Chemical Oceanographic Data From the Western Mediterranean

by

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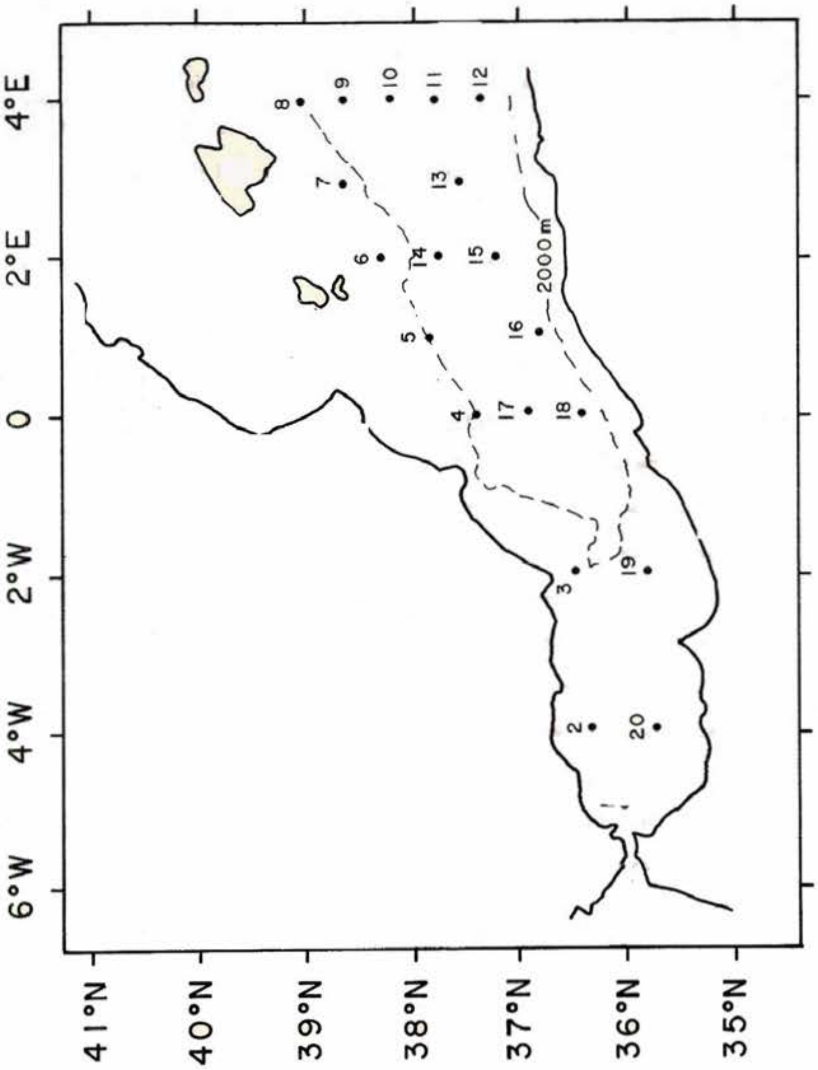
Introduction

During September of 1976 a cruise was made in the Western Mediterranean Sea on the R/V GILLISS. This report contains the chemical oceanographic data obtained from the samples collected on the cruise. The purpose of the cruise was to examine the physical properties (density and sound speeds) of evaporated seawaters and to characterize the carbonate system in the Mediterranean Sea. The discussion of the scientific results of this cruise is given in the scientific papers resulting from the cruise (Millero, Means, and Miller, 1978; Millero, Morse, and Chen, 1979).

Measurements

The samples were taken in 3 liter Niskin bottles. The locations of the stations are shown in Figure 1. The samples for physical chemical measurements were stored in 900 ml glass bottles. The samples for nutrient analysis were stored in 200 ml plastic bottles (poisoned with $HgCl_2$). The temperatures were obtained from reversing thermometers. The salinities were measured on board with a Beckman Salinometer. The laboratory salinities were measured with a Guildline salinometer. The values given in this report are from the laboratory measurements. The shipboard salinometer malfunctioned during the cruise. On stations where both systems were used, the salinities agreed to $\pm$ 0.02°/oo. The laboratory measurements were frequently higher by ∿0.01°/oo due to evaporation. Oxygen measurements were not made on the cruise because the reagents were lost on the trip from Miami to Gibraltar (in two hurricanes). The phosphate, nitrate and silicate analyses were made on an autoanalyzer by the Miami Water Analysis Laboratory.

The concentrations of nutrients in the surface were undetectable by the methods used. The nitrate and phosphate data for the deep waters

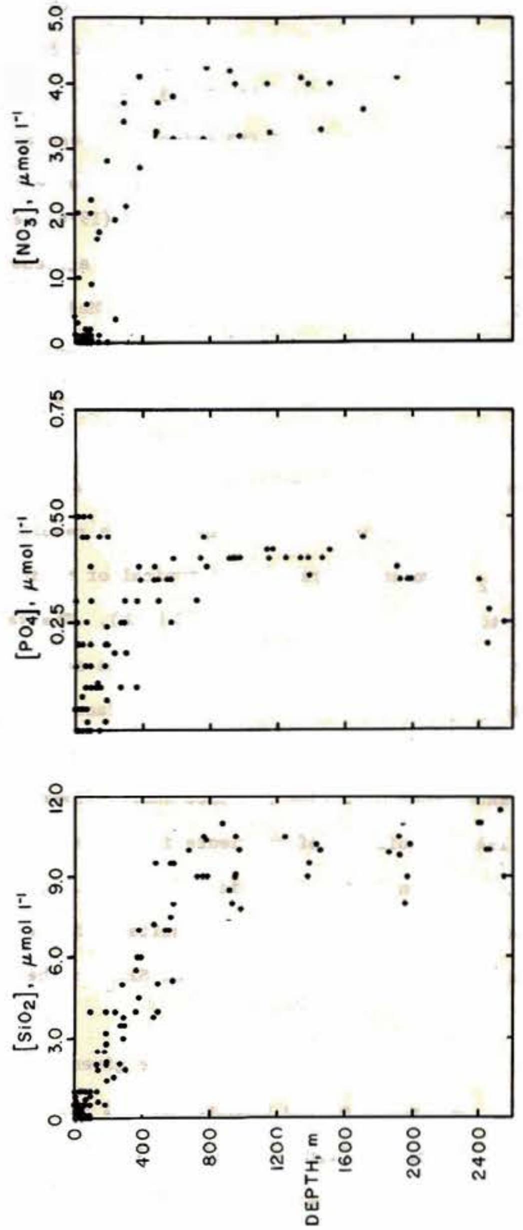


41°N
40°N
39°N
38°N
37°N
36°N
35°N
6°W
4°W
2°W
0
2°E
4°E
2000 m
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Figure 1

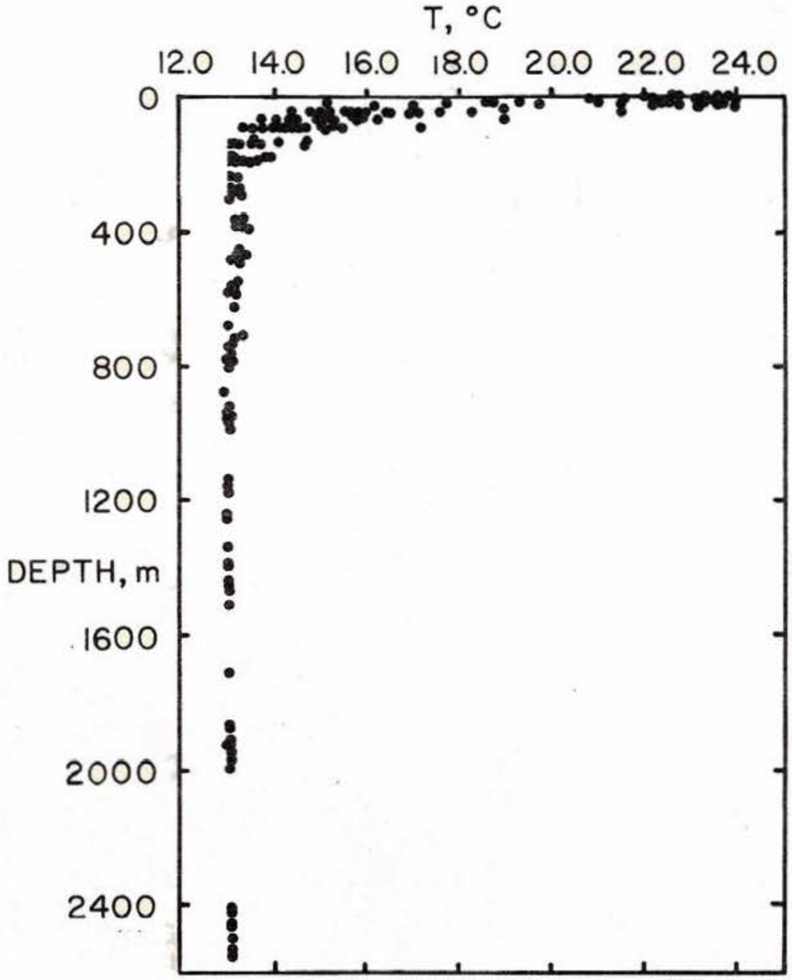
showed quite a lot of scatter apparently due to the methods used to store the samples. The average values of NO_3 and PO_4 for the deep waters, (below 500m) were respectively, 3.8 ± 0.5 μ mol ℓ^{-1} (33 points) and 0.3 ± 0.1 μ mol ℓ^{-1} (53 points). These average values are in reasonable agreement with the values of NO_3 = 5.0 μ mol ℓ^{-1} and PO_4 = 0.25 μ mol ℓ^{-1} found by Chernyakova (1976) near the Straits of Sicily. Our results are also in reasonable agreement with the recent GEOSECS test (404) station in the Eastern Mediterranean (NO_3 = 4.8 μ mol kg^{-1} and PO_4 = 0.2 μ mol kg^{-1} for deep water). The average values of SiO_2 = 9.1 ± 1.5 μ mol kg^{-1} (47 points) for the deep waters are in reasonable agreement with the values of SiO_2 = 9.0 μ mol kg^{-1} from the GEOSECS test station in the Eastern Mediterranean. Due to the poor quality of our nutrient data, we have not reported the results. The profiles of NO_3, PO_4 and SiO_2 shown in Figures 2, are typical of Mediterranean waters (compared to results stored in the NODC bank). The values in the deep waters are quite low compared to waters at the same depth in the Atlantic. This is largely due to the fact that the surface waters of the Atlantic are almost depleted of nutrients and the river imput is quite low. Since the deep water turn over time is quite short, (Sverdrup, Johnson and Fleming, 1942) a build up of nutrients in the deep waters does not take place as is common in the Atlantic and Pacific. Schink (1967) has made a chemical balance for SiO_2 and his results indicate that the river imput is approximately equal to the outflow of SiO_2 in the deep waters into the Atlantic.

The temperature and salinity data are given at various depths in Appendix I. A summary of the temperature and salinity data is shown as a function of depth in Figures 3 and 4. A summary of the average salinities and temperatures for the surfaae (0 to 100m) and deep waters (300 m to the bottom) are given in Table I.



[NO3], μmol l-1
0
1.0
2.0
3.0
4.0
5.0
[PO4], μmol l-1
0.25
0.50
0.75
[SiO2], μmol l-1
0
3.0
6.0
9.0
12.0
0
400
800
1200
1600
2000
2400
DEPTH, m

Figure 2



T, °C
12.0
14.0
16.0
18.0
20.0
22.0
24.0
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 3

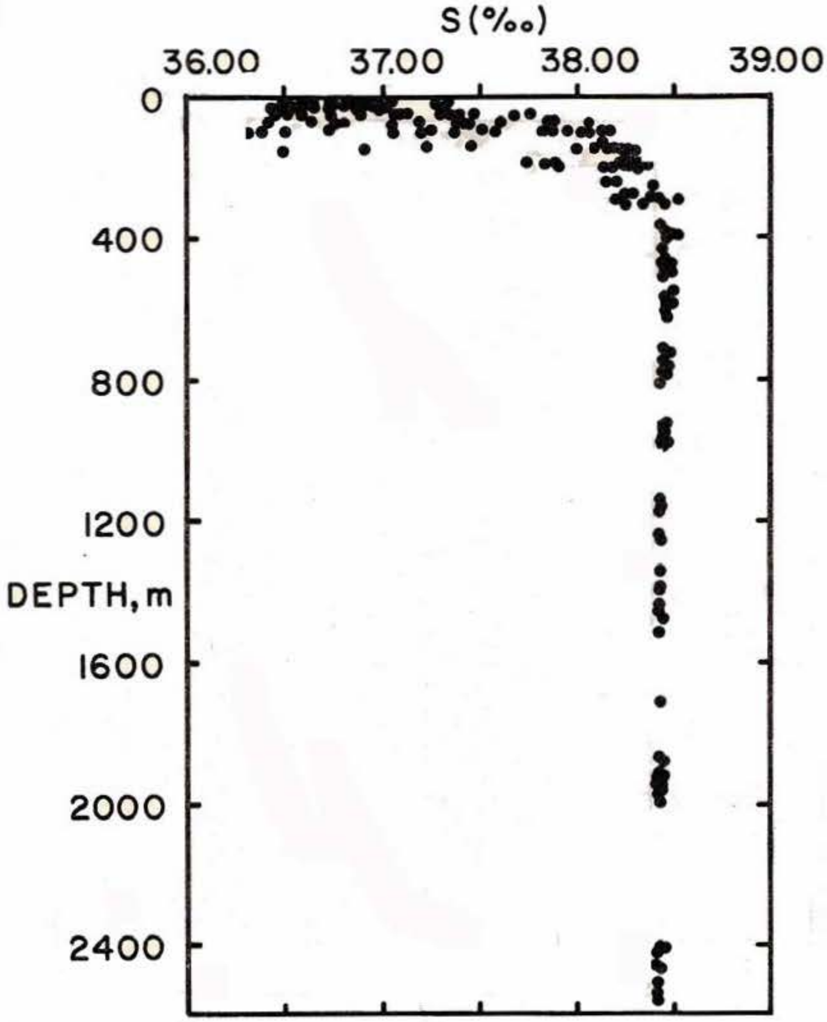


Figure 4

TABLE I

Summary of Results for the Mediterranean Sea[a]

Parameter	Surface Waters (0 to 100m)	Deep Waters (300m to bottom)
S(‰)	36.8 ± 0.2 (43)	38.44 ± 0.02 (67)
t(°C)	23.5 ± 0.5 (20)	13.05 ± 0.05 (81)
θ(°C)	-	12.83 ± 0.07 (71)
SiO_2, μ mol kg^{-1}	0	9.1 ± 1.5 (47)
NO_3, μ mol kg^{-1}	0	3.8 ± 0.5 (33)
PO_4, μ mol kg^{-1}	0	0.3 ± 0.1 (53)
$pH_{25°C}$	8.19 ± 0.02 (41)	$8.05 \pm 0.01_4$ (109)
pH_{insitu}	8.20 ± 0.02 (41)	$8.17 \pm 0.01_4$ (109)
A_T(meq kg^{-1})	2.39 ± 0.03 (78)	2.63 ± 0.03 (163)
A_T/Cl (‰)	$0.121_8 \pm 0.001$ (99)	$0.124_3 \pm 0.001_6$ (123)
$[HCO_3]$, mmol kg^{-1}	1.91 ± 0.03 (51)	2.18 ± 0.03 (110)
$[CO_3]$, mmol kg^{-1}	0.23 ± 0.01 (52)	$0.17_9 \pm 0.006$ (139)
$[CO_2]$, mmol kg^{-1}	$0.012_5 \pm 0.001$ (73)	$0.016_4 \pm 0.001$ (145)
ΣCO_2, mmol kg^{-1}	2.18 ± 0.05 (81)	2.36 ± 0.03 (136)
P_{CO_2}, 10^6 atm	393 ± 31 (80)	425 ± 23 (100)
Ωcalcite	5.2 ± 0.2 (41)	2.44 ± 0.06 (8)[b]
Ωaragonite	3.1 ± 0.1 (41)	1.43 ± 0.03 (8)[b]

a) The number of data points used are given in parenthesis.

b) From the deepest stations (∼ 2500m)

The Atlantic surface waters flowing into the Mediterranean have a temperature of 23.5 ± 0.5°C and a salinity of 36.8 ± 0.2°/oo. The deep Mediterranean waters have an insitu temperature of 13.05 ± 0.5°C, adiabatic temperature θ = 12.83 ± 0.07°C and a salinity of 38.44 ± 0.02°/oo. The deep waters are quite uniform, while the surface waters have large changes in temperature and salinity due to the mixing of the two water masses. For most of the stations a maximum occurs in the salinity at ~400m. This feature is normally attributed to the Lavintine Intermediate waters (Wust, 1961). The north-south section of stations 8 to 12 (Figure 5) clearly show the core of this water which has a maximum salinity of 35.52°/oo. The scatter in the salinities between 0 to 300m is due to advection. This is shown in north-south section of stations 8 to 12 (Figure 6) of the waters between 0 and 200 meters. The surface salinities (Figure 7) show that the low salinity waters in the surface waters near Africa are due to the input waters from the Atlantic.

