

On the Distribution of Calcium, Magnesium, Sulphate and Boron in the South-Western Indian Ocean Region of the Southern Ocean

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ABSTRACT

The major ions namely, calcium, magnesium, sulphate and boron are studied in the south-west Indian Ocean. The concentrations and their ratios to chlorinity of these ions are found to be 418 ± 5 mg/kg and 0.02191 ± 0.00017 for calcium, 1285 ± 17 mg/kg and 0.06730 ± 0.00057 for magnesium, 2.67 ± 0.004 mg/kg and 0.01399 ± 0.000067 for sulphate and 4.62 ± 0.44 mg/kg and 0.242 ± 0.023 for boron.

Calcium showed distinct variations at sub-tropical convergence and Antarctic divergence whereas magnesium, though a conservative element, did not show any regular pattern of variation. Sulphate, a biologically inactive anion was found to be most conservative. Boron shows dissimilar pattern of variation in the Antarctica and sub-tropical region and varies inversely with chlorinity in the sub-tropical region. The depthwise variations of all these four ions have been described.

INTRODUCTION

The concept of ratio between constant major ion and chlorinity is well known. But deviations from this conservative behaviour are many a times encountered due to slight changes in the physical properties of sea water brought about by factors such as precipitation, evaporation, dilution by influx of land water, mostly in the coastal region and melting of ice, mixing of different water masses in the open ocean. Thus, a study of major ions becomes a useful index of identifying changes in the physical properties of sea water. The major ions calcium, magnesium and fluoride have been studied in the Northern Indian Ocean by several workers (Sen Gupta *et al* 1978, Naqvi *et al*, 1979, Noronha *et al*, 1981, Naqvi & Naik, 1982).

Southern region of the Indian Ocean and the Antarctic region needs a considerable attention to understand the influence of physical processes on the major constituents and their relations with chlorinity since the waters in this region influence the deep and bottom waters of all the oceans in the Northern region. In view of this, water samples were collected along a section from 32°S to 70°S during the First Indian Expedition to Antarctica. The present report deals with the distribution of some major constituents like calcium, magnesium, sulphate and boron in the South-West Indian Ocean region of the Southern Ocean. An attempt has also been made to correlate the data with the physical properties of sea water.

MATERIALS AND METHODS

Water samples were collected from standard depths at 17 hydrographic stations lying between 32°06'S to 69°58'S latitudes and 11° 06'E to 50° 12'E longitudes as shown in Fig. 1, Samples were analysed on board the ship for salinity and stored in stoppered plastic bottles which were subsequently analysed in the shore laboratory. Salinity was estimated using an "Autosal" salinometer. Calcium and magnesium were determined by the method of Culkin & Cox (1966). Magnesium values were corrected for strontium (0.6%) and for the end-point overestimate (1%) as suggested by Carpenter and Manella (1973).

Sulphate was analysed indirectly according to the method of Kwiecinski (1965), This method, despite its limitations, is fairly accurate for the determination of sulphate in the salinity range encountered for ocean water (Howarth 1978).

