

Carbonate chemistry in marine pore waters: MANOP sites C and S

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Calculations of the alkalinity and total CO₂ response to organic matter diagenesis in a closed system containing CaCO₃ indicate that the traditional stoichiometric reactions for organic matter degradation and the accompanying CaCO₃ reaction are approximations at the pH of seawater. These approximations are different from the true values by about 10% during oxygen and MnO₂ reduction and about 40% during denitrification.

Intercalibration of in situ and box core methods of pore water sampling from deep-sea carbonate-rich and carbonate-deficient sediments indicates that the sampling artifact on carbonate system measurements due to pressure change is variable in magnitude and apparently related to the carbonate content of the sediments. Previously proposed methods for predicting the effect are not general, implying that there is no alternative to in situ sampling for the evaluation of the carbonate system parameters.

In situ results from a carbonate ooze sediment at MANOP site C reveal that the pore waters are slightly supersaturated with respect to calcite. Ion activity products fall within the range predicted for equilibrium with aragonite. The diagenetic model applied to an open system using molecular diffusion coefficients adequately predicts the pore water alkalinity and total CO₂ changes in response to organic matter degradation. This result provides clear evidence that the transport mechanism for dissolved species near the sediment-water interface at this location is by molecular diffusion and is not enhanced by biological or physical processes. At a siliceous ooze site, MANOP site S, the alkalinity increases in the pore waters in response to CaCO₃ rain to the sediment-water interface. Calcium carbonate is not preserved, and the stoichiometric model predicts a particulate CaCO₃/organic carbon rain ratio of 0.4–1.2. This ratio is in the same range as that measured in sediment traps deployed at this site as part of the MANOP program.

1. Introduction

The utility of the carbonate system for interpreting reactions during early diagenesis in pore waters of deep-sea sediments was demonstrated by Emerson et al. [1] and has been elaborated by others [2,3]. There remain uncertainties in the conclusions drawn in the original paper because of questions with regard to the expected stoichiomet-

ric ratios during organic matter degradation and the sampling artifacts caused by pressure change during core recovery. In this paper we clear the air with respect to these questions and present results from cruise K79-05 of the R.V. "Knorr" in May of 1979 to MANOP (Manganese Nodule Project) sites C and S. This paper is a companion to Jahnke et al. [4] and Klinkhammer et al. [5] in which the nutrient and trace metal results from the same cruise are discussed.

MANOP site C (1°03'N, 138°56'W, see Fig. 1) is located in a calcareous ooze province beneath the biologically active waters that upwell along the equator. The bottom slopes gently from 4430 to

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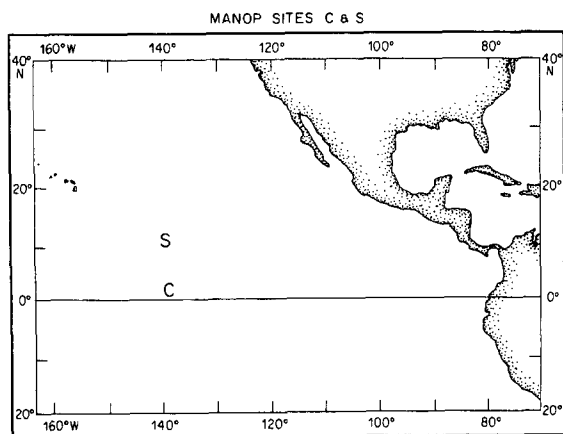


Fig. 1. Location of MANOP sites C and S.

4460 m in the area, and the highest sedimentation rates exceed 2 cm/1000 years. Manganese nodules are rare in this region. Site S (11°2'N, 140°W) is a province of siliceous ooze/clay which lies to the north of site C. The region is one of extensive manganese nodule coverage. The siliceous clay is underlain by a mid-Tertiary nannofossil ooze which has in some places been reworked into the overlying siliceous sediments. The water depth is 4910 m and the sedimentation rate is a few millimeters per 1000 years or non-existent (some areas of the site are erosional rather than depositional).

2. Theory: the stoichiometric equations

The change in alkalinity and total CO_2 during organic matter degradation in a closed system is usually modeled using Redfield stoichiometry and the relationships of the type presented in Table 1 [1,2,6–8]. Prediction of alkalinity and total CO_2 changes in carbonate sediments using a combination of equation (6) and the organic matter degradation reactions (equations (1) to (5)) is not strictly correct because one should not expect the CaCO_3 precipitation or dissolution (reaction (6)) to go entirely to the right or left. The degree to which CO_2 reacts with CaCO_3 depends upon the ratio of alkalinity to total CO_2 that is added to the water during organic matter diagenesis.

To illustrate this point we calculate the expected alkalinity and total CO_2 change during organic matter degradation according to equations (1) through (3). We do not consider iron oxide or sulfate reduction as they are usually unimportant in deep-sea sediment early diagenesis. The change in total alkalinity ($\text{TA} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{H}_2\text{BO}_3^- + \text{OH}^- - \text{H}^+$) or total CO_2 ($\text{TC} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2$) with respect to the oxidant concentration, $[N]$, is described by:

$$\frac{d\text{TC}}{d[N]} = \left. \frac{\partial \text{TC}}{\partial [N]} \right|_{\text{Ca}} + \left. \frac{\partial \text{TC}}{\partial [N]} \right|_{\text{OM}} \quad (7)$$

TABLE 1

Stoichiometry of organic matter oxidation reactions [1]

