

## ON THE CO<sub>2</sub>—O<sub>2</sub> SYSTEM IN THE NORTHEASTERN PACIFIC

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### ABSTRACT

Ben-Yaakov, S., 1972. On the CO<sub>2</sub>—O<sub>2</sub> system in the Northeastern Pacific. *Mar. Chem.*, 1: 3–26.

The TCO<sub>2</sub>, O<sub>2</sub>, TA and δ<sup>13</sup>C data of the 1969 Geosecs Intercalibration Cruise was analyzed and found to be consistent with a vertical mixing model which assumes that each point along a vertical profile is a mixture of the upper and lower boundaries. Calculated regression coefficients are in agreement with the model of Redfield et al. (1963) and with the assumption that TA variation is due to carbonate reaction. Oxygen consumption and TCO<sub>2</sub> production decrease exponentially with depth and approximately 80% of ΔCO<sub>2</sub> can be accounted for, on average, by O<sub>2</sub> consumption. The remaining 20% are probably due to carbonate solution which seems to take place at depths below 2,500 m. The present study suggests that the isotopic composition (δ<sup>13</sup>C) of the carbon source, required to account for most of the oxygen consumed, may be heavier than the value of –23‰ assigned to dissolved organic carbon and particulate organic carbon.

### INTRODUCTION

The primary objective of the 1969 Geosecs Intercalibration Cruise was the “refinement of techniques and intercalibration of results obtained by various participating laboratories” (Turekian, 1970). However, the intercalibration cruise did not only provide a framework for comparing analytical techniques, but also produced the most comprehensive set of geochemical data ever measured at one station. The results of this expedition have been extensively discussed by the participating scientists and reported in the *Journal of Geophysical Research* (75: 7639–7695; 1970). It is imperative, however, that the 1969 Geosecs data be analyzed by as many techniques as possible to help in evaluating the results and planning the Geosecs program.

This paper is an attempt to study the CO<sub>2</sub>—O<sub>2</sub> system in the Northeastern Pacific by analyzing the TCO<sub>2</sub>, O<sub>2</sub>, TA and δ<sup>13</sup>C of the 1969 Geosecs Station. These data have been analyzed by Craig and Weiss (1970) and Kroopnick et al. (1970), who concluded that the data is not inconsistent with a diffusion-advection mixing model. The present study, however, is an attempt to study the system without pre-assuming a specific mixing mechanism, using multiple regression analyses (Ben-Yaakov, 1971) and other linear calculations to determine which model the calculated results fit most closely. The analyses were designed

to study: (1) the exchange coefficient  $TCO_2-O_2$  and  $TCO_2-TA$ ; (2) to estimate the  $\delta^{13}C$  of the  $CO_2$  sources; (3) to estimate the percentage contribution of  $O_2$  and  $TA$  variations to  $CO_2$ ; and (4) to estimate the rate of in situ processes.

#### $TCO_2$ REGRESSION ANALYSIS

The hydrographic data of the 1969 Geosecs Intercalibration Station ( $28^\circ 29' N$   $121^\circ 38' W$ ) show a linear relation between salinity and potential temperature over the 0.85-km to 4-km depth section. Craig and Weiss (1970) have fitted a vertical diffusion–advection mixing model to the data and calculated the parameter  $z^*$  (the ratio of vertical eddy-diffusion coefficient to vertical velocity; Craig, 1969) for the stable conservative tracers data. The values obtained for the salinity and potential-temperature fit were found to be identical to within the measurement accuracy of these variables. These results indicate that the water column between 0.85 km and 4 km can be described by a diffusion–advection mixing model. Namely, each point along this section can be considered to be a mixture of the boundary waters.

It was shown by Ben-Yaakov (1971) that the concentration of total dissolved  $CO_2$  ( $TCO_2$ ) of each point along a vertical profile, under the above mixing conditions, can be expressed as:

$$TCO_2 = A + A_T \cdot T + A_O \cdot O_2 + A_A \cdot TA \quad (1)$$

where  $T$ ,  $O_2$  and  $TA$  are temperature, total dissolved  $O_2$  and total alkalinity, respectively, and the  $A$ 's are constants. Eq.1 pre-assumes that  $TCO_2$  variations, along the mixing path, are linearly proportional to  $O_2$  and  $TA$  variations. The stable conservative variable (temperature) in the equation serves as a measure to the amount of mixing that has taken place. The relation can be extended to the general case in which each point is a mixture of  $n$  water sources. In such a case, one would have to incorporate in eq.1,  $n - 1$  stable conservative tracers (Ben-Yaakov, 1971).

Eq.1 can be fitted to a set of data by the multivariable regression analysis method (Draper and Smith, 1966; Ben-Yaakov, 1971) from which the constants  $A$ 's can be estimated. These constants reflect the dependencies between  $TCO_2$  and the other variables in the regression. Hence, the constant  $A_O$  reflects the  $TCO_2-O_2$  relation given that all the other variables are constant. Namely:

$$A_O = \frac{\partial TCO_2}{\partial O_2} \quad (2)$$

Similar definitions hold for  $A_A$  and  $A_T$ .

An important feature of the multivariable regression analysis technique is that it extracts the constants  $A$ 's directly from the raw data by applying the least square fitting method. The technique is essentially an extension of the well-known two-dimensional regression analysis and one can calculate statistical measures, such as multiple correlation coefficients and  $F$  ratios, to estimate the goodness of fit.

Using the least square method, the TCO<sub>2</sub> data of the 1969 Geosecs station was fitted to the model of eq.1. Calculations were carried out by a computer program (BMD02R) prepared by the biomedical research group of the University of California at Los Angeles (Dixon, 1970). This program calculates a sequence of regressions according to a pre-specified code. Using this process, one can evaluate the relative importance of a given variable to the regression.

Table I summarized some of the TCO<sub>2</sub> regression analyses of the 1969 Geosecs Intercalibration station data. The TCO<sub>2</sub> and O<sub>2</sub> data were measured by Weiss (Craig and Weiss, 1970) while the total alkalinity data was measured by Edmond (Takahashi et al., 1970). Since the two sets of data were not measured on the same cast, Edmond's TA data had to be interpolated to the depths reported by Weiss. Interpolation was accomplished by fitting the TA data to a fifth order polynomial in depth. The polynomial was then used to calculate the TA values corresponding to the Weiss data. Accuracy of interpolation was tested by re-calculating the original TA values. Maximum deviation was 0.04 mequiv./kg while the standard error of estimate (square root of the variance) was found to be 0.014 mequiv./kg, which is approximately 0.6% of the mean value of TA along the profile. This is about twice the estimated precision and accuracy of the measuring technique. However, higher degree polynomials (up to seventh degree) did not improve the fitting. The polynomial interpolation technique was favored over the Lagrange-type interpolation scheme since the least square method, used during the polynomial fitting, tends to smooth some errors due to the finite accuracy of measurement and due to sample handling. This point will be further discussed below.

Table I demonstrates that TCO<sub>2</sub> along the vertical profile of the 1969 Geosecs Station can closely be described by eq.1. Since addition of salinity to the regression does not markedly improve the fit, one can conclude that the TCO<sub>2</sub> profile is not inconsistent with a two-source mixing model. Also, replacing  $T$  by potential temperature ( $\hat{T}$ ) does not seem to improve the fitting. This can be explained perhaps by the fact that the major TCO<sub>2</sub>-O<sub>2</sub> and TA changes occur at the upper layer where the difference between temperature and potential temperature is negligible.

Regression analysis with  $T$  (or  $\hat{T}$ ) instead of  $S$  yields, in general, a better fit. This should probably be attributed to the non-linearity of the  $S$ - $T$  diagram at the upper water layer (Craig and Weiss, 1970). The non-linearity is probably reflecting seasonal variations which may vary the temperature and salinity of the upper layer in a non-linear manner. The solubility of gases in seawater is strongly dependent on temperature and, to a lesser degree, on salinity. Hence, the contribution of  $T$  to the regression not only serves as a measure for the mixing process (Ben-Yaakov, 1971), but also reflects the variable conditions at the upper layer of the ocean.