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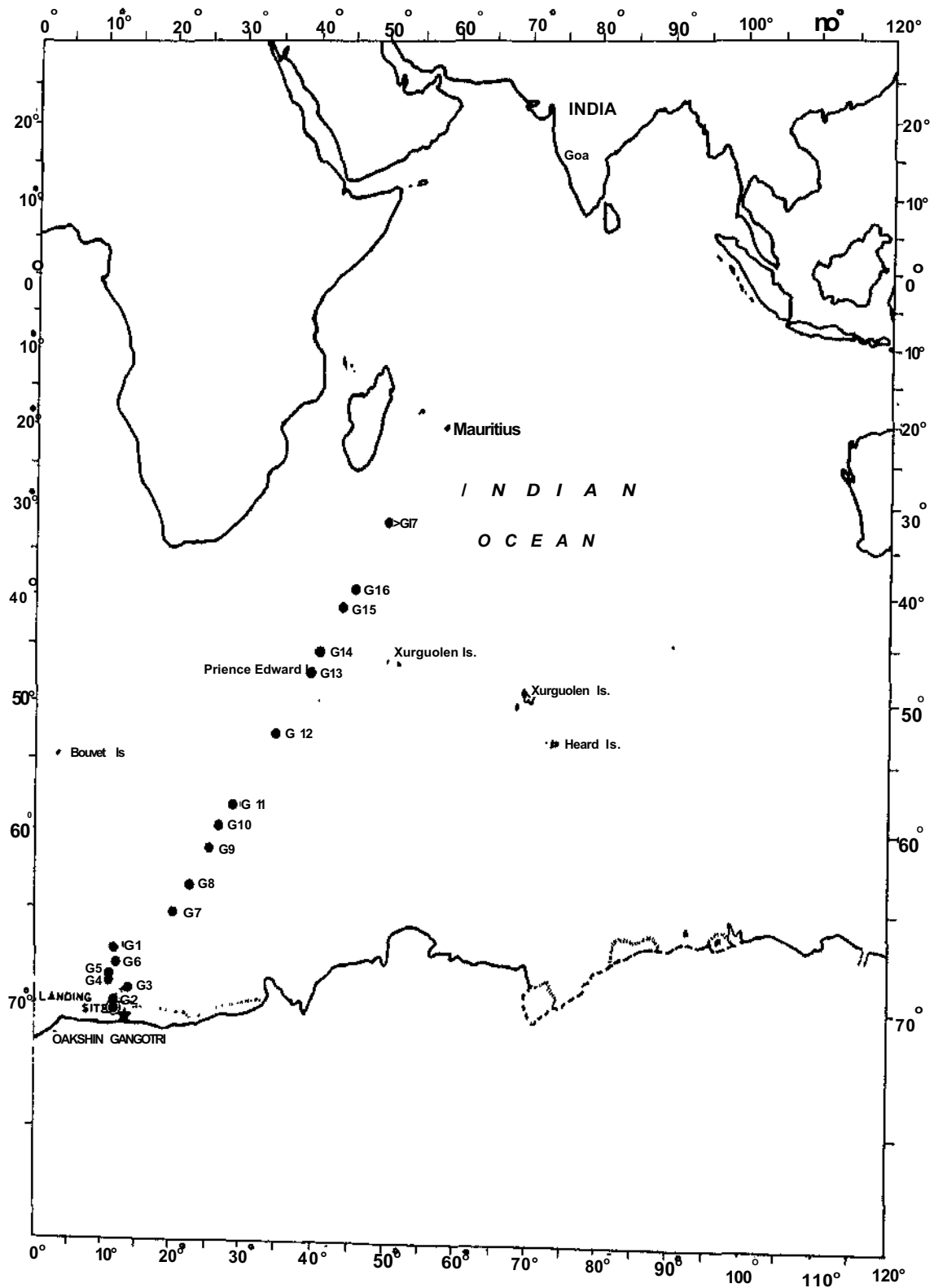


Fig. 1 : Map showing the stations position

Samples were analysed for boron content by the method of Hulthe *et al* (1970) with slight modification. The method involves treatment of the water sample with 1:1 concentrated sulphuric acid/glacial acetic acid so that organic matter is destroyed and any particulate matter is dissolved. Propionic anhydride and oxalyl chloride were replaced by acetic anhydride and hydrochloric acid and acetone with iso-butyl methyl ketone.

The precision of analyses for calcium and magnesium was determined by carrying out ten replicate analyses of a mixture of samples and expressed as coefficient of variation which was found to be $\pm 0.30\%$ for calcium and $\pm 0.29\%$ for magnesium. The precision of the method for sulphate was determined by six replicate analyses on 1 ml of I.A.P.S.O. standard sea water ($\text{Cl}^{\circ}\text{oo} = 19.375$). This showed an average sulphate concentration of 2.1762 ± 0.01162 gm/kg ($\text{SO}_4/\text{Cl} = 0.14019$), which corresponds to a coefficient of variation of $\pm 0.43\%$. Boron was estimated with a precision of 0.51% .

RESULTS AND DISCUSSION

Following Gamberoni *et al* 1982, the stations have been grouped together according to their geographical location as those in the Antarctic region (G_1 - G_{14}) and the sub-tropical region (G_{15} - G_{17}).

