

## The Buffer Capability of the Ocean to Increasing Atmospheric CO<sub>2</sub>

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### ABSTRACT

The CO<sub>2</sub>-seawater system and the method for calculating the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in seawater are studied. The buffer capability of the ocean to increasing atmospheric CO<sub>2</sub> is expressed in terms of the differential buffer factor and buffer index. Dissolutions of aragonite and calcite have a significant influence on the differential buffer factor. The trend of change in the buffer factor is obtained by a box model.

### 1. INTRODUCTION

After CO<sub>2</sub> gains through the interface between the atmosphere and the oceans, it dissolves in seawater. Molecular CO<sub>2</sub> then undergoes hydrolysis and dissociation reactions forming H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup>. This is often called the carbonate system. If chemical equilibrium is reached, the system may be defined using any two of four quantities, pCO<sub>2</sub>, pH, total CO<sub>2</sub> (TC) and total alkalinity (TA). These four quantities, together with temperature, pressure and salinity are inexorably linked by fundamental thermodynamic relationships although there is still debate over the exact form and numerical values of the various constants defining this linkage. Some researchers have dealt with the method for calculating pCO<sub>2</sub> (Broecker and Takahashi, 1978; Peng et al., 1987).

The formulation of total alkalinity has not been agreed between different researchers. In Peng et al.'s definition (1987), the expression of TA is:

$$TA = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{H}_2\text{BO}_3^-) + (\text{H}_3\text{SiO}_4^-) + (\text{H}_2\text{PO}_4^-) + 2(\text{HPO}_4^{2-}) \\ + 3(\text{PO}_4^{3-}) + (\text{OH}^-) - (\text{H}^+) \quad (1)$$

where parentheses indicate the concentrations of dissolved species. Eq.(1) suggests that all anions are proton acceptor. However, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is also a proton donor. In this sense, a reference level is needed. Dickson (1981) has proposed a suitable definition using a zero level of protons, in which pK<sub>c1</sub> > φ > pK<sub>f</sub> has been considered. pK<sub>c1</sub> and pK<sub>f</sub> are the negative common logarithms of the constants of the first order dissociation of carbonic acid and the dissociation of hydrofluoric acid, respectively. φ has been assigned the value of 4.5 at 25°C and zero ionic strength. Acids with a dissociation constant > 10<sup>-4.5</sup> are considered as proton donors, whilst those bases formed from weak acids with dissociation constants < 10<sup>-4.5</sup> are considered as proton acceptors. From this definition, the TA in the ocean can be expressed by:

$$TA = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{H}_2\text{BO}_3^-) + (\text{H}_3\text{SiO}_4^-) + (\text{HS}^-) + 2(\text{S}^{2-}) + (\text{HPO}_4^{2-}) + 2(\text{PO}_4^{3-}) \\ + (\text{NH}_3) + (\text{OH}^-) - (\text{H}^+) - (\text{HF}) - (\text{H}_3\text{PO}_4) - (\text{HSO}_4^-) \quad (2)$$

It is obvious that not all the components on the right side of Eq.(2) are important for the calculation of pCO<sub>2</sub>.

For the exchange of  $\text{CO}_2$  between the atmosphere and the oceans, the buffer factor is often used to describe the buffer role of seawater in discussing oceanic uptake of atmospheric  $\text{CO}_2$ . The concept of the buffer factor  $\beta_{rs}$  was first proposed by Revelle and Suess (1957):

$$\beta_{rs} = \left( \frac{d\text{PCO}_2}{\text{PCO}_2} \right) / \left( \frac{dT\text{C}}{T\text{C}} \right), \quad (3)$$

where  $T\text{C}$  and  $\text{PCO}_2$  are the total  $\text{CO}_2$  in seawater and the partial pressure of  $\text{CO}_2$  in the atmosphere, respectively.

