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**Oxygen-Total Inorganic Carbon Dioxide Relationship
in the Pacific Ocean***

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Abstract: The total inorganic carbon dioxide-oxygen relationship in the ocean has been studied previously using two different approaches, one of which is theoretical and the other is statistical. Discrepancies between the two sets of results have been solved in this work by applying multiple linear regression analysis to express total inorganic carbon dioxide, normalized to constant S‰, as a function of potential temperature and total alkalinity and oxygen normalized to constant S‰. Results of the regression are in agreement with the assumption that total alkalinity changes in the open ocean are only due to S‰ changes and calcium carbonate dissolution or precipitation; and with Redfield's model for the prediction of the total inorganic carbon dioxide-oxygen ratio for the biochemical oxidation.

I. Introduction

REDFIELD (1934) proposed a model to explain the proportions of organic derivatives in sea water based on dissolved oxygen concentration (O₂), phosphate (PO₄), nitrate (NO₃) and total inorganic carbon dioxide (TCO₂) data from the Western Atlantic Ocean and on the elementary composition of plankton. The model is based on the assumption that, when biological oxidation occurs, the ratios of the consumption of dissolved oxygen to the production of nutrients and carbon dioxide are constant. So that, if we want to estimate the contribution of biological oxidation to the concentration of nutrients and total inorganic carbon dioxide, we only need to calculate the amount of dissolved oxygen that has been utilized and multiply it by the respective constants associated with each of the nutrients and the inorganic carbon dioxide (ALVAREZ-BORREGO *et al.*, 1973).

When O₂ and TCO₂ are expressed in mg-at/l and mM respectively, the ratio predicted by Redfield's model is $\Delta TCO_2 : \Delta O_2 \doteq -106 : 276 \doteq -0.384$; and when O₂ is expressed in ml/l and

TCO₂ is expressed in mM the predicted ratio is $\Delta TCO_2 : \Delta O_2 \doteq -0.106 : 3.1 \doteq -0.0342$ (REDFIELD *et al.*, 1963).

POSTMA (1964) and CRAIG (1969) questioned the validity of Redfield's model because they did not find a linear relationship between O₂ and TCO₂. But CULBERSON and PYTKOWICZ (1970) have shown that when changes in TCO₂ due to all the processes other than oxidation are compensated for, linear relationships between apparent oxygen utilization (AOU) (REDFIELD, 1942) and TCO₂ with essentially the slope predicted by Redfield's model are found. CULBERSON (1972) showed that the vertical and horizontal distribution of TCO₂ in the Pacific, Indian and South Atlantic Oceans conform to Redfield's model.

CULBERSON and PYTKOWICZ (1970) and CULBERSON (1972) used a direct approach to correct their AOU and TCO₂ data. Based on theoretical considerations they corrected the data so that only the changes due to biological processes were left. Their work was essentially a test of Redfield's model. The assumptions involved in their calculations are that the specific alkalinity at the source of the waters is constant, and that changes in total alkalinity (TA) are only due to changes of S‰ and precipitation or dissolution of carbonates.

BEN-YAAKOV (1971, 1972) has introduced multiple linear regression analysis to the study

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of the relationships between TCO_2 , O_2 , TA, $T^\circ\text{C}$ and $\text{S}\%$ in the ocean. He has shown that there is a linear relation between TCO_2 , O_2 , TA and $T^\circ\text{C}$ along vertical profiles in the Eastern Pacific. For his 1971 paper he used the data of CULBERSON and PYTKOWICZ (1970) and found that the data are consistent with Redfield's model; but he suggested that two other processes, besides carbonate reaction, may be responsible for TA changes. For his 1972 paper he used data from a GEOSECS intercalibration station (CRAIG and WEISS, 1970; TAKAHASHI *et al.*, 1970) and found the 95% confidence interval for the TA regression coefficient being consistent with the assumption that, besides the $\text{S}\%$ effect, TA changes are only due to carbonate dissolution or precipitation. He indicated that possibly the inconsistency shown in his 1971 results is due to some systematic errors in the data. In his 1972 work he reports that the best estimate for the $\Delta\text{TCO}_2:\Delta\text{O}_2$ ratio, at the 95% confidence level, is -0.042 ± 0.004 mM/ml, which is not consistent with Redfield's value of -0.0342 . Thus, there exists a discrepancy between the results of CULBERSON and PYTKOWICZ (1970) and CULBERSON (1972) and the results of BEN-YAAKOV (1971), and also between the results of BEN-YAAKOV (1972) and Redfield's model.

The purpose of the present work is to solve the discrepancy between the theoretical and statistical approaches by introducing corrections to the data before the application of the statistical method.

2. Sources of data

For this study we used the data that BEN-YAAKOV (1971, 1972) used, that is, data from Stations 70 and 127 of YALOC-69 (CULBERSON and PYTKOWICZ, 1970) and data from the 1969 GEOSECS intercalibration station (CRAIG and WEISS, 1970; TAKAHASHI *et al.*, 1970). In addition to these, data from YALOC-66 cruise (BARSTOW *et al.*, 1968) are used. TCO_2 data from YALOC-66 and YALOC-69 were calculated from pH and TA data, and TCO_2 data from the 1969 GEOSECS station were measured by gas chromatography. The locations of the stations are shown in Figure 1.

