The Chemistry of Water and Sediment from the Benthic Boundary Layer at a Site in the Northwest Atlantic Ocean

R. L. Schmidt

June 1979

**Work Supported by
the U.S. Department of Energy
and General Electric Company
(Knolls Atomic Power Laboratory)
under Related Services Agreement 300A01157**

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from

National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00049 3983

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INTRODUCTION

The corrosion of metal alloys resulting from planned or accidental exposure to the deep-sea environment may proceed at rates or produce corrosion products different from those resulting from exposure to surface waters. Since few corrosion studies have been conducted in the deep sea (Boyd and Fink 1978), estimates of corrosion rates in this milieu were made through comparison of environmental conditions at deep-sea locations with those for sites where corrosion rates have been experimentally determined. A primary objective of this study was to characterize the corrosive potential of the benthic boundary layer at a site where selected metal alloys were being exposed. Those properties of sea water and sediment likely to affect the corrosion of alloys that were measured in this study include salinity, pH, scale-forming cations, redox potential, dissolved gases, heavy metal ions, abrasive particulates, and microorganisms (LaQue, 1975).

Determination of the chemical properties of the benthic boundary layer of the deep sea presents unique analytical problems. The properties of water and the extent and rates of chemical reactions are affected by pressure (Hamman 1957), and the inability to make in situ measurements necessitated the application of thermodynamic relationships and/or empirical equations to analytical values determined for deep-sea samples under normal atmospheric conditions to estimate their actual chemical properties. In this study the chemical properties of abyssal seawater and sediment samples were measured using state-of-the-art methodology and correction factors were applied to estimate values in the deep sea.

Another objective for this program was the development of information concerning the biogeochemical cycling of corrosion products in the benthic boundary layer. Sediments and sea water were analyzed for total trace metals and sediments were subjected to selective extraction methods to evaluate the chemical forms of sediment trace metals. The distribution of trace metals in the sediment profile, the relationships of trace metal concentrations with other sediment components, and the variability of trace element interactions were examined to assess the impact of diagenetic processes on the mobility and accumulation of sediment trace metals.

This work, which is sponsored by the Knolls Atomic Power Laboratory, was performed at the Pacific Northwest Laboratory (PNL), operated for the Department of Energy by Battelle Memorial Institute. The laboratory studies were conducted at the PNL Marine Research Laboratory, Sequim, Washington.

MATERIALS AND METHODS

SEAWATER AND SEDIMENT SAMPLES

Seawater and sediment samples used in this study were collected at a site in the North Atlantic where accidental and planned exposures of several types of metal alloys are occurring. This sampling site is located on the continental slope at 41°45'N, 65°00'W at a depth of about 2,500 m. Sampling was conducted from a deep-sea submersible research vessel. Sea water was collected with TFE-coated sampling bottles and sediment cores of up to 50 cm in length were obtained using 5-cm diameter plastic tubes.

The seawater samples were received at PNL in 1-liter polyethylene bottles and stored at 4°C. Sediment cores were shipped in both frozen and unfrozen (4°C) conditions and were stored accordingly.

SEAWATER CHEMISTRY

The chemical properties of three 1-liter seawater samples were measured in replicate. Since limited sample quantity was available, analytical procedures were selected on the basis of evaluations using surface seawater at the Marine Research Laboratory. The values of some measured parameters such as pH, alkalinity and dissolved organic C may alter slightly during sample storage, however, the extent of changes during storage were likely insufficient to affect the overall evaluation of corrosion potential for the benthic waters that these samples represent.

pH

Measurements of pH for this study were made against National Bureau of Standards phthalate and phosphate buffers using a combination Ag/AgCl-calomel electrode. Meter calibration was monitored with an uncertified tris buffer made in sea water having a salinity approximating that of the samples.

Salinity

Although the most widely-used method for salinity measurements is by conductimetric techniques (Wilson 1975), for this study salinity was calculated from chlorinity values determined using argentometric titration. Of great importance for these samples was the small amount of sample required for chlorinity titrations compared to the amount required for determinations by conductivity.

Chlorinity was determined by titrating AgNO_3 into sea water using K_2CrO_4 as indicator. The silver nitrate solution was standardized with standard sea water having a chlorinity of 19.374 parts per thousand as prepared by the International Association for Physical Sciences of the Ocean. A piston burette capable of dispensing 5 μl increments of titrant was employed.

Alkalinity

Total alkalinity was determined by adding standardized 0.020 M HCl to sea water, boiling for 5 minutes and cooling. The sample was then titrated with NaOH using bromothymol blue as indicator. During cooling and titration, CO_2 -free N_2 was bubbled through the sample. The NaOH titrant was standardized using the same procedure but the sea water was replaced by distilled CO_2 -free water.

Dissolved Organic Carbon

Aliquots of benthic water were filtered through porous silver membranes using a stainless steel filtration apparatus. The apparatus and filters were heated to 550°C prior to use to pyrolyze any organic residue. The filtered water was preserved by freezing.

To determine dissolved organic carbon, seawater samples were added to ampules containing saturated potassium persulfate and 10% phosphoric acid. Following purging with N_2 , the ampules were sealed and autoclaved along with a set of potassium biphthalate standards. After cooling, the ampule seal was broken and the CO_2 purged from the sample with N_2 through an infrared detector.

Suspended Particulates

An aliquot of sea water was filtered through preweighed polycarbonate 0.4 μm membranes. Double filters were used; the suspended matter was collected on the top membrane and the bottom filter served as an analytical blank. The filters were rinsed with distilled water, dried, and weighed. The filtered sea water was used for analyses of other soluble inorganic components. Elemental analysis of suspended matter deposited on the membranes was determined by x-ray fluorescence spectroscopy.

Sulfate

Sulfate was measured in the seawater samples by titration with $\text{Pb}(\text{ClO}_4)_2$ employing a microliter syringe burette and a lead sulfate selective ion electrode to indicate the end point. Standard sea water was used as a standard for comparison.

Mg, Ca and Sr

The concentrations of Mg, Ca and Sr were determined using standard additions and atomic absorption spectrophotometry following dilution in lanthanum chloride to suppress interferences. Concentrations of these elements in standard sea water were also determined to verify the accuracy of this method.

Elemental Analysis

Aliquots of sea water were acidified with ultrapure HNO_3 to pH 2 and analyzed by inductively-coupled plasma emission spectroscopy.

INTERSTITIAL WATER

Sediments were extruded from the core tubes and segmented under N_2 in a glove box. Following centrifugation at 5000 rpm at 4°C , interstitial waters were decanted, again under N_2 . The interstitial waters were analyzed for chemical properties by the same methods described for sea water. In addition, analysis for sulfide ion concentration was undertaken.

Sulfide

The sulfide concentration was determined by titrating with 0.01 M $\text{Pb}(\text{ClO}_4)_2$. A silver/sulfide selective ion electrode was employed to detect the end point. Prior to titration the sample was diluted with an anti-oxidant buffer in N_2 atmosphere.

SEDIMENTS

Following extrusion from the core tubes, the redox potential of the sediments was measured by inserting a platinum/calomel electrode directly into sediments to record the potential measured with a specific-ion meter. The measurements were conducted under N_2 . Samples of sediment were then taken for microbiological analyses. After centrifugation to remove interstitial water, the wet sediments were homogenized and samples were removed for particle size and mineralogical analysis. The remaining sediments were dried at 60°C and crushed in an agate mortar and subsampled for trace metal, organic and radiological analysis.

Particle Size and Mineralogy

Sand and coarse silt-sized materials were removed from sediment samples by sieving. The clay and fine silt fractions were subjected to a centrifuge separation procedure (Kittrick and Hope 1963). The mineralogical components of size fractions were defined using x-ray diffraction analysis employing a selective solvation procedure (Jackson 1973).

Organic Carbon

Organic carbon concentrations were determined using microcombustion techniques (Hajek and Wildung 1969).

Microbiology

Methods were developed for enumerating sulfate-reducing anaerobic bacteria present in deep-sea sediments using a collection of certified anaerobic organisms. Samples of the deep-sea sediments were held at 40°C under anoxic conditions preparatory to conducting the bacteriological assays. Sampling and culture transfers were conducted in controlled N₂ atmosphere. The method selected for the microbiological assay involved culturing in Starkey's medium (Butlin et al. 1949) using the multiple-tube most-probable-number technique (Alexander 1965).

