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Sediment Geochemical Processes: Field Participation at Eckernförde Site (Coastal Benthic Boundary Layer Special Research Project)

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13. Abstract *(Maximum 200 words).*

The Naval Research Laboratory (NRL) 6.1 Core Program "Sediment Geochemical Processes" participated in field experiments in the Baltic Sea near Eckernförde, Germany during May 1993 in conjunction with the NRL Coastal Benthic Boundary Layer Special Research Project. Samples from box cores BC244 ("APL-2/Stanic-towers" site) and BC250 (Mittelgrund area) were analyzed for water content, average grain density, and grain size distribution. Porosity, void ratio, and wet bulk density were calculated from the water content and average grain density. The electrical resistivity of core BC250 was measured downcore, from which formation factors were calculated. These data are reported in this memorandum report. In addition, cores BC244 and BC250 were sampled for microfabric, clay-fraction mineralogy, inorganic and organic carbon contents, and total nitrogen content. These analyses are in progress. BC244, BC250, and BC265 (also from the "APL-2/Stanic-towers" site) were analyzed for dissolved porewater concentrations of nutrients and key chemical species (pH, salinity, titration alkalinity, oxygen by microelectrode, ammonia, nitrate plus nitrite, Mn, Fe, Ca, phosphate, silicate, and sulfide) and total and microbial methane by GEOMAR, a research institute located in Kiel, Germany. The electrical resistivity of core BC265 was tested as well by GEOMAR. The GEOMAR results will be reported elsewhere.

14. Subject Terms.

Sediment Physical Properties, Clay Mineralogy, Bottom Water Salinity, Suboxic Sediment Diagenesis, Sediment Porewater Geochemistry

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Sediment Geochemical Processes:
Field Participation at Eckernförde Site
(Coastal Benthic Boundary Layer Special Research Project)

Introduction

Eckernförde Bay, located in the Baltic Sea near the town of Eckernförde, Germany, was the site of the first field exercise of the Coastal Benthic Boundary Layer Special Research Program (CBBL-SRP). The CBBL-SRP, which is funded by the Office of Naval Research (ONR), is a multidisciplinary program to model quantitatively the effects of environmental processes on sediment structure and sediment properties. The Naval Research Laboratory (NRL) 6.1 Core Research Program "Sediment Geochemical Processes" participated in these field experiments by examining the relationship between sediment geochemistry, clay-fraction mineralogy, physical properties, and microfabric at two areas studied as part of the CBBL-SRP field program in Eckernförde Bay.

Sampling Locations and Analytical Methods

Three box cores were retrieved near the mouth of Eckernförde Bay aboard the R/V *Kronsort* for the geochemistry-related studies (Fig. 1). An Ocean Instruments spade box corer (20 cm x 30 cm x 50 cm deep) was used to take BC244 at 54°29'36.2"N, 10°00'13.8"E and BC250 at 54°29'57.7"N, 10°01'56.1"E. An Ocean Instruments USNEL-type (United States Naval Electronics Laboratory; Hessler and Jumars 1974) spade box corer (50 cm x 50 cm x 50 cm deep) was used to retrieve BC265 located at 54°29'36.98"N, 9°59'18.88"E. BC244 and BC265 were taken from a muddy site designated the "APL-2/Stanic-towers" site in water ~24 m deep (Figs. 1 and 2). BC250 was taken from an area of sandy muds in water ~16 m deep on a nearby rise called "Mittelgrund" (Babenerd and Gerlach 1987) (Figs. 1 and 2). Subcores were taken using acrylic tubing with mild suction applied during subcoring. All subcores were capped with overlying water filling the space above the sediment to exclude air and stored upright at 6°C (if not tested aboard ship) until extruded or otherwise analyzed.

Samples from BC244 and BC250
Approximately 10 cm of bottom water of 18°/oo salinity covered BC244. The brown color of the top 2 cm of sediment suggested an oxidized surface layer; deeper sediment was black and smelled of

hydrogen sulfide. Four subcores (6-cm inside diameter, 1.4-mm wall acrylic tubing) were taken from BC244. Approximately 15 cm of bottom water of 16⁰/oo salinity covered BC250. Three subcores were taken from BC250. The least disturbed subcore (based on inspection of subcore and box core surfaces) from both of these box cores was extruded and cut into 2-cm-thick sections for porewater analysis by GEOMAR, a national marine research institute located in Kiel, Germany. (See section outlining GEOMAR participation.) Porewaters were extracted by centrifugation, and the sediment remaining after centrifugation was used for grain size and clay-fraction mineralogy analyses. One subcore from each box core was extruded and sampled for microfabric analysis. Another subcore was extruded and sampled for water content, average grain density, inorganic and organic carbon analyses, and total nitrogen analysis; this subcore from BC250 was sampled for electrical resistivity as well. The fourth subcore from BC244 was reserved for total methane analysis by GEOMAR.

Samples from BC265
Three subcores (10-cm inside diameter, 3-mm wall thickness, acrylic tubing) were taken from this box core. One subcore was used for oxygen microprobe and electrical resistivity measurements by GEOMAR. One subcore was used for porewater analyses by GEOMAR, and one subcore was reserved for microbial methane analysis by GEOMAR. Mass physical property and grain size distribution analyses were not made on sediments from this box core; however, these sediments are assumed to be similar to those of BC244 retrieved nearby.

