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An Investigation of the Relation between Chlorinity and Electric Conductivity in Baltic Water

by

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Introduction

Recent developments in oceanographical instruments have made possible the measurement of some properties of sea water with greater accuracy than could be achieved with earlier methods. This, however, makes necessary a revision of some hitherto accepted relations in sea water, if the new instruments are to be used. Conductance, H, in particular, is used to determine the salinity of the sea with an exactness of a few thousands of per mille. In this way, not only is a more exact measure of the salinity, S, obtained, but also of, among other things, the density, which is of great importance for dynamic calculations. However, the relations between H and density, Cl and S respectively are not yet known with satisfactory precision.

The transition from the determination of salinity by chlorine titration (Cl - S) to instrumental determination of salinity via H (H - S) requires an exact knowledge of the relation between chlorinity and H. It is essential that the results of chlorine titration (Cl - S) and those of salinometric measurements (H - S) shall be comparable. To achieve this we must know whether the relation H/Cl is the same in all sea water. If it is not, each instrument must be recalibrated for the sea to be investigated. Our knowledge of the relations between the various elements of sea water is based almost exclusively of Dittmar's studies, published in the Challenger Reports, 1885. These analyses were of excellent quality for their time, but they have not the precision we can achieve nowadays with modern methods. Dittmar's result showed that the composition of different sea waters was approximately constant, with only few exceptions. There was no consistency in the deviations. Dittmar himself observed, for instance, that two samples of ocean water of the same chlorinity might vary by about 0.15°/oo in salinity. Dittmar's samples did not include the Baltic Sea, the Mediterranean, the Red Sea or the Arctic and Antarctic regions, where deviations may be expected.

Three years ago, the British National Institute of Oceanography began the collection of samples of water from all the seas in the world in order to determine these relationships. The first result of the investigation showed that the relation between Cl and density (Knudsen 1901), accepted formerly, is unsatisfactory, and that there is good relation between H and density, but great variations in the relation Cl - H. Cox (1962) has analyzed about 300 samples with salinity ranging from 33 to 39°/oo, and has found appreciable variations in the relation H - Cl; samples with the same H may differ in Cl by as much as 0.03°/oo.

The investigation

There has thus been considerable recent work on ocean water of normal and high salinity. In the Baltic, with its specific hydrographical conditions, the problem is a complicated one. Voipio (1962) has found great differences between Cl - S and H - S, while Gripenberg (1937) proved that Ca/Cl is quite different in the Baltic than in ocean water.

In order to make clear this relation for the Baltic Sea, an investigation was begun in the autumn of 1962 at seven stations, as shown in the map in Fig. 1. Conductance was determined with the help of an Australian salinometer according to Hamon and Brown (1961), while the salinity (H - S) was calculated from the tables belonging to the instrument (mainly Thomas, Thompson and Utterback, 1934, for lower salinities). Precision is 0.003°/oo S. The chlorinity was measured potentiometrically, mainly according to Bather and Riley (1953), but with silver indicator and reference electrodes. It is a precision titration in which a weighted sample of sea water W, is titrated with a balanced amount of $AgNO_3$ solution, T, and equivalence point is attained volumetrically with a recording millivoltmeter, type 'Speedomax'. Standard seawater was titrated every day, and factor F was calculated, with the help of which the chlorinity was determined according to $Cl = \frac{T\ F}{W}$; precision is 0.003°/oo Cl. From the chlorinity was calculated the salinity, S°/oo, according to Knudsen, designated Cl - S. Then the difference Δ S between H - S and Cl - S was calculated. The Ca content was determined titrimetrically with the help of EDTA according to Malmstedt-Hadjioanou (1959), with a precision of 1 mg Ca/L. The Ca content is considered to be the most important factor as regards deviations in the relations H - S and Cl - S. The Ca content determined in this way was compared with a Ca content calculated from the relations for ocean water, Ca/Cl = 0.02106. The difference is designated ΔCa.

Results

The diagram for Vinga, Måseskär and Bornö shows that ΔS is higher in the surface water, approximately $0.030^{o}/oo$ S than below the halocline. The surplus of calcium in the surface water is about 8 mg Ca/L, and declines rapidly below the halocline; in the diagram the Ca curve is like a reversed picture of the salinity curve. Below the halocline, ΔCa follows closely upon ΔS, although both are small and in the vicinity of the zero line. See Figs. 2 and 3.

