Evaluation of the calcium problem in the South Pacific

Chen-Tung A Chen, Ricardo M. Pytkowicz, and Eric J. Olson

School of Oceanography, Oregon State University, Corvallis, OR 97331, U.S.A.

(Received August 6, 1981: Accepted October 31, 1981)

Previous estimates of the decomposition of calcium carbonate and organic carbon in deep ocean water are subject to inaccuracies due to (1) the effect of phosphate released from the decomposition of organic matter on titration alkalinity not being properly evaluated, (2) the variation of the preformed properties not being considered, and (3) the input of anthropogenic CO₂ not being corrected for. More accurate results are presented here for selected stations in the South Pacific.

INTRODUCTION

Calcium carbonate (CaCO₃) exhibits increased solubilities at the lower temperatures and higher pressures found in deep waters (Pytkowicz and Connors, 1964; Pytkowicz, 1965; Li et al., 1969). Dissolution of CaCO₃ into ions produces one mole of carbonate and, hence, two equivalents of titration alkalinity (TA), per mole of calcium (Ca). The acids derived from the oxidative decomposition of organic matter may contribute to the in situ titration of alkalinity (Goldman et al., 1972; Gundersen and Mountain, 1973, Brewer and Goldman, 1976). Therefore, the effect of organic matter must be considered when attempting to calculate the calcium concentration from alkalinity data (Brewer et al., 1975; Skirrow, 1975; Almgren et al., 1977; Dyrsen, 1977). Brewer et al. (1975) reported that no apparent excess of calcium was found in the South Pacific when the organic acid contribution was considered.

A mass balance of the oxidation reactions associated with the decomposition of organic matter and of the resulting effect on the titration alkalinity was presented by Chen (1978) following the concepts of Brewer et al. (1975). Precise vertical profiles of the calcium increase were used to calculate the Inorganic Carbon to Organic Carbon ratios. There were, however, three inaccuracies which required correction: the effect of the release of phosphate on TA which was not properly evaluated, the preformed values which were not considered, and the anthropogenic CO₂ input which was not corrected. Data from selected stations in the South Pacific studied before (Brewer et al., 1975; Chen, 1978) were reanalyzed. More accurate profiles for calcium increase and for Inorganic Carbon to Organic Carbon ratios were obtained as a result of this study. Details are given below.

CHANGE IN TA GENERATED BY THE DECOMPOSITION OF ORGANIC MATTER

The decomposition of 106 moles of organic carbon (Org C) yields 106 moles of CO₂, 16 moles of HNO₃, and 1 mole of H₃PO₄, according to the Redfield-Ketchum-Richards model (Redfield et al., 1963):

\[
(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3\text{PO}_4 = 106 \text{CO}_2 \]

\[
+ 16 \text{HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} \quad (1)
\]

Brewer et al. (1975) suggested that the change in TA (ΔTA) for the above equation equals the sum of the changes in NO₃⁻ (ΔNO₃) and in PO₄³⁻ (ΔPO₄). In seawater CO₂, HNO₃, and H₃PO₄ pro-
duced in situ react with CO$_3^{2-}$ (KESTER and PYTKOWICZ, 1967; BREWER et al., 1975; CHEN, 1978) to form, respectively HCO$_3^-$, NO$_3^-$, and HPO$_4^{2-}$. Then Eq. (1) becomes

$$
\begin{align*}
\text{(CH$_2$O)$_{106}$ (NH$_3$)$_{16}$ H$_3$PO$_4$} & + 138 \text{ O$_2$} \\
+ 124 \text{ CO}_2^{2-} & = 16 \text{ NO}_2^- + \text{HPO}_4^{2-} \\
+ 230 \text{ HCO}_3^- & + 16 \text{ H}_2\text{O}
\end{align*}
$$

(2)

CHEN (1978) concluded that, even though HPO$_4^{2-}$ is capable of reacting with two hydrogen ions, it contributes only 1 eq/kg to TA. Since the determination of TA is normally carried out to a pH of 3, HPO$_4^{2-}$ is hence converted to H$_2$PO$_4^-$ and only one hydrogen ion is used (KESTER and PYTKOWICZ, 1967). Consequently, a decrease of 17 eq/kg in TA occurs with the decomposition of one mole of organic matter per kg of seawater.

