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# Geochemical **characterization** of a marine sediment **core** from Terra Nova Bay, **Ross Sea, Antarctica**

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## **Abstract**

The chemical fractionation of ten metals (Al, Ti, Cr, Fe, Cd, Cu, Mn, Pb, Zn and Ni) is reported for a marine sediment collected offshore in the Terra Nova Bay, Ross Sea, Antarctica. To evaluate their mobility and availability, the BCR sequential extraction procedure was applied on 11 sections of the sediment. The analyses, performed both by ICP-OES and GF-AAS, highlighted that most of the elements were in the residual phase, showing a strong binding with the matrix and a low availability. **The BCR sequential procedure allowed us to have an insight into the chemical properties of the sediment and provided useful information about the redox state of the sediment itself and important indication on the availability and partitioning of different metals.** A chemometric treatment was

24 applied on the dataset and it showed a separation between the superficial and the lowest sections of  
25 the core, the first being more influenced by the presence of Mn and the second by an increase in Al,  
26 Ti, Fe, Cr and Pb concentrations.

27 **Keywords:** Antarctica, Ross Sea, marine sediment, sequential extraction procedure, sediment  
28 diagenesis

## 29 1. Introduction

30 The Southern Ocean is the fourth largest ocean of the world. From the biological point of  
31 view, it is a so-called High-Nutrient Low-Chlorophyll (HNLC) region. In other words, it is  
32 characterized by a high concentration of nutrients, such as nitrates and phosphates, but it shows a  
33 very low productivity (Martin and Fitzwater, 1988; Martin et al., 1990). The main reason, as  
34 highlighted by Martin in 1990, is that this environment is Fe-limited. Through artificial (Smetacek et  
35 al., 2012) and natural (Duprat et al., 2016) Fe fertilization, it has been shown that the productivity  
36 increased with a significant atmospheric CO<sub>2</sub> drawdown to the surface ocean. Considering that one  
37 of the main Fe source to the ocean is the Aeolian mineral dust (Jickells et al., 2005), during the coldest  
38 and dustiest glacial periods, the increase in Fe supply caused an enhancement of the marine  
39 productivity in the Subantarctic zone of the Southern Ocean (Martínez-García et al., 2011) that likely  
40 contributed to part of the total 100 ppm decrease in atmospheric CO<sub>2</sub> from the interglacial periods  
41 (Lambert et al., 2015).

42 The Ross Sea, which is the southernmost sea on Earth, is comprised between Victoria Land  
43 and Marie Byrd Land. It shows high marine productivity that contributes to at least half the annual  
44 biological production of the entire Antarctic continental shelf (48 Tg C yr<sup>-1</sup>) (Arrigo and Van Dijken,  
45 2003). Nowadays, the primary production has a peak during the austral spring and, according to  
46 satellite observations, can rise up to 4 g C m<sup>-3</sup> d<sup>-1</sup> (Rhodes et al., 2009). The productivity in the Ross  
47 Sea has been associated to the availability of Fe and it was found that algal community growth can

48 be limited by iron deficiency in much of the Southern Ross Sea during summer, excluding the areas  
49 where punctual iron sources exist (Sedwick et al., 2000). Taking advantage of the general absence  
50 of pollution (Caroli et al., 2001), the Ross Sea is a privileged spot where performing biogeochemical  
51 studies. On this purpose, marine sediment cores represent a unique archive to reconstruct the past  
52 seawater composition. The low-sedimentation rate that characterizes the off-shore regions of polar  
53 oceans (centimetres per thousand years) provides low-resolution records that can cover up to the last  
54 millions of years of the Earth history (Martínez-García et al., 2011). The knowledge of their  
55 composition and of the involved sedimentation processes (i.e. biogenic, lithogenic and chemical  
56 processes) can be extremely helpful to address several environmental and climatic questions. For  
57 instance, through the determination of trace metals, it is possible to gain insight into the geochemical  
58 and environmental processes that took place in the water column or into the diagenetic processes that  
59 took place in the sediments themselves (Froelich et al., 1979).

60        Depending on how chemicals are bounded and on any pH or redox potential changes, sea  
61 sediments can act not only as a sink, but also as a new sources of trace metals and pollutants (Ianni  
62 et al., 2010). Therefore, to assess the environmental quality of a sediment core and to evaluate the  
63 more available fractions, it is crucial to perform fractionation studies using sequential extraction  
64 procedures. These methods are based on the use of a series of reagents chosen to solubilise in  
65 sequence different fractions thought to be responsible for retaining the trace metals (Gleyzes et al.,  
66 2002). The outcomes of sequential extraction procedures must be interpreted with caution because  
67 the reagents are not very selective and metal re-adsorption and redistribution may take place after  
68 each step. Nevertheless, such procedures provide useful information on metal binding mode and the  
69 possible presence of anthropogenic contamination (Bacon and Davidson, 2008). One of the most  
70 widespread sequential extraction procedures is the Tessier protocol (Tessier et al., 1979), that  
71 partitions the elements into five operationally-defined geochemical fractions including: exchangeable  
72 fraction; carbonate-bound fraction (acid-soluble); bound to Fe and Mn oxides fraction (reducible);  
73 bound to the organic matter fraction (oxidable) and residual fraction. However, considering the

74 diversity of existing procedures and the lack of uniformity among the different methods, a  
75 standardized three-step procedure was proposed by the former Community Bureau of Reference  
76 (BCR), now the Standards, Measurements and Testing Programme (Quevauviller, 1998). It involves  
77 three extractions steps with reagents of different strength in order to have information on the  
78 exchangeable, water- and acid-soluble (first step), reducible (second step) and oxidizable (third step)  
79 fractions. A comparison between the Tessier and the BCR protocol was performed on a Ross Sea  
80 sediment core. It highlighted higher extraction percentages for the Tessier procedure, mainly because  
81 of the stronger reagents and more drastic conditions (Casalino et al., 2013). In any case, considering  
82 the availability of a certified reference material, shorter extraction times, an easier sample handling  
83 and a detailed protocol, the adoption of the BCR procedure is preferable, especially if a comparison  
84 among different sites is subsequently performed. Nevertheless, the Tessier protocol can be  
85 advantageous when a distinction between a mobile and mobilizable fraction is object of studies  
86 (Casalino et al., 2013).

87 This paper reports the results of a geochemical investigation performed on one sediment core  
88 collected in Terra Nova Bay, Ross Sea, Antarctica, for ten metals: Al, Ti, Cr, Cd, Cu, Mn, Fe, Pb, Zn  
89 and Ni. We reconstructed both their total concentration and their partitioning in the different fractions  
90 according to the BCR procedure providing an insight on the diagenetic processes that might have  
91 taken place in the sediment itself. An X-Ray Diffraction (XRD) investigation to understand if the  
92 lithology of the sediment has changed over time is also reported.

## 93 2. Regional setting

94 The sediment core, coded sediment B, was sampled during the XX Italian Antarctic Survey  
95 in 2004-2005 at the mooring B (73°59.7' S, 175°0.8' E) in an offshore area of the Ross Sea. The  
96 collected sediment was located in the northern part of the Joides Basin at 588 meters depth (Figure  
97 1). According to recent surveys performed at this location, the sinking particles are constituted mainly  
98 by lithogenic (40-62% of the composition of particles in the near-bottom trap) and biogenic materials

99 (29-47% of the bulk dry material in the near-bottom trap) (Langone et al., 2000). Their composition  
100 is strongly linked to the seasonal sea-ice cover: the lowest fluxes of biogenic silica were recorded  
101 during austral autumn and winter, when the sea-ice extent was at its maximum (Langone et al., 2000;  
102 Mezgec et al., 2017).

