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Long term constraints on the global marine carbonate system

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ABSTRACT

As a result of the interaction between biological cycles and the abyssal circulation, the modern North Pacific Ocean has a lower degree of calcite saturation (Ω) and a shallower carbonate compensation depth (and lysocline) than does the North Atlantic. Results of simple calculations show that an increase in the sea water $[CO_3^=]/[Ca^{++}]$ ratio or a decrease in the sea water $[PO_4^=]$ (which is assumed to be coupled with the input of metabolic CO_2) would make the Atlantic and Pacific more similar with respect to Ω and the compensation depth, whereas a decrease in the sea water $[CO_3^=]/[Ca^{++}]$ ratio or an increase in the sea water $[PO_4^=]$ would enhance the existing geographical contrast in these parameters.

1. Introduction

In a general sense, the object of this paper is to examine the significance of an oceanographic parameter that has not previously been extensively considered: the preformed carbonate concentration of deep ocean water masses (i.e., their carbonate ion concentration prior to modification by $CaCO_3$ dissolution and metabolic CO_2 and NO_3^- addition).

More specifically, this study argues and discusses the implications of the following two propositions concerning long term controls on seawater and sediment chemistry: 1) the difference in lysocline and carbonate compensation depths between the Atlantic and Pacific Oceans is fixed by the amount of metabolic CO_2 added to North Pacific deep water and the $CO_3^=$ ion concentration of North Atlantic deep water and 2) the average $[CO_3^=]/[Ca^{++}]$ ratio of seawater is currently fixed at a value where the oceans are particularly well poised to compensate for surface water biogenic calcite overproduction (relative to the riverine and hydrothermal calcium input with which removal must be in balance). Following Redfield et al. (1963) and Broecker (1971), we regard $PO_4^=$ as the limiting nutrient in the oceans over a long time scale. The amount of metabolic CO_2 in North Pacific deep water is fixed by the $PO_4^=$ content and the P/C ratio in the Redfield relationship; hence we will argue that the difference between North Atlantic and North Pacific carbonate compensa-

tion depths is fixed by the $[PO_4^\equiv]$ in the North Pacific and the $[CO_3^\equiv]$ in the North Atlantic.

In qualitative terms, the argument for these points is straightforward. Calcium carbonate is assimilated into tests of calcareous marine organisms more rapidly than calcium is delivered to the oceans by rivers. In order that seawater chemistry remains at steady-state, the chemistry of the oceans is adjusted such that water into which most tests fall is undersaturated with respect to $CaCO_3$ (Broecker, 1971; Berger, 1970). The corrosive deep and bottom waters dissolve an amount of $CaCO_3$ equal to the excess surface water production with respect to the riverine input. There are two mechanisms responsible for regulating deep water carbonate dissolution, and while these mechanisms are coupled, each could probably completely balance overproduction on its own and will be discussed separately.

Mechanism I invokes the fact that $CaCO_3$ solubility increases with increasing pressure and decreasing temperature. Thus, the degree of $CaCO_3$ saturation tends to be lower in deep than in surface water. Compensation for overproduction of $CaCO_3$ in surface waters occurs in part by adjustment of seawater chemistry such that the rate at which biogenic $CaCO_3$ falls into undersaturated deep water and dissolves equals the rate of excess $CaCO_3$ production.

Mechanism II involves the effect of organisms and the abyssal circulation on the distribution of tracers in the deep oceans. There is net flow of deep water from the North Atlantic around the circumpolar to the North Pacific. Along with other biogenic constituents, CO_2 (from CH_2O oxidation) and $CO_3^\equiv$ (from $CaCO_3$ dissolution) are constantly being added to the deep water. The average input ratio of CH_2O-C/$CaCO_3$-C is greater than one (four according to Li *et al.*, 1969); i.e., carbonic acid is added in greater abundance than carbonate ion. Some of the added CO_2 is used up to neutralize the added $CO_3^\equiv$ according to the reaction:

$$CO_2 + H_2O + CO_3^\equiv \longrightarrow 2HCO_3^-$$
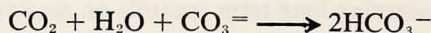
However, since CO_2 is added in excess, some remains after added $CO_3^\equiv$ is neutralized, and reacts with, and neutralizes, $CO_3^\equiv$ which was present in the water mass at the time of its formation. Thus as deep water progresses along the grand tour the carbonate ion concentration decreases, and North Pacific deep water is thus more acidic and corrosive than North Atlantic deep water. Carbonate compensation for surface water overproduction relative to the riverine input could be produced by adjustment of seawater chemistry so that the deep waters at the start of the abyssal grand tour are supersaturated and those at the middle and end are undersaturated.