Upon more careful evaluation of the proton balances, we concluded recently that, in theory, the release of H$_3$PO$_4$ due to the decomposition of organic matter should have no effect on TA. The explanation for this is that in normal seawater, the TA is related to pH-dependent ions of weak electrolytes.

$$
\begin{align*}
\text{TA} & = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] \\
& + [\text{HPO}_4^{2-}] + [\text{OH}^-] - [\text{H}^+] \\
& = (\text{Na}^+) + (\text{K}^+) + 2(\text{Mg}^{2+}) + 2(\text{Ca}^{2+}) + \ldots \\
& - (\text{Cl}^-) -(\text{Br}^-) -(\text{NO}_3^-) - 2(\text{SO}_4^{2-}) - \ldots
\end{align*}
$$

(3)

The value for TA can also be represented by the non-pH-dependent ions of strong electrolytes in order to satisfy the electroneutrality condition (STUMM and MORGAN, 1970; BROECKER, 1974):

$$
\begin{align*}
\Delta \text{TA} & = 2x - 17y \\
\Delta \text{TCO}_2 & = x + 106y
\end{align*}
$$

(6) (7)

The increases in Ca, TA, and TCO$_2$ (total CO$_2$) are 1 mole, 2 eq, and 1 mole, respectively, for the dissolution of 1 mole of CaCO$_3$. Assuming that $x \mu$mole of CaCO$_3$ and $y \mu$mole of organic matter decompose in 1 kg of seawater, the changes in TA ($\mu$eq) and TCO$_2$ ($\mu$mol) can be presented as follows:

Solving for $x$ using Eqs. (6) and (7) yields
Evaluation of the calcium problem

\[ \Delta Ca = x = 0.46288 \Delta TA + 0.074236 \Delta TCO_2 \]  

(8)

The ratio of the in situ Inorganic C and Organic C variation can be calculated from

\[ \frac{\text{Inorg C}}{\text{Org C}} = \frac{x}{106y} = \frac{0.16038 \Delta TCO_2 + \Delta TA}{2 \Delta TCO_2 - \Delta TA} \]  

(9)

The surface waters above the deeper waters under study were taken as the references in previous studies (BREWER et al., 1975; CHEN, 1978), with the \( \Delta Ca \) and Inorg C/Org C results as demonstrated in Fig. 1 and in CHEN (1978). However, the use of surface values as reference points neglects variations in initial boundary conditions (SHILLER and GIESKES, 1980). As ocean water mixes predominantly laterally (EDMOND et al., 1979) and deeper waters at most stations undoubtedly have surface origins which are different from those directly above them it is not certain whether the increase in \( \Delta Ca \) or the change in Inorg C/Org C ratios in the deeper layer is indeed due to the in situ dissolution of CaCO_3 and organic matter oxidation. It may simply reflect the different initial (preformed) chemical properties of the deep waters (KEELING and BOLIN, 1968; EDMOND et al., 1979; SHILLER and GIESKES, 1980). In order to calculate the contribution of Ca, Inorg C, and Org C due to in situ particle dissolution, preformed concentrations need to be taken into account.

Since no theory at present can be used to predict the preformed TA and TCO_2 (TA^0 and TCO_2^0, respectively, salinity normalized to 35‰), we will use the empirical equations, reported by CHEN and PYTKOWICZ (1979) on the basis of the GEOSECS data for waters in the South Pacific. The numbers in parentheses give one standard deviation of the least squares fit.

