ARCTIC OCEAN SECTION 1994

FINAL REPORT OF SEDIMENT POREWATER CHEMISTRY

by

John P. Christensen
Bigelow Laboratory
W. Boothbay Harbor, ME 04575
Receptionist: 207-633-9600
Fax: 207-633-9641
Internet: jchristensen@bigelow.org

Bigelow Internal Lab Report
No. 099971202

Date: 28 February 1998

25 pages total

Purpose

The Arctic Ocean Section 1994 cruise was undertaken to provide basic data about the central ice-covered Arctic ocean. This principal investigator. was funded by the Office of Polar Programs, National Science Foundation, grant No. OPP-9400058, "Oxygen consumption, denitrification, and carbon oxidation rates in near-surface sediments of the Arctic Ocean". The purpose of this research was to provide the first description of porewater chemistry and diagenetic processes in near-surface sediments of the central Arctic Ocean. Thirteen subcores from boxcores were collected. Analyses for a variety of solutes from the pore waters (O_2, dissolved iron and manganese, phosphate, and titration alkalinity) were conducted on board. Samples were taken for additional tests to be performed at Bigelow Laboratory and for other investigators.

This report provides a final listing of porewater chemical analyses. This data has been submitted to the Arctic System Science (ARCSS) Data Coordination Center (ADCC) at the National Snow and Ice Data Center (CIRES, Campus Box 449, University of Colorado at Boulder, Boulder CO 80309-0449, 1-303-492-6199) and should be posted on the ARCSS home page at the web site (http://arcss.colorado.edu/). Alternately, a disk file with the text in asc format and the three data tables in comma separated value format will be provided by contacting the Principal Investigator.

CONTENTS

METHODS

The 1994 Arctic Ocean Section expedition was a joint Canadian- U.S. expedition in which multidiscilinary investigations were done on two ice breakers sailing north from Bering Strait and crossing the ice-covered central Arctic Ocean. The cruise track started from the continental shelf and slope in the Chukchi Sea, crossed the Chucki Cap and basin, the Alpha Ridge, entered the Markov Basin, crossed the Lomonosov Ridge at the North Pole, and ended at Iceland. Sediment sampling was limited to 1 or 2 cores per station which were shared by a large number of investigators. Near surface sediments were collected using the U.S. Geological Survey (Menlo Park) box core which was slightly smaller than a typical Mark IV. On some of the casts, a 1.5L Niskin bottle was mounted to the corer frame and was tripped when the corer's shovel closed. After the corer arrived on deck and the box of sediments removed, core tubes were pushed vertically into the sediments while attempting to retain a portion of the waters above the sediments for subsequent analysis. Cores were stored typically at <4 ^{o}C until analysis.

To obtain sediment porewater and bulk sediment samples, cores were sectioned in horizontal strata. For porewater used in nutrient and chemical analysis, 20-30 cc of whole sediments were centrifuged on board the ship at 10,000 g for 20 min. After centrifuging, pore waters were decanted and filtered through 25 mm 0.40 mm Nucleopore polycarbonate filters. These waters were subdivided. For analysis of nitrate and nitrite, porewater aliquots of 1.0 ml were preserved by addition of 0.025 ml of 0.108 M $HgCl_2$, and then frozen for return to Bigelow. A small volume autoanalyzer method based on the cadmium copper reduction was used (Wood et al., 1967). In the present analysis, mercuric chloride preservative acts to poison the cadmium column, so the added Hg was removed by addition of imidazole. A porewater sample (0.9 ml) which contained $HgCl_2$ was mixed with 0.020 ml of a 2.00 M imidazole solution. A white precipitate formed, an imidazole-Hg complex, which was removed by centrifuging at 10,000 g for 5 min. in a microfuge. The clear supernatant was decanted and used directly in the autoanalyzer. With imidazole treatment, the adverse affect of mercury on the cadmium column was eliminated. Standards were prepared with $HgCl_2$ and imidazole in an identical fashion. For silicate, 1.0 ml aliquots were frozen in polyethylene micro vials. Samples were returned to Bigelow for small volume autoanalyzer determination based on the method of Armstrong et al. (1967). For alkalinity, 0.5 ml were stored at room temperature until analysis on the ship by Gran titration (Edmond, 1970). The pH electrodes were equilibrated with seawater. Substandard seawater (collected at Site 6, 400 m, 34.820 psu, and used throughout the cruise) was used as the running standard for alkalinity measurements and was calibrated against 10.624 meq/L Na_2CO_3. As a measure of precision, the coefficient of variation of four replicate substandard seawaters samples typically was 1.0%. For phosphate, dissolved iron, and dissolved manganese, a 3.0 ml aliquot of porewater was acidified with 0.100 ml of 4.0 N HCl and then refrigerated until on board analysis using an autoanalyzer. The phosphate method was that of Murphy and Riley (1962). From the same aliquots used for phosphate analyses, dissolved reduced manganese and iron were determined via autoanalyzer based on the manual methods of Armstrong et al. (1979) and Murray and Gill (1978). Both of these latter methods had detection limits of about 1 mM.