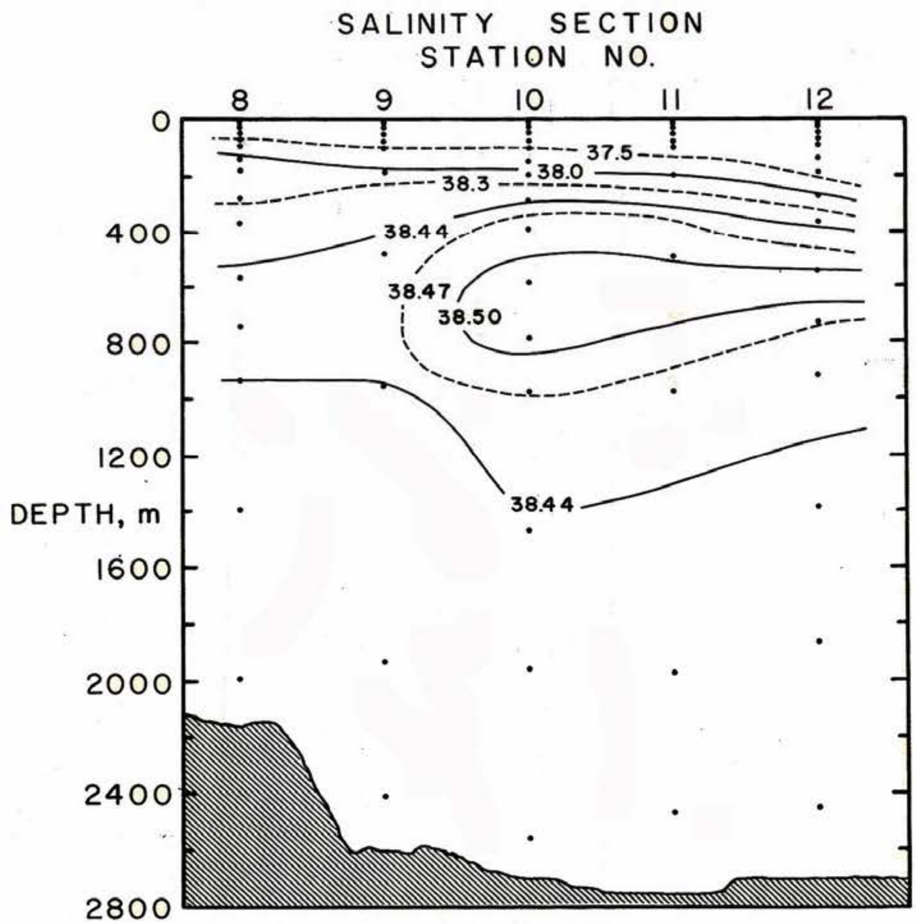
The pH measurements were made on the water as soon as the samples were taken from the Niskin water samples. The combination glass electrode (Corning) and pH meter (Leeds and Northrup) were calibrated before and after each series of measurements (at a given station) with NBS buffers (pH = 4.0, 7.0, and 9.0). The precision of the pH measurements was 0.003 pH units and the accuracy is thought to be 0.02 pH units. The values of the pH at 25°C were determined from the measured values at a given temperature (t°C) using

$$t \geq 20^\circ C \qquad pH_{25} = pH_t + X_1 \; (t-25) \qquad (1)$$

$$t \leq 20^\circ C \qquad pH_{25} = pH_t + X_1 \; (20-25) + Y_1 \; (t-20) \qquad (2)$$

The values of X_1 and Y_1 from Harvey (1963) were fit to the equations

$$X_1 = 0.011-4.7 \times 10^{-4}(S-35) + 0.0013(pH_t-8) \qquad (3)$$



SALINITY SECTION
STATION NO.
8
9
10
11
12
0
400
800
1200
DEPTH, m
1600
2000
2400
2800
37.5
38.0
38.3
38.44
38.47
38.50
38.44

Figure 5

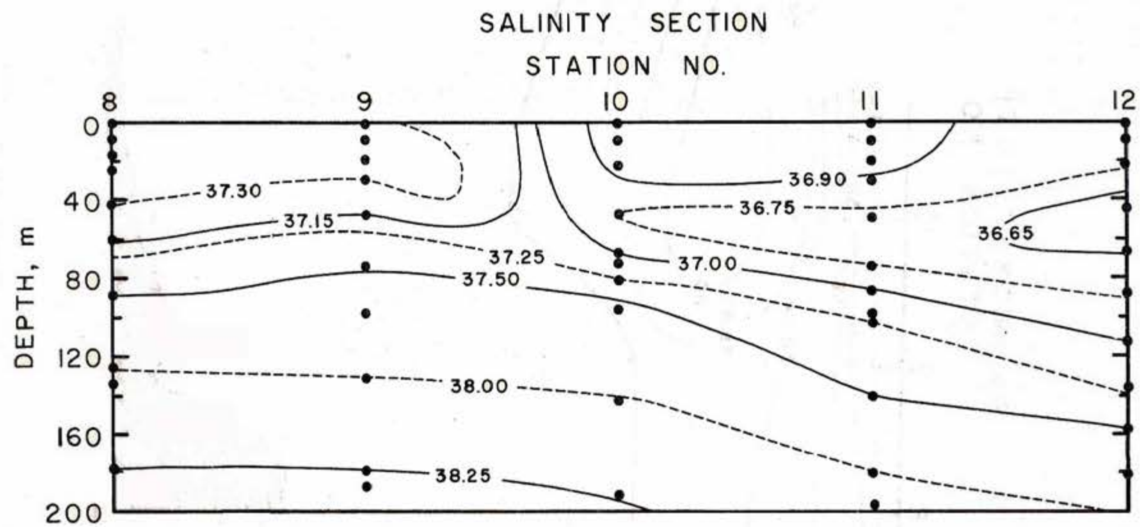

SALINITY SECTION
STATION NO.
8
9
10
11
12
0
40
80
120
160
200
DEPTH, m
37.30
37.15
37.25
37.50
38.00
38.25
36.90
36.75
36.65
37.00

Figure 6

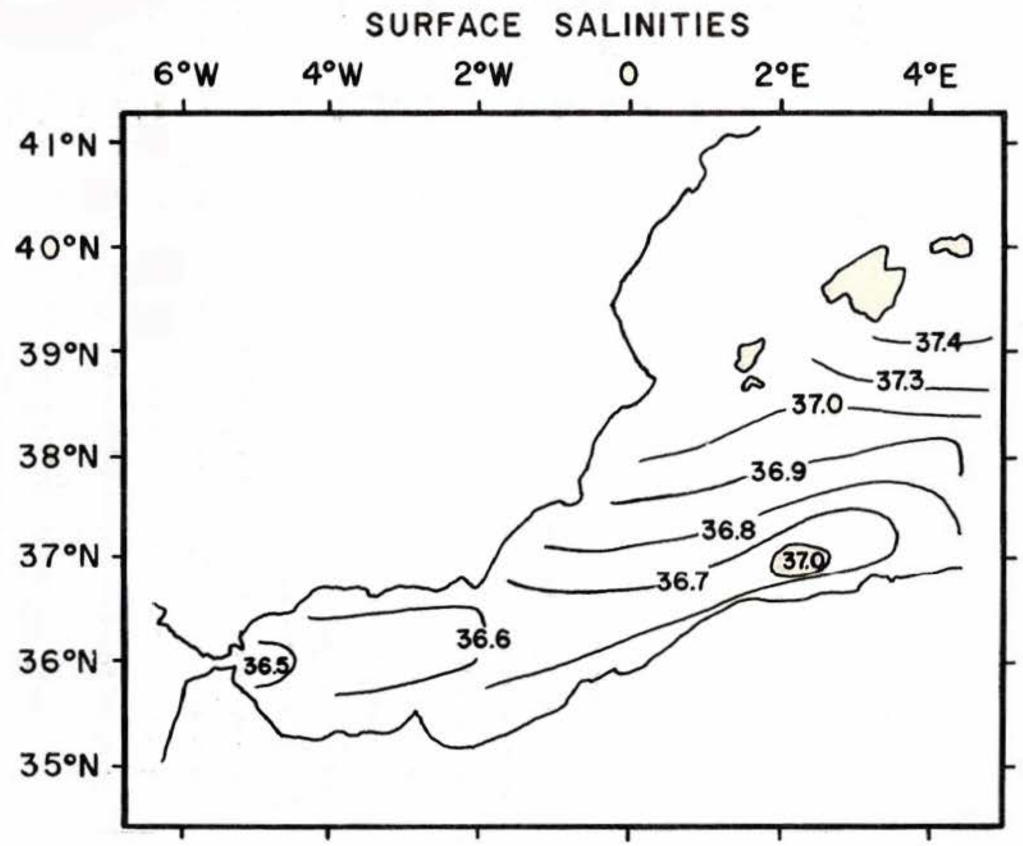

SURFACE SALINITIES
6°W
4°W
2°W
0
2°E
4°E
41°N
40°N
39°N
38°N
37°N
36°N
35°N
37.4
37.3
37.0
36.9
36.8
37.0
36.7
36.6
36.5

Figure 7

$$Y_1 = 0.011-7.3 \times 10^{-5}(S-35) + 0.0022(pH_t-8) \qquad (4)$$

The values of X_1 and Y_1 are based on the work of Buch and Nynäs(1939). The values of $pH_{25}-pH_t$ calculated from these equations agree with those derived by Ben-Yaakov (1970) [based on Lymans(1956) constants] to 0.007 over the temperature and pH range of our measurements. Equations (1) to (4) also give values of $pH_{25}-pH_t$ that agree within $\pm$ 0.008 (Millero, paper in preparation) with the values calculated using the constants of Mehrbach et al. (1973).

The total alkalinity (A_T) measurements were made by the methods developed by Edmond (1970). The titration with 0.1m HCl (in 0.6m NaCl) were made at 25 $\pm$ 0.01°C. The emf measurements were made with an Orion or Leeds and Northrup pH meter, and combination glass electrode. The end point of the titration was determined by using a Gran method and computer program developed by Gieskes (personal communication). The volume alkalinities were converted to weight values using the densities measured on the same samples (Millero, Means, and Miller, 1978). The precision of the total alkalinity was 0.003 meq kg^{-1} and the accuracies are thought to be 0.01 meq kg^{-1}. The values of pH and A_T at 25°C for the samples are given in Appendix I. A summary of pH and A_T data is shown in Figures 8 and 9. The average values of pH and A_T for the surface and deep waters are given in Table I. The surface waters have a pH_{25} = 8.19 $\pm$ 0.02 and A_T = 2.39 $\pm$ 0.03 and deep waters have a pH_{25} = 8.05 $\pm$ 0.01 and A_T = 2.63 $\pm$ 0.03 meq kg^{-1}. The in situ pH_t has been determined using the rearranged form of equations (1) and (2). The correction of pressure on the pH has been determined by using the data of Culberson and Pytkowicz (1968) fitted to the equation

$$pH_{in\ situ} = pH_t - P\ [.000428 \times 10^{-4} \times t - (pH_t - 7.8) \times 4 \times 10^{-5}] \qquad (5)$$

Since the temperature of the surface waters (23.5 $\pm$ 0.5°C) is close to

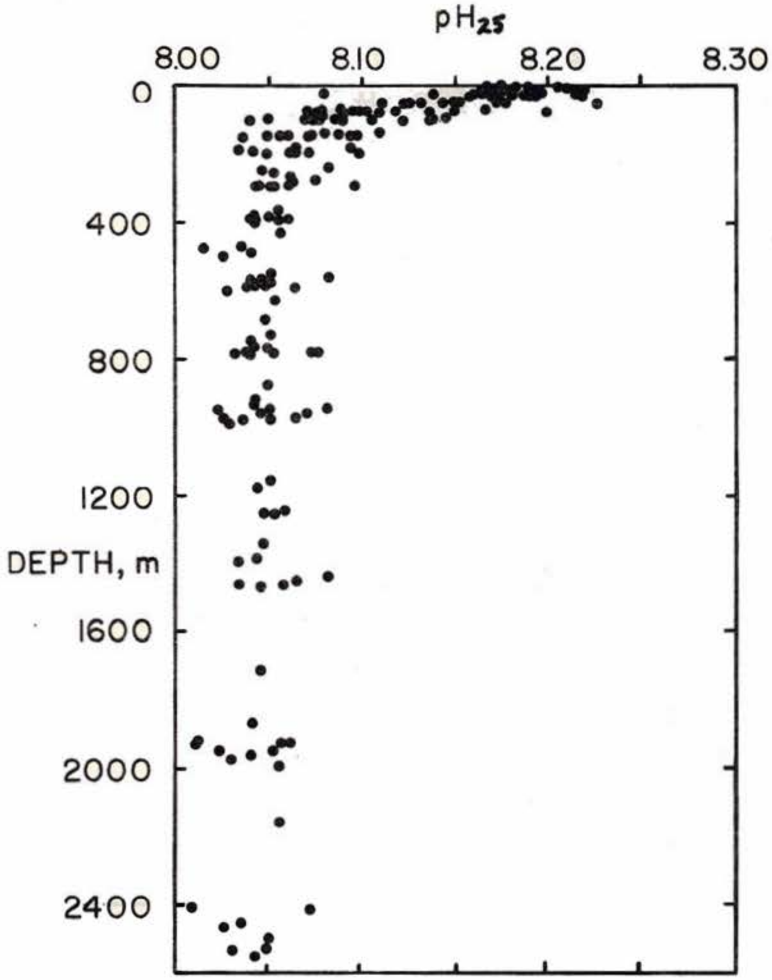


Figure 8

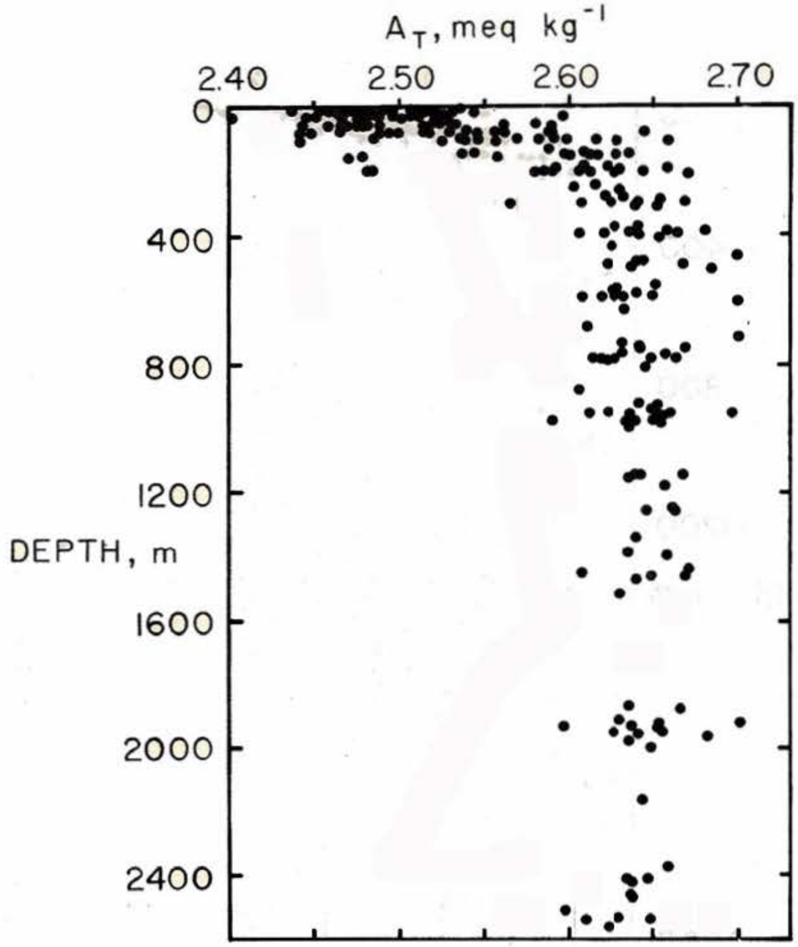


Figure 9

25°C, the $pH_{in\ situ}$ is only 0.01 pH unit higher than pH_{25}. The average value of $pH_{in\ situ}$ in the deep waters is equal to 8.17 ± 0.01, which is only 0.03 pH units lower than the surface values. The pressure and temperature correction is shown for Station 11 in Figure 10. The specific alkalinity S.A. = $A_T/Cl(^o/oo)$ where $Cl(^o/oo) = S(^o/oo)/1.80655$ (UNESCO, 1965) nave also been calculated for the samples. A plot of S.A. for all the stations is shown as a function of depth in Figure 11. The scatter in the data is due to the error of the values of A_T (an error of ± .02 meq kg^{-1} A_T yields an error of ± 0.001 in S.A.). The surface waters have an S.A. = 0.122 ± 0.001 while the deep waters have an S.A. = 0.124 ± 0.0016. Our results indicate that the specific alkalinity increases by 0.002 in the deep waters (which is within the scatter of the data).

The summary of the data represented in Figures 2 to 11 show quite a lot of scatter in the various properties. Part of this scatter is due to experimental errors; however, most of it is due to variations in the waters. This can be demonstrated by examining the temperature, salinity pH_{25}, A_T, and S.A. for one station. The station selected is Station 11 since we have tritium data for this station (see Table II and Figure 12 measurements from the Tritium Laboratory under the direction of Dr. Gote Ostlund). The values of the various parameters plotted as a function of depth are given in Figures 13 and 14.

