting the ocean photosynthesis and new production.

A sediment deposit collects particles in transit and/or formed within the water column above, which eventually settle by gravity onto the bottom of a given water body. Particles in the water column originate from multiple processes driven by basin geology and hydrology, trophic chains, and atmospheric transport.

A sediment deposit constitutes a continuous record of the processes occurring in the water column in a chronological sequence, where the chemical information along a depth profile provides a more or less clearly defined image of a period in the ecosystem history.

The knowledge of the total content of elements and of the phases to which they are bound permits both to obtain an estimate of the natural variability of inorganic species and/or to point out the occurrence of a possible local and/or global anthropogenic contamination (Ciaralli et al. 1998; Frignani et al. 2003). The sources of the elements have different intensities in the course of time; furthermore they are able to produce fractionation/enrichment of single elements with respect to a purely geophysical environment: for these reasons the concentration profiles of such elements with depth are not generally uniform, yielding a chronological sequence of chemical data useful to understand each particular ecosystem.

Many studies on ocean sediments have been and still are conducted in Antarctica, with the aim of either investigating ocean circulation and basin characteristics on the geological time scale or studying the role of primary and net production at this high latitude, especially in connection with the role Antarctic Ocean plays against the build-up of atmospheric CO₂ in the Earth troposphere (Diekmann and Kuhn 1999; Isla et al. 2004; Wilson et al. 2007; Pike et al. 2008). In any case, the studies focused on recent sedimentation in this region are less common and limited. Top sediments, due to their recent formation, may contain traces of local and/or distant anthropogenic pollution following the inception of the Industrial Era. They are widely studied in highly anthropized areas where pollution history can be effectively reconstructed by sediment layers dating and chemical characterization.

In this work, we determined the concentrations of 20 elements (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V, and Zn) in a short sediment core collected in the polynya of TNB during the Italian Expedition carried out in 2003–2004 within the framework of the Italian National Program for Research

in Antarctica (PNRA). The data obtained were analyzed by chemometric techniques. Finally, in order to acquire information on the element mobility and on the geological and/or biological components with which the metals can be associated, the partitioning of eight metals, namely Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, into different fractions was determined with the modified Bureau of Community Reference (BCR) three-step sequential extraction procedure.

Experimental

Study area

The polynya of TNB is characterized by high productivity (Saggiomo et al. 2002), although it is less productive than the southernmost Ross Sea polynya (Goffart, Catalano, and Hecq 2000).

In this study, we considered a site, indicated as “site D”, located in the western sector of the Ross Sea continental shelf within the polynya of TNB at 75° 06' S and 164° 28' 5" E, as shown in Figure 1. The sediment core was collected in this area at a depth of 972 m during the 2003–2004 PNRA Campaign. Surface sediments in the Ross Sea are usually composed of unsorted ice-rafted debris, siliceous, and calcareous biogenic debris and terrigenous silt and clays (Dunbar et al. 1985). Coarse terrigenous deposits predominate in site D, due to the inputs of the David and Campbell glaciers.

Sampling and sample pre-treatment

A box corer was used in order to collect the sediment, then a plastic cylinder was inserted into the sediment to obtain one core, 22 cm long and with a diameter

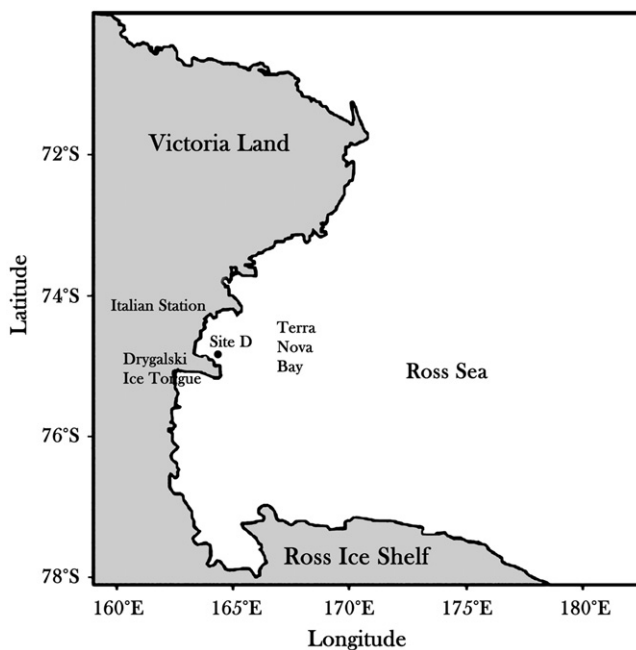


Figure 1. Map of Terra Nova Bay. The study site is marked with a black circle.

of 12 cm. Immediately after collection, the sediment core was sub-sampled to obtain sections 1 cm thick and stored at -20°C in precleaned polycarbonate Petri capsules until chemical processing and analysis. Before analysis, the core sections were left to thaw out and air-dry, and visible marine organisms were removed by hand in a clean environment under a Class-100 laminar flow bench-hood. Afterwards they were stored in polycarbonate bags for all subsequent analyses. Sample handlings were always performed under controlled conditions to minimize the contamination. The moisture content of the sediment was determined by drying a sub-sample of sediment at 105°C for 24 h until constant mass was attained. Moisture contents were used to calculate all sediment characteristics on a dry mass basis.

Apparatus and reagents

A Varian Liberty 100 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was used to determine the elements whose concentrations were higher than the detection limits of the instrument. Element concentrations close to or lower than the detection limits for ICP-AES were determined with a Perkin Elmer Analyst 600 or a Perkin Elmer 5100 Graphite Furnace Absorption Spectrometer (GF-AAS) equipped with Zeeman-effect background correction. A Milestone MLS-1200 Mega microwave laboratory unit was used for the dissolution of the samples. All the reagents used were of analytical grade. Water was purified in a Milli-Q[®] system. Standard element solutions were prepared from concentrated stock solutions (Merck Titrisol).

Analytical procedure

Determination of total concentrations

Sediment samples were digested in a microwave oven. Sample aliquots of 100 mg were treated with a mixture of 5 mL of aqua regia and 2 mL of hydrofluoric acid in PTFE bombs. Four heating steps of 5 min each (at 250, 400, 600, and 250 W respectively), followed by a ventilation step of 25 min, were applied. Finally 0.7 g of boric acid was added, and the bombs were further heated for 5 min at 250 W and again cooled by ventilation for 15 min. At the end of the treatment, the samples appeared completely dissolved. Prior to the instrumental analysis, the resulting solutions were centrifuged at 4500 rpm for 15 min and diluted to 50 mL with HPW. Elements were determined by ICP-AES or GF-AAS depending on the element concentration level. Lutetium (1 mg L^{-1}) was used as an internal standard in ICP-AES determinations. Matrix modifiers were employed to determine As, Cd, Co, and Pb by GF-AAS.

All experiments were performed in triplicate and blanks were run simultaneously. The standard solutions for the instrumental calibrations were prepared in aliquots of blanks. Accuracy and precision of total concentrations were evaluated through the use of standard reference materials (NIST SRM 2702 Marine sediment and MURST-ISS-A1 Antarctic marine sediment). Concentrations of organic matter and carbonates were determined by thermogravimetry with a Setaram TAG24 double furnace apparatus.

Element fractionation

The modified Bureau of Community Reference (BCR) sequential extraction procedure was used to obtain information about the nonresidual fractionation of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The procedure used is reported in detail elsewhere (Quevauviller 2002; Malandrino et al. 2009).

Extracts were analyzed by ICP-AES or GF-AAS depending on the metal concentration levels. Calibrations were performed with standard solutions prepared in aliquots of sample blanks. To determine cadmium and lead in the extracts of the third fraction, it was necessary to use the standard additions method. Matrix modifiers were employed to determine Cd, Cr, Cu, and Pb.

All experiments were performed in triplicate and the corresponding blanks were run simultaneously. The relative standard deviations of the results were generally within 10%. Higher uncertainties were observed, in some cases, when low concentrations were extracted. The analytical accuracy of the data was confirmed by applying the sequential extraction procedure to a standard reference material (BCR 701 Lake sediment). Quality assurance of the BCR technique was measured by comparing the sum of the four BCR steps to the independent aqua regia extraction of the standard reference material used, with the four steps of the BCR procedure extracting 88–101% of the elements recovered by aqua regia digestion.

Marine sediment data relative to both total element concentration and different BCR fractions were processed by principal component analysis (PCA) and hierarchical cluster analysis (HCA) with XlStat 4.4 software package. When the concentrations were below the detection limit, a random value (chosen with the “Random” function of Microsoft Excel) between zero and that limit was inserted, in order to be able to apply PCA and HCA without losing any data.

Results and discussion

Sediment morphology

A visual inspection showed that the sediment core had a likely oxidized brownish top layer of 1 cm. From 1 cm to the end the sediment was pale grey with black stripes, which were particularly pronounced from 17 to 22 cm. The visual lithology seems to indicate oxic conditions at the sediment–water interface and anoxic–sulphidic conditions in the rest of the core. The sandy component was higher in the lowermost part of the core and the presence of gravel was significant. This can be due to the proximity of continental sources which can supply coarse sediment by glacial drainage.

The sediment accumulation rates in the Ross Sea and in general in Antarctica are very low (Demaster, Ragueneau, and Nittouer 1996; Domack et al. 1999). Recently, Frignani et al. (2003) estimated a value of the order of 1.73 cm ka^{-1} associated with a flux of $19.46 \text{ g m}^{-2} \text{ y}^{-1}$ for sediments of the polynya region considered in the present study.

