Journal of the Oceanographical Society of Japan
Vol. 38, pp. 57 to 62, 1982

Calcium-Alkalinity Relationship in the North Pacific*

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Abstract: The dissolution of calcium carbonate in deep ocean water causes variation in calcium concentration (ΔCa) and alkalinity (ΔTA) in the ratio of one to two. The decomposition of organic matter generates nitric acid, phosphoric acid and sulfuric acid. A proton flux which is derived from this process also changes alkalinity. Using the variation in nitrate concentration (ΔNO_3) as an index of the proton flux, the relationship between ΔCa, ΔTA and ΔNO_3 is expressed as

$$\Delta Ca = 0.5\,\Delta TA + 0.63\,\Delta NO_3$$

The values of ΔCa obtained from direct measurements in the North Pacific are in good agreement with the values estimated from this equation.

1. Introduction

Alkalinity is one of the most fundamental parameters in the chemistry of sea water. The nature and mechanism of alkalinity distribution is a subject of interest in chemical oceanography.

It is a well-known fact that the concentration of calcium and alkalinity are higher in deep water than in surface water as a result of the dissolution of biogenic calcium carbonate particles. The dissolution of one mole of calcium carbonate adds one mole of calcium and two equivalents of alkalinity to the sea water. The concentration of calcium and alkalinity in sea water are, therefore, expected to change in this proportion if other processes which change calcium concentration or alkalinity are absent. Recent developments in the high-precision determination of calcium in sea water have made it possible to compare the variation in calcium concentration with that in alkalinity.

By using the calcium and alkalinity data obtained in the Pacific Ocean along 170°W, TSUNOGAI *et al.* (1973) calculated the following value:

$$(2TA - Ca)/Cl$$

where TA, Ca and Cl are titration alkalinity, concentration of calcium and chlorinity, respectively. They found that this value was not constant, and suggested the existence of calcium sources other than the dissolution of calcium carbonate.

HORIBE *et al.* (1974) plotted calcium concentration normalized to 35‰ salinity versus titration alkalinity normalized to same salinity (35‰) for data obtained at four stations between American Samoa and Tonga. The regression line of the plot had a slope of 0.734, which is higher than the slope of 0.5 expected from the dissolution of calcium carbonate. They found, however, that a plot of calcium concentration versus carbonate alkalinity gave a regression line with a slope close to 0.5. BREWER *et al.* (1975) pointed out that it is not carbonate alkalinity but titration alkalinity that changes stoichiometrically with the dissolution of calcium carbonate.

BREWER *et al.* (1975) calculated the difference in calcium concentration (ΔCa) and that in alkalinity (ΔTA) from an arbitrary surface sea water as a reference using the same data as used by HORIBE *et al.* (1974). Although the dissolution of calcium carbonate should give $\Delta Ca/\Delta TA = 0.5$, the ratio obtained in the water column below 500 m was larger than 0.5. They suggested that this could be attributed to the decomposition of organic matter. In other words, the proton flux associated with the decomposition of organic matter changes alkalinity. This concept was first suggested by LYMAN (1959).

We examined the relationship between calcium concentration and alkalinity from the view-

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* Received June 10, 1981, revised Apr. 9 and accepted Apr. 14, 1982.

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point that the proton flux changes alkalinity.

2. Sampling and chemical analysis

Sea water samples were collected at Stns. 4 (34°55′N, 152°10′E), 8(38°00′N, 179°45′W) and 9(30°00′N, 170°00′W) for the determination of calcium, magnesium and alkalinity during the KH-80-2 Cruise of the R. V. Hakuhō Maru (April-June, 1980) of the Ocean Research Institute, University of Tokyo. Hydrographic data including salinity and nutrients will be published in the near future as a cruise report by the Ocean Research Institute.

Alkalinity was determined on board by the computer-processed potentiometric titration method, which is based on Edmond's method (EDMOND, 1970). The volume of the titration cell was about 30 ml and the full volume of the syringe burette (Metrohm Dosimat: E412) was 1 ml. The titrant, standard hydrochloric acid (ca. 0.3N), was adjusted to an ionic strength of 0.7 by adding sodium chloride, and was standardized against a borax standard solution which was also adjusted to an ionic strength of 0.7 by adding sodium chloride. The precision of this method is 0.2%.