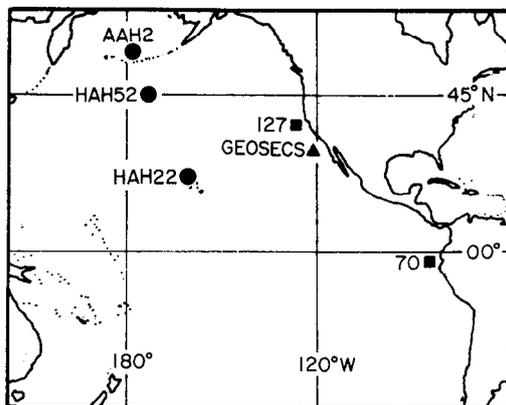


Fig. 1. Location of the stations used in this study. HAH22: $24^\circ30.6'N$, $161^\circ30.0'W$; HAH52: $45^\circ52.8'N$, $174^\circ02.3'W$; AAH2: $52^\circ56.1'N$, $177^\circ55.0'W$; 70: $04^\circ00.0'S$, $082^\circ00.0'W$; 127: $38^\circ00.2'N$, $124^\circ45.0'W$; GEOSECS: $28^\circ29.0'N$, $121^\circ38.0'W$.

3. Results and discussion

From PARK (1965):

$$\text{TCO}_2 = \text{P. TCO}_2 + \Delta\text{TCO}_{2_{\text{ox}}} + \Delta\text{TCO}_{2_{\text{CO}_3^-}} \quad (1)$$

where P. TCO_2 is the preformed total inorganic carbon dioxide, $\Delta\text{TCO}_{2_{\text{ox}}}$ is the increment of total inorganic carbon dioxide due to biological processes, and $\Delta\text{TCO}_{2_{\text{CO}_3^-}}$ is the increment of total inorganic carbon dioxide due to carbonate dissolution or precipitation.

$$\Delta\text{TCO}_{2_{\text{ox}}} = a_R(\text{AOU}) = a_R(\text{O}_2' - \text{O}_2) \quad (2)$$

$$\Delta\text{TCO}_{2_{\text{CO}_3^-}} = k(\text{TA} - \text{P. TA}) \quad (3)$$

where a_R is the $\Delta\text{TCO}_2:\Delta\text{O}_2$ ratio for biological processes, O_2' is the oxygen concentration at saturation, k is the $\Delta\text{TCO}_2:\Delta\text{TA}$ ratio, and P. TA is the preformed total alkalinity. Substituting Equations (2) and (3) in Equation (1) we have

$$\text{TCO}_2 = \text{P. TCO}_2 + a_R(\text{O}_2' - \text{O}_2) + k(\text{TA} - \text{P. TA}) \quad (4)$$

$$\text{TCO}_2 = (\text{P. TCO}_2 + a_R\text{O}_2' - k\text{P. TA}) - a_R\text{O}_2 + k\text{TA} \quad (5)$$

If a_R and k are constants, the quantity $(P. TCO_2 + a_R O_2' - kP. TA)$ is a conservative variable in the sense that it is not affected by biological or geological processes; it is only gained or lost at the boundaries. If we make a regression of TCO_2 on O_2 , TA, temperature and/or salinity, the temperature and/or salinity terms may represent the conservative fractions of total inorganic carbon dioxide, oxygen and total alkalinity, namely $(P. TCO_2 + a_R O_2' - kP. TA)$, so that the O_2 and TA terms represent only the non-conservative fractions.

According to POSTMA (1964) two of the processes that affect TA and TCO_2 are changes in $S_{\text{‰}}$ by evaporation or precipitation and formation or solution of particulate calcium carbonate. $S_{\text{‰}}$ changes cause the P. TA and P. TCO_2 to change. POSTMA (1964), CULBERSON and PYTKOWICZ (1970) and CULBERSON (1972) applied corrections to their data to account for these effects by normalizing to a constant $S_{\text{‰}}$ and constant alkalinity. They normalized the data to $S_{\text{‰}}=34.68$ which is the value that corresponds to the deep Pacific waters. When normalizing to a constant alkalinity they used $k=0.5$ based on the assumption that there are no other processes affecting TA besides those mentioned above. The factor 0.5 is to transform milliequivalents of TA to millimoles of TCO_2 . BEN-YAAKOV (1971) found the TA regression coefficient consistently higher than 0.5 (as high as 0.93) in most of the cases.