The density measurements were made with a vibrating densimeter that is described in detail elsewhere (Picker, Tremblay, and Jolicoeur, 1974). The densimeter was calibrated with nitrogen, water and standard seawater. The values of the relative density, $d-d_o$. (where d is the density of the sample and d_o is the density of pure water) obtained for standard seawater during the cruise are given in Table III. The precision for these calibrations was ± 3 x 10^{-6} g cm^{-3}. The temperature of the densimeter

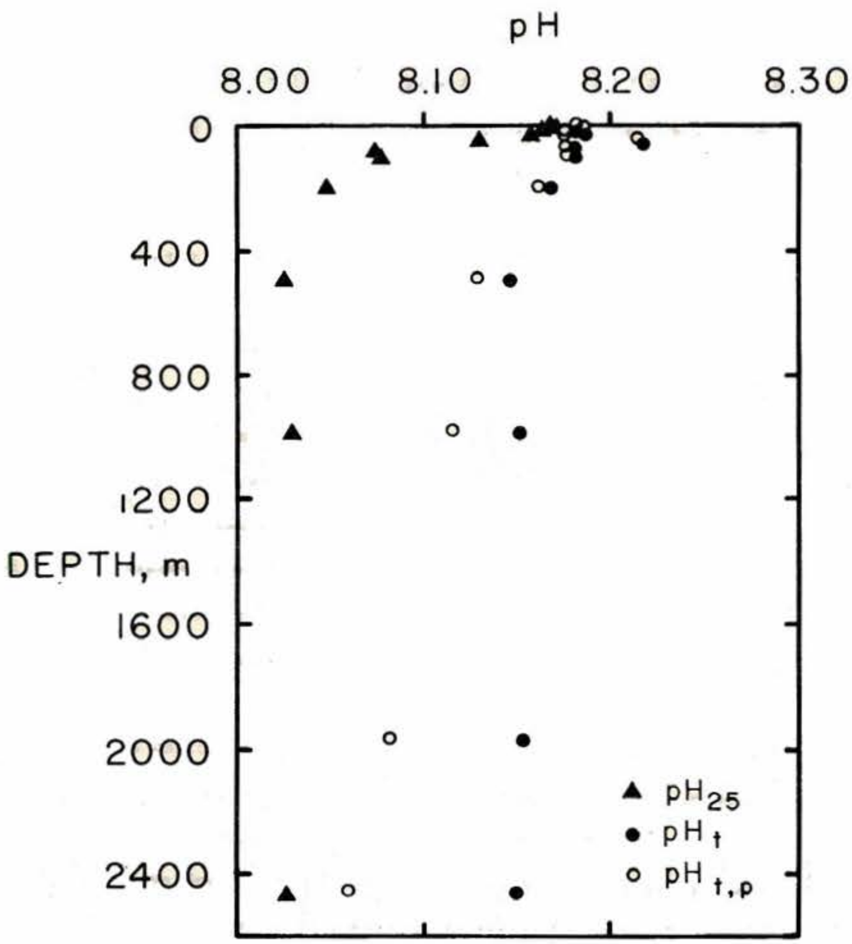
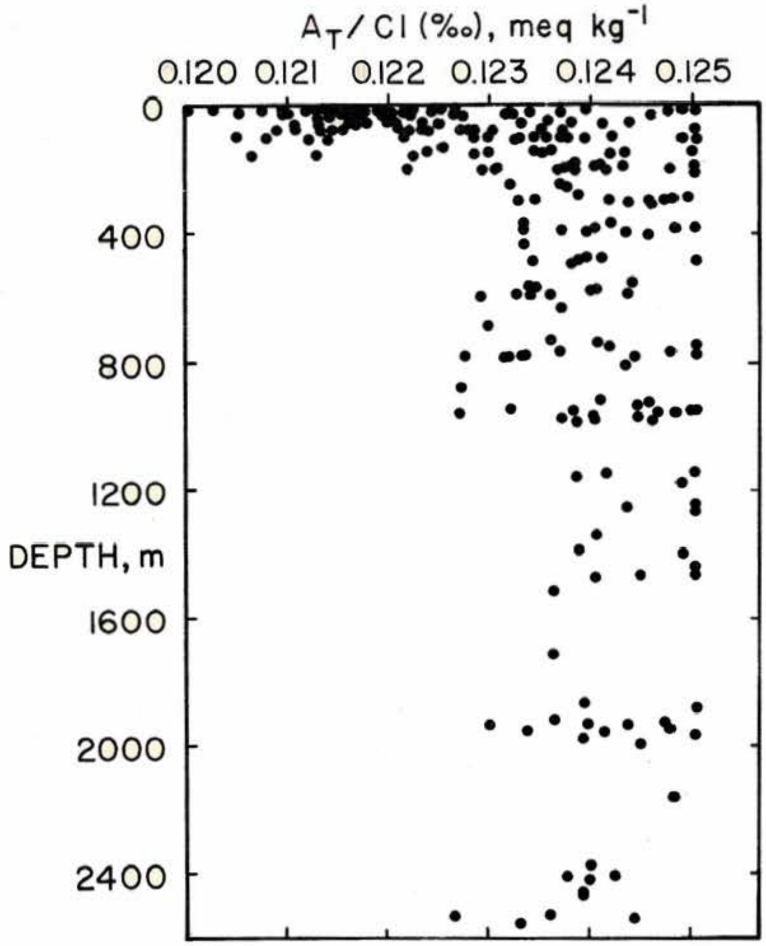

pH
8.00
8.10
8.20
8.30
0
400
800
1200
DEPTH, m
1600
2000
2400
pH25
pH t
pH t,p

Figure 10



A_T / Cl (‰), meq kg^{-1}
0.120 0.121 0.122 0.123 0.124 0.125
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 11

Table II

Tritium Data for Station 11

Depth	t^oC	S^o/oo	TU
1	23.74	36.937	6.23 ± 0.19
10	23.73	36.944	6.39 ± 0.19
20	23.72	36.925	6.37 ± 0.19
30	23.17	36.844	6.05 ± 0.18
49	16.95	36.715	5.28 ± 0.16
74	15.31	36.727	5.32 ± 0.17
98	15.12	37.181	5.99 ± 0.18
197	13.46	38.108	contaminated
494	13.26	38.473	3.37 ± 0.12
985	13.06	38.449	1.04 ± 0.06
1972	13.08	38.394	0.64 ± 0.06
2464	13.10	38.423	0.46 ± 0.06

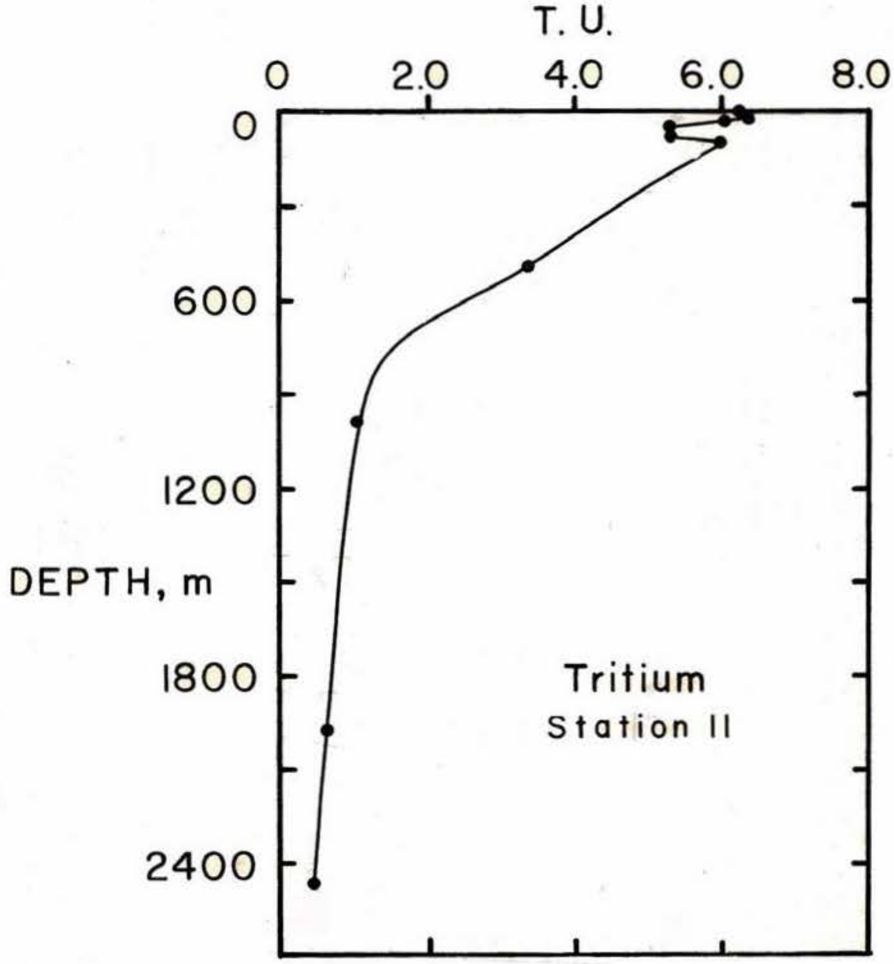


Figure 12

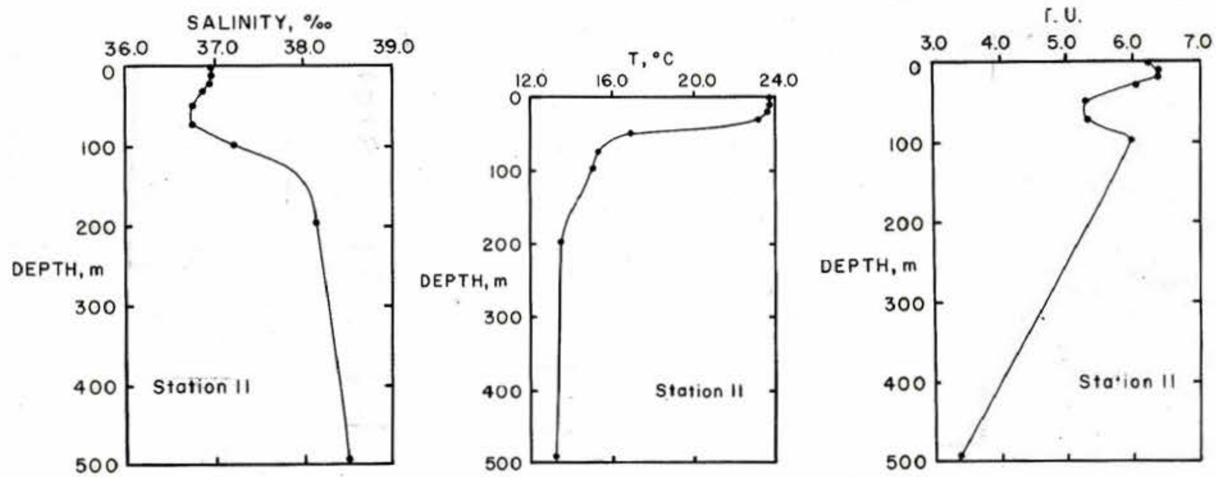

SALINITY, ‰
36.0
37.0
38.0
39.0
0
100
200
DEPTH, m
300
400
500
Station II
T, °C
12.0
16.0
20.0
24.0
0
100
200
DEPTH, m
300
400
500
Station II
T. U.
3.0
4.0
5.0
6.0
7.0
0
100
200
DEPTH, m
300
400
500
Station II

Figure 13

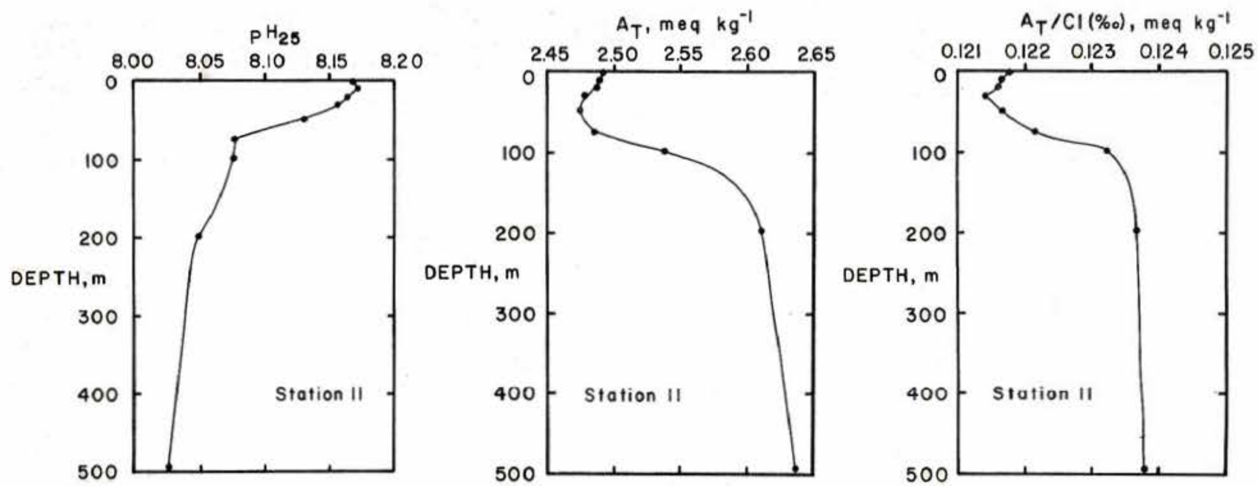

pH25
8.00 8.05 8.10 8.15 8.20
DEPTH, m
0
100
200
300
400
500
Station II
AT, meq kg-1
2.45 2.50 2.55 2.60 2.65
DEPTH, m
0
100
200
300
400
500
Station II
AT/Cl (‰), meq kg-1
0.121 0.122 0.123 0.124 0.125
DEPTH, m
0
100
200
300
400
500
Station II

Figure 14

Table III

CALIBRATIONS OF THE FLOW DENSIMETER ONBOARD SHIP IN THE MEDITERRANEAN

Run	Measured Relative Density	Deviation, 10^6 b
1	26.298	3
2	26.299	2
3	26.293	8
4	26.298	3
5	26.295	6
6	26.300	1
7	26.306	5
8	26.301	0
9	26.303	2
10	26.309	8
11	26.303	2
12	26.297	4
13	26.300	1
14	26.304	3
15	26.300	1
16	26.303	2
17	26.304	3
18	26.303	2
19	26.300	1
20	26.201	0
	ave. 26.301 ± 0.003	

a) Relative density = $d_{SW} - d_{H_2O}$ times 10^3 where the seawater is P_{73} with Cl^o/oo = 19.375.

b) Deviation = measured - calculated densities from the equation of state of Millero, Gonzalez and Ward (1976).

on the ship was set to 25 ± 0.01°C with a Brooklyn thermometer calibrated with a platinium resistance thermometer. The laboratory densimeter was set to 25 ± 0.003°C with a platinium resistance thermometer. The densimeters have been shown (Millero, Lawson and Gonzalez, 1976) to measure the relative density of seawater solutions to an accuracy of $\pm 3 \times 10^{-6}$ g cm^{-3}.

The solutions were pressure filtered before the densities were measured. The salinities were measured on the samples after the densities were measured. Due to a malfunction of the ship-board salinometer, the onboard salinities were found to be unreliable. Thus, although the densities measured onboard the ship showed a precision of $\pm 4 \times 10^{-6}$ g cm^{-3}, it was not possible to compare the results with those calculated from our equation of state (Millero, Gonzalez and Ward, 1976). All the results reported in Appendix II are based on laboratory measurements.

A summary of the excess densities

$$\Delta d(\text{excess}) = d(\text{meas}) - d(\text{calc}) \qquad (6)$$

are given in Table IV and are shown plotted versus depth in Figure 15. The overall average value of Δd(excess) is ±3.9 x 10^{-6} g cm^{-3}; while the standard deviation is 4.8 x 10^{-6} g cm^{-3}. These results indicate the Mediterranean sea waters have the same density as evaporated standard seawater.

We also made density measurements on Mediterranean seawater from 2554m (Station 10) diluted by weight with pure water. These results are given in Table V. The measured densities agree very well with those calculated from the 1 atm equation of state at the weight or conductivity salinity. Thus, although the earlier density measurements of Knudsen et al. (1902) and Cox, McCartney and Culkin (1970) indicated that Mediterranean seawater contained less dissolved solids than evaporated seawater at the same chlorinity, our results indicate that the major constituents of Mediterranean and Atlantic waters are the same.

TABLE IV

SUMMARY OF DENSITY RESULTS FOR THE MEDITERRANEAN SEA

Station	No. Samples	Ave. Dev.	Std. Dev.
1	11	$\pm 3.5 \times 10^{-6}$	4.4×10^{-6}
2	12	4.9	5.6
3	16	4.3	5.2
4	16	4.6	5.6
5	12	3.3	4.4
6	16	4.2	5.3
7	12	3.8	4.6
8	16	3.3	4.1
9	12	3.6	4.1
10	16	4.1	4.9
11	12	3.8	4.9
12	16	3.4	5.1
13	12	4.3	5.3
14	16	3.8	4.6
15	16	4.3	5.5
16	12	4.1	5.1
17	16	4.4	5.3
18	16	3.1	3.9
19	16	2.9	3.6
20	12	5.0	6.1
Overall	283	3.9	4.8

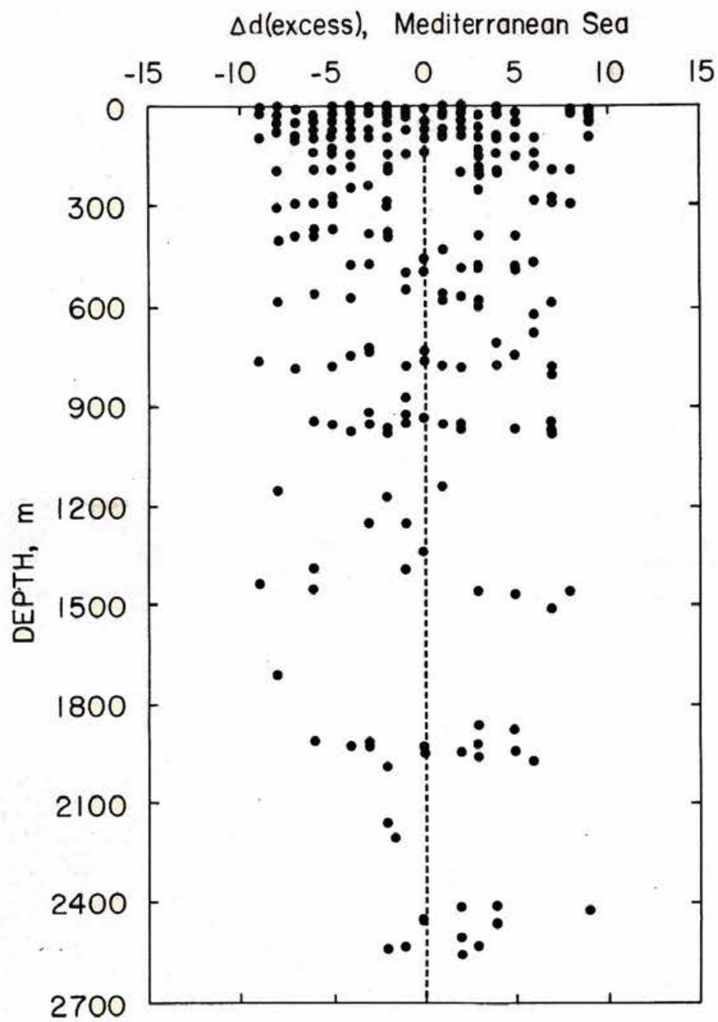

Δd(excess), Mediterranean Sea
-15
-10
-5
0
5
10
15
0
300
600
900
1200
1500
1800
2100
2400
2700
DEPTH, m

Figure 15

TABLE V

COMPARISON OF THE MEASURED AND CALCULATED DENSITIES OF WEIGHT DILUTED MEDITERRANEAN SEAWATERS AT 25°C

Salinity		[d(meas) - d(calc)]	
Wgt[a]	Cond[b]	$10^6\Delta_{wgt}$[c]	$10^6\Delta_{cond}$[d]
38.417	38.417	-2	-3
34.930	34.930	-4	-4
29.644	29.645	1	2
25.159	25.160	0	0
19.946	19.951	-2	2
14.940	14.946	-2	3
10.002	10.004	-1	1
5.161	5.167	-3	-1
		± 2.1	± 2.0

a) weight diluted salinities of Mediterranean sample with S(°/oo) = 38.417.

b) Calculated from conductivity ratio using equation of Millero, Gonzalez, and Ward (1976).

c) Δ_{wgt} = d(meas) - d (calc) using weight salinity.

d) Δ_{cond} = d(meas) - d(calc) using conductivity salinity.

