

*The Alkalinity and Total Carbon Dioxide Concentration in the World Oceans**

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ABSTRACT

The titration alkalinity and total carbon dioxide concentration data obtained during the GEOSECS Expeditions, 1972–1977, in the Atlantic, Pacific and Indian Oceans have been summarized. The oceans have been divided into seven oceanic regions, and the mean vertical distributions of the alkalinity and total CO₂ concentration have been computed. In addition, the vertical distributions of these quantities as well as salinity and potential temperature for the mean world ocean have been computed using the regional mean values. Based upon these values, the total CO₂ content of the world oceans has been estimated to be 3.16×10^{12} MCO₂. The CO₃²⁻ ion concentration at the *in situ* temperature and pressure conditions have been computed using the alkalinity and total CO₂ data. The regional mean vertical profiles for the CO₃²⁻ ion in seawater are presented and discussed.

1. INTRODUCTION

The Geochemical Ocean Sections Study (GEOSECS) program was initiated in 1970 with the support of the International Decade of Ocean Exploration Program of the U.S. National Science Foundation. The major objective has been to establish baselines for the concentrations of various chemical species and radio-isotopes in the world oceans. This paper summarizes the alkalinity and total CO₂ concentration data obtained by the GEOSECS program for the three major oceans of the world. Since the distribution of these quantities in the surface waters of the world oceans has already been presented elsewhere (Takahashi *et al.*, 1980-a), this paper will describe these quantities in sub-surface waters.

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2. THE METHOD OF DETERMINATIONS AND QUALITY OF THE DATA

The titration alkalinity and the total dissolved CO₂ concentration were both determined by means of the Gran (1952) potentiometric titration method using an automated titrator system similar to that described by Edmond (1970). The titrator was calibrated using gravimetrically prepared solutions of Na₂B₄O₇ · 10 H₂O or Na₂CO₃, of which the ionic strength was adjusted to that of seawater using NaCl or KCl. The accuracy of the measurements was tested against the results of other methods including the volumetric and infrared analysis methods (Takahashi *et al.*, 1970).

The results of the Atlantic GEOSECS have been critically evaluated by Takahashi *et al.* (1976a) based on the consistency of the partial pressure of CO₂ (pCO₂) measured by the equilibrator-infrared system (Takahashi *et al.*, 1976b) with that calculated from the alkalinity and total CO₂. It has been shown that the GEOSECS Atlantic data are entirely consistent with the measured pCO₂ values, the first and second dissociation constants of carbonic acid in seawater by Mehrbach *et al.* (1973), the CO₂ solubility in seawater by Weiss (1974) and the first dissociation constant of boric acid in seawater by Lyman (1956). However, while the data for the Pacific Ocean were being obtained, it became apparent that the measured pCO₂ values were about 20% smaller than those computed using the alkalinity and total CO₂ data and the set of constants stated above. This inconsistency was observed throughout the Pacific as well as the Indian Ocean data. This means that the observed alkalinity/total CO₂ ratio is too small. On the other hand, it has been demonstrated by Takahashi *et al.* (1980-a) that the alkalinity-salinity relationship observed in the Atlantic sector of the Circumpolar Water (CPW) is consistent with that observed in the Pacific sector. Furthermore, the alkalinity data obtained by Weiss *et al.* (1979) in the Weddell Sea are in agreement with the GEOSECS Atlantic data obtained along the 60°S parallel. These observations indicate that the GEOSECS alkalinity values appear to be reliable, and that the cause for the internal inconsistency among the alkalinity-total CO₂-pCO₂ values is an over-estimation of the total CO₂ concentrations. Using the pCO₂ data for surface and sub-surface water samples in the Pacific, Broecker and Takahashi (1978) therefore concluded that a correction of -15 μM/kg for the GEOSECS total CO₂ data (obtained by the titrimetric method) is needed to achieve the internal consistency of the alkalinity, total CO₂ and pCO₂ data. A similar conclusion was reached for the GEOSECS Indian Ocean data. Furthermore, Keeling (personal communication) has reported that the total CO₂ concentrations determined by his volumetric method for a dozen or more samples collected during the GEOSECS Expeditions in the Indian Ocean are consistently lower than the corresponding GEOSECS total CO₂ values by 17 μM/kg.

David Bos (private communication) of the Physical and Chemical Oceanographic Data Facilities, Scripps Institution of Oceanography, has investigated the source of this over-estimation of total CO₂ by the titrimetric method, and observed that the assumption of the ideal electrode sensitivity (-59.19 millivolts per pH unit at 25°C) used in the Gran titration calculation leads to an over-estimation of the total CO₂

concentration. If an electrode sensitivity of 98% of the ideal value (due presumably to the difference in asymmetry and liquid junction potentials for the standard buffer solutions and seawater) is used for the Gran calculation, the resulting alkalinity and total CO_2 values are reduced by $4 \mu\text{eq/kg}$ and $21 \mu\text{M/kg}$ respectively compared to the values obtained using the ideal electrode sensitivity. In view of the observations made by Hawley and Pytkowicz (1973) for a glass electrode, such a deviation of electrode sensitivity from the ideal value appears to be reasonable. Thus, according to the observations made by Bos, it is speculated that the glass electrodes used for the GEOSECS Atlantic Expeditions had sensitivities close to the ideal, whereas those used for the Pacific and Indian Ocean Expeditions had sensitivities of about 98% of the ideal. Although this explanation can account for the internal consistency of the alkalinity, total CO_2 and pCO_2 data observed for the Atlantic data and for the lack of internal consistency observed for the Pacific and Indian Ocean data, it can not be substantiated due to the absence of records pertaining to the glass electrodes used for the respective expeditions. Recently, Bradshaw *et al.* (in press) have found that the effect of the CO_3^{2-} ion on the Gran F_1' function was omitted in the GEOSECS program used for the reduction of the Pacific and Indian Ocean titration data. They have shown that the omission would cause an over estimation of the total CO_2 concentration by about $12 \mu\text{M/kg}$.

