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The Distribution of Some Chemical Elements
Between Dissolved and Particulate Phases in the Ocean

Report to the Atomic Energy Commission on Contract No. AT(11-1)-3556

[Formerly AT(30-1)-4150]

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Personnel: Derek W. Spencer
 Peter G. Brewer
 Peter L. Sachs
 C. L. Smith
 J. W. Murray

MASTER

Introduction

During the three year period from August 1, 1969 to July 31, 1972, our research has been directed toward an understanding of the fundamental chemical behavior of elements in the ocean. Particularly we have been concerned with the trace element cycle and the flux of these elements through the ocean from their input by rivers to their incorporation into sediments.

In pursuit of these objectives we initiated a program of analysis of sea water for several trace elements.

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Earlier work in the Gulf of Maine (supported by AEC Contract AT(20-1)-1918) had indicated that, except for the upper 50 meters, the suspended matter in the water column was dominated by clay minerals that were resuspended from the bottom (Spencer and Sachs, 1970). Chemical analysis of the suspended matter using atomic absorption spectrometry of ashed and dissolved filters showed that, in the deep water below 50 meters, the concentrations of particulate Fe, Cu, Ni, Zn and Al was dominately controlled by the occurrence of the resuspended clays.

The suspended matter was collected by filtration on 0.5 μ membrane filters and we have used this as a definition of "particulate" element and the metal passing through the filter we define as "dissolved." This early work determined that atomic absorption spectrometry did not have sufficient sensitivity to be of general use in the analysis of oceanic suspended matter and it was necessary for us to develop a more sensitive technique. Spencer, Brewer and Sachs (1972) describe a technique using instrumental neutron activation analysis of pelletized filters that is sufficient for the analysis of particulates in many ocean areas with filtration of 5 - 10 liters of sea water. Using this technique we have determined the particulate concentrations of elements such as Mn, Fe, Co, Hg, Sc, Zn, La, Sr, Cr and Au. In many samples we can identify γ -ray peaks from Ag, U, Th²³², As and Ba but we have not yet established quantitative procedures for these elements.

Early work on trace metals dissolved in sea water employed a solvent extraction atomic absorption technique for the analysis of Fe, Cu, Zn and Ni. Traces of Co, Pb and Cd can be detected but not with suf-

ficient precision to supply useful data (Spencer, Brewer and Smith, 1969). We are still using the technique but have recently developed colorimetric procedures that give us greater precision for Fe and permit measurement of Mn (Brewer and Spencer, 1971; this report).

We are not satisfied with the precision of any of the techniques we currently employ and our search for better methods continues (Section 4, this report).

During the funding period we have investigated the distribution of "dissolved" and "particulate" trace metals in several areas including the Black Sea, the Cariaco Trench, the North East Pacific Ocean, the North West Atlantic Ocean and the Gulf of Maine. This report gives an account of our progress in these investigations together with a list of publications resulting from the work.

The report is in five sections entitled:

1. Preliminary Report of Studies of the Deep Nepheloid Layer in the N. W. Atlantic Ocean.
2. Preliminary Report on the Chemistry of the Cariaco Trench
3. Trace Element Profiles at the GEOSECS II North Atlantic Station
4. Trace Metal Analysis of Sea Water by Gas Chromatography of Metal Chelates
5. Surface Chemistry of Hydrrous Manganese Dioxide

A sixth section on the suspended matter in the Gulf of Maine could not be completed before the preparation of this report owing to a breakdown of our analyzer system. Although the data acquisition is now

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complete, we have not yet been able to condense and analyze the information.

List of Publications and Reports

Supported by Contract AT(11-1)-3566

Formerly AT(30-1)-4150

- NYO-4150-1 Sachs, P. L. and D. W. Spencer (1970)
In situ measurement of light scattered from a laser beam
compared to suspended particulate concentrations derived
from concurrently collected samples

W. H. O. I. Technical Report
- NYO-4150-2 The distribution of some chemical elements between dissolved
and particulate phases in the ocean

Report to AEC on Contract
AT(30-1)-4150, 1969-70
- NYO-4150-3 Turner, J. S., T. G. Shirtcliffe and P. G. Brewer (1970)
Variations of transport coefficients across density
interfaces in multiple diffusive systems

Nature, 228, 1083
- NYO-4150-4 Spencer, D. W., D. E. Robertson, K. K. Turekian and
T. R. Folsom (1970)
Trace element intercalibrations and profiles at the
GEOSECS test station in the north east Pacific Ocean

J. Geophys. Res., 75, 7688
- NYO-4150-5 Brewer, P. G. and D. W. Spencer (1970)
Trace element intercalibration study

W. H. O. I. Technical Report
No. 70-62
- NYO-4150-6 Brewer, P. G. and D. W. Spencer (1971)
Colorimetric determination of manganese in anoxic waters

Limnol. & Ocean., 16, 107
- Limnol.*

List of Publications, cont.

- NYO-4150-7 Spencer, D. W. and P. G. Brewer (1971)
Vertical advection, diffusion and redox potentials as
controls on the distribution of Mn and other trace
metals dissolved in waters of the Black Sea

J. Geophys. Res., 76, 5877

- NYO-4150-8 Spencer, D. W., P. G. Brewer and P. L. Sachs (1971)
Aspects of the distribution and trace element composi-
tion of suspended matter in the Black Sea

Geochim. et Cosmochim. Acta,
36, 71

- NYO-4150-9 Distribution of some chemical elements between dissolved
and particulate phases in the ocean.

Report to AEC on Contract
AT(30-1)-4150, 1970-71

- COO-3566-1 Brewer, P. G. and D. W. Spencer (1972)
The distribution and flux of some trace elements between
dissolved and particulate phases in the Black Sea

AAPG Memoir, E. T. Degens
and D. A. Ross, eds. (in press)

- COO-3566-2 Brewer, P. G., D. W. Spencer and D. E. Robertson (1972)
Trace element profiles from the GEOSECS test station in
the Sargasso Sea

Earth & Planet. Sci. L.
(in press)

Section I

Preliminary Report on Studies of the Deep Nepheloid Layer in the N. W. Atlantic Ocean

Introduction

During September, 1970, we participated in R/V KNORR cruise # 12. The track of the vessel and station locations are shown in Figure 1.

The purpose of our participation in this cruise was to sample and analyze the suspended matter in the nepheloid layer in the N. W. Atlantic Ocean that was reported by Eittrheim et al (1969). This study indicated the presence of the nepheloid layer by an in situ light scattering technique and documentation of the quantity and nature of the suspended matter was lacking.

In addition to sampling for the suspended matter, we obtained detailed temperature and salinity profiles in the near bottom waters together with data on dissolved silica, particulate organic carbon (analyzed by T. C. Loder of Dalhousie University) and excess Rn^{222} (analyzed by G. Matthieu of the Lamont-Doherty Geological Observatory).

In this manuscript, we report our studies of distribution of the suspended matter related to hydrography, the size frequency variation, mineralogical and chemical composition determined by X-ray diffraction, electron scanning microscopy and neutron activation analysis.

This work is a part of our long range program concerned with

the distribution of trace metals between dissolved and particulate phases of the ocean.

Sampling and Analytical Methods

At each of the stations shown in Figure 1, we collected up to twelve 30 liter water samples covering the water column up to about 500 meters off the bottom. These samples were collected in P. V. C. Niskin samplers and, interspersed with the Niskin bottles, we ran up to nine Nansen bottles equipped with reversing thermometers. The top Nansen bottle was set at up to 2000 meters off the bottom to be sure that we covered the profile across the potential temperature-salinity break between the Antarctic Bottom Water (ABW) and the North Atlantic Deep Water (NADW). At five to six depths within 100 meters of the bottom, the water from the 30 liter samplers was run into evacuated glass bottles and the radon gas removed and measured on board ship, using the helium stripping and freezing technique developed by Broecker (1965).

Aliquots of the remaining 30 liter samples were filtered according to the following scheme:

- A. 5 liters through 0.5 μ Nuclepore filter
- B. 10 liters through pairs of 0.5 μ Millipore EH filters (pre-weighed)
- C. 10 liters through 0.5 μ Nuclepore filter (pre-weighed)
- C. 2 - 4 liters through 0.5 μ Sela Flotronics silver filter (pre-ignited)

These aliquots were filtered using the pressure filtration technique described by Spencer and Sachs (1970). Each filter, except for

D above, was well washed with distilled deionized water immediately after the filtration.

The A samples were used for electron scanning microscopy studies; the B and C samples, for weighing of total suspended matter and for chemical and mineralogical studies; and the D samples, for particulate organic carbon.

The pre-weighed Millipore EH and Nuclepore filters were returned to the laboratory and, after equilibration with the temperature and humidity conditions in the balance room, were reweighed to determine the total suspended matter concentrations. The quantity of water filtered was retained in containers and measured gravimetrically in the laboratory.

Our intention in collecting samples on the EH filters was to test and compare these with both the Millipore HA and Nuclepore filters that we had used previously. We had had verbal reports that the trace element background in the EH filters was extremely low.

However, our experience showed that the EH filters, after having sea water passed through them, lost up to 10 times the weight of the suspended matter collected, probably through flushing out of the detergent used in their manufacture. This loss was so large that it could not be adequately compensated for by the second blank filter and, consequently, the total suspended matter determinations on the EH filters had very poor precision. The negligible weight loss from Nuclepore filters makes them ideal for this purpose.

Although we determined, by later activation analyses, that several EH filters did indeed have low background concentrations of trace elements, the variation was very large between batches and this contri-

buted to high detection limits (Spencer, Brewer and Sachs, 1972).

In view of these problems, the data we report here are taken entirely from the Nuclepore filters.

Activation analyses of the filters were performed using the technique described by Spencer, Brewer and Sachs (1972).

Particulate organic carbon was determined using the technique recommended by Gordon (1969).

Salinity and silicate concentrations were determined on board ship using a Schliecher-Bradshaw salinometer and the silico-molybdenum blue method described by Grasshoff (1964).

Hydrographic Setting

Hydrographic and dissolved silica data are presented in Table 1.

The potential temperature-salinity diagram shown in Figure 2 is typical for the deep waters, colder than 3° , in the N. W. Atlantic Ocean (Wright and Worthington, 1970). The sharp break at about 2.05°C - 34.907 ‰ is frequently referred to as the break between the North Atlantic Deep Water (NADW) and the Antarctic Bottom Water (ABW) masses. Wright and Worthington have pointed out that the deep water in the North Atlantic probably has five major sources. Three of these, the ABW, the Denmark Straits and the Iceland-Scotland overflow, are predominant in water colder than 3°C . In the North Atlantic, the ABW runs from 2.0°C , 34.89 ‰ to 0.5°C , 34.76 ‰ and Metcalf (1969) has shown that it is characterized by high silica concentrations. The principal sources of the

NADW are the Denmark Straits overflow water which is found at potential temperature from 0° - 4°C and salinities of 34.90 ‰ and the Iceland-Scotland overflow water, from 2° - 3° at 34.98 - 35.02 ‰. From the θ -Sal. diagram, Figure 2, it appears that the bottom water at Station 22 is much more representative of the Denmark Straits overflow water that resides predominately in the Labrador Basin.

Spencer and Craig (1972) in discussing the hydrographic and nutrient profiles at the GEOSECS Atlantic test station (36°N , 68°W) point out that a slight oxygen maximum exists at 3600 - 3800 meters (θ , 2.1° ; Sal., 34.91 ‰) and a slight phosphate maximum and inflexion in the silicate profile occurs at 3200 meters (θ , 3°C ; Sal., 34.95 ‰). Further, Brewer, et al (1972) and Clarke et al (1972) show that the 3200 meter level at the GEOSECS station is characterized by sharp maxima in the profiles of dissolved Fe, Zn, Cu and excess H^3 , and it appears likely that this level represents the core of the Iceland-Scotland overflow water while the break in the θ -Sal. diagram at 2°C , 34.905 ‰ represents the core of the Denmark Straits overflow. However, as Worthington and Wright (1970) indicate, the Denmark Straits overflow water exists at potential temperatures from 0° - 4°C .

The potential temperature section, Figure 3, shows a curious bulge in the bottom water at Station 25. As can be seen from Figure 1, this section runs south from 44°N to 36°N . Further, the dissolved silica section, Figure 4, shows that a marked reversal in the dissolved silica profiles occurs at Stations 24, 25 and 26. It is likely that these features are the result of the intrusion of dense Denmark Straits overflow water

into the deep ABW. This interpretation is further verified by the silica-calinity diagram shown in Figure 5 in which the mixing between the ABW and the Denmark Straits overflow water is seen to be more pronounced in the stations to the north and west.

Total Suspended Matter

Figures 6 and 7 show the total dry suspended matter concentrations at most of the stations. It is immediately apparent that the highest concentrations of suspended matter are found well away from the continental slope at Stations 26, 27 and 28. Also apparent is that the low silica Arctic water seems to coincide with minima in the profiles of total suspended matter. The light scattering profiles published by Eittrem et al (1969) frequently show a characteristic step at distances from 100 to 600 meters off the bottom. It is not unlikely that this step is a function of the same relatively clear Arctic water.

The existence of the clear layer implies that it is a barrier to vertical diffusion of particles and further that the settling time of the particles must be long compared with the rates of horizontal advection and diffusion.

The highest concentrations of suspended matter are clearly associated with the highest dissolved silica concentrations characteristic of the ABW. It is unlikely, however, that the suspended matter is a significant source of the dissolved silica for the linear salinity-silica relationships shown in Figure 5 and the data presented by Spencer and Craig (1972) suggest that silica is conservative in the deep western Atlantic Ocean. It is more likely that the high dissolved silica represents an Antarctic contribution

and that the association of high suspended matter concentrations with the ABW is the source of the relationship.