BEN-YAAKOV (1971, 1972) used a regression equation of the type

$$TCO_2 = A_0 + A_1 T^{\circ}C + A_2 O_2 + A_3 TA \quad (6)$$

where A_0 , A_1 , A_2 and A_3 are constant regression coefficients. At first it may seem that to properly apply Equation (6) to the data it is necessary to choose a portion of the water column where mixing between no more than two water types is occurring, since there is only one conservative variable in the equation. But, by comparing Equations (5) and (6) we can see that the only necessary and sufficient condition for the proper application of Equation (6) is that the conservative quantity $(P. TCO_2 + a_R O_2' - kP. TA)$ be a linear function of $T^{\circ}C$,

that is

$$P. TCO_2 + a_R O_2' - kP. TA = A_0 + A_1 T^{\circ}C \quad (7)$$

according to Equation (7) the $T^{\circ}C$ term of Equation (6) has to be able to extract the changes in the preformed fractions of total inorganic carbon dioxide, oxygen and total alkalinity, otherwise the results of the regression analysis are not correct.

The variation of the O_2 and TA regression coefficients shown by Ben-Yaakov's (1971, 1972) results may be due to either one of the following reasons: a) Equation (6) was not applied to the proper portion of the water column in all the cases; b) the changes of TCO_2 and TA due to $S_{\text{‰}}$ changes were not properly extracted by the $T^{\circ}C$ term. According to his results, when $S_{\text{‰}}$ is added to Equation (6) the adjustment of the regression coefficients is not made towards intervals consistent with the theoretical considerations. There is a significant correlation between all the variables of Equation (6) and $S_{\text{‰}}$ (BEN-YAAKOV, 1971). There are different possibilities that may happen by chance, *i.e.*: the correlations may be such that the TA term of Equation (6) represents the changes of TCO_2 due to both the $S_{\text{‰}}$ changes and the carbonate reaction. In this case the regression coefficient would not be 0.5 but a higher one. When $S_{\text{‰}}$ increases, TA and TCO_2 increase. If all the TA increase, due to $S_{\text{‰}}$ increase, would consist of carbonate ions, the factor to transform ΔTA (milliequivalents) to ΔTCO_2 (millimoles) would be 0.5. If all the TA increase would consist of bicarbonate ions, the factor to transform ΔTA to ΔTCO_2 would be 1.0. Since the borate alkalinity is small percentage-wise ($\approx 4\%$ of the TA) and since about 90% of the carbonate alkalinity consists of bicarbonate ions in the open ocean, the factor to transform ΔTA , due to changes of $S_{\text{‰}}$, to ΔTCO_2 is between 0.5 and 1.0.

If the $S_{\text{‰}}$ effect is causing the disagreement between the results obtained by BEN-YAAKOV (1971, 1972) and those obtained by CULBERSON and PYTKOWICZ (1970) and CULBERSON (1972), the results obtained by applying regression analysis to data normalized to constant $S_{\text{‰}}$

should be consistent with the results of CULBERSON and PYTKOWICZ (1970) and CULBERSON (1972).

To test the hypotheses the a_R is the value predicted by Redfield's model and k is equal to 0.5 the data were normalized to a constant $S\%$ of 34.68, and the regression equation

$$\begin{aligned} \text{TCO}_{2n} = a_0 + a_1\theta^\circ\text{C} + a_2\text{O}_{2n} + a_3\text{TA}_n \\ + \text{TCO}_{2n_{\text{res}}} \end{aligned} \quad (8)$$

was applied to the data; $\text{TCO}_{2n} = \text{TCO}_2(34.68/S\%)$, $\text{O}_{2n} = \text{O}_2(34.68/S\%)$, $\text{TA}_n = \text{TA}(34.68/S\%)$; a_0, a_1, a_2 and a_3 are constant regression coefficients, and $\text{TCO}_{2n_{\text{res}}}$ are the residuals of TCO_{2n} after regression on $\theta^\circ\text{C}, \text{O}_{2n}$ and TA_n . After normalization of the data Equation (5) is transformed to

$$\begin{aligned} \text{TCO}_2(34.68/S\%) = (P.\text{TCO}_2 + a_R\text{O}_2' \\ - kP.\text{TA})(34.68/S\%) - a_R\text{O}_2(34.68/S\%) \\ + k\text{TA}(34.68/S\%) \end{aligned} \quad (9)$$

By comparing Equations (8) and (9) we can see that the only necessary and sufficient condition for the proper application of Equation (8) is that the conservative quantity $(P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%)$ be a linear function of $\theta^\circ\text{C}$, that is:

$$\begin{aligned} (P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%) \\ = a_0 + a_1\theta^\circ\text{C} \end{aligned} \quad (10)$$

This is equivalent to saying that Equation (8) must be applied to data from a portion of the water column where the diagram of $(P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%)$ versus $\theta^\circ\text{C}$ is able to detect only two-water types mixing. We use potential temperature instead of *in situ* temperature to avoid the adiabatic heating effect of pressure.

A classical way to detect two-water-types mixing has been to look for straight portions of the temperature-salinity (T-S) diagram. But, a straight T-S diagram is a necessary but not sufficient condition for two-water-types mixing (ALVAREZ-BORREGO *et al.*, 1973). The (P.

$\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%)$ versus $\theta^\circ\text{C}$ or other diagrams may show water types that the T-S diagram does not show.

To separate the water column into portions for which Equation (10) applies we use a method similar to the one ALVAREZ-BORREGO *et al.* (1973) used when they applied regression analysis to test Redfield's model for the oxygen-nutrients relationships.

