DANMARKS GEOLOGISKE UNDERSØGELSE
II. Række. Nr. 107
Geological Survey of Denmark. II. Series. No. 107

Late- and Post-glacial sediments in the Randers fjord area

Geochemical, sedimentological, and geoelectric investigations

BY

Arne Villumsen and Holger Lykke Andersen

DANSK SAMMENDRAG

Sen- og post-glaciale sedimenter i Randers fjord området
Geokemiske, sedimentologiske og geoelektriske undersøgelser

I kommission hos C. A. Reitzels Forlag . København 1976

Danmarks Geologiske Undersøgelse. II. Række. Nr. 107
Geological Survey of Denmark. II. Series. No. 107

Late- and Post-glacial sediments in the Randers fjord area

Geochemical, sedimentological, and geoelectric investigations

By

Arne Villumsen and
Holger Lykke Andersen

Dansk sammendrag:
Sen- og post-glaciale sedimenter i
Randers fjord området.
Geokemiske, sedimentologiske og
geoelektriske undersøgelser.

I kommission hos C. A. Reitzels Forlag
København 1976

D.G.U. II. rk. nr. 107
er sat med Fotosats Times
og trykt i offset i 1000 eksemplarer
hos Andelsbogtrykkeriet i Odense.
Bogen er trykt på Thai-Cote, 115 g
fra a/s De forenede Papirfabrikker.
ISBN 87–421–0648–6

With 5 plates

Date of publication: 1976–03–31

Contents

Abstract

Thickness and distribution of Late- and Post-glacial sediments in an Eastern Jutland valley system have been mapped, and their sedimentogenetic and diagenetic relations have been studied. The chemical and sedimentological methods used are discussed in detail. Post-glacial marine sediments formed in a tidal fjord environment are the most important deposits in the area, and it is shown that river supplies of freshwater control the salinity of the environment and were responsible for the rather high content of allochthonous material in the sediment. The marine sediments rest on Late-glacial sand, whose surface topography indicates that the valleys were formed by subglacial erosion. Local occurrences of dead ice were present at least until the *Littorina* sea (Atlantic) transgression. Depth conditions for Early Post-glacial peat are used to estimate the groundwater level and the course of the river Gudenå in the Continental Period. Sedimentary facies in the Atlantic *Littorina* sea are discussed, including salinity, tidal activity, water depth, nutrient conditions, and exchange of stagnant bottom water from the deepest parts of the fjord area. The sequence seems to have been influenced only by minor syndiagenetic and weathering processes.

With the intention of providing supplementary information to that obtained from mapping of the Post-glacial sediments of the region 161 electric soundings have been carried out in the Randers fjord area. The specific resistivity of the sediments has been determined and the principle limitations of the methods applied have been investigated. Interpretation of the electric soundings has been done using a new system of computer programs. Maps showing the thickness relationships and variations in specific resistivity in the uppermost, largely Post-glacial deposits in the area have been prepared, and a map showing the location of the surface of the Danian limestone and occurrence of Tertiary clay is also presented.

Introduction

The investigation of Late- and Post-glacial sediments in the Randers fjord area can be taken as a natural continuation of earlier research carried out in the Rosenholm depression (Villumsen 1973), where Late- and Post-glacial sediments from a freshwater basin were studied. The Randers fjord area includes Rosenholmå valley, Allingå valley, Virring bay, Grund fjord, and the parts of Randers fjord situated on the RANDERS MAP SHEET. For some time during the Post-glacial time this area was covered by the Atlantic *Littorina* sea, and a study of the Late- and Post-glacial deposits from this area and a comparison with results from the Rosenholm study will therefore permit interpretations of many different sedimentary facies in the transition zone from a pure freshwater to a marine environment.

The investigation is divided into three main parts, namely:
a geochemical and sedimentological study (by Arne Villumsen)
a geoelectric investigation (by Holger Lykke Andersen), and
a paleontological investigation (by Anne-Lise Lykke Andresen and Jytte Christensen).

The present paper describes the results of the geochemical, sedimentological, and geoelectric investigations. Some preliminary results from the paleontological study have kindly been provided from the authors mentioned above, and these results are included here. The entire results of the paleontological study will be published at a later date.

Geochemical and sedimentological investigations

Arne Villumsen

History of research

The geological development of the Randers area is complex (Larsen et al. 1972) and up to now is not known in detail. In order to illustrate some main features of the genetic history of the area, Sorgenfrei's (1952) investigations can be mentioned. He demonstrated that tectonic movements of the pre-Quaternary deposits have played an important role in the foundation of the great east-west trending valleys which today dominate the morphology of the northern part of the RANDERS MAP SHEET. The area was further modelled during the Quaternary glaciations. Concerning this A. Jessen (1918) writes:

"The large, wide valleys around Randers fjord, the rivers Gudenå and Nørreå, are very old an can be traced back to at least the Würm glaciation. During the last phase of glaciation, when the great outwash plains were formed, and during the subsequent melting of the ice, these valleys were the bed for subglacial and later extramarginal meltwater-rivers. These rivers with their great floods and tremendous material transport transformed the original valleys, first by erosion, later by filling irregularities in the valley bottom, so that the original V-formed cross-section was transformed to a U-form with flat bottom and steep flanks". (A. Jessen 1918, p. 11 (translated)).

It is generally accepted that the southern part of Denmark was situated above sea-level during the Late-glacial period (see for example Krog's (1968) outline concerning the distribution of Late- and Post-glacial marine sediments in Denmark) and this explains why Late-glacial marine deposits are not found in the Randers area. Different investigators have found peat deposits underlying the Post-glacial marine sediments in the Randers area and in the adjoining valleys. Feddersen, who made a boring in the Nørreå valley in 1881 (according to A. Jessen 1918) was one of the first to report this, but peat layers were later found at a number of localities below the marine sediments in the Randers area (A. Jessen 1918). These freshwater deposits are normally dated to "fastlandstiden" (the "Continental Period"), a chronostratigraphical unfortunate name, which roughly includes the Preboreal and Boreal Chrons in this area. During the following *Littorina* transgression most of the Randers area was covered by the sea, the maximum extension of which was mapped by A. Jessen (1918, 1920). The estuary of the river Gudenå, which in "fastlandstiden" was situated some distance out in the recent Kattegat (Mörner 1969), retired to the vicinity of the present town of Langå (A. Jessen 1918) when the *Littorina* sea reached its maximum extent. Wave motions and tidal activity were more intense than today (Nielsen 1938) and this contributed to the formation of the steep coasts which are often seen limiting the *Littorina* sea deposits in the Randers area.

The development of the vegetation in Randers fjord was studied by K. Jessen (1918). Temperature and salinity conditions were discussed by Johansen (1918) based on the fauna of the *Littorina* deposits. Both temperature and salinity were higher in the *Littorina* sea than they are today in the remaining part of the fjord system (Johansen 1918).

By investigations carried out around the small peninsula of Dyrholmen in Virring bay (see fig. 1) Troels-Smith (1942) demonstrated the presence of 3 separated *Littorina* transgression layers which he dated by their pollen content to the Atlantic. According to Mertz (1924), the uplift of the Randers area after the maximal *Littorina* transgression and up to today has amounted to some 3–4 metres. An important part of the area, especially around the recent Randers fjord and Grund fjord, has quite recently been effectively drained and has become permanent dry land after the establishment of major pump stations.

Description of localities

The investigated area includes an Eastern Jutland valley system. The valleys are today covered by Post-glacial marine and freshwater sediments, while the surroundings are build up of sandy tills from the Würm glaciation and Late-glacial outwash sands. Only the Late- and Post-glacial deposits in the valley system have been included in this study. Fig. 1 shows location of the investigated area which includes Rosenholmå valley, Allingå valley, Virring bay, Grund fjord and Randers fjord.

The Rosenholmå valley is quite narrow. The bottom of the valley slopes from about 12 m (above sea level) in the south-eastern end to 5 m in the northwest where the small river Rosenholmå flows into the Allingå valley. The river Rosenholmå drains the Rosenholm depression which has been geologically described by Villumsen (1973). The Rosenholmå valley is covered by a thin layer of Post-glacial peat.

The Allingå valley has a total length of about 15 km. It includes the low lying area between the village of Robdrup and the recent Grund fjord. The western part of the area – around Klausholm castle – is up to 1 km across, and is covered by a few metres of peat resting mostly on sand. A few km northeast of Klausholm the valley is very narrow (about 200 metres) and here the youngest deposits are also Post-glacial peat, but below the peat marine sediments are often seen. The valley bottom is about 7–8 m above sea level at Robdrup and some 3 m at Vester Alling. A little northeast to the village of Vester Alling the valley opens to an extensive, almost horizontal area, part of which, Virring bay, extends a few kilometres to the west. Nearly half way between Vester Alling and the castle of Gammel Estrup the Allingå valley has a narrow connection to the southeast (to Kolindsund). The last part of the Allingå valley (from Gammel Estrup to Grund fjord) is about 1 km across. The valley bottom slopes gently from ca. 3 m at Vester Alling to about + 0.2 m at the inner part of Grund fjord. The sediments in this part of the valley are mainly Post-glacial peat underlain by marine clay and gyttja.

Virring bay. The western part of this area lies 3–4 m above sea level and is made up of peat without marine sediments. In the area between the village of Virring and the Allingå valley the peat rests on marine clay and silt. Virring bay is approximately 1 km across.

Grund fjord includes the northeastern part of the investigated area. It is demarcated from Randers fjord by a north-south line through the village of Ugelhuse. The area is horizontal at about 0.2–0.5 metres above sea level. The youngest sediments consist of alternating layers of sand and clay with a minor content of organic matter. The sediments in the recent Grund fjord are not included in this investigation.

Randers fjord. Only the valley between the village of Ugelhuse and the town of Randers has been studied in this connection. The area is about one kilometer wide and is covered by a relatively thin peat layer, which overlies Post-glacial marine sediments. The river Gudenå runs from west to the east and at the village of Ugelhuse it turns at a right angle to the north. The sediments below the recent Randers fjord are not included in this investigation.

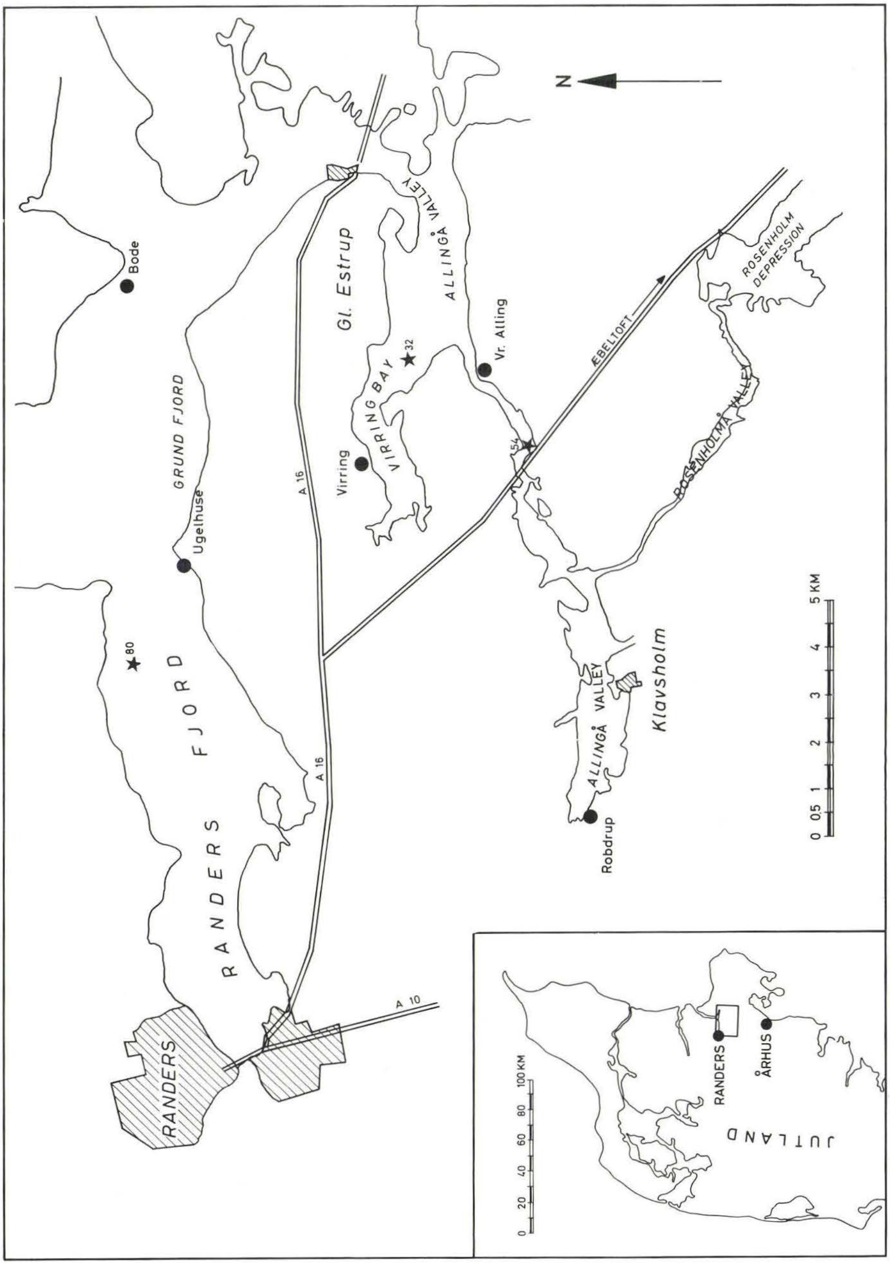


Fig. 1. Location map for the Randers fjord area. The asterisks indicate type localities.

Working methods and discussion of their applicability

Field work

Depth mapping. During the field work systematic depth mapping of the area was carried out, using a Hiller-type corer. The localities of borings (about 85 in total) can be seen in plate 1. Nearly all the borings stopped for technical reasons in a sand deposit below the Post-glacial sediments. This sand deposit is believed to be roughly Late-glacial in age. (A detailed discussion concerning the age of the sand is given on p. 43). Plate 1 shows the topography of the sandsurface. An investigation of the thickness of the Post-glacial sediments and the deeper lying deposits of the area has been carried out by H. L. Andersen using geolectric methods and the results of his study are presented in this paper (pp. 93–110).

During the depth mapping a total of 6–700 samples of mainly Post-glacial marine sediments were taken for paleontological and other studies. Some preliminary results of this investigation are incorporated in the present paper (kindly communicated by Mrs. A.-L. Andersen), but the final report concerning the faunal conditions will be published at a later date.

Field measurement of pH and Eh was carried out for a few borings as described by Villumsen (1973).

Type localities: Based on the results of the depth mapping 3 type localities were selected as representatives for three of the main facies. The type localities are indicated in fig. 1 and plate 1 by asterisks. At these localities undisturbed sediment cores were taken using a Geonor A/S 54 mm sampler. With a few exceptions only this material was used for the chemical and sedimentological laboratory investigations.

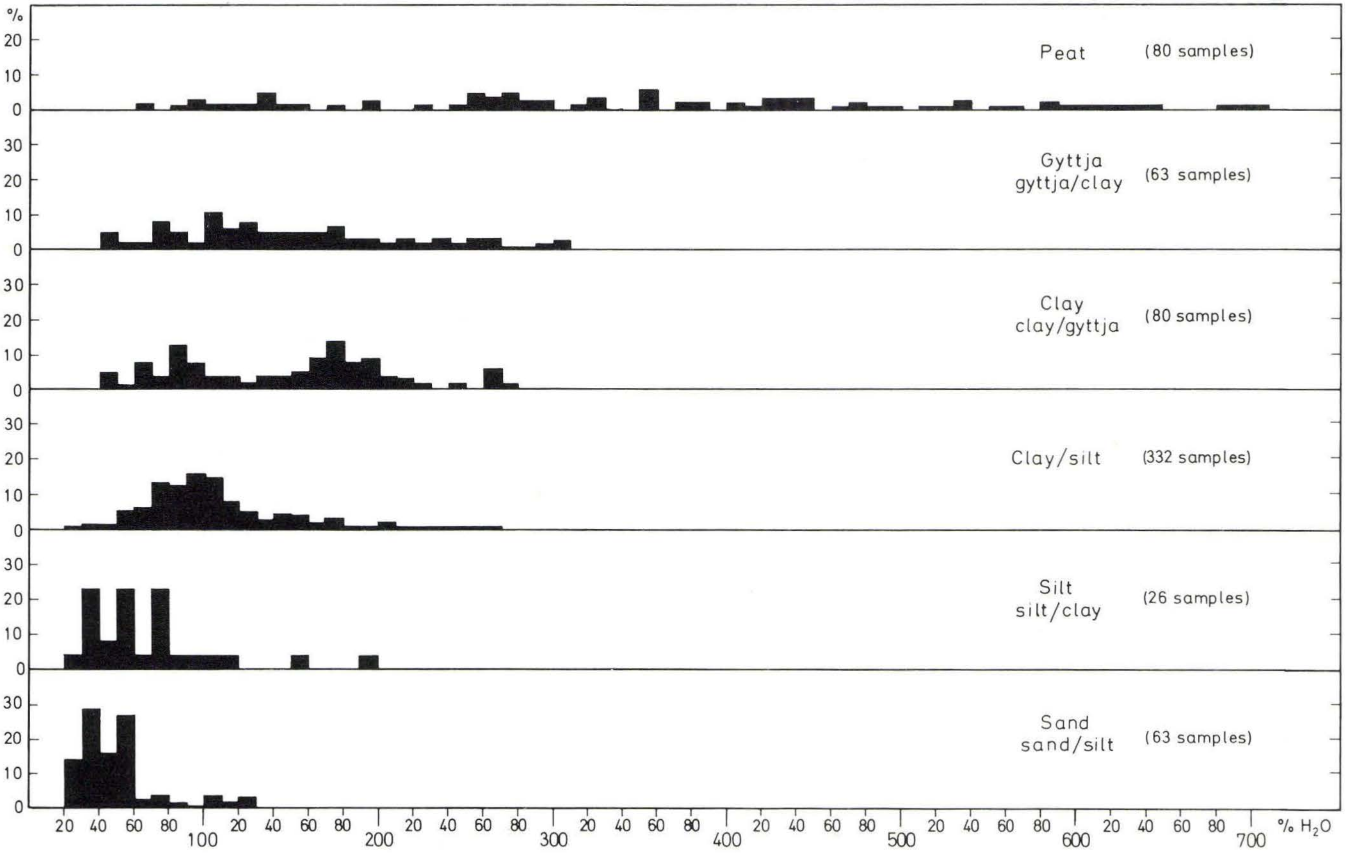
Laboratory work

X-ray radiographs were taken of most of the core material following the method described by Thiede and Larsen (1971).

Water content. The water content of all the samples collected during the depth mapping was determined by weight loss after drying in an oven for 24 hours at 110°C. This determination of the water content is an excellent and rapid method which often gives an indication of the lithological differences, especially for sediments which are saturated with water. Very often small variations in the content of organic matter will clearly influence the water content of the sediment. Fig. 2 shows the correlation between water

Fig. 2.

Correlation between water content and sediment type.



content (% of dry matter) and the sediment types in the investigated area, based on about 600 determinations. It is clearly seen that an increase of clay and organic matter in the sediment causes the water content to rise. The peat varies widely in its water content mainly because it was not fully water saturated when the material was sampled. Further the Early Postglacial peat, which lies below some 10 m of marine sediments, might have lost some water during compaction. Generally the peat in the area is very sandy, which of course also influences its water content.

The investigated sediments, which contain several compounds that are unstable under oxidizing conditions will, during drying in an oven as described above, undergo major changes in chemistry and mineralogy such that subsequent laboratory analysis will be of a questionable value. Therefore the samples from the type borings were dried by freezing under vacuum (−50°C, 0.05 mm Hg). By this method very small transformations of the material will occur. All the analytical results are converted to dry weight at 110°C.

Grain size distribution was determined by wetsieving. Silt and clay contents were calculated using Stokes law. The content of organic matter and sulphides caused some difficulties in the grain size determination: The samples were treated by H_2O_2 for destruction of the organic matter, but some sulphuric acid was produced by oxidation of the sulphides and this attacked some of the sample material. Presumably the uncertainty of the method is about 10 %.

The loss on ignition was determined after ignition at 1000°C for 20 minutes to ensure a total removal of CO_2 from carbonates. The results could be reproduced with a relative uncertainty of $\pm$ 5 %. This determination is rather simple, but it has in many cases been used successfully to obtain a measure of the total content of organic matter in a sediment, for example in pure organogenic deposits. Generally, however, the change in weight of a sediment by the ignition is a result of many, often mutually dependent, processes, and therefore it is difficult to interpret the loss on ignition. Its application as a direct measure of the content of organic matter can often be highly questionable:

By the ignition at 1000°C not only organic matter will disappear. In the present case the changes in weight will further include: loss of chemically combined water from opal, clay and other hydrous silicates; loss of CO_2 from the carbonates; increase in weight caused by oxidation of reduced iron compounds ($FeO \rightarrow Fe_2O_3$); decrease or increase in weight caused by the sulphur content (by base deficit part of the sulphur will disappear with the combustion products, resulting in a weight decrease). If the sample has a sufficient content of bases (for example as $CaCO_3$), the sulphur in the ignited sample will remain as sulphates, causing an increase in weight by the oxygen uptake.

In calcareous sediments the *reduced loss on ignition* (i.e. the total loss on ignition – CO_2 loss from carbonates) might be an acceptable measure of the caustobiolithic fraction, but still better this part of the sediment is indicated by the content of organic C, which is used in the present context.

CO_2 in carbonates. By using 10 % HCl the CO_2 was expelled from the samples, absorbed in sodium asbestos and then determined gravimetrically. The uncertainty on the double determinations lies within ± 2 % relatively.

In many cases the CO_2 content originates from $CaCO_3$ alone. In such cases the CO_2 content is often determined by titration, but as for this sample material the presence of $FeCO_3$ and organic matter could make the titration uncertain. Therefore the above mentioned method was used, although it is more time consuming.

Total C. The total carbon content was determined gravimetrically after combustion in a Leco 521 induction furnace. The uncertainty is ± 2 % (relative).

Organic C was calculated as the difference between total C and CO_3-C. This is one of the best measures of the content of organic matter in the samples, and today it is normally used. The total content of *organic matter* has sometimes been estimated, based on the content of organic C using different conversion factors (Orr, Emery & Grady 1958). However, as the organic fraction normally has a wide range in composition, partly because of differences in the organic source material, partly because diagenetic transformations can give different alteration products, conversions like these should normally be avoided.

Total N. The N content was determined by a normal Kjeldahl analysis, by which nitrogenous compounds except NO_3-N are converted into $(NH_4)_2SO_4$ in a boiling mixture of K_2SO_4, $CuSO_4$, HgO and H_2SO_4 (conc.). The nitrogen content is then determined by distillation and titration of NH_3. The uncertainty of the method is about ± 2 % (rel.). Qualitative NO_3 tests (see below) were in all cases negative, and thus the nitrogen content determined by the Kjeldahl method gives the total N content of the samples.

NO_3-N, qualitative. Qualitative NO_3 tests were carried out on a water extract of the samples using the brucine method. All the NO_3 tests were negative, which means under the present conditions that the NO_3 concentration in the sediment is less than 0.01 %.

NH_4-N. In a reduced environment the pore solution often contains appreciable quantities of ammonia, some of which might be preserved in the sample after the freeze-drying process used in the present case. This contribution to the nitrogen content of the samples is presumably of minor importance. On the other hand ammonia can react with the clay minerals, and this often makes interpretations of the total N content of the samples difficult (see below).

Fixed and exchangeable NH_4-N. NH_4^+ can either neutralize negative charges within the clay mineral lattice (fixed NH_4^+) or at the clay mineral surfaces exchangeable NH_4-N was determined: After repeated treatment by 1 N KCl amount of NH_4^+ which can be extracted by 1 N KCl (Stevenson & Cheng 1972). The nitrogen, which is incorporated in the sediment, in this way, depends, among other things, on the clay mineral type. According to Nielsen (1971) Allison & Roller (1955) indicated that vermiculite can, on average, fix 50 meq NH_4^+ per 100 g clay mineral, which corresponds to 0.7 % N. For montmorillonite and illite they found 6 meq and 1 meq NH_4^+, respectively, per 100 g clay mineral. According to the authors above, kaolinite could not fix NH_4^+.

In a representative series of 6 samples from the investigated area the exchangeable NH_4-N was determined: After repeated treatment by 1 N KCl MgO was added to the extract, and then NH_3 was distilled, accumulated and determined spectrophotometrically following Nessler's method. The results showed that exchangeable NH_4-N amounted to 10 % of the total nitrogen content.

The content of fixed NH_4-N was not determined. An estimate based on the above mentioned ability to fix NH_4 for different clay minerals, knowledge of the clay mineral type, and the grain size distribution for the present samples, gives the same order of magnitude for fixed NH_4-N as for exchangeable NH_4-N. It may thus be concluded that about $^1/_5$ of the total nitrogen content might be combined with the clay fraction. This is of importance in a discussion of the applicability of some of the parameters which have often been used to characterize the composition of the organic fractions and their degree of transformation (for example the C/N ratio and the total nitrogen content as determined by the Kjeldahl method).

As systematic determinations of the fixed and exchangeable NH_4-N were not performed, the contents of organic N cannot be calculated (= total N − (fixed N + exchangeable N)). Therefore the nitrogen content given in this paper is less suitable as a measure of the sediment's total caustobiolithic fraction than the content of organic C.

The C/N-ratio. The ratio between organic carbon and nitrogen in a sediment often varies widely and is normally difficult to interpret. According to Arrhenius (1950), Gripenberg (1934) investigated the C/N ratio in Baltic Sea sediments and related the high C/N values to supply of land-derived organic matter which were supposed to have entered the Baltic Sea in solution or suspension. Hansen (1959, 1962) classified modern freshwater lake sediments using among other parameters the C/N ratio. A high ratio is characteristic of the lake sediment type "dy", and Hansen believed that a supply of terrestrial humus to lakes generally increases the C/N ratio in the sediment. Hansen also found that the C/N ratio could be used for a classification of fossil lake sediments. An interpretation of small variations in the C/N ratio should be avoided (Hansen 1964a) because post depositional transformations will effect the C/N ratio. – Based on investigations of the Red Sea sediments Mohamed (1949, according to Arrhenius 1950) believed that the C/N ratio was like the value found in living plankton. It is possible that the special chemical conditions of the Red Sea water can explain Mohamed's surprising conclusion (Red Sea water has a high Mg content, which can prevent chlorophyll decomposition (see the later section on the chlorophyll content)). Arrhenius (1950) showed that higher C/N ratios occur with greater total content of organic matter in the sediments. According to Stevenson & Cheng (1972) the reason for this could be that the content of NH_4-N fixed in the clay minerals contributes only to a relatively minor extent to the total nitrogen content in samples where the concentration of organic matter is high. Bordovskiy (1965) states that the contents of N and P in planktonic material will be selectively effected by aerobic decomposition processes, and therefore the C/N ratio of the organic matter in a marine sediment will normally be higher than in the plankton. Generally this means that allochthonous organic matter will have higher C/N values than the source material because the allochthonous fraction has normally been under oxidizing conditions for a greater period of time. Stevenson & Cheng (1972) showed that the content of amino acids was great in sediments with low C/N ratios which supports Bordovskiy's theory (1965) concerning selective decomposition of compounds rich in nitrogen. Stewart & Gorsline (1962) assumed that high C/N values which they found for marine near-shore sediments were caused by the large content of land-derived plant material. – The conclusion of this is that by the C/N ratio it is possible to distinguish between allochthonous and autochthonous organic components of a modern sediment. The allochthonous part of the material has the highest C/N ratio. This primary difference, however, cannot be expected to be preserved during the diagenetic alterations to which the organic fraction of the sediment will be subjected. Decisive importance should not be attached to small variations in the C/N ratio, neither for modern nor for ancient sediments. As a closing remark to the discussion of the C/N ratio it should again be underlined that only the ratio between the *organic* carbon and the *organic* nitrogen has a real meaning when characterizing the organic content of a sediment. A Kjeldahl determination of the nitrogen will not, as earlier mentioned, be usable as a direct measure of the organic N in sediments where a certain amount of clay is present.

Total S (1st method) was determined using a Leco 532–000 type automatic sulphur titrator. Results from this apparatus are normally slightly low because SO_3 from the combustion products is not included in the titration. To test this method another, more time-consuming, technique was used (see below). It appeared that the Leco method gave a mean sulphur content of 97 % of the total S, and therefore the results are here used without correction.

Total S (2nd method). By using a modified version of Eschka's method (Dansk Standard No. 155) the total sulphur content was determined in the following way: A weighed subsample was ignited in a crucible with a mixture of Na_2CO_3 and MgO for two hours at 850°C. By this means all the sulphur in the sample is converted to SO_4^{-2} and SO_3^{-2}. The sample is then oxidized in a porcelain container by bromine water ($SO_3^{2-} + 0 \rightarrow SO_4^{2-}$) and acidified by HCl before evaporation to precipitate SiO_2. The evaporated rest is soaked with HCl, and the sulphates are dissolved in distilled water. SiO_2 was then removed by filtration, and after adding $BaCl_2$ the total S content was determined from the precipitated amount of $BaSO_4$. The uncertainty is about 5 % relative.

SO_4-S. A weak HCl solution is added to the sample, and the sulphates are dissolved by boiling. After filtration the sulphates are precipitated by $BaCl_2$ and determined gravimetrically. The uncertainty is about ± 1 mg SO_4. In the actual case only minor amounts of SO_4-S were found.

Elementary S. After chloroform extraction the sample was filtered, evaporated (at 60–70°C) and weighed. In addition to elementary S, fat and waxes will be extracted by the chloroform, and thus the method has an inbuilt uncertainty.

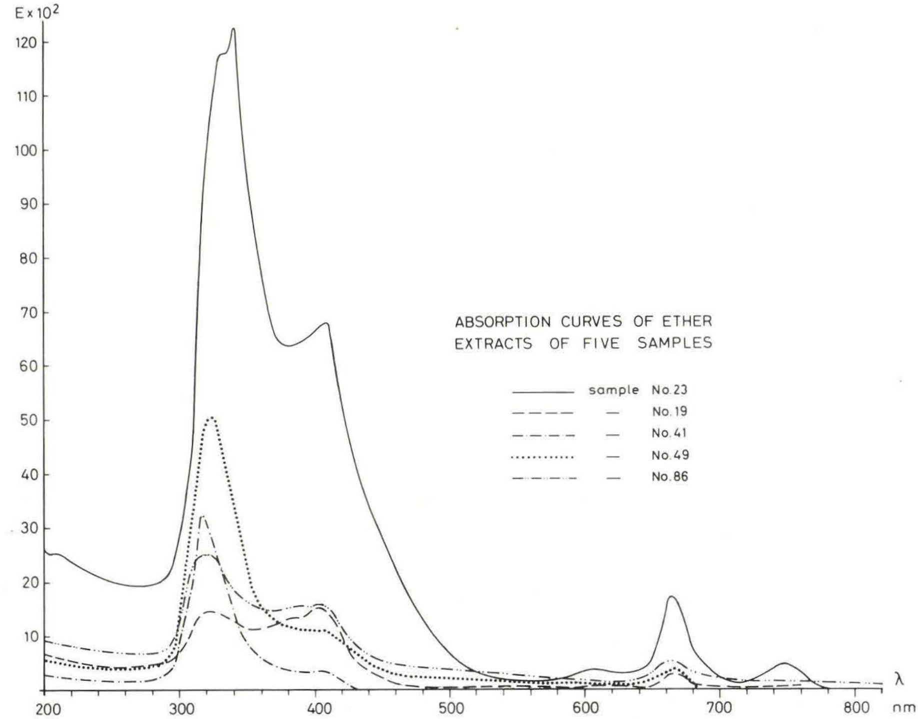


Fig. 3. Absorption spectra of 5 samples from the Randers fjord area. Absorption maxima at λ = ca. 750 nm originate from bacteriochlorophyll a, which is produced by purple sulphur bacteria. Absorption maxima at λ = ca. 660 nm originate from chlorophyll remains (see text p. 20).

Elementary S from purple sulphur bacteria. Some of the bacteria of the sulphur cycle are photoauthotrophic. For example this applies to purple sulphur bacteria, which can live in shallow, anaerobic environments where light is admitted. The bacterial activity results in an accumulation of elementary sulphur, produced from H_2S or sulphides. In a few samples the content of pigment from purple sulphur bacteria (bacteriochlorophyll a) was determined as follows:

2 g pulverized sample was extracted by 25 ml ether for about 1 hour. After centrifugation the extinction of the filtrate for wavelengths between 200 nm and 1000 nm was measured using a Hitachi-type spectrophotometer. In only one of the samples, No. 23, was an extinction maximum of about 750 nm found (see fig. 3), and presumably this originates from a content of bacteriochlorophyll a as other pigments show no extinction in this wavelength area (Fenchel & Straarup 1971). As the content of elementary S in

sample No. 23 is anomalously high (2.2 % – see table 2), it seems reasonable to assume that only this sample has a content of bacteriochlorophyll a. Sample No. 23 was sedimented in a special environment, which is not characteristic for the investigated area as a whole. It may therefore be concluded that normally elementary S originating form either purple or green sulphurbacteria (which have the same requirements for light, se page 20) has generally been of minor importance in controlling the sulphur content of the sediments in the area. The absorption has not been converted into an absolute measure of bacteriochlorophyll a.

The sulphur isotope ratio was determined according to the method of Hartmann & Nielsen (1969) and Thode et al. (1961):

To 1 g of pulverized, vacuum dried sediment sample a few drops of H_2O_2 and bromine water were added, and then the sample was slowly evaporated. This treatment and the following evaporation with bromine water and aqua regia transforms all the sulphur compounds into sulphates. The nitric acid was then removed by evaporation with HCl. After this the sulphates were transformed into H_2S by a reduction solution (500 ml HI (density 1.7), 816 ml conc. HCl, 245 ml H_3PO_2, after Thode et al. (1961)). The evolved H_2S was bubbled through distilled water using a nitrogen current and then precipitated as CdS in a hydrous solution of cadmiumacetate. After filtration and vacuum drying the CdS was ignited at about 700°C in evacuated quartz ampoules, by which the sulphide content was transformed into SO_2. The ratio between $^{32}SO_2$ and $^{34}SO_2$ was then measured using a mass spectrometer (type Varian MAT.CH5, ionsource electron bombardment). As standard CdS (from Riedl de Haën/Hannover) with a $\delta^{34}S$ value of $+\ 10.8\ ‰$ was used.

$$(\delta^{34}S\ ‰ = \frac{(^{34}S/^{32}S)\text{sample} - (^{34}S/^{32}S)\text{ meteorite standard}}{(^{34}S/^{32}S)\text{ meteorite standard}} \times 1000)$$

As the mass spectrometer had a molecular flow gas admission system, and as the measurings were taken in a series, the calculated $\delta^{34}S$ values (‰) cannot be given more accurately than in table 2.

As the maximum content of total S is found in the marine sediments it may be assumed that the sulphate content of the *Littorina* sea was important for the accumulation of sulphur in the sediments. Hartmann & Nielsen (1969) described a similar model for the formation of sulphides in recent Baltic Sea sediments: The reduction of sea water sulphate takes place by means of bacteria, whose activity in the Baltic Sea is restricted to the uppermost few cm of sediment which has a diffusion contact with the sea water (Hartmann & Nielsen 1969). The sulphate reduction results in fractioning of the S isotopes, so that the $\delta^{34}S$ values for the sediment sulphides are often found to be negative, while sea water sulphate has a $\delta^{34}S$ value of about + 20 ‰ (the sediment sulphur is isotopically lighter than sea water sulphate). Hartmann & Nielsen (1969) investigated the relationship between the degree of isotopic fractionation and the sedimentary environment and found that the sedimentation rate was the most important factor. For the actual samples from the Randers area the $\delta^{34}S$ values give some support to Hartmann & Nielsen's model (1969) as the highest S contents and the most negative $\delta^{34}S$ values are found where the rate of sedimentation seems to have been relatively slow.

The content of residual chlorophyll. From a small subsample (normally 1 g) the pigment content was extracted with 100 ml 85 % ethylalcohol for 20 hours. The absorption for the filtrate was measured at 662.5 nm using a Perkin-Elmer, Hitachi type spectrophotometer. – Fresh chlorophyll as well as many of its decomposition compounds show a maximum extinction at about 660 nm (Orr & Grady 1957), and therefore a good measure of the pigment content can be obtained based on the extinction intensity at this wavelength.

Green sulphur bacteria also show a maximum extinction at 660 nm, and it is not immediately possible to distinguish between chlorophyll and pigment from green sulphur bacteria (Fenchel & Straarup 1971). In the present case, however, green sulphur bacteria have presumably contributed very little to the absorption at 662.5 mm because green sulphur bacteria approximately have the same requirements for light as purple sulphur bacteria, which as earlier mentioned have only been found in one case in a special sedimentary environment in the investigated area.

In order to correct the measured extinction intensities at 662.5 nm the mean extinction of the extract in the wavelength interval from 520 nm to 800 nm was subtracted from the readings. After this the corrected measurements (table 3) should give a reliable impression of the chlorophyll content in the sediments (Sanger & Gorham 1972). Most of the autochthonous organic fraction in the marine environment is produced by the flora through photosynthetic activity. In marine areas of shallow water the bottom vegetation might make an important contribution, but generally floating plants or phytoplankton are the main source of the organic matter in the sea, and in order to sustain their production, nutrients, light and CO_2 are required. The application of the chlorophyll content as a measure of the organic matter in the marine productive layer is rather problematical, partly because different types of phytoplankton have different clorophyll contents, and also because the chlorophyll content of the same type of phytoplankton may depend on the growing rate. As a mean value it is presumed that organic matter in surface sea water contains 6 % green pigment, expressed as chlorophyll. Phytoplankton contain much more chlorophyll than terrestrial plants. Thus green leaves contain only about 0.8 % chlorophyll (Orr, Emery & Grady 1958). Chlorophyll is unstable under oxidizing conditions, with the result that the sediment sometimes only receives a very small part of the primarily produced chlorophyll. Decomposition processes cause chemical changes in the chlorophyll molecule, and therefore the green organic pigment of a sediment cannot always properly be named chlorophyll. In most cases the first step in the chlorophyll decomposition is liberation of Mg, and pheophytin is formed. Further change in the organic fraction can result in the formation of porphyrin, which is a vanadium-bearing organic-chemical complex (Welte 1969). In the geological literature chlorophyll-resembling compounds have been described as sediment chlorophyll, chlorophyll remains, green pigment, pheophorbide or pheophytin (Orr & Grady 1957). The greatest content of chlorophyll remains have been found in dark, cold anaerobic environments, and under these conditions differences in the primary production are supposed to be preserved, and the pigment content can thus be used as a measure of the nutrient conditions in the environment of formation (Sanger & Gorham 1972). Besides anaerobic conditions (and thus low benthonic activity) a high Mg content seems to stabilize the chlorophyll content of the sediment (Nissenbaum, Baedecker & Kaplan 1972). From Danish deposits chlorophyll content has been described from the interglacial lake sediment at Rodebæk (Andersen & Gundersen 1955).

Quantitative measures of the content of chlorophyll remains are given by Parsons & Strickland (1963), who calculated the pigment content including chlorophyll. If for the Randers fjord sediments it is assumed that the original chlorophyll content has been transformed to pheophytin, it is possible to give a quantitative measure of the pigment content using the extinction intensities at 662.5 nm. Data from Strickland & Parsons (1968) and Orr & Grady (1957) have been used to calculate the specific absorption coefficient of 50 l/g cm, which is valid for pheophytin in an ethylalcohol solution. This numerical value indicates that 1 g of pheophytin dissolved in 1 litre of ethylalcohol will give an extinction (absorption) of 50 when the light beam in the spectrophotometer passes through 1 cm of the solution. The absolute pheophytin content which is found by this conversion procedure is of course not a totally correct value of the pigment content as its exact composition is not known. In spite of this reservation the pigment content expressed as pheophytin should for the present sediment be more reliable than the semiquantitative measures given by the extinction intensities, and also more relevant than a conversion of the extinction measurements to an absolute quantity of chlorophyll using another specific absorption coefficient.