At the transition to the Baltic stations, ΔS and ΔCa rise considerably, and the highest values are at the surface; ΔS follows, on the whole, ΔCa, and is almost a reversed picture of the salinity curve. Both ΔS and ΔCa decline greatly below the halocline, after which they drop gradually with depth (Figs. 4, 5, 6 and 7). There is a clear geographical distribution of ΔS and ΔCa, both with regard to size and variation with depth. For surface conditions, the highest values of ΔS and ΔCa are found at S 24, while F 81 has a lower value; the lowest values are found at F 78 and SS 29 B. The situation is the opposite with reference to the values of ΔS and ΔCa in the bottom water. The highest values are found at SS 29 B and F 78, while F 81 has a lower value and S 24 the lowest. The greatest difference between the surface and bottom for ΔS and ΔCa was found at S 24, the smallest at SS 29 B.

Discussion

Koroleff (in Granquist 1955, and in Hela and Koroleff 1957) made determinations of calcium in water from the same stations as above with samples taken during the summers of 1954 and 1955. The values of ΔCa from these analyses have also been inserted into Figs. 4, 5, 6 and 7. Here, too, is a geographical distribution, and the values decline in the same way from S 24 to F 78. Unlike the present investigation, ΔCa increases with depth, however; S 24 is an obvious example (see Fig. 4). For deep water, ΔCa is also geographically distributed, greatest at S 24, less at F 81 and F 78.

The difference between the Ca values given here and the corresponding values given by Koroleff is probably due to different degrees of stagnation when the two measurements were made. Koroleff's samples were taken in 1954-55, during, according to Fonselius (1962), a great period of stagnation, while the result presented here refers to the year 1962, after an inflow of fresher water (1959 for the Bornholm basin and 1961 for the Gotland basin, according to Fonselius, ibid.). Salinity declines gradually during stagnation, while ΔCa increases. Koroleff's high values for bottom water are probably due to the great calcium-dissolving ability of the water. The factors facilitating the solution of calcium are, according to Buch (1945), low temperature, low salinity and acid pH, the last-named being of dominant importance. Buch found the greatest undersaturation with reference to $CaCO_3$ in the Gotland basin, where undersaturation values between -0.56 and -0.48 correspond to pH-values varying between 7.00 and 7.12. Water of a low pH-value is formed during stagnation periods, when oxygen is consumed in the oxidation of carbon to carbon dioxide, whereby the acidity of the water increases (pH declines when ΣCO_2 increases without any considerable change taking place in alkalinity). Conditions for the solution of calcium are therefore much more favourable in the Baltic than in the oceans.

There is a great increase in Δ S and Δ Ca from the Skagerack to the Baltic Sea. Although there does not seem to be any simple relation between salinity and Δ S and Δ Ca respectively, it may be said that, in a 'healthy' condition, the more salty water has lower values of Δ S and Δ Ca; the values are practically zero in the very salt water from the Skagerak.

It will be observed that the surface water is also rich in Ca. Generally speaking, the surface water is undersaturated as regards $CaCO_3$ (Buch 1945), at least in the northern parts of the Baltic. In the southern parts a great influx of Ca takes place from the Ca-rich riverwater flowing from Central Europe, while in the north the influx from the Ca-poor regions of northern Europe is slight.

Although the increase in Δ S usually follows that of Δ Ca, there is no constant relation between them. There must be other disturbing elements. Wittig (see Buch 1945) has shown, among other things, that the increase of Ca-ions is not equivalent to the increase in alkalinity. The fact that the alkalinity increases more than Ca may mean that other carbonates than $CaCO_3$ were released, in the first place $MgCO_3$, according to Wittig. This conclusion is also in keeping with the small surpluses of Mg which Koroleff found in the Baltic in 1954-55.

Deviations in the relation between Cl - S and H - S provide convincing evidence that the determination of salinity should be made via conductance. With a view to elucidating the problem further, more analyses should be made of H - S, Cl - S, Ca and Mg; but the effect of the whole carbonic acid system on H should be explained, in which the pH-value and alkalinity must be determined.

