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# **DISTRIBUTION OF INORGANIC COMPONENTS IN ANTARCTIC DEEP AND SURFACE SEAWATERS**

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The composition of seawater is the result of the interaction of chemical, biological, physical and geological processes, which together give rise to the biogeochemical cycle. Great influence is exerted by water currents and living organisms. Moreover, the chemical composition and the biological activities in seawaters from Antarctica are strongly influenced by the formation, presence and melting of pack-ice, the low temperature and the absence of light for several months of the year.

Polar regions have a strong influence on the global planetary climate and water and air circulation. For this reason, we studied the distribution of major, minor and trace elements in four sampling sites in Ross Sea, defined as: CA, CA2, D1, B10. CA (72°10.40'S, 174°10.43'E) and CA2 (71°58.52'S, 172°29.51'E) are localized near Cape Adare. Site D1 (75°06.00'S, 164°28.00'E) is near the Drygalsky glacier, in the zone of polynya. Site B10 (74°41'S, 164°05'E) is localized in Gerlache Inlet. In the first three sites we studied the distribution of K, Ca, Na, Mg, Li, B, Si, Sr, Ba, Mn, Cd, Fe and Ni along the column of water, whereas the temporal variation of concentrations were investigated in site B10.

## **EXPERIMENTAL**

The samples were collected during the 2000-2001 (CA, CA2 and D1) and 2001-2002 (B10) expeditions to Antarctica. They were immediately filtered and frozen and were defrozen and acidified before analysis. All precautions were adopted during sample collection, pretreatment and analysis in order to avoid contaminations. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the determination of major (Na, K, Ca and Mg) and minor (B, Ba, Li, Si, Sr) elements. Cd, Fe and Ni were determined

by adsorptive cathodic stripping voltammetry at a hanging mercury drop electrode after complexation with the proper ligand. The steps of sample introduction, reagent and standard addition were automated with the aid of an autosampler and delivering units. Mn was determined by atomic absorption spectroscopy after preconcentration by solid phase extraction.

The accuracy of the procedures was confirmed by analysis of standard reference seawater.

## RESULTS AND DISCUSSION

The results obtained for the elements considered are reported in Tab 1 for samples CA, CA2, D1 and in Tab. 2 for samples B10. The concentrations found are in agreement with the typical values found in literature for clean seawater.

Tab.1. The concentrations of major, minor and trace elements in the samples collected from sites CA, CA2 and D1 (expressed in mmol/l for Ca, Na, Mg, K;  $\mu\text{mol/l}$  for Li, B, Ba, Si, Sr; nmol/l for Cd, Fe, Mn, Ni)