In order for mechanism II to operate, the amount of carbonic acid added during the grand tour must be comparable to the $[CO_3^\equiv]$ of North Atlantic deep water. As a very crude first approximation, neglecting deep water $CaCO_3$ dissolution and many other factors to be considered later, and taking deep and bottom water $[PO_4^\equiv]$

as a parameter which controls CO_2 input (by the Redfield relationship), we can express this condition as follows:

$$106 \times ([PO_4^{\equiv}]_{deep}^{N.\ Pacific} - [PO_4^{\equiv}]_{deep}^{N.\ Atlantic}) \sim [CO_3^{\equiv}]_{deep}^{N.\ Atlantic}$$

If the right-hand term is much larger than the left-hand term, then CO_2 addition during the grand tour would not significantly lower the original $[CO_3^{\equiv}]$ and there would be very little Atlantic-Pacific contrast in either the degree of calcite saturation (Ω) or the carbonate compensation depth. In this case all compensation would occur by Mechanism I. On the other hand, if the left-hand term in the above equation is much larger than the right-hand term, most $CO_3^{\equiv}$ initially present in North Atlantic deep water would eventually be titrated to HCO_3^{-}. In this case the Pacific Ω would be less and the compensation depth shallower than values in the Atlantic; here all compensation would be by Mechanism II, with all of the North Atlantic sea floor and virtually none of the Pacific sea floor lying above the compensation depth. In the present ocean the relation in the above equation is strongly obeyed— the left-hand term is about 109 $\mu M\ kg^{-1}$, while the right-hand term is about 112 $\mu M\ kg^{-1}$ — and both mechanisms are important.

The fact that both potential mechanisms of carbonate compensation are active is an interesting feature of the modern oceans; it may allow the oceans to correct imbalances in throughput with chemical changes smaller than those which would be required if either mechanism were operating on its own.

To further argue the points raised in the first paragraph, we present the results of simple calculations which show how Ω (the degree of calcite saturation, i.e., the ion concentration product, $[Ca^{++}][CO_3^{\equiv}]$, divided by the apparent solubility product of calcite, $K'sp$) of different water masses changes with variations in the seawater $[CO_3^{\equiv}]/[Ca^{++}]$ ratio and in the seawater $PO_4^{\equiv}$ concentration. The models used are simple but suitable in that they provide reliable estimates of the changes in the relative degree of saturation of different water masses caused by changes in the sea-water $[CO_3^{\equiv}]/[Ca^{++}]$ ratio and $PO_4^{\equiv}$ concentration. However, these models are not suited for more demanding applications.

The model changes in $[Ca^{++}]$ and $[CO_3^{\equiv}]$ are not outside the range over which, according to Holland (1972), these parameters may have varied in the paleo-oceans. No evidence known to us indicates that model $PO_4^{\equiv}$ concentrations are outside the range of real ocean variations either, although if (as assumed in some models) the real world $[PO_4^{\equiv}]$ doubled, the oceans would become anoxic in the absence of a sympathetic increase in the pO_2 of the atmosphere. Whether real ocean $[Ca^{++}]$, $[CO_3^{\equiv}]$ and $[PO_4^{\equiv}]$ ever approached model values is, of course, completely unknown. Nevertheless the results of model calculations are useful in understanding some of the characteristics of sea water chemistry, and gaining insights into chemical paleoceanography.

2. Methods

The effect on Ω of changes in water mass properties at two depths (3500m and the bottom) is considered at each of six Geochemical Ocean Section Study (GEOSECS) stations. Station numbers, locations, present properties, and degree of carbonate saturation (calculated from GEOSECS leg report data using the methods of Takahashi (1975) for the apparent dissociation constants of carbonic and boric acid determined by Lyman (1957), the $K'sp$ as determined by Ingle *et al.* (1973) at 1 atmosphere pressure, and the pressure effect on $K'sp$ for calcite as determined by Culberson, 1972) are given in Table 1. The bottom-water chemistry is taken as the average of near-bottom values before depth gradients in potential temperature and salinity appear (i.e., as bottom mixed layer values); the depth range of each of the well-mixed bottom water layers is listed in the table (as the $\pm$ values under the "depth" column). The preformed phosphate is calculated as the difference between the observed *in situ* phosphate concentration, and the apparent oxygen utilization (AOU) divided by 138, using the O_2 solubility data of Kester (1975).

Obviously one can alter $[Ca^{++}]$ and $[CO_3^=]$ in any arbitrary way and determine the effect upon Ω of the various water masses in Table 1. Altering $[Ca^{++}]$ and $[CO_3^=]$ in specific ways summarized below gives useful insights into the behavior of the sediment-water system. Models I-IV were designed to demonstrate that the difference between Ω of deep waters in the Pacific and Atlantic depends on the average $[CO_3^=]/[Ca^{++}]$ ratio in these waters. In models I-IV (outlined in Table 2), it was assumed that, despite changes in $[Ca^{++}]$ and $[CO_3^=]$, biogenic components (including nutrients, $CaCO_3$, CH_2O, etc.) continue to cycle through the oceans exactly as they do today. Hence phosphate and nitrate concentrations, for example, remain constant and, more relevant to our purpose, the differences in total alkalinity (TA) and total carbon dioxide (TCO_2) between various water masses are the same as in the real ocean. In other words, we examined carbonate saturation in hypothetical oceans in which the present day ocean *variations* in $[Ca^{++}]$, TCO_2, TA, (and hence $[CO_3^=]$) were superimposed on different *background* levels of these parameters. Parameters in models I-IV were chosen as follows (note that "d" denotes deep water and "b" denotes bottom water);