103 Ross Sea waters are generally oversaturated with respect to both calcite and aragonite,  
104 showing a saturation state greater than 1 (Hauck et al., 2012; Rivaro et al., 2014). The occurrence of  
105 calcium carbonate species was well documented both in bottom traps (Bergami et al., 2009; Langone  
106 et al., 2000) and in deep sediment cores (Casalino et al., 2013). However, the high productivity of the  
107 Ross Sea and the respiration of the organic matter in the sediments can alter the sediment carbonate  
108 chemistry, modifying their preservation (Hauck et al., 2012). The mean  $\text{CaCO}_3$  content in the Ross  
109 sea is 2% ( $714 \text{ g CaCO}_3 \text{ m}^{-2}$ ) with the highest values ( $> 10\%$ ) being located in the Drygalsky Basin  
110 (Domack et al., 1999).

111 Sediment B features were investigated in previous studies (Ravaioli et al., 1999) where it was  
112 classified as siliceous mud. In particular, sediment B is constituted by olive-gray siliceous mud and  
113 ooze without gravels. The sediment is characterized by a high concentration of biogenic silica (20 to  
114 30% of the total sediment mass). The concentration of organic carbon, ranging from 0.86 to 1.23%,  
115 does not show any clear trend along the core and it is the highest among all the investigated sediment  
116 cores in the Ross Sea (Frignani et al., 2003; Langone et al., 2000; Ravaioli et al., 1999). Compared  
117 to other sediment cores collected in different areas of the Ross Sea, sediment B is the one that shows  
118 the highest concentration of macrobenthos species, especially polychaetes (up to the 75%). These  
119 species, mainly located (80%) in the first 5 centimetres of the sediment, can provide potential  
120 bioturbation of the sediment itself (Ravaioli et al., 1999).

121 The Ross Sea topography is shaped by glacial erosion and it is characterised by a complex  
122 and heterogeneous morphology. This, results in a high variability in the sedimentation rates that can  
123 change up to two-orders of magnitude within a distance of less than 600 km (DeMaster et al., 1992).

124 In the Joides Basin, the  $^{14}\text{C}$  sedimentation rate ranges from 4.5 cm kyr<sup>-1</sup> to 42 cm kyr<sup>-1</sup> (DeMaster et  
125 al., 1996; Langone et al., 1998; Mezgec et al., 2017; Salvi et al., 2004).

126 For sediment B, neither a  $^{14}\text{C}$  dating nor a magnetic susceptibility profile were performed. For  
127 this reason, we compared the sediment accumulation rates (SAR) from different sediment cores  
128 collected close to sediment B (Figure 1; Table 1). Moreover, we observed that the diatomaceous mud  
129 layer, representative of Holocene open water conditions, has the same thickness both in site B and in  
130 site ANTA19-C14 (Corradi et al., 2003) which indicates similar sedimentation rates. In addition, site  
131 ANTA19-C14 has a  $^{14}\text{C}$  sediment accumulation rate (38.3 cm kyr<sup>-1</sup>) similar to the one calculated for  
132 sediment Y5 (38 cm kyr<sup>-1</sup>), located less than 10 km away from site B. For these reasons, we assume  
133 that sediment B should preserve a SAR similar to the one calculated for the nearby sediments which  
134 ranges from 37 to 42 cm kyr<sup>-1</sup>.

135 In this paper, we performed a comparison with other sea sediment cores collected in the Terra  
136 Nova Bay, which were analysed using the BCR extraction procedure. These sediments, coded D and  
137 H, were collected in a polynya area and on the outer continental shelf respectively (Casalino et al.,  
138 2013; Malandrino et al., 2010). They are characterized by a lower biogenic silica concentration than  
139 sediment B (1-4.5% and 5-8% respectively) and with low sediment accumulation rates of 1.7 cm kyr<sup>-1</sup>  
140 (Frignani et al., 2003). The organic content is higher in sediment H ( $\approx 0.3\%$ ) than in sediment D ( $\approx$   
141 0.15%), with an enrichment at surface in both sites.

### 142 3. Material and methods

#### 143 3.1 Sample processing

144 A stainless-steel box corer was used to sample 50 cm of sediment. The core was extruded  
145 from the corer and subsampled in different sections using a knife with a Teflon blade (Table 2). To  
146 avoid contamination from any metallic part, only the inner part of the core was collected and  
147 transferred into polycarbonate Petri boxes, stored at -25 °C and shipped to the University of Turin

148 (Italy). Subsequently, all the sections were defrosted for 18 hours in previously cleaned polycarbonate  
149 boxes under a Class-100 laminar flow hood located in a Class-100.000 clean room. They were dried  
150 under a Class-100 laminar hood, homogenized at 320 rpm for 15' and then stored in polycarbonate  
151 boxes. To take into account the moisture content, a sub-sample of sediment was dried at 105°C until  
152 constant mass was attained. Moisture contents were used to calculate all sediment characteristics on  
153 a dry mass basis.

154 We performed a sequential extraction procedure following the three-step Modified BCR  
155 protocol (Rauret et al., 2000). We will refer to the three extracted phases as the labile, reducible and  
156 oxidizable fractions respectively. All the bottles and vessels used during this process were previously  
157 filled for 7 days with a 5% solution of 65% HNO<sub>3</sub> (Sigma Aldrich Merck, USA), then rinsed with  
158 Ultrapure Water (UPW) and filled until their use with a 2% solution of 37% HCl (Sigma Aldrich  
159 Merck, USA). All the acids were purified by sub-boiling distillation in a quartz still and UPW was  
160 used throughout.

161 The labile fraction was extracted adding 20 ml of 0.11 M acetic acid (ACS Reagent,  
162 Honeywell, USA) to 0.5 g of sample in a reaction vessel. The sample was shaken for 16h at room  
163 temperature. The supernatant was then filtered and collected in previously cleaned polyethylene  
164 bottles, acidified with 100 µl of 65% HNO<sub>3</sub> (Sigma Aldrich Merck, 65%) and made up to 50. The  
165 residue was then washed with 10 ml of UPW.

166 The reducible fraction was extracted adding to the washed solid residual, 20 ml of a 0.1 M  
167 hydroxylamine hydrochloride (ACS Reagent, Merck, DE) solution adjusted to pH 2. The sample was  
168 shaken for 16h at room temperature. The supernatant was then filtered and collected in previously  
169 cleaned polyethylene bottles, acidified with 100µl of 65% HNO<sub>3</sub> (Sigma Aldrich Merck, USA) made  
170 up to 50 ml. The residue was then washed with 10 ml of UPW.



171 The oxidizable fraction was extracted adding to the washed solid residual, 5 ml of 33% H<sub>2</sub>O<sub>2</sub>  
172 (Extrapure, Honeywell, USA) at room temperature for 1h. The solution was occasionally shaken.  
173 Then, the uncovered reaction vessel was heated at 85°C using a water bath for 2h until the total  
174 volume was reduced to 2 ml. 5 ml of 33% H<sub>2</sub>O<sub>2</sub> were further added and kept for 1h at 85°C. Then the  
175 vessel was uncovered again until the final volume of 0.5 ml was reached. At this point, 25 ml of 1 M  
176 ammonium acetate (trace metal basis, Sigma Aldrich Merck, USA) (adjusted to pH 2 with 65%  
177 HNO<sub>3</sub>) were added and the covered vessel was shaken for 16h at room temperature. The supernatant  
178 was then filtered and collected in previously cleaned polyethylene bottles, acidified with 100µl of  
179 65% HNO<sub>3</sub> (Sigma Aldrich Merck, USA) and made up to 50 ml.