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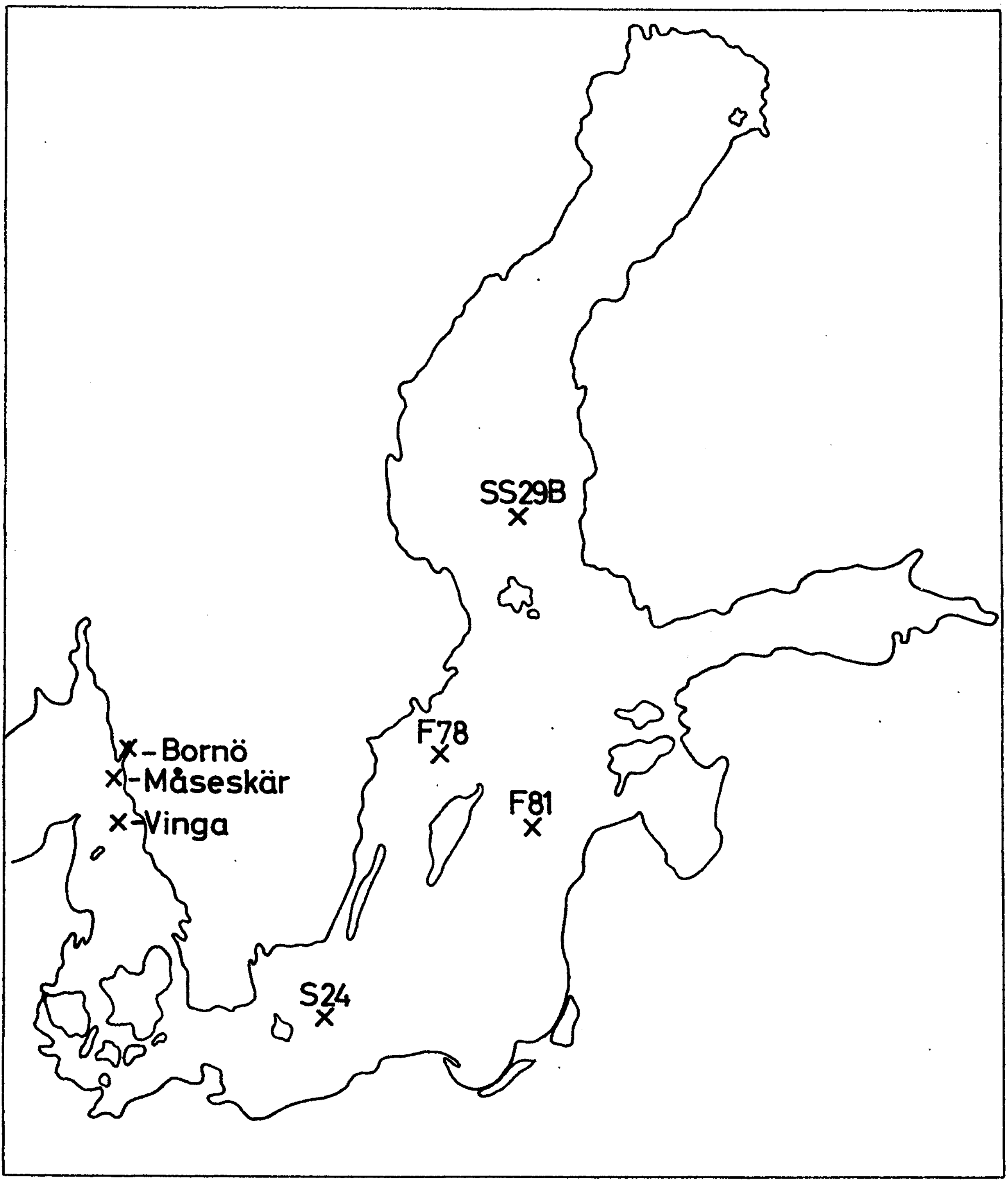
Fig 1