They pointed out that the increase in  $\text{PCO}_2$  was ten times larger than the increase in total  $\text{CO}_2$  concentration when total alkalinity remained constant. Bolin and Eriksson (1959) used a simple calculation to obtain a buffer factor of 12.5 but ignored the effect of borate. However, Kanwisher (1960) obtained a larger buffer factor of 16.3 based on his experimental data, and gave same results at temperatures of 10°C and 20°C, respectively. A smaller buffer factor of  $7.8 \pm 1.0$  was obtained by Rebello and Wagener (1976) for 7 seawater samples from different locations at  $\text{PCO}_2$  of 330 ppmv. Recently Maier-Reimer and Hasselmann (1987) have proposed the differential buffer factor, assuming that  $T\text{A}$  is constant.

Here a brief derivation of the differential buffer factor for different cases will be given, including the influence of the dissolution of sediments on the differential buffer factor. In addition, the differential buffer factor will be considered together with the buffer index (or buffer capacity), which is a concept of buffer solution. The buffer capability of the seawater should be in agreement with the buffer index. The trend of change in the buffer factor will be demonstrated by a box model.

## II. CALCULATION OF $\text{pCO}_2$

Hydrogen sulphide and ammonia often occur in anoxic water. In the anoxic oceans concentrations of sulphides of 2 and  $60 \mu\text{mol kg}^{-1}$  at depths of 150 and 200 m in the Black Sea were observed (Richards, 1965). It can be shown that  $\text{HS}^-$  is almost equal to the concentration of sulphides and that  $\text{S}^{2-}$  is obviously negligible. However, in the open ocean, concentrations of sulphides are small.

If concentrations of  $\text{SO}_4^{2-}$ ,  $\text{F}^-$  and  $\text{NH}_4^+$  of  $3 \times 10^4$ , 80 (Pytkowicz and Hawley, 1974) and  $2 \mu\text{mol kg}^{-1}$  (Menzel and Spaeth, 1962) are used, according to their thermodynamic equilibrium equations  $\text{HSO}_4^-$ ,  $\text{HF}$  and  $\text{NH}_3$  concentrations of less than  $0.1 \mu\text{mol kg}^{-1}$  can be obtained, respectively, which are smaller than the error of measurement of  $T\text{A}$ . Therefore,  $\text{HSO}_4^-$ ,  $\text{HF}$ ,  $\text{H}_2\text{S}$  and ammonia may be ignored for the calculation of  $T\text{A}$ , and the expression of  $T\text{A}$  is reduced to:

$$T\text{A} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{H}_2\text{BO}_3^-) + (\text{H}_3\text{SiO}_4^-) + (\text{HPO}_4^{2-}) + 2(\text{PO}_4^{3-}) + (\text{OH}^-) - (\text{H}^+) \quad (4)$$

The term total carbon carbon dioxide is also called the total dissolved inorganic carbon dioxide, which is expressed as:

$$T\text{C} = (\text{CO}_2(\text{aq})) + (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \quad (5)$$

By mass balance, we obtain the following formulae for the calculation of total  $\text{CO}_2$ , total borate, total silicate and total phosphate:

$$T\text{C} = (\alpha_p \text{PCO}_2) + (\text{HCO}_3^-) + (\text{CO}_3^{2-}) \quad (6)$$

$$T\text{B} = (\text{H}_3\text{BO}_3) + (\text{H}_2\text{BO}_3^-) \quad (7)$$

$$T\text{Si} = (\text{H}_3\text{SiO}_4) + (\text{H}_3\text{SiO}_4^-) \quad (8)$$

$$TP = (\text{H}_2\text{PO}_4^-) + (\text{HPO}_4^{2-}) + (\text{PO}_4^{3-}) \quad (9)$$

When  $\text{CO}_2$  is added to seawater, if biological processes of  $\text{CO}_2$  are not taken into account,  $TB$ ,  $TSi$ , and  $TP$  are unchanged.  $TA$  is also unchanged because  $\text{CO}_2$  reacts with  $\text{HCO}_3^-$  to form  $\text{H}^+$  and  $\text{CO}_3^{2-}$  so that there is no net charge change.