- | | |
|-----|--|
| (a) | (C : N : P = 106 : 16 : 1) Organic matter degradation |
| (1) | Oxygen reduction:
$138 \text{ O}_2 + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 18 \text{ HCO}_3^- \Rightarrow 124 \text{ CO}_2 + 16 \text{ NO}_3^- + \text{HPO}_4^{2-} + 140 \text{ H}_2\text{O}$ |
| (2) | Nitrate reduction:
$94.4 \text{ NO}_3^- + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} \Rightarrow 13.6 \text{ CO}_2 + 92.4 \text{ HCO}_3^- + 55.2 \text{ N}_2 + 84.8 \text{ H}_2\text{O} + \text{HPO}_4^{2-}$ |
| (3) | Mn^{4+} reduction:
$236 \text{ MnO}_2 + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 364 \text{ CO}_2 + 104 \text{ H}_2\text{O} \Rightarrow 470 \text{ HCO}_3^- + 8 \text{ N}_2 + 236 \text{ Mn}^{2+} + \text{HPO}_4^{2-}$ |
| (4) | Fe^{3+} reduction:
$212 \text{ Fe}_2\text{O}_3 + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 740 \text{ CO}_2 + 316 \text{ H}_2\text{O} \Rightarrow 846 \text{ HCO}_3^- + 424 \text{ Fe}^{2+} + 16 \text{ NH}_3 + \text{HPO}_4^{2-}$ |
| (5) | Sulfate reduction:
$53 \text{ SO}_4^{2-} + \text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} \Rightarrow 39 \text{ CO}_2 + 67 \text{ HCO}_3^- + 16 \text{ NH}_4^+ + 53 \text{ HS}^- + 39 \text{ H}_2\text{O} + \text{HPO}_4^{2-}$ |
| (b) | Calcium carbonate dissolution |
| (6) | $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + 2 \text{ HCO}_3^-$ |

$$\frac{dTA}{d[N]} = \left. \frac{\partial TA}{\partial [N]} \right|_{Ca} + \left. \frac{\partial TA}{\partial [N]} \right|_{OM} \quad (8)$$

where $\partial TC/\partial [N]_{Ca}$ indicates the change in total CO_2 during organic matter degradation with the calcium concentration held constant (i.e., no $CaCO_3$ reaction) and $\partial TC/\partial [N]_{OM}$ is the change in total CO_2 as a result of $CaCO_3$ reaction in the absence of organic matter degradation. The partial derivatives with the subscripts "Ca" are derived from the stoichiometric equations (1) through (3). The changes in alkalinity and total CO_2 due to $CaCO_3$ reaction, the last term in equations (7) and (8), can be derived from an equilibrium model in which the response of the carbonate parameters to conditions brought about by organic matter degradation is calculated from the definitions for the alkalinity and total CO_2 , and the first and second dissociation constants for carbonic acid [9].

We calculated $dTA/d[N]$ and $dTC/d[N]$ using a computer program in which the initial condition is a closed system saturated with respect to calcite. Organic matter degradation changed the alkalinity, total CO_2 and oxidant ratios of the water according to the stoichiometry in equations (1) through (3). A new carbonate ion concentration was calculated from the carbonate system parameters and compared with the saturation value. Alkalinity, total CO_2 and calcium were then allowed to increase or decrease according to the stoichiometry in equation (6) until saturation was reattained. The calculation was made for small intervals of oxidant concentration, ΔN . The value of ΔN was decreased until further decrease caused no change in the result.

Fig. 2 is a graphical representation of the results of these calculations for oxygen, nitrate and manganese. Both the pH at which the calculations were made and the pH change during the reaction are indicated in the figures. The stoichiometric oxygen reaction (equations (1) and (6)) overpredicts the alkalinity increase by about 10%. The ratio dTA/dO_2 for organic matter degradation in the presence of $CaCO_3$ in marine systems should be about -1.50 rather than -1.67 . The extent of $CaCO_3$ precipitation during manganese reduction is also overpredicted by equation (3) by about 10%. Only about 60% of the CO_2 released during

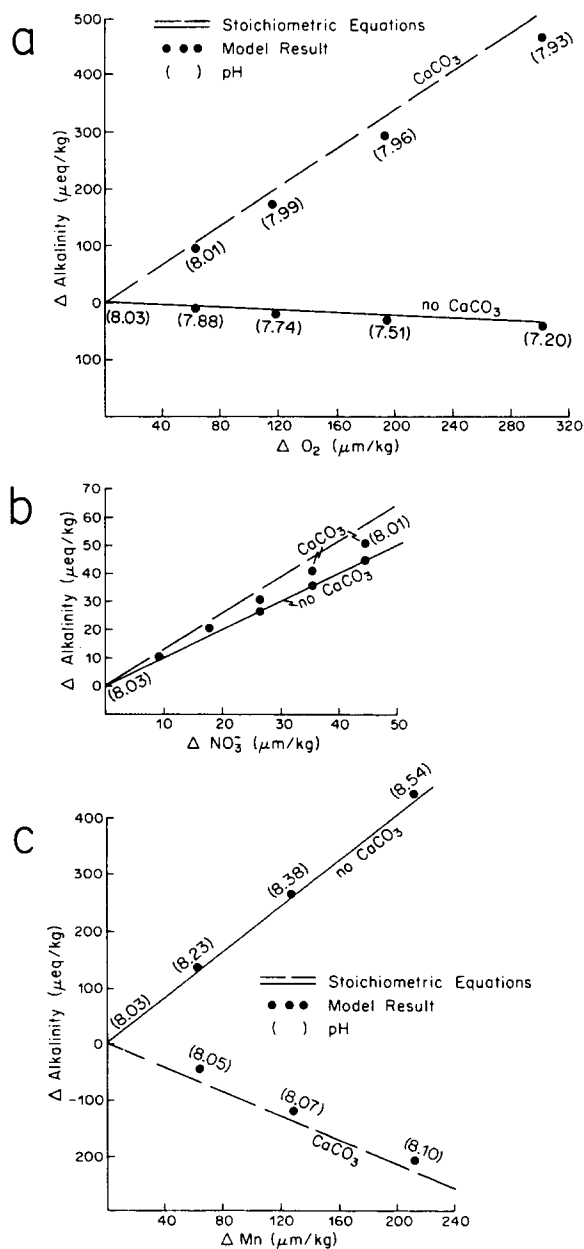


Fig. 2. The changes in alkalinity during organic matter degradation in a closed system in the presence and absence of $CaCO_3$. Lines represent the values predicted by the equations in Table 1. Symbols are the model derived results, and pH values are in parentheses. The initial condition is given in Table 2. The results are for the electron acceptors; (a) oxygen, (b) nitrate, and (c) manganese.

organic matter degradation by nitrate reduction dissolves calcium carbonate. Differences between the simple stoichiometric model values and the equilibrium model results may be viewed as resulting from the ratio of alkalinity/total CO₂ released during organic matter degradation. If this ratio is near 1, then the difference between alkalinity and total CO₂ (CO₃²⁻-CO₂) remains nearly constant; there can be very little change in [CO₃²⁻], and hence little reaction with CaCO₃. The greatest inaccuracies in the stoichiometric model occur when the $\Delta A/\Delta TC$ is near unity, as in the case for denitrification. The equilibrium and stoichiometric model predictions approach each other as $\Delta A/\Delta TC$ during organic matter degradation becomes greater or smaller than one.