Model I-d: the $[CO_3^=]$ of deep water at station 115 was increased by 20% (model Ids) and 100% (model Idl) respectively. TCO_2 was assumed to change at all deep stations by the amount of the change in carbonate ion at station 115. Calcium was decreased at all deep stations so that Ω of deep water at station 115 remained constant. Note that $[Ca^{++}]$ decreases by less than 50% in the $[CO_3^=]$ doubling model due to the change in the fraction of $CO_3^=$ ion paired by the new Ca^{++} concentration.

Model I-b: same as I-d, except that calculations were done for bottom waters only.

Table 1. Summary of present characteristics of water masses discussed here. Numbers in parentheses are GEOSECS station numbers. Maximum ranges of depth, salinity, and temperature are given below average bottom water values. Ω = degree of calcite saturation. All data are from GEOSEC leg reports, except for station 215 alkalinity and total CO_2 data, which are revised acording to Taro Takahashi (personal communication). $[Ca^{++}] = 1.026 \times 10^{-2}$ (salinity, ‰)/(35.00), M/kg (Carpenter, 1957).

Water Mass, Station and Location	Depth (m)	Salinity (‰)	Temperature, in situ (°C)	$[PO_4 \equiv]$ (μM/kg)	Preformed $[PO_4 \equiv]$ (μM/kg)	$[Ca^{++}]$ (mM/kg)	Total Alkalinity (μEq/kg)	Total CO_2 (μM/kg)	Ω (%)
Gibbs Fracture Zone Water (24)	2460	35.000	3.017						
53°46'N 33°37'W	±77	±0.003	±0.007	1.05	0.69	10.26	2292	2168	120
Eastern Basin Water (115)	3354	34.992	2.62	1.49	0.92	10.24	2340	2184	122
28°6'N 25°50'W	5156	34.886	2.455	1.52	0.91	10.23	2344	2187	90
	±145	±0.002	±0.018						
Weddell Sea Water (85)	3558	34.656	−0.209	2.14	1.29	10.16	2341	2233	87
57°31.8'S 17°26'W	4595	34.650	−0.276	2.12	1.32	10.16	2340	2235	71
	±123	±0.001	±0.001						
Antarctic Water (68)	3387	34.713	1.035	2.20	1.22	10.18	2371	2239	106
48°38.5'S 45°58'W	5881	34.665	0.267	2.24	1.33	10.16	2374	2270	57
	±85	±0.004	±0.010						
Circumpolar Water (76)	3464	34.711	0.961	2.10	1.10	10.18	2354	2242	93
57°42.5'S 66°5.5'W	4471	34.710	0.996	2.11	1.12	10.17	2354	2245	76
	±120	±0.001	±0.019						
North Pacific Water (215)	3384	34.668	1.488	2.53	1.06	10.16	2419	2339	79
37°28.6'N 177°19.4'W	5420	34.684	1.600	2.43	1.08	10.17	2426	2327	63
	±95	±0.003	±0.015						

Model II-*d*: the $[CO_3^=]$ of deep water at station 115 was decreased by 20% (model II*ds*) and 50% (model II*dl*). TCO_2 was assumed to change at all deep stations by the amount of the change in carbonate ion at station 115. Calcium was increased at all deep stations so that Ω of deep water at station 115 remained constant. Note that $[Ca^{++}]$ increases by less than 100% in the $[CO_3^=]$ halving model due to the change in the fraction of $CO_3^=$ ion paired by the new Ca^{++} concentration.

Model II-*b*: same as II-*d*, except that calculations were done for bottom waters only.

Model III-*d*: the carbonate ion concentration at station 115 deep water was increased by 20% and 100% at constant pH. Calcium was decreased at all deep stations so that Ω of deep water at station 115 remained constant.

Model III-*b*: same as model III-*d*, except that calculations were done for bottom waters only.

Model IV-*d*: the carbonate ion concentration at station 115 deep water was decreased by 20% and 50% at constant pH. Calcium was increased at all deep stations so that Ω at station 115 remained constant.

Model IV-*b*: same as model IV-*d*, except that calculations were done for bottom waters only.