Considering the discussions presented above, we have chosen to correct the total CO_2 values for the Pacific and Indian Oceans by $-15 \mu\text{M/kg}$ and to present these adjusted values in the following sections. Although the accuracy of the alkalinity and total CO_2 values reported here can not be rigorously assessed, the data set presented is internally consistent. The precision for the alkalinity and total CO_2 values has been estimated to be $\pm 0.15\%$ and $\pm 0.3\%$ (one standard deviation) respectively for the Atlantic and Indian Ocean data based upon 350 measurements for each of these quantities in water samples below 4000 m depth, and to be $\pm 0.2\%$ and $\pm 0.5\%$ respectively for the Pacific Ocean data also based upon about 350 measurements in water samples below 4000 m. The accuracy of alkalinity and total CO_2 (corrected for $-15 \mu\text{M/kg}$ in the Pacific and Indian Ocean) values reported here is probably no better than $21 \mu\text{eq/kg}$ and $21 \mu\text{M/kg}$ respectively due to the blank in titration measurements. However, since the blank correction affects the alkalinity in the same proportion as it does to the total CO_2 concentration, it does not affect the ratio of the alkalinity to total CO_2 . All the data presented here are listed in Takahashi *et al.* (1980-b).

3. DISTRIBUTION OF THE ALKALINITY AND THE TOTAL CO₂ CONCENTRATIONS

3.1. Regional Distributions

For the purpose of data analysis, the three major oceans of the world have been divided into seven regions: a) the North Atlantic between 35°N and the equator, b) the South Atlantic between the equator and 45°S, c) the North Pacific between 50°N (the Aleutian Island arc) and the equator, d) the South Pacific between the equator and 45°S, e) the North Indian north of the equator, f) the South Indian between the equator and 45°S, and g) the Antarctic, south of 45°S. The locations of the GEOSECS stations in each of these oceans are shown elsewhere (e.g., Broecker and Takahashi, 1978, for the Atlantic and Pacific, and Takahashi *et al.* (1980-a and 1980-b) for the three oceans. The North Atlantic Ocean data are limited to observations from stations south of 35°N due to a malfunction of the titrators in the early stage of GEOSECS. In terms of the GEOSECS stations, all the data for the station numbers less than 31 have been excluded from this study. The southern limit of 45°S in the southern oceans was chosen to coincide with the approximate northern boundary of the west wind drift surface currents around the Antarctic Continent. All the data for the south of 45°S in the three oceans are grouped in the Antarctic section. In order to illustrate the quality and quantity of the GEOSECS alkalinity and total CO₂ concentrations, the alkalinity (1242 determinations) and total CO₂ (1245 determinations) data obtained in the North Pacific (north of the equator) are shown in Fig. 1 as a function of the depth. In addition, an arithmetic mean (with equal weight) and a standard deviation for the alkalinity and total CO₂ values in each 100 m depth interval were computed for the sample above 1200 m, and those in each 200 m depth interval were computed for the samples below 1200 m. These values are also plotted in Fig. 1. The values for the standard deviation shown in Fig. 1 are typical of the data set obtained for other regions of the oceans.

The mean alkalinity and total CO₂ values in the depth intervals computed for each of the seven oceanic regions are plotted as a function of the depth in Figs. 2-a and 2-b respectively. For both quantities, the Atlantic values are low, the Pacific and Indian Ocean values are high, and the Antarctic values lie in the middle, although the values for the South Atlantic Ocean below about 4500 m tend to be indistinguishable from those for the deep Antarctic values. The alkalinity minimum seen at a depth of about 800 m in the South Atlantic profile appears to represent the core of Antarctic Intermediate Water (salinity minimum). The broad alkalinity and total CO₂ minimum observed in depth range of 1500 to 3500 m in the North and South Atlantic profiles appear to represent North Atlantic Deep Water. The regional mean values computed for the potential temperature, salinity, alkalinity and total CO₂ concentration in the three depth intervals of 0–50, 50–1200 and >1200 m, representing the surface, thermocline and deep water, are tabulated in Table 1.

Alkalinity depends primarily on salinity. Since a number of model calculations that have appeared in recent literature are based on a constant salinity ocean, alka-