Calculation of Parameters for the Carbonate System

The various components of the carbonate system can be determined from pH and A_T using the equations

$$[HCO_3^-] = A_c \ / \ [1+2K_2'/a_H] \tag{7}$$

$$[CO_3^{2-}] = A_c K_2' / (a_H + 2K_2') \tag{8}$$

$$[CO_2] = (A_c a_H \ / \ K_1') \ / \ (1 + 2K_2' \ / \ a_H) \tag{9}$$

$$\Sigma CO_2 = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \tag{10}$$

$$P_{CO_2} = [CO_2] \ / \tag{11}$$

$$I.P. = [Ca^{2+}] \ [CO_3^{2-}] \tag{12}$$

$$\Omega = I.P. \ / \ K_{sp}' \tag{13}$$

The definitions of the symbols used in these equations are given in Table VI. In this section we will outline the methods used to calculate the various parameters in equations (7) to (13).

The apparent activity of the proton (a_H) was calculated from the in situ $pH_{t,p}$ which were determined from equations (1) to (5). The pressure and temperature corrections are valid to $\pm$ 0.007 for the Mediterranean Sea waters. The activity of the proton is given by

$$a_H = 10^{-pH_{t,p}} \tag{14}$$

The carbonate alkalinity (A_c) is calculated from

$$A_c = A_T - [B(OH)_4^-] \tag{15}$$

where the borate ion is given by

$$[B(OH)_4^-] = K_B' \ [B]_T \ / \ (K_B' + a_H) \tag{16}$$

TABLE VI

Symbols used to Characterize the Carbonate System

Symbol	Definition
A_T	Total alkalinity (meq kg^{-1})
A_C	Carbonate alkalinity (meq kg^{-1})
K_B'	The apparent dissociation constant of boric acid
K_1'	The first apparent dissociation constant for carbonic acid
K_2'	The second apparent dissociation constant for carbonic acid
pH	The negative $\log_{10}$ of the activity of H^+ (relative to the National Bureau of Standards scale)
$a_H = 10^{-pH}$	The apparent activity of the proton
$[HCO_3^-]$	The concentration of bicarbonate ion (mmol kg^{-1})
$[CO_3^{2-}]$	The concentration of carbonate ion (mmol kg^{-1})
$[CO_2]$	The concentration carbon dioxide (CO_2 and H_2CO_3, mmol kg^{-1})
ΣCO_2	The total carbon dioxide (HCO_3^- + CO_3^{2-} + CO_2, mmol kg^{-1})
P_{CO_2}	The partial pressure of carbon dioxide (atm^{-1})
$[Ca^{2+}]$	The concentration of calcium (mmol kg^{-1})
$[B]_T$	Total boron (m mol kg^{-1})
$[B(OH)_4^-]$	The concentration of borate anion (mmol kg^{-1})
S	The salinity in parts per thousand (°/oo)
t	Temperature (C°)
T	Absolute temperature (t°C + 273.15)
P	Applied pressure in bars (equated to depth in meters x 10^{-1})
α	Henry's law coefficient for the solubility of CO_2
ΔV_i	The "apparent" volume change for a given process (cm^3 mol^{-1})
ΔK_i	The "apparent" compressibility change for a given process (cm^3 mol^{-1} bar^{-1})
R	The gas constant (82.0597 cm^3 bar K^{-1} mol^{-1})

The total concentration of boron, $[B]_T$, was determined from (Culkin, 1965)

$$[B]_T = 1.212 \times 10^{-2} S \quad (17)$$

The apparent constant for the ionization of boric acid (K_B') at 1 atm was taken from the equation of Takakashi et al. (1970) which is a fit of Lyman's results (1965)

$$K_B' = 2.121302 \times 10^{-7} - 1.677761 \times 10^{-9} T - 1.67712 \times 10^{-10} S + 2.206332 \times 10^{-12} T^2 + 9.770430 \times 10^{-15} T^3 - 2.10475 \times 10^{-17} T^4 + 6.8943376 \times 10^{-13} ST \quad (18)$$

The effect of pressure on K_B' was determined from

$$\ell n(K_B{}^P/K_B{}^0) = (\Delta V_B/RT)P + (0.5\Delta K_B/RT)P^2 \quad (19)$$

The volume change (ΔV_B) and compressibility change (ΔK_B) for the ionization of boric acid have been determined from the work of Culberson and Pytkowicz (1968). The values of ΔV_B and ΔK_B at various temperatures (t°C) are given by

$$-\Delta V_B = 29.69 - 0.300\ (S-35) - 0.1674t + 1.66 \times 10^{-3} t^2 \quad (20)$$

$$-10^3 \Delta K_B = 3.34 - 0.368\ (S-35) - 9.173 \times 10^{-3} t - 2.16 \times 10^{-3} t^2 \quad (21)$$

As shown elsewhere (Ward and Millero, 1975) the values of $K_B{}^P/K_B{}^0$ determined from the direct measurements of Culberson and Pytkowicz (1968) are in good agreement with partial molal volume and compressibility measurements. The in situ value of K_B' is given by

$$K_B'(\text{insitu}) = [K_B'] \, [\exp(\ell n K_B{}^P/K_B{}^0)] \quad (22)$$

The 1 atm values of the apparent constants for the ionization of carbonic

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 13, (37° 39'N, 002° 59'E)

Depth (m)	Temp (C)	S^{o}/o	A_T (meq kg^{-1})	pH_{25}
1	2 .78	36.718	-----	-----
9	22.69	36.729	-----	-----
18	22.54	36.749	-----	-----
28	22.19	36.730	-----	-----
47	15.82	37.091	-----	-----
71	14.30	37.379	-----	-----
94	13.98	37.863	-----	-----
190	13.10	38.252	-----	-----
478	13.21	38.497	-----	-----
956	13.05	38.446	-----	-----
1927	13.07	38.421	-----	-----
2421	13.11	38.417	-----	-----

acid K_1' and K_2' were taken from the equations of Mehrbach et al (1973)

$$-\log K_1' = -13.7201 + 0.031334\ T + 3235.76\ /\ T + 1.3 \times 10^{-5}\ ST - 0.1032\ S^{1/2} \quad (23)$$

$$-\log K_2' = 5371.9645 + 1.671221\ T + 0.22913\ S - 18.3802 \times \log S - 128375.28\ /\ T - 2194.3055 \log T - 8.0944 \times 10^{-4}\ ST - [5617.11\ (\log S)\ /\ T + 2.136\ S/T] \quad (24)$$

The effect of pressure on the apparent constants was determined from

$$\ell n(K_i^P\ /\ K_i^0) = (\Delta V_i\ /\ RT)P + (0.5\Delta K_i /\ RT)\ P^2 \quad (25)$$

The values of ΔV_i and ΔK_i have been determined from the measurements of Culberson and Pytkowicz (1968). The values of ΔV_i and ΔK_i are given by

$$-\Delta V_1 = 25.02 + 0.1757\ (S-35) + 0.0629t - 8.225 \times 10^{-3}t^2 \quad (26)$$

$$-10^3\Delta K_1 = 2.17 + 0.2865\ (S-35) + 0.2789t - 1.59 \times 10^{-2}t^2 \quad (27)$$

$$-\Delta V_2 = 15.91_5 - 0.327\ (S-35) + 0.0120\ t \quad (28)$$

$$-10^3\Delta K_2 = -0.64 + 0.262\ (S-35) + 0.02098t + 4.355 \times 10^{-3}\ t^2 \quad (29)$$

The insitu values of K_1' and K_2' are given by

$$K_1'(\text{in situ}) = 10^{-pK_1}[\exp(\ell n\ K_1^P/K_1^0) \quad (30)$$

$$K_2'(\text{in situ}) = 10^{-pK_2}[\exp(\ell n\ K_2^P/K_2^0) \quad (31)$$

The values of α, the Henry's law coefficient for the solubility of CO_2 in seawater, have been determined from the equation of Weiss (1974) which is based on the measurements of Murray and Riley (1971).

$$\ell n\ \alpha = -60.2409 + 93.4517(100/T) + 23.3585\ \ell n\ (T/100) + S\ [0.023517 - 0.023656\ (T/100) + 0.0047036\ (T/100)^2] \quad (32)$$

The various parameters for the carbonate system, $[HCO_3^-]$, $[CO_3^{2-}]$, $[CO_2] = [H_2CO_3] + [CO_2]$, ΣCO_2, and PCO_2 for the Mediterranean stations are given in Appendix III. Profiles summarizing all the data is shown as a function of depth in Figures 16 to 20. A summary of the average values of $[HCO_3^-]$, $[CO_3^{2-}]$, $[CO_2]$, ΣCO_2 and PCO_2 for the surface and deep waters are given in Table 1. The ΣCO_2 increases by 0.18 ± 0.08 m mol kg^{-1} from the surface to deep waters, while PCO_2 shows little or no change within the scatter of the data ($\pm$ 30 x 10^{-6} atm). The increase in ΣCO_2 (as well as the other carbonate parameters) with depth is largly due to the increase in the salinity of the water. The small changes in PCO_2 indicate that little biological oxidation occurs in the Mediterranean waters (in contrast to deep Atlantic and Pacific waters). The fast turn over time of the Mediterranean waters causes the deep waters to have nearly equilibrium values of PCO_2. Our results for the various components of the carbonate system are in good agreement with the results of Chernyakova (1976) in the Straits of Sicily and the GEOSECS test station (404) in the Eastern Mediterranean. The values of the ion product (I.P. = $[Ca^{2+}]$ $[CO_3^{2-}]$were calculated from equation (12) where the values of $[Ca^{2+}]$ were determined from

$$[Ca^{2+}] = 0.01027\ (S/35) \qquad (33)$$

The solubility product, K_{sp}', of calcite at 1 atm was calculated from the equation (Ingle, 1975)

$$10^7 K_{sp}'(\text{calcite}) = -34.452 - 39.866\ S^{1/2} + 110.21 \log S - 7.5752 \times 10^{-6} T^2 \qquad (34)$$

The effect of pressure on the solubility of calite was determined from

$$\ell n(K_{sp}^{P}/K_{sp}^{0}) = \frac{\Delta Vc\ P}{RT} + \frac{0.5 \Delta Kc\ P^2}{RT} \qquad (35)$$

where ΔV_c and ΔK_c for the solubility of calcite (Ingle, 1975) are given by

$$\Delta V_c = -35.5 - 0.53\ (25-t) \qquad (36)$$

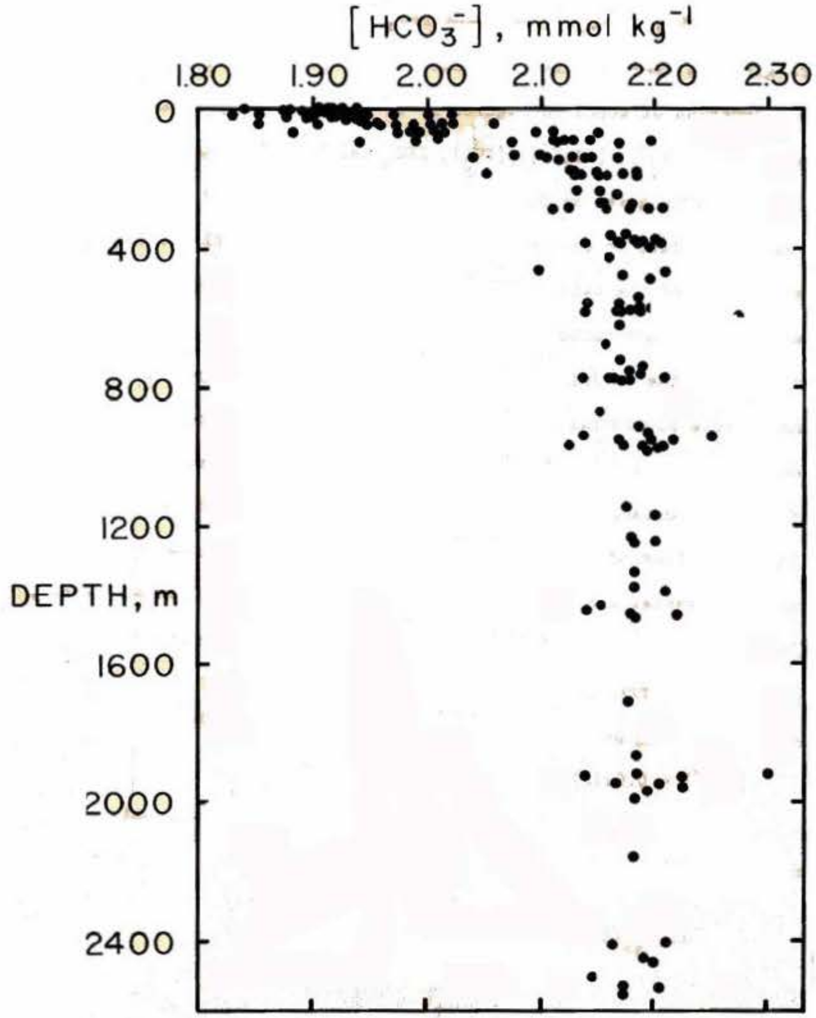
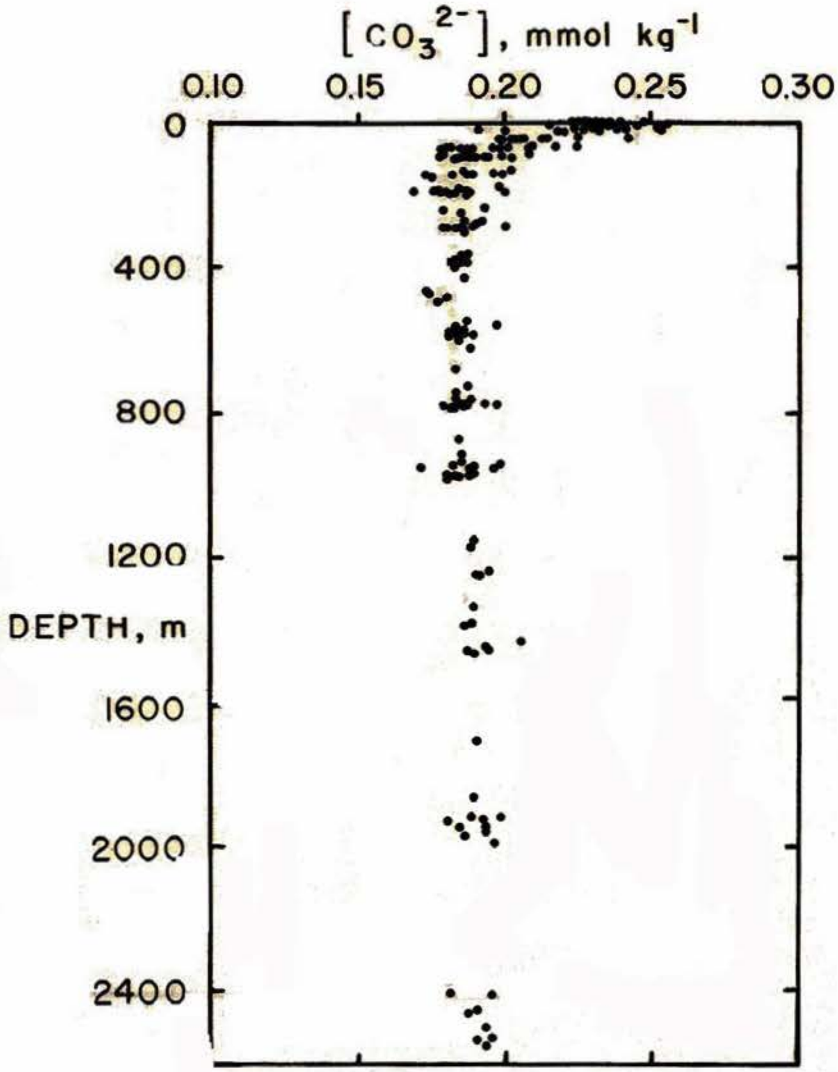

[HCO3-], mmol kg-1
1.80
1.90
2.00
2.10
2.20
2.30
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 16



[CO3 2-], mmol kg-1
0.10
0.15
0.20
0.25
0.30
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 17