Fig. 1. \( \Delta Ca \) estimated (closed circles) by Eq. (8) and measured (open circles), using the local surface quantities as reference values. The data were taken from the Antipode 15 Expedition (GEOSECS, 1972) and the work of HORIBE et al. (1974).
TCO₂\textsuperscript{o} (µmol/kg)
\[ = 2236 - 9.4 \theta (\pm 21) \theta \leq 25^\circ C \]
\[ = 2500 - 20.0 \theta (\pm 21) \theta > 25^\circ C \quad (10) \]

TA\textsuperscript{o} (µeq/kg)
\[ = 2383 - 3.1 \theta (\pm 10) \theta \leq 25^\circ C \]
\[ = 2306 (\pm 10) \theta > 25^\circ C \quad (11) \]

Recently, Takahashi et al. (1980) reported that the GEOSECS surface TA data can be related linearly to salinity but is independent of temperature in three cases: a) the Antarctic trend for waters south of the Antarctic Convergence, b) the warm water trend which applies to the warm waters north of the Subtropical Convergence, and c) the transition one which is shown to result from a straight mixing line between the Antarctic and the warm waters. Our approach is similar to theirs in several aspects: a) we have normalized the alkalinitities to a constant salinity to take into consideration the linear dependence of alkalinity on salinity, b) the waters near 0°C and the waters above 25°C can be considered as the Antarctic and warm water components, respectively, and c) the transition between 0°C and 25°C is represented by a straight mixing line between the warm and cold waters. Takahashi et al. also reported an anomaly in the northern North Pacific which we detected in the Northwest Pacific (Chen and Pytkowicz, 1979).

A similar correlation between calcium and temperature has been given here to provide a means of calculating the values for preformed calcium in the Pacific Ocean (Fig. 2) using the comprehensive data of Tsunogai et al. (1973). The values for surface calcium show a decrease with increasing temperature similar to the trends observed in the TA\textsuperscript{o} and TCO₂\textsuperscript{o} correlations. The break in slope, however, seems to come approximately at 20°C in the calcium correlation. The equations representing the salinity normalized surface distribution are:

\[ Ca\textsuperscript{o} (µmol/kg) \]
\[ = 10,255 - 3.53 \theta (\pm 6) \theta \leq 20^\circ C \]
\[ = 10,184 (\pm 5) \theta > 20^\circ C \quad (12) \]

It is not yet known to what degree the various factors controlling the calcium concentration are reflected in the slope of the preformed calcium correlation. The break in the slope at 20°C (and at 25°C for TA\textsuperscript{o} and TCO₂\textsuperscript{o} correlations) is unexplained at present. Relationships between the preformed values for TA, TCO₂, and Ca, the change in the biological and chemical activities, and the changes of physical processes, such as current flow patterns and the equatorial upwelling (Broecker et al., 1978) are currently under investigation.

It should be mentioned that the breaks in the slopes may cause errors in estimations of preformed values, because the nonlinear effects of mixing may occur. However, this is relatively unimportant from a global point of view, since

![Fig. 2. Surface calcium concentration versus temperature. The data were taken from Tsunogai et al. (1973) and normalized to 35‰.](image-url)
the vast majority of subsurface waters do not mix with waters warmer than 20°C. We calculated the results presented below by ignoring the nonlinear effects of mixing.

**CORRECTION FOR THE ANTHROPOGENIC CO₂ INPUT**

The changes in TCO₂ are often used to calculate the Inorg C/Org C ratios (Eqs. (8) and (9) and Li et al., 1969; Kroopnick et al., 1972; Ben-Yaakov, 1972; Kroopnick, 1974; Edmond, 1974; Chen, 1978). However, the surface waters have an anthropogenic CO₂ input of as much as 40 μmol/kg (Chen and Millero, 1979; Chen and Pytkowicz, 1979), so the use of present day TCO₂ preformed values as reference states in Eqs. (8) and (9) causes a significant systematic error in ΔTCO₂ for deep waters.

To correct this error, the anthropogenic CO₂ signal is subtracted from the TCO₂₀ values when calculating Inorg C/Org C ratios for deep waters. Anthropogenic CO₂ also affects Ca calculations, but the effect is slight and the correction made in this study is not important.

**RESULTS AND DISCUSSION**

The preformed values calculated from Eqs. (10) and (11) were used as the references for the

---

**Fig. 3.** ΔCa estimated (closed circles) by Eq. (8) and measured (open circles), using the Antipode 15 data (GESECS, 1972) and preformed estimates as reference points.
\( \Delta \) quantities in Eqs. (8) and (9). The results for \( \Delta \text{Ca} \) are seen in vertical profiles in Fig. 3 for four Antipode stations (GESECS, 1972; Horibe et al., 1974).