Water Content and Average Grain Density
Approximately 40 g of wet sediment were placed in a preweighed aluminum pan, dried in a 110⁰C oven for approximately 16 hours, cooled to room temperature in a desiccator, and reweighed. Water content was calculated as the water lost in percent of dry weight. The dry weight was first corrected for the weight of salt using the salinity of bottom water, which was measured with a hand-held, calibrated Atago salinity refractometer. Calculations follow:

$$w_{sea\ salt} = \frac{(w_{water})(s)}{(1000-s)},$$

$$W\% = \frac{(w_{water})(100)}{(w_{sample} - w_{sea\ salt})},$$

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where w represents a weight in grams of sea salt, water, and sample (including sea salt) as indicated by subscript, s is the salinity in parts per thousand and W is the water content in percent of salt-free, dry weight.

The average grain density, G, was measured in a Quantichrome Model MVP-1 Multi-Pycnometer. Ottawa sand was used to check the accuracy of the pycnometer. Sediment was stored in a desiccator (following drying in a oven at 110°C) prior to weighing between 2 and 7 g for measurement. The data reported here represent single measurements; replicate measurements will be made in the future. All measurements were corrected for the mass and volume of sea salt present, for which a density of 2.18 g/cm^3 was assumed, using the following equations:

$$G = \frac{w_{sample} - w_{sea\ salt}}{v_{sample} - v_{sea\ salt}},$$

$$v_{sea\ salt} = \frac{w_{sea\ salt}}{\rho_{sea\ salt}}.$$

v refers to volume, w to weight, and ρ to density for components specified by the subscript. v_{sample} is the volume measured in the pycnometer. In all calculations given here, the subscript "sample" refers to dry sediment with sea salt present, and the subscript "sediment" refers to dry sediment free of salt.

Porosity, Void Ratio, and Wet Bulk Density

Porosity, void ratio, and wet bulk density were calculated from the water content and the average grain density data. Porosity, P, is calculated as follows:

$$P = \frac{v_{voids}}{v_{voids} + v_{sediment}},$$

$$v_{voids} = \frac{(w_{water} + w_{sea\ salt})}{(\rho_{bottom\ water})},$$

$$v_{sediment} = \frac{(w_{sample} - w_{sea\ salt})}{(\rho_{sediment})}.$$

Densities at 25°C of 1.01061 g/cm^3 and 1.00911 g/cm^3 were used for bottom water salinities of 18⁰/oo (BC244) and 16⁰/oo (BC250), respectively. A fully water-saturated sediment was assumed. Based on acoustic and X-ray results on pressurized cores (M. Richardson, pers. comm.), gas bubbles are found in sediments at these sites only below 50 cm.

The void ratio, e, is calculated as shown, with symbols as defined previously:

$$e = \frac{v_{voids}}{v_{sediment}}.$$

The wet bulk density, ρ_{wet}, is calculated using the following equations:

$$\rho_{wet} = \frac{w_{porewater} + w_{sediment}}{1\ cm^3},$$

Per 1 cm^3 of wet sediment,

$$w_{porewater} = (P)(\rho_{porewater}) \sim (P)(\rho_{seawater}),$$

$$w_{sediment} = (1-P)(\rho_{sediment}).$$

Grain Size Distribution

The grain size distribution results presented here are for the natural sample, i.e., no pretreatment was employed to remove iron and manganese oxides, organic carbon, etc., prior to disaggregation. A method employing separation by settling based on that of Folk (1974) was used. Only the data for the sand (>63 μm), silt (<63 μm, >2 μm) and clay (<2 μm) fractions are reported here; however, the silt fraction was analyzed in greater detail (half-phi intervals from 4 to 6ϕ and whole-phi intervals from 6 to 9ϕ) and will be published in a future report.

Formation Factor

Electrical resistivity measurements were made with a resistivity probe patterned after Andrews and Bennett (1981). This probe used four platinum wires, each 0.5 mm in diameter, embedded in plastic, and spaced 0.5 cm apart. The tip of the probe was bevelled at approximately $45°$ to expose wire cross-sectional areas of approximately 0.24 mm^2. The associated electronics were designed by Peter Kauffman of the Applied Physics Laboratory at the University of Washington.

For BC250, bottom water resistivity, $R_{bottom\ water}$, was measured at a level ~1.5 cm above the sediment-water interface. Surface water was removed, and the probe was inserted 1 cm into the sediment for the measurement of sediment resistivity, $R_{sediment}$, at a depth of 1 cm. Following extrusion and removal of each 2-cm interval, measurements were made by insertion of the probe to a depth of 1 cm. The formation factor, F, is calculated as follows:

$$F = \frac{R_{sediment}}{R_{bottom\ water}} .$$

The formation factor is used to calculate a bulk sediment diffusion coefficient, D_x, from the diffusion coefficient in open solution, $D_{x,o}$, which, in this case, would be a solution identical in composition to porewater (Manheim and Waterman 1974):

$$D_x = \frac{D_{x,o}}{F} .$$

The greater the value of F, the slower a dissolved species is able to diffuse for a given concentration gradient.