The ratios predicted by the stoichiometric and equilibrium models are summarized in Table 2. Equilibrium model values are dependent upon the initial pH and to a lesser degree on temperature and pressure, so the exact result must be solved for each specific case. In general, however, for typical seawater conditions, the alkalinity increase in response to O₂ reduction in a CaCO₃-saturated solution is 5–10% less than the stoichiometry predicted value and the alkalinity increase due to CaCO₃ dissolution during denitrification is one half to two thirds that indicated by equation (6). In section 4 of this paper we apply the results of the model to an open system to interpret the carbonate chemistry data at sites C and S.

3. Analytical methods and results: the pressure effect

The predicted change in alkalinity and total CO₂ in sediment pore waters caused by CaCO₃ precipitation during core recovery was shown by Murray et al. [3] to be in close agreement with measured differences between core centrifugation and harpoon (in situ) sampling. The comparison was made at a location in the Guatemala Basin in hemipelagic sediments with a carbonate content of 0.5–1.0%. At MANOP sites M and H, Emerson et al. [1] assumed a thermodynamically predictable pressure effect and corrected the alkalinity data accordingly. One of the resulting conclusions was that the pore water alkalinity/nitrate ratio could be explained only if HCO₃⁻ and NO₃⁻ were assumed to diffuse at the same rate. This conclusion led to the hypothesis that surface sediment pore waters were bioturbated or mixed at a rate greater than that due to molecular diffusion.

At sites C and S we had the opportunity once again to compare results from core centrifugation and in situ methods. Alkalinity was measured by Gran titration using the extended calculation method [10]; total CO₂ was determined by gas chromatography; and calcium was analyzed by EGTA titration. The error in these measurements is on the order of $\pm 0.7\%$. The data are tabulated in the companion paper by Jahnke et al. [4] and summarized in Fig. 3a and b. Calcium data from

TABLE 2

The ratios of alkalinity/oxidant, total CO₂/oxidant and calcium/total CO₂ predicted from the stoichiometric equations (Table 1) and the model (see text). The final column represents the change in calcium with respect to the amount of total CO₂ added to the water by organic matter degradation (initial conditions: TA = 2.446×10^{-3} ; TC = 2.278×10^{-3} ; pH = 8.03; T = 1.5°C; P = 437 atm)

	$\partial TA/\partial [N]$	$\partial TC/\partial [N]$	$\frac{(\Delta Ca)}{(\Delta \Sigma CO_2)_{org \ deg}}$
$[N] = O_2$			
stoichiometric value	-1.68	-1.67	1.17
model result	-1.50	-1.58	1.06
$[N] = NO_3^-$			
stoichiometric value	-1.29	-1.27	0.13
model result	-1.15	-1.21	0.08
$[N] = MnO_2$			
stoichiometric value	1.08	1.09	-3.43
model result	0.96	1.05	-3.24

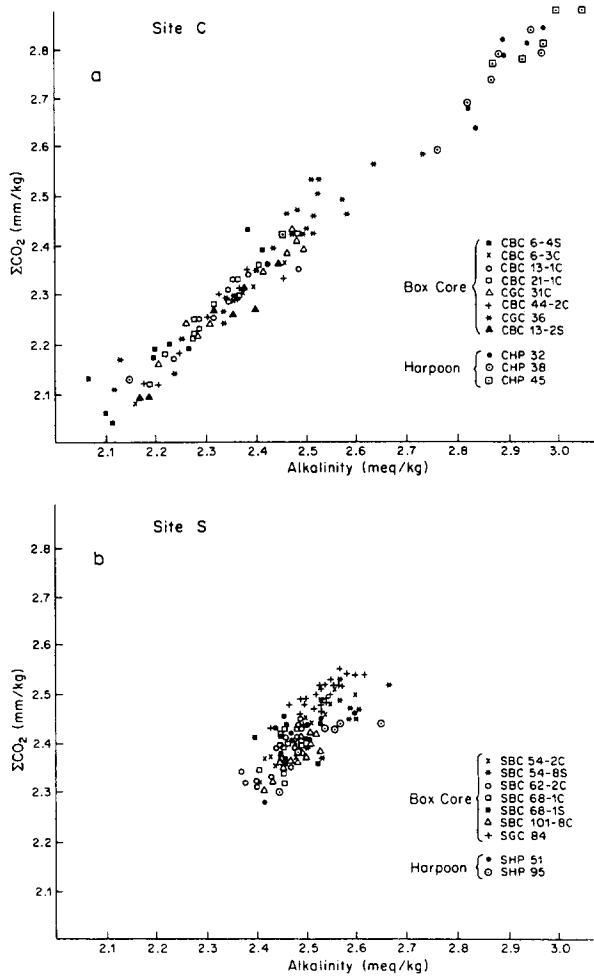


Fig. 3. Alkalinity and total CO_2 results from MANOP pore waters at sites C (a) and S (b). The data are tabulated in Jahnke et al. [4].

two cores and harpoons are presented in Fig. 4. The changes in alkalinity and total CO_2 due to the pressure effect predicted by the methods of Murray et al. [3] are roughly $100 \mu\text{eq/kg}$ and $50 \mu\text{mol/kg}$, respectively. The differences between core and harpoon results are about $500 \mu\text{mol/kg}$ and the measured ratio of alkalinity change to total CO_2 change is about 1. The offset in calcium below 20 cm at site C is even greater than that for alkalinity and ΣCO_2 —approximately $800 \mu\text{mol/kg}$. At site S there are almost no differences in the alkalinity and total CO_2 concentrations measured