Figure 3 represents values of \( \Delta \text{Ca} \) (estimated, closed circles) and \( \Delta \text{Ca} \) (measured, open circles) for the four Antipode stations. The estimated \( \Delta \text{Ca} \) has an uncertainty of approximately \( \pm 4 \mu \text{mol/kg} \) owing to uncertainties in \( \Delta \text{TA} \) (\( \pm 5 \mu \text{eq/kg} \)) and \( \Delta \text{TCO}_2 \) (\( \pm 10 \mu \text{mol/kg} \)). It should be noted that the measured data of Horibe et al. (1974) have been systematically shifted down by \( 127 \mu \text{mol/kg} \) so that they are consistent with the more comprehensive data of Tsunogai et al. (1973). The agreement between the estimated and measured values is quite good. For most of the points presented, the measured and estimated values agree within \( \pm 15 \mu \text{mol/kg} \), which is the total precision of the two values.

It can be seen that the value for \( \Delta \text{Ca} \) decreases with depth near the surface, increases with depth below 500m, and reaches a maximum of 35 \( \mu \text{mol/kg} \) at approximately 2,900m. The value decreases rapidly to 5 \( \mu \text{mol/kg} \) below 2,900m and shows a distinct change between 3,650 and 3,800m, corresponding to the depth of the benthic front (Craig et al., 1972). Although the profiles given in Fig. 3 look similar to those shown in Fig. 1, they are reflecting different things.

Since the local surface seawaters were taken as the references for the \( \Delta \text{Ca} \) values in Fig. 1, the large increase in \( \Delta \text{Ca} \) (up to 80 \( \mu \text{mol/kg} \)) with depth represents higher preformed Ca concentrations in deeper waters in addition to the in situ \( \text{CaCO}_3 \) dissolution at these locations. On the other hand, the \( \Delta \text{Ca} \) values given in Fig. 3 represent only the effect of \( \text{CaCO}_3 \) production and dissolution since the water left the Southern Ocean. These values show clearly that there is a net \( \text{CaCO}_3 \) dissolution in the water column below 500m.

The water at 2,900m has maximum silicate, phosphate and nitrate concentrations (GESECS, 1972) and probably represents the southward flowing North Pacific Deep Water (NPDW). Since the \( \text{CaCO}_3 \) saturation depth is rather shallow in the North Pacific (Pytkowicz, 1970), up to 35 \( \mu \text{mol/kg} \) of \( \text{CaCO}_3 \) probably has dissolved in NPDW by the time it reaches the study area. This compares with a maximum of 80 \( \mu \text{mol/kg} \) in Fig. 1 and suggests that as much as 45 \( \mu \text{mol/kg} \)
kg of $\Delta$Ca at 2,900 m shown in Fig. 1 is due to the higher initial Ca concentration of the deeper waters.

Below the benthic front the water shows little change in $\Delta$Ca values (5 $\mu$mol/kg) since it left the Southern Ocean, indicating little CaCO$_3$ dissolution between the Southern Ocean and the study sites. By way of comparison, as much as 50 $\mu$mol/kg of the apparent increase in $\Delta$Ca concentration shown in Fig. 1 is due to the higher preformed Ca in the deeper waters. This agrees with the work of Keeling and Bolin (1968) in that a large portion of the apparent increase in calcium concentration found in the deep oceans is due to calcium transported by the water itself, and not by gravitational settling and subsequent dissolution of particles.

Figure 4 shows vertical profiles of $\Delta$Ca (meas) - crosses - and $\Delta$a (est) - circles - for stations from 35°N to 69°S centered along 170°W. The measured values south of 30°N were determined from the data of Tsunogai et al. (1973) during the Japanese Southern Cross Cruise. The calcium data from the Southern Cross Cruise has excellent quality, but the alkalinity data shows large scatter. As a result we have calculated the estimated $\Delta$Ca values using TA and TCO$_2$ data for nearby stations occupied in the GEOSECS program. The profile at 35°N was calculated using the data of Shiller and Gieskes (1980).

