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NEUTRALIZATION OF FOSSIL FUEL CO₂ BY MARINE CALCIUM CARBONATE

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ABSTRACT

The CaCO₃ stored in marine sediments will ultimately neutralize the CO₂ generated by fossil fuel combustion. Details of this process are explored and a model of the early phases of this process in the western basin of the deep Atlantic Ocean is presented. The amount of CaCO₃ available for dissolution is derived from the calcite content of marine sediments and the extent to which these sediments are stirred by benthic organisms. The conclusion is that the available calcite is about equivalent to the CO₂ which would be released if our known resources of natural gas, oil and coal were burned. The rate at which this dissolution will proceed is estimated from the rate at which natural dissolution has proceeded during the Holocene. The conclusion is that if linear kinetics are followed, the time constant will be on the order of 1500 years. On the other hand, if the exponential kinetics found in the laboratory by Berner and Morse (1972) apply, then the time constant will be much shorter. It is possible that the dissolution process will become limited by the rate stirring of the mixed layer in deep sea sediments. The insoluble residue of clay minerals and opal built up in the upper few millimeters of the sediment as the result of dissolution must be mixed down into the underlying sediment if more than the upper few millimeters of sediment is to be attacked.

In order to model the change in the carbonate ion content of the waters in the deep Atlantic Ocean over the next few hundred years it is necessary to know:

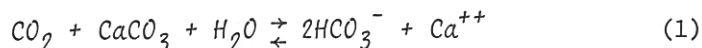
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Present address: Lamont-Doherty Geological Observatory

- 1) the rate of chemical fuel use over this period;
 - 2) the distribution of this CO_2 between the terrestrial biosphere, upper ocean and atmosphere;
 - 3) the relationship between the $\text{CO}_3^{=}$ content of newly formed deep water and the $p\text{CO}_2$ in the atmosphere;
 - 4) the ventilation time of the northern component of the deep water in the Atlantic Ocean and the distribution of this component in the deep mixing zone;
 - 5) the relationship between the *in situ* $\text{CO}_3^{=}$ content of deep water and the $\text{CO}_3^{=}$ content necessary to trigger dissolution;
 - 6) the relationship between the rate of dissolution of deep sea sediments and the degree of undersaturation of the bottom water.
- Preliminary estimates have been made of these factors and they have been combined into a dissolution model.

INTRODUCTION

CO_2 generated by the combustion of fossil fuels will ultimately be neutralized through combination with sedimentary calcium carbonate via the reaction



Regardless of whether this dissolution takes place on land or in the sea, the calcium and bicarbonate ions generated will end up as part of the ocean's dissolved salt load. In this paper some of the details of this process are considered.

The primary contributor to this neutralization will be deep sea sediments. The deep sea will be gradually "acidified" by the downward mixing of surface water enriched in fossil fuel CO_2 and its sediments will become subject to enhanced calcium carbonate dissolution. Shallow marine deposits are less promising because of their relatively small area and their generally low CaCO_3 content, and because the water in which they are bathed is highly saturated with respect to both calcite and aragonite (see Figure 1). It is unlikely that the CO_2 content of the atmosphere will ever become great enough to bring these waters to a state of undersaturation. Although enhanced continental weathering will contribute to the neutralization, the fact that the decay of organic material maintains the CO_2 content of soil and ground waters far higher than the atmospheric equilibrium content suggests that the higher atmospheric CO_2 contents will not have a very large impact.

For the purposes of this discussion, the sediments of the sea will be divided into five categories.

- 1) Those lying beneath the calcite compensation depth. As these sediments contain little calcium carbonate they will not contribute significantly to the neutralization process.
- 2) Those lying between the calcite compensation depth and the

Fig. 1a. CO_2 water depth in the western North Atlantic content for 1972. They are based on data with a temperature increasing water column calculated from the station 30 the leg 1 bring the leg 3 the results from titanium results are in Sept. 1972.

lysocline horizon zone between is small and depth moves virtually a (see Figure 3).