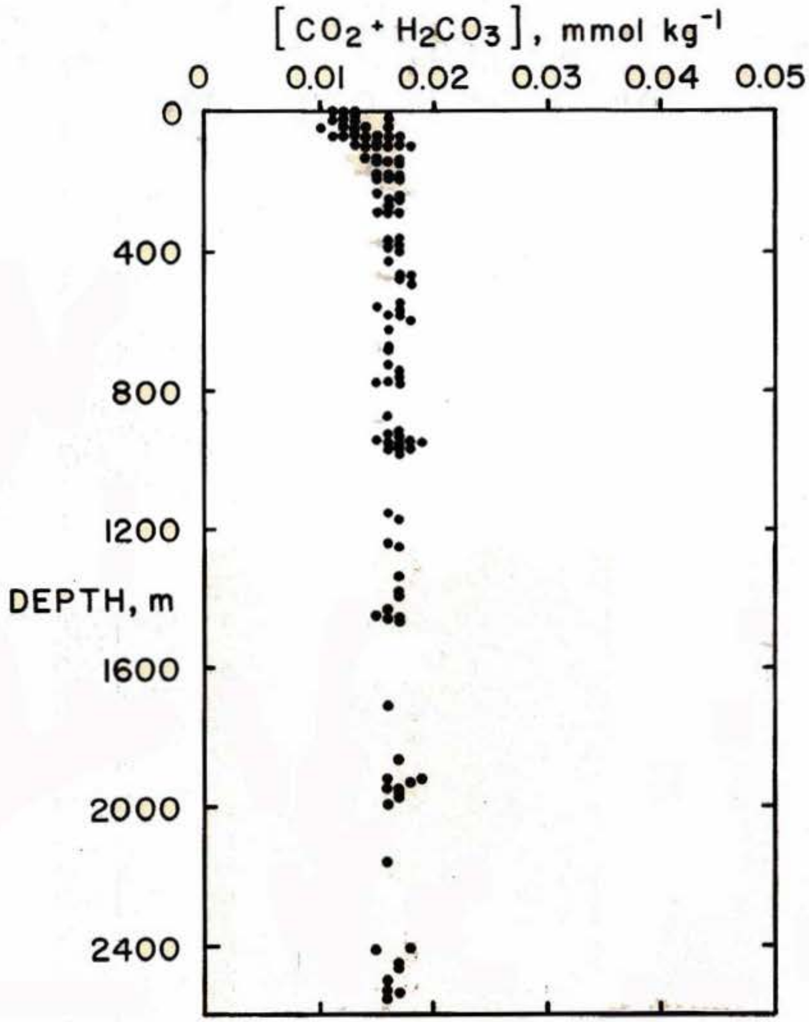
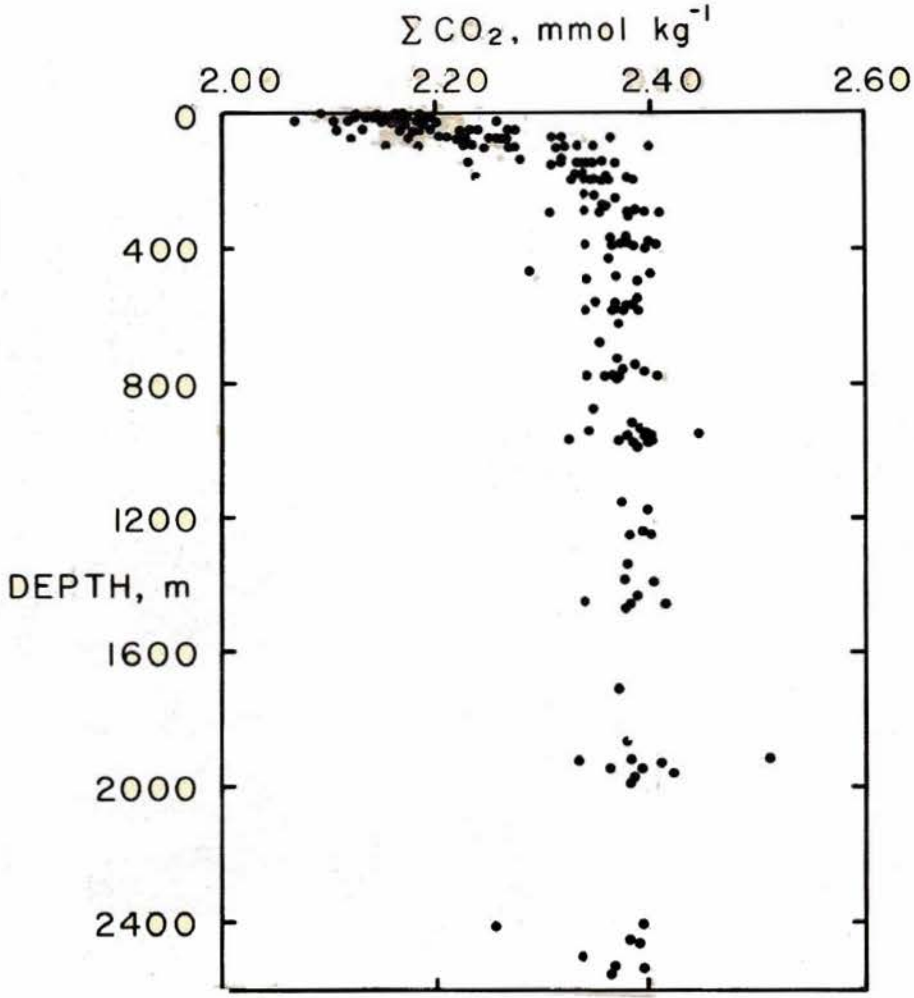
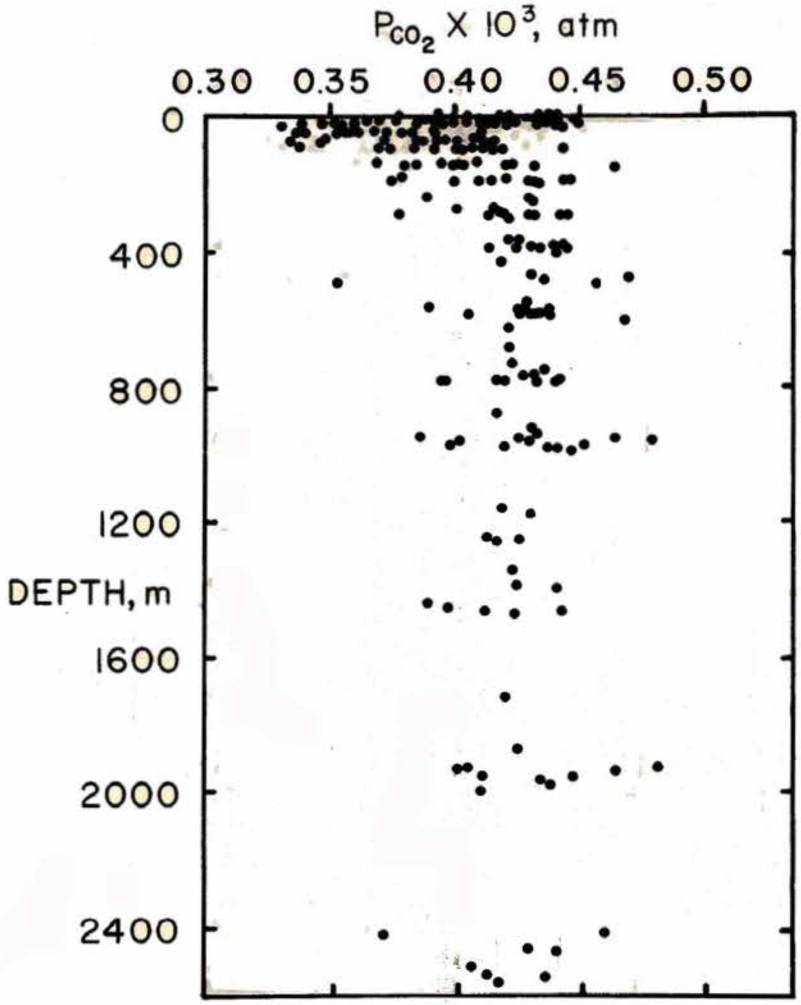

[CO2 + H2CO3], mmol kg-1
0
0.01
0.02
0.03
0.04
0.05
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 18



ΣCO2, mmol kg-1
2.00
2.20
2.40
2.60
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 19



P_{CO_2} X 10^3, atm
0.30
0.35
0.40
0.45
0.50
0
400
800
1200
DEPTH, m
1600
2000
2400

Figure 20

$$10^3 \Delta K_c = 2.529 + 0.369\ (25-t) \qquad (37)$$

As shown elsewhere (Millero, 1977) the values of ΔVc from Ingle (1975) are in reasonable agreement with the values determined from molal volume data. The insitu K_{sp}' for calcite is given by

$$K_{sp}'(\text{insitu}) = K_{sp}'(1\ \text{atm})\ [\exp(\ell n K_{sp}^P / K_{sp}^0)] \qquad (38)$$

The K_{sp}' for the solubility of aragonite at 1 atm has been estimated from the work of Berner (1976)

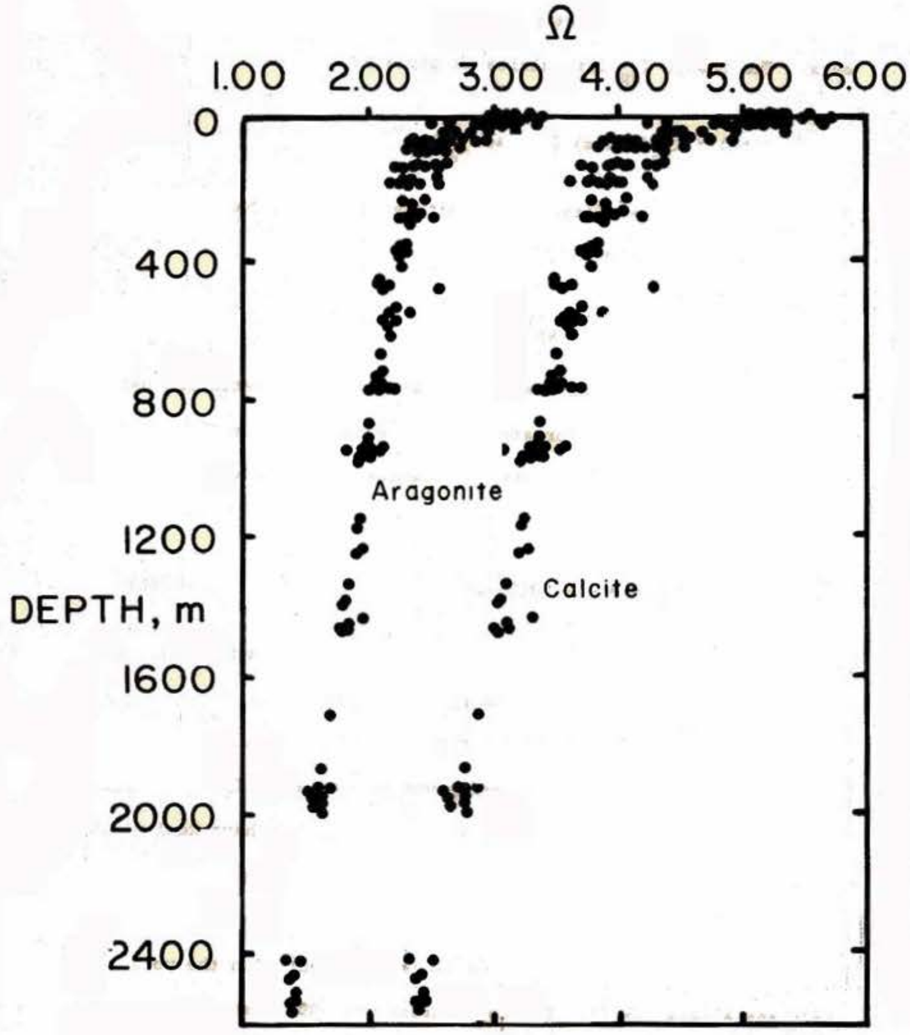
$$K_{sp}'(\text{aragonite})/K_{sp}'(\text{calcite}) = 1.68-[2.5 \times 10^{-3}(25-t)] \qquad (39)$$

The effect of pressure on the K_{sp}' for aragonite was estimated using equation (35). The value of ΔV_a for aragonite was estimated from the calcite data by making an adjustment for the differences in the volumes of the solid phases.

$$\Delta V_a = -38.3 - 0.53(25-t) \qquad (40)$$

The value of ΔK_a was assumed to be equal to ΔK_c (equation 37). The insitu K_{sp}' for aragonite was calculated from equation (38).

The values of Ω, calculated from eq. (13) for calcite and aragonite for the Mediterranean samples are given in Appendix III. A summary of the results are shown in Figure 21. The surface waters have $\Omega cal = 5.0$ and $\Omega arag = 2.8$, while the deep waters have values as low as $\Omega cal = 2.5$ and $\Omega arag = 1.5$. All the Mediterranean waters are supersaturated with respect to calcite and aragonite (which is in agreement with the work of Chernyakova, 1976 and Alekis, 1972). The deep waters are ~50% less saturated than the surface waters. This decrease is largly due to the effect of pressure on the solubility of $CaCO_3$. The deep waters of the Mediterranean are more highly saturated with respect to calcite and aragonite when compared with



Ω
1.00
2.00
3.00
4.00
5.00
6.00
0
400
800
1200
1600
2000
2400
DEPTH, m
Aragonite
Calcite

Figure 21

Atlantic waters (GEOSECS Station 115) at the same depth - see Figures 22 and 23. This is due to the higher values of PCO_2 in deep Atlantic waters (due to more biological oxidation).

The computer program used to calculate the various components for the carbonate system on a Hewlett Packard 9830 computing calculator is given in Appendix IV.

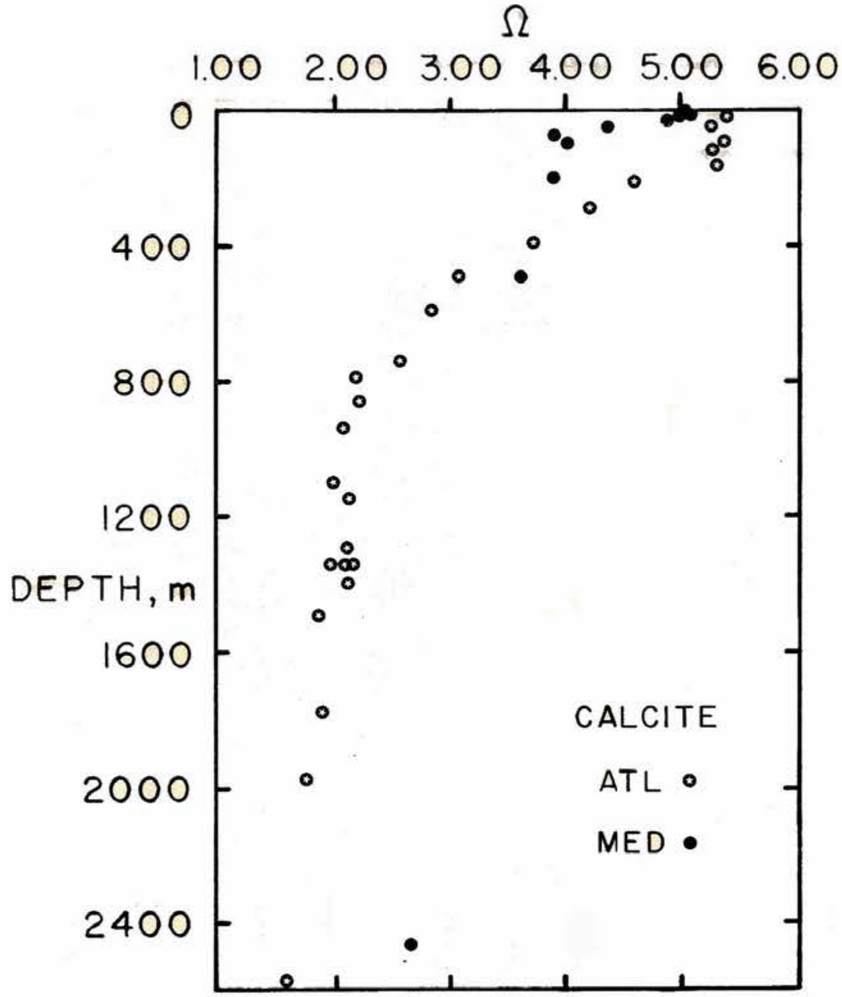

Ω
1.00 2.00 3.00 4.00 5.00 6.00
0
400
800
1200
DEPTH, m
1600
2000
2400
CALCITE
ATL
MED

Figure 22

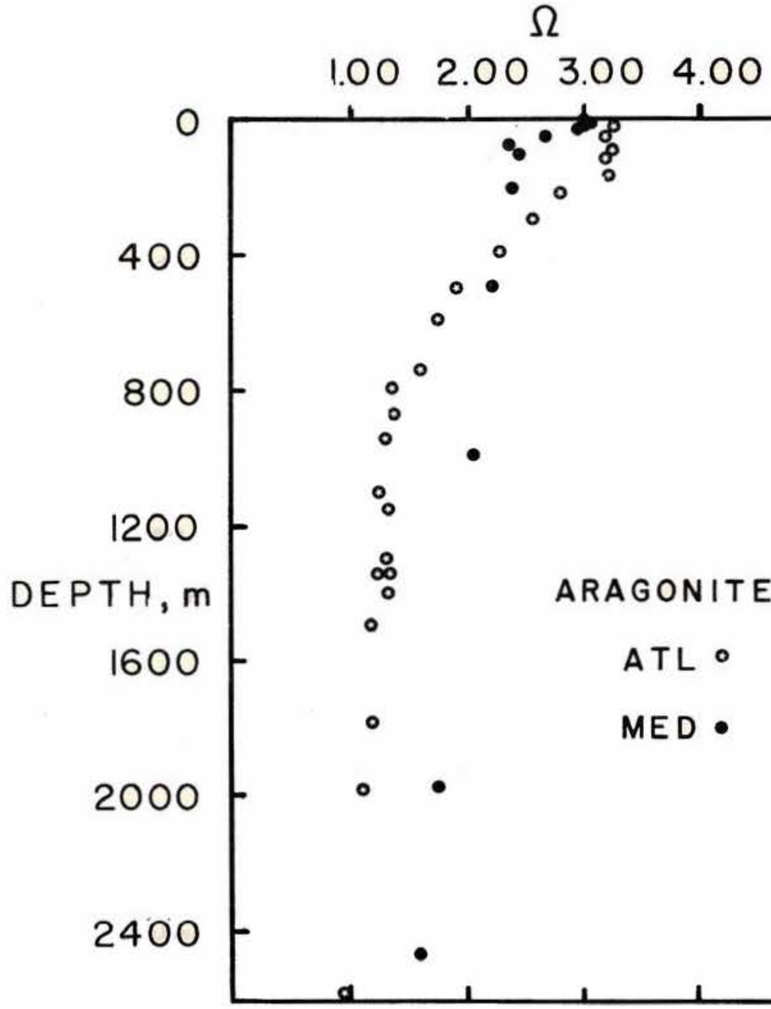

Ω
1.00 2.00 3.00 4.00
0
400
800
1200
DEPTH, m
1600
2000
2400
ARAGONITE
ATL
MED

Figure 23

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APPENDIX I

CARBONATE DATA FOR MEDITERRANEAN STATIONS

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 1 (36° 01.5'N, 04° 52.2'W)