$TB$  has a relationship with salinity (Culkin, 1965):

$$TB = 4.106 \times 10^2 (S / 35.) \mu\text{mol} / \text{kg} \quad (10)$$

For convenience of calculation, we can use  $AC$ ,  $AB$ ,  $ASi$ ,  $AP$  and  $AW$  which are often called the alkalinity of the different acids. We have the following formulae based on the thermodynamic equilibrium equations.

$$TC = \alpha_s p\text{CO}_2 (1 + K_{c1} a_H^{-1} + K_{c1} K_{c2} a_H^{-2}) \quad (11)$$

$$AC = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \\ = TC(K_{c1} a_H + 2K_{c1} K_{c2}) / (a_H^2 + K_{c1} a_H + K_{c1} K_{c2}) \quad (12)$$

$$AB = (\text{H}_2\text{BO}_3^-) = TBK_b / (a_H + K_b) \quad (13)$$

$$ASi = (\text{H}_3\text{SiO}_4^-) = TSiK_{s1} / (a_H + K_{s1}) \quad (14)$$

$$AP = (\text{HPO}_4^{2-}) + 2(\text{PO}_4^{3-}) = TP(K_{p2} a_H + 2K_{p2} K_{p3}) / (a_H^2 + K_{p2} a_H + K_{p2} K_{p3}) \quad (15)$$

$$AW = (\text{OH}^-) - (\text{H}^+) = K_w f_h / a_H - a_H / f_h \quad (16)$$

$$TA = AC + AB + ASi + AP + AW \quad (17)$$

where:

$a_H$  indicates the activity of hydrogen ions;  $\alpha_s$  indicates the solubility of  $\text{CO}_2$  in surface seawater;  $K_{c1}$ ,  $K_{c2}$ ,  $K_b$ ,  $K_{s1}$ ,  $K_{p2}$ , and  $K_{p3}$  are the first and second dissociation constants of carbonic acid, the first dissociation constant of boric acid, the first dissociation constant of silicic acid, the second and third dissociation constants of phosphonic acid, and dissociation constant of seawater, respectively; and  $f_h$  is the total activity coefficient of hydrogen ions. The value for  $\alpha_s$  is computed using the expression given by Weiss (1974). The values for  $K_{c1}$  and  $K_{c2}$  are computed using the expressions obtained by Mehrbach et al. (1973). The value of  $K_b$  is computed using the expression given by Li et al. (1969) based on the experimental data of Lyman (1956). A value of 9.51 for  $pK_{s1}$  obtained by Ingri (1959) in a 0.5 M NaCl solution at 25°C is used. The expressions for  $K_{p2}$  and  $K_{p3}$  are based on the data of Kester and Pytkowicz (1967) at a salinity range of 33‰ to 36‰. The expressions for  $K_w$  and  $f_h$  were proposed by Millero (1979) and Takahashi et al. (1981), respectively, according to the data of Culberson and Pytkowicz (1973). Under conditions of known  $TA$  and  $TC$ , we have seven equations and seven unknowns from (11) to (17). Since these equations are linked through  $a_H$  that is sensitive. An iteration method is used to calculate  $a_H$  at the initial condition of  $\text{pH} = 8.0$ . We can calculate  $a_H$  from (12) in terms of  $AC$ , calculated from (17) in which  $AB$ ,  $ASi$ ,  $AP$  and  $AW$  are calculated using an iterative  $a_H$ .  $p\text{CO}_2$  is calculated from (11) using  $a_H$ . An iteration error of  $1. \times 10^{-5}$  is used.