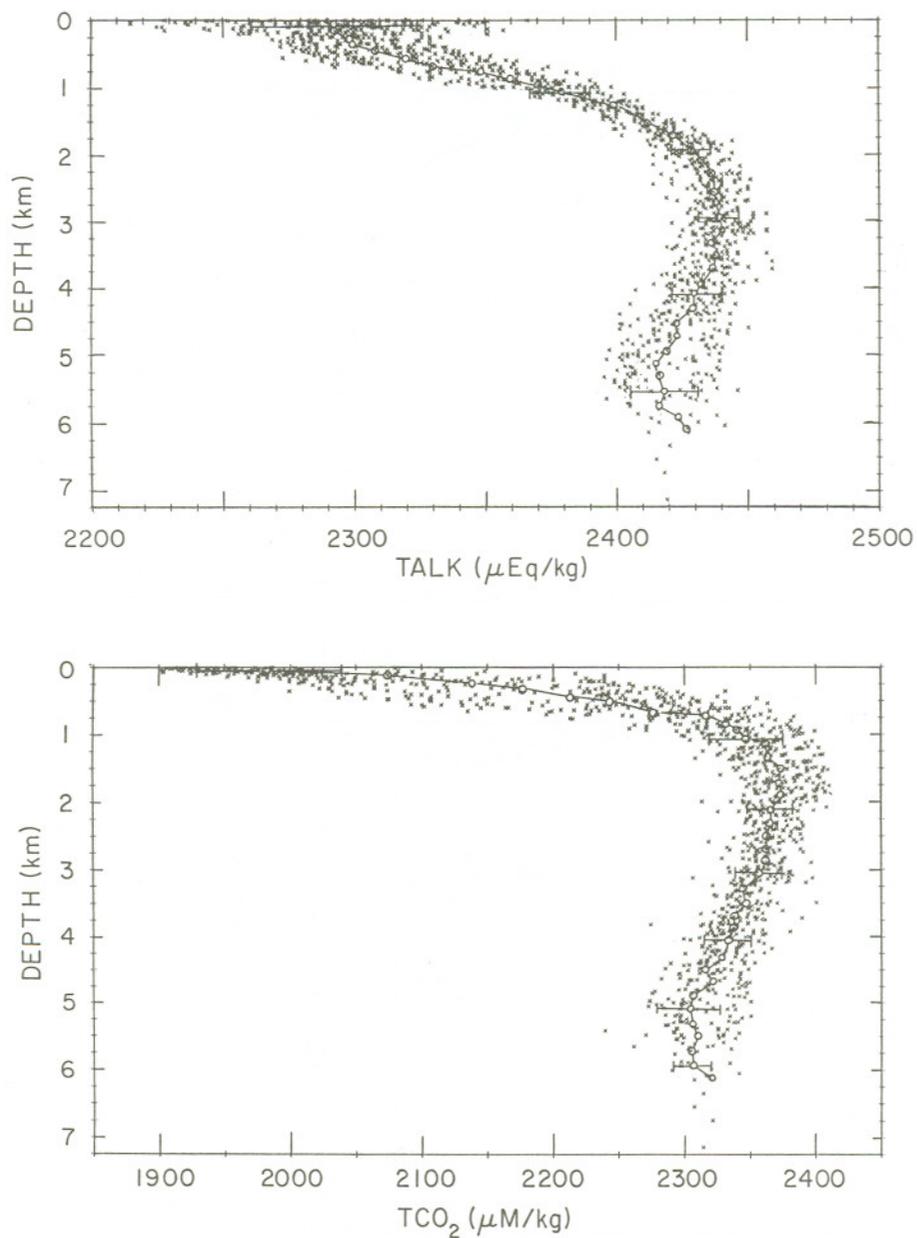


Figure 1: The GEOSECS (a) alkalinity and (b) total CO_2 concentration data in the North Pacific Ocean north of the equator. The arithmetic mean for the 100 meter depth interval for above 1200 meters in depth and the 200 meter depth interval for below 1200 meters in depth is indicated by an open circle, and one standard deviation for selected depth intervals is shown by a horizontal bar.

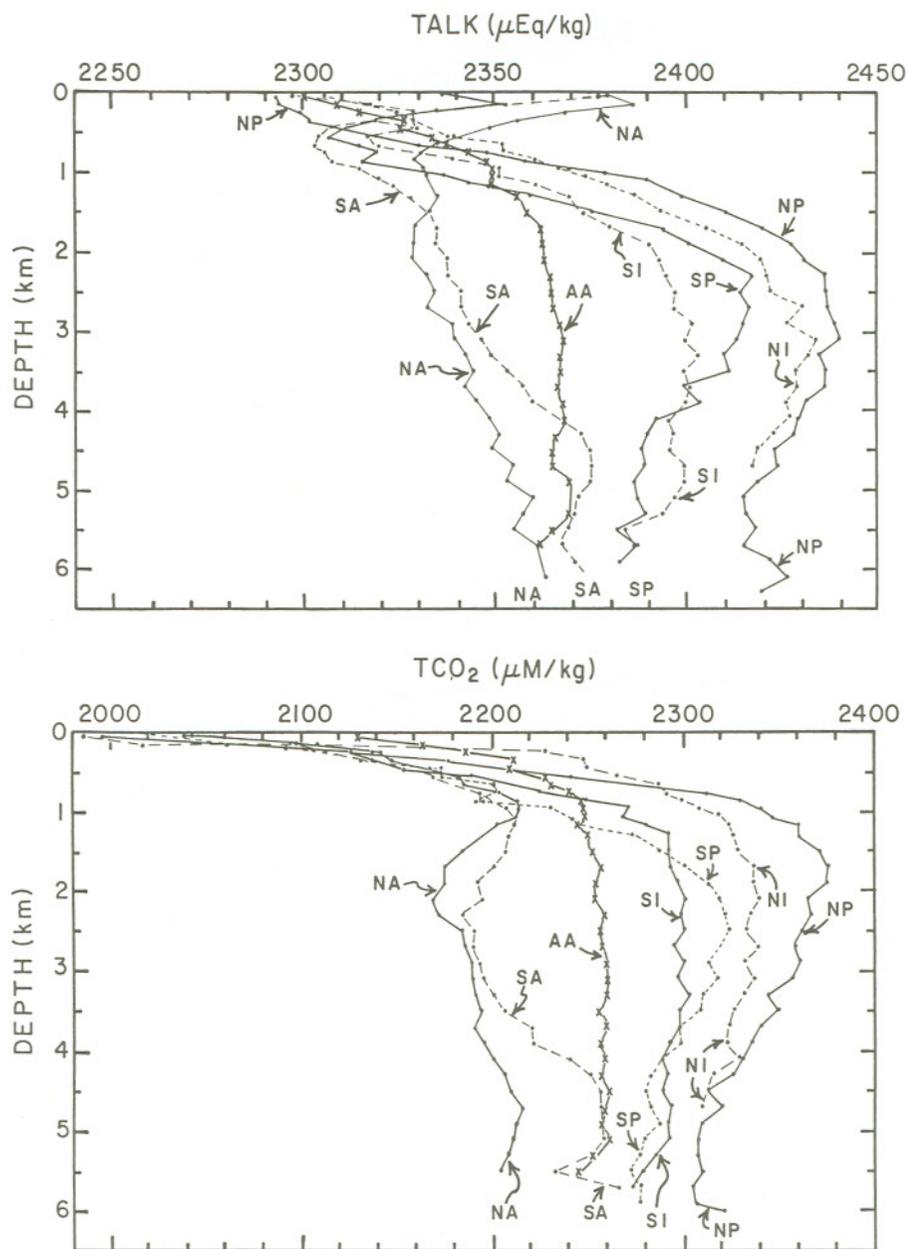


Figure 2: The mean vertical distribution of (a) the alkalinity and (b) the total CO_2 concentration in the seven regions of the world oceans. NA = North Atlantic, SA = South Atlantic, NP = North Pacific, SP = South Pacific, NI = North Indian, SI = South Indian, and AA = Antarctic region (south of 45°S). The mean values for each depth intervals in the first six oceanic regions are indicated by solid circles, and those in the Antarctic region are indicated by X's.