Depth (m)	Temp (C)	S^o/oo	A_T(meq kg^{-1})	pH_{25}
5	-----	36.486	--------	-----
10	23.20	36.524	2.482	8.189
100	17.00	36.317	2.556	8.122
150	-----	36.493	2.469	-----
200	-----	38.184	2.671	-----
300	-----	38.346	2.639	-----
428	13.18	38.448	2.625	8.056
488	-----	38.473	-----	-----
623	13.13	38.471	2.633	8.053
738	13.08	38.458	2.641	-----
778	13.02	38.445	2.648	8.076
805	13.01	38.433	2.645	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 2, (036° 18'N, 003° 59'W)

Depth (m)	Temp (C)	S^{o}/oo	A_T (meq kg^{-1})	pH_{25}
20	23.00	36.546	2.496	8.179
50	21.53	37.682	2.586	-----
100	17.00	38.019	2.628	8.139
125	17.50	38.141	2.587	-----
150	15.00	38.301	2.557	8.035
200	13.60	38.324	2.627	-----
250	13.50	38.400	2.630	8.052
300	13.40	38.461	2.652	-----
400	13.20	38.476	2.653	8.042
500	13.11	38.455	2.685	-----
600	13.12	38.458	2.727	8.027
710	13.30	38.454	2.728	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 3, (036° 26'N, 001° 58'W)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	22.68	36.637	2.468	-----
9	20.84	36.529	2.467	8.189
18	18.70	36.588	2.495	-----
27	17.05	36.427	2.474	8.181
46	15.53	36.586	2.481	-----
71	15.07	36.759	2.517	8.095
93	14.23	37.371	2.569	-----
139	13.48	38.104	2.636	8.087
184	13.06	38.230	2.658	-----
281	13.14	38.381	2.654	8.062
379	13.20	38.460	2.681	-----
560	13.16	38.488	2.629	8.082
745	13.05	38.450	2.669	-----
943	13.04	38.446	2.622	8.081
1142	13.00	38.432	2.667	
1241	12.98	38.429	2.661	8.059

CARBONATE DATA FOR MED[illegible]ANEAN STATIONS

Station 4 (037° 72'N, 000° 05'W)

Depth (m)	Temp (C)	S^{o}/oo	A_T(meq kg^{-1})	pH_{25}
1	23.75	36.885	2.500	-----
18	21.02	36.917	2.395	8.196
46	15.87	37.402	2.532	-----
68	14.35	37.419	2.539	8.166
90	14.09	37.514	2.568	-----
237	13.02	38.208	2.615	8.082
302	13.03	38.254	2.643	8.056
472	13.38	38.477	2.640	-----
490	13.27	38.486	2.646	8.123
720	13.13	38.487	2.579	-----
948	13.02	38.447	2.659	8.050
1140	13.01	38.435	2.641	-----
1338	13.00	38.431	2.639	8.047
1512	13.03	38.424	2.629	-----
1711	13.02	38.431	2.630	8.046
1910	13.08	38.427	2.629	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 5, (37° 52.7'N, 00° 59.5'E)

Depth (m)	Temp (C)	S^{o}/oo	A_T (meq kg^{-1})	pH_{25}
1	23.57	37.039	-----	-----
3	23.55	37.046	-----	-----
9	23.55	37.054	-----	-----
18	18.56	36.610	-----	-----
27	16.18	36.650	-----	-----
70	15.18	36.798	-----	-----
91	15.01	37.252	-----	-----
137	14.09	37.454	-----	-----
182	13.83	37.890	-----	-----
455	13.23	38.464	-----	-----
926	13.04	38.460	-----	-----
1876	13.05	38.442	-----	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 6, (38° 20.0'N, 02° 00.2'E)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	23.60	36.980	2.480	8.167
9	23.57	36.985	2.480	8.175
18	23.53	36.984	2.488	8.176
27	21.50	37.023	2.486	8.159
47	16.48	37.367	2.561	8.122
71	14.50	37.850	2.645	8.089
96	13.60	38.067	2.659	8.049
145	13.26	38.184	2.625	8.049
193	13.06	38.278	2.644	8.048
281	13.30	38.449	2.652	8.042
383	13.16	38.465	2.635	8.040
583	13.08	38.464	2.632	8.042
781	13.01	38.447	2.620	8.032
975	13.01	38.440	2.638	8.036
1173	13.01	38.430	2.656	8.044
1252	12.98	38.430	2.645	8.053

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 7, (38° 31.4'N, 003° 00.1'E)

Depth (m)	Temp (C)	S^{o}/oo	A_T (meq kg^{-1})	pH_{25}
1	24.06	37.252	2.510	8.189
9	24.02	37.274	2.463	8.173
18	24.02	37.276	2.510	8.170
27	23.61	37.286	2.518	8.172
46	16.47	37.340	2.523	8.125
70	14.90	37.600	2.556	8.118
94	14.00	37.841	2.582	8.073
142	13.50	38.160	2.597	8.056
189	13.19	38.278	2.483	8.041
466	13.40	38.481	2.533	8.035
946	13.05	38.446	2.695	8.023
1920	13.04	38.442	2.760	8.013

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 8, (38° 44'N, 3° 59.3'E)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
0	24.00	37.360	2.521	8.205
9	24.23	37.335	2.530	8.219
17	24.06	37.312	2.525	8.214
25	23.93	37.291	2.523	8.218
43	18.96	37.301	2.519	8.172
66	15.73	37.190	2.513	8.149
89	14.44	37.499	2.535	8.144
134	13.55	38.122	2.608	8.109
178	13.07	38.251	2.622	8.094
273	13.07	38.289	2.632	8.074
367	13.18	38.466	2.626	8.054
562	13.06	38.457	2.636	8.046
745	13.02	38.450	2.642	8.040
934	12.98	38.442	2.648	8.042
1392	13.02	38.431	2.657	8.034
1992	13.05	38.426	2.647	8.056

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 9 (38° 27'N, 3° 58'E)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	23.85	37.300	2.513	8.168
9	23.97	37.338	2.515	8.164
19	24.00	37.304	2.520	8.165
29	23.97	37.317	2.519	8.169
48	18.27	37.132	2.514	8.123
73	15.79	37.449	2.545	8.109
98	14.56	37.823	2.591	8.077
187	13.02	38.290	2.629	8.034
472	13.13	38.486	2.643	8.015
952	13.03	38.443	2.635	8.002
1930	13.07	38.434	2.651	8.011
2408	13.10	38.450	2.633	8.010

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 10, (38° 08.4'N, 004° 00.2'E)

Depth (m)	Temp (C)	S°/oo	A_T (meq kg^{-1})	pH_{25}
1	23.32	36.937	2.486	8.175
9	23.25	36.929	2.468	8.179
23	23.25	36.964	2.496	8.180
47	16.43	36.745	2.477	8.149
72	15.10	37.050	2.488	8.098
96	14.37	37.582	2.525	8.105
143	13.67	38.001	2.598	8.094
192	13.33	38.242	2.605	8.048
291	13.30	38.436	2.641	8.050
390	13.44	38.516	2.642	8.042
586	13.20	38.498	2.619	8.038
783	13.10	38.467	2.622	8.040
977	13.03	38.473	2.653	8.036
1468	13.04	38.443	2.639	8.046
1960	13.09	38.441	2.681	8.041
2554	13.13	38.424	2.622	8.044

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 11 (37° 49.9'N, 004° 01.2'E)

Depth (m)	Temp (C)	S°/oo	A_T (meq kg^{-1})	pH_{25}
1	23.74	36.954	2.491	8.168
10	23.73	36.962	2.489	8.172
20	23.72	36.948	2.487	8.163
30	23.17	36.868	2.478	8.157
49	16.95	36.735	2.474	8.130
74	15.31	36.748	2.485	8.075
98	15.12	37.200	2.538	8.076
197	13.46	38.140	2.611	8.048
494	13.25	38.487	2.637	8.026
985	13.06	38.445	2.635	8.029
1972	13.08	38.418	2.635	8.031
2464	13.10	38.440	2.636	8.027

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 12, (37° 31'N, 004° 01'E)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	23.55	36.822	2.480	8.164
9	23.54	36.823	2.474	8.178
22	23.53	36.809	2.480	8.186
45	17.11	36.504	2.465	8.152
67	15.91	36.634	2.464	8.088
88	15.31	36.727	2.484	8.078
136	14.71	37.232	2.543	8.080
182	13.91	37.741	2.592	8.064
272	13.23	38.254	2.622	8.061
364	13.28	38.431	2.641	8.054
547	13.22	38.502	2.651	8.051
728	13.12	38.470	2.631	8.051
918	13.02	38.461	2.641	8.043
1385	13.01	38.428	2.635	8.044
1866	13.07	38.42[illegible]	2.635	8.042
2454	13.11	38.41[illegible]	2.635	8.036

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 13, (37° 39'N, 002° 59'E)

Depth (m)	Temp (C)	S^o/o	A_T(meq kg^{-1})	pH_{25}
1	2 .78	36.718	-----	-----
9	22.69	36.729	-----	-----
18	22.54	36.749	-----	-----
28	22.19	36.730	-----	-----
47	15.82	37.091	-----	-----
71	14.30	37.379	-----	-----
94	13.98	37.863	-----	-----
190	13.10	38.252	-----	-----
478	13.21	38.497	-----	-----
956	13.05	38.446	-----	-----
1927	13.07	38.421	-----	-----
2421	13.11	38.417	-----	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 14, (37° 42'N, 001° 58'E)

Depth (m)	Temp (C)	S^o/oo	A_T (meq kg^{-1})	pH_{25}
1	23.51	36.874	2.436	8.210
9	23.35	36.873	2.486	8.216
23	19.72	36.800	2.498	8.194
47	14.76	37.067	2.530	8.130
71	14.30	37.611	2.561	8.136
95	13.74	37.954	2.599	8.089
144	13.26	38.192	2.628	8.097
193	13.01	38.273	2.630	8.098
288	13.24	38.420	2.625	8.096
387	13.35	38.501	2.605	8.060
584	13.16	38.489	2.607	8.064
776	13.07	38.460	2.613	8.073
968	13.01	38.445	2.589	8.064
1450	13.01	38.424	2.606	8.065
1926	13.00	38.432	2.595	8.057
2502	13.12	38.417	2.596	8.051

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 15, (37° 13.0'N, 001° 59.1'E)

Depth (m)	Temp (C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	23.63	37.004	2.494	8.183
9	23.48	36.984	2.484	8.186
23	23.29	36.985	2.596	8.178
47	15.01	37.471	2.580	8.143
71	14.05	37.873	2.590	8.098
95	13.52	38.127	2.616	8.069
144	13.17	38.269	2.616	8.071
193	13.12	38.364	2.628	8.061
289	13.29	38.522	2.669	8.043
386	13.27	38.500	2.664	8.041
582	13.10	38.478	2.649	8.048
775	13.07	38.458	2.663	8.038
970	13.00	38.452	2.649	8.026
1460	13.02	38.425	2.669	8.034
1949	13.08	38.424	2.640	8.024
2536	13.13	38.422	2.647	8.032

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 16, (36° 48.2'N, 001° 00.2'E)

Depth (m)	Temp(C)	S°/oo	A_T(meq kg^{-1})	pH_{25}
1	22.22	36.646	-----	-----
9	22.18	36.634	-----	-----
18	19.31	36.478	-----	-----
27	17.02	36.469	-----	-----
47	15.67	36.518	-----	-----
71	14.97	36.805	-----	-----
95	14.68	37.057	-----	-----
192	13.17	38.213	-----	-----
483	13.24	38.489	-----	-----
968	13.03	38.444	-----	-----
1944	13.07	38.427	-----	-----
2533	13.11	38.418	-----	-----

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 17, (36° 5.2'N, 000° 00.5'W)

Depth (m)	Temp (C)	S°/oo	A_T (meq kg^{-1})	pH_{25}
1	22.00	36.817	2.471	8.182
9	18.68	36.825	2.471	8.166
23	15.14	36.992	2.477	8.138
47	14.37	37.758	2.560	8.110
71	13.71	38.062	2.587	8.078
95	13.32	38.168	2.598	8.068
144	13.04	38.238	2.600	8.071
193	13.03	38.309	2.608	8.071
291	13.22	38.438	2.564	8.053
387	13.34	38.523	2.637	8.055
583	13.14	38.493	2.626	8.049
777	13.06	38.457	2.626	8.052
972	13.00	38.451	2.633	8.051
1459	13.03	38.438	2.648	8.058
1946	13.08	38.444	2.625	8.053
2530	13.12	38.419	2.628	8.050

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 18 (36° 24'N, 000° 00')

Depth (m)	Temp (C)	S^o/oo	A_T(meq kg^{-1})	pH_{25}
1	22.57	36.677	2.535	8.188
9	21.58	36.633	2.530	8.191
23	17.74	36.658	2.528	8.189
46	15.20	36.893	2.523	8.132
70	14.38	37.612	2.516	8.070
94	13.79	38.056	2.538	8.078
142	13.13	38.216	2.611	8.072
190	12.99?	38.324	2.626	8.064
285	13.14	38.423	2.654	8.060
392	13.29	38.467	2.640	8.050
573	13.13	38.477	2.640	8.051
764	13.05	38.471	2.657	8.049
955	12.99	38.442	2.652	8.070
1435	13.03	38.427	2.670	8.082
1921	13.07	38.421	2.652	8.062
2413	13.11	38.424	2.523	8.073

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 19, (35° 44.8'N, 002° 00.2'W)

Depth (m)	Temp (C)	S^{o}/oo	A_T(meq kg^{-1})	pH_{25}
1	23.27	36.674	2.455	8.190
9	23.14	36.655	2.453	8.193
23	22.78	36.643	2.444	8.186
47	17.61	36.447	2.442	8.177
71	16.24	36.414	2.440	8.102
95	15.47	36.501	2.440	8.085
144	14.67	36.908	2.477	8.060
193	13.63	37.904	2.579	8.048
242	13.18	38.158	2.602	8.046
290	13.05	38.205	2.607	8.044
386	13.18	38.384	2.620	8.043
482	13.07	38.387	2.622	8.040
581	12.99	38.384	2.621	8.041
679	12.99	38.351	2.610	8.048
777	12.97	38.361	2.618	8.052
875	12.90	38.349	2.605	8.049

CARBONATE DATA FOR MEDITERRANEAN STATIONS

Station 20 (35° 41.9'N 004° 00.5'W)

Depth (m)	Temp (C)	S^o/oo	A_T (meq kg^{-1})	pH_{25}
9	23.28	36.632	2.457	8.196
23	22.37	36.554	2.447	8.215
47	21.53	36.517	2.457	8.226
70	18.97	36.411	2.447	8.199
94	17.18	36.379	2.440	8.138
189	13.67	37.835	2.590	8.040
378	13.20	38.456	2.658	8.041
569	13.12	38.474	2.640	8.040
761	13.06	38.460	2.631	8.042
955	13.02	38.445	2.656	8.046
1152	12.99	38.435	2.635	8.051
1250	12.99	38.443	2.662	8.048

APPENDIX II

DENSITY DATA FOR MEDITERRANEAN STATIONS

STATION 1

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
10	36.524	27.456	27.454	2
100	36.317	27.301	27.297	4
150	36.498	27.434	27.437	3
200	38.189	28.720	28.716	4
300	38.346	28.833	28.835	-2
428	38.461	28.923	28.922	1
488	38.473	28.934	28.931	3
623	38.471	28.936	28.930	6
738	38.462	28.923	28.923	0
778	38.445	28.917	28.910	7
805	38.433	28.908	28.901	7

STATION 2

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
20	36.550	27.470	27.474	-4
50	37.682	28.324	28.332	-8
100	38.019	28.580	28.587	-7
125	38.140	28.674	28.679	-5
150	38.301	28.806	28.801	5
200	38.328	28.824	28.821	3
250	38.400	28.879	28.876	3
300	38.461	28.914	28.922	-8
400	38.476	28.926	28.934	-8
500	38.452	28.915	28.916	-1
600	38.458	28.923	28.920	3
710	38.454	28.921	28.917	4