If Equation (8) is applied to the proper portion of the water column, a plot of $\text{TCO}_{2n_{\text{res}}}$ versus $\theta^\circ\text{C}$ should be completely random, because $\text{TCO}_{2n_{\text{res}}}$ should result only from the random errors in the measurements of $\text{TCO}_2, \text{O}_2, \text{TA}, S\%$ and $\theta^\circ\text{C}$. Thus, if we apply Equation (8) to the whole water column and plot $\text{TCO}_{2n_{\text{res}}}$ versus $\theta^\circ\text{C}$, the pattern shown by the diagram, if any, would give us an indication of how to separate the water column into suitable portions.

To illustrate this procedure let us examine a hypothetical example similar to the one used by ALVAREZ-BORREGO *et al.* (1973). Suppose we have data from the whole water column of a certain station, and suppose the $(P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%)$ versus $\theta^\circ\text{C}$ diagram is like the one shown in Figure 2a where at least three water types A, B and C are being detected. Since $(P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68/S\%)$ is not a linear function of $\theta^\circ\text{C}$, the plot of $\text{TCO}_{2n_{\text{res}}}$ versus $\theta^\circ\text{C}$ would generate a diagram as shown in Figure 2b which would

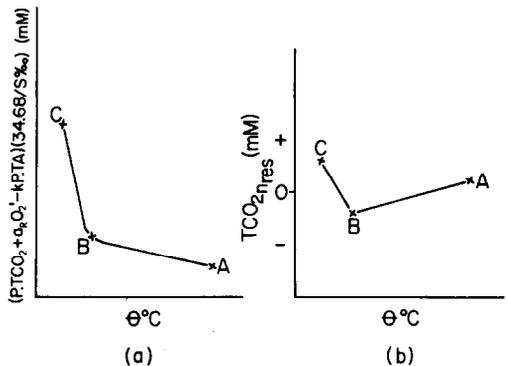


Fig. 2. $(P.\text{TCO}_2 + a_R\text{O}_2' - kP.\text{TA})(34.68\%)$ versus $\theta^\circ\text{C}$ diagram (a), and $\text{TCO}_{2n_{\text{res}}}$ versus $\theta^\circ\text{C}$ diagram (b), of a hypothetical station.

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Table 1. Regression equations expressing total inorganic carbon dioxide as a function of potential temperature, oxygen and total alkalinity. The confidence intervals are at the 95% confidence level.

STATION	TYPE OF DATA	DEPTH RANGE (METERS)	REGRESSION EQUATIONS (SHOWING 95% CONFIDENCE INTERVALS)	R ²	n-p-1 ^a	EQUATION NUMBER
HAH22 (YALOC-66) (24°30.0'N, 161°30.0'W) (near Hawaii)	Normalized to S _w = 34.68	0-4545	TCO _{2n} = (1.136±0.298) - (0.0118±0.0011)θ°C - (0.0356 ± 0.0034)O _{2n} + (0.567±0.118)TA _n	0.997	32	11†
		74-414 414-4545	TCO _{2n} = (0.961±0.654) - (0.0151±0.0007)θ°C - (0.0416 ± 0.0122)O _{2n} + (0.669±0.257)TA _n TCO _{2n} = (1.005±0.575) - (0.0089±0.0040)θ°C - (0.0339±0.0020)O _{2n} + (0.614±0.224)TA _n	0.999 0.996	7 15	12† 13†
	Not Normalized	74-414	TCO ₂ = (0.843±0.552) - (0.0131±0.0014)θ°C - (0.0421±0.0133)O ₂ + (0.706±0.208)TA	0.999	7	14†
		414-4545	TCO ₂ = (0.743±0.394) - (0.0090±0.0038)θ°C - (0.0332±0.0019)O ₂ + (0.716±0.153)TA	0.997	15	15†
70 (YALOC-69) (04°00.0'S, 082°00.0'W) (off Ecuador)	Normalized to S _w = 34.68	0-3432	TCO _{2n} = (0.511±0.710) - (0.0088±0.0028)θ°C - (0.366±0.070)O _{2n} + (0.805±0.294)TA _n	0.998	22	16‡
		0-98 398-3432	TCO _{2n} = (1.766±3.892) - (0.0053±0.0042)θ°C - (0.376±0.112)O _{2n} + (0.234±1.68)TA _n TCO _{2n} = (0.904±0.528) - (0.0091±0.0033)θ°C - (0.333±0.077)O _{2n} + (0.641±0.220)TA _n	0.998 0.991	4 11	17‡ 18‡
	Not Normalized	0-98	TCO ₂ = (1.749±2.044) - (0.0058±0.0034)θ°C - (0.394±0.062)O ₂ + (0.25±0.87)TA	0.999	4	19‡
		398-3432	TCO ₂ = (0.729±0.396) - (0.0074±0.0024)θ°C - (0.316±0.079)O ₂ + (0.709±0.176)TA	0.992	11	20‡
127 (YALOC-69) (38°00.2'N, 124°45.0'W) (off California)	Normalized to S _w = 34.68	0-3843	TCO _{2n} = (1.556±0.378) - (0.0123±0.0028)θ°C - (0.332±0.028)O _{2n} + (0.386±0.154)TA _n	0.998	22	21‡
		197-3843	TCO _{2n} = (1.766±3.892) - (0.0053±0.0042)θ°C - (0.376±0.112)O _{2n} + (0.234±1.68)TA _n TCO _{2n} = (0.868±0.924) - (0.0072±0.0065)θ°C - (0.346±0.016)O _{2n} + (0.650±0.372)TA _n	0.997	14	22‡
	Not Normalized	197-3843	TCO ₂ = (0.939±0.638) - (0.0105±0.0077)θ°C - (0.346±0.013)O ₂ + (0.631±0.252)TA	0.999	14	23‡
		0-4000	TCO _{2n} = (1.570±0.398) - (0.0078±0.0024)θ°C - (0.0387±0.0045)O _{2n} + (0.346±0.169)TA _n	0.991	24	24‡
GROSECS 1969 (28°29'N, 121°38'W) (off Baja California)	Normalized	0-4000	TCO _{2n} = (1.570±0.398) - (0.0078±0.0024)θ°C - (0.0387±0.0045)O _{2n} + (0.346±0.169)TA _n	0.991	24	24‡
	Not Normalized	0-4000	TCO ₂ = (1.241±0.334) - (0.0082±0.0026)θ°C - (0.0410±0.0042)O ₂ + (0.482±0.138)TA	0.993	24	25‡