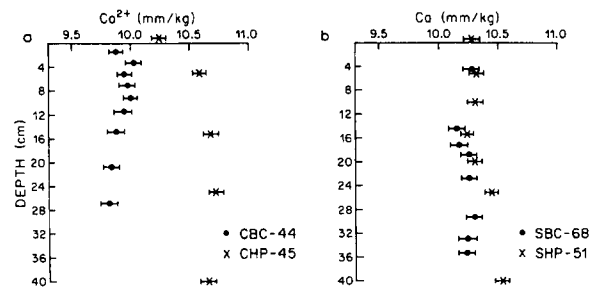


Fig. 4. Calcium results from a core and a harpoon from sites C (a) and S (b). The data are tabulated in Jahnke et al. [4].

by the harpoon and centrifugation methods. The offset in calcium at this location is small, but slightly greater than the analytical error, $\pm 70 \mu\text{mol/kg}$.

Clearly, the results from sites C and S are not in agreement with the thermodynamically predicted trends. The degree of change in carbonate system parameters brought about by pressure decrease appears to depend upon the presence of CaCO_3 in the sediments. There is very little evidence for a pressure effect at the siliceous ooze site, presumably due to the lack of nucleation sites for CaCO_3 ; in sediments with a low carbonate content (i.e., the Guatemala Basin [3]), the carbonate system responds to the pressure change in a thermodynamically predictable way; and in nearly pure CaCO_3 (site C), the chemical differences resulting from the pressure decrease are much greater than would be predicted.

A probable explanation for the very large pressure effect observed at site C is that the pH of the pore waters is not controlled by the carbonate system, but held constant during core recovery. If this is the case then the $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ ratio must have remained constant while CaCO_3 precipitated during pressure change. The resulting alkalinity change would be much larger than otherwise predicted, and the ratio of the alkalinity to total CO_2 change could be one. The predicted response of alkalinity and total CO_2 by both variable and constant pH models at sites C and S is presented in Fig. 5. The data from site C are in accordance with the constant pH model using a

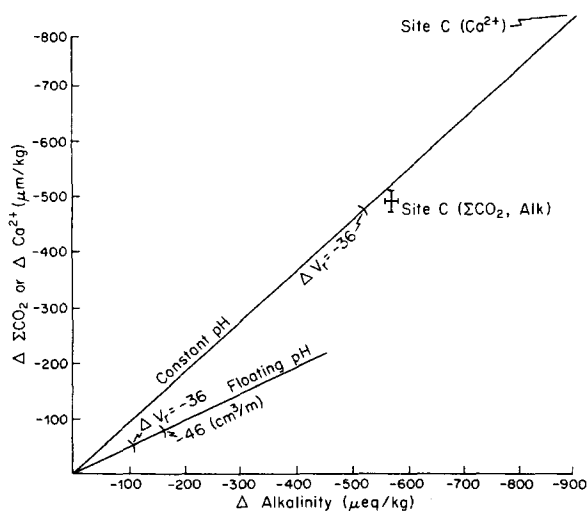
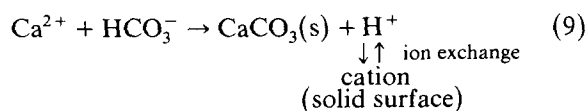


Fig. 5. The change in alkalinity (Δ alkalinity) and total CO_2 ($\Delta\Sigma\text{CO}_2$) resulting from a pressure change of 437 atm. The line for floating pH was calculated by the methods outlined in Murray et al. [3]. Site C alkalinity and total CO_2 and calcium results are indicated on the figure.

partial molal volume change, ΔV_r , for calcite of $-36 \text{ cm}^3/\text{mol}$. The preferred value of ΔV_r ranges from $-36 \text{ cm}^3/\text{mol}$ at 25°C to $-48 \text{ cm}^3/\text{mol}$ at 2°C [11]. A possible explanation for constant pH during pressure change is that the hydrogen ion released during precipitation is adsorbed by a solid surface:



A comparison of the pH measured on samples from the harpoon and cores (Fig. 6) indicates that the most frequently measured values are different by at most 0.05 units. If reaction (9) were not

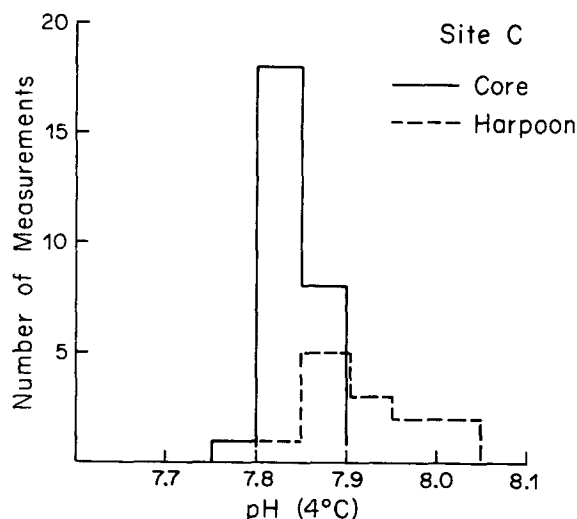


Fig. 6. A comparison of pH measured at site C on samples from the harpoon and from cores. Data are tabulated in Jahnke et al. [4].

operative, the core pH should be 0.15–0.2 units lower than that derived from the harpoon. If this mechanism is the explanation for the observations, it appears to be viable only in calcium carbonate-rich sediments.

The reason for the anomalously large offset in calcium between the in situ sampler and cores at site C ($800 \mu\text{mol}/\text{kg}$) compared to $500 \mu\text{mol}/\text{kg}$ for total CO_2) and the slight offset at site S is not at all clear. We can only speculate that these results may represent an ion exchange with another major ion of seawater at particle surfaces.

