

The Total Carbon Dioxide in the Ocean

by

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Abstract

The total carbon dioxide in sea water was determined by means of the micro-diffusion method on the cruises of JEDS-3 and JEDS-4. It was confirmed that the total carbon dioxide to AOU plots gave a straight line with a slope $\Delta C/\Delta O_2$ of about 106/272 in atoms for the waters for which the phosphate to AOU plots gave a straight line with a slope $\Delta P/\Delta O_2$ of 1/272. Nearly the same ratio as above was also found in the Antarctic Circumpolar Water. The significance of the reserved total carbon dioxide was pointed out.

1. Introduction

The total carbon dioxide is a name given to a group composed of free CO_2 or H_2CO_3 , HCO_3^- and CO_3^{--} . A number of studies have been made on the vertical distribution of the total carbon dioxide in the ocean. THOMPSON and HAMM (1941) determined the vertical variation of the total carbon dioxide in the Northeastern Pacific down to the depth of 2000 m. MIYAKE and SARUHASHI (1956) showed that the gradual increase of carbon dioxide with the depth was mainly due to the oxidation of the organic matter in sea water and that the ratio of $(\Sigma CO_2 - \Delta C)/\text{chlorosity}$ was nearly constant to the depth of 2000 m from the surface, where the amount of CO_2 calculated from the consumed oxygen was denoted by ΔC .

In the ocean, there are various kinds of carbon compounds besides the members of the total carbon dioxide. Most of them are related to marine biomass. Members of the total carbon dioxide are converted into organic compounds by photosynthesis, which, in turn, are decomposed into members of the total carbon dioxide.

Biochemical processes accompanied by photosynthesis and decomposition of organic matter in sea water are complicated, but the over-all balance of the elements seems to be simple. For example, as previously pointed out by the present author (1964, 1965), if sea waters with the same concentration of reserved phosphate are chosen in a certain region and phosphate concentration is plotted against AOU (the difference between saturated and observed amount of dissolved oxygen), a straight line with the slope $(\Delta P/\Delta O_2)$ of 1/272 in atoms is obtained. According to FLEMING (1940), the average C : N : P ratio of marine plankton is 106 : 16 : 1.

Basing on these figures, REDFIELD *et al* (1963) assumed that the chemical formula of the substance of marine plankton could be expressed as $(CH_2O)_{106}(NH_2)_{16}(PO_4)$ and when plankton was decomposed the substance changed into CO_2 and H_2O with

discharge of nitrate and phosphate. He pointed out that the ratio of liberated phosphate to consumed oxygen $\Delta P/\Delta O_2$ is 1/276. In short, the ratio of increase in phosphate to decrease in oxygen actually observed in sea water is nearly equal to the value expected from an analysis of plankton.

From the approximate coincidence between expected and observed values of the ratio ($\Delta P/\Delta O_2$), it may be anticipated that the ratio $\Delta C/\Delta O_2$ will be nearly in agreement with the value of 106/272 in sea water when organic compounds are completely converted into carbon dioxide.

2. Analytical method

Measurement of the total carbon dioxide was done after SARUHASHI's micro-diffusion method (1953). Two flasks were used as a "micro-diffusion apparatus". A conical glass flask (100 ml) was connected with another flask (50 ml) with a U-shaped glass-tubing as shown in Fig. 1. A sea water sample (20 ml) was put in a larger flask aboard a ship soon after sampling. Immediately, sulfuric acid 2 N solution (2 ml) was added, and a larger flask and a smaller one into which $Ba(OH)_2$ 0.1 N solution (3 ml) was put in advance were connected through a glass tubing. The connected flasks were stood for about 20 hours or longer. After that, the remaining part of $Ba(OH)_2$ was titrated with HCl 0.05 N solution. A Metrohm piston buret (20 ml whole scale, 0.02 ml minimum scale, Metrohm AG Herisau Co., Switzerland) was employed for titration.