Calcium

The average concentration of calcium for the entire region ± 5 mg/kg with an average Ca/Cl ratio of 0.02191 ± 0.00017 . Average calcium was found to be 416 mg/kg for the Antarctic region and 425 mg/kg for the sub tropical region. There is not much data available to compare our results in this area. Tsunogai *et al* (1971) obtained a Ca/Cl ratio of 0.01295 for the Antarctic Ocean. The Ca/Cl ratio in this region lies in between those reported so far in the Northern Indian Ocean. Our value of Ca/Cl seems to be somewhat higher compared to those reported in the other parts of the world oceans. The average chlorinity for the two regions, in which the area under observations is divided, is 18.99‰ and 19.35‰ respectively. The higher Ca/Cl ratio is probably the result of high calcium concentration associated with comparatively low chlorinity in the waters. It may also be the effect of averaging.

Fig. 2 shows the depth profiles of calcium and Ca/Cl ratio in the two regions. The values at stations

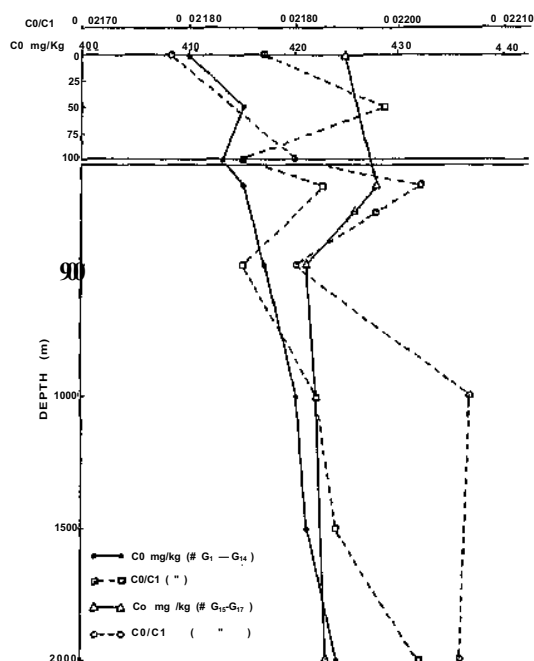


Fig. 2 : Vertical distribution of integrated values of calcium and calcium/chlorinity in the Antarctic and sub-tropical region.

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G_1 to G_{14} have been pooled together depthwise and those at G_{15} to G_{17} have been arranged separately. It can be seen from the figure that in curve (1) the calcium concentration increases from surface to 2000 m whereas in curve (2) concentration of calcium gradually increases from 0 to 200 m below which there is a rapid decrease up to 500 m. At higher depths calcium concentration is found to remain constant. It can also be noted that concentrations in the calcium profiles are of a higher order in curve (2) than in curve (1). The profiles of Ca/C1 for the Antarctic region, (curve (3)) follow a similar pattern of variation as that of its calcium profiles except between 200 to 500 m. Tsunogai *et al* observed that the Ca/C1 ratio was lower for the surface Indian Ocean water than the Antarctic Ocean which they attributed to lower concentration of calcium in the warm waters. The decrease in Ca/C1 at this depth can be attributed to the increase in the chlorinity from 200 m to 500 m and shows a sudden increase upto 1000 m. This may be the result of Antarctic intermediate water of low salinity at this depth. The effect of the change in salinity is more evident in the sub-tropical region due to greater difference in chlorinity of the two watermasses than in the Antarctic region.

An attempt was made to identify the physical processes and their influence on different watermasses using calcium as an indicator. Fig. 3 shows the latitudinal variation of calcium. Calcium profile shows