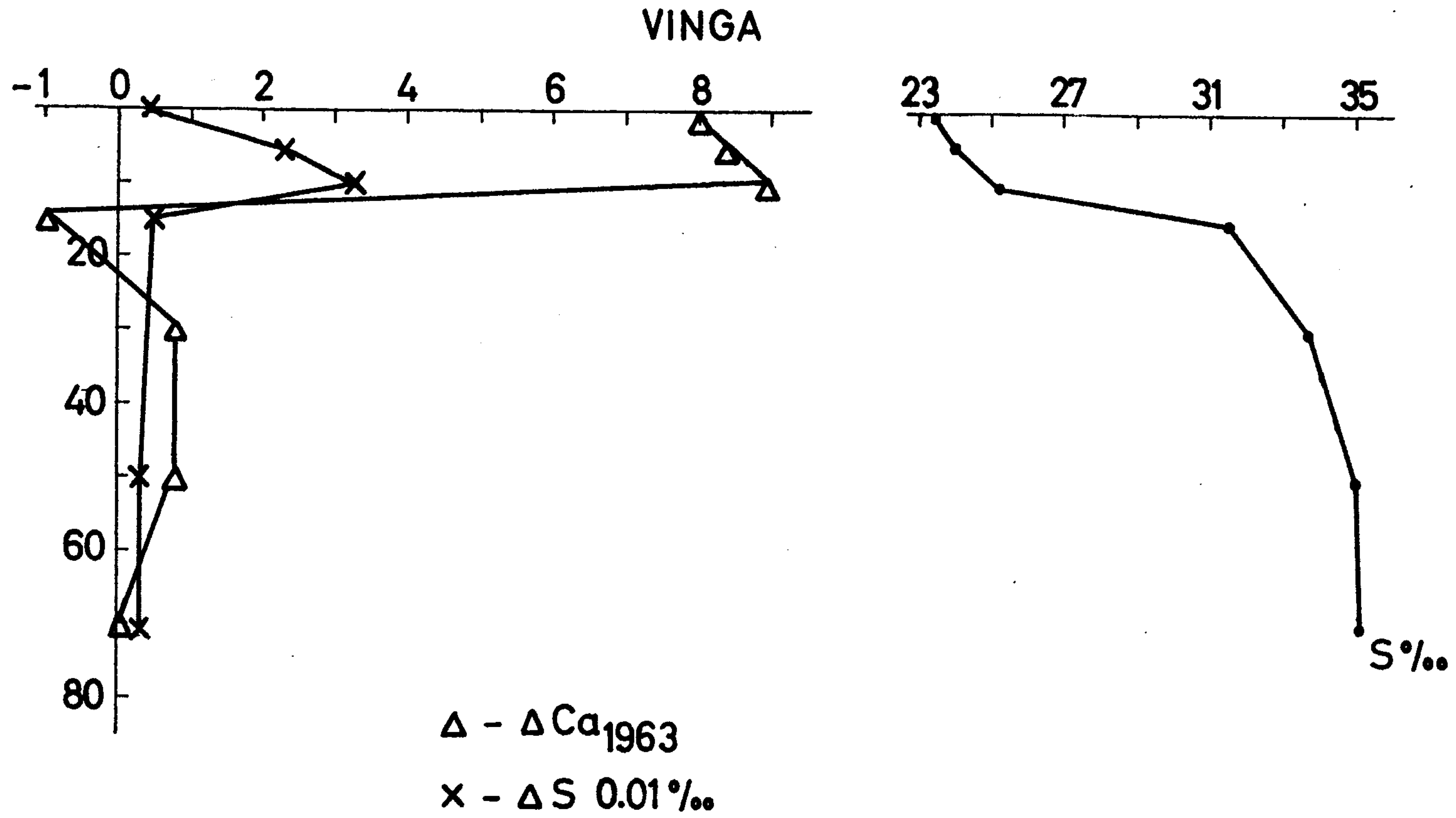
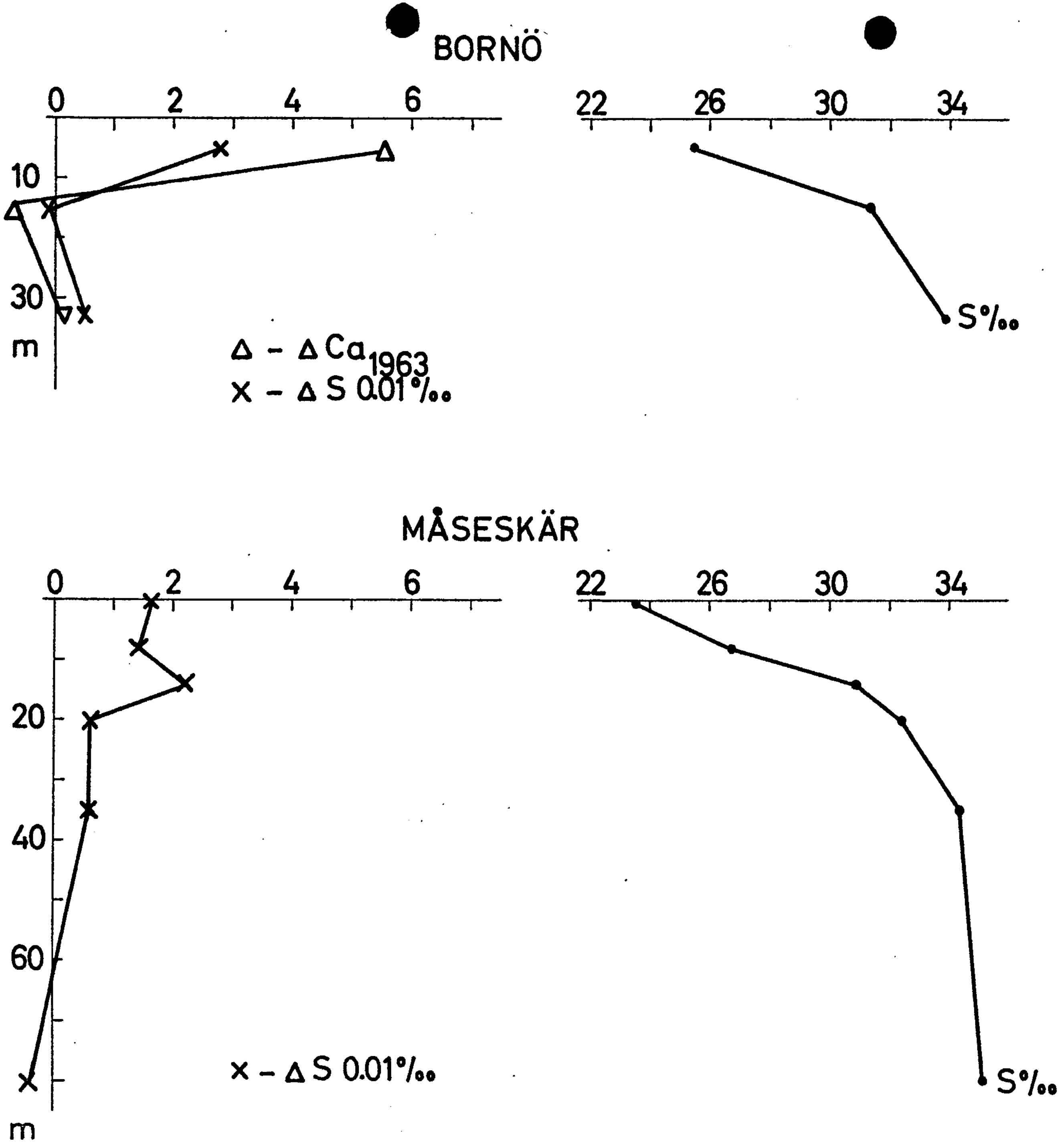