Size Frequency and Mineralogical Analysis

Particle size data has been obtained by grain counting on electron scanning photomicrographs. Figure 8 gives examples of electron scanning photomicrographs of samples from various depths at Station 27 where the suspended matter concentration increases monotonically as the bottom is approached. Each photograph represents approximately the same amount of water filtered onto 0.5 μ Nuclepore filters. The round holes are the 0.5 μ pores of the filters. The figures illustrate dramatically the increase in suspended matter as the bottom is approached and also give an indication of the increase in median particle size with depth

For each depth at Station 27, we have selected at random three areas of the filter to be scanned. On each of the photomicrographs we have placed a 1 μ grid and determined the maximum dimension of each particle located in a randomly selected set of 200 such 1 μ squares. The resulting size frequency distributions are shown in Figure 9 and these confirm the intuitive results obtained from inspection of the photographs.

Further size frequency analyses are being made on samples from other stations and, while these are not yet complete, the electron photomicrographs reveal that when the total particulate matter concentration is low (<50 μ g/kg), particles larger than 2 μ are very rare and it is likely that the size frequency distributions of all the samples from the slope stations (#22, 23, 31 and 34) will not be very different from the 257 m

samples from Station 27.

The nature of suspended matter is seen to be predominately flat clay particles with occasional diatom and coccolith fragments.

A number of X-ray diffraction scans have been run by resuspending the particles using an ultrasonic probe and refiltration onto a small area of a silver filter, using the techniques described by Spencer and Sachs (1970). The X-ray diffraction data show predominant peaks from illite, chlorite and quartz with minor amounts of kaolite.

Further mineralogical studies are being made.

Chemical Data

The suspended matter collected on 0.5 μ Nuclepore filters has been analysed for Mn, Au, La, Mg, Cr, Sb, Sc, Fe, Zn and Co, using the neutron activation analysis technique mentioned earlier. The results are presented in Table 2. Figure 10 shows the excellent correlation that exists between Fe and total suspended matter for all of the samples and indicates that Fe is present at an almost constant percentage, 6.4%, of the total. Figures 11, 12, 13, 14, 15 and 16, showing respectively the relationships between Fe and Sc, Fe and La, Fe and Co, Fe and Mn, Fe and Cr and Mn and Co, are remarkable in illustrating the extreme uniformity in composition of the suspended matter at most stations. The La/Fe and Co/Fe ratios are virtually constant in all of the samples at about 5×10^{-4} and 2.5×10^{-4} respectively. These ratios are close to those expected for fine grained clay material.

Figure 11 shows that the Fe-Sc plot is not linear even though

the scatter is quite low. We believe that this may be due to an incorrect blank and are currently investigating this problem. At Sc levels above $1 \mu\text{g/kg}$, the Sc/Fe ratio is constant at about 6×10^{-4} which again is close to the values expected in fine grained clay. In contrast to the constancy of the La/Fe, Co/Fe and Sc/Fe ratios, the Mn/Fe and Cr/Fe ratios show significant differences with location. Figure 14 shows that, while most samples have Mn/Fe ratios of about 2×10^{-2} , those from Station 27, south of the New England Seamount chain on the Bermuda Rise, have a significantly lower ratio and those from Station 34, on the continental slope south of Georges Bank, have significantly higher ratios. Similarly, the Cr/Fe ratios of the stations on the continental slope (#22, #23, #31 and #34) can be seen to be about a factor of 3 higher than the remaining samples. Figure 17 shows that at a single station there is a rough correlation between particulate organic carbon and Fe (total suspended matter) but the POC/Fe ratio is very much higher at the continental slope stations.

This same fact is true in general for elements like Sb and Zn (see Figure 18) but it is also true that none of the elements determined show a very high degree of correlation with P. O. C. Further interpretation of this data awaits statistical analysis but it seems probable that the major compositional variations in the suspended matter of the nepheloid layer can be explained by resuspension of the bottom sediments and size sorting within the turbulent bottom water column.

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Table 1

Hydrographic Data - R/V KNORR Cruise # 12

Station No.	Location	Distance Off Bottom (m)	Depth (m)	Salinity ($^{\circ}$ / $^{\circ}$)	Temp. ($^{\circ}$ C)	Potential Temp. ($^{\circ}$ C)	Silica μ M/kg	Remarks
22	42 $^{\circ}$ 00'N 62 $^{\circ}$ 26'W	720		34.930	3.27	3.08	18.4	
		520		.919	3.11	2.90	19.2	
		320		.910	2.88	2.66	20.9	
		270		.911			20.0	
		170		.909	2.80	2.56	20.2	
		145		.904			21.0	
		110		.905	2.72	2.48	20.6	
		95		.902			20.6	
		60		.904	2.68	2.43	20.2	
		30		.905	2.67	2.42	21.3	
		25		.926				
		20	3020	.931			15.79	{Bottles tripped higher in water column
23	43 $^{\circ}$ 51'N 56 $^{\circ}$ 45'W	1510		34.951	3.81	3.69	13.2	
		1002		.933	3.46	3.31	16.0	
		697		.946	3.20	3.01	17.9	
		498		.936	2.99	2.78	18.4	
		301		.929	2.82	2.60	19.5	
		255		.930				
		151		.932	2.79	2.55	19.2	
		132		.928			19.5	
		93		.929	2.76	2.51	20.2	
		87		.925			19.4	
		45		.928	2.76	2.51	19.9	
		21		.925	2.76	2.51	20.1	
		15		.921				
		10	3169	.919			19.8	

Table 1 (cont.)

Station No.	Location	D. Off Bot. Depth	Salinity	Temp.	Pot. Temp.	Silica	Remarks
24	42°00'N 57°10'W	1541	34.928	2.82	2.54	21.6	
		1040	.913	2.45	2.12	25.0	
		740	.903	2.37	2.01	25.9	
		535	.903	2.32	1.94	27.5	
		318	.900	2.31	1.90	27.2	
		271	.946			26.4	
		161	.897	2.28	1.85	26.8	
		136	.895			28.8	
		112	.895	2.28	1.85	30.4	
		90	.899			25.6	
		44	.895	2.28	1.86	32.4	
		24	.895	2.28	1.84	33.4	
		18	.889				
		11	.889			34.7	
		4729					
25	39°51'N 57°30'W	2506	34.951	3.26	3.03	19.9	
		2008	.929	2.78	2.51	24.0	
		1507	.903	2.38	2.05	30.1	
		1006	.896	2.35	1.97	33.3	
		706	.889	2.35	1.93	33.9	
		506	.892	2.38	1.92	35.2	
		307	.892	2.38	1.92	35.2	
		156	.892	2.39	1.91	34.3	
		109	.889			34.3	
		84	.887			34.8	
		59	.889			34.5	
		21	.898	2.39	1.91	34.5	
		9	.894			33.9	
		5146					

Table 1 (cont.)

Station No.	Location	D. Off Bot.	Depth	Salinity	Temp.	Pot. Temp.	Silica	Remarks
26	37°45'N 57°45'W	2368		34.940	~	~	21.8	
		1892		.927	2.70	2.42	24.6	
		1471		.909	2.47	2.14	28.7	
		991		.898	2.33	1.96	35.3	
		699		.898	2.30	1.89	35.9	
		501		.884	2.31	1.88	36.0	
		316		.890	2.29	1.83	37.0	
		168		.890	2.31	1.83	36.3	
		123		.881			36.0	
		75		.887			37.5	
		38		.885	2.31	1.83	38.5	
		27	5141	.884			40.8	
27	35°30'N 59°14'W	2515		34.969	3.44	3.23	20.5	
		2012		.943	2.99	2.72	22.9	
		1510		.914	2.54	2.23	28.1	
		1006		.899	2.32	1.95	33.9	
		704		.892	2.28	1.87	37.4	
		504		.895	2.27	1.84	38.5	
		303		.883	2.23	1.78	40.4	
		153		.882	2.26	1.79	42.1	
		107		.936			42.6	
		82		.876			43.0	
		32		.875			44.5	
		19		.877	2.26	1.77	44.9	
		7	5057	.883			44.6	

Table 1 (cont.)

Station No.	Location	D. Off Bot.	Depth	Salinity	Temp.	Pot. Temp.	Silica	Remarks
28	37°49'N 61°15'W	2506		34.964	3.58	3.58	16.8	
		2005		.946	3.13	2.87	20.9	
		1506		.927	2.78	2.46	24.9	
		1006		.906	2.44	2.07	30.1	
		707		.897	2.36	1.95	32.8	
		507		.895	2.34	1.91	34.4	
		307		.888	2.32	1.87	35.5	
		157		.891	2.33	1.85	36.3	
		111		.885			39.2	
		85		.883			38.3	
		40		.893			38.9	
		22		.890	2.32	1.83	36.8	
		10	5063	.884			39.1	
29	39°59'N 63°22'W	2265		34.942	3.08	2.86	21.1	
		1763		.925	2.63	2.37	25.0	
		1261		.901	2.39	2.08	29.7	
		1009		.897	2.30	1.96	32.6	
		708		.892	2.27	1.89	34.2	
		506		.887	2.27	1.87	34.1	
		306		.889	2.25	1.83	36.4	
		156		.882	2.23	1.79	38.5	
		110		.881			39.5	
		84		.880			39.9	
		39		.876			43.9	
		22	4846	.876	2.20	1.74	42.8	

Table 1 (cont.)

Station No.	Location	D. Off Bot.	Depth	Salinity	Temp.	Pot. Temp.	Silica	Remarks
30	40°00'N 65°19'W	1512		34.936	2.86	2.62	20.9	
		1010		.916	2.47	2.19	22.4	
		710		.907	2.37	2.05	24.5	
		510		.904	2.31	1.98	27.5	
		310		.900	2.27	1.91	30.0	
		160		.894	2.24	1.87	34.6	
		113		.889			34.9	
		99		.890	2.23	1.85	35.9	
		88		.889			35.3	
		49		.887	2.22	1.83	36.4	
		42		.909			24.2	Bottle tripped higher in water column
		34		.889	2.23	1.84	36.4	
		13	4314	.888			37.4	
31	40°00'N 66°21.5'W	1296		34.953	3.36	3.18	18.2	
		900		.949	3.02	2.80	20.9	
		406		.922	2.56	2.28	22.5	
		158		.911	2.35	2.06	26.0	
		113		.906			26.1	
		99		.905	2.31	2.02	26.6	
		87		.902			26.3	
		48		.901	2.25	1.95	27.5	
		23		.988			13.7	{Bottles tripped {higher in water column
		13	3535	.980			14.2	

Table 1 (cont.)

Station No.	Location	D. Off Bot.	Depth	Salinity	Temp.	Pot. Temp.	Silica	Remarks
32	37°00'N 66°58'W	2218		34.951	3.13	2.90	21.0	
		1808		.928	2.74	2.47	22.8	
		1411		.911	2.48	2.17	27.2	
		978		.904	2.34	1.97	31.6	
		705		.898	2.32	1.93	33.5	
		526		.895	2.32	1.91	34.8	
		328		.891	2.31	1.87	35.4	
		178		.889	2.31	1.85	36.9	
		132		.899			32.1	
		108		.901			31.4	
		63		.898			32.4	
		43		.902	2.34		30.6	
		33	4927	.903			31.7	
								All post tripped
33	37°57'N 68°27'W	2521		34.963			15.0	
		2021		.954	3.20	3.00	18.8	
		1021		.903	2.32	2.03	27.7	
		770		.896	2.27	1.96	31.5	
		320		.890	2.25	1.89	33.8	
		281		.891	2.24	1.88	34.3	
		170		.892	2.25	1.87	34.1	
		101		.890	2.23	1.85	35.4	
		71		.884			37.4	
		56		.885	2.23	1.84	36.9	
		37		.884			37.4	
		18		.886	2.23	1.83	36.6	
		9	4312	.885			37.0	
34	38°49'N 69°00'W	1208		34.965	3.68	3.52	15.2	
		809		.962	3.38	3.18	18.3	
		406		.941	2.95	2.72	21.1	
		297		.933	2.83	2.60	20.9	
		258		.927			20.9	
		133		.921	2.57	2.33	22.8	
		58		.911			24.6	
		20	3085	.917	2.41	2.16	26.0	

TABLE 2

Particulate Element Concentrations - R/V KNORR Cruise #12

Concentration ng/Kg (Sea Water)

Station No.	Depth	Mn	Au	La	Hg	Cr	Sb	Sc	Fe	Zn	Co	POC
22	25	0.35	.01	< .02	.367	< .2	2.98	.031	<50	8.14	< .01	
	50	24.4	.02	< .02	< .05	10.1	2.65	.023	863	23.9	.032	
	100	1.13	< .002	< .02	< .05	< .2	6.66	.035	<50	7.55	< .01	
	145	16.5	.068	.142	.614	7.9	155	.296	959	15.8	.672	
	270	< 1	.003	< .02	< .05	< .2	< .5	.013	<50	2.94	< .01	
23	15	31.9	.040	.754	.332	4.2	13.2	.95	1430	39.1	.47	9.0
	39	4.97	.017	.206	.178	.36	3.2	.22	175	17.0	.15	2.0
	87	14.6	.033	.290	.434	5.9	5.9	.31	425	31.7	.16	2.4
	132	25.9	.014	.625	.250	13.8	29.9	.76	1380	187.5	.28	2.8
	255	8.1	.055	.127	< .05	2.5	6.3	.14	114	46.8	< .05	2.0
24	18	58.0	.095	1.52	.356	9.46	21.04	1.51	2410	56.5	.488	3.0
	37	10.4	.366	.045	.385	< .2	6.08	0.22	153	29.2	< .01	2.9
	95	12.6	.031	.343	< .05	< .2	8.35	0.42	471	38.7	.150	2.0
	136	3.9	.037	.057	< .05	.69	4.0	0.099	<50	99.2	< .01	1.7
	271	18.7	< .01	< .02	.343	.63	9.46	0.305	276	32.9	.010	1.9

Table 2, cont.