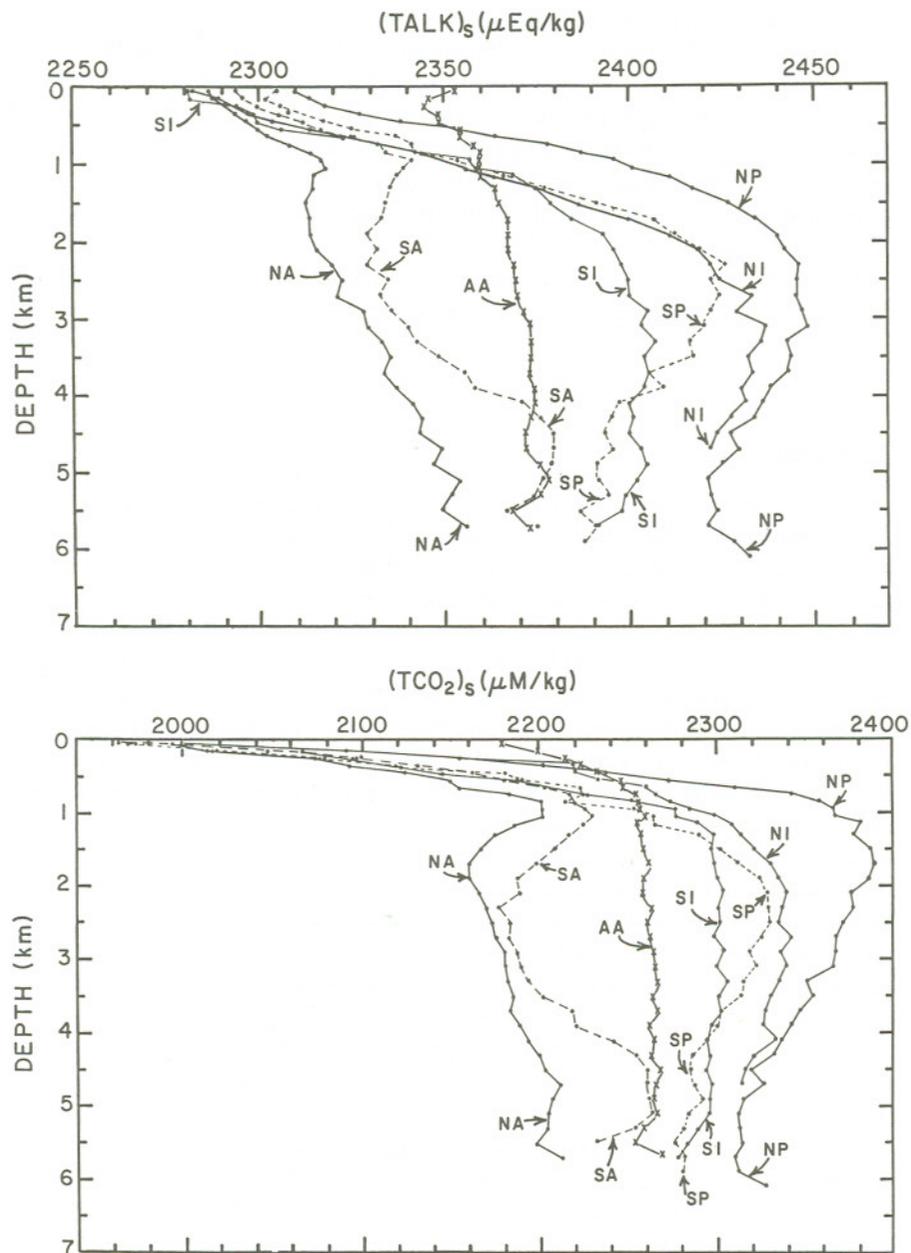


Figure 3: The mean vertical distribution of (a) the alkalinity and (b) the total CO_2 concentration normalized to the mean world ocean salinity value of 34.78‰. NA = North Atlantic, SA = South Atlantic, NP = North Pacific, SP = South Pacific, NI = North Indian, SI = South Indian, and AA = Antarctic region. The values for the Antarctic region are indicated by X's, and those for other regions by solid circles.

linity values used should be normalized to a constant salinity. For this reason, alkalinity and total CO₂ values normalized to the mean world ocean salinity of 34.78‰ have been computed for the depth intervals and plotted as a function of the depth in Figs. 3-a and 3-b. It is seen that the alkalinity minima observed at about 800 m depth in some profiles on the alkalinity vs. depth plot (Fig. 2-a) are eliminated, and that the large spread of the alkalinity values in the surface waters is greatly reduced. The normalized alkalinity values for the Antarctic region show a small increase (about 25 $\mu\text{eq/kg}$) from the surface to 5300 m.

The regional mean values for the normalized alkalinity and total CO₂ concentration values in the three depth intervals are listed in Table 1.

