1985

THE INFLUX OF BLACK MAGNETIC SPHERULES TO THE LAKES OF THE ENGLISH LAKE DISTRICT

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2ND YEAR APPLIED CHEMISTRY
THE UNIVERSITY OF SALFORD

CONTENTS

Introduction to the Freshwater Biological Association

The Freshwater Biological Association was founded in 1929 to meet the lack of facilities for freshwater research in the United Kingdom.

The Association was originally based at Wray Castle near the northern end of Windermere. In 1950 the headquarters and main laboratories were moved to their present location at The Ferry House, which is situated at the western landing of the ferry, which traverses Windermere. These laboratories provide the study centre for lakes, reservoirs and upland streams and rivers. A laboratory is also maintained in Dorset for the study of lowland streams and rivers in southern England and a unit (the Teesdale unit) is situated at Lartington, Co. Durham for the study of upland streams and rivers.

The research projects undertaken by the Association are financed partly by the Natural Environment Research Council and partly through contracts from regional water authorities, commercial and international organisations and government departments.

Research within the Association covers the fields of Algology, Chemistry, Fish, Invertebrates, Macrophytes, Microbiology and Palaeolimnology. Substantial administrative, library, stores and workshop facilities support this research.

The Chemistry department has two roles to fulfill, acting in both a service and a research capacity. As a service department it undertakes: analyses of water for nutrients, sediment analysis and analysis of fish and other tissues,for the biologists. In a research role, the chemical processes within freshwaters are studied and topics covered include: the geochemical cycling of iron and manganese species within lakes and studies of the organic and magnetic fraction of sediments. The department is equiped with modern instrumentation and has a staff of about a dozen full-time scientists.

Project Summary

The project undertaken during the period 18-2-85 to 23-8-85 was to determine whether the influx of Black Magnetic Spherules (B.M.S.) into lakes was directly from the atmosphere or via the catchment.

The method of solution of this problem was to collect samples of sediment from a number of lakes. These samples would then be analysed for B.M.S. and the flux to the lake surface calculated.

A statistical link between the fluxes for several lakes would show the input to be independant of the catchment area (and type) of the lake (since lakes with widely differing catchments were to be studied). This would give reasonable proof that input was primarily atmospheric and did not include material from the catchment.

Background Information

Black Magnetic Spherules

These particles are part of the total magnetic fraction found in sediment. Previously these particles have been found in ocean sediments, peat sections and have been collected on filtration of the air, although no detailed study of their presence in lake sediments has been conducted.

The origin of these particles was originally thought to be extra-terrestrial but recently it has been shown that they are produced as a result of fossil fuel burning.

Occasionally these particles may have a diameter greater than 100 microns but they are usually less than 70 microns and their abundance increases almost exponentially with decrease in diameter. Most of the particles found during this study were of less than 10 microns diameter. Externally these particles are spherical, black and have a smooth or sculptured surface, sometimes with projections from the surface (fig.1).

Analysis of the spherules has shown them to be constructed of a core of alpha-iron, followed by a layer of Wüstite containing some alpha-iron and an outer layer of Magnetite. The iron content of the spherules is of the order 60-70% and high percentages of nickel and cobalt are found together with traces of iridium (Delmonte, M. 1976).

Magnetic Susceptibility

This technique gives a measure of the volume concentration of magnetic minerals within a sample. The value obtained depends not only on the mineral but also on its grain size. It has been shown that decreasing grain size results in a slight decrease in susceptibility (Bloemendal J. 1982) .

This technique was used in two ways:

Firstly it was used to gain a rough guide to the distribution of magnetic material within a core of sediment (as detailed later). Measurements were taken and a graph of sediment depth against susceptibility was plotted to reveal a profile of the ´Whole Core Susceptibility´.

Secondly this technique was used to determine the magnetic content of each section of core. After extraction, as detailed later, the susceptibility of the sample was measured and converted back to magnetic material using a ´standard´. The standard consisted of a sample of magnetic material from sediment thoroughly washed several times. By using this method, the interference of grain size could be virtually overlooked.

The units of measurement were $x10^{8}$S.I. units

Experimental Method

Sampling

Samples of sediment for analysis were obtained using a Mackereth 1 metre corer (Mackereth 1958), from Windermere North Basin, Esthwaite Water, Blelham Tarn and Wastwater in the Lake District National Park ,Cumbria (fig.2). Twenty cores were taken from each of the first two sites and ten from each of the remaining two. Cores were taken, one at the deepest point of the water body and the rest evenly spread over lower water depths (fig.3). The cores were taken over as wide an area as possible so as to try to prevent localised abnormalities in sedimentation from influencing the results.

Analysis of Cores

Whole Core Susceptibilities

The Magnetic Susceptibility Profile of each core was taken using the susceptibility meter linked to a purpose designed rig. The rig (fig.4a) consisted of a framework with a large screw-thread which was able to move the detector down over the core. The detector consists of a coil of wire encased within a plastic box with a hole in the centre to clear the core. The core was mounted in the rig and the detector head moved down the core a set distance by the screw thread and readings taken at constant time intervals, indicated by a beep from the instrument. A reading was omitted each time the detector head was moved. This procedure was repeated all the way down the core from the sediment surface. Blank readings were taken on the water above the sediment at the begining and end of each set of core readings.

A computer program was employed to correct the readings for instrument drift, using the blanks. This calculation assumed the drift of the instrument to be linear between the blanks and so the blank for any particular reading could be calculated and subtracted from the reading.

The resultant set of figures were plotted as a graph of depth of sediment against corrected magnetic susceptibility to yield a profile (fig.5) .

Analysis of Deep Core

The second stage of analysis was to slice the core obtained at the deepest water depth. This was done at 1cm intervals.

A plastic seal and aluminium piston were inserted into the lower end of the tube which was then placed into a water-tight cylinder (fig.6) which locked around the bottom of the core. Water was introduced into the cylinder via a small hand pump and the resultant pressure forced the piston and seal against the sediment which moved out of the core. At the top of the core, a square perspex sampling platform was affixed and a piece of perspex, with a hole of identical diameter to the inside of a core tube and 1cm thick, was placed on top of the platform. The sediment was extruded into the perspex plate yielding the necessary slice. A syringe (1ml) of sediment was taken for sulphide determination. The wet density of the sediment was determined using a variety of methods including density bottle and a calibrated syringe (the sample then being dried to determine the percentage dry weight which is given as

$$\frac{\text{weight of dry sediment} \times 100}{\text{weight of wet sediment}}$$

The remainder of the slice was then dried for later analyses.

Spherule Extraction Technique

The remaining cores were extruded using the same equipment, but were sliced into four or five equal slices each of 17.5cm, using a section of pipe similar to core tube instead of the perspex plate.

The sections were sealed into polythene bags, from which as much air as possible was excluded to reduce oxidation, and were stored at 10°C.

Each core section was weighed and a sub-sample of approximately 200g was taken from the previously homogenized section. This sample was placed in a 1 litre beaker and heated with Hydrochloric acid 1M (400ml) for four hours at 80 C to disaggregate the sample. (Hydrogen peroxide had previously been used in an effort to decompose the organic matter, but due to the high percentage of organics, this was not entirely successful. Therefore the acid method was used as it was just as successful in recovering the magnetic fraction, provided the solution was not allowed to stand for more than two days, after which time the magnetic fraction dissolved in the acid.)

After disaggregation, the sample was transferred to a circular glass trough and any magnetic material present was removed using a magnet, which had small plastic bags placed over its poles. The magnet was swirled in the sample and removed, the clay minerals and other non-magnetic matter washed off the plastic bags with deionized water, the plastic bags removed from the magnet and the magnetic material washed into a beaker from the bags. This procedure was continued until no magnetic matter was detected on the plastic bags.

The extract was filtered onto a 2.4cm glass fibre filter (previously dried in an oven at 60°C and weighed). A blank was obtainded by the filtration of a few ml of the solution from which the magnetic material had been extracted. The filter was again dried in an oven, reweighed to reveal the amount of material deposited, and placed into a plastic pot (10ml) for the determination of its susceptibility.

The pots were placed into a susceptibility detector (fig.4b) (again a coil contained within a plastic box, bench mountable, but with a hole of sufficient diameter to clear the pot) and the susceptability read, a blank being taken using an empty pot before and after each reading. Readings were corrected by subtracting the mean of the blanks either side of the reading and the values noted.

A further computer program was used to calculate the load on the core. This was done by converting the susceptibility values back to magnetic material using a standard of very clean magnetic material of weight 0.0496g and susceptability 174.

The mean and standard deviation of the loads were determined.

Results

The load on a core was calculated as follows:

The magnetic material after extraction contained some clay minerals and although they were of smaller susceptibility than the magnetic fraction, they were taken into account by subtracting an amount from the Magnetic susceptibility reading, calculated by:

$$\frac{\text{Magnetic weight x Clay susceptibility}}{\text{Clay weight}}$$

which gave the susceptibility of the magnetics assuming it to be all clay (the largest error possible).

Each magnetic susceptibility reading was then converted into a weight using the 'standard'. This was performed by:

$$\frac{\text{'Corrected' magnetic susceptibility X 'standard' weight}}{\text{'standard' susceptibility}}$$

The weights thus obtained were then corrected to the same sample size (200g) by:

$$\frac{\text{200 x magnetic weight (from above)}}{\text{weight of subsample}}$$

Histograms of magnetic susceptibility of section against section depth (fig.7) reveal a peak at the surface followed by a depression. This depression was taken as the background reading and the mean of the magnetic weights within this region was subtracted from the peak weights to obtain an input weight for each subsample. This value was corrected back to the whole section weight. The sum of these values gave the load on the core.

Plots of load against depth (fig.8) reveal linear relationships but with widely differing deviations from the regression line.

The means and standard deviations of the loads were obtained and these values are given below:

	x	s	n	
Esthwaite	0.00986	0.00618	19	
Blelham	0.00642	0.00315	9	
Windermere	0.02954 0.01391	0.01802	19	47 I
Wastwater	0.03270 0.02126	0.01990	9	65% accum?

(mg Magnetite / $34cm^2$)

Discussion

Statistical tests were performed on the data to check its significance.

A Students t-test was used to test whether or not the means obtained were significantly different. This test required the variances of the two sets of data to be similar and this was checked using an F-test.

$$F = \left\{ s_1^2/(n_1 - 1) \right\} \Big/ \left\{ s_2^2/(n_2 - 1) \right\}$$

Values obtained:

Test	F	Degrees of Freedom	Critical values 95%	99%
BT/EW	1.71	8/18	2.51	3.71
W/EW	8.50	18/18	2.20	3.10
WW/EW	23.33	8/18	2.51	3.71
W/BT	14.54	18/8	3.20	5.42
BT/WW	39.91	8/8	3.44	6.03
WW/W	2.74	8/18	2.51	3.71

The values obtained show the variances for BT/EW at 95% and WW/W at 99% confidence limits to be not significantly different. The other values show significant difference and this is taken into account by using Welch's test instead of the t-test to check the difference in the means.

Welch's test uses the statistics:

$$Z = \left\{ x_1 - x_2 \right\} \Big/ \left\{ (s_1^2/n_1) + (s_2^2/n_2) \right)^{1/2}$$

and

$$C = \left\{ s_1^2/n_1 \right\} \Big/ \left\{ (s_1^2/n_1) + (s_2^2/n_2) \right\}$$

In the t-test, t is similar to Z but s_1 and s_2 are replaced by s given by:

$$s = \frac{(x_1 - \bar{x}_1)^2 + (x_2 - \bar{x}_2)^2}{n_1 + n_2 - 2}$$

and C is not used.

The values obtained are:

t-test

Test	t	Degrees of freedom	Critical value 95%	97.5%
EW/BT	1.95	26	1.71	2.06
WW/W	0.40	26	1.71	2.06

Welch´s test

Test	Z	C	Degrees of Freedom v	v	Critical value for z at 99%
W/EW	4.50	0.89	18	18	2.51
WW/EW	3.37	0.96	8	18	2.58
W/BT	5.42	0.94	18	8	2.74
WW/BT	3.91	0.98	8	8	2.72

From the t-test, the values for Wastwater and Windermere are significantly different at 95% confidence limits and those for Blelham and Esthwaite at 97.5% confidence limits.

The values obtained for Welch´s test show there to be significant difference between the means in all cases at 99% confidence limits.

Therefore, the means for Esthwaite and Blelham are not significantly different as are those of Windermere and Wastwater, but the latter pair are larger than the former by a factor of 3.8

Windermere and Wastwater are large deep lakes whereas Esthwaite and Blelham are small and shallow this was thought to be having an effect on the results.

In Esthwaite Water and Blelham Tarn sediment was found covering the entire lake bed, whereas the beds of Windermere and Wastwater had areas devoid of sediment. It was proposed that sediment which should have been found in the latter two lakes had been transported, by wave action or the slope of the bank, towards the deeper parts of the lake. This would result in increased sedimentation on some areas of the lake bed and so an increased load. We would therefore expect the values of the load means of Wastwater and Windermere to be greater than those for Esthwaite and Blelham as shown in the results. (Esthwaite and Blelham do not suffer from transportation since they have shallow sloping beds and wave action generally disturbs all sediments, not just that at the banks)

The problem was now to estimate the area of the lake bed over which sediment was accumulating and correct the load means back to a flux to the lake surface.

A recent paper (Hakanson 1976) has shown that for large lakes, no sedimentation will occur on slopes of greater than 14%. This factor was used to try and correct the results. All areas of greater than 14% slope were marked on a contour map of the lake, and by a cut and weigh method, the percentage of the bed on which sedimentation would settle was determined.

Values obtained were:

Wastwater	38%	)	accumulation area as
Windermere	75%	)-	a percentage of total
Blelham Tarn	48%	)	lake surface area

These values do not fit our observations that shallow lakes are covered in sediment, since they show a low value for Blelham Tarn which is covered in sediment. This observation therefore throws doubt on the other values obtained. A reason for this inaccuracy could lie in the fact that the method was only designed for use with large lakes, and it appears to fall down when applied to shallow small lakes.

A further method of determining accumulation area was to plot a graph of the peak of the whole-core susceptabiliy profiles against water depth. Since all profiles have a similar shape varying only in depth within the sediment, lower accumulation rates at the edges yielding a more compressed profile (fig 5), it was proposed that such a plot would yield a straight line which could be extrapolated to the x-axis where the peak was at the surface of the sediment. This depth of water would be the dividing point between accumulation and non-accumulation. From this depth, charts could be used to calculate the percentage of the lake bed upon which sediment would accumulate.

Shallow lakes should have sedimentation in all areas and so the extrapolation would be expected to a depth of water less than or equal to zero.

Deeper lakes should have an area without sediment deposition, due to wave action, and so extrapolation should yield a depth of greater than zero.

Results (fig.9) follow these proposals for Blelham Tarn and Esthwaite Water but for Windermere and Wastwater, the graph has too much of a scatter for a reliable intercept to be evaluated.

Conclusions and Recommendatons

Although the results from this project do not show a direct correlaton between the fluxes to each lake surface, they do give some weight to the hypothesis of direct atmosphere input to lakes. This information lies in there being two sets of means, each of a pair of values not significantly different, despite having different catchments. Also, two of the lakes, Windermere and Wastwater are a considerable distance apart and yet yield similar means which again tends to rule out geographical position as being important to B.M.S. input.

A further study of the extent of the sedimentation would reveal the correlation or otherwise of these results but at the moment, they cannot be compared truly since inaccuracy in determining sediment accumulation area is complicating the problem.