Trace Metals

Sediments were ground to a fine powder and mixed with a binding agent, micro-crystalline cellulose, in a ball-mill. A quantity of sediment-cellulose mixture was subjected to 20,000 psig in a hydraulic press to form a wafer suitable for analysis by energy-dispersive x-ray fluorescence (Currie 1977).

Total metals in sediments were also determined by atomic absorption and inductively-coupled plasma optical emission spectrometry following treatment with HNO₃-HF-HClO₄ (Gupta and Chen 1975). Although plasma emission spectrometry provides simultaneous analysis of 30 elements (Schleicher and Barnes 1975), it lacks the degree of sensitivity required for several trace metals. Atomic absorption methods, flame and non-flame, were required for total Co analysis and analysis of those elements of interest present in relatively low concentrations.

Selective Extraction

A selective extraction method was employed to define the forms of trace metals in the sediments. Core segments were extruded from frozen cores and samples were removed from the central region at each end of each segment. Employing a dry sediment-to-solution ratio of 1:25, wet sediments were sequentially extracted using the method presented in Table 1. The remaining sediment was dried at 50°C and analyzed for total trace metals and organic carbon.

RESULTS AND DISCUSSION

SEAWATER CHEMISTRY

pH

Measurement of pH governs to a great extent the ability to make an accurate evaluation of the thermodynamic properties of sea water (Bates 1975). This is especially important when experimental pH numbers are used to determine the kinetic properties or state of equilibrium of chemical and biological processes occurring in sea water. Unfortunately the difference in ionic strength of standard NBS solutions and that of sea water introduces a systematic error in pH measurement mainly caused by junction-potential differences (Grasshoff 1976). For this reason, secondary standards were prepared in synthetic sea water using tris and tris hydrochloride. However, each salinity value requires preparation of a separate set of tris/seawater buffers and their use is not practicable for routine analysis of widely varying sea waters. Consequently, pH measurements for this study were made against standard NBS phthalate and phosphate buffers. Meter calibration was monitored with an uncertified tris buffer made in sea water having a salinity approximating that of the samples.

The difference in liquid junction potential between seawater samples and standard NBS solutions is in the order of one-tenth of a pH unit (Grasshoff 1976); this magnitude of difference was noted for the tris buffer prepared in our laboratory. The measured pH of tris buffer in sea water of 34 parts per thousand salinity was 8.453 at 21°C; the pM_h of this solution is reported to be 8.340, where M_h = moles free hydrogen ion per kilogram sea water (Hansson 1973).

The pH of sea water is altered not only by changes in acidic and basic species concentrations, but also by changes in temperature and pressure and appropriate corrections must apply to estimate in situ pH. In this study corrections were applied according to the temperature and pressure values reported for the North Atlantic Ocean at 2,500 m. These values were assumed to be 3.0°C and 249 atm (Reid 1974), respectively. A temperature coefficient was calculated using the following equation:

$$pH_{t_2} = pH_{t_1} + 0.0114(t_1 - t_2)$$

where t_1 = measuring temperature
 t_2 = in situ temperature (Hood and Pytkowicz 1974, Skirrow 1975).

The uncertainty of the temperature coefficient is such that the accuracy of the correction is about ± 0.02 pH units.

The effects of hydrostatic pressure on the dissociation constants of carbonic acid in sea water require that the pH value measured at 1 atm be reduced to obtain an estimate of in situ pH. A pressure compensation value of 0.098 pH units was applied to measured values in this study (Riley and Chester 1971). Table 2 lists the measured pH at the given temperature, and the pH corrected for both temperature and pressure. Although the values were measured and corrected to three decimals, the limits of accuracy are about ± 0.02 pH units and the values were rounded to two decimal places.

Salinity

Table 3 lists the titration volumes and estimated salinities of the 3 benthic boundary layer seawater samples examined in this study. The relationship between salinity and chlorinity as determined by argentometric titration is:

$$S \text{ ‰} = 1.80655 \text{ Cl ‰}.$$

This equation was established by an International Panel of UNESCO (Wilson 1975) and has been experimentally verified as an accurate estimate of salinity.

Alkalinity

The total alkalinity of sea water is produced by excess anions of weak acids and corresponds to the amount of strong acid in millimoles required to neutralize 1 kg of sea water. Total alkalinity in well-aerated sea water at ca pH 8 is essentially the sum of the concentrations of bicarbonate, carbonate and borate ions. The most convenient way to estimate concentrations of the species at in situ conditions is to measure total alkalinity in pressure- and temperature-independent units as millimoles/liter. After reducing the measured alkalinity for borate contribution (Dyrssen and Wedborg 1974), the concentrations of carbonate species at in situ temperature and pressure were estimated by applying corrected dissociation constants.

Among several methods based on empirical equations for determining corrected dissociation constants, the method of Gieskes (1974) was selected. The dissociation constants were calculated from the measured chlorinity of the seawater samples for this study and corrected for a temperature of 3.0°C and a pressure of 249 atm. Assuming that total titrable alkalinity is independent of pressure and temperature, and that no CO₂ exchange in the samples had occurred, corrected dissociation constants were then used to estimate the concentrations of the dissociation products of carbonic acid in the benthic boundary layer sea water. These data are given in Table 4. The estimated species distribution of CO₂ is applied in a following section of this report to estimate the in situ degree of calcium carbonate saturation.

Dissolved Organic Carbon

The quantity of dissolved organic carbon (DOC) found in these samples is listed in Table 5. These values (1.02 to 1.22 mg/l) are somewhat higher than those generally reported for deep-sea bottom waters. Menzel (1970) and Menzel and Ryther (1970) report DOC concentrations of about 0.4 to 0.6 mg/l for the deep North Atlantic. The method of analysis used by these investigators is identical to that used in this study. Although the higher values in our water samples may have resulted from contamination by organic substances leaching from the plastic storage containers, dissolved organic C may have diffused from the sediments since the samples were taken near the sediment-water interface.

Suspended Particulate Material

The quantities and trace metal concentrations of suspended particulate material are given in Table 6. The large variations in trace metal concentrations among the samples indicate that the chemical nature of suspended particulates found in the seawater samples was not consistent among samples. Although it was possible that the samples were contaminated by artifacts from the sampling operation, it was just as likely that the trace metals may have resulted from direct or resuspended corrosion products emanating from exposed metals at the site. The differences among samples may have arisen from situational variations during sampling with regard to corroding metal surfaces or resuspended sediments.

Sulfate

The measured quantities of sulfate, Table 7, approximate the sulfate content of standard sea water. The distribution of sulfate among its species at 2,500 m, estimated using Millero's approach (Millero 1971), is approximately: free SO_4^{2-} , 35%; NaSO_4^- , 40%; MgSO_4 , 21%; and CaSO_4 , 4%.

Mg, Ca and Sr

The concentrations of Mg, Ca and Sr in the benthic seawater samples are listed in Table 8. The measured values appear to match closely those expected from chlorinity measurements for open ocean surface sea water. The slight discrepancies may result from the effect of depth on equilibria or the interactions of these elements between sea water and sediment.

Elemental Analysis

The trace metal content of the benthic seawater samples as determined by plasma emission spectrometry, Table 9, displays similar inconsistencies as the

trace metal concentration of suspended particulate matter. As noted above the difference may be related to sampling locations. The concentrations of Cr, Fe, and Ni were below detectable limits, and the plasma method is not routinely used for Co analysis due to high Fe interference encountered in most environmental samples. More refined analytical methods were not pursued for trace metal concentrations in these samples because larger sample sizes are required for preconcentration techniques.

INTERSTITIAL WATER CHEMISTRY

Sediments from cores 2, 7, 9 and 14 were extruded in 5 cm segments. The sediment segments of cores 2 and 9 and of cores 7 and 14 were combined before centrifugation. Following centrifugation, the interstitial waters of the cores from sediment depths 0-5 and 5-10 cm, and from 10-15 and 15-27 cm were mixed to provide sufficient quantities of samples for analysis. The interstitial water samples were filtered by methods described for sea water.