These profiles show, as do the others, a good deal of scatter in the measured values and a much more detailed profile using the estimated values. The precisions in $\Delta$Ca (est) and $\Delta$Ca (meas) in these profiles are similar to those previously described. The agreement between the estimated and measured values is, in most cases, within the $\pm 15\mu$mol/kg sum of the precisions. This agreement is very reasonable in view of the fact that the GEOSECS stations
were occupied in different seasons in different years and also in somewhat different locations as compared to the Southern Cross Stations.

The profiles indicate strong vertical mixing for calcium in the southernmost stations and the gradual formation, deepening and erosion of the benthic front when moving north. Evidence of the benthic front is gone by 12°N.

The Inorg C/Org C ratios for the Antipode 15 stations were calculated using Eq. (9), and the results are plotted in Fig. 5. The ratios for the near-surface samples are negative because there is a net loss of Inorg C due to the formation of CaCO₃ since the water left its origin. This is probably a mixture of near local surface water and the Southern Ocean water. Consequently, we will limit our discussion to waters below 1,000 m.

Figure 5 shows that there is an increase of the proportion of Inorganic Carbon below 1,000 m. It reaches a maximum at approximately 2,900 m. This is what we expected, because the amount of the dissolution of CaCO₃ increases with depth.

The Inorg C/Org C ratio decreases below 3,000 m and shows a sharp decrease at approximately 3,650 m, which corresponds to the depth of the benthic front (CRAIG et al., 1972). The low Inorg C/Org C ratio for bottom water deeper than the benthic front indicates that a relatively smaller amount of CaCO₃ has decomposed in this water. Also, the bottom water is probably coming from the Southern Ocean (CRAIG et al., 1972), which is rich in siliceous organisms. Because of this, low ratios can be expected according to EDMOND (1974), and our values agree with his work for the circumpolar waters. Overall, the CaCO₃ contributes approximately 12% of the total CO₂ input (using 0.135 as the average ratio of the Inorg C to Org C) below 1,000 m in the water column in the South Pacific Ocean. This is lower than most of the previous estimates (Li et al., 1969; CRAIG, 1970; CHEN, 1978), but agrees with the results of EDMOND (1974).

It should be pointed out that equations (10) to (12) are not exact because they were derived without data from the important oceanic source water regions, thus the possibility of systematic errors in ΔCa and Inorg C/Org C calculations should not be ruled out. Nevertheless, we feel that the correction for the preformed values is conceptually important and our results represent a step forward. More data in the Polar regions are clearly in order.

**CONCLUSION**

It is concluded that (1) in theory, the phosphate released by organic matter decomposing does not affect TA, but in practice, it actually does; (2) the preformed values need to be considered in order to differentiate between the inorganic and organic carbon delivered to the deep waters by gravitational settling of particles or by the transport of water itself; (3) when calculating ΔTCO₂, the anthropogenic CO₂ input needs to be deleted; (4) a large portion of the apparent calcium concentration increase reported previously is probably not due to the in situ CaCO₃ dissolution in the water column.

![Fig. 5. The ratio of Inorg C to Org C flux versus the depth calculated from Eq. (9).](image-url)
but due to the transport by the water itself; and (5) the dissolution of CaCO$_3$ contributes approximately 12% of the total CO$_2$ input into the deep waters of the South Pacific below 1,000m.

NOTE ADDED IN PROOF
The preliminary GEOSECS TA and TCO$_3$ data used in this study are currently being revised. [BRADSHAW, A. L., BREWER, P. G., SHAFTER, D. K. and WILLIAMS, R. T. (1981) Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS Program, Earth Planet. Sci. Lett. 55, 99–115.] Since the correction is mostly in a systematic way, it does not significantly affect the calculation of $\Delta$ quantities used in this study and should not noticeably affect our results.

Acknowledgement—We thank S. TSUNOGAI for sending us unpublished data; P. BREWER, D. DYRSSEN and J. GIESKES for stimulating discussions; and P. BREWER, J. GIESKES and T. TAKAHASHI for sending us manuscripts before publication. This research was supported by grants from NSF (OCE77-00018 A04, OCE78-20449 and OCE80-18770), DOE (81 EV-10611), and ONR (N00014-78C-0004).

REFERENCES