Total concentrations

The element concentrations and relative standard deviations for each core section, together with mean and concentration ranges are reported in Table 1. For the sake of comparison, Table 2 shows the elemental concentrations in other Antarctic marine

Table 1. Concentrations of inorganic constituents (mg kg^{-1}) and organic matter and carbonates (percentages w/w) for each section of the sediment core collected at site D. Concentrations are shown as mean values \pm standard deviations.

	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	La
D0	44,560 \pm 1330	600 \pm 27	14,280 \pm 360	0.52 \pm 0.04	9.64 \pm 0.5	39.6 \pm 2.4	21.4 \pm 1.4	18,960 \pm 360	6660 \pm 350	29.5 \pm 2.4
D1	46,010 \pm 2780	518 \pm 25	12,190 \pm 550	0.48 \pm 0.01	11.0 \pm 0.2	51.8 \pm 3.2	109 \pm 3	24,900 \pm 260	22,470 \pm 230	31.1 \pm 2.1
D2	42,700 \pm 1850	463 \pm 16	11,390 \pm 200	0.58 \pm 0.04	9.16 \pm 0.3	52.1 \pm 4.5	109 \pm 2	25,120 \pm 520	20,860 \pm 150	30.4 \pm 3.1
D3	44,780 \pm 1690	530 \pm 15	11,790 \pm 290	0.56 \pm 0.04	9.44 \pm 0.5	50.3 \pm 3.7	112 \pm 4	24,330 \pm 730	21,270 \pm 1060	31.7 \pm 1.9
D4	45,630 \pm 1130	550 \pm 16	11,960 \pm 110	0.62 \pm 0.01	8.58 \pm 0.5	57.2 \pm 3.0	112 \pm 4	23,330 \pm 800	21,840 \pm 430	32.9 \pm 3.1
D5	46,000 \pm 600	520 \pm 13	11,890 \pm 100	0.70 \pm 0.05	8.08 \pm 0.4	49.9 \pm 2.3	115 \pm 2	22,760 \pm 550	12,820 \pm 390	34.5 \pm 2.1
D6	44,100 \pm 110	500 \pm 10	11,090 \pm 410	0.59 \pm 0.05	8.74 \pm 0.4	51.1 \pm 2.3	111 \pm 5	23,460 \pm 290	19,060 \pm 340	31.1 \pm 1.4
D7	48,920 \pm 590	496 \pm 27	13,980 \pm 600	0.53 \pm 0.02	9.18 \pm 0.3	52.8 \pm 3.1	32.2 \pm 1.4	26,130 \pm 290	16,220 \pm 430	37.0 \pm 0.8
D8	51,920 \pm 2430	513 \pm 23	12,700 \pm 60	0.58 \pm 0.02	10.8 \pm 0.5	56.1 \pm 3.0	39.3 \pm 1.6	29,680 \pm 590	18,370 \pm 810	38.6 \pm 2.0
D9	48,280 \pm 820	498 \pm 12	12,430 \pm 340	0.56 \pm 0.04	10.4 \pm 0.6	54.4 \pm 2.5	39.8 \pm 0.4	24,270 \pm 410	16,860 \pm 350	33.9 \pm 0.8
D10	46,720 \pm 2030	435 \pm 20	11,980 \pm 90	0.65 \pm 0.02	11.4 \pm 0.3	52.1 \pm 3.5	38.2 \pm 1.8	28,820 \pm 180	15,720 \pm 190	33.9 \pm 3.2
D11	54,870 \pm 1650	483 \pm 18	12,910 \pm 310	0.62 \pm 0.05	10.2 \pm 0.7	61.4 \pm 3.3	52.2 \pm 2.5	31,900 \pm 860	18,460 \pm 1000	38.8 \pm 2.5
D12	55,000 \pm 2600	510 \pm 25	12,530 \pm 600	0.62 \pm 0.05	11.0 \pm 0.2	62.8 \pm 3.6	44.5 \pm 2.1	31,430 \pm 180	20,150 \pm 240	44.9 \pm 4.6
D13	51,450 \pm 2010	467 \pm 22	11,520 \pm 390	0.69 \pm 0.05	11.6 \pm 0.3	56.0 \pm 1.6	54.1 \pm 2.4	33,360 \pm 310	19,000 \pm 1160	45.2 \pm 2.3
D14	62,340 \pm 1590	484 \pm 10	11,490 \pm 500	0.57 \pm 0.04	12.4 \pm 0.1	62.0 \pm 2.2	48.2 \pm 2.0	37,570 \pm 720	20,150 \pm 550	51.2 \pm 0.9
D15	57,540 \pm 1370	470 \pm 9	11,160 \pm 490	0.54 \pm 0.03	10.6 \pm 0.6	58.3 \pm 3.6	44.9 \pm 2.2	34,660 \pm 1690	19,560 \pm 160	48.9 \pm 2.0
D16	55,680 \pm 2720	483 \pm 25	12,330 \pm 130	1.17 \pm 0.04	15.5 \pm 0.5	61.9 \pm 4.0	41.4 \pm 2.3	33,410 \pm 1690	20,630 \pm 440	49.9 \pm 3.7
D17	54,220 \pm 610	958 \pm 47	14,770 \pm 190	0.74 \pm 0.05	16.6 \pm 0.7	54.1 \pm 1.1	35.3 \pm 1.7	29,250 \pm 550	21,230 \pm 640	28.0 \pm 0.4
D18	56,590 \pm 850	467 \pm 4	15,240 \pm 320	0.65 \pm 0.03	19.0 \pm 0.4	11.5 \pm 1.6	35.6 \pm 0.8	34,520 \pm 240	19,440 \pm 920	29.6 \pm 1.5
D19	51,720 \pm 600	796 \pm 10	13,620 \pm 280	0.65 \pm 0.02	17.7 \pm 0.3	45.0 \pm 0.8	33.8 \pm 0.9	33,360 \pm 190	18,800 \pm 630	33.0 \pm 1.2
D20	61,930 \pm 2100	975 \pm 5	14,490 \pm 150	0.65 \pm 0.03	16.6 \pm 0.1	62.3 \pm 3.4	31.4 \pm 1.5	41,120 \pm 460	21,140 \pm 500	32.7 \pm 2.8
D21	58,970 \pm 2520	880 \pm 40	12,300 \pm 540	0.67 \pm 0.04	20.5 \pm 0.1	58.2 \pm 3.9	30.9 \pm 1.8	39,930 \pm 940	21,600 \pm 1190	31.1 \pm 1.8
Mean	51,360	573	12,640	0.64	12.2	52.8	58.8	29,650	18,740	36.3
Minimum	42,700	435	11,090	0.49	8.08	11.5	21.4	18,960	6660	28.0
Maximum	62,340	976	15,240	1.17	20.5	62.8	116	41,120	22,470	51.2

(continued)

Table 1. Continued.