Although the constant pH model appears to adequately explain the alkalinity and total CO_2 data from site C, one must be careful about gener-

TABLE 3

A summary of the differences between the pore water alkalinity sampled by in situ and centrifugation methods

Location	Depth (m)	Δ Alkalinity (harpoon-core) ($\mu\text{eq}/\text{kg}$)	Alkalinity predicted		
			floating pH	constant pH	references
Guatemala Basin	3500	~ 80	88	425	[3]
MANOP site C	4450	580	112	540	this work
MANOP site S	4900	0	122	585	this work

alizing this effect to long-term, in situ processes. If the in situ pH of pore waters were to be held constant by H^+ exchange onto a solid surface and the carbonate ion controlled by calcium carbonate equilibrium, then there could be no increase in alkalinity or total CO_2 during organic matter diagenesis. (If two of the system unknowns are fixed then the remaining variables are also fixed.) We know this not to be the case as in situ alkalinity and total CO_2 do increase in the sediments at site C (Fig. 3; see also the profiles in Jahnke et al., [4]).

A summary of the observed pressure effects (Table 3) indicates that one must be very careful in correcting carbonate system measurements on pore water samples extracted from cores. Previous predictions of the pressure effect [3] hold true only in very special cases. Conclusions drawn about the rates of mixing of surface pore waters based on measurements from cores [1] may well be incorrect and must be tested by in situ measurements.

4. Discussion

In this section we evaluate the in situ data from sites C and S in terms of the pore water saturation state; and the alkalinity, total CO_2 and calcium response to organic matter degradation. The data are reproduced from Jahnke et al. [4] in Table 4. Carbonate ion concentration and pH are calculated from alkalinity and total CO_2 by the methods described in Emerson et al. [1].

4.1. The pore water saturation state

A comparison of the measured and calculated pH from the harpoon results is presented in Fig. 7. With a few exceptions the data fall within ± 0.1 pH units indicating the internal consistency of the results. (An error of 0.5% in alkalinity and total CO_2 causes an uncertainty in pH of about ± 0.08 units. The measured pH is probably not accurate to better than ± 0.05 units.) The ion concentration product for calcite ($pICP = -\log([Ca^{2+}][CO_3^{2-}])$) from site C data is presented in Fig. 8. The apparent solubility products for calcite and aragonite in seawater were derived from the compilation by Millero [11] and are indicated on the abscissa of

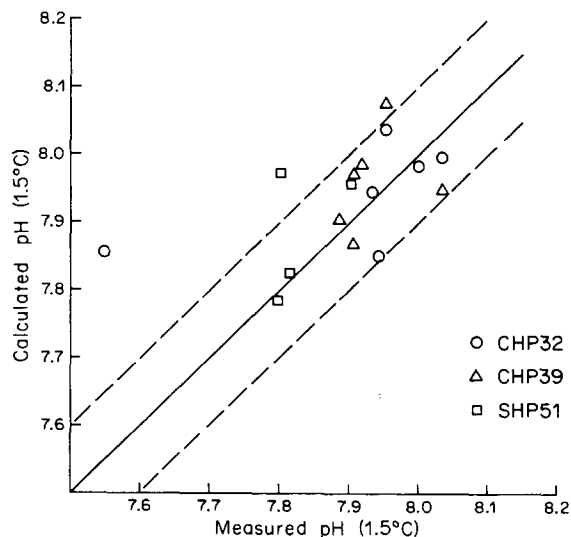


Fig. 7. Comparison of the measured and calculated pH results from the in situ sampler (see Table 3).

the figure. The apparent constant for calcite, K'_{sp} , is consistent with the 1-atm solubility products of Ingle [12] and Morse et al. [13] and a partial molal volume change of $-48 \text{ cm}^3/\text{mol}$ at 2°C [12]. The aragonite solubility product is consistent with the data of Morse et al. [13] at 1 atm and a ΔV_r of $-45 \text{ cm}^3/\text{mol}$ at 2°C (see Millero [11]). The error bars in the figure represent one standard deviation of the results for both bottom water and pore water. The bottom water values used to calculate

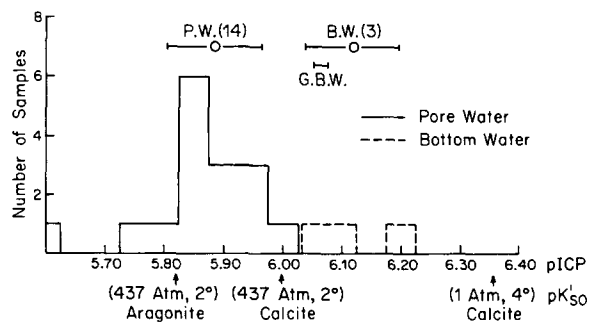


Fig. 8. The $pICP (-\log([Ca^{2+}][CO_3^{2-}]))$ for site C pore waters. All data are from harpoon samples. Error bars represent one standard deviation of the pore water (P.W.) and bottom water (B.W.) results. G.B.W. indicates the $pICP$ calculated from carbonate ion data of GEOSECS: the carbonate ion content of Pacific bottom water at 4370 m was taken to be $79-84 \times 10^{-6} \text{ mol/kg}$ [14]; the calcium content used was $10.3 \times 10^{-3} \text{ mol/kg}$. (See text for the sources for the pK' values.)