Results and Discussion

Mass Physical Properties

Box cores 244 and 250 represent very different areas from a physical property standpoint and should provide an interesting comparison with respect to geochemistry. The decrease with depth in

water content is much less in BC244 compared to BC250 (Table 1; Fig. 3). As discussed below, shifts in grain size distribution to coarser sediment occur with depth and correlate closely with decreases in water content. Organic carbon content may be important as well to water content, which will be evaluated when data become available. The average grain densities (Table 1; Fig. 4) follow a similar trend downcore; surface values are low, probably due to the presence of greater quantities of low-density organic matter. The average value for both cores is ~ 2.70 g/cm^3. This value seems a little high, particularly if organic carbon content is high. The average grain density values shown in Table 1 and Figure 4 represent single measurements; replicate analyses are planned. The differences between the two cores with respect to water content is reproduced in porosity, void ratio and wet bulk density plots (Table 1; Figs. 5, 6, and 7).

Grain Size Distributions

In general, sediments at both sites become coarser in texture with depth; a transition to coarser grained sediment (higher silt content for BC244, higher sand content for BC250) occurs at 8 to 10 cm (Table 2; Fig. 8) at both sites. Using a range of sedimentation rates from 3.2 mm/y estimated for Eckernförde Bay to 0.2 mm/y for the area south of Mittelgrund (Balzer et al. 1987), the transition depth corresponds to a period ranging from 25 to 500 years ago, suggesting an anthropomorphic or episodic (e.g., a storm) reason for the transition. Since grain size distributions were determined without pretreatment to remove cements, the effects of chemical aggregation cannot be assessed; additional grain size analyses following pretreatment to remove cementing agents are planned. For BC250, the fact that porosity continues to decrease below 28 cm, despite the increase in the silt and clay fractions, suggests that sand grains are in contact and the voids between sand grains are being infilled with matrix (Bennett et al. 1980). Resolution of this question must await the microfabric results.

Formation Factors

For BC250, the formation factor variation with depth (Table 3; Fig. 9) is consistent with the downcore changes in porosity. The formation factor increases with depth, with the largest increase occurring at a depth of 8 to 10 cm. This increase is most likely due to the decrease in porosity accompanying a shift to coarser sediment.

Analyses in Progress

Microfabric, additional grain size, clay-fraction mineralogy, total and organic carbon, and total nitrogen determinations are in progress. Since these samples have a significant silt component, scanning electron microscopy will probably be the primary instrument used to examine the microfabrics of these sediments. The microfabric will be examined on samples that have been embedded in epoxy and polished; unembedded, fractured samples will be studied also. Image analysis and elemental analysis of individual particles and cements, if present, will be performed as well.

To improve the statistics of the analyses, the average grain densities of all samples will be rerun in duplicate. A second measurement of grain size distribution will be made on samples for which enough material remains. This second determination will involve pretreatment of the sediment to remove organic matter and other cementing agents.

Clay-fraction mineralogy will be determined using material from the grain size determinations (both untreated and treated to remove cementing agents and organic matter). For each sample, a porous porcelain tile will be covered with ~2.5 mL of suspended clay fraction (<2 μm) following the removal of coarser grained material by settling during grain size analysis. After 5-10 minutes, the deflocculent solution (from grain size analysis) soaks into the tile, leaving the clay-sized particles as a thin veneer on the surface of the tile. A Scintag XDS 2000 X-Ray Diffractometer equipped with software to aid in the identification of minerals will be used for the analyses. The tiles will be scanned from 0 to 70° 2θ, and the counts per second will be recorded as a spectrum. Peak parameters, e.g., height, full-width-at-half-maximum, etc., will be evaluated by computer and digitally stored. Blank tiles will be scanned to check for a substrate contribution to sample spectra. All tiles will be rescanned following heating at 600°C for 2-3 hours to check for mineral transformations that aid in verifying the presence of certain minerals.

Carbon, hydrogen, and nitrogen (CHN) analysis will be performed on samples to measure total-carbon and organic-carbon contents. The carbonate-carbon content is approximated by the difference between total carbon and organic carbon. CHN analysis will also measure total nitrogen.

GEOMAR Participation

Dr. Michael Schlüter and M. Kreuz from GEOMAR, a national marine research institute located in Kiel, Germany, analyzed sediment samples from all three cores for dissolved porewater constitutents. These include: pH, salinity, titration alkalinity, oxygen by microelectrode, ammonia, nitrate plus nitrite, Mn, Fe, Ca, phosphate, silicate, and sulfide. Box cores were extruded in 2-cm intervals. The porewater of each interval was extracted by centrifugation and then filtered to remove any remaining particulates prior to analysis. The electrical resistivity of a subcore from BC265, located near BC244, was measured for comparision with BC250. BC265 is presumed similar to BC244 based on location and appearance; porewater geochemical similarities will help to support this presumption. Dr. S. Lammers, GEOMAR, retained a subcore of BC244 for total sedimentary methane analysis, and I. Bussman sampled BC265 for microbial methane analysis. The results from these studies will be reported by the GEOMAR scientists.