Suppose that input data are as follows:

$$\begin{array}{ll} T = 20.0^\circ\text{C}; & S = 35.0\text{‰} \\ TC = 2000 \mu\text{mol} \cdot \text{kg}^{-1}; & TA = 2320 \mu\text{mol} \cdot \text{kg}^{-1}; \\ TP = 1.5 \mu\text{mol} \cdot \text{kg}^{-1}; & TSi = 5.0 \mu\text{mol} \cdot \text{kg}^{-1}. \end{array}$$

The results are:

$$\begin{array}{ll} AC = 2209.65 \mu\text{eq} \cdot \text{kg}^{-1}; & AB = 103.0 \mu\text{eq} \cdot \text{kg}^{-1}; \\ AP = 1.8 \mu\text{eq} \cdot \text{kg}^{-1}; & ASi = 0.35 \mu\text{eq} \cdot \text{kg}^{-1}; \end{array}$$

$$AW = 5.2 \mu\text{eq.kg}^{-1}.$$

We see that  $AP$ ,  $ASi$  and  $AW$  are much smaller than  $AB$ , although large values of  $TP$  and  $TSi$ , typical of surface water, are used. We deduce that  $AP$  and  $ASi$  can be ignored for the calculation of total alkalinity, as the error in measuring  $TA$  is about  $3 \mu\text{eq kg}^{-1}$ . In general, surface water has lower concentrations of total phosphate and total silicate.  $AW$  is retained in our calculation because it is not directly associated with any measurements.

### III. BUFFER ROLE OF SEAWATER TO ATMOSPHERIC $\text{CO}_2$

#### 1. Deduction of the Differential Buffer Factor and Buffer Index

Total  $\text{CO}_2$  in surface seawater increases with an increase in atmospheric  $\text{CO}_2$ . The buffer role of seawater versus the increase of atmospheric  $\text{CO}_2$  can be described in terms of the differential buffer factor defined as follows:

$$\beta_d = \left( \frac{d\ln\rho\text{CO}_2}{d\ln TC} \right)_{T,S,TA} = \left( \frac{d\ln C}{d\ln TC} \right)_{T,S,TA}, \quad (18)$$

where  $C$  indicates total dissolved  $\text{CO}_2$  ( $\text{CO}_2(aq) + \text{H}_2\text{CO}_3$ ). Initially the change of  $TA$  is not considered and the buffer role of water is ignored. According to the above discussion, we have the following expressions for  $TA$  and  $TC$ :

$$TC = (1 + K_{c1}a_H^{-1} + K_{c1}K_{c2}a_H^{-2})C, \quad (19)$$

$$TA = (K_{c1}a_H^{-1} + 2K_{c1}K_{c2}a_H^{-2})C + AB. \quad (20)$$

At a given temperature and salinity, differentiating Eqs.(19) and (20) yields:

$$dTC = \frac{\partial TC}{\partial a_H} \frac{\partial a_H}{\partial C} dC + \frac{\partial TC}{\partial a_H} \frac{\partial a_H}{\partial TA} dTA + \frac{\partial TC}{\partial C} dC. \quad (21)$$

Because  $dTA = 0$  is assumed, if the buffer role of borate is ignored ( $AB = 0$ ), the differential buffer factor is deduced as follows:

$$\beta_{dc} = \frac{(a_H + 4K_{c2})(a_H^2 + a_H K_{c1} + K_{c1} K_{c2})}{(a_H^3 + 4a_H^2 K_{c2} + a_H K_{c1} K_{c2})}. \quad (22)$$

If borate is included, we have the following equation:

$$\begin{aligned} \beta_{db} = & (a_H^2 + K_{c1} a_H + K_{c1} K_{c2})(C(a_H + K_b)^2 K_{c1} a_H + 4C \\ & (a_H + K_b)^2 K_{c1} K_{c2} + TBK_b a_H^3) / ((a_H^2 + K_{c1} a_H + K_{c1} K_{c2}) \\ & TBK_b a_H^3 + C(a_H + K_b)^2 (a_H^3 K_{c1} + 4a_H^2 K_{c1} K_{c2} + a_H K_{c1}^2 K_{c2})). \end{aligned} \quad (23)$$

Both Eqs.(22) and (23) show that the differential buffer factor is a function of temperature, salinity and pH. Eq.(23) consists of the two buffer systems of carbonate and borate, which can be clearly seen from the buffer index or buffer capacity. Next, we will use the theory of buffered solution to discuss it further.