Station No.	Depth	Mn	Au	La	Hg	Cr	Sb	Sc	Fe	Zn	Co	POC
25	13	30.6	.036	.638	< .05	3.14	11.12	.732	1110	13.0	.188	1.2
	39	3.6	.0098	.111	.207	2.67	2.82	.161	70		< .01	0.8
	89	16.5	.023	.500	.184	1.53	4.60	.457	650	22.4	.084	4.6
	134	32.8	.031	.739	.064	5.11	8.61	.907	1430	19.6	.224	3.1
	259	32.7	.079	.913	.094	3.82	19.12	1.094	1660	18.5	.321	2.3
26	27				.228	17.4	26.4	5.76	9110	34.8	1.68	10.5
	57				.411	23.8	22.6	3.51	6000	24.9	1.17	11.5
	104	187	.010	3.2	.609	15.4	30.9	4.94	8510	29.9	1.76	6.3
	148				.163	.87	9.8	0.80	1270	17.4	0.5	2.0
	750	27.6			.064	2.55	10.9	0.66	1070	25.5	0.27	1.2
27	12	199	0.015	9.21	0.70	39.9	80.6	12.13	19200	102.2	4.45	6.7
	87	97.8	< .01	4.95	0.69	19.4	44.1	6.34	9520	98.9	2.25	2.0
	132	34.8	0.032	4.13	0.14	15.7	46.8	5.43	8140	31.5	1.88	2.7
	257	66.7	0.031	3.45	0.18	17.6	29.7	4.02	5160	24.1	1.39	5.9

Table 2, cont.

Station No.	Depth	Mn	Au	La	Hg	Cr	Sb	Sc	Fe	Zn	Co	POC
28	15	308	0.013	5.83	0.367	35.3	41.6	6.1	15870		3.56	10.8
	40	507	0.052	10.86	0.78	59.6	67.6	3.2	24250	1040	5.61	11.8
	90	375	0.048	7.17	0.305	41.5	66.5		19220		4.41	13.1
	135	181	0.06	4.49	0.358	15.0	59.7	5.4	9200	57.8	2.11	10.6
	260	32	0.015	10.4		3.0	10.3	0.9	1380	13.7	0.25	1.9
29	15	144	0.022	3.24	.663	20.3	33.4	5.51	7920	45.5	1.88	13.2
	39	177	0.0236	4.11	.332	24.2	49.3	6.70	9850	66.7	2.33	10.9
	89	48.9	0.0319	1.06	.604	7.1	22.1	1.91	2640	30.9	0.586	2.1
	135	52.3	0.1033	1.02	.677	12.7	41.7	1.82	4270	87.5	0.604	1.5
	258	18.7	0.0168	0.31	.276	2.3	13.4	0.61	770	13.2	0.09	5.2
30	18	202	0.032	4.79	.269	15.4	46	6.26	9730	82.3	2.25	12.2
	42	20.2	0.051	.275	.311	2.86	13.3	0.21	630	94.5	.116	6.6
	98	100	0.143	2.08	.381	22.7	25.4	2.84	4600	36.5	1.04	
	139	41.8	0.054	1.04	.618	7.65	26.9	1.17	1930	48.2	.364	1.2
	263	8.2	0.027	.167	.430	1.89	7.3	0.26	290	32.2	< .05	2.0

Table 2, cont.

Station No.	Depth	Mn	Au	La	Hg	Cr	Sb	Sc	Fe	Zn	Co	POC
31	92	27.6	.030	.345	.195	6.55	15.2	.506	744	26.4	.287	3.2
	138				.368	7.36	14.3	.529	905	37.9	.264	1.9
	260				.227	2.50	3.9	.161	32	18.2	.136	3.7
32	37	7.86	.048	.092	< .01	.833	4.43	.15	29.7	19.0	< .01	
	63	3.21	.022	< .01	.108	2.35	8.53	.11	< 50	12.3	<	
	112	7.00	.030	.019	.102	3.75	4.71	.20	164	13.8	< .01	
	157	7.38	.013	.075	.023	2.77	5.44	.20	184	13.3	< .01	
	281	13.44	.052	.344	.132	3.75	5.22	2.73	375	20.8	< .01	
33	27	48.1	0.043	.859	.275	8.19	10.5	.97	1540	22.7	.35	3.2
	136	27.4	0.046	.47	.157	4.7	12.1	.69	1050	26.9	.18	3.0
	221	20.6	0.024	.45	.331	4.51	12.1	.64	850	22.1	.17	3.1
	271	10.4	0.029	.013	.01	24.35	2.6	.23	170	12.1	< .01	2.9
34	9	46.1	0.023	.267	.512	6.25	14.15	.499	635	11.30	.19	7.5
	33	34.0	0.049	.304	.0130	2.24	6.08	.374	446	10.74	.09	8.6
	68	24.0	0.0068	.120	.418	.9	4.79	.321	290	4.99	.03	3.4
	108	12.3	0.0046	.104	.213	1.23	6.06	.161	125	.47	.04	3.1
	258	10.5	0.019	.153	.391	1.82	16.38	.172	93	23.95	.67	8.4

Fig.1

Potential Temperature °C

Fig. 3

R/V Knorr Cruise #12 Si μ M/Kg in Deep Water

Fig. 4

Fig. 5

Total Particulate Matter R/V Knorr Cruise #12

Fig. 6

Total Particulate Matter

R/V Knorr Cruise #12

Fig. 7

Figure 8 - Electron Scanning Photomicrographs of Suspended Matter
from R/V KNORR # 12, Sta 27. (2400 x) Nuclepore 0.5 μ Filters

A. 257 m off bottom
B. 132 m off bottom

C. 87 m off bottom
D. 12 m off bottom

*Size Frequency Distribution
Particulate Matter
Station 27 R/V Knorr Cruise #12
(depths are meters off bottom)*

Fig. 9

Fe vs Total Suspended Matter R/V Knorr Cruise #12

Fig. 10

Fig. 11

Particulate Fe vs La

R/V Knorr Cruise 12

Fig. 12

Fig. 13

Fig. 14

Fig. 15

Particulate Mn vs Co

R/V Knorr Cruise #12

Fig. 16

Fig. 17

Fig. 18

Section II

PRELIMINARY REPORT ON CHEMISTRY OF CARIACO TRENCH

Introduction

In previous work we have examined in detail the distribution of trace elements in the Black Sea (Spencer and Brewer, 1971; Spencer, Brewer and Sachs, 1972). The Black Sea is the most prominent example of a permanent anoxic basin and at all depths greater than ca. 250m hydrogen sulfide is found. The chemical consequences of this are striking; precipitation of certain metallic sulfides takes place, the redox potential of the system is lowered abruptly and reduction of iron and manganese to their divalent states occurs. The biological and biochemical consequences are equally drastic; all normal marine life ceases and only sulfate reducing bacteria survive, phosphate and ammonia build up in large excess of the normal concentrations and the ΣCO_2 -pH-alkalinity relationships are driven to extremes.

In view of this it is important to document these consequences of anoxicity as exactly as possible and even more important to understand the mechanism by which this is brought about. What causes anoxic basins to be formed and, once formed, how stable are they? In order to answer questions such as these we need to compare several basin systems, to assess the similarities between anoxic basins and to look for differences between them and oxygenated systems.

We know that vertical density stratification inhibits mixing and renewal of the deep water, leading to depletion of oxygen; yet the necessary degree of stratification has not been defined.

In July and August of 1971 we visited the Cariaco Trench, a truly marine anoxic basin, and the preliminary results are given in this report.

The Cariaco Trench: General Description

The Cariaco Trench is a depression situated on the northern Venezuelan continental shelf at roughly 10° 30'N, 65° 30'W. It is approximately 100 miles long and 40 miles wide and the greatest depth is close to 1400m. The location, together with the cruise track and station numbers, is shown in Figure 1. The sill surrounding the basin is nowhere deeper than 150m and above that depth the waters may mix freely with the surrounding Caribbean waters. The deep water of the basin is made up from this source and is close to 36.19 ‰ in salinity and has a temperature of 16.75°C. Observations in December, 1954 at Atlantis Station 5231 indicated that the deep water contained hydrogen sulfide and this was confirmed by a more detailed investigation in February, 1955 (Richards and Vaccaro, 1956). Since that time a great many cruises have investigated the area, but few significant conclusions have been reached. The basin is apparently permanently anoxic; sulfide is present at all depths below 400m and reaches a maximum value close to 34 μM $\text{H}_2\text{S-S/l}$.

In Table 1 we compare several features of the Cariaco Trench with reported data for the Black Sea. It is evident that the chemical effects are less extreme here, but show many similar features.

Account of the Cruise and Collection of Samples

R/V ATLANTIS II left Trinidad on July 14, 1971 for a 14 day cruise to carry out an interdisciplinary study (geological, geochemical, biological) in the Cariaco Trench. Personnel on board supported by this contract were:

Dr. P. G. Brewer	W.H.O.I.
Mr. J. W. Murray	W.H.O.I./M.I.T.
Mr. Eric Sundquist	Harvard/Lamont Doherty

Plans for measurement of ^{222}Rn did not come to fruition; however, all other objectives were accomplished. Basically, two stations were occupied in a series of hydrocasts extending over several days at a location in the eastern basin (Stations 1789, 1794) and in the western basin (Stations 1799, 1804, 1809). Composite profiles were made up from these hydrocasts in order to provide data for a detailed study of the vertical distribution of properties.

Salinity, temperature, oxygen, sulfide and silicate samples were taken from Nansen bottles. Large volume samples for trace metal analysis were taken with 30 l. Niskin bottles. Samples for pCO_2 were also taken with the 30 l. Niskin bottles and samples for ^{14}C determination were taken with 150 l. Bodman bottles loaned for the purpose by Dr. Vaughan Bowen.

Samples for trace metal analysis were filtered through 0.45μ preweighed Nuclepore filters immediately after collection using a totally enclosed N_2 gas pressure filtering system to prevent contamination and oxidation. The samples were acidified to pH 1.5 using pure hydrochloric acid from an all silica still and stored in high density linear polyethylene jerry cans. Samples for pCO_2 and ^{14}C were equilibrated and purged of CO_2 immediately after collection using apparatus supplied by Lamont-Doherty Geological Observatory.

A total of 55 samples were taken and filtered for trace metal analyses both in the dissolved and particulate phases, and in addition, we supplied 33 samples of particulate matter, taken in identical manner to Dr. Brian Price of the University of Edinburgh, Scotland. Dr. Price was a guest investigator on the cruise and will analyze the particulate matter using X-ray fluorescence, thus providing additional data and a much needed check on our own analyses by the instrumental neutron activation technique.

We collected 20 samples for pCO_2 and ΣCO_2 determinations in conjunction with the ^{14}C program and analyses of these are being run at Harvard and at Lamont-Doherty; 10 samples for ^{14}C determination were taken and processed and these analyses will be carried out at the University of Miami.

The ATLANTIS II returned to Woods Hole in late August, 1971 and analysis of the samples and data has proceeded since then. Time has not permitted completion of the project; however, the results to date are of considerable interest.

Temperature, Salinity and Density

Salinity determinations were carried out at Woods Hole using a Schleicher-Bradshaw conductive salinometer. Temperatures were corrected and thermometric depths calculated, using the W.H.O.I. hydrographic computer program HYLOG.

Figure 2 shows the vertical profile of salinity at a location in the eastern basin of the trench compiled from data from Stations 1789 and 1794. In general a smooth curve is shown from a minimum of 36.185 ‰ in the deep water to ca. 36.8 ‰ close to the surface. Some points scatter badly from the curve and give evidence of either a miscast or poor salinity determinations. A similar composite profile in the western basin from Stations 1799, 1804 and 1809 gave an identical curve, but many more points were erratic. Examination of the data revealed the possibility of poisoning of the platinum electrodes of the salinometer by the sulfide present in the samples, and the salinities were re-determined with an inductive salinometer (c.f. Brewer, 1971). Considerable improvement was noted, but not all samples were available for re-analysis and the problem is still disturbing.

A vertical profile of potential temperature (θ) is shown in Figure 3, again giving a smooth curve from the deep water at 16.75°C to the surface at >19.0°C.

Since the deep water is less salty than the surface water, it must be colder to preserve the density balance. The deep water is unusually warm and this indicates a somewhat delicate balance for an anoxic basin, and a vertical profile of potential density (σ_θ) is shown in Figure 4. The density of the deep water lies close to 26.50 σ_θ units. The boundary between the oxygenated and sulfide containing waters occurred at 300m and at this depth we find $\sigma_\theta = 26.46$, a difference of only .04 units. (Compared with a Black Sea $\Delta\sigma_\theta$ between the deep water and the interface of ca. 1.0 units). The stability maximum of the water column occurs at a depth of close to 150m, corresponding to the sill depth connecting the basin with the nearby Caribbean. The density here is 26.35 and if the deep water were to reach this value (an increase of 0.15 σ_θ units) the basin would mix rapidly and would no longer be anoxic.