The best fit (highest multiple correlation coefficient and  $F$  ratio) was obtained for the 0-3,598 m depth section when the variables in regression were TCO<sub>2</sub>, O<sub>2</sub>, TA and  $T$  (or  $\hat{T}$ ). The high correlation coefficient and  $F$  ratio (approximately 0.997 and 1,500, respectively) suggest that this fit is highly significant and that eq.1 is adequately (statistically speaking) representing the data. The fit for the 0-4,100-m depth section has a somewhat lower

TABLE I

Regression coefficients of  $TCO_2$  measured during 1969 Geosecs Intercalibration Cruise

Depth range	Variables in regression	$A_T$ (mmole/kg °C)		$A_S$ (mmole/kg ‰)		$A_O$ (mmole/ml)		$A_A$ (mmole/mequiv.)		A (mmole/kg)	R	F
		value	S	value	S	value	S	value	S			
0-4100	T, O <sub>2</sub> , TA	-0.00673	0.00158	-	-	-0.04365	0.00227	0.55270	0.08639	1.07321	0.9951	1057.478
0-4100	S, T, O <sub>2</sub> , TA	-0.00651	0.00157	0.05430	0.04074	-0.04018	0.00344	0.35160	0.17331	-0.32762	0.9954	813.436
0-4100	T̄, O <sub>2</sub> , TA	-0.00661	0.00158	-	-	-0.04394	0.00225	0.54922	0.08877	1.08050	0.9951	1042.338
0-4100	S, T̄, O <sub>2</sub> , TA	-0.00638	0.00157	0.05365	0.04110	-0.04051	0.00344	0.35141	0.17513	-0.30537	0.9953	799.932
0-3598	T̄, O <sub>2</sub> , TA	-0.00662	0.00134	-	-	-0.04186	0.00198	0.63104	0.07737	0.88778	0.9972	1464.914
0-3598	S, T, O <sub>2</sub> , TA	-0.00650	0.00134	0.04086	0.03606	-0.03930	0.00300	0.47244	0.15972	-0.14890	0.9973	1111.487
0-3598	T, O <sub>2</sub> , TA	-0.00658	0.00133	-	-	-0.04200	0.00196	0.62533	0.07830	0.90060	0.9972	1467.521
0-3598	S, T̄, O <sub>2</sub> , TA	-0.00645	0.00133	0.03916	0.03614	-0.03956	0.00298	0.47417	0.15982	-0.09500	0.9973	1108.615
300-3598	S, O <sub>2</sub> , TA	-	-	0.08630	0.10033	-0.03954	0.00398	0.57427	0.36172	-1.98258	0.9788	152.452
300-3598	T, O <sub>2</sub> , TA	-0.02529	0.00881	-	-	-0.03614	0.00307	-0.14748	0.36089	2.80097	0.9845	210.075
300-3598	T̄, O <sub>2</sub> , TA	-0.02216	0.00831	-	-	-0.03750	0.00289	-0.04208	0.35163	2.53777	0.9838	200.576
800-3598	T, O <sub>2</sub> , TA	-0.09436	0.02850	-	-	-0.06251	0.01113	-1.99648	0.81384	7.48115	0.9354	16.319
800-3598	S, T, O <sub>2</sub> , TA	-0.10657	0.03732	-0.11606	0.21072	-0.06347	0.01186	-2.08799	0.87358	11.75056	0.9386	11.097

<sup>1</sup> Calculations are based on  $TCO_2$  and  $O_2$  data measured by R. Weiss; TA data measured by J. Edmond (Craig and Weiss, 1970; Takahashi et al., 1970).

S = standard error of estimate; R = multiple correlation coefficient; F =  $\sqrt{\text{regression variance/residuals variance}}$ .

correlation coefficient and  $F$  ratio. This is perhaps due to CO<sub>2</sub> diffusion from sea floor (approximately 4,100 m) as suggested by Weiss' data. One would not expect, therefore, that eq.1 should hold in the water mass overlying the sediment since it represents a different water source.

Analyses of portions of the profile (300–3,598 m and 800–3,598 m) produced a somewhat lower degree of fitting as indicated by the smaller correlation coefficients and  $F$  ratios. This should be attributed to the loss of degrees of freedom – as less data points are available for the analysis – and to the fact that all the variables undergo only a slight variation at depth. For example, TCO<sub>2</sub> variation between 800 and 3,598 m is only 0.03 mmole/kg which is approximately 1% of the mean value. Since the precision and accuracy of analysis of TCO<sub>2</sub> were estimated to be approximately 0.3% and 0.5%, respectively (Takahashi et al., 1970) one would expect a rather large relative error in TCO<sub>2</sub> over the 800–3,500 m section.

Fig.1 is a plot of TCO<sub>2</sub> residuals (the difference between measured and calculated values) versus depth. The range of the residuals is approximately  $\pm 0.020$  mmole/kg which is approximately 0.6% of the mean value. However, the residuals reflect not only the error in TCO<sub>2</sub>, but also errors in other variables in the regression. Hence, the precision of the gas chromatographic TCO<sub>2</sub> determination, used by Weiss, was probably better than 0.6%.

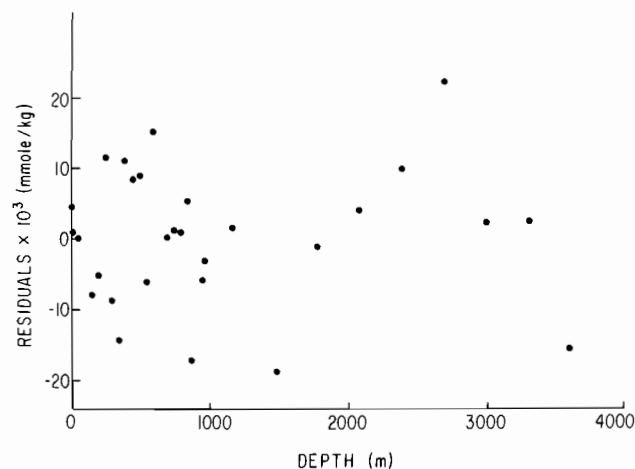


Fig.1. Residuals of TCO<sub>2</sub> regression. Analysis range: 0–3,598 m. Variables in regression: TCO<sub>2</sub>, O<sub>2</sub> (measured by Weiss, Craig and Weiss, 1970), TA (measured by Takahashi, et al., 1970) and  $T$ . (See Table I.)

The exchange coefficient between TCO<sub>2</sub> and O<sub>2</sub> ( $A_O$ ) was found to be (Table I) approximately  $-0.04$  mmole/ml for all the analyses. The higher values, obtained by analyzing the 800–3,500 m segment, are not significant since the standard error of estimate ( $S$ ) was approximately 0.01 mmole/ml so that the actual 95% confidence range of  $A_O$  for this analysis is approximately  $-0.04$  to  $-0.08$  mmole/ml. The best estimate (lowest  $S$ ) seems to have been obtained from the analysis on the 0–3,598 section. The

exchange coefficient is estimated from this analysis to be  $0.042 \pm 0.004$  mmole/ml where the plus-minus value covers the 95% confidence limits.

The best estimate for  $A_A$  (exchange coefficient between  $TCO_2$  and  $TA$ ) was also obtained from the analysis on the 0–3,598 m section. The 95% confidence limits range estimated from the present analysis is  $0.63 \pm 0.14$  mmole/mequiv. The standard error of estimate ( $S$ ) for  $A_A$  is somewhat higher than that for  $A_O$  (10% for  $A_A$  as compared to 5% for  $A_O$ ), which may be due, partly, to errors introduced during the interpolation process. It should be recalled that  $TA$  and  $TCO_2$  were not measured on the same water samples.

During the 1969 Geosecs Intercalibration Cruise,  $TCO_2$  was measured on board ship both by R. Weiss (Craig and Weiss, 1970) and J. Edmond (Takahashi et al., 1970). The two sets of data were found to be inconsistent to within 2% with Edmond's data systematically higher. The discrepancy was attributed by Takahashi et al. (1970) to an error in Edmond's  $TCO_2$  values due to the use of chloroform as a poisoning agent. The postulated error in Edmond's data offers one the opportunity to check the effects of such practical inaccuracies on the results of the multivariable regression analysis. Some of the analyses were, therefore, repeated on Edmond's  $TCO_2$  data and the results are summarized in Table II.

The regression coefficients obtained during these calculations are, as one would expect, systematically different from the coefficient calculated from Weiss' data. The absolute value of the  $TCO_2$ – $O_2$  exchange coefficient,  $A_O$ , is lower by about 10% when compared to the results of Table I.

The calculated variation of the regression coefficients due to an error in  $TCO_2$  are somewhat larger than estimated by Ben-Yaakov (1971) for a systematic error in  $TCO_2$ . However, the previous error analysis was made under the assumption that the percentage error is constant. This is different from the present case since the deviation between Edmond's and Weiss' data is not constant and generally increases with depth.