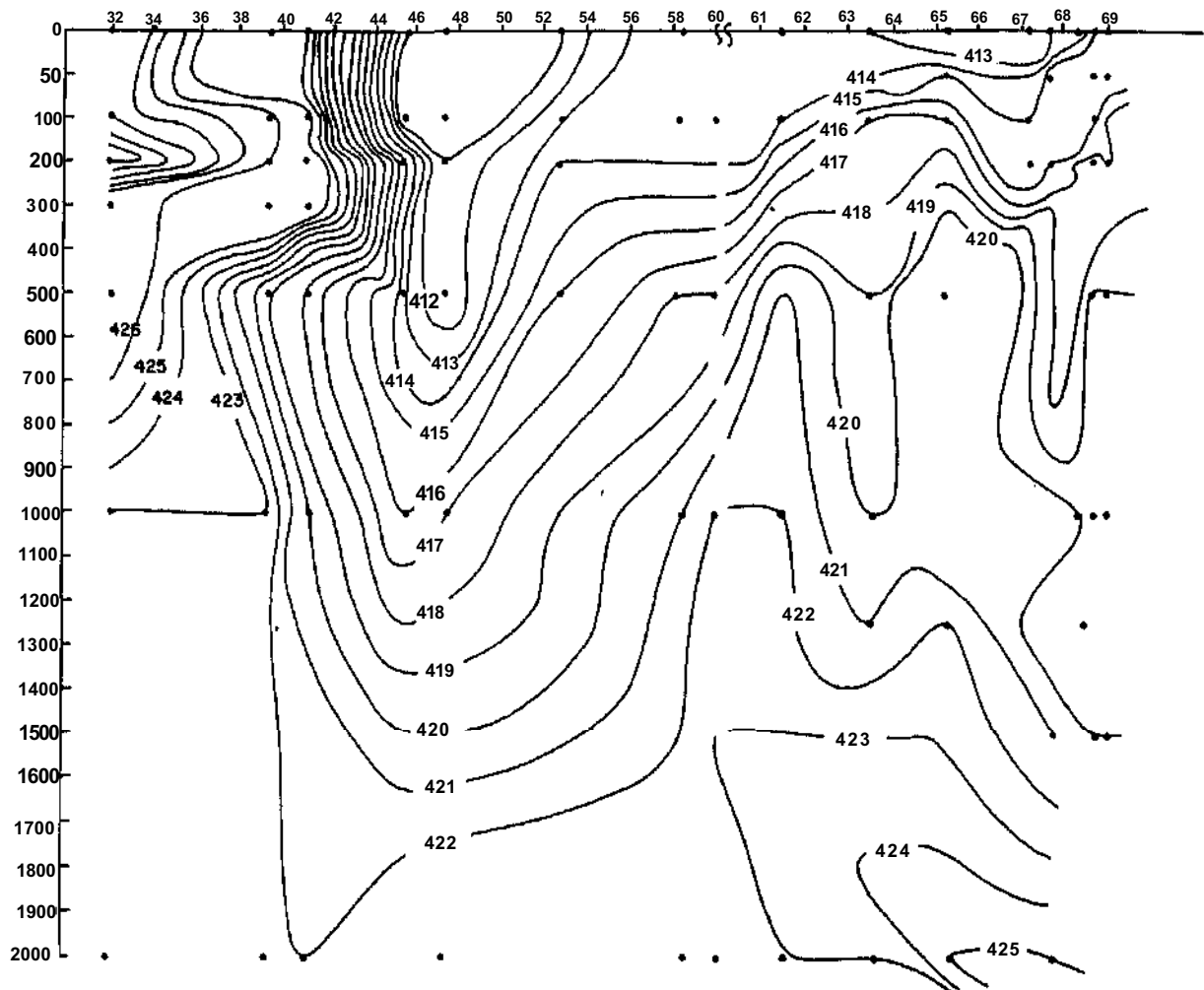


Fig. 3 : Profiles of latitudinal variation of calcium.

distinct variation at sub-tropical convergence region between 40°S to 42°S, the sinking of watermass at 46°S and the Antarctic divergence around 68 to 69°S. The Antarctic intermediate water is seen around 200 m at 61 to 62°S which sinks towards the north and flows at a depth of about 1000 m. Thus, variations in the calcium concentration in this region depend on the characteristic of the watermass as they vary with the physical changes in sea water, without significant indication of geochemical processes.

Magnesium

The average concentration of magnesium is 1285 ±17 mg/kg with a Mg/C1 ratio of 0.06730 ± 0.00057. Average magnesium concentration in the Antarctic region is 1281 mg/kg and in the sub-tropical region it is 1298 mg/kg. Our Mg/C1 ratio exceeds those reported for the other world oceans. A comparison of the present Mg/C1 with 0.06692, reported by Culkin & Cox (1966) for the world oceans, shows that this value exceeds by 0.00038 which is within the standard deviation of the Mg/C1 ratio.