3.2. Global Average

Although regional differences in the distribution of the alkalinity and the total CO₂ concentrations are clearly depicted in Figs. 2 and 3, some CO₂ model studies such as those using a single average ocean, require a global mean distribution of the alkalinity and total CO₂ concentration in the oceanic system. To obtain such a global ocean average, an area-weighted arithmetic mean of the seven regional mean values for a respective quantity in each 100 m depth interval for the upper 1200 m, and in each 200 m depth interval for the waters below 1200 m has been computed. The fractional weighting factors representing the areas of the seven oceanic regions are listed in the footnote of Table 2. As mentioned earlier, the GEOSECS alkalinity and total CO₂ data are limited to the area south of 35°N. However, due to the lack of reliable data in the north of 35°N, it is assumed that the mean values for the North Atlantic from the equator to 35°N (which comprises 7.0% of the world oceanic area) represent the entire North Atlantic Ocean (which comprises 11.9% of the world oceanic area). For the calculation of the world mean temperature and salinity, only the GEOSECS data have been used. Since the GEOSECS expeditions were undertaken mostly during the summer months in both hemispheres, the mean values for the shallow depths are presumably skewed in favor of the summer values. Because of this reason, the mean temperature for the upper 50 m listed in Table 2 appears to be higher by a few degrees than the space-time average value. No seasonal effect is expected for the values for deeper waters.

The global mean potential temperature, salinity, alkalinity (normalized to 34.78‰ salinity) and total CO₂ concentration (normalized to 34.78‰ salinity) are plotted in Fig. 4 as a function of the depth. The uncertainties in the mean values for the normalized alkalinity and total CO₂ concentration are expressed in two ways. First, if the world ocean is horizontally homogeneous, and the vertical distribution and the standard deviation in each depth interval for a given quantity in each oceanic region are represented by a depth profile (as shown in Figs. 1 through 3), then the mean world ocean value (\bar{X}) and the standard deviation (σ) are given according to the statistical formalities (Bevington, 1969):

$$\begin{aligned}\bar{X} &= \sum W_i \cdot X_i \\ \sigma &= (\sum (W_i^2 \cdot \sigma_i^2))^{1/2}\end{aligned}\quad \dots (1)$$

where W_i is the fractional weight ($\sum W_i = 1$) for a value X_i , and σ_i is the standard deviation for a value X_i . The values for the world mean alkalinity and total CO_2 and the standard deviation σ thus computed for the mean world ocean value in each depth interval are shown in Fig. 4 by the solid circles and horizontal bars respectively. It is, however, noted that the standard deviation does not appear to indicate the magnitude of the regional variations observed in Fig. 3. Therefore, to express the regional differences in the alkalinity and total CO_2 concentration, another standard deviation was computed by using the following equations:

$$\begin{aligned}\sigma' &= [\sum (X_i - \bar{X}')^2 / (N - 1)]^{1/2} \\ \bar{X}' &= \sum X_i / N\end{aligned}$$

where N is the number of the data points and is 7 for the averaging of the seven oceanic regions. The values for σ' thus computed are shown by the dashed curves in Fig. 4. These curves coincide roughly with the depth profiles for the North Atlantic and North Pacific Oceans.

The global averages for the potential temperature, salinity, alkalinity and total CO_2 in three depth intervals were computed by averaging (area weighted) the regional mean values presented in Table 1, and are listed in Table 2. Using these values, the total volume of the ocean water of 1370 km^3 , and the mean seawater density of 1.025 gm/cm^3 , the total alkalinity and total CO_2 content of the oceans have been estimated to be $3.33 \times 10^{12} \text{ eq}$ and $3.16 \times 10^{12} \text{ MCO}_2$ ($= 1.39 \times 10^8 \text{ metric tons CO}_2$).

The value for pCO_2 in the surface mixed layer in this mean world ocean of a constant salinity of 34.78‰ has been calculated to be $300 \times 10^{-6} \text{ atm.}$ at the mean temperature of 19.20°C (with $(\text{TALK})_s = 2311 \mu\text{eq/kg}$ and $(\text{TCO}_2)_s = 2002 \mu\text{M/kg}$). This compares with the mean atmospheric pCO_2 of $321 (\pm 3) \times 10^{-6} \text{ atm.}$ in 1973, and indicates that the surface water of this idealized ocean is undersaturated with respect to the atmospheric CO_2 . If a mean CO_2 gas exchange rate of $20 \text{ MCO}_2/\text{m}^2 \text{ yr}$ is assumed, the net transfer flux of CO_2 from the atmosphere to the ocean is estimated to be $(20 \times (321 - 300) / 321 =) 1.3 (\pm 0.2) \text{ MCO}_2/\text{m}^2 \cdot \text{yr}$. This corresponds to 130 (± 15)% of the fossil fuel CO_2 production rate in 1973. If a temperature of 20.26°C is assumed for the surface water, the pCO_2 in the surface water is increased to $313 \times 10^{-6} \text{ atm.}$ In this case, the net transfer flux of CO_2 to the oceans is estimated to be about 50% of the fossil fuel CO_2 production rate, and is consistent with that estimated on the basis of the fossil fuel production rate (Baes *et al.*, 1977) and the rate of increase of the atmospheric CO_2 concentration observed by Keeling *et al.*, (1976).