In Figure 5 we show a θ - Sal diagram and note that it is essentially linear over the depth range 1400m - 150m. Over this mixing interval we have applied the vertical advection diffusion model described by Wyrski (1962), developed by Craig (1969) and used to model the Black Sea data (Spencer and Brewer, 1971). Horizontal gradients are taken to be negligible and the profile is assumed to be stationary in time $\frac{\partial C}{\partial t} = 0$. The profile is then represented by the equation for vertical diffusion (κ) and advection (ω):

$$\frac{\kappa \partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} + J = \frac{\partial C}{\partial t} = 0 \quad (1)$$

and the ratio κ/ω , or z^* in the notation of Craig (1969), is taken to be constant over the entire mixing interval. For a conservative tracer J equals zero and the solution to (1) is:

$$(C - C_0) = (C_m - C_0) \frac{(e^{z/z^*} - 1)}{(e^{z_m/z^*} - 1)} \quad (2)$$

where z is positive upwards, C_m and C_o are the concentrations at the upper and lower boundaries and z_m is the mixing interval.

An approximate solution was obtained using a Wang 500 desk calculator and a least squares fit of equation (2) to the salinity and potential temperature data was accomplished using a program originally supplied to us by H. Craig.

In Tables 2 and 3 we show the fit of the model to the salinity and temperature data; the mixing parameter obtained (z^*) is 0.143 km for salinity and 0.146 for potential temperature. The difference is not significant. The standard deviation of the residuals is $0.009^\circ/\text{oo}$ and 0.04°C which is good considering the composite nature of the profile.

Two points are of immediate interest. First, the value of z^* is similar to that obtained for the Black Sea (0.09 km), and dissimilar to typical values for oxygenated systems, such as the deep Pacific (1.0 km, Craig, 1969) and the Mindanao deep (1.3 km, Munk, 1966). It may be that this value of z^* is characteristic of anoxic basins where the assumption of a κ constant with depth is in doubt.

Secondly, we seek to test the assumption that $\partial c/\partial t = 0$ and re-examine the old data for this purpose. In Figure 6 we have plotted a vertical profile of temperature from our data and compared it to data from Worthington (1954) and Richards and Vaccaro (1956). It is obvious that a significant difference exists and the evidence suggests that the deep water of the Cariaco Trench has warmed 0.07°C over the 16 year period. Data from a 1965 cruise of the R/V Thomas G. Thompson (Richardo, 1970) give deep water temperatures about 0.02°C lower than ours and 0.05°C higher than the 1954 data. If correct, then this is a most important observation and we can postulate these things:

1. There is an error
2. The deep water has warmed by geothermal heat flow
3. The 1954 deep water is being replaced by warmer water from outside the trench

There appears to be no chance of error in the 1954/1955 data. We have checked Woods Hole data files and talked with Worthington to verify this. We have manually corrected several of the new data points to check on the computer program and have checked the thermometer calibration records. Thus, at the time of writing, there seems to be little chance of error.

Postulate (2) seems the most probable and the third postulate seems most unlikely; for warmer water to replace the deep water, it must be more dense. A simple calculation shows that such a water should have a salinity in excess of 36.21‰, and no water of this salinity is observed below 500m. The density of the deep water has decreased by about $0.014 \pm .002 \sigma_\theta$ units in 16 years, and it is interesting to speculate that if this trend continues linearly then the basin would become unstable in about 150 years.

The assumption is that $\partial c / \partial t = 0$ is thus not valid; however, the change is small and we will persist with the model, being fully aware of the problem.

Oxygen, Sulfide and Silicate

The vertical distribution of dissolved oxygen and hydrogen sulfide is shown in Figure 7. Oxygen begins to decrease rapidly below 100m and below 250m is at the limit of detection. Hydrogen sulfide occurs at ca. 300m and considerable scatter is observed between different casts indicating mixing processes taking place at the interface.

Inspection of the data shows that sulfide analyses on samples taken from P.V.C. Niskin bottles gave significantly higher results than samples from Teflon lined Nansen bottles (~15% higher). This is attributable to attack of the metallic surfaces by sulfide and indicates the need for non-metallic samplers for this kind of work.

The highest sulfide values lie close to $34 \mu\text{M}$, slightly higher than the $30 \mu\text{M}$ reported by Richards and Vaccaro (1956). The analytical error is such that this difference is not significant; what is important is that the $\text{H}_2\text{S} - \text{O}_2$ interface appears to have moved 150 meters up the water column in the 16 year interval, since the interface was first reported at a depth close to 450m. Thus, the temperature and oxygen balance of the basin is not in a steady state and we must seek the mechanisms driving these changes.

Figure 8 shows a vertical profile of dissolved silicate. The data were obtained with the silico-molybdenum blue method of Mullin and Riley (1955). Silicate increases rapidly below 100m depth, and at the $\text{O}_2 - \text{H}_2\text{S}$ interface is at a level of $40 - 45 \mu\text{M}$; here the profiles are erratic, as are the sulfide data, indicating mixing in this region. Below 400m a smooth increase to a maximum value of close to $60 \mu\text{M}$ occurs and this is twice the amount of silicate contained in Caribbean waters of comparable depth outside the confines of the trench.

Iron and Manganese

We have carried out analyses for dissolved iron and manganese in all our samples and the vertical profiles are shown in Figures 9 and 10. The data are most interesting, and can be compared to similar profiles in the Black Sea. Both elements show a sharp break in the profile at 300m where the transition from an oxidizing to a reducing environment takes place; this is due to reduction of Fe

(III) to Fe (II) and Mn (IV) to Mn (II) and reflects the greater solubility of the divalent species. Both elements also show a maximum in mid-water and curve smoothly to a constant value in the deep water. We have previously described this phenomenon in the Black Sea (Spencer and Brewer, 1971) and seek to describe it in similar terms here. The basic cycle consists of upward mixing of divalent Fe and Mn from the reducing to the oxidizing environment, precipitation of MnO_2 and $Fe(OH)_3$ at the interface and settling and dissolution of this precipitate. The chemical driving force is the abrupt change in redox potential and the dynamics of the system are controlled by advection and diffusion.

For a stable non-conservative tracer, the term J in equation (1) is not zero and describes the rate of production or consumption of the tracer species. We will allow J to vary exponentially with depth and the basic equation becomes:

$$K \frac{\delta^2 c}{\delta z^2} - \frac{\delta c}{\delta z} + J_0 e^{-\mu z} = \frac{\delta c}{\delta t} = 0 \quad (3)$$

The solution to this equation is (Craig and Weiss, 1970):

$$(C - C_0) = (C_m - C_0) f(z) + \frac{J_0/\omega}{\mu(1 + \mu^2 \star)} \cdot [(1 - e^{-\mu z}) - (1 - e^{-\mu z_m}) f(z)] \quad (4)$$

where

$$f(z) = \frac{(e^{z/z^*} - 1)}{(e^{z_m/z^*} - 1)} \quad (5)$$

We have fit equation (4) to the Fe and Mn profiles, and the least squares fit is illustrated in Figures 9 and 10. The data are given in Table 4 for the two parameter fit for manganese and the values obtained are $J_0/\omega = 3.1 \times 10^{-9}$ and $\mu = -25$. For iron the corresponding values were $J_0/\omega = 2.1$ and $\mu = -3.2$. The standard deviation of the residuals was $\pm 2.3 \mu\text{g Fe/kg}$ and $\pm 3.5 \mu\text{g Mn/kg}$.

The scatter is partly due to analytical error, but mostly from combining samples from different days and locations on to a single profile with inadequate salinity information. The scatter, as in sulfide and silicate values, at the interface can also be seen here. The analytical method used was developed for this project and consisted of pre-concentration of a 1 l. sample on a 10 cm column of Chelex 100 ion exchange resin in the ammonium form at pH 7. The column was eluted with 40 ml. of 2N HCl and the eluate evaporated to ca. 5 ml. volume in a Teflon beaker. The concentrate was made up to 10.0 ml. and split into two fractions; Mn was determined by atomic absorption spectroscopy on one aliquot and Fe was determined spectrophotometrically with 2, 2¹-dipyridyl on the other.

A recent advance in technique has enabled us to determine Mn directly by a modified formaldoxime procedure that eliminates the Fe interference. The method uses only 35 ml. of sample and is simple; we have applied the method to our samples and now have two sets of data obtained by completely independent technique. Both sets of data are shown in Figure 10; the first profile took more than one month to complete, whereas the second profile was obtained in a single day.

Particulate Matter

Particulate matter samples were collected on 0.45 μ pore size preweighed Nuclepore filters and in Figure 11 we show the profile of dry weight of total suspended matter. The data range from a high value of ca. 2.0 mg/kg at the surface to a mini-

mum of 0.2 mg/kg between 400 - 1200 m, with a slight increase being detectable close to the bottom. Considerable scatter, indicative of the complexity of the region, exists in the region from 250 - 400m, covering the H_2S and O_2 interface. Samples from the eastern basin, closer to the Gulf of Cariaco, are generally higher in suspended matter than samples from the western basin.

We have not yet begun analysis of these samples; however, some data from Price (personal communication) indicates that the particulate manganese peak above the interface is of the order of $0.5 \mu g/kg$ and that the particulate iron peak is ca. $2 - 5 \mu g/kg$.

Discussion

The data as given in the preceding sections presents several problems.

Firstly, we wish to estimate the rate of mixing, and the chemical fluxes within the basin. The scale height we have derived (κ/ω) is only a ratio and we need specific values for either κ or ω . In our study of the Black Sea we derived ω from the observed rate of input of bottom water through the Bosphorous. This path is not open to us here, and indeed it is hard to see any probable advective input of bottom water into the Cariaco Trench. An alternative approach is to model the distribution of a radioactive tracer in the system and to use the radiochemical half-life to put real time into the model (Craig, 1969). It is to this end that we have taken samples for ^{14}C determinations and we await the data. The problem is not easy and may well prove perplexing.

The rates we derive in this way are, of course, model dependent. We assume a mean upward flow (ω) which is conceptually separated from the diffusive motions (κ) of the system. These models are derived from open ocean studies and limits on ω were set from estimates of, for instance, the freezing of Antarctic pack ice

(Munk, 1966). Similarly, limits for the allowed values of κ ($.01 < \kappa < 10 \text{ cm}^2 \text{ sec}^{-1}$) are set from a knowledge of the molecular diffusion coefficients of heat and salt, and the observation that these properties are not separated by mixing within the ocean. The model is not perfect and the situation has been lucidly stated by Robinson and Stommel (1959): "The inclusion of an eddy-conductivity (κ) is a parametric way of including small scale vertical mixing processes into the theoretical model....It means that we simply do not know anything about the physics of the mixing process....Thus, we envisage the ocean as being slowly and evenly stirred by some physical process which we cannot specify...." If, in fact, there is no clearly defined upward advection the convex shapes of the temperature and salinity profiles are generated solely by an eddy diffusion coefficient that varies with depth. In this case the advection-diffusion model would give rates for the upward transport of properties that are too high, and for the downward transport of properties that are too low.

In our previous attack on the anoxic basin problem in the Black Sea we derived a vertical eddy diffusion coefficient of $0.014 \text{ cm}^2 \text{ sec}^{-1}$; this is only ten times the molecular diffusion coefficient of heat, and is an order of magnitude less than the lower limit for κ ($0.1 \text{ cm}^2 \text{ sec}^{-1}$) in the open ocean models described above. These limits are somewhat intuitive, but they are based on a set of self-consistent ideas about the ocean which we should not discard lightly. We propose to examine the problems in future work and to test the validity of the advection-diffusion model in the Cariaco Trench by examining the distribution of ^{14}C , temperature, and the rate of production of particulate manganese at the oxygen-sulfide boundary. We hope to reconcile the separate constraints of dynamic mixing and chemical kinetics.

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Table I

Comparison of existing data from the Cariaco Trench and the Black Sea

	<u>Cariaco Trench</u>	<u>Black Sea</u>
Deep water residence time	ca. 200 years	ca. 2000 years
Maximum depth of basin	1400 meters	2000 meters
Factor contributing to density stratification	Temperature	Salinity
Maximum sulfide concentration	34 μM	400 μM
Salinity of deep water	36.19%	22.4%
Temperature of deep water	16.75°C	8.9°C
Maximum phosphate concentration	2.5 μM	7.5 μM
Maximum silicate concentration	60 μM	180 μM
Maximum ammonia concentration	9 μM	100 μM

2218379

GAUSHAUS AUSPUT...CONTRL= 1

CARIACO TRENCH SALINITY DATA STATIONS 1789, 1794

FIT TO STABLE CONSERVATIVE TRACER MODEL

DEPTH	CONCENTRATION	CALCULATED	DIFFERENCE
.186	36.349	36.368	-.019
.197	36.323	36.355	-.032
.201	36.344	36.350	-.006
.246	36.300	36.307	-.007
.260	36.278	36.297	-.019
.279	36.285	36.284	.001
.284	36.282	36.280	.002
.296	36.261	36.273	-.012
.298	36.274	36.272	.002
.316	36.264	36.263	.001
.326	36.261	36.258	.003
.333	36.260	36.255	.005
.345	36.260	36.250	.010
.348	36.246	36.249	-.003
.356	36.253	36.245	.008
.373	36.253	36.239	.014
.376	36.252	36.238	.014
.396	36.239	36.232	.007
.397	36.231	36.232	-.001
.421	36.232	36.226	.006
.437	36.221	36.222	-.001
.443	36.219	36.221	-.002
.446	36.213	36.220	-.007
.450	36.231	36.220	.011
.478	36.219	36.215	.004
.481	36.224	36.214	.010
.533	36.212	36.207	.005
.629	36.201	36.200	.001
.689	36.194	36.197	-.003
.872	36.183	36.193	-.010
1.021	36.194	36.192	.002
1.147	36.190	36.192	-.002
1.246	36.179	36.192	-.013
1.315	36.187	36.192	-.005
1.321	36.191	36.192	-.001
1.335	36.194	36.192	.002
1.345	36.195	36.192	.003
1.355	36.191	36.192	-.001
1.365	36.195	36.192	.003
1.371	36.197	36.192	.005
1.375	36.180	36.192	-.012