In models I and II, the changes in $[CO_3^=]$ and TCO_2 at station 115 are specified (to repeat, $\Delta [TCO_2] = \Delta [CO^=_3]$), and the changes in TA are computed from this information. The changes in Ω of the various water masses are then calculated by adding these same changes in TCO_2 and TA to each water mass. In models III and IV, the changes in $[CO_3^=]$ and pH at station 115 are specified and the changes in TA and TCO_2 are computed from this information. Again, the changes in Ω of the various water masses are again calculated by adding these same TCO_2 and TA changes to each water mass. The purpose of presenting both sets of models for $[CO_3^=]$ increase (I and III) and $[CO_3^=]$ decrease (II and IV) is to show that assuming constant cycling, the difference between Atlantic and Pacific carbonate saturations is relatively insensitive to assumptions about the ways in which carbonate system parameters are varied to meet the model requirements of variable $[Ca^{++}]$ and $[CO_3^=]$.

Models V and VI (outlined in Table 2) demonstrate the effect on the degree of carbonate saturation of carbonic acid injection to the deep ocean resulting from organic matter decomposition. We previously held $[PO_4^\equiv]$ constant (models I-IV); in these models $[PO_4^\equiv]$ is assumed to vary.

Model V: the $[PO_4^\equiv]$ is increased by 20% and 100% throughout the oceans, heralding an increase in the carbonic acid input to the deep and bottom waters. In the case of the $[PO_4^\equiv]$ doubling, the TCO_2 of each water mass changes then according to the following equation:

$$\Delta [TCO_2] = 106 \, ([PO_4^=] - [PO_4^=]_{PRE}) + \frac{106}{4} \, ([PO_4^=] - [PO_4^=]_{PRE})$$

$$= 133 \, ([PO_4^=] - [PO_4^=]_{PRE})$$

The first term in the equation results from 106 moles of CO_2 released, by organic matter decomposition, per mole of phosphate released (Redfield *et al.*, 1963). The second term represents the addition of 0.25 moles of CO_2, from $CaCO_3$ dissolution, for each mole of CO_2 added by organic matter decomposition (Li *et al.*, 1969). This term results from analyses of Pacific Ocean data, but we assume it to be representative of the marine environment in general. Addition of biogenic debris will make seawater more acidic as long as the dissolution ratio of $CaCO_3$-C/CH_2O-C is <1.1 (the critical ratio is slightly greater than 1.0 because of nitric acid production during organic matter oxidation). To be qualitatively correct our model calculations require that biogenic debris input increases seawater acidity, and this requirement holds over wide excursions of the $CaCO_3$-C/CH_2O-C input ratio.

A doubling of the global seawater $[PO_4^=]$ increases the TCO_2 by an amount proportional to the oxidative phosphate input, assuming that the preformed $[PO_4^=]$ remains a constant fraction of the observed $[PO_4^=]$. Since the preformed $[PO_4^=]$ of a water mass depends on nutrient dynamics, light limitation, etc., the foregoing assumption may not be rigorously followed in any paleo- or hypothetical ocean, but in the absence of drastic violations the qualitative conclusions drawn from our model obtain.

The change in TA (again for the case of $[PO_4^=]$ doubling) is given by

$$\Delta [TA] = 2 \left(\frac{106}{4} \right) \, ([PO_4^=] - [PO_4^=]_{PRE}) - 16 \, ([PO_4^=] - [PO_4^=]_{PRE})$$

$$= 37 \, ([PO_4^=] - [PO_4^=]_{PRE})$$

since for each mole of $CaCO_3$ which dissolves, two equivalents of alkalinity are added to the system, and for each mole of phosphate released by organic matter decomposition, 16 equivalents of alkalinity are simultaneously titrated by nitrate added to the system (Brewer *et al.*, 1975). There are analogous equations for the model in which $[PO_4^=]$ is increased by 20%.

Model VI: same as model V, except that phosphate concentrations were decreased by 20% and 50%. Then for decreasing $[PO_4^=]$ by 50%

$$\Delta TCO_2 = 133 \, (-0.5) \, ([PO_4^=] - [PO_4^=]_{PRE}) \text{ and}$$

$$\Delta TA = 37 \, (-0.5) \, ([PO_4^=] - [PO_4^=]_{PRE}) \,.$$

Again there are analogous equations for decreasing $[PO_4^=]$ by 20%.

In models V and VI, the $[Ca^{++}]$ at each station changes by a constant factor, which is determined by the change in $[Ca^{++}]$ required at station 115 in order to maintain a constant Ω there. The values of Ω of each of the water masses are cal-

Table 2. Changes in the chemistry of sea water associated with models I-VI. In all cases the degree of calcite saturation at station 115 remains constant. It is assumed that charge balance is preserved by a change in the chloride concentration.