Fig 2


BORNÖ
0
2
4
6
22
26
30
34
10
30
m
S°/oo
Δ – ΔCa1963
x – ΔS 0.01°/oo
MÅSESKÄR
0
2
4
6
22
26
30
34
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40
60
m
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S°/oo

Fig 3

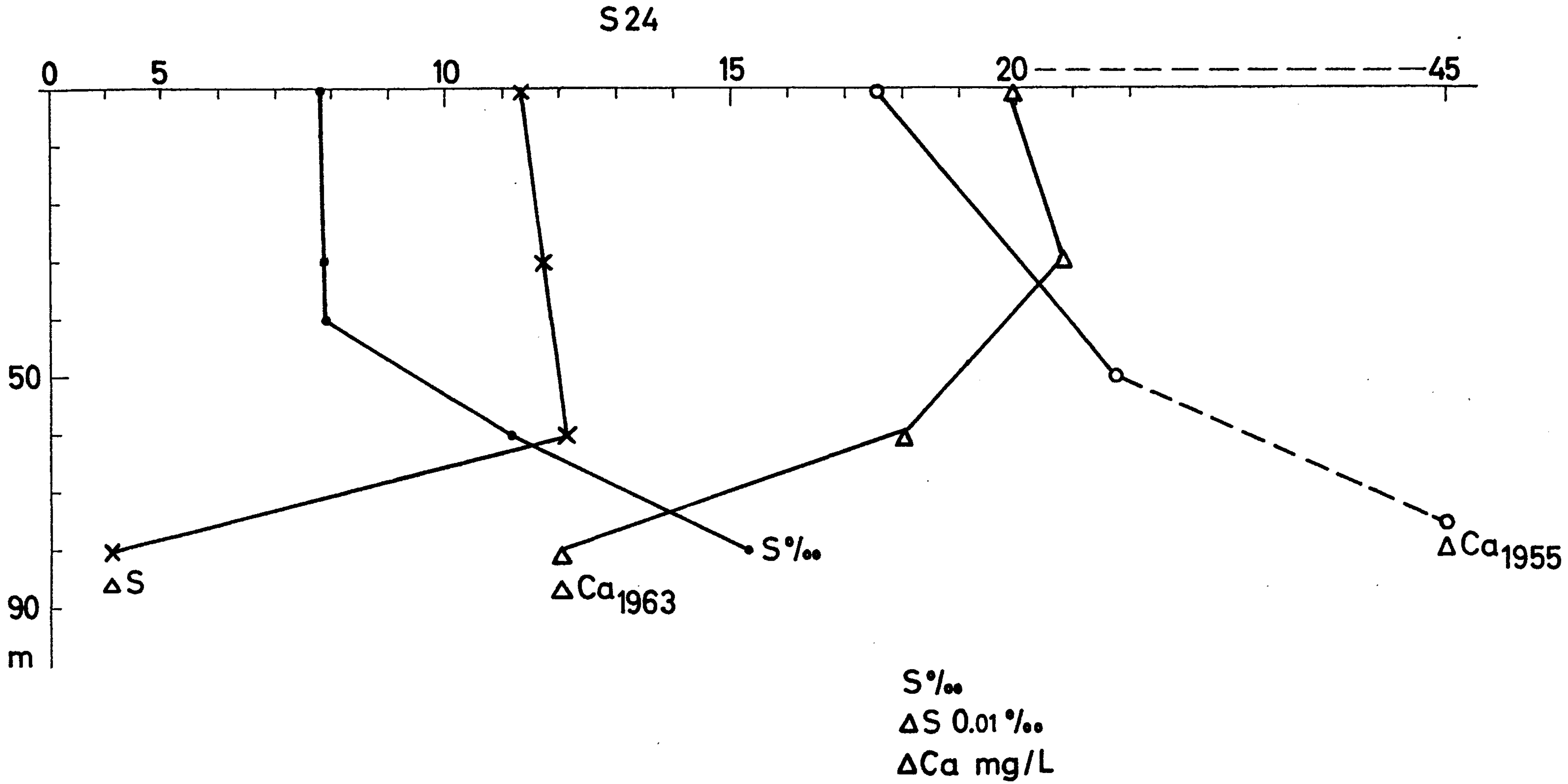
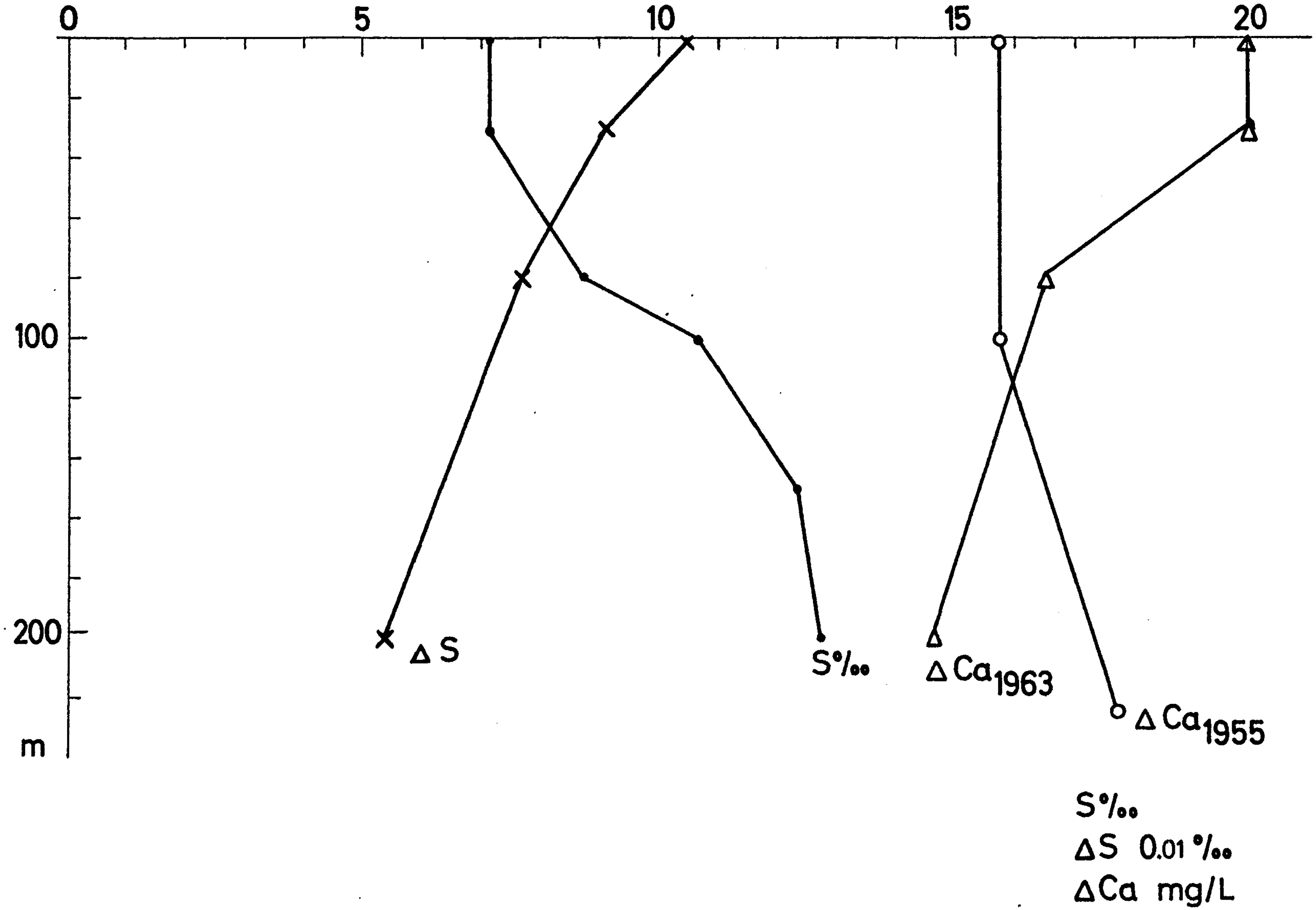