STATION 3

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.637	27.533	27.539	-6
9	36.537	27.462	27.463	-1
18	36.588	27.506	27.502	4
27	36.427	27.381	27.380	1
46	36.586	27.496	27.501	-5
71	36.759	27.633	27.632	1
93	37.371	28.087	28.096	-9
139	38.104	28.652	28.652	0
184	38.233	28.752	28.749	3
281	38.381	28.868	28.862	6
379	38.460	28.916	28.922	-6
560	38.488	28.937	28.943	-6
745	38.453	28.921	28.916	5
943	38.450	28.908	28.914	-6
1142	38.433	28.902	28.901	1
1241	38.431	28.908	28.900	8

STATION 4

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.886	27.720	27.728	-8
18	36.919	27.761	27.753	8
46	37.407	28.132	28.123	9
68	37.421	28.128	28.134	-6
90	37.517	28.208	28.206	2
237	38.209	28.728	28.731	-3
302	38.266	28.772	28.774	-2
472	38.479	28.932	28.936	-4
490	38.486	28.946	28.941	5
720	38.515	28.960	28.963	-3
948	38.448	28.911	28.912	-1
1140	38.437	28.905	28.904	1
1338	38.432	28.900	28.900	0
1512	38.424	28.901	28.894	7
1711	38.442	28.900	28.908	-8
1910	38.429	28.892	28.898	-6

STATION 5

		$(d - d^{o})10^{3}$		
Depth(m)	S‰	Measured	Calculated	$(\Delta d)10^{6}_{excess}$
1	37.040	27.845	27.845	0
3	37.046	27.853	27.849	4
9	37.055	27.856	27.856	0
18	36.612	27.530	27.521	9
27	36.659	27.559	27.556	3
70	36.798	27.657	27.661	-4
91	37.254	28.008	28.004	4
137	37.457	28.155	28.161	-6
182	37.891	28.486	28.490	-4
455	38.465	28.925	28.925	0
926	38.462	28.922	28.923	-1
1876	38.442	28.914	28.909	5

STATION 6

Depth(m)	S°/oo	$(d - d^{\wedge})10^3$ Measured	Calculated	$(\Delta d)10^6$ excess
1	36.981	27.809	27.800	9
9	36.986	27.812	27.804	8
18	36.986	27.802	27.804	-2
27	36.944	27.766	27.772	-6
47	37.374	28.092	28.098	-6
71	37.862	28.467	28.468	-1
96	38.071	28.627	28.627	0
145	38.190	28.715	28.717	-2
193	38.287	28.798	28.790	8
291	38.467	28.920	28.927	-7
383	38.482	28.932	28.938	-6
583	38.483	28.942	28.939	3
781	38.448	28.914	28.912	2
975	38.434	28.898	28.902	-4
1173	38.429	28.896	28.898	-2
1252	38.433	28.900	28.901	-1

STATION 7

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	37.252	28.004	28.006	-2
9	37.274	28.022	28.022	0
18	37.276	28.022	28.024	-2
27	37.286	28.035	28.031	4
46	37.340	28.077	28.072	5
70	37.603	28.274	28.272	2
94	37.841	28.450	28.452	-2
142	38.160	28.698	28.694	4
189	38.278	28.792	28.784	8
466	38.529	28.980	28.974	6
946	38.446	28.918	28.911	7
1920	38.422	28.890	28.893	-3

STATION 8

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
0	37.360	28.084	28.087	-3
9	37.343	28.073	28.075	-2
17	37.312	28.049	28.051	-2
25	37.291	28.040	28.035	-5
43	37.301	28.043	28.043	0
66	37.223	27.987	27.984	3
89	37.499	28.186	28.193	-7
134	38.122	28.668	28.665	3
178	38.254	28.771	28.765	6
273	38.402	28.885	28.878	7
367	38.466	28.920	28.926	-6
562	38.464	28.926	28.925	1
745	38.450	28.910	28.914	-4
934	38.475	28.933	28.933	0
392	38.438	28.904	28.905	-1
1992	38.442	28.906	28.908	-2

STATION 9

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	37.303	28.042	28.044	-2
9	37.345	28.078	28.076	2
19	37.306	28.041	28.046	-5
29	37.320	28.055	28.057	-2
48	37.137	27.920	27.918	2
73	37.452	28.149	28.157	-8
98	37.829	28.447	28.443	4
187	38.294	28.791	28.796	-5
472	38.495	28.945	28.948	-3
952	38.451	28.912	28.915	-3
1930	38.520	28.964	28.967	-3
2408	38.450	28.918	28.914	4

STATION 10

Depth(m)	S^{o}/oo	$(d - d^{o})10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.937	27.764	27.767	-3
9	36.929	27.763	27.761	2
23	36.964	27.792	27.787	5
47	36.748	27.624	27.624	0
72	37.050	27.844	27.852	-8
96	37.582	28.261	28.256	5
143	38.015	28.582	28.584	-2
192	38.242	28.760	28.756	4
291	38.436	28.911	28.903	8
390	38.516	28.962	28.964	-2
586	38.498	28.958	28.951	7
783	38.467	29.920	28.927	-7
977	38.479	28.934	28.936	-2
1468	38.457	28.924	28.919	5
1960	38.457	28.922	28.919	3
2554	38.412	28.887	28.885	2

STATION 11

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.956	27.782	27.781	1
10	36.964	27.796	27.787	9
20	36.949	27.772	27.776	-4
30	36.869	27.714	27.715	-1
49	36.736	27.619	27.614	5
74	36.755	27.628	27.629	-1
98	37.212	27.981	27.975	6
197	38.142	28.682	28.680	2
494	38.500	28.952	28.944	0
985	38.448	28.919	28.912	7
1972	38.423	28.900	28.894	6
2464	38.449	28.917	28.913	4

STATION 12

Depth(m)	S^{o}/oo	$(d - d^{o})10^{3}$ Measured	Calculated	$(\Delta d)10^{6}_{excess}$
1	36.826	27.678	27.683	-5
9	36.825	27.681	27.682	-1
22	36.808	27.660	27.669	-9
45	36.506	27.434	27.440	-6
67	36.634	27.532	27.537	-5
88	36.739	27.618	27.617	1
136	37.232	27.990	27.990	0
182	37.741	28.374	28.376	-2
272	38.254	28.760	28.765	-5
364	38.431	28.895	28.900	-5
547	38.502	28.952	28.953	-1
728	38.470	28.926	28.929	-3
918	38.461	28.919	28.922	-3
1385	38.428	28.891	28.897	-6
1866	38.423	28.897	28.894	3
2454	38.418	28.890	28.890	0

STATION 13

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	$(d - d^o)10^3$ Calculated	$(\Delta d)10^6_{excess}$
1	36.723	27.606	27.605	1
9	36.730	27.610	27.610	0
18	36.770	27.637	27.640	-3
28	36.675	27.560	27.568	-8
47	37.088	27.874	27.881	-7
71	37.379	28.101	28.102	-1
94	37.864	28.467	28.470	-3
190	38.252	28.770	28.763	7
478	38.490	28.947	28.944	3
956	38.462	28.918	28.923	-5
1927	38.429	28.894	28.898	-4
2421	38.420	28.900	28.891	9

STATION 14

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.875	27.721	27.720	1
9	36.882	27.729	27.725	4
23	36.807	27.666	27.668	-2
47	37.068	27.864	27.866	-2
71	37.610	28.279	28.277	2
95	37.954	28.534	28.538	-4
144	38.191	28.714	28.718	-4
193	38.275	28.782	28.790	-8
288	38.420	28.886	28.891	-5
387	38.503	28.948	28.954	-6
584	38.490	28.932	28.944	-8
776	38.460	28.917	28.922	-5
968	38.448	28.910	28.912	-2
1450	38.426	28.890	28.896	-6
1926	38.438	28.905	28.905	0
2502	38.416	28.890	28.888	2

STATION 15

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	37.007	27.816	27.820	-4
9	36.992	27.801	27.808	-7
23	36.988	27.796	27.805	-9
47	37.476	28.173	28.175	-2
71	37.884	28.484	28.485	-1
95	38.136	28.676	28.676	0
144	38.276	28.777	28.782	-5
193	38.374	28.863	28.856	7
289	38.663	29.070	29.076	-6
386	38.711	29.105	29.112	7
582	38.484	28.932	28.940	-8
775	38.462	28.924	28.923	1
970	38.462	28.925	28.923	2
1460	38.440	28.914	28.906	8
1949	38.437	28.904	28.904	0
2536	38.452	28.914	28.916	-2

STATION 16

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6$ excess
1	36.666	27.556	27.561	-5
9	36.636	27.548	27.539	9
18	36.489	27.423	27.427	-4
27	36.471	27.423	27.414	9
47	36.540	27.464	27.466	-2
71	36.816	27.674	27.675	-1
95	37.240	27.999	27.996	3
192	38.236	28.756	28.752	3
483	38.508	28.960	28.958	2
968	38.460	28.926	28.921	5
1944	38.460	28.926	28.921	5
2533	38.444	28.908	28.909	-1

STATION 17

Depth (m)	S°/oo	$(d - d^o)10^3$ Measured	$(d - d^o)10^3$ Calculated	$(\Delta d)10^6$ excess
1	36.817	27.668	27.676	-8
9	36.825	27.673	27.682	-9
23	36.992	27.810	27.808	2
47	37.758	28.384	28.389	-5
71	38.062	28.616	28.620	-4
95	38.168	28.694	28.700	-6
144	38.238	28.752	28.753	-1
193	38.309	28.805	28.807	-2
291	38.438	28.900	28.905	-5
387	38.523	28.974	28.969	5
583	38.493	28.939	28.947	-8
777	38.457	28.918	28.919	-1
972	38.451	28.922	28.915	7
1459	38.438	28.908	28.905	3
1946	38.455	28.920	28.918	2
2530	38.424	28.897	28.894	3

STATION 18

Depth (m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6$ excess
1	36.678	27.574	27.571	3
9	36.633	27.533	27.536	-3
23	36.658	27.556	27.555	1
46	36.893	27.735	27.733	2
70	37.612	28.278	28.278	0
94	38.056	28.620	28.615	5
142	38.216	28.742	28.736	6
190	38.324	28.813	28.818	-5
285	38.423	28.892	28.894	-2
382	38.467	28.924	28.927	-3
573	38.477	28.930	28.934	-4
764	38.471	28.930	28.930	0
955	38.442	28.909	28.908	1
1435	38.427	28.888	28.897	-9
1921	38.433	28.904	28.901	3
2413	38.495	28.946	28.948	2

STATION 19

Depth(m)	S^o/oo	$(d - d^{\sim})10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
1	36.675	27.570	27.568	2
9	36.655	27.552	27.553	-1
23	36.643	27.542	27.544	-2
47	36.450	27.394	27.398	-4
71	36.417	27.376	27.373	-3
95	36.502	27.438	27.437	1
144	36.908	27.744	27.745	-1
193	37.928	28.516	28.518	-2
242	38.179	28.704	28.708	-4
290	38.230	28.754	28.747	7
386	38.394	28.882	28.879	3
482	38.395	28.877	28.872	5
581	38.404	28.880	28.879	1
679	38.351	28.845	28.839	6
777	38.361	28.850	28.846	4
875	38.349	28.836	28.837	-1

STATION 20

Depth(m)	S^o/oo	$(d - d^o)10^3$ Measured	Calculated	$(\Delta d)10^6_{excess}$
	36.632	27.532	27.536	-4
23	36.555	27.476	27.477	-1
47	36.520	27.460	27.451	9
70	36.412	27.364	27.369	-5
94	36.379	27.353	27.344	9
189	37.837	28.443	28.449	-6
378	38.467	28.925	28.927	-2
569	38.476	28.936	28.934	2
761	38.466	28.917	28.926	-9
955	38.445	28.912	28.910	2
1152	38.440	28.898	28.906	-8
1250	38.446	28.908	28.911	-3

APPENDIX III

PARAMETERS FOR THE CARBONATE SYSTEM

IN

THE MEDITERRANEAN SEA

STATION 1

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
10	5.17	3.08	1.909	0.233	0.012	402	2.154
100	4.42	2.66	2.052	0.204	0.014	395	2.269
428	3.80	2.29	2.164	0.183	0.016	417	2.364
623	3.65	2.19	2.175	0.182	0.016	419	2.373
778	3.71	2.23	2.168	0.191	0.015	393	2.374

STATION 2

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
20	5.10	3.04	1.930	0.230	0.012	413	2.172
100	4.86	2.93	2.080	0.221	0.013	385	2.314
150	3.80	2.29	2.119	0.174	0.017	463	2.311
250	3.92	2.37	2.171	0.183	0.017	429	2.371
400	3.76	2.27	2.200	0.181	0.017	439	2.398
600	3.61	2.17	2.279	0.180	0.018	467	2.476

STATION 3

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
9	5.06	3.03	1.902	0.228	0.011	366	2.142
27	4.84	2.92	1.926	0.220	0.011	324	2.157
71	4.13	2.49	2.045	0.189	0.014	389	2.248
139	4.27	2.58	2.146	0.196	0.015	391	2.357
281	4.00	2.41	2.184	0.188	0.016	415	2.388
560	3.90	2.35	2.145	0.193	0.015	387	2.352
943	3.59	2.15	2.142	0.190	0.015	382	2.347
1241	3.29	1.97	2.197	0.184	0.016	409	2.397

STATION 4

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
18	5.00	2.99	1.833	0.226	0.011	349	2.069
68	4.80	2.90	1.992	0.219	0.012	312	2.222
237	4.11	2.48	2.134	0.192		386	2.341
302	3.90	2.36	2.181	0.185	0.016	419	2.382
490	4.31	2.60	2.119	0.210	0.014	349	2.343
948	3.43	2.05	2.202	0.182	0.016	422	2.400
1338	3.13	1.87	2.189	0.178	0.016	419	2.383
1711	2.89	1.71	2.184	0.176	0.016	416	2.376

STATION 6

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
1	5.04	3.00	1.923	0.226	0.013	432	2.162
9	5.10	3.04	1.915	0.229	0.012	422	2.157
18	5.12	3.05	1.921	0.230	0.012	422	2.163
27	4.89	2.92	1.940	0.221	0.013	410	2.174
47	4.55	2.74	2.048	0.206	0.014	387	2.268
71	4.37	2.64	2.151	0.199	0.015	406	2.365
96	4.04	2.44	2.200	0.184	0.017	441	2.401
145	3.94	2.39	2.171	0.181	0.017	429	2.369
193	3.93	2.38	2.188	0.182	0.017	430	2.387
291	3.84	2.32	2.199	0.181	0.017	441	2.397
383	3.73		2.187	0.179	0.017	437	2.382
583	3.59	2.16			0.017	431	2.379
781	3.37	2.02	2.183	0.173	0.017	439	2.373
975	3.29	1.97	2.196	0.175	0.017	435	2.388
1173	3.24	1.93	2.205	0.179	0.017	427	2.401
1252	3.23	1.93	2.188	0.181	0.016	414	2.385

STATION 7

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.35	3.19	1.921	0.240	0.012	417	2.172
9	5.10	3.04	1.899	0.228	0.012	427	2.140
18	5.16	3.08	1.940	0.232	0.013	439	2.184
27	5.18	3.09	1.945	0.233	0.013	432	2.190
46	4.50	2.71	2.013	0.204	0.013	378	2.231
70	4.45	2.69	2.050	0.203	0.014	368	2.266
94	4.10	2.48	2.114	0.187	0.015	407	2.316
142	3.96	2.40	2.141	0.182	0.016	420	2.339
189	3.64	2.20	2.056	0.169	0.016	413	2.240
466	3.50	2.11	2.103	0.170	0.017	429	2.289
946	3.30	1.98	2.256	0.175	0.018	462	2.449
1920	2.73	1.61	2.326	0.172	0.019	478	2.517

STATION 8

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
0	5.55	3.31	1.911	0.248	0.011	399	2.171
9	5.70	3.40	1.903	0.255	0.011	388	2.170
17	5.62	3.35	1.905	0.252	0.011	390	2.169
25	5.64	3.36	1.900	0.253	0.011	384	2.165
43	4.99	3.00	1.958	0.226	0.012	364	2.196
66	4.63	2.79	1.986	0.211	0.012	342	2.209
89	4.59	2.77	2.009	0.210	0.013	333	2.232
134	4.41	2.67	2.101	0.203	0.014	365	2.318
178	4.27	2.58	2.128	0.197	0.015	375	2.340
273	4.05	2.45	2.155	0.190	0.016	397	2.361
367	3.84	2.31	2.167	0.183	0.016	420	2.366
562	3.63	2.18	2.175	0.179	0.017	426	2.371
745	3.48	2.09	2.195	0.178	0.017	433	2.390
934	3.37	2.02	2.199	0.178	0.017	430	2.394
1392	3.04	1.81	2.216	0.175	0.017	437	2.408
1992		1.66	2.191	0.180	0.016	406	2.386

STATION 9

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.16	3.08	1.944	0.231	0.013	440	2.188
9	5.13	3.06	1.949	0.230	0.013	447	2.192
19	5.14	3.06	1.953	0.231	0.013	447	2.196
29	5.17	3.08	1.948	0.232	0.013	441	2.193
48	4.51	2.71	2.005	0.205	0.014	406	2.224
73	4.37	2.64	2.048	0.199	0.014	388	2.261
98	4.16	2.51	2.116	0.190	0.015	412	2.322
187	3.81	2.30	2.188	0.176	0.017	443	2.381
472	3.50	2.11	2.215	0.170	0.018	469	2.404
952	3.09	1.85	2.222	0.164	0.019	478	2.404
1930	2.60	1.54	2.232	0.165	0.018	461	2.415
2408	2.34	1.38	2.219	0.162	0.018	456	2.399