Acknowledgements

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Figures

fig.1 Electron micrographs of the magnetic extract from the sediment of Esthwaite Water.

fig.2 The geographical location of Windermere, Esthwaite Water, Blelham Tarn and Wastwater, within the Lake District National Park.

fig.3 The location and depths of all cores taken (The circled values are core references).

fig.4 The equipment used to determine Magnetic Susceptibility on:

(a) The whole core
(b) The 10ml pot

fig.5 Whole core susceptibility profiles of Magnetic Susceptibility ($x10^8$ S.I. units) versus depth of sediment (cm). Prefix indicates lake i.e. W = Windernere, E = Esthwaite Water, B = Blelham Tarn and WW = Wastwater. Number in brackets indicates depth of water above lake bed at that point (m).

fig.6 The equipment used to extrude the core.

fig.7 Histograms of magnetic susceptibility of magnetic and clay extract of core sections versus section depth. Histograms for the same lake are plotted on the same axes, the y-axis giving core depth. Each section is 17.5cm thick.

fig.8 Plots of load versus depth of core for the four water bodies (and the regression lines).

fig.9 Plots of the depth of the main peak of the Profiles(cm) versus water depth (m) -to aid determination of the extent of sedimentation(see discussion).

fig.2

Location of Water Bodies Studied

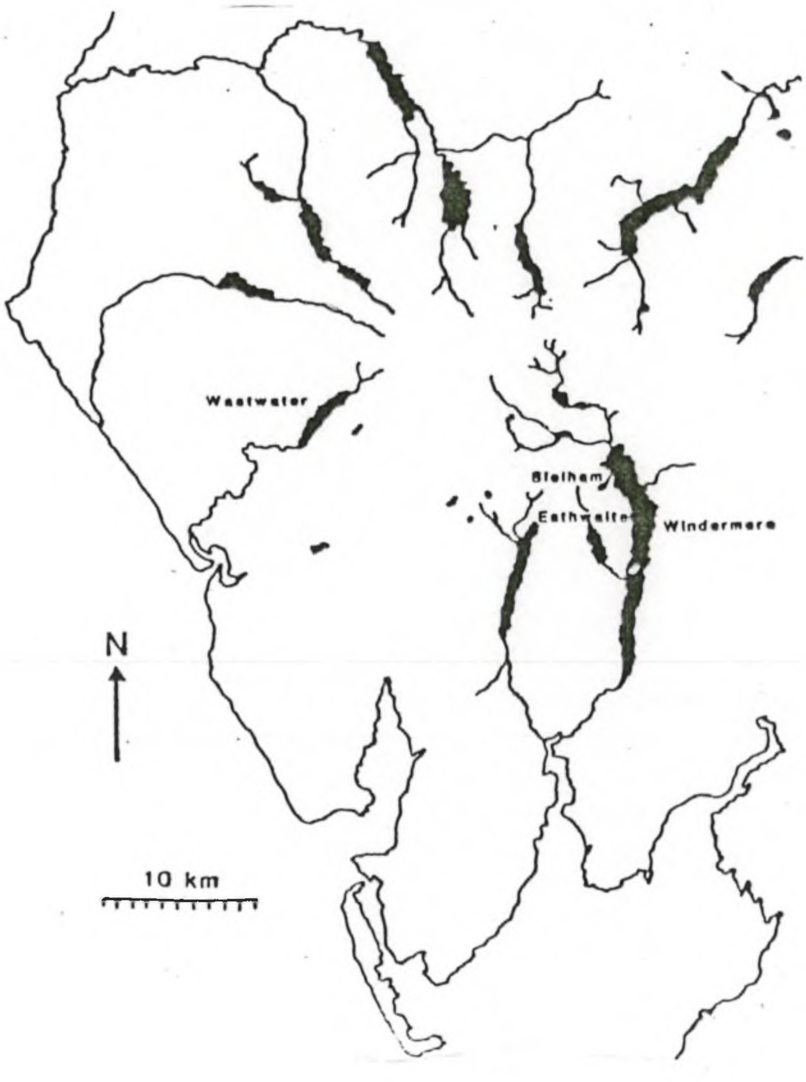
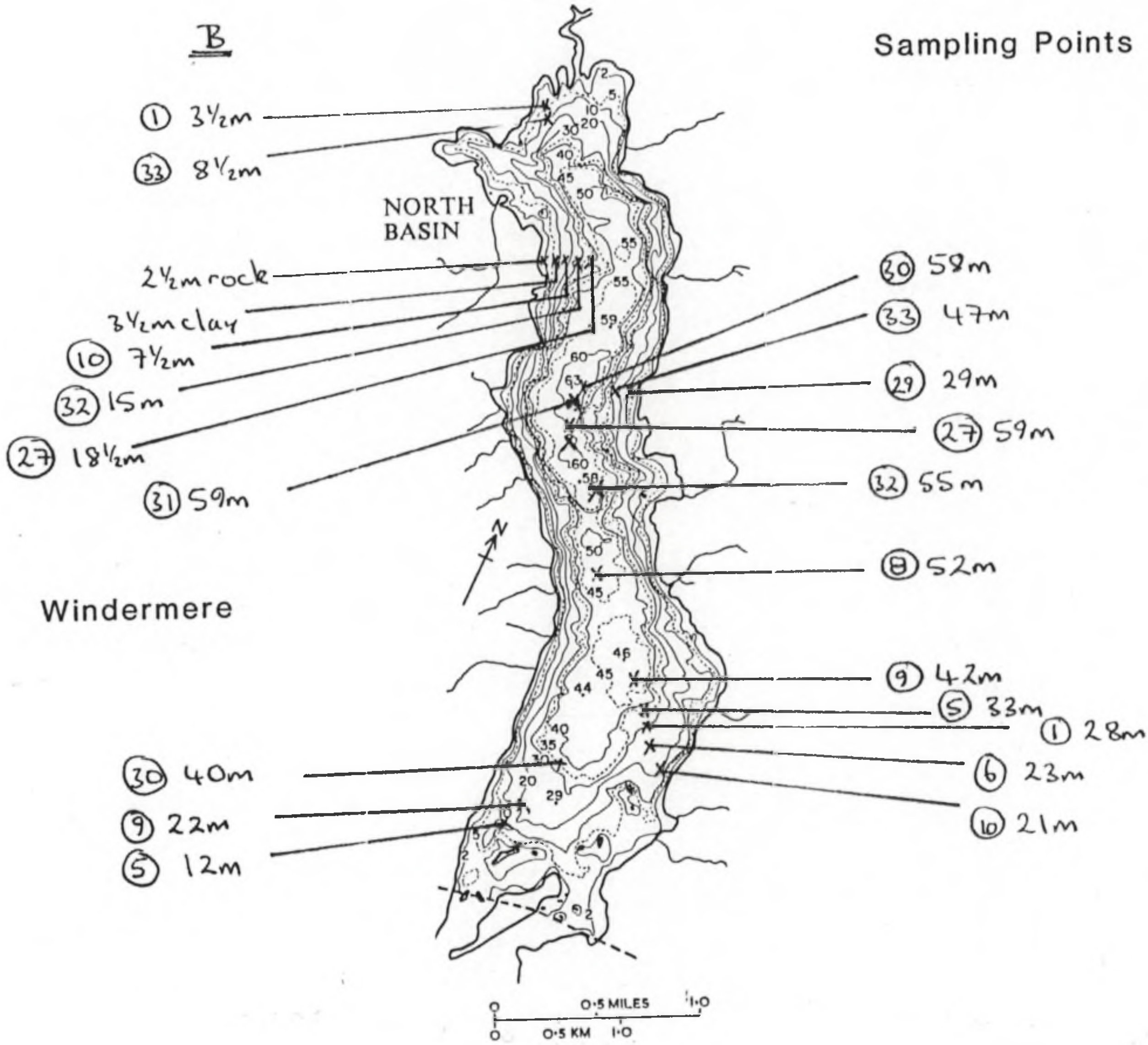


fig.3

Sampling Points



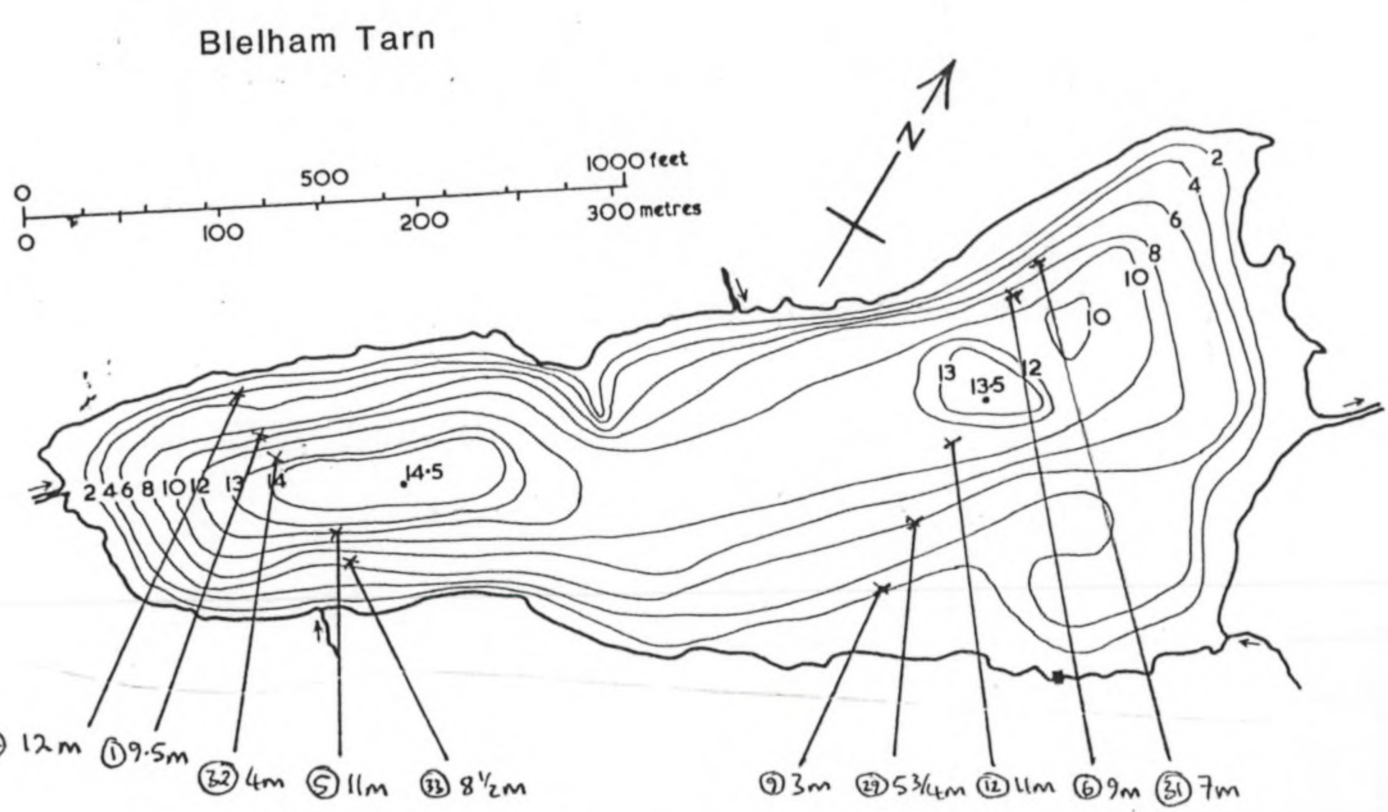
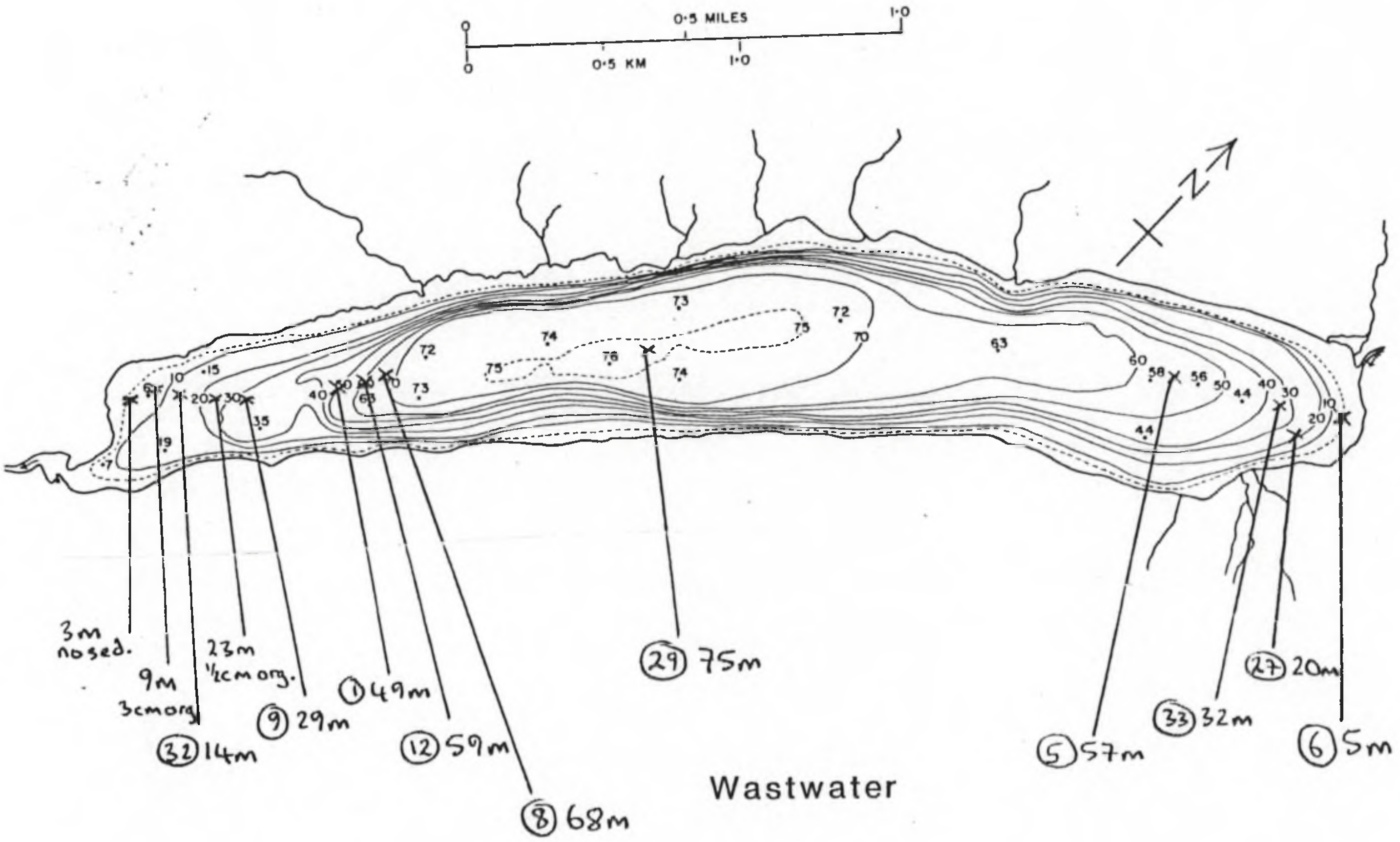