Calcium and magnesium were determined by the computer-processed potentiometric titration method developed by KANAMORI and IKEGAMI (1980). The error is estimated to be less than 0.1%. Calcium was determined by an EGTA titration using a calcium-selective electrode (Orion: Model 92-20) as the end-point detector, and total alkaline earth metals by an EDTA titration with a divalent cation electrode (Orion: Model 92-32). The concentration of strontium was estimated by the use of the strontium/chlorinity ratio reported by CULKIN and COX (1966), and the concentration of magnesium was obtained by subtracting the strontium concentration from the difference between the EDTA and EGTA titrations. Sea water samples, which were unfiltered, were stored in sealed polyethylene bottles. Although a few months lapsed before the analysis at the laboratory, no changes in salinity were detected.

3. Modeling of calcium-alkalinity relationship

According to the generally accepted model ot REDFIELD *et al.* (1963), the decomposition of average planktonic organic matter can be formulated as

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4+138O_2= 106CO_2+16HNO_3+H_3PO_4+122H_2O \quad (1)$$

Estimating from the dissociation constants of phosphoric acid in sea water (KESTER and PYTKOWITZ, 1967), addition of 1 mole of phosphoric acid causes a decrease in titration alkalinity which is very close to 1 equivalent. Therefore, as a result of the reaction given by Eq. (1), TA decreases by 17 equivalents. When x moles of calcium carbonate and y moles of organic matter decompose in 1 kg of sea water, the variation in titration alkalinity (ΔTA), total carbon dioxide ($\Delta\Sigma CO_2$), nitrate concentration (ΔNO_3) and apparent oxygen utilization (AOU) are represented as follows:

$$\Delta TA=2x-17y \quad (2)$$

$$\Delta\Sigma CO_2=x+106y \quad (3)$$

$$\Delta NO_3=16y \quad (4)$$

$$AOU=138y \quad (5)$$

From Eqs. (2) and (3), (2) and (4), and (2) and (5), the variation in calcium concentration (ΔCa), which is equal to x, is given by the following equations (6), (7) and (8), respectively.

$$\Delta Ca=0.463\Delta TA+0.074\Delta\Sigma CO_2 \quad (6)$$

$$\Delta Ca=0.5\Delta TA+0.53\Delta NO_3 \quad (7)$$

$$\Delta Ca=0.5\Delta TA+0.062AOU \quad (8)$$

Here, their practical applicabilities to the real oceans of the three equations given above, are compared to find the best choice for a check of our calcium-alkalinity model. Equations (1) and (2) are fundamental ones in the construction of the present model, and are assumed to hold.

Equations (3), (4) and (5) express the stoichiometry among chemical species in regard to organic matter decomposition and calcium carbonate dissolution reactions. However, the observable $\Delta\Sigma CO_2$ and AOU are also affected by other processes, in particular carbon dioxide and oxygen exchange between the atmosphere and sea water. Thus, the relations of Eqs. (3) and (5) are not observed as long as the water remains at the surface. Water mixing in subsurface water may also complicate these relationships.

On the other hand, the exchange of nitrate between the atmosphere and sea is negligible.

Further, the decomposition (or formation) of organic matter is the only process that brings about significant variation in nitrate concentration. Therefore, whatever path the water takes, the concentration of nitrate in this water records the integral amount of the decomposition of organic matter, and Eq. (4) would be applicable all over the oceans.

The disagreement of the relation between AOU and nitrate or phosphate observed among different water masses with the relation expected from Eq. (1), which is a common experience of oceanographers, can be attributed mainly to the phenomena described above. Consideration of the above suggests that among Eqs. (6), (7) and (8), Eq. (7) which is based on Eqs. (1), (2) and (4) is the best choice for the present model.

The atomic ratio of sulfur to carbon in marine organisms is approximately 0.015 (DEUSER, 1970; BREWER *et al.*, 1975; CHEN, 1978). If all reduced sulfur is oxidized to sulfate, the sulfate contribution to alkalinity would be 20 % of the nitrate contribution. Equation (2) is, then, converted to

$$\Delta \mathrm{TA} = 2x - 20.2y \qquad (9)$$

From Eqs. (4) and (9), ΔCa is given by

$$\Delta \mathrm{Ca} = 0.5\Delta \mathrm{TA} + 0.63\Delta \mathrm{NO_3} \qquad (10)$$

Table 1. Analytical data for calcium, alkalinity and nitrate at Stns. 4, 8 and 9.