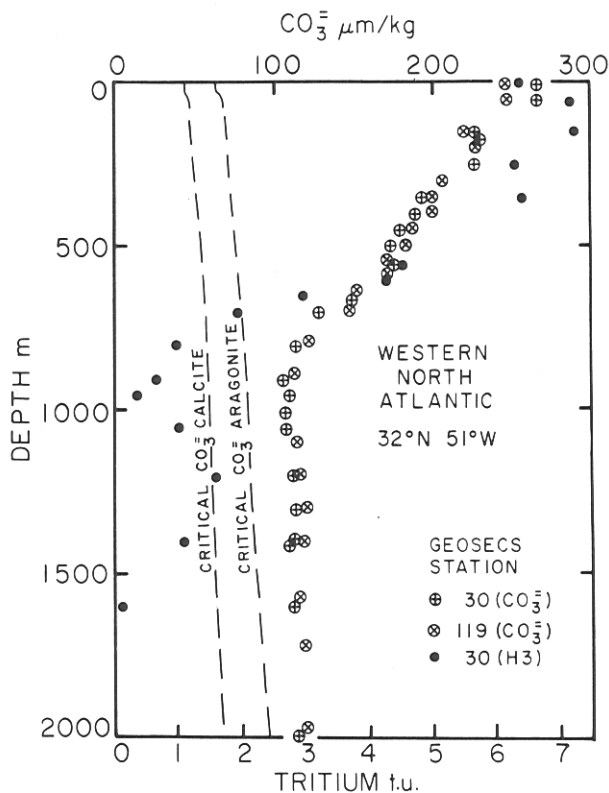


Fig. 1a. $\text{CO}_3^{=}$ and tritium concentration as a function of water depth in the upper water column at 32°N and 51°W in the western North Atlantic Ocean. Curves for the critical carbonate ion content for calcite and for aragonite are given for reference. They are based on those given by Broecker and Takahashi (in press) with a temperature correction for the decrease in solubility with increasing water temperature. The carbonate ion results were calculated from the titration data given in the GEOSECS leg reports using the constants adopted by Takahashi et al. (1976). At station 30 the leg report ΣCO_2 results were decreased by $15 \mu\text{m}/\text{kg}$ to bring the leg 3 results into agreement with the $p\text{CO}_2$ data and with the results from the other GEOSECS Atlantic Ocean legs. The tritium results are those of Ostlund et al. (1974) on samples collected in Sept. 1972.

lysocline horizon (see Figure 2). These sediments lie in the transition zone between depths where natural dissolution by bottom water is small and depths where natural dissolution by bottom water removes virtually all of the calcite from the accumulating sediment (see Figure 3). These sediments still have calcite available for

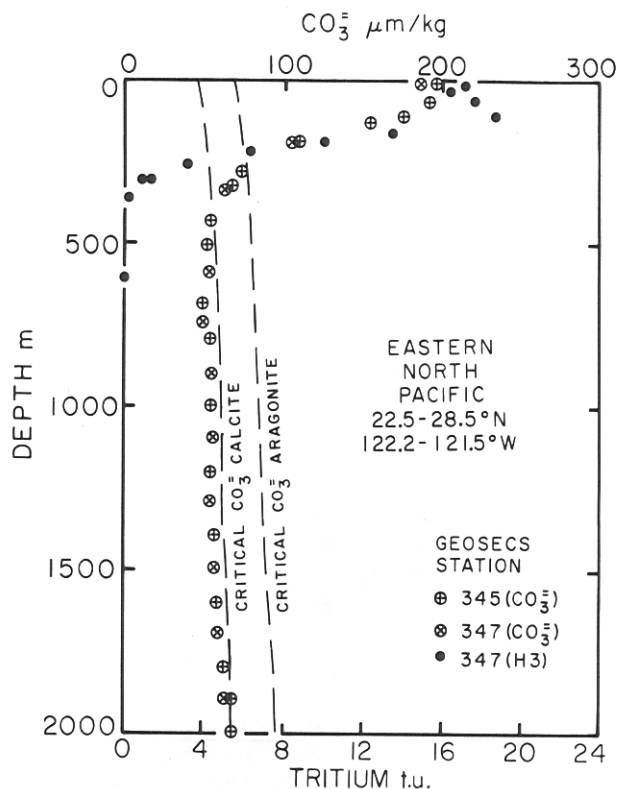


Fig. 1b. Similar results for the North Pacific Ocean (ST 345 23°N; 122°W; ST 347 29°N; 122°W). In accord with the study by Broecker and Takahashi (in press) the Pacific Ocean leg report ΣCO_2 results were reduced by $15 \mu\text{m}/\text{kg}$ to bring the Pacific Ocean results into agreement with Pacific Ocean $p\text{CO}_2$ results and with the Atlantic Antarctic results. This correction increases the CO_3^{2-} concentrations by about $8 \mu\text{m}/\text{kg}$. The tritium results are those of Roether (1974) for samples collected in November 1971.

the neutralization of fossil fuel CO_2 . As the bottom water with which they are in contact is already understaturated, any further decrease in CO_3^{2-} content will produce an immediate effect.

3) Those lying above the lysocline and below a water depth of 2800 meters. These sediments are located mainly on the flanks of the oceanic ridges and rises and are on the average very rich in calcium carbonate (i.e., >80%). Although they currently lie in non-corrosive water, as the CO_3^{2-} content of the deep sea falls they will eventually come under attack. The time elapsed before the onset of dissolution in any given area will increase with elevation above