	Mg	Mn	Na	Ni	P	Pb	Sr	Ti	V	Zn	OM + CO ₂ ⁻
D0	8430 ± 80	477 ± 12	19,170 ± 200	23.4 ± 0.3	591 ± 5	14.9 ± 0.8	198 ± 1	2670 ± 80	57.1 ± 4.0	75.7 ± 3.3	1.73 ± 0.03
D1	8060 ± 80	540 ± 38	21,060 ± 580	18.6 ± 0.5	583 ± 1	14.5 ± 1.0	218 ± 1	3010 ± 80	68.0 ± 2.9	83.5 ± 4.8	2.23 ± 0.10
D2	7820 ± 80	496 ± 24	21,210 ± 590	17.3 ± 0.7	550 ± 5	14.8 ± 0.6	197 ± 11	2900 ± 50	57.5 ± 1.7	97.8 ± 5.5	1.76 ± 0.05
D3	8440 ± 340	501 ± 17	22,600 ± 630	16.0 ± 0.6	548 ± 4	15.2 ± 0.1	197 ± 5	2970 ± 110	59.5 ± 2.0	94.9 ± 5.2	2.61 ± 0.08
D4	8680 ± 330	487 ± 12	23,080 ± 410	20.1 ± 1.1	530 ± 1	15.5 ± 0.2	207 ± 13	2980 ± 140	65.9 ± 4.1	90.9 ± 1.3	1.85 ± 0.00
D5	8570 ± 90	502 ± 16	23,070 ± 780	20.1 ± 0.8	723 ± 7	15.7 ± 0.7	204 ± 9	3090 ± 200	62.9 ± 4.2	85.8 ± 2.1	1.32 ± 0.02
D6	8210 ± 290	477 ± 2	23,130 ± 280	20.5 ± 1.4	554 ± 7	15.7 ± 0.2	186 ± 7	2800 ± 40	67.3 ± 3.1	91.3 ± 0.8	2.10 ± 0.05
D7	9880 ± 300	425 ± 5	23,160 ± 430	20.3 ± 1.4	575 ± 2	16.1 ± 0.2	208 ± 6	2860 ± 90	71.8 ± 4.8	91.5 ± 4.1	1.51 ± 0.03
D8	10,040 ± 250	466 ± 7	22,640 ± 190	25 ± 1.1	607 ± 2	16.9 ± 0.2	203 ± 2	3150 ± 90	83.4 ± 4.3	93.5 ± 2.3	1.28 ± 0.00
D9	9720 ± 210	435 ± 12	21,560 ± 110	28.2 ± 0.4	572 ± 7	16.7 ± 0.2	186 ± 7	3100 ± 200	81.3 ± 4.7	88.9 ± 3.5	1.76 ± 0.04
D10	9950 ± 210	453 ± 30	20,460 ± 120	28.8 ± 0.3	580 ± 2	17.6 ± 1.0	163 ± 6	2810 ± 270	87.2 ± 5.4	89.5 ± 4.6	1.73 ± 0.04
D11	11,130 ± 240	517 ± 19	22,770 ± 90	33.9 ± 2.3	602 ± 9	18.6 ± 0.2	191 ± 6	3340 ± 120	91.4 ± 6.1	102 ± 2.2	1.26 ± 0.01
D12	10,920 ± 600	563 ± 31	22,000 ± 580	35.0 ± 2.2	618 ± 6	19.4 ± 0.1	196 ± 10	3260 ± 150	96.5 ± 1.6	101 ± 5.9	1.88 ± 0.00
D13	10,600 ± 600	617 ± 37	22,120 ± 320	28.1 ± 1.4	665 ± 6	18.9 ± 0.0	205 ± 14	2920 ± 180	105 ± 5.8	105 ± 3.4	1.73 ± 0.09
D14	12,580 ± 310	637 ± 9	22,780 ± 520	27.9 ± 1.2	665 ± 5	20.9 ± 0.3	168 ± 8	3240 ± 140	105 ± 4.1	109 ± 2.6	1.74 ± 0.01
D15	11,490 ± 520	611 ± 21	20,870 ± 420	24.2 ± 1.3	487 ± 6	20.3 ± 0.7	159 ± 4	3060 ± 160	92.7 ± 1.3	97.7 ± 3.8	1.77 ± 0.03
D16	11,770 ± 680	597 ± 30	21,280 ± 810	26.2 ± 1.4	498 ± 4	20.6 ± 1.0	98 ± 6	3020 ± 200	90.8 ± 6.5	97.1 ± 4.3	1.68 ± 0.05
D17	10,660 ± 160	596 ± 13	19,970 ± 40	25.7 ± 1.8	581 ± 4	31.3 ± 1.1	155 ± 2	3370 ± 80	104 ± 2.8	97.9 ± 6.5	1.18 ± 0.04
D18	10,420 ± 160	623 ± 13	20,320 ± 360	21.8 ± 2.0	585 ± 3	21.1 ± 1.2	150 ± 3	3430 ± 70	107 ± 1.1	89.9 ± 1.3	1.37 ± 0.01
D19	10,750 ± 220	535 ± 8	19,890 ± 220	20.6 ± 1.6	569 ± 2	16.9 ± 0.1	147 ± 2	3190 ± 70	106 ± 0.8	78.4 ± 1.5	1.77 ± 0.06
D20	12,800 ± 650	714 ± 36	21,970 ± 150	32.2 ± 0.8	607 ± 7	17.2 ± 0.6	154 ± 4	3440 ± 180	112 ± 1.8	97.9 ± 5.5	2.07 ± 0.03
D21	12,210 ± 660	692 ± 20	22,960 ± 330	36.1 ± 1.8	562 ± 6	17.4 ± 1.1	132 ± 5	3120 ± 40	115 ± 3.6	105 ± 5.0	3.06 ± 0.06
Mean	10,140	544	21,730	25.01	585	18.02	178	3080	85.95	93.95	1.79
Minimum	7820	425	19,170	16.03	487	14.49	97.88	2670	57.11	75.74	1.18
Maximum	12,800	714	23,160	36.07	723	31.27	218	3440	116	109	3.06

Table 2. Concentrations of major, minor, and trace elements (mg kg^{-1}) in sedimentary rocks (shales), deep-sea sediments (clay), and Antarctic marine sediments collected in Terra Nova Bay during the Antarctic summer of 1993/94 and in Windmill Islands (East Antarctica) during the Antarctic summer of 1998/99 (Turekian and Wedepohl 1961; Ciaralli et al. 1998; Gasparon et al. 2007).

	Sedimentary rocks (shales)	Deep-sea sediments (clay)	Terra Nova Bay	Windmill Islands
Al	80,000	84,000	98,444	
Ba	580	2300		423
Ca	22,100	29,000		
Cd	0.30	0.42	2.21	1.7
Co	19	74		4.86
Cr	90	90	68.44	27.7
Cu	45	250		17.4
Fe	47,200	65,000	53,667	
K	26,600	25,000		
La	92	115		26.5
Mg	15,000	21,000		
Mn	850	6700	1274	
Na	9600	40,000		
Ni	68	225	22.37	13.1
P	700	1500		
Pb	20	80	44.27	16
Sr	300	180		143
Ti	4600	4600		
V	130	120		36.4
Zn	95	165	142.34	65

sediments collected in TNB during the 1993–1994 Campaign (Gerlache Inlet) (Ciaralli et al. 1998) and in the Windmill Islands (East Antarctica) during the Antarctic summer 1998–1999 (Gasparon et al. 2007); background values for elements in sedimentary rocks (shales), adopted by several researchers as background values for marine sediments (Förstner and Wittmann 1983; Rubio, Nombela, and Vilas 2000); and background values in marine clay-like sediments (Turekian and Wedepohl 1961).

In comparison with element concentrations in the shales, the contents of elements in this marine sediment core are usually lower, with the exception of Cd, Cu, and Na. This may be due to a “dilution effect” of the biogenic component, likely to be present in this core, on the lithogenic element content. The different behavior of cadmium and copper may be caused by their capability of substituting calcium in carbonates. The high concentrations of sodium may be due to the contribution of interstitial marine water. Also the concentration of strontium (178 mg kg^{-1}) is lower in core D than in shales (300 mg kg^{-1}), but is similar to that reported for deep-sea sediments composed principally by clays (180 mg kg^{-1}) (Turekian and Wedepohl 1961). This can be considered as an initial indication of the absence of pollution in this area and of the possibility to use the element concentrations reported here as reference values for future studies in the polynya of TNB.

The element content in this marine sediment core is usually lower than the values reported in Table 2 for other marine Antarctic sediments; this is likely due to a combination of several factors such as a different watershed lithology, spatial

and temporal variations in clastic sediment supply, different grain-size, and primary production. It is, however, interesting to note that some elements, namely Ba, Cd, and Pb, have a similar behavior in marine sediments collected in different areas of Antarctica. In particular, the low temporal and spatial variability of lead content in all the sites considered is further evidence that this element can be considered a good indicator of anthropogenic contamination because its baseline concentrations in sea water and soils are low and it is an ubiquitous pollutant.

As to depth profiles, the concentrations of some lithophile elements (Al, Fe, Mg, and Mn) are high at the bottom of the core, implying a high proportion of mineral detritus derived from the nearby coast. A relatively coarser grain size of the bottom sediments, compared to the upper sections of the core, supports this hypothesis. Also Co, V, and to a lesser degree Pb and Ti follow the trend of Al, Fe, and Mn, and their fluctuations are due to varying proportions of clastic input over time.

Among the typically lithophile elements, i.e., the alkali and alkaline-earth metals sodium, magnesium, potassium, and calcium, that together with aluminum and silicon are the major constituents of aluminosilicates, only Mg is strongly correlated to Al (Pearson correlation coefficient = 0.959, $\alpha = 0.01$). This indicates that clay minerals are not primary constituents of clastic sediment supply. Since Mg correlates well also with Fe (Pearson correlation coefficient = 0.920, $\alpha = 0.01$), it is very likely that they derive from the presence of orthopyroxenes. In fact, magnesium and iron represent the major elements building up these silicates.

Na and K follow a different pattern in comparison with the other lithophiles, with higher concentrations in the ranges 3–8 cm and 12–15 cm for Na and 2–5 cm for K. Furthermore, K content sharply decreases in the top layer compared to the rest of the core. The trend observed for K and Na might be due to an additional source of these elements, such as marine salts deriving from interstitial waters, likely present at higher levels in the sections of core closer to the seafloor, or also other K and Na bearing minerals. Also Ca presents a different depth profile from the other lithophile elements, with a slightly higher concentration in the first 2 cm and between 18 and 21 cm: the distribution of this element is principally believed to reflect changes in the sedimented organic matter, but this association in core D is not so evident. This is supported by studies on the water column in the Ross Sea which show how biogenic carbonates are unstable at depths well above the sea bottom as a result of dissolution processes leading to the limited deposition of calcium in the sedimentary bed (Manno et al. 2007).

Among the elements typically present at high concentrations in productive ecosystems, Sr, Cu, and partially P are characterized by higher contents in the upper sections of the core. Particularly Sr has, in general terms, an opposite distribution relative to the major elements along the sediment core, i.e., with a clear increase in content towards the uppermost part of the core. This may be indicative of the presence of aragonite (Fernández-Bastero et al. 1998), where strontium easily substitutes calcium. The main sources of aragonite are pteropod shells. Strontium may, in part, be derived also from the tests of rapidly dissolving acantharians, which are common inhabitants of all oceans and secrete a skeleton made of the mineral celestite, SrSO_4 . A possible common reason for the increase of Sr, Cu, and partially P might be an increment of biological productivity in the water column and in the sediment itself over time, induced by climatic improvements that favored primary production. A partial confirmation of this increment is the organic matter and carbonates trend that actually decreases with increasing depth (Table 1).

Alternatively, if the primary production was constant over time, the lower concentrations of these elements at the bottom could be explained by a higher degree of degradation. In fact, the material buried in the deepest sections of the sediment was exposed to microbial degradation processes for a longer time than in the upper parts of the core, with a consequent reduction in the amount of nutrients. Under this scenario, the increase in Cu, Sr, and P from the bottom to the top of the core would simply be a consequence of the lower degree of decomposition of the younger sediment. The other investigated trace and minor elements do not show well-defined trends.