Fig. 4 shows the depth profiles of magnesium and Mg/C1 ratio in the two regions. Comparison of Fig. 4 with Fig. 3 indicates similar pattern of variation in both the regions. Magnesium as well as Mg/C1 show large variations with depth. These variations have been attributed to geological and biological activity of magnesium (Culkin and Cox, 1966).

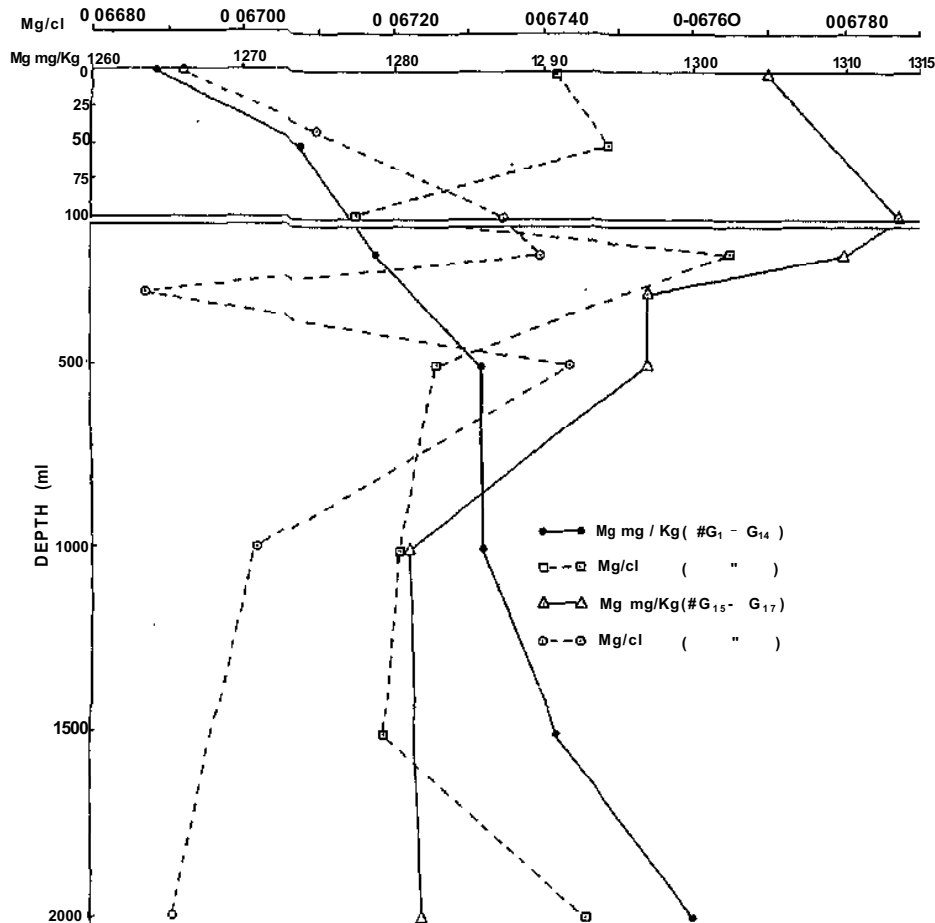


Fig. 4 : Vertical distribution of integrated values of magnesium and magnesium/chlorinity in the Antarctic and sub-tropical region.

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Magnesium did not show any regular pattern of variation geographically due to large and irregular pattern of its distribution. This suggests that calcium is a better index for identifying different water masses than magnesium. However, we feel that the high concentration of this element and perhaps some systematic error in analysis, involved in its estimation, may be responsible for the large scatter of this element, as preparation of standard solution always has the inherent risk of introducing systematic error in the final result.

Sulphate

Average SO_4^{2-} concentration and the corresponding SO_4^{2-}/Cl ratio in the region under study are 2.67 ± 0.004 gm/kg and 0.1399 ± 0.000067 respectively. The SO_4^{2-}/Cl ratio was observed to be fairly constant over depth range and location studied, ranging from 0.1394 to 0.1414. Our present value agrees remarkably well, with the SO_4^{2-}/Cl ratio reported by several other workers; 0.1400 (Morris & Riley, 1966) for surface and deep water samples from major seas and ocean basins; 0.1395 (Bather & Riley, 1954), for the Irish Sea, 0.1395 (Thompson, Johnston & Wirth, 1931) in ocean water. However, for the Baltic Sea, the ratio tends to vary (Kwiecinski, 1965).