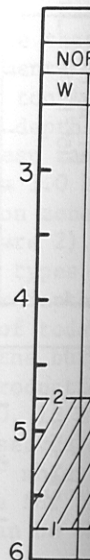


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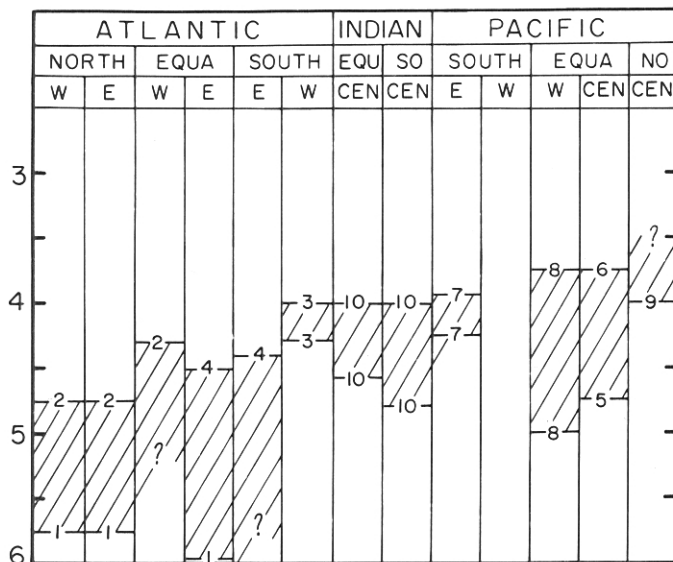


Fig. 2. Summary of lysocline and carbonate compensation depths for various oceanic regions as given by Broecker and Takahashi (in press). The numbers refer to the source of the information as given in the original paper.

the lysocline. (The shallower the sediment the more the $\text{CO}_3^{=}$ content will have to fall before dissolution is triggered.)

4) Those sediments lying above the ridge crests but beneath the 100 fathom contour. These sediments lie primarily along the continental rises and in marginal seas. They are in general low in calcite content (e.g., ~25%) because of dilution with continental detritus. Since the acidification of the waters which they contact will occur more rapidly than that of the subridge crest waters, their contribution could be significant during the early stages of the neutralization process.

5) Shallow water sediments (e.g., <200 meter depths). The waters in this depth range will respond very quickly (i.e., a few years) to changes in atmospheric CO_2 content. Those sediments in contact with mixed layer water (i.e., upper 30-150 meters) will not, however, be subject to attack because the mixed layer is too highly supersaturated with respect to calcite and aragonite to ever become corrosive. However, as the $\text{CO}_3^{=}$ content drops sharply with depth below the mixed layer in some regions of the ocean, dissolution of sediments in contact with upper thermocline waters could contribute to the neutralization of fossil fuel CO_2 . Assessment of this potential will prove complex. Region by region studies will be