TABLE 4
Carbonate system parameters from sites C and S in situ measurements

Cast	Depth (cm)	Alkalinity	Measured values			Calculated values ^a	
			ΣCO_2 (mmol/kg)	Ca	pH (1.5°C)	pH	$[\text{CO}_3^{2-}]$ ($\mu\text{mol/kg}$)
CHP 32	0	2.444	2.343	–	7.54	7.86	80
	5	2.863	2.693	–	7.95	8.04	138
	10	2.919	2.777	–	7.93	7.95	115
	15	2.915	2.810	–	7.94	7.85	93
	25	2.968	2.798	–	8.00	7.99	128
	40	3.004	2.828	–	8.03	8.00	128
CHP 38	0	2.407	2.301	–	7.91	7.87	81
	5	2.845	2.681	–	7.92	7.99	122
	10	2.897	2.732	–	7.91	7.98	124
	15	2.911	2.778	–	7.88	7.91	107
	25	3.000	2.783	–	7.95	8.08	157
	40	2.983	2.831	–	8.04	7.95	119
CHP 45	0	2.472	2.424	10.25	–	7.69	57
	5	2.903	2.767	10.55	–	7.92	108
	10	2.956	2.774	–	–	8.02	135
	15	3.003	2.803	10.68	–	8.05	147
	25	3.009	2.866	10.72	–	8.10	169
	40	3.077	2.865	10.65	–	8.07	156
SHP 51	0	2.437	2.281	10.29	–	7.98	107
	5	2.525	2.410	10.32	–	7.87	87
	10	2.569	2.407	10.31	7.80	7.98	113
	15	2.488	2.401	10.26	7.80	7.79	73
	25	2.548	2.445	10.45	7.81	7.83	82
	40	2.619	2.460	10.53	7.90	7.97	113
SHP 69 ^b	0	2.452	–	–	7.97	–	–
	5	2.531	–	–	7.77	–	–
	10	2.549	–	–	7.75	–	–
	25	2.555	–	–	7.72	–	–
	40	2.574	–	–	–	–	–
SHP 95	0	2.462	2.302	–	–	7.99	110
	5	2.506	2.379	–	–	7.90	93
	10	2.555	2.435	–	–	7.88	91
	25	2.584	2.444	–	–	7.93	102
	40	2.666	2.443	–	–	8.10	150

^a Calculated by the methods outlined in Emerson et al. [1].

^b Total CO_2 data are deleted because of standardization problems.

the pICP in Fig. 8 are from the top harpoon port which was designed to remain above the sediment-water interface during deployment; thus, all the results derive from data sampled in the same way. The pICP calculated from GEOSECS North Pacific carbonate estimates [14] and a

calcium concentration of 10.3 mmol/kg is plotted in Fig. 8 for comparison.

The pore water results indicate that the sediments are supersaturated with respect to calcite at site C. Although the degree of supersaturation is slight and not greatly outside the measurement

error, the internal consistency of the data represented in Fig. 7 and the agreement with GEO-SECS bottom water results are arguments for its validity. Since the bottom water in this region of the ocean is undersaturated with respect to marine calcite, the most viable means of creating pore waters that are supersaturated is aragonite dissolution and preservation in the sediments. The pore waters are saturated with respect to aragonite (Fig. 8). The rain of aragonite to the sediments may be sufficient [15] in this highly productive region of the ocean to result in a small amount of aragonite preservation in the sediments.

4.2. The stoichiometric model

The “potential alkalinity increase” (PAI; [1]) in oxic and suboxic [7] sediment pore waters is defined as:

$$\begin{aligned} \text{PAI} = \Delta\text{TA}_{\text{inorg}} + & \left(\frac{\partial\text{TA}}{\partial\text{O}_2} \right) \frac{D_{\text{O}_2}}{D_{\text{HCO}_3^-}} \Delta\text{O}_2 \\ & + \left(\frac{\partial\text{TA}}{\partial\text{NO}_3^-} \right) \frac{D_{\text{NO}_3^-}}{D_{\text{HCO}_3^-}} \Delta\text{NO}_3^- \\ & + \left(\frac{\partial\text{TA}}{\partial\text{MnO}_2} \right) \frac{D_{\text{Mn}^{2+}}}{D_{\text{HCO}_3^-}} \Delta\text{Mn} \end{aligned} \quad (10)$$

where $\Delta\text{TA}_{\text{inorg}}$ is the increase in total alkalinity brought about by purely inorganic dissolution of CaCO_3 required to resaturate the pore waters in sediments that are below the saturation horizon in the ocean. The derivatives are the stoichiometric ratios from Table 2 (e.g., $(\partial\text{TA}/\partial\text{O}_2) = -1.50$ in the presence of calcium carbonate). Diffusion coefficients are $D_{\text{HCO}_3^-} = 11.8 \times 10^{-6} \text{ cm}^2/\text{s}$, $D_{\text{O}_2} = 23 \times 10^{-6} \text{ cm}^2/\text{s}$, $D_{\text{NO}_3^-} = 19.0 \times 10^{-6} \text{ cm}^2/\text{s}$, and $D_{\text{Mn}^{2+}} = 6.9 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C [16]. The delta terms are the differences between bottom water and pore water concentrations of oxygen, nitrate, and manganese. The “potential total CO_2 increase” (PCI) is exactly analogous to equation (10) except that $\Delta\text{TC}_{\text{inorg}}$ replaces $\Delta\text{TA}_{\text{inorg}}$ and ∂TC replaces ∂TA (e.g., $\partial\text{TC}/\partial\text{O}_2 = -1.58$ in the presence of carbonate). Since oxygen was not measured on harpoon samples, we assume that the change in oxygen, $\Delta\text{O}_2 = \text{O}_{2,\text{bottom water}} (167 \mu\text{mol}/\text{kg}) - \text{O}_{2,\text{pore water}}$ is related to the change in

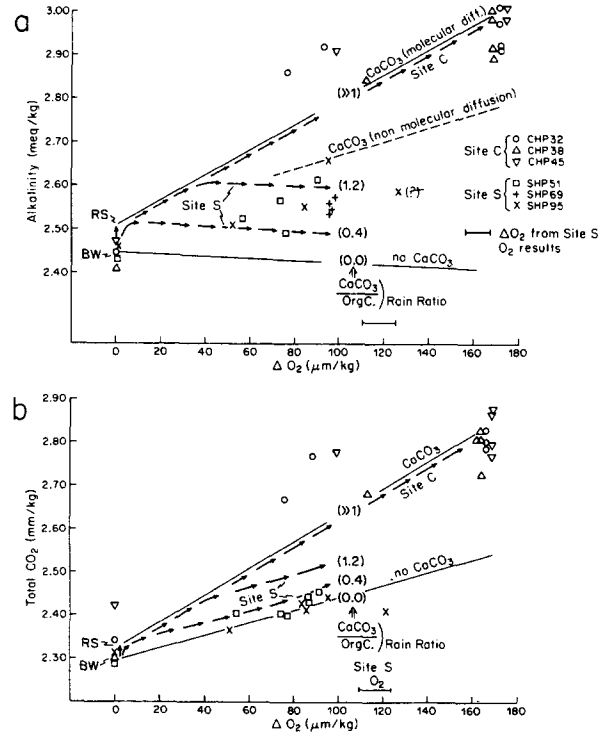


Fig. 9. Alkalinity (a) and total CO_2 (b) changes as a function of organic matter degradation during oxygen reduction at sites C and S. Dashed lines are the predicted values for various particulate CaCO_3 /organic carbon rain ratios (see text). B.W. indicates bottom water values. R.S. is the value of alkalinity and total CO_2 attained when the pore waters become resaturated with respect to calcite by “inorganically” driven CaCO_3 dissolution. Symbols represent data from sites C and S in situ measurements.