Model	ΔTA (μEq/kg)	ΔTCO_2 (μM/kg)	new[Ca⁺⁺][1]	ΔpH	$\Delta[PO_4\equiv]$
I$d(l)$	280	112	0.518[Ca⁺⁺][1]	variable	0
I$d(s)$	58	22	0.843[Ca⁺⁺]	variable	0
I$b(l)$	276	109	0.518[Ca⁺⁺]	variable	0
I$b(s)$	58	22	0.843[Ca⁺⁺]	variable	0
II$d(l)$	-160	-56	1.87[Ca⁺⁺]	variable	0
II$d(s)$	-60	-22	1.23[Ca⁺⁺]	variable	0
II$b(l)$	-157	-54	1.87[Ca⁺⁺]	variable	0
II$b(s)$	-60	-22	1.23[Ca⁺⁺]	variable	0
III$d(l)$	2276	2184	0.523[Ca⁺⁺]	0	0
III$d(s)$	455	437	0.843[Ca⁺⁺]	0	0
III$b(l)$	2277	2187	0.523[Ca⁺⁺]	0	0
III$b(s)$	455	437	0.843[Ca⁺⁺]	0	0
IV$d(l)$	-1138	-1092	1.85[Ca⁺⁺]	0	0
IV$d(s)$	-455	-437	1.23[Ca⁺⁺]	0	0
IV$b(l)$	-1139	-1094	1.85[Ca⁺⁺]	0	0
IV$b(s)$	-455	-437	1.23[Ca⁺⁺]	0	0
V(l)	37([PO₄≡]−[PO₄≡]$_{PRE}$)[3]	133([PO₄≡]−[PO₄≡]$_{PRE}$)	(5)	variable	+[PO₄≡][2]
V(s)	37(0.2)([PO₄≡]−[PO₄≡]$_{PRE}$)	133(0.2)([PO₄≡]−[PO₄≡]$_{PRE}$)		variable	+(0.2)[PO₄≡]
VI(l)	37(−0.5)([PO₄≡]−[PO₄≡]$_{PRE}$)[4]	133(−0.5)([PO₄≡]−[PO₄≡]$_{PRE}$)	(6)	variable	(−0.5)[PO₄≡]
VI(s)	37(−0.2)([PO₄≡]−[PO₄≡]$_{PRE}$)	133(−0.2)([PO₄≡]−[PO₄≡]$_{PRE}$)		variable	(−0.2)[PO₄≡]

(1) $[Ca^{++}]$ = present calcium concentration.

(2) $[PO_4\equiv]$ = present phosphate concentration.

(3) $[PO_4\equiv]-[PO_4\equiv]_{PRE}$ = present phosphate concentration-preformed phosphate concentration (i.e., doubling of oxidative phosphate input).

(4) i.e., halving of oxidative phosphate input.

(5) see footnotes (1) and (2) of Table 4.

(6) see footnotes (3) and (4) of Table 4.

*Note that (*l*) and (*s*) denote large and small changes, respectively, according to the various models described in the text (i.e., in models I, III and V, (*l*) denotes a doubling, while (*s*) denotes a 20% increase; in models II, IV, and VI, (*l*) denotes a halving, while (*s*) denotes a 20% decrease).

culated from the model $[Ca^{++}]$ and the model values of TA and TCO_2 at each station resulting from changes in the $[PO_4^{\equiv}]$.

In models I-VI, the seawater Cl^- concentration is assumed to change by the amount required to maintain charge balance.

Ω values were calculated from the model $[Ca^{++}]$, alkalinity and TCO_2 using the methods of Takahashi (1975). The values thus calculated are not precisely correct: since the free $CO_3^{\equiv}$ concentration is a function of $[Ca^{++}]$ (Garrels and Thompson, 1962), the apparent constants for our hypothetical solutions are not identical to the seawater apparent constants. Values of Ω were calculated using seawater apparent constants and then corrected to account for changes in the fraction of free carbonate, using Garrels and Thompson's ion pairing values at 25°C and 1 atmosphere pressure. All tabulated Ω values have been corrected in this way. The maximum correction is 7% in the free $CO_3^{\equiv}$ concentration.

Results of the changes in Ω (defined as $\Delta\Omega$) for models I-IV are given in Table 3. Results for models V and VI are given in Table 4.

The difference in the degree of carbonate saturation between GEOSECS stations 115 in the Atlantic and 215 in the Pacific at 3500 m depth due to the combined effects of simultaneously varying the $[CO_3^{\equiv}]/[Ca^{++}]$ ratio at station 115 and the global $[PO_4^{\equiv}]$ was determined. In all cases the degree of carbonate saturation at station 115 was held constant. Initially, values of 0.25, 0.50, 1.00, 2.50, and 4.00 were chosen for the $[CO_3^{\equiv}]/[Ca^{++}]$ ratio in the Atlantic normalized to the modern value. A value of 0.25 corresponds to a halving of $[CO_3^{\equiv}]$ and a doubling of $[Ca^{++}]$, 4.00 corresponds to a doubling of $[CO_3^{\equiv}]$ and a halving of $[Ca^{++}]$, and a value of 1.00 represents today's ratio. Changes in alkalinity and total CO_2 were then computed as in models I and II. Next, a new $[PO_4^{\equiv}]$ at each station was calculated for factors of 0, 0.5, 1.0, 1.5, and 2.0 times the present $[PO_4^{\equiv}]$. This results in a simultaneous but additional change (calculated as in models V and VI) in TA and TCO_2 for each selected $[CO_3^{\equiv}]/[Ca^{++}]$ ratio at station 115. The new $[CO_3^{\equiv}]$ at station 115 was calculated and the $[Ca^{++}]$ was then readjusted to keep the degree of carbonate saturation constant there. This results in the final $[CO_3^{\equiv}]/[Ca^{++}]$ ratio at station 115. The Ω at station 215 in the Pacific is then computed from combined changes in alkalinity and total CO_2 induced from the variations of the $[CO_3^{\equiv}]/[Ca^{++}]$ ratio in the Atlantic (as calculated in models I and II), the $[PO_4^{\equiv}]$ in the Pacific (as calculated in models V and VI), and the $[Ca^{++}]$ of seawater. The results are expressed in Figure 1.