180 To have information on the total metal concentrations, an acid digestion in a Milestone MLS-  
181 12000 MEGA Microwave was also performed. 100 mg of dried sample were treated with 5 ml of  
182 *aqua regia* and 2 ml of hydrofluoric acid (48%, ACS Reagent, Sigma Aldrich Merck, USA) in PTFE  
183 bombs. The applied digestion program was: 300s at 250 W, 300s at 400 W, 300s at 600 W, 300s at  
184 250 W. A ventilation step of 25 minutes followed. 0.7 g of boric acid were added and the bombs  
185 were further heated for 300s at 250 W and cooled again with a ventilation step of 15 minutes. The  
186 final solution was filtered and made up to 50 ml with UPW.

187 All experiments were executed in triplicate and the same procedure was performed for the  
188 blanks.

### 189 3.2 Apparatus and reagents

190 All the extracts were analysed either by ICP-OES (Varian Liberty 100 Inductively Coupled  
191 Plasma-Optical Emission Spectrometer) equipped with a V-groove nebulizer or by GF-AAS (Perkin  
192 Elmer 5100 Graphite Furnace Atomic Absorption Spectrometer) equipped with a heated graphite  
193 atomizer and Zeeman-effect background correction, depending on the concentration of the analytes  
194 in the samples and on the Limit of Detection (LoD) and Limit of Quantification (LoQ) (Table S2).

195 LoD, LoQ and more details on the instruments used for the determination of the different species are  
196 reported in the following sections. Calibration curves were performed using the external standard  
197 calibration method for all the ten elements of interest. Standards were prepared from single element  
198 1000 mg L<sup>-1</sup> stock solutions (Merck Titrisol).

199 X-ray powder diffraction (XRD) data were collected on specimens hand ground with an agate  
200 mortar and mounted on a zero-background Si-monocrystal flat sample holder, using an automated  
201 PW3050/60 PANalytical X'Pert-PRO diffractometer in Bragg-Bretano geometry with  $\Theta$ - $\Theta$  setup,  
202 ~~Real-Real-~~Time Multile Strip detector and Cu-K $\alpha$  radiation. Data were analysed in the 3-70° 2 $\Theta$  range  
203 with the Diffrac Plus (2005) software (EVA 11,00,3).

## 204 4. Results

### 205 4.1 Quality assurance

206 The measurement trueness was evaluated both for the total digestion and for the sequential  
207 extraction method. For the total digestion, the MURST-ISS-A1 (Antarctic sediment) reference  
208 material (Caroli et al., 1998) was analysed using three replicates, while for the BCR protocol the  
209 BCR-701 (Lake Sediment) reference material was analysed (Casalino et al., 2013) using three  
210 replicates for each step. Regarding the total digestion of the sediment core and focusing on five main  
211 elements, the average recovery was  $86 \pm 9\%$  (Table 3). Relatively to the BCR sequential extraction  
212 protocol, we found average recoveries of:  $81 \pm 23\%$  for the first step,  $91 \pm 15\%$  for the second step  
213 and  $79 \pm 15\%$  for the third one (Table 4). Overall, our results underestimated the real concentration  
214 of some elements, in particular Zn (51%) in the first fraction and Cd (52%) in the third one. The  
215 uncertainty associated to each concentration value is comparable to the ones found in other studies  
216 (Cuong and Obbard, 2006).

217 The Limit of Detection (LoD) and the Limit of Quantification (LoQ) were determined through  
218 the ICP-AES and GF-AAS analyses of the blanks (number of readings: 3). The returned average

values were then summed to three times (for the LoD) and ten times (for the LoQ) the standard deviation of the blank measurements. The results are summarized in Table S1.

4.2 Total metal concentration and sediment lithology

Total metal concentrations in the core sections are reported in Table 5. Al, Fe and Ti are the metals with the highest concentrations. This indicates that they are the main constituents of the sediment lithology. The variability of each element along the core, expressed as relative standard deviation (RSD%), did not exceed 15%, apart from Mn (47%) and Cd (60%). This suggests that the lithology of the sediment did not significantly change within the studied period. Additional clues come from the XRD analysis performed on selected samples (B01, B02, B12, B17, B22, B27, B32, B37, B42, B45), which does not highlight any modification in the sediment composition (Figure S1). The sediment is mainly constituted by quartz ( $\text{SiO}_2$ ), plagioclase  $((\text{Na,Ca})(\text{Si,Al})_4\text{O}_8)$ , K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ), mica  $(\text{Ca,Na})(\text{Al,Mg,Fe})_{2,3}(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$  and halite ( $\text{NaCl}$ ).

To quantify the carbonate concentration in the sediment we applied the Loss of Ignition method, based on the combustion of 1 g of dried sediment at 950°C for 2 hours (Heiri et al., 2001). More details on the analytical procedure and on the results are reported in the Supplementary Material (Figure S5). The results show that the carbonate content of the sediment ranges from 2% to 5% of the total dried mass reflecting the average calcium carbonate concentration retrieved from 52 sediments collected in the Ross Sea (Hauck et al., 2012). In our record, we found a significantly amount of trace elements associated to ~~to~~ with the first BCR fraction. This fraction, as we will discuss deeply in the following, extracts metals that can be associated with carbonates. For this reason, and according to former interpretations of similar extraction results (Casalino et al., 2013; Ianni et al., 2010; Malandrino et al 2010), we hypothesize the presence of carbonate minerals, such as otavite ( $\text{CdCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ) and siderite ( $\text{FeCO}_3$ ) in our sediment core. Nevertheless, to better assess their occurrence, more focused investigations need to be performed (e.g. through Scanning Electron Microscope analyses).

#### 244 4.3 Metal partitioning

245 The results of the metal partitioning will be interpreted assuming the following features  
246 (Abollino et al., 2006; Reddy et al., 2001): a) the first fraction corresponds to loosely held metal ions,  
247 including the exchangeable and soluble forms, that can be readily extracted and are therefore  
248 potentially available for the biota. Metals associated with carbonates and easily soluble  
249 oxide/hydroxides in mildly acidic conditions are present in the first fraction as well; b) the second  
250 fraction is composed of additional metal oxides/hydroxides soluble at acidic pH and metals associated  
251 with Fe-Mn oxides; c) the third fraction comprises metal ions associated with easily oxidizable solids  
252 or compounds, including organic matter and sulphides.

253 Figures 2-4 summarize the distribution of the elements in the four fractions. All the  
254 concentration values for each fraction and section are reported in the Supplementary Material (Table  
255 S4, Table S5 and Table S6)

256 Iron, aluminium, titanium and chromium (Figure 2): these elements are mainly present in the  
257 residual phase (> 80%) as silicates. This is consistent with the inert feature of these metals. Fe, despite  
258 its biological relevance, is also a key constituent of sedimentary rocks and it is mainly present in the  
259 sediment in its insoluble form (Gleyzes et al., 2002).

260 Zinc and copper (Figure 3): they are mainly extracted in the residual phase (> 50%). However,  
261 they are also present in high concentration along the whole core in the second and third fraction. This  
262 trend suggests that these elements are scavenged by amorphous oxides (Casalino et al., 2013) and can  
263 be associated with humic and fulvic acids (10% and 20% for Zn and Cu respectively) (Braguglia et  
264 al., 1995). Low extraction percentages (from 4 to 14% and from 2% to 4% for Zn and Cu respectively)  
265 are recorded in the first fraction.