fig.3

Sampling Points



Wastwater

Esthwaite Water

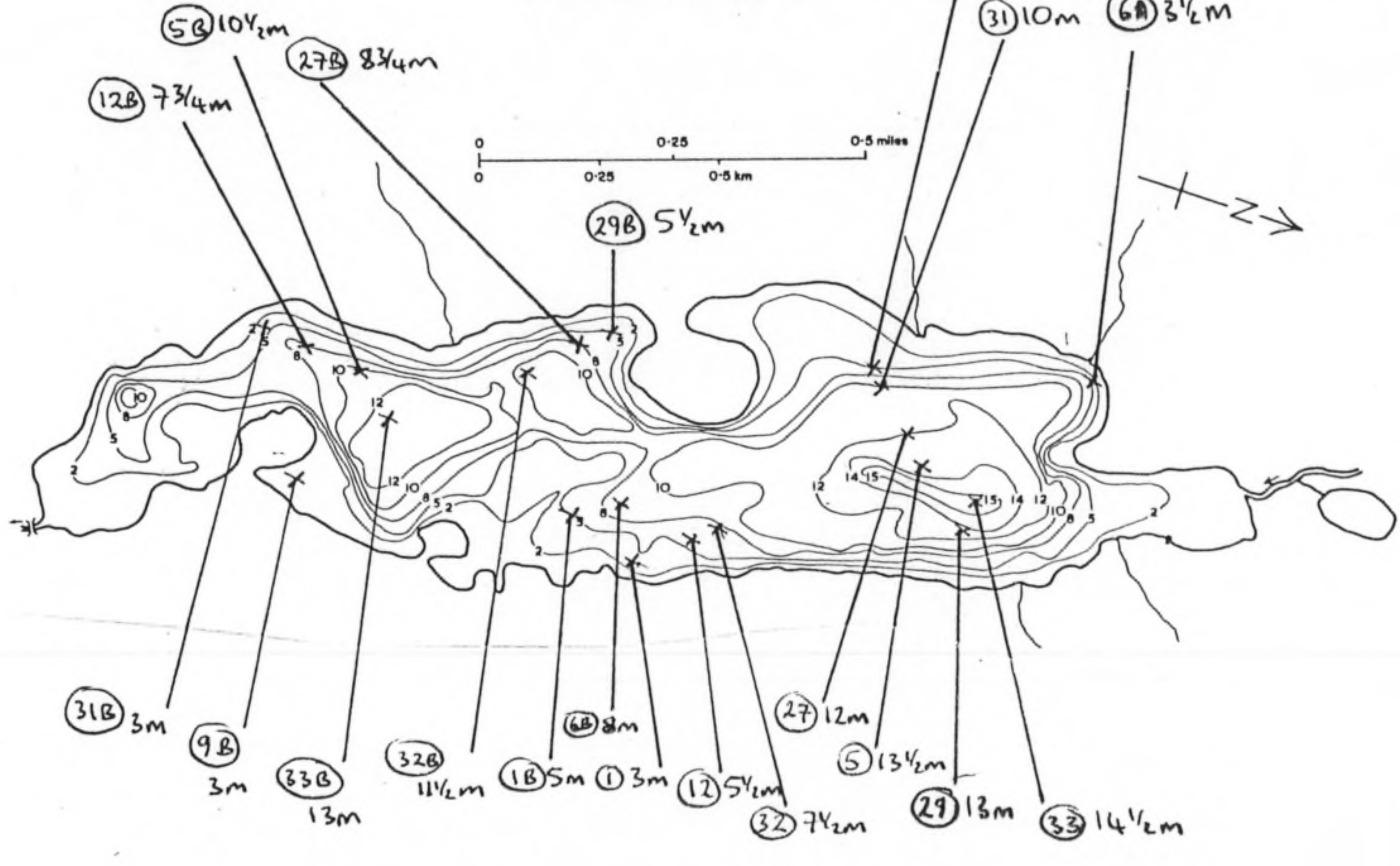
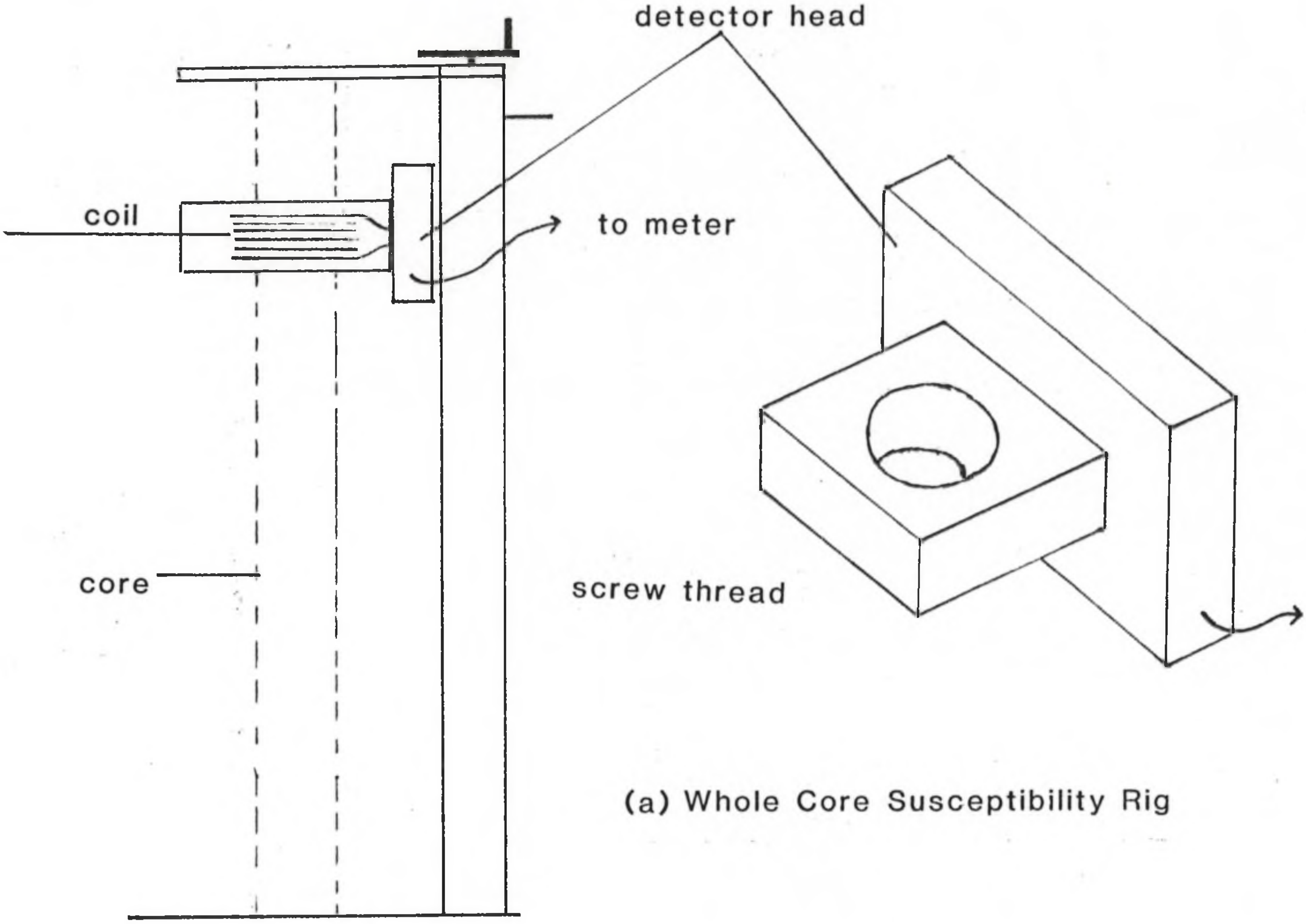
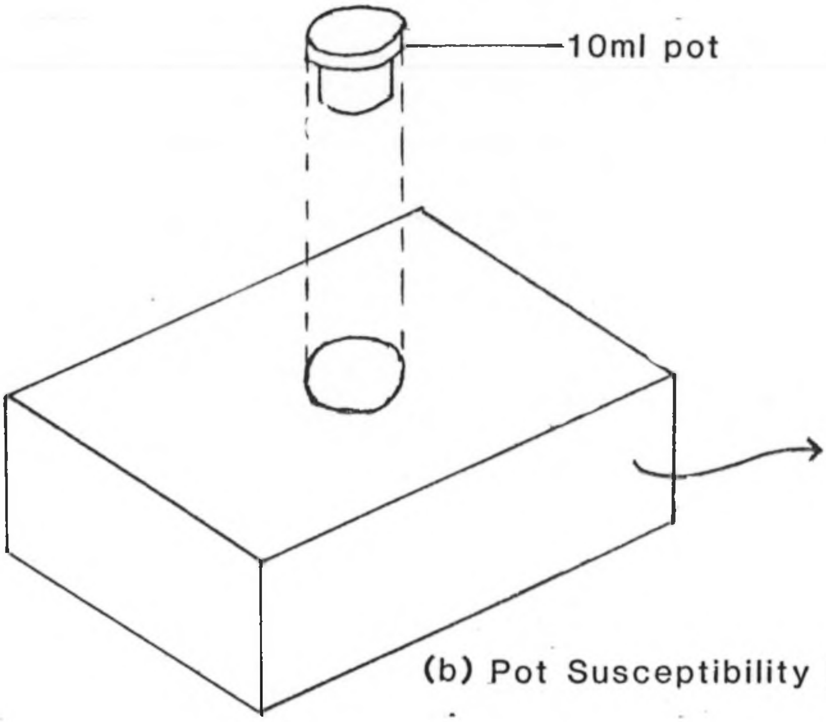


fig.4



(a) Whole Core Susceptibility Rig



(b) Pot Susceptibility Rig

fig.5

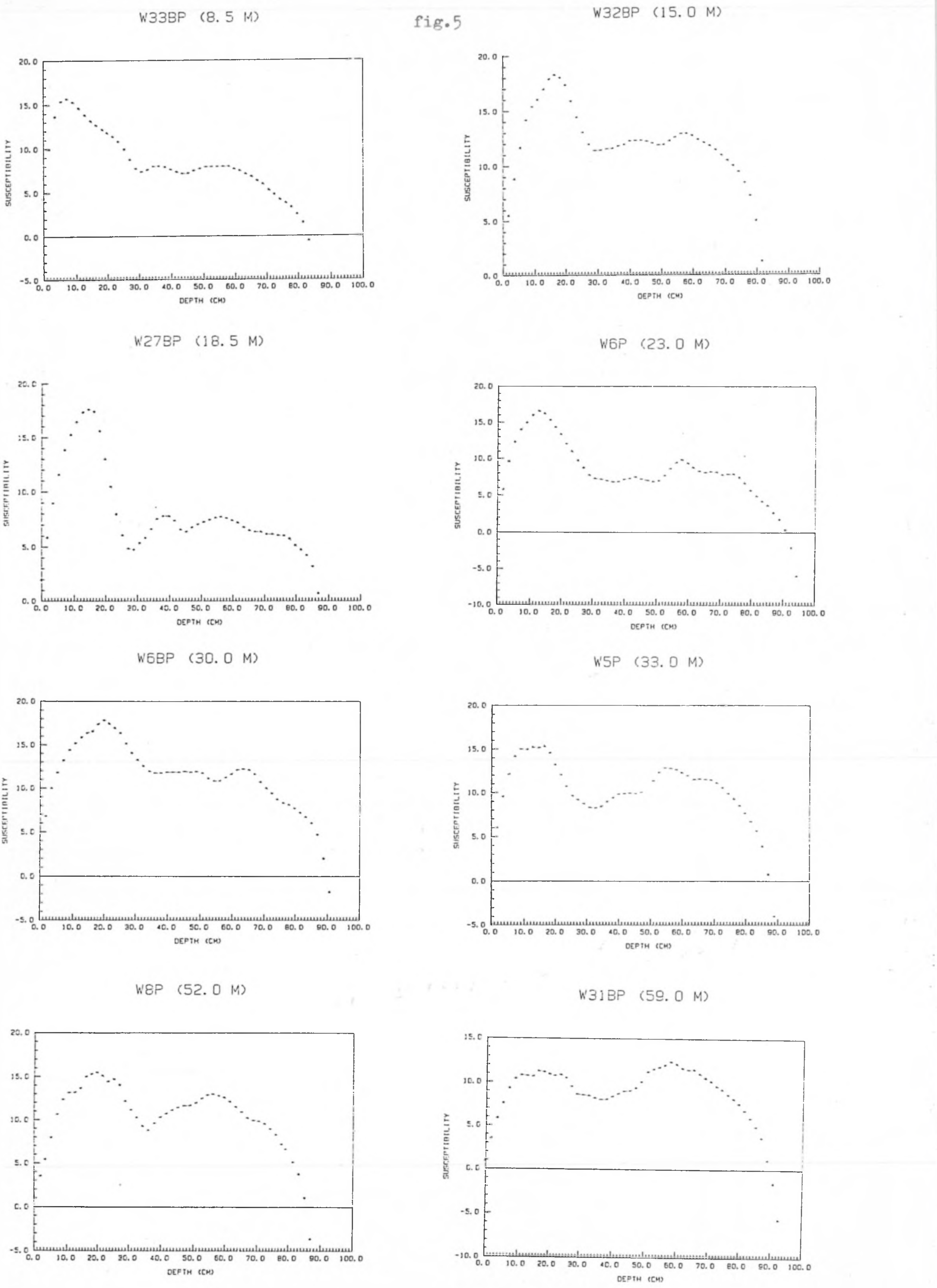
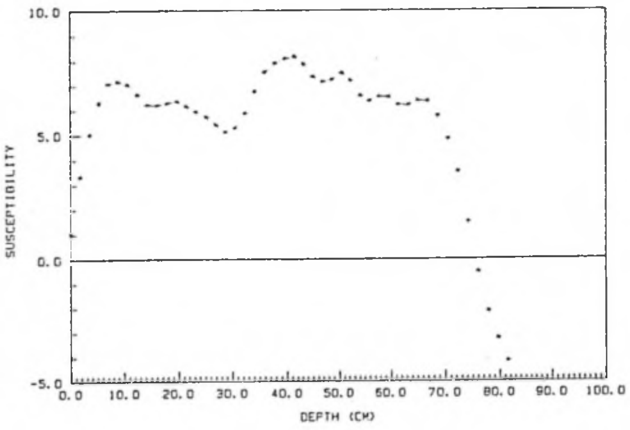
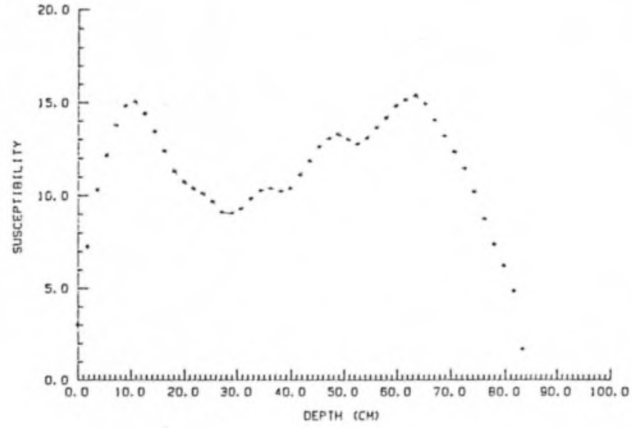

W33BP (8.5 M)
W32BP (15.0 M)
W27BP (18.5 M)
W6P (23.0 M)
W6BP (30.0 M)
W5P (33.0 M)
W8P (52.0 M)
W31BP (59.0 M)
SUSCEPTIBILITY
DEPTH (CM)

fig.5

E31BP (3.0 M)



E1BP (5.0 M)