It can be considered that the seawater is a buffered solution consisting of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{BO}_3^-$ . It can be shown that at about the pH of seawater there exist buffer pairs. The buffer index is defined as:

$$\beta_1 = dC_b / dpH = d((\text{H}_2\text{BO}_3^-) + (\text{HCO}_3^-) + 2(\text{CO}_3^{2-})) / dpH, \quad (24)$$

where  $C_b$  represents basic species.

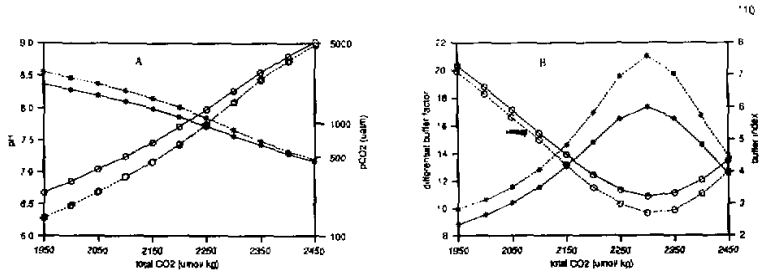


Fig.1. Plots (A) pH ( \* ) and  $pCO_2(O)$ ; and (B) differential buffer factor ( \* ) and buffer index ( O ) vs total  $CO_2$ . ( $T=20^\circ C$ ,  $S=35\text{‰}$ ,  $TA=2317 \mu\text{mol} / \text{kg}$ ) dashed curves indicate  $TB=0.0$ .

If we ignore borate ( $(H_2BO_3^-)=0$ ), we have the following equation, by using a simple deduction:

$$\beta_{ic} = \frac{a_H K_{c1} TC(a_H^2 + 4a_H K_{c2} + K_{c1} K_{c2}) \ln 10}{(a_H^2 + a_H K_{c1} + K_{c1} K_{c2})^2} \quad (25)$$

If borate is included, the buffer index is expressed as:

$$\beta_{ib} = \beta_{ic} + \frac{a_H K_b TB \ln 10}{(a_H + K_b)^2} \quad (26)$$

Eq.(26) clearly demonstrates that the buffer role of the oceans is due to carbonate and borate.

2. Relationships between TC and the Differential Buffer Factor, and TC and Buffer Index

For an ideal system in which there is only exchange of  $CO_2$  between the atmosphere and the ocean mixed layer, and in which TC in the mixed layer is only responding to atmospheric  $CO_2$  according to thermodynamic equilibriums, we can calculate  $pCO_2$  and pH in surface seawater. It can be seen from Fig. 1a that pH decreases and  $pCO_2$  increases with increasing total  $CO_2$ . The relationships between TC and the differential buffer factor, TC and buffer index are shown in Fig. 1b. An interesting feature is that the differential buffer factor first increases with the increase in TC, then it decreases with increasing TC after it reaches a maximum. The buffer index varies with increasing TC, an opposite variation to the differential buffer factor. The minimum buffer index is consistent with the maximum differential buffer factor. If Figs. 1a and 1b are considered together, it can be seen that maximum differential buffer factor and minimum buffer capacity occur at a pH of about 7, which indicates that the buffer pairs of seawater are just being changed from  $CO_3^{2-}+HCO_3^-$  to  $HCO_3^-+H_2CO_3$ , and from  $H_2BO_3^-+H_3BO_3$  to  $H_3BO_3$ .

These demonstrate that the buffer role of seawater first decreases with an increase in atmospheric  $CO_2$  and, after a maximum, it then increases with an increase in atmospheric  $CO_2$ . Borate increases the buffer capability of the ocean to atmospheric  $CO_2$  but it does not affect the trend. It can be shown that there is a limit to the differential buffer factor of = 1. Nevertheless, the system should be changed because  $HSO_4^-$ ,  $F^-$  and others will play important buffer roles after the value of pH is smaller than 4. In fact, even if there were no other processes, including exchange between the mixed layer and the deep water, it would be unlikely to happen because atmospheric  $pCO_2$  could not approach infinity.