Summary

The two sites sampled by these cores are very different with respect to physical properties. The "APL-2/Stanic-towers" site sampled by BC244 shows little change in water content (and derived parameters) over the surface 28 cm, despite a drop in the clay-to-silt weight ratio from ~4:1 to ~1:1, the result of both an increase in silt and a decrease in clay downcore (the percent sand remains approximately constant with depth). It is likely that organic carbon content is a contributing factor to the maintanence of high water content at this site. In contrast, BC250 from the Mittelgrund area shows a decrease in water content from over 300% in the surface sediment to less than 50% at 20-22 cm. These changes correlate with a shift in texture from a mud to a muddy sand or sand (Folk 1974). The formation factor increases greatly over this transition in grain size distribution. The additional analyses planned for these sediments and the data from other authors will improve the interpretations of the data presented here.

Acknowledgments

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Table 1. Measured and Derived Mass Physical Properties for Box Cores 244 and 250.

Box Core	Depth, cm	Water Content, %	Average Grain Density, g/cm³	Porosity	Void Ratio	Wet Bulk Density, g/cm³
BC244	0-2	356	2.62	0.904	9.39	1.17
	2-4	296	2.72	0.890	8.10	1.20
	4-6	285	2.73	0.887	7.83	1.21
	6-8	269	2.70	0.880	7.34	1.21
	8-10	272	2.72	0.882	7.44	1.21
	10-12	281	2.70	0.884	7.64	1.21
	12-14	257	2.69	0.875	6.97	1.22
	14-16	262	2.71	0.877	7.16	1.22
	16-18	259	2.75	0.878	7.17	1.22
	18-20	266	2.69	0.878	7.22	1.22
	20-22	275	2.64	0.879	7.29	1.21
	22-24	259	2.67	0.874	6.96	1.22
	24-26	262	2.64	0.875	6.67	1.21
	26-28	259	2.68	0.875	7.00	1.22
BC250	0-2	322	2.63	0.895	8.54	1.18
	2-4	269	2.74	0.881	7.43	1.21
	4-6	260	2.80	0.880	7.33	1.22
	6-8	193	2.71	0.841	5.28	1.28
	8-10	122	2.69	0.767	3.30	1.40
	10-12	82.2	2.72	0.693	2.25	1.54
	12-14	61.4	2.76	0.631	1.71	1.66
	14-16	55.8	2.73	0.605	1.53	1.69
	16-18	47.8	2.75	0.569	1.32	1.76
	18-20	44.4	2.73	0.550	1.22	1.78
	20-22	41.7	2.71	0.533	1.14	1.81

Table 2. Grain Size Distribution for Box Cores 244 and 250.

Box Core	Depth, cm	Sand, % (>63 μm)	Silt, % (<63 μm, >2 μm)	Clay, % (<2 μm)
BC244	0-2	2.3	50.6	47.1
	2-4	4.3	17.6	78.1
	4-6	3.1	18.8	78.1
	6-8	2.2	33.5	64.3
	8-10	1.9	46.5	51.6
	10-12	2.2	49.6	48.2
	12-14	2.3	51.3	46.4
	16-18	2.0	46.7	51.3
	18-20	1.5	51.5	47.4
	30-32	0.9	42.1	57.0
	34-36	1.1	44.1	54.8
BC250	0-2	17.0	41.3	41.7
	2-4	16.1	40.1	43.8
	6-8	21.6	37.0	41.4
	8-10	39.7	46.8	13.5
	10-12	56.7	21.3	22.0
	12-14	74.9	12.3	12.8
	14-16	83.0	11.5	5.5
	16-18	82.7	11.0	6.3
	18-20	80.9	8.0	11.1
	20-22	91.5	0.0	8.5
	22-24	89.8	5.2	5.0
	24-26	91.2	5.4	3.4
	26-28	94.2	4.9	0.9
	28-30	72.2	24.7	3.1
	30-32	64.1	15.8	20.1
	32-34	76.5	10.6	12.9

Table 3. Formation factors for Box Cores 250 and 265.