nitrate above the nitrate maximum by [17]:

$$\begin{aligned} \Delta\text{O}_2 = & (\text{NO}_3^-_{\text{bottom water}} - \text{NO}_3^-_{\text{pore water}}) \\ & \times \left(\frac{138}{16} \right) \left(\frac{D_{\text{NO}_3^-}}{D_{\text{O}_2}} \right) \end{aligned} \quad (11)$$

Below the nitrate maximum, i.e., in the zone of denitrification, we assume that the oxygen in the pore water is zero or very close to zero. At site C the alkalinity and total CO_2 changes due to the slight decrease in nitrate and increase in manganese are ignored because they have a negligible effect.

Measured and predicted alkalinity and total CO_2 are plotted versus ΔO_2 in Fig. 9. The lines are predictions for various rain ratios of particulate

CaCO₃ and organic carbon. For a CaCO₃/organic carbon rain ratio much greater than one ($\gg 1$ in Fig. 9) calcium carbonate would be preserved in the sediments and the alkalinity response is predicted by equation (10). If the ratio is zero—no particulate CaCO₃ reaches the sediment-water interface—the predicted response is that of equation (1). The intermediate cases were derived by computing the PAI for conditions in which a fraction of the total oxygen consumption occurs in the presence of CaCO₃. For example, if it requires 35 $\mu\text{mol/kg}$ of O₂ consumption to exhaust the sediments of CaCO₃ (an intermediate case in Fig. 9), then the PAI to this point is:

$$\text{PAI} = \Delta\text{TA}_{\text{inorg}} + \left(\frac{\partial\text{TA}}{\partial\text{O}_2} \right) \frac{D_{\text{O}_2}}{D_{\text{HCO}_3^-}} 35 \mu\text{mol/kg}$$

where $\Delta\text{TA}_{\text{inorg}} = 60 \mu\text{eq/kg}$. (The bottom water $[\text{CO}_3^{2-}]$ is $80 \mu\text{mol/kg}$ and the $[\text{CO}_3^{2-}]_{\text{sat}}$ is $\sim 95 \mu\text{mol/kg}$. To raise the $[\text{CO}_3^{2-}]$ by $15 \mu\text{mol/kg}$ by CaCO₃ dissolution requires an increase of $60 \mu\text{eq/kg}$ of alkalinity and $30 \mu\text{mol/kg}$ of total CO₂.) The second term on the right side of the above equation is: $-1.50 \times 1.95 \times -35 \mu\text{mol/kg} = 102 \mu\text{eq/kg}$. Once CaCO₃ is totally dissolved, the PAI follows the course described by equation (1).

The $\Delta\text{Ca}/\Delta\text{TA}$ ratios during “inorganic” and “organic” CaCO₃ dissolution are 0.5 (equation (6)) and 0.54 (equations (1) and (6)), respectively. The amount of CaCO₃ dissolved during the process depicted by the above equation is, therefore, $85 \mu\text{mol/kg}$. Since the organic carbon consumption in the sediments, and hence the presumed carbon rain rate, is directly related to the amount of the oxygen depletion ($\partial(\text{org C})/\partial\text{O}_2 = 106/138$), the ratio of particulate CaCO₃ to organic carbon reaching the sediment-water interface in the intermediate case can be estimated from the pore water results. (In this case the ratio is 85 divided by 0.77 times the estimated oxygen depletion.)

Alkalinity and total CO₂ results at site C (Fig. 9) are greater than the values predicted from the nitrate model (equation (12)) in the region of incomplete oxygen consumption ($\Delta\text{O}_2 = 70\text{--}100 \mu\text{mol/kg}$ in Fig. 9). This result probably reflects the approximate nature of the O₂-NO₃⁻ relationship. Jahnke et al. [4] and Galoway and Bender

[18] show that the prediction of oxygen from the stoichiometric O₂-NO₃⁻ relationship can significantly overestimate the oxygen concentration at this site. The maximum measured changes in alkalinity and total CO₂ at site C, however, are within $\pm 10\%$ of the model predicted change. Thus, to a first approximation, the PAI and PCI models adequately explain the alkalinity and total CO₂ data after aerobic respiration is complete.

If the dissolved constituents of the pore water were transported by a mechanism which is faster than molecular diffusion (i.e.,urbation induced by biological or physical activity), the predicted alkalinity at $\Delta\text{O}_2 = 167 \mu\text{mol/kg}$ would be 2.76 meq/kg (Fig. 9a). The alkalinity and total CO₂ data are inconsistent with a hypothesis that transport in the pore waters is by processes which enhance the molecular diffusion rates [1].

With the site C data as verification for the stoichiometric model we can use it to interpret the pore water results from the non-carbonate sediments at site S. First, we note that the alkalinity measurements from site S (Fig. 9a) fall between those predicted for organic matter degradation in the presence and absence of CaCO₃, implying that some CaCO₃ has dissolved in the sediment even though CaCO₃ is not preserved. Both total CO₂ and alkalinity fall below the line predicted for organic matter degradation in the presence of CaCO₃, indicating that the CaCO₃ which rains to the sediments is exhausted before organic matter diagenesis is complete.