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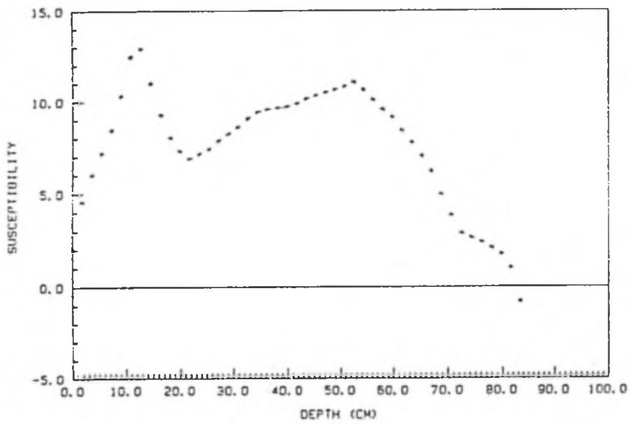
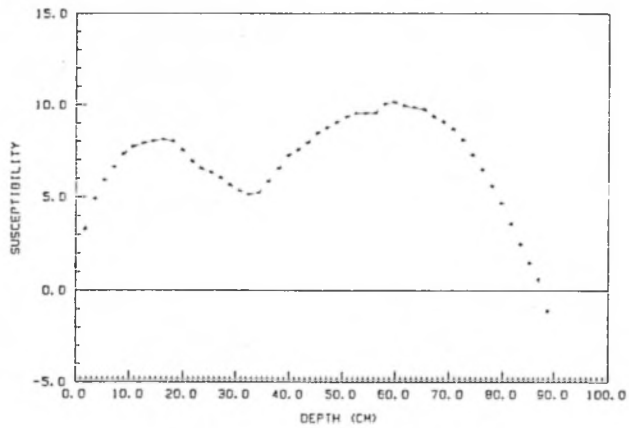
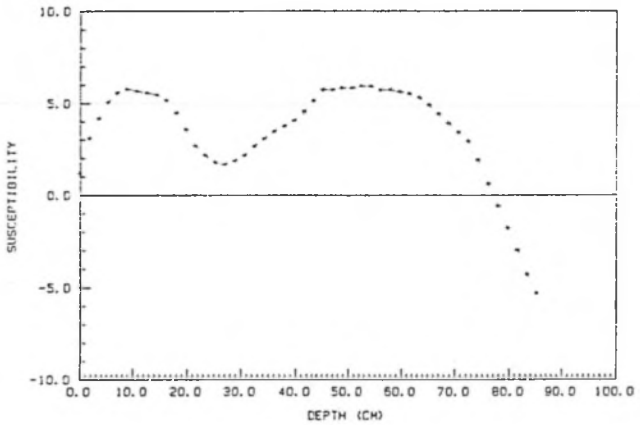


E27BP (8.75 M)



E5BP (10.5 M)



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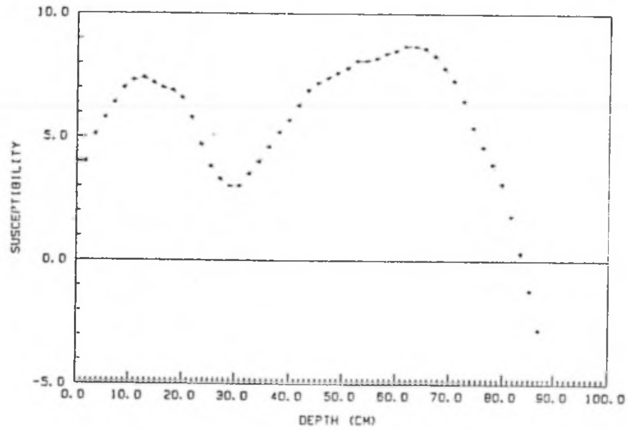
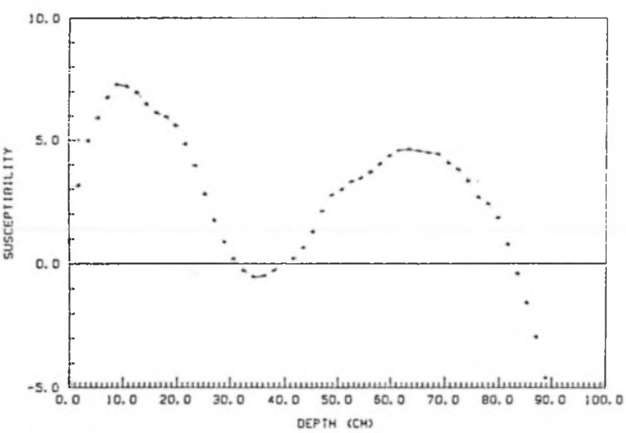


E33BP (13.0 M)



E33P (14.5 M)

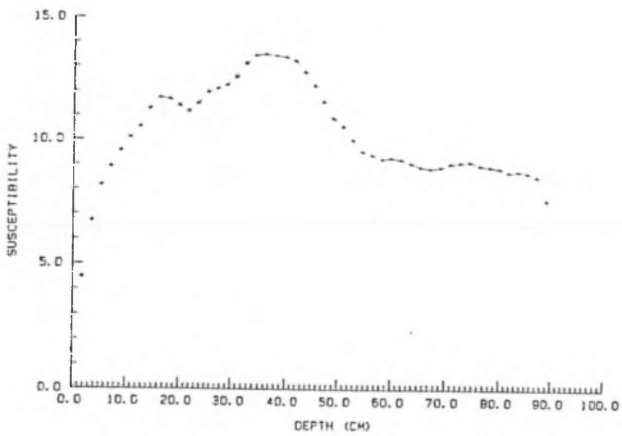
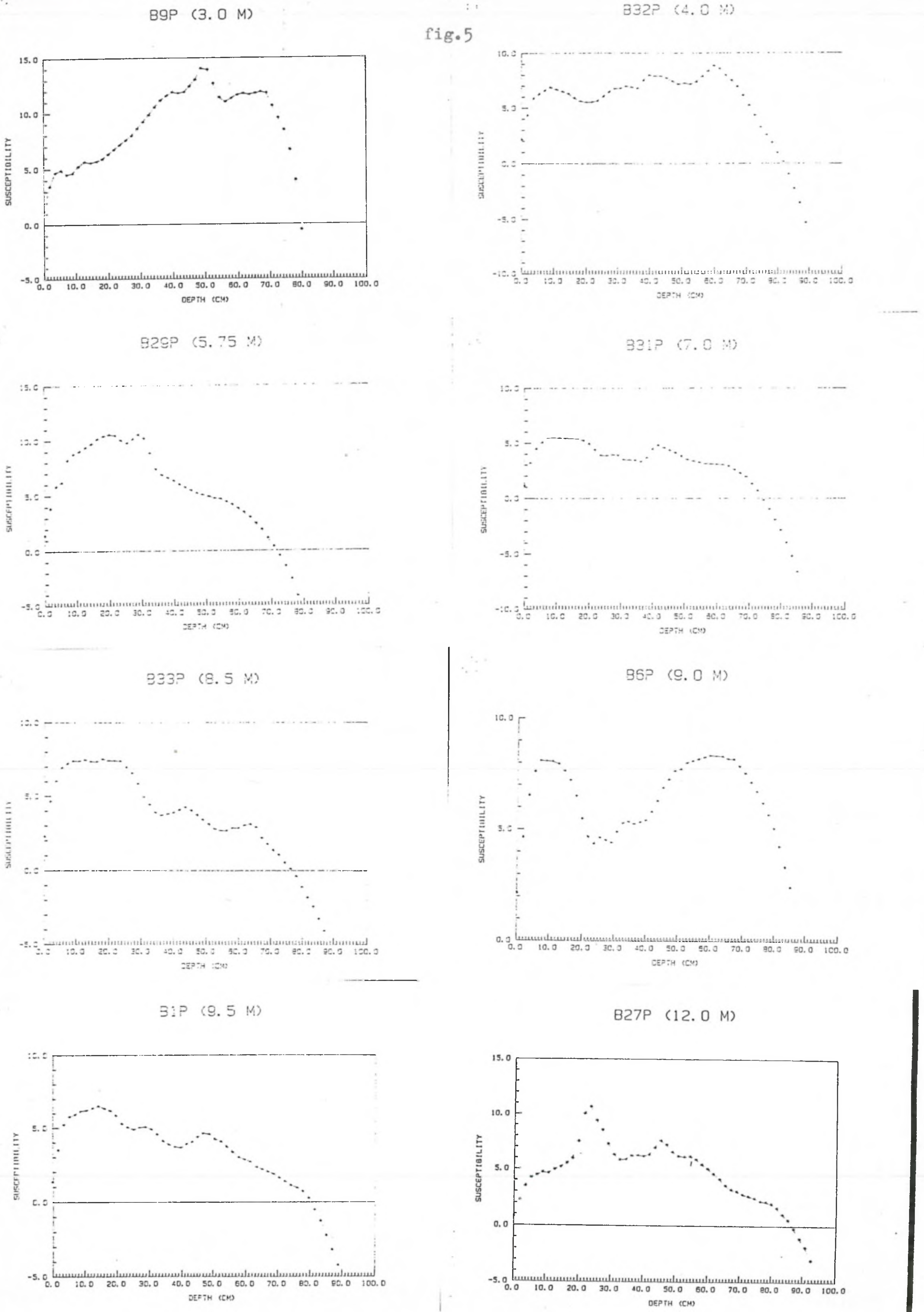


fig.5



B9P (3.0 M)
B32P (4.0 M)
B29P (5.75 M)
B31P (7.0 M)
B33P (8.5 M)
B6P (9.0 M)
B1P (9.5 M)
B27P (12.0 M)
SUSCEPTIBILITY
DEPTH (CM)

fig.5

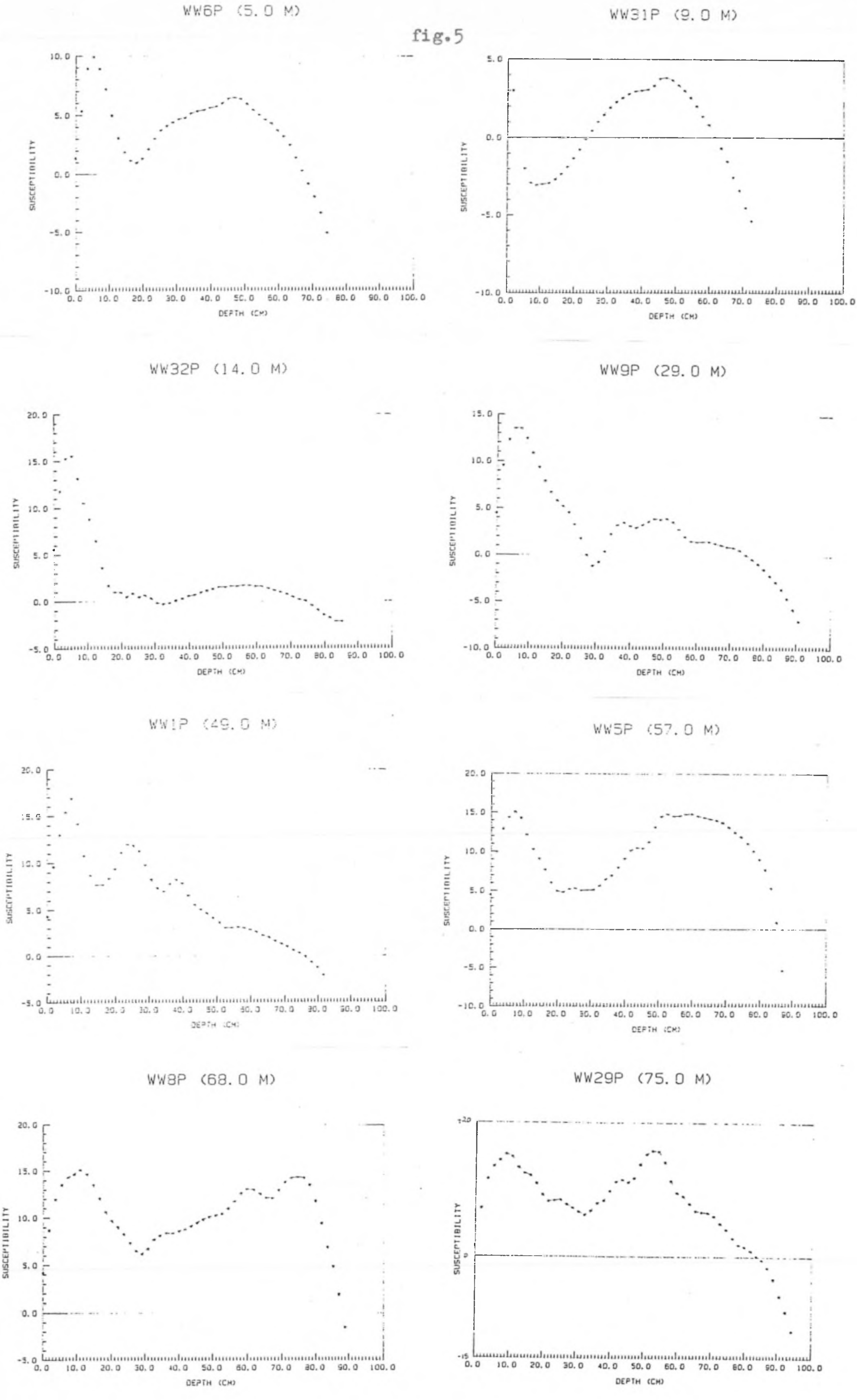

WW6P (5.0 M)
WW31P (9.0 M)
WW32P (14.0 M)
WW9P (29.0 M)
WW1P (49.0 M)
WW5P (57.0 M)
WW8P (68.0 M)
WW29P (75.0 M)
SUSCEPTIBILITY
DEPTH (CM)
0.0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0