The depth and temperature corrections applied to the parameters of seawater chemistry were also used to estimate in situ values for the interstitial waters.

pH

The pH of the deep-sea interstitial water, Table 10, is somewhat reduced from the seawater pH (Table 2) likely due to increased concentrations of bicarbonate.

Salinity

The titration values and estimated salinities of the interstitial water samples are listed in Table 11. Salinity was calculated assuming that the ratio of salinity to chlorinity used for sea water obtains for interstitial waters.

Alkalinity

The alkalinity measurements for interstitial water were corrected for temperature and depth and the concentration of carbonic acid species, shown on Table 12, was estimated using the same assumptions and equations that were applied to seawater alkalinity. The average concentrations of HCO_3^- in interstitial waters of pelagic clays reported for the Deep Sea Drilling Project is 3.10 mM/l; for terrigenous sediments, 7.20 mM/l (Manheim 1975). Thus, the values determined for this study, 5.14 - 5.54 mM/l, appear to be intermediate between those for pelagic clays and terrigenous sediments.

Dissolved Organic Carbon

The concentration of dissolved organic carbon (DOC) in the interstitial waters of segments from cores 18 and 26 are listed in Table 13. The DOC concentration increases with depth and appears to be correlated with changes with depth for organic C in the sediments (Table 21).

Sulfate

The concentration of sulfate in the interstitial waters was found to be 0.70 mM/l and 0.19 mM/l in the 0-10 cm and 10-27 cm samples, respectively. Since these values are substantially lower than those found in deep-sea interstitial waters separated from sediment immediately after sampling (Manheim 1975), it is suspected that microbial reduction of sulfate has occurred during storage of these cores under possibly anoxic conditions in sealed containers.

Sulfide

Although reduction of SO_4^{2-} in the interstitial waters appears to have occurred as noted above, no detectable levels of soluble sulfide were measured. Interaction of S^{2-} with transition metal ions in the interstitial water may have led to the formation of insoluble metal sulfides and reduced the concentration of S^{2-} to extremely low amounts.

Mg, Ca and Sr

The concentrations of Mg, Ca and Sr in the interstitial waters (Table 14) are less than those in the overlying boundary layer water (Table 8). A reduction in the Ca:Cl ratio of interstitial waters was also noted for deep-sea hemipelagic sediments in the Northeast Pacific (Manheim 1975). This loss in Ca concentration may result from calcium carbonate precipitation due to the increased alkalinity of interstitial water (Table 12).

Elemental Analysis

The results of plasma emission spectrometric analysis of the interstitial waters are shown in Table 15. The analysis of major ions in these samples by this method appears to be reliable. However, the limited quantity of sample prevented the application of concentration techniques to improve the detectability of trace metals. Further analytical development is being undertaken to provide reliable analysis of trace concentrations of metals in samples of limited amount having a high salt matrix by non-flame atomic adsorption spectrometry.

DEGREE OF SATURATION OF CALCITE

The formation of scale deposits consisting of insoluble carbonate salts of calcium, magnesium, and strontium on mild steel exposed to sea water appears to retard its corrosion. However, for metals, such as stainless steel, which depend on oxygen-induced passivity for corrosion protection, the formation of scale may set up corrosion cells and induce accelerated corrosion (LaQue 1975).

Formation of several insoluble carbonates may be possible, including calcite, CaCO_3 ; aragonite, metastable CaCO_3 ; magnesite, MgCO_3 ; dolomite, $\text{CaMg}(\text{CO}_3)_2$; and huntite, $\text{CaMg}_3(\text{CO}_3)_4$. Little data has been developed for carbonate species other than calcite, the predominant scale-former, and, thus, discussion of degree of saturation and formation of scale will be limited to calcite in this paper.

The degree of saturation of CaCO_3 is usually given as the ratio of the ion activity product to the apparent solubility product (Skirrow 1975):

$$\Omega = \frac{\text{IAP}}{K'_{\text{sp}}}$$

At the ocean's surface, the degree of saturation generally exceeds 100%, i.e., surface sea water is supersaturated with respect to CaCO_3 . But calcium carbonate has the property of becoming increasingly soluble with increasing pressure (depth) and decreasing temperature (Gieskes 1974). Thus, it is expected that at some depth in the ocean, sea water would become undersaturated with respect to CaCO_3 and the removal of CaCO_3 would exceed the addition by sedimentation. This phenomenon has been observed and efforts have been made to develop models to describe it (Berner 1965, Ingle 1974, Leyendekkers 1975, Pytkowicz 1968).

In this discussion, the method of Ingle (1974) was applied to estimate the apparent solubility product of calcite at 3.0°C and 249 atm. The apparent ion activity product was calculated using data from Elgquist and Wedborg (1975). Although all the models for describing CaCO_3 saturation are empirical and also suffer by neglecting the interactions of Ca with organic matter, the estimated values of degree of saturation may be useful for evaluating the corrosive potential of the deep-sea environment. The estimated degree of saturation of calcite in benthic boundary layer sea water and sediment interstitial waters are listed in Table 16. These data indicate that no calcite scale would be expected to form in the benthic boundary layer sea water. However, scale formation appears possible in the upper 10 cm of the sediment.

SEDIMENT CHEMISTRY

Redox Potential

The potential differences in the sediments were measured with a combination electrode pair consisting of an inert Pt and a saturated calomel reference electrode. The measured emf, E_m , is the difference between the oxidation-reduction potential of the sample and the potential of the reference electrode:

$$E_m = E_H - E_{\text{ref.}}$$

The reference potential was estimated by be 255 mv under the conditions of measurement (Stumm and Morgan 1970). The measured and estimated potentials for the sediment samples from the deep-sea are given in Table 17. The pE values shown are logarithmic equilibrium expressions of the electron activity:

$$pE = \frac{E_h}{2.3} \frac{RT}{F} - 1$$

The sediments may be considered to be anaerobic; the redox potential of a system containing 0.01 mg/l O₂ at pH 8 is approximately 700 mv (pE = 12.5) (Stumm and Morgan 1970). Thus, the sediment samples have relative electron activities 5 to 9 orders of magnitude greater than very slightly oxygenated sea water. Figure 1, a diagram of the distribution of a NO₃⁻ - NH₄⁺ system, shows that redox potentials of the sediments collected for this study are at about the level where NO₃⁻ is being reduced to NH₄⁺. As shown on Figure 2, the redox potentials determined for this study decrease linearly with depth. By extrapolation, the depth at which SO₄²⁻ would be reduced to HS-(~225 mv) is about 50 cm (Goldhaber and Kaplan 1974).

Particle Size and Mineralogy

The particle size distribution of the sediments in Cores 2, 9 and 7, 14 (Table 18) as a function of depth indicates that a gradient exists from larger- to smaller-sized material. This distribution is anomalous for undisturbed abyssal sediments, and indicates a modification of the normal sedimentary processes by turbidity currents or mechanical disturbance (Riley and Chester 1971). The distribution of minerals in the sediments (Table 19) indicates the presence of smectite, a clay mineral apparently derived from marine weathering of volcanic material, and the absence of montmorillonite, probably of terrigenous origin in this area (Riley and Chester 1971, Elderfield 1976), in the surface layer (0-10 cm). This phenomenon may be further evidence of recent disturbance to the sediments.

Microbiology

The numbers of sulfate-reducing anaerobic bacteria per gram of wet sediment in segments from cores 2, 7, 9, and 14 are given in Table 20. The variability of the data suggests that there is no significant difference in the distribution of these bacteria with depth. Generally, the quantity of total bacteria in marine sediment decreases with sediment depth (Bordovskiy 1965, Price 1975) as shown in Figure 3. However, the results of this study are in accord with data cited by Bordovskiy (1965) showing that the fraction of spore-forming bacteria, a class which includes SO₄²⁻ reducers, of the total bacteria count increases with depth. The presence of sulfate-reducing bacteria indicates that there is a potential for corrosion to occur in the sediment under conditions in which the concentration of O₂ is reduced by mechanical or chemical means (LaQue 1975).

Organic Carbon

The quantities of organic carbon in segments of sediment cores 2 and 9, 7 and 14; and 29 are given in Table 21 which also includes the estimated quantities of inorganic C as determined by difference between total C and organic C measurements.