FINAL PARAMETERS ZSTAR= .143

Table 2

2217764

GAUSHAUS AUSPUT...CONTROL 1

CARIACO TRENCH POTENTIAL TEMPERATURE DATA STATIONS 1789,1794

FIT TO STABLE CONSERVATIVE TRACER MODEL

DEPTH	CONCENTRATION	CALCULATED	DIFFERENCE
.186	17.830	17.717	.113
.197	17.550	17.646	-.096
.201	17.610	17.621	-.011
.246	17.310	17.387	-.077
.260	17.260	17.328	-.068
.279	17.240	17.256	-.016
.284	17.230	17.239	-.009
.296	17.210	17.200	.010
.298	17.150	17.193	-.043
.316	17.140	17.141	-.001
.326	17.100	17.114	-.014
.333	17.060	17.097	-.037
.345	17.120	17.069	.052
.348	17.060	17.062	-.002
.356	17.020	17.045	-.025
.373	17.040	17.011	.029
.376	17.020	17.006	.014
.396	16.970	16.972	-.002
.397	17.010	16.970	.040
.421	16.980	16.935	.045
.437	16.920	16.915	.005
.443	16.940	16.908	.032
.446	16.890	16.904	-.014
.450	16.940	16.900	.040
.478	16.920	16.872	.048
.481	16.920	16.869	.051
.533	16.850	16.830	.020
.629	16.760	16.787	-.027
.689	16.790	16.771	.019
.872	16.760	16.749	.011
1.021	16.740	16.743	-.003
1.147	16.750	16.741	.009
1.246	16.710	16.740	-.030
1.315	16.740	16.740	-.000
1.321	16.740	16.740	-.000
1.335	16.800	16.740	.060
1.345	16.820	16.740	.080
1.355	16.760	16.740	.020
1.365	16.710	16.740	-.030
1.371	16.740	16.740	-.000
1.375	16.750	16.740	.010

FINAL PARAMETERS ZSTAR .146

Table 3

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GAUSHAUS AUSPUT...CONTROL= 1

CARIACO TRENCH MANGANESE DATA STATIONS 1789,1794,1799,1804,1809

TWO PARAMETER FIT TO STABLE NON-CONSERVATIVE TRACER MODEL

DEPTH	CONCENTRATION	CALCULATED	DIFFERENCE
.300	1.800	1.800	-.000
.308	3.800	7.019	-3.219
.318	18.000	12.074	5.926
.328	.200	15.846	-15.646
.334	17.700	17.618	.082
.338	21.100	18.629	2.471
.369	25.200	23.171	2.029
.381	25.300	23.895	1.405
.393	21.900	24.281	-2.381
.416	27.800	24.415	3.385
.440	26.300	24.090	2.210
.449	25.800	23.906	1.894
.467	21.900	23.490	-1.590
.485	21.900	23.050	-1.150
.485	21.600	23.050	-1.450
.516	23.600	22.312	1.288
.541	24.500	21.774	2.726
.581	23.700	21.043	2.657
.622	21.100	20.455	.645
.678	20.000	19.866	.134
.721	19.100	19.541	-.441
.775	18.200	19.248	-1.048
.790	17.200	19.184	-1.984
.874	18.700	18.925	-.225
1.073	17.400	18.676	-1.276
1.142	20.200	18.644	1.556
1.197	17.300	18.627	-1.327
1.296	20.100	18.609	1.491
1.346	18.600	18.604	-.004
1.346	18.600	18.604	-.004
1.396	18.700	18.600	.100

FINAL PARAMETERS JZER0/W= .000 MU= -.250E 02

BOUNDARY VALUES...DM= .300 OZER0=1.400 CM= 1.800 CZER0=18.600

Table 4

Fig. 1

Fig. 4

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Section 3

TRACE ELEMENT PROFILES FROM THE GEOSecs TEST STATION

IN THE SARGASSO SEA

P. G. Brewer and D. W. Spencer
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

and

D. E. Robertson
Battelle Northwest
Richland, Washington 99352

Woods Hole Oceanographic Institution Contribution No. _____.

Submitted to EPSL

ABSTRACT

During the second GEOSECS test cruise a profile of 25 large volume water samples were collected, filtered and stored in the acidified condition. Two laboratories have together determined Fe, Cu, Zn, Ni, Sc, Co, Sb, Cs and U in these samples. Both laboratories determined Zn and the correlation is good; Zn, Fe and Cu show a maximum in the North Atlantic Deep Water, Cs and U are essentially conservative and Ni, Co and Sb show variability within the uncertainty of the technique. Sc is more abundant in deep water than surface water in both the Atlantic and Pacific Oceans.

TRACE ELEMENT PROFILES FROM THE GEOSECS TEST STATION IN THE
SARGASSO SEA

P. G. Brewer, D. W. Spencer and D. E. Robertson

Introduction

Data on the trace element composition of seawater are presently somewhat erratic (Brewer and Spencer, 1970) due to the sampling, storage and analytical problems involved in the determination. The potential use of these components as tracers and indicators of geochemical processes (Spencer and Brewer, 1971) has led to systematic attempts to resolve these problems. During the first GEOSECS test cruise in September 1969, a profile of 16 large volume water samples was collected; the samples were divided into filtered and unfiltered groups and aliquots of the samples from each group were stored both at their natural pH and in the acidified (pH = 1.8) state in 2 l. polyethylene bottles. Analyses of these samples were carried out by three laboratories and the data are presented in Spencer, et al., (1970). From these results it was apparent that filtered samples (0.45 μ Nuclepore filter) stored in the acidified state provided the most accurate data and subsequent work has been carried out with this in mind.

During the second GEOSECS test cruise a profile of 25 large volume water samples was collected and analyzed by two laboratories.

The purpose was to examine the trace element profiles for evidence of non-conservative behavior, to compare the Atlantic and Pacific profiles and to assess the precision of the measurements by inter-laboratory comparison.

Sample Collection and Storage

Details of the hydrographic casts are given in Spencer (1970). Briefly the samples were collected on three casts over a two day period in 30 l. P.V.C. Niskin bottles identical to those used in the Pacific test cruise. The samples were filtered immediately upon collection, using a totally enclosed filtering system pressured by nitrogen gas, and stored in 2-1/2 gallon linear polyethylene jerry cans. Acidification of the filtered samples to pH 1.8 was carried out with the addition of 50 ml. of 6N HCl distilled from an all silica still.

Methods of Analysis

Copper, zinc, iron and nickel were determined at Woods Hole by a combination of solvent extraction and atomic absorption spectroscopy (Brewer et al., 1969) using the method of standard additions on 400 g aliquots of sample. Analyses were carried out during January and February 1971, approximately five months after collection.

Scandium, cobalt, antimony, cesium, uranium and zinc were determined at Battelle by instrumental neutron activation analysis of evaporated sea salts (Robertson, et al., 1968). Briefly, 25 ml.

aliquots of seawater were repeatedly pipetted into a 7 ml. polyethylene vial until a total of 20 ml. had been evaporated to dryness under a heat lamp. The vials were irradiated with an integral thermal neutron flux of about 3×10^{18} n/cm² and counted five weeks after irradiation. Cs, U, Sb, Co and Sc were determined with a multidimensional gamma ray spectrometer using NaI (Tl) crystals; zinc was determined with a Ge (Li) detector. Samples were analyzed in duplicate one month apart.

Results

The data obtained by the Woods Hole group is given in Table I and that obtained by Battelle, in Table 2. In Table I, we have also listed the salinity and potential temperature at the sample depth as an indication of the oceanographic environment from which the sample came. In Table 2, the duplicate analyses and the mean are given.

Zinc

Only one element, zinc, was analyzed by both groups and the vertical profiles illustrating both sets of data are shown in Figure I. Considerable variation exists over a range from 1 to 7 µg/kg. Both sets of data are characterized by 3 maxima: one at 190 m (see discussion of the iron data); a second one at 960 m which correlates with the oxygen minimum; and a third peak at 3200 m in the North Atlantic deep water. The correlation between the two sets of data is reasonable considering recent intercalibration results (Brewer and Spencer, 1970) and a scatter diagram is shown in Figure 2. The least squares regression through the points has a standard error of 0.69 µg

and correlation coefficient of 0.72. The line indicates a blank discrepancy of 0.6 μg between the two sets of data and a greater range for the Woods Hole analyses, indicating a small calibration difference between the two laboratories.

Examination of the data from the filtered, acidified samples on the first GEOSECS test cruise (Spencer, et al., 1970) gave a correlation coefficient of 0.64 and a standard error of 1.0 μg . The blank discrepancy again was in the same sense and equal to 0.8 μg , and the Woods Hole data had the greater range. These differences can be eliminated by exchange of standard solutions and it is gratifying to report the improvement in the correlation between the two laboratories.

Iron

The dissolved iron profile is shown in Figure 3. The data range from 1 - 20 $\mu\text{g}/\text{kg}$ and between 1200 and 4000 m bear a strong resemblance to the zinc profile with a maximum in the North Atlantic deep water of 3200 m. Iron shows a sharp spike at 190 m, as does zinc, and there exists the possibility of contamination of the sample from fine particulate material corroded from the hydrographic wire (Robertson, 1968). The third peak in the profile occurs at 760 m and does not appear to be correlated with the oxygen minimum, but rather with the stability maximum at the base of the Sargasso Sea water (Spencer and Craig, 1972) and may be due to the production of iron in the water column by the dissolution of sinking particles held up by the density gradient.

Copper

The profile of dissolved copper (Figure 4) can be drawn more

smoothly than for the preceding elements and only shows two distinct maxima at 760 m and at 3200 m.

The upper peak correlates with the iron maximum at the density break and the lower peak matches both the iron and zinc data in indicating strong positive trace metal anomaly in the North Atlantic deep water.

Antimony

The antimony profile does not show readily interpretable variations and, although a line has been drawn through all the points (Figure 5), we feel that most of the variability is due to analytical error. There is no significant difference between surface and deep waters.

Scandium

Figure 6 shows the profile of dissolved scandium. Scandium is a congener of aluminum and is similar in its chemical characteristics to the lanthanides. We would expect it to be associated with silicates and we have here evidence of its enrichment in deep waters. The mean of all samples above 2020 m is .00064 $\mu\text{g/kg}$ and below, is .0092 $\mu\text{g/kg}$ and there is <1% probability that these means are the same.

Cobalt

The data for dissolved cobalt (Figure 7) range from 0.007 to 0.051 $\mu\text{g/kg}$ and show no systematic pattern. Two samples, at the surface and at 390 m, gave anomalously high results (Table 2) and have not been plotted. The apparent lack of correlation with the other data lead us to believe that most of the variability is due to analytical error.

Uranium and Cesium

Uranium is generally considered to be a conservative component of seawater and the vertical profile (Figure 8) shows no significant variation with depth. Similarly, cesium (Figure 9) is remarkably constant throughout the water column.

Conclusions

The lack of comparable data from different locations makes it difficult to draw conclusions from a single profile. Spencer and Brewer (1969) have discussed the distribution of copper, zinc and nickel in the Sargasso Sea. The previous data for copper and zinc are similar to those reported here but the previous iron data are significantly lower and this can be attributed to the fact that previously samples were stored in the unacidified state. Alexander and Corcoran (1967) have determined copper in sea water from the Straits of Florida and found offshore values to be about 2 $\mu\text{g/kg}$, in approximately the same range as we report here. Menzel and Spaeth (1962) have reported on dissolved iron in the Sargasso Sea and give a mean value of about 1.5 $\mu\text{g Fe/l}$ in the upper 1000 m. It is not clear whether the samples were acidified on storage and this low value could be due to loss by adsorption.

Spencer and Craig (1972) report on the hydrographic data taken at this same station. They indicated that an intensely layered water column exists and it appears that all five sources of deep North Atlantic water (Worthington and Wright, 1970) can be identified in the profile. The profiles of zinc, iron and copper are clearly related to the cores of deep water. The Antarctic Bottom Water with a core at about 4800 - 4950 m is characterized by relatively uniform zinc and copper

concentrations of 2.4 $\mu\text{g/kg}$ and 0.6 $\mu\text{g/kg}$ respectively. Dissolved iron appears to show a maximum at this same depth. The slight increase of copper and zinc and decrease in iron noted for the sample at 4998 m may be real for reversals are also noted in the bottom profiles of salinity and silica and it is not unlikely that the bottom water represents part of the very cold, dense Denmark Straits overflow water. Breaks in the potential temperature - salinity curve exist at 1.9°C, 34.9 ‰ at 4000 m and at 3°C, 34.954 ‰ at 3200 m. Spencer and Craig suggest that these represent cores of Denmark Straits overflow and Iceland-Scotland overflow waters that mix to form the North Atlantic Deep Water. They show that the profile of phosphate shows a slight maximum at 3200 m while a slight oxygen maximum exists at about 3600 - 3800 m.

The region at about 4000 - 3800 m is characterized by distinct minima in the zinc and iron profiles but these elements and copper have very pronounced maxima at 3200 m. These maxima together with the phosphate maximum, the inflexion in the silica profile (Spencer and Craig, 1972) and a distinct maxima in the profile of excess He^3 (Clark, et al, 1972) appear to mark the core of the Iceland-Scotland overflow water. The excess He^3 may well be contributed to this water as it flows across the Reykjanes Ridge north of 52°N in the Atlantic Ocean. That copper, zinc and iron are contributed by this same source is not at all certain but we would point out that a correlation between He^3 and Fe was also observed in the deep north Pacific Ocean. (Spencer, et al, 1970; Clarke, et al, 1970).