266 Nickel (Figure 3): it is present in a significant amount into all the different fractions showing  
267 a heterogeneous behaviour.

268 Manganese (Figure 3): it shows a peculiar fractionation as a function of depth. In the upper  
269 sections it is mainly extracted in the first and second fractions probably as rhodochrosite ( $\text{MnCO}_3$ )  
270 and as oxide (33% and 34% respectively), while below 6.5 centimetres depth, it mainly occurs in the  
271 residual phase.

272 Cadmium and lead (Figure 4): cadmium is mainly present in the acid-soluble phase ranging  
273 from 0.03 to 0.262 mg kg<sup>-1</sup> with maximum values between 20 and 30 cm depth. Acid-soluble Cd  
274 constituted up to the 70% of the total Cd present in the sediment, while the remaining part is  
275 associated to Fe-Mn oxides. Cd is not detected in the oxidizable fraction. Lead is mainly extracted in  
276 the second and third fraction showing an opposite trend between these two fractions. In particular,  
277 lead associated with Fe oxides become increasingly more relevant with depth (from 17% to 67%),  
278 while a significant drop is observed in the oxidizable Pb fraction from 6 cm downwards (from 40%  
279 to 10%).

## 280 5. Discussion

### 281 5.1 Discussion on the total metal concentration

282 To determine if any anthropogenic contamination or any extra source affects the chemical  
283 composition of the sediment, we calculated the enrichment factors (EF) using the upper crustal  
284 elemental abundances (Hans Wedepohl, 1995) such that  $EF = ([x]/c)_{\text{sample}} / ([x]/c)_{\text{upper crust}}$  where c is  
285 one of the conservative crustal elements (i.e. Ti for our aims) and x the element we wanted to  
286 investigate (Table S3). Values higher than 10 indicate potential additional sources (e.g. pollution).  
287 However, we did not appreciate any value greater than 10. This confirms that all the geochemical  
288 evaluations that follow, are related to natural processes only.

289 Mn is more concentrated in the first 2 centimetres of the sediment, while its concentration  
290 decreases below 3.5 centimetres to a lower and almost constant value. Comparing our results with  
291 other studies performed in other locations of the Ross Sea (Casalino et al., 2013; Malandrino et al.,

2010), we found that sediment B represents a *unicum* concerning the total Mn behaviour. Both in site H (Casalino et al., 2013) and in site D (Malandrino et al., 2010), the total Mn concentration was higher (average: 1000 mg kg<sup>-1</sup> and 544 mg kg<sup>-1</sup> respectively) and with a lower variability along the core (RSD: 8% and 15% respectively). We interpreted this difference between sediment B and sediment D and H, as a consequence of different diagenetic processes related to the different sediment redox conditions that will be discussed in the following.

In sediment B, the Cd concentration increases with depth from an average of 0.06 mg kg<sup>-1</sup>, recorded in the first 3 cm, to a maximum of 0.4 mg kg<sup>-1</sup> at 27 cm depth. The average concentration along the whole core is 0.2 mg kg<sup>-1</sup>, similar to the one recorded in site H (Casalino et al., 2013), but lower than the one recorded in site D (Malandrino et al., 2010).

The lower crustal element (e.g. Al, Fe, Ti, Mn) concentration recorded at site B than at site D and H can be linked to the higher SAR that characterizes this site. Considering that, at site D the highest values for these elements are recorded in the deepest parts of the sediment, we hypothesize that, accordingly to the available sediment accumulation rate and <sup>14</sup>C dating (Frignani et al., 2003; Malandrino et al., 2010), this part corresponds to colder and dustier periods (e.g. Antarctic Cold Reversal). Alternative explanations can rely on the higher exposure to continental weathering (e.g. due to the strong katabatic winds) or on the faster degradation of the biological component than the mineralogical one in the bottom part of the sediment (Malandrino et al., 2010). This hypothesis is consistent with the progressive decrease in the total organic carbon concentration recorded in this sediment as a function of depth (Frignani et al., 2003).

A Principal Component Analysis (PCA) and a Hierarchical Cluster Analysis (HCA) were performed on the total element content (Figure 5). The PCA shows a clear correlation among Al, Ti, Fe, Cr and Pb which constituted the lithological bulk of the sediment, while the HCA shows a separation among the samples as a function of depth: 1) B01 and B02 forms one distinct group, mainly influenced by the high concentration of Mn. According to ~~with~~ the presence of macrobenthos in the

upper sections of the core (Langone et al., 1998), ~~it is possible that the first centimetres at~~ the first centimetres may be affected also by bioturbation processes; 2) from B07 to B22; 3) the sections from B27 to B37 are mainly influenced by Cu, Cd, Zn and Ni; 4) B42 and B45 are characterized by an increase in crustal elements such as Al, Ti, Fe, Cr and Pb. ~~Contrarily to what described for sediment D, in this context, we exclude that this increase in the crustal element concentration can be linked to an increase in the organic matter degradation. Indeed, the organic matter concentration appears to be constant throughout the entire sediment (Ravaoli et al., 1999). This increase can be likely associated to external inputs that are difficult to identify in the absence of an absolute dating of the core.~~

We compared the average total concentrations of the elements in sediment B with the ones retrieved from other sites in the Terra Nova Bay (Table 6). The higher concentrations of Al and Fe in site D than in site B and H suggest that site D is more exposed to continental weathering. Furthermore, site D shows higher Cd concentration than sediment H and B. However, how we will discuss in the metal partitioning section, this increase is likely due to a stronger terrigenous input that characterizes the polynya than the other two sites. Site H and Site B show similar trace metals concentration ranges, likely because they are both located offshore.

## 5.2 Discussion on the metal partitioning

The distribution of manganese in marine sediments provides useful information on the sediment oxidation potentials (Pedersen and Price, 1982). In some circumstances, the presence of Mn(II)-carbonate is also considered a proxy for short oxygenation events in regions where anoxic conditions prevail (Lenz et al., 2014). Under these conditions, Mn, present in its reduced and soluble form ( $Mn^{2+}$ ), is leached from the sediment and enriched in the anoxic stratified bottom waters. In case of short-term oxygenation events, soluble  $Mn^{2+}$  can be oxidized back to Mn-oxide. When the anoxic conditions are restored, it is reduced back to Mn(II) and, thanks to the alkalinity increase promoted by sulphur reducing bacteria, it can precipitate as rhodochrosite. These events are clearly visible in the sediment core stratigraphies as thin rhodochrosite layers (Huckriede and Meischner, 1996).

342 Mn species are also involved in the diagenesis of marine organic matter together with nitrate,  
343 Fe, and sulphate. Under semi-anoxic conditions, the organic carbon is oxidized by Mn(IV), which  
344 releases soluble  $Mn^{2+}$  to the porewater.  $Mn^{2+}$  can diffuse upwards in layers where more oxic  
345 conditions prevail and it can accumulate as  $MnO_2$  (Froelich et al., 1979). This process provides a  
346 mechanism for stripping manganese from the deepest and anoxic sections of the sediment,  
347 accumulating and redepositing Mn oxides at the sediment-water interphase.