Cores 2, 9 and 7, 14

Organic C increased with depth in cores 2, 9, and 7, 14, a condition not usually prevalent in deep-sea sediments. The distribution of organic C usually decreases with depth as a result of microbial degradation and deposition of particulate organic matter (Bordovskiy 1965, Price 1975). The distribution of organic C in these cores appears to arise from biological oxidation of sediment organic matter following a recent disturbance which produced a distribution of sediment particles decreasing in size with depth (see Table 18).

The rate of biological oxidation would be expected to decrease with sediment depth as a function of O_2 concentration. This phenomenon is illustrated by changes with depth in E_h (Table 17) and numbers of sulfate-reducing bacteria (Table 20). The effect of sedimentation on organic C concentration during the relatively short time required for oxidation would be minimal in the deep ocean. For a sediment initially containing 5.8 mg C per g which was well-mixed and then left undisturbed for 15 years, the annual rates of oxidation required to approximate the present distribution of organic C in these 4 cores would be 5.9, 3.3, and 0.9% at 2.5, 7.5, and 12.5 cm depth, respectively. The rate of biological oxidation of sediment organic matter has been determined by in situ measurements and is in the order of 1-4% per year for sediments at 2,000 m depth in the Northwest Atlantic south of New England (Smith and Teal 1973, Degens and Mopper 1975).

If the organic C concentrations in these cores are normalized against the fraction of material having a particle diameter $<5\mu m$, their coefficient of variation (COV) is 0.11. The COV for non-normalized organic C is 0.38. Alternatively, the data can be normalized to the concentrations of Rb, an element that exhibits conservative behavior under marine conditions (Brewer 1975) and is associated with the clay size fraction of the sediment, substituting for potassium in aluminosilicate minerals (Calvert 1975). Using the data in Table 27, the COV for Rb-normalized organic C is calculated to be 0.08. The sediment represented by these cores appears to have been disturbed, but not well-mixed, resulting in larger material being deposited over smaller grain-size material, and producing the observed distribution of organic C.

The quantity of inorganic C in cores 2, 9, and 7, 14 appears to have a nearly stoichiometric relationship with Ca in the sediment through the formation of calcite, $CaCO_3$. The correlation coefficient of the regression of inorganic C on Ca, $y = 1.59 + 2.17x$, is $r = 0.955$ which is significant at

$p < 0.001$. The stoichiometry of inorganic C to Ca is illustrated in Table 22. When the Ca concentration in sediment is corrected for the formation of gypsum, CaSO_4 , the mean molar ratio of Ca to inorganic C almost equals unity.

Core 29

As shown in Table 21, core 29 appears to come from an area where the sediments are continuously well-mixed with no apparent strong differences in C concentration with depth. The mean concentration of organic C, 5.8 mg/g, in core 29 closely approximates that in the bottom portions of cores 2, 9, and 7, 14. Normalizing the organic C values against Rb content has no significant effect on the variability of the data.

Elemental Analysis

The concentrations of elements in sediment cores 2, 9, and 7, 14 are given in Table 23. Table 24 lists the elemental content of core 29. Analyses by x-ray fluorescence (XRF) were performed on 2 or 3 aliquots of the sediment samples. The accuracies of the analytical methods were verified by analyzing standard rock and soil samples (Table 25). Extremely good agreement between analytical data and certified standard values is demonstrated. The mean analytical measurements for the trace elements are listed on Table 26.

No component in core 29 appears to have a strong correlation with depth which indicates a fairly well-mixed sediment to at least 43 cm. However, the concentrations of most of the elements in cores 2, 9 and 7, 14 appear to exhibit a relationship with sediment depth. The distribution of trace metals with depth likely results from the particle size distribution which, for cores 2, 9 and 7, 14, consists of larger, lower-surface area particles at the surface grading with depth to smaller materials. The strong correlations with depth will produce spurious correlations among total concentrations of elements and could lead to erroneous conclusions about biogeochemical processes influencing the distribution of trace metals in the sediment. To minimize the particle size effect, the concentrations of trace elements were normalized against the Rb concentration, as was done above for organic C distribution. Table 27 lists the Rb-normalized values for elements in core segments from cores 2, 9; 7, 14; and 29.

Selective Extraction

The reagents employed in this procedure, as listed on Table 1, were selected from those suggested by several investigators for removing specific fractions of trace metals from sediments and soils. Dilute acetic acid was selected to remove trace metals principally associated with inorganic sorption sites or weakly complexed by organic moieties. Copper specifically adsorbed on inorganic sites was extracted from soil with this reagent (McLaren and Crawford 1973) and Hodgson (1960) successfully separated exchangeable Co from

montmorillonite using 2.5% acetic acid. Other reagents commonly used for removing so-called "exchangeable" or "available" metals may also dissolve metals associated with amorphous metallic oxide coatings (Gibbs 1973) or the mineral lattice (Aleksandrova 1967).

Trace metals associated with organic materials were removed using 0.1 M sodium pyrophosphate. This reagent was the most efficient extractant of organic matter from soil of various sodium salt solutions tested by Bremner and Lees (1949). Alteration of organic complexes (Bremner and Lees 1949), collapse of the clay lattice (Aleksandrova 1967, Lahann 1976), or dissolution of amorphous oxide materials (McLaren and Crawford 1973) may result from using more rigorous treatments to remove organic matter. Residual organic matter which may be coating sediment particles is removed with sodium hypochlorite at 100°C. This treatment was found important in order to efficiently extract trace metals associated with metal oxides in the following step.

Treatment with hydroxylamine hydrochloride in acetic acid was selected for extraction of trace metals sorbed to or coprecipitated with the amorphous metal oxides of, primarily, Mn and Fe. This portion of trace metals is referred to as the reductant-soluble fraction. This reagent dissolved almost all total Fe and Mn from ferromanganese nodules (Chester and Hughes 1967) and appears to remove free oxides in soils and sediments without affecting the lattice structure of clay minerals (Lahann 1976). Other reagents commonly used for this step required repeated treatment and/or uv irradiation (McLaren and Crawford 1973, Grimme 1967, LeRiche and Weir 1963).

The quantities of Cr, Mn, Fe, Co, Ni and Cu extracted from the sediment segments of core 29 are listed in Table 28. Analytical detection of Cr and Co in the Na-pyrophosphate extracts for organically-complexed metals was limited due to matrix interferences.

Distribution of Trace Elements in the Sediment Profile

The distribution of trace elements may be related to long-term diagenetic equilibrium processes. Microbial degradation of organic matter, oxidation: reduction reactions, and sorption/desorption are known to influence trace metal concentrations in sediments. As an example of the influence of microbial metabolic activity, the variation of Ca concentrations in the sediment with depth is indicative of the accumulation of CaCO_3 as CO_3^{2-} , produced by microbial decomposition of organic matter, interacts with Ca^{2+} in the pore waters. The degree of saturation of calcite was shown by thermodynamic relationships to exceed 100% in the top 10 cm of the sediment layer (Table 16) and, thus, precipitation of CaCO_3 is possible. In addition, a nearly perfect stoichiometric relationship between Ca and inorganic C in the sediments was demonstrated (Table 22).

Often a fraction of sediment trace metals is of biogenic origin, likely in fecal pellets. Microbial metabolic processes may produce soluble organic complexes of these metals which may diffuse from the sediment. On the basis of data for trace metal concentrations in sea water and suspended matter

(see Bibliography), the average fluxes from North Atlantic Ocean deep-sea sediments are estimated to be: Fe, 0.38×10^{-3} ; Co, 15×10^{-6} ; and Ni, 35×10^{-6} mg/cm²/year. Manheim (1975) estimated fluxes for the world-wide ocean as follows: Fe, 7.8×10^{-6} ; Co, 0.31×10^{-6} ; and Ni, 0.44×10^{-6} mg/cm²/year. If the North Atlantic receives a high proportion (60%) of total dissolved solids from the world's runoff, as suggested by Schutz and Turekian (1965), while constituting only 29% of the world's oceanic volume (Reid 1974), then a high rate of trace metal accumulation will result. This likely leads to greater concentrations of metals in North Atlantic sediment interstitial water and increased diffusive flux of trace metals compared to the world average.