Another distinct break in the θ -Sal curve occurs at 4°C, 34.97 ‰ at 2000 m. This level is characterized by broad minima

in the nutrient copper, iron and zinc profiles and appears to represent Labrador Sea water (Worthington and Wright, 1970).

The pronounced peak in the zinc profile at 1000 m is coincident with the oxygen minimum and maxima in the nutrient profiles.

It is curious that both iron and copper exhibit maxima at 758 m, distinctly above the oxygen minimum. Whether or not this is real, or the result of sample confusion during the analysis, is not clear at this time for we did not have sufficient sample remaining to be able to duplicate the data. Confirmation will have to await the results from the GEOSECS cruise starting in July, 1972.

It is clear from the data we present that many trace elements have distributions that are clearly related to the water mass structure and their determination should provide important information to the forthcoming GEOSECS program.

Acknowledgments:

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TABLE I

Trace Element Data from the Woods Hole Laboratory

Depth (m)	S ⁰ /oo	θ	Fe	Cu	Zn
1	36.075	26.50 ^c	4.6	1.70	1.67
90	36.536	20.30	2.6	1.70	1.03
190	36.550	18.30	19.8	1.30	3.90
290	36.524	17.80	2.4	1.25	2.35
390	36.500	17.60	1.8	0.63	2.40
490	36.469	16.70	3.3	0.70	1.85
758	35.886	14.20	8.9	3.90	2.65
960	35.210	9.30	2.9	1.90	3.30
1263	34.991	5.40	4.4	0.40	1.73
1515	34.983	4.20	2.1	0.65	--
2020	34.968	3.60	1.7	0.98	1.58
2525	34.957	3.25	9.9	1.10	3.58
2983	34.947	2.85	10.9	2.54	3.65
3232	34.929	2.55	19.7	7.90	6.55
3667	34.918	2.15	2.3	1.03	3.10
4160	34.895	2.00	0.9	0.88	3.10
4509	34.893	1.90	1.1	0.73	2.05
4780	34.890	1.86	0.8	0.68	2.45
3998	34.900	1.95	3.2	0.93	1.37
4748	34.886	1.85	13.2	0.70	2.35
4823	34.885	1.85	5.0	0.60	2.31
4878	34.884	1.85	5.45	0.48	2.35
4923	34.883	1.84	10.54	0.65	2.32
4963	34.882	1.83	6.56	0.48	2.43
4998	34.895	1.83	2.05	1.15	2.68

TABLE 2

Trace Element Data from the Battelle Northwest Laboratory

Depth (m)		Element Concentrations in $\mu\text{g/Kg}$										
		Sc	Co		Sb		Cs		U		Zn	
1	.0007 .009	.0008	.456 .455	* .455	.22 .24	.23	.29 .31	.30	3.3 3.3	3.3	2.6 2.5	2.5
90	.0004 .0004	.0004	.010 .019	.015	.18 .22	.20	.29 .30	.30	3.2 3.6	3.4	1.4 1.5	1.4
190	.0010 .0010	.0010	.013 .015	.014	.21 .21	.21	.29 .30	.29	3.9 3.5	3.7	3.6 3.5	3.5
290	.0005 .0006	.0006	.010 .012	.011	.19 .18	.19	.29 .30	.30	3.4 3.4	3.4	1.2 1.3	1.2
390	.0004 .0003	.0004	.147 .143	.145*	.24 .23	.24	.28 .31	.29	3.6 3.4	3.5	2.1 2.3	2.2
490	.0006 .0007	.0007	.013 .016	.014	.19 .19	.19	.28 .28	.28	3.7 3.6	3.6	1.2 1.4	1.3
758	.0007 .0005	.0006	.011 .009	.010	.20 .19	.20	.29 .29	.29	3.3 3.1	3.2	1.2 1.5	1.4
960	.0008 .0007	.0007	.013 .015	.014	.21 .21	.21	.28 .29	.28	3.5 3.5	3.5	5.0 5.0	5.0
1263	.0006 .0006	.0006	.013 .015	.014	.18 .19	.19	.28 .29	.28	3.4 3.4	3.4	1.0 2.0	1.5
1515	.0007 .0007	.0007	.024 .024	.024	.21 .23	.22	.28 .29	.29	3.3 3.6	3.5	1.5 1.6	1.6
2020	.0004 .0006	.0005	.015 .014	.014	.20 .19	.20	.29 .30	.29	3.4 3.3	3.3	1.4 2.1	1.8
2525	.0008 .0009	.0008	.051 .051	.051	.19 .20	.19	.25 .26	.26	3.2 3.1	3.2	2.9 3.0	3.0
2983	.0009 .0011	.0010	.019 .023	.021	.24 .27	.25	.26 .30	.28	3.1 3.5	3.3	2.8 3.3	3.0
3232	.0010 .0010	.0010	.016 .017	.016	.26 .24	.25	.27 .27	.27	3.2 3.2	3.2	4.5 4.4	4.4
3667	.0009 .0012	.0010	.035 .042	.039	.18 .27	.22	.25 .30	.28	3.1 3.5	3.3	2.0 3.0	2.5
4160	.0010 .0010	.0010	.011 .015	.013	.24 .21	.22	.28 .27	.27	3.4 3.3	3.3	2.4 3.1	2.7
4509	.0010 .0010	.0010	.022 .027	.024	.19 .28	.23	.25 .30	.28	3.2 3.7	3.5	1.4 2.7	2.1
4780	.0010 .0010	.0010	.008 .011	.010	.17 .26	.21	.26 .30	.28	3.1 3.7	3.4	2.5 2.9	2.7
3998	.0010 .0010	.0010	.008 .010	.009	.18 .19	.19	.28 .26	.27	3.5 3.2	3.3	1.1 1.3	1.2
4748	.0010 .0010	.0010	.008 .012	.010	.19 .20	.20	.29 .28	.29	3.6 3.2	3.4	1.9 1.5	1.7
4823	.0010 .0010	.0010	.008 .009	.009	.18 .20	.19	.28 .29	.29	3.5 3.5	3.5	3.1 3.0	3.1
4878	.0008 .0007	.0008	.007 .007	.007	.22 .21	.22	.31 .28	.29	3.6 3.4	3.5	1.2 1.5	1.4
4923	.0009 .0010	.0009	.031 .043	.037	.18 .20	.19	.27 .26	.27	3.5 3.6	3.5	2.7 2.5	2.6
4963	.0010 .0010	.0010	.008 .009	.008	.18 .17	.18	.29 .27	.28	3.5 3.2	3.4	1.5 1.6	1.5
4998	.0004 .0004	.0004	.005 .008	.006	.25 .23	.24	.29 .28	.29	3.4 3.3	3.4	1.7 1.6	1.7
4919	.0010 .0010	.0010	.018 .016	.017	.21 .23	.22	.29 .29	.29	3.5 3.4	3.4	1.8 2.5	2.1
4944	.0010 .0010	.0010	.018 .010	.014	.22 .23	.22	.29 .27	.28	3.6 3.4	3.5	1.4 1.8	1.6
5044	.0010 .0010	.0010	.018 .014	.016	.25 .24	.24	.29 .28	.29	3.5 3.4	3.4	1.6 2.2	1.9
5069	.0009 .0010	.0010	.017 .018	.017	.23 .23	.23	.28 .28	.28	3.2 3.3	3.3	3.6 4.4	4.0

Figure Captions

Figure 1 : Dissolved zinc profile from both laboratories

Figure 2 : Correlation of the two sets of zinc data

Figure 3 : Dissolved iron profile

Figure 4 : Dissolved copper profile

Figure 5 : Dissolved antimony profile

Figure 6 : Dissolved scandium profile

Figure 7 : Dissolved cobalt profile

Figure 8 : Dissolved uranium profile

Figure 9 : Dissolved cesium profile

Section 4

RESEARCH IN NEW ANALYTICAL TECHNIQUES:

TRACE METAL ANALYSIS OF SEAWATER BY GAS CHROMATOGRAPHY OF METAL CHELATES

Background

With a view toward extending and improving our capabilities in the analysis of trace metals in seawater, a program has been initiated during the last year to investigate recent sensitive techniques involving gas chromatography of volatile transition metal chelates. A principal drawback to atomic absorption analysis, the mainstay of our present soluble trace metal determinations is that analyses must be performed close to the limits of detection, even with sample pre-concentration, with subsequent loss of accuracy and precision; for several trace metals, the limits on precision are insufficient to allow meaningful fitting of the data to geochemical models.

Reports in the recent literature have demonstrated the feasibility of trace metal analysis by gas chromatography for a variety of sample types, including steels, non-ferrous alloys, ores, blood plasma, urine, lunar soil, and atmospheric particulate matter. This technique combines the high volatility of chelates formed by transition metals with fluorinated β -diketones and the extreme sensitivity of the electron capture detector to halogenated compounds. Detection limits have been demonstrated to be in the picogram to sub-picogram range (10^{-12} - 10^{-14} grams). It is expected, therefore, that extension of this method to seawater analyses will result in improved trace metal measurements and, to a large extent, reduced sampling requirements.

Brief Methods Description

The analytical procedure consists of simultaneous chelation and solvent extraction of the metal of interest using 1,1,1-trifluoro-2, 4-pentanedione (Htfa) or related β -diketones, followed by quantitative electron capture gas chromatography. A small aliquot of the sample (5 ml) is pipetted into a Pyrex culture tube and adjusted to the appropriate pH with acetic acid-sodium acetate buffer. A benzene solution of the chelating reagent containing an internal standard is added, and the tube is tightly capped and shaken for 30 to 180 minutes, depending on the metal being determined. The organic phase is then drawn off, washed briefly with a solution of sodium hydroxide to remove excess reagent and measurements of the relative peak heights of the metal chelate and internal standard peaks are then compared with known calibration curves to give the amount of trace metal present. The method is rapid, highly sensitive and reduces sample storage requirements by a factor of one hundred. Batch extraction of samples may be performed at sea.

Preliminary Results

Initial studies have focused on the determination of chromium, an element not feasibly determined by atomic absorption due to formation of the refractory sesquioxide. Chromium is an important geochemical indicator and appears to show interesting oxidation-reduction chemistry in seawater. Attempts to establish chromium speciation have shown a state of thermodynamic non-equilibrium between the Cr(III) - Cr(VI) oxidation states, which is important in determining not only the distribution of naturally occurring

chromium, but also that of ^{51}Cr introduced to the hydrosphere via nuclear reactor cooling effluent.

Our preliminary results indicate that the above procedure will allow precise determinations of chromium in seawater. Using ^{51}Cr as a radio-tracer, the extraction of chromium has been studied as a function of pH, reagent concentration and extraction time. Although the extraction of chromium is kinetically slow (Figure 1), approximately 93 ± 2 percent of the chromium can be extracted at the optimum pH (5.71) and reagent concentration (0.25 M) within 180 minutes.

A typical chromatogram obtained by injection of 1 μl of a standard solution containing 10 picograms of chromium and a smaller amount of lindane ($\text{C}_6\text{H}_6\text{Cl}_6$) as an internal standard is illustrated in Figure 2; even at this low concentration, the chromium chelate produces a large, well-defined peak. The ratio of the $\text{Cr}(\text{tfa})_3$ peak height to the internal standard peak height is reproducible to within approximately 3 percent as determined by repeated injections of 10 picogram amounts of chromium.

Figure 3 illustrates a chromatogram obtained from a seawater extract; while two of the peaks are readily identifiable from their retention times as $\text{Cr}(\text{tfa})_3$ and lindane (added as internal standard), additional peaks appear in the trace. These components have tentatively been identified as contaminants arising from the plastic vessels used for storage of the seawater samples; the use of glass or Teflon storage bottles eliminates these contaminants and the chromatograms obtained from uncontaminated samples are similar to that of Figure 2.

Since chromium forms only the Cr(III)-trifluoroacetylacetonate, the above procedure provides a means of determining the distribution of chromium between its principal oxidation states, Cr(III) and Cr(VI). Analysis of duplicate samples, one treated with a suitable reducing agent, gives values for Cr(III) and total chromium, respectively, from which the [Cr(III)/Cr(VI)] ratio can be determined. Samples will be collected during an upcoming cruise to the Sargasso Sea in May-June, 1972 to test this particular aspect, as well as the overall reliability of the gas chromatographic method.

FIGURE CAPTIONS

Figure 1. Extraction of a 10^{-5} M spike of ^{51}Cr from seawater medium as a function of time under various conditions.

Figure 2. Chromatogram of $\text{Cr}(\text{tfa})_3$ standard solution containing 1×10^{-11} g of chromium.

Figure 3. Chromatogram of $\text{Cr}(\text{tfa})_3$ extracted from seawater.

Figure 1.

Figure 2.

Figure 3.

SECTION 5

THE SURFACE CHEMISTRY OF HYDROUS MANGANESE DIOXIDE

James W. Murray
Department of Chemistry
Woods Hole Oceanographic Institution

INTRODUCTION

Manganese dioxide is an important phase in marine geochemistry. Along with hydrous iron oxide, it is a major component of manganese nodules, averaging 22% by weight (Horne, 1970). It has also been found to be an important component in the sediments of the East Pacific Rise. Bostrom and Peterson (1969) have suggested that this phenomenon is the result of precipitation following the injection of volcanic emanations into the sea water near the crest of the rise. In yet another context Spencer and Brewer (1972) have found relatively high concentrations of suspended manganese just above the anoxic interface in the Black Sea.