S 24
0
5
10
15
20
45
50
90
m
ΔS
ΔCa_{1963}
S ‰
ΔCa_{1955}
S ‰
ΔS 0.01 ‰
ΔCa mg/L

Fig 4

F 81



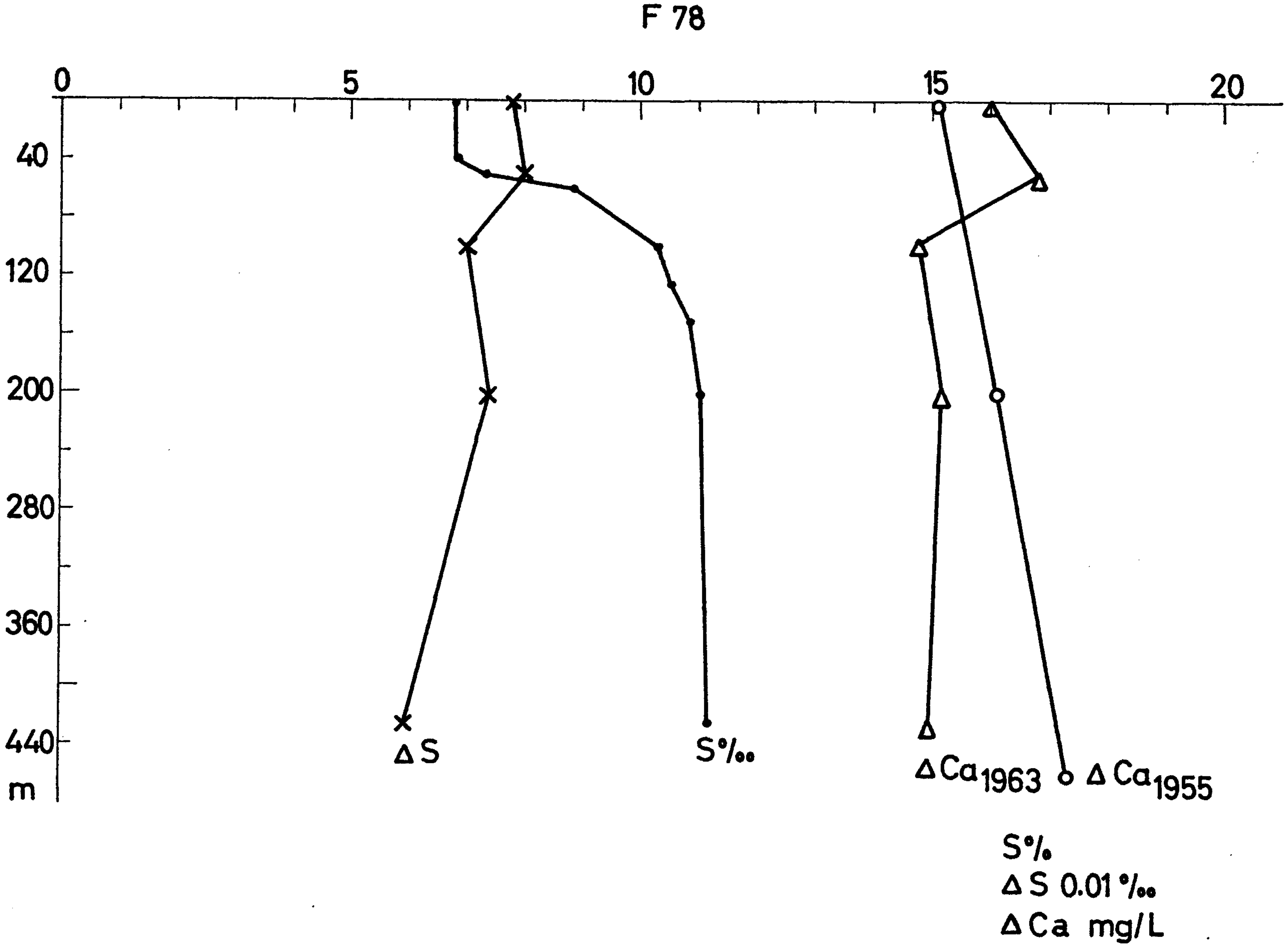

F 78
0
5
10
15
20
40
120
200
280
360
440
m
ΔS
S°/oo
ΔCa1963
ΔCa1955
S°/o
ΔS 0.01 °/oo
ΔCa mg/L