#### $\delta^{13}C$ REGRESSION ANALYSIS

The linear mixing model expressed by eq.1 should hold not only for  $TCO_2$ , but also for each stable isotope of the gas. Consider, in particular, the variation  $T^{13}CO_2$  along a vertical profile. If one assumes that the variation of  $TCO_2$ , and hence  $T^{13}CO_2$ , are linearly proportional to variations in total dissolved oxygen and total alkalinity, then one can express  $T^{13}CO_2$  as:

$$\Delta^{13}C = \Delta^{13}C_{org.} + \Delta^{13}C_c \quad (3)$$

where  $\Delta^{13}C$  is the variation in  $T^{13}CO_2$  at a given point along the profile and  $\Delta^{13}C_{org.}$  and  $\Delta^{13}C_c$  are the  $T^{13}CO_2$  contributions of the organic matter and carbonate reaction to  $\Delta^{13}C$ . The two  $\Delta^{13}C$  contributions can be written explicitly as:

$$\Delta^{13}C = A_O \Delta O_2 \left( 1 + \frac{\delta^{13}_{org.}}{1,000} \right) R_S + A_A \cdot \Delta TA \left( 1 + \frac{\delta^{13}_c}{1,000} \right) R_S \quad (4)$$

TABLE II

Regression coefficient of TCO<sub>2</sub> of the 1969 Geosecs Intercalibration Cruise

Depth range	Variables in regression	AT (mmole/kg °C)		AS (mmole/kg %)		AO (mmole/ml)		AA (mmole/mequiv.)		A (mmole/kg)	R	F
		value	S	value	S	value	S	value	S			
49-3598	T, O <sub>2</sub> , TA	-0.00777	0.00208	-	-	-0.03652	0.00205	0.74180	0.10225	0.66504	0.9967	1154.970
0-3598	T̄, O <sub>2</sub> , TA	-0.00775	0.00202	-	-	-0.03665	0.00199	0.73358	0.10199	0.68376	0.9968	1176.773
300-3598	T, O <sub>2</sub> , TA	-0.00943	0.00551	-	-	-0.03194	0.00192	0.61440	0.22577	0.96806	0.9942	574.562
300-3598	T̄, O <sub>2</sub> , TA	-0.00910	0.00509	-	-	-0.03227	0.00176	0.61841	0.21384	0.95666	0.9943	581.465
300-3598	S, O <sub>2</sub> , TA	-	-	0.02025	0.05741	-0.03356	0.00228	0.92598	0.20696	-0.50451	0.9934	503.490
800-3598	T, O <sub>2</sub> , TA	0.03622	0.02330	-	-	-0.01641	0.00917	1.90833	0.65389	-2.29490	0.9052	15.115
800-3598	T̄, O <sub>2</sub> , TA	0.04968	0.02548	-	-	-0.00763	0.01166	2.25794	0.70113	-3.17927	0.9151	17.175

Calculations are based on O<sub>2</sub> data measured by R. Weiss; TCO<sub>2</sub> and TA data measured by J. Edmond (Craig et al., 1970; Takahashi et al., 1970). S = standard error of estimate; R = multiple correlation coefficient; F = √(regression variance/residuals variance).

where  $A_O$  and  $A_A$  are  $TCO_2-O_2$  and  $TCO_2-TA$  exchange constants, respectively, and  $R_S$  is the isotopic standard through which  $\delta^{13}C$  ( $\delta^{13}$ ) is defined (Craig, 1957). The last equation is a first-order approximation which is justified by the large difference in the natural abundance of  $^{13}C$  and  $^{12}C$  (Craig, 1970).

The  $\Delta$  values in eq.4 are the differences between the observed values and the preformed values which would have been measured if the variables were stable conservative. Hence:

$$\Delta^{13}C = R_S \left( 1 + \frac{\delta^{13}}{1,000} \right) TCO_2 - {}^{13}C' \quad (5)$$

$$\Delta O_2 = O_2 - O_2' \quad (6)$$

$$\Delta TA = TA - TA' \quad (7)$$

where the prime stands for preformed value. However, the preformed quantities can be expressed as a linear function of temperature for a two-source mixing model (Ben-Yaakov, 1971), i.e.,:

$$C' = K_C T + P_C \quad (8)$$

where  $K$  and  $P$  are constants. Hence,

$$C = C' - K_C T - P_C \quad (9)$$

By combining eq.4, 5, 6, 7 and replacing the preformed values by expression similar to eq.9, one obtains:

$$\left( 1 + \frac{\delta^{13}}{1,000} \right) TCO_2 = B + B_T \cdot T + A_O \cdot \left( 1 + \frac{\delta^{13}_{org.}}{1,000} \right) \cdot O_2 + A_A \cdot \left( 1 + \frac{\delta^{13}_c}{1,000} \right) TA \quad (10)$$

where the  $A$ 's and the  $B$ 's are constants. The last equation can further be simplified by subtracting eq.1 from it which produces the relation:

$$\delta^{13} \cdot TCO_2 = A + A_T \cdot T + A_O \delta^{13}_{org.} \cdot O_2 + A_A \delta^{13}_c \cdot TA \quad (11)$$

It should be noted that eq.11 is similar in form to eq.1, the only difference being the  $\delta^{13}C$  values which are multiplying the corresponding variables. Assuming that  $\delta^{13}C_{org.}$  and  $\delta^{13}_c$  are constant along the profile, one can apply the multivariable regression analysis on  $\delta^{13} \cdot TCO_2$ ,  $O_2$ ,  $TA$  and  $T$  data and extract the coefficients  $A_O \cdot \delta^{13}_{org.}$ ,  $A_A \cdot \delta^{13}_c$ . The constants  $A_O$  and  $A_A$  can be obtained from the analysis on the  $TCO_2$  data and hence, one can calculate  $\delta^{13}C_c$  and  $\delta^{13}C_{org.}$  by dividing the corresponding regression coefficients from the two analyses.

Table III summarized the regression analysis performed on the  $\delta^{13}C \cdot TCO_2$  data. The correlation coefficients and the  $F$  ratios of these analyses are, in general, smaller than the corresponding value calculated during the regression analysis on  $TCO_2$ . This should be expected due to the increase in the data scatter resulting from the inaccuracies of the  $\delta^{13}$  values. The  $\delta^{13}C$  used in the present analysis are those measured at SIO (Kroopnick et al., 1970). However, since the agreement between the SIO and WHOI was within  $0.05\text{‰}$

TABLE III

Regression coefficients of  $\delta^{13}\text{C}$  · TCO<sub>2</sub> of the 1969 Geosecs Intercalibration Cruise

Depth range	Variables in regression	AT (% mmole/kg °C)		AS (mmole/kg)		AO (% mmole/ml)		AA (% mmole/mequiv.)		R	F
		value	S	value	S	value	S	value	S		
0-3598	T, O <sub>2</sub>	0.17187	0.01260	-	-	0.55289	0.03908	-	-	0.9919	427.828
0-3598	T, O <sub>2</sub> , TA	0.26547	0.02830	-	-	0.46588	0.03823	5.77047	1.64621	0.9959	519.264
0-3598	$\bar{T}$ , O <sub>2</sub>	0.16825	0.01243	-	-	0.55949	0.03908	-	-	0.9918	421.992
0-3598	$\bar{T}$ , O <sub>2</sub> , TA	0.26358	0.02773	-	-	0.47257	0.03722	5.99053	1.64642	0.9959	531.677
149-3598	T, O <sub>2</sub>	0.14923	0.01577	-	-	0.53294	0.03648	-	-	0.9830	185.829
149-3598	T, O <sub>2</sub> , TA	0.40601	0.07940	-	-	0.40418	0.04808	12.08754	3.69507	0.9910	219.902
300-3598	T, O <sub>2</sub>	0.08881	0.01506	-	-	0.40615	0.03287	-	-	0.9630	76.546
300-3598	T, O <sub>2</sub> , TA	0.10681	0.12767	-	-	0.40355	0.03888	0.73088	5.14511	0.9630	46.870
300-3598	$\bar{T}$ , O <sub>2</sub>	0.08674	0.01477	-	-	0.40967	0.03328	-	-	0.9628	76.085
300-3598	$\bar{T}$ , O <sub>2</sub> , TA	0.09361	0.11919	-	-	0.40893	0.03700	0.28562	4.91296	0.9628	46.512
300-3598	O <sub>2</sub> , TA	-	-	-	-	0.41691	0.03500	-3.54084	0.62553	0.9606	71.750
300-3598	S, O <sub>2</sub> , TA	-	-	0.29380	1.20702	0.42254	0.04321	-4.55120	4.20850	0.9609	44.102
800-3598	T, O <sub>2</sub>	0.13115	0.07147	-	-	0.46409	0.0500	-	-	0.9707	65.312
800-3598	T, O <sub>2</sub> , TA	0.09676	0.32439	-	-	0.45444	0.12675	-1.01058	9.26416	0.9708	38.167
800-3598	$\bar{T}$ , O <sub>2</sub>	0.13464	0.07267	-	-	0.47831	0.09152	-	-	0.9709	65.712
800-3598	$\bar{T}$ , O <sub>2</sub> , TA	0.12845	0.37388	-	-	0.47596	0.16952	-0.17731	10.47093	0.9709	38.333

Calculations are based on O<sub>2</sub> data measured by R. Weiss (Craig and Weiss, 1970); TA and TCO<sub>2</sub> data measured by J. Edmond (Takahashi et al., 1970);  $\delta^{13}\text{C}$  data measured at SOI (Kroopnick et al., 1970).