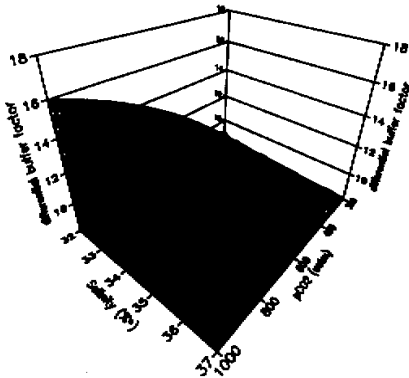


Fig.2. Differential buffer factor as a function of salinity and pCO<sub>2</sub> at the temperature of 20°C (TA = 50.3x(S-35.)+2317).

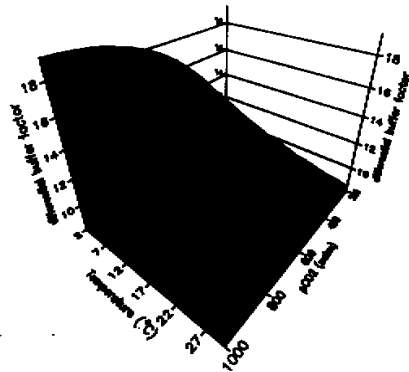


Fig.3. Differential buffer factor as a function of temperature and pCO<sub>2</sub> at the salinity of 35‰ (TA = 50.3x(S-35.)+2317).

Total alkalinity is not constant for the whole ocean. The buffer factor may be affected by the total alkalinity which can be estimated from salinity, although the relationship between total alkalinity and salinity is approximate. We can develop a diagram which shows the differential buffer factor as a function of atmospheric pCO<sub>2</sub> and oceanic salinity at a temperature of 20°C.

Suppose that atmospheric CO<sub>2</sub> varies from 200 to 1000 μatm which is within the range before dissolution of carbonate takes place, and that salinity varies from 32‰ to 37‰, which covers the whole scope of salinity in the oceans. The dependence of the differential buffer factor on salinity and pCO<sub>2</sub> is shown in Fig.2. In the calculation, the following relationship between TA and S is used:

$$TA = 50.26 (S-35.)+2317 . \tag{27}$$

The differential buffer factor decreases slightly with increasing total alkalinity. the dependence of the differential buffer factor on temperature is shown in Fig.3, which demonstrates that the differential buffer factor decreases with an increase in temperature.

### 3. The Influence of the Dissolution of Sediments on the Buffer Role of Seawater

The dissolution of calcium carbonate may take place as seawater changes from a weak base to a weak acid, so that surface seawater will eventually be undersaturated with respect to carbonate. In surface water, there exists an equilibrium, that is formation of calcium carbonate:



The apparent solubility product (K<sub>spc</sub>) for calcite is calculated using the expression given in Takahashi et al. (1981) according to Ingle et al. (1973). The apparent solubility product (K<sub>spa</sub>) for aragonite can be approximately obtained by multiplying (K<sub>spa</sub>) by 1.45 based on the experimental data given by Berner (1976). From the thermodynamic point of view, aragonite is easier to dissolve than calcite because of their difference in solubility products. As CO<sub>2</sub> enters the surface water of the oceans, the concentration of CO<sub>3</sub><sup>2-</sup> decreases. If the concentration of CO<sub>3</sub><sup>2-</sup> is smaller than K<sub>spa</sub> / (Ca<sup>2+</sup>), aragonite begins to dissolve. It can be ob-

tained from a simple calculation that aragonite begins to dissolve when atmospheric  $\text{CO}_2$  reaches a value of  $1531 \mu\text{atm}$ , corresponding to a  $TC$  of  $2270 \mu\text{mol kg}^{-1}$  under the conditions of a temperature of  $20^\circ\text{C}$ , salinity of 35‰ and total alkalinity of  $2317 \mu\text{eq kg}^{-1}$ , again assuming equilibrium.