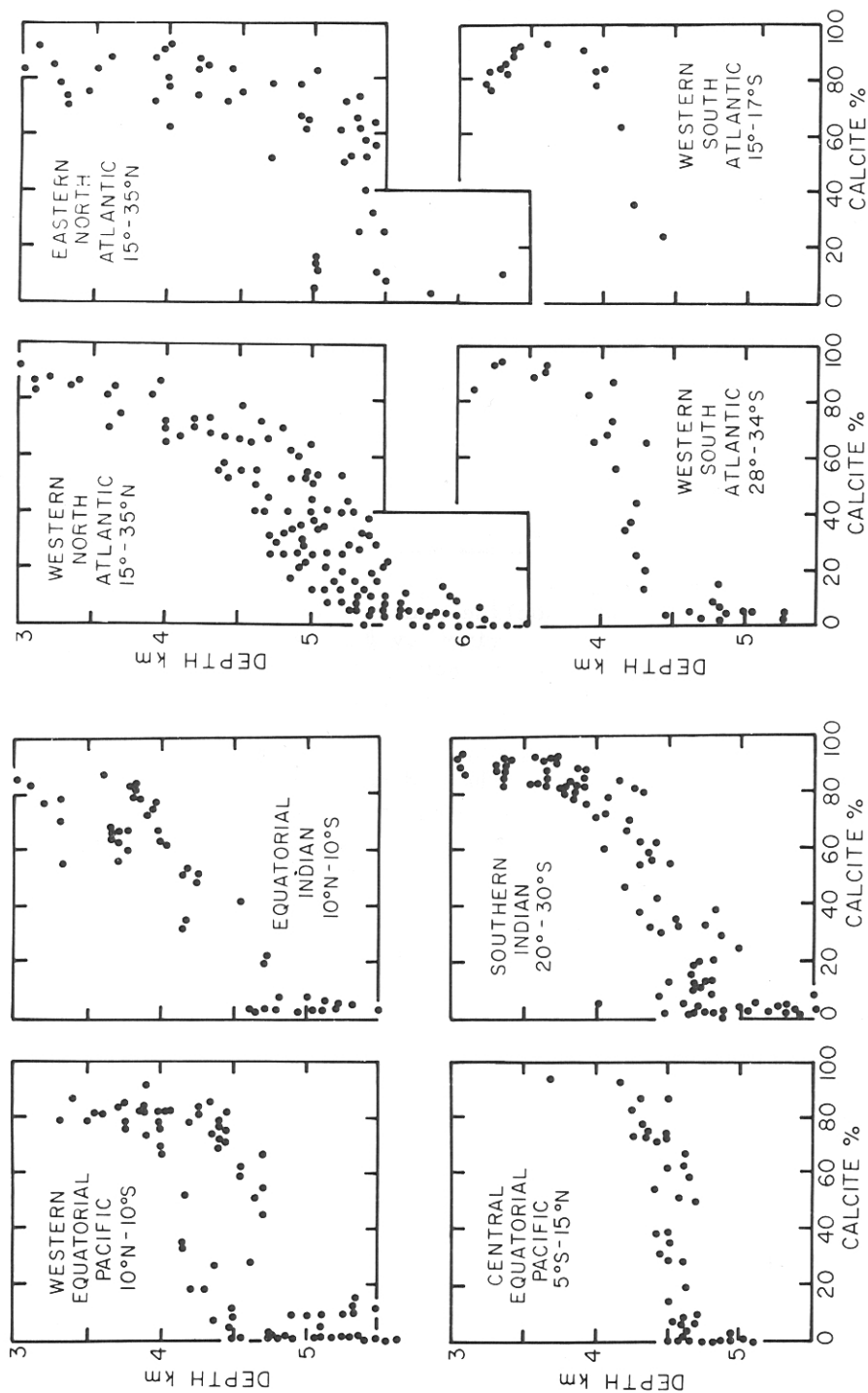


Fig. 3. CaCO_3 versus water depth plots as given by Broecker and Takahashi (in press).

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Above Shelf break
Shelf break to Ridge crest
Ridge crest to Lysocline
Lysocline to Compensation
Below Compensation
TOTAL

* Based on the area
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necessary. Examples are given in Figure 1. Certainly on the long time scale these sediments will prove far less important than deep sea sediments in neutralizing CO₂. Their area and CaCO₃ content are just too low.

The depth of the lysocline varies from place to place in the world ocean ranging from 4.7 km in the North Atlantic Ocean to less than 3.0 km in the North Pacific Ocean. The thickness of the transition zone beneath the lysocline varies from 200 to 1000 meters (see Figure 2). Using this information, the area of each of these sediment types has been estimated (see Table 1) using the area versus water depth data given by Sverdrup *et al.* (1942).

As of today about 1.4×10^{16} moles of CO₂ have been generated through the burning of gas, oil and coal (Broecker *et al.*, 1971). If the production rate is increased by 2% per year, then in the year 2100, 18×10^{16} moles of CO₂ will have been produced. Our total reserves of coal, oil and gas, if burned, would produce about 50×10^{16} moles of CO₂ (Hubbert, 1972). How much sediment CaCO₃ is available for the neutralization of this CO₂? An estimate of this amount can be obtained from the following expression:

$$\text{Sediment density} \times \text{frac. CaCO}_3 \times \frac{\text{burrowing depth}}{\text{frac. non-CaCO}_3} \quad (2)$$

TABLE 1. Sediment Area Distribution*

(Units 10¹⁴ m²)

Region	Depth Range	Atlantic	Indian	Pacific	Total
Above Shelf break	<200	0.14	0.03	0.10	0.55 ^{0.27}
Shelf break to Ridge crest	200-2800	0.22	0.11	0.21	0.54
Ridge crest to Lysocline	-	0.35	0.18	0.18	0.71
Lysocline to Compensation	-	0.21	0.14	0.14	0.49
Below Compensation	-	0.14	0.30	1.15	1.59
TOTAL	-	1.06	0.76	1.78	3.60

* Based on the area versus water depth data given in Sverdrup (1942) and the lysocline and compensation depths given in Fig. 2.

The assumption is that once a carbonate-free layer one burrowing depth thick mantles the sea floor, the underlying calcium carbonate will be immune to dissolution regardless of the acidity of the overlying water. From radiocarbon data on deep sea cores it appears that the mean depth of burrowing is about 9 cm (see Peng *et al.*, 1977). The following average CaCO_3 contents are adopted for the sediment provinces mentioned above:

shelf break - ridge crest	25%
ridge crest - lysocline	85%
lysocline - compensation	40%

The corresponding amounts of available CaCO_3 are shown in Table 2. Two points stand out. First, the amount of "available" CaCO_3 is about equivalent to the amount of CO_2 locked up in recoverable fuel. Second, about half of this calcium carbonate lies in the Atlantic Ocean.

BASIS FOR FUTURE DISSOLUTION RATE ESTIMATES

In order to calculate the rate at which the deep sea CaCO_3 will dissolve, four basic pieces of information are needed:

- 1) projected atmospheric CO_2 contents;
- 2) the carbonate ion content of newly formed deep water;
- 3) the rate of fossil fuel CO_2 neutralization by sediment per unit drop in the carbonate ion content of the ocean water in contact with the sediment; and
- 4) the ventilation times for various deep water masses.

TABLE 2. Available CaCO_3 in Deep Sea Sediment*

Region	(Units 10^{16} moles)			
	Atlantic	Indian	Pacific	Total
Shelf break to Ridge crest	0.7	0.3	0.6	1.6
Ridge crest to Lysocline	18.0	9.2	9.2	36.4
Lysocline to Compensation	1.3	0.8	0.9	3.0
TOTAL	20.0	10.3	10.7	41

* = Dry density (i.e., $\sim 1 \text{ gm/cm}^3$) x Area x

$$\frac{\text{Mixing Depth (i.e., 9 cm)}}{\text{Frac. non-}\text{CaCO}_3} \times \text{Frac. CaCO}_3$$

For the decadal use of chemical fertilizers, the petroleum price, energy policies, and nuclear fuel use into the future. For the calculation of the growth rate of the atmosphere (see Figure 4) has no further increase. This choice allows a constant growth rate to the atmosphere.