S = standard error of estimate; R = multiple correlation coefficient; F =  $\sqrt{\text{regression variance/residuals variance}}$ .

(Kroopnick et al., 1970) one would expect similar results with the WHOI data. The best fit was again obtained when the regression was fitted to the 0–3,598 m segment.

Using the results of the analyses of eq. 1 and 2, one can calculate the  $\delta^{13}\text{C}$  of the organic and carbonate fraction contributing to  $\text{TCO}_2$ . These calculations are summarized in Table IV. The plus–minus values in this table represent the 95% confidence limits for the computed  $\delta^{13}\text{C}$  values. The confidence limits were calculated by adding the percentage standard error of estimate of the corresponding A and  $\delta^{13}\text{A}$ , used in the division, and multiplying the resulting (s) by the proper factor according to the  $-t$  statistics.

TABLE IV

Estimated  $\delta^{13}\text{C}$  of the in situ organic and carbonate  $\text{TCO}_2$  sources.

Depth range (m)	Variables in regression	$\delta^{13}\text{C}_{\text{Org.}}$ (‰)	$\delta^{13}\text{C}_{\text{C}}$ (‰)
0–3598	$\hat{T}, \text{O}_2, \text{TA}$	$-11.1400 \pm 2.80926$	$9.16078 \pm 7.55127$
0–3598	$T, \text{O}_2, \text{TA}$	$-11.02388 \pm 2.86848$	$8.73450 \pm 7.35604$
0–3598	$S, \hat{T}, \text{O}_2, \text{TA}$	$-10.2786 \pm 4.15774$	$21.4798 \pm 27.8175$
0–3598	$S, T, \text{O}_2, \text{TA}$	$-10.01781 \pm 4.16659$	$22.10331 \pm 28.2803$
300–3598	$T, \text{O}_2, \text{TA}$	$-10.9643 \pm 3.99283$	$-6.95742 \pm 103.127$
300–3598	$\hat{T}, \text{O}_2, \text{TA}$	$-10.7155 \pm 3.60521$	$-13.8099 \pm 461.991$
800–3598	$T, \text{O}_2, \text{TA}$	$-7.10686 \pm 6.59765$	$0.397129 \pm 9.63066$
800–3598	$S, T, \text{O}_2, \text{TA}$	$-6.51205 \pm 5.85924$	$1.78909 \pm 9.12172$
0–4100	$\hat{T}, \text{O}_2, \text{TA}$	$-10.59990 \pm 2.65378$	$10.03398 \pm 8.82575$
0–4100	$T, \text{O}_2, \text{TA}$	$-10.50676 \pm 2.73266$	$9.46222 \pm 8.52952$
0–4100	$S, \hat{T}, \text{O}_2, \text{TA}$	$-10.2056 \pm 4.15786$	$26.2148 \pm 42.9373$
0–4100	$S, T, \text{O}_2, \text{TA}$	$-9.98183 \pm 4.20147$	$26.4721 \pm 43.0577$

Calculations are based on  $\text{TCO}_2$  and  $\text{O}_2$  data measured by R. Weiss and  $\text{TA}$  measured by J. Edmond, Craig and Weiss (1970), Takahashi et al. (1970). Plus and minus ranges are 95% confidence limits.

Table IV also demonstrates that the best statistics are obtained for the analyses on the 0–3,598 m section, when  $\text{O}_2$ ,  $\text{TA}$  and  $T$  (or  $\hat{T}$ ) are included. The present analysis suggests that  $\delta^{13}\text{C}_{\text{Org.}}$  should be in the range  $-8.34\text{‰}$  to  $-14.0\text{‰}$  while  $\delta^{13}\text{C}_{\text{C}}$  should be in the range  $1.2\text{‰}$  to  $16.6\text{‰}$ . The statistics of the  $\delta^{13}\text{C}_{\text{C}}$  estimate is rather poor, which may reflect the error introduced through the interpolation process (see p. 00).

The calculations were repeated on Edmond's  $\text{TCO}_2$  data (Takahashi et al., 1970) to investigate the effect of practical errors in  $\text{TCO}_2$  on the estimation of  $\delta^{13}\text{C}$ . The results of these analyses are summarized in Table V. It should be noted that although the estimates of  $\text{A}_\text{O}$  and  $\text{A}_\text{A}$  for these data were consistently lower (Table II), the  $\delta^{13}\text{C}$  estimates obtained from Edmond's  $\text{TCO}_2$  data are only slightly heavier than the values estimated from Weiss' data and there seems to be no significant statistical difference between the two. This is perhaps a result of the present calculation procedure in which the corresponding regression coefficients from the  $\text{TCO}_2$  and  $\delta^{13}\text{C} \cdot \text{TCO}_2$  analyses are divided to obtain  $\delta^{13}\text{C}$ . This has probably the effect of partially cancelling systematic errors in the coefficients.

TABLE V

Estimated  $\delta^{13}\text{C}$  of the in situ organic and carbonate  $\text{TCO}_2$  sources

Depth range (m)	Variables in regression	$\delta^{13}\text{C}_{\text{Org.}}$ (‰)	$\delta^{13}\text{C}_{\text{C}}$ (‰)
0-3598	$T, \text{O}_2, \text{TA}$	$-12.7569 \pm 3.52582$	$7.77901 \pm 6.58294$
0-3598	$\hat{T}, \text{O}_2, \text{TA}$	$-12.8941 \pm 3.43134$	$8.16616 \pm 6.75942$
49-3598	$T, \text{O}_2, \text{TA}$	$-11.0674 \pm 3.87558$	$16.2949 \pm 14.4546$
300-3598	$T, \text{O}_2, \text{TA}$	$-12.6346 \pm 3.95357$	$1.18958 \pm 17.6227$
300-3598	$\hat{T}, \text{O}_2, \text{TA}$	$-12.6722 \pm 3.67543$	$0.461862 \pm 16.2084$
800-3598	$\text{O}_2, \text{TA}$	$-27.6929 \pm 46.3966$	$-0.529563 \pm 10.0721$
800-3598	$\hat{T}, \text{O}_2, \text{TA}$	$-62.3801 \pm 235.091$	$-0.07853 \pm 9.3253$
300-3598	$S, \text{O}_2, \text{TA}$	$-12.5906 \pm 4.28585$	$-4.91501 \pm 11.2869$

Calculations are based on  $\text{TCO}_2$  and  $\text{TA}$  data measured by J. Edmond (Takahashi et al., 1970);  $\text{O}_2$  data measured by Weiss (Craig and Weiss, 1970). Plus and minus ranges are 95% confidence limits.

#### O<sub>2</sub> CONSUMPTION AND $\text{TCO}_2$ PRODUCTION

The regression analysis presented above suggests that the mixing model, which assumes that the intermediate waters are a mixture of the upper and lower boundaries, fits the data for the water column at the 1969 Geosecs Intercalibration Station. If this model is accepted, one can calculate the amount of  $\text{O}_2$  consumed and the amount of  $\text{TCO}_2$  produced in a given parcel of water. The preformed value of a given non-conservative tracer (say  $\text{O}_2$ ) is a linear function of  $\hat{T}$  (Ben-Yaakov, 1971) and can be calculated from an expression similar to eq.8. By subtracting the measured value from the calculated preformed value, one can obtain an estimate for the amount of tracer utilized or produced. This calculation procedure is illustrated graphically in Fig.2. The straight line  $A-B$  is the locus of the preformed  $\text{O}_2$  that would have resulted from a mixture of water types  $A$  and  $B$ . Hence, the vertical distance between the straight line and any given data point is a measure of the amount of  $\text{O}_2$  consumed ( $\Delta\text{O}_2$ ) from the water parcel under consideration. The magnitude of the calculated  $\Delta\text{O}_2$  (or  $\Delta\text{TCO}_2$ ) clearly depends on the selection of the boundary points  $A$  and  $B$ . However, if the same boundaries are selected for both  $\Delta\text{O}_2$  and  $\Delta\text{TCO}_2$  calculations, one would obtain a relative measure of oxygen consumed and carbon dioxide produced in a given parcel of water. It should be emphasized that this calculation does not produce an estimate of in situ processes, but rather reflects the total change in the considered components as compared to the parent boundary waters. The problem of in situ processes will be treated in detail in the next section.