348 The adoption of the BCR protocol allowed us to investigate both the acid-leachable phase of  
349 Mn, where it is likely present as rhodochrosite (I fraction), and the reducible fraction, where it is  
350 present as oxide (II fraction). Our record shows that manganese extracted in the first fraction exhibits  
351 a maximum at 1 cm depth (40% of the total Mn, which corresponds to  $201\text{ mg kg}^{-1}$ ) followed by a  
352 decrease to the 3% of the total Mn concentration ( $4.6\text{ mg kg}^{-1}$ ) from 8 cm depth to the bottom (Figure  
353 3, Table S4). Mn-oxide concentration decreases sharply from 35% of the total Mn concentration ( $193$   
354  $\text{mg kg}^{-1}$ ) at the surface, to 10% at 6 cm depth ( $21\text{ mg kg}^{-1}$ , Figure 3, Table S5). This is consistent with  
355 what postulated by Froelich et al., (1979), which described an enrichment of Mn species at the  
356 sediment-water interphase and a subsequent pauperization of Mn-oxides in the anoxic part of the  
357 sediment. Thus, the Mn-oxide enrichment recorded at the surface can be explained as the re-oxidation  
358 of  $Mn^{2+}$ , which has migrated upwards from the anoxic section of the sediment through the sediment  
359 porewaters (Froelich et al., 1979).

360 The presence of a high concentration of labile-Mn, together with the high concentration of  
361 Mn-oxides at the water-sediment interphase, suggests that part of the Mn-oxides can be reduced by  
362 the respiration of the organic matter. Alternatively, a fraction of the total  $Mn^{2+}$  that diffuses upwards  
363 can precipitate as rhodochrosite instead of being oxidized by the  $O_2$  excess. Lastly, the role of  
364 bioturbation in influencing the distribution of the Mn solid phase cannot be excluded *a priori*,  
365 considering the presence of different ~~macrozoobenthos~~ macrozoobenthos species localized in the first  
366 5 cm of the core (Ravaioli et al., 1999).



367 The interpretation of the Mn species distribution is consistent with the behaviour of the Fe  
368 species. Indeed, Fe is involved in the respiration of the organic matter under stronger anaerobic  
369 conditions (Wersin et al., 1991). In sediment B, we observed that, in the uppermost 3.5 cm, Fe  
370 extracted in the II fraction, builds up the 10-12% (from 1500 to 2500 mg kg<sup>-1</sup>) of the total Fe. Below  
371 this horizon, the concentration of Fe oxides decreased down to the 4% ( $\approx$ 740-1000 mg kg<sup>-1</sup>) of the  
372 total Fe (Table S4, Figure 2). This suggests that Fe(III) has been dissolved into soluble Fe(II) species  
373 accordingly to a plausible increase in the sediment anoxicity with depth. This interpretation is  
374 endorsed by the increase in the oxidizable Fe fraction with depth. Contrarily to what observed for the  
375 Mn species, the recycling of Fe upwards is reduced because of its tendency to be more easily captured  
376 by sulphide to form FeS species (Calvert and Pedersen, 1996).

377 Taking advantage from the availability of other two sediment cores in the Ross Sea (sediment  
378 H and sediment D) on which a BCR extraction procedure was performed, we investigated the  
379 differences in their redox states (Casalino et al., 2013; Malandrino et al., 2010). Neither sediment H  
380 nor sediment D show a significant variability in the Mn-oxides fraction that ranges from 3-7% and 2-  
381 6% of the total Mn concentration respectively. However, in sediment H the concentration of Mn-  
382 oxides is one order of magnitude higher ( $554 \pm 134$  mg kg<sup>-1</sup>, 70% of total Mn) than in sediment D  
383 ( $25 \pm 6$  mg kg<sup>-1</sup>). This, together with the absence of any enrichment in labile Mn along the whole  
384 core, indicates an overall oxic condition at this location. To the contrary, an increase in labile-Mn, is  
385 observed in the uppermost 3 cm of sediment D (15-6% vs 1% at the bottom). This layer, in the  
386 absence of a Mn-oxide enrichment, might indicate anoxic conditions of the site D bottom waters.

387 Organic complexes dominate the total concentration of Fe, Zn and Cu in seawater (Morel and  
388 Price, 2003). This behaviour is reflected in sediment B, where these metals, and especially Zn and  
389 Cu, are extracted in significant concentrations in the third fraction. In particular, these species exhibit  
390 an enrichment at intermediate depths (20-25 cm) where their concentration in the oxidizable fraction  
391 rise up to the 11% (for Zn), 26% (Cu) and 5% (Fe). Even if for Fe, a significant contribution can

392 come from the FeS species formed as a consequence of the respiration of the organic matter under  
393 anaerobic conditions, Zn and Cu are strongly bound to the organic matter as shown in another study  
394 performed close to site B (Calace et al., 2005). This can reflect the high productivity in this area,  
395 which causes a greater amount of organic and biogenic remains to get buried (Ianni et al., 2010).

396 In seawater, Cd shows a nutrient-like behaviour. Moreover, having, in its hydrated form, a  
397 similar ionic radius to that of the Ca ion, it can be taken up through the Ca-ion pumps by several  
398 marine organisms (Merian et al., 2004). This, can result in ~~an~~ enrichment in the biogenic calcareous  
399 debris (Ciaralli et al., 1998; Ianni et al., 2010). The PCA performed on the first fraction (Figure S2)  
400 showed that Cd influences mainly the bottom sections of the core.

401 Comparing sediment B with sediment D, we observed that sediment D has a significantly  
402 lower average concentration of Cd associated to the first fraction, with the average value of  $5.4 \pm 4.8$   
403 %, but a higher total Cd content (up to  $1.17 \text{ mg kg}^{-1}$ ). Considering that site D is a coastal site, this  
404 higher content in total Cd concentration can derive from a stronger terrigenous input (Malandrino et  
405 al., 2010). The lower concentration obtained in the first fraction might indicate a lower uptake from  
406 the marine phytoplankton at this location. This is consistent with the higher productivity recorded in  
407 site B than in site D (Frignani et al., 2003; Langone et al., 2000), that might have led to different Cd  
408 biological uptakes.

409 Accordingly with previous studies, we found that Mn and, especially, Fe oxides are good Pb  
410 scavengers (Ianni et al., 2010) since the largest fraction of Pb is associated with the II fraction. This  
411 is true in particular below 3.5 cm depth, where its concentration increased up to the 68% of the total  
412 Pb. It is also well known that the organically complexed lead fraction in seawater can constitute a  
413 significant portion of the total Pb (Capodaglio et al., 1998). In sediment B, a high amount of Pb is  
414 extracted in the oxidizable fraction (25-40%) in the uppermost 3.5 cm of the sediment. Considering  
415 the redox state of the sediment discussed above, we assume that Pb is bound to the organic matter  
416 rather than present as PbS. The increase in this fraction can be explained by the low concentration of

other micronutrients, which might have led to an increase in the Pb organic complexation in the water column. However, below 3.5 cm depth, the oxidizable Pb fraction decreased down to 8-10% of the total Pb. This is mirrored by an increase in the Zn and Cu extracted in the third fraction, which suggests a higher affinity of these micronutrients to the organic matter and produces a decrease in the concentration of organically bounded Pb, in favour of an increase in Pb scavenged by Fe-oxides (II fraction).

## 6. Conclusions

In this study, we showed the geochemical features of a sediment core collected in the Terra Nova Bay (Antarctica). Through a mineralogical study, we evaluated the lithology of the sediment and we found that it was mainly constituted by felsic rocks and it did not significantly change along the whole core. Most of the elements were present in the residual phase, indicating a strong binding with the sediment matrix and a low availability.