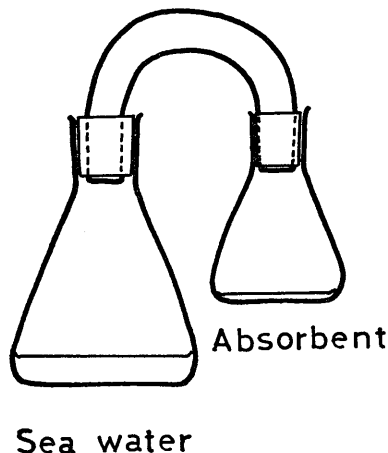


Fig. 1. A set of glass flasks for measurement of carbon dioxide in sea water.

3. Absorption rate of CO_2 into $Ba(OH)_2$ solution

Results of measurement of the absorption rate of CO_2 into $Ba(OH)_2$ solution are shown in Table 1.

Table 1. Absorption rate of CO_2 into $Ba(OH)_2$ solution

Time in hours after the addition of acid to the sol'n.	CO_2 determined in mg-at/l
11	1.80
21	2.31
28	2.30
45	2.28
53	2.30

Table 2. Precision of analysis

ΣCO_2	mg-at/l
	2.28
	2.30
	2.26
	2.30
	2.27
	2.28

Average: 2.28₂

Standard deviation, σ : 0.035₇

1.96 σ : 0.070₀

From the results shown in Table 1, it can be concluded that 20 hours are enough for complete absorption of CO_2 into the absorbent.

To examine the precision of analysis, six samples of sea water stored in the same bottle were treated in the same way and analyzed in 45 hours after the addition of acid to the water. Results are shown in Table 2.

From the result of Table 2, the concentration ranging from 2.21 to 2.35 mg-at/l can not be significantly distinguished at the 95% confidential level.

4. Results and discussion

Results of determination of the total carbon dioxide will be shown together with results for phosphate and AOU determined simultaneously on the cruises of JEDS-3

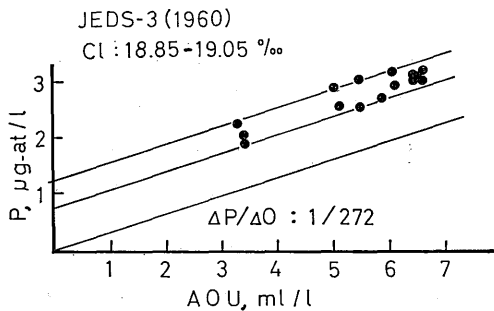


Fig. 2. Relation between phosphate and AOU for waters with Cl 18.85 to 19.05‰ at JEDS-3.

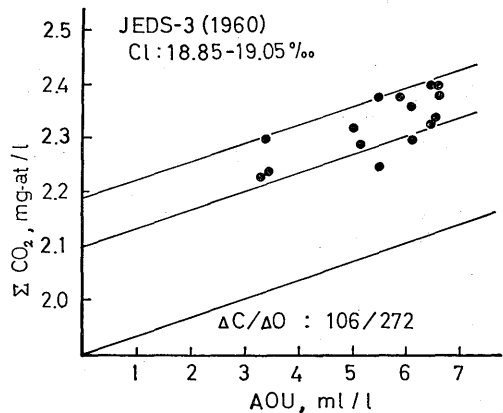


Fig. 3. Relation between total carbon dioxide and AOU for waters with Cl 18.85 to 19.05‰ at JEDS-3.

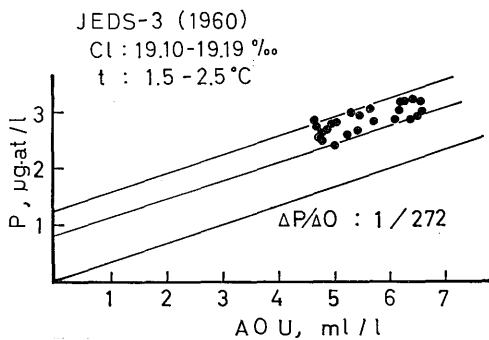


Fig. 4. Relation between phosphate and AOU for waters with Cl 19.10 to 19.19‰ at JEDS-3.