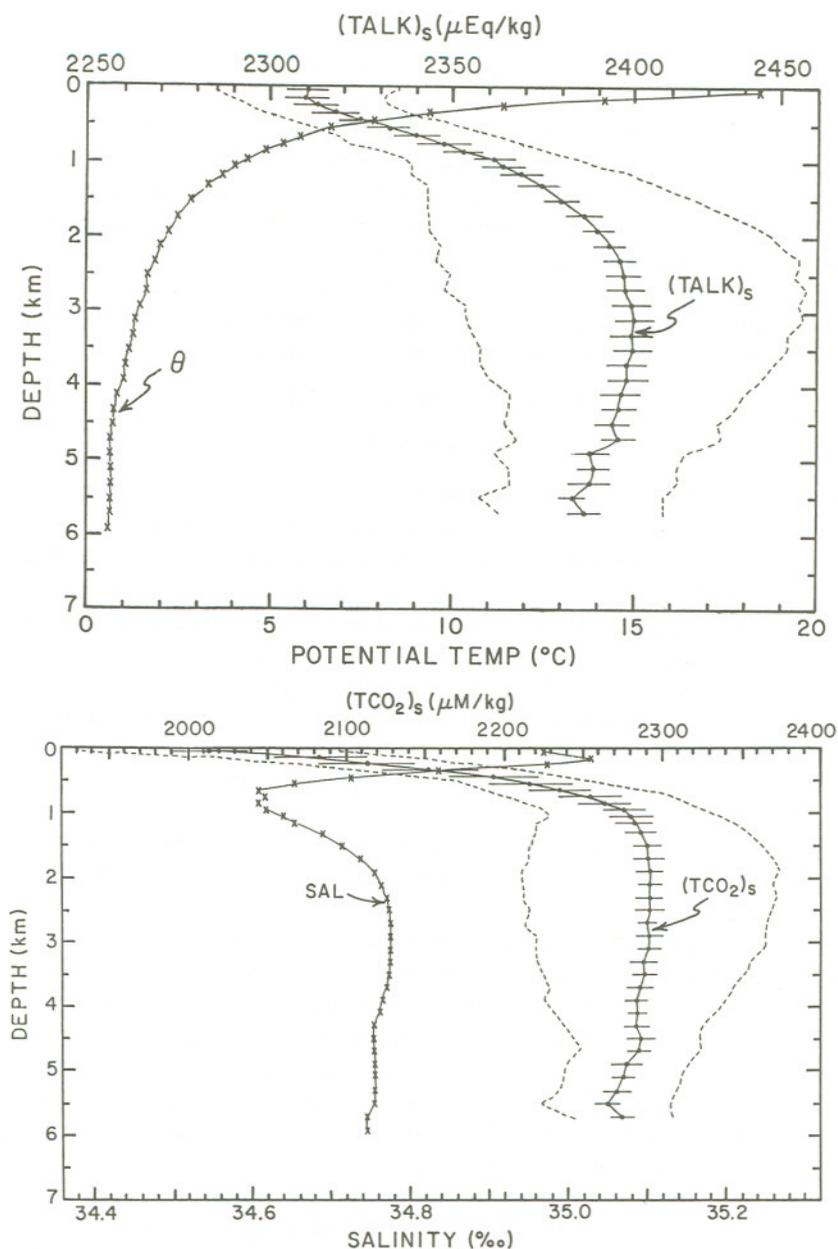


Figure 4: The vertical distribution of the mean world ocean values for (a) the normalized alkalinity and potential temperature, and (b) the normalized total CO_2 concentration and salinity. The mean values for the alkalinity and total CO_2 concentrations are indicated by solid circles, and those for the potential temperature and salinity by X's. The horizontal bars attached to the solid circles indicate the standard deviation calculated for each depth interval using Eq. (1), the dashed curved indicate the standard deviation calculated for each depth interval using Eq. (2).

Table 1. Mean values for the potential temperature, salinity, titration alkalinity and total CO₂ in the three depth ranges in the seven areas of the world oceans. The mean values are the arithmetic means of the GEOSECS data (equally weighted) in each depth range, and the \pm values are one standard deviation of the data set for each depth range. (TALK)_s and (TCO₂)_s are respectively the alkalinity and total CO₂ concentration normalized to the mean world ocean salinity value of 34.78‰.

	Depth Range (m)	θ (°C)	SAL. (‰)	TALK ($\mu\text{eq/kg}$)	(TALK) _s	TCO ₂ ($\mu\text{M/kg}$)	T(CO ₂) _s
N. Atl. (35°N to Equator)	0–50	17.1±9.1	35.4 ±1.1	2371±37	2287± 9	2023± 48	1944± 25
	50–1200	8.1±6.1	35.3 ±0.6	2351±34	2302±16	2167± 58	2124± 96
	1200–5800	2.2±1.5	34.93±0.07	2340±13	2328±16	2192± 18	2181± 21
S. Atl. (Equator to 45°S)	0–50	22.5±5.3	35.8 ±0.7	2375±48	2295± 8	2027± 37	1961± 34
	50–1200	9.7±6.0	35.0 ±0.7	2326±32	2315±18	2151± 63	2142± 94
	1200–5800	1.8±1.3	34.8 ±0.1	2350±17	2348±21	2214± 32	2212± 38
N. Pac. (50°N to Equator)	0–50	20.7±8.0	34.5 ±0.8	2293±34	2310±24	1969± 49	1985± 77
	50–1200	9.9±6.6	34.5 ±0.4	2323±37	2349±39	2202±133	2227±140
	1200–6200	1.5±0.7	34.65±0.05	2427±15	2436±13	2347± 30	2356± 32
S. Pac. (Equator to 45°S)	0–50	24.6±4.3	35.3 ±0.5	2332±36	2307±10	1993± 46	1971± 52
	50–1200	11.8±7.2	34.9 ±0.6	2329±30	2325±25	2148± 88	2146±112
	1200–5900	1.5±0.7	34.67±0.05	2400±23	2408±22	2301± 31	2309± 31
N. Ind. (20°N to Equator)	0–50	27.9±1.5	34.9 ±1.1	2303±58	2283±12	1950± 61	1933± 13
	50–1200	13.1±5.4	35.3 ±0.4	2337±29	2308±29	2238± 82	2211± 83
	1200–4800	2.2±1.4	34.78±0.09	2419±18	2420±21	2330± 16	2330± 16
S. Ind. (Equator to 45°S)	0–50	26.3±3.2	34.9 ±0.6	2292±36	2282±6	1944± 47	1936± 25
	50–1200	11.6±5.9	34.9 ±0.3	2327±25	2317±31	2168± 98	2160±109
	1200–5800	1.7±1.0	34.72±0.05	2393±18	2397±17	2294± 19	2298± 17
Antarctic (south of 45°S)	0–50	3.6±3.9	33.9 ±0.4	2297±15	2354±20	2120± 38	2172± 49
	50–1200	2.5±2.6	34.4 ±0.3	2328±28	2353±17	2207± 57	2230± 47
	1200–5800	0.7±0.9	34.69±0.05	2365± 9	2371± 9	2257± 13	2263± 13

Table 2. The mean values of the potential temperature, salinity, alkalinity and total CO₂ concentration in the world oceans. (TALK)_s and (TCO₂)_s are respectively the alkalinity and total CO₂ values normalized to the world average salinity of 34.78‰. The numbers in the parentheses indicate the number of determinations.