The BCR protocol allowed us to investigate in details the geochemical properties of the sediment highlighting several sediment diagenetic processes due to the respiration of the organic matter. Furthermore, we were able to understand which elements were bounded to the organic matter and which was their behaviour accordingly with their abundance and availability in the water column. Lastly, we discussed the role of Cd, which was mainly extracted in the first fraction. Because of the high organic carbon flux recorded at sediment B, we propose that the observed enrichment in labile Cd was mainly due to a non-selective biological uptake.

## 7. Data availability

All data are available upon request to the authors

## Aknowledgments

439 This work was financially supported by the Italian National Antarctica Research Program (PNRA).  
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441 oceanographic campaigns performed in the Ross Sea.

442 **Tables and figures**

443 **Table 1** – Locations and sediment accumulation rates for sediments collected in the same area of  
444 sediment B.

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Core	Coordinates	Sediment Accumulation Rate	References
Site B <i>(red dot)</i>	73°59.7'S; 175°0.8' E	n.a.	<i>This work</i>
ANTA91-14 <i>(violet dot)</i>	73°52.4' S; 175°24.8' E	38.3 cm kyr <sup>-1</sup>	(Frignani et al., 1998)
Y5 <i>(green dot)</i>	74°00.0' S; 174°44.0' E	38 cm kyr <sup>-1</sup>	(Calace et al., 2004)
WRS_JB <i>(blue dot)</i>	73°49.0' S; 174°39.0' E	42 cm kyr <sup>-1</sup>	(Mezgec et al., 2017)
Site D <i>(black dot)</i>	75°06.0' S; 164°13.0' E	1.7 cm kyr <sup>-1</sup>	(Malandrino et al., 2010)
Site H <i>(yellow dot)</i>	75°56.0' S; 177°36.0' W	1.7 cm kyr <sup>-1</sup>	(Casalino et al., 2013)

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453 **Table 2** – Sections of the sediment and associated depth

Section	Depth /cm
B01	0-0.5
B02	0.5-1
B07	3-3.5
B12	5.5-6
B17	8.0-8.5
B22	11-12
B27	16-17
B32	21-22
B37	26-27
B42	32-34
B45	38-40

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455 **Table 3** – Cu, Cr, Zn, Mn and Mn recovery from the standard reference material MURST-ISS-A1.

456 All values are reported in mg kg<sup>-1</sup>.

	Analysed CRM value	Certified CRM value	Recovery %
Cu	5.15 ± 0.09	5.79 ± 1.59	89 %
Cr	30.8 ± 0.8	42.1 ± 3.4	71%
Zn	45.5 ± 0.1	53.3 ± 2.7	85%
Mn	420 ± 12	446 ± 19	94%
Fe	2.25 ± 0.07	2.44 ± 0.07	92%

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460 **Table 4** – Results of analysis of standard reference material BCR-701 in comparison with certified  
461 values for the different step of the BCR Protocol. All values are reported in mg kg<sup>-1</sup>.

	Analyzed CRM value	Certified CRM value	Recovery %
<b>Step 1</b>			
Cd	5.7 ± 0.6	7.3 ± 0.4	78%
Cr	2.16 ± 0.05	2.3 ± 0.2	94%
Cu	57.7 ± 0.3	49.3 ± 1.7	117%
Ni	12.4 ± 0.4	15.4 ± 0.9	81%
Pb	1.97 ± 0.08	3.2 ± 0.2	62%
Zn	104 ± 8	205 ± 6	51%
<b>Step 2</b>			
Cd	4.18 ± 0.02	3.8 ± 0.3	110%
Cr	41.3 ± 0.3	46 ± 2	90%
Cu	82 ± 1	124 ± 3	66%
Ni	25.6 ± 0.7	27 ± 1	95%
Pb	108.0 ± 0.1	126 ± 3	86%
Zn	112 ± 2	114 ± 5	98%
<b>Step 3</b>			
Cd	0.14 ± 0.03	0.27 ± 0.06	52%
Cr	121 ± 5	143 ± 7	85%
Cu	38 ± 2	55 ± 4	69%
Ni	14.0 ± 0.6	15.3 ± 0.9	92%
Pb	7.4 ± 0.3	9 ± 2	82%
Zn	42 ± 1	46 ± 4	91%

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Depth /cm	Cr	Mn	Zn	Ti	Cu	Al	Fe	Cd	Pb	Ni
<b>-0.5</b>	39.3 ± 0.6	624 ± 5	94.1 ± 0.5	2560 ± 20	29.5 ± 0.5	37000 ± 4000	24000 ± 2000	0.10 ± 0.01	9.0 ± 0.3	19.9 ± 0.4
<b>-1</b>	39.5 ± 0.4	544 ± 9	89 ± 1	2560 ± 20	29.4 ± 0.3	34000 ± 3000	22000 ± 1000	0.06 ± 0.02	8.7 ± 0.4	18.4 ± 0.2
<b>-3.5</b>	40.7 ± 0.5	321 ± 7	89.8 ± 0.6	2680 ± 40	29.0 ± 0.9	33500 ± 100	23500 ± 200	0.04 ± 0.01	9.1 ± 0.4	16.8 ± 0.3
<b>-6</b>	40.6 ± 0.4	248 ± 6	88 ± 2	2570 ± 20	30 ± 1	36000 ± 2000	23000 ± 1000	0.12 ± 0.01	11.6 ± 0.3	17.1 ± 0.8
<b>-8.5</b>	42 ± 1	226 ± 4	87 ± 1	2600 ± 20	31.1 ± 0.5	35000 ± 2000	21000 ± 1000	0.24 ± 0.02	11.4 ± 0.3	22 ± 5
<b>-11</b>	39.3 ± 0.2	210 ± 4	82 ± 2	2500 ± 40	34.4 ± 0.9	37000 ± 6000	22000 ± 2000	0.25 ± 0.01	10.6 ± 0.5	18 ± 1
<b>-17</b>	38.5 ± 0.3	204 ± 3	94 ± 2	2420 ± 40	33.3 ± 0.9	33000 ± 2000	19600 ± 900	0.48 ± 0.02	7.7 ± 0.2	19.9 ± 0.1
<b>-22</b>	40.4 ± 0.5	210 ± 2	100.4 ± 0.2	2530 ± 50	35 ± 1	35000 ± 2000	22000 ± 2000	0.37 ± 0.01	8.4 ± 0.1	21.2 ± 0.3
<b>-27</b>	43 ± 1	237 ± 6	109 ± 3	2780 ± 90	31.3 ± 0.2	36000 ± 1000	24000 ± 1000	0.37 ± 0.01	10.2 ± 0.3	22.9 ± 0.6
<b>-34</b>	47.1 ± 0.6	274 ± 3	110 ± 2	3070 ± 60	27.4 ± 0.7	45000 ± 6000	28000 ± 3000	0.28 ± 0.02	11.2 ± 0.7	23.7 ± 0.6
<b>-40</b>	45 ± 3	270 ± 20	95 ± 8	3000 ± 200	24 ± 1	43000 ± 7000	25000 ± 4000	0.37 ± 0.04	12 ± 1	20 ± 2
<b>AV</b>	41.3	306.1	94.4	2651.8	30.4	36772	23100	0.2	10	19.9
<b>MAX</b>	47.1	623.7	110.1	3069.8	34.7	45000	28000	0.5	12.2	23.7
<b>MIN</b>	38.5	204.4	81.5	2420.0	24.2	33000	19600	0.04	7.7	16.8
<b>DEV</b>	6	47	10	8	10	10	10	60	15	12

**Table 5** – Total metal content. All concentrations are expressed in mg/kg. AV = average concentration. MAX = maximum concentration. MIN = minimum concentration. DEV = standard deviation (%)