Biogenous lime. From a known sample quantity the shell material in the fraction > 1 mm was separated, and the lime content was determined by weighing. This biogenic lime is dominated by benthonic molluscs while lime from foraminifers is subordinate (pers.comm. A. L. Andersen). In a brackish or marine environment, like main part of the investigated area, it is assumed that the importance of the flora for the primary lime sedimentation is minor compared to the contribution from the molluscs. As an important source of error it should be mentioned that in many cases partly dissolved and crushed shell material will pass the 1 mm sieve, and will therefore not be included as biogenous lime.

The opal content. The determination of opal is performed in order to obtain an impression of the content of diatoms in the sediment. The determination was carried out using a modified version of the method of Lunge and Millberg (Hillebrand et al. 1955, p. 852): ½–1 g sample (depending on the diatom content) was weighed in a porcelain container, and a few drops of soda solution and about 10 ml 30 % H_2O_2 were added to oxidize the organic matter. After this the sample was treated with 75 ml of a 10 % Na_2CO_3 solution for 2 hours at 90–100°C. The solution was then filtered, and the filtrate acidified with HCl, and then evaporated to dryness for precipitation of SiO_2. After ignition at 900°C the precipitated amount of SiO_2 was determined gravimetrically. As it is possible that the soda solution can attack other SiO_2 compounds than the diatom opal, some uncertainty for the determinations cannot be excluded. Experiments with reaction time and concentration of the soda solution have shown that the solubility is strongly dependent on the sediment's age, presumably because of differences in dehydration of the opal. Therefore differences in the opal content of less than 1 % are not considered to be significant.

The content of acid soluble components. The determination of the contents of Al, Fe, Mn, Ca, Mg, Na, K, Cr, Cu, Zn, Pb, V, Li, Rb, and P were determined in a solution of the sample produced by boiling with aqua regia (⅔ HCl, 20 % + ⅓ HNO_3, 68 %) as follows: A subsample of 1 g was boiled with 50 ml aqua regia for 2 hours followed by evaporation (120°C) to dryness for total precipitation of SiO_2. The evaporation residue was moistened with HCl, and distilled water was added. The insoluble residue and precipitated SiO_2 were filtered, washed and determined gravimetrically. The filtrate was used for the determination of metals and P. – The treatment with aqua regia leads to solution of carbonates, sulphides, phosphates, hydroxides and some silicates (in the present case mainly the clay minerals), while quartz, feldspars, amphiboles, and well-crystallized clay minerals etc.

will remain undissolved. Some elements were determined in solutions produced by boiling of the sample with 20 % HCl. This treatment seems to dissolve the same compounds as the boiling with aqua regia, besides some of the sulphides. Unless otherwise stated the indicated content of elements is determined in solutions produced by aqua regia treatment of the samples.

Ca, Fe, Mn, Mg, Cr, Cu, Zn, V, and Li. The content of these elements was determined in a diluted solution using atomic absorption (Perkin-Elmer, 303). The uncertainty of the determinations is strongly dependent on the concentration. For Ca, Fe, Mn, and Mg the uncertainty varies from ±2 % (rel.) for the highest concentrations to approximately ±20 % (rel.) for small contents. For the contents of Cr, Cu, and V differences below 10 ppm are not considered to be significant. Variations in the Li content greater than 5 ppm are significant. The uncertainty on the Zn determinations is presumably higher than for the other elements (e.g. Cr, Cu, and V) because it is difficult to entirely avoid contamination during the preparation work.

Pb was determined on an extract (see below) from the aqua regia solution by atomic absorption (Perkin-Elmer model 300) using graphite furnace (HGA72) and Deuterium background corrector. The extraction was performed as follows: a sub-sample of the aqua regia solution was buffered with 1 M sodiumcitrate, extracted by xylene with DDDC (diethylammonium-diethyldithicarbominat) as complex-forming agent and dithizone as indicator.

Rb was determined by atomic absorption in a solution produced by boiling with 20 % HCl. The uncertainty has the same order of magnitude as stated for Li.

Na and K were determined using an EEL type flame photometer. Uncertainty 2–5 % (rel).

Al was determined by spectrophotometer (Perkin-Elmer, Hitachi). Uncertainty ± 10 % (relative).

P. The determination was performed spectrophotometrically on a weak sulphuric acid solution. Uncertainty 10–20 % (rel.).

SiO_2 from acid-soluble silicates was determined in a selected series of samples after the treatment with aqua regia using the same method as for the determination of the opal content (p. 22).

Insoluble residue is the ignited remains of the sample after the treatment with aqua regia. It includes quartz, opal, feldspars, amphiboles, and well-crystallized clay minerals.

Semi-quantitative modal analysis. The mineralogical composition (modus) of the samples was determined for the total material as well as for the clay fraction using a Philips X-ray diffractometer with Cu-Kα-radiation. For each mineral the intensity of the reflections will be a usable, semi-quantitative expression of its concentration and thus of its variation throughout the investigated sequence.

Modus of the bulk sample was determined directly for the dried and pulverized sediment. Quartz, feldspar and calcite are the dominating minerals; amphibole is sometimes present. Most of the samples contain pyrite. In one sample a small content of marcasite was found. About half of the investigated samples were found to contain a mixed carbonate mineral ((Mn, Ca, Mg, Fe) CO_3, see later).

Modus of the clay fraction was determined for the fraction $< 2\ \mu m$ from a selected series of samples. To obtain a precise identification and a reliable quantitative measure, orientated preparations and treatment with ethylene-glycol and hydrochloric acid were used.

Norm calculations. The modus, determined by X-ray diffractometry, and the chemical composition of the acid-soluble fraction were used as the basis for a calculation of the mineralogical composition (norm) of the investigated sediments.

As earlier mentioned the treatment with aqua regia will leave part of the sample undissolved, and therefore the chemical composition of this insoluble residue is not known. In the present case the insoluble residue are more or less dissolved by the aqua regia treatment (Villumsen & Nielsen 1976). The acid soluble fraction of the material is dominated by Fe, Al, S, and Ca, while the content of Mg, K, Na, P_2O_5, Cr, Cu, Pb, Zn, V, Li, and Rb is relatively small.

Norm of the bulk sample

FeS_2. As the modus showed pyrite content in almost all samples, the FeS_2 norm was first calculated. The values are shown in table 2 where the excess either of Fe (indicated as Fe_2O_3) or of S is also shown. The same table gives the contents of elementary S and SO_4-S. The correlation between the FeS_2

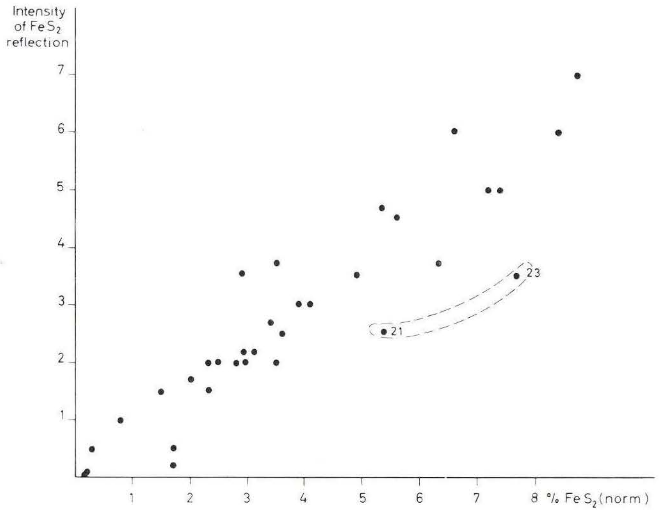


Fig. 4. Correlation between X-ray intensity of FeS_2 (at d = 2.709 Å) and FeS_2-norm. For samples Nos. 21 and 23 (framed) the FeS_2-norm is too high because these samples contain considerable amounts of elementary S.

norm and the intensity of the pyrite reflection (measured at d = 2.709 Å) is fairly good (fig. 4) with a few exceptions: Samples Nos. 21 and 23 (framed in fig. 4) have a very high FeS_2 norm which must be too high, as the remaining content of S (after the norm calculation) is lower than the content of elementary sulphur found in these two samples. The correspondence between the pyrite X-ray intensity and the FeS_2 norm shows that the sulphur content occurs mainly as FeS_2, and that possible FeS_x is quantitatively of minor importance. It may also indicate that the content of organic combined sulphur is not essential for the amount of total sulphur in the sediment, as the content of organic matter shows a wide range of variation (cf. table 3) in the investigated samples. Presumably the FeS_2 norm is, in most cases, a little too high because the samples are believed to contain a small amount of elementary sulphur and sulphate S (table 2). A systematic determination has not been performed, and correction of the FeS_2 norm is therefore not possible.

$CaCO_3$ norm was calculated similarly (table 4). As it appeared that parts of the investigated sequence had a surplus of carbonate (CO_2) relative to the amount of CaO, the sediment must contain other carbonates besides $CaCO_3$. The intensity of the $CaCO_3$ reflection (X-ray diffractometry) corresponds poorly with the $CaCO_3$ norm, and it is therefore possible that a

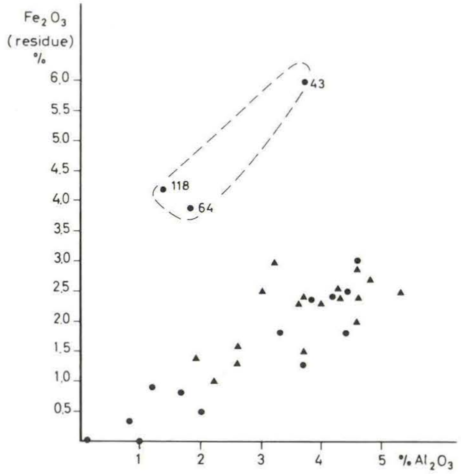


Fig. 5. Correlation between Al_2O_3 and Fe_2O_3-residue (= total Fe_2O_3 – Fe_2O_3 from FeS_2). Samples containing mixed carbonate are indicated by a solid triangle. – The figure shows that an increase in Al_2O_3 corresponds to an increase in Fe_2O_3-residue, but the correlation is rather poor. A better correlation is obtained if a variable amount of iron is incorporated in the mixed carbonates. Samples Nos. 43, 64, and 118 (framed) have abnormally high contents of Fe_2O_3-residue, probably because of epidiagenesis or weathering.

certain amount of carbonate (CO_2) should be related to other carbonates than $CaCO_3$. This implies that the $CaCO_3$ norm (table 4) may be to high.

Other carbonates. The CO_2 remaining after the $CaCO_3$ norm was calculated and, as mentioned above, possibly a certain amount of CO_2 already included in the $CaCO_3$ norm must belong to other carbonate minerals. It is most reasonable that this amount of CO_2 is combined with Fe, Mn, Mg, and Ca in a mixed carbonate; the justification of this is given below:

Fig. 5 shows that what is left of Fe_2O_3 (= total Fe_2O_3 minus Fe_2O_3 from the FeS_2 norm) shows a tendency to correlate with the content of Al_2O_3 except for 3 samples – Nos. 43, 64, and 118 (see fig. 5). These samples have abnormally high iron content, presumably because they have been subject to oxidizing and acid conditions after deposition. The correlation indicates that in normal cases a certain amount of iron is combined with the clay fraction, as Al_2O_3 can only be present in clay minerals (see page 29). As it seems reasonable that iron carbonate can exist in chemical equilibrium in the investigated samples, the amount of Fe_2O_3 equivalent to the carbonate CO_2 (= total carbonate CO_2 minus CO_2 in the $CaCO_3$ norm)

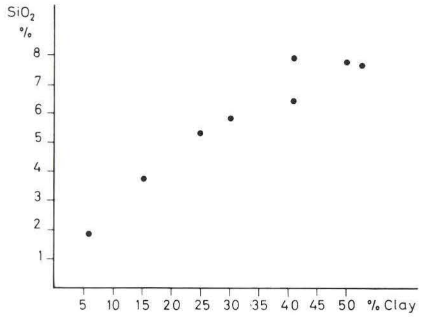


Fig. 6. Correspondance between clay content and SiO_2 from acid-soluble silicates (8 samples).

was subtracted from the Fe_2O_3 residue in order to obtain a better correlation between Al_2O_3 and iron than shown in fig. 5. The new calculated Fe_2O_3 values, however, correlate in many cases less well with Al_2O_3 than previously, and therefore it is hardly possible that the carbonate mineral is pure iron carbonate. The best correlation between Al_2O_3 and the iron residue is obtained if varying amounts of Fe_2O_3 is subtracted, and therefore it is assumed that a certain amount of iron is combined with the carbonate mineral. – In fig. 5 samples which contain a surplus of CO_2 after the $CaCO_3$ norm has been calculated are shown by triangles. Characteristic of these samples is a relatively high MnO content, and therefore it is assumed that the carbonate mineral also contains some Mn. As the MgO content of the same samples is slightly higher than the amount which correlates with Al_2O_3 (see fig. 8), it is suggested that the carbonate mineral is also Mg-bearing. From an anaerobic basin in the Baltic Sea Hartmann (1964, p. 13) de-

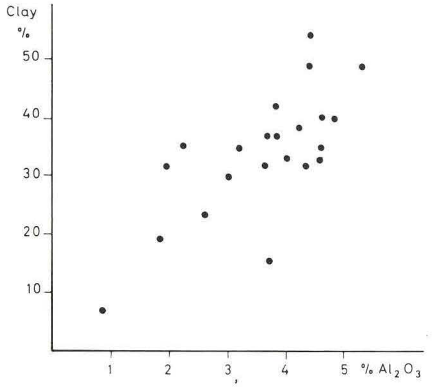


Fig. 7. Correlation between Al_2O_3 and clay content (23 samples).

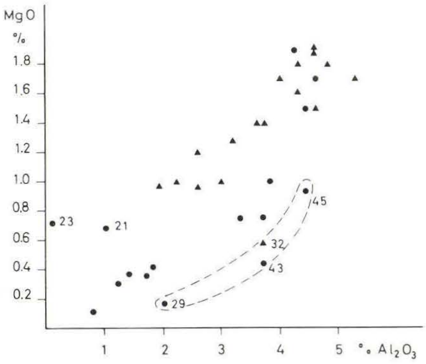


Fig. 8. Correlation between Al_2O_3 and MgO. Samples containing mixed carbonate are shown by solid triangles.

scribed a mixed carbonate mineral which may be analogous to the carbonate mineral found in the Randers fjord area. Hartmann published its chemical composition as $Mn_{56.8}$ $Ca_{25.46}$ $Mg_{9.72}$ $Fe_{8,02}$ CO_3, and by X-ray diffractometry he found its main reflection at d = 2.89 Å. In 17 of the investigated samples from the Randers fjord area this reflection was also found (table 4), and this is considered the final evidence of the existence of the mixed carbonate mineral. As the 2.89 Å reflection is observed not only in the samples which contain a surplus of CO_2 relative to the $CaCO_3$ norm, it seems likely that the $CaCO_3$ norm has been overestimated, and the mixed carbonate may therefore also contain Ca. The conclusion of this is that the carbonate content of the sediment consists of $CaCO_3$ and a mixed carbonate mineral to which Mn, Ca, Mg, and Fe is combined. The exact chemical composition of the mixed carbonate is not known.

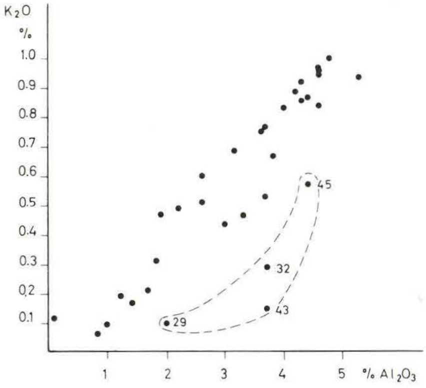


Fig. 9. Correlation between Al_2O_3 and K_2O.

Norm of the clay fraction. As mentioned earlier the clay minerals are not assumed to be totally dissolved by the aqua regia treatment. On the other hand an increasing amount of SiO_2 from acid soluble silicates corresponds to an increasing clay content (fig. 6), and in fig. 7 it is shown that an increase in clay content corresponds to an increase in Al_2O_3. Chemical analyses of the clay fraction have not been performed, and as the mineralogical composition of the sediment is relatively complex it is not satisfactory to carry out a regular norm calculation for the clay fraction. This applies especially to elements which are in the present case combined to several minerals, for example Fe, which is present in FeS_2, mixed carbonate, clay minerals and perhaps in phosphates. Instead of a norm calculation for the clay fraction its mineralogical composition is illustrated for each of the elements determined to discuss its relation to Al_2O_3, which presumably is present only in clay minerals. If an element has a positive correlation with the Al_2O_3 content, that element may be combined with a clay mineral, but other explanations are possible (for example fine-grained organic matter can be sedimented selectively with the clay).

Fe_2O_3. A certain amount of the acid soluble iron in the samples, here stated as Fe_2O_3, is combined with pyrite and with a mixed carbonate (see page 27). Fig. 5 shows that after subtraction of the Fe in the pyrite norm, the Fe_2O_3 residue increases with increasing Al_2O_3 content, both for samples which contain mixed carbonate and for samples where the presence of mixed carbonate is not demonstrated. This indicates a certain iron content of the clay fraction.

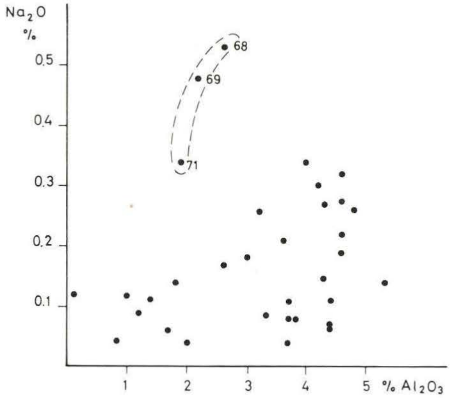


Fig. 10. Correlation between Al_2O_3 and Na_2O. Samples Nos. 68, 69, and 71 have high water contents, which may have increased the Na_2O contents of the samples.

CaO. The surplus of CaO (table 4) shows no relationship to the Al_2O_3 content. It is possible that some Ca is combined with P_2O_5 or with the organic fraction instead of clay minerals.

MgO. As mentioned on page 27 samples which contain mixed carbonate have the greatest MgO content. In fig. 8, which shows the relationship between MgO and Al_2O_3, samples which contain mixed carbonate are indicated by triangles. By subtracting a certain amount of MgO from these samples a fairly good correlation between MgO and Al_2O_3 for almost all samples can be obtained, and thus it is reasonable that the clay fraction contains Mg. In accordance with this the modal analysis showed that clay minerals rich in Mg (montmorillonite and chlorite) are often strongly represented in the clay fraction. Samples Nos. 29, 32, 43, and 45 (framed in fig. 8) contain relatively less MgO than the other samples, which may be due to solution processes. No accordance between MgO and Al_2O_3 can be demonstrated for the peat samples (Nos. 21 and 23).

K_2O. Fig. 9 shows the dependence that K_2O shows on Al_2O_3. It is seen that samples with the lowest MgO contents (fig. 8) have abnormally low contents of K_2O. Otherwise the correlation is so good that it may reasonably be concluded that K_2O is combined with the clay minerals.

Na_2O. In fig. 10 the content of Na_2O is plotted against Al_2O_3. The marked samples (Nos. 68, 69, and 71) are taken from the upper part of boring No. 80*, where the content of organic matter, and hence the water content, is relatively great. It is possible that a saline pore solution has increased the Na_2O content. No correlation with Al_2O_3 can be demonstrated, even if these three samples are excluded, and the Na_2O content thus does not seem to originate from the clay fraction.

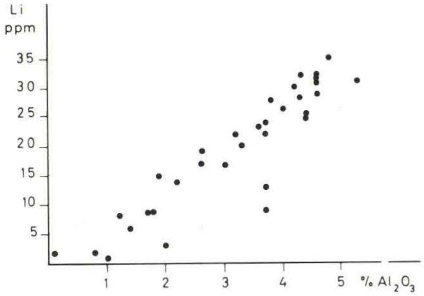


Fig. 11. The positive correlation between Al_2O_3 and Li indicates that Li is combined to the clay fraction.

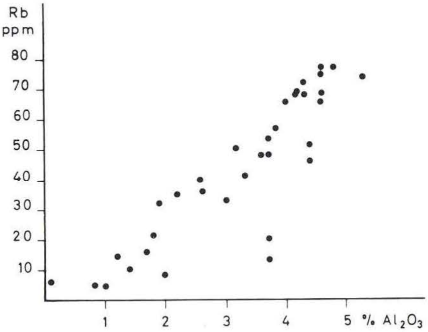


Fig. 12. Correlation between Al_2O_3 and Rb.

MnO. No correlation with Al_2O_3 can be seen, presumably because an important part of the MnO content is combined with the mixed carbonate mineral as mentioned on page 27.

Li and Rb. Bulk sample analysis of Li and Rb shows a fairly good correlation with the Al_2O_3 content (figs. 11 and 12.) A more detailed investigation of Li and Rb (and B) (Villumsen & Nielsen 1976) has demonstrated that paleosalinity does not control the Li and Rb contents.

Cr, Pb, Zn, Cu, and V. Figs. 13–17 show the relation between Al_2O_3 and these elements. A common feature is a tendency to increase with greater Al_2O_3 content, but in most cases a wide scattering of the observations is apparent. The mutual relationships between Cr, Pb, Zn, Cu, and V have

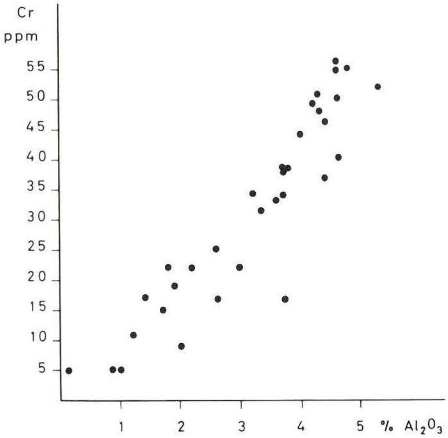


Fig. 13. Correlation between Al_2O_3 and Cr.

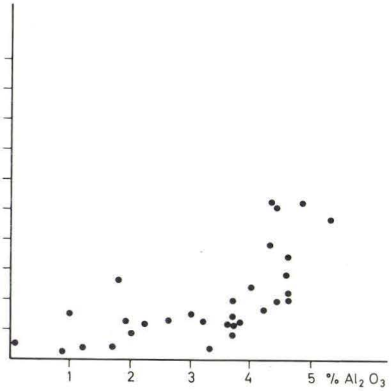


Fig. 14. Correlation between Al_2O_3 and Pb.

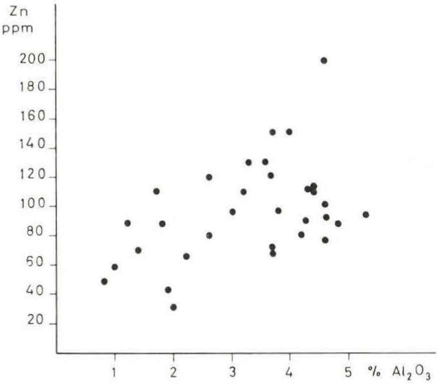


Fig. 15. Correlation between Al_2O_3 and Zn.

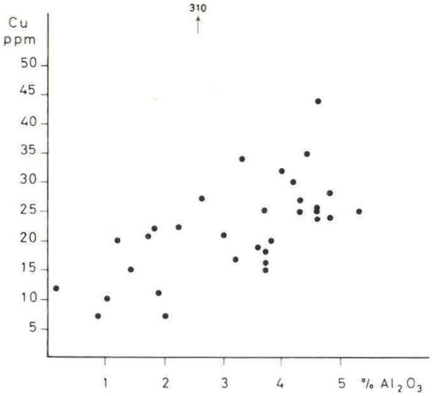


Fig. 16. Correlation between Al_2O_3 and Cu.

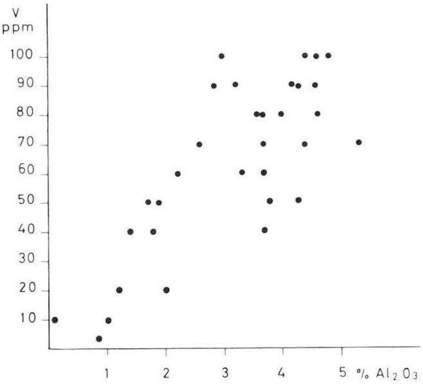


Fig. 17. Correlation between Al_2O_3 and V.

been tested, and there is a positive correlation between Cu and Zn. Concerning the other elements the correlation tendency is weaker, but a certain relation between Cr and Zn, V and Zn, and between Pb and Zn cannot be excluded. Furthermore, the Cu content seems to increase concurrently with the FeS_2 norm, but for the Zn content this tendency is extremly weak. As the contents of these elements are fairly low (see table 5), and as the sample material consisted of only 33 samples, it does not seem reasonable to discuss their interrelations in further detail.

Final comments on the composition of the clay fraction. By the use of a series of diagrams is was shown above that the Al_2O_3 content is related to some extent to Fe_2O_3, MgO, K_2O, Rb, Li, and Cr. These elements increase when the Al_2O_3 content increases, and therefore they belong essentially to the clay fraction. It cannot be finally decided whether these elements are combined with clay minerals or with another component which fluctuates parallel to the Al_2O_3 content. (A more detailed discussion of the chemistry and mineralogy of the clay fraction is given by Villumsen & Nielsen 1976).

Humic acids. The term humic acid has been used in the geological literature with a variety of meanings. Humic acid (HA) in this connection includes the part of the organic fraction which, after removel of fat, wax etc., can be extracted by 0.2 N NaOH and precipitated by HCl.

The process of formation of HA is not yet known in details. Lignin and cellulose are mainly believed to be the source material of HA, but sometimes other components (for example protein) may be involved (Francis 1961). According to Degens (1967) the chemical composition of HA depends on the composition of the source material, but others (for example Uspenskiy

& Radchenko 1955, according to Bordovskiy 1965) are of the opinion that the source material does not influence the composition of the HA formed. HA formation occurs as a result of microbiological processes under aerobic conditions (humification) for example in the upper, dry parts of peat bogs or on land (Teichmüller & Teichmüller 1967). Under anaerobic conditions the continuous microbiologic reactions will hardly alter the HA content, and therefore fossil layers of humufied peat are preserved in, for example, Danish raised bogs (Bahnson 1968).

Degens (1967) states that as lignin is presumably the main source of organic matter which is transformed to HA, the HA content in marine sediments must be of continental origin as lignin is not important in marine plants. In agreement with this Skopintsev (1950, according to Bordovskiy 1965) states that the humus content in marine sediments is an allochthonous component, which has a low nutrient value and characteristically has a high C/N ratio. Veber et al. (1956, according to Bordovskiy 1965) found that the HA content in the anaerobic zone in the Black Sea amounts to 10–20 % of the organic fraction, and stated that anaerobic HA formations cannot be excluded. According to Nissenbaum et al. (1972) Otsuki & Hamya (1967) stated that HA may originate from planktonic organic matter. Based on C-isotope investigations Brown et al. (1972) considered that HA can only be of continental origin. Thus there is no general agreement about the origin of HA, but concerning the Randers fjord area it seems most reasonable that HA is an allochthonous component as many other observations (for example the great amount of detrital material in the sediment, see page 75) make admission of considerable amounts of allochthonous material to the fjord area likely. Quantitative determinations of the HA content have not been performed.

Normally HA or other types of organic matter in solution or in colloidal form are belived to be very active in sedimentogenesis as well as in diagenesis. In order to illustrate this a short review is presented below:

Chemical weathering for example is described by Baker (1973), who states that HA can be very effective during mineral degradation and mobilization of metals in podsol profiles. Bader et al. (1960) and Bordovskiy (1965) refer to the interaction between clay and organic matter present either in solution, as a suspension or in colloidal form. They point out that during the transportation this type of organic matter can react with clay to form complex compounds which will later on be deposited. This is one of the reasons why fine grained sediments often have the highest content of organic matter. Khan & Schnitzer (1972) demonstrated that HA was able to prevent flocculation of other types of organic matter. According to Bader (1956), Turner (1932) and Gedroiz (1933) stated that organic matter may be 7–8 times more effective for ion exchange than clay minerals. Diagenetic transformations of organic material, which is initially controlled by microbiologic activity, can be restricted, partly because somewhat transformed lignin compounds (presumably mainly HA) may form the so-called lignoprotein complexes which are difficult to decompose and therefore prevent nitrogen uptake by the organisms (Bader 1956). Diagenetic reactions are thus retarded by a nutrient deficit.

Electron spin resonance (ESR) investigations of the humic acid content. ESR investigations have received increasing interest for the characterization of humic acids (HA) during recent years. The ESR method is described, and its validity is discussed by Pedersen and Villumsen (1974). By the ESR method it seems possible to classify HA from fossil sediments according to the pH of the environment of formation and to divide them into two classes (see fig. 18). Empirically a pH value of about 4.6 has been found to separate the two classes (class I: $pH < 4.6$, class II: $pH > 4.6$, Cheshire and Cranwell 1972). ESR spectra obtained from the HA from the Randers fjord area in all cases belonged to class II. As the HA content is believed to be an allochthonous component of the sediment this means that the pH level during the Late- and Post-glacial epoch has been above 4.6 in the area round the investigated sediment basin where HA formation has occurred.

Carbon isotope ratio. The ratio between the stable isotopes ^{13}C and ^{12}C is often used to distinguish between organic matter produced in a marine environment and that from terrestrial and limnic environments. Marine plants (except marine phytoplankton) and animals have a $^{13}C/^{12}C$ ratio slightly higher than limnic and terrestrial organisms, and this difference seems to be preserved during the diagenetic transformation processes ("einkohlung", oil formation etc.), to which the organic fraction is subject after deposition. The C isotope ratio for marine phytoplankton is roughly the same as for terrestrial plants (Wickmann 1952; Craig 1953; Schwarz 1969; Newmann et al. 1973). The isotope ratio also depends on the temperature in the formation environment. Thus Rogers and Koons (1969) found a decreasing $^{13}C/^{12}C$ ratio in sediments containing glacial fauna. This means that a temperature decrease can influence the isotope ratio for marine sediments in the same way as an increase in content of terrestrial or freshwater organic matter. When knowledge of temperature conditions is available, as in the present case (Iversen 1973), the $^{13}C/^{12}C$ ratio is one of the most suitable parameters for evaluation of the importance of non-marine supplies to a

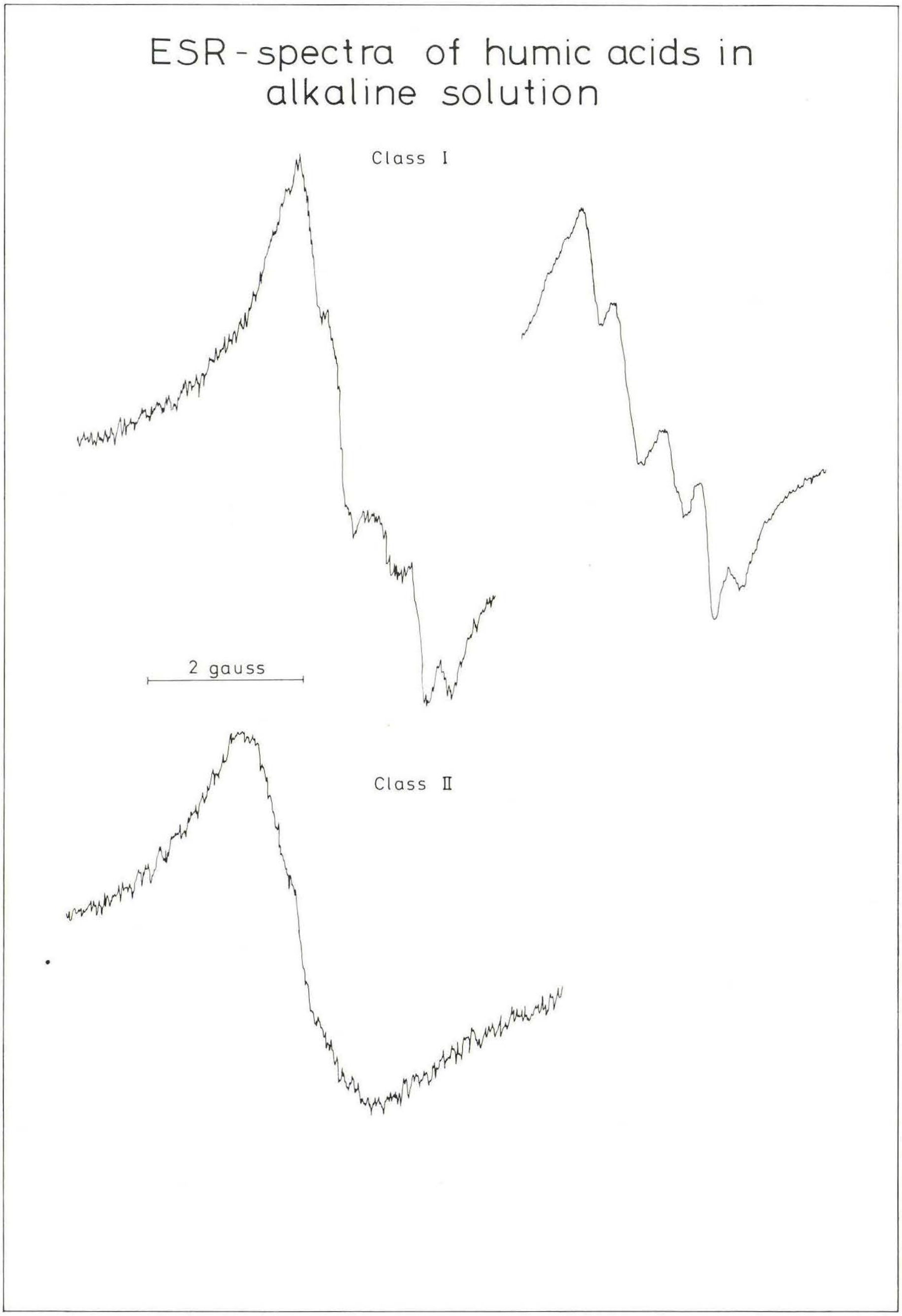


Fig. 18. ESR-spectra of acid-boiled humic acids (ABHA). Humic acids formed in acid environments will give class I ESR-spectra, while class II spectra are obtained from ABHA formed in more alkaline environments. The figure shows two class I spectra from raised bog peats and an example of a class II spectrum found in all ABHA from the Randers fjord area.

marine sediment basin. The carbon isotope ratio was determined in a few representative samples from the Randers fjord area in the following was:

From a suitable amount of sample $CaCO_3$ was removed by treatment with dilute HCl. After this the sample was combusted at about 900°C in pure oxygen. The evolved combustion products were purified using a series of absorption phases for amongst others NH_3, SO_2, and halogens. The remaining pure CO_2 was absorbed in a NH_4OH solution, and precipitated as $CaCO_3$ by $CaCl_2$. $CaCO_3$ was then dissolved by dilute phosphorous acid treatment, and the ratio $^{13}C/^{12}C$ determined on the expelled CO_2 using a mass spectrometer. The results (see table 3) are indicated as $\delta^{13}C$ ‰, i.e. in a form immediately comparable to the international standards.

$$(\delta^{13}C\ ‰ = \frac{(^{13}C/^{12}C)\text{sample} - (^{13}C/^{12}C)\text{standard}}{(^{13}C/^{12}C)\text{standard}} \times 1000)$$

Composition of the sequence

Depth mapping of the investigated area included the upper 10–15 metres of sediment. For technical reasons thicker sand deposits (i.e. above ½–1 m) were not drilled. The area is dominated by Post-glacial marine sediments, which rest upon a sand deposit of presumed Late-glacial age. One of the type borings (No. 32*) included a few metres of the Late-glacial sediment, and it appeared that at this locality the sequence includes Late-glacial freshwater gyttja. Below this lake sediment, whose upper part has been dated by pollen analysis to Younger Dryas, stratified outwash sand and gravel were found. Fig. 19 shows a generalized standard profile, composed of observations from the entire Randers fjord area. In stratigraphical order the sequence includes:

Post-glacial freshwater peat
Post-glacial brackishwater gyttja
Post-glacial marine clay and silt (*Littorina* deposits)
Early Post-glacial fresh- and brackishwater peat
Late-glacial sand
Late-glacial freshwater gyttja
Late-glacial sand.

In the following pages each unit of the profile is described, based mainly on the observations from the three type localities.

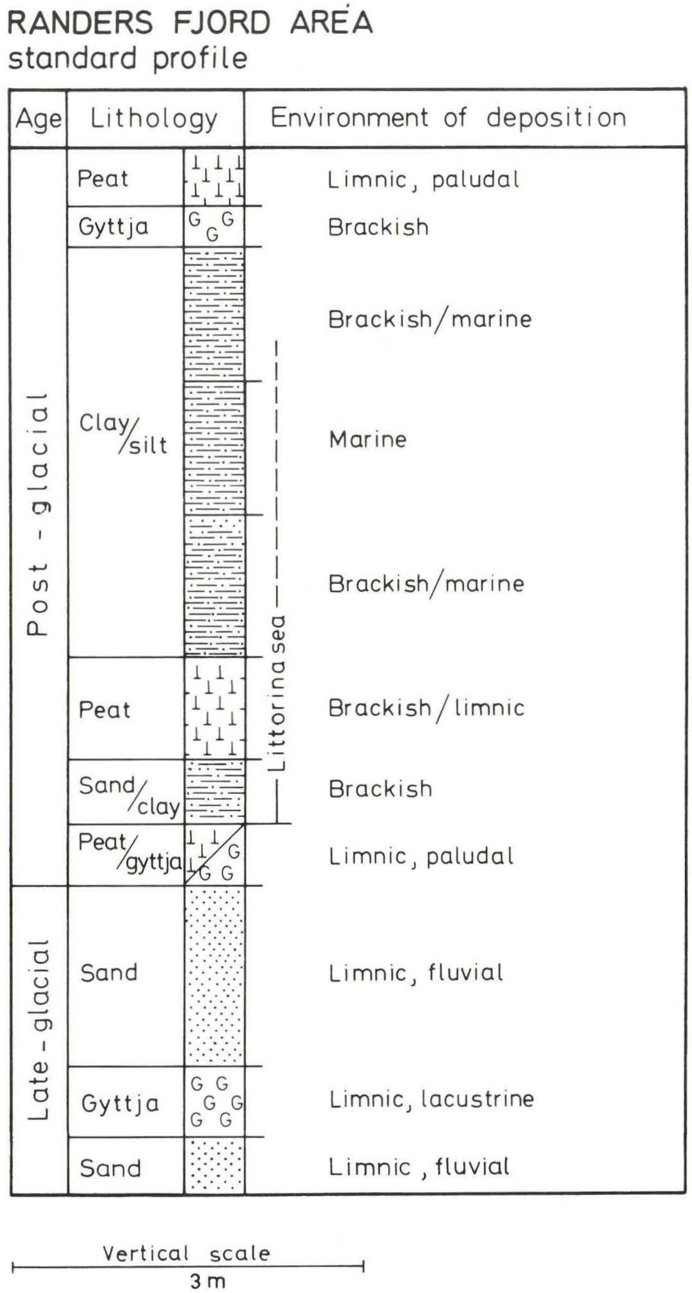


Fig. 19. Generalized lithologic profile for the investigated section.