Figure 2 reports the depth profiles for the Fe/Mn, Cu/Zn and Al/Ti ratios, and Ba_{excess} . The first ratio has been used by various authors (Tolonen and Meriläinen 1983; Sohlenius and Westman 1998) as a paleoredox indicator in sediment cores. Since manganese oxides are dissolved from the sediment at a higher redox potential than iron oxides, a high Fe/Mn ratio may be the result of reducing conditions at the sediment–water interface. Nevertheless the use of this ratio is limited, as manganese and iron can form minerals under both anoxic and oxic conditions, depending also on the bacterial reduction of sulphates to sulphides. Also the Cu/Zn ratio can be used to describe sediment redox conditions (Sohlenius and Westman 1998); its application is restricted to areas where an anthropogenic input of these elements can reasonably be excluded, like the area considered in this study. A clear difference of both ratios is evident between the uppermost (from the top to –7 cm) and the deeper parts of the core. This trend indicates a change in the sedimentation conditions very likely correlated with the beginning of deglaciation. Unfortunately, when the Fe/Mn ratio decreases at 1–7 cm of depth, indicating oxic or nearly oxic sea-bottom conditions, the Cu/Zn ratio increases, indicating anoxic or nearly anoxic conditions. Since climatic conditions improved after deglaciation and a higher primary production of silica-based organisms likely determined an increase of Cu concentration, it is possible that the Cu/Zn ratio is not usable as a paleoredox indicator in this period of time: therefore we think that the Fe/Mn ratio is more reliable than the Cu/Zn ratio. It is hence probable that the lowermost part of the core was deposited in reducing conditions, while for its uppermost part it is not possible to make any affirmation. Further studies are necessary to explain these experimental results.

The Al/Ti ratio instead is used as an index of sediment origin; increasing ratios suggest an increase in felsic sources, whereas low values generally indicate a prevalence of mafic material. Our results suggest that there have been pulses in sediment provenance, with two episodes characterized by high values of the ratio, possibly related to the contribution of detritus from the “Granite Harbor Intrusives” (according to the geological sketch in Licht, Lederer, and Swope 2005), and a decreasing trend from 15 cm upcore, controlled by the increased contribution from the erosion of the McMurdo volcanic group, similarly to what was reported by Damiani and Giorgetti (2008).

Barium is the element most frequently used as a paleoproductivity proxy (Dymond, Suess, and Lyle 1992; Murray, Leinen, and Isern 1993; Bonn et al. 1998). An excess barium is often calculated ($Ba_{\text{excess}} = Ba_{\text{total}} - (Ba/Ti_{\text{litho}} \times Ti_{\text{total}})$), which is related to the biological contribution of the element according to the formulation reported by Dymond, Suess and Lyle (1992), replacing Al with Ba as a proxy for detrital contribution (Murray, Leinen, and Isern 1993). We used a crustal value of Ba/Ti of 0.126 in agreement with Bonn et al. (1998), in order to compare our results with their data on other sites around the continental margin of Antarctica.

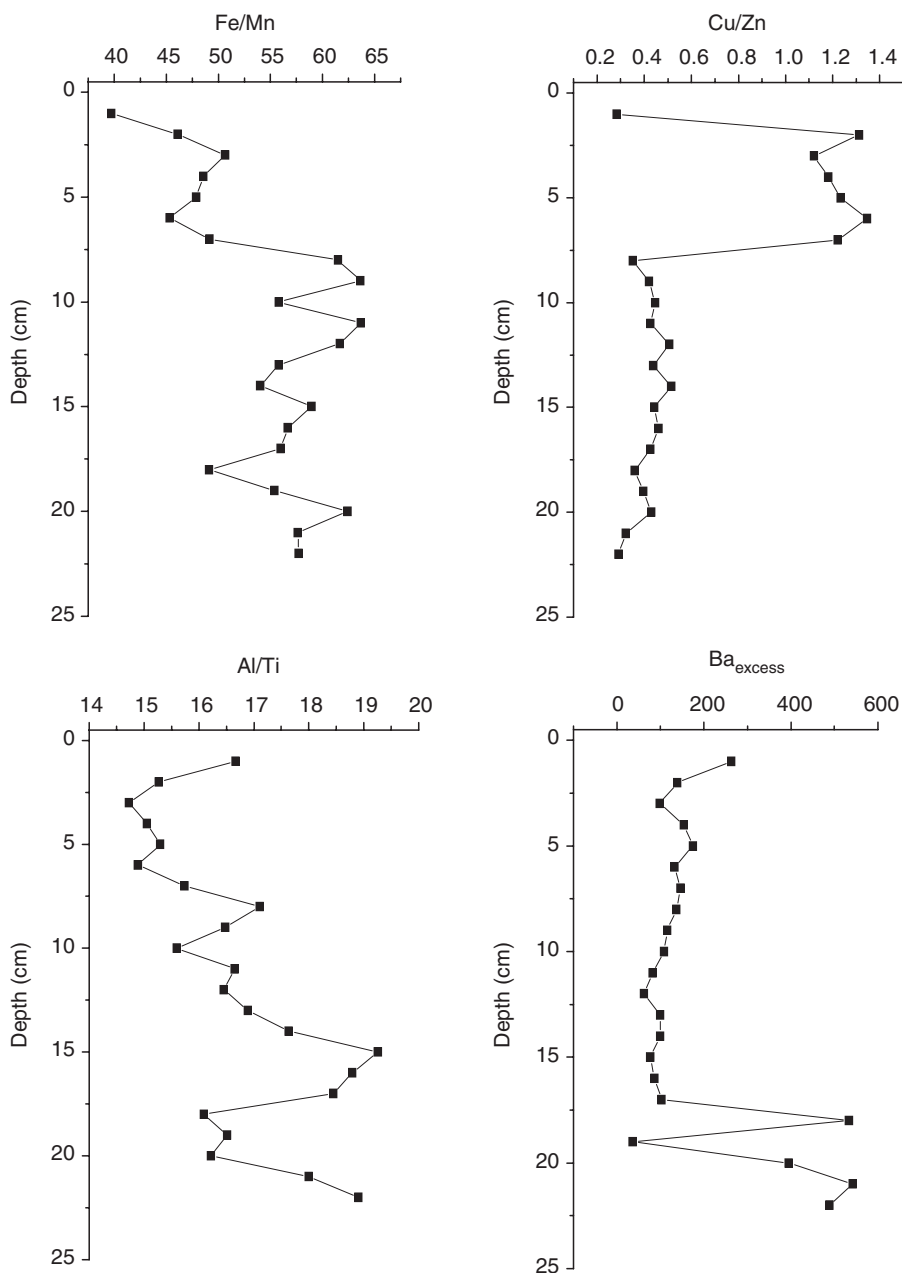


Figure 2. Fe/Mn, Cu/Zn, Al/Ti ratios, and Ba_{excess} profiles for core D.

Compared to such data our records indicate lower Ba_{excess} values, which is probably dependent on the geographic position (very close to the continental margin) and on the different water depth, since high water depths generally record higher barium fluxes.

Several authors (Loring 1990; Daskalakis and O'Connor 1995; Covelli and Fontolan 1997; Veinott, Perron-Cashman, and Anderson 2001) suggested

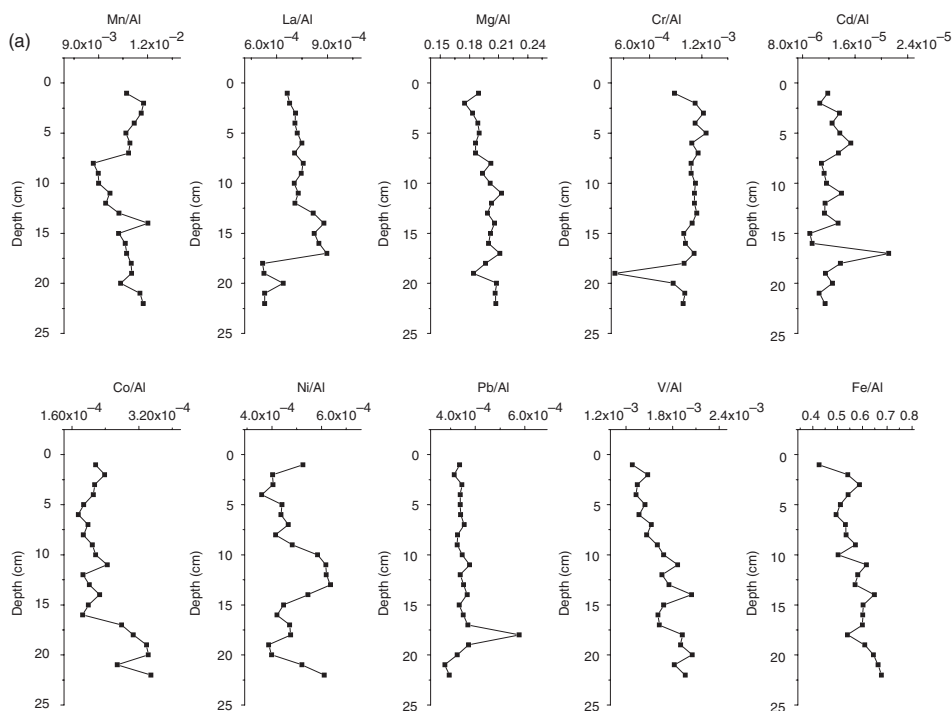


Figure 3. Metal concentrations normalized as ratios to aluminum along core D: (a) elements having increasing or constant values with increasing depth; (b) elements having decreasing values with increasing depth. (*Continued*).

normalizing the data to correct for the natural variability in the element concentrations due to parent material or grain size and to evidence anthropogenic and/or biogenic inputs. Among the various methods of normalization proposed (e.g., using Al, Li, and Fe), we applied aluminum that is widely used in the literature (Summers et al. 1996; Balls et al. 1997), since it is a conservative element and a major constituent of aluminosilicates; in addition, it is not used in biological processes and is inert during diagenesis. The normalized element *versus* depth profiles are shown in Figure 3. This normalization permits us to clearly distinguish the elements influenced at a higher degree by primary production in the water column. These elements (Ba, Ca, Cu, K, Na, P, Ti, and Zn) show a decreasing trend with increasing depth and confirm an increase of biological productivity in the area from the beginning of deglaciation, probably induced by a warmer climate.