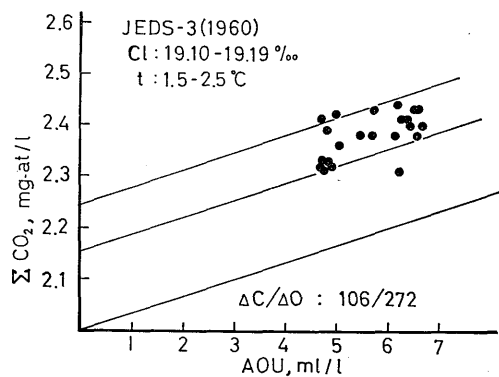


Fig. 5. Relation between total carbon dioxide and AOU for waters with Cl 19.10 to 19.19‰ at JEDS-3.

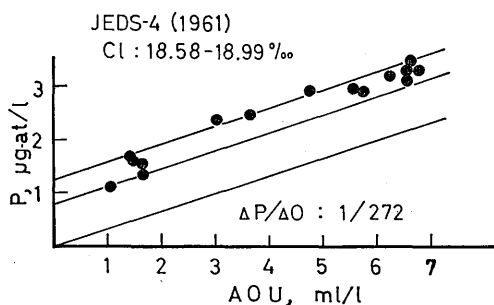


Fig. 6. Relation between phosphate and AOU for waters with Cl 18.58 to 18.99‰ at JEDS-4.

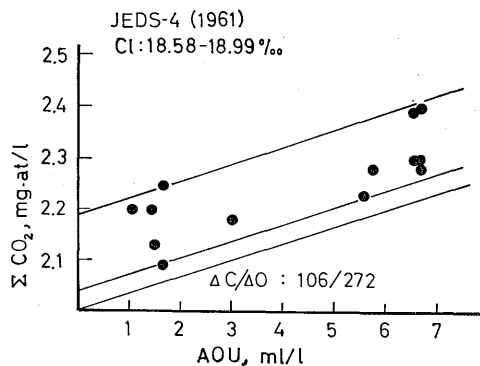


Fig. 7. Relation between total carbon dioxide and AOU for waters with Cl 18.58 to 18.99‰ at JEDS-4.

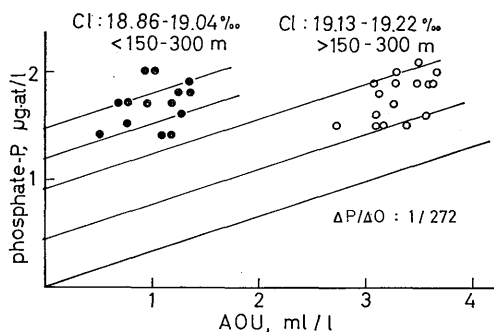


Fig. 8. Relation between phosphate and AOU for the Antarctic Circumpolar water off Prins Olaf Coast.

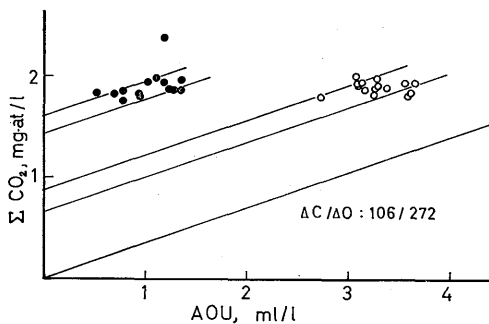


Fig. 9. Relation between total carbon dioxide and AOU for the Antarctic Circumpolar water off Prins Olaf Coast.

(The third Japanese Expedition of Deep Sea carried out in May 1960 between 139°30'E and 147°30'E along 30°N) and JEDS-4 (in June 1961 between 143°E and 148°E along 38°N).

Fig. 2 shows the relation between phosphate concentration and AOU for waters with a chlorinity of 18.85 to 19.05‰ collected on the cruise of JEDS-3. Fifteen points on the diagram fall along a straight line whose slope gives the ratio ($\Delta P/\Delta O_2$) of 1/272. Fig. 3 shows the relation between the total carbon dioxide concentration and AOU in the same waters as above. Fifteen points on the diagram fall along a straight line whose slope gives the ratio ($\Delta C/\Delta O_2$) of 106/272. Figs. 4 and 5 show the same inclination as mentioned in Figs. 2 and 3 in waters with a chlorinity of 19.10 to 19.19‰ and temperature of 1.5 to 2.5°C collected on the cruise of JEDS-3. Figs. 6 and 7 show also the same inclination as mentioned in Figs. 2 and 3 for waters with a chlorinity of 18.58 to 18.99‰ in JEDS-4.