^a n-p-1 are the residual degrees of freedom, n is the number of observations and p is the number of independent variables already in the regression equation.

[†] O₂ and O_{2n} expressed in ml/l, and TCO₂ and TCO_{2n} in mM/l.

[‡] O₂ and O_{2n} expressed in mg-at O₂/kg, and TCO₂ and TCO_{2n} in mM/kg.

[§] O₂ and O_{2n} expressed in ml/kg, and TCO₂ and TCO_{2n} in mM/kg.

detect the three water types A, B and C. Thus, each minimum and maximum in the TCO_{2n,RES} versus θ°C diagram represents a different water type.

This procedure was applied to some field data. Both regression Equations (6) and (8) were applied to the data to show that in some cases Equation (6) gives a confidence interval for the TA regression coefficient inconsistent with the expected value of 0.5, and in other cases it gives a confidence interval for the O₂ regression coefficient inconsistent with Redfield's model while Equation (8) gives confidence intervals consistent with the theoretical values. The regression analysis was performed by a computer program (SIPS) (OREGON STATE UNIVERSITY, 1971). The results are shown in Table 1. Confidence levels of 95% are given for each of the coefficients of the resulting regression equations. In Table 1, for each station, equations are given for the whole water column first and then for the depth ranges

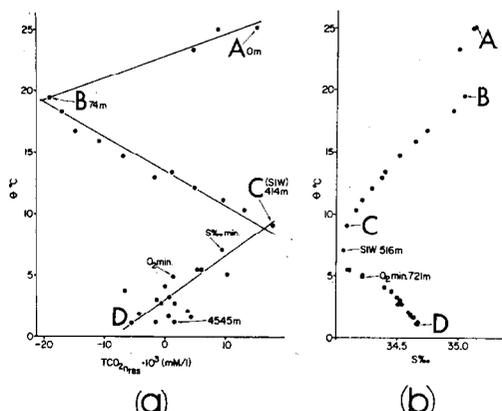


Fig. 3. θ°C-TCO_{2n,RES} diagram (a), and θ°C-S_w diagram (b) for the whole water column of Station HAH22. A, B, C and D denote water types. SIW means Subarctic Intermediate water.

chosen according to the TCO_{2n,RES} versus θ°C diagrams.

This treatment is illustrated with Station

HAH22 as follows. The $\text{TCO}_{2_{n_{\text{res}}}}$ versus $\theta^{\circ}\text{C}$ and the $\theta^{\circ}\text{C}$ - $\text{S}\%$ diagrams for the whole water column of Station HAH22 are shown in Figures 3a and b, respectively. A definite dependency of $\text{TCO}_{2_{n_{\text{res}}}}$ on $\theta^{\circ}\text{C}$ is shown in Figure 3a. Both diagrams (Figures 3a and b) show very distinctly four water types A, B, C and D, where C is the Subarctic Intermediate water. Equation (11) (Table 1) has confidence intervals for the O_2 and TA regression coefficients consistent with Redfield's number and 0.5, respectively. We consider this agreement fortuitous since, according to Figure 3a, there is no oceanological or statistical basis to justify the coefficient for $\theta^{\circ}\text{C}$ as a valid one. According to Figure 3a Equation (11) is not properly describing the data.

A separation of the data from HAH 22 into two subsets was done; one from B to C and another from C to D; and Equations (6) and (8) were applied to them. Between A and B (Figure 3a) there are only two data points; therefore, no regression was applied to that portion of the water column. Although not shown here, if we apply Equation (6) to the whole water column of Station HAH 22 and plot $\text{TCO}_{2_{n_{\text{res}}}}$ versus $\theta^{\circ}\text{C}$, the resulting diagram is very similar to Figure 3a, with the same points as maxima and minima. A similar statement applies to the other stations.