The dissolution of aragonite changes the concentration of carbonate ions, which leads to variation in total alkalinity. The change in total alkalinity can be expressed in terms of changing calcium concentration:

$$dTA = 2d(\text{Ca}^{2+}) . \quad (29)$$

The change in total  $\text{CO}_2$  due to the increase of atmospheric  $\text{CO}_2$  must be:

$$dTC_g = dTC - d(\text{Ca}^{2+}) . \quad (30)$$

The differential buffer factor is written as:

$$\beta_{da} = \frac{TC}{C} \left( \frac{dC}{dTC_g} \right)_{T,S} . \quad (31)$$

We can deduce the following equation for the calculation of the differential buffer factor  $\beta_{de}$ :

$$\beta_{da} = \left( 1 - \frac{(a_H C^2 K_{c1} K_{c2} + 2C^2 K_{c1} K_{c2}^2 + 2a_H^4 K_{spa}) DH}{C a_H K_{c1} K_{c2} B_0} + \frac{a_H^4 K_{spa}}{C^2 K_{c1} K_{c2} B_0} \right)^{-1} , \quad (32)$$

where:

$$B_0 = a_H^2 + K_{c1} a_H + K_{c1} K_{c2} , \quad (33)$$

$$DH = \frac{a_H K_{c1} K_{c2} C^2 B_1^2 (K_{c1} a_H + 2K_{c1} K_{c2}) + 2a_H^5 K_{spa} B_1^2}{4a_H^4 C K_{spa} B_1^2 + K_{c1} K_{c2} C^3 B_1^2 B_2 + T B K_b a_H^3 K_{c1} K_{c2} C^2} , \quad (34)$$

$$B_1 = a_H + K_b , \quad (35)$$

$$B_2 = K_{c1} a_H + 4K_{c1} K_{c2} . \quad (36)$$

We see that  $\beta_{de}$  is a function of pH and  $\text{pCO}_2$  at a given temperature and salinity, but pH and  $\text{pCO}_2$  can be calculated from  $TC$  and  $TA$  since  $TA$  does not change much. A  $\beta_{de}$  value of 3.8 can be obtained under the conditions of a temperature of  $20^\circ\text{C}$ , salinity of 35‰, total alkalinity of  $2317 \mu\text{eq kg}^{-1}$  and total  $\text{CO}_2$  of  $2270 \mu\text{mol kg}^{-1}$ .  $\beta_{da}$  is much smaller than  $\beta_{de}$  and  $\beta_{db}$ . This indicates the buffer capability of seawater increases because of the dissolution of sediments.

After equilibrium between the formation and dissolution of aragonite, the  $\text{CO}_2$  from the atmosphere partly makes the equilibrium move towards dissolution, and reduces the pH values of seawater. As the ocean contains 60 times more  $\text{CO}_2$  than the atmosphere, the excess  $\text{CO}_2$  put into the atmosphere will eventually be distributed in the proportion of 15:1 between the oceans and the atmosphere.

#### IV. THE CHANGE OF THE BUFFER FACTOR WITH TIME IN TERMS OF BOX MODEL

The situation described above is an ideal one, which may not happen in the future. Here we concentrate on the change of the buffer factor with time by using a box-diffusive model (Hoffert et al., 1981; Bacastow and Bjorkstrom, 1981). The assumptions and conditions of the model will be given.

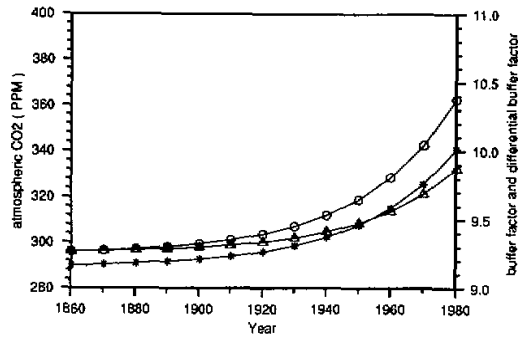


Fig.4. Variations of atmospheric  $\text{CO}_2$  (\*), buffer factor (o) and differential buffer factor ( $\Delta$ ) with time.