The chlorinity values from stations G_1-G_{14} were seen to increase with depth, however, at stations G_5-G_7 $Cl\%$ values decrease with the depth. For this purpose, values of $SO_4^{2-}/Cl\%$ and for the two regions, were pooled together and arranged out then plotted against depth to give a generalised picture of the vertical distribution of these parameters (Fig. 5a & 5b). As observed from either figure, it can be seen that as the $Cl\%$ increases (Fig. 5a) or decreases (Fig. 5b) with depth, there is a corresponding increase or decrease in the SO_4^{2-} concentration. The SO_4^{2-}/Cl ratio profile does vary marginally with depth, but this is hardly significant and as such can be assumed to be constant over depth range studied.

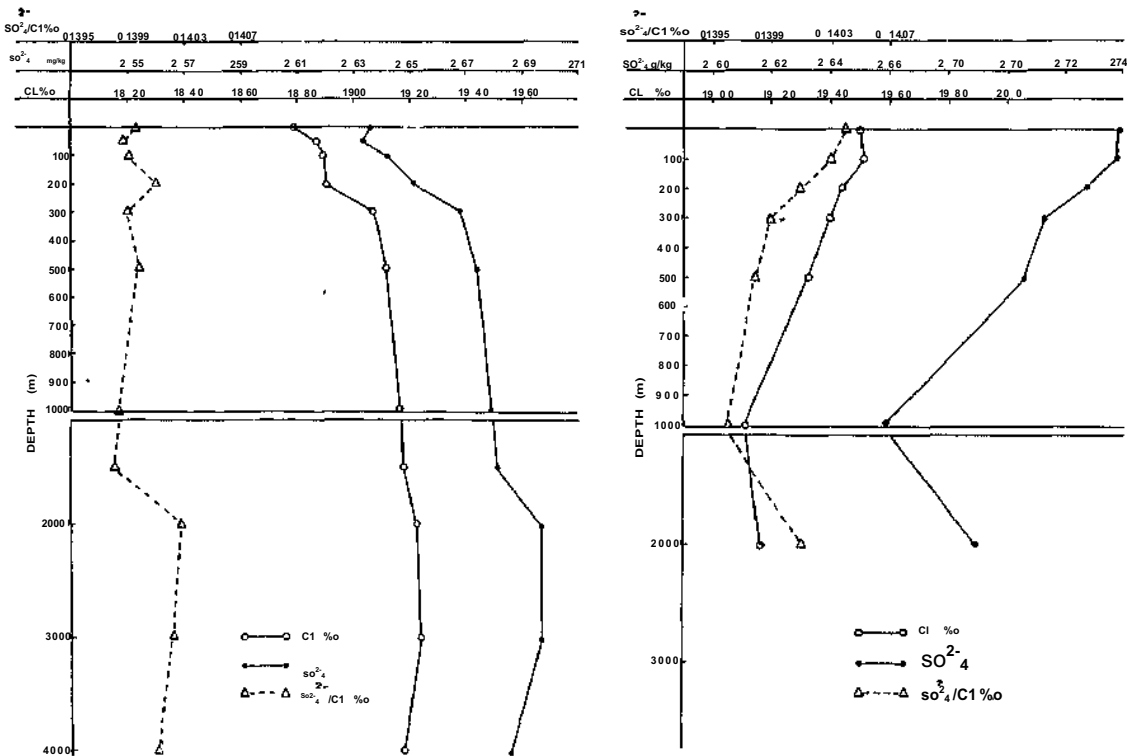


Fig. 5a & 5b : Vertical distribution of integrated values of chlorinity, sulphate and sulphate/chlorinity in the Antarctic (a) and sub-tropical region (b).

Average mean values of SO_4^{2-} and $\text{SO}_4^{2-}/\text{Cl}$ are 2.6617 gm/kg and 0.1399 for the Antarctic and 2.7108 mg/kg and 0.1402 for the subtropical region. A comparison of these average values shows that for the Antarctic region the values are lower than those in the sub-tropical region. This increase in sulphate concentration is attributed to the higher chlorinity values, the $\text{SO}_4^{2-}/\text{Cl}$ ratios in both the cases almost being constant, indicating that sulphate is a biologically inactive and the most conservative anion in ocean water.