Clearly there are many oversimplifications behind the Ω estimates. However, the models satisfy this basic requirement: they reliably indicate how the difference in carbonate saturation between various water masses would change due to changes, by a specified amount, in the carbonate ion concentration of seawater, or by a constant fraction in the phosphate concentration of seawater, with the physical circula-

Table 3. Changes in degree of calcite saturation produced by North Atlantic carbonate chemistry models. For model notation see Table 2.

Station	Water Mass	I(l) Ω %	I(l) ΔΩ %	I(s) Ω %	I(s) ΔΩ %	II(l) Ω %	II(l) ΔΩ %	II(s) Ω %	II(s) ΔΩ %	III(l) Ω %	III(l) ΔΩ %	III(s) Ω %	III(s) ΔΩ %	IV(l) Ω %	IV(l) ΔΩ %	IV(s) Ω %	IV(s) ΔΩ %
GFZW																	
(24)	Bottom	129	9	122	2	111	−9	117	−3	128	8	122	2	109	−11	117	−3
EBW	Deep	122	0	122	0	122	0	122	0	122	0	122	0	122	0	122	0
(115)	Bottom	90	0	90	0	90	0	90	0	90	0	90	0	90	0	90	0
WSW	Deep	98	11	90	3	77	−10	83	−4	98	11	90	3	74	−13	83	−4
(85)	Bottom	81	10	74	3	63	−8	68	−3	80	9	74	3	60	−11	68	−3
AAW	Deep	112	6	107	1	100	−6	104	−2	111	5	107	1	100	−6	104	−2
(68)	Bottom	65	8	59	2	50	−7	54	−3	65	8	59	2	48	−9	54	−3
CPW	Deep	103	10	96	3	84	−9	91	−2	103	10	95	2	81	−12	89	−4
(76)	Bottom	85	9	79	3	68	−8	74	−2	85	9	78	2	66	−10	73	−3
NPW	Deep	95	16	83	4	69	−10	74	−5	95	16	83	4	61	−18	74	−5
(215)	Bottom	72	9	65	2	56	−7	60	−3	71	8	65	2	53	−10	60	−3

Table 4. Changes in degree of calcite saturation produced by global phosphate chemistry models. It is assumed that charge balance is preserved by a change in the chloride concentration. For model notation, see Table 2.

		Model									
		V(l) $\Delta[PO_4\equiv]=+[PO_4\equiv]^{(1)}$					V(s) $\Delta[PO_4\equiv]=+0.2[PO_4\equiv]^{(2)}$				
Station	Water Mass	new $[PO_4\equiv]$ (μM/kg)	new TA (μEq/kg)	new TCO$_2$ (μM/kg)	Ω (%)	$\Delta\Omega$ (%)	new $[PO_4\equiv]$ (μM/kg)	new TA (μEq/kg)	new TCO$_2$ (μM/kg)	Ω (%)	$\Omega\Delta$ (%)
GFZW											
(24)	Bottom	2.10	2305	2216	134	14	1.12	2295	2178	122	2
EBW	Deep	2.98	2361	2260	122	0	1.60	2344	2199	122	0
(115)	Bottom	3.04	2367	2268	90	0	1.64	2349	2203	90	0
WSW	Deep	4.28	2372	2346	68	−19	2.31	2347	2256	83	−4
(85)	Bottom	4.24	2370	2341	59	−12	2.28	2346	2256	68	−3
AAW	Deep	4.40	2407	2368	80	−26	2.40	2378	2265	100	−6
(68)	Bottom	4.48	2408	2391	43	−14	2.42	2381	2294	54	−3
CPW	Deep	4.20	2391	2375	66	−27	2.30	2361	2269	87	−6
(76)	Bottom	4.22	2391	2376	56	−20	2.31	2361	2271	72	−4
NPW	Deep	5.06	2473	2534	41	−38	2.82	2430	2378	69	−10
(215)	Bottom	4.86	2476	2506	36	−27	2.70	2436	2363	56	−7