It is interesting to note that Ba and Ca also belong to this group, confirming an association with a biogenic sedimented fraction. In fact, calcium, in connection with P and Sr, constitutes residues of hard parts of organisms, such as brachiopods (shells) or arthropods (crustaceans). These parts mainly consist of skeletal apatite (amorphous Ca-phosphate and Ca-carbonate-phosphate). Instead, barium is present in the sedimentary solid-phase in the form of barite (BaSO_4): the formation and precipitation of barite from the water column occurs either in sulphate-rich microenvironments produced during the decay of organic matter or within the tests of rapidly dissolving acantharians (McManus et al. 2002). The second hypothesis is

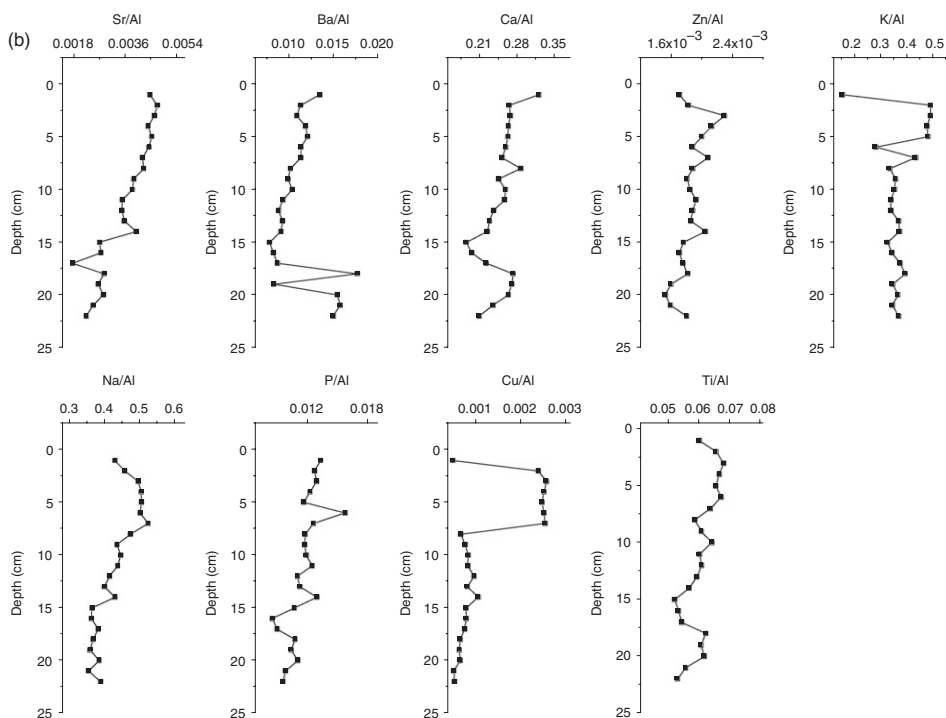


Figure 3. Continued.

presumably more likely because, as reported above, an increase in strontium content in upper sections is also evident. Furthermore, from the depth profile of Zn it is evident that this element is also supplied by mineral detritus but its distribution in uppercore sections is influenced by association with organic matter. Finally, it is surprising to see that also a typically lithogenic and refractory element like Ti seems to have a trend similar to that of the biogenic elements. It is possible to hypothesize an association between Ti and organic matter: several authors (Skrabal, Ullman, and Luther III 1992; Skrabal 1995; Kryc, Murray, and Murray 2003) have observed a pairing of Ti and organic matter and it was postulated that dissolved organic matter may influence the removal of dissolved Ti by metal-organic colloids.

As to elements associated to anthropogenic sources (e.g. Pb, Cd, Zn, Cr, and Ni), no evidence of enrichment is recorded in the top layer of the core (D0), suggesting that this area can be considered free from contamination.

As several marine sediment cores were collected in the Ross Sea during the Italian Expedition of 2004–2005, the sedimentological record preserved in this core can be confirmed or rejected by further studies on these samples. However, our study demonstrates that a thorough understanding of detrital and organic material inputs is necessary before the extent of human impact can be quantified.

Statistical analysis

A chemometric study on the analytical data was carried out to obtain a visual representation of the element distribution along core D and to find out similarities among samples and correlations among variables. PCA and HCA were applied to

the experimental dataset. All of these statistical methods are well-known and described in the literature (e.g., Einax, Zwanziger, and Geiß 1997; Vandeginste et al. 1998). We consider that the basic principles and the theoretical fundamentals are known to a substantial part of the readers and there is no need for a detailed explanation here.

The combined plot of the first two principal components is shown in Figure 4(a). The sample numbers correspond to the core sections, e.g., sample 0 is the top layer

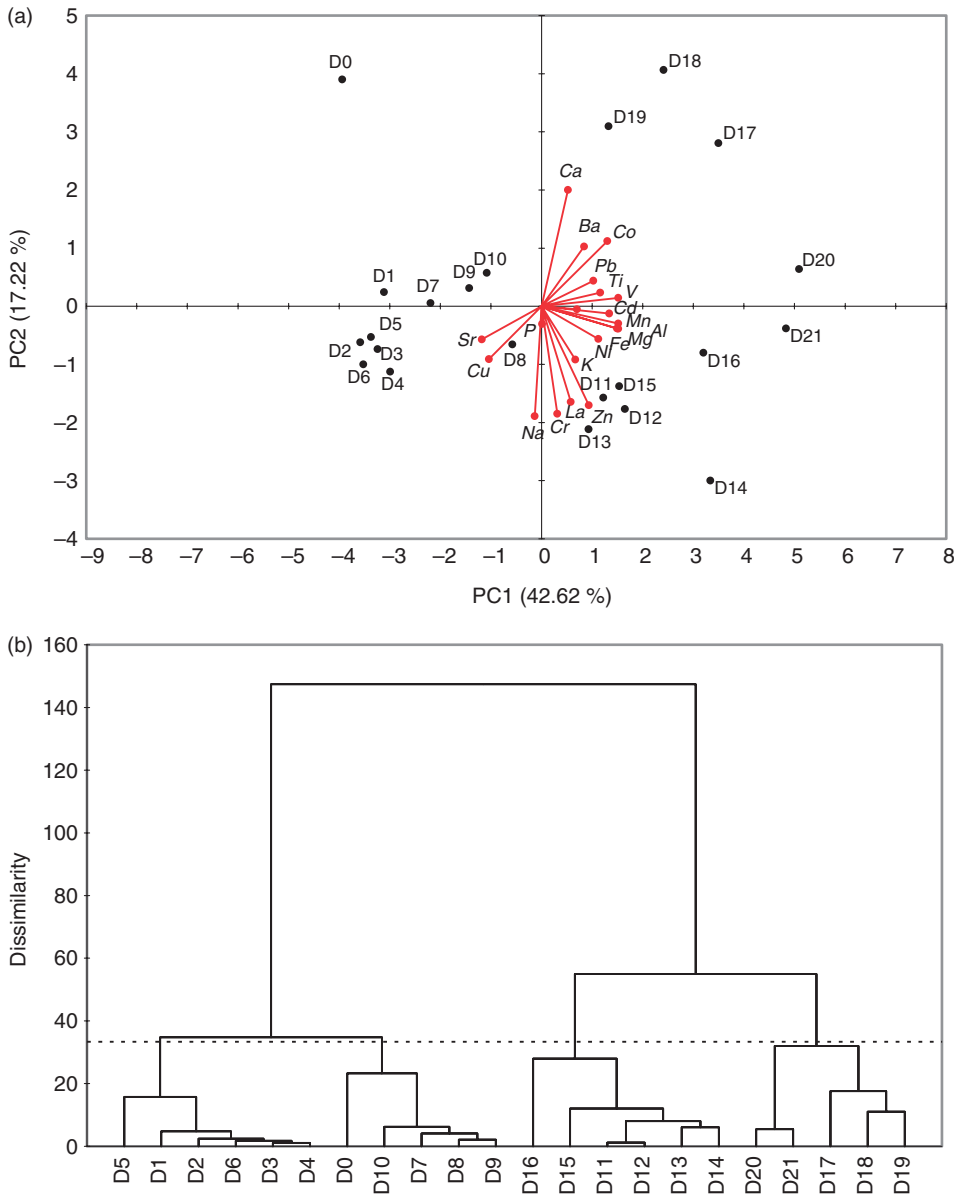


Figure 4. Metal concentrations: (a) combined plot of scores and loadings on PC1–PC2 and (b) dendrogram obtained by HCA.

of the sediment and sample 21 is the deepest one. An interesting trend appears: the sections are grouped as a function of their depth along the sediment core. Six distinct groups, i.e., six different phases of development can be identified along the core:

- The top layer, 1 cm thick, forms its own “cluster” in this dataset due to low concentrations in most of the elements considered. For this reason we named it the “reactive layer” of the sediment. Rather than the environmental history of the area, it reflects the dynamic character of the water–sediment interface.
- Samples from D1 to D6 are characterized by a higher concentration of Cu and Sr, i.e., the nutrient elements, indicating the biogenic input in the area. These layers were hence settled when the primary production in the water column was high.
- The next group of samples (D7–D10) reflects a change in the sedimentary conditions which may be due to a variation in the sedimentation rate and/or in the grain size. Unfortunately, at the moment we have no experimental evidence to confirm this hypothesis.
- The group formed by D11–D16 samples is influenced by the variables identified by the vectors of the elements having either a geological or biological source, namely Cr, K, La, and Zn.
- Samples from D17 to D19 are characterized by some of the elements associated with organic matter, namely Ba and Ca.
- Finally, the group formed by the samples D20 and D21 are aligned with the direction of the vectors representing the main constituents of the clay minerals (Al, Fe, and Mn).