Using the above procedure,  $\Delta\text{O}_2$  and  $\Delta\text{TCO}_2$  were estimated for the 1969 Geosecs Intercalibration Station and the results of these calculations are depicted in Fig.3, 4 and 5. The  $\text{TCO}_2$  and  $\text{O}_2$  data used in these calculations were measured by Weiss (Craig and Weiss, 1970) and the three figures summarize the results for various boundary selections

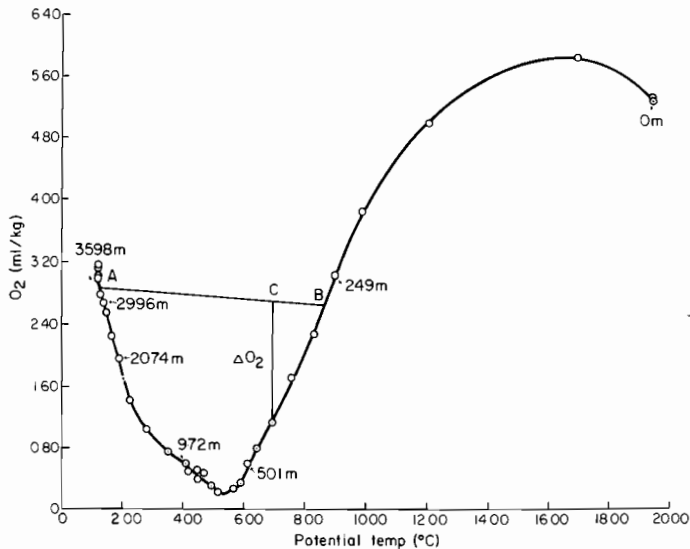


Fig.2. Dissolved oxygen versus potential temperature for the 1969 Geosecs Intercalibration Station. Oxygen data was measured by R. Weiss (Craig and Weiss, 1970). The vertical line,  $\Delta O_2$ , illustrates the computation procedure for estimating the amount of  $O_2$  utilized from a given parcel of water.

using both potential temperature (Fig.3 and 4) and salinity (Fig.5) as the stable conservative tracer. The two left columns of the figures summarize the  $\Delta O_2$  and  $\Delta TCO_2$  values calculated for all the data points between the boundaries. The boundary points (A and B in Fig.2) are averaged values of two upper and two lower points along the profile. The averaging procedure was used in order to minimize the error due to data scatter. The function  $P(\Delta O_2)$  is an estimate of the percentage contribution of  $\Delta O_2$  to  $\Delta TCO_2$ . A 100% value means that  $\Delta TCO_2$  can be completely explained by  $\Delta O_2$  and hence the contribution of carbonate reaction is negligible. The function  $P(\Delta O_2)$  was calculated by assuming that the model of Redfield Ketchum and Richards (1963) is valid in the North-eastern Pacific. The analyses presented in this study as well as previous analyses (Ben-Yaakov, 1971) seem to support this assumption (this point is further discussed below). The function given in the last column of Fig.3, 4 and 5,  $P(f\Delta O_2)$  is similar to  $P(\Delta O_2)$  but is calculated for the whole segment between the upper boundary and any given point along the profile. For example, a value of 80% at 1,500 m implies that 80% of  $TCO_2$  variation in the water column – between the upper boundary and 1,500 m – should be attributed to oxidation of organic matter and 20% are a result of carbonate solution.

The accuracy of the calculation at the upper layer of the profile is rather poor, because the system is open to diffusion from and to the atmosphere. This probably explains the sharp variations in the function  $P(\Delta O_2)$  and  $P(f\Delta O_2)$ . The results, however, are fairly consistent for the water column below some 250 m and suggest that most of  $TCO_2$  variations along the profile are due to  $TCO_2$ - $O_2$  exchange. Carbonate reaction is pronounced at the upper layer and at depth, below 2,500 m. However, the accumulative contribution of  $TA$  to  $\Delta TCO_2$  in the water column is no more than 20%.

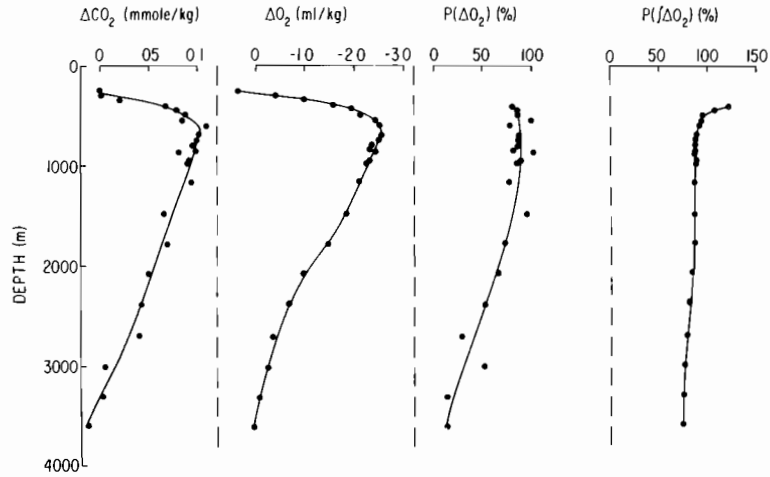


Fig.3. Estimate of O<sub>2</sub> utilization and TCO<sub>2</sub> production in the 1969 Geosecs Intercalibration Station. TCO<sub>2</sub> and O<sub>2</sub> data were measured by Weiss (Craig and Weiss, 1970). Potential temperature was used here as a stable conservative tracer and the upper and lower boundaries were set at 249 m and 3,598 m. The functions  $P(\Delta\text{O}_2)$  and  $P(f\Delta\text{O}_2)$  are an estimate of the percent contribution of oxygen consumption to TCO<sub>2</sub> at a given point and along a given segment, respectively. See text for details of calculation procedures.

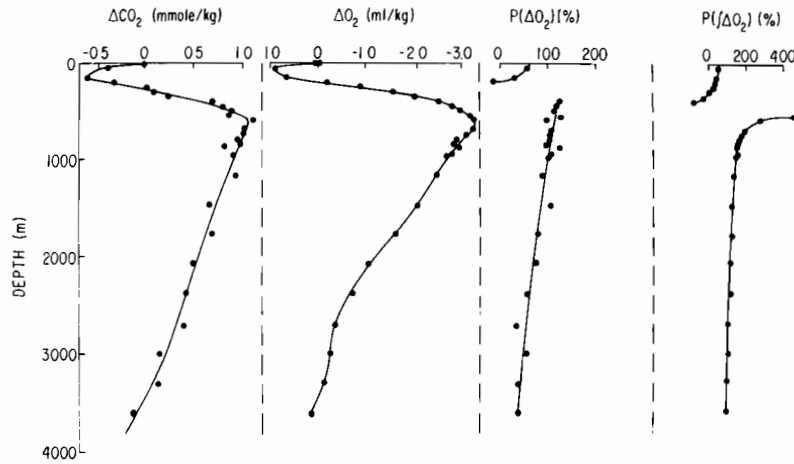


Fig.4. Estimate of O<sub>2</sub> utilization and TCO<sub>2</sub> production in the 1969 Geosecs Intercalibration Station. TCO<sub>2</sub> and O<sub>2</sub> data were measured by Weiss (Craig and Weiss, 1970). Potential temperature was used here as a stable conservative tracer and the upper and lower boundaries were set at the surface and 3,598 m. The functions  $P(\Delta\text{O}_2)$  and  $P(f\Delta\text{O}_2)$  are an estimate of the percent contribution of oxygen consumption to TCO<sub>2</sub> at a given point and along a given segment, respectively. See text for details of calculation procedures.

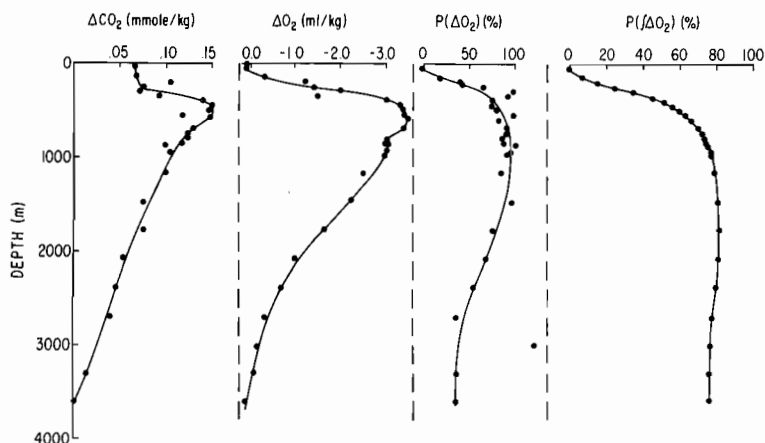


Fig.5. Estimate of  $\text{O}_2$  utilization and  $\text{TCO}_2$  production in the 1969 Geosecs Intercalibration Station.  $\text{TCO}_2$  and  $\text{O}_2$  data were measured by Weiss (Craig and Weiss, 1970). Salinity was used here as a stable conservative tracer and the upper and lower boundaries were set at the surface and 3,598 m. The functions  $P(\Delta\text{O}_2)$  and  $P(f\Delta\text{O}_2)$  are an estimate of the percent contribution of oxygen consumption to  $\text{TCO}_2$  at a given point and along a given segment, respectively. See text for details of calculation procedures.