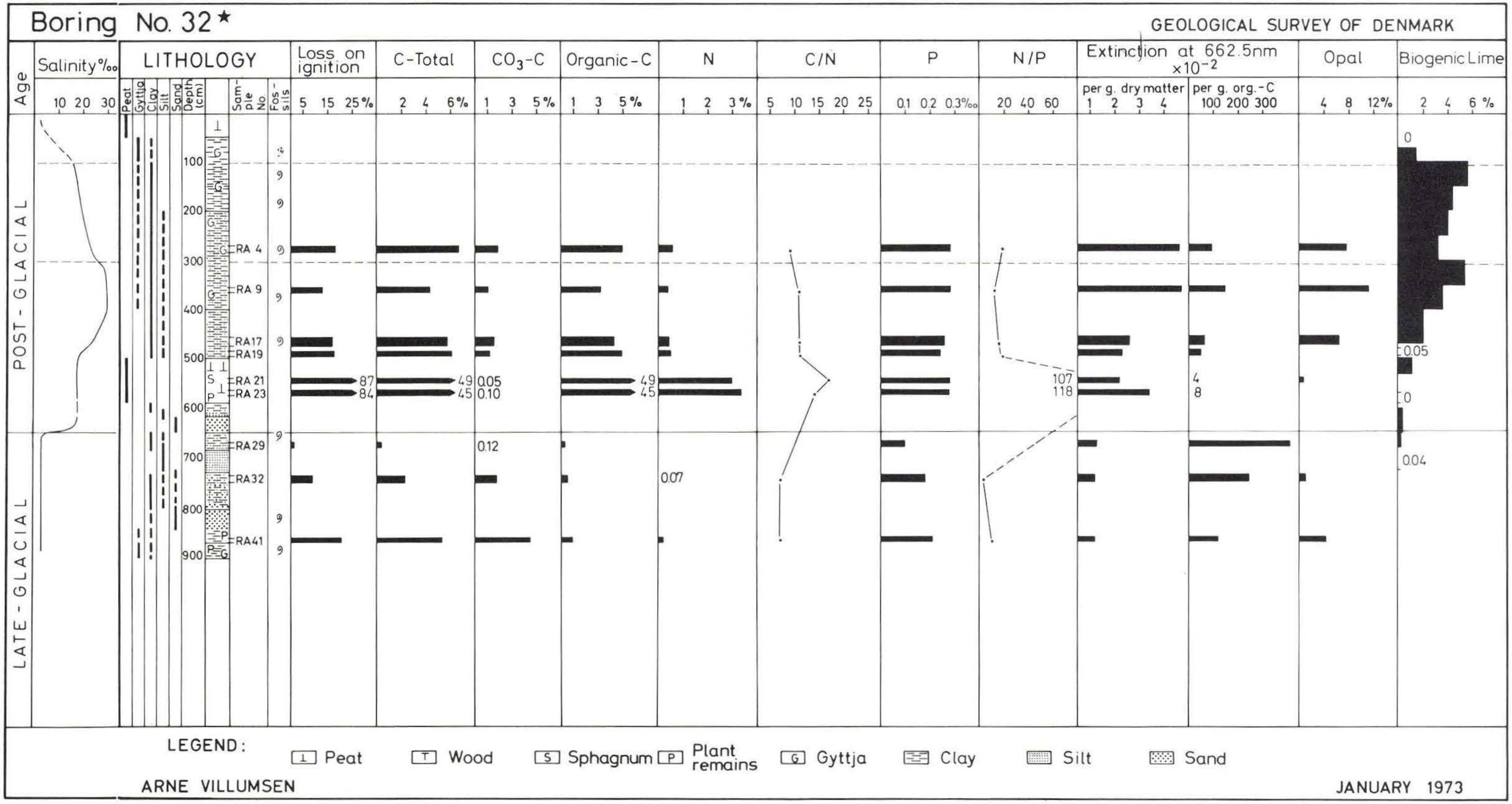


Fig. 20. Type locality boring 32*. Lithology and composition of the organic fraction.

1. Late-glacial sediments

Younger Dryas gyttja. At type locality No. 32* (for location see fig. 1) a blackish grey clay gyttja with light grey burrows was found. This lake deposit rests on outwash sand and gravel and is also overlain by outwash material. Pollenanalytically the upper part of the gyttja is assigned to Younger Dryas. It contains a freshwater fauna (including a.o. *Pisidium* sp. and *Bithynia* sp.) which seems to indicate that sedimentation occurred in a shallow lake (water depth less than 3 metres). The burrows were hardly recognizable on X-ray radiographs, and the gyttja thus seems to be a homogeneous mixture as regards mineralogy and grain size. Figs. 20, 21, and 22 shows that the gyttja (sample No. 41) is rich in organic matter, lime and diatoms (opal). So the environment of deposition seems to have been strongly influenced by biological activity, which is also indicated by the C/N ratio (= 7) (Hansen 1964 b). The gyttja has a low content of minerogenic material (low insoluble residue), and therefore the transport of clastic material to the lake where the gyttja was formed has presumably been relatively minor. The gyttja contains about 30 % clay, of which some 40 % is montmorillonite, 40 % illite, and 20 % kaolinite + chlorite (Villumsen and Nielsen 1976). The content of total S is about 1 %, and the FeS_2 also amounts to 1 %. It is possible that the observed colour variations for the burrows in the gyttja are controlled by the iron content, partly because a considerable amount of iron remains after the FeS_2 norm has been calculated (fig. 21 and table 2). If this is correct, the redox potential in the light grey burrows was higher than in the blackish grey gyttja at the time of formation.

Lithological and paleontological change at the Late-/Post-glacial transition. The gyttja described above differs greatly from the stratified sediment which overlays the Younger Dryas gyttja in boring No. 32*. Figs. 20 and 21 show some of its most important characteristics: Low content of organic matter and high amount of insoluble minerogenic material. At a depth of about 6 metres (below surface) a distinct lithological change mainly from sand to clay is observed. Investigations of the molluscs and diatoms (A.-L. Andersen and J. Christensen, personal comm. 1973) showed that freshwater conditions had prevailed during the deposition of the sediments found below 6.60 metres, and that the sand layer immediately above this (see fig. 20) contains molluscs and diatoms which indicate a salinity of 15-20 ‰. The fauna resembles a Post-glacial *Littorina* fauna, and the resemblance is so exact that the possibility that this marine sediment is Late-glacial can

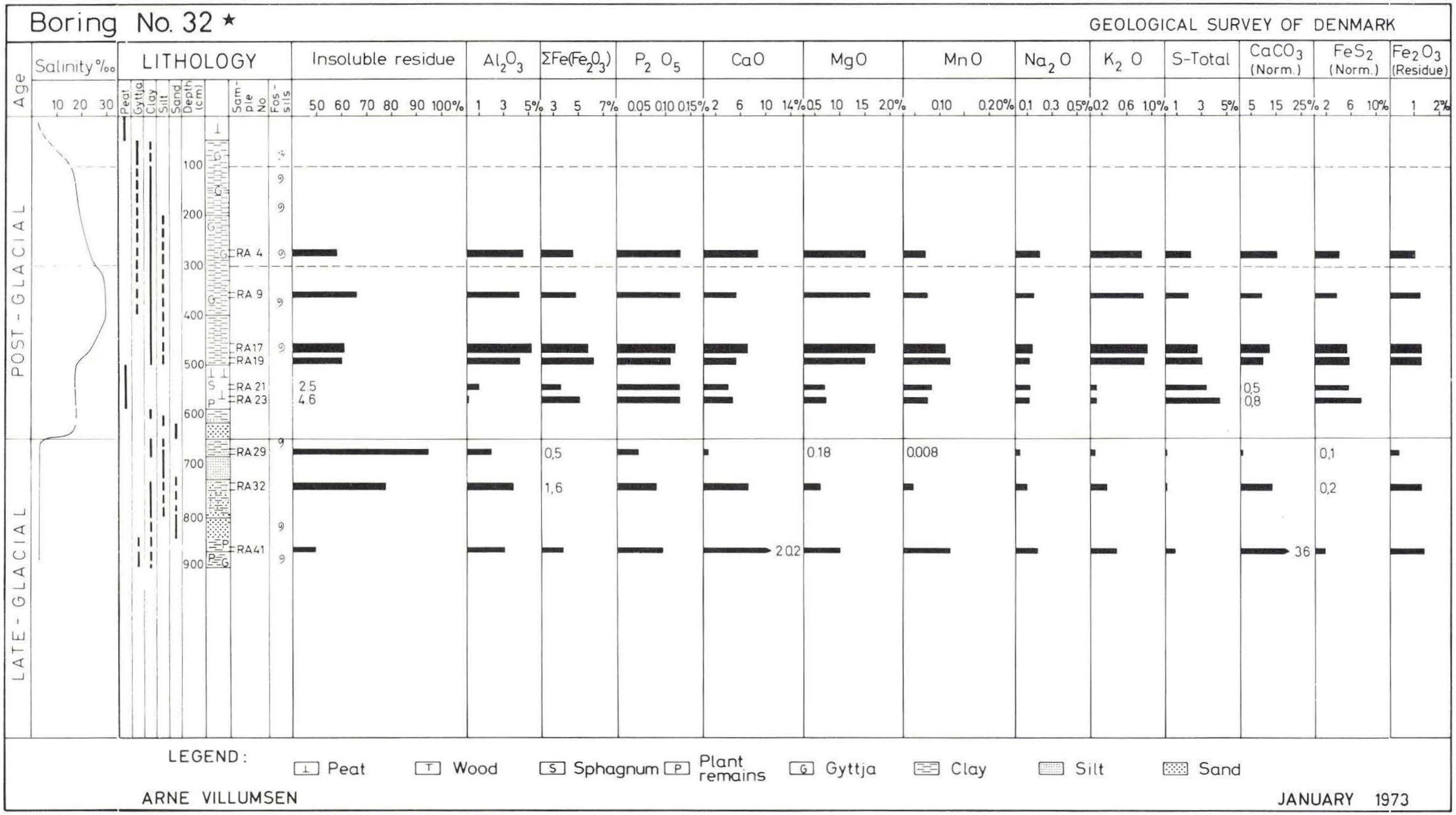


Fig. 21. Type locality boring 32*. Lithology and chemical composition.

Fig. 22. Type locality boring 32*. Lithology and content of trace elements.

be excluded. Results of a pollenanalytical examination of the lower part of this marine deposit may indicate that the transgression is younger than Boreal, but exact dating was not possible partly because of the considerable content of rebedded pollen. As earlier mentioned the freshwater sediments below the *Littorina* transgression layer are characterized by large amounts of minerogenic material, and as this increases upwards through the section it is assumed that the whole series of freshwater sediments below the marine deposit is of Late-glacial age. Thus the transition between the Late- and the Post-glacial sediments is fixed at a depth of 6.60 m below surface (4.18 m below sea level) as for boring No. 32*. The transgression layer seems, as stated above, to be younger than Boreal, and as the first *Littorina* transgression hitherto reported from this area is the Middle Atlantic transgression (Troels-Smith 1942), sediments representing Preboreal, Boreal, and possibly Early Atlantic seem to be absent at this locality. From this it appears that age determinations in boring No. 32* are based on paleontological and lithological observations and supported by a few pollen examinations. In the remaining part of the investigated area the stratigraphic division of the sediment is exclusively based on lithology, and paleontology, such that sediments with large contents of minerogenic material are referred to Late-glacial time, while sediments containing organic matter or a marine fauna are considered to be Post-glacial. Of course datings like these cannot be very precise, and do not allow a general discussion of discontinuities in sedimentation etc. at the transition between the Late- and Post-glacial.

Late-glacial sand. In most of the borings which were carried out during the depth mapping a sand deposit was found below the marine sediments which could not be drilled for technical reasons. Accordingly, this sand deposit covers the sedimentation basin which was filled with sediments during the Post-glacial. As it seems to correspond in age with the Late-glacial sand which limits the investigated area in the valleys, the sand in the present context is considered to be Late-glacial although its age is stated with a high degree of uncertainty.

Plate 1 shows the topography of the Late-glacial sand surface compiled from the depth mapping data. In the area round borings Nos. 25, 69, 78, and 79, north of Ugelhuse, the age of the sand is especially questionable: The sand bank which stretches from the north a small distance southwest into Randers fjord interrupts the morphological system formed by the elongate east-west depressions in Randers fjord and Grund fjord. As the upper part of the sand bank contains marine molluscs, it seems reasonable to assume that this sand bank was formed in the Post-glacial *Littorina* sea. This assumption is supported by other observations (see the discussion of Early Post-glacial sediments, p. 51).

The bottom topography in Randers fjord, Grund fjord and Virring bay, which is dominated by the elongate east-west depressions, supports the theory of subglacial erosion as an important factor in the formation of the valley system, as mentioned by A. Jessen (1918). According to him irregularities in the valley bottom were filled by Late-glacial outwash sediments after the ice had left the area. As the surface of Late-glacial sand is obviously still characterized by an irregular relief, it can be assumed that during the melting period the deep depressions were filled with dead ice. It will later be demonstrated (p. 58) that dead ice was also present in the Post-glacial time. Unlike these valleys, that of Rosenholmå was presumably not formed by subglacial erosion; instead it is assumed to have been eroded by the outward flow from the Late-glacial Rosenholm depression (Villumsen 1973). The Late-glacial outwash sand which demarcates the area of investigation in the western part of Allingå valley is presumably only a minor remnant of a large sand deposit which might once have covered most of the Allingå valley, the older genetic relations of which are unknown.

The part of the Allingå valley which was filled with Post-glacial sediments was presumably eroded by a Late-glacial river running from west to east. According to Harder (1908) the Late-glacial sand below the *Littorina* sediments in the Allingå valley round the castle of Gl. Estrup were probably sedimented by the meltwater river, which flowed from southeast to northwest, passed Gl. Estrup, and had its outlet near the village of Bode (plate 1). Thus the sand bottom in the investigated area is not a well-defined chronostratigraphic unit, but instead forms a lithological main type which must roughly be of Late-glacial age in the whole area.

2. *Post-glacial sediments*

Early Post-glacial deposits. It was mentioned in the introduction that there have been earlier reports on shallow-water deposits from different localities in the valley which border the Randers fjord area. These sediments are normally referred to "fastlandstiden" (the Continental Period), i.e. the section of the Post-glacial during which most of Denmark was situated above sea level. This period closes with the transgression of the *Littorina* sea. During the depth mapping peat and gyttja were found below the *Littorina* sediments at several localities. The chronostratigraphical use of the term "fastlands"-sediment (Continental sediment) has earlier been discussed, and in the following context the term "Early Post-glacial" is used instead. Fig. 23 shows the localities and the level at which Early Post-glacial peat has

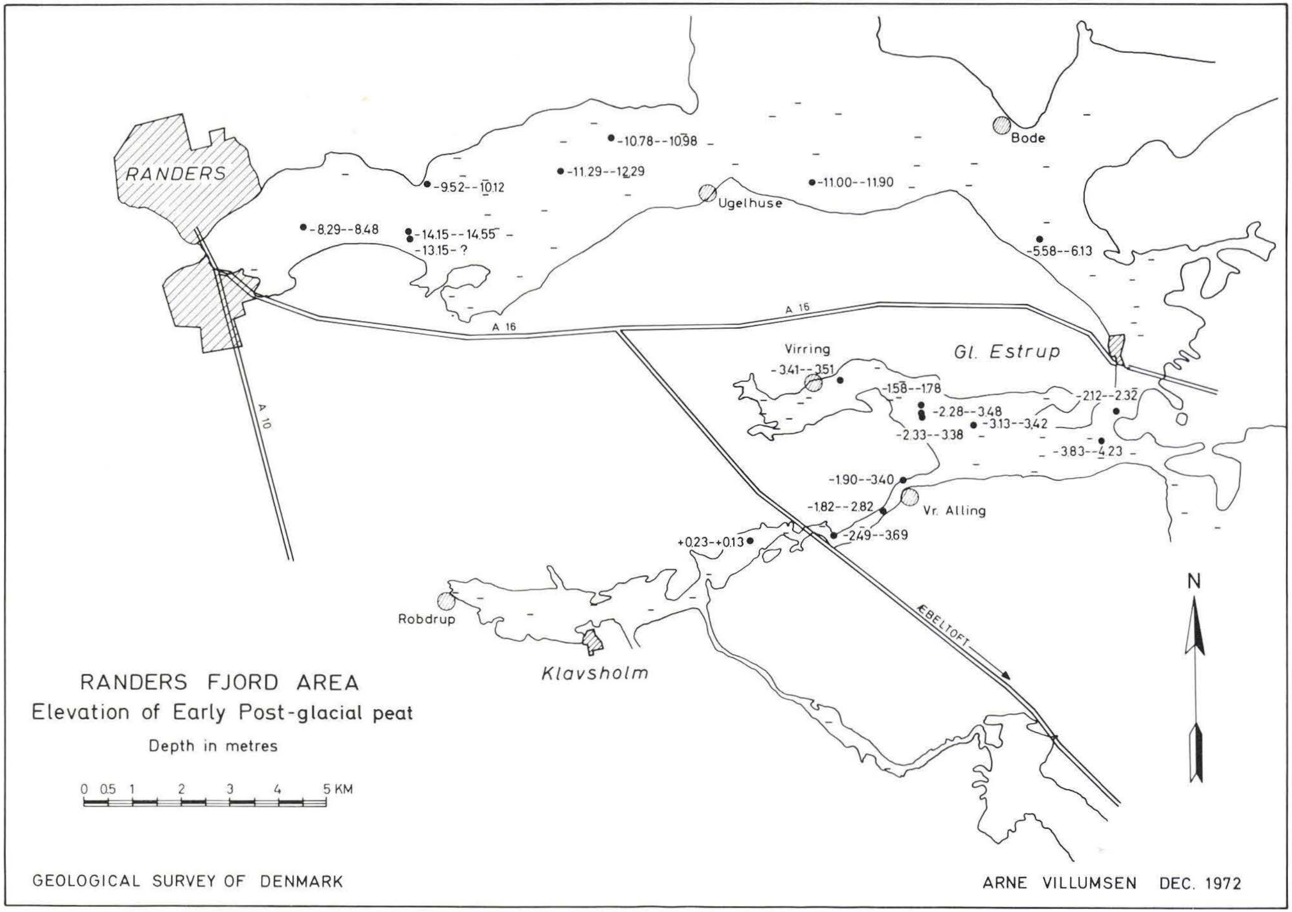

RANDERS FJORD AREA
Elevation of Early Post-glacial peat
Depth in metres
0 0.5 1 2 3 4 5 KM
RANDERS
-8.29--8.48
-9.52--10.12
-14.15--14.55
-13.15-?
-11.29--12.29
-10.78--10.98
Ugelhuse
-11.00--11.90
Bode
-5.58--6.13
A 16
A 10
Virring
-3.41--3.51
Gl. Estrup
-1.58--1.78
-2.28--3.48
-2.33--3.38
-3.13--3.42
-2.12--2.32
-3.83--4.23
-1.90--3.40
Vr. Alling
-1.82--2.82
-2.49--3.69
+0.23-+0.13
Robdrup
Klavsholm
ÆBELTOFT
N
GEOLOGICAL SURVEY OF DENMARK
ARNE VILLUMSEN DEC. 1972

Fig. 23.

Boring No. 53

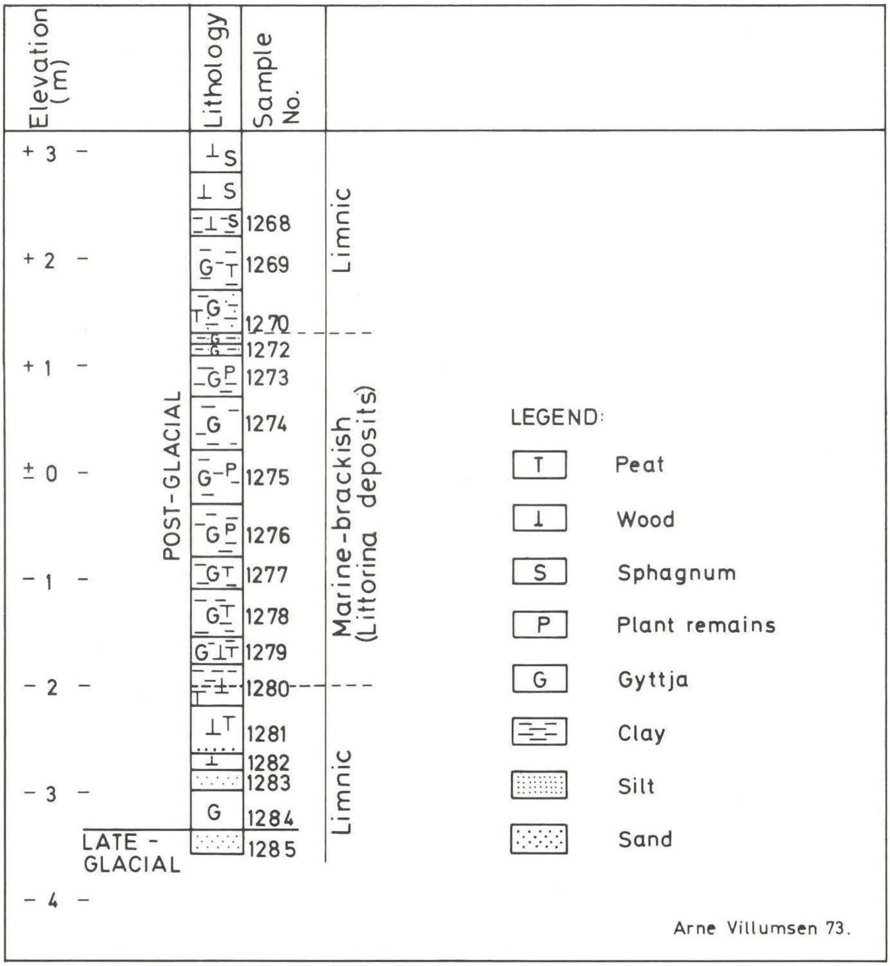


Fig. 24. Lithology of Late- and Post-glacial sediments found by boring No. 53.

been found within the investigated area. In boring No. 53, carried out in the Allingå valley about ½ km SW of Vester Alling sediments from the oldest *Littorina* transgression are found about 5 m below surface, i.e. at a level of –2 metres (see fig. 24).Immediately below the marine sediments peat without calcareous molluscs is present (samples Nos. 1280 & 1281), and below the peat freshwater sediments occur. For lithological reasons the transition from sand (sample No. 1285) to gyttja (sample No. 1284) is believed to correspond to the Late-/Post-glacial boundary. Characteristic

Fig. 25. X-ray radiograph (× 1) of core material from type locality boring 32*. Depth 5.48–5.63 m below surface. The figure shows the autochthonous peat with distinct traces of roots.

Fig. 26. X-ray radiograph (× 1) of core material from type locality boring 80*. Depth 11.03–11.19 m below surface. The photo shows the allochthonous, layered peat deposit.

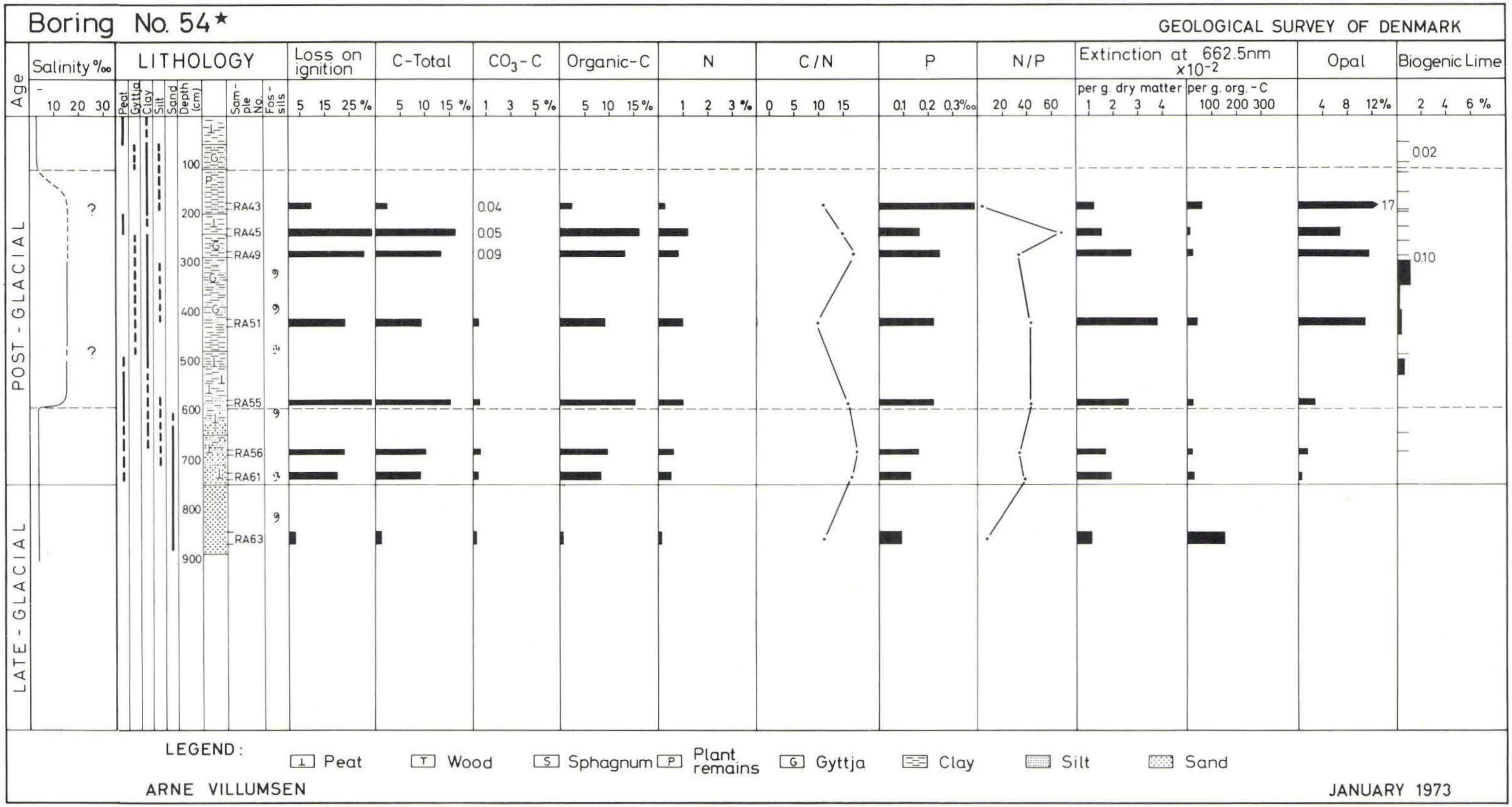


Fig. 27. Type locality boring 54*. Lithology and composition of the organic fraction.

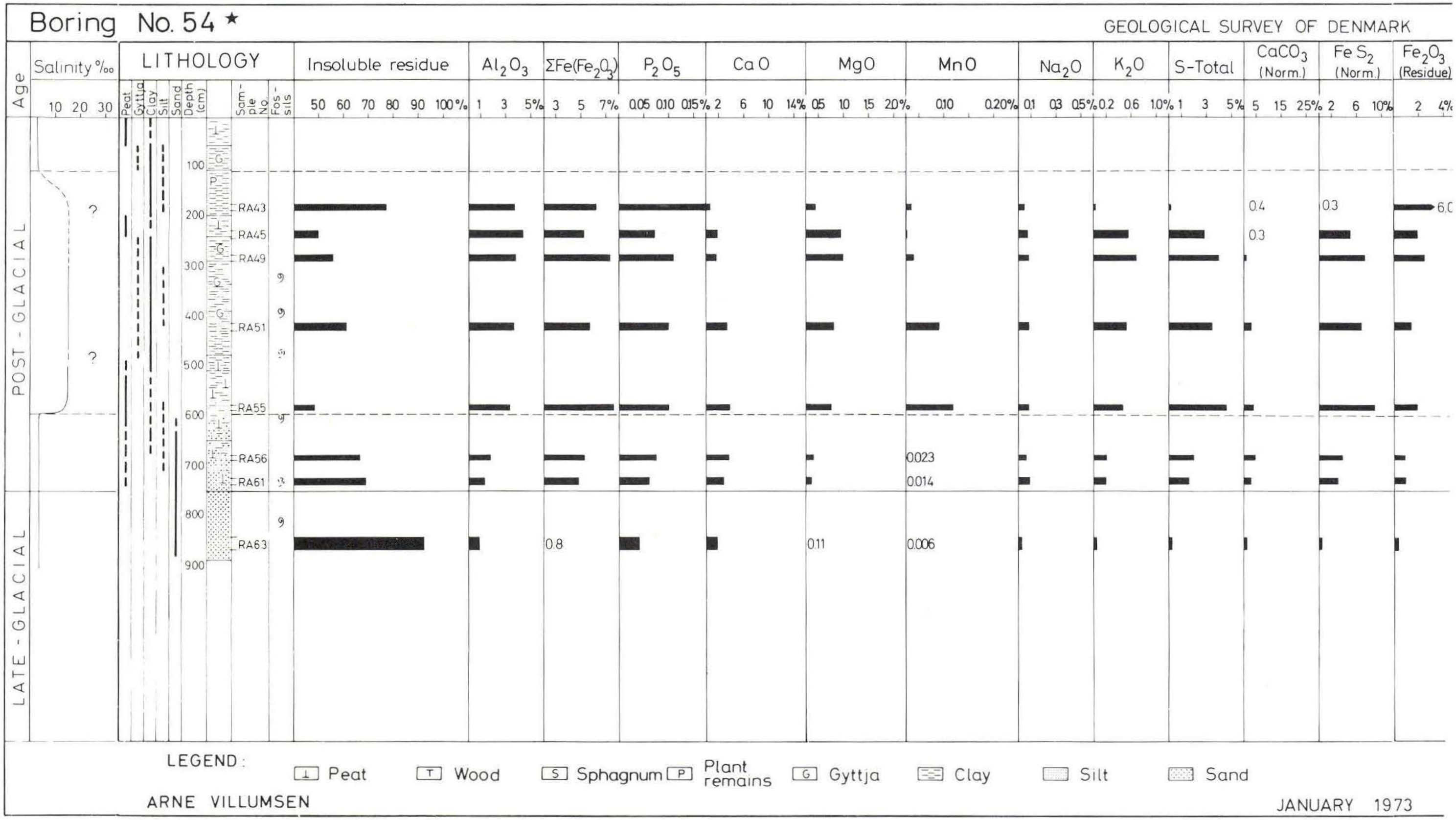


Fig. 28. Type locality boring 54*. Lithology and chemical composition.

of this boring and also of boring No. 13 which was drilled at Vester Alling, is the presence of Post-glacial freshwater sediments below the *Littorina* deposits. Normally Post-glacial freshwater sediments have not been found below the Early Post-glacial peat in the other borings. The general impression is that the peat, as well as the underlying sand sediment normally contains a brackish fauna. As a presumably representative example for Randers fjord and Grund fjord some observations from boring No. 80* can be mentioned. The paleosalinity of the sand deposit below the Early Post-glacial peat (fig. 30) is about 10 ‰, while the peat itself contains a fauna indicating more freshwater conditions (salinity about 4 ‰).

The various laboratory investigations showed that the peat within the area had a rather varying composition:

The Early Post-glacial peat found in boring No. 32* has a high content of organic matter (org. C about 50 %), while minerogenic material is subordinate (2–5 %). Wood is very scarce in the peat. On the X-ray radiograph (fig. 25) which shows a sequence of this peat, well-developed root traces have been observed. Thus this peat seems mainly to be of autochthonous origin, and a preliminary paleobotanical investigation of the peat shows that it can be classed as eutrophic freshwater peat with *Dryopteris*. Pollen of *Pinus* are present (S. Th. Andersen, personal comm.). The peat contains about 3 % of nitrogen and has a high S-content (about 4 % S-total). A considerable amount of elementary sulphur (2.2 %) was found in it, and this is believed to have been formed by photoautotrophic sulphur bacteria as a high quantity of their pigments was found in the peat (see page 18). These bacteria required an anaerobic environment and shallow water. The peat contains diatoms indicating brackish conditions (salinity 17–20 ‰). This information indicate that the peat was formed in a freshwater bog area, which was temporarily covered by sea water.

Quite another type of Early Post-glacial peat was found in boring Nos. 80* and 54*: In the field the peat from boring No. 80* (fig. 30) was characterized as clayey and sandy. In accordance with this the loss on ignition is only about a third as much as for the peat in boring No. 32*. Fig. 26 (X-ray radiograph) shows a section of this deposit where there are abundant layers of wood. Although wood and bark remains seem to constitute an important part of the peat (S. Th. Andersen, pers.comm.), its C/N ratio is only 14. The peat thus seems to be a mainly allochthonous formation like that found in boring No. 54* (fig. 27). Structurally the lower parts of this peat especially resembles the deposit found in boring No. 80*, and many other points of similarity between the peat from the two localities are demonstrated in figs. 27–32. The low C/N values of the peat in both borings might indicate a low degree of decomposition, but there might be other reasonable explanations for this, such as a differing composition of the organic source material.

As stated above, there are sedimentogenetic differences between the Early Post-glacial peat found at the three type localities:

In boring No. 32* autochthonous peat almost without minerogenic material occurs. In borings Nos. 54* and 80*, on the other hand, an allochthonous deposit was found, composed mainly of wood mixed with sand and clay. Salinity conditions of the allochthonous peat support the assumption that the peat is older than the *Littorina* deposits, but it has been rebedded during the first marine transgression, which according to Troels-Smith (1942) reached the area during the Atlantic. In the Allingå valley at Vester Alling (boring No. 54*) the *Littorina* sea has not reworked the Early Post-glacial peat material.

Early Post-glacial peat as indicator of the groundwater level. The Early Post-glacial peat deposits, in spite of the above mentioned differences, can generally be taken as shallow water sediments. Thus the peat is an important indicator of the sedimentary environment during the Early Post-glacial Continental Period. The courses of the rivers Gudenå and Allingå in the Early Post-glacial time are not known in detail, but they must have flowed along Randers fjord and the Allingå valley respectively on their way to a probably common outlet to the sea, presumably several kilometres north of the investigated area as no other connections to the sea were possible (see plate 1). The distribution of the Early Postglacial peat (fig. 23) gives a possibility of obtaining a more detailed impression of the river courses in the valley systems, and at the same time provides a good basis for discussion of the age relations for the so-called Late-glacial sand surface. If the morphology of the sand substratum during the Early Post-glacial period appeared as today (plate 1), the river Gudenå should pass a system of local depressions on its way downstream. Depressions below the level of the highest sand barrier then would be filled up with water, and therefore lake sediments should be present in the deepest depressions today. This, however, is not the case, and therefore it must be assumed that either the sand barriers were not present or the deep depressions were not formed in Early Post-glacial time. The last possibility again involves dead ice as a genetic element. Both theories generally seem reasonable, but in some cases, for example in the area north of Ugelhuse, the sand barrier was present in Early Post-glacial time. Thus Randers fjord and Grund fjord seem to have been free of larger lakes. In this area most of the peat occurs at levels between –8.5 and –11.5 m. This means that the groundwater table or at least the surface of the river Gudenå in the Early Post-glacial time was situated at about the

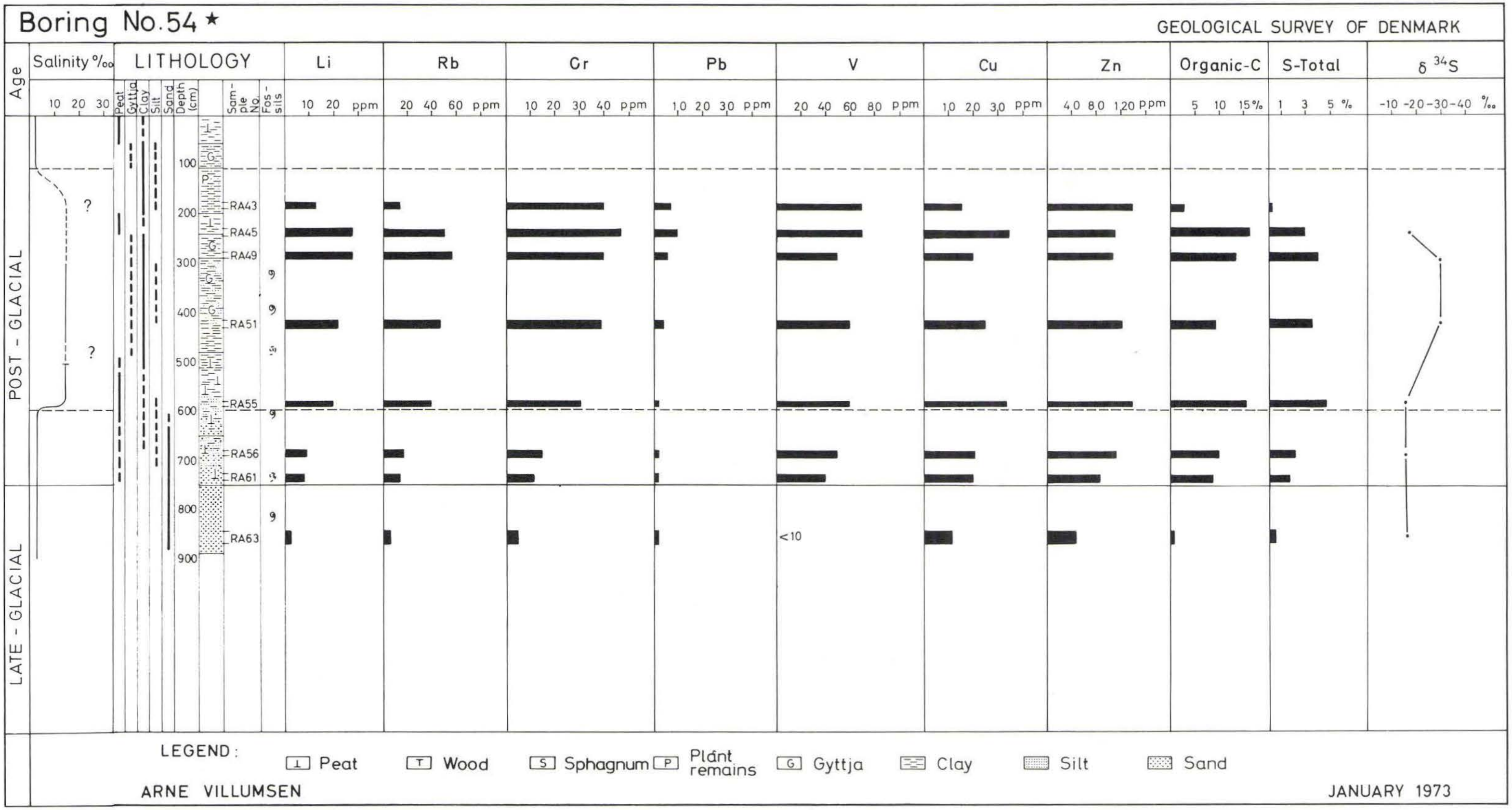


Fig. 29. Type locality boring 54*. Lithology and content of trace elements.