fig.6

Core Extrusion Equipment

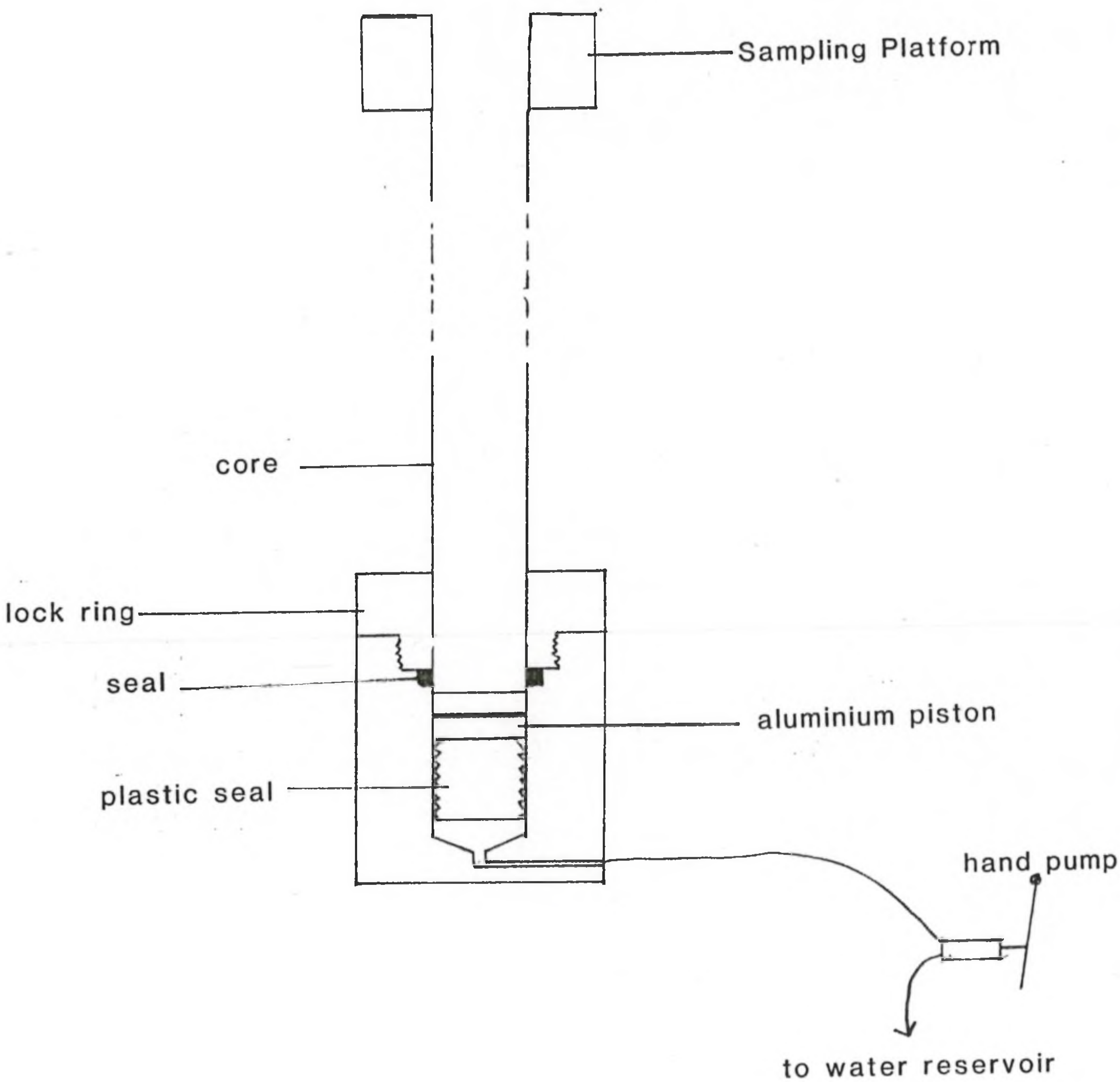


fig.7

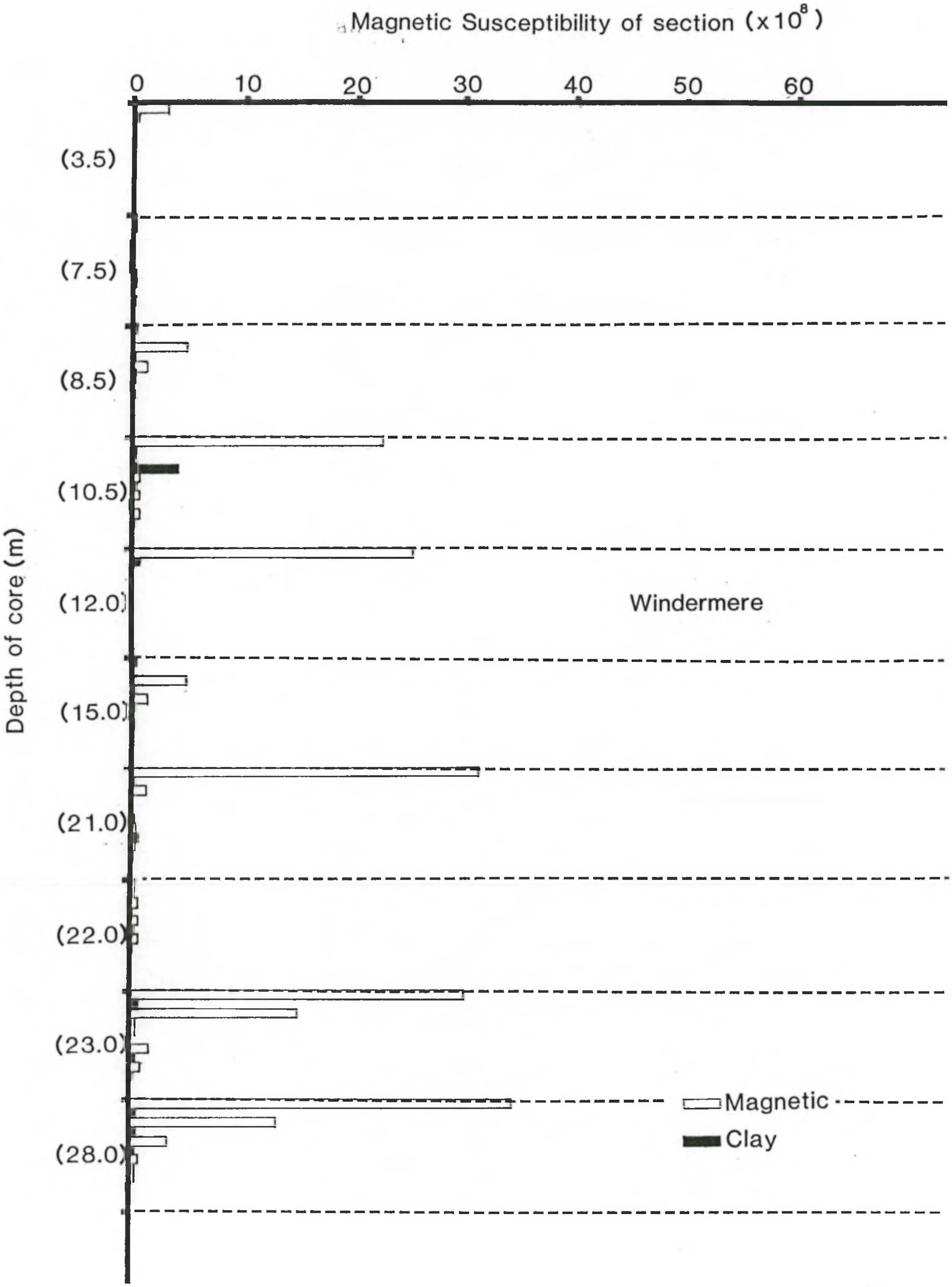
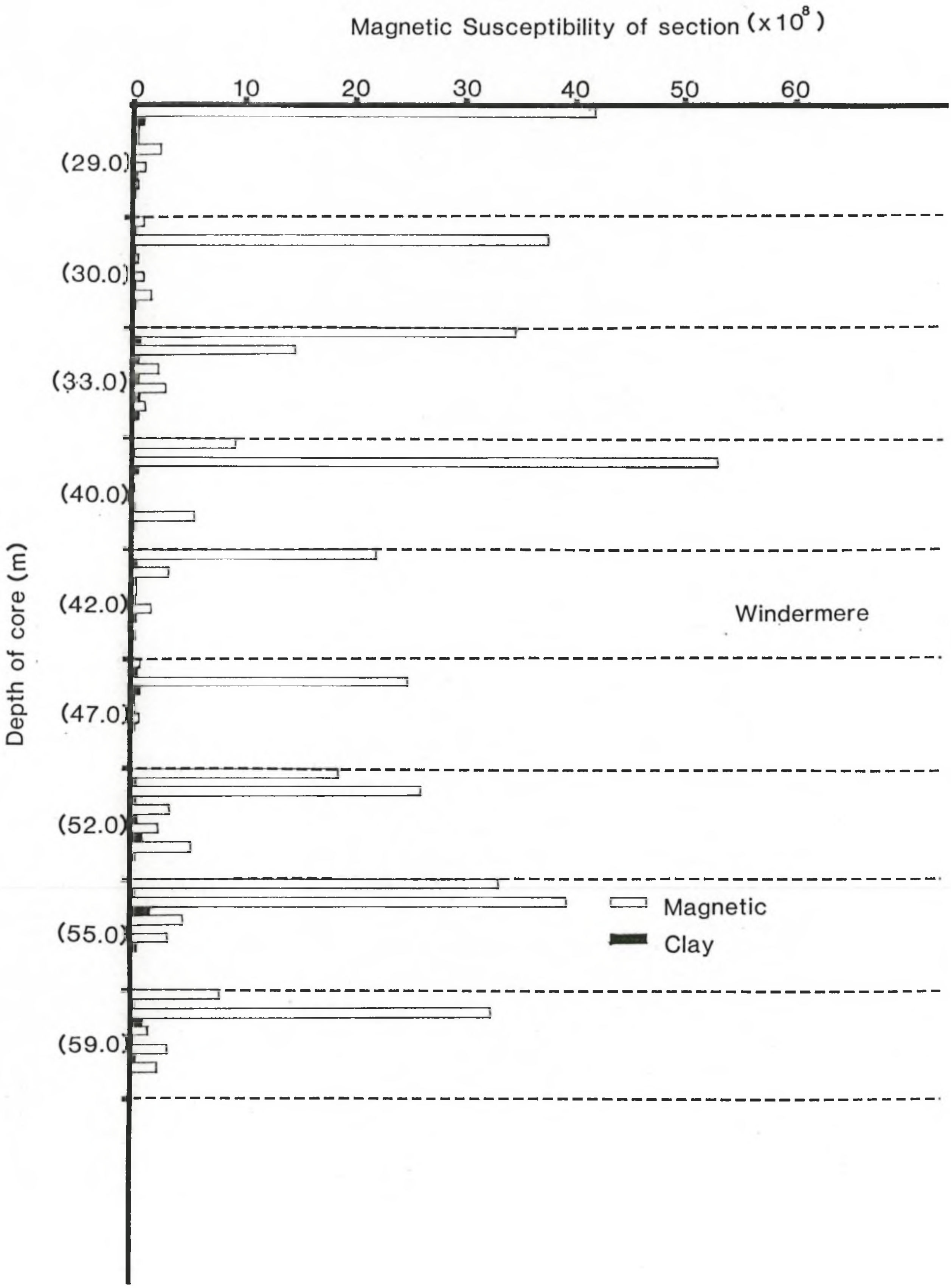

Magnetic Susceptibility of section (x10^{8})
0
10
20
30
40
50
60
Depth of core (m)
(3.5)
(7.5)
(8.5)
(10.5)
(12.0)
(15.0)
(21.0)
(22.0)
(23.0)
(28.0)
Windermere
Magnetic
Clay

fig.7



Magnetic Susceptibility of section (x10⁸)
0
10
20
30
40
50
60
Depth of core (m)
(29.0)
(30.0)
(33.0)
(40.0)
(42.0)
(47.0)
(52.0)
(55.0)
(59.0)
Windermere
Magnetic
Clay

fig.7

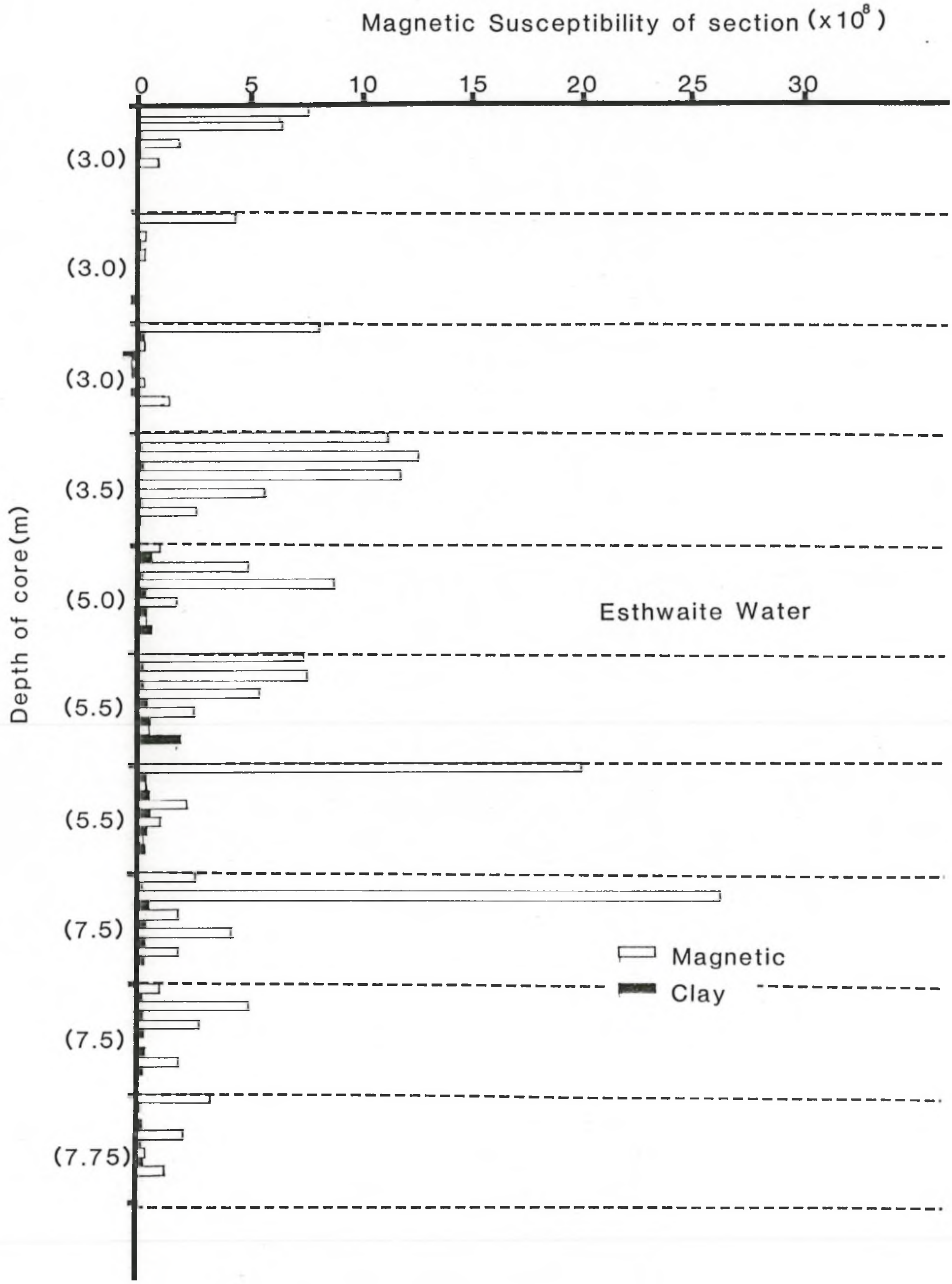

Magnetic Susceptibility of section (x10⁸)
0
5
10
15
20
25
30
Depth of core(m)
(3.0)
(3.0)
(3.0)
(3.5)
(5.0)
(5.5)
(5.5)
(7.5)
(7.5)
(7.75)
Esthwaite Water
Magnetic
Clay