Fig.4 and 5 show the results of the calculation over the water column – down to 3,500 m. As one would expect, the calculations of Fig.4 and 5 produce different results for the upper layer due to the non-linearity of the  $T$ - $S$  diagram in this range. The calculations of Fig.4, in which potential temperature was used, produce results which are consistent with the expected  $\text{TCO}_2$  and  $\text{O}_2$  variation in the upper layer of the ocean. Total dissolved  $\text{CO}_2$  is somewhat depleted and  $\text{O}_2$  is in excess in the upper layer due to biological activity. These fine details were not observed when  $S$  was used as a stable conservative tracer (Fig.5). This further substantiates the conclusion, drawn above, that potential temperature is a more effective parameter for the analyses used here.

By using the calculated  $\Delta\text{O}_2$  along the profile (Fig.3, 4, 5), and assuming that the model of Redfield et al. (1963) holds in the Northeastern Pacific, one can estimate the amount of organic carbon ( $\Delta\text{C}$ ) that apparently has been oxidized by  $\Delta\text{O}_2$ . The results of these calculations, for the data of Fig.3, are summarized in Table VI. These calculations pre-assume that the oxygen is consumed only through oxidation of organic matter and that the ratio  $\Delta\text{C}/\Delta\text{O}_2$  is 276/106 (Redfield et al., 1963). Since the estimate of  $\Delta\text{C}$  is linearly proportional to  $-\Delta\text{O}_2$ , the parameters show identical variation with depth reaching a maximum at the oxygen-minimum zone (approximately 700 m). The magnitude of  $\Delta\text{C}$  at the maximum zone is estimated to be approximately 1 mg/kg.

The  $\Delta\text{C}$  calculated here cannot be accounted for by the variation of total dissolved organic carbon (DOC) in the water column. The average value of DOC was reported (Menzel and Ryther, 1968; Williams and Gordon, 1970) to be in the range of 0.4–0.7 mg/kg while the variations along a vertical profile (excluding the upper layer) are less than 0.2 mg/kg. These variations are clearly too small to account for the observed  $\Delta\text{O}_2$  with depth.

TABLE VI

Estimate of the amount of organic carbon ( $\Delta C$ ) which may account for  $\Delta O_2$  along the profile

Depth (m)	$\Delta C$ (mg/kg)
300	0.161
350	0.402
400	0.816
450	0.797
501	0.880
511	0.990
602	1.027
702	1.050
756	1.020
804	0.959
854	0.945
869	0.994
955	0.954
972	0.918
1171	0.860
1483	0.747
1779	0.603
2074	0.386
2387	0.266
2697	0.137
2997	0.093
3297	0.053
3598	0.053

Calculations are based on the results presented in Fig.3. See text for details.

Furthermore, the data of Williams et al. (1969) suggests that the "age" of DOC, sampled from the Northeastern Pacific, is approximately 3,400 years and hence, the contribution of DOC to  $TCO_2$  must be only a small fraction of the DOC concentration. Namely, most of the oxidized carbon is apparently introduced in a particular form or through the metabolism of higher-level animals (Sverdrup, 1938).

#### IN SITU PROCESSES

The results presented in Fig.3, 4 and 5 suggest that  $TCO_2$  variation along a vertical profile, in the Northeastern Pacific, are correlated with  $O_2$  variations. However, the above calculations do not reveal where these variations have taken place, as the calculations reflect the total change since the waters have left the boundaries. The results of the multi-variable regression analyses suggest that the  $TCO_2$  and  $O_2$  profiles are consistent with a mixing model which assumes that each point represents a mixture of the layers above and below it. If this model is accepted, then one can estimate the incremental change in a

non-conservative tracer, per unit depth, by subtracting the measured concentration from the expected one. This method of calculation is depicted in Fig.6. The straight  $C-T$  line is the locus of all possible mixtures of the boundary waters if the tracer were conservative. In particular, the concentration of tracer at the mid-temperature point would be equal to the average of the boundary concentration. Hence, by subtracting the actual concentration from this average, one would obtain a relative measure for the amount of tracer consumed over the depth range ( $D_1-D_2$ ).

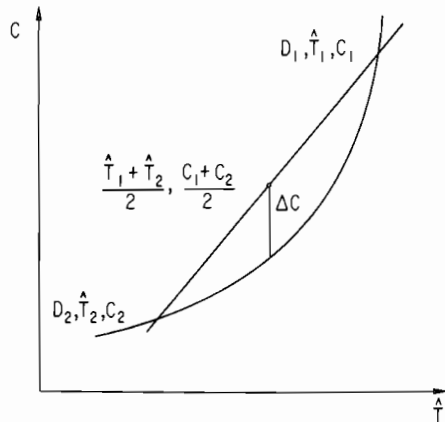


Fig.6. Illustration of the calculation method used to estimate the amount of a non-conservative tracer consumption per unit depth. The upper and lower points are chosen at regular depth increments. An estimate of tracer consumed is obtained by subtracting the measured concentration, at the mid-temperature point, from the expected one due to linear mixing.

The suggested calculation calls for interpolation of the original data to regular depth intervals. Since the concentration of the two boundary points ( $C_1, C_2$ ) are close, any interpolation inaccuracy will result in a large error in the calculated  $\Delta C$  and the procedure requires, therefore, maximum interpolation accuracy. Also, the scatter of the original data, due to finite analytical accuracy, may also produce large percentage errors as one subtracts two close numbers with random errors. Hence, one should consider these calculations only as a first approximation of the amount of tracer variation per unit depth.

Calculation was carried out in 100-m depth increments using two methods of interpolation. Fig.7 summarizes the results of one set of calculations of  $O_2$  consumption (per unit depth) in which a two-polynomial Lagrange-type interpolation was utilized (Borkowski and Goulet, 1971). This method uses four original data points, two above and two below the interpolated point. Two second-order polynomials are fitted to three points each and the average of the values calculated from the polynomial is taken as the interpolated value. The calculation requires two interpolations. First, potential temperature is interpolated to 100-m depth interval. The temperature values are then used to interpolate dissolved oxygen to the given depths and to the mid-temperature point. This procedure

produces interpolated values of temperature and O<sub>2</sub> at 100-m depth intervals, and also the interpolated value of the "measured" mid-temperature oxygen concentrations. The latter is subtracted from the mean of the neighboring O<sub>2</sub> values which is by definition  $\Delta O_2$  per 100-m depth (see Fig.6).

The large scatter in Fig.7 is probably due to interpolation errors as well as random error in the original data. The broken line is an average of two regression models calculated by the least square methods. The slope of the average line suggests that the amount of oxygen consumed per unit depth is decreasing exponentially with depth at a rate of ten-fold per 1,500 m.

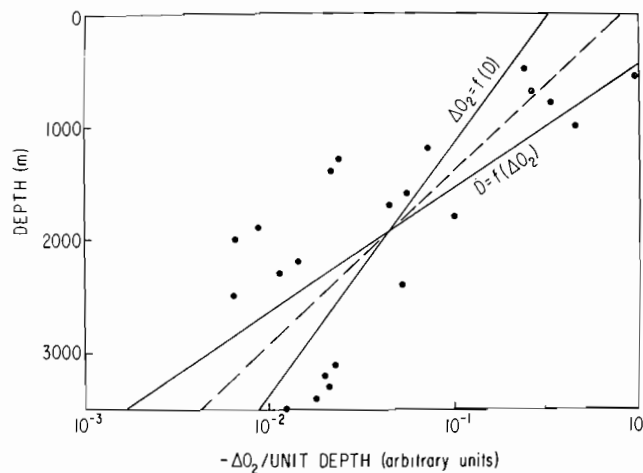


Fig.7. Estimate of oxygen utilization per unit depth using the calculation method illustrated in Fig.6. Results are for two-polynomials Lagrange-type interpolation. Dissolved oxygen data was measured by R. Weiss (Craig and Weiss, 1970).