Boron

The average concentration of boron for the entire region is 4.62 ± 0.44 mg/kg and the B/Cl ratio is 0.242 ± 0.023 . The relation $B(\text{mg/kg}) = 0.227 \times \text{Cl}\text{‰} + 0.050$ with the observed mean $\text{Cl}\text{‰}$ in this case as 19.124 gives boron concentration as 4.39 mg/kg and the corresponding B/Cl as 0.230. The ratio, as calculated, is somewhat higher than that obtained from low chlorinity Baltic Sea water by Dyrssen and Uppstrom (1973), which was 0.230. Culkin (1965) has reported the average concentration of boron to be 4.5 mg/kg at a salinity of 35‰. Goldschmidt and Peters (1932), after making a systematic study of boron in sea water from different locations and depths observed a wide range of variation. These observations suggest that some systematic relationship exists between boron content of sea water, the sediment formed in this water and the salinity of water at the time of deposition. The concentration of boron observed in the Antarctic region is higher than the calculated value. The difference is due to higher salinity in Antarctic oceans, as compared to Baltic waters.

Boron also shows dissimilar pattern of variation in the two regions. Values of boron at stations G_1 to G_{14} and at stations G_{15} to G_{17} are pooled together depthwise to present a general picture. Graphical representations are shown in Fig. 6a and 6b. The depthwise variations of boron content in the two regions is compared with that of chlorinity shown in Fig. 5a and 5b respectively. It can be observed from Fig. 5a that chlorinity increases with the depth. In the case of boron and B/Cl ratio (Fig. 6a) two minima are observed, one at 100 m and the other at 1000 m beyond which the boron concentration goes on increasing upto 4000 m depth.

A reverse pattern of variation of boron is observed as compared to chlorinity at stations G_{15} - G_{17} (Fig. 6b), where boron and B/Cl ratio generally increases from surface upto 1000 m while a decreasing

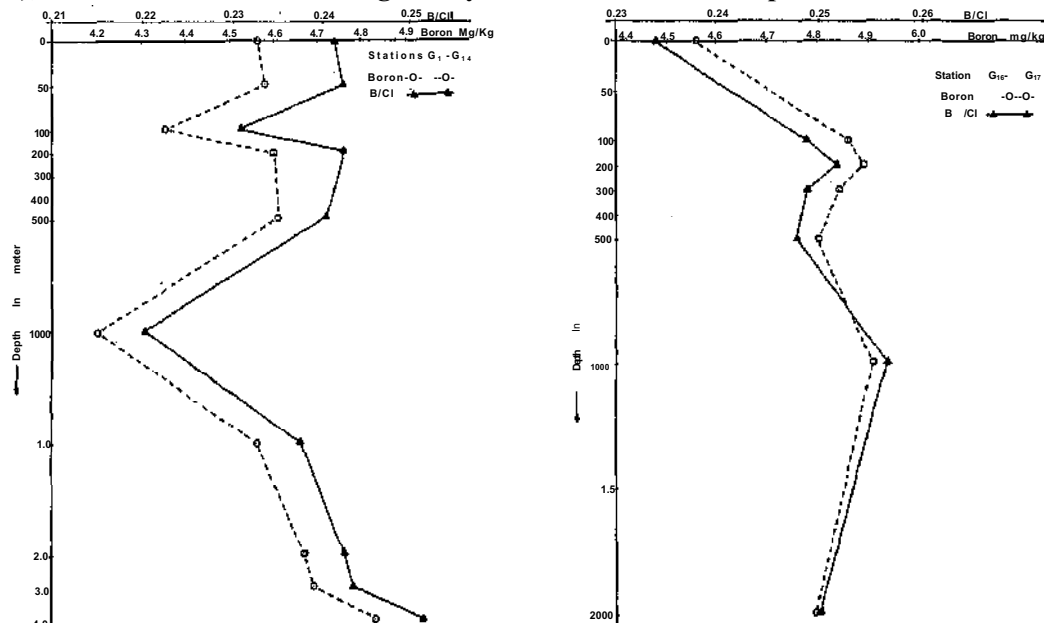


Fig. 6a & 6b : Vertical distribution of integrated values of boron and boron/chlorinity in the Antarctic and sub-tropical region.