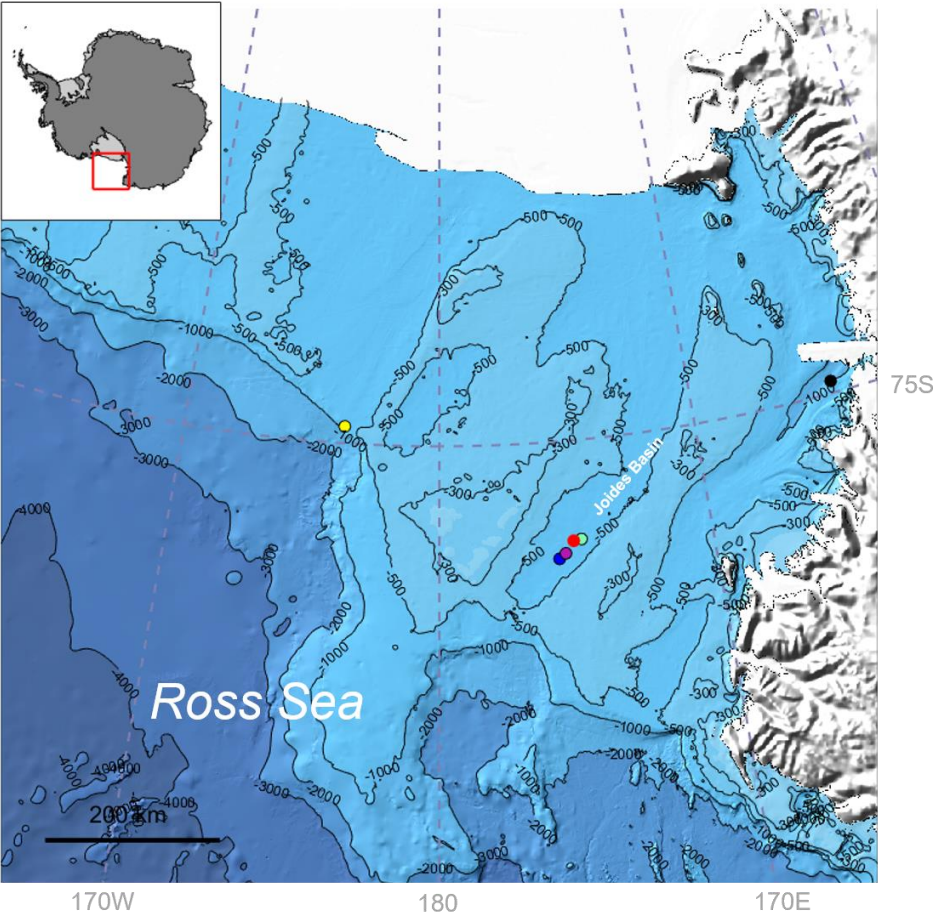
466 **Table 6** - Concentration ranges found in the sediment H (Casalino et al., 2013), sediment D  
467 (Malandrino et al., 2010) and sediment B (this work). Values are in mg kg<sup>-1</sup>.

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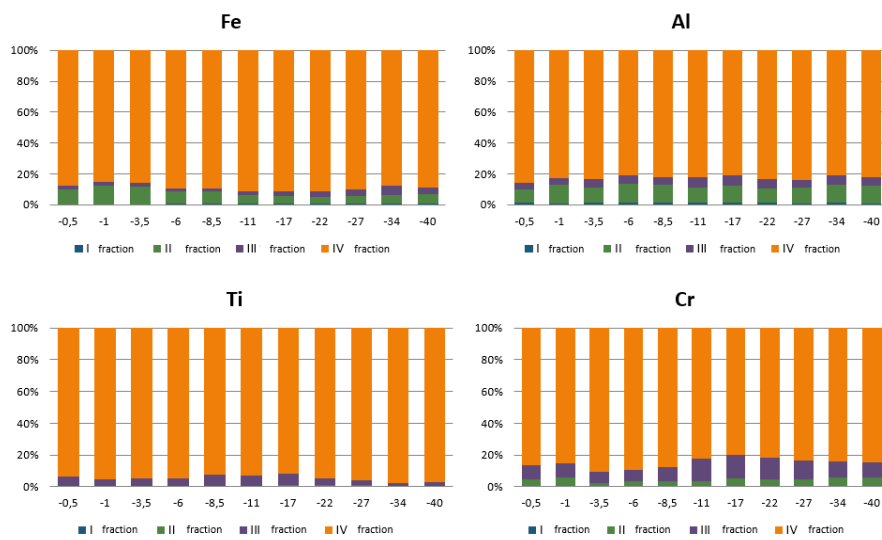
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Element	Site D	Site H	Site B
Al	42 700-62 340	35 310-53 040	<b>33 000-45 000</b>
Cd	0.49-1.17	0.23-0.86	<b>0.04-0.5</b>
Cr	12-63	33-51	<b>39-47</b>
Cu	21-116	32-66	<b>24-35</b>
Fe	18 960-41 120	19 043-33 475	<b>19 600-28 000</b>
Mn	425-714	849-1176	<b>204-624</b>
Ni	16-36	13-34	<b>17-24</b>
Pb	15-31	10-15	<b>8-12</b>
Ti	2 670-3440	1 858-3 327	<b>2 420-3 070</b>
Zn	75-109	74-114	<b>81.5-110</b>

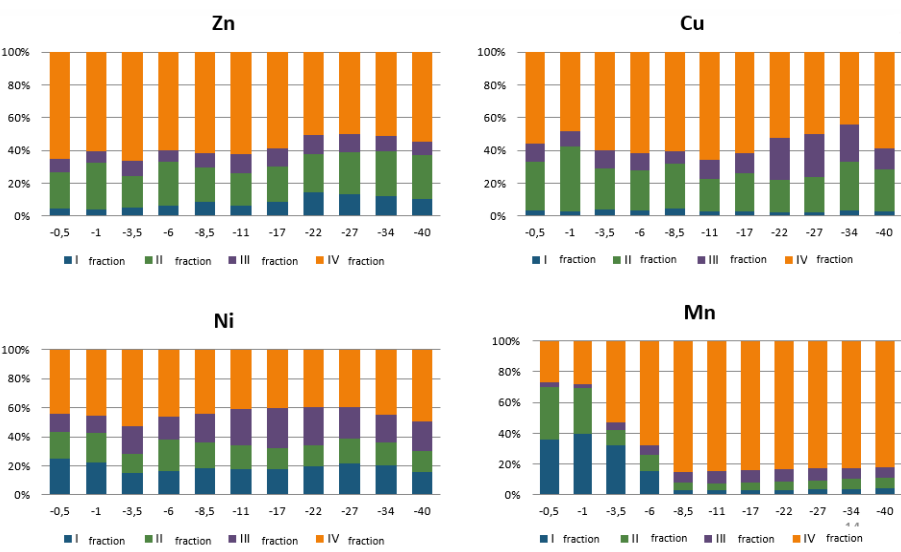
470 **Figure 1** – Map of the Ross Sea. The red circle represents the sediment B (this study). The other  
471 cores are also shown: Y5 (green dot), WRS-JB (blue dot) and ANTA91-14(violet dot) where used  
472 for a better evaluation of the sediment accumulation rate. Site D (black dot) and site H (yellow dot)  
473 where used to perform a comparison. Credits: Antarctic Mapping Tools for Matlab (Greene et al.,  
474 2017)



**Figure 2** – Fe, Al, Ti and Cr partitioning among the BCR fractions: labile (Fraction I), reducible (Fraction II), oxidizable (Fraction III) and residual (total extracted minus the sum of the three fractions, Fraction IV).