Depth Range (m)	θ (°C)	S (‰)	TALK	(TALK) _s $\mu\text{eq/kg}$	TCO ₂	(TCO ₂) _s $\mu\text{M/kg}$
0-50*	19.2 (1032)	34.9 (1032)	2322 (317)	2311 (317)	2012 (300)	2002 (300)
50-1200*	9.1 (5244)	34.8 (5244)	2332 (2309)	2332 (2309)	2181 (2217)	2182 (2217)
> 1200*	1.5 (7876)	34.76 (7876)	2390 (3519)	2393 (3519)	2284 (3399)	2288 (3399)
Whole Ocean**	3.9 (14,152)	34.78 (14,152)	2372 (6145)	2374 (6145)	2251 (5916)	2254 (5916)

* The area-weighted arithmetic mean. The following weighting factors were used to represent each of the seven oceanic regions:

N. Atlantic = 11.9%,
 S. Atlantic = 9.7%,
 N. Pacific = 21.9%,
 S. Pacific = 21.4%,
 N. Indian = 3.4%,
 S. Indian = 13.6%,
 Antarctic (S of 45°S) = 18.2%.

** The volume-weighted arithmetic mean. The mean world ocean depth (excluding the adjacent seas) of 4100 meters, and the following areal percentage for each depth range were used:

0-50 = 100% of the oceanic area
 50-1200 = 99.3% of the oceanic area
 > 1200 = 93.9% of the oceanic area.

4. DISTRIBUTION OF CARBONATE IONS IN THE OCEANS

Since the dissolution of marine carbonates in the deep oceans constitutes a feedback mechanism in the cycle of alkalinity and total CO₂, it is important to know the distribution of CO₃⁼ ion concentrations in the oceans. Therefore, the the CO₃⁼ concentration in seawater at the *in situ* temperature and pressure conditions has been computed using the GEOSECS alkalinity, total CO₂, temperature, salinity and pressure data. The first and second apparent dissociation constants of carbonic acid in seawater determined by Mehrbach *et al.* (1973), the first apparent dissociation constant of boric acid in seawater determined by Lyman (1956), and the effect of pressure on these dissociation constants determined by Culberson *et al.* (1967) were used for the computation. Details for the computational scheme are described in Broecker and Takahashi (1978), and the values are listed in Takahashi *et al.* (1980-b).

4.1. Regional Distribution

The mean vertical distributions of $\text{CO}_3^{=}$ ion concentrations in the seven regions of the world oceans are shown in Fig. 5. The averaging scheme for the $\text{CO}_3^{=}$ ion concentration is identical to that used for the alkalinity and total CO_2 concentration. It is seen that among the deep waters (i.e., below 2000 m) of the world oceans, the North Atlantic water contains the highest concentration of the $\text{CO}_3^{=}$ ion, ranging from 100 to 110 $\mu\text{M}/\text{kg}$, whereas the North Pacific water contains the lowest, ranging from 65 to 85 $\mu\text{M}/\text{kg}$. This is a manifestation of greater values for the $(\text{ALK})/(\text{TCO}_2)$ ratio in the Atlantic water than that in the Pacific water.

Also shown in Fig. 5 are the critical carbonate dissolution curves for calcite and aragonite proposed by Broecker and Takahashi (1978):

$$(\text{CO}_3^{=})_{\text{CC}} (\mu\text{M}/\text{kg}) = 90 \exp [0.16 (Z-4)], \quad \dots (3)$$

$$(\text{CO}_3^{=})_{\text{CA}} (\mu\text{M}/\text{kg}) = 120 \exp [0.15 (Z-4)], \quad \dots (4)$$

where CC and CA denote the critical concentration for calcite and aragonite respectively and Z is the depth of water in kilometers. These curves define the concentration of $\text{CO}_3^{=}$, at which the skeletal calcium carbonate matter in deep sea sediments begins to dissolve into seawater. For example, the $\text{CO}_3^{=}$ concentration curve (marked NA) for the North Atlantic intersects with these critical curves CA and CC in Fig. 5-a at a depth of 3.2 km and 4.6 km respectively. This indicates that aragonitic and calcitic skeletal matter is being dissolved into seawater at water depths greater than 3.2 km and 4.6 km respectively. Similarly, in the North Pacific, the dissolution of aragonite and calcite should start at water depths of 0.6 km and 0.8 km respectively.

The distribution of the $\text{CO}_3^{=}$ concentration in the mean world ocean has been computed by averaging (area weighted) the seven regional values in the respective depth intervals as done for other quantities, and is plotted in Fig. 5-b. It was also computed using the mean world ocean values for temperature (Fig. 4-a), $(\text{TALK})_s$ and $(\text{TCO}_2)_s$ (Fig. 4-a and b) at a constant salinity of 34.78‰. The $\text{CO}_3^{=}$ concentration values thus computed for the mean world ocean agree within 2% with the mean world ocean values computed by averaging the regional mean values. Thus, the distribution of the $\text{CO}_3^{=}$ concentration in the mean world ocean appears to be independent of the averaging schemes. In the mean world ocean, the aragonite and calcite start to dissolve into seawater at depths of 1.0 km and 3.8 km respectively. Below these critical depths, the difference between the $\text{CO}_3^{=}$ concentrations given by Eqs. (3) and (4) and those in the ocean water increases with depth. This means that the chemical driving force for dissolution increases with depth. Therefore, the carbonate matter should dissolve at an accelerated rate with increasing depth. This concept has been applied to quantitative model computations for estimating the distribution of calcium carbonate in deep sea sediments (e.g., Schink and Guinasso, 1977; Takahashi and Broecker, 1977) and for forecasting the effect of increased CO_2 concentrations in the deep North Atlantic water on the dissolution flux of calcium carbonate (Broecker and Takahashi, 1977).