Manganese is by far the most mobile of the metals in deep-sea sediments as shown by the large quantities dissolved from the sediments of core 29 by 2.5% acetic acid (Table 28). The effect of redox equilibria on Mn is illustrated by the differences in concentration in the sediment profile. Redox processes, occurring at the pE level measured for these sediments (Table 17), result in reduction of MnO₂ and formation of Mn²⁺ (Stumm and Morgan 1970). The accumulation of Mn near the sediment surface (Table 27) is likely due to the oxidation of Mn²⁺ following diffusive transport. Apparently in the sediments represented by core 29, reductant-soluble Mn has migrated from 6-10 cm and has been deposited at 4-6 cm, perhaps as MnO₂ or MnCO₃. The quantity of lithogenous Mn, the difference between total and extracted Mn, shows little variation throughout the profile. In core 29 the mean quantity of extracted or non-lithogenous Mn is 38% of total Mn; in a sediment core taken about 1300 km east of site 1, this fraction was 42% of total Mn (Chester and Messiha-Hanna 1970).

Selective extraction (Table 28) indicates that ~9% of Cr is in the non-lithogenous fraction of the sediment. Chester and Messiha-Hanna (1970) found that 12% of Cr is in non-lithogenous positions in three sediments collected along the continental slope near New England. Cr, which is less soluble under reduced conditions, exhibits a distribution with depth which indicates that it may also be affected by redox equilibrium and diffusion processes. The small fraction removed from the sediment upon treatment with acidic reducing agent may be Cr(OH)₃ which formed from CrO₄²⁻ under the relatively reduced conditions in the sediment.

The distribution of Fe in core 29 is typical for hemipelagic sediments, i.e., little variation in concentration. Although some oxidized Fe species (reductant-soluble fraction) may be solubilized under reduced conditions, they are likely immobilized again as relatively insoluble sulfides (Bonati et al. 1971). The non-lithogenous fraction in core 29 is 11% of total Fe; this value is typical of that for deep-sea sediments throughout the North Atlantic (Chester and Messiha-Hanna 1970).

The geochemistry of cobalt and nickel in marine sediments is strongly affected by redox processes involving Mn-oxide precipitates (Hem 1978). This is illustrated by considering the ratio of non-lithogenic Co or Ni against

non-lithogenic Mn. In core 29 the mean ratio for Co is 0.0125 ± 0.0010 ; in 37 North Atlantic deep-sea sediments, the mean ratio is 0.0222 ± 0.0035 . The t statistic, testing the null hypothesis that the difference between the ratios is zero, is 1.43 with 45 degrees of freedom and indicates no significant difference between the ratios. Similarly, the mean ratios of non-lithogenic Ni to non-lithogenic Mn are 0.0338 ± 0.0038 for core 29 and 0.0608 ± 0.0156 for 37 North Atlantic deep-sea sediments. Again the t statistic, 0.90 with 45 degrees of freedom, shows no significant difference between the ratios. Apparently non-lithogenic Ni and Co do not form discrete minerals but are incorporated into pelagic sediments in association with Mn species. However, under reduced conditions Ni and Co do not appear to migrate as readily as Mn and may be retained by Fe species (Bonati et al. 1971).

CONCLUSIONS

The chemical properties of water from the benthic boundary layer do not appear to differ substantially from those of surface sea water. Salinity, pH and major ion content of this water appear to be representative of well-oxygenated, unpolluted oceanic water. On the basis of the properties examined, it is expected that corrosion of metals exposed in the deep sea would not differ greatly from that in surface waters having similar properties. However, the effect of pressure on corrosion rates and chemical forms of corrosion products may be an unknown factor of major importance. Increased calcite solubility at depth has been well-documented and the resulting inhibited formation of protective scale may be indicative of the effects of pressure on corrosion. Corrosion rates for stainless steel appear to be reduced in the deep sea, however this phenomenon has been attributed to lower temperatures (Boyd and Fink 1978). The effect of pressure on corrosion independent from other variables apparently has not received emphasis.

The presence of sulfate-reducing bacteria in the bottom sediments at this site indicates that, if diffusion of O_2 into the sediment was inhibited, stainless steels buried in the mud would lose passivity and corrosion rates would increase.

The eventual fate of corrosion products is dependent on their properties and the properties of their environment. In benthic boundary layer sea water it might be expected that corrosion products would be released as metal oxides. Oxidic corrosion products that become incorporated in the sediment will likely be immobilized in the oxic zone, however if anoxic conditions should develop, redox processes may lead to their accumulation of the sediment surface as in the case of Mn, or to their complexation by sediment organic ligands. Corrosion products from metals exposed to reduced conditions in the sediment may be ionic in nature and interact with insoluble sediment components or become complexed with soluble organics in the interstitial water. Organo-metallic complexes may be labile and undergo further chemical changes and, perhaps, eventually diffuse to the overlying sea water, or they may have a more refractory nature and help to immobilize the corroded metals in the sediment.

RECOMMENDATIONS

Since accurate evaluation of the corrosive potential of the deep-sea environment depends on estimations of in situ conditions, in future studies shipboard measurements under controlled temperature and atmosphere immediately following sample acquisition are recommended for several critical parameters including pH, redox potential, alkalinity, sulfide and sulfate concentrations, and microbial populations. The nature of these measurements and the need for extreme care to prevent contamination of biological, water, and sediment samples may require the participation in sampling cruises of two or more experienced research staff.

Although this study has provided data about the geochemistry of trace metals at a particular site, there exists a large degree of uncertainty as to the applicability of this information to corrosion products. Apparent is the need for investigations of the chemical nature and eventual fate of released corrosion products in the deep sea. Initial experiments of this nature are currently being undertaken at the Pacific Northwest Laboratory under the sponsorship of the Department of Energy through the auspices of the Knolls Atomic Power Laboratory. A series of experiments is planned to determine the rate of release and form of corrosion products removed from neutron-activated metal specimens upon exposure to sea water and sediments under oxidized and reduced conditions. In addition, biological uptake and effect studies using a variety of representative marine animals exposed to sea water and sediments containing released corrosion products will be initiated. Geochemical alterations of long-lived corrosion products and their possible biological uptake and effects may occur over a long term. Experiments following the course of these possible long-term chemical changes and biological effects are being planned as extensions of the current research at PNL.

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Department of Energy through the Knolls Atomic Power Laboratory, Schenectady, N.Y. Sherman Williams, KAPL's technical representative for this project, supplied the seawater and sediment samples for this study. Laboratory research was capably assisted by Lisa Veneroso and technical guidance was provided by T. R. Garland and R. E. Wildung. J. E. Rogers conducted the microbiological studies. This report was prepared with the much-needed and untiring assistance of Judy Jensen.

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TABLE 1. Sequential extraction of trace metals in marine sediments

Fraction	Extractant	Treatment
Trace metals in weakly-complexed organic form or specifically sorbed on inorganic sites	2.5% Acetic acid	Shake 48-72 hours. Centrifuge.
Trace metals specifically sorbed or strongly-complexed by organic material	0.1 M Sodium pyrophosphate	Shake 48-72 hours. Centrifuge Repeat.
Residual organic matter	5% Sodium hypochlorite	Shake overnight. Centrifuge.
Trace metals associated with amorphous Mn- and Fe-oxides	1 M Hydroxylamine hydrochloride in 25% Acetic acid	Shake 48-72 hours. Centrifuge. Repeat.

TABLE 2. pH of seawater samples from the benthic boundary layer

	Sample		
	1	2	3
Temperature, °C	14.0	14.0	14.5
Measured pH	8.159 8.143	8.120 8.131	8.188 8.209
Mean	8.151	8.126	8.198
Corrected to 3.0°C	8.276	8.251	8.329
Corrected to 249 atm	8.174	8.149	8.227
Say	8.17 ± 0.02	8.15 ± 0.02	8.23 ± 0.02

TABLE 3. Salinity of benthic boundary layer sea water

	Standard sea water	Sample		
		1	2	3
Titrant volume, ml	15.63	15.34	15.25	15.08
	15.67	15.40	15.31	15.19
Chlorinity, ‰	19.374	18.99	18.88	18.67
		19.06	18.95	18.80
Salinity, ‰ (calculated from Cl ‰)	35.00	34.31	34.11	33.73
		34.43	34.23	33.96
Mean		34.37 ± 0.06	34.17 ± 0.06	33.85 ± 0.09

TABLE 4. Total alkalinity and estimated concentration of dissociation products of carbonic acid in benthic boundary layer seawater samples, corrected to 3.0°C and 249 atm.