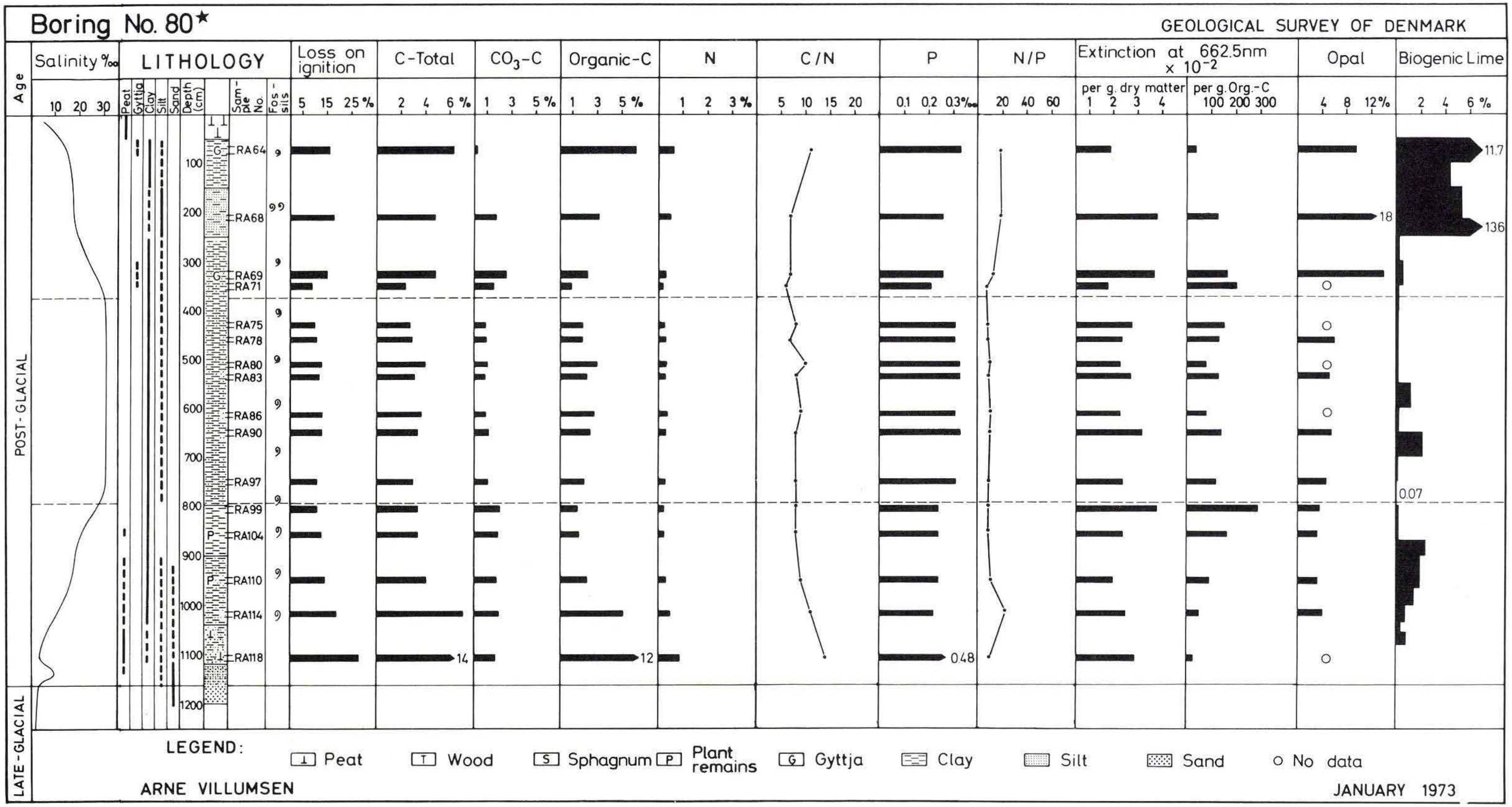


Fig. 30. Type locality boring 80*. Lithology and composition of the organic fraction.

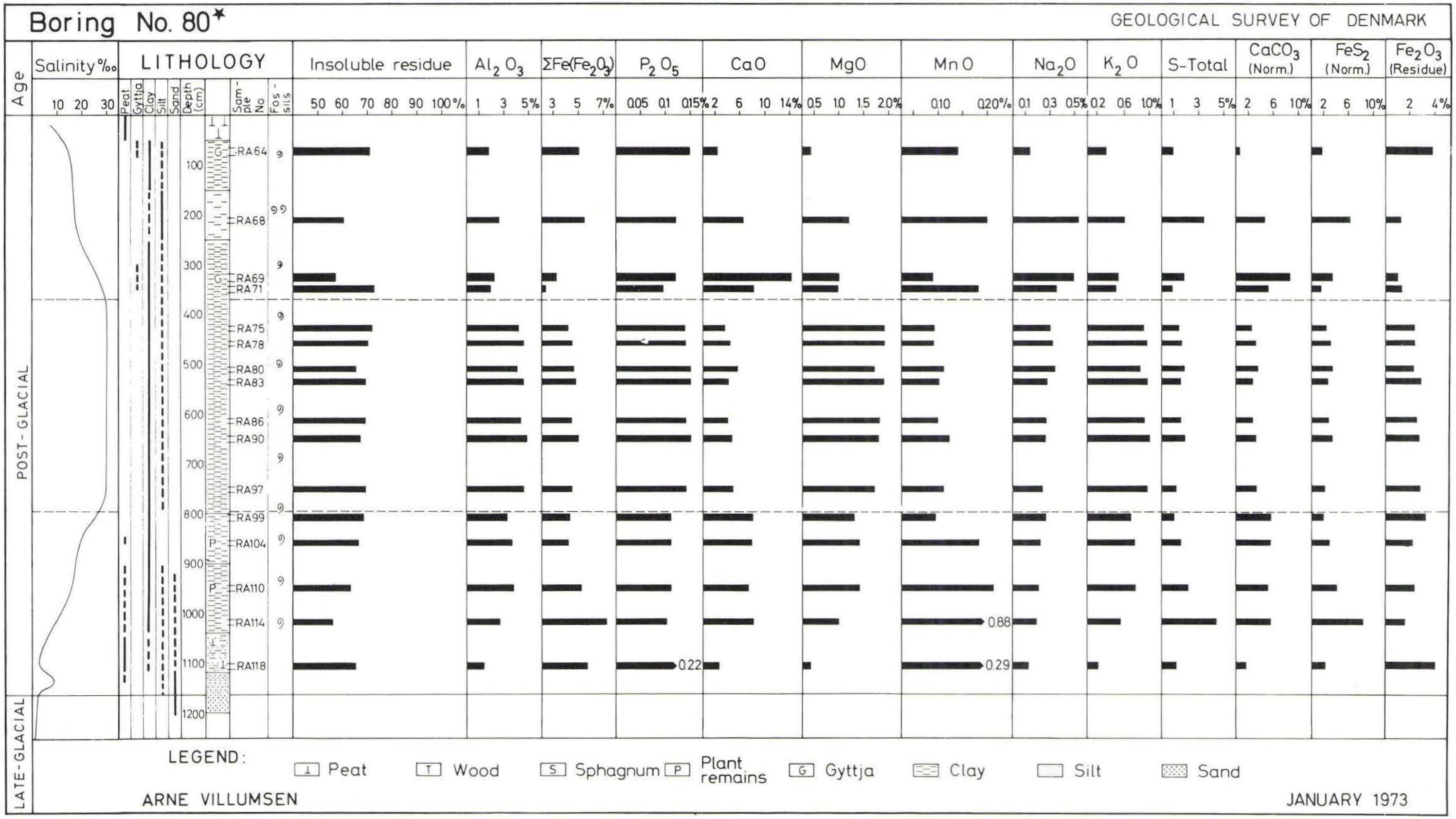


Fig. 31. Type locality boring 80*. Lithology and chemical composition.

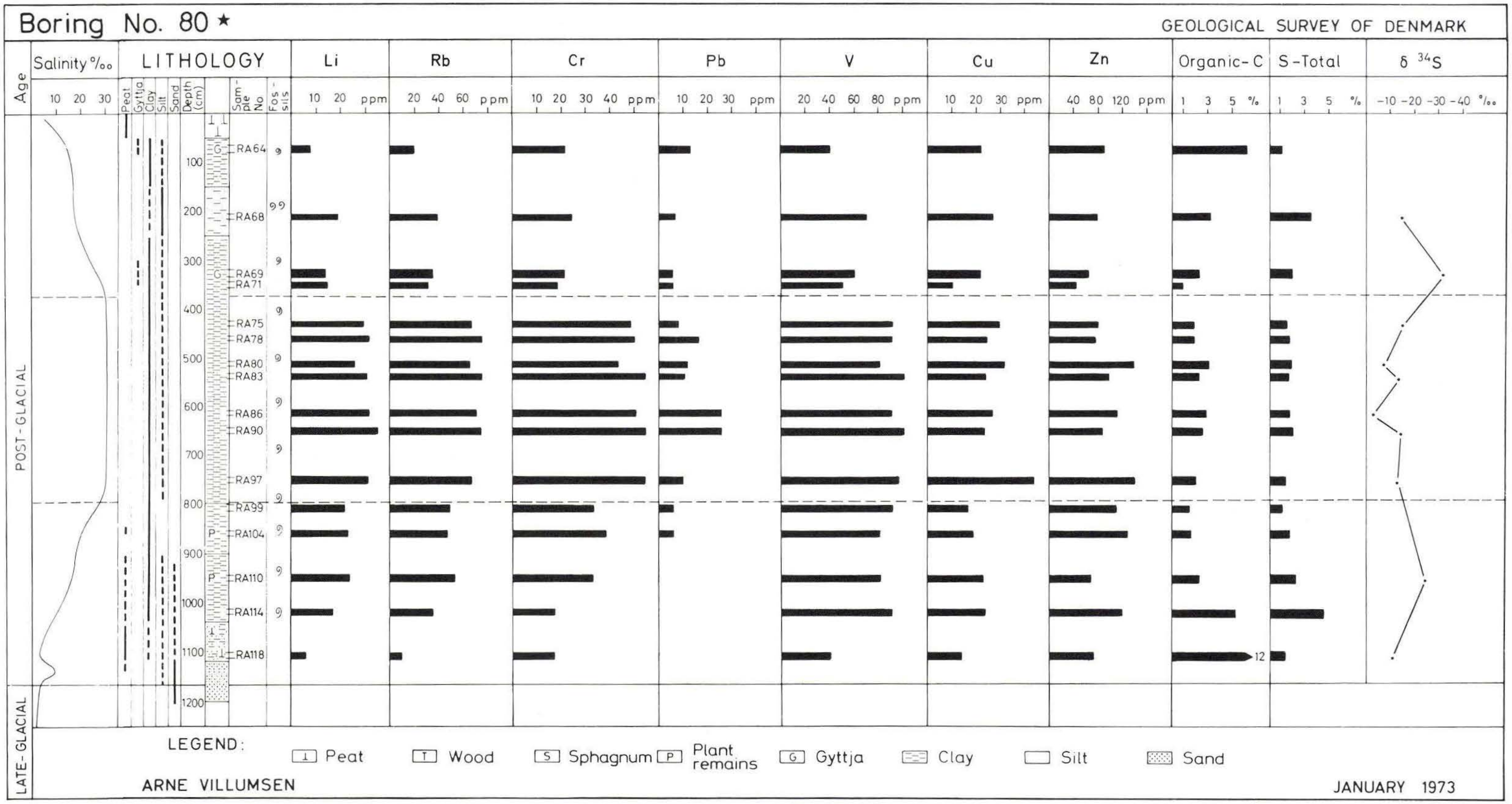


Fig. 32. Type locality boring 80*. Lithology and content of trace elements.

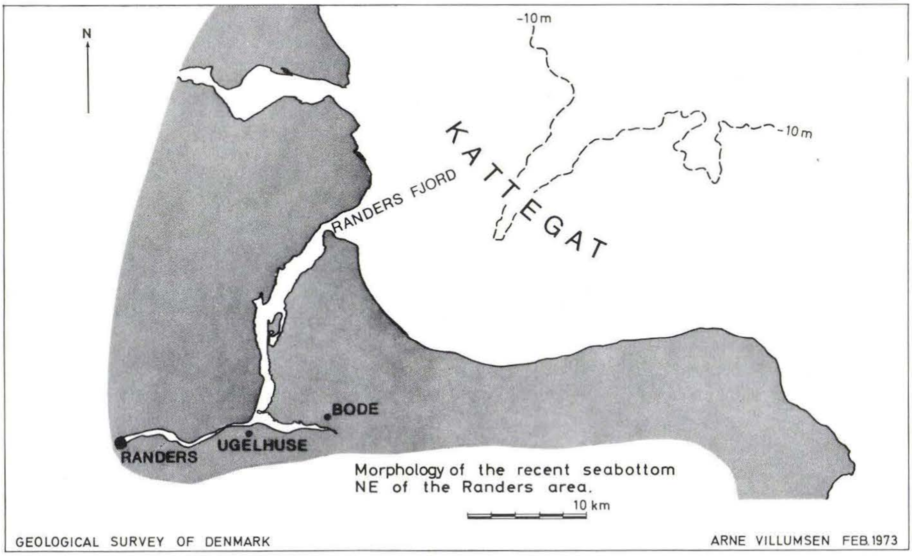


Fig. 33.

level –10 m in this area. As an objection it could be assumed that the whole Randers fjord contained such great quantities of dead ice that sedimentation took place at a higher level, but as all the peat deposits with only one exception (boring No. 33) were found at fairly constant levels, this objection cannot be very important. Dead ice might have been locally significant for example in the area around boring No. 33 (see below). As indicated above, it can be assumed that the river Gudenå left the investigated area with its surface at about the –10 m level. It is natural then to try to estimate its course outside the area studied. An impression of the slope of the river can be obtained from plate 1 fig. 23, and assuming that the river Gudenå continued towards the sea with constant slope a good correspondance with the recent morphology of the sea bottom can be obtained (see fig. 33): In the area about 20 km north of Ugelhuse the –10 m level limits a narrow, deeper north-south trending part of the recent sea bottom, and it is believed that this locally marks the course of the river Gudenå in Early Post-glacial time.

Compared to the slope of the river Gudenå, the river Allingå seems to have had a steeper gradient. Based on the elevation of the peat found in borings Nos. 54*, 53, and 13 the surface of the river Allingå in the area around Vester Alling seems to have been at a level of about –3 m in Early Post-glacial time (fig. 23). 10 km downstream the surface drops to –6 m as peat was found at this level in boring No. 64 (north of Gammel Estrup). The

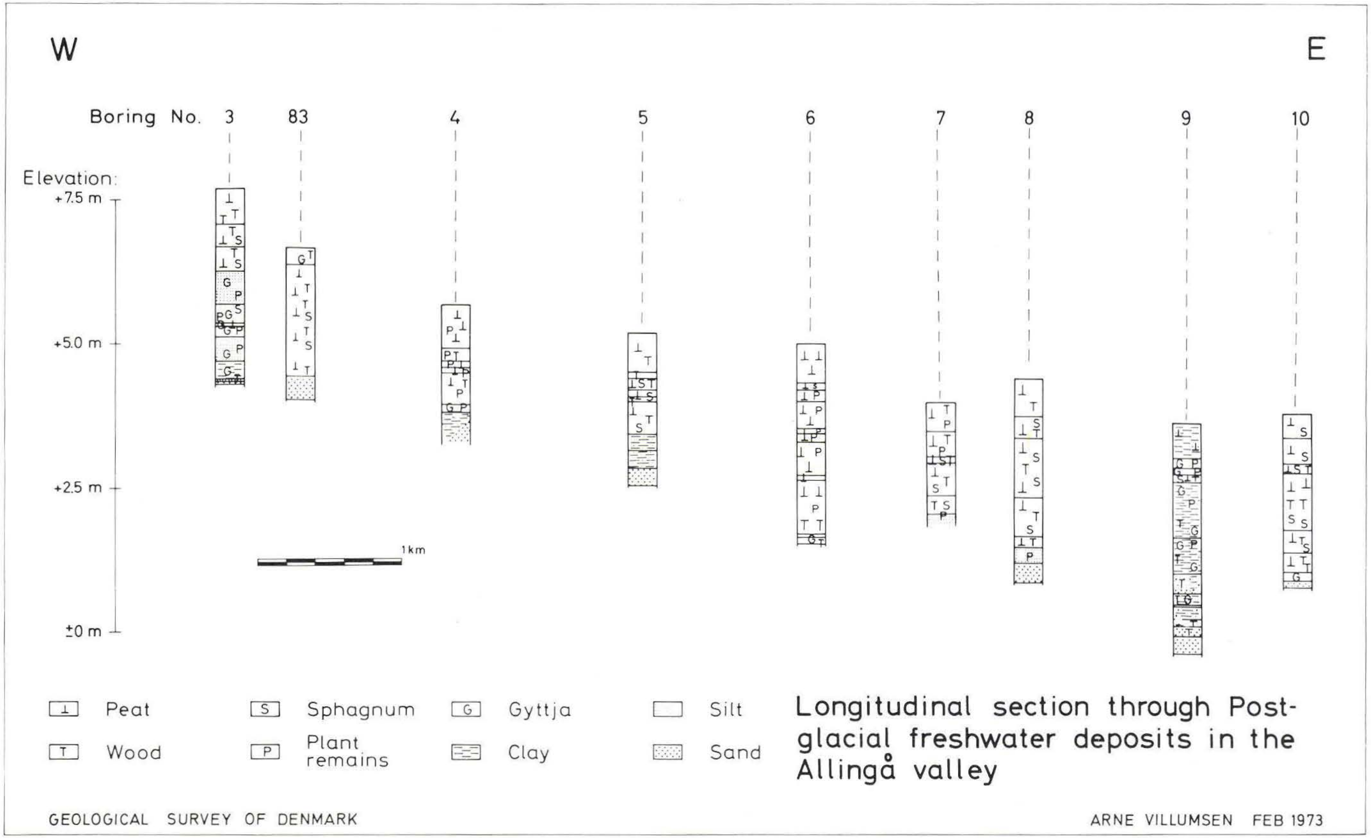


Fig. 34. For localization of the borings, see plate 1.

mean slope for the river within this section is about 30 cm per km. Fig. 34 illustrates the slope for the upper part of the river (around Klavsholm castle) and shows that the sand substratum drops from +4 m in boring No. 83 to ca. – 0.5 m in boring No. 9. As lake sediments (gyttja) have only been found between the sand barriers at one locality (boring No. 6), it is believed that the river Allingå during the Early Post-glacial time had about the same slope as the sand bottom. This means that the upper section of the river had a mean slope of 1 m per kilometre. It is possible that the slope of the river was even greater at that time, because it undoubtedly deepened its bed later in the Post-glacial time.

Local ocurrences of dead ice in Early Post-glacial time. As mentioned above the Early Post-glacial peat in Randers fjord and Grund fjord is situated at approximately the same level. The peat found in boring No. 33 (fig. 35) makes an exception, since here a thin layer of sandy freshwater gyttja (depth 14.20–14.40 m below surface) was found above the peat, while in boring No. 33 A (about 20 m from No. 33) a clayey gyttja more than 1 m thick was found above the peat (depth 12.50–13.50 m). Based on their lithology and fauna these gyttja occurrences are believed to be roughly synchronous. The content of sand and the thickness of the gyttja deposit in boring No. 33 might indicate a more marginal environment of formation than for the thicker, clayey gyttja found in boring No. 33 A, i.e. the gyttja found in boring No. 33 A must have been formed at the lowest level. Thus a vertical dislocation of these Early Post-glacial peat and gyttja deposits seems to have occurred, and as occurrences of dead ice were likely within the area, it is assumed that this is caused by melting of dead ice in the substratum. It does not seem possible to decide when the dislocation ceased.

It can be stated conclusively that the Early Post-glacial sediments are dominated by allochthonous peat, which for most of the area can be assumed to have been rebedded during the first *Littorina* transgression. The peat, which generally is taken as an indicator of shallow water environments, shows by its distribution that the Early Post-glacial groundwater table in Randers fjord and Grund fjord was situated at a level of −8.5 to −10 m, and that the river Gudenå during this period had a moderate slope, contrary to at least the upper part of the river Allingå. Depth conditions for the peat around boring No. 33 indicate the presence of local occurrences of dead ice in Early Post-glacial time.

Post-glacial marine sediments. The Early Post-glacial shallow water deposits are overlain by marine sediments in most of the investigated area. These marine sediments are the thickest deposits within the area (fig. 19). Large

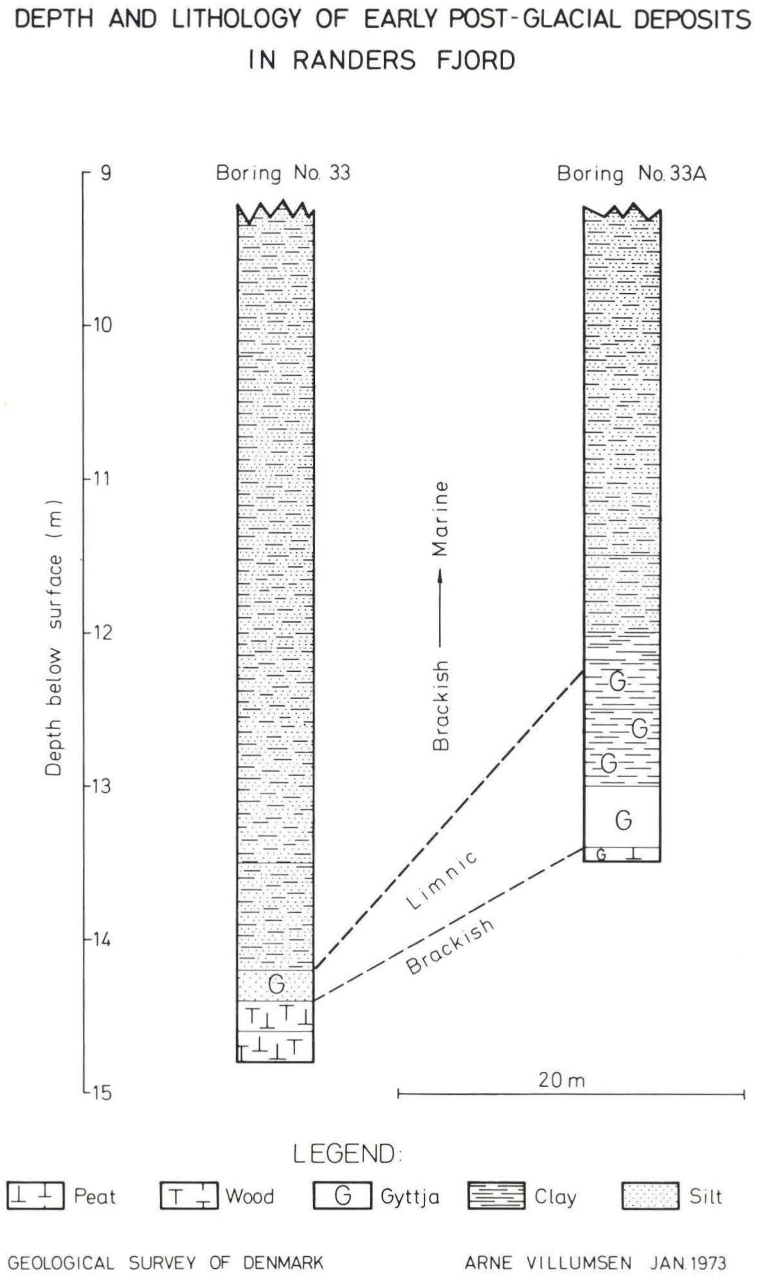

DEPTH AND LITHOLOGY OF EARLY POST-GLACIAL DEPOSITS IN RANDERS FJORD
Boring No. 33
Boring No. 33A
Depth below surface (m)
9
10
11
12
13
14
15
Brackish ⟶ Marine
Limnic
Brackish
G
G
G
G
G
G
20 m
LEGEND:
Peat
Wood
Gyttja
Clay
Silt
GEOLOGICAL SURVEY OF DENMARK
ARNE VILLUMSEN JAN. 1973

Fig. 35.

parts of the marine sequence certainly were formed in the *Littorina* sea, but as marine conditions persisted from Atlantic time (Iversen 1937; Troels-Smith 1942) until today (Johansen 1918), it is hardly possible to distinguish between *Littorina* sediments and younger, marine deposits using sedimentological and chemical methods. In the following context the marine sediments are therefore discussed collectively.

The marine sediments include a locally more than 10 m thick series of silty clay and gyttja, which normally is grey, greenish grey or blackish grey in colour. The macroscopic fauna is dominated by molluscs with calcareous shells, which locally have a corroded surface, especially when the shells are found in sand layers. Normally, however, the shell material is well-preserved, often with an intact epidermis. At some localities, for example in the area between Bode and Gammel Estrup, larger occurrences of shell-breccia dominated by *Ostrea* and *Cardium* are present. The marine sediments are somewhat diverse within the investigated area. The 3 type localities (fig. 1) were selected as representing the most important marine sedimentary environments:

*Boring No. 80** is assumed to contain the most complete and the most marine series of sediments, because it is located in the largest and deepest valley, and closest to the sea.

*Boring No. 54** was drilled in the Allingå valley at a locality which was covered by the *Littorina* sea only for a short period; therefore this boring illustrates the marginal facies where a river flowed into the *Littorina* sea.

*Boring No. 32** also represents a marginal sedimentary environment, but contrary to boring No. 54* it is situated in a relatively quiet environment without freshwater supply. A detailed characterization of these 3 type borings supplemented by field data from the other borings should accordingly give a reliable, general impression of the sedimentogenetic development of the whole area.

Boring No. 80:* The drilled sequence includes in total 12 m of sediment of which the lowermost 50 cm is believed for lithological reasons to be of Late-glacial age. The early Post-glacial peat at about 11 m depth was, as earlier mentioned, presumably rebedded during the *Littorina* transgression. The overlying ca. 10.5 m of sediment is a silty, blackish-grey deposit containing marine molluscs. Chemical, sedimentological, and palaeontological studies show that this sediment profile consists of 3 units (see figs. 30, 31, 32):

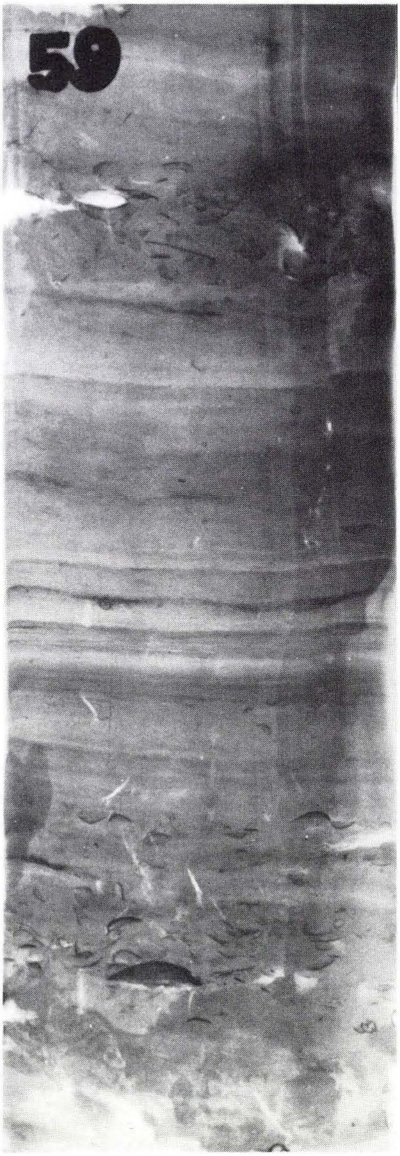
Lower part of boring No. 80* (between 10.5 m and 8 m below surface). An example of the sediment is given by the photo fig. 36 which shows the core section 9.55–8.93 m below surface. The deposit is a silty, blackish-grey clay which upon oxidation rapidly becomes totally black. The content of organic matter is concentrated in thin layers, and sand laminae are common,

Fig. 36. Photo showing the lower part of the sediments from type locality boring 80* (depth 8.93–9.55 m below surface). The layered appearance is essentially caused by thin laminae of organic matter.

thus giving the sediment a layered appearance. The fauna indicates a paleosalinity of 10 ‰ immediately above the Early Post-glacial peat where *Theodoxus fluminalis* is present. Between ca. 9.5 and 8 m below surface the fauna is dominated by *Hydrobia* while *Cardium* and *Littorina* are also present. This indicates an increase in salinity to 15–20 ‰. The presence of *Theodoxus fluminalis* is indicative of an agitated, shallow and brackish environment. Investigations of the organic fraction (fig. 30) show an upwards decrease of organic matter, and as the content of nitrogen is almost constant throughout the section, a decrease in the C/N ratio can be observed. It is possible that this can be explained by benthonic activity.

The central part of boring No. 80* (between 8 m and 3.5 m below surface). This sediment can, like the lower part, be described as a silty blackish-grey clay, but is characterized by its content of several millimetre-thin alternating light and bluish-black layers. These laminae are believed to represent frequent changes in redox potential at the sea bottom during sediment formation. X-ray radiographs (figs. 37–41) show that this central part of the marine section is markedly layered also after oxidation of the material. On fig. 37 a grain size variation between the different thin layers can be seen (dark layers = clay; light layers = silt). The fauna in this central part is poor in species. Almost exclusively small specimens of *Spisula subtruncata* and *Corbula gibba* have been found, indicating a salinity of up to 30 ‰ and quieter conditions. The fauna seems to be present only in certain horizons, separated by clearly layered fossil-free sequences. Within the fossiliferous layers (e.g. lower part of fig. 37) the shells are found separated, and a faint tendency for an orientation of the shell material can be observed. A little higher in the profile (see fig. 38) the orientation seems to be quite random. Fig. 39 gives a good example of well developed layering in the sediment and its fauna, which like the whole central part of this boring only includes small forms of molluscs. Fig. 40 shows the only sign of bioturbation found in the central part. Fig. 41 shows the same layered sediment, but in this case the fossils are concentrated in a single layer and the bivalves are preserved coherent. No orientation of the shells in this layer can be seen. Concerning chemical composition the central part of boring No. 80* differs from the lower and the upper part of the sequence. The central part has a lower content of MnO, CO_3-C, and CaO thus giving a lower $CaCO_3$-norm (table 4). In agreement with this the content of biogenic lime is lower. Al_2O_3, K_2O, MgO, Fe_2O_3, and P_2O_5 are higher in the central part, possibly because the clay content is higher or easier soluble than in the lower and upper parts. Illite seem to be more common in the central part.

Upper part of boring No. 80* (between 3.5 m below and up to the surface): Characteristic for the upper part is a slightly higher sand and silt



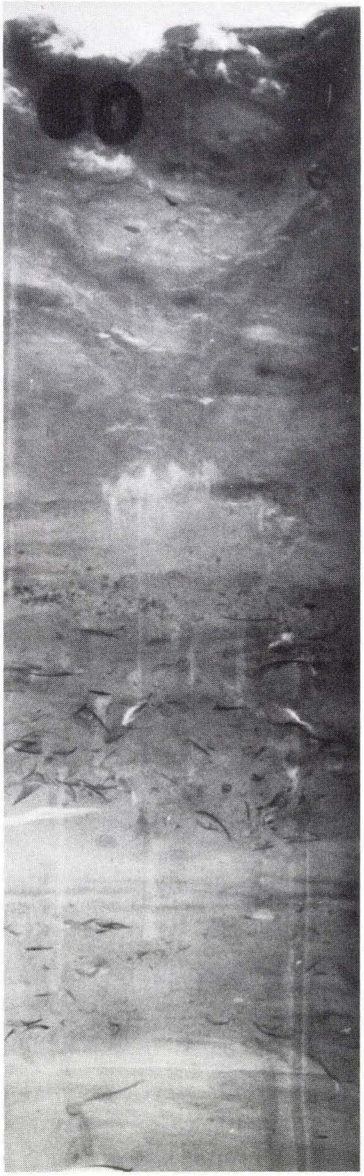


Fig. 37. X-ray radiograph (× 1) from type locality boring 80* (depth 6.21–6.35 m below surface). The photo gives an impression of the layered sediment which is present in the middle of the marine section from this type locality (light layers = silt; dark layers = clay). The fauna which includes almost exclusively *Spisula subtruncata,* is found in special horizons. A faint tendency for the shell material to be oriented can be seen.

Fig. 38. X-ray radiograph (× 1) from the middle part of the marine sediment at type locality boring 80* (depth 6.07–6.21 m below surface). The fauna is, as in fig. 37, dominated by *Spisula subtruncata,* but here the shell material shows a random orientation.

Fig. 39. X-ray radiograph (× 1) from the middle part of the marine sediment at type locality boring 80* showing an almost non-fossiliferous, clearly layered sediment. Depth 5.35–5.49 m below surface (light layers = silt; dark layers = clay).

Fig. 40. X-ray radiograph (× 1) from the middle part of the marine sediment found at boring 80*. Depth 5.20–5.35 m below surface. There are traces from a burrowing organism which has disturbed the layering of the almost fossil-free sediment.

content, and accordingly the content of acid soluble components originating from the clay fraction decreases (e.g. Al_2O_3, MgO, K_2O). The content of organic matter is higher in the upper than in the central part, and roughly of the same order of magnitude as in the lower part. The opal content (from diatoms) has a maximum in the upper part of the sequence, and the biogenic lime goes up to 13.6 %. The fauna includes *Cardium* and *Littorina* and as in the lower section *Hydrobia* dominates. This indicates an approximate salinity of 15–20 %, and in the uppermost part the salinity was even lower than this. The fauna is either evenly distributed in the sediment or concentrated in occurrences of shell-breccia.

Boring No. 32:* The marine part of boring No. 32* embraces slightly more than 5 m of sediment (figs. 20, 21, and 22). The oldest marine deposits include about 0.5 m of sand and clayey silt (depth 6.60 m to ca. 6 m below surface) followed by about 1 m peat which is in turn overlain by ca. 4 m of blackish-grey silty clay or clay-gyttja. The fauna in the sand deposit below the peat indicates that the salinity has been 10–20 ‰, and as mentioned earlier its composition is like a quite normal *Littorina* fauna. In the layer of clay and silt immediately below the peat no molluscs or diatoms were found, presumably because of solution processes. The peat, which as stated earlier contains brackish-water diatoms, is assumed to have been deposited in a bog area which was temporarily covered by the *Littorina* sea. The fauna and sediment investigations show that the marine deposits above the peat are composed of 3 different parts:

The lower part (depth 5–4.5 m below surface) contains *Cardium* and *Hydrobia,* which indicate a salinity of 15–20 ‰. Fig. 42 is an example of the sediment immediately above the peat. It is characteristic for the lower part that no layering can be observed, and that the fossils are scattered in the sequence. The bivalves are sometimes preserved with their shells coherent, but separate shells are also often found.

Within the next 1.5 m of the profile (between 4.5 and 3 m below surface) a more marine fauna including *Littorina* and *Cardium* is present, indicating a paleosalinity of 25–30 ‰ and a tidal environment. Alternating layers of clay and silt are characteristic for this central part of the marine sediment. The fossils seem to occur mostly in the silt layers. No preferred orientation of the shells can be observed within the silt layers. The photo, fig. 43, is an example of the layered sediment: At the bottom of the photo there is a thick silt layer with *Hydrobia* and *Cardium* amongst others. Above this clay without shells is present. The limit between the silt and clay is well-defined and might represent a hiatus. Above the clay layer an increase in grain size occurs (to silt), and at the same time the content of molluscs increases

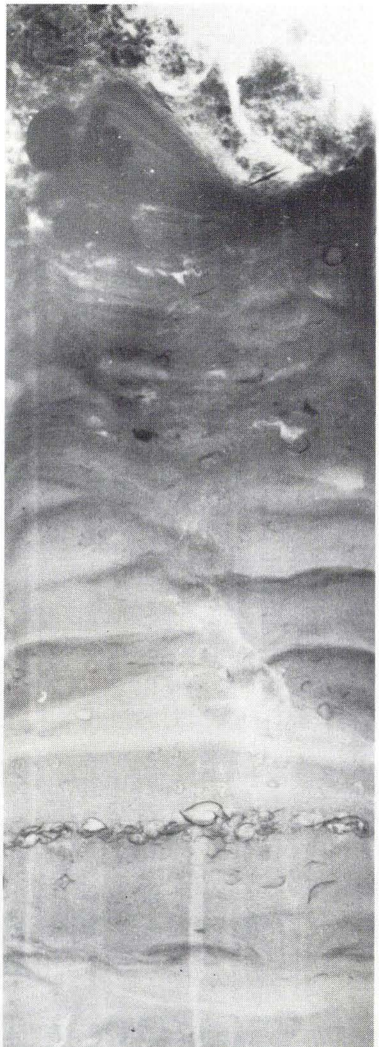


Fig. 41. X-ray radiograph (× 1), same locality and same part of marine sediment as fig. 40. Depth 5.05–5.20 m below surface. The small specimens of *Spisula* are here concentrated in a single layer.

Fig. 42. Photo from type locality boring 32*, depth 4.26–4.93 m below surface. The photo gives an example of the marine sediment found above the Early Post-glacial peat. Lack of layering and large specimens of, amongst others, Cardium which are evenly distributed through the profile, are characteristic for this deposit.

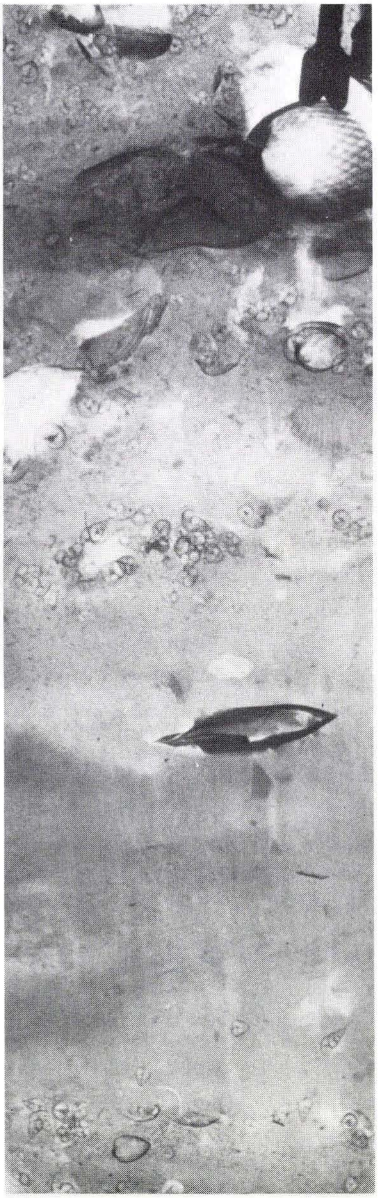
(*Hydrobia, Littorina, Cardium, Mytilus*). Upwards the single layers are thinner, but still a correspondance between grain size and fossil content seems to exist (fig. 44).

In the upper part of this section (from 3 m to 1 m below surface) the silt content decreases while its gyttja character increases. Compaction of the sediment core during the drilling has disturbed the sequence so that no reliable structural information can be obtained. Investigations of the fauna show that the salinity was a little lower (20–25 ‰) than in the central part, and effects of tidal water are absent. The bivalves are preserved coherent, and as the content of silt decreases, there is evidence of quieter environments. Through the upper part of the boring the salinity decreases to very low values. The uppermost metre is presumably formed in a freshwater environment.

Thus investigations of both fauna and sediment show that the marine deposit above the peat (i.e. from 5 to 1 m below surface) can be taken as a section separated in 3 units: 1) Between 5 and 4.5 m (below surface) a non-layered, silty, greyish black clay. 2) From 4.5 to 3 m (below surface) alternating layers of silt and clay. The general impression is that the fauna, which is influenced by tidal activity is found especially in the silt layers. 3) Between 3 and 1 m (below surface) the fauna and lithology indicates a quieter environment without tidal movements.

It is obvious that the moderate number of samples investigated from the marine part of boring No. 32* restricts the posibility of deciding whether the above mentioned division of the sequence can also be found by chemical methods. Taken as a whole the marine sediment found above the Early Post-glacial peat in boring No. 32* is similar to the upper and lower marine parts of boring No. 80*, although some minor differences should be noticed: The content of organic matter is a little higher in boring No. 32*, the C/N ratio is 10–12 in boring No. 32*, while it is about 8 in boring No. 80*. The contents of Al_2O_3, K_2O, and MgO in boring No. 32* are of the same order of magnitude as in the central part of boring No. 80*. So it seems that the content of soluble clay and organic matter is somewhat higher in the marine sediments in Virring bay (boring No. 32*) than in the remaining part of the investigated area. The reason for this is possibly that boring No. 32* is situated in an area where freshwater supplies have been subordinate.