Depth (m)	Salinity (‰)	Ca (mmole/kg)	TA (meq/kg)	NO_3 (μmole/kg)
Stn. 4				
0	34.603	10.09_7	2.314	3.8
10	34.589	10.08_9	2.302	3.6
50	34.546	10.06_6	2.297	3.7
100	34.463	10.06_2	2.290	10.4
199	34.260	10.02_1	2.300	12.8
497	34.023	9.95_4	2.310	32.6
596	34.107	9.99_5	2.315	37.0
695	34.219	10.04_3	2.332	39.1
794	34.305	10.06_6	2.356	39.4
992	34.384	10.10_8	2.377	41.5
1241	34.451	10.13_0	2.398	42.2
1490	34.519	10.16_0	2.406	42.1
2128	34.611	10.18_1	2.425	39.9
2620	34.647	10.20_3	2.422	38.0
3107	34.665	10.20_1	2.430	36.4
3599	34.683	10.20_6	2.436	36.0
4095	34.684	10.20_2	2.440	35.6
4590	34.726	10.20_9	2.430	35.3
5579	34.692	10.20_4	2.426	34.5
6076	34.698	10.21_3	2.430	34.2
Stn. 8				
0	34.484	10.05_8	2.286	5.8
10	34.476	10.05_8	2.296	5.8
30	34.456	10.05_3	2.295	6.4
49	34.465	10.05_0	2.291	7.1
98	34.416	10.03_0	2.299	7.9
195	34.211	9.98_7	2.293	13.6
487	33.979	9.94_3	2.318	25.4
584	34.000	9.96_1	2.327	32.4
682	34.081	9.99_4	2.331	37.0
779	34.160	10.01_4	2.344	39.8
974	34.293	10.07_0	2.371	42.9
1219	34.408	10.11_7	2.389	44.1
Stn. 8				
1465	34.483	10.14_4	2.402	44.4
2106	34.602	10.18_3	2.424	42.1
2596	34.645	10.18_8	2.420	39.7
3087	34.668	10.18_9	2.426	37.8
3578	34.681	10.20_5	2.439	36.7
4067	34.682	10.20_3	2.425	36.1
4558	34.690	10.19_8	2.430	36.2
5050	34.689	10.20_0	2.427	36.1
5542	34.689	10.20_0	2.429	35.9
Stn. 9				
0	35.213	10.27_7	2.358	0.1
10	35.196	10.27_1	2.350	0.0
30	35.150	10.26_1	2.348	0.0
49	35.075	10.23_1	2.345	0.0
98	34.898	10.17_1	2.329	1.4
195	34.601	10.10_1	2.292	4.9
292	34.390	10.04_7	2.292	10.7
388	34.256	10.00_8	2.289	14.6
485	34.124	9.97_9	2.300	19.2
583	34.037	9.96_3	2.310	25.9
680	34.021	9.97_9	2.333	33.8
974	34.291	10.07_1	2.368	42.9
1220	34.446	10.13_9	2.404	43.6
1708	34.584	10.17_5	2.423	41.5
1952	34.614	10.19_0	2.430	40.4
2195	34.631	10.19_5	2.436	39.5
2439	34.646	10.19_0	2.446	38.5
2683	34.660	10.20_2	2.434	38.0
3415	34.679	10.20_5	2.442	36.4
3904	34.688	10.20_6	2.437	35.8
4394	34.692	10.20_4	2.437	35.5
4884	34.695	10.29_9	2.442	35.2
5374	34.698	10.21_3	2.435	34.6