In general, from Figure 4(a) it is evident that the deepest sections of the core are composed by a higher percentage of detritus having mineral origin relative to the most recent ones. Similarly, a decrease of the elements having a predominantly mineralogical origin was observed in the surface sections where, on the contrary, there is a prevalence of detritus with a biological origin. The determination of Si content would allow us to verify the validity of this hypothesis. This trend can be either due to the fact that the biological component of the sediment is subjected to faster and stronger processes of degradation and transformation relative to the mineralogical component or, more likely, to a warmer climate during the deposition of the uppercore sections that determined a greater primary production in the water column.

Finally, the PCA plot confirms that an anthropic influence on the composition of the sediment can be excluded because the section D0, corresponding to the most recent sedimentation period, does not show higher metal ion concentrations than the lower sections. Therefore, it can be presumed that the composition of the sediment derives from natural biogeochemical processes. In particular, the terrestrial contribution is evidenced by the correlation among typically lithogenic elements such as Al, Fe, Mg, and Mn, while we can suppose that the biogenic source is evidenced by the correlation between Sr and Cu.

Also the dendrogram (Figure 4b) obtained by HCA shows a clear association of the core samples as a function of depth, indicating the occurrence of coherent and consistent layers of sediments characteristic of differently prevailing processes of sedimentation in the course of time: in particular, there are two main clusters split into several smaller groups of samples, showing different behavior, probably due to

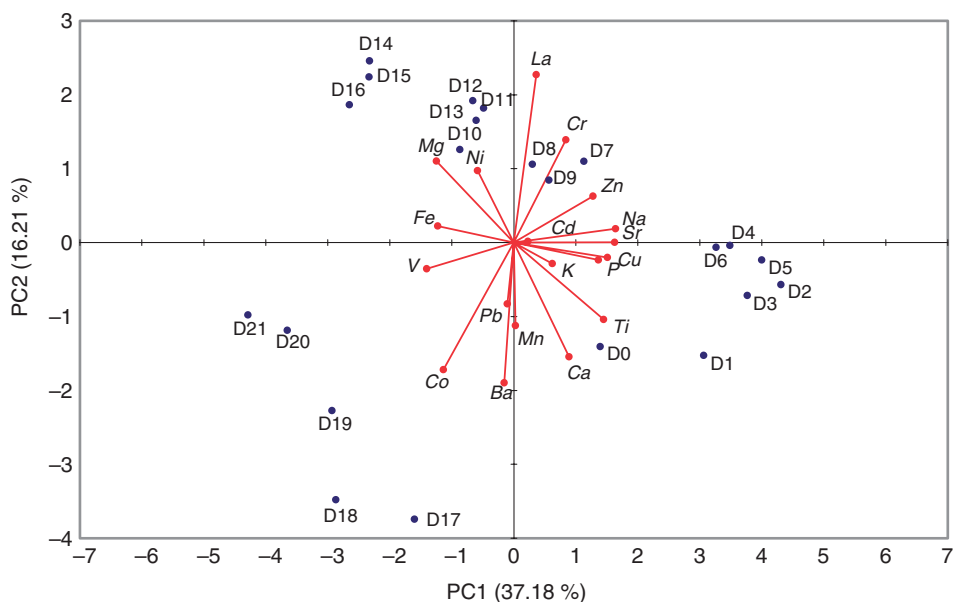


Figure 5. Combined plot of scores and loadings on PC1–PC2 of metal concentrations normalized as ratios to aluminum.

a prevalence of biogenic features in the top layers (D0–D10), and a more typically mineral composition in the deeper half of the core (D11–D21).

PCA was also applied to the Al-normalized data (Figure 5). PC1 is interpreted as the biogenic component since Cu, P, and Sr have high loadings on it (Fernández-Bastero et al. 1998; Calace et al. 2005; Gasparon et al. 2007). It is not possible to give a single interpretation for PC2 because the most significant elements characterizing this component are La and Ba that are usually indicative of clastic and biological sources, respectively. It is, however, interesting to note that the core sections form the same groups evidenced in Figure 4(a) with the exception of sample D10, hence the different phases of development in the considered sediment chronology are further confirmed.

Finally, taking into account the classification observed by applying PCA and HCA, we chose the most interesting sections of the core, representative of the groups evidenced, and determined the mobility of eight metals in such sections.

BCR partitioning

We studied the fractionation of metals with the BCR method. This procedure has been applied and accepted by a large group of specialists (Ho and Evans 1997; Lopez-Sanchez et al. 1998; Smeda and Zyrnicki 2002) even if, like all others sequential extraction procedures, it suffers from several drawbacks, such as the lack of selectivity and element redistribution during extraction, and it provides operationally defined results (Bermond and Yousfi 1997). For this reason, fractions of metals extracted are reported using the corresponding operational mechanisms of

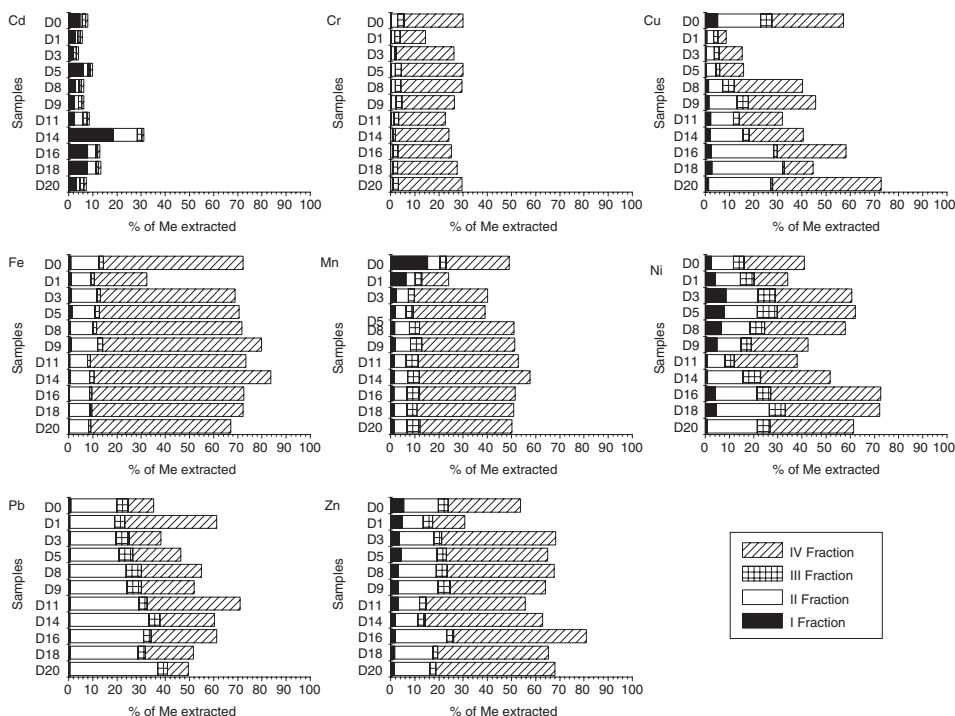


Figure 6. BCR partitioning of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in selected sediment samples.

release, such as weak acid-extractable, reducible, and oxidizable, rather than the sediment phases they target.

Figure 6 reports the results of the BCR sequential extraction for Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from the most significant sections of the marine sediment core investigated. The data are reported as percent fractions of the total concentration, the first four fractions being measured experimentally, while the fifth one (i.e., the residual fraction, bound to the silicate structures of the sediment) being computed from the total concentration by subtraction.

The investigated elements have been chosen according to the following criteria: (i) Cu, Fe, Mn, and Zn for their geochemical relevance, their role in redox cycles, and, for Fe and Mn, also for their tendency to form colloids onto which other elements may be adsorbed and, for Cu and Zn, for their role as micronutrients; (ii) Cd, to prove or disprove its association with carbonate content; (iii) Cr and Ni, for their role in the biogeochemical processes; (iv) Pb, as principal indicator of possible global or local pollution of anthropic origin.

The results obtained show that the upper part of the core has a different behavior compared with that of the deeper part for fractions I, II, and III. In particular, the deepest sections of the core are characterized by a larger level of extraction into the second fraction for most of the metals in comparison with the top sections, while the opposite trend is observed for the third fraction. This is explainable considering that the percentage of debris, having principally mineral origin, is greater in the deeper part of the core. The upper part, instead, is characterized by a greater

percentage of biogenic debris in which trace elements are mainly associated with organic material. This is in agreement with the findings of other authors who reported a close association of trace elements such as Cu and Zn to humic and fulvic acids in other Antarctic sediment cores (Braguglia et al. 1995; Calace et al. 2005). Some sections are particularly different from the others. For example, the D0 sample shows, in the first fraction, higher percentages of extraction than the following sections, likely because, as reported above, it represents the most “reactive layer” of the core. The D1 sample presents low levels of extracted metals both in fractions II and IV and percentages similar to the other samples in fractions I and III; it is deducible that the remaining proportion of non-extracted metal ions is bound to the silicatic component, which is not dissolved by aqua regia.