It is generally found that when a geochemical enrichment of manganese occurs certain other elements are enriched as well. Statistical analysis of the data reveal that the enriched elements are frequently correlated with manganese (Riley and Sinhaseni, 1958; Cronan, 1969; Spencer and Brewer, 1972). Adsorption onto the manganese dioxide surface is one of the mechanisms frequently proposed to explain these metal ion enrichments (Goldberg, 1954; Krauskopf, 1956; Jenne, 1969). Several different factors, of which adsorption onto the manganese dioxide surface is only one, could explain these correlations. Unfortunately, relatively little is known about the electrochemistry of the manganese dioxide surface that can be used to evaluate this mechanism.

The nature of the electrochemical double layer separating metal oxides from aqueous solution has been studied for a number of metal oxides. DeBruyn

and Stumm and their co-workers have been especially successful in looking at the oxide-solution interface in the same way that an electrochemist views the interface at a polarized electrode (Grahame, 1947). Because construction of reversible metal oxide electrodes is not always feasible (i. e., Covington, et al., 1972), and thus direct measurement of the double layer parameters is not possible, the reversible interface model has been developed (Stumm, et al., 1970). The distinction between the reversible (i. e., metal oxides) and the polarizable interface (i. e., Hg) is related to the mechanism by which the separation of charge originates. For a polarizable interface, the potential difference across the double layer is applied externally using an external potentiometer. The change in electrostatic potential across the reversible interface has been found to be the result of the transfer of potential determining ions across the solid-solution interface.

For the reversible metal oxide interface, it has been observed that hydrogen and hydroxyl ions play a unique role in determining the sign and magnitude of the surface charge. Thus the model has been adapted so that H^+ and OH^- are the potential determining ions (P. D. I.) for the surface. Because of the potential determining role of $H^+(OH^-)$, metal oxides can be characterized by a solution pH for which the charge on the surface is zero. This pH, the pH(ZPC) [at the zero point of the charge], is a convenient reference point that characterizes the amphoteric nature of the metal oxide. For a pH below the pH(ZPC), the surface charge is positive; for a pH above the pH(ZPC), the surface charge is negative. Furthermore, the location of the pH(ZPC) is useful in predicting the nature of the surface reactions (Stumm, et al.,

since it is a function of the acidity of the central metal ion and the electrostatic field strength of the solid (Healy, et al., 1966).

Healy et al. (1966) investigated the location of the pH(ZPC) for a number of different crystal modifications of manganese dioxides using electrophoresis and coagulation techniques. They found that the pH(ZPC) ranged from 1.5 for Mn(II)-Manganite to 5.0 for βMnO_2 . Several adsorption experiments have been performed using a variety of inorganic electrolytes (Gabano, 1965; Murray et al., 1968; Posselt et al., 1968; Kozawa, 1959). However, only Morgan and Stumm (1964) have reported measuring directly the adsorption of H^+ and OH^- ions using the alkalimetric titration method initially used by Parks and deBruyn (1962) to study the ferric oxide-solution interface. Morgan and Stumm's results were ambiguous, however, as the net OH^- bound to the solid as a function of pH was obtained at only one ionic strength. The values that have been reported for pH(ZPC) of hydrous manganese dioxides (βMnO_2 -Mn(II)-Manganite) range from 1.5 to 4.5. Some of this variation is, most likely, due to the effect of crystal structure noted by Healy et al. (1966a). However, a source of variation potentially as important is due to sample preparation and subsequent aging effects. Neither has been well documented in the literature. In order to evaluate the sign and magnitude of the charge on the hydrous manganese dioxide (i. e., δMnO_2) surface and to evaluate what possible roles adsorption and/or reaction play in metal ion enrichments and correlations, a detailed study of the δMnO_2 -solution interface has been undertaken. This paper discusses the direct measurement of the adsorption density of $\text{H}^+(\text{OH}^-)$ ions on a preparation of δMnO_2 and attempts to use these measurements to construct a model for the electrochemical double layer at the surface.

II MATERIALS AND METHODS

Because the dehydration of the surface with drying or simply aging while in solution can have such a pronounced effect on the location of the pH(ZPC) of the solid (Parks, 1964), it is important that the history of the sample in any experiment be described thoroughly.

The manganese dioxide used in these experiments was prepared by the oxidation of manganous ion by permanganate.

The procedure used was to add the required stoichiometric amount of NaMnO₄ (Mallinkrodt, reagent grade) to a 4 liter Erlenmeyer flask. An equivalent amount of base (NaOH) was added initially to neutralize the acid evolved and to keep the pH of the solution basic throughout the preparation. This tends to create a situation favoring kinetically the oxidation of Mn(II) (Morgan and Stumm, 1964). Distilled water was added to bring the volume up to approximately 3 liters and then the stoichiometrically required amount of standardized MnCl₂ (B&A, reagent grade) was added dropwise while the entire solution was well mixed with a magnetic stirrer. The NaMnO₄ was standardized using sodium oxalate (Skoog and West, 1963) and the MnCl₂ was standardized using the method of Lingane and Karplus (1946). The suspension was washed repeatedly until the ionic strength was approximately 1×10^4 . Several suspensions of MnO₂ were prepared at a concentration level of 5×10^{-3} m/l and then combined to produce a 4 liter stock suspension of 4.8×10^{-2} m/l MnO₂. The stock suspension was well mixed before each experiment and then a suitable aliquot was withdrawn. Twenty-five ml (containing 0.106 gms of MnO₂) of the mixed stock suspension was used for the majority of the experiments described in this paper. To prevent possible dehydration of the surface, the MnO₂ was kept in solution at all times.

The stoichiometry of the resulting hydrous manganese dioxide was determined by the O-Tolidine method (Morgan and Stumm, 1964). The oxide was found to have the composition of $\text{MnO}_{1.92}$. The X-ray powder and oriented patterns (Cu radiation with a curved crystal monochromator) of the air dried (25°) oxide showed a low degree of crystallinity. X-ray reflections were generally found at approximately 7.4 Å, 4.04 Å, 2.43 Å and 1.63 Å. The results of the stoichiometry and X-ray analyses indicate that this synthetic manganese dioxide is similar structurally to the naturally occurring mineral Birnesite (Jones and Milen, 1956) and the synthetic product studied by Giovanoli (1969, 1970) called Manganate-IV, by Morgan (1965) called δMnO_2 and by Healy *et al.* (1966) called Mn(II)-Manganite. For ease of reference, the manganese dioxide used in these experiments will be referred to as δMnO_2 .

Transmission electron microscope pictures (fig. 1) show that the particles of δMnO_2 range in length from 0.2 to 1.0μ and appear to be aggregates of much smaller spherically shaped particles. The surface area was obtained by using the B. E. T. method (Brunauer *et al.*, 1938). The required amount of δMnO_2 suspension was centrifuged and the separated δMnO_2 colloid was freeze dried. The sample was resuspended in acetone and dried again under vacuum. The B. E. T. method was performed using N_2 gas with a He carrier. Triplicate measurements gave a surface area of $263 \pm 5 \text{ m}^2/\text{gm}$. A t-plot, calculated from the N_2 adsorption data is shown in figure 2 (de Boer, 1966). The linearity of the t-plot suggests that there is no capillary condensation or closing of micropores during the adsorption process and there are no porous capillaries with openings larger than the diameter of the nitrogen gas molecules (3.54 Å).

The alkalimetric titrations were performed using 25 ml of the MnO_2 stock suspension. After the required adjustments of ionic strength using NaCl, the total volume was brought to 200 ml. The acid and base portions of the titration curves were done in different experiments. The procedure used was to add small aliquots (0.03 - 0.15 ml) of standardized 0.1N HCl or 0.1N NaOH to the titration cell and to read the pH after 2 minutes. pH measurements were made using a Fisher combination glass electrode and an Orion pH meter (Model 801). The blank titrations were prepared in an identical manner. After equilibration the δMnO_2 was removed by centrifugation and the titration was performed on the supernatant solution. To calculate the adsorption density, the pH values were corrected to concentrations using the Debye-Huckel equation. The operational definition of pH used in these experiments was:

$$pH = -\log \gamma_{salt} C_H^+$$

where γ_{salt} is the mean ionic activity coefficient of the salt used to adjust the ionic strength.

The electrophoresis measurements were measured using a Briggs micro-electrophoresis cell. The electrochemical cell can be represented by:

and the mobility was calculated as

$$U = \frac{C}{i R T}$$

where U = mobility ($\mu\text{sec}^{-1} / \text{volt cm}^{-1}$)

i = applied d. c. current (amps)

R = solution resistance (ohms)

T = average time for a particle to travel 69μ (sec)

C = cell constant (12.4 for the cell used)

RESULTS

A. Electrophoresis Measurements: Na^+ and K^+ Adsorption

Because the alkalimetric titration method is inaccurate at low pH values and because there is a lack of agreement regarding the location of the pH (ZPC) for the various modifications of MnO_2 , the location of the pH (ZPC) for the δMnO_2 used in these experiments was determined using electrophoresis measurements and Na^+ and K^+ adsorption.

The electrophoresis measurements were made at low ionic strength (1×10^{-4}) except above pH 4 where the ionic strength was controlled by the strong acid added to adjust the pH. Measurements were not possible for pH values less than about 2.5 because the combined effects of the reduction in surface charge and increase in ionic strength made the δMnO_2 suspension unstable causing the colloidal particles to settle out of the plane of focus. The calculated electrophoretic mobilities are plotted vs. pH in fig. 3. A positive mobility was never observed. The mobilities were strongly negative over most of the pH range and decreased rapidly below about pH 4. Extrapolation of the electrophoretic mobilities to zero gives a maximum value for the pH (SPC) of 2.40. The strong dependence of the mobility on pH supports the model that H^+ and OH^- are potential determining ions for the δMnO_2 surface.

The adsorption of Na^+ and K^+ was also used as an independent check on the location of the pH (ZPC). Assuming that Na^+ and K^+ do not exhibit specific adsorption on the δMnO_2 surface, these cations should be completely desorbed at the pH (ZPC). Suspensions of MnO_2 were spiked with NaCl and KCl . The pH of the suspensions was adjusted by dropwise addition of 3 N

NH OH. After equilibration, suitable aliquots of the suspensions were withdrawn and filtered and analyzed by atomic adsorption. The amounts of Na^+ and K^+ adsorbed vs. pH are shown in fig. 3. Na^+ and K^+ were completely desorbed from the surface at pH 2.25 and 2.15 respectively. The kinetics of adsorption were rapid and the amounts of Na^+ and K^+ adsorbed were completely reversible vs. pH (i. e., the amount adsorbed did not depend upon the direction from which the pH was approached).

B. Kinetics

Before undertaking the alkalimetric titration experiments on the δMnO_2 surface, it was necessary to evaluate the rate of response of the surface to the addition of various amounts of acid or base. De Bruyn (1966, 1967, 1968, 1969, 1970) has found that the reaction of protons with the metal oxide surface appears to be a two step process. For pH values greater than the pH (ZPC), an aliquot of base produces a rapid rise in pH (although not as large a rise as would take place in an unbuffered solution) followed by a slow downward drift. The slow drift was found to last about 80 hours for Fe_2O_3 and 800 hours for TiO_2 . A similar rapid drop in pH occurred after the addition of acid for pH values less than the pH (ZPC). However, the occurrence of the slow step seemed to depend on the oxide used.

The pH drift after the addition of various amounts of base to suspensions of δMnO_2 is shown in fig. 4. The initial pH of the suspensions was about 3.25. The figure shows that there is a downward pH drift that increases with the size of the aliquot of base added. The time to reach equilibrium was a function of the amounts of strong base added, implying that the pH drift is a function of H^+ or OH^- gradients

produced by the addition. Fig. 5 shows the pH drift over an extended period of time. Equilibrium, in this example, appears to have been reached by about 200 hours. In Fig. 6, the H^+ ion activity is plotted as $T^{\frac{1}{2}}$. After the rapid equilibration of the solution with the surface following the addition of base, protons are released to the bulk solution (or OH^- is consumed by the surface) giving a linear response as $T^{\frac{1}{2}}$ for up to approximately 10 minutes, whereupon the drift appears to assume a quasiexponential character. Similar $T^{\frac{1}{2}}$ plots have been observed by Gallagher and Phillips (1968) and Wytttenbach (1961) for tritium diffusing into $\alpha FeOOH$ and by Luce et al. (1972) for proton exchange with Mg^{+} in magnesium silicates. These authors 11 found that their data could best be described using the parabolic diffusion model that results from solving Fick's second law (eqn. 1).

$$\frac{a \cdot C}{a \cdot t} = D \frac{a^2 \cdot C}{a \cdot x^2} \quad (1)$$

for extraction from a semi-infinite slab into a well-stirred aqueous solution.

Berube and de Bruyn (1968) and Onoda and de Bruyn (1966) showed that if the titration is performed fast enough, the slow, diffusion controlled step may be suppressed. They concluded that under these conditions the experimental results should reflect only changes characteristic of a surface process. The short-term response of the δMnO_2 surface after the addition of small aliquots of base was found to be rapid and as a result of adding small aliquots the pH drift was minimized. When the titrations were performed with the aliquots (.05 - .15 ml) of base and acid added at regular two minute intervals, they were found to be reversible to within 0.1 pH units.