Model

		VI(*l*) $\Delta[PO_4\equiv]=-0.5[PO_4\equiv]^{(3)}$					VI(*s*) $\Delta[PO_4\equiv]=-0.2[PO_4\equiv]^{(4)}$				
Station	Water Mass	new $[PO_4\equiv]$ (μM/kg)	new TA (μEq/kg)	new TCO_2 (μM/kg)	Ω (%)	$\Delta\Omega$ (%)	new $[PO_4\equiv]$ (μM/kg)	new TA (μEq/kg)	new TCO_2 (μM/kg)	Ω (%)	$\Delta\Omega$ (%)
GFZW											
(24)	Bottom	0.53	2285	2144	115	−5	0.98	2289	2158	119	−1
EBW	Deep	0.75	2329	2146	122	0	1.38	2336	2169	122	0
(115)	Bottom	0.76	2333	2147	90	0	1.40	2339	2171	90	0
WSW	Deep	1.07	2325	2177	96	9	1.97	2335	2210	91	4
(85)	Bottom	1.06	2325	2182	77	6	1.96	2334	2214	74	3
AAW	Deep	1.10	2353	2174	118	12	2.00	2364	2213	111	5
(68)	Bottom	1.12	2357	2210	64	7	2.06	2367	2246	60	3
CPW	Deep	1.05	2335	2176	105	12	1.90	2347	2215	99	6
(76)	Bottom	1.06	2336	2179	86	10	1.91	2347	2219	81	4
NPW	Deep	1.27	2392	2242	104	25	2.24	2408	2300	89	10
(215)	Bottom	1.22	2401	2238	77	14	2.16	2416	2291	70	7

(1) Changes in water mass characteristics due to doubling oxidative phosphate input at each station while keeping the degree of calcite saturation at station 115 constant (by increasing the Ca^{++} concentration of seawater appropriately). New $[Ca^{++}]$ = 1.34 (original $[Ca^{++}]$) for bottom water; new $[Ca^{++}]$ = 1.32 (original $[Ca^{++}]$) for deep water.

(2) Changes in water mass characteristics due to increasing oxidative phosphate input at each station by 20% while keeping the degree of calcite saturation at station 115 constant (by increasing the Ca^{++} concentration of seawater appropriately). New $[Ca^{++}]$ = 1.05 (original $[Ca^{++}]$) for both deep and bottom water.

(3) Changes in water mass characteristics due to halving oxidative phosphate input at each station while keeping the degree of calcite saturation at station 115 constant (by decreasing the Ca^{++} concentration of seawater appropriately). New $[Ca^{++}]$ = 0.880 (original $[Ca^{++}]$) for bottom water; new $[Ca^{++}]$ = 0.887 (original $[Ca^{++}]$) for deep water.

(4) Changes in water mass characteristics due to decreasing oxidative phosphate input at each station by 20% while keeping the degree of calcite saturation at station 115 constant (by decreasing the Ca^{++} concentration of seawater appropriately). New $[Ca^{++}]$ = 0.951 (original $[Ca^{++}]$) for both deep and bottom water.
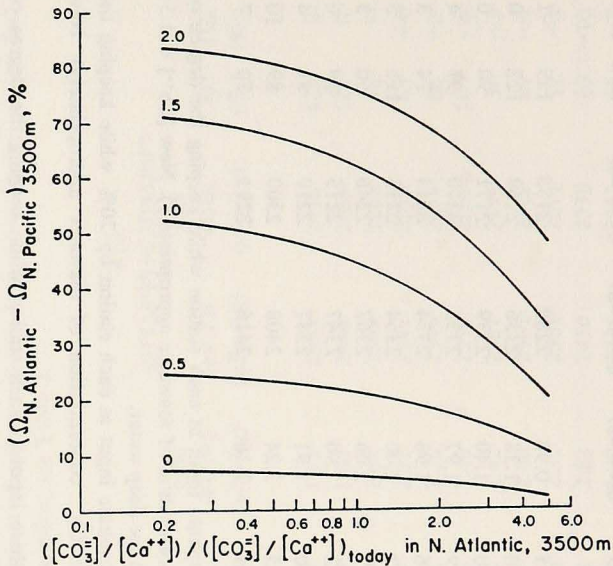
Figure 1. Difference in degree of $CaCO_3$ saturation between North Atlantic (GEOSECS station 115) and North Pacific (GEOSECS station 215) Oceans at 3500m depth vs. assumed $[CO_3^=]/[Ca^{++}]$ ratio at GEOSECS station 115 relative to the present value, for various concentrations of $PO_4^=$. (Numbers above curves are values of assumed $[PO_4^=]$ normalized to the present value; thus the curves are labelled for oceans with no $PO_4^=$ (0), half the present $PO_4^=$ (0.5), the present $PO_4^=$ concentration (1), 1.5 times the present $PO_4^=$ (1.5), and twice the present $PO_4^=$ (2).

tion of seawater held constant and with the flux of all biogenic components related as at present to the deep sea phosphorus concentration.