| Site | Dept (m) | K    | Ca   | Na  | Mg   | Li   | B    | Ba   | Si   | Sr   | Cd   | Fe   | Mn   | Ni   |
|------|----------|------|------|-----|------|------|------|------|------|------|------|------|------|------|
| CA   | - 50     | 10.1 | 9.01 | 445 | 54.5 | 27.4 | 0.36 | 70.6 | 96.1 | 83.9 | 0.46 | 1.04 | 0.22 | 4.04 |
|      | -150     | 9.69 | 9.14 | 470 | 54.6 | 23.0 | 0.38 | 80.1 | 121  | 85.0 | -    | -    | 0.62 | -    |
|      | -200     | 10.3 | 9.31 | 488 | 55.9 | 23.0 | 0.39 | 87.4 | 114  | 84.7 | 0.65 | 1.86 | 0.20 | 4.99 |
|      | -280     | 10.0 | 9.07 | 472 | 55.0 | 25.9 | 0.44 | 94.7 | 146  | 84.6 | 0.61 | 1.09 | 0.22 | 5.37 |
|      | -300     | 10.4 | 9.15 | 454 | 55.3 | 23.0 | 0.37 | 80.1 | 125  | 85.5 | 0.57 | 1.59 | 0.53 | 4.94 |
|      | -350     | 10.0 | 9.22 | 488 | 56.1 | 20.2 | 0.37 | 80.1 | 103  | 85.7 | 0.52 | 3.64 | 0.40 | 3.79 |
|      | -400     | 9.63 | 8.88 | 438 | 54.5 | 18.7 | 0.38 | 72.8 | 99.7 | 82.0 | 0.61 | -    | 1.34 | -    |
|      | -440     | 10.1 | 9.56 | 471 | 56.3 | 34.6 | 0.42 | 87.4 | 157  | 84.9 | 0.55 | 1.59 | 0.36 | 5.06 |
|      | -545     | 9.59 | 9.29 | 485 | 55.3 | 27.4 | 0.39 | 80.1 | 135  | 85.0 | 0.68 | 2.01 | 0.24 | 3.25 |
| CA2  | - 40     | 10.9 | 10.3 | 462 | 55.4 | 24.0 | 0.40 | 76.3 | 51.2 | 82.9 | 0.83 | 3.52 | 0.20 | 3.10 |
|      | - 100    | 10.3 | 10.0 | 494 | 62.0 | 25.6 | 0.34 | 80.4 | 60.1 | 87.8 | 0.74 | 3.87 | 0.27 | 2.96 |
|      | - 450    | 10.7 | 10.6 | 475 | 58.1 | 19.2 | 0.36 | 82.6 | 69.3 | 88.5 | 0.72 | 4.66 | 0.10 | 4.04 |
|      | - 600    | 10.4 | 10.5 | 463 | 59.4 | 21.4 | 0.36 | 92.7 | 61.6 | 77.9 | 0.99 | 1.90 | 0.06 | 4.99 |
|      | - 700    | 10.3 | 10.2 | 470 | 59.0 | 19.4 | 0.35 | 84.5 | 75.9 | 78.8 | 0.88 | 1.83 | 0.16 | 3.82 |
|      | - 800    | 9.48 | 10.6 | 484 | 58.4 | 16.0 | 0.42 | 91.3 | 54.8 | 78.3 | 0.56 | 1.81 | 0.20 | 3.85 |
|      | -1000    | 10.1 | 10.4 | 441 | 56.6 | 30.1 | 0.39 | 88.7 | 74.1 | 77.1 | 0.90 | 3.71 | 0.22 | 3.49 |
|      | -1200    | 10.5 | 10.5 | 455 | 60.1 | 23.7 | 0.43 | 92.3 | 80.0 | 84.0 | 0.82 | 0.88 | 0.44 | 3.68 |
|      | -1580    | 10.8 | 10.4 | 466 | 60.7 | 36.9 | 0.35 | 91.1 | 65.5 | 80.0 | 0.58 | 1.72 | 0.18 | 3.12 |
| D1   | -30      | 9.78 | 10.5 | 481 | 57.6 | 28.9 | 0.40 | 82.8 | 61.6 | 87.1 | 0.46 | 2.56 | 0.42 | 3.88 |
|      | -75      | 9.86 | 10.1 | 466 | 57.5 | 23.3 | 0.35 | 70.1 | 62.1 | 86.1 | 0.77 | 3.56 | 0.60 | 4.09 |
|      | -100     | 10.2 | 11.2 | 498 | 57.9 | 22.9 | 0.37 | 69.7 | 70.5 | 91.0 | 0.77 | 2.47 | 0.82 | -    |
|      | -300     | 9.78 | 10.1 | 488 | 55.0 | 22.8 | 0.35 | 97.4 | 84.3 | 82.4 | 0.71 | -    | 0.15 | -    |
|      | -400     | 10.6 | 10.4 | 459 | 56.3 | 27.5 | 0.40 | 81.9 | 68.0 | 85.9 | 0.64 | 1.49 | 0.82 | 3.80 |
|      | -600     | 10.0 | 10.1 | 465 | 56.6 | 32.7 | 0.45 | 94.0 | 50.4 | 89.2 | 0.80 | 3.15 | 0.78 | 3.44 |
|      | -700     | 9.75 | 10.4 | 440 | 57.5 | 25.4 | 0.36 | 73.5 | 48.5 | 87.0 | 0.76 | 2.47 | 0.64 | 3.12 |
|      | -900     | 10.2 | 10.4 | 502 | 57.5 | 32.0 | 0.49 | 102  | 58.5 | 89.0 | 0.60 | 1.40 | 1.11 | 3.15 |
|      | -1000    | 9.09 | 10.7 | 475 | 56.6 | 16.4 | 0.40 | 87.4 | 50.6 | 83.1 | 0.30 | 1.45 | 1.16 | 2.47 |

Tab.2. The concentrations of major, minor and trace elements in the samples collected from site B10 (expressed in mmol/l for Ca, Na, Mg, K;  $\mu\text{mol/l}$  for Li, B, Ba, Si, Sr; nmol/l for Cd, Fe, Mn, Ni)