As about half of the northern end of the waters in the North Atlantic composition of a deep water mass in the Atlantic Ocean. These waters are much warmer than those descending. If these waters are exposed to the atmosphere, then, in their ΣCO_2 content, they are in equilibrium with the atmosphere. To answer this question, the data shown in Figure 5 are used. The CO_2 produced at the surface of the sea in the Norwegian Sea over the Denmark Strait Sea which enters the North Atlantic from Scotland rise follows the same trend.

Fig. 4. Part of the data shows that the 0.9 ppm/yr increase in CO_2 by the coworkers of Scripps Institution of Oceanography in 1958. The annual increase in CO_2 over the next 30 years will increase to 1.8 ppm/yr .

For the decade prior to the sharp increase in oil prices, the use of chemical fuels was increasing by about 4.5% per year. Since the petroleum price hike this pace has slowed. As comprehensive energy policies have yet to be developed, any projection of chemical fuel use into the future is bound to be little more than a guess. For the calculations presented here, a 2% per year increase in the growth rate of the atmospheric CO₂ content until the year 2100 (see Figure 4) has been adopted and it has been further assumed that no further increase will occur during the following century. This choice allows a contrast of the situation during a period of exponential growth to that during a period of atmospheric stability.

As about half of the deep water in the ocean is generated at the northern end of the Atlantic Ocean, it is appropriate to take the waters in this region as an example. Table 3 summarizes the composition of a number of surface waters in the northern Atlantic Ocean. These waters are more saline and, of course, much warmer than those descending to form North Atlantic Deep Water (NADW). If these waters are cooled and freshened at equilibrium with the atmosphere, then, as shown in Table 4, they must change significantly in their ΣCO₂ content. The question is whether these waters maintain equilibrium with the atmosphere as they are cooled. The best way to answer this question is to look at newly produced deep water. As shown in Figure 5 there are three major contributors to NADW; water produced at the surface of the Labrador Sea (LSW), water produced in the Norwegian Sea which enters the Atlantic Ocean by spillage over the Denmark Straits (DSW) and water produced in the Norwegian Sea which enters the Atlantic Ocean by spillage over the Iceland-Scotland rise followed by passage through the Gibbs Fracture Zone

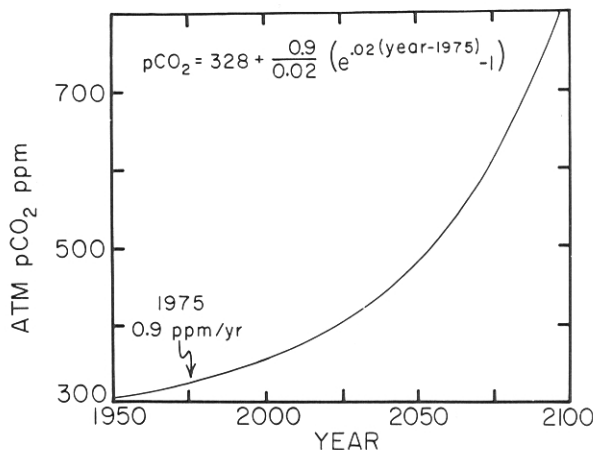


Fig. 4. Partial pressure of CO₂ versus time calculated assuming that the 0.9 ppm/yr increase rate measured by Dr. C. Keeling and his coworkers of Scripps Institution of Oceanography over the last several years will increase by 2% per year through the next century.

TABLE 3. Composition of Some North Atlantic Warm Surface Water Samples*

GEOSECS STATION NO.	24	25	26	27	28	29	30	119
T °C	11.2	20.3	21.8	22.4	25.0	25.2	26.6	21.1
S ‰	34.7	35.6	35.8	36.1	36.4	36.0	36.6	36.7
O ₂ μm/kg	291	229	220	218	210	209	205	230
SiO ₂ μm/kg	1.9	-	0.5	0.8	0.6	1.3	0.9	0.8
PO ₄ μm/kg	0.41	-	0.09	0.03	0.02	0.05	0.04	0.04
NO ₃ μm/kg	5.0	-	0.0	0.1	0.0	0.0	0.1	0.0
ALK μeq/km	2278	2308	2308	2359	2377	2357	2384	2389
ΣCO ₂ μm/kg	2088	2073	2064	2085	2039	2007	2020	2040
H ₂ BO ₃ ⁻	67	79	82	90	110	112	116	113
2CO ₃ ⁼ +HCO ₃ ⁻	2211	2229	2226	2269	2267	2245	2268	2276
HCO ₃ ⁻² /CO ₃ ⁼ CO ₂	1555	1345	1310	1285	1233	1233	1187	1306
HCO ₃ ⁻ μm/kg	1931	1885	1872	1873	1789	1749	1752	1784
CO ₃ ⁼ μm/kg	140	172	177	198	239	248	258	246
CO ₂ μm/kg	17.0	15.3	15.1	13.8	10.8	10.0	10.0	9.9
pCO ₂ 10 ⁻⁶ atm	407	480	490	455	383	355	368	315

* Based on the titration alkalinity and total dissolved inorganic carbon data, nutrient element and dissolved oxygen and hydrographic data given in the GEOSECS leg reports. The constants used are those adopted by Takahashi *et al.* (in press).