An attempt was made to reduce the large scatter in the results by smoothing the original data. This was accomplished by fitting a high-order polynomial to the original data of temperature and oxygen by the least square method. Third and fourth order polynomials were fitted to express potential temperature as a function of depth and O<sub>2</sub> as a function of potential temperature. However, the O<sub>2</sub> variations at the oxygen-minimum zone were found to be too sharp to be faithfully reproduced by a least square fitting. The problem was circumvented by breaking the profile into two sections and fitting two high-order polynomials for each set of data. Goodness of fit was checked by re-calculating the original data points by the polynomials. These tests have shown that the estimated standard deviation of a re-calculated value is approximately equal to the analytical precisions, suggesting that the fitted polynomials are reproducing the original data to within the precision of measurement. The fitting of O<sub>2</sub> is illustrated in Fig.8 which is a plot of the interpolated value versus the measured data. As can be seen, the errors seem to be random, suggesting that the smoothing procedure did not introduce systematic errors.

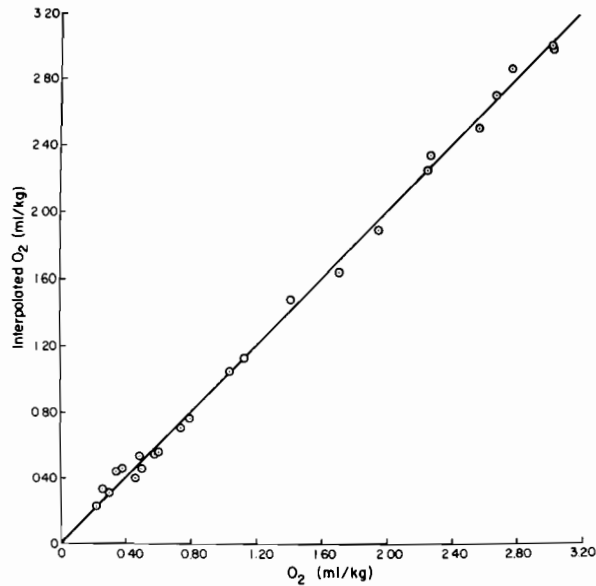


Fig.8. Interpolated versus measured  $O_2$  concentration. Points were calculated by a two-stage least square polynomial fitting:  $\hat{T} = f(D)$  and  $O_2 = f(\hat{T})$ . Separate fittings were used for the 249–702 m and 702–3,598 m depth ranges. Dissolved oxygen data was measured by R. Weiss (Craig and Weiss, 1970).

Fig.9 summarizes the calculation for oxygen utilization per unit depth using the data smoothing technique. The end points of each of the two profile segments have been omitted since a relatively large error could be expected at the fitting ends. These errors are probably responsible for the tailing around 1,000 m and 3,000 m which are the ends of lower segment (702–3,598 m). However, it is evident from Fig.9 that the least square

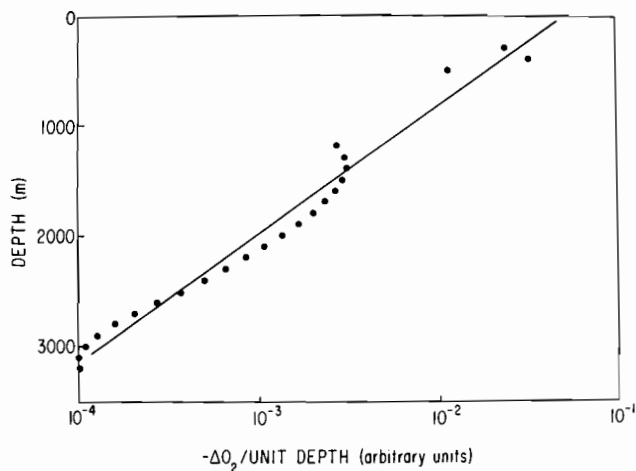


Fig.9. Estimate of oxygen utilization per unit depth using the method of calculation illustrated in Fig.6. Results are for the least square polynomial interpolation. Oxygen data measured by R. Weiss (Craig and Weiss, 1970).

smoothing technique is very effective in reducing the scatter of the calculated value. The results of this set of calculations also suggest that oxygen utilization per unit depth is decreasing exponentially with depth. The slope is somewhat different from the one calculated by the Lagrange-type interpolation and is estimated here to decrease by ten-fold every 1,200-m depth interval.

Using the least square polynomial interpolation technique, I have also estimated the amount of CO<sub>2</sub> production per unit depth using the CO<sub>2</sub> data measured by R. Weiss (Craig and Weiss, 1970). The *TCO*<sub>2</sub> production per unit depth (Fig.10) seems also to follow the exponential function with a slope close to the one estimated for O<sub>2</sub>: a ten-fold decrease for every 1,500 m depth interval. These results are consistent with the conclusion, arrived at above, that *TCO*<sub>2</sub> production is mainly due to oxidation of organic matter.

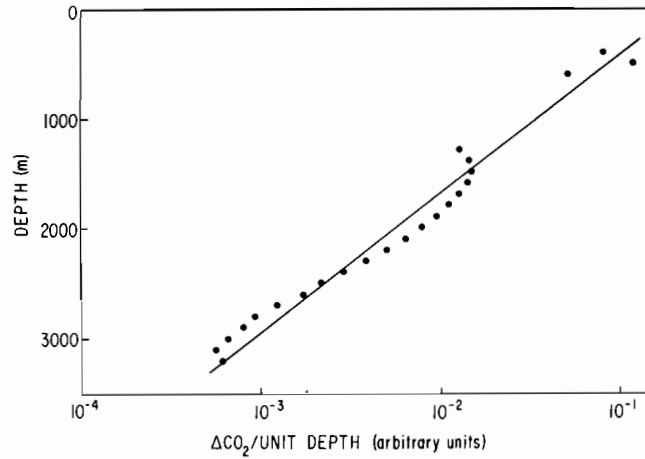


Fig.10. Estimate of *TCO*<sub>2</sub> production per unit depth using the method of calculation illustrated in Fig.6. Results are for least square polynomial interpolation. Dissolved carbon dioxide data measured by R. Weiss (Craig and Weiss, 1970).

The amount of oxygen utilized and *TCO*<sub>2</sub> produced per unit depth is related to the rates of consumption and production through a parameter  $\tau$  which is defined as the residence time of a water parcel at a given depth. This relation can be expressed mathematically as:

$$J_c \propto \frac{C_D}{\tau_D} \quad (12)$$

where  $J_c$  is the rate of tracer variation per unit time and unit depth and  $C_D$  is the amount of tracer produced (or consumed) per unit depth — as calculated above. The residence time,  $\tau_D$ , is not necessarily constant along a profile as its value depends on the eddy diffusivity and vertical velocity at any given point. However, Craig and Weiss have shown that the 1969 Geosecs Intercalibration data over the depth range 0.86–3.5 km, is not inconsistent with a mixing model which assumes a constant eddy-diffusivity to vertical-velocity ratio. If we assume that this ratio does not change markedly over the analyses

range (0.5–3.5 km) then the results of Fig.7, 9 and 10 reflect also the depth dependence of the consumption and production rates of the tracers. The present calculations suggest that the rates of O<sub>2</sub> consumption and TCO<sub>2</sub> utilization decrease exponentially with depth with a ten-fold decrease every 1,200–1,500 m. Namely, O<sub>2</sub> consumption and TCO<sub>2</sub> production ( $J$ ) rates can be expressed as:

$$J = J_0 e^{-\mu z} \quad (13)$$

where  $J_0$  and  $\mu$  are constants and  $z$  is depth.

The present estimate for the value of  $\mu$  for the Northeastern Pacific is in the range 1.92–1.53 km<sup>-1</sup>. This value is very close to the figure 1.54 km<sup>-1</sup> estimated by Craig and Weiss (1970) from a diffusion-advection mixing model. The estimates are within a factor of two to the estimate of Riley (as quoted from Wyrтки, 1962) for the Atlantic Ocean.

#### DISCUSSION

The results of the analyses presented here in general confirm with the results obtained by using the diffusion-advection mixing model (Craig and Weiss, 1970), although no a priori assumption was made here of any particular mixing mechanism (Ben-Yaakov, 1971). The results suggest that the intermediate waters of the Northeastern Pacific can be considered as a mixture of the deep and upper layers and that the production of TCO<sub>2</sub> is a linear function of O<sub>2</sub> consumption and  $TA$  variations.

The TCO<sub>2</sub>–O<sub>2</sub> exchange coefficient  $A_O$  (Table I), estimated from the present analysis, is close to – but consistently higher than – the value previously estimated from a different set of data (Ben-Yaakov, 1971; using the data reported by Culberson and Pytkowicz, 1970). This difference is probably a reflection of the discrepancy between TCO<sub>2</sub> measurement of Weiss and the other investigators during the 1969 Geosecs cruise (Takahashi et al., 1970). Regression analysis of the TCO<sub>2</sub> measured by Edmond (Table II) produces lower values which are more consistent with the earlier results and with the model of Redfield et al. (1963), who estimated the value to be –0.0343 mmole/ml. It appears, therefore, that the discrepancy in the TCO<sub>2</sub> measurements during the intercalibration cruise reflects perhaps some inherent difference between the gas chromatographic method used by Weiss and the other analytical methods.