A nearly equal inclination was confirmed in the Antarctic Circumpolar Water off

Prins Olaf Coast. Antarctic data employed here are taken from a report by TORII, YOSHIDA and HIRAYAMA (1959). Waters were classified into two groups; the upper water (depth <150–300 m, Cl 18.86–19.04‰) and the lower water (depth >150–300 m, Cl 19.13–19.22‰). Fig. 8 shows the relation between phosphate and AOU. Fig. 9 shows the relation between the total carbon dioxide concentration and AOU. In waters in which the phosphate concentration to AOU plots give a straight line with a slope ($\Delta P/\Delta O_2$) of 1/272, the total carbon dioxide concentration to AOU plots also give a straight line with a slope ($\Delta C/\Delta O_2$) of approximately 106/272. Assuming the chemical formula of the substance of marine plankton as $(CH_2O)_{106}(NH_2)_{15}(PO_4)$, the ratio of $\Delta C : \Delta P : \Delta O$ will be 106 : 1 : 272 on the complete oxidation assumed.

Extention to zero AOU of the straight line in the total carbon dioxide to AOU diagram gives the concentration of the reserved total carbon dioxide as mentioned in the case of phosphate. The reserved total carbon dioxide will be a factor more significant than the total carbon dioxide itself for identification of water masses like the reserved phosphate.

Here it is noteworthy that in the Antarctic Circumpolar Water, two water masses, i.e. the upper and the lower water can be distinguished in terms of the reserved total carbon dioxide as well as the reserved phosphate, in connection with the fact pointed out by REDFIELD and FRIEDMAN (1965) that in the same region the deuterium to salinity plots have two straight lines with each different slope which meet at the point representing the water occupying the 300 m depth. According to them, the upper water is a mixture of sea water and melt of sea-water ice.

An average concentration of the reserved total carbon dioxide in each water mass is shown in Table 3 for the five water masses.

Table 3. Concentrations of reserved total carbon dioxide and their ratios to chlorosity

	Conc'n of reserved ΣCO_2 mg-at/l	Chlorinity Cl ‰	Chlorosity Cl' ‰	Ratio of reserved $\Sigma CO_2/Cl'$
JEDS-3 (1960)	2.20	19.15	19.61	0.11
	2.15	18.95	19.41	0.11
JEDS-4 (1961)	2.12	18.78	19.24	0.11
Antarctic Circumpolar Water	1.60	18.95	19.41	0.08
	0.85	19.18	19.65	0.04

As shown in Table 3, the ratios of the reserved total carbon dioxide to chlorosity are equal among the Pacific waters off Japan, while it is much lower in the Antarctic Circumpolar Waters. To make clear the reason of the difference in the reserved carbon dioxide between the Pacific and the Antarctic Ocean, further studies will be needed on the basis of more data.