(GFZW). As shown in Table 5 these three sources have similar alkalinities and ΣCO₂. All are deficient in O₂, presumably because of respiration at depth in their source regions. If the composition of these waters prior to alteration by *in situ* respiration is reconstructed by bringing the O₂ content to the atmospheric contact value (i.e., 5% supersaturated), then the CO₂ partial pressure drops to roughly the atmospheric value and the ΣCO₂ content and CO₃⁼ contents become similar to that for the cooled and freshened northern Atlantic Ocean surface water (see Table 4). Hence, the contact time between the atmosphere and the cooling water appears to be long enough to bring the ΣCO₂ content to equilibrium with the atmosphere. Thus, an estimate as to how the CO₃⁼ content of downwelling deep water will change with atmos-

TABLE 4.

HCO ₃ ⁻
ALK
H ₂ BO ₃
2CO ₃ ⁼
HCO ₃ ⁻
CO ₃ ⁼
CO ₂
pCO ₂
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TABLE 4. Station 119 Surface Water Freshened and Cooled at Equilibrium with the Atmosphere*

	21.1°C	2.25°C
119	36.7%	34.93%
21.1		
36.7		
230		
0.8		
0.04		
0.0		
2389		
2040		
113		
2276		
1306		
1784		
246		
9.9		
315		

* The constants used are those adopted by Takahashi *et al.* (in press).

spheric CO₂ content can be obtained by considering either "freshened and cooled" northern Atlantic Ocean surface water (Table 4) or "oxygenated" NADW (Table 5). An example using the latter is shown in Table 6. For a 50% increase in atmospheric CO₂ content, the CO₃⁼ content drops by 27%. As shown in Table 7 this result is not dependent on the exact composition of the water. When the same calculation is made for warm surface water, the carbonate ion content drops by 24% for a 50% increase in atmospheric CO₂ content. In Figure 6 a plot of the fractional change in CO₃⁼ content of "oxygenated" NADW against atmospheric CO₂ content is given.

The most reliable way to assess the rate of attack caused by a given lowering of the CO₃⁼ content of the water in contact with the sediment is to use the Holocene record for calibration. This record is interpreted to indicate that no measurable calcite dissolution will occur until the CO₃⁼ content drops below what is herein called the critical carbonate ion content given by the following equation (Broecker and Takahashi, in press).

$$[CO_3^{=}]_{CRIT} = 93 e^{0.14(z - 4)} \mu\text{m/kg} \quad (3)$$

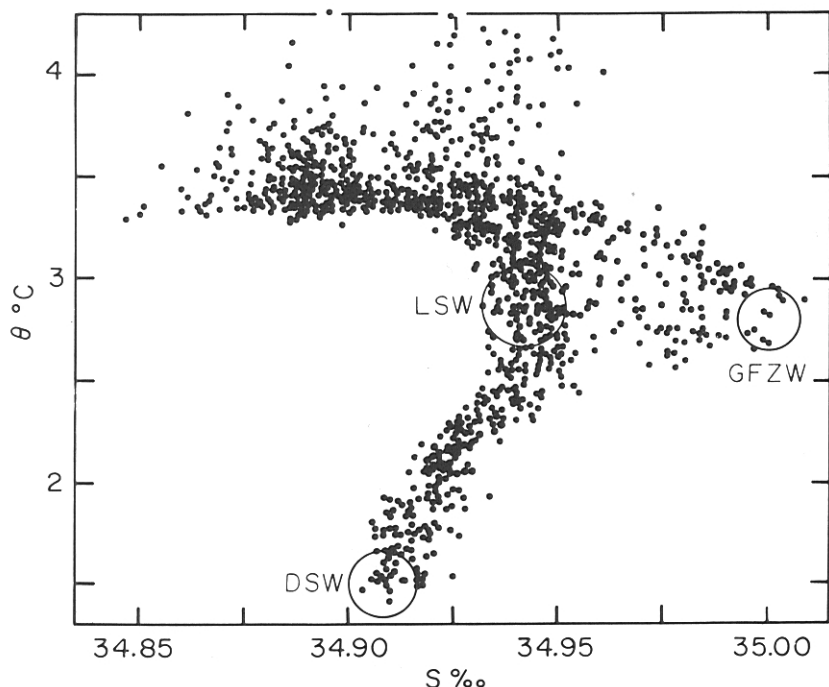


Fig. 5. Potential temperature versus salinity diagram for deep waters found at the northern end of the western basin of the North Atlantic Ocean. The end members are DSW, water spilling over the Denmark Straits; GFZW, water entering the western basin through the Gibbs Fracture Zone; and LSW, water generated at the surface of the Labrador Sea. A mixture of these three end members forms the northern component to basal North Atlantic Deep Water (NADW).