Box Core	Depth, cm	Formation Factor
BC250	1	1.14
	3	1.53
	5	2.07
	7	2.57
	9	5.35
	11	6.99
	13	7.15
	15	7.13
	19	7.15
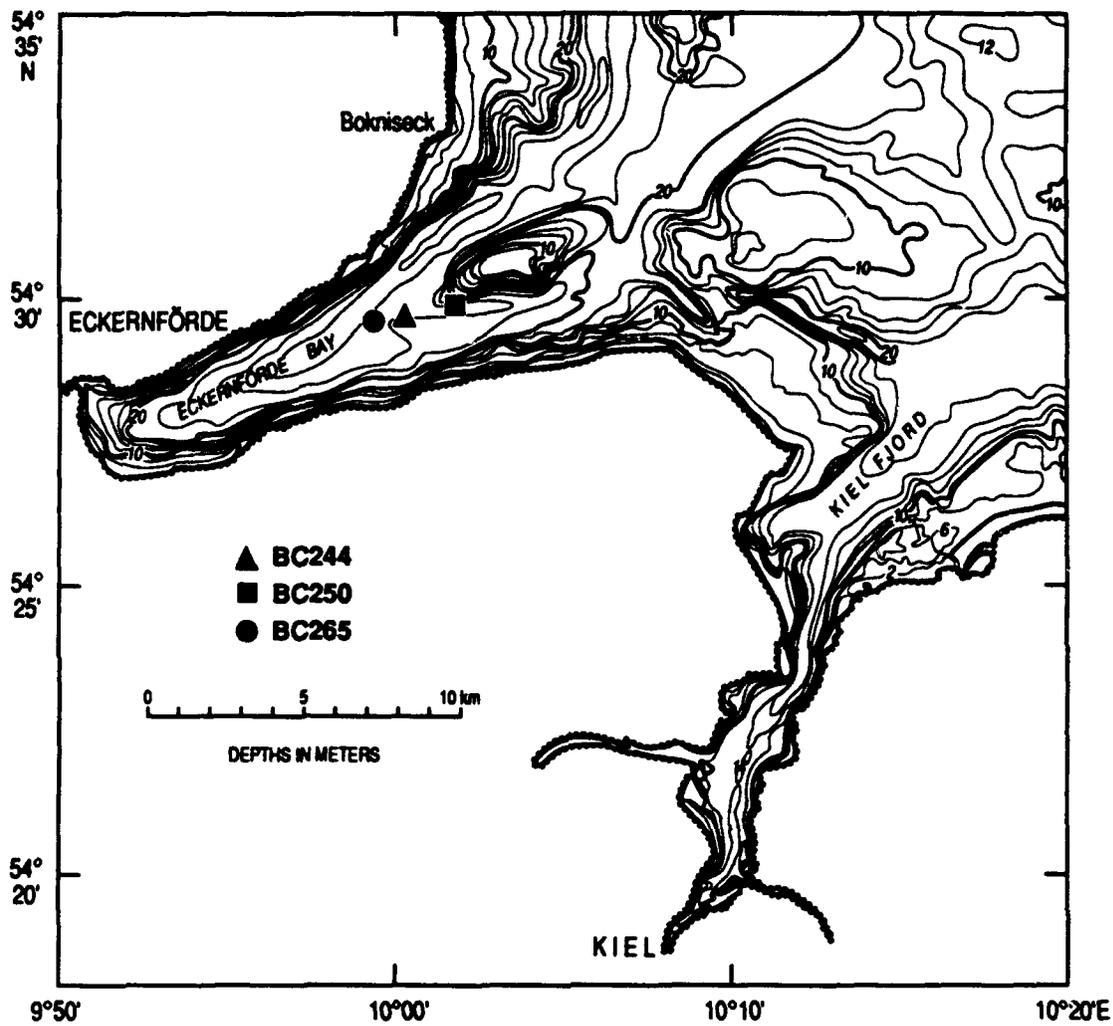
Fig. 1 - Bathymetric map of Eckernförde Bay showing locations of box cores. Redrawn from Babenerd and Gerlach 1987.
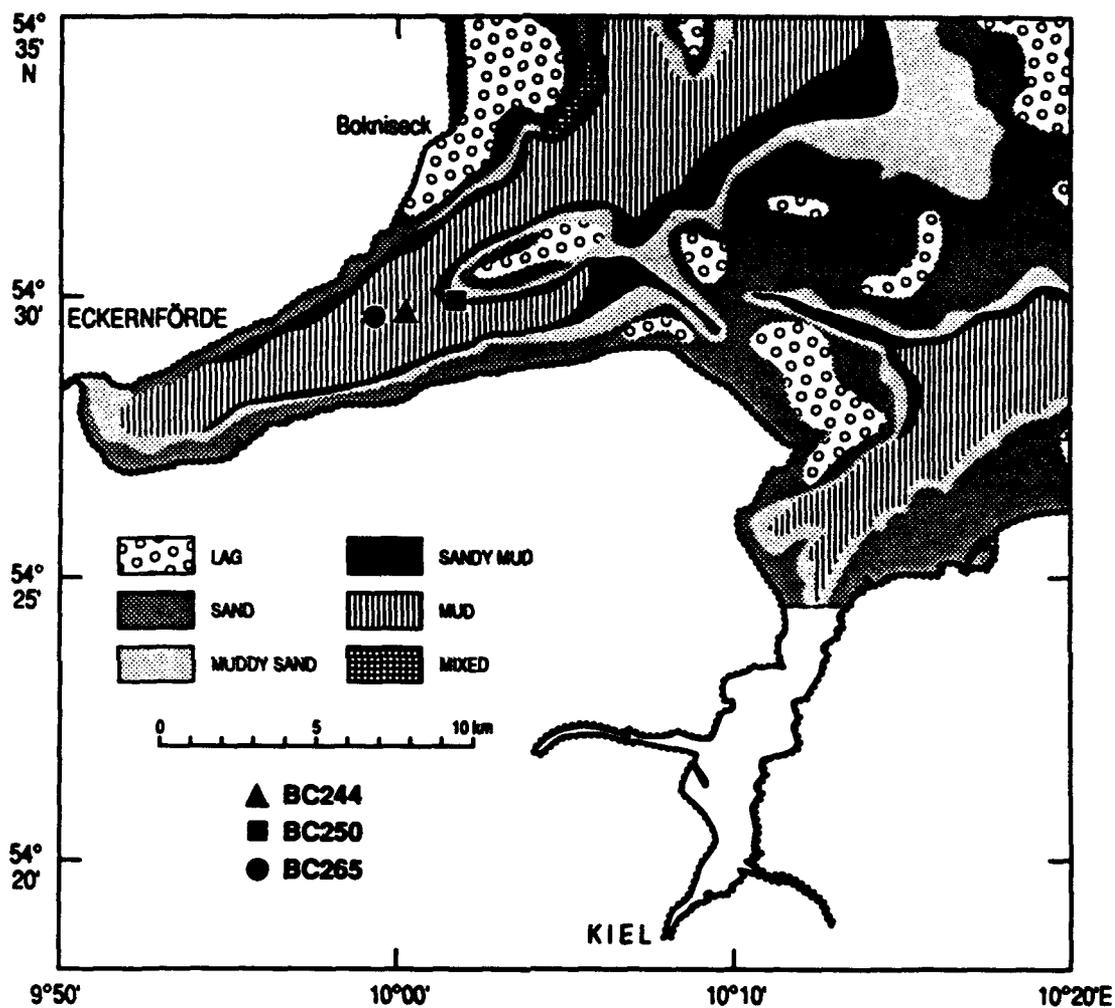
Fig. 2 - Map of Eckernförde Bay showing texture of bottom sediments and locations of box cores. Redrawn from Babenerd and Gerlach 1987.
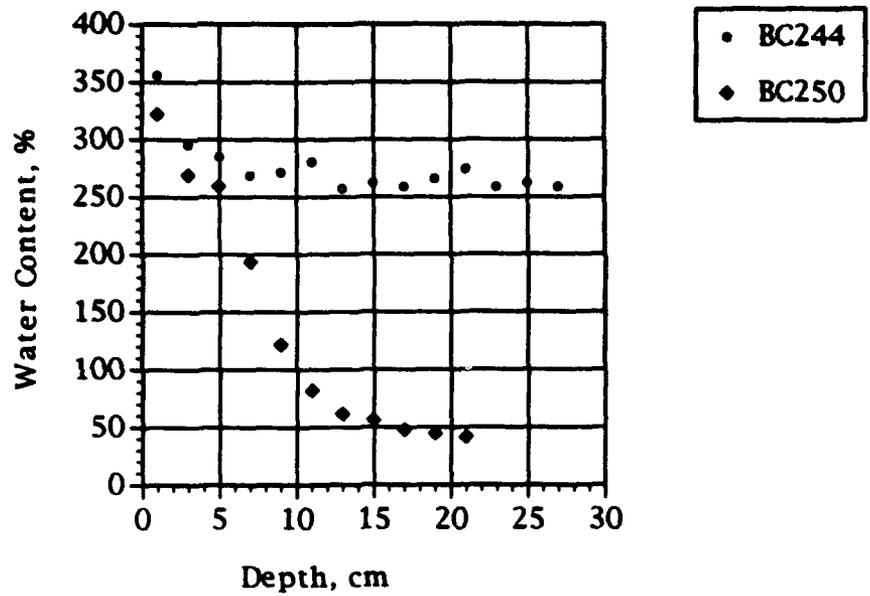
Fig. 3 - Water content as percent dry weight versus sediment depth at center of sampling interval.
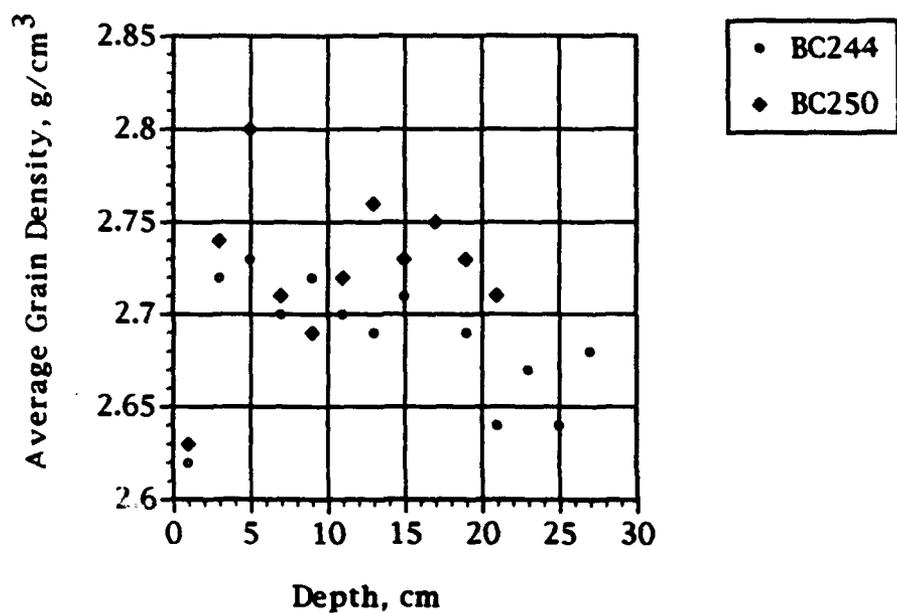
Fig. 4 - Average grain density versus sediment depth at center of sampling interval.