STATION 10

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
1	5.11	3.05	1.921	0.229	0.012	419	2.163
9	5.10	3.04	1.903	0.229	0.012	410	2.144
23	5.16	3.08	1.924	0.232	0.012	414	2.168
47	4.56	2.75	1.958	0.208	0.012	347	2.178
72	4.13	2.49	2.015	0.189	0.014	381	2.218
96	4.25	2.57	2.037	0.194	0.014	369	2.246
143	4.26	2.57	2.108	0.196	0.015	381	2.318
192	3.88	2.34	2.155	0.180	0.017	427	2.351
291	3.89	2.35	2.183	0.183	0.017	430	2.382
390	3.77	2.27	2.190	0.180	0.017	441	2.387
586	3.55	2.14	2.175	0.176	0.017	436	2.369
783	3.43	2.06	2.178	0.176	0.017	431	2.371
977	3.31	1.98	2.209	0.176	0.017	438	2.402
1468	3.04	1.81	2.190	0.177	0.016	420	2.384
1960	2.78	1.64	2.233	0.177	0.017	430	2.426
2554	2.42	1.42	2.182	0.172	0.016	413	2.370

STATION 11

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.07	3.02	1.931	0.228	0.013	435	2.171
10	5.10	3.04	1.925	0.229	0.012	430	2.167
20	5.00	2.98	1.933	0.225	0.013	440	2.171
30	4.89	2.92	1.933	0.221	0.013	437	2.167
49	4.41	2.66	1.972	0.201	0.013	373	2.186
74	3.93	2.37	2.035	0.180	0.015	410	2.230
98	4.03	2.43	2.076	0.185	0.015	414	2.276
197	3.88	2.34	2.160	0.180	0.017	431	2.357
494	3.56	2.14	2.201	0.174	0.018	455	2.392
985	3.24	1.94	2.199	0.173	0.017	444	2.389
1972	2.66	1.58	2.202	0.170	0.017	434	2.389
2464	2.39	1.41	2.208	0.167	0.017	435	2.392

STATION 12

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	4.99	2.98	1.928	0.224	0.013	436	2.165
9	5.10	3.04	1.909	0.229	0.012	418	2.151
22	5.17	3.08	1.906	0.233	0.012	409	2.151
45	4.57	2.75	1.946	0.208	0.012	352	2.166
67	4.01	2.42	2.005	0.184	0.014	401	2.203
88	3.94	2.38	2.031	0.181	0.015	406	2.227
136	4.03	2.43	2.077	0.186	0.015	403	2.279
182	3.97	2.40	2.131	0.184	0.016	416	2.332
272	3.94	2.38	2.158	0.185	0.016	413	2.359
364	3.86	2.33	2.180	0.184	0.016	424	2.380
547	3.72	2.24	2.191	0.183	0.017	427	2.391
728	3.56	2.14	2.175	0.181	0.016	420	2.373
918	3.38	2.03	2.192	0.178	0.017	428	2.387
1385	3.07	1.83	2.188	0.176	0.016	422	2.381
1866	2.78	1.65	2.192	0.174	0.016	421	2.383
2454	2.44	1.44	2.199	0.170	0.017	424	2.386

STATION 14

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.32	3.17	1.846	0.239	0.011	374	2.095
9	5.48	3.27	1.879	0.246	0.011	374	2.137
23	5.14	3.08	1.922	0.233	0.011	350	2.166
47	4.47	2.70	2.021	0.204	0.013	350	2.238
71	4.59	2.77	2.038	0.209	0.013	342	2.260
95	4.26	2.57	2.113	0.194	0.015	388	2.322
144	4.33	2.62	2.130	0.199	0.015	376	2.344
193	4.30	2.60	2.131	0.199	0.015	371	2.345
288	4.22	2.55	2.127	0.199	0.015	375	2.340
387	3.84	2.32	2.143	0.184	0.016	412	2.343
584	3.72	2.24	2.142	0.184	0.016	403	2.343
776	3.65	2.19	2.141	0.187	0.015	391	2.343
968	3.41	2.05	2.129	0.182	0.015	395	2.326
1450	3.13	1.86	2.145	0.182	0.015	393	2.342
1926	2.78	1.65	2.145	0.176	0.015	396	2.337
2502	2.45	1.44	2.153	0.173	0.016	401	2.341

STATION 15

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.22	3.11	1.918	0.234	0.012	416	2.164
9	5.21	3.11	1.907	0.234	0.012	408	2.153
23	5.36	3.20	2.006	0.241	0.013	434	2.260
47	4.72	2.85	2.046	0.214	0.013	348	2.273
71	4.34	2.62	2.097	0.197	0.014	381	2.309
95	4.13	2.50	2.145	0.188	0.016	409	2.349
144	4.11	2.48	2.143	0.189	0.016	401	2.348
193	4.01	2.43	2.162	0.186	0.016	413	2.364
289	3.89	2.35	2.212	0.183	0.017	443	2.412
386	3.79	2.28	2.210	0.181	0.017	443	2.409
582	3.66	2.21	2.193	0.182	0.017	428	2.391
775	3.47	2.09	2.215	0.178	0.017	440	2.410
970	3.24	1.94	2.214	0.173	0.018	449	2.404
1460	3.01	1.79	2.227	0.175	0.017	439	2.419
1949	2.65	1.57	2.212	0.168	0.017	443	2.398
2536	2.39	1.41	2.214	0.170	0.017	431	2.400

STATION 17

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.08	3.04	1.906	0.229	0.012	390	2.147
9	4.81	2.89	1.930	0.217	0.012	360	2.160
23	4.47	2.70	1.969	0.203	0.013	340	2.185
47	4.41	2.66	2.061	0.200	0.014	369	2.274
71	4.17	2.53	2.112	0.190	0.015	397	2.317
95	4.09	2.47	2.131	0.186	0.016	404	2.333
144	4.07	2.46	2.130	0.187	0.015	396	2.333
193	4.05	2.45	2.137	0.188	0.016	397	2.340
291	3.79	2.29	2.114	0.178	0.016	412	2.309
387	3.85	2.32	2.174	0.184	0.016	423	2.375
583	3.64	2.19	2.172	0.181	0.016	423	2.369
777	3.52	2.11	2.171	0.181	0.016	417	2.368
972	3.38	2.03	2.179	0.180	0.016	417	2.375
1459	3.13	1.87	2.187	0.182	0.016	408	2.385
1946	2.79	1.65	2.174	0.177	0.016	407	2.367
2530	2.46	1.45	2.182	0.175	0.016	407	2.372

STATION 18

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
1	5.28	3.15	1.952	0.238	0.012	402	2.201
9	5.25	3.14	1.948	0.237	0.012	384	2.196
23	5.08	3.05	1.957	0.230	0.011	333	2.199
46	4.48	2.70	2.014	0.204	0.013	354	2.231
70	3.98	2.41	2.061	0.181	0.015	405	2.257
94	4.08	2.47	2.071	0.186	0.015	391	2.272
142	4.10	2.48	2.139	0.189	0.016	398	2.343
190	4.03	2.44	2.159	0.187	0.016	407	2.361
285	3.98	2.40	2.185	0.187	0.016	418	2.389
392	3.81	2.30	2.182	0.183	0.017	428	2.381
573	3.68	2.21	2.182	0.182	0.016	423	2.381
764	3.55	2.13	2.200	0.182	0.017	425	2.398
955	3.55	2.13	2.178	0.188	0.016	398	2.382
1435	3.32	1.98	2.184	0.193	0.015	385	2.392
1921	2.88	1.71	2.189	0.182	0.016	401	2.387
2413	2.53	1.49	2.071	0.175	0.014	366	2.261

**

STATION 19

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	ΣCO_2
1	5.15	3.07	1.884	0.231	0.012	397	2.127
9	5.16	3.08	1.880	0.232	0.012	391	2.124
23	5.05	3.01	1.881	0.228	0.012	392	2.120
47	4.75	2.86	1.902	0.217	0.011	331	2.130
71	4.06	2.45	1.973	0.186	0.014	387	2.174
95	3.[illegible]	2.35	1.989	0.180	0.014	394	2.184
144	3.74	2.26	2.041	0.174	0.016	415	2.230
193	3.82	2.31	2.134	0.178	0.016	428	2.328
242	3.81	2.30	2.155	0.178	0.017	427	2.350
290	3.76	2.27	2.161	0.178	0.017	427	2.355
386	3.72	2.25	2.172	0.178	0.017	432	2.367
482	3.63	2.19	2.177	0.177	0.017	433	2.371
581	3.56	2.15	2.176	0.177	0.017	429	2.370
679	3.53	2.12	2.161	0.178	0.016	419	2.356
777	3.50	2.10	2.165	0.180	0.016	414	2.361
875	3.39	2.03	2.157	0.177	0.016	414	2.350

STATION 20

Depth	Ω_{cal}	Ω_{arg}	$[HCO_3]$	$[CO_3]$	$[CO_2]$	$10^6 P_{CO_2}$	$\sum CO_2$
9	5.19	3.10	1.880	0.234	0.011	391	2.125
23	5.30	3.16	1.855	0.239	0.011	356	2.106
47	5.37	3.21	1.854	0.244	0.010	336	2.108
70	4.97	2.99	1.882	0.227	0.011	328	2.120
94	4.36	2.62	1.939	0.201	0.013	363	2.152
189	3.78	2.28	2.151	0.175	0.017	440	2.343
378	3.78	2.28	2.206	0.181	0.017	441	2.403
569	3.60	2.17	2.192	0.178	0.017	436	2.387
761	3.47	2.08	2.184	0.178	0.017	429	2.378
955	3.39	2.03	2.203	0.180	0.017	427	2.399
1152	3.27	1.95	2.181	0.180	0.016	415	2.377
1250	3.22	1.92	2.207	0.180	0.017	422	2.404

APPENDIX IV

DEFINITION OF PARAMETERS FOR THE COMPUTER PROGRAM

Definition of Parameters for the Computer Program

Symbol	Definition
S1	Station number
D	Depth (m)
T1	Temperature at Depth (°C)
S2	Salinity at Depth (^{o}/oo)
A1	Titration Alkalinity (meq kg^{-1})
P1	pH_{25} at 25°C of Sample
P2	Applied pressure (atm or bar)
C	Chlorinity of Sample (^{o}/oo)
K	Absolute temperature (°K)
P3	pH_t at insitu temperature
P4	pH_t at insitu temperature and pressure
B3	Total concentration of B, mol kg^{-1}
B4	log K_{HB}' for boric acid at 1 atm insitu t and S (^{o}/oo)
B5	K_{HB}'at 1 atm
B6	ΔpK_{HB} for effect of pressure
B7	K_{HB}'at insitu pressure
A6	Ac, carbonate alkalinity (meq kg^{-1})
G1	log K_1' for carbonic acid at 1 atm
G2	K_2 at 1 atm
F3	ΔpK_2' for effect of pressure
G3	K_2 at insitu P and t
G4	Concentration of CO_3^{2-} (mol kg^{-1})
C3	Concentration of Ca^{2+} (mol kg^{-1})
Z1	log K_{CaCO_3} at 1 atm
Z3	ΔV for solubility of $CaCO_3$
Z2	ΔK for solubility of $CaCO_3$
Z4	$\Delta p\ K_{CaCO_3}$ for calcite
X2	[Ca] [$CO_3^=$] insitu
Z5	Ion product for calcite

Symbol	Definition
O1	Ω for calcite
D1	Difference between calcite and aragonite solubility
Y1	ΔpK_{CaCO_3} for aragonite
Y3	Ion product for aragonite
O4	Ω for aragonite
G5	log K_1 for carbonic acid at 1 atm
G6	K_1' for carbonic acid at 1 atm
F5	ΔpK_1' for effect of pressure
G7	K_1' for carbonic acid at insitu t and P
G8	ln α for solubility of CO_2
G9	α for solubility of CO_2
H1	$[HCO_3]$ insitu conditions (mol kg^{-1})
H2	$[CO_3]$ insitu conditions (mol kg^{-1})
H3	P_{CO_2} insitu conditions (atm^{-1})
H4	ΣCO_2 insitu conditions (mol kg^{-1})

```
10 REM Calculation of Parameters for the Carbonate System (Input pH&AT)
20 DISP "Station Number";
30 INPUT S1
40 PRINT
50 PRINT
60 WRITE (15,70)"Station Number",S1
70 FORMAT F5.0
80 REM
90 REM
100 PRINT
110 PRINT "Depth   0-cal   0-arg   HCO3   CO3   CO2   PCO2   TCO2"
120 REM INPUT
130 DISP "Depth=";
140 INPUT D
150 DISP "Temp. at Sample Depth in deg. C   ";
160 INPUT T1
170 DISP "Enter Salinity in o/oo            ";
180 INPUT S2
190 DISP "Titration Alkalinity in meq/kg";
200 INPUT A1
210 DISP "Enter measured pH at 25 deg.      ";
220 INPUT P1
230 REM
240 REM Conversions
250 REM
260 REM
270 P2=D/10
280 REM
290 C=S2/1.80655
300 REM
310 K=T1+273.15
320 REM
330 REM
340 REM  Calculation of Activity H+ In Situ  (A5)
350 REM
360 REM Effect of Temp. on a(H+)
370 X5=0.011-4.7E-04*(S2-35)+0.0013*(P1-8)
380 X6=0.011-7.3E-05*(S2-35)+0.0022*(P1-8)
390 REM
391 IF T1<20 THEN 395
392 P3=P1-X5*(T1-25)
393 GOTO 400
394 REM
395 P3=P1-X5*(20-25)-X6*(T1-20)
396 REM
397 REM Effect of Pressure on a(H+)
```

```
400 P4=P3-P2*(4.28E-04-4E-06*T1-(P3-7.8)*4E-05)
410 REM
420 REM
430 A5=10^(-P4)
470 REM
490 REM
500 REM Calculation of Carbonate Alkalinity In Situ  (A6)
510 REM
520 B3=0.237*C/10.82
530 B4=2.121302E-07-1.677761E-09*K-1.67712E-10*S2+2.206332E-12*K^2
540 B4=B4+9.77043E-15*K^3-2.10475E-17*K^4+6.8943376E-13*S2*K
541 REM
542 E1=-29.69+0.3*(S2-35)+0.1674*T1-1.66E-03*T1^2
543 E2=-3.34+0.368*(S2-35)+9.173E-03*T1+2.16E-03*T1
544 B6=(-E1*P2)/(82.0597*K*2.30259)+(0.5*E2*P2^2)/(1000*82.0597*K*2.30259)
560 B7=B4*10^(B6)
570 A6=A1-(B7*B3)/(A5+B7)
650 REM
690 REM  Calculation of  CO3 In Situ using Mehrbach  (G4)
700 REM
710 G1=5371.9645+1.671221*K+0.22913*S2+18.3802*LGT(S2)-128375.28/K
720 G1=G1-2194.3055*LGT(K)-0.00080944*S2*K-5617.11*LGT(S2)/K+2.136*S2/K
730 G2=10^(-G1)
731 REM
732 E3=-15.915+0.327*(S2-35)-0.012*T1
733 E4=0.64-0.262*(S2-35)-0.02098*T1-4.355E-03*T1^2
734 F5=(-E3*P2)/(82.0597*K*2.30259)+(0.5*E4*P2^2)/(1000*82.0597*K*2.30259)
740 G3=G2*10^F5
750 G4=A6*G3/(A5+2*G3)
760 REM
770 REM
780 REM  Calculation of  Ca  (C3)
790 REM
800 C3=0.01027*(S2/35)
810 REM
820 REM
830 REM  Calculation of IMP (X1,Lyman,X2,Mehrbach)
840 REM
860 X2=C3*G4/1000
870 REM
880 REM
890 REM  Calculation of Omega Calcite using Ingle/Mehrbach  (O1)
900 REM
910 Z1=(-34.452-39.866*S2^(1/3)+110.21*LGT(S2)-7.5752E-06*K*K)/1E+07
920 Z2=(2.529+0.369*(25-T1))/1000
```

```
930 Z3=-35.5-0.53*(25-T1)
940 Z4=(-Z3*P2+0.5*Z2*P2^2)/(2.30259*K*82.0597)
950 Z5=Z1*10^Z4
960 01=X2/Z5
980 REM
1040 REM
1080 REM  Calculation of Omega Aragonite Best Guess (04)
1090 Z9=-38.3-0.53*(25-T1)
1100 Y1=(-Z9*P2+0.5*Z2*P2*P2)/(2.30259*K*82.0597)
1110 Y2=Z8*10^Y1
1131 REM
1132 D1=1.68-(0.0025*(25-T1))
1133 Y3=D1*Z1*10^Y1
1134 04=X2/Y3
1140 REM
1150 REM
1160 REM
1200 REM CALCULATION OF HCO3(H1), CO2(H2),PCO2(H3),TCO2(H4)
1210 REM
1220 G5=-13.7201+0.031334*K+3235.76/K+1.3E-05*S2*K-0.1032*S2^0.5
1230 G6=10^(-G5)
1240 E5=-25.02-0.1757*(S2-35)-0.0629*T1+8.225E-03*T1^2
1241 E6=-2.17-0.2865*(S2-35)-0.2789*T1+1.59E-02*T1^2
1242 F6=(-E5*P2)/(82.0597*K*2.30259)+(0.5*E6*P2^2)/(1000*82.0597*K*2.30259)
1250 G7=G6*10^F6
1260 G8=-60.2409+93.4517*(100/K)+23.3585*LOG(K/100)
1270 G8=G8+S2*(0.023517-0.023656*(K/100)+0.0047036*(K/100)^2)
1280 G9=10^(G8/2.30259)
1290 H1=A6/(1+2*G3/A5)
1300 H2=(A6*A5/G7)/(1+2*G3/A5)
1310 H3=H2/(G9)
1320 H4=A6*(1+G3/A5+A5/G7)/(1+2*G3/A5)
1330 REM
1340 REM OUTPUT
1350 REM
1370 WRITE (15,1380)D,01,04,H1,G4,H2,H3,H4
1380 FORMAT F5.0,3X,F5.2,5X,F5.2,5X,F6.3,3X,F6.3,3X,F6.3,3X,F6.3,3X,F6.3,
1390 GOTO 120
1400 STOP
1410 END
```