| Date                            | Depth (m) | K    | Ca   | Na  | Mg   | Li   | B    | Ba   | Si   | Sr   | Cd   | Fe   | Mn   | Ni   |
|---------------------------------|-----------|------|------|-----|------|------|------|------|------|------|------|------|------|------|
| Dec <sup>th</sup><br>10<br>2001 | -14       | 11.4 | 11.0 | 418 | 60.3 | 19.8 | 0.34 | 62.1 | 67.0 | 93.1 | 0.36 | 0.99 | 0.75 | 7.30 |
|                                 | -30       | 8.89 | 9.64 | 425 | 51.2 | 23.3 | 0.37 | 65.0 | 59.7 | 85.4 | 0.30 | 5.09 | 0.38 | 8.75 |
|                                 | -100      | 8.79 | 9.55 | 445 | 52.0 | 22.4 | 0.34 | 73.1 | 48.8 | 78.4 | 0.37 | 0.51 | 0.33 | 6.12 |
|                                 | -240      | 11.1 | 10.0 | 514 | 53.7 | 21.4 | 0.34 | 65.6 | 41.5 | 84.4 | 0.50 | 0.72 | 1.18 | 11.0 |
| Dec <sup>th</sup><br>29<br>2001 | -10       | 5.46 | 7.83 | 337 | 30.6 | 9.94 | 0.16 | 48.2 | 50.0 | 54.0 | 0.34 | 4.28 | 0.35 | 3.64 |
|                                 | -35       | 9.13 | 10.4 | 425 | 51.0 | 21.0 | 0.38 | 61.0 | 40.8 | 83.4 | 0.41 | 1.78 | 0.42 | 6.67 |
|                                 | -60       | 8.73 | 9.55 | 432 | 50.3 | 15.2 | 0.34 | 86.3 | 56.6 | 82.4 | 0.33 | 2.51 | 0.82 | 12.4 |
|                                 | -240      | 9.14 | 10.2 | 466 | 51.7 | 22.2 | 0.36 | 64.7 | 51.6 | 81.0 | 0.40 | 1.25 | 0.40 | 6.48 |
| Jan <sup>th</sup><br>16<br>2002 | -1        | 10.1 | 11.4 | 438 | 51.5 | 22.2 | 0.35 | 56.5 | 53.5 | 85.0 | 0.11 | 21.6 | 2.57 | 7.13 |
|                                 | -10       | 9.20 | 9.89 | 414 | 55.5 | 27.1 | 0.35 | 65.8 | 54.7 | 93.3 | 0.14 | 1.60 | 2.06 | 7.40 |
|                                 | -50       | 10.5 | 10.4 | 475 | 55.1 | 24.5 | 0.47 | 94.2 | 61.5 | 92.0 | 0.44 | 9.51 | 1.84 | 8.69 |
|                                 | -240      | 11.0 | 10.8 | 500 | 54.7 | 16.7 | 0.34 | 75.7 | 82.6 | 85.3 | 0.51 | 39.2 | 1.53 | 10.1 |

Na, K, Ca and Mg are present with uniform distribution along the column of water in samples CA, CA2 and D1. In site B10, all the major elements were present at low concentrations in the sample collected at  $-10$  m on December 29<sup>th</sup>, probably because of the dilution with the water from the ice. The concentrations of Na in site B10 increase with depth, reflecting the trend of salinity in the water of Gerlache inlet<sup>1</sup>. Concerning minor elements, CA, CA2 and D1 sites show a greater variability of the concentrations along the water column than for the major elements. In site CA2 Si and Sr have a similar profile. Site CA is characterized by a greater concentration of Si than CA2 and D1, probably because of a stronger effect of erosion of rocks. In site D1 there is a decrease of all elements in the deepest layer. We can see a similar behaviour of Li, B, Ba, and Sr under  $-400$  m. Barium is a bio-intermediate element, whose distribution is influenced both by its involvement in biological processes and by the equilibrium between the dissolved form and barite crystal. In the samples from CA, CA2 and D1 sites, Ba has greater concentrations in deep waters, probably because of the mineralization of shells and skeletons. Also for the minor elements in B10 site we can observe the lowest concentrations in the sample collected on December 29<sup>th</sup>.

As to trace elements, low concentrations of cadmium were found in sites CA and D1 for sub-surface waters in comparison to deep waters, probably as a consequence of bioaccumulation phenomena. Cadmium has a nutrient-type profile also in the samples collected on January 16<sup>th</sup> in site B10. Iron did not show a particular trend with depth. The

distribution of this element in seawater is strongly influenced by its tendency to form oxides and hydroxides and its capacity to exist in different states of oxidation. The concentrations of nickel in sites CA and CA2 are lower in sub-surface than in deep waters, whereas they tend to decrease with depth in site D1; the causes of such decrease are not explained at the moment. No remarkable trends were observed for manganese. In sites CA and CA2, for which also the profiles of temperature and salinity are known, we found a correlation between the highest values of temperature and the highest concentrations of Fe and Ni.

The data were treated with principal component analysis (PCA) and hierarchical cluster analysis (HCA)<sup>2</sup>. The combined plot of scores and loadings on PC1-PC2 obtained by PCA and the dendrogram obtained by HCA are reported in Fig. 1a and b respectively. Fig. 1a shows that the samples from sites CA, CA2 and D1 form a unique group. The samples from B10 are separated from such group; in particular sample B10 collected on December 29<sup>th</sup> at – 10 m is differentiated from all other samples because it has the lowest major and minor metal concentrations, as discussed above.