16
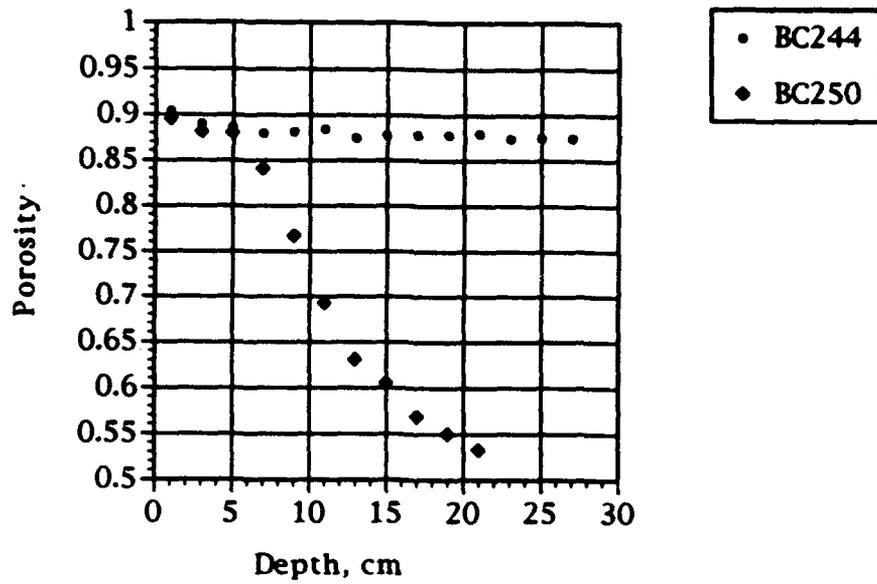
Fig. 5 - Porosity versus sediment depth at center of sampling interval.
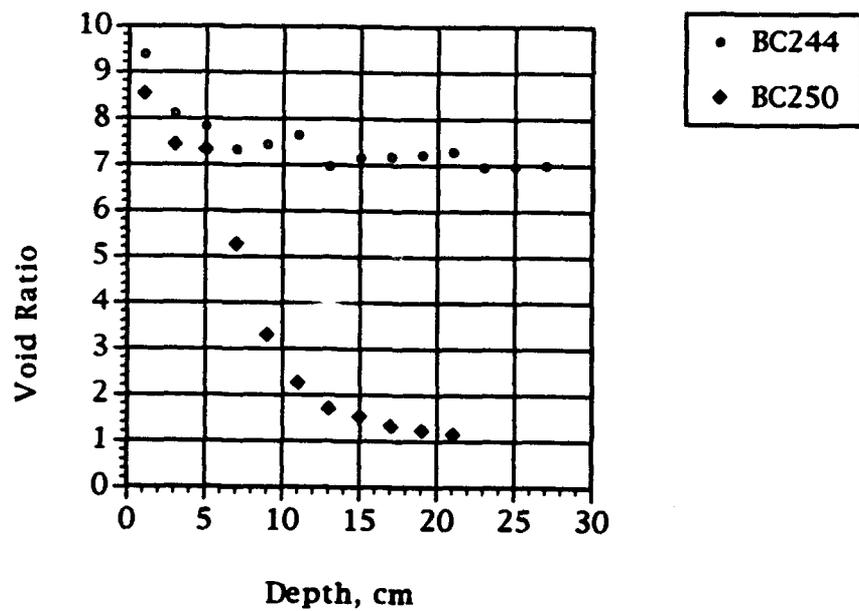
Fig. 6 - Void ratio versus sediment depth at center of sampling interval.