fig.7

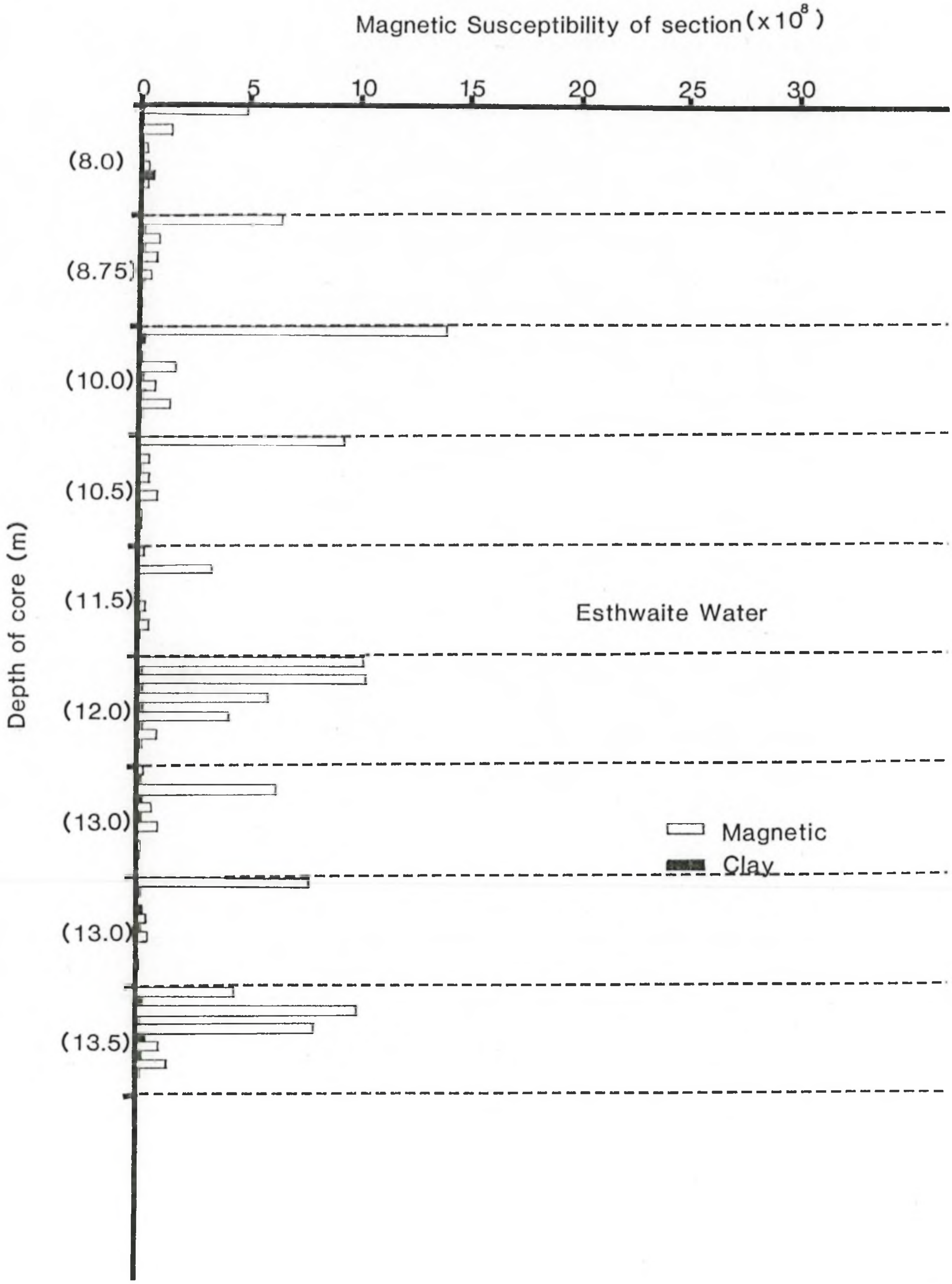
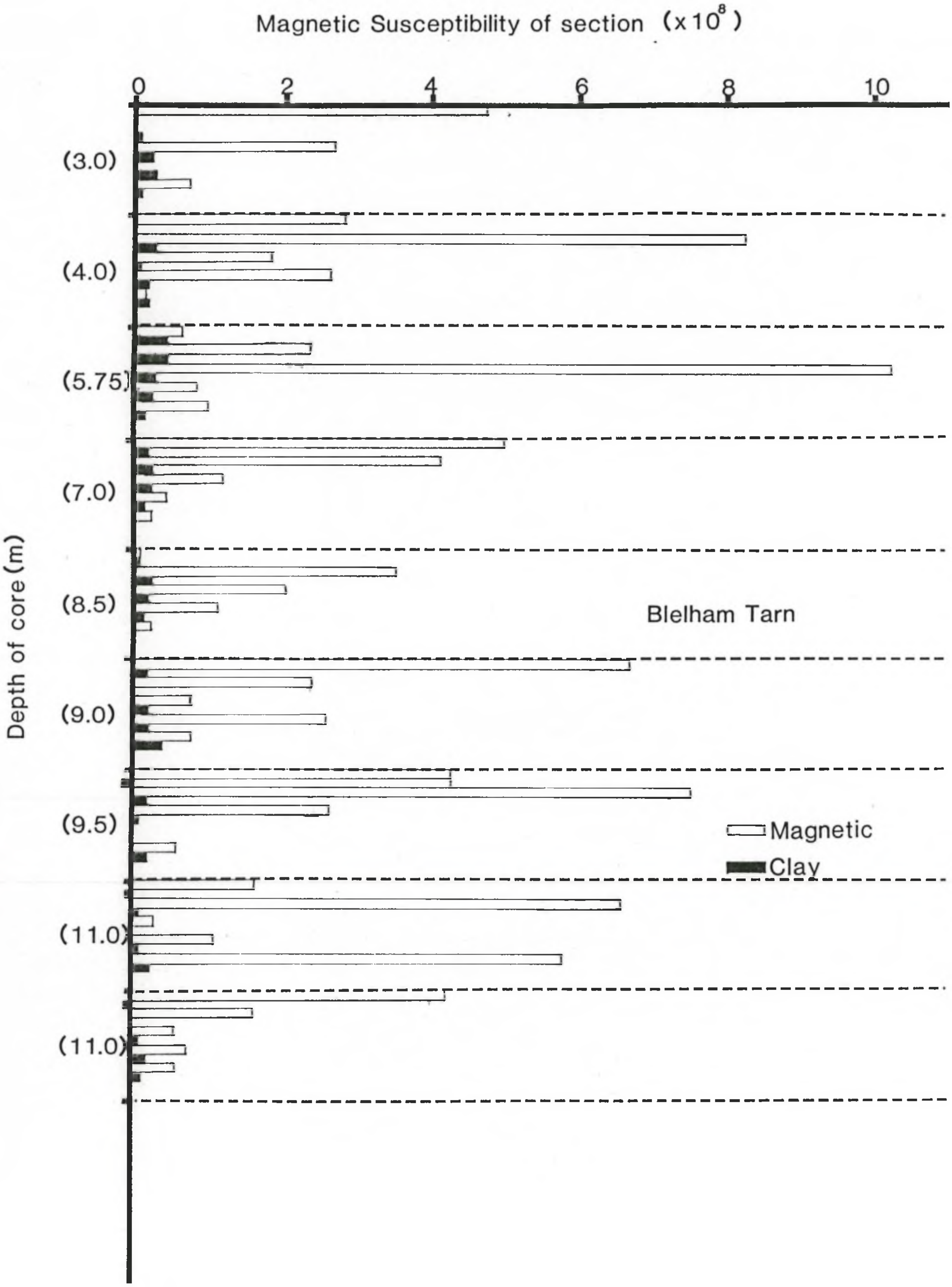
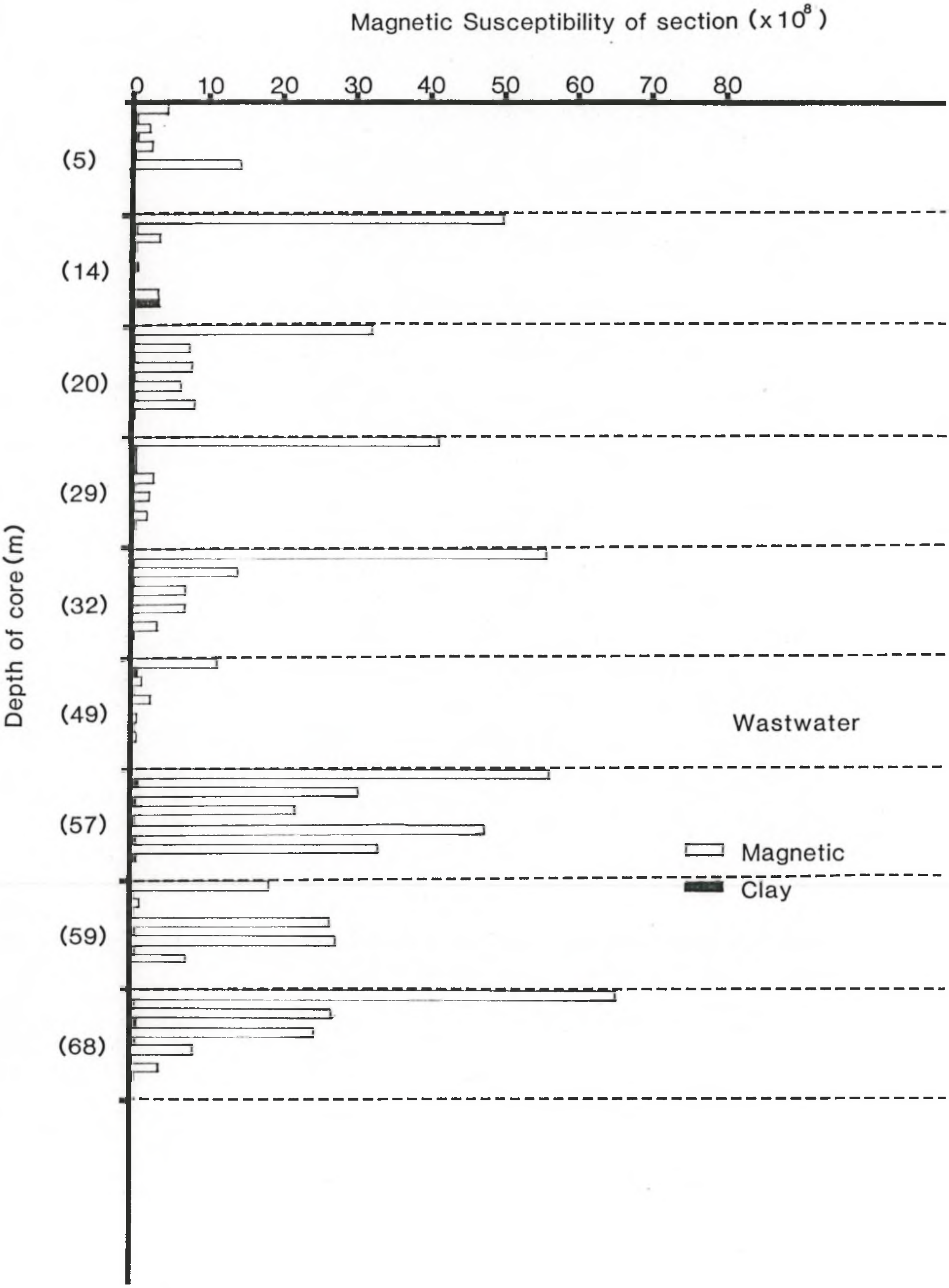

Magnetic Susceptibility of section (x10^8)
0
5
10
15
20
25
30
Depth of core (m)
(8.0)
(8.75)
(10.0)
(10.5)
(11.5)
(12.0)
(13.0)
(13.0)
(13.5)
Esthwaite Water
Magnetic
Clay

fig.7



Magnetic Susceptibility of section (x10^8)
0
2
4
6
8
10
(3.0)
(4.0)
(5.75)
(7.0)
(8.5)
(9.0)
(9.5)
(11.0)
(11.0)
Depth of core (m)
Blelham Tarn
Magnetic
Clay

fig.7



Magnetic Susceptibility of section (x10^8)
0
10
20
30
40
50
60
70
80
(5)
(14)
(20)
(29)
(32)
(49)
(57)
(59)
(68)
Depth of core (m)
Wastwater
Magnetic
Clay

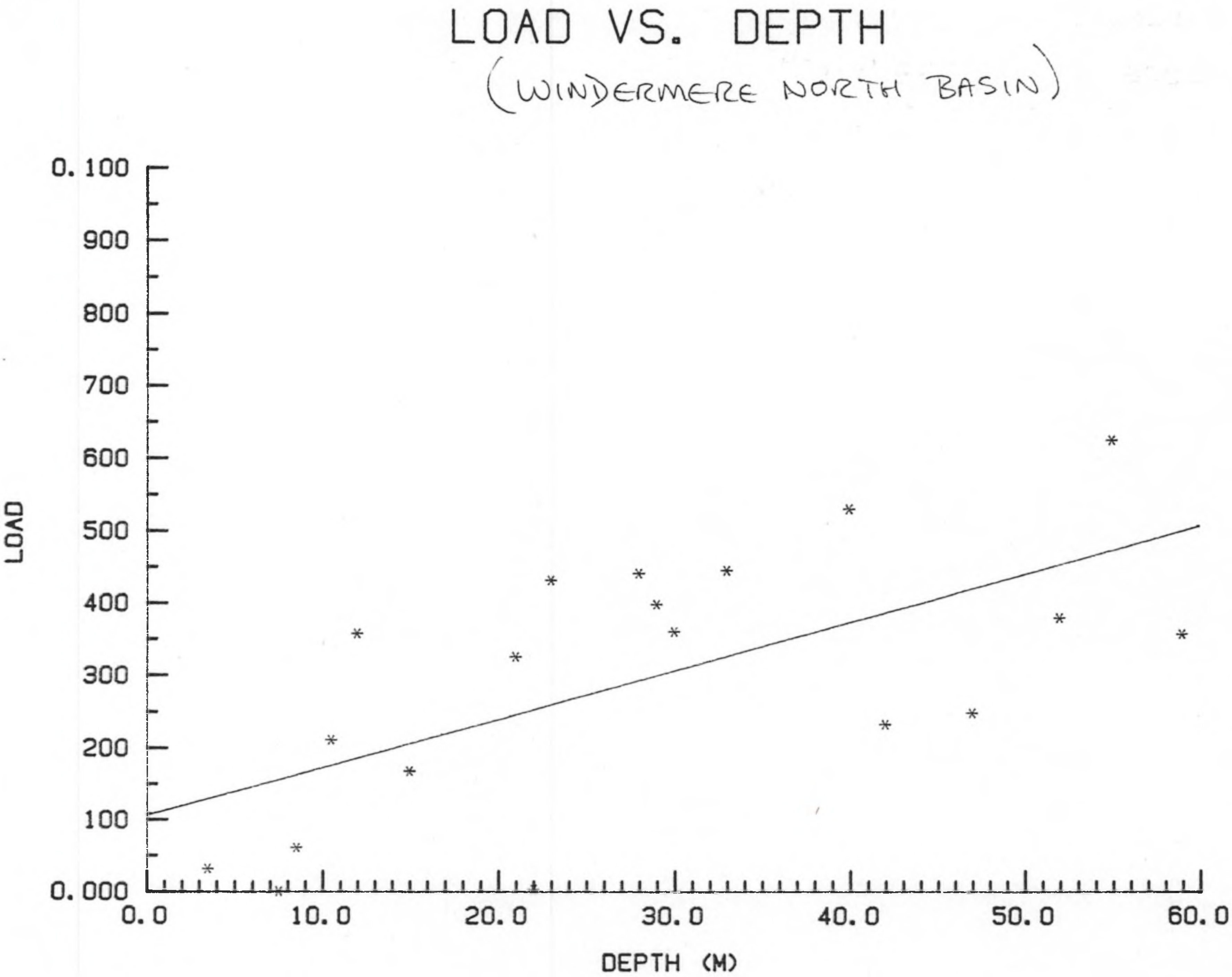

LOAD VS. DEPTH
(WINDERMERE NORTH BASIN)
0.100
900
800
700
600
500
400
300
200
100
0.000
LOAD
0.0
10.0
20.0
30.0
40.0
50.0
60.0
DEPTH (M)

fig.8

LOAD VS. DEPTH (ESTHWAITE)