The loadings of the major and minor metals are positive with respect to PC1 component, that is an increase of the concentrations of these elements causes an increase of PC1. This component might depend on the natural factors that normally influence these elements, that is physical factors like the effect of dilution or the presence of marine currents. The PC2 component is heavily influenced by Ni, Fe and Mn; this suggest its dependence on biological factors. Calcium and strontium are correlated, presumably owing to their similar chemical properties; the correlation between iron and manganese might be due to their involvement in redox cycles. Silicon and cadmium are probably correlated because of their nutrient-type behaviour.

In the dendrogram, samples CA, CA2 and D1 form three clusters. Therefore HCA allows to better differentiate these three sampling sites in comparison to PCA.

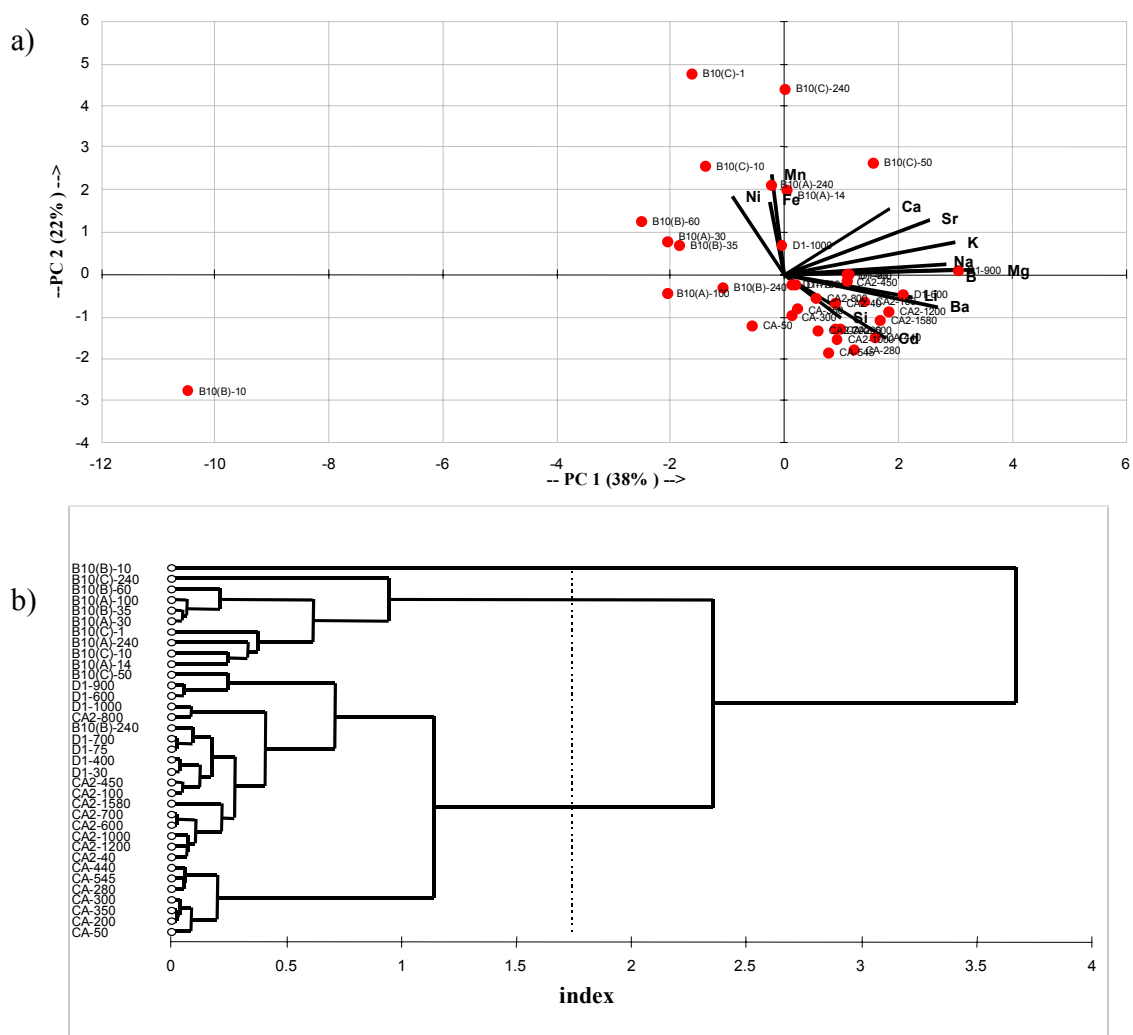


Fig. 1. a) Plot of scores and loadings on PC1-PC2 and b) dendrogram obtained by HCA (A: Dec 10<sup>th</sup> 2001; B: Dec 29<sup>th</sup> 2001; C: Jan 1<sup>st</sup> 2002)

## REFERENCES

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