Equations (12) and (14) (Table 1) have confidence intervals, for the oxygen and total alkalinity regression coefficients, consistent with the theoretical values. They show that, with or without normalization of the data, from the depth range 74-414 m of HAH 22, to constant $\text{S}\%$, we obtain essentially the same results.

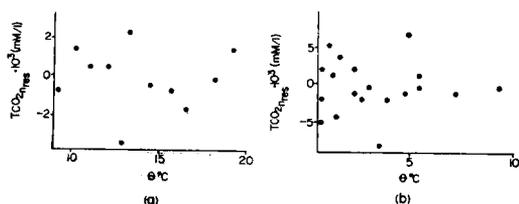


Fig. 4. $\text{TCO}_{2_{n_{\text{res}}}}$ versus $\theta^{\circ}\text{C}$ diagrams for the portions of the water column between (a) 74 and 414 m, and (b) 414 and 4,545 m of Station HAH 22.

But, while Equation (13) shows confidence intervals consistent with the theory, Equation (15) has a confidence interval for the TA regression coefficient that is not consistent with the value 0.5. Thus, in this case normalization to a constant $\text{S}\%$ improved the results of the regression.

Figures 4a and b show the $\text{TCO}_{2_{n_{\text{res}}}}$ versus $\theta^{\circ}\text{C}$ diagrams for the depth ranges 74-414 m and 414-4,545 m of HAH 22. These diagrams do not show any particular trend. This indicates that $\text{TCO}_{2_{n_{\text{res}}}}$ result from only the random errors in the measurements of TCO_2 , O_2 , TA, $\text{S}\%$ and $\theta^{\circ}\text{C}$, and that Equations (12) and (13) are properly describing the data.

The total alkalinity regression coefficients of Equations (17) and (19) are not significantly different from zero. This indicates that possibly solution or precipitation of calcium carbonate does not significantly affect TCO_2 in the depth range 0-98 m of Station 70. PYTKOWICZ (1972) (and previous authors cited therein) indicates that sea water is supersaturated with respect to calcite in the upper few hundred meters in the open ocean. Thus, no net dissolution of calcium carbonate is expected to occur in the upper few hundred meters. The confidence intervals for the oxygen regression coefficients of Equations (17) and (19) (Table 1) are consistent with Redfield's model. This indicates that, in the depth range 0-98 m of Station 70, TCO_2 is not only controlled by air-sea exchange, but biological oxidation is an important factor. For Equation (17), without the TA_n term, the O_{2_n} regression coefficient is -0.365 ± 0.062 , and for Equation (19), without the TA term, the O_2 regression coefficient is -0.388 ± 0.052 . These two intervals are consistent with Redfield's model. CULBERSON and PYTKOWICZ (1970) found agreement with Redfield's model only below 98 m at Station 70. Possibly the disagreement found by them in the upper 98 m was due to their assumed constant initial specific alkalinity not applying to this depth range.

Equations (18) and (20) (Table 1) have confidence intervals for the oxygen regression coefficient consistent with Redfield's model. But, while Equation (18) has a confidence interval for the TA_n regression coefficient consistent

with 0.5, the one for Equation (20) is not consistent with 0.5. Again, normalization of the data before application of regression analysis has improved the results.

For the depth range 197 to 3,843 m of Station 127 the results are essentially the same with or without normalization of the data to constant S‰ (Equations 22 and 23, Table 1). The confidence intervals for the total alkalinity regression coefficients of Equations (22) and (23) are consistent with 0.5. But the confidence intervals for the oxygen regression coefficients of these equations are not consistent with Redfield's model, they are a little too low. This is the only case in which we found disagreement between our results and Redfield's model. CULBERSON and PYTKOWICZ (1970) found agreement between their corrected data and Redfield's model below 400 m for Station 127.

Equation (24) has confidence intervals for the O_{2n} and TA_n regression coefficients consistent with Redfield's model and 0.5, respectively. Equation (25) (Table 1) has a confidence interval for the TA regression coefficient consistent with 0.5, but it has a confidence interval for the O_2 regression coefficient inconsistent with Redfield's model. Once again, the normalization improved the results of the regression. BEN-YAAKOV (1972) applied regression analysis to data without normalization, from this station, and reported as his best estimate for the O_2 regression coefficient a confidence interval that is not consistent with Redfield's model.

The coefficients of determination (R^2) (DRAPER and SMITH, 1966) are higher than 0.99 for all of our results (Table 1). This indicates that a very high fraction of the variability of TCO_{2n} and TCO_2 has been explained by the regressions. The results of the regressions with and without normalization of the data to constant S‰ (Table 1) are not statistically different. The 95% confidence intervals overlap in all cases. However, they are different in that, while the results obtained without normalization sometimes are consistent and sometimes are not consistent with the theoretical considerations, the results obtained with normalization are always consistent with the theory. The values

of R^2 for the regression equations with and without normalization of the data (Table 1) are not significantly different.