*Boring No. 54** was drilled in the Allingå valley at a locality which was covered by the *Littorina* sea for a short period only. The exact demarcation of the marine sequence in boring No. 54* (see fig. 27) is complicated partly because the core recovery was relatively bad and partly because the molluscs



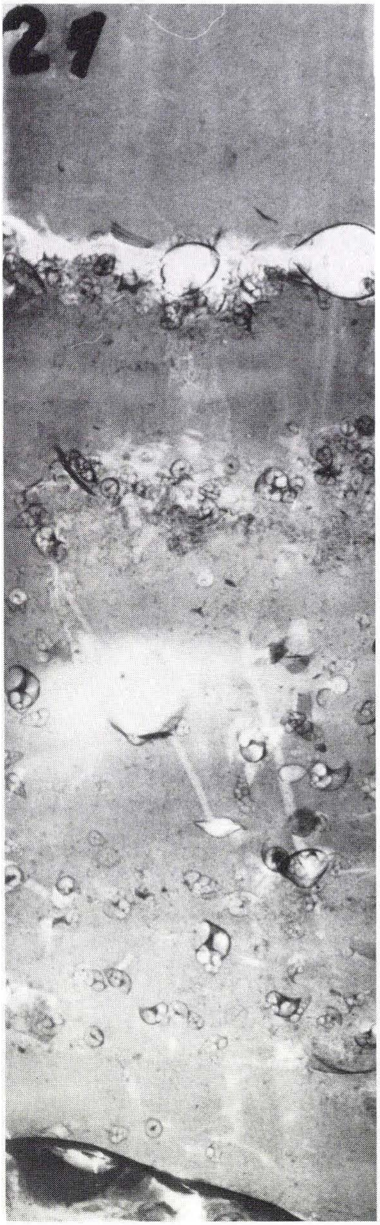


Fig. 43. X-ray radiograph (× 1) from boring 32*. Depth 3.77–3.93 m below surface. In the lower part of the photo a silty layer containing *Hydrobia* sp. and *Cardium* sp. is seen. Above this there is a discordant clay layer without fossils. In the upper part of the photo the sediment is rich in silt, and contains large forms of *Hydrobia*, *Cardium*, and *Littorina*. The large bivalve just above the fossil-free clay layer is a *Mytilus*.

Fig. 44. X-ray radiograph (× 1) from boring 32*. Depth 3.61–3.77 m below surface. The fauna is dominated by *Hydrobia* and *Cardium*, which is found preferentially in the most silty layers.

have been dissolved from the uppermost 3 m of sediment. – The lower boundary for the marine sediment is fixed at a depth of 6 m below surface (level −3.17 m) where marine molluscs are present in thin sandlayers in the Early Post-glacial peat. The upper boundary is assumed to be about 1 m below surface (level +1.80 m) because fossils including *Cardium* were found at this level in another boring in the vicinity (boring No. 12). This marine sequence which in thickness amounts to 5 m contains a varied series of brackish- and freshwater sediments, in which allochthonous minerogenic and organogenic components are present in varying amounts. Lithologically the deposit can be described as a grey and greyish-brown silty clay which contains some gyttja. Layers of clayey peat occur locally. The content of organic matter and the C/N ratio is higher than in the two other type borings. The insoluble residue does not differ significantly from boring No. 32* and 80*, presumably because boring No. 54* has a higher loss on ignition. The $CaCO_3$-norm and the content of biogenic lime is lower in boring No. 54*, possibly because of the solution processes already mentioned. Pollenanalytical dating of the oldest marine sediment (depth 5.70 m below surface) was not possible as the pollen content was strongly decomposed and presumably rebedded. It was, however, possible to date the lowest part of the thickest marine (brackish) layer in the boring (between 4.40 and ca. 3 m below surface) to Atlantic time based on samples taken at 4.30 and 4.00 m below surface. The sediment is layered and contains many relatively large, separate *Cardium* shells with random orientation.

The marine sediments found in the 3 type borings can thus be taken to illustrate 3 different facets of the sedimentogenesis during the *Littorina* period. In borings Nos. 80* and 32* a marine deposit which can be subdivided into three parts is present, and in boring No. 54* there is a profile through alternating freshwater and brackish sediments. In a later chapter (p. 73) the sedimentary environment and its development will be discussed based on the observations mentioned above. An attempt is now made to clarify for which parts of the investigated area each of the type borings is representative. The data available for this interpretation, besides the lithological field description, includes only a systematic determination of the water content of the samples. The water content varies from 25 % to more than 600 % within the area (fig. 2), but normally values between 50 % and 150 % are found. The lowest values are generally found (normally less than 100 %) in samples from Randers fjord, Grund fjord and Allingå valley north of Gammel Estrup. In the remaining part of the Allingå valley and in Virring bay the water content is normally around 150 %. Lower values are found for deposits just above the sand substratum. This regional tendency, combined with the analytical results from the type borings, is assumed to indicate that the content of organic matter is greatest in the sediments in Virring bay and in the upper part of the Allingå valley.

The above mentioned 3-fold division of the marine sequence is confirmed by the determination of water contents at a number of localities. In Randers fjord, Grund fjord, and Allingå valley north of Gammel Estrup the highest water content was found in the central part of the marine sequence, as for boring No. 32* and 80*. Characteristic for boring No. 80* is a slightly higher content of clay and organic matter in the central part, while other parameters which might influence the water content are relatively constant through the profile. The observed variations in water content for the sediments in Randers fjord, Grund fjord and the lower part of Allingå valley are therefore assumed to express differences in the clay content and in the content of organic matter which consequently are greatest in the central parts of the marine profile. Another characteristic feature of the central part of boring No. 80* is the presence of thin light and blackish- or bluish-grey laminae. These thin layers have been found in many other borings. Fig. 45 shows the area in which the water content is greatest in the central part of the marine sediments and where alternating thin layers of light- and bluish-grey colours have been found at the same level as in boring No. 80*. Based on this boring No. 80* is assumed to be representative of the area shown in fig. 45 which includes most of Randers fjord, Grund fjord and parts of Allingå valley.

The central parts of the *Littorina* deposits in boring No. 32* seems, as earlier mentioned, to be influenced by tidal activity, and to contain slightly more silt than the rest of the profile. Therefore the water content of the central part is the lowest. Likewise, fig. 45 shows the area for which boring No. 32* is typical, that is the area covered by borings where minima in water content occur in levels corresponding to boring No. 32*, and where at the same time the content of sand or silt is greatest. Boring No. 32* is, as shown at fig. 45, only characteristic for a minor part of the investigated area (Virring bay and parts of Allingå valley). It is difficult to demarcate the area for which boring No. 54* is representative. Based on lithology, water content and the geographical conditions it is assumed that it is only characteristic for a small area in the immediate vicinity of boring No. 54* (see fig. 45). In parts of the investigated area deposits are found which are not represented by the type borings: in the area around the village of Bode where the drilled sequence is only a few metres thick, alternating thin layers of clay, silt and sand were found, and it is assumed that this deposit represents a marshy sediment. Laboratory investigations of this deposit have not been performed.

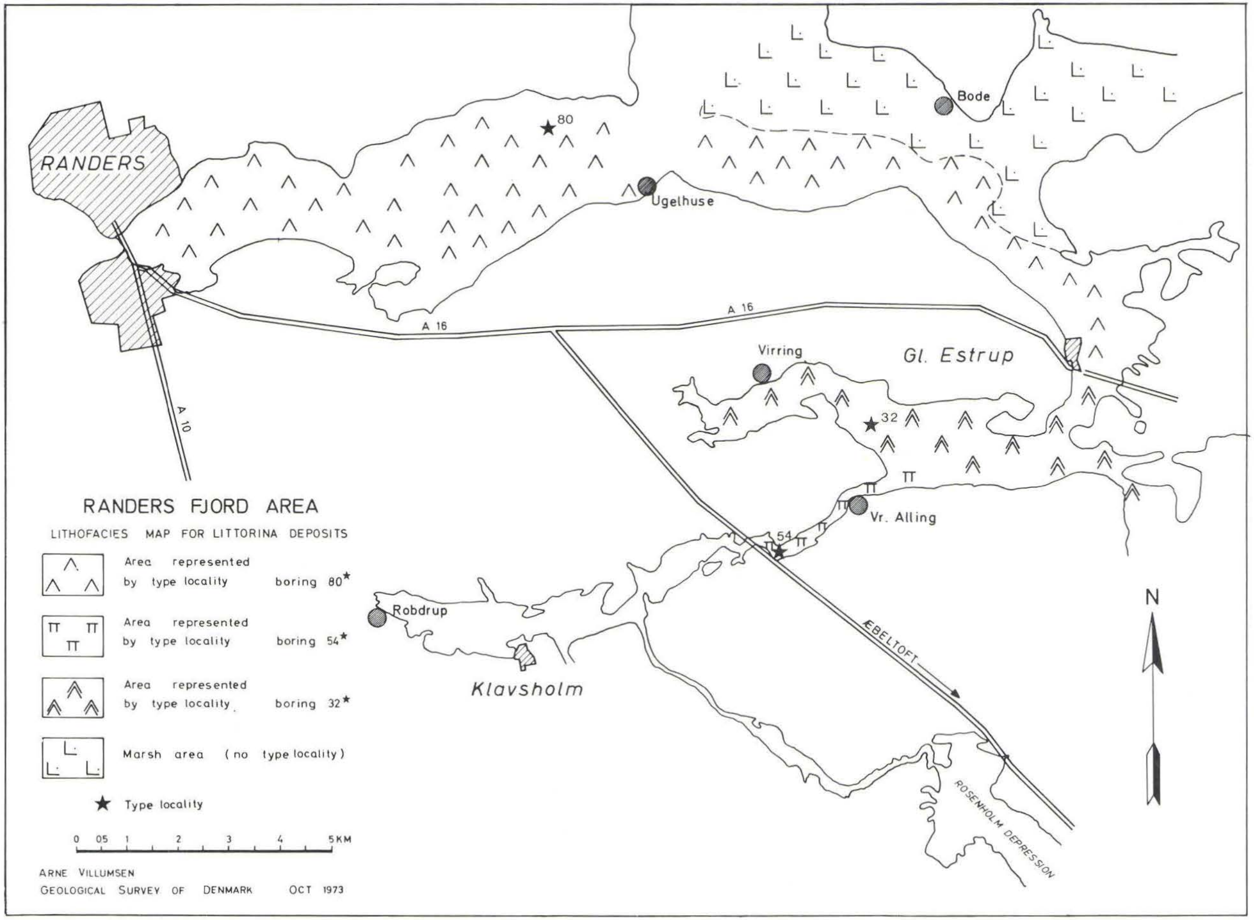

RANDERS
80
Bode
Ugelhuse
A 16
A 16
A 10
Virring
Gl. Estrup
32
Vr. Alling
54
Robdrup
Klavsholm
ÆBELTOFT
ROSENHOLM DEPRESSION
N
RANDERS FJORD AREA
LITHOFACIES MAP FOR LITTORINA DEPOSITS
Area represented by type locality boring 80★
Area represented by type locality boring 54★
Area represented by type locality boring 32★
Marsh area (no type locality)
★ Type locality
0 05 1 2 3 4 5KM
ARNE VILLUMSEN
GEOLOGICAL SURVEY OF DENMARK OCT 1973

Fig. 45.

Post-glacial freshwater deposits. As earlier mentioned the *Littorina* sea during its maximum transgression reached a few km west of Vester Alling. In the Allingå valley west of this the only major freshwater deposit of the investigated area is present. The profile which attains a maximum thickness of a little more than 3 m (fig. 34) includes up to 2 m gyttja resting on the Late-glacial sand substratum; above the gyttja fen peat is present. At some localities no gyttja is found, and the peat rests directly on Late-glacial sand. Fig. 34 shows a longitudinal section through the freshwater sediments. It can be seen that the gyttja formation occurred in 3 small lakes, separated by sand barriers, which were not found during the depth mapping. The top of the sand barriers must have been a little higher than the level of the top of the gyttja which they demarcate (some uncertainty may be caused for example by later compaction of the sediment). The following overgrowth of the area, by which the peat formation became possible, might correspond to the final regression phase of the *Littorina* sea. Formation of freshwater deposits became possible as the sea regressed, and it seems that most of the investigated area had a freshwater phase after the marine. At some localities this has hardly been registered in the sediments, and in part of the area freshwater environment has not yet replaced the marine. This is especially the case for the meadows around Randers fjord and Grund fjord, where overgrowth is still taking place, and where an important decrease in the fjord-area has been noticed in the last 200 years (Johansen 1918). The thickness of the freshwater deposits decrease from the inner parts of the Allingå valley towards the recent fjords. Intensive agricultural use of the area has reduced the possibility of detailed geological interpretations of the freshwater sediments.

Description of the sedimentary environments

The present investigation supports the preexisting overall impression of the Late- and Post-glacial developments of Denmark, but some general aspects of the sedimentary environment in a protected fjord area can be illustrated.

Salinity: The determination of the salinity in the environment of formation is based on the fauna and in a few cases also on the content of diatoms. The Late-glacial sediments are all deposited in freshwater, the Younger Dryas gyttja in a lacustrine environment, while the Late-glacial sand is interpreted as a fluviatile deposit. Early Post-glacial, undisturbed freshwater sediments (peat and gyttja) are apparently present only in the upper part of Allingå valley (SW of Vester Alling). The remaining occurrences of Early

Post-glacial peat within the area were presumably redebbed by the first *Littorina* transgression. All the marine sediments are believed to be Post-glacial in age, based on the composition of the fauna. As earlier mentioned it is hardly possible to separate *Littorina* sediments from younger marine sediments, and therefore the marine sediment is discussed as a whole: The salinity of the marine sequence seems to vary in the same way throughout the whole area: the lower and upper parts were formed under more brackish conditions than the central part, where the fauna indicating the highest salinity is present. The central part of boring No. 80* was formed at a salinity of ca. 30 ‰ and as expected the salinity were lower at the two other type localities. In boring No. 32* the maximum was 25 ‰ while it was only about 15 ‰ in boring No. 54*. A pollen analytical dating of the most marine sediment found in boring No. 54* showed an Atlantic age, and it is therefore assumed that the salinity culminated in the area as a whole when the *Littorina* sea had its maximum extension in Atlantic time. Freshwater supplies through the Allingå valley must be responsible for the much lower salinity in boring No. 54* than in boring No. 32* which are located only 3–4 km apart but in the more protected Virring bay. A. Jessen (1918) stated that the marine surface water of the *Littorina* sea, like the present Randers fjord (Jacobsen 1918), was less saline than the bottom water, which possibly could have stabilized the water in the deepest parts of the area and thus promoted stagnant conditions.

In a recent paper (Villumsen and Nielsen 1976) the possibility of using certain chemical elements (Li, Rb, B) as indicators of paleosalinity was discussed for the Randers fjord area. It was demonstrated that effects other than paleosalinity governed the chemical composition of the sediments, and no supplementary information concerning the paleontological salinity interpretations can therefore be given.

Supplies of freshwater to the area. During the Late- and Post-glacial time the investigated area received large amounts of freshwater from the rivers Gudenå and Allingå and from many local creeks opening to the valley system. In many ways these influxes of freshwater have influenced the sedimentary development of the area, for example by lowering the salinity.

The sediments content of allochthonous material. The sediment can be taken as a variable mixture of minerogenic and biogenic components. Allochthonous, minerogenic matter includes quartz, feldspars, amphiboles, lime, etc., while the organogenic fraction consists of living fauna and flora elements as well as dead organic matter in different stages of decomposition.

Biogenic material can be divided into two main groups: a non-combustible (acaustobiolithic) and a combustible (caustobiolithic) fraction (Pettijohn 1957).

a. Allochthonous, minerogenic material: Treatment with acids leads to solution of part of the sediment, while quartz, felspars, amphiboles etc. and SiO_2 from decomposed silicates (including clay) and from opal (diatoms) will remain as an insoluble residue. After correction for the content of diatom-SiO_2 and addition of non-biogenic lime a fairly reliable expression of the size of the total minerogenic fraction can be obtained (table 1). It is seen from the table that the minerogenic content is very high for the Late-glacial sediments. The supply of minerogenic material via the river Allingå seems only locally to have influenced the sediments, although the slope of the river Allingå, as mentioned on page 56, was rather high. The highest content of minerogenic material in the Post-glacial sediments is found in Randers fjord. In the marine sequence the highest salinity and the lowest content of minerogenic material seem to correlate within the area represented by typelocality No. 80* (fig. 45).

b. Allochthonous, biogenous material: The acaustobiolithic fraction is dominated by biogenic lime and silica from diatoms. It is believed that the acaustobiolithic fraction is mainly authocthonous, although some rebedding cannot be excluded. In a few cases larger occurrences of shell-breccia have been found, and these of course make the specification of the trophic state uncertain when based on the content of biogenic lime.

The caustobiolithic fraction is expected to include varying amounts of organic matter produced and sedimented within the sedimentary basin and organic material formed in the surrounding area and from there transported to the investigated area. Here it seems generally possible to distinguish between allochthonous and autochthonous organic matter: organic material is normally sensitive to oxidative processes, and as the allochthonous organic fraction normally spends the longest period in oxidizing environments, the allochthonous components will attain a more stable composition than the autochthonous. This means that the allochthonous organic matter will have:

higher C/N ratios
greater contents of humic acids and
lower pheophytin contents

than the autochthonous organic material. For the marine sediments the allochthonous organic material will mainly be of terrestrial, lacustrine or fluviatile origin. A possible content of wood in the marine sediment can therefore only be allochthonous. Besides this the ratio $^{13}C/^{12}C$ is different for organic material produced in fresh and marine environments. In the present case several different possibilities therefore seem to exist to separate the two types of organic material.

In the following context an attempt is made to illustrate the amount and variation of the allochthonous organic material through the investigated sequence and within the area as a whole. The Younger Dryas gyttja (boring No. 32*) contains so little minerogenic material that the freshwater lake where the gyttja was formed must have been free from great freshwater supply. On the other hand the Late-glacial sand which in boring No. 32* overlies the gyttja as well as the Late-glacial sand bottom represents a period in which clastic supplies dominated. While the older parts of the Late-glacial sand according to Harder (1908) were formed when the ice melted from the area, the younger sand deposits, for example the sand above the Younger Dryas gyttja (boring No. 32*), must consist of local outwash material supplemented by clastic material from the source area of the rivers Gudenå and Allingå as the inland ice in the last part of the Late-glacial time had long since disappeared from Denmark. The Early Post-glacial peat found in the deepest levels of the valley system contains, as already mentioned, a fauna indicating brackish conditions. As the layering is marked and the sand content rather large, most of the peat occurrences seem to be allochthonous. However, the ca. 1 m thich Early Post-glacial peat found in boring No. 32* (Virring bay) is assumed to be autochthonous as the peat is extremely rich in organic carbon and contains many traces of roots. The minerogenic part of the Post-glacial marine sediment decreases as earlier mentioned rather uniformly for the main part of the area to a minimum value which was attained during the maximum *Littorina* transgression in the Atlantic. At the same time the highest content of clay is found. The minerogenic content is generally highest in Randers fjord (60–75 % in boring No. 80*), while the smallest content is found in Allingå valley. The river Allingå was apparently not so important for the supply of minerogenic material as could be expected from the relatively steep slope of the river. Throughout the area the lowest content of organic matter corresponds to the maximum transgression, which might indicate a mainly allochthonous origin for the organic matter in the marine sediment. This assumption is supported by other observations:

1) The total autochthonous biomass (the amount of organic matter estimated on the base of the pheophytin content) only amounts to 5–20 ‰ of the sediment which corresponds to not more than 10 % of the sediment's total content of organic matter.

2) The δ^{13}C-values (table 3) which were determined on a selected series of samples from the area where the allochthonous contributions were assumed to be the lowest (boring No. 80*, Randers fjord) all indicate that the organic C was either formed in a terrestrial or limnic environment or originates from marine phytoplankton. But as the total content of organic matter containing pheophytin is subordinate in quantity, marine phytoplankton cannot have influenced the δ^{13}C-value much. It is therefore believed that the organic matter is mainly of terrestrial or limnic origin, and thus the organic matter is an allochthonous component of the marine sediment.

The C/N ratio varies in the same manner through the sediment profiles within the investigated area. The lowest C/N ratios are found in the level corresponding to the maximum transgression. The highest values (10–18) occur in the sediments from Allingå valley (boring 54*), but towards the more open sea the C/N values decrease (C/N is 6–10 in boring No. 80*, except for the Early Post-glacial peat, see fig. 30). Corresponding to this decrease a drop in the content of organic C from 10–15 % in boring No. 54* to 1–5 % in boring No. 80* can be noted. The lowest C-contents are found in all borings at levels corresponding to the maximum transgression. The quantitative distribution of humic acids seems to vary in the same way as the content of organic C.

The total pheophytin content does not vary much, but an increase in pheophytin relative to total organic C is seen towards the sea. As the conditions for benthonic decomposition of the organic matter (which might cause a decrease in C/N ratio, Hansen 1964 b) seems to have been unfavourable at least during the formation of the central part of boring No. 80*, it is assumed that the C/N ratios have remained roughly unchanged since sedimentation. The regional variation in the C/N ratios, pheophytin contents, organic C, and of humic acids, might indicate that the importance of autochthonous organic material increased towards the open sea. As stated earlier the allochthonous organic matter is quantitatively the most important. As a final comment it should be mentioned that the N/P ratio varies roughly parallel to the C/N ratio, but a detailed discussion of the N/P quotient is not possible on the investigated data.

Tidal movements: The tidal activity of the *Littorina* sea was more intense than in the Danish sea area today (Nielsen 1938). Fauna investigations from the Randers area show the greatest tidal effect in the *Littorina* sea up to the maximum transgression (Atlantic time). After this the amplitude of the tides decreased again. This observation corresponds to Nielsen's (1938) explanation of the hydrological conditions in the *Littorina* sea. He stated that a decrease of the tidal movements occurred when the land connection between England and Denmark ceased to exist. The tidal range cannot be given with reasonable certainty before the faunal investigation is finished. Yet it seems probable, estimated on lithology and the morphology of the Late-glacial sand deposit, that the difference between low- and high-tide was about 2 m. This tidal activity, combined with the wind action, must have been able to erode the Quaternary sediments just outside the investigated area. That this was so is readily seen in the steep *Littorina* cliffs in the area.

Marine, tidal sediments: Boring No. 32* includes a fauna characteristic for tidal environments. At the same time the fauna is that requiring the highest salinity (20–25 ‰) in this boring. As the maximum salinity must have prevailed synchronously throughout the area, the most marine sequence of the borings must therefore have been formed in a tidal environment. The core recovery from boring No. 54* was as earlier mentioned so bad that interpretations based on sediment structures were not possible. But for boring No. 32* and 80* the cores were good enough for X-ray radiographs. At these two type localities two widely different facies are met with.

Boring No. 32.* The photos, figs. 43 and 44 show examples of the sediment structures and the distribution of the fauna. It is seen that alternating clay and silt layers occur, and that the molluscs are predominantly present in the most silty layers. The transition between clay and silt layers is sometimes so abrupt that it seems most reasonable that the transition represents a hiatus. It is therefore assumed that these sediments were formed in a shallow, littoral environment.

Boring No. 80.* The sediment structures (figs. 37–41) in the part of boring No. 80* where the fauna demanding the highest salinity is present indicates quite another type of environment from that in boring No. 32*. The sediment which is laminated and clayey was no doubt deposited below wave base. The composition and distribution of the fauna and the absence of traces of benthonic activity show that conditions were unfavourable for the higher biological life. The content of diatoms (which assumedly includes benthonic as well as planktonic forms) is not to the same extent as the content of biogenic lime low within this sequence, and therefore nutrient conditions do not seem to have been generally poor. The great number of alternating light and bluish-black laminae might indicate a fluctuation in oxygen content at the sediment water contact, and it seems probable that periodic anaerobic conditions alternated with periods where the supply of oxygen made a short period of benthonic life possible. It might seem paradoxical that the minimum water exhange occurs in the fjord area nearest to the open sea. The explanation must be that the water depth was so great around boring No. 80* that no exhange of water occurred at the bottom. It seems most probable that this was caused by a system of barriers lying at a level just permitting exchange of water in Virring bay, but not in the deepest parts around boring No. 80*. As boring No. 80* is taken as representative of the sedimentary environment in Randers fjord, Grund fjord, and the northern part of Allingå valley (fig. 45), the system of barriers may have been located in the area north of Ugelhuse, as no other connexion to the sea is possible. Just around borings Nos. 78–69–70–71 a sand barrier is present (plate 1) which as earlier stated might be Post-glacial in age (p. 43). The maximum height of the barrier is at a level of –3 to –4 m, which roughly corresponds to the highest level where the laminated sediment occurs in boring No. 80*. Thus it seems possible that the sand barrier north of Ugelhuse has prevented the exhange of bottom-water in much of the investigated area.

Water dept: The distribution of the different sediment types combined with knowledge of the topography of the sedimentary basin makes an estimation of the water depth possible.

The Late-glacial gyttja (boring No. 32*) was, as earlier mentioned, formed in a shallow freshwater lake where the water depth estimated by the fauna was less than 3 m. The Early Post-glacial freshwater sediments in the upper part of Allingå valley (mainly peat) are generally taken as shallow-water deposits formed in a paludal environment with a subordinate fluviatile character. The allochthonous peat deposits in Randers fjord, Grund fjord, and the lower part of Allingå valley are also shallow-water sediments which were rebedded during the first *Littorina* transgression (see p. 51). The *Littorina* transgressions within a part of Virring bay were investigated by Troels-Smith (1942) working around Dyrholmen, a small peninsula about 1 km west of boring No. 32*. He showed that the earliest *Littorina* transgression which reached Dyrholmen was the Middle Atlantic. Sediments from this period were found at a level of –1.5 m and higher (Troels-Smith 1942). The deepest level at which marine sediments are found in boring No. 32* is –4.18 m (see p. 43). It is not impossible that a marine transgression older than the Middle Atlantic could have reached the area, as the topography of the Late-glacial sand surface (plate 1) shows no barriers higher than ca. –2 m in the area between boring No. 32* and the open sea. However, this interpretation is too speculative for detailed discussion based on the data available at present.

Assuming that the first *Littorina* transgression reached the –2 m level the increase in water depth of Randers fjord and Grund fjord must have amounted to 6–8 m, as the Early Post-glacial peat deposits here are found at levels between –8.5 and –10.5 m. An analogous sudden increase of water depth is reported to have occurred in Præstø fjord in Atlantic time (Mikkelsen 1949, op.cit. Krog 1968). During the maximum transgression (the Middle Atlantic) the *Littorina* sea reached even higher levels. Troels-Smith (1942) thus mentions a level of at least +3 m. During the remaining part of the Post-glacial the sedimentation and land elevation in combination resulted in a decrease of water depth, and today formation of marine sediments takes place only in a rather limited part of the area investigated.

Nutrient conditions: The content of nutrients is only one of several factors influencing the biological activity which might take place in a sedimentary basin. Rawson (1939, according to Stewart and Rohlich 1967) presented a schematic outline concerning the complicated interrelationship which might exist between for example the topography of the source area, the shape, water depth, and the oxygen conditions of the sedimentary basin. The nutrients which normally are believed to be the most important are N and P, but a number of compounds which are normally present in small amounts can be of enormous importance for the biological life. Many authors have tried to quantify the nutrient conditions (trophic state) for fossil sedimentary environments by chemical analysis of the sediments. As a Danish example of this Hansen's (1964 b) method is mentioned. He calculated the trophy for lake sediments using the ratio:

$$\frac{\text{opal} + CaCO_3}{\text{opal} + CaCO_3 + \text{minerogenic matter}}$$

Other authors consider that the nutrient state is better expressed by the content of chlorophyll remains (Sanger and Gorham 1972). Using a modified version of the Hansen (1964 b) method where the sum of biogenic lime + opal is given in percent of the sum $CaCO_3$-norm + insoluble residue (including SiO_2 from diatoms, see p. 24) the nutrient condition for the Randers area has been calculated. The result is shown in table 6 where the pheophytin content (originating from the primary chlorophyll content) is also given. There is no correspondance between the two measures of the trophic state, but this is not surprising: Under the assumption that no rebedding or solution of diatoms, biogenic lime or pheophytin has occurred, the two expressions for the nutrient conditions will be illustrative for the trophy in two different zones, i.e. the pheophytin content representing the trophogene zone (zone of photosynthetic activity), while the biogenic lime + part of the diatom silica formed at the bottom of the sediment basin. The content of nutrients may have been optimum throughout the water column, but as earlier stated the benthonic life was restricted for a certain period because of lack of oxygen in the deepest part of the area. Besides oxygen deficit the presence of toxic compounds released from the euxinic environment might have inhibited benthonic life without influencing the biological production in the upper layers of water. In the shallow parts of the fjord system the oxygen supply seems to have been good, but here secondary processes (rebedding, solution) have disturbed the original sediment to a considerable extent. Therefore measurement of the trophic state is very uncertain. Thus it must be concluded that no reliable measurements of the trophic state can be given based on the chemical parametres determined in this study.

Summary of the development of the sedimentary environment during the Late- and Post-glacial times. The Late-glacial sediments included in this investigation are dominated by fluviatile freshwater deposits transported to the area by the river Gudenå, Allingå, and local creeks. Late-glacial freshwater gyttja formed in a shallow lake has been found at a single locality. Late-glacial marine sediments have not been found in the area. In the Early Post-glacial (the Continental Period) the Randers fjord area was covered by bogs and small freshwater lakes. Occurrences of dead-ice have been present at least until the *Littorina* sea transgressed the deepest parts of Randers fjord. By the *Littorina* transgression rebedding of the Early Post-glacial peat took place in most of the area. The water depth in Randers fjord suddenly increased by 6–8 m (possibly more). During the maximum extension of the *Littorina* sea most of the area investigated was sea covered. Only the area around Klavsholm remained a freshwater environment but the water table in this area seems to have been closely linked to fluctuations in sea level. The river supply of minerogenic and organic material was least during the maximum transgression. Freshwater supplies from the Allingå river caused, as expected, a relatively low salinity in Allingå valley and from here an increase to about 30 ‰ towards the open sea can be noticed. In the Littorina sea tidal fluctuations with an amplitude of abouth 2 m occurred. These caused a total water exchange in the shallow marine areas while euxinic conditions prevailed in the bottom region in the deepest part of the fjords. No satisfactory measurement of the nutrient conditions has been obtained in the present investigation, but it seems that the total content of autochthonous organic matter in the sediment amounts to less than 10% of the total content of organic matter. After the maximum extension of the *Littorina* sea the tidal effect decreased and as a combined effect of isostatic uplift, sedimentation, and overgrowth the sea regressed, and freshwater deposits (gyttja and peat) formed in the area abandoned by the sea. This regression still continues and today a minor part of the original fjords are sea covered.

General outline concerning the changes in a sediment during diagenesis and weathering

A newly formed sediment will normally immediately be subjected to diagenetic transformations. Diagenesis here includes the period from when a particle hits the sediment surface and becomes part of the sediment until the start of metamorphism, or until the sediment is subject to erosion and weathering (Fairbridge 1967, p. 32). The most sensitive parts of the sediment (especially clay and organic matter) might, even before diagenesis starts, have been altered by aquatolytic and halmyrolytic processes (Müller 1967, 140 pp.). According to Fairbridge (1967) the diagenesis can be divided in 3 phases:

> A. Syndiagenesis which occurs at the time of sedimentation and includes the processes in the sediment governed by biological activity.
> B. Anadiagenesis, during with the sediment becomes indurated as a result of physical and chemical influences (compaction, squeezing of pore solutions, cementing etc.)
> C. Epidiagenesis, which includes alterations occuring in the sediment after it has been elevated and brought into contact with groundwater.

If the sediment is raised above the groundwater level the epidiagenesis will be replaced by erosion and weathering, by which for example oxidation of iron sulfides can take place. These three main phases of diagenesis are characterised by the fact that the pore solutions of the sediment lie in different part of a normal Eh/pH diagram (see for example Fairbridge 1967, fig. 1 p. 26).

The syndiagenesis occurs at positive as well as negative Eh-values, and pH between 6 and about 10. The anadiagenesis takes place within roughly the same pH interval as syndiagenesis but the Eh is slightly lower. Epidiagenesis is normally characteristic by an oxidizing, rather acid environment (pH = 4–6). During weathering which might follow epidiagenesis, the pH can decrease to extremly low values (pH = 2–3), while Eh at the same time is high. Assuming that the sediment attained equilibrium under the different conditions to which it was submitted during diagenesis, it might be possible to judge how far the diagenetic development reached, and possibly also which diagenetic phases the sediment has passed through.

As stated above the organic fraction is much more sensitive to diagenetic processes than the inorganic part of the sediment. It has been demonstrated that detailed investigations of the organic matter might give very good illustration of the course of diagenesis (Degens 1967; Prashnowsky 1971). Plant material which, via the peat and the brown coal stage, is transformed first to bituminous coal and then to anthracite has passed the transition between syn- and anadiagenesis when the peat stage is left (biological activity ceases during the peat stage). The anadiagenesis only includes that part of the coalification in which plant remains are visible (the so called "soft brown coal stage"). Normally soft brown coal is found together with lightly consolidated sand and clay which are not yet subject to anadiagenetic alterations. This underlines the suitability of the organic matter as an indicator of especially the early diagenetic conditions. But as mentioned above, the organic and inorganic fractions of the sediment will normally be at different diagenetic stages; it is therefore worth mentioning which sediment fraction the different diagenetic concepts are used on.

In the Randers fjord area the sediment as a whole seems to have been subject to syn- and epidiagenetic influences. It is possible that compaction and squeezing of pore water from the Early Post-glacial peat should be referred to the anadiagenetic stage, but at the inorganic part of this deposit seems unaffected by anadiagenesis it is assumed that no anadiagenetic transformations occurred in the investigated sediments.

A short outline is now given of the syn- and epidiagenetic processes and their traces, which might be recognized in the Randers fjord area by the methods used.

The syndiagenesis includes as earlier mentioned that part of the diagenesis in which biological activity takes place. Normally syndiagenesis is subdivided into an *initial* phase and an *early burial* phase, separated by a zero value for Eh (initial phase $Eh > 0$, early burial $Eh < 0$). The processes of *the initial phase* are at first governed by the chemical composition of the water in which the sedimentation occurs. By continued deposition the sediment will lose its direct contact with the overlying water, and the pore solution will start its own development, regulated by biological processes. Often a certain amount of organic material will be present in the sediment, and throughout syndiagenesis this will strongly influence the reactions in the pore solution. The organic matter serves as a source of nutrients – or energy – for the biological life, the macroscopic as well as the microbiologic life. The benthonic activity occuring in the bottom layer and the uppermost few millimetres or centimetres of sediment might destroy the stratification. For the biological processes the most decomposible organic material with the highest nutrient content will be used first. This leads to a decrease in the N content as compounds rich in nitrogen (for example free amino acids) are normally the most unstable (Degens 1967). The decomposition of the organic matter corresponds to hydrolysis by which NH_4^+ and PO_4^{3-} are lost, and the organic remains are oxidized to H_2O and CO_2 (Richards 1965). The CO_2 formation will contribute to a lowering of the pH level in the pore solution from about 8 (in normal sea water) to 7 or 6.5 (Fairbridge 1967), which makes the solution of lime possible. The NH_4^+ released is unstable when O_2 is present, and by bacterial activity (or by pure chemical reactions) it will be converted to N_2, NO_2^- and NO_3^-. The intensity of the biological activity depends on the amount and nutrient value of the organic material; the rate of sedimentation; the migration rate of the bacteria etc., which cause the decomposition; and on the grain size distribution (Oppenheimer 1960; Bordovskiy 1965; Fenchel 1969). The decomposition of the organic material will use all the oxygen available, and continued decomposition of the organic fraction takes place with NO_3^- and NO_2^- as suppliers of oxygen, thus enabling a continued release of CO_2 and H_2O (Richards 1965). It should here be noticed that Eh is still positive when all the oxygen is used up. Thus Mortimer (1941) mentioned a laboratory experiment where E_7 (i.e. Eh at $pH = 7$) was $+300$ mV to $+200$ mV in a fluid free of oxygen. The transition from positive to negative Eh values occurs normally very abruptly in the sediment, often in only a few mm of sediment ('redox discontinuity layer'). The negative Eh values are mainly buffered by a sulphide-sulphate system (Fenchel and Riedl 1970; Fenchel 1969), while the systems govering the higher Eh values are not known in detail (Fenchel 1969).

The authigenic mineral paragenesis of the initial phase is stable at $Eh > 0$ and pH about 7. Often iron compounds will dominate, and therefore yellow and grey layers, corresponding to the oxides of the initial phase, are often seen in recent sediments, while black sediments, which are in many cases found below the grey layers, take their colour from iron sulphides, and are accordingly formed in the early burial stage (Fenchel and Riedl 1970, p. 259).

The zone of the initial phase of the diagenesis is restricted to the upper part of the sediment, normally to depths ranging from a few millimeters to 30–50 cm (Fairbridge 1967). In extreme cases, for example below the surf zone, it extends to a few metres (Fenchel and Riedl 1970). Sometimes the initial phase is totally omitted, for example in cases where the oxygen supply is unable to reach the sediment surface. In eutrophic lakes and fjord areas bottom stagnations with an annual periodicity are common, and in these cases the initial phase might be rhythmically omitted (often to be seen as alternating layers of light and black sediments). Thus sediments which have been subject to the initial phase of syndiagenesis might be characterized by

lack of layering,
low content of nitrogen,
corroded surfaces of lime shells,

light grey or yellow collours,
an authigenic mineral paragenesis which is stable at positive
Eh and a pH of about 7,

but none of these characteristics can alone be final evidence of reactions in the initial phase. For this a series of negative observations are necessary in addition (H_2S, for example, is not present), or more advanced organochemical investigations which have not been included in the present study.

Early burial. The course of diagenesis during the early burial phase is extremely different from the initial phase. The lack of oxygen enables a series of decomposition processes to occur, causing release of toxic components (for example H_2S) which destroy the possibilities of higher biological life. The active biomass of the early burial stage forms a complex ecological system, exclusively built up of microorganisms (Fenchel and Riedl 1970) which cannot change the sedimentary structures (the layering is preserved), but which greatly influence the chemical composition of the pore solution, its redox-potential and pH. The microorganisms cause, analogously to the initial stage, oxidation of the organic material, using SO_4, NO_3, CO_2, and H_2O as sources of oxygen. The end products are H_2S, NH_3, CH_4, and H_2 (Fenchel and Riedl 1970). The release of these compounds will lead to an increase in pH to more than 9 (Zobell 1942, according to Fairbridge 1967), and Eh will decrease to extremely low values (–400 to –600 mV). If the pH rises to values of about 9, important parts of the sediment will be subject to solution processes (diatoms for example become unstable). Generally the new pH/Eh environment will stabilize a new mineral paragenesis. The sulphate reduction, which is one of the most important processes in the early burial stage, occurs by the action of the bacteria *Desulfovibrio* sp. which is able to start its activity at an Eh value of about + 100 mV (Fenchel and Riedl 1970). In cases where the initial stage is omitted the sulphate reducing bacteria will get a continuous supply of fresh SO_4 from the sea water. If the initial stage is established the SO_4 will be supplied by diffusion through the upper few centimetres of sediment. Thus an accumulation of sulphides will take place, and this is believed to be the most important contribution to the sulphur content of the sediment (Hartmann and Nielsen 1969). When the diffusion contact with sea water ceases (normally below a few centimetres of sediment), the sulphate content will rapidly be used up, and the sulphate reduction replaced by other processes.

As stated on p. 19 the sulphate reduction leads to fractionation of the different sulphur isotopes, so that the content of the heavier ^{34}S isotope is less in H_2S – or in the authigenic minerals formed by H_2S – than in the original sea water sulphate (the sediment sulphur has become "isotopically lighter") (Thode et al. 1961; Ault 1959; Hartmann & Nielsen 1969; Rees 1973). The degree of fractionation depends on many different environmental parameters as for example the redox potential, the rate of sedimentation, and the duration of the diffusion contact to the water rich in sulphate. Thus the ratio of the sulphur isotopes might be a valuable indicator of the changes to which the sediment has been subjected during the early burial phase.