Each metal shows a characteristic fractionation pattern. In particular, cadmium presents high percentages of extraction into the first fraction, which confirms its preferential association with carbonates as it has previously been reported (World Health Organization (WHO) 1992; Daskalakis and O'Connor 1995). Chromium is extracted at lower extent into the first three fractions, in agreement with its features of inert metal. A large proportion of iron is found into the fourth fraction, probably deriving from the dissolution of crystalline oxides containing this element; however, a portion of these oxides, along with amorphous oxides, is extracted into the second fraction. Nickel and manganese are extracted in considerable amounts into all fractions, even if higher percentages are found into the fourth one. Copper is extracted at a higher extent into the deepest sections of the core than into the surface sections. This different behavior is a further confirmation of the fact that the higher Cu concentration in the uppermost part of core is due to its biogenic origin. Lead is principally extracted into the second and fourth fractions. Even if it is possible that this element is adsorbed onto amorphous and crystalline oxides, it is likely that this partitioning is, in part, due to a redistribution of the metal present as sulphide in the anoxic sediment from the oxidizable to the reducible fraction, as also reported by other authors (Zehl and Einax 2005; Larner et al. 2008). Copper and zinc partitioning could also be influenced by this redistribution, which principally occurs in anoxic sediments. In the absence of experimental evidence on the sulfur content, we speculate this. Finally zinc, like manganese and nickel, is extracted in considerable amounts into all fractions and it is the most mobile metal investigated yielding a maximum of 81% of extraction into the four fractions for sample D16. This result is in agreement with the well-known high mobility of zinc in sediments and soils.

We have also treated these analytical data with PCA and HCA. The PC and dendrogram plots will not be shown in this article, but they are available on request from the authors. From this chemometric elaboration, we formulated some hypotheses about the origin and behavior of these metals. The results obtained by PCA and HCA concerning the first three fractions show a differentiation between the surface (D0–D9) and bottom samples (D11–D20, with the exception of D14 for the third fraction). This feature is not evident in the PC and dendrogram plot of the fourth fraction. This likely indicates that the minerogenic component of the core, mainly associated to such fraction, is similar in all sections considered, while the weak acid-extractable, reducible and oxidizable fractions are characterized by a larger variability over time. In fact, these fractions are certainly influenced to a greater extent by the changes occurring in the water column.

Altogether, the results obtained show that most of the metals are present in the fourth and fifth fractions, therefore strongly bound to the sedimentary matrix, and are hardly released. These findings confirm that the metals present in core D mainly have a natural, and not anthropogenic, origin. In fact, various investigations have shown that metals derived from human activities are usually present in easily available forms (Quevauviller 2002; Chun-gang et al. 2004).

Finally, we observed the following correlations in the PC plots: between Fe and Mn, typically lithogenic elements, in the fourth fraction; among Cr, Fe, and Ni in all four fractions: this could indicate a common terrigenous origin; and among Cu, Fe, and Zn in the third fraction: this could indicate an involvement of these elements in biological processes. Cadmium instead does not show significant correlations with others variables in any fraction. This confirms that the behavior of this element is different from that of the other metals investigated by BCR sequential extraction procedure.

Conclusions

This study permits to increase the knowledge of the natural sediment conditions in a particularly important area as the polynya of TNB. The variability in element concentrations observed as a function of depth is the result of variations in elastic input and in the amount and type of biological production, which likely reflect the climatic variations that took place over the sedimentation time of the core. Furthermore, the element concentration values reported here can be helpful to identify possible local and/or global anthropogenic input in this area in the future.

Acknowledgments

This study has been conducted with the financial support of the Italian National Research Program for Antarctica (PNRA). We are indebted with the Italian participants to the XIX Expedition to Antarctica, in the year 2003/04, for carrying out the samplings.

References

- Arrigo, K.R., G.R. Ditullio, R.B. Dunbar, D.H. Robinson, M. Van Woert, D.L. Worthen, and M.P. Lizotte. 2000. Phytoplankton taxonomic variability in nutrient utilization and primary production in the Ross Sea. *Journal of Geophysical Research* 105: 8827–46.
- Balls, P.W., S. Hull, B.S. Miller, J.M. Pirie, and W. Proctor. 1997. Trace metal in Scottish estuarine and coastal sediments. *Marine Pollution Bulletin* 34: 42–50.
- Bathmann, U., J. Priddle, P. Tréguer, M. Lucas, J. Hall, and J. Parslow. 1999. Plankton ecology and biogeochemistry in the Southern Ocean: A review of the Southern Ocean JGOFS. In *The changing ocean carbon cycle. A midterm synthesis of the Joint Global Ocean Flux Study*, eds. R.B. Hanson, H.W. Ducklow and J.G. Field, 300–37. Cambridge: Cambridge University Press.
- Bermond, A.P., and I. Yousfi. 1997. Reliability of comparisons based on sequential extraction procedures applied to soil samples: The thermodynamic point of view. *Environmental Technology* 18: 219–24.
- Bonn, W.J., F.X. Gingele, H. Grobe, A. Mackensen, and D.K. Futterer. 1998. Palaeoproductivity at the Antarctic continental margin: Opal and barium records for the last 400 ka. *Palaeogeography Palaeoclimatology Palaeoecology* 139: 195–211.

- Braguglia, C.M., L. Campanella, B.M. Petronio, and R. Scerbo. 1995. Sedimentary humic acids in the continental-margin of the Ross Sea (Antarctica). *International Journal of Environmental Analytical Chemistry* 60: 61–70.
- Bromwich, D.H., and D.D. Kurtz. 1984. Katabatic wind forcing of the Terra Nova Bay polynya. *Journal of Geophysical Research* 89: 3561–72.
- Budillon, G., and G. Spezie. 2000. Thermohaline structure and variability in the Terra Nova Bay Polynya (Ross Sea) between 1995–98. *Antarctic Science* 12: 493–508.
- Calace, N., C. Cremisini, M. Galletti, S. Mirante, and B.M. Petronio. 2005. Copper and other trace elements strongly bound to humic acids along sediment cores in the Ross Sea, Antarctica. *Journal of Environmental Monitoring* 7: 1281–86.
- Chun-gang, Y., J. Shi, B. He, J. Liu, L. Liang, and G. Jiang. 2004. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International* 30: 769–83.
- Ciaralli, L., R. Giordano, G. Lombardi, E. Beccaloni, A. Sepe, and S. Costantini. 1998. Antarctic marine sediments: Distribution of elements and textural characters. *Microchemical Journal* 59: 77–88.
- Covelli, S., and G. Fontolan. 1997. Application of a normalization procedure in determining regional geochemical baselines. *Environmental Geology* 30: 34–45.
- Damiani, D., and G. Giorgetti. 2008. Provenance of glacial–marine sediments under the McMurdo/Ross Ice Shelf (Windless Bight, Antarctica): Heavy minerals and geochemical data. *Palaeogeography Palaeoclimatology Palaeoecology* 260: 262–83.
- Daskalakis, K.D., and T.P. O'Connor. 1995. Normalization and elemental sediment contamination in the coastal United States. *Environmental Science and Technology* 29: 470–7.
- Demaster, D.J., O. Ragueneau, and C.A. Nittrouer. 1996. Preservation efficiencies and accumulation rates for biogenic silica and organic C, N and P in high-latitude sediments: The Ross Sea. *Journal of Geophysical Research* 101: 18501–18.
- Diekmann, B., and G. Kuhn. 1999. Provenance and dispersal of glacial–marine surface sediments in the Weddell Sea and adjoining areas, Antarctica: Ice-rafting versus current transport. *Marine Geology* 158: 209–31.
- Ditullio, G.R., J.M. Grebmeier, K.R. Arrigo, M.P. Lizotte, D.H. Robinson, A. Leventer, J.P. Barry, M.L. Van Woert, and R.B. Dunbar. 2000. Rapid and early export of *Phaeocystis antarctica* blooms in the Ross Sea, Antarctica. *Nature* 404: 595–8.
- Domack, E.W., E.A. Jacobson, S. Shipp, and J.B. Anderson. 1999. Late Pleistocene-Holocene retreat of the West Antarctic ice sheet system in the Ross Sea: Part 2. Sedimentologic and stratigraphic signature. *Geological Society of America Bulletin* 111: 1517–36.
- Dunbar, R.B., J.B. Anderson, E.W. Domack, and S.S. Jacobs. 1985. Oceanographic influences on sedimentation along the Antarctic continental shelf. *Antarctic Research Series* 43: 291–312.
- Dymond, J., E. Suess, and M. Lyle. 1992. Barium in deep-sea sediments: A geochemical proxy for paleoproductivity. *Paleoceanography* 7: 163–181.
- Einax, J.W., H.W. Zwanziger, and S. Geiß. 1997. *Chemometrics in environmental analysis*. Weinheim, Germany: Wiley-VCH.
- Fernández-Bastero S., I. Alejo, M.A. Nombela, S. García-Gil, G. Francés, B. Rubio, and M. Pérez-Arlucea. 1998. Chemical factors controlling the steady-state distribution of mixed carbonate-siliciclastic sediments in Baiona Bay (NW of Spain). Paper presented at Proceedings of the 15th International Sedimentological Congress, April 12–17: 327–8. Alicante, Spain.
- Förstner, U., and G.T.W. Wittmann. 1983. *Metal pollution in the aquatic environment*. Berlin, Germany: Springer.
- Frignani, M., F. Giglio, A. Accornero, L. Langone, and M. Ravaioli. 2003. Sediment characteristics at selected sites of the Ross Sea continental shelf: Does the sedimentary record reflect water column fluxes? *Antarctic Science* 15: 133–9.