	Sample		
	1	2	3
Total alkalinity, mM/l (as titrated)	2.521 2.488 2.485	2.503 2.473 2.541 2.534	2.607 2.627 2.674 2.605 2.590
Mean	2.498	2.513	2.621
Standard error	0.012	0.016	0.015
Carbonate alkalinity, mM/l	2.417	2.436	2.533
[CO ₃ ²⁻], mM/l	0.160	0.154	0.187
[HCO ₃ ⁻], mM/l	2.090	2.119	2.159
[CO ₂] _t , mM/l	0.016	0.017	0.014
ΣCO ₂ , mM/l	2.266	2.290	2.360

TABLE 5. Dissolved organic carbon concentrations in benthic boundary layer seawater samples

	Sample		
	1	2	3
Dissolved organic carbon, mg/l	1.02 1.00 1.03	1.37 1.20 1.13 1.16	1.19 1.05 1.00 1.07 1.03
Mean	1.02	1.22	1.07
Standard error	0.01	0.05	0.03

TABLE 6. Quantity of suspended particulate material and concentration of particulate trace metals in benthic boundary layer sea water

Sample	mg/l	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
-----μg/g-----									
1	0.43	8870	322	<30	11,000	27.7	11,800	1650	1260
2	0.45	592	<1	57,600	9,500	165	52,300	13,400	5850
3	0.31	<1	<1	41,000	8,500	<1	11,500	10,200	1370

TABLE 7. Concentration of sulfate in benthic boundary layer seawater samples

<u>Sample</u>	<u>0.1 M Pb(ClO₄)₂ titration volume, ml</u>	<u>Sulfate, mM/l</u>
<u>Standard sea water</u> expected*		27.6
as measured	1.375 1.384	27.5 27.7
Mean		27.6
<u>Seawater</u> 1	1.376	27.5
2	1.365	27.3
3	1.353	27.1

* Wilson 1975

TABLE 8. Concentrations of Mg, Ca, and Sr in benthic boundary layer seawater as determined by atomic absorption (AA) and plasma emission spectroscopy (PES).

		<u>Sample</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
		<u>mM/l</u>		
Mg, mM/l	AA	57.2	52.0	56.1
	PES	56.4	56.8	56.8
	expected *	53.4	53.1	52.6
Ca, mM/l	AA	10.8	10.3	10.7
	PES	10.2	10.4	10.3
	expected *	10.3	10.3	10.2
Sr, mM/l	AA	0.088	0.085	0.093
	expected *	0.093	0.093	0.092

*Dyrssen and Wedborg 1974.

TABLE 9. Elemental analysis of benthic boundary layer sea water by plasma emission spectrometry

Sample	B	Na	Mg	Al	K	Ca	Cr
	-----mg/l-----						
1	4.18	11900	1370	0.087	387	407	<0.028
2	4.10	11900	1380	0.097	390	417	<0.028
3	4.16	11900	1380	0.090	391	412	<0.028
Detection Limits	0.01	0.10	0.001	0.05	6.0	0.007	0.028
Expected*	4.44	10770	1290	0.002	380	412	0.0003

Sample	Mn	Fe	Ni	Cu	Zn	Sr
	-----mg/l-----					
1	<0.003	<0.04	<0.02	0.26	0.09	6.37
2	4.30	<0.04	<0.02	0.083	0.38	6.36
3	4.04	<0.04	<0.02	0.012	<0.011	6.29
Detection Limits	0.003	0.04	0.020	0.012	0.011	0.100
Expected*	0.0002	0.002	0.0017	0.0005	0.049	8.00

* Brewer 1975

TABLE 10. pH of interstitial water from deep-sea sediments

	Sample	
	0-10 cm	10-27 cm
Temperature	20°C	19°C
Measured pH	7.98	7.92
Corrected to 3.0°C	8.17	8.10
Corrected to 249 atm	8.07	8.00

TABLE 11. Salinity of deep-sea interstitial water

	Standard sea water	Sample	
		0-10 cm	10-27 cm
Titrant volume, ml	14.54	12.94	13.96
	14.54	13.03	13.94
	14.59		
	14.60		
	14.58		
Mean	14.57		
Standard error	0.013		
Chlorinity, ‰	19.374	17.21	18.56
		17.33	18.54
Salinity, ‰	35.00	31.09	33.53
		31.31	33.49
Mean		31.20	33.51

TABLE 12. Total alkalinity and estimated concentration of dissociation products of carbonic acid in deep-sea sediment interstitial waters corrected to 3.00°C and 249 atm

	Sample	
	0-10 cm	10-27 cm
Total alkalinity, mM/l	6.239	5.652
(as titrated)	6.226	5.811
Mean	6.232	5.732
Carbonate alkalinity, mM/l	6.162	5.666
[CO ₃ ²⁻], mM/l	0.309	0.261
[HCO ₃ ⁻], mM/l	5.544	5.144
[CO ₂] _t , mM/l	0.055	0.058
ΣCO ₂ , mM/l	5.905	5.463

TABLE 13. Dissolved organic carbon concentrations in interstitial waters of deep-sea sediments

Sample	Depth	Dissolved organic carbon mg/l			
		Mean			
Core 26	0-10 cm	6.36	6.27	6.24	6.29 ± 0.04
	10-20	7.83	7.56	7.05	7.48 ± 0.23
	20-30	12.84	12.45		12.64 ± 0.29
	30-44	11.49	11.73	11.79	11.67 ± 0.09
Core 18	0-10	4.32	3.96	3.84	4.04 ± 0.14

TABLE 14. Concentrations of Mg, Ca and Sr in sediment interstitial waters from the benthic boundary layer as determined by atomic absorption (AA) and plasma emission spectrometry (PES)

		Sample	
		0-10 cm	10-27 cm
Mg, mM/l	AA	53.1	53.7
	PES	51.4	53.5
Ca, mM/l	AA	8.6	8.6
	PES	8.7	8.7
Sr, mM/l	AA	0.081	0.085

TABLE 15. Elemental analysis of interstitial waters by plasma emission spectrometry

Sample	B	Na	Mg	Al	K	Ca	Cr
-----mg/l-----							
0-10 cm	4.94	10300	1250	0.63	436	350	<0.028
10-27 cm	5.10	10900	1300	0.14	475	350	<0.028
Expected*	4.2	10800	1250	--	380	415	--

Sample	Mn	Fe	Ni	Cu	Zn	Sr
-----mg/l-----						
0-10 cm	0.40	0.26	<0.02	0.023	0.15	5.44
10-27 cm	0.32	0.083	<0.02	<0.012	<0.011	5.70
Expected*	1.0	0.02	0.005	0.005	0.025	7.80

* Manheim 1975

TABLE 16. Estimated degree of saturation of calcite
in benthic boundary layer sea water and
sediment interstitial waters

Sample	Degree of Saturation, %
Benthic boundary layer sea water	
1	65.6
2	64.0
3	79.4
Interstitial water	
0-10 cm	120
10-27 cm	92.6

TABLE 17. Redox potential of sediments from the deep sea

Depth, cm	-----Core-----				Mean	pE
	2	7	9	14		
E_m , measured potential, mv						
0-5	158	159	170	159	161	
5-10	78	168	132	225	151	
10-15	23	72	-12	-40	12	
15-27	-80	-3	-	-108	-64	
E_h , redox potential, mv						
0-5	413	414	425	414	416	7.4
5-10	333	423	387	480	406	7.2
10-15	278	332	243	215	267	4.8
15-27	175	252	-	147	191	3.4

TABLE 18. Particle size analysis of sediments from Cores 2, 9 and 7, 14.