The bacterial metabolism leads to H_2S production which will, in the case of a low concentration of metal ions (for example in calcarous rocks, Hunt 1967) be accumulated, and thereby possibly inhibit continued microbiological transformation. On the other hand, if the content of metal ions is great, as in clayey sediments, H_2S will be combined in some sulphide mineral (normally iron sulphide), and continued sulphate reduction is possible. The newly formed iron sulphide will be converted into hydrotroillite ($FeS_x \cdot (H_2O)_y$) and afterwards to pyrite or marcasite (Galliher 1933; Kaplan, Emery, and Rittenberg 1963). The pH value is assumed to control whether the end product will be pyrite or marcasite. Normally pyrite is believed to be formed in weakly alkaline environments, and especially in clay sediments, while marcasite is found under more sandy, neutral or light-acid conditions (Fairbridge 1967, p. 54). Traces of the early burial stage thus include

no macroscopic fauna (or possibly a special or one-sided fauna),
distinct layering,
smell of H_2S,
content of metal sulphides with a low quantity of ^{34}S.
solution tendency for the diatom content,
an authigenic mineral assemblage stable at negative Eh values and neutral or alkaline conditions.

The changes of the organic fraction during the syndiagenesis includes decomposition of the relatively unstable biochemical macromolecules and condensation of the decomposition products (Degens 1967). During this some of the hydrolysis products will escape from the sediment and return to the biological cyclus (PO_4, NO_3, etc.). During the syndiagenesis the microbiological activity gradually ceases, and the changes of the sediment through the subsequent anadiagenesis takes place by pure physical and chemical reactions leading to induration of the inorganic fraction and maturing of the organic part which will finally turn to either coal or oil.

Epidiagenesis and weathering. If by uplifting the sediment is brought into contact with the groundwater zone, Eh and pH will change, depending on the chemistry of the groundwater. The mineral assemblage will again become unstable, and it must be expected that certain epidiagenetic transformations will occur, leading to an equilibrium between the minerals and the new environment. If the sediment is raised above the groundwater level, the transition between epidiagenesis and *weathering* is passed. The most important changes occurring in the sediment during epidiagenesis and weathering involve the oxidation of the sulphides, which leads to a strong decrease in pH.

Solution tendencies and a mineralparagenesis stable under acid and oxidizing conditions are therefore evidence of epidiagenesis and weathering.

Diagenetic transformations of the Late- and Post-glacial sediments in the Randers fjord area

Syndiagenetic changes. As the total Late- and Post-glacial sequence contains FeS_2, and as about half of the investigated samples contain mixed carbonate, it is concluded that the sediment as a whole has been subjected to syndiagenetic early burial processes where Eh was negative. As FeS_2 is normally present as pyrite, the environment seems to have been neutral or slightly alkaline. Marcasite was found only in a single sample (No. 110) indicating local weakly acidic conditions. Within the central part of the marine Post-glacial sediment in Randers fjord and Grund fjord the initial stage of syndiagenesis seems to have been omitted rhythmically, as well preserved alternating light and bluish-black laminae are found. In the same sequence the biogenic lime content is very low and originates from a benthonic mollusc fauna poor in species. Apart from these special conditions which prevailed in the central part of the marine sequence in Randers fjord, Grund fjord and the lower part of Allingå valley, the sediments generally seem to have been marked by the initial stage: The light burrows in the black Late-glacial gyttja (boring No. 32*), and the rich benthonic mollusc fauna in the marine sediment are the most evident traces of a positive redox potential at the time of deposition. The lime content of the Late-glacial gyttja shows that the environment was alkaline. The fluviatile Late-glacial sediments (clay, silt, sand) and the Early Post-glacial peat deposits formed in shallow water, and it is therefore hardly possible that the initial stage of this part of the sequence was omitted. Before the *Littorina* transgression the Early Post-glacial peat, about 1 m thick, found in boring No. 32* (Virring bay), must have been subject to an aerobic influence as its content of humic acids is high. Its content of pigments from photoautotrophic sulphur bacteria shows that after it was covered by the *Littorina* sea the peat was in an anaerobic, shallow marine environment. The shell material from the molluscs in the marine series sometimes has corroded surfaces, especially when present in sand layers. It is possible that this solution tendency is synsedimentary (i.e. occurs in the initial stage), but it might also be caused by a later (epidiagenetic) supply of acid water through these more permeable layers.

Epidiagenetic changes. From many of the borings carried out in the valley around Gl. Estrup and in Virring bay it appears that in the strongly permeable Late-glacial sand deposit below the marine, clayey sediments more alkaline water without direct contact with the overlying sediments is present. Especially around Gl. Estrup there is sufficient pressure to raise the water about ½ m above the surface through the borehole. The same situation possibly exists in the remaining part of the area. In boring No. 80, for example, Eh is higher in the deepest and most sandy part of the sequence. These water movements, occurring below the groundwater table in the area, might lead to transformations of the sediments which should be considered epidiagenetic.

Transformations of the sediments caused by weathering

The isostatic elevation of the area, combined with the drainage carried out recently, has led to a general drop in the groundwater level, and today large parts of the sequence are situated above the groundwater zone. Around the recent fjords, Randers fjord and Grund fjord, the groundwater table lies about 1 m below surface, while in Allingå valley it is 2–3 m below surface. Within the upper 1–3 m of sediment conditions favourable for weathering processes (Christensen 1962) have therefore been established, and evidence of this is present in most of the area: In boring No. 54* molluscs with lime shells are not present in the uppermost 3 m of the profile, and presumably for the same reason the MnO content is very low in this section. The Na_2O content is low through the whole boring, while K_2O is only low in the upper 2½ m of the core. The iron content does not seem to be influenced by the acid environment. A minor quantity of gypsym, which was found in the boring at a depth of 3 m, indicates that the sulphides are unstable. In boring No. 32* molluscs with lime shells are either totally absent or show marked signs of solution within the uppermost one metre of the profile. As expected the weathering is the least intense in boring No. 80* where the lime has only been removed from the uppermost ½ m of the sequence.

Recent pH and Eh conditions

As expected measurements of pH and Eh showed (fig. 46) that pH is lower in Virring bay (boring No. 82) than in Randers fjord (boring No. 80). This because of the weathering which is, as mentioned, the most prevalent in areas with a low groundwater table. While pH shows only a minor fluctuation through the core from Randers fjord, a pH rise to about 8 is noticed in the lowest part of boring No. 82 from Virring bay. This is considered to result from the water movement which takes place in the more permeable Late-glacial sand substratum. The Eh values are generally highest in the sediments above the groundwater table. In the remaining part of the sequence Eh is roughly the same (around 0 mV), but in the lowest part of boring No. 80 (Randers fjord) an increase to an Eh of about +100 mV occurs. As stated earlier this is taken to indicate that a water course is present in the Late-glacial sand without connection to the pore solutions in the overlying sediments.

Conclusions

This study includes only sediments from the youngest part of the Late-glacial period and the Post-glacial period. Below the Post-glacial sediments Late-glacial outwash sand has been found. The morphology of this sand substratum (plate 1) supports the assumption that the area has been subjected to subglacial erosion. The deep depressions in the sand surface indicate occurrence of dead ice in the Late-glacial outwash period, and other observations show that the dead ice persisted for a long time during Post-glacial time.

During the Early Post-glacial shallow freshwater sediments (peat) were deposited in the area. The areal distribution and the depth of the peat (fig. 23) show that the Early Post-glacial groundwater level was about –10 m in Randers fjord and Grund fjord and a little higher in the remaining part of the area.

During Atlantic time the investigated area, which received freshwater supplies from the rivers Allingå and Gudenå during the Late- and Post-glacial period, was transgressed by the *Littorina* sea. The Early Post-glacial peat deposits were rebedded during this event. The *Littorina* sea seems to have transgressed the main part of the area very abruptly, the water depth suddenly increasing by at least 6–8 m in the deepest parts. Later on during the Atlantic the *Littorina* sea reached its maximum extension, and at the same time it attained its maximum salinity presumably because the tidal movements

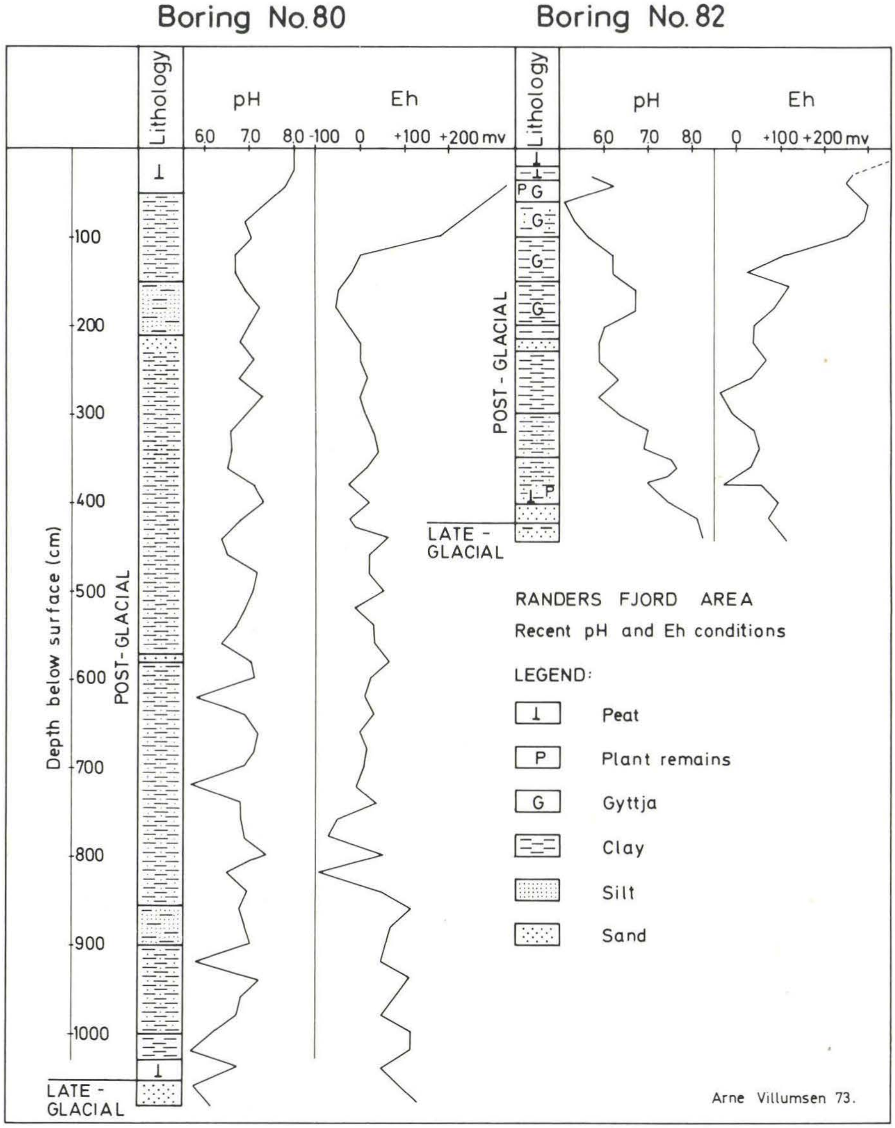


Fig. 45.

were rather strong. The difference between the high and low tide is estimated at 2 m. Shortly after the *Littorina* transgression a great sand barrier was built up across the valley north of Ugelhuse (plate 1) which seems to have restricted the exchange of water between the open sea and the Randers fjord area when the *Littorina* sea had its maximum extension. The oxygen supply to the bottom water in the area was therefore insufficient for a normal benthonic fauna despite the rather strong tidal movements. As expected the freshwater supply from the rivers caused a decrease in the salinity of the inner parts of the fjords. Furthermore, the two main rivers were of great importance for the transportation of allochthonous material to the sedimentary basin. Different investigations of the content of organic matter have proved that allochthonous organic material forms the main part of the organic fraction. Corresponding to the maximum extension of the *Littorina* sea the supply of allochthonous material was at a minimum. The tidal effect and the salinity decreased shortly after the main transgression, and subsequently because of isostatic uplift of the area and the continued sedimentation the sea regressed towards the recent Randers fjord. After this regression, Post-glacial freshwater sediments extended to still larger parts of the area.

Generally, the sequence seems to have been subject to processes of the syndiagenetic initial stage as well as the early burial stage. In the deepest parts of the fjord system where lack of oxygen periodically prevailed, the initial phase seems to have been omitted rhythmically. In the Late-glacial gyttja light burrows were found in the otherwise black gyttja, which presumably shows that the initial and early burial stages occurred side by side. The sediments seem unaffected by anadiagenetic reactions. Different observations show that weathering processes which are still occurring in the area have resulted in solution of molluscs with lime shells from the youngest parts of the sediments. The very permeable Late-glacial sand deposits seem to have water flowing through them, locally under considerable pressure, which has no direct connection to the pore fluid of the overlying sediments. As this water movement occurs below the groundwater table, transformations of the sediments should be considered epidiagenetic. However, during this study it has not been possible to demonstrate with certainty any results of such an epidiagenetic influence.

Acknowledgements

It is a great pleasure for me to express my gratitude to the many individuals and institutions who have supported and inspired this study. Special thanks are directed to Professor Dr. Phil. *Gunnar Larsen,* Århus University, to State Geologists Dr. Phil. *Helge Gry* and *Werner Christensen*, Geological Survey of Denmark, who supervised the investigations. To colleagues and staff at the Geological Institute, Århus University, and at the Geological Survey of

Denmark thanks are given for assistance and guidance during field work and laboratory work, for typing the manuscript, and for the drawings. I especially would like to thank Senior Geologist *Henning Kristiansen,* Geological Survey of Denmark, who assisted in the description of the methods, Cand. Scient. *Bent Aaby* for the pollenanalytical work, and the staff of the Geochemical Department of the Geological Survey for the chemical analyses. Further more thanks are offered to Professor, Dr. Phil. *Tom Fenchel,* Århus, for many inspiring discussions concerning the pigment content, to Dr. *Jens Arne Pedersen,* Århus, for the ESR measurements, to Stud. Scient. *Bjørn Buchardt*, Copenhagen, for the C-isotope analyses, to Civil Engineers *E. Larsen* and *E. Sørensen,* Risø, for the S-isotope measurements and to Professor, Dr. Phil. *M. Køie,* Copenhagen, for the Rb-determinations.

Geoelectric investigations

Holger Lykke Andersen

Purpose and methods of the investigations

In connection with sedimentological and geochemical investigations in the Randers fjord area, geoelectric investigations have been carried out with the primary intention of obtaining information on the sedimentary sequence in the area. To attempt to map the boundary between the Late- and Post-glacial deposits was of particular significance, but deeper boundaries were also of interest.

Geoelectric methods have been used previously in Denmark to investigate similar problems. These earlier attempts have shown that there are problems associated with this type of application of geoelectric techniques. These problems are partly associated with insufficient knowledge of the specific resistivity of the sediments, and partly with theoretical difficulties of the method in determing the depths of boundaries and the specific resistivity of layers.

With the present investigation, emphasis has been laid on drawing attention to the problems attendant to the method. An attempt is made to describe the relationship between specific resistivity and other properties of the sediment, and to clarify the limitations of the methods in connection with typical sedimentary succession in the area. This analysis of these considerable problems is far from being complete, but the results can serve as a complement to previously published experiences (Dinesen 1961; Klitten 1972) related to the possibilities and limitations of geoelectric methods in connection with the mapping of Post-glacial basins.

As the major aim of the investigation was to describe the lithological variation with depth in the Randers fjord area, electric soundings were carried out. A total of 161 electric soundings were made using a Schlumberger electrode configuration (see for example Kunetz 1966) with a constant potential electrode distance of 0.5 m and a maximum current electrode distance (L/2) of 100 m.

The soundings were arranged in as regular a network as possible using the existing roads. The localities are shown in plates 2 and 3.

The measurements were carried out using direct current equipment constructed by N. Breiner and O. Larsen of the Geophysical Laboratory, Aarhus

University. The field measurements were carried out by Ole Houmøller, Torben Søgaard Jensen, Jens Bach Jepsen, Knud Pedersen, and John Tychsen between March and June, 1972.

Electric resistivity af Post-glacial sediments

General review

Knowledge of the specific electric resistivity of the sediments being studied is a vitally important factor in trying to carry out geological interpretations of electric soundings. Without this information it is impossible to decide which of the many theoretically possible models should be selected. Normally the mathematical interpretation of the soundings can neither definitely fix the thickness nor the specific resistivity of the individual horizons. One of the conditions to be able to make a reasonable estimate of the thickness of a layer is that its specific resistivity is known as precisely as possible.

Several different methods have been used to try to obtain values of specific resistivity for the sediments in the Randers fjord area.

a. Measurement with a roughly 2 m long probe in principle constructed in the same way as a lateral probe for borehole measurements (Lynch 1962; Andersen 1974). With this probe it is possible to determine the specific resistivity in situ for soft sediments, such as Post-glacial clay and mud.

   Measurements with this probe have been carried out at the bottom of canals and ditches in the area around Randers fjord. The determined values are for sediments which lie under the groundwater table.

b. Measurements on cores from the type borings Nos. 32* and 80* described in the previous chapters, and also on cores from investigation borings by the Århus District Road Authority, between Kristrup and Dronningborg (borings Nos. V 1–3, see plate 2).

   These measurements were carried out immediately after the arrival of the sealed cores at the laboratory. The principles involved in the determinations are similar to those earlier described for sand samples (Andersen 1974).

c. It has sometimes been possible to obtain average values for sediments directly on the basis of the electric soundings in those places where the soundings could be correlated with existing borings.

   This method has especially been used in connection with Quaternary (glacial) and Pre-quaternary sediments.

d. With the intention of estimating the possible variation within the sand sediments, the specific resistivity of the groundwater in the area has been

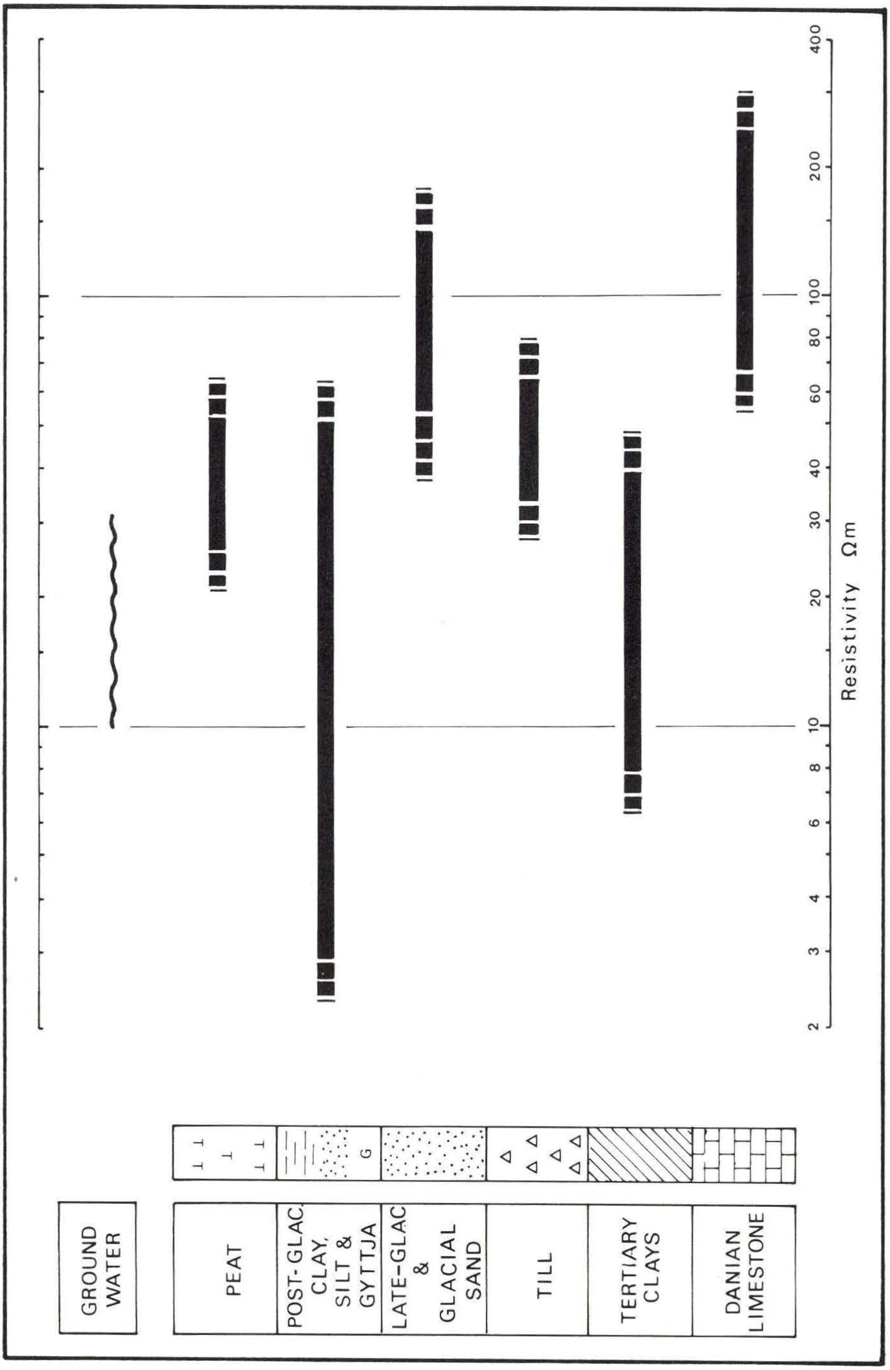


Fig. 47. Summary of specific resistivity values for some characteristic sediments from the Randers fjord area.

determined. Calculations based on chemical analyses from water borings in the area have been carried out following Andersen (1974) and the sand sediment's specific resistivity has been estimated using Archie's equation (Archie 1942) assuming the formation factor to be about 3–5.

The results of the determinations of specific resistivity are summarised in fig. 47 in which the length of the columns represents the range of values for each sediment type. This does not mean that individual cases cannot be found in which the values for a sediment fall outside the presented intervals, especially for the four lowest groups in fig. 47 for which the number of determinations is relatively low.

The main reason for the large range of specific resistivity for the sand sediments is the considerable variation in the resistivity of the groundwater (about 10–30 ohmm at 8°C). The variation given for the Danian limestone is an estimate and the spread can similarly mainly be referred to the resistivity of the groundwater.

Because of uncertainty relating to the stratigraphic placing of the Tertiary clays in the borings, they are grouped together, though it is known that the lowest values come from borings in Eocene clay.

Fig. 47 clearly demonstrates that none of the presented sediment groups can immediately be identified by its specific resistivity. Apart from Post-glacial clay and gyttje with very low resistivity and Danian limestone with very high values, many of the sediments overlap each other, especially in the region between about 25 and 50 ohmm.

This naturally complicates the geological interpretation of the electric soundings. Sometimes the problem is reduced when it is possible to judge the depth at which a particular specific resistivity occurs and thereby estimate its stratigraphic position.

Investigation of cores

There were two purposes for the investigation of the specific resistivity in the cores. Firstly to illustrate how the specific resistivity varies with depth for the Post-glacial sediments and at the boundary between Late- and Post-glacial sediments in order to investigate to what extent the specific resistivity can be used to indicate the sedimentary sequence. Secondly to determine any relationship between lithology and specific resistivity for more detailed interpretation of the electric soundings.

The results from the measurements of cores from borings Nos. 32* and 80* are shown in figs. 48 and 49 together with the lithology of the stratigraphic succession. It is apparent that the two borings show rather different

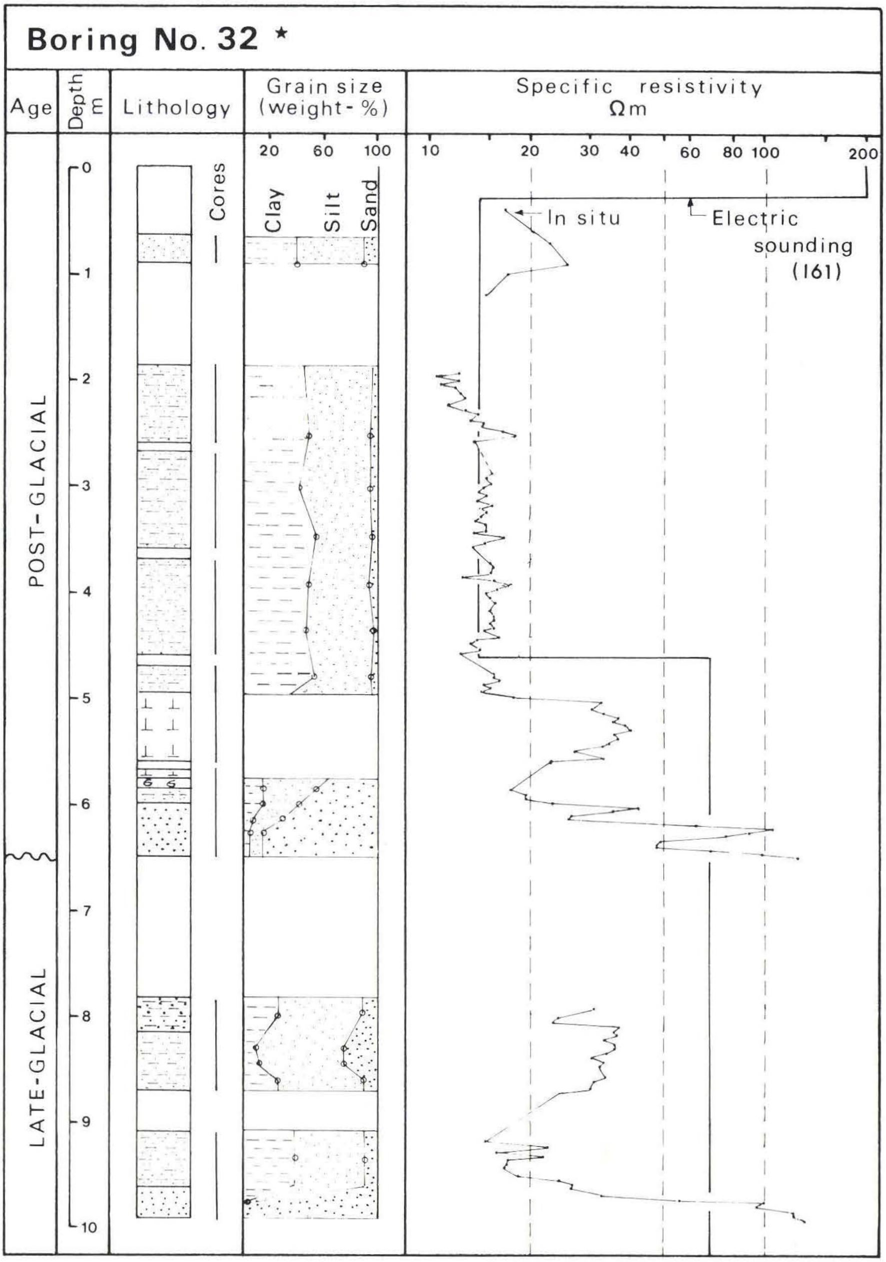

Boring No. 32 *
Age
Depth m
Lithology
Grain size (weight-%)
Specific resistivity Ωm
0
1
2
3
4
5
6
7
8
9
10
POST-GLACIAL
LATE-GLACIAL
Cores
20
60
100
Clay
Silt
Sand
10
20
30
40
60
80
100
200
In situ
Electric sounding (161)

Fig. 48.

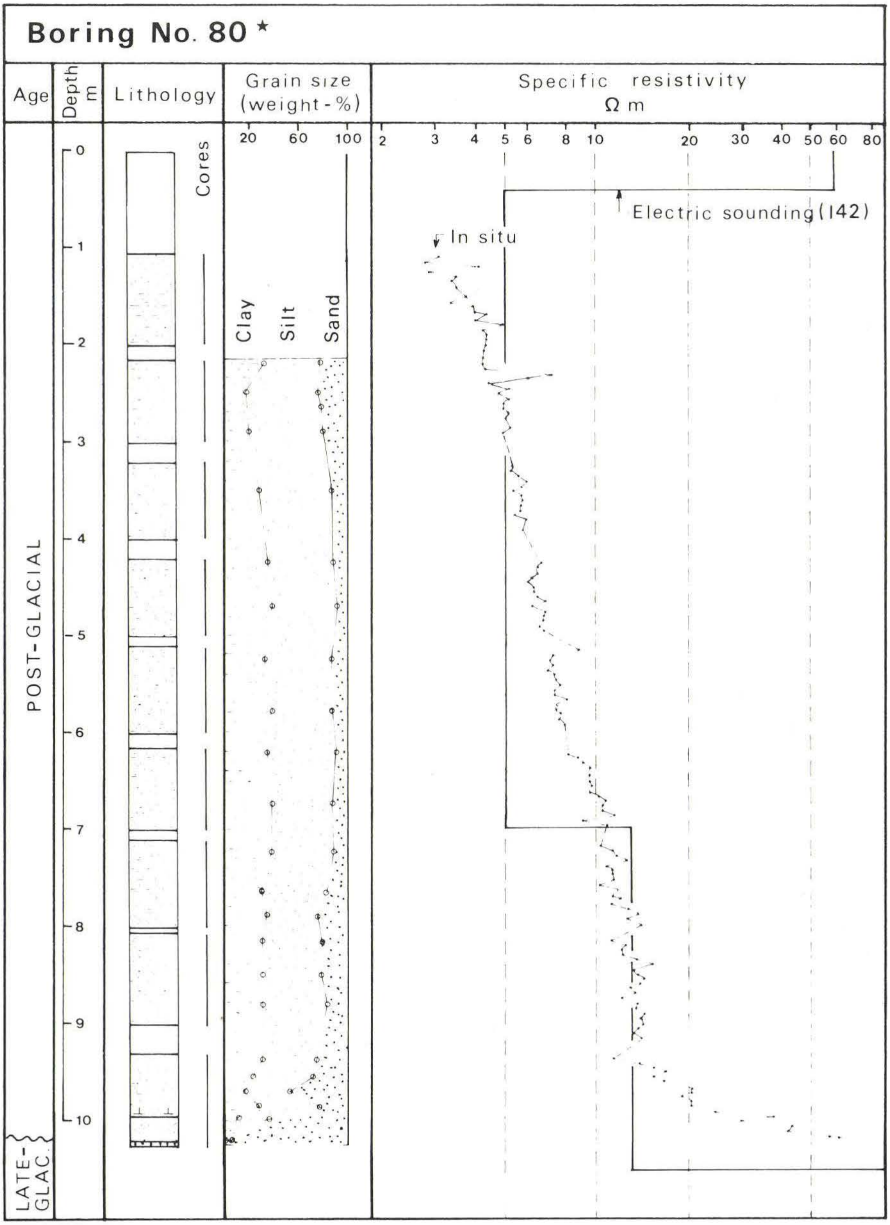

Boring No. 80 *
Age
Depth m
Lithology
Grain size (weight-%)
Specific resistivity
Ω m
20 60 100
2 3 4 5 6 8 10 20 30 40 50 60 80
0 1 2 3 4 5 6 7 8 9 10
Cores
Electric sounding (142)
In situ
Clay
Silt
Sand
POST-GLACIAL
LATE-GLAC.

Fig. 49.

trends. Both however show an increase in specific resistivity in the vicinity of the boundary between Late- and Post-glacial deposits.

Relationship between lithology and specific resistivity. Within the Post-glacial sediments, boring 32* shows little variation except where related to peat horizons. In boring 80* the specific resistivity gradually rises with depth and the resistivity in the upper part is much lower than in boring 32*. It is not until the base of the Post-glacial clay sediments in boring 80* are reached that the values are equivalent to those in the clay deposits in boring 32*.

With the intention of showing an expected relationship between clay content and specific resistivity, grain size analyses have been carried out at reasonable intervals in the clastic parts of borings 32* and 80*. The distributions, in weight percent of clay, silt and sand fractions are shown in figs. 48 and 49. As shown in fig. 50 there is a fairly simple relationship which can be closely compared with Archie's equation (Archie 1942).

Hill and Milburn (1956) have shown that ion concentration of the pore water is significant for the effect of clay on the specific resistivity of a sediment. The ion concentration of the pore water is not known here and therefore the determined relationship can only be of local significance, despite the occurrence of similar relationships elsewhere (Andersen 1974).

Boring 80* shows no apparent relationship between clay content and specific resistivity. This can be seen in fig. 49 which shows rather constant grain size distribution throughout the Post-glacial sequence, while the specific resistivity increases with depth.

The explanation for this probably lies in the variation of the ion concentration in the pore water through the sediments. While carrying out the borings it was noted that at this locality the pressure of the pore water in the Late-glacial sand was more than a meter above ground level (−0.4 m). An upward flow of pore water is therefore possible and since the ion concentration of the pore water in the Late-glacial sand is relatively low (as indicated by the electric soundings) it is reasonable to assume that the pore water of the Post-glacial material is being flushed out from below. The low specific resistivity at the top of the sequence is interpreted as expressing the marine environment with relatively high ion concentration in the pore water.

Relationship between specific resistivity and electric soundings. Variations in resistivity have been derived from electric soundings carried out near the two borings as shown in figs. 48 and 49, together with the actual trends.

There are two features of general significance which are expressed in figs. 48 and 49:

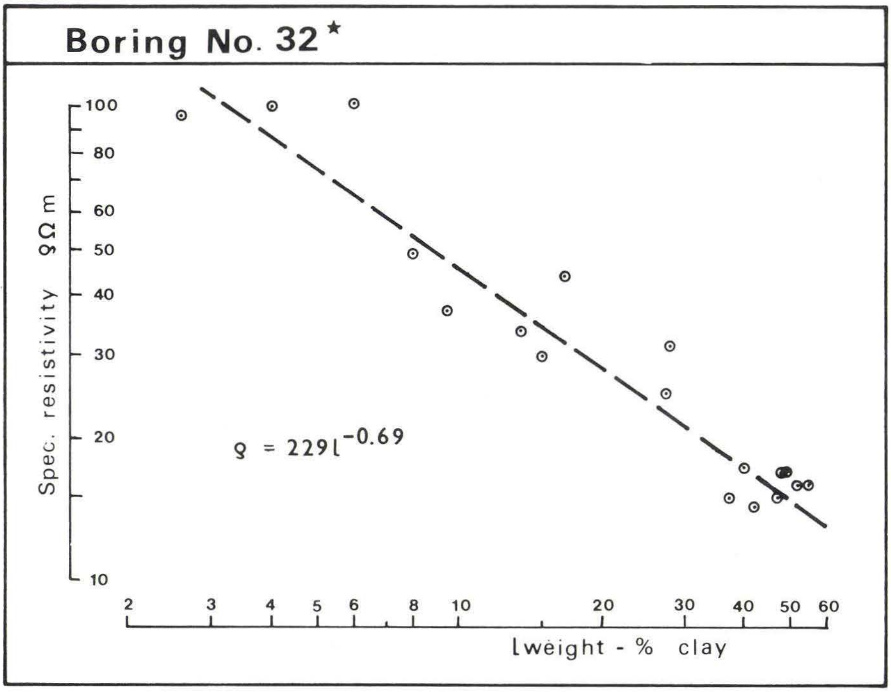


Fig. 50. Specific resistivity as a function of clay content in Late- and Post-glacial sediments in boring 32* from Virring bay.

a. gradual change in resistivity is very badly reproduced by the electric sounding. It is represented by a series of relatively thick homogeneous layers (boring 80*, 1–10 m).
b. a layer, which is thin in comparison with its depth below surface, is not represented in the electric sounding (boring 32*, 5.5–6 m and 9–9.5 m).

This last point infers uncertainty in the determination of the location of the boundary between Post- and Late-glacial sediments. While this boundary appears to be accurately represented in sounding 142 at boring 80* where the Post-glacial sequence is homogeneous, there is a considerable discrepancy in sounding 161 at boring 32* because of a peat layer in the lowest part of the Post-glacial sediments.

Relationship between organic content and specific resistivity. The manner in which organic material effects the specific resistivity of sediments, such as those developed here, is virtually unknown. In connection with borings carried out by the Århus Council Road Authority in the western part of

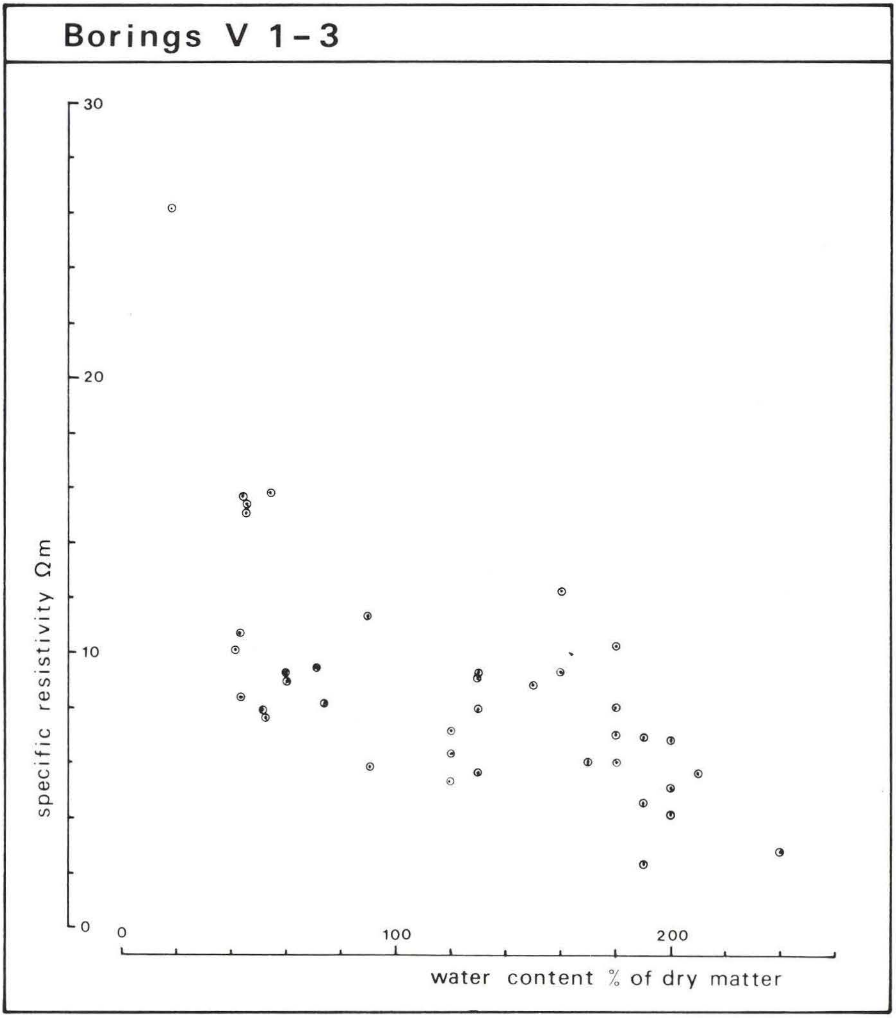


Fig. 51. Specific resistivity as a function of water content in Late- and Post-glacial sediments in three borings (V 1–3) between Kristrup and Dronningborg (see plate 2).

Randers fjord (V 1–3, in plate 2) it has been possible to compare the specific resistivity of the samples of Post-glacial sediments with their water content and their loss on ignition as determined on a routine basis in Århus Council Road Authority's laboratory.

No relationship between specific resistivity and loss on ignition was apparent. However, the water content of the material seems to be related to the resistivity, but as shown in fig. 51 there is a considerable spread in the data. This is probably because of the dependance of the specific resistivity of the sediments on other factors which are unknown.

Interpretation of electric soundings

General

As a rule the interpretation takes place in two separate steps. The first is purely mathematical and consists of the conversion ϱ_a (L/2) → ϱ (Z) in order to derive the true specific resistivity of the layers (ϱ), as a function of depth (Z), from the apparent specific resistivity (ϱ_a) measured as a function of the half distance (L/2) between the current electrodes.