- Gasparon, M., K. Ehrler, J. Matshullat, and M. Melles. 2007. Temporal and spatial variability of geochemical backgrounds in the Windmill Islands, East Antarctica: Implications for climate changes and human impacts. *Applied Geochemistry* 22: 888–905.
- Goffart, A., G. Catalano, and J.H. Hecq. 2000. Factors controlling the distribution of diatoms and *Phaeocystis* in the Ross Sea. *Journal of Marine Systems* 27: 161–75.
- Ho, M.D., and G.J. Evans. 1997. Operational speciation of cadmium, copper, lead and zinc in the NIST standard reference materials 2710 and 2711 (Montana soil) by the BCR sequential extraction procedure and flame atomic absorption spectrometry. *Analytical Communications* 34: 363–4.
- Isla, E., P. Masque, A. Palanques, J. Guillen, P. Puig, and J.A. Sanchez-Cabeza. 2004. Sedimentation of biogenic constituents during the last century in western Bransfield and Gerlache Straits, Antarctica: A relation to currents, primary production, and sea floor relief. *Marine Geology* 209: 265–77.
- Jacobs, S.S., R.G. Fairbanks, and Y. Horibe. 1985. Origin and evolution of water masses near the Antarctic continental margin: Evidence from $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ ratios in seawater. *Antarctic Research Series* 43: 59–85.
- Kryc, K.A., R.W. Murray, and D.W. Murray. 2003. Al-to-oxide and Ti-to-organic linkages in biogenic sediment: Relationships to paleo-export production and bulk Al/Ti. *Earth and Planetary Science Letters* 211: 125–41.
- Kurtz, D.D., and D.H. Bromwich. 1985. A recurring atmospherically forced polynya in Terra Nova Bay. *Antarctic Research Series* 43: 177–201.
- Larner, B.L., A.S. Palmer, A.J. Seena, and A.T. Townsend. 2008. A comparison of an optimised sequential extraction procedure and dilute acid leaching of elements in anoxic sediments, including the effects of oxidation on sediment metal partitioning. *Analytica Chimica Acta* 608: 147–57.
- Licht, K.J., J.R. Lederer, and R.J. Swope. 2005. Provenance of LGM glacial till (sand fraction) across the Ross embayment, Antarctica. *Quaternary Science Reviews* 24: 1499–520.
- Lopez-Sanchez, J.F., A. Sahuquillo, H.D. Fiedler, R. Rubio, G. Rauret, H. Muntau, and P. Quevauviller. 1998. CRM 601, A stable material for its extractable content of heavy metals. *Analyst* 123: 1675–77.
- Loring, D.H. 1990. Lithium – A new approach for the granulometrical normalization of trace metal data. *Marine Chemistry* 29: 156–8.
- Malandrino, M., O. Abollino, S. Buoso, A. Giacomino, C. La Gioia, and E. Mentasti. (2009) Geochemical characterisation of Antarctic soils and lacustrine sediments from Terra Nova Bay. *Microchemical Journal* 92, 21–31.
- Manno, C., S. Sandrini, L. Tositti, and A. Accornero. 2007. First stages of degradation of *Limacina helicina* shells observed above the aragonite chemical lysocline in Terra Nova Bay (Antarctica). *Journal of Marine Systems* 68: 91–102.
- McManus, J., J. Dymond, R.B. Dunbar, and R.W. Collier. 2002. Particulate barium fluxes in the Ross Sea. *Marine Geology* 184: 1–15.
- Murray, R.W., M. Leinen, and A.R. Isern. 1993. Biogenic flux of Al to sediment in the central equatorial Pacific Ocean: Evidence for increased productivity during glacial periods. *Paleoceanography* 8: 651–670.
- Nelson, D.M., D.J. De Master, R.B. Dunbar, and W.O. Smith Jr. 1996. Cycling of organic carbon and biogenic silica in the Southern Ocean: Estimates of water-column and sediment fluxes on the Ross Sea continental shelf. *Journal of Geophysical Research* 101: 18519–32.
- Pike, J., C.S. Allen, A. Leventer, C.E. Stickley, and C.J. Pudsey. 2008. Comparison of contemporary and fossil diatom assemblages from the western Antarctic Peninsula shelf. *Marine Micropaleontology* 67: 274–87.
- Quevauviller, P. 2002. *Methodologies in soil and sediment fractionation studies*. Cambridge, UK: Royal Society of Chemistry.

- Rubio, B., M.A. Nombela, and F. Vilas. 2000. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. *Marine Pollution Bulletin* 40: 968–80.
- Saggiomo, V., G. Catalano, O. Mangoni, G. Budillon, and G.C. Carrada. 2002. Primary production processes in ice-free waters of the Ross Sea (Antarctica) during the austral summer 1996. *Deep-Sea Research Part II* 49: 1787–1801.
- Saggiomo, V., G.C. Carrada, O. Mangoni, M. Ribera D'Alcalà, and A. Russo. 1998. Spatial and temporal variability of size fractioned biomass and primary production in the Ross Sea (Antarctica) during austral spring and summer. *Journal of Marine Systems* 17: 115–27.
- Sarmiento, J.L., T.M.C. Hughes, R.J. Stouffer, and S. Manabe. 1998. Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature* 393: 245–9.
- Schlitzer, R. 2002. Carbon export fluxes in the Southern Ocean: Results from inverse modelling and comparison with satellite-based estimates. *Deep-Sea Research Part II* 49: 1623–44.
- Skrabal, S.A. 1995. Distributions of dissolved titanium in Chesapeake Bay and the Amazon River Estuary. *Geochimica et Cosmochimica Acta* 59: 2449–58.
- Skrabal, S.A., W.J. Ullman, and G.W. Luther III. 1992. Estuarine distributions of dissolved titanium. *Marine Chemistry* 37: 83–103.
- Smeda, A., and W. Zyrnicki. 2002. Application of sequential extraction and the ICP-AES method for study of the partitioning of metals in fly ashes. *Microchemical Journal* 72: 9–16.
- Smith Jr, W.O., and R.B. Dunbar. 1998. The relationship between new production and vertical flux on the Ross Sea continental shelf. *Journal of Marine Systems* 17: 445–457.
- Smith Jr, W.O., and L.J. Gordon. 1997. Hyperproductivity of the Ross Sea (Antarctica) polynya during austral spring. *Geophysical Research Letters* 24: 233–6.
- Sohlenius, G., and P. Westman. 1998. Salinity and redox alternations in the northwestern Baltic proper during the late Holocene. *Boreas* 27: 101–14.
- Sullivan, C.W, K.R. Arrigo, C.R. McClain, J.C. Comiso, and J. Firestone. 1993. Distributions of phytoplankton blooms in the Southern Ocean. *Science* 262: 1832–7.
- Summers, J.K., T.L. Wade, V.D. Engle, and Z.A. Malaeb. 1996. Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* 19: 581–94.
- Sweeney, C., D.A. Hansell, C.A. Carlson, L.A. Codispoti, L.I. Gordon, J. Marra, F.J. Millero, W.O. Smith, and T. Takahashi. 2000. Biogeochemical regimes, net community production and carbon export in the Ross Sea, Antarctica. *Deep-Sea Research Part II* 47: 3369–94.
- Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzi, B. Tilbrook, N. Bates, et al. 2002. Global sea-air CO₂ flux based on climatological surface ocean CO₂, and seasonal biological and temperature effects. *Deep-Sea Research Part II* 49: 1601–22.
- Tolonen, K., and J. Meriläinen. 1983. Sedimentary chemistry of a small polluted lake, Gallträsk, S. Finland. *Hydrobiologia* 103: 309–18.
- Tréguer, P., and P. Pondaven. 2002. Climatic changes and the carbon cycle in the Southern Ocean: A step forward. *Deep-Sea Research Part II* 49: 1597–600.
- Turekian, K.K., and K.H. Wedepohl. 1961. Distribution of the elements in some major units of the Earth's Crust. *Geological Society of America Bulletin* 72: 175–92.
- Vandeginste, B.G.M., D.L. Massart, L.M.C. Buydens, S. De Jong, P.J. Lewi, and J. Smeyers-Verbeke. 1998. *Handbook of chemometrics and qualimetrics (data handling in science and technology)*. Amsterdam, The Netherlands: Elsevier Science B.V.
- Veinott, G., S. Perron-Cashman, and M.R. Anderson. 2001. Baseline metal concentrations in coastal Labrador sediments. *Marine Pollution Bulletin* 42: 187–92.
- WHO-World Health Organization. 1992. *Cadmium: Environmental aspects. Environmental health criteria*. Geneva. Switzerland.

- Wilson, G., D. Damaske, H.D. Moller, K. Tinto, and T. Jordan. 2007. The geological evolution of southern McMurdo Sound – New evidence from a high-resolution aeromagnetic survey. *Geophysical Journal International* 170: 93–100.
- Zehl, K., and J.W. Einax. 2005. Influence of atmospheric oxygen on heavy metal mobility in sediment and soil. *Journal of Soils and Sediments* 5: 164–70.