The shape of the transition zone calcite content profile can be satisfactorily explained if the dissolution rate, R , is assumed to follow the equation

$$R = \sqrt{f} \cdot 0.025 \left(\frac{[CO_3^{=}]_{CRIT}}{[CO_3^{=}]} - 1 \right) \text{ moles/m}^2 \text{ yr} \quad (4)$$

Where f is the fraction of calcite in the sediment (Broecker and Takahashi, in prep.)*. For small drops in $CO_3^{=}$ content (i.e., up to $15 \mu\text{m/kg}$) this relationship should be quite valid. For larger

*EDITOR'S NOTE: Since this paper was written, the authors have found the coefficient of dissolution, 0.025, to be a factor of two lower than that used in this contribution.

Water Type
Station
Depth (m)
θ °C
S ‰
O_2 $\mu\text{m/kg}$
SiO_2 $\mu\text{m/l}$
NO_3^- $\mu\text{m/kg}$
$PO_4^{=}$ $\mu\text{m/kg}$
ALK $\mu\text{eq/l}$
CO_2 $\mu\text{m/l}$
$H_2BO_3^-$ $\mu\text{m/l}$
$2CO_3^{=} + HCO_3^-$
HCO_3^-
$CO_3^{=}$
CO_2
$P_{CO_2} \cdot 10^{-6}$

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TABLE 5. North Atlantic Deep Water Components (GFZW, DSW, LSW); Their Average and Their "Oxygenated" Average+

Water Type	GFZW	DSW	LSW	NADW	NADW*
Station	24	25	26	-	-
Depth (m)	2470	4550	1990	-	-
θ °C	2.81	1.78	3.62	2.25	2.25
S ‰	35.00	34.91	34.95	34.93	34.93
O ₂ $\mu\text{m/kg}$	276	288	274	280	345
SiO ₂ $\mu\text{m/kg}$	13.9	-	12.0	13	-
NO ₃ ⁻ $\mu\text{m/kg}$	16.1	-	16.8	17	10
PO ₄ ⁼ $\mu\text{m/kg}$	1.06	-	1.16	1.14	0.66
ALK $\mu\text{eq/kg}$	2292	2290	2288	2290	2290
ΣCO_2 $\mu\text{m/kg}$	2168	2172	2168	2168	2119
H ₂ BO ₃ ⁻ $\mu\text{m/kg}$	50	48	48	49	63
2CO ₃ ⁼ +HCO ₃ ⁻	2242	2242	2240	2241	2227
HCO ₃ ⁻	2044	2051	2046	2046	1975
CO ₃ ⁼	99	95	97	98	126
CO ₂	25	25	25	24	18
P _{CO₂} 10 ⁻⁶ atm	436	433	463	430	310

* to 5% O₂ supersaturation assuming $\Delta\text{O}_2/\Delta\Sigma\text{CO}_2 = -1.33$

+ The hydrographic, nutrient element and dissolved oxygen data are from the GEOSECS leg reports. The constants used are those adopted by Takahashi *et al.* (in press).

drops (20-50 $\mu\text{m/kg}$), its validity depends on whether dissolution follows linear kinetics or Morse-Berner exponential kinetics (Morse and Berner, 1972). As it is not yet known what constitutes the rate limiting step for dissolution, it is not possible to say for sure which type of kinetics applies. Therefore, both will be considered.

Through radiocarbon dating, a general idea of the ventilation times for most parts of the deep sea has been developed. They range up to about 1500 years for the deep water in the North Pacific Ocean (Bien *et al.*, 1965). The deep Atlantic Ocean, which is of considerable interest because of its large calcite reserves,

TABLE 6. Change in Composition of Sinking NADW with Increasing Atm. CO₂ Content*

Year	1975	2050	Δ	$\frac{2050}{1975}$
$\text{HCO}_3^- / \text{CO}_3^{2-} \cdot \text{CO}_2$	1725	1725	-	-
ALK μeq/kg	2290	2290	0	-
H ₂ BO ₃ ⁻ μm/kg	63	46	-17	-
2CO ₃ ⁼ + HCO ₃ ⁻	2227	2244	+17	-
HCO ₃ ⁻ μm/kg	1975	2062	+85	-
CO ₃ ⁼ μm/kg	126	91	-35	0.73
CO ₂ μm/kg	18	27	+ 9	1.50
pCO ₂ 10 ⁻⁶ atm	310	468	-	1.50
ΣCO ₂ μm/kg	2119	2180	+61	1.029

$$\frac{\% \text{ inc atm CO}_2}{\% \text{ inc ocean CO}_2} = \frac{50}{2.9} = 17.2$$

* The constants used are those adopted by Takahashi *et al.* (in press).

is ventilated on the time scale of several hundred years (Broecker *et al.*, 1960; Stuiver, 1976). The presence of bomb-produced tritium and radiocarbon in upper thermocline waters demonstrates that this region of the sea is ventilated on the time scale of a few years to a few tens of years (see Figure 1).