The second step is a geological evaluation of the true specific resistivity for the layers.

An "indirect" method has been used for the first step in which the measured soundings are compared with theoretically calculated model curves. This has been based on the calculation procedure originally used by Ghosh (1971) and further developed by H. K. Johansen of the Laboratory of Geophysics, Århus. Use of this method means that calculations of model curves for an arbitrary number of homogenous and horizontal layers can be completed in a very short time.

A system of programs has been established based on this calculation procedure which makes it possible to calculate model curves and comparisons with measured soundings using a display terminal, here linked to a CDC 6400 computer at Aarhus University's Computing Centre (Johansen 1975).

The procedure starts with the display of the required sounding. Then one attempts to estimate a sequence of layers that correspond to the sounding. The proposed layer thicknesses and specific resistivities are then input to the computer which immediately calculates the appropriate model curve. This is then displayed in such a way that it can be compared with the measured values.

If there is an unacceptable difference between the measured and calculated curves, corrected values are input for one or more of the layers and/or maybe the number of layers is altered. The corrected model curve is calculated and displayed, the process being repeated until a satisfactory agreement is obtained (I, table 7 p. 120).

It has been found that using this procedure it can often be difficult to arrive at an acceptable model within a reasonable time. The most rational

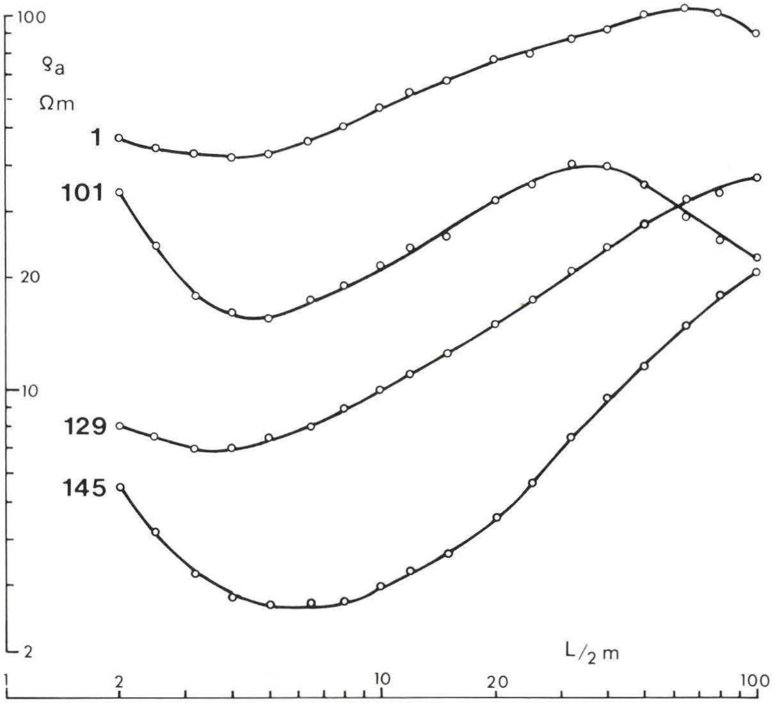


Fig. 52. Characteristic sounding curves for the Randers area.

procedure is to make the first estimate by means of the traditional method using an atlas with two- and three-layer master curves, combined with auxilliary curves (Deppermann et al. 1961).

When a reasonably good agreement has been reached between the measured and calculated curves, an automatic process of fine adjustment of the layer parameters takes place. This is done using a calculation method and computer program also developed by Johansen (1976). In addition to fine adjustment, extreme values of layer thickness and specific resistivity are calculated for each layer in the model (II in table 7, p. 120).

Characteristic soundings and their properties

Most of the electric soundings can be represented by the type of curves shown in fig. 52. The left part of the curves corresponds to layers which lie above the groundwater table. The location of this part of the curve depends

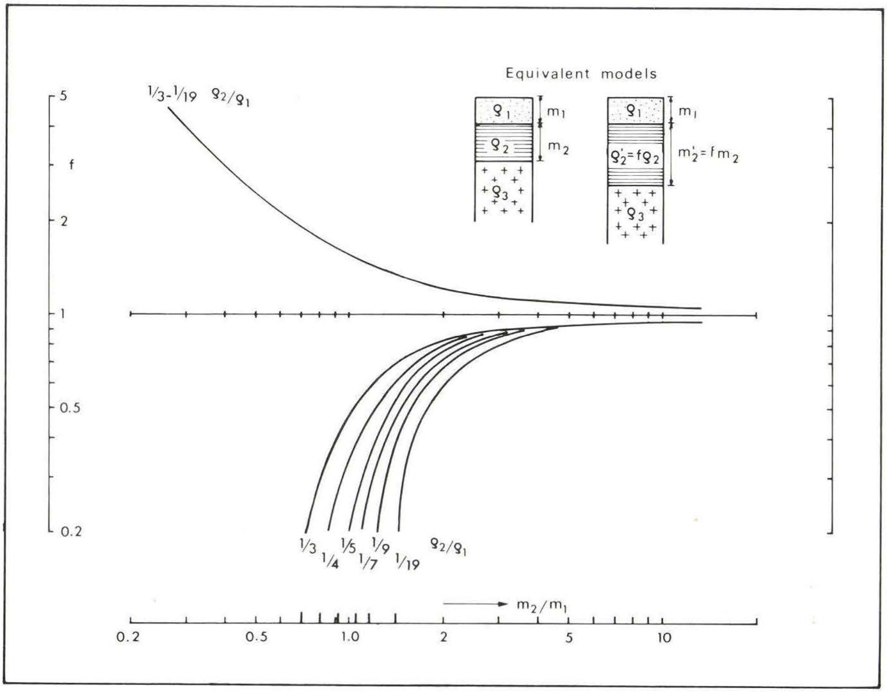


Fig. 53. Range of validity of the principle of equivalence for minimum curves.

on the height above sea level and the lithology of the uppermost layers. The size of the curve's minimum varies with the thickness and character of the Post-glacial sediments.

The most extreme minimum has been measured in the area around Randers fjord, while minima are less or totally lacking in other parts of the valley system. There can be a maximum towards the right hand end of the curves if there is Tertiary clay with low specific resistivity or saline groundwater under the Quaternary sediments (sounding No. 101 in fig. 52). The curves can end with increasing values, because the Quaternary is sandy and thick or because it is underlain directly by Danian limestone with fresh groundwater (sounding No. 145 in fig. 52).

The main interest has been concentrated on the minimum of the sounding curves since these are related to Late- and Post-glacial sediments.

Principle of equivalence. According to the principle of equivalance (see for example Keller and Frischknecht 1966) it is not possible with certainty to determine both thickness (m_2) and specific resistivity (ϱ_2) for a layer which occurs as a minimum on an electric sounding curve.

Only the value m_2/ϱ_2 can be determined with confidence. This shortcoming in the properties of a minimum curve is however here especially related to situations in which the Post-glacial sediments below the groundwater table are thin compared to the thickness of the overlying layers.

This uncertainty associated with the principle of equivalence has been investigated and the results are presented in fig. 53. The problem has been looked at for sequences with three layers with specific resistivity $\varrho_1 > \varrho_2 < \varrho_3 = \infty$ and thickness m_1, m_2, $m_3 = \infty$. A sequence of model curves were calculated in series characterised by definite values of m_2/ϱ_2. For selected values of ϱ_2/ϱ_1 within each series (shown as curve parameters in fig. 53) the amount of change in ϱ_2/ϱ_1 which brought about variation of ± 5 % in the specific resistivity was investigated.

As ± 5 % is that uncertainty which is traditionally associated with the apparent specific resistivity in an electric sounding, the change found in this way expresses the uncertainty which is associated with ϱ_2 and m_2.

On the ordinate the curves in fig. 53 give the factor f which is a measure of the uncertainty with which m_2/m_1 and ϱ_2/ϱ_1 can be determined from sounding curves corresponding to sequences with m_2/m_1 as given on the abscisse and ϱ_2/ϱ_1 given as curve parameters.

As can be seen from fig. 53, the greatest uncertainty is associated with small relative thicknesses of the second layer (m_2/m_1) and for a small relative values of specific resistivity of the second layer (ϱ_2/ϱ_1). In a large part of the Randers fjord area the ratio m_2/m_1 (that is the thickness of the marine Post-glacial sediments below the groundwater table divided by the depth to the groundwater table) is greater than about four or five which means that the uncertainty in the determination of the thickness and specific resistivity can be expected to be rather small (see also table 7, p. 120).

Principle of suppression. Boring 80* indicates that the Post-glacial section is most often composed of what, from a specific resistivity view point can be considered as two layers as the lowest part has a relatively high resistivity. Characteristically its value is greater than that of the layer above, less than that of the underlying sediments. This sequence of specific resistivity values gives rise to considerable difficulties in the determination of the thickness and specific resistivity of ther intermediate layer, or in its identification at all.

Fig. 54 illustrates the nature of this problem. The basis for fig. 54 is a series of four-layer model curves which are compared with three-layer model curves. Taking into consideration that the four-layer curves have a ± 5 % uncertainty, the four-layer model curves, which are identical with the three-layer model curves are found, as shown in fig. 54.

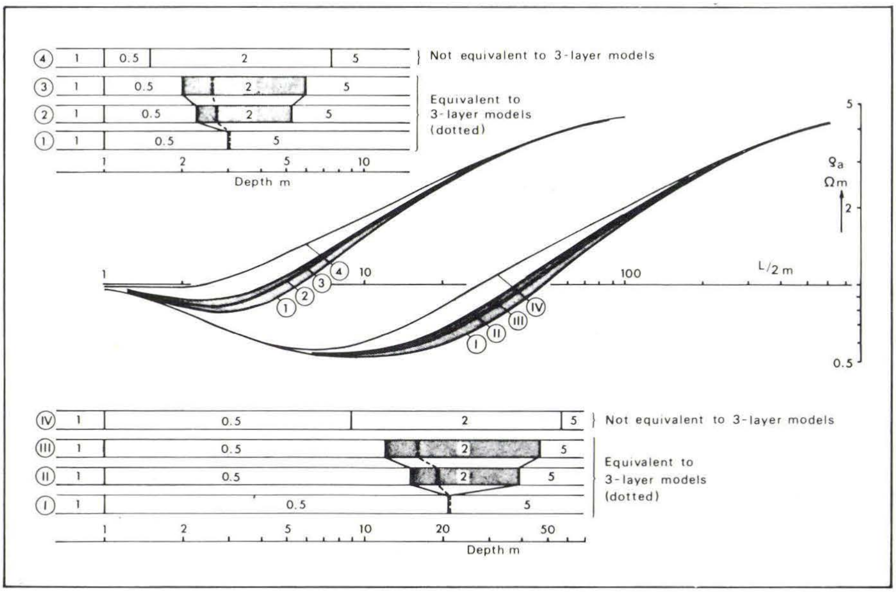


Fig. 54. Range of validity of the principle of suppression for some characteristic sequences.

For the selected, rather characteristic resistivity ratio and the selected uncertainty, the following apply:

a. The intermediate layer (third layer in the model) is only recognised as a separate layer when its thickness is about twice that of the total overlying (critical thickness is equal to about two). For lower values of specific resistivity for the second layer, other factors being constant, the critical thickness for the intermediate layer is greater than two.
b. If the intermediate layer is less than about 0.8 times the thickness of the total overlying layers, the following relationship holds:

$$\frac{m_2{}^4}{\varrho_2{}^4} + \frac{m_3{}^4}{\varrho_3{}^4} = \frac{m_2{}^3}{\varrho_2{}^3}$$

where m_i^j = thickness of the i-th layer in a j-layer model

ϱ_i^j = specific resistivity of the i-th layer in a j-layer model.

For lower values of specific resistivity for the second layer, the same relation holds for thickness of the third layer greater than 0.8. This relation generally means that, within certain limits, it is possible to estimate the thickness of an intermediate layer using three-layer model curves.

Within the Randers fjord area the thickness of a possible intermediate layer is generally less than the critical thickness. This means that an intermediate layer can only be included in the interpretation when there is other independent evidence for its existence, as for example from boring 80*.

Interpretation procedure

As shown above, the electric sounding method cannot normallly provide unequivocal information as to the number of layers, their thickness or specific resistivity.

A subjective estimate, based on independent geological information, therefore plays an important part in arriving at a final geological interpretation.

In this investigation the main problem has been to arrive at an estimate or to the existence of, and specific resistivity for, possible intermediate layers in the lower part of the Post-glacial deposits. On the other hand, the principle of equivalence has also given some problems with the determination of the thickness of Post-glacial sediments with low specific resistivity.

Even within the Randers fjord area, where there are a considerable number of borings, it has by no means always been possible to arrive at a reliable estimate as to the nature of the sedimentary sequence. It has therefore been necessary to define a general rule after which the interpretation should be carried out. The following general rule has been applied:

Variations in both number of layers and the specific resistivity are made as small as possible, of course in such a way that no obvious conflict with information from boreholes in the area arises. This "conservative principle" means that information as to facies variation which may be included in the electric soundings are suppressed to a minimum.

In practice the procedure has been thus:

a. The first models obtained from the automatic procedure (II in table 7, p. 120) are drawn in profiles together with the existing borehole information.
b. The specific resistivity of the different layers is selected using the abovementioned rule, being kept within the calculated extreme values.
c. Final fine adjustment are carried out where the specific resistivity is fixed for as many layers as possible (III in table 7, p. 120). Then the final profile can be drawn using those layer parameters that give the best fit (see plate 5).

Results and conclusions

Pre-quaternary deposits

An excellent presentation of the Pre-quarternary geology of the Randers fjord area has been prepared by Sorgenfrei (1954), including an elevation map for the surface of the Danian limestone. Schrøder (1974) later presented an elevation map for the surface of the Tertiary.

The electric soundings carried out in connection with the present study can to some extent supplement the picture already obtained concerning the location of the Danian limestone surface and occurrence of Paleocene and Eocene clays (plate 4).

As can be seen in fig. 47 the Danian limestone occurs with a higher specific resistivity than the other sediments in the area. This means that it is sometimes possible to estimate the depth to the surface of the Danian limestone as for example in the eastern part of the investigated area.

The Tertiary clays are represented by a wide range of specific resistivities. Paleocene sediments with relatively high values cannot be distinguished from, for example till. On the other hand, Eocene clays with relatively low values can be distinguished from the Quaternary deposits with which they are most likely in contact, namely till and glacial sand. However, it must be pointed out that Eocene clay could be confused with other types of sediment which contain saline groundwater.

Therefore, the electric soundings can only be expected to provide very limited information as to the Tertiary clays which, according to Sorgenfrei (1954), can be expected to occur in the Randers fjord region.

Only in a small area, near Neder Romalt, are there indications from the electric soundings which suggest the presence of Eocene clays.

Similarly, the soundings only sporadically indicate the presence of Paleocene clay, though its presence can often not be excluded.

The distribution pattern shown in plate 4 is therefore somewhat uncertain for the Paleocene clay.

When Tertiary clays are shown as absent in the central area around Randers fjord, it is because those indications which could be interpreted as Paleocene clay present such a disjointed picture that it seems more reasonable to refer it to Quaternary deposits.

As can be seen in plate 4 the surface of the Tertiary deposits is essentially conformable with the ground surface. The marine Late- and Post-glacial deposits are thus located in areas where Tertiary limestone and clays are particularly deep. As demonstrated by Sorgenfrei (1954) the occurrence of Eocene and Paleocene clay in the area around Randers fjord, and depressions in the Danian surface, are tectonically controlled by sinking in connection with the rise of salt structures at Gassum and Voldum.

It seems appropriate to point out that valley development has been emphasised by erosion which has probably removed most of the Tertiary clay sequence.

Post-glacial deposits

The main aim of the geoelectric investigation was to attempt to describe the thickness relationships and variations in lithology of the Post-glacial deposits of the Randers fjord area. The results are presented in map form in plates 2 and 3. The map in plate 2 shows the main trends in elevation of what is called a "high resistivity substratum". The reason for this neutral term is that it is apparent that there is not necessarily a coincidence between the stratigraphic boundary Late-/Post-glacial and the break in resistivity values determined with the electric soundings.

Comparison of this map with the elevation map for the "Late-glacial sand surface" (plate 1) constructed on the basis of borings shows an acceptable agreement in the part of the valley system south of Gl. Estrup, while in the rest of the area there is a tendency for the "high-resistivity substratum" to be deeper than the boundary found from the borings. This lack of agreement may be related to erroneous interpretations related to the existence of an intermediate layer which, due to the principle of suppression, could not be recognised in the electrical soundings.

It could be that the depth found by borings, because of the equipment used, is only the depth to the first recorded sand layer which could be so thin that it does not register on the electric soundings.

It cannot be excluded that clay and gytje horizons may occur below the elevations shown in plate 1.

Since the map plate 2 is based on an interpretation, it would be meaningless to discuss the uncertainty of the elevations given.

The map in plate 3 presents the main trends of variation of specific resistivity for the Post-glacial sediments. The lowest specific resistivity for the Post-glacial deposits has been chosen, partly because its value has been relatively well determined and partly because it appears that this value expresses some essential properties of the Post-glacial deposits.

The variations expressed in plate 3 are largely related to two factors – lithological and pore water properties. It is not possible with the available material at the present time to determine the relative importance of these two factors. Information from boring 80* indicates that the ion concentration of the pore water plays a considerable role in the area around Randers fjord.

With the intention of supporting this indication, measurements of specific resistivity have been carried out on water in canals and ditches throughout the area. The measurements were carried out in the autumn of 1975 after a long period with low rainfall, so that the groundwater contribution would be relatively large.

The determinations revealed considerable variation within the area around Randers fjord. Low values (10 ohmm) occurred around the fjord and high values (about 20 ohmm) at the margins of the area. In the rest of the area, that is south of Gl. Estrup, the values were more constant (about 20 ohmm). With this in mind, the map in plate 3 should be interpreted differently in the area around Randers fjord and the area south of Gl. Estrup. In the Randers fjord-part of the area the map would appear essentially to show variations in the salinity of the groundwater, with relatively saline groundwater in a zone stretching along, and mostly north of, Randers fjord.

A small offshoot exists to the southwest near Holmen (north of Assentoft), and an area between Allingåbro and Ørsted. Comparison with plates 1 and 2 shows that these areas to some extent relate to regions with large thicknesses of Post-glacial sediments. This coincidence can indicate that the saline groundwater has not yet been completely washed out, as known from boring 80*, but there may also be a relatively clay-rich facies developed in these areas.

South of Gl. Estrup it is believed that the specific resistivities shown in plate 3 largely reflect lithological variations in the Post-glacial sediments.

Acknowledgements

Economic support for the geoelectric investigations was provided by the Geological Survey of Denmark and the Laboratories for Exogene Geology and Geophysics of Aarhus University.

I would like to thank the students and colleagues from the Geophysical Laboratory who have helped with the fieldwork, often under difficult weather and road conditions.

It has only been possible to carry out the necessary calculations because of the advanced system of programs developed by *H. K. Johansen*.

Århus Council Road Authority kindly allowed me to examine core material from between Kristrup and Dronningborg. Special gratitude is extended to *Vagn Lerskov* who helped me to examine this material.

I would like to thank Mrs. *J. Gerdel* for drawing the figures so expertly, Mr. *R. Wilson* for translating and Mrs. *E. Moltke Nielsen* for typing the manuscript.

Dansk sammendrag

Sen- og post-glaciale sedimenter i Randers fjord området. Geokemiske, sedimentologiske og geoelektriske undersøgelser

De geokemiske og sedimentologiske undersøgelser af Randers fjord områdets aflejringer har sigtet på at beskrive sedimenternes dannelsesforhold og deres diagenese. Undersøgelsen er arealmæssigt begrænset til det område, der er dækket af post-glaciale dannelser (fig. 1). Gennem en dybdekartering foretaget med mosebor er påvist tilstedeværelsen af en 10–15 m mægtig lagserie, hvoraf hovedparten er marint ler, gytje og silt. På basis af resultaterne fra dybdekarteringen udvalgtes 3 typelokaliteter, hvorfra der optoges intakte sedimentkerner til laboratoriebearbejdelse. De kemiske metoder, der hertil har været benyttet, er beskrevet, og deres anvendelighed er indgående diskuteret.

Den gennemborede lagserie (se fig. 19) underlejres af en sandaflejring, som anses stort set for at være af sen-glacial alder. Sandets overflademorfologi (tavle 1) støtter en tidligere fremsat teori (A. Jessen 1918) om at dele af dalsystemet har været udsat for subglacial erosion, og at dødis har spillet en rolle for bevarelsen af det ujævne relief. Andre observationer (se fig. 35) tyder på at dødis lokalt har været tilstede i området, i hvert fald indtil *Littorina*-havet transgredierede området.

Områdets sen-glaciale sedimenter består overvejende af smeltevandssand. I et enkelt tilfælde (boring 32*) fandtes ferskvandsgytje (yngre dryas) afsat i en lavvandet sø. Sen-glaciale, marine sedimenter er ikke påvist. Ved en række boringer fandtes over sandet tynde tørvelag, som antagelig dannedes tidligt i post-glacialtiden (fastlandstiden). Tørveforekomsternes dybdebeliggenhed (fig. 23) anvendes som grundlag for en bedømmelse af beliggenheden af fastlandstidens grundvandsspejl og med dette som udgangspunkt fremsættes betragtninger vedrørende havspejlets niveau udenfor undersøgelsesområdet. Hovedparten af undersøgelsesområdet dækkedes i atlantisk tid af *Littorina*-havet. Det ser ud til at vanddybden i de dybeste dele af Randers fjord og Grund fjord herunder hurtigt er øget med 6–8 m. Senere i atlantisk tid nåede havet sin maksimale udbredelse og havde samtidig sin højeste saltholdighed, antagelig fordi tidevandsbevægelserne i *Littorina*-havet var ret kraftige. Det anslås at forskellen mellem ebbe og flod inden for området har været af størrelsesorden 2 m. Ferskvandstilførslerne til området har, som man måtte vente, bevirket at saltholdigheden i de inderste fjordarme var lavest. Samtidig har områdets to største vandløb, Gudenåen og Allingåen, haft stor betydning for tilførslen af alloktont materiale, som udgør en væsentlig del af de marine aflejringer.

Formentlig ret tidligt i atlantisk tid opbyggedes en sandtærskel tværs over dalstrøget nord for Ugelhuse (tavle 1), som tilsyneladende har været stærkt medvirkende til at hindre en fri vandudveksling mellem Randers fjord området og det åbne hav, mens *Littorina*-havets udbredelse var størst. Iltforsyningen til bunden af dele af fjordsystemet har i perioder været utilstrækkelig for en normal bundfauna, til trods for at tidevandsbevægelserne på denne tid som nævnt har været betydelige.

Det vises, at den post-glaciale marine lagserie generelt må opfattes som bestående af 3 enheder, der er indbyrdes forskellige, såvel kemisk som strukturelt. Ved at kombinere typeboringernes udsagn om de marine lags beskaffenhed med resultaterne fra dybdekarteringen er der foretaget en lithologisk provinsinddeling af undersøgelsesområdet (fig. 45). – Næringsforholdene i sedimentationsmiljøet er søgt belyst, dels ved en modificeret udgave af Hansens (1964 a) metode, dels ved en angivelse af sedimenternes pheophytinindhold, men nogen endelig afklaring af næringssituationen synes dog ikke at kunne fremlægges. Efter dannelsen af de marine sedimenter har området gennemløbet en ferskvandsfase. Ferskvandssedimenterne svarende hertil er kun i mindre grad undersøgt i denne sammenhæng. – Omtalen af lagseriens diagenetiske forhold støttes i det væsentlige på Fairbridges (1967) model for diagenesen, suppleret med nyere informationer fra litteraturen. Kun syndiagenetiske påvirkninger kan tydeligt spores i det undersøgte materiale. Epidiagenetiske ændringer synes stedvis at kunne foregå i øjeblikket. Områdets forvitringstilstand og den nuværende pH og Eh situation er illustreret ved fig. 46. Målingerne indicerer, at der i det sen-glaciale sandunderlag forekommer en vandtype, der ikke har nogen forbindelse med den overliggende lerseries porevæske.

I fortsættelse af de sedimentologiske og geokemiske undersøgelser er der gennemført en geoelektrisk undersøgelse i Randers fjord området. Der er udført 161 elektriske sonderinger med schlumberger elektrode konfiguration. Lokaliseringen fremgår af tavle 2 og 3.

Med henblik på fortolkningen af de elektriske sondringer er det forsøgt at belyse eventuelle sammenhænge mellem sedimenternes lithologiske egenskaber og deres specifikke modstand. I Virring bugt har der i typeboring 32* kunnet påvises en simpel sammenhæng, som vist på fig. 50. I området omkring Randers fjord synes en anden faktor at spille en væsentlig rolle for den specifikke modstand, nemlig grundvandets varierende saltholdighed.

Ved undersøgelser af boringer i den vestligste del af Randers fjord, antydes der en vis indvirkning på den specifikke modstand af sedimenternes vandindhold (fig. 51).

Ved den matematiske fortolkning af de elektriske sonderinger er der benyttet et regneprogram-system, som i de seneste år er udviklet ved Laboratoriet for Geofysik ved Århus Universitet af H. K. Johansen. Systemet gør det muligt at foretage fortolkningen efter den indirekte metode ved interaktiv benyttelse af en grafisk skærmterminal, som i dette tilfælde er tilkoblet en CDC 6400 computer på Århus Universitets Regnecenter (RECAU). Systemet kan endvidere foretage automatisk finjustering af lagparametre, således at jordmodellen bringes til bedst opnåelige overensstemmelse med den målte elektriske sondering. Endelig beregnes ekstremværdierne for lagparametrene. Den praktiske fremgangsmåde ved benyttelse af dette fortolkningssystem beskrives.

Forhold, som kan henføres til det såkaldte ækvivalensprincip og især til det såkaldte suppressionsprincip medfører alvorlige begrænsninger for anvendelsen af den elektriske sonderingsmetode i områder med en geologisk opbygning som i Randers fjord området. Virkningen af disse principper er nærmere undersøgt (fig. 53 og 54).

Den geologiske fortolkning af de elektriske sonderinger har hentet værdifuld støtte i informationer fra de mange boringer i området. Fortolkningen er iøvrigt gennemført efter det overordnede princip, at variationerne fra sondering til sondering i såvel lagantal som specifik modstand for de enkelte lag er gjort mindst mulig.

Som resultat af undersøgelsen er der fremstillet kort over beliggenheden af "underlag med høj specifik modstand" (tavle 2), som anses for at være den bedst opnåelige beskrivelse af grænsen mellem sen- og post-glaciale aflejringer. Desuden er der konstrueret et kort som illustrerer variationer i de postglaciale aflejringers specifikke modstand (tavle 3). Endelig har materialet givet anledning til fremstilling af et kort over Danienkalkens overflade og udbredelsen af Tertiære lerarter (plate 4).

	Sample No.	Insoluble residue + SiO_2 %	Al_2O_3 %	Fe_2O_3 %	P_2O_5 %	CaO %	MgO %	MnO %	Na_2O %	K_2O %	Loss on ignition %	Total	Total minerogenic matter %
Boring 32*	RA 4	58.2	4.6	4.6	0.13	8.6	1.5	0.070	0.20	0.84	18.2	96.94	62
	– 9	66.1	4.3	4.8	0.13	5.5	1.6	0.074	0.15	0.86	12.9	96.41	59
	– 17	60.5	5.3	5.8	0.12	7.2	1.7	0.11	0.14	0.94	16.7	98.51	63
	– 19	60.0	4.4	6.2	0.11	5.3	1.5	0.12	0.11	0.87	17.6	96.21	64
	– 21	2.5	1.0	3.6	0.13	4.1	0.68	0.086	0.12	0.10	86.5	98.82	3
	– 23	4.6	0.11	5.1	0.13	4.8	0.72	0.077	0.12	0.12	83.6	99.38	5
	– 29	95.2	2.0	0.53	0.046	0.80	0.18	0.008	0.04	0.10	1.4	100.31	96
	– 32	77.7	3.7	1.6	0.083	7.5	0.59	0.043	0.11	0.29	8.6	100.21	90
	– 41	49.1	3.0	3.6	0.095	20.2	1.0	0.12	0.19	0.44	20.6	98.35	–
Boring 54*	– 43	76.5	3.7	6.2	0.18	0.62	0.45	0.035	0.04	0.15	9.1	96.98	60
	– 45	49.7	4.4	5.3	0.073	1.8	0.93	0.026	0.07	0.55	34.6	97.45	43
	– 49	55.9	3.8	7.3	0.11	1.5	1.0	0.042	0.08	0.67	31.0	101.40	45
	– 51	61.2	3.7	5.7	0.10	3.1	0.78	0.088	0.08	0.53	23.0	98.28	52
	– 55	48.4	3.3	7.6	0.10	3.9	0.77	0.12	0.08	0.46	34.5	99.23	49
	– 56	66.5	1.7	3.3	0.075	3.7	0.37	0.023	0.06	0.21	22.5	98.44	69
	– 61	68.6	1.2	2.8	0.059	2.9	0.32	0.014	0.09	0.19	20.5	96.67	71
	– 63	91.7	0.83	0.84	0.039	1.5	0.11	0.006	0.04	0.07	2.9	98.04	93
Boring 80*	– 64	70.8	1.8	5.0	0.15	2.3	0.41	0.14	0.14	0.31	15.7	96.75	–
	– 68	60.7	2.6	5.5	0.12	6.6	1.2	0.20	0.53	0.60	17.6	95.65	–
	– 69	57.2	2.2	3.3	0.12	14.2	1.0	0.086	0.49	0.49	14.7	93.79	65
	– 71	73.3	1.9	2.4	0.096	8.3	0.98	0.18	0.35	0.47	8.8	96.69	76
	– 75	72.3	4.2	4.1	0.14	3.7	1.9	0.080	0.30	0.89	9.8	97.41	73
	– 78	69.7	4.6	4.5	0.14	4.4	1.9	0.083	0.32	0.95	10.9	97.49	72
	– 80	65.6	4.0	4.6	0.15	5.6	1.7	0.11	0.34	0.84	13.1	96.04	68
	– 83	68.6	4.6	4.8	0.15	4.0	1.9	0.10	0.28	0.97	12.0	97.40	70
	– 86	69.1	4.3	4.5	0.14	4.0	1.8	0.097	0.27	0.92	12.5	97.64	61
	– 90	66.7	4.8	5.0	0.15	4.6	1.8	0.12	0.26	1.0	12.6	97.03	67
	– 97	69.0	4.6	4.5	0.14	4.7	1.7	0.11	0.23	0.96	11.2	97.14	73
	– 99	68.4	3.2	4.3	0.11	8.1	1.3	0.094	0.26	0.69	11.4	97.85	79
	– 104	66.2	3.6	4.2	0.11	7.8	1.4	0.18	0.21	0.75	12.6	97.05	76
	– 110	63.2	3.7	5.1	0.11	7.3	1.4	0.21	0.20	0.77	14.1	96.09	71
	– 114	55.3	2.6	7.2	0.10	8.0	0.98	0.88	0.18	0.51	18.8	94.55	65
	– 118	64.9	1.4	5.7	0.22	2.3	0.39	0.29	0.11	0.17	27.8	103.28	64

Table 1. Chemical analysis (aqua regia treatment). The last column shows the calculated content of total minerogenic matter (= (insoluble residue + SiO_2) – (opal-SiO_2) + ($CaCO_3$-norm) – (biogenous lime)).

	Sample No.	ΣFe (Fe_2O_3 %)	Total S %	Calculated FeS_2-norm %	Residue Fe_2O_3 %	Residue S %	Elementary S %	SO_4-S %	$\delta^{34}S$ ‰
Boring 32*	4	4.6	2.08	3.9	2.0				– 34
	9	4.8	1.90	3.6	2.4				– 20
	17	5.8	2.62	4.9	2.5				– 38
	19	6.2	3.01	5.6	2.5		0.4	0.14	– 34
	21	3.6	3.36	5.4		0.5			– 41
	23	5.1	4.54	7.7		0.5	2.2	0.04	– 10
	29	0.5	0.075	0.1	0.5				– 16
	32	1.6	0.11	0.2	1.5				
	41	3.6	0.88	1.7	2.5		0.4	0.08	– 38*
Boring 54*	43	6.2	0.18	0.3	6.0				
	45	5.3	2.85	5.3	1.8				– 17
	49	7.3	3.93	7.4	2.4		0.9	0.76	– 29
	51	5.7	3.50	6.6	1.3				– 29
	55	7.6	4.63	8.7	1.8				– 15
	56	3.3	1.97	3.7	0.8				– 15
	61	2.8	1.55	2.9	0.9				– 16
	63	0.8	0.45	0.8	0.3				
Boring 80*	64	5.0	0.91	1.7	3.9				
	68	5.5	3.38	6.3	1.3			0.28	– 14
	69	3.3	1.82	3.4	1.0				
	71	2.4	0.81	1.5	1.4				– 31
	75	4.1	1.31	2.5	2.4				– 14*
	78	4.5	1.63	3.1	2.4				
	80	4.6	1.88	3.5	2.3				– 7
	83	4.8	1.51	2.8	2.9				– 13
	86	4.5	1.56	2.9	2.6		0.6	0.07	– 2*
	90	5.0	1.87	3.5	2.7				– 13
	97	4.5	1.21	2.3	3.0				– 12
	99	4.3	1.05	2.0	3.0				
	104	4.2	1.56	2.9	2.3				
	110	5.1	2.17	4.1	2.4				– 23
	114	7.2	4.50	8.4	1.6				
	118	5.7	1.23	2.3	4.2				– 10

Table 2. Norm-calculation of FeS_2, based on the content of acid soluble Fe (expressed as Fe_2O_3) and the total S content. The contents of elementary S, SO_4-S, and $\delta^{34}S$ values are shown ('*' indicates a higher degree of uncertainty on the measurement).

					Extinction (× 10^{-2}) at λ = 662.5 nm		
	Sample No.	Organic C %	Total N %	C/N	pr. g dry matter	pr. g org. C	$\delta^{13}C$‰
Boring 32*	RA 4	4.90	0.52–0.52	9	4.4	90	
	– 9	3.25	0.31–0.31	11	4.5	138	
	– 17	4.28	0.40	11	2.4	56	
	– 19	4.93	0.43	11	2.1	22	
	– 21	49.13	3.0 –2.9	17	2.0	4	
	– 23	45.12	3.3 –3.4	14	3.2	7	
	– 29	0.29			1.0	345	
	– 32	0.46	0.070	7	1.0	217	
	– 41	0.97	0.13	7	1.0	103	
Boring 54*	– 43	2.28	0.21	11	1.0	44	
	– 45	15.93	1.1	15	1.3	8	
	– 49	13.01	0.78	17	2.5	19	
	– 51	8.94	0.93	10	3.6	40	
	– 55	15.10	0.96	16	2.4	16	
	– 56	9.74	0.55	18	1.5	15	
	– 61	8.22	0.49	17	1.7	21	
	– 63	0.74	0.070	11	0.9	122	
Boring 80*	– 64	6.14	0.58	11	1.7	28	
	– 68	3.09	0.46	7	3.6	117	– 29.93
	– 69	2.22	0.30	7	3.5	158	
	– 71	0.88	0.15	6	1.6	182	– 27.79
	– 75	1.87	0.23	8	2.6	139	
	– 78	1.82	0.28	7	2.2	121	
	– 80	3.01	0.29	10	2.1	70	
	– 83	2.14	0.26	8	2.5	117	– 20.64
	– 86	2.78	0.32	9	2.1	76	
	– 90	2.36	0.29	8	3.0	127	
	– 97	1.96	0.25	8	2.2	112	
	– 99	1.38	0.18–0.17	8	3.6	261	
	– 104	1.47	0.18–0.18	8	2.2	150	
	– 110	2.26	0.24–0.25	9	1.8	80	– 36.74
	– 114	5.14	0.46	11	2.3	45	– 27.15
	– 118	11.96	0.86	14	2.7	23	

Table 3. The contents of organic carbon and total nitrogen. Based on these the C/N ratio is calculated. The extinction measurement shown gives a semiquantitative expression of the chlorophyll content. The carbon isotope ratios are shown to the right of the table.

	Sample No.	CaO %	CO_2 %	Calculated $CaCO_3$-norm %	Residue CaO %	Residue CO_2 %	+ = mixed carbonate mineral present
Boring 32*	4	8.6	6.51	14.8	0.3		+
	9	5.5	3.89	8.8	0.6		+
	17	7.2	5.39	12.2	0.4		+
	19	5.3	3.96	9.0	0.3		
	21	4.1	0.22	0.5	3.8		
	23	4.8	0.37	0.8	4.4		
	29	0.8	0.44	1.0	0.2		
	32	7.5	6.23	13.4		0.3	+
	41	20.2	15.86	36.0	0	0	+
Boring 54*	43	0.6	0.16	0.4	0.4		
	45	1.8	0.13	0.3	1.6		
	49	1.5	0.34	0.8	1.0		
	51	3.1	1.14	2.6	1.6		
	55	3.9	1.32	3.0	2.2		
	56	3.7	1.85	4.2	1.4		
	61	2.9	1.24	2.8	1.3		
	63	1.5	0.68	1.5	0.7		
Boring 80*	64	2.3	0.55	1.2	1.7		
	68	6.6	6.71	11.8		1.5	+
	69	14.2	9.67	22.0	1.9		+
	71	8.3	5.68	12.9	1.1		+
	75	3.7	3.28	6.6		0.4	
	78	4.4	3.56	8.1	0	0	+
	80	5.6	3.92	8.9	0.6		+
	83	4.0	3.57	7.1		0.5	+
	86	4.0	3.54	7.1		0.4	+
	90	4.6	3.89	8.2		0.3	+
	97	4.7	4.02	8.4		0.3	
	99	8.1	7.52	14.5		1.1	+
	104	7.8	7.11	13.9		1.0	+
	110	7.3	7.01	13.0		1.3	+
	114	8.0	7.08	14.3		0.8	+
	118	2.3	1.72	3.9	0.1		

Table 4. Norm-calculation of $CaCO_3$, based on the content of acid soluble Ca (expressed as CaO) and the content of carbonate-CO_2. In the last column the presence of a mixed carbonate mineral (Mn, Fe, Mg, Ca, $-CO_3$) is indicated by '+'. (This mineral gives an X-ray peak at d = 2.88–2.89 Å).

	Sample No.	Pb ppm	V ppm	Cr ppm	Cu ppm	Zn ppm	Rb ppm	Li ppm
Boring 32*	4	14	80	40	26	92	66	29
	9	18	50	48	25	90	68	28
	17	23	70	52	25	93	74	31
	19	25	100	37	28	110	46	28
	21	7.5	10	5	10	59	5	1
	23	2.4	10	5	12	160	7	2
	29	4.4	20	9	7	30	8	3
	32	9.8	40	17	15	72	20	9
	41	7.4	100	22	21	96	33	17
Boring 54*	43	6.8	70	39	16	150	13	13
	45	9.4	70	46	35	110	51	28
	49	6.0	50	39	20	96	57	28
	51	3.6	60	38	25	120	48	22
	55	2.1	60	31	34	150	41	20
	56	2.0	50	15	21	110	16	9
	61	1.9	20	11	20	89	14	8
	63	1.2	<10	5	7	48	5	2
Boring 80*	64	13	40	22	22	88	21	8
	68	6.3	70	25	27	80	40	19
	69	5.9	60	22	22	66	36	14
	71	6.2	50	19	11	43	32	15
	75	8.3	90	49	30	80	69	30
	78	17	90	50	25	77	75	32
	80	12	80	44	32	150	66	26
	83	11	100	55	24	100	76	31
	86	26	90	51	27	110	72	32
	90	26	100	55	24	87	77	35
	97	10	100	56	44	200	69	31
	97	10	90	55	24	120	67	32
	99	6.4	90	34	17	110	50	22
	104	6.9	80	33	19	130	48	23
	104	6.9	80	42	19	120	49	22
	110		80	34	23	69	54	24
	114		90	17	310	120	36	17
	118		40	17	15	70	10	6

Table 5. The samples content of trace elements.