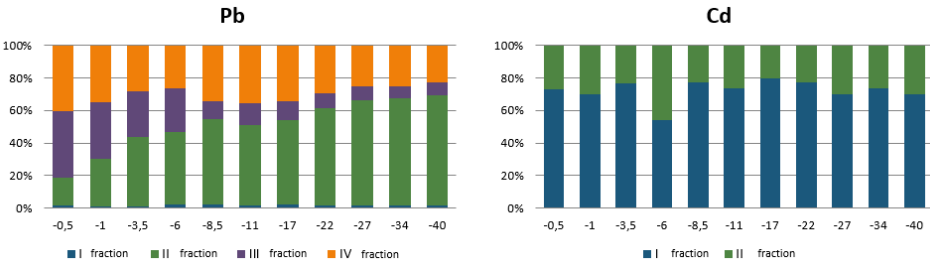
490 **Figure 3** – Zn, Cu, Ni and Mn partitioning among the BCR fractions: labile (Fraction I), reducible  
491 (Fraction II), oxidizable (Fraction III) and residual (total extracted minus the sum of the three  
492 fractions, Fraction IV).



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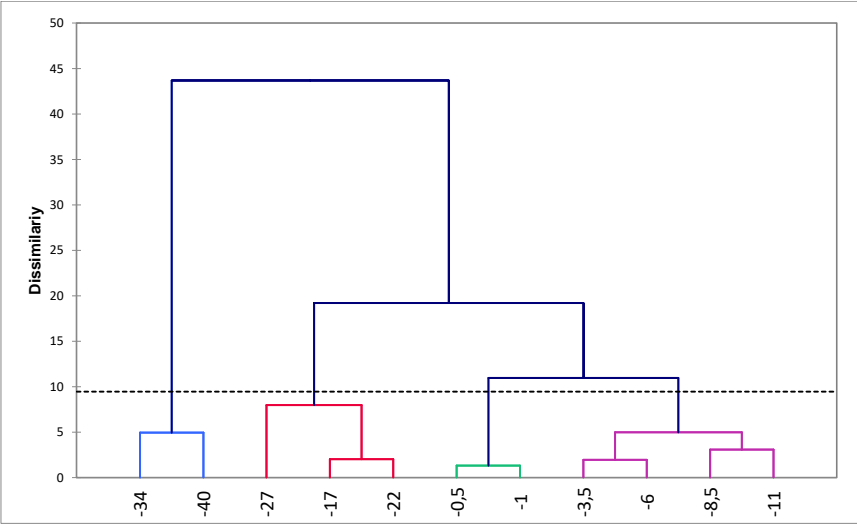
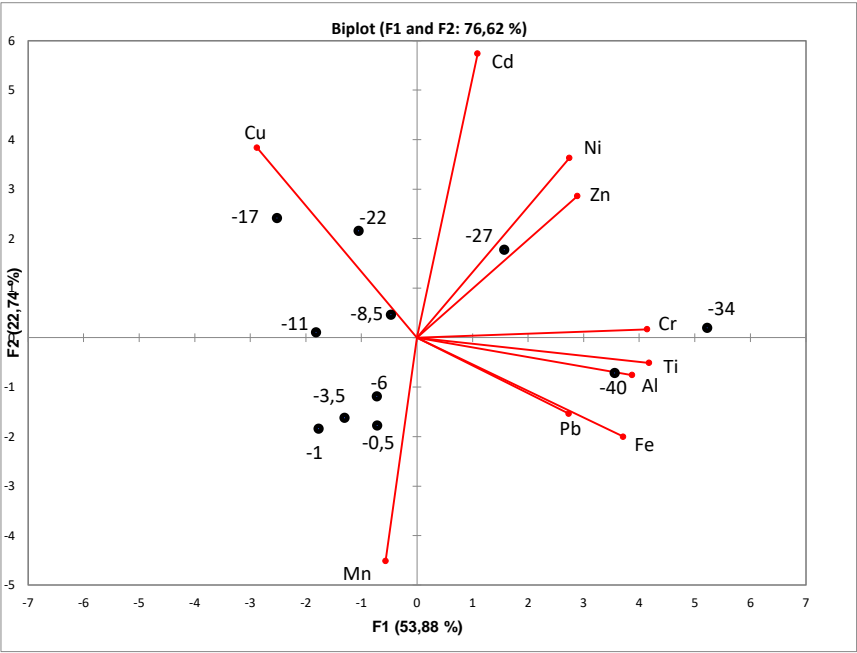
495 **Figure 4** – Pb and Cd partitioning among the BCR fractions: labile (Fraction I), reducible (Fraction  
496 II), oxidizable (Fraction III) and residual (total extracted minus the sum of the three fractions, Fraction  
497 IV).



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500 **Figure 5** – Chemometric treatments on the total element content. *First panel:* bi-plot of scores and  
501 loadings on PC1-PC2; *Second panel:* dendrogram obtained by HCA.



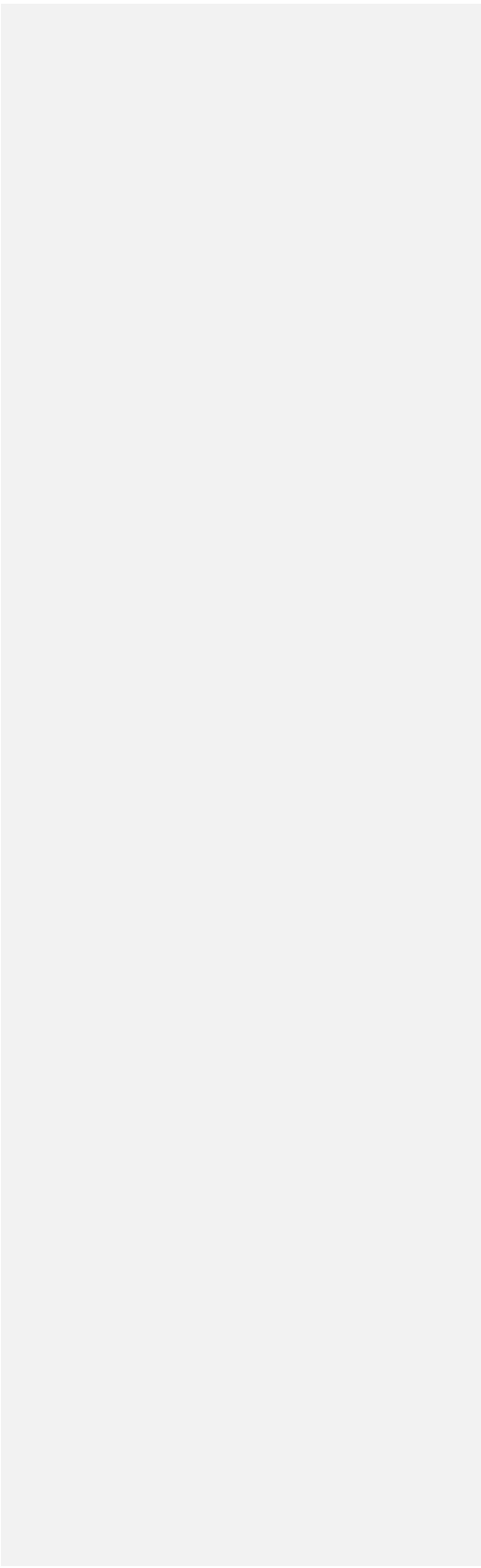
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