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References

- FLEMING, R.H., 1940: The composition of plankton and units for reporting population and production. Proc. 6th Pacific Sci. Cong. Calif. 3, 533-540.
- MIYAKE, Y. and K. SARUHASHI, 1956: On the vertical distribution of the dissolved oxygen in the ocean. Deep-Sea Res., 3, 242-247.
- REDFIELD, A.C., B.H. KETCHUM and F.A. RICHARDS, 1963: The influence of organisms on the composition of sea water. M.N. HILL, ed., "The Seas". Vol. 2. The Composition and Descriptive Oceanography. Intersci. Publ., New York. pp. 554.
- REDFIELD, A.C. and I. FRIEDMAN, 1965: Factors affecting the distribution of deuterium in the ocean. D.R. Schink and J. T. Corless, ed., "Marine Geochemistry" Narragansett Marine Lab., Univ. Rhode Is. Occasional Publ. No. 3., 149-168.
- SARUHASHI, K., 1953: On the total carbonaceous matter and hydrogen ion concentration in sea water—a study on the metabolism in natural water (1). Pap. Met. & Geophys. 3, 202-206.
- SUGIURA, Y. and H. YOSHIMURA, 1964: Distribution and mutual relation of dissolved oxygen and phosphate in the Oyashio and the northern part of Kuroshio Regions. J. Oceanogr. Soc. Japan. 20, 14-23.
- SUGIURA, Y., 1965: Distribution of reserved (preformed) phosphate in the Subarctic Pacific Region. Rap. Met. & Geophys. 15, 208-215.
- THOMPSON, T.G. and R.E. HAMM, 1941: Dissolved nitrogen in the sea water of the Northeast Pacific with notes on the total carbon dioxide and the dissolved oxygen. J. Mar. Res., 4, 11-27.
- TORII, T., Y. YOSHIDA and Z. HIRAYAMA, 1959: Chemical studies on the nutrient matter in sea water between Cape Town and Lutzow-Holm Bay, Antarctica. The Antarctic Record. No. 8, 482-498.

海洋中の全炭酸

杉浦吉雄

全炭酸とは、海水中に溶存する CO_2 あるいは H_2CO_3 と HCO_3^- と CO_3^{--} とからなる一群の炭酸物質に対して名付けられる。海洋中にはこれらの炭酸物質の外にも、各種の炭素化合物があるが、その多くは海洋生物と関係が深い。光合成、酸化分解に際し、上記の炭酸物質と各種の炭素化合物は相互に変化し合う。その過程はきわめて複雑であるが、その際の元素の収支を全般的にみると案外簡単のように思われる。著者が海水について最近明らかにした事実はこのことを示唆する。海水中のリン酸塩濃度と AOU (酸素の飽和量と観測値の差) の関係から $\Delta P/\Delta O_2$ 比の値を求めると、原子比で 1/272 となる。Fleming のプランクトンの元素分析による C : N : P 比 106 : 16 : 1 に基いて Redfield らはプランクトン物質の平均的な化学式を $(\text{CH}_2\text{O})_{106}(\text{NH}_2)_{16}(\text{PO}_4)$ とし、これが完全に分解することを仮定して $\Delta P/\Delta O_2$ 比として 1/276 なる値を得た。これは前述の 1/272 にきわめて近い。このことは、プランクトンの C : P 比がほぼ 106 : 1 に近いことを示すものと考えられる。然らば、海水の $\Delta C/\Delta O_2$ 比は 106/272 に近い値になるのではないか、この場合、有機物の完全酸化は海水中の CO_2 を増加させ、従つて、全炭酸を増加させることを考えれば、 $\Delta C/\Delta O_2$ 比は全炭酸と酸素の量比として海水の値から求められるはずである。

海水中の全炭酸は、微量拡散法で求めた。試料として JEDS-3 と JEDS-4 の海水を用いた。分析は勿論現場で行なう。その結果、海水の $4C/4O_2$ 比が確かに 106/272 に近い値であることを認めた。南極周辺水についても、この点をチェックしたが、ほぼ同様の結果を得た。

リン酸塩と酸素の関係について、著者はすでに別報で詳しく述べたが、それによるとリン酸塩は一般に、保存性と非保存性の二種に分けられる。同様のことは全炭酸についても云える。リン酸塩の場合と全く同様に、水塊の標識としては、全炭酸そのものよりも保存性全炭酸の方が合理的である。南極周辺水のうち、深さ 150~300m 以深の水と以浅の水について保存性全炭酸濃度を求めると、それぞれ 0.85, 1.60 mg-at/l となり、明瞭に差が認められる。これは、最近 Redfield と Friedman が重水と塩分の組合せから求めた水塊の区分とよく一致し、注目される。保存性全炭酸濃度の値とクロロシティとの比を二、三の日本周辺水と南極周辺水について求めてみると、前者ではいずれも 0.11 となるのに、後者では、0.08, 0.04 というかなり低い値になる。これは注目すべき点であるが、さらに多くの試水について確かめることが望ましい。