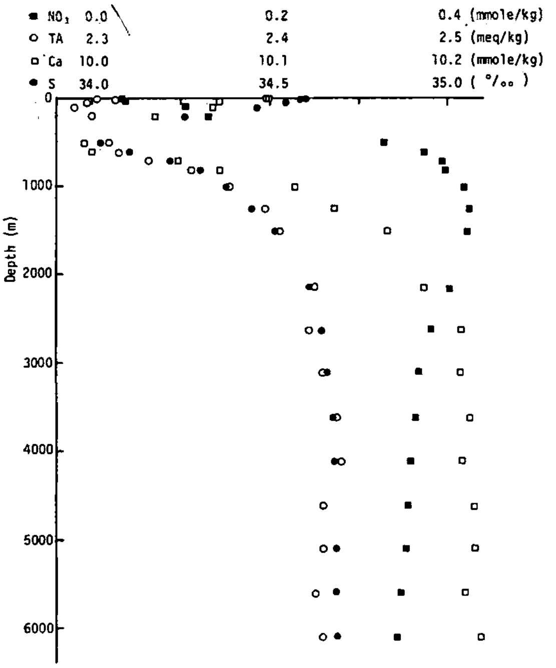

Fig. 1. Vertical distributions of salinity, calcium, alkalinity and nitrate at Stn. 4.

4. Observed relationship between calcium and alkalinity

The vertical distributions of salinity, calcium, alkalinity and nitrate at Stn. 4 are shown in Fig. 1. These analytical data at Stns. 4, 8 and 9 are given in Table 1.

The concentration variation in substance $A(\Delta A)$ is obtained by taking the difference from a reference sea water sample, which is, in this case, a surface sea water sample at each station. The observed ΔA is, therefore, given by

$$\Delta A = A - A_{surf}(S/S_{surf}) \qquad (11)$$

where A, A_{surf}, S and S_{surf} are the concentrations of substance A observed in deep and surface waters and the salinities of these waters, respectively.

The plots of observed ΔCa versus estimated ΔCa, which is calculated from ΔTA and ΔNO_3

Fig. 2-1.

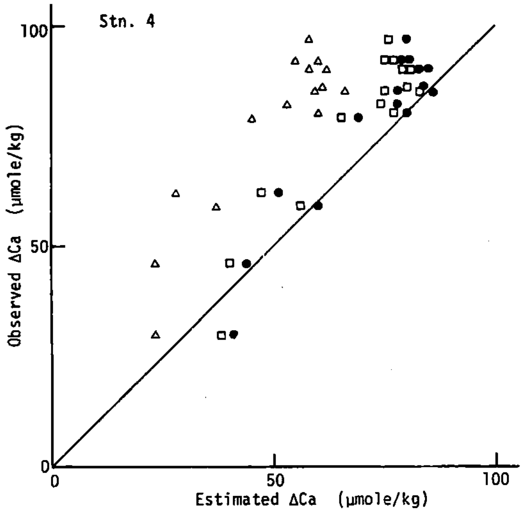

Fig. 2-2.

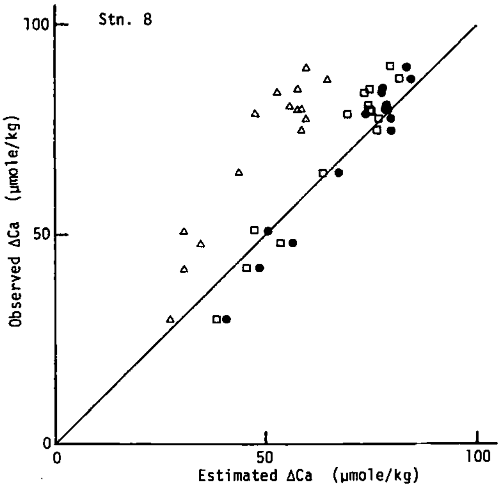

Fig. 2-3.

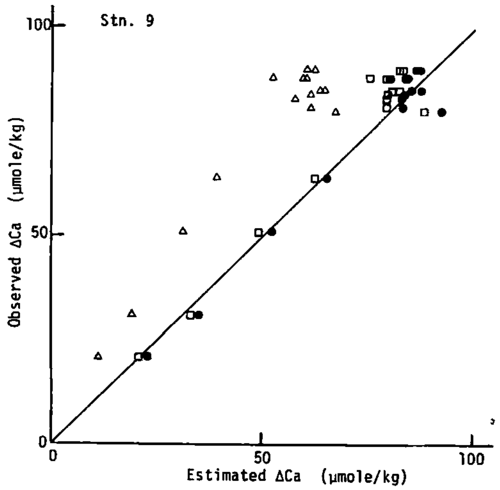

Fig. 2. Relationships between the observed and → estimated values of ΔCa in the water column below 500 m for Stns. 4, 8 and 9. Estimated ΔCa is calculated from 0.5ΔTA (open triangles), 0.5ΔTA+0.53ΔNO_3 (open squares) and 0.5ΔTA +0.63ΔNO_3 (solid circles). The solid lines represent one to one correlation between observed and estimated ΔCa.