Fig 6

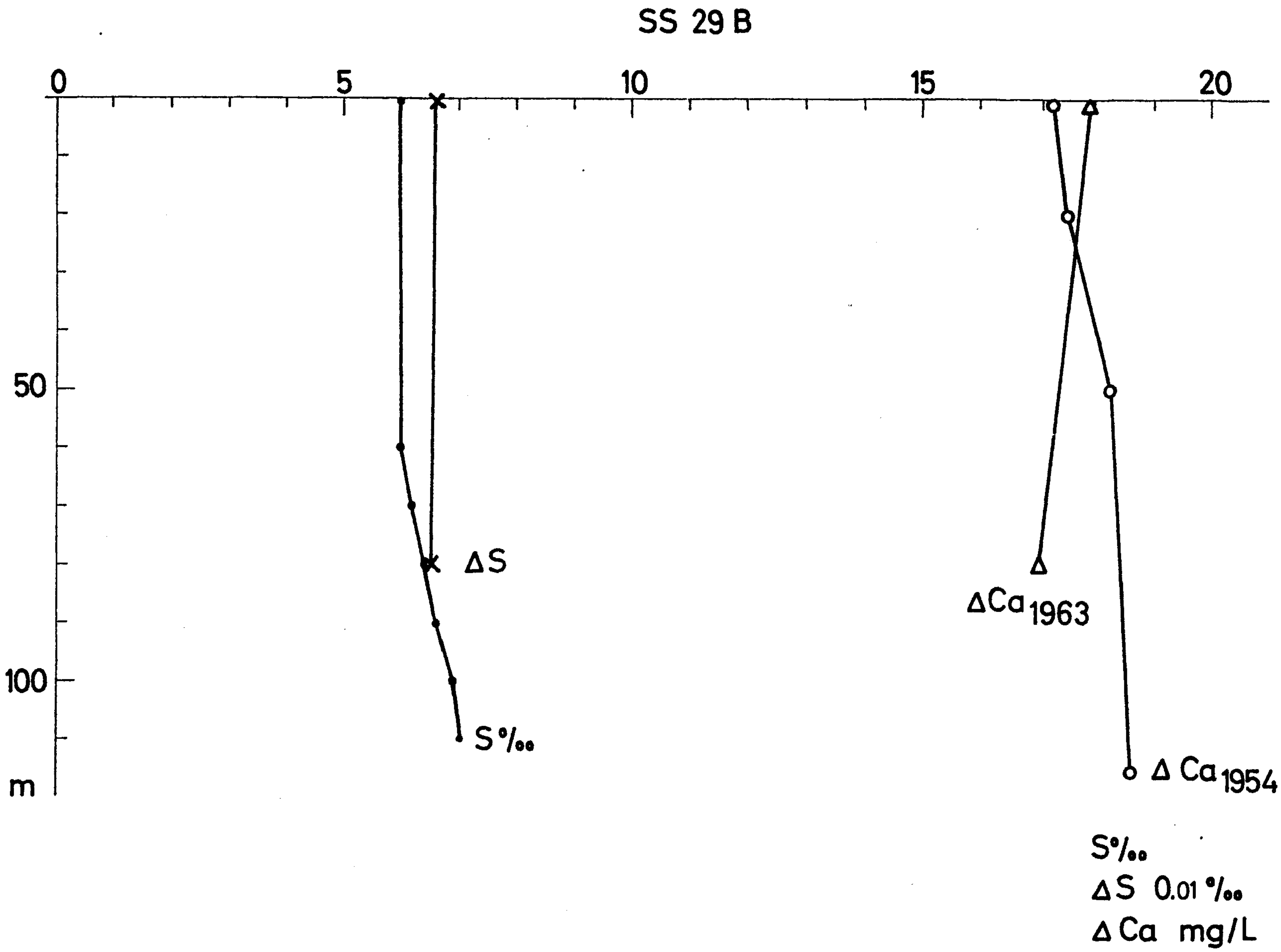


Fig 7