Whole sediment subsamples from each strata were frozen in tightly sealed screw-capped glass vials and returned to Bigelow for determination of porosity by weight loss after freeze drying. Porosity was calculated as ml of porewater per cc of whole sediment after correction for sea salt left behind after freeze drying. Also, to correct for evaporation that occurred in each porosity sample during sample shipping and storing, small aliquots of porewater, extracted from the porosity sample just before freeze drying, were analyzed for chlorinity based on titration with $AgNO_3$.

Salinity and nutrient samples were also taken from waters overlying each sediment core, from the boxcore's Niskin bottle, and from bottom water obtained from accompanying CTD casts. Salinities were run during the cruise on an Autosal salinometer to typical physical oceanographic precision. Nutrients from these water samples were run with the same methods as done for the pore waters.

Oxygen profiles were determined on separate subcores using a Transidyne oxygen electrode (Model 1201) and model 768 microelectrodes made within a 20 guage stainless steel canula. The electrodes were mounted on a computer controlled manipulator which was driven by a stepping motor with a single step distance of 0.001 inch. The output from the Model 1201 was recorded digitally with a laptop computer. A hand-made resistivity probe with a width of 0.4 cm was also mounted on the manipulator and its output was digitally recorded as well. A temperature probe monitored conditions of the core or the standardization beaker that was being analyzed. Following boxcore recovery, the sediment subcore used for electrode profiling was stored in a small refrigerator. The electrode manipulator was mounted above the refrigerator and extended down through a door in the top so that electrodes operated within the cooled interior of the refrigerator. Prior to analyzing each subcore, the electrodes were standardized by immersion in a 500 ml beaker containing substandard seawater. This water had been collected from 400 m depth at station 6 (salinity of 34.820 psu) and was used throughout the cruise. To standardize the oxygen electrode, this seawater was bubbled with air and subsequently with industrial grade N_2 until stable readings were obtained. Following standardization, the electrodes were immersed in the unstirred waters over the subcore. A depth profile of the overlying waters were obtained to assure that they were vertically homogeneous. Then the electrodes were positioned 2-4 cm above the sediment water interface. Water was withdrawn by slow-speed pumping and samples collected for small volume Winkler titration oxygen (Carpenter 1965), nutrient concentrations, and salinity. Following these collections, the electrodes were lowered in increments and readings of the electrode outputs were taken. For oxygen, the computer made a set of 22-24 readings over 4 seconds, averaged this set, and then repeated this measurement set 10-15 times. Then the computer read the resistivity and temperature probes, averaging 3-4 readings for each electrode over a two-second sampling period. The resistivity and temperature probes were sequentially resampled until ten averages were obtained from each. The results from each 4 second average (for oxygen) and each 2 second average (for resistivity) were recorded. Then the manipulator lowered the electrodes the prescribed depth interval, and the sequence of measurements repeated. Penetration of the oxygen and resistivity probes into the sediments were individually monitored by sight. A painted vertical depth probe mounted adjacent to the electrodes helped the investigator evaluate the depth at which the tips of the probes entered the sediments. Typically, the depth of the sediment water interface was visually ascertained to within a millimeter. Following the attainment of maximum depth of the electrodes (about 6 cm), the electrodes were returned to the overlying waters and measurements of the overlying waters were continued in order to verify electrode stability. Then, the level of zero oxygen was checked again in N_2 bubbled substandard seawater and the resistivity electrode was reimmersed in substandard seawater. The oxygen electrode readings were converted to oxygen concentrations based on a two point standard curve, using the oxygen concentrations measured by the Carpenter technique and the reading made of zero oxygen standards.

The purpose for measuring resistivity was twofold; to obtain an estimate of porosity nearer the sediment water interface than possible with core sectioning, and to obtain porosity estimates in cores where no core sectioning was performed. Consequently, the resistivity profiles were ultimately correlated with the measured porosity profiles following Winsauer et al., 1952; Li and Gregory, 1974; Ullman and Aller, 1982; Reimers et al., 1992. Profiles of the raw resistivity output in millivolts were first converted to profiles of formation factor, f:

$$f = R_z / R_{bw}. \qquad \text{(Eq. 1)}$$

R_z is the resistance at a particular depth and R_{bw} is the resistivity in the bottom water well away from boundaries such as the sediment-water interface and the air-water interface. The formation factor was statistically correlated with porosity based on the relationship:

$$1/f = a \; p^b. \qquad \text{(Eq. 2)}$$

Since 1/f is R_{bw} / R_z, porosity of the bottom water equals 1 when a = 1. Thus, regressions of ln(1/f) versus

ln(1/P) were evaluated where the regression line passed through the origin. In other studies, all data from near-surface porosity profiles were regressed against 1/f. However, in the central Arctic sediments sedimentation rates are low (1 cm/1000 yr) and the longer section profiles extended deep enough to sample one or more glacial epochs. To best use resistivity for estimating near-surface porosities, the regression of porosity to resistivity was made with data for 2.5 cm depth or less. The resulting coefficient, b, for each regression is included with its respective core (Cores 6, 7, 13, 25, and 26). Slopes were similar for all central basin cores (all cores except the slope station, 6). Thus, the general coefficient, 1.99789 calculated as the average of the deeper 4 cores, was used to calculate estimated fine-scale porosity profiles, particularly for cores where no porosity measurements were made.