Cores 2, 9	Depth, cm			
	0-5	5-10	10-15	15-27
	-----weight %-----			
Particle size				
<0.2 μm	13.0	16.3	20.6	22.0
0.2 - 2 μm	11.0	21.0	30.2	40.0
2 - 5 μm	8.7	15.4	3.6	5.0
5 - 20 μm	8.6	11.3	12.3	16.9
20 - 50 μm	6.1	4.7	8.6	3.9
0.05 - 0.10 mm	24.5	18.6	11.7	10.5
0.10 - 0.25 mm	12.5	7.2	7.0	0.9
0.25 - 0.50 mm	7.2	3.0	3.0	0.4
0.50 - 1.00 mm	6.2	2.0	1.6	0.4
1.00 - 2.00 mm	2.2	0.5	1.4	0.0
Median particle size, μm	54	4.2	1.8	1.0
Sediment type	silty clayey sand	sandy silty clay	sandy silty clay	silty clay
Cores 7, 14				
Particle size				
<0.2 μm	11.3	14.2	24.9	18.1
0.2 - 2 μm	9.3	19.4	45.0	41.6
2 - 5 μm	7.4	14.4	5.7	4.8
5 - 20 μm	7.0	11.2	12.9	24.9
20 - 50 μm	7.5	4.2	1.7	0.8
0.05 - 0.10 mm	25.2	18.9	8.4	8.1
0.10 - 0.25 mm	15.4	8.7	1.2	0.9
0.25 - 0.50 mm	8.9	4.7	0.7	0.4
0.50 - 1.00 mm	6.8	3.3	0.5	0.4
1.00 - 2.00 mm	1.2	0.5	0.0	0.0
Median particle size, μm	62	6.4	0.73	1.2
Sediment type	silty clayey sand	sandy silty clay	silty clay	silty clay

TABLE 19. Mineralogy of fine clay fractions (<0.2 μ m) of sediments in Cores 2, 9 and 7, 14. M = major, m = minor, t = trace component

Component	Depth, cm			
	0-5	5-10	10-15	15-27
<u>Cores 2, 9</u>				
Montmorillonite			M/m	M/m
Chlorite	m	m	m	m
Mica (Illite)	M/m	M/m	M/m	M/m
Kaolinite	m	m	m	m
Highly-charged smectite	M	M	M/m	M/m
<u>Cores 7, 14</u>				
Montmorillonite			M/m	
Chlorite	m	m	m	m
Mica (Illite)	M/m	M/m	M/m	M/m
Kaolinite	m	m	m	m
Highly-charged smectite	M	M	M/m	M

TABLE 20. Numbers of sulfate-reducing bacteria per gram of wet sediment in core segments

Core	Depth, cm			
	0-5	5-10	10-15	15-27
2	7×10^7	3×10^4	$\sim 2 \times 10^6$	$\sim 1 \times 10^7$
7	1.1×10^4	2.1×10^5	9.3×10^4	1.2×10^5
9	$\sim 1 \times 10^6$	$\sim 4.5 \times 10^5$	1.4×10^4	-
14	1.4×10^4	9.2×10^3	6.4×10^3	6.4×10^4

TABLE 21. Organic and inorganic C in sediment core segments

	Depth cm	Organic C --mg/g dry	Inorganic C sediment---
Cores 2, 9	0-5	2.6	20.3
	5-10	4.2	11.3
	10-15	3.9	8.4
	15-27	5.8	10.3
Cores 7, 14	0-5	2.3	16.1
	5-10	2.9	14.5
	10-15	6.2	9.1
	15-27	6.0	8.1
Core 29	0-2	6.1	7.5
	2-4	6.4	7.4
	4-6	5.0	10.4
	6-10	5.2	11.2
	10-15	5.8	7.4
	15-20	5.5	6.1
	20-25	6.0	7.7
	25-30	6.2	7.0
	30-35	6.0	7.4
	35-43	4.8	8.9

TABLE 22. Relationship of inorganic C and Ca in sediments

	Total Ca	CaSO ₄ (s)*	Difference -----meq/g-----	CO ₃ ²⁻	Ratio Ca/CO ₃ ²⁻

Cores 2, 9					
0-5 cm	1.78	0.10	1.68	1.69	0.99
5-10	1.26	0.13	1.13	0.94	1.20
10-15	0.93	0.18	0.75	0.70	1.07
15-27	0.93	0.11	0.82	0.86	0.95
Cores 7, 14					
0-5	1.71	0.12	1.59	1.34	1.17
5-10	1.67	0.11	1.56	1.21	1.29
10-15	0.96	0.18	0.78	0.76	1.03
15-27	0.73	0.12	0.61	0.68	0.90
			Mean	1.08 ± 0.05	

*Estimated from S concentration by XRF

TABLE 23. Analytical determinations of total elements in sediment cores 2, 9, and 7, 14. The methods of analyses are: X, x-ray fluorescence spectrometry, and P, HF-HClO₄ digestion followed by either plasma emission or atomic spectrometry.

Depth, cm		Si	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr
cm	Method	-----	%	-----	---µg/g---		%	-----			µg/g-----		
Cores 2, 9													
0-5	X	25.9	7.22	0.32	71	525	2.11	--	26	11	--	56	264
	X	27.3	7.05	0.32	54	514	1.98	--	22	13	10	52	240
	P	--	5.90	--	32	435	1.75	7	18	21	37	--	224
5-10	X	31.8	4.64	0.30	70	308	2.43	--	30	27	33	89	264
	X	31.1	5.44	0.35	68	373	2.48	--	32	30	--	62	210
	P	--	4.50	--	50	336	2.70	10	28	30	64	--	204
10-15	X	28.5	3.94	0.31	74	390	2.47	--	30	32	35	80	192
	X	27.7	3.54	0.32	44	389	2.31	--	30	24	--	64	173
	P	--	3.70	--	42	390	2.30	12	28	27	62	--	182
15-27	X	25.8	3.65	0.46	130	578	4.45	--	55	23	102	112	200
	X	29.1	3.79	0.46	112	630	4.39	--	51	27	101	109	212
	P	--	2.86	--	74	520	3.50	16	40	23	84	--	168
Cores 7, 14													
0-5	X	22.4	6.60	0.27	42	680	1.82	--	24	20	91	41	203
	X	30.0	6.58	0.32	59	683	1.93	--	25	14	56	49	238
	X	28.4	7.40	0.31	56	690	2.03	--	25	20	95	49	261
	P	--	5.30	--	30	515	1.70	7	18	25	115	--	218
5-10	X	28.8	6.53	0.37	63	520	2.52	--	30	11	--	59	237
	X	27.2	6.89	0.34	96	480	2.45	--	32	17	25	55	248
	P	--	5.40	--	42	390	2.30	10	23	26	58	--	232
10-15	X	26.7	3.74	0.43	90	520	4.00	--	46	21	77	103	198
	X	28.6	3.96	0.45	121	587	4.39	--	54	31	83	104	192
	P	--	3.00	--	68	449	3.25	15	39	25	75	--	170
15-27	X	28.9	2.85	0.51	117	640	4.73	--	58	27	100	125	188
	X	29.6	2.99	0.42	118	657	4.96	--	64	30	96	128	177
	P	--	2.40	--	80	555	3.75	18	44	25	82	--	156

TABLE 24. Total element determinations in sediments from core 29. All values were determined by x-ray fluorescence spectrometry except Co which was analyzed by atomic absorption spectrophotometry following HF/HClO₄ digestion.

Depth cm	Si ----- %	Ca ----- %	Ti ----- %	Cr ----- --µg/g--	Mn ----- %	Fe ----- %	Co ----- --µg/g--	Ni ----- %	Cu ----- --µg/g--	Zn ----- --µg/g--	Rb ----- %	Sr ----- %
0-2	25.7	2.43	0.45	115	614	4.43	12	48	18	89	113	174
2-4	25.3	2.63	0.46	105	685	4.92	11	53	25	95	123	181
4-6	26.5	4.45	0.43	98	913	4.08	12	43	18	80	98	210
6-10	24.5	4.31	0.41	115	543	3.82	13	40	22	76	95	211
10-15	25.7	2.82	0.46	103	625	4.44	15	53	21	93	120	189
15-20	25.2	2.24	0.45	105	696	4.60	14	48	22	89	128	171
20-25	23.7	2.39	0.43	94	622	4.22	17	46	19	87	116	186
25-30	25.2	2.30	0.45	109	672	4.76	16	52	21	93	121	174
30-35	25.4	2.56	0.46	124	714	4.93	18	50	24	98	125	190
35-43	23.7	3.20	0.45	93	715	4.32	16	45	18	89	108	185

TABLE 25. Total element determinations in standard reference materials.