data by the use of Eqs. (7) and (10), for the three stations are shown in Fig. 2. The plots of observed ΔCa versus 0.5ΔTA are also shown in Fig. 2. As is evident from the figure, ΔCa obtained from direct measurements is in good agreement with ΔCa estimated from Eq. (10) (solid circle in Fig. 2), and the validity of the model represented by Eq. (10) is proved. It is evident that the sulfate contribution to alkalinity can not be ignored.

5. Vertical distribution of magnesium

Some investigators (BILLINGS *et al.*, 1969; ALMGREN *et al.*, 1977) found the variation in magnesium/chlorinity ratio to be as large as a few per cent. This phenomenon suggests the presence of fluxes of calcium, alkalinity or protons derived from other processes than that considered here. For instance, TSUNOGAI *et al.* (1973) suggested the dissolution or ion-exchange of silicate materials.

The vertical distribution of the magnesium/chlorinity ratio at Stn. 4 is shown in Fig. 3. Within an experimental error of 0.1%, no noteworthy variation is recognized. In order to discuss the distribution of magnesium, more accurate determinations are required.

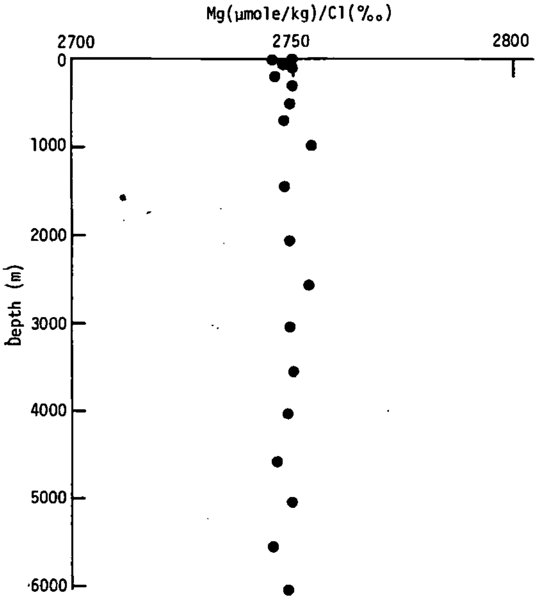

Fig 3. Vertical distribution of the magnesium/chlorinity ratio at Stn. 4.

6. Conclusions

Taking into account the proton flux associated with the decomposition of organic matter, the relationship between calcium and alkalinity is proved to be expressed by a formula. Further examination of the sulfate contribution to alkalinity should be undertaken because positive proof of its importance is still lacking. SHILLER and GIESKES (1980) suggested that calcium concentration and alkalinity can change independently due to interactions at boundaries, i.e., basalt-sea water interactions. Influence of these processes was not found in this study.

Although more observations are required to reach a universal conclusion, the authors believe that the line of approach presented here is useful for understanding the nature of alkalinity and carbonate system in the oceans.

Acknowledgements

The authors are sincerely grateful to Professor Yasushi KITANO for his continuing encouragement and helpful advice. This study was supported by a grant from the Ministry of Education, Science and Culture (56030048).

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北太平洋におけるカルシウムとアルカリ度の関係

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要旨：海洋深層水中における炭酸カルシウムの溶解によって，カルシウムの濃度変化 (ΔCa) とアルカリ度の変化 (ΔTA) が生じる．また，有機物の分解によって，硝酸，りん酸および硫酸が生成され，この結果放出されるプロトンによってもアルカリ度は変化する．このプロトンの放出量を示す指標として硝酸イオンの濃度変化 (ΔNO_3) を用いると，ΔCa，ΔTA と ΔNO_3 の関係は以下のように表わされる．

$$\Delta \mathrm{Ca} = 0.5\,\Delta \mathrm{TA} + 0.63\,\Delta \mathrm{NO_3}$$

北太平洋において直接測定した ΔCa の値は，上式を用いて見積もった ΔCa の値とよく一致した．

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