REFERENCES

Armstrong, F.A.J., C.R. Stearns, J.D.H. Strickland 1967 The measurement of upwelling and subsequent biological processes by means of the Technicon autoanalyzer and associated equipment. Deep-Sea Res. 14: 381-389.

Armstrong, P.B., W.B. Lyons, H.E. Gaudette 1979 Application of formaldoxime colorimetric method for the determination of manganese in the pore water of anoxic estuarine sediments. Estuaries 2: 198-210

Carpenter, J.H. 1965 The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr. 10: 141-143.

Edmond, J.M. 1970 High precision determination of titration alkalinity and total carbon dioxide content of seawater by potentiometric titration. Deep-Sea Res. 17: 737-750.

Li, Y-H., S. Gregory 1974 Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmo. Acta 38: 703-714.

Murphy, J., J.P. Riley 1962 A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 12: 162-176.

Murray, J.W. G.Gill 1978 The geochemistry of iron in Puget Sound. Geochim. Cosmo. Acta 42: 9-19.

Reimers, C.E., R.A. Jahnke, D.C. McCorkle 1992 Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle. Global Biogeochem. Cycles 6: 199-224.

Ullman, W.J., R.C. Aller 1982 Diffusion coefficients in nearshore marine sediments. Limnol. Oceanogr. 27: 552-556.

Winsauer, W.W., H.M. Shearin, Jr., P.H. Masson, M. Williams 1952 Resistivity of brine-saturated sands in relation to pore geometry. Bull. Am. Assoc. Petro. Geol. 36: 253-277.,

Wood, A.B., F.A.J. Armstrong, F.A. Richards 1967 J. Marine Biol. Assoc. U.K. 47: 25.

D A T A

T A B L E S

TABLE 1 (NP-LOC01). Locations, sampling times, and water depths of boxcores used in this study.

Abbreviations: LATDEG = degrees of latitude, LATMIN = minutes of latitude, DECDEG = degrees and minutes in decimal degrees, LNG = longitude, LNGDEG = degrees of longitude, LNGMIN = minutes of longitude, LNGNEG = negative decimal degrees of longitude, WIRE-Z = deep-sea wire length at core impact, SONIC-Z = sonic water depth at core impact, JD-GMT = Julian day based on the date using GMT, JDAY = Julian day based on the date using ship's time, JD-DEC = Julian day using date and time based on ship's time.

TABLE 2 (NPW-TCH2). Porewater and porosity data from sectioned cores.

Abbreviations: DEPTH TOP = depth in sediment of the top of the sectioned strata, DEPTH BTM = depth in sediment of the bottom of the sectioned strata, DEPTH AVE = depth at the mid point of the section, UGAT/L = microgram atoms of the key element per liter of porewater, TALK = titration alkalinity, MEQ/L = milliequivalents of alkalinity per liter, DENSITY = density of porewater given CTD bottom water salinity and laboratory analysis temperature of 25^{o}C, TEMP INSITU = temperature based on deepest CTD readings at nearby hydrographic stations, SALINITY INSITU = salinity based on deepest CTD readings at nearby hydrographic stations, SALINITY BOTTLE = salinity measured with an on-board salinometer, UGAT/KG = microgram atoms of the key element per kilogram of seawater based on the density of the sample at analysis temperature, OLW = water within the box core which overlays the sediments, CTD BTMWTR = deepest data collected with the CTD for the station (usually from the CCG Louie St. Loraine), LSLxx = CTD station number for stations from the CCG Louie St. Loraine, -9 or -99 = data not measured.

TABLE 3 (NP-O2RES). Profiles of dissolved oxygen, formation factors and estimated porosities from resistivity data, and measured porosities.

Abbreviations: DEPTH = depth of probe tip above (negative) or below (positive) the sediment-water interface. DEPTH TOP = depth in sediment of the top of the sectioned strata, DEPTH BTM = depth in sediment of the bottom of the sectioned strata, UGAT/L = microgram atoms of the key element per liter of porewater, UGAT/KG = microgram atoms of the key element per kilogram of seawater based on the density of the sample at the in situ temperature and salinity (deepest readings of CTD at the associated hydrographic station), COEF B OF CORE = regression coefficient b (equation 2) for the relationship between formation factor and porosity from the core (includes only data from 2.5 cm depth or less), POROSITY /W CORE COEF B = estimated porosity based on the measured formation factor and the core coefficient B, GENERAL COEF B = average coefficient B for the 4 deeper cores, POROSITY /W GEN. COEF B. = estimated porosity based on the general coefficient B, MEASURED POROSITY = measured porosity data from TABLE 2 for the same station as used in the oxygen and resistivity measurements. -9 or -99 = data not measured.

LAST PAGE

IS

BLANK