Diagrammatic illustration of the extraction of the mixing effect, the S‰ effect and the carbonate reaction effect

According to the results given above, data from the depth range 197-3,843 m of Station 127 of YALOC-69, and data from the whole water column of the 1969 GEOSECS station (Table 1) can be properly described by regression Equation (8). This gives us an opportunity to illustrate diagrammatically the extraction of the mixing, S‰ and carbonate reaction effects on the TCO_2 by applying regression analysis to normalized data; so that only the biological effect is left and, in agreement with Redfield's model, a linear relationship between dissolved oxygen and total inorganic carbon dioxide is left.

When regressing TCO_{2n} on O_{2n} , TA_n and $\theta^\circ C$, since O_{2n} , TA_n and $\theta^\circ C$ are correlated to a certain extent, the O_{2n} term represents the regression of the residuals of TCO_{2n} , after regression on $\theta^\circ C$ and TA_n , on the residuals of O_{2n} , after regression on $\theta^\circ C$ and TA_n . In other words, if we do the regression in a stepwise manner, adding $\theta^\circ C$ and TA_n first we have

$$TCO_{2n} = c_0 + c_1\theta^\circ C + c_2TA_n + TCO_{2n_r} \quad (26)$$

and implicitly and simultaneously

$$O_{2n} = d_0 + d_1\theta^\circ C + d_2TA_n + O_{2n_r} \quad (27)$$

where c_0 , c_1 , c_2 , d_0 , d_1 and d_2 are constant regression coefficients and TCO_{2n_r} and O_{2n_r} are the TCO_{2n} and O_{2n} residuals after regression on $\theta^\circ C$ and TA_n .

When we add O_{2n} to regression Equation (26), what we are doing is regressing TCO_{2n_r} on O_{2n_r}

$$TCO_{2n_r} = f_0 + a_2O_{2n_r} + TCO_{2n_{res}} \quad (28)$$

where f_0 and a_2 are constant regression coefficients and $TCO_{2n_{res}}$ is as defined for Equation (8); substituting the value of O_{2n_r} from Equation (27) into Equation (28) we have

$$\text{TCO}_{2_{n_r}} = (f_0 - a_2d_0) - a_2d_1\theta^\circ\text{C} + a_2\text{O}_{2_n} - a_2d_2\text{TA}_n + \text{TCO}_{2_{n_{res}}} \quad (29)$$

substituting Equation (29) into Equation (26)

$$\text{TCO}_{2_n} = (c_0 + f_0 - a_2d_0) + (c_1 - a_2d_1)\theta^\circ\text{C} + a_2\text{O}_{2_n} + (c_2 - a_2d_2)\text{TA}_n + \text{TCO}_{2_{n_{res}}} \quad (30)$$

$(c_0 + f_0 - a_2d_0)$, $(c_1 - a_2d_1)$ and $(c_2 - a_2d_2)$ are constants, we can represent them by the symbols a_0 , a_1 and a_3 respectively; Equation (30) is the same as Equation (8). The O_{2_n} regression coefficient of Equation (8), a_2 , is the slope of the $\text{TCO}_{2_{n_r}}$ versus $\text{O}_{2_{n_r}}$ diagram.

The $\text{TCO}_2 - \text{O}_2$ and $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagrams for the depth range 197-3,843 m of Station 127 of YALOC-69 are shown in Figures 5a and b. Figures 6a and b show the $\text{TCO}_2 - \text{O}_2$ and

$\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagrams for the whole water column (0-4,000 m) of the 1969 GEOSECS station. Figures 5a and 6a show that the $\text{TCO}_2 - \text{O}_2$ diagrams for these stations are not linear, they have a hook-like shape. Figures 5b and 6b show that after normalizing the data and regressing $\text{TCO}_{2_{n_r}}$ and $\text{O}_{2_{n_r}}$ on $\theta^\circ\text{C}$ and TA_n , the hook-like shape disappeared. For Station 127 the $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ correlation coefficient is -0.997 , and for the GEOSECS station it is -0.964 . In Figures 5b and 6b the data points do not follow a sequence, with reference to depth, along the line. In other words, the points at one end are not necessarily the near surface points, and the points at the other end are not necessarily the deep points. The data points at the upper end of the $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagrams correspond to the O_2 minimum zone. $\text{TCO}_{2_{n_r}}$ and $\text{O}_{2_{n_r}}$ should not be regarded as the oxidative fractions of TCO_{2_n} and O_{2_n} . By definition the $\text{TCO}_{2_{n_r}}$'s and $\text{O}_{2_{n_r}}$'s add to zero, respectively. The $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagram is useful only for calculating the ratio of the oxidative fractions of TCO_{2_n} and O_{2_n} .

TCO₂ - O₂ relationship in the Northeastern Pacific Ocean and Southeastern Bering Sea

In the Northeastern Pacific the $\text{TCO}_2 - \text{O}_2$ relationship for the region of the water column above the O_2 minimum zone varies systematically with latitude (Figure 7). The slope of this relationship is highest near Hawaii and lowest in the Bering Sea. In the entire water column the slope changes with depth. This correlates very well with the results obtained by ALVAREZ-BORREGO *et al.* (1973) for the O_2 -nutrient relationships. According to the results discussed above these variations of the $\text{TCO}_2 - \text{O}_2$ relationship with latitude and with depth are due to mixing between different water types with different preformed fractions of TCO_2 and O_2 ; and to the TA varying with depth as a result of $\text{S}\%$ changes and calcium carbonate reaction.