17
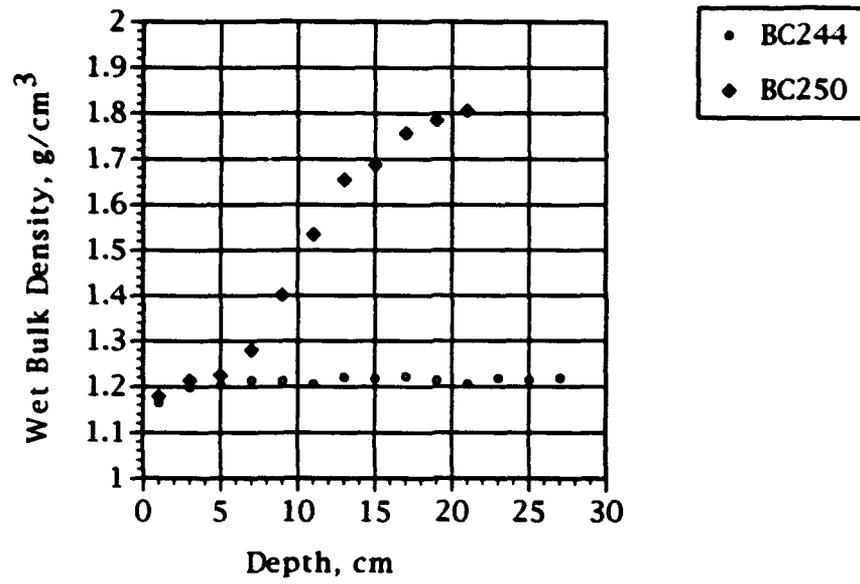
Fig. 7 - Wet bulk density versus sediment depth at center of sampling interval.