Reference Material	Method	Si ----- %	Ca ----- %	Ti ----- %	Cr ----- --µg/g--	Mn ----- %	Fe ----- %	Co ----- --µg/g--	Ni ----- %	Cu ----- --µg/g--	Zn ----- %	Sr ----- %
SO-1 Clay	PES ^a	--	1.85	0.49	165	876	5.81	33	92	62	144	299
	Cert.	--	1.80	0.53	160	890	6.00	33	94	61	146	300
SO-2 Podzol	PES	--	1.71	0.79	20	583	5.18	11	10	6	101	340
	Cert.	--	1.95	0.86	16	700	5.56	13	12	7	124	340
SO-3 Calcar.	PES	--	14.50	0.19	21	525	1.50	9	16	16	52	223
	Cert.	--	14.81	0.19	26	520	1.51	12	16	17	52	217
SO-4 Chernozem	PES	--	1.04	0.27	59	596	2.09	12	23	20	84	160
	Cert.	--	1.11	0.34	61	600	2.31	15	26	22	94	170
W-1	XRF ^b	23.5	7.51	0.61	135	1206	7.27	--	77	114	82	182
	Cert.	24.6	7.83	0.64	119	1278	7.76	--	76	110	84	190
BCR-1	XRF	26.3	4.88	1.32	--	1379	9.61	--	--	20	119	324
	Cert.	25.5	4.95	1.32	--	1400	9.37	--	--	18	120	330

a PES indicates plasma emission and atomic absorption spectrophotometry following HF/HClO₄ digestion.

b XRF indicates analysis by x-ray fluorescence spectrometry.

TABLE 26. Concentrations of trace elements in sediments.

	Depth	Ca	Cr	Mn	Fe	Co	Ni	Cu	Rb
	cm	mg/g	--µg/g--		mg/g			µg/g	
Cores 2, 9	0-5	71	62	520	20	7	24	12	54
	5-10	50	69	340	25	10	31	28	75
	10-15	37	59	390	24	12	30	28	72
	15-27	37	121	604	44	16	53	25	110
Cores 7, 14	0-5	68	52	684	19	7	25	18	46
	5-10	67	80	500	25	10	31	14	57
	10-15	38	106	554	42	15	50	26	104
	15-27	29	118	648	48	18	61	28	126
Core 29	0-2	24	115	614	44	12	48	18	113
	2-4	26	105	685	49	11	53	25	123
	4-6	44	98	913	41	12	43	18	98
	6-10	43	115	543	38	13	40	22	95
	10-15	28	103	625	44	15	53	21	120
	15-20	22	105	696	46	14	48	22	128
	20-25	24	94	622	42	17	46	19	116
	25-30	23	109	672	48	16	52	21	121
	30-35	26	124	714	49	18	50	24	125
	35-43	32	93	719	43	16	45	18	108

TABLE 27. Concentrations of trace elements normalized against Rb concentration.

	Depth	C	Ca	Cr	Mn	Fe	Co	Ni	Cu
	cm	--mg/g---		--µg/g---		mg/g		--µg/g---	
Cores 2, 9	0-5	5.5	152	132	1100	43	15	51	25
	5-10	6.4	77	105	520	38	15	47	43
	10-15	6.2	57	90	600	37	18	46	43
	15-27	6.0	39	126	630	46	17	55	26
Cores 7, 14	0-5	5.7	171	130	1700	48	17	62	45
	5-10	5.8	135	161	1000	50	20	62	28
	10-15	6.8	42	117	611	46	17	55	29
	15-27	5.5	26	107	590	41	16	55	25
Core 29	0-5	6.2	25	117	623	45	12	49	18
	2-4	6.0	25	98	638	46	10	49	23
	4-6	5.8	52	115	1070	48	14	50	21
	6-10	6.3	52	138	656	46	16	48	27
	10-15	5.5	27	98	597	42	14	51	20
	15-20	4.9	20	94	624	41	13	43	20
	20-25	5.9	24	93	615	42	17	45	19
	25-30	5.9	22	103	637	45	15	49	20
	30-35	5.5	23	114	655	45	17	46	22
	35-43	5.1	34	99	764	46	17	48	19

TABLE 28. Trace metal concentrations in sediment fractions in Core 29.

Depth cm	I	O	R	TE	TM	I	O	R	TE	TM
	-----µg/g-----					-----µg/g-----				
	Cr					Mn				
0-2	<0.2	<0.5	8.8	9.5	115	121	21	52	194	614
2-4	<0.3	<0.7	10.2	11.2	105	124	24	120	268	685
4-6	<0.4	<0.6	8.4	9.0	98	256	48	97	401	913
6-10	<0.4	<0.5	8.4	9.3	115	88	15	60	163	543
10-15	<0.4	<0.5	8.6	9.5	103	106	18	81	205	625
15-20	<0.6	<0.5	10.1	11.2	105	124	22	114	260	696
20-25	<0.4	<0.5	8.7	9.6	94	124	29	120	273	622
25-30	<0.3	<0.5	10.6	11.4	109	113	21	115	249	672
30-35	<0.5	<0.6	8.9	10.0	124	142	25	127	294	714
35-43	<0.5	<0.4	7.2	8.1	93	149	24	112	285	715
Mean	<0.4	<0.5	9.0	9.9	106	135	25	100	259	680
	Fe, mg/g					Co				
0-2	0.47	1.53	3.45	5.45	44.3	1.1	<0.6	0.7	2.4	12
2-4	0.85	1.11	4.15	6.11	49.3	1.0	<0.9	1.2	3.1	11
4-6	0.69	1.07	2.59	4.35	40.8	1.2	<0.8	1.3	3.3	12
6-10	0.44	0.77	2.14	3.35	38.2	1.2	<0.6	1.4	3.2	13
10-15	0.58	0.81	2.87	4.26	44.4	1.2	<0.6	1.2	3.0	15
15-20	0.82	0.95	3.57	5.34	46.0	1.1	<0.6	1.2	2.9	14
20-25	0.78	0.99	3.08	4.85	42.2	0.9	<0.6	1.6	3.1	17
25-30	0.94	1.02	4.34	6.30	47.6	0.8	<0.6	2.0	3.4	16
30-35	0.99	1.13	4.69	6.81	49.3	0.9	<0.8	1.7	3.4	18
35-43	0.75	0.90	2.39	4.04	43.2	0.8	<0.5	1.8	3.1	16
Mean	0.73	1.03	3.33	5.09	44.5	1.0	<0.7	1.4	3.1	14
	Ni					Cu				
0-2	1.5	0.4	4.4	6.3	48	2.9	8.4	5.9	17.2	18
2-4	1.2	<0.9	5.7	7.8	53	0.4	3.7	9.1	13.2	25
4-6	2.1	0.8	5.6	8.5	43	0.9	5.0	8.1	14.0	18
6-10	2.6	2.1	5.3	10.0	40	0.8	6.1	9.1	16.0	22
10-15	2.0	1.8	6.1	9.9	53	0.3	4.0	8.3	12.6	21
15-20	1.5	1.3	4.9	7.7	48	0.5	4.3	9.3	14.1	22
20-25	1.2	1.4	4.7	7.3	46	0.3	3.5	11.7	15.5	19
25-30	1.3	1.2	5.1	7.6	52	0.3	3.4	9.3	13.0	21
30-35	1.4	1.1	5.7	8.2	50	0.5	4.4	9.1	14.0	24
35-43	1.0	1.4	6.3	8.7	45	0.3	3.3	7.9	11.5	18
Mean	1.6	1.2	5.4	8.2	48	0.7	4.6	8.8	14.1	21

I = inorganically-sorbed and/or weakly complexed

O = organically-complexed

R = reductant-soluble

TE = total extractable

TM = total sediment metal concentration

FIGURE 1. Equilibrium distribution of NO_3^- - NH_4^+ as a function of pE in sea water at pH 8 and 10°C. $[\text{NH}_4^+] + [\text{NO}_3^-] = 5 \times 10^{-4} \text{ M}$ (from Stumm and Morgan, 1970).

FIGURE 2. Redox potential distribution in sediments.

FIGURE 3. The logarithm of the total number of bacteria in marine sediment as a function of depth (data from Price, 1975).

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