C. Alkalimetric Titration Curves

Recording the pH during the course of a titration of a suspension of MnO_2

and comparing it with the pH of a similar solution minus the MnO colloid provides data that can be interpreted in terms of adsorption of hydrogen or hydroxyl ions. The adsorption density ($\overline{[H^+]} - \overline{[OH^-]}$) is obtained from a mass balance between the titration curve of the suspension and that of the supernatant of the suspension.

$$\frac{C_B - C_A + [H^+] - [OH^-]}{S} = \overline{[OH^-]}^* - \overline{[H^+]}^* = - \frac{\delta_0}{F} \quad (7)$$

C_B = strong base

C_A = strong acid

S = surface area (cm^2)

$\overline{}^*$ = specific adsorption density ($\frac{\text{equivalents}}{\text{cm}^2}$)

= surface charge (coul/cm^2)

F = Faraday constant ($9.65 \times 10^4 \text{ coul}/\text{eq.}$)

The quantity of acid or base that cannot be balanced in the solution phase and is present in the system is ascribed to the surface. Fig. 7 shows the alkalimetric titration curves and Fig. 8 the net adsorption curves for the MnO_2 surface at several different ionic strengths. The net adsorption curves result from subtracting the blank titration curves from the suspension titration curves. Such a procedure takes into account any strong acid or strong base present in the system. The error in subtracting these curves increases at low pH values because of the decrease in slope. The surface charge is conventionally calculated relative to the intersection of the titration curves at different ionic strengths. This intersection generally agrees well (except in the presence of specific adsorbable cations or anions) with the pH (ZPC) located by other methods

such as electrophoresis. For δMnO_2 the pH (ZPC) located by electrophoresis and Na and K adsorption cannot be reached by the alkalimetric titration method used. Thus, the surface charge calculated directly from the data gives only a minimum value as the correct value must be calculated from the pH (ZPC). In order to obtain a more quantitative value for the surface charge, an alternate method must be used for extending the net titration curves to the pH (ZPC).

In this instance, the adsorption of Na^+ has been found to be a suitable means of extrapolating the titration curves. For constant potential surfaces, such as metal oxides, the surface charge on the solution side is equal but opposite in sign to the charge on the solid (Stumm and Morgan, 1971). When the surface is negatively charged, the charge on the solution side is given by the sum of δ^+ (charge due to a surplus of cations) and $-\delta^-$ (charge due to a deficiency of anions).

$$\delta_{\text{solution}} = F (\delta^+ + \delta^-)$$

Assuming that both Cl^- and Na^+ react non-specifically with the surface and that the number of equivalents of Na^+ adsorbed on the surface equals the number of equivalents of Cl^- desorbed, the surface charge can be approximated at constant ionic strength by:

$$\text{surface} = F (2 \sqrt{[\text{Na}^+]})$$

Fig. 9 shows the net titration curves for MnO extrapolated to pH 2.25 on the basis of measurements of Na^+ adsorption for $I = 10^{-3}$ and $I = 10^{-2}$. The surface charge has been calculated relative to this intersection.

The alkalimetric titration experiments were repeated after one month and it was found that they had decreased by approximately 10 - 15%. Parks (1964) has noted that treatment likely to lead to bulk or surface dehydra-

tion often results in more acid pH (ZPC). Thus it is likely that the decrease observed above is due to the aging of the freshly precipitated "active form of MnO into a more stable form. This aging is probably due to the condensation and dehydration of the metal oxide and may explain some of the variability that exists in the literature regarding the location of the pH (ZPC) for δMnO_2 .

DISCUSSION

The thermodynamics and coordination chemistry of the metal oxide-electrolyte interface have been described in detail by Parks and de Bruyn (1962), de Bruyn and Agar (1962), Berube and de Bruyn (1968), Atkinson et al. (1967) and Stumm et al. (1970).

The origin of the charge at the metal oxide-solution interface is viewed as a two step process. The surface hydrates by pulling H^+ ions, OH^- ions or water molecules from solution as the surface atoms attempt to complete their coordination. The metal hydroxide groups formed in this manner participate in acid-base reactions to produce a positively or negatively charged surface. The surface metal hydroxide groups can either dissociate or accept H^+ or OH^- ions.

It is impossible to determine experimentally whether the reaction is due to the adsorption of H^+ and OH^- ions or to the dissociation of surface sites.

The exact location of the pH(ZPC) will depend on the relative acidity of the surface groups.

The pH(ZPC) will lie at the pH value for which an equal number of Me - OH₂⁺ and Me - O⁻ groups are present, i.e. when the surface is uncharged. Using reaction (3) the pH(ZPC) will be characterized by:

$$\begin{aligned} & [\text{Me} - \text{OH}_2^+] = [\text{Me} - \text{O}^-] \\ \text{and } & [\text{H}^+_{\text{ZPC}}] = [K_1 K_2]^{1/2} \text{ or } \text{pH(ZPC)} = 1/2 (\text{p}K_1 + \text{p}K_2) \quad (4) \end{aligned}$$

where K₁ and K₂ define the acidity constants of the surface sites (Stumm, et al., 1970). The location of the pH(ZPC) will thus depend on such factors as the acidity of the metal ion and the electrostatic field strength of the solid (Healy, et al., 1965, 1966). Table 1 compares the pH(ZPC) of several metal oxides. In general the pH(ZPC) is inversely proportional to the charge of the metal ion and the size of the unit cell of the solid.

As shown in reactions (1) and (2) only H⁺ and OH⁻ are potential determining. This is a simplification of the more general model proposed by Parks and de Bruyn (1962) in which the establishment of the surface charge can also be explained by the adsorption from solution of dissolved metal hydrolysis species. If the affinity of all the dissolved metal hydrolysis species in equilibrium with a metal oxide for the surface of that metal oxide were equal then one would expect good agreement between the pH(ZPC) and the iso-electric point of the complex solution.

The results of this study indicate that H^+ and OH^- are potential determining ions for the δMnO_2 surface and that the pH(ZPC) is located at approximately pH 2.25. As MnO_2 is highly insoluble ($K_{so} = 10^{-56}$ Morgan, 1965) the adsorption from solution of dissolved Mn(IV) hydrolysis species can be neglected. This low pH(ZPC) implies that compared with most other metal oxides δMnO_2 is relatively strong acid. Combining reactions 1 and 2 gives an overall reaction for the surface of:

which has an equilibrium constant of:

$$K_{12} = \frac{[\text{MnO}^-]}{[\text{MnOH}_2^+]} \times \frac{\gamma_- (\text{surface})}{\gamma_+ (\text{surface})} \times \text{Cl}_H^2$$

Assuming that at the pH(ZPC) the positive and negative sites are equal and the activity coefficients for the sites are equal $K_{12} = 10^{-4.5}$ for MnO_2 . This value compares with a K_{12} of 10^{-17} calculated in a similar manner for Fe_2O_3 (Parks and de Bruyn, 1962) and shows that δMnO_2 attracts protons much less strongly than Fe_2O_3 .

A more rigorous theoretical treatment of the δMnO_2 surface is not feasible because of the uncertainties in the extrapolation of the titration curves. An additional uncertainty is related to the assumption that H^+ and OH^- are the sole potential determining ions. As discussed previously the solubility of δMnO_2 is extremely low and thus, Mn(IV) solution species can be neglected. However, at low pH values Mn is released to solution. Morgan (1965) reported that Mn(II) may be released from δMnO_2 in acid solu-

tions. He attributed this to H^+/Mn^{+2} exchange. Figure 10 shows the release of Mn to solution versus time for suspensions adjusted to different initial pH values. Mn was released to solution in increasing quantities, versus time and as the experiment progressed the pH decreased indicating that H^+ ions were being released to solution. The shape to these curves suggest that the release of Mn from the solid is not due to H^+/Mn^{+2} exchange. Such a reaction would tend to increase the solution pH as the solid consumed protons and the release of Mn versus time should decrease as the gradients decreased. The observation that the release of Mn was not observed for any samples above pH 3.0 suggests an alternative mechanism for the release. Figure 11 shows a pE - pH diagram for manganese. From the relative positions of the $MnO_2 - Mn^{+2}$ and $O_2 - H_2O$ lines it is apparent that MnO_2 becomes unstable with respect to the oxidation of water at pH values below 3. This suggests that the reduction of MnO_2 by H_2O takes place liberating Mn^{+2} and H^+ to solution.

Though there is a considerable time lag before any Mn can be detected in solution for pH values between 2 and 3 it is highly possible that small amounts of Mn^{+2} are released during the course of an alkalimetric titration and re-adsorbed specifically by the negative surface thus acting as another potential determining ion. Participation of Mn^{+2} as a P.D.I. below pH 3.0 would mean that the location of the pH(ZPC) at 2.25 is not entirely due to reversible H^+ (OH^-) adsorption, thus indicating that MnO_2 has even less affinity for protons than was previously calculated. The pH(ZPC) has been

located for βMnO using the alkalimetric titration method (Jenkins 1971) so it is reasonable to expect that H^+ and OH^- should be considered the potential determining ions for δMnO_2 for pH values greater than 3.

Table 1 indicates that the material that has the most comparable pH(ZPC) to MnO_2 is SiO_2 . Figure 12 compares the charge versus pH values for amorphous SiO_2 obtained by Tadros and Lyklema (1968) with the charge versus pH data for MnO_2 obtained in this paper. The pH(ZPC) for Tadros and Lyklema's SiO_2 was 3.0. The calculated surface charge increases much more rapidly for δMnO_2 , reaching approximately $100 \mu \text{ coul/cm}^2$ by pH 8.0. This demonstrates the much greater surface activity for δMnO_2 compared with SiO_2 even though they have similar pH(ZPC). A possible explanation for this difference may be due to the fact that Mn^{+2} may be acting as a potential determining ion below pH 3.

SUMMARY AND CONCLUSIONS

An experimental investigation of the pH(ZPC) and surface charge was made for a sample of hydrous manganese dioxide (δMnO_2). As for other metal oxides, H^+ and OH^- were found to be potential determining ions, however, below pH 3 Mn^{+2} may be acting as a potential determining ion as well.

The alkalimetric titration curves failed to provide a unique location for the pH(ZPC). In order to locate the pH(ZPC) electrophoretic mobilities and Na^+ and K^+ adsorption measurements were used. These methods agreed well and gave a pH(ZPC) of approximately 2.25 ± 0.20 for the sample studied. Once the pH(ZPC) was located the net alkalimetric titration curves were extrapolated to that point using the adsorption of Na^+ . The charge values calculated by this procedure give values of approximately $100 \mu \text{ coul/cm}^2$ at pH 8, con-

siderably higher than the charge on SiO_2 which has a similar $\text{pH}(\text{ZPC})$. The difference in surface charge for these two substances gives a possible explanation of why manganese rich sediments and manganese nodules have much larger concentrations of rare metals than silica rich sediments (Krauskopf, 1956).

TABLE 1

COMPARISON OF THE pH OF ZPC FOR VARIOUS METAL OXIDES

<u>OXIDE</u>	<u>pH(ZPC)</u>	<u>REFERENCE</u>
WO_3	0.5	El Wakkad and Rizk (1957)
SiO_2 (Qtz.)	2.0	Li (1958)
(Amorphous)	3.5	Bolt (1957)
	3.0	Tadros and Lyklema (1968)
TiO_2	6.0	Berube and de Bruyn (1968)
γ - Al_2O_3	7.6	Stumm, Huang and Jenkins (1970)
α - Fe_2O_3	8.5	Parks and de Bruyn (1962)
ZnO	8.9	Blok and de Bruyn (1970)
Ag_2O	11.2	Parks and de Bruyn (1962)

Figure 1

Transmission electron microscope picture of δMnO_2

Magnification: 15,000 x

Figure 2

The nitrogen gas adsorption data for two samples of δMnO_2 plotted as a t-plot (de Boer et al., 1966). The specific surface area can be calculated using the slope of this line:

$$S = 15.47 (V_a / t)$$

where V_a is the volume of adsorbed nitrogen gas and t is the average thickness of the adsorbed layer in Angstroms. The same data give a surface area of $263 \text{ m}^2/\text{g}$ using a B. E. T. plot. The surface area as determined by the t-plot is $270 \text{ m}^2/\text{g}$.

Fig. 2

Figure 3

Electrophoresis mobilities and Na^+ and K^+ adsorption
measurements for δMnO_2 .

Fig. 3.

Figure 4

PH drift versus pH for δMnO_2 .

Fig. 4

Figure 5

Long Term pH Drift

Fig. 5

Figure 6

pH Drift Plotted Versus $\sqrt{t}$

Fig. 6

Figure 7a

Alkalimetric titration curves for δMnO_2 at several ionic strengths. The titrations were performed using 0.1 gm (26m^2) of δMnO_2 and the ionic strength was adjusted using NaCl. Total volume of the titration cell was 200 ml. The acid and base portions of the titration curves were done in different experiments.

Figure 7b

Blank titration curves performed on the supernatant solutions after the removal of the δMnO_2 .

δ MnO₂ ALKALIMETRIC TITRATION CURVES

Fig. 7a

Fig. 7b

Figure 8

Net alkalimetric titration curves for δMnO_2

Fig. 8

Figure 9

Surface charge calculations for the alkalimetric titration curves extrapolated to the $\text{pH}(\text{ZPC})$ using Na^+ adsorption data. Charge values in $\mu\text{coul}/\text{cm}^2$ were calculated relative to the intersection of the titration curves using equation 7.

Fig. 9

Figure 10

The release of manganese to solution from suspensions of δMnO_2 adjusted to different initial pH values.

Curve	pH
1	1.50
2	2.30
3	2.45

Fig. 10

Figure 11

Eh - pH Diagram for Manganese

FIG. II. POTENTIAL DIAGRAM SHOWING THE RELATION OF A NUMBER OF OXIDATION-REDUCTION REACTIONS TO MAJOR MANGANESE SPECIES.

Figure 12

A comparison of the charge versus pH values for δMnO_2 and SiO_2 . The charge values for δMnO_2 were calculated using alkalimetric titration curves extrapolated to the $\text{pH}(\text{ZPC})$ using Na^+ adsorption. The charge values for SiO_2 were taken from Tadros and Lykleme (1968).

Fig. 12

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