a

b
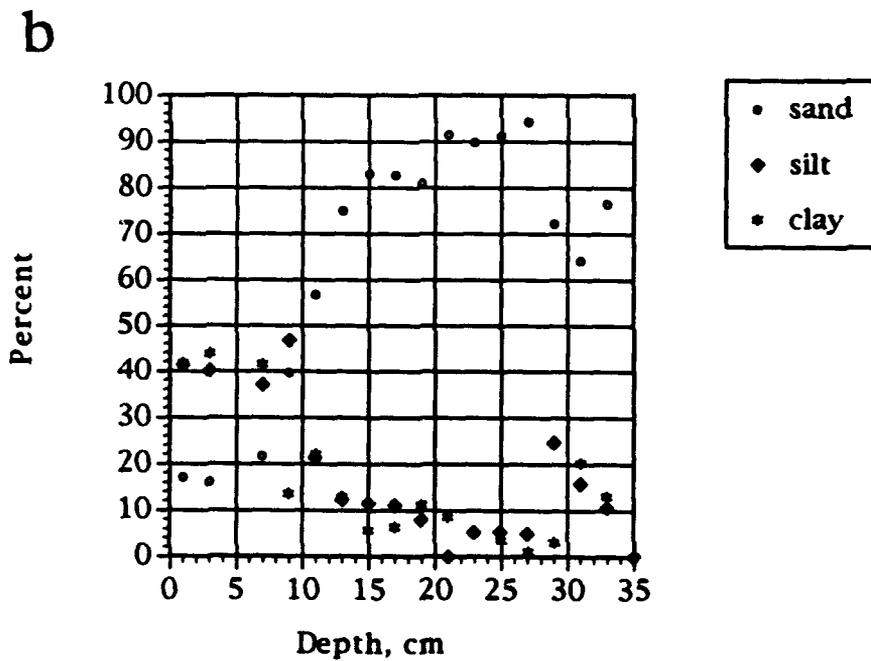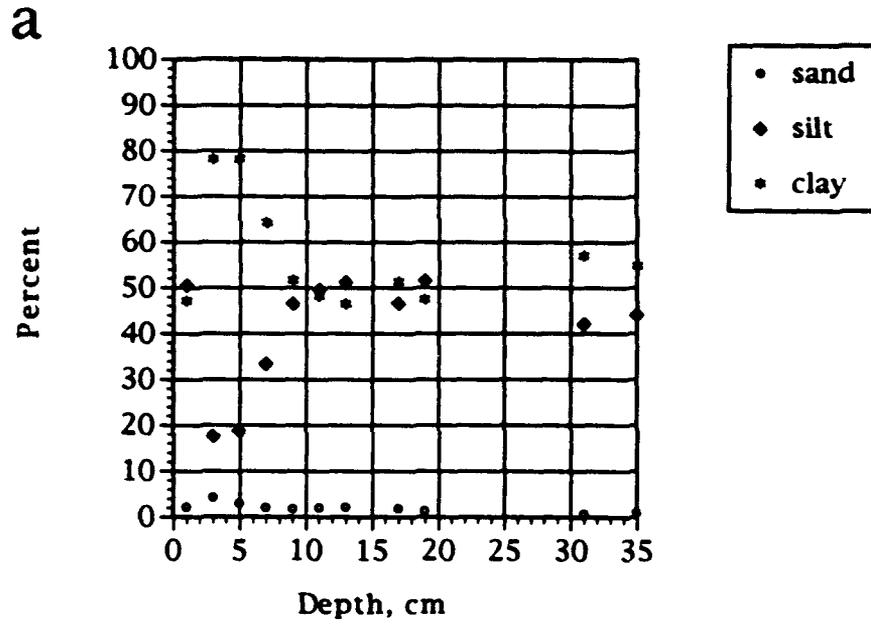
Fig. 8 - Grain size distribution in percents by weight sand, silt, and clay versus sediment depth at center of sampling interval: a. BC244; b. BC250.
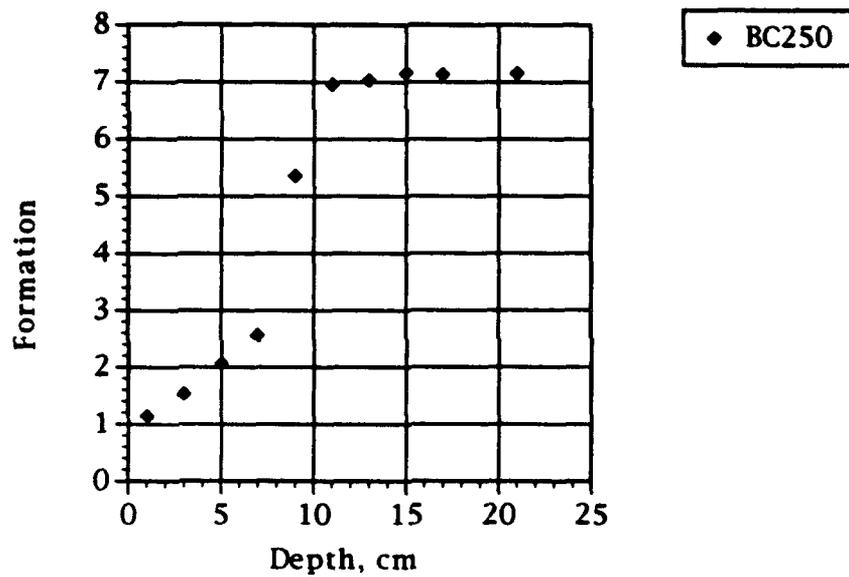
Fig. 9 - Formation factor versus sediment depth at center of sampling interval for BC250 only.