4. Conclusions

When applying multiple linear regression analysis to express total inorganic carbon dioxide as a function of oxygen, total alkalinity and

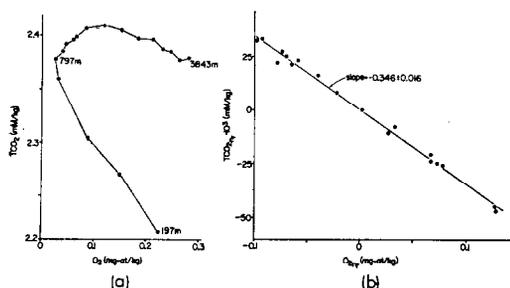


Fig. 5. $\text{TCO}_2 - \text{O}_2$ diagram (a), and $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagram (b), for the portion of the water column between 197 and 3,843 m of Station 127.

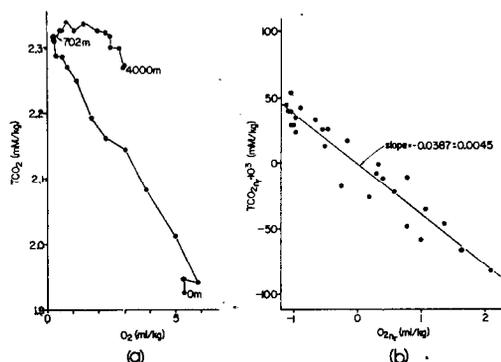


Fig. 6. $\text{TCO}_2 - \text{O}_2$ diagram (a), and $\text{TCO}_{2_{n_r}} - \text{O}_{2_{n_r}}$ diagram (b), for the whole water column of the 1969 GEOSECS station.

Oxygen-Total Inorganic Carbon Dioxide Relationship in the Pacific Ocean

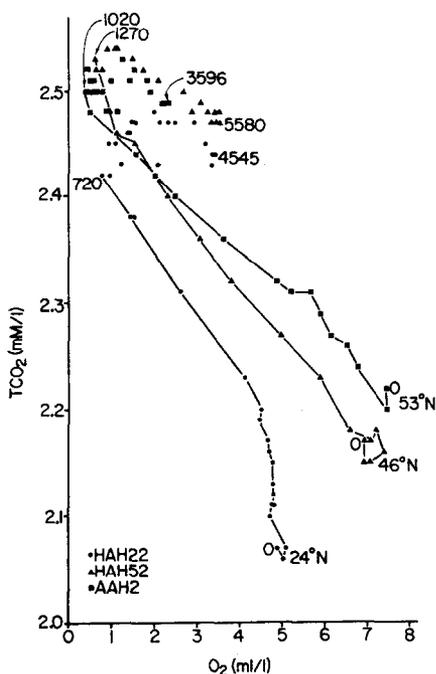


Fig. 7. TCO_2 - O_2 diagrams for the whole water column of Stations HAH22, HAH52, and AAH2. The numbers by the data points represent depth in meters.

potential temperature, better results are obtained if the data are first normalized to a constant $S_{\text{‰}}$. If the normalization is not done, it is difficult to properly associate any physical meaning to the regression coefficients. Without the normalization sometimes the results are misleading due to the fact that total alkalinity or oxygen terms may represent not only the carbonate reaction or biological oxidation effects, respectively, but also the $S_{\text{‰}}$ effect on the TCO_2 .

Results obtained by applying multiple linear regression analysis to data normalized to constant $S_{\text{‰}}$ are consistent with the hypothesis that TA changes are only due to $S_{\text{‰}}$ changes and dissolution or precipitation of calcium carbonate. These results are also consistent, with only one exception, with Redfield's model.

In the Northeastern Pacific Ocean and Southeastern Bering Sea the total inorganic carbon dioxide-oxygen relationship varies with depth.

For the region of the water column above the oxygen minimum zone it varies systematically with latitude. These variations are due to mixing between different water types with different preformed portions of total inorganic carbon dioxide and oxygen, and to total alkalinity varying with depth as a function of $S_{\text{‰}}$ and carbonate reaction.

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太平洋における溶存酸素と全炭酸の関係

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要旨: 海洋における全炭酸と溶存酸素の関係は、従来、理論および統計の両面から研究が進められてきたが、その結果は一致しないことが多かった。本研究では、ポテンシャル水温と全アルカリ度を用い、一定の塩分量に換算した全炭酸と、一定の塩分量に換算した酸素とを用いて、多変数解析法を適用し、両方法の結果を一致させる

ことができた。この結果、外洋における全アルカリ度の変化は、塩分量の変化と、炭酸カルシウムの溶解・沈殿だけで済むという仮定が正しいことが明らかになり、さらに、生化学的酸化の際の全炭酸・酸素比に関する REDFIELD のモデルとも一致することがわかった。