3. Discussion of results

a. Relevance to Proposition I. The effect of varying the $[CO_3^=]/[Ca^{++}]$ ratio of seawater on Ω has been considered in models I-IV. Values of Ω calculated for the various water masses for models I and II are similar to Ω values calculated for models III and IV, indicating that differences between water mass Ω values calculated from the various models are relatively insensitive to the exact assumptions made about the pH, TA, and TCO_2 values of seawater.

Increasing the $[CO_3^=]$ while decreasing $[Ca^{++}]$ such that Ω at station 115 remains constant, and assuming that biogenic components continue to cycle in the oceans as they do today (models I and III), increases the degree of carbonate saturation of all other water masses, and results in decreasing the difference in Ω between waters at the beginning and end of the circulation path. In such an ocean Ω of the Pacific would be larger, and the compensation depth deeper, than at present. Calcium removal would exceed input. Due to this imbalance Ω would decrease globally,

and the compensation depth would rise globally, until cessation of excess calcite deposition. Thus in a hypothetical steady-state ocean with a higher than present $[CO_3^=]/[Ca^{++}]$ ratio, the Atlantic compensation depth would rise, the Pacific compensation depth would fall, and the Atlantic-Pacific contrast would decrease. By the same kind of argument, starting with results of models II and IV, we can readily show that, in a hypothetical steady-state ocean with a lower $[CO_3^=]/[Ca^{++}]$ ratio, Atlantic Ω and compensation depth would fall, the Pacific Ω and compensation depth would rise, and the Atlantic-Pacific contrast would obviously increase.

b. Relevance to Proposition II. As noted earlier, calcite compensation in the modern oceans occurs by two mechanisms: depth control and abyssal circulation control. However, the calculations above show that, if the $[CO_3^=]/[Ca^{++}]$ ratio or the $[PO_4^\equiv]$ of seawater were much different from the modern value, one of the mechanisms would dominate: if the $[CO_3^=]/[Ca^{++}]$ ratio were lower or the $[PO_4^\equiv]$ higher, the Atlantic-Pacific Ω contrast would increase and compensation would be dominantly by abyssal circulation control. Ca^{++} and HCO_3^- throughput could still be balanced by either mechanism acting alone. Thus it is conspicuous that the $[CO_3^=]/[Ca^{++}]$ ratio is set at a value where both mechanisms act in concert. We speculate that the present $[CO_3^=]/[Ca^{++}]$ ratio is near the most stable value— i.e., that value requiring the smallest change to rebalance the Ca^{++} budget following a change in input. It is tempting to further speculate that the $[CO_3^=]/[Ca^{++}]$ ratio in deep ocean source waters is fixed near the most stable value, but there are no obvious feedback mechanisms which would accomplish this.

c. Paleoceanographic Implications. While no one has succeeded in documenting a change in the major cation or nutrient content of seawater, recent data make it more and more plausible to postulate that such changes have occurred. To take one example: in the Paleogene, when abyssal temperatures were about 15°C (Emiliani, 1954; Douglas and Savin, 1971), O_2 solubility would have been 200 μM kg^{-1}. If the $PO_4^\equiv$ content of seawater and the Redfield ratios had been the same as today, a large part of the deep ocean would have been anoxic. There is, however, no evidence for widespread anoxia; hence it is likely that the pO_2 of the Paleogene atmosphere was higher, or the $[PO_4^\equiv]$ of the abyssal Paleogene oceans was lower, than the modern values.

The ideas in this paper provide a framework for making certain inferences about paleocean abyssal chemistry. Firstly, they confirm the intuitively obvious notion that we can trace paleo abyssal water circulation from relative carbonate compensation depths: net flow must have been in the direction along which the compensation depth shoals. The only ways in which this conclusion could be violated are if input of $CO_3^=$ to the deep sea exceeded input of $CO_2 + NO_3^-$, or if the $[CO_3^=]/[Ca^{++}]$ ratio of seawater was so high that dissolution of biogenic debris lowers the $[CO_3^=]/$

$[Ca^{++}]$ by producing a fractional $[Ca^{++}]$ increase greater than the fractional $[CO_3^=]$ decrease. It seems very unlikely that such conditions ever prevailed.

Secondly, our results suggest that, at any time in the past when the interoceanic variation in compensation depths was similar to the present difference, the $[CO_3^=]$ at the deep water mass source regions was approximately equal to 106 ($[PO_4^\equiv]$increase) during the abyssal grand tour. The summary work of Van Andel (1975) on Atlantic, Pacific, and Indian Ocean compensation depths shows that, except at times of crossovers, maximum compensation depth differences have been similar to the present value, indicating that, during the Cenozoic and much of the Mesozoic, the $[CO_3^=]$ in deep water source regions has been comparable to 106 times the maximum interoceanic range in the abyssal $PO_4^\equiv$ concentration.

Finally, our arguments indicate factors which must be considered in discerning cause of variations in the relative carbonate compensation depths of the oceans as inferred from DSDP data.

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