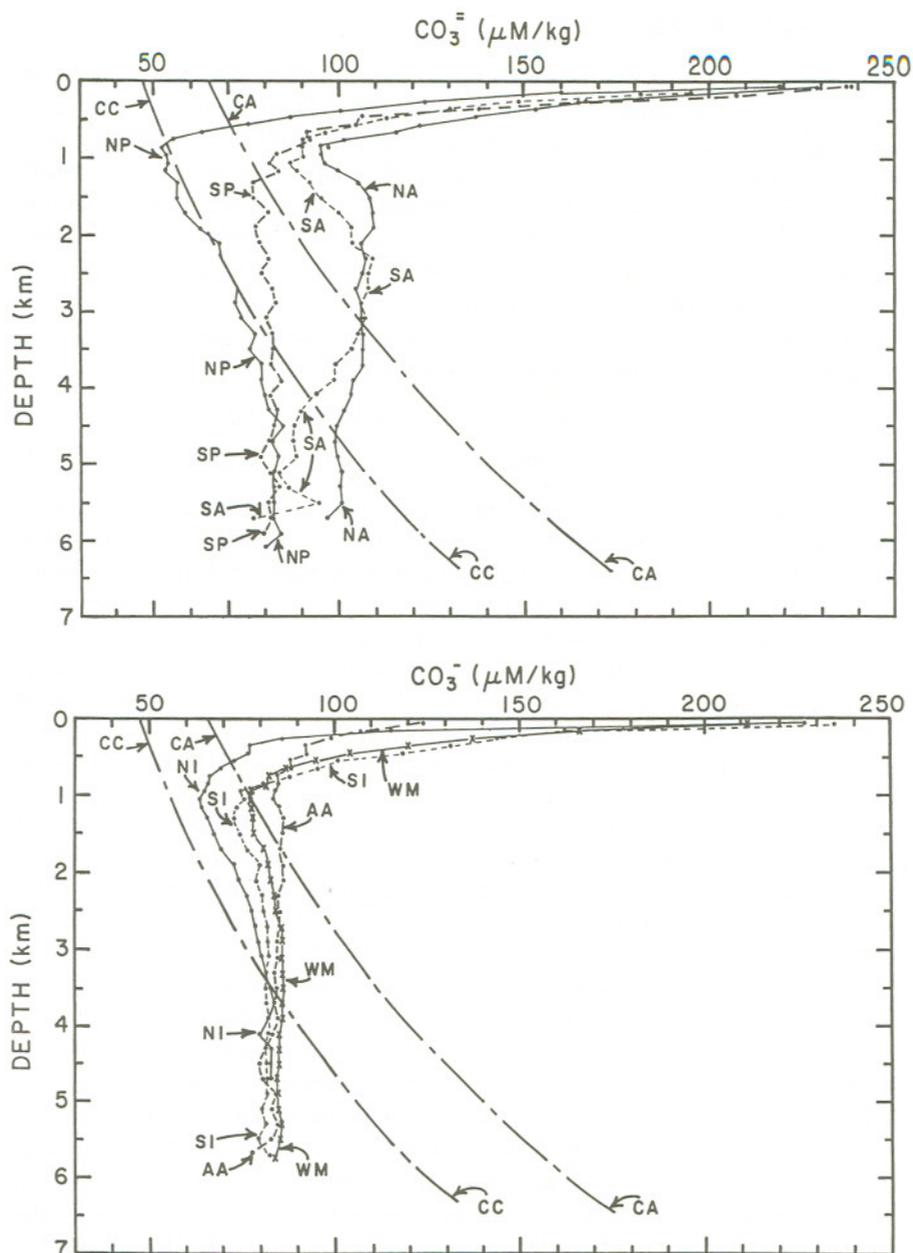


Figure 5: The vertical distribution of the CO_3^{2-} ion (a) in the Atlantic and Pacific Oceans, and (b) in the Indian Ocean, Antarctic region and mean world oceans. NA = North Atlantic, SA = South Atlantic, NP = North Pacific, SP = South Pacific, NI = North Indian, SI = South Indian, AA = Antarctic, and WM = Mean of the world oceans. The critical dissolution curves (Eqs. 3 and 4) for calcite (CC) and aragonite (CA) are also shown to indicate the depth at which marine carbonates start to dissolve into the ocean water.

5. SUMMARY

A total of approximately 6000 measurements each made for the alkalinity and total CO₂ concentration in the three major oceans of the world during the GEOSECS Expeditions, 1972–1977, has been summarized. The oceans were divided into seven regions, and the mean vertical distributions for these quantities in each region have been presented. The alkalinity and total CO₂ concentration are highest in the deep water (>2000 m) of the North Atlantic. The North Pacific deep water contains about 5% greater alkalinity and about 10% greater total CO₂ concentration than the North Atlantic deep water. These quantities in the North and South Indian Oceans are similar to those in the North and South Pacific Oceans respectively, but are in average about 1% smaller than the Pacific values.

The distribution of these quantities as well as the salinity and potential temperature in a mean world ocean was computed by averaging (area weighted) the seven regional mean values in 100 m depth intervals above 1200 m, and in 200 m depth intervals below 1200 m.

The mean vertical distribution profiles in the seven oceanic regions for the concentration of CO₃⁼ ions at *in situ* temperature and pressure conditions have been computed by averaging the individual values calculated from each pair of the alkalinity and total CO₂ measurements in a given depth interval. The CO₃⁼ concentrations are highest in the North Atlantic, and are lowest in the North Pacific region, the former being 20 to 40 μM/kg higher in the depths greater than 2 km than the latter depending upon the depth. This accounts for the position of the calcite lysocline deepest in the North Atlantic (~4.7 km) and shallowest in the North Pacific (0.8 to 2.7 km).

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