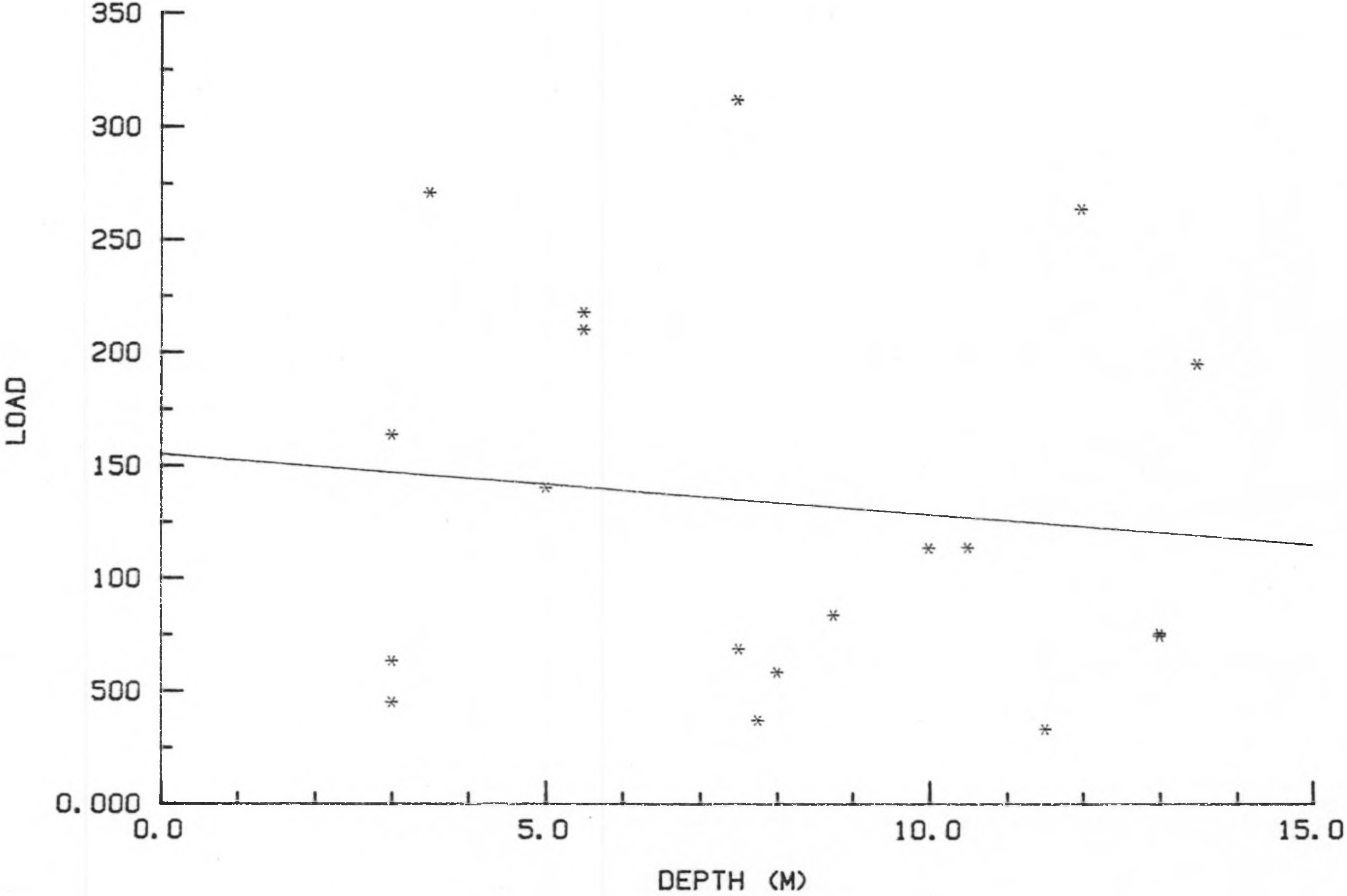
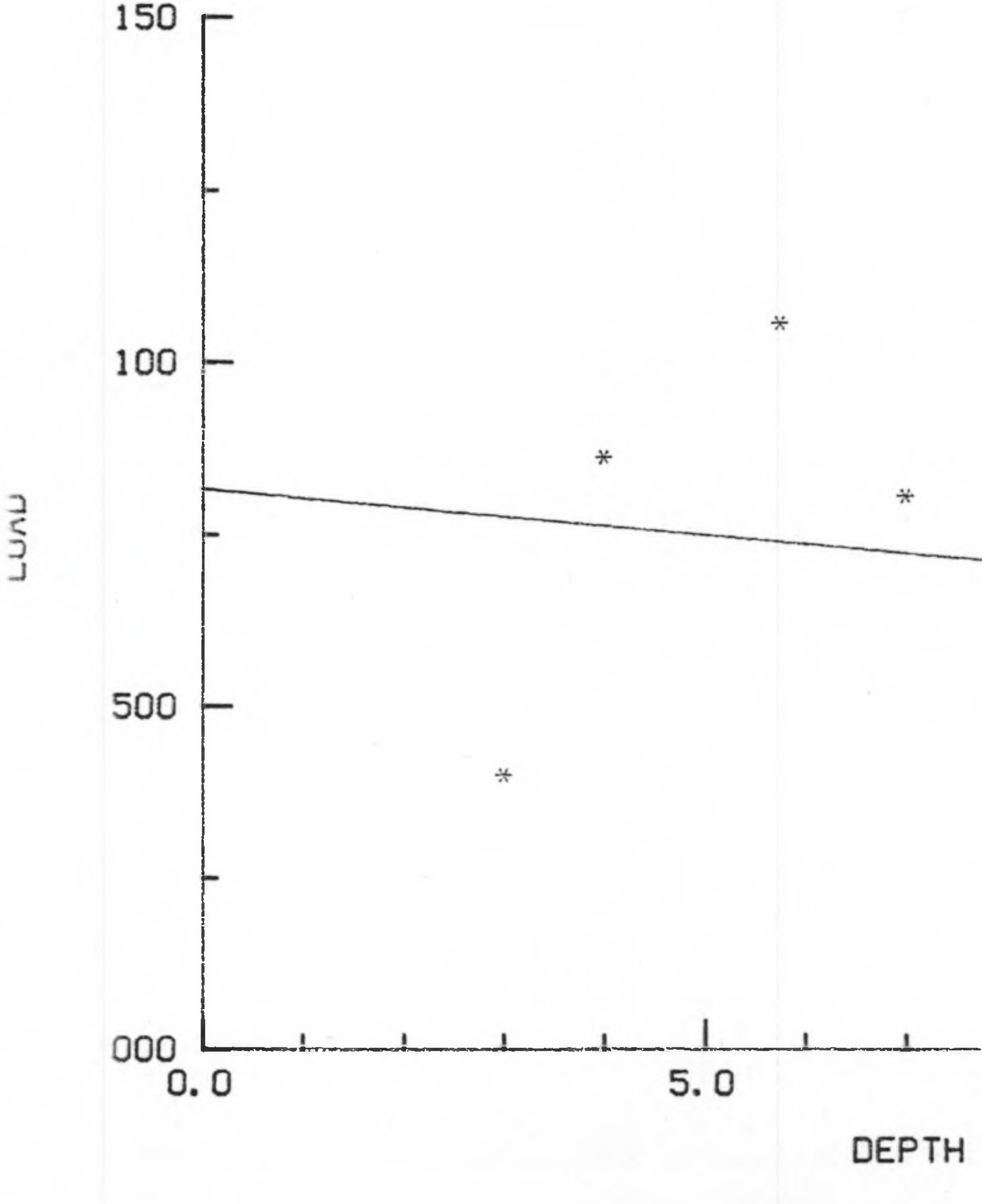


fig.8

LOAD VS.



DEPTH (BLELHAM)

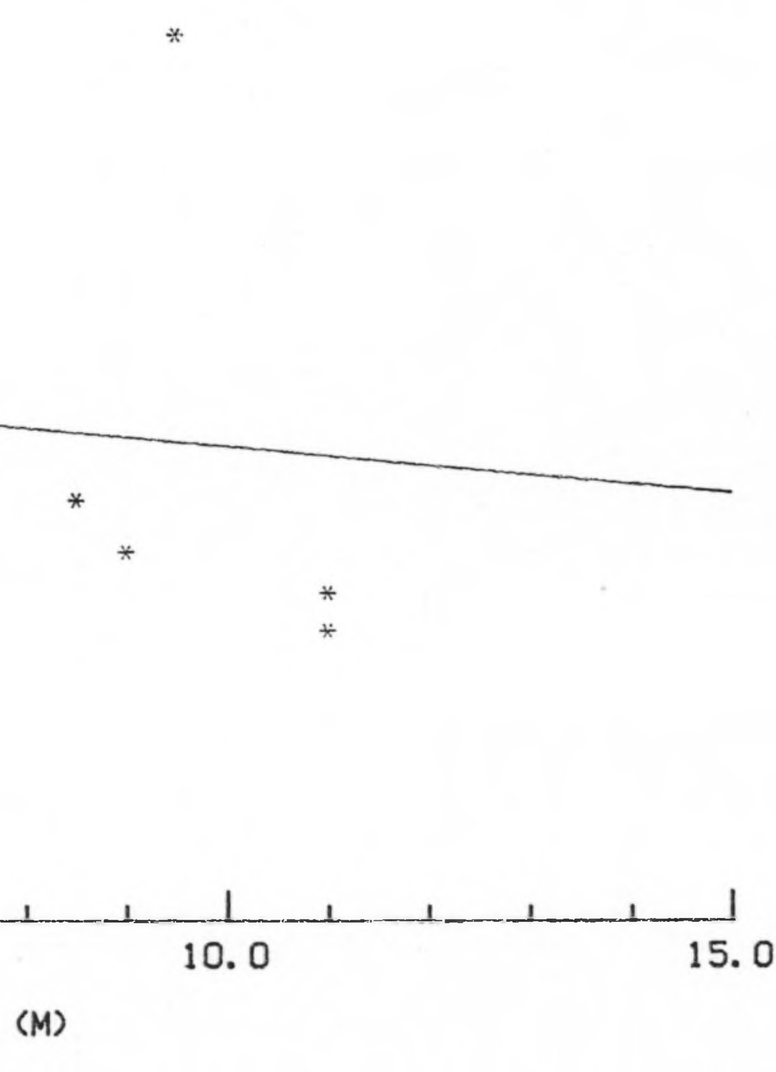


fig.8

DEPTH (WASTWATER)

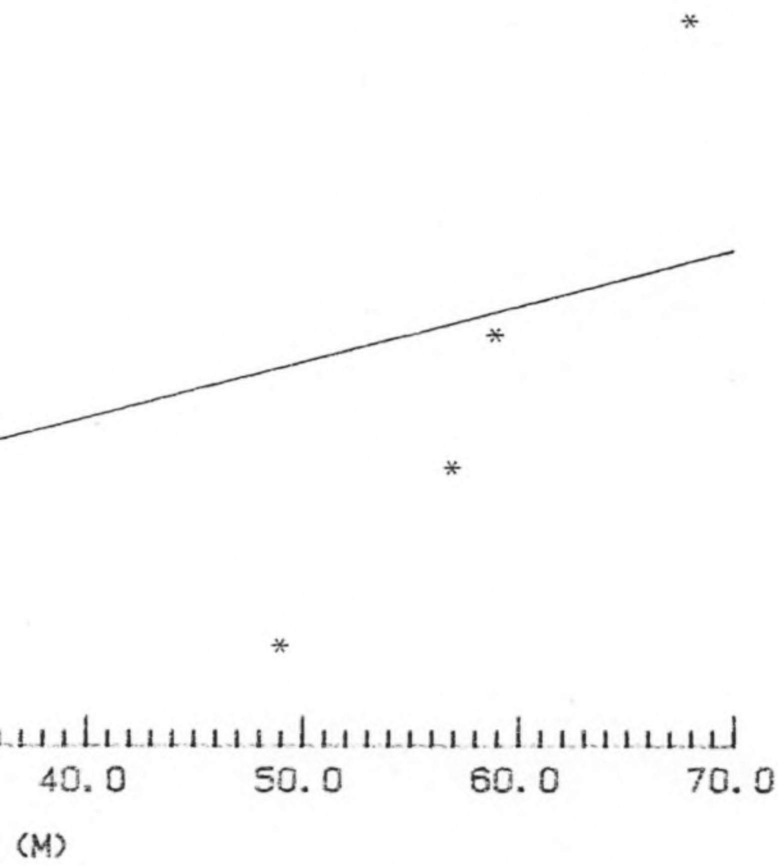
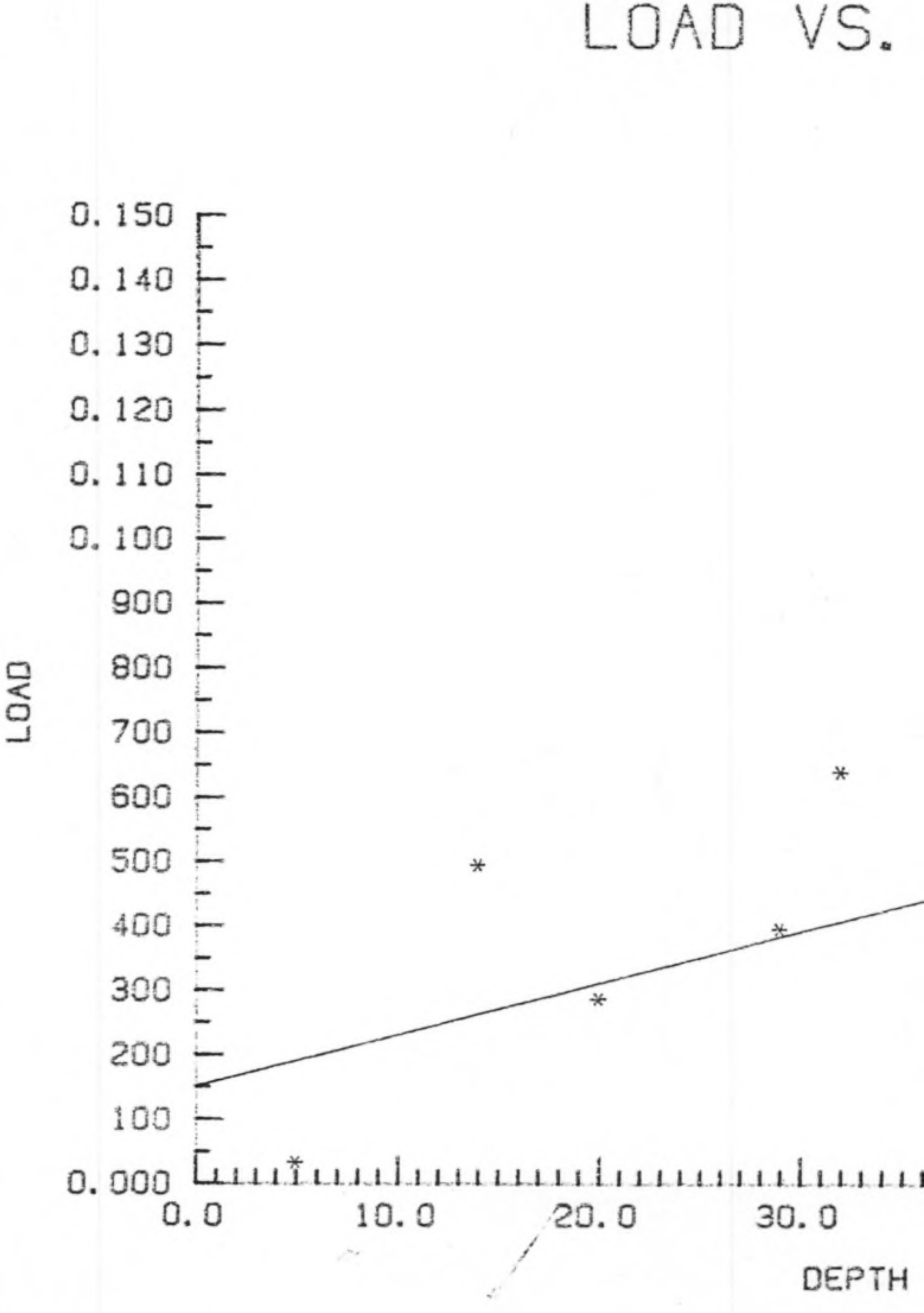
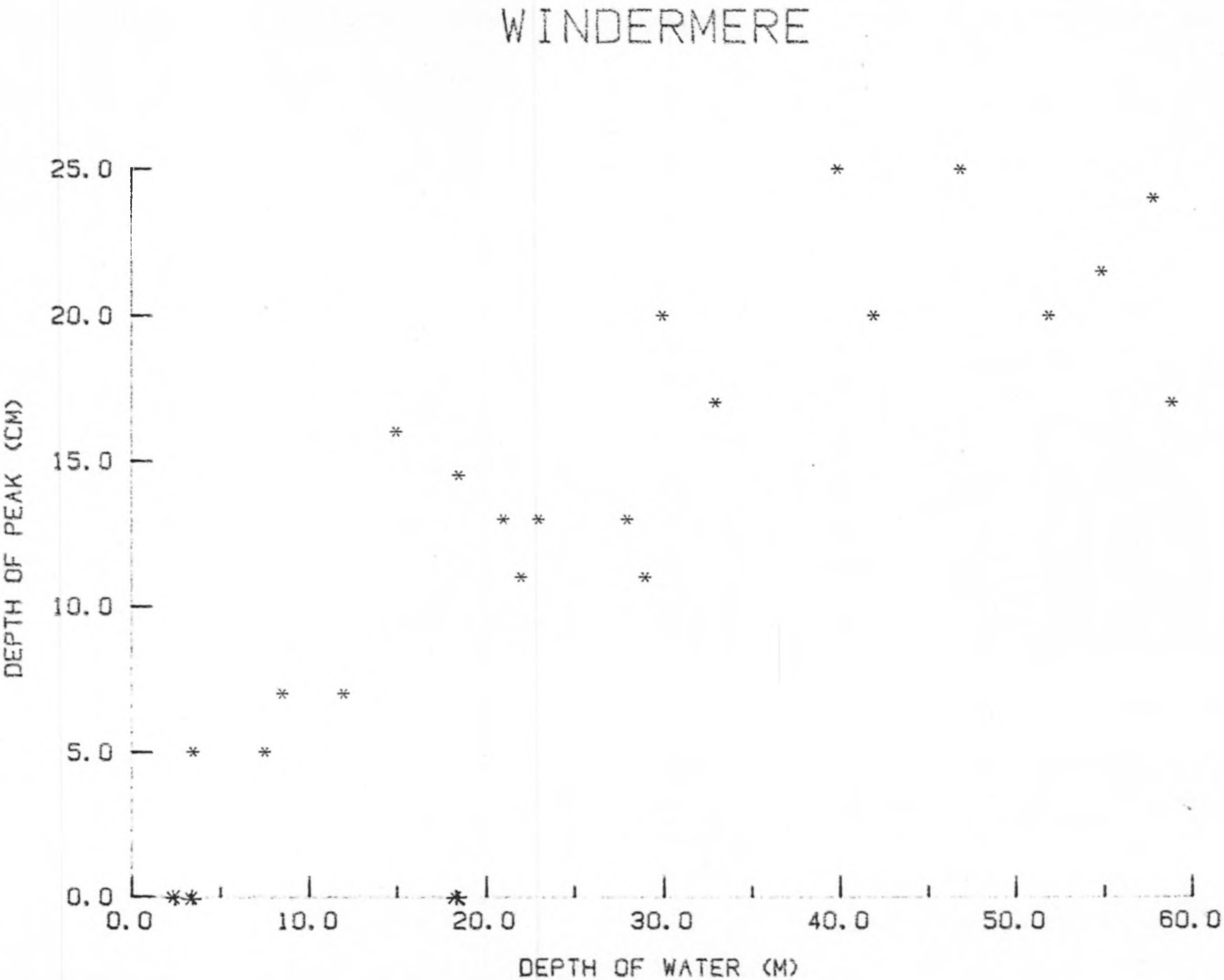