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trend is observed in case of chlorinity at this depth interval. Below 1000 m, chlorinity increases slightly with a corresponding decrease in boron and B/C1 ratio. Boron as well B/C1 ratio show a maxima at 100 and 1000 m which is the reverse of what is observed in previous stations.

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REFERENCES

- Barther J. M. and Riley J. P. (1954)
The chemistry of the Irish Sea Part I: The sulfate chlorinity ratio. *Jr. Con perm. int. Explor. Mer.* 20; 145-152
- Carpenter J. H. and Manella M. E. (1973)
Magnesium to chlorinity ratios in sea water. *J. Geophys. Res.*, 78; 3621-3626.
- Culkin F. (1965)
In *Chemical Oceanography vol. 1*; ed. by J. P. Riley and G. Skirrow (Academic Press) London, 121.
- Culkin F. and Cox R. A. (1966)
Sodium, potassium, magnesium, calcium and strontium in sea water. *Deep Sea Res.* 13; 789-804.
- Dyrssen D. W. and Uppstrom L. R. (1974)
B/C1 ratio in the Baltic Sea water. *Ambio*; vol. 3; No. 1 pg. 44-46
- Dyrssen D. W. and Uppstrom L. R. (1973) -
In *Report on the chemistry of sea water. IX*, Univ. Gotingen 1-6.
- Gamberoni, Ceronimi and Jeannin P. F. and Marail J.F. (1982)
Study of frontal zones in the Crose-Kerguelen region. *Oceano acta*, vol. 5,3, (1982)
- Goldschmidt V. M. and Peters G. (1932)
Zur geochemie des Bors. *Nachr. gesselsch, Naturwissench*, Gottingen, Mathphys. Klasse III, 25IV, 402.
- Howarth R. W. (1978)
A rapid and precise method for determining sulfate in sea water; estuarine waters and sediment pore water. *Limnology and Oceanography* 23 :1066-1069.
- Hulthe P., Uppstrom L and Ostling G. (1970)
An automatic procedure for the determination of boron in sea water. *Anal Chim. Acta*, 51; 31.
- Kwiccinski B. (1965)
The sulfate content of Baltic sea water and its relationship to chlorinity. *DeepSeaRes.*, 12,797-804.
- Morris A. W. and Riley J. P. (1966)
The bromide-chlorinity and sulfate chlorinity ratio in sea water. *Deep-Sea Res.*, 13,699-705,
- Naqvi S. W. A. and Reddy C. V. G. (1978)
On the variation in calcium content of the waters of Laccadives (Arabian Sea). *Mar-Chem.* 8,1-7.
- Naqvi S. W. A. and Naik S. (1983)
Calcium/chlorinity ratio and carbonate dissolution in the northwestern Indian Ocean. *Deep-Sea Res.*, 30,381-392.
- Noronha R. J., Moraes, C. and Sen Gupta R. (1981)
Calcium, magnesium and fluoride concentration in the Andaman Sea. *Ind. J. mar. Sci.* 10,234-237.
- Sen Gupta R., Naik S., Singhal S. Y. S. (1978)
A study of fluoride, calcium and magnesium in the Northern Indian Ocean. *Marine Chem.* 6,125-141.
- Shirodkar P. V. (1982)
Distribution of boron in shallow waters over the Wadge Bank. *Mahasagar-Bull. Nam. Inst. Oceanogr.* (In press)
- Shirodkar P. V., Singhal S. Y. S. and Sen Gupta R. (1982)
Studies on boron along the Central West Coast of India. *Ina. J. mar. Sci.* 11,251-252.
- Thompson T. G., Johnston W. R. and Wirth H.E., (1931)
The sulfate chlorinity ratio in ocean-water. *Jr. cons. perm. int. Explor. Mer.*, 6,246-251
- Tsunogai S., Yamazaki T and Nishimura M. (1971)
Calcium in the Antarctic ocean. *Journal of the Oceanography, Society of Japan*, 27, 5,191-196.