The TCO<sub>2</sub>–O<sub>2</sub> exchange coefficient,  $A_A$ , (Table I) is estimated here to be  $0.63 \pm 0.14$  mmole/mequiv. (95% confidence limits) which is very close to the expected value, 0.5 mmole/mequiv., that should result from carbonate reaction. Previous estimates (Ben-Yaakov, 1971) did not produce the expected value. This was tentatively interpreted as due to contribution of processes other than carbonate reaction to  $TA$ . The present data do not support this assumption and the earlier results may have been inaccurate due to systematic errors in the data.

Residual analysis on the present regression calculations (Fig.1) seem to indicate that the precision of the 1969 Geosecs measurements were lower than the YALOC 69 determinations (Culberson and Pytkowicz, 1970). The residual range for the present

calculations was found to be  $\pm 0.02$  mmole/kg whereas residual range for the calculation based on the YALOC 69 data (Ben-Yaakov, 1971) was only  $\pm 0.005$  mmole/kg. It appears, therefore, that the problem of  $TCO_2$  determination is still open and additional intercalibration tests are probably needed. It is imperative, however, that intercalibration be made on waters drawn from the same bottles to avoid errors inherent in any interpolation method.

The analysis on the relative contribution of O<sub>2</sub> consumption and  $TA$  variation to  $\Delta TCO_2$  (Fig.3, 4 and 5) suggest that the 80% of  $TCO_2$  variation along the profile is correlated with  $\Delta O_2$ . These results are close to the value estimated by Craig (1970) for the South Pacific using the diffusion-advection mixing model. He estimated the  $\Delta O_2$  contribution to  $\Delta TCO_2$  to be 70% and the carbonate contribution to be 30%. However, the analyses of the  $\delta^{13}C$  Geosecs data by Kroopnick et al. (1970) produced quite different estimates. They conclude that 70% of  $\Delta TCO_2$  is due to carbonate solution and only 30% are due to  $\Delta O_2$ . This estimate is both in conflict with the present analyses and also inconsistent with the data of Ben-Yaakov and Kaplan (1971), which suggest that Northeastern Pacific is close to saturation down to 2,500 m.

The present study and the data of Ben-Yaakov and Kaplan (1971) suggest that the rate of CO<sub>2</sub> production due to carbonate solution is not constant along the water column. However, Kroopnick et al. (1970) have assumed that CO<sub>2</sub> production rate due to carbonate solution is constant with depth. This a priori assumption may also have contributed to the discrepancy between the results of Kroopnick et al. (1970) and this study regarding the average contribution of carbonate solution to CO<sub>2</sub> production.

Menzel and Ryther (1968) and Menzel (1970) have made the point that the lack of variability in the concentration of dissolved organic carbon (DOC) in deep water may indicate that the amount of in situ organic carbon oxidation is insignificant. They have suggested, therefore, that the entire biochemical cycle of organic matter is confined to the upper 200–300 m of the ocean. This argument was further discussed by Menzel (1970) who showed linear regression between O<sub>2</sub> and salinity in Intermediate Water Cores, and concluded that O<sub>2</sub> is a quasi-conservative tracer in these waters. Our analyses are clearly in conflict with these conclusions. The present calculations suggest that oxygen is consumed in situ in the Northeastern Pacific and that the consumption rate is exponential with depth. It is possible, of course, that oxygen consumption rate at the Atlantic Intermediate Water Cores analyzed by Menzel (1970) is indeed insignificant when compared to consumption rates in the Northeastern Pacific. In any case, the data of the 1969 Geosecs Station does not show linear correlation between O<sub>2</sub> and salinity or potential temperature (Fig.2). This study supports the conclusion of Craig (1971) regarding the role of in situ metabolism.

The present analyses suggest that  $\delta^{13}C_{org}$  is in the range from  $-9.3\text{‰}$  to  $-16.3\text{‰}$  (95% confidence levels). This isotopic composition seems to be too heavy when compared to the isotopic composition of DOC and POC which was reported to be in the range of  $-22\text{‰}$  to  $-24\text{‰}$  for the Northeastern Pacific (Williams and Gordon, 1970). One possible explanation is that the  $\delta^{13}C_{org}$  estimate is inaccurate due to systematic errors and scatter

in the 1969 Geosecs data. At any rate, the  $\delta^{13}\text{C}$ ,  $\text{TCO}_2$ ,  $\text{O}_2$  and  $TA$  data of the Geosecs station is inconsistent with the assumption that  $\delta^{13}\text{C}_{\text{org}}$  is  $-23\text{‰}$  (Williams and Gordon, 1970) – if one accepts the idea of vertical mixing in the Northeastern Pacific. This was checked by forcing  $\delta^{13}\text{C}_{\text{org}}$  to be  $-23\text{‰}$  and  $\delta^{13}\text{C}_c$  to be  $+2\text{‰}$  or  $0\text{‰}$  (Craig, 1954) in eq.11 which is a corollary of the vertical mixing concept. It was found that the data of Geosecs 1969 does not obey eq.11 if  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_c$  are set as above.

The present  $\delta^{13}\text{C}$  analyses were performed under the assumption that  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_c$  are constant along the profile. This is justified for  $\delta^{13}\text{C}_c$  because the stable isotope composition of the carbonate fraction was reported to be in a narrow range (Craig, 1954; Kroopnick et al., 1970). However, Sackett et al. (1965) have shown that the carbon isotope composition in marine plankton and sediments is a function of temperature and one may conclude that  $\delta^{13}\text{C}_{\text{org}}$  should be made perhaps temperature-dependent. This procedure, however, would be inconsistent with the concept of vertical mixing. The primary source of the oxidizable organic carbon must be particulate organic carbon that originates at the surface – if a vertical mixing model is assumed. The data of Williams and Gordon (1970) supports this idea as they have found that  $\delta^{13}\text{C}$  of POC and DOC is essentially constant along a vertical profile in the Northeastern Pacific. If  $\delta^{13}\text{C}_{\text{org}}$  is nevertheless arbitrarily forced to be temperature-dependent and the analysis is repeated, one obtains inferior statistical results.

Little can be said about the present  $\delta^{13}\text{C}_c$  estimate (Table IV) since the 95% confidence band is very broad. However, the estimated range,  $+9.2 \pm 7.5\text{‰}$ , covers the value  $+2\text{‰}$  which is the  $\delta^{13}\text{C}$  of the carbonate fraction of Foraminifera (Craig, 1954). The wide error band of the estimated  $\delta^{13}\text{C}_c$  is probably partially due to interpolation errors. It should be recalled that  $\text{TCO}_2$  and  $TA$  were not measured on the same water samples and an interpolation procedure had to be used to interpolate  $TA$  to the  $\text{TCO}_2$  points.

## CONCLUSION

The results of the present analyses suggest that the  $\text{TCO}_2$ ,  $\text{O}_2$  and  $TA$  data of the 1969 Geosecs Station is not inconsistent with a vertical mixing model which assumes that intermediate waters are a mixture of the upper layer and abyssal waters. The calculated regression coefficients are in close agreement with the model of Redfield Ketchum and Richards (1963) and with the assumption that the  $TA$  variation is due to carbonate reaction. Oxygen consumption and  $\text{CO}_2$  production are not confined to one particular layer, but seem to occur over the whole profile. The rate of  $\text{O}_2$  consumption and  $\text{TCO}_2$  production is depth-dependent and decreases by ten-fold every 1,200–1,500 m. Hence, more than 50% of the oxygen is consumed in the upper 500 m.

The analyses further suggest that an average of 80% of  $\Delta\text{TCO}_2$  can be accounted for by oxygen consumption and 20% are probably due to carbonate reaction. However, these percentages are not constant along the profile and the contribution of carbonate reaction to  $\Delta\text{TCO}_2$  is greater than 50% at the depths below 2,500 m.

The present estimate of  $\delta^{13}\text{C}_{\text{org}}$  ( $-9.3\text{‰}$  to  $-16.3\text{‰}$  for 95% confidence limits) suggest that the isotopic composition of the oxidizable organic carbon is heavier than the

$\delta^{13}\text{C}$  of PDC and DOC reported for the Northeastern Pacific (Williams and Gordon, 1970) — unless our analyses are inaccurate due to systematic error in the data. The latter is not unlikely considering the inconsistencies in the 1969 carbonate data (Takahashi et al., 1970).

Regression calculations on short segments of the profile have produced scattered results due to poor statistics. Closely-spaced data points would facilitate analyses of the fine structure along the profile.

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