fig.8


LOAD VS.
LOAD
0.150
0.140
0.130
0.120
0.110
0.100
900
800
700
600
500
400
300
200
100
0.000
0.0
10.0
20.0
30.0
DEPTH



WINDERMERE
25.0
20.0
15.0
10.0
5.0
0.0
DEPTH OF PEAK (CM)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
DEPTH OF WATER (M)

fig.9

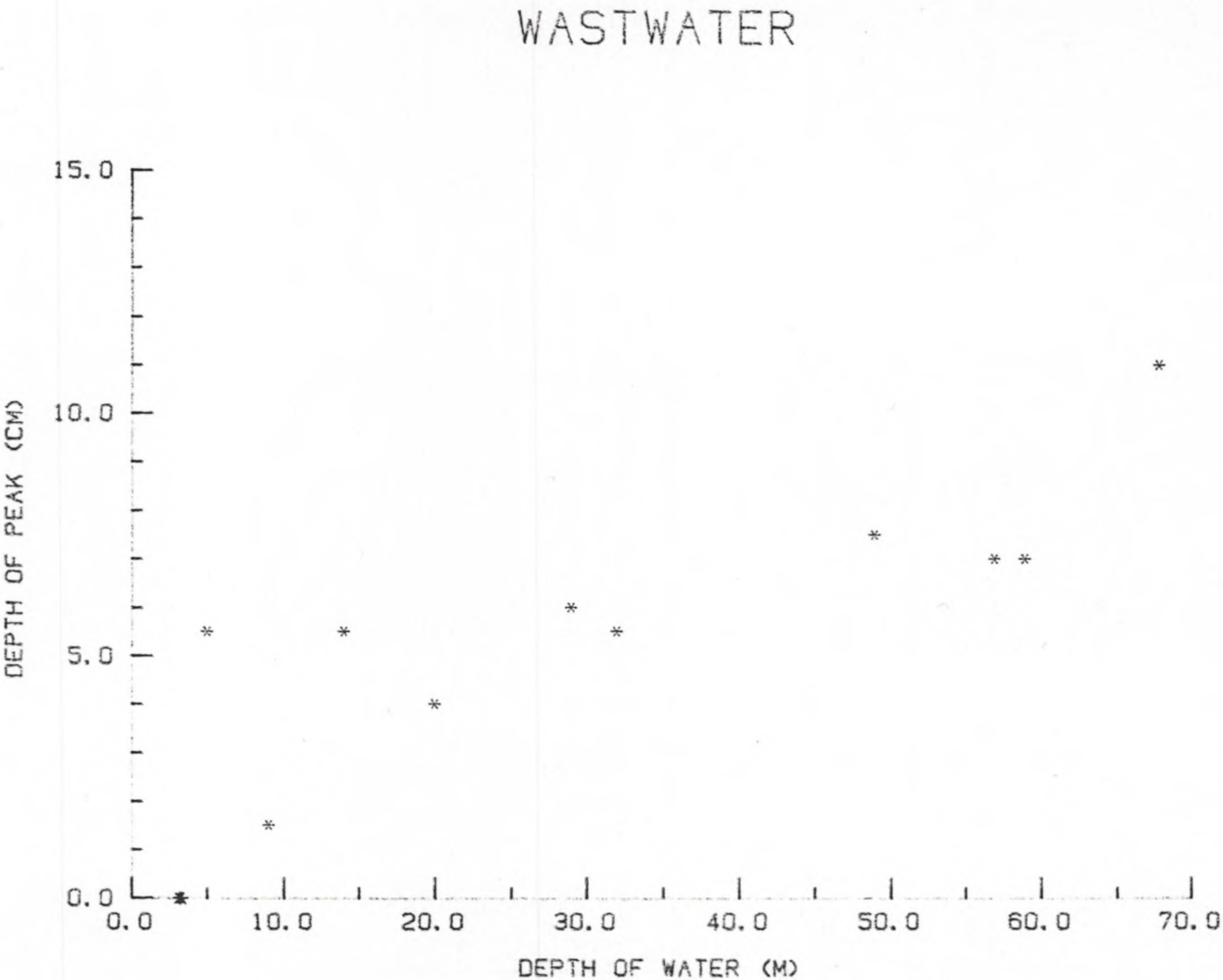

WASTWATER
DEPTH OF PEAK (CM)
15.0
10.0
5.0
0.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
DEPTH OF WATER (M)

fig.9

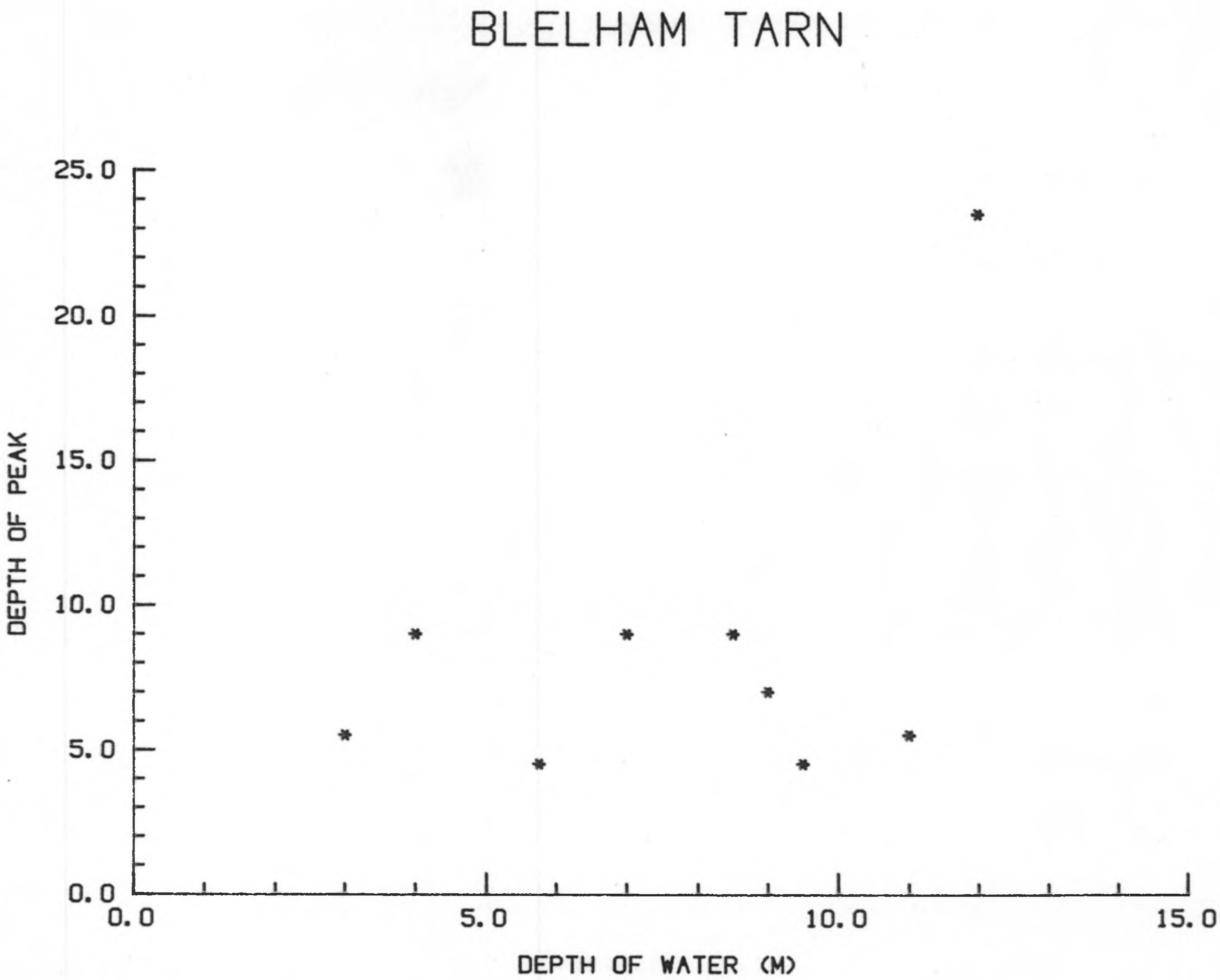

BLELHAM TARN
25.0
20.0
15.0
10.0
5.0
0.0
DEPTH OF PEAK
0.0
5.0
10.0
15.0
DEPTH OF WATER (M)

fig.9

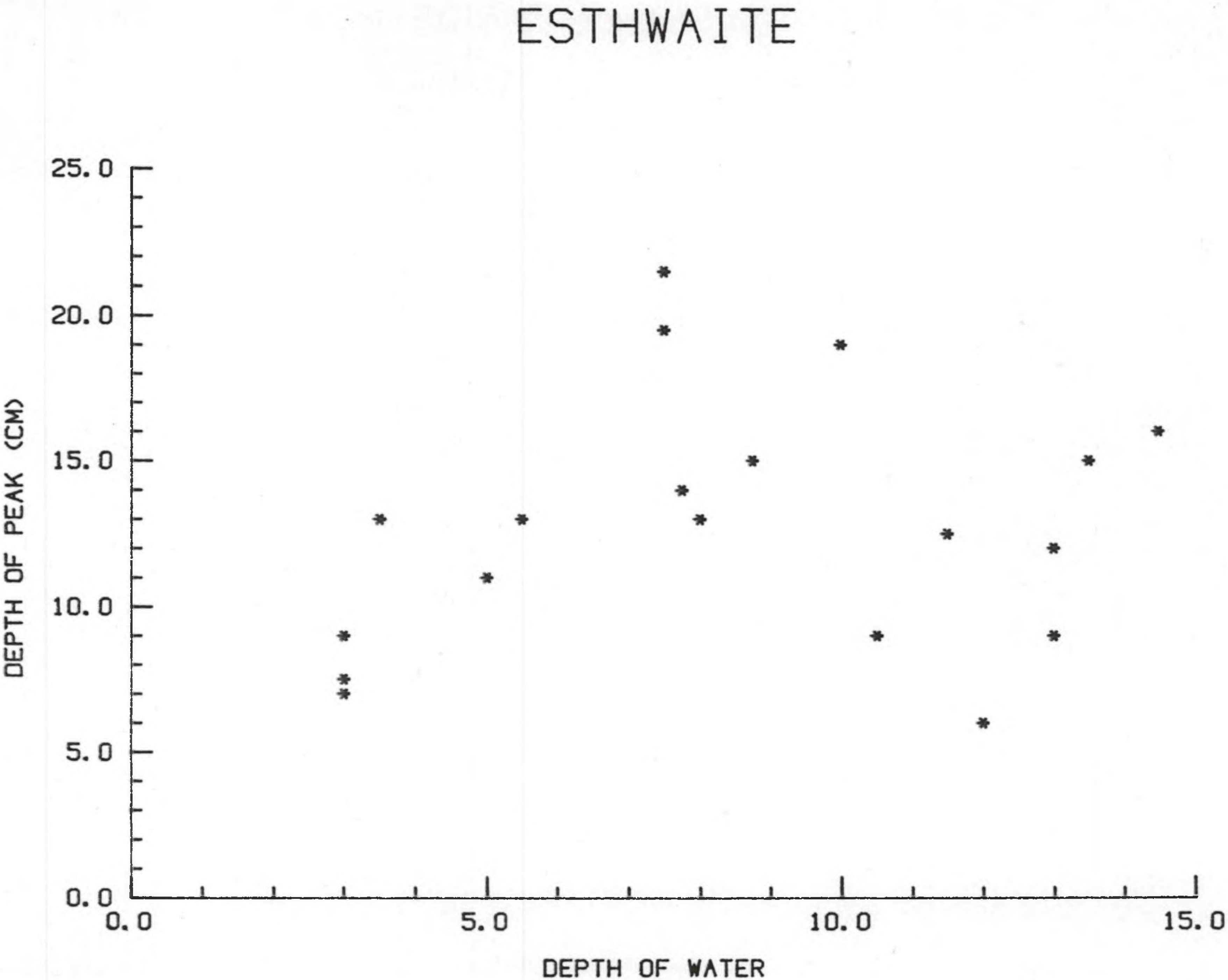

ESTHWAITE
25.0
20.0
15.0
10.0
5.0
0.0
DEPTH OF PEAK (CM)
0.0
5.0
10.0
15.0
DEPTH OF WATER

fig.9