The ΔO_2 estimate from the nitrate data at this site is about $95 \mu\text{mol/kg}$. The difference between bottom water oxygen and oxygen measured in the pore waters at site S [4] is $115 \mu\text{mol/kg}$ (see Fig. 9). The inconsistency in these ΔO_2 estimates could be due to the approximate nature of the nitrate model (equation (12)) or from real variations in pore water chemistry at the site. Using the value estimated from the nitrate model, because the data are from the same samples as those for alkalinity and total CO₂, we estimate that the CaCO₃/organic carbon rain ratio required to explain the alkalinity data from site S is 0.4–1.2 (Fig. 9a). The total CO₂ data (Fig. 9b) are less sensitive than alkalinity to this type of analysis but indicate a rain ratio not greater than 0.5. As the alkalinity

result is more sensitive, we assign it more weight and take the best estimate for the rain ratio to be 0.4–1.2. Sediment trap estimates of the carbon flux at 4630 m at this site are 2.5 mol C/cm² and 2.3 mol CaCO₃/cm² (Jack Dymond and Kathy Fischer, O.S.U. sediment trap group, personal communication). These data fall within the range predicted from the pore water analysis.

The contention that the alkalinity increase observed at both sites C and S can be explained solely as a result of calcium carbonate dissolution is supported by the calcium-alkalinity relationship in Fig. 10. The calcium results from in situ measurements are in agreement with that predicted from the stoichiometric model and a diffusion correction:

$$\Delta TA = \left(\frac{\partial TA}{\partial Ca} \right) \frac{D_{Ca}}{D_{HCO_3}} \Delta Ca$$

where $(\partial TA/\partial Ca)$ is 1.84 during oxygen consumption (Table 2) and $D_{Ca} = 7.93 \times 10^{-6}$ cm²/s at 25°C [16]. The slight alkalinity excess (or Ca deficiency) is not significantly outside of the measurement error. The alkalinity deficiency reported by Sayles [19] for the South Atlantic and Caribbean pore waters is not observed at these sites.

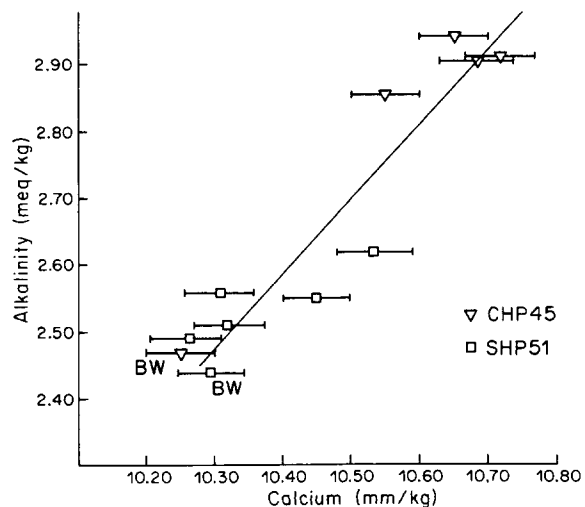


Fig. 10. The alkalinity and calcium data from in situ measurements. B.W. indicates bottom water values. The line represents the stoichiometrically predicted trend.

5. Summary and conclusions

The main conclusions that we wish to emphasize in this study concern the stoichiometry of predicted alkalinity and total CO₂ response to organic matter degradation, the problems of predicting the pressure effect during sampling in the deep sea, the calcite saturation state in equatorial Pacific carbonate sediments, and the utility of stoichiometric theory in predicting the pore water alkalinity and total CO₂ response to organic matter degradation.

The stoichiometry of the alkalinity and total CO₂ increase during organic matter degradation in a closed system is not simply represented by a combination of equations (1) to (5) and (6). The degree of reaction represented by equation (6) is dependent upon the alkalinity and total CO₂ released to the pore water during organic matter degradation. An extreme example is that of denitrification in which only slightly more than half of the CaCO₃ predicted to dissolve by equations (2) and (6) actually dissolves at the pH of seawater. The alkalinity and total CO₂ increase during oxygen reduction is about 90% of the value predicted from equations (1) and (6).

With a greater number of comparisons of pore water carbonate system measurements between in situ and shipboard sampling methods, it has become clear that previous explanations for the pressure effect [3] are not general. Conclusions drawn from centrifuged pore water measurements that were corrected to in situ conditions [1] by this method may be incorrect. The alkalinity offset varies between 0 and 500 μeq/kg, while the thermodynamically predicted value [3] is ~100 μeq/kg. The magnitude of the effect appears to be dependent on the abundance of CaCO₃ in the sediments. At present there is no alternative to measuring the carbonate system parameters in deep-sea pore waters by in situ methods.

In situ alkalinity, total CO₂ and pH measurements from MANOP site C are internally consistent, and the calculated bottom water carbonate ion concentration agrees with GEOSECS deep Pacific results within the error of the measurements. The pore water data indicate supersaturation with respect to calcite. The most likely explanation for this result is the dissolution of aragonite in the sediments.

Alkalinity and total CO₂ increases follow the trends predicted by the model for organic matter degradation in the presence of CaCO₃ at site C. Alkalinity and total CO₂ changes in the interstitial waters are inconsistent with a hypothesis that pore water transport is enhanced by biological or physical turbation processes. At site S, the siliceous ooze, the pore water alkalinity results indicate dissolution of CaCO₃ in the sediments near the sediment-water interface. The stoichiometric model is used to show that the particulate CaCO₃/C_{organic} ratio entering the sediments must be 0.8 ± 0.4 . Measured values for this ratio from bottom sediment traps at this site fall within this prediction (CaCO₃/C_{organic} ~ 0.9).

Organic carbon rain rates predicted by the companion paper to this one, Jahnke et al. [4], are in excellent agreement with the sediment trap fluxes measured at site S. This result and the compatibility of the predicted and measured CaCO₃/organic carbon rain ratio show that we are on the threshold of understanding the inter-relationships between particulate carbon and carbonate rain, degradation, dissolution and preservation in deep-sea sediments. Once the processes controlling carbon fluxes at the sediment-water interface are firmly quantified we can be more confident in our ability to interpret past changes in the sedimentary record.

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