	Sample No.	Insoluble residue + SiO_2 + $CaCO_3$-norm %	Biogenic lime + opal %	Trophy %	Pheophytin ppm
Boring 32*	4	73.0	11.4	16	88
	9	74.9	15.6	21	90
	17	72.9	10.1	14	48
	19	69.0			42
	21	3.0	0.5	17	40
	23	5.4			64
	29	96.2			20
	32	91.1	1.0	1.1	20
	41	85.1			20
Boring 54*	43	76.9	17.0	22	20
	45	50.0	7.3	15	26
	49	56.7	12.7	22	50
	51	63.8	11.4	18	72
	55	51.4	2.4	4.7	48
	56	70.7	1.6	2.3	30
	61	71.4	tr	tr	34
	63	93.2			18
Boring 80*	64	72.0	21.2^{+}	29^{+}	34
	68	72.5	31.6^{+}	44^{+}	72
	69	79.2	14.1	18	70
	71	86.2			32
	75	78.9			52
	78	77.8	5.7	7.3	44
	80	74.5	6.9	9.3	42
	83	75.7	5.8	7.6	50
	86	76.2			42
	90	74.9	7.8	10	60
	97	77.4	4.7	6.1	44
	99	82.9			72
	104	80.1	4.6	5.7	44
	110	76.2	5.2	6.8	36
	114	69.6	4.8	6.9	46
	118	68.8			54

Table 6. Comparison between trophic state calculated as (biogenic lime + opal) in per cent of (insoluble residue + SiO_2 + $CaCO_3$-norm) and the sediments content of pheophytin. Values marked by '+' are abnormally high because the samples contain shell-breccia.

		I	II			III		
layer No.	x)	first estimate	best fit	min.	max.	best fit	min.	max.
1	ϱ_1	35	29	25	37	30	fixed	
	m_1	2	1	0.8	1.2	1	1	1.1
2	ϱ_2	13	12	10	13	10	fixed	
	m_2	6	4	3	5	3	3.2	3.7
3	ϱ_3	30	24	19	33	30	fixed	
	m_3	5	9	7	14	11	10	13
4	ϱ_4	120	135	100	197	100	fixed	
	m_4	25	30	14	53	50	41	66
5	ϱ_5	50	31	16	51	30	fixed	

x) ϱ = resistivity in ohm
m = thickness in m

Table 7. Three steps of the interpretation of electric soundings. I: first estimate obtained on graphic display. II: 1st automatic calculated best fit and extreme parameters. III: 2nd automatic calculated best fit with some parameters fixed.

References

Andersen, H. L. 1974: Kortlægning af undergrunden i omegnen syd og vest for Århus. – Århus, Laboratory for Geophysics, pp. 58–101.

Andersen, S. T. & Gundersen, K. 1955: Ether soluble Pigments in Inter-glacial Gyttja. – Experientia, 11 (9), pp. 345–353.

Archie, G. E. 1942: The electrical resistivity log as an aid in determining some reservoir characteristics. – Trans. A.I.M.E., 146, pp. 54–62.

Arrhenius, G. 1950: Carbon and nitrogen in subaquatic sediments. – Geochim. cosmochim. Acta, 1, pp. 15–21.

Ault, W. U. 1959: Isotopic Fractionation of Sulfur in Geochemical Processes. – *In*: Abelson, P. H. (editor) Researches in Geochemistry, pp. 241–259. – New York: John Wiley & Sons, Inc.

Bader, R. G. 1954: The role of organic matter in determining the distribution of pelecypods in marine sediments. – J. mar. Res., 13, pp. 32–47.

Bader, R. G. 1956: The lignin fraction of marine sediments. – Deep-Sea Res., 4, pp. 15–22.

Bader, R. G., Hood, D. W. & Smith, J. B. 1960: Recovery of dissolved organic matter in sea-water and organic sorption by particulate material. – Geochim. cosmochim. Acta, 19, pp. 236–243.

Bahnson, H. 1968: Kolorimetriske bestemmelser af humificeringstal i højmosetørv fra Fuglsø Mose på Djursland. – Meddr dansk geol. Foren., 18, pp. 56–64.

Baker, W. E. 1973: The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization. – Geochim. cosmochim. Acta, 37, pp. 269–281.

Bordovskiy, O. K. 1965: Accumulation and transformation of organic substances in marine sediments. – Mar. Geol., 3, pp. 3–114.

Brown, F. S., Baedecker, M. J., Nissenbaum, A., and Kaplan, I. R. 1972: Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia – III. Changes in organic constituents of sediment. – Geochim. cosmochim. Acta, 36, pp. 1185–1203.

Cheshire, M. V. & Cranwell, P. A. 1972: Electron-spin resonance of humic acids from cultivated soils. – J. Soil Sci., 23, pp. 424–430.

Christensen, W. 1962: Betragtninger over den geokemiske udvikling i de øvre jordlag i Danmark. – Meddr dansk geol. Foren., 15, pp. 112–122.

Craig, H. 1953: The geochemistry of the stable carbon isotopes. – Geochim. cosmochim. Acta, 3, pp. 53–92.

Degens, E. T. 1967: Diagenesis of organic matter. – *In*: Larsen, G. & Chilingar, G. V. (editors) Developments in Sedimentology, 8, pp. 343–390. – Amsterdam: Elsevier.

Deppermann, K. et al. 1961: Die geoelektrischen Verfahren der angewandten Geophysik. – *In*: Bentz, A. (editor) Lehrbuch der Angewandten Geologie, 1, pp. 718–770. – Stuttgart: Ferdinand Enke.

Dinesen, B. 1962: Geoelektrisk kortlægning af Limfjordsengene ved Vester Hassing. – Danm. Geol. Unders. III. række, 35, 63p.

Fairbridge, R. W. 1967: Phases of diagenesis and authigenesis. – *In*: Larsen, G. & Chilingar, G. V. (editors) Developments in Sedimentology, 8, pp. 19–89. – Amsterdam: Elsevier.

Fenchel, T. 1969: The ecology of marine microbenthos. – IV. Structure and function of the benthic eco-system, its chemical and physical factors and the microfauna communities with special reference to the ciliated protozoa. – Ophelia, 6, pp. 1–182.

Fenchel, T. & Riedl, R. J. 1970: The Sulfide System. – Mar. Biol., 7, pp. 255–268.

Fenchel, T. & Straarup, B. J. 1971: Vertical distribution of photosynthetic pigments and the penetration of light in marine sediments. – Oikos, 22, pp. 172–182.

Francis, W. 1961: Coal. (2nd ed.). – New York: Arnold. 816 p.

Galliher, E. W. 1933: The Sulphur Cycle in Sediments. – J. sedim. Petrol., 3, pp. 51–63.

Ghosh, D. P. 1971: The Application of Linear Filter Theory to the Direct Interpretation of Geoelectrical Resistivity Sounding Measurements. – Geophysical Prospecting, 19, pp. 192–217.

Hansen, K. 1959: The Terms Gyttja and Dy. – Hydrobiologia, 13, pp. 309–315.

Hansen, K. 1962: The Dystrophic Lake Type. – Hydrobiologia, 19, pp. 183–191.

Hansen, K. 1964a: The Post-glacial development of Grane Langsø. – Meddr dansk geol. Foren., 15, pp. 446–458.

Hansen, K. 1964b: Oversigt over danske Søsedimenter. – Meddr dansk geol. Foren., 15, pp. 428–430.

Harder, P. 1908: En østjydsk Israndslinie og dens Indflydelse på Vandløbene. – Danm. geol. Unders. II række, 19, 262 p.

Hartmann, M. 1964: Zur Geochemie von Mangan und Eisen in der Ostsee. – Meyniana, 14, pp. 3–20.

Hartmann, M. & Nielsen, H. 1969: $\delta^{34}S$ – Werte in rezenten Meeres-sedimenten und ihre Deutung am Beispiel einiger Sedimentprofile aus der westlichen Ostsee. – Geol. Rdsch., 58, pp. 621–655.

Hill, H. J. & Milburn, J. D. 1956: Effect of clay and Water Salinity on Electrochemical Behaviour of Reservoir Rocks. – Trans A.I.M.E., 207, pp. 65–72.

Hillebrand, W. F. et al. 1955: Applied Inorganic Analysis. (2nd ed.). – New York: John Wiley & Sons, Inc. 1034 p.

Hunt, J. M. 1967: The Origin of Petroleum in Carbonate Rocks. – *In*: Chilingar, G. V., Bissell, H. J., and Fairbridge, R. W. (editors) Development in Sedimentology, 9B, pp. 225–251. – Amsterdam: Elsevier.

Iversen, J. 1937: Undersøgelser over Litorinatransgressioner i Danmark (Foreløbig Meddelelse). – Meddr dansk geol. Foren., 9, pp. 223–232.

Iversen, J. 1973: The Development of Denmarks Nature since the Last Glacial (Ed.: S. T. Andersen). – Danm. geol. Unders., V række nr. 7 – c, 126 p.

Jessen, A. 1918: Udstrækningen af Randers Fjord i Litorinatiden. – *In*: Johansen, A. C. (ed.) Randers Fjords Naturhistorie, pp. 11–19. – København: Reitzel.

Jessen, A. 1920: Stenalderhavets Udbredelse i det nordlige Jylland. – Danm. geol. Unders., II række, 35, 112 p.

Jessen, K. 1918: Bidrag til Vegetationens Historie i Randers Fjord-Dal. – *In*: Johansen, A. C. (ed.) Randers Fjords Naturhistorie, pp. 21–43. – København: Reitzel.

Johansen, A. C. 1918: Randers Fjords Naturhistorie. – København: Reitzel. 520 p.

Johansen, H. K. 1975: An Interactive Computer/Graphic-Display-Terminal System for Interpretation of Resistivity Soundings. – Geophysical Prospecting, 23, pp 449–458.

Johansen, H. K. 1976: A man/computer interpretation system for resistivity soundings over a horizontally stratified earth. – Geophysical Prospecting (in press).

Kaplan, I. R., Emery, K. O. & Rittenberg, S. C. 1963: The distribution and isotopic abundance of sulphur in recent marine sediments off southern California. – Geochim. cosmochim. Acta, 27, pp. 297–331.

Keller, G. V. & Frischknecht, F. C. 1966: Electrical Methods in Geophysical Prospecting. – Oxford: Pergamon Press, 517 p.

Khan, S. U. & Schnitzer, M. 1972: The retention of hydrophobic organic compounds by humic acid. – Geochim. cosmochim. Acta, 36, pp. 745–754.

Klitten, K. 1972: Geoelektrisk Kortlægning af Postglaciale Bassiner. – Afhandl. fra Inst. for Tekn. Geol. No. 1. 74 p.

Krog, H. 1968: Late-Glacial and Post-Glacial shoreline Displacement in Denmark. – Means of Correlation of Quarternary Successions, 8, pp. 421–435.

Kunetz, G. 1966: Principles of Direct Current Resistivity Prospecting. – Berlin: Gebrüder Bornträger. 103 p.

Larsen, G., Liboriussen, J. & Villumsen, A. 1972: Kvartærgeologiske undersøgelser på kortbladet Randers. – Dansk geol. Foren. Årsskrift 1971, pp. 27–40.

Lynch, E. J. 1962: Formation Evaluation. – New York: Harper and Row. 422 p.

Mertz, E. L. 1924: Oversigt over de sen- og postglaciale Niveauforandringer i Danmark. – Danm. geol. Unders. II række, 41, 50 p.

Mortimer, C. H. 1941: The Exchange of Dissolved Substances between mud and water in Lakes. – J. Ecol., 29, pp. 280–329.

Müller, G. 1967: Diagenesis in argillaceous sediments. – *In*: Larsen, G. & Chilingar, G. V. (editors) Developments in Sedimentology, 8, pp. 127–177. – Amsterdam: Elsevier.

Mörner, N. A. 1969: The Late Quarternary History of the Kattegatt Sea and the Swedish West Coast. – Sver. geol. Unders. Afh. Ser. C., 640, 473 p.

Newmann, J. W., Parker, P. L. & Behrens, E. W. 1973: Organic Carbon isotope ratios in Quarternary cores from the Gulf of Mexico. – Geochim. cosmochim. Acta, 37, pp. 225–238.

Nielsen, J. D. 1971: Fiksering og frigørelse af ammonium. – Tidsskrift for Planteavl, 75, pp. 239–255.

Nielsen, E. S. 1938: De danske farvandes hydrografi i Litorinatiden. – Meddr dansk geol. Foren., 9, pp. 337–348.

Nissenbaum, A., Baedecker, M. J. & Kaplan, I. R. 1972: Organic geochemistry of Dead Sea sediments. – Geochim. cosmochim. Acta, 36, pp. 709–727.

Oppenheimer, C. H. 1960: Bacterial activity in sediments of shallow marine bays. – Geochim. cosmochim. Acta, 19, pp. 244–260.

Orr, W. L., Emery, K. O. & Grady, J. R. 1958: Preservation of chlorophyll derivatives in sediments off southern California. – Bull. Am. Ass. Petrol. Geol., 42, pp. 925–962.

Orr, W. L. & Grady, J. R. 1957: Determination of Chlorophyll derivatives in marine sediments. – Deep-Sea Res., 4, pp. 263–271.

Parsons, T. R. & Strickland, J. D. H. 1963: Discussion of Spectrophotometric Determination of Marine-plant Pigments, with Revised Equations for Ascertaining Chlorophylls and Carotenoids. – J. mar. Res., 21, pp. 155–163.

Pedersen, J. A. and Villumsen, A. 1974: ESR investigations of humic acids. – Danm. geol. Unders., Årbog 1973, pp. 133–140.

Pettijohn, F. J. 1957: Sedimentary Rocks. – New York: Harper and Bros. 718 p.

Prashnowsky, A. A. 1971: Biogeochemische Untersuchungen an Gesteinen der Bohrung Münsterland I. – Neues Jb. Geol. Paläont. Abh., 138, pp. 37–55.

Rees, C. E. 1973: A steady-state model for sulphur isotope fractionation in bacterial reduction processes. – Geochim. cosmochim. Acta, 37, pp. 1141–1162.

Richards, F. A. 1965: Chemical observations in some anoxic, sulfide-bearing basins and fjords. – Advances in water pollution research, 3, pp. 215–243.

Rogers, M. A. and Koons, C. B. 1969: Organic carbon δ C^{13} values from Quarternary marine sequences in the Gulf of Mexico: a reflection of paleotemperature changes. – Trans. Gulf Cst. Ass. geol. Socs. 19, pp. 529–534.

Sanger, J. E. & Gorham, E. 1972: Stratigraphy of fossil pigments as a guide to the Post-glacial history of Kirchner Marsh, Minnesota. – Limnol. Oceanogr., 17, pp. 840–854.

Schrøder, N. 1974: De geofysisk-geologiske undersøgelser af området nord for Århus. – Århus, Laboratory for Geophysics, pp. 12–55.

Schwartz, H. P. 1969: Carbon Isotopes in Nature. – *In*: Wedepohl, K. H. (ed.) Handbook of Geochemistry. Chapt. 6 B. – Berlin: Springer.

Sorgenfrei, T. 1952: Geologiske og hydrologiske erfaringer fra Randers og omegn. – Vandteknikeren, pp. 1–6.

Sorgenfrei, T. & Berthelsen, O. 1954: Geologi og Vandboring. – Danm. geol. Unders. III række, 31, 106 p.

Stevenson, F. J. 1960: Some aspects of the distribution of biochemicals in geologic environments. – Geochim. cosmochim. Acta, 19, pp. 261–271 .

Stevenson, F. J. & Cheng, C.-N. 1972: Organic geochemistry of the Argentine Basin sediments: Carbon-nitrogen relationships and Quarternary Correlations. – Geochim. cosmochim. Acta, 36, pp. 653–671.

Stewart, R. A. & Gorsline, D. S. 1962: Recent sedimentary history of the St. Joseph Bay, Florida. – Sedimentology, 1, pp. 256–286.

Stewart, K. M. & Rohlich, G. A. 1967: Eutrophication. – A review. – California State Water Quality Control Board, Publication No. 34.

Strickland, J. D. H. & Parsons, T. R. 1968: A Practical Handbook of Seawater Analysis. – Fisheries Research Board of Canada, Bull. No. 167. – Ottawa. 311 p.

Teichmüller, M. & Teichmüller, R. 1967: Diagenesis of Coal (Coalification). – *In*: Larsen, G. & Chilingar, G. V. (editors) Developments in Sedimentology, 8, pp. 391–415. – Amsterdam: Elsevier.

Thiede, J. & Larsen, G. 1971: Radiographies of consolidated calcareous sediments from Denmark. – Bull. geol. Soc. Denmark, 20, pp. 307–328.

Thode, H. G., Monster, J. & Dunford, H. B. 1961: Sulphur isotope geochemistry. – Geochim. cosmochim. Acta, 25, pp. 159–174.

Troels-Smith, J. 1942: Geologisk Datering af Dyrholm-Fundet. – Arkæol. – Kunsth. skr. K. dansk. Vidensk. Selsk. 1 (1), pp. 137–212.

Villumsen, A. 1973: Geochemical and sedimentological investigations of the Rosenholm Depression. – Danm. geol. Unders. II række, 100, 66 p.

Villumsen, A. & Nielsen, O. B. 1976: The influence of paleosalinity, grain size distribution and clay minerals on the content of B, Li, and Rb in Quarternary sediments from Eastern Jutland, Denmark. – Sedimentology (in press).

Welte, D. 1969: Organic Geochemistry of Carbon. – *In*: Wedepohl, K. H. (ed.) Handbook in Geochemistry. Chapter 6L. – Berlin: Springer.

Wickmann, F. E. 1952: Variations in the relative abundance of the carbon isotopes in plants. – Geochim. cosmochim. Acta, 2, pp. 243–254.

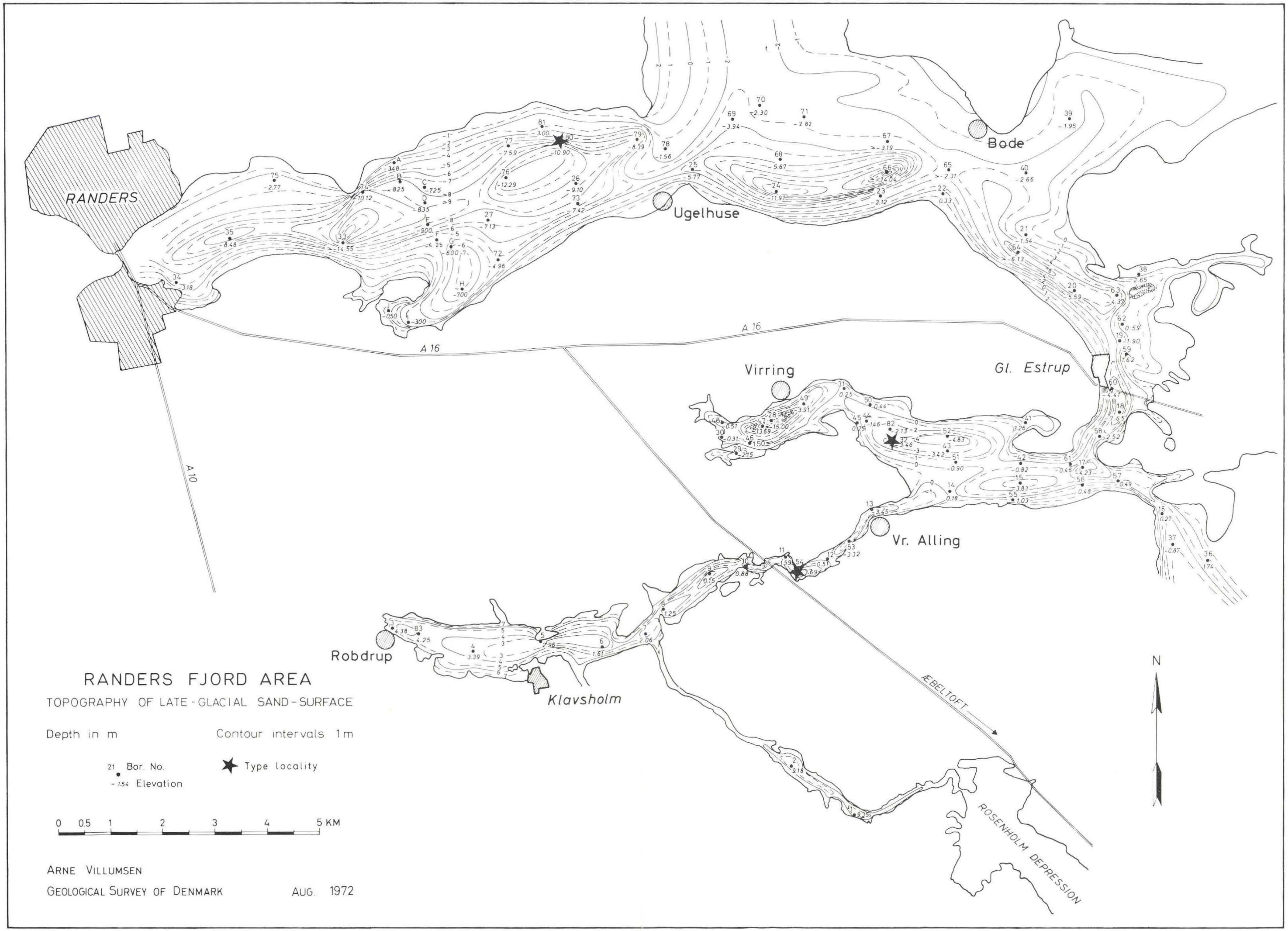

RANDERS
Ugelhuse
Bode
Virring
Gl. Estrup
Vr. Alling
Robdrup
Klavsholm
A 16
A 10
ÆBELTOFT
ROSENHOLM DEPRESSION
N
RANDERS FJORD AREA
TOPOGRAPHY OF LATE-GLACIAL SAND-SURFACE
Depth in m
Contour intervals 1m
21 Bor. No.
-1.54 Elevation
Type locality
0 0.5 1 2 3 4 5 KM
ARNE VILLUMSEN
GEOLOGICAL SURVEY OF DENMARK
AUG. 1972

Plate 1.

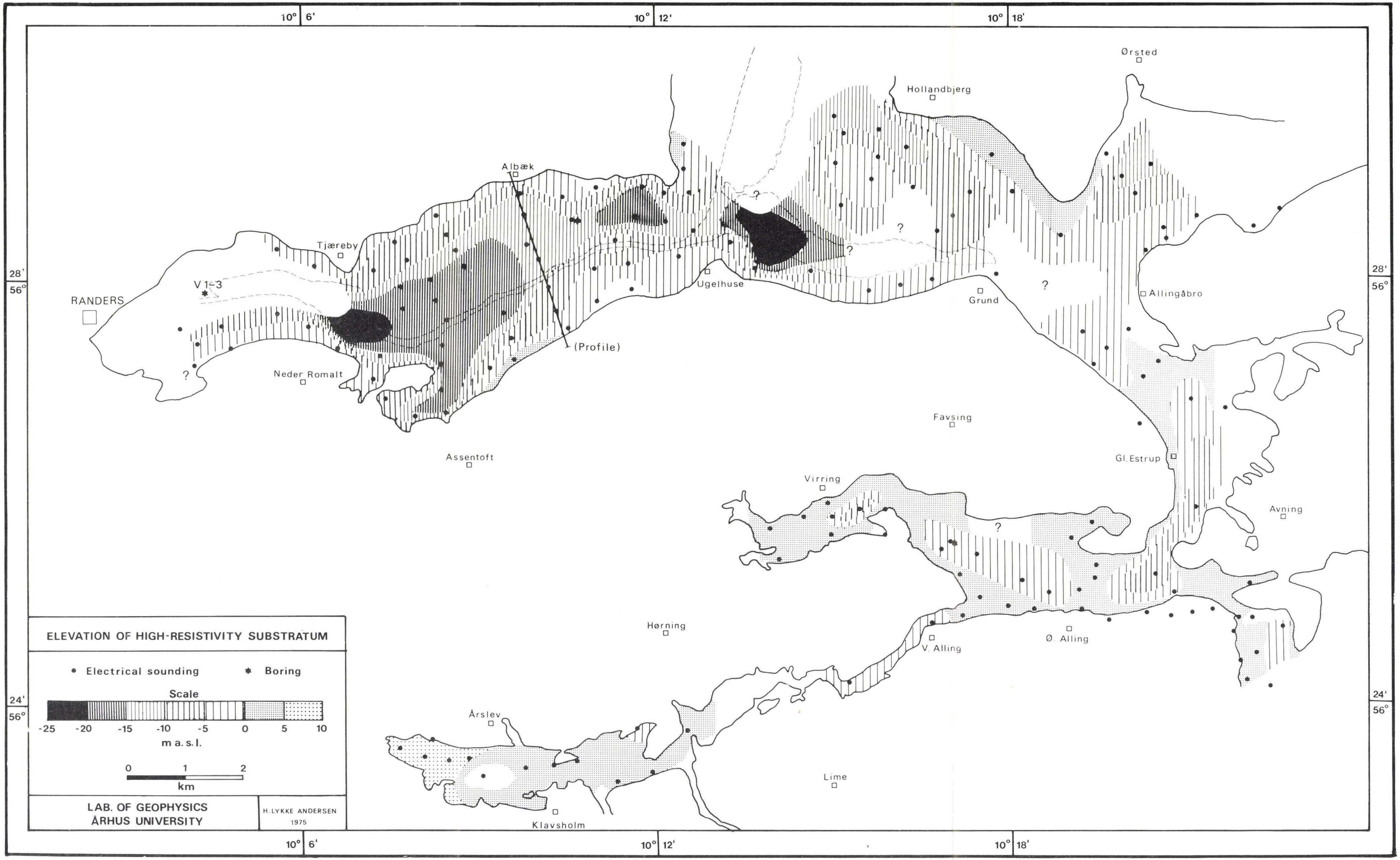

10° 6'
10° 12'
10° 18'
Ørsted
Hollandbjerg
Albæk
Tjæreby
V 1-3
RANDERS
Ugelhuse
Grund
Allingåbro
(Profile)
Neder Romalt
Favsing
Assentoft
Gl. Estrup
Virring
Avning
V. Alling
Ø. Alling
Hørning
Årslev
Lime
Klavsholm
?
28'
56°
24'
56°
ELEVATION OF HIGH-RESISTIVITY SUBSTRATUM
● Electrical sounding
✱ Boring
Scale
-25 -20 -15 -10 -5 0 5 10
m a.s.l.
0 1 2
km
LAB. OF GEOPHYSICS
ÅRHUS UNIVERSITY
H. LYKKE ANDERSEN
1975

Plate 2.

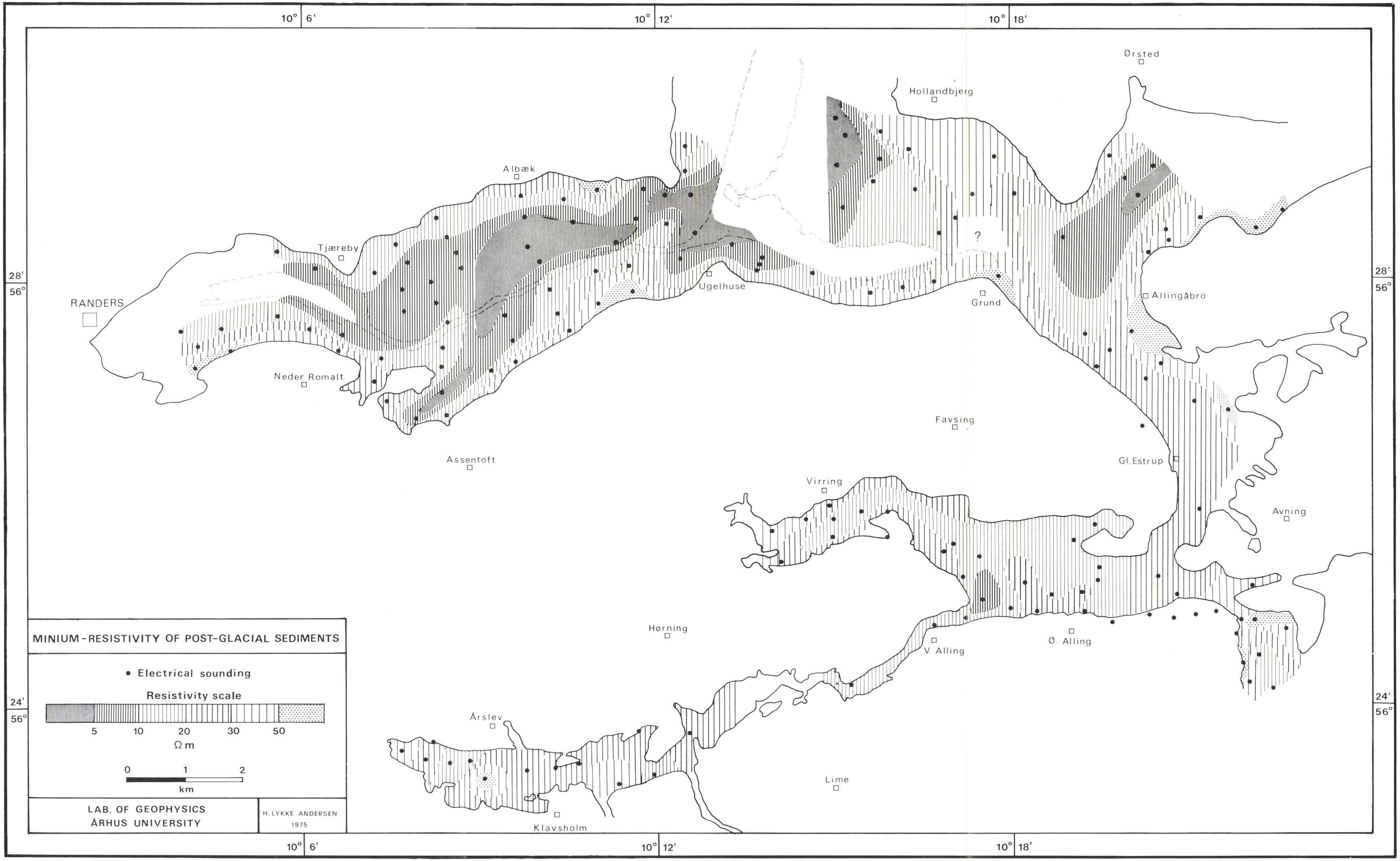

10° 6'
10° 12'
10° 18'
28' 56°
24' 56°
Ørsted
Hollandbjerg
Albæk
Tjæreby
RANDERS
Ugelhuse
Grund
Allingåbro
Neder Romalt
?
Favsing
Assentoft
Gl. Estrup
Virring
Avning
Hørning
V. Alling
Ø. Alling
Århslev
Lime
Klavsholm
MINIUM-RESISTIVITY OF POST-GLACIAL SEDIMENTS
● Electrical sounding
Resistivity scale
5
10
20
30
50
Ωm
0
1
2
km
LAB. OF GEOPHYSICS
ÅRHUS UNIVERSITY
H. LYKKE ANDERSEN
1975

Plate 3.

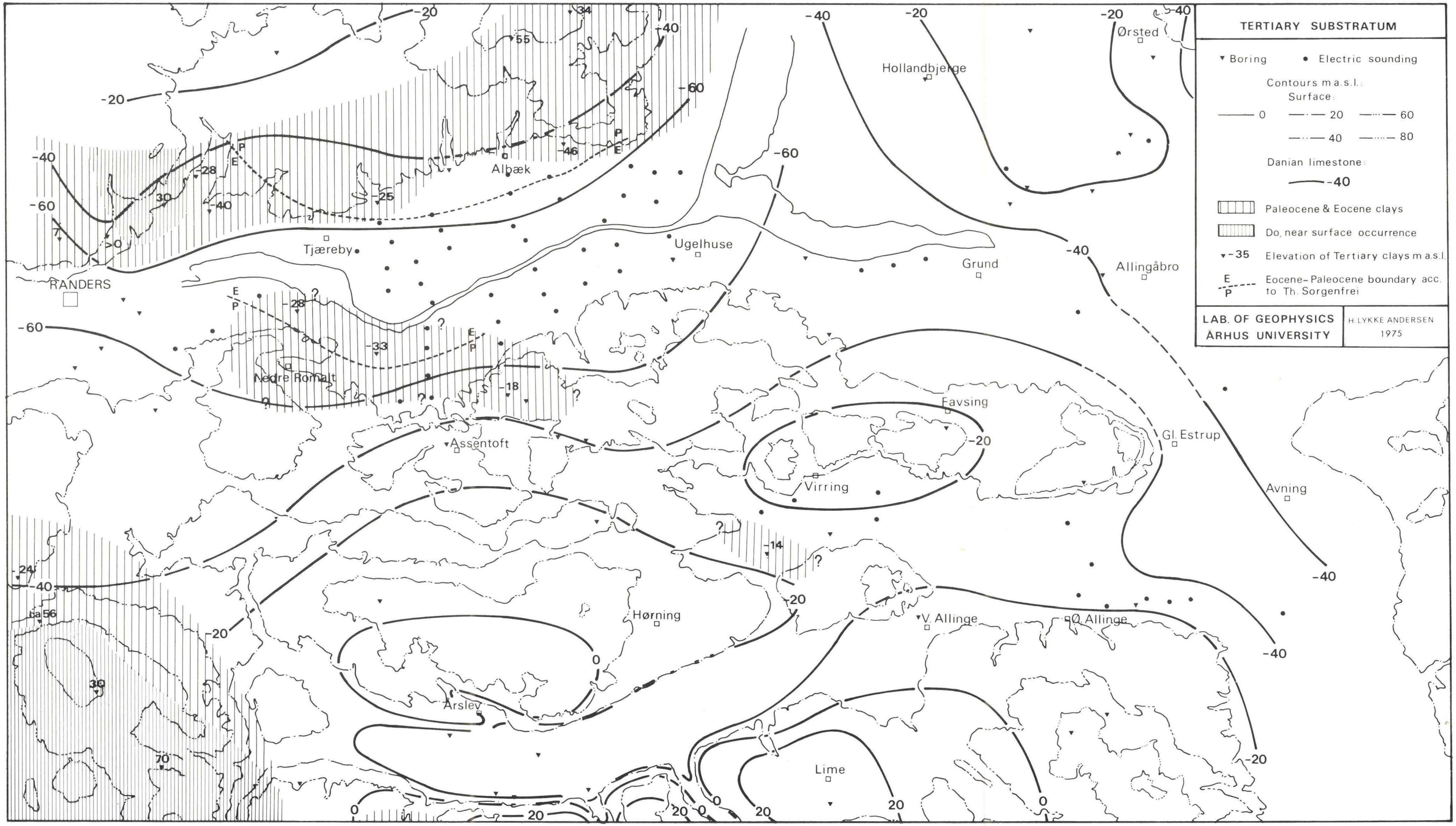

TERTIARY SUBSTRATUM
▾ Boring
● Electric sounding
Contours m a.s.l.:
Surface:
0
20
60
40
80
Danian limestone:
-40
Paleocene & Eocene clays
Do, near surface occurrence
▾-35 Elevation of Tertiary clays m a.s.l.
E P Eocene-Paleocene boundary acc. to Th. Sorgenfrei
LAB. OF GEOPHYSICS ÅRHUS UNIVERSITY
H. LYKKE ANDERSEN 1975
RANDERS
Tjæreby
Albæk
Nedre Romalt
Assentoft
Ugelhuse
Hollandbjerge
Ørsted
Grund
Allingåbro
Favsing
Virring
Gl. Estrup
Avning
Hørning
V. Allinge
Ø. Allinge
Århus
Årslev
Lime
-20
-40
-60
-20
0
20
-34
-55
-28
30
-40
-25
-46
7
>0
-28
-33
-18
-14
-24
ca 56
30
70

Plate 4.

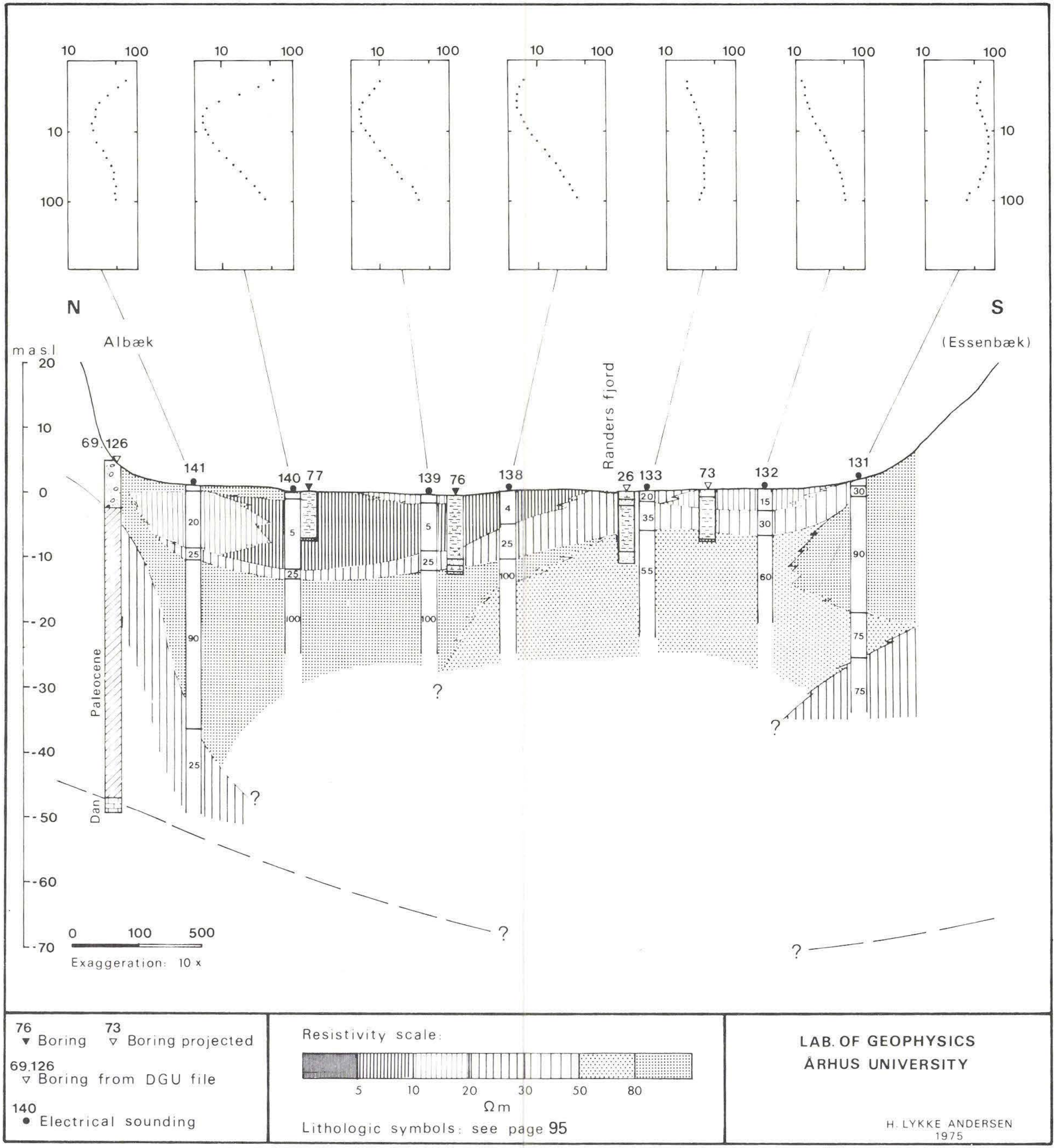


Plate 5. Cross section drawn on the basis of electric soundings and borings. Location shown in plate 2.