The atmosphere is considered as a chemically well mixed system that exchanges  $\text{CO}_2$  with the oceans and terrestrial ecosystem. The exchange of  $\text{CO}_2$  between the atmosphere and the ocean mixed layer is driven by a difference between atmospheric  $\text{PCO}_2$  and mixed layer  $\text{pCO}_2$ , which is represented by the buffer factor  $\beta_{rs}$ . The net exchange between the atmosphere and the terrestrial ecosystem is assumed to be zero.

The global  $\text{CO}_2$  emission from commerce has been increasing at an exponential growth depending on the time period (Keeling, 1973; Marland and Rotty, 1984). Here the production rate of  $\text{CO}_2$  is approximately expressed by the following equation from 1860 to 1980:

$$R_a(t) = 7.67 \times 10^{18} \exp(0.0345(t - 1860)) \mu\text{mol yr}^{-1} (t \geq 1860) \quad (37)$$

This production equation approximately represents the mean production rate in this time period, which indicates that the integrated amount of carbon dioxide from fossil fuels is nearly equal to that obtained by Rotty (1981).

The values of input parameters and initial conditions are listed in table 1, in which the meanings of symbols are the same as those in Hoffert et al. (1981).

Suppose that the initial status is that the atmosphere, the mixed layer and the deep ocean are in equilibrium with each other. The model is run from 1860 to 1980, in which a time step of 0.1 yr and 25 vertical levels in the deep water are used. Fig.4 shows the variations of atmospheric  $\text{CO}_2$  and buffer factor, as well as differential buffer factor, with time. The modeled atmospheric  $\text{CO}_2$  is nearly consistent with the observed global value of atmospheric  $\text{CO}_2$  at 340 ppmv in 1980. The buffer factor has increased from about 9.3 to 10.4. The differential buffer factor is always smaller than the buffer factor. Nearly 35% of the amount of  $\text{CO}_2$  from fossil fuels has been absorbed by the oceans.

Table 1. Input Parameters and Initial Conditions

$H_m = 75. \text{ m}$ ;	$H_d = 5000 \text{ m}$
$A = 3.34 \times 10^{14} \text{ m}^2$	
$K = 3000 \text{ m}^2\text{yr}^{-1}$ ;	$K_{om} = 0.13 \text{ yr}^{-1}$
$N_{so} = 5.19 \times 10^{22} \mu\text{mol}$ ;	$N_{m0} = 6.865 \times 10^{22} \mu\text{mol}$
$T = 15. \text{ }^\circ\text{C}$ ;	$S = 35.14\%$
$TA = 2324 \mu\text{eq kg}^{-1}$ ;	$C_d(Z,0) = 1987. \mu\text{mol kg}^{-1}$
$\text{PCO}_2(0) = 290 \text{ ppmv}$ ;	$\beta_{rs}(0) = 9.27$



## V. CONCLUSIONS

An iteration method for calculating  $p\text{CO}_2$  in surface seawater is discussed. The consideration of phosphates and silicates as well as other components should be made in the calculation of total alkalinity if measurements of total alkalinity and total  $\text{CO}_2$  are improved and highly precise results of  $p\text{CO}_2$  are required.

An ideal system, assuming thermodynamic equilibrium and only exchange of  $\text{CO}_2$  between the atmosphere and the ocean mixed layer, is used to discuss for the ability of the oceans to take up atmospheric  $\text{CO}_2$ . The simulated results show that the buffer capability of the oceans is decreasing, and that the excess  $\text{CO}_2$  put into the atmosphere will be distributed in the ratio of about 6 between the oceans and the atmosphere until carbonate reaches undersaturation in the surface water. This leads to the dissolution of calcium carbonate and movement of lysocline upwards. The dissolution of sediments considerably increases the buffer role of the oceans to atmospheric  $\text{CO}_2$ .

The results from the box model show that the present buffer factor and differential buffer factor is about 10.4 and 9.9, suggesting that a 10% increase of atmospheric  $\text{CO}_2$  only produces a 1% increase of total  $\text{CO}_2$  in the upper layer of the oceans.

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