THE TIME CONSTANT FOR SEDIMENT DISSOLUTION

A rough idea of the rate at which deep sea sediments will dissolve can be obtained. Assume that 23×10^{16} moles of CO₂ are generated through fossil fuel burning and allowed to come to equilibrium with the ocean. For simplicity, the ocean will be taken to be entirely NADW. In such a case the pCO₂ of the atmosphere would be 660×10^{-6} atm. The deep ocean ΣCO₂ content would then be

HCO₃⁻
ALK
H₂BO₃⁻
2CO₃⁼
HCO₃⁻
CO₃⁼
CO₂
pCO₂
ΣCO₂

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TABLE 7. Change in Composition of Warm Surface Water with Increasing Atm. CO₂ Content*

Year	1975	2050	Δ	$\frac{2050}{1975}$
HCO ₃ ⁻² /CO ₃ ⁼ · CO ₂	1306	1306	-	-
ALK μeq/kg	2389	2389	0	-
H ₂ BO ₃ ⁻ μm/kg	114	87	-27	-
2CO ₃ ⁼ + HCO ₃ ⁻	2275	2302	+27	-
HCO ₃ ⁻ μm/kg	1785	1924	143	-
CO ₃ ⁼ μm/kg	245	187	-58	0.76
CO ₂ μm/kg	10	15	+ 5	1.50
P _{CO₂} 10 ⁻⁶ atm	317	484	-	1.50
ΣCO ₂ μm/kg	2040	2130	90	1.044

$$\frac{\% \text{ inc. atm CO}_2}{\% \text{ inc. ocean CO}_2} = \frac{50}{4.4} = 11.4$$

* The constants used in these calculations are those adopted by Takahashi *et al.* (in press).

120 μm/kg higher than during pre-industrial time and the CO₃⁼ content of the deep water about half its pre-industrial value (i.e., down by about 55 μm/kg). Of the 23 x 10¹⁶ moles of CO₂ generated, 6.7 x 10¹⁶ would reside in the atmosphere and 16.3 x 10¹⁶ in the ocean. The amount of excess CO₂ per m² of ocean surface would be 640 moles.

Under such circumstances, deep sea sediments would be subjected to waters with carbonate ion deficiencies (relative to the critical carbonate ion content) ranging from about 55 μm/kg for the transition zone to between 15 and 25 μm/kg at the ridge crests. The average for all the CaCO₃-bearing sediments would be about 40 μm/kg. Using the dissolution coefficient of 0.025 moles/m² yr per μm/kg undersaturation obtained for Holocene dissolution in the ocean (Broecker and Takahashi, in prep.) and linear kinetics, yields an average of 1 mole/m² yr excess dissolution from the carbonate-bearing

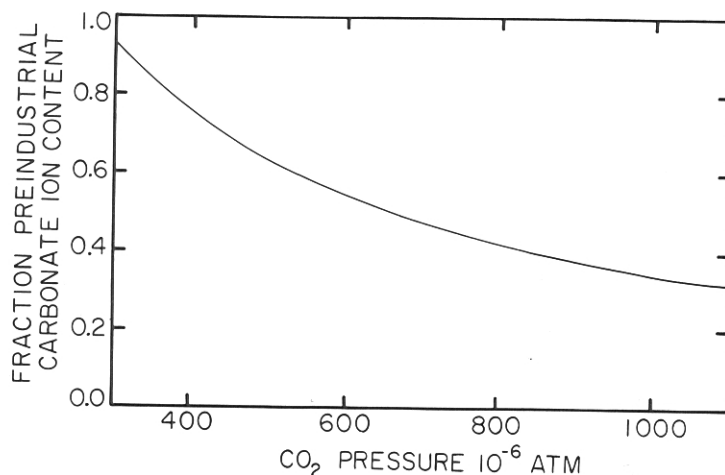


Fig. 6. $\text{CO}_3^{=}$ content of input northern component water (Table 6) relative to its pre-industrial value as a function of atmospheric CO_2 content. The pre-industrial $\text{CO}_3^{=}$ ion content is calculated to be $135 \mu\text{m}/\text{kg}$ (compared to $126 \mu\text{m}/\text{kg}$ in 1975).

sediments of the deep ocean. Since the area of deep floor bearing CaCO_3 -rich sediment is about half the total area (see Table 1), this corresponds to $0.5 \text{ mole}/\text{m}^2 \text{ yr}$ dissolution rate as referred to the entire ocean floor. Thus, the initial rate of dissolution in this well mixed ocean would be an amount of CaCO_3 equivalent to one part in 1280 of the excess CO_2 in the ocean-atmosphere system. This yields a time constant (i.e., about 1280 years) for neutralization comparable to the time scale for deep ocean ventilation. Thus, any realistic model must consider dissolution and deep mixing together.

If Morse-Berner exponential kinetics (Morse and Berner, 1972) are used, then as shown in Figure 7, dissolution rates many times higher would be expected. They would be so high in fact, that the sediments would neutralize the excess CO_2 roughly as fast as it arrived in the deep sea.

Of course, as the dissolution proceeded, dilution of the sedimentary calcite by the buildup of a non-calcite residue would slow down the dissolution process. Eventually dissolution would become limited by the rate at which the residue was stirred into the sediment column by benthic burrowers. Thus, any realistic model of the fate of CO_2 will have to simultaneously deal with oceanic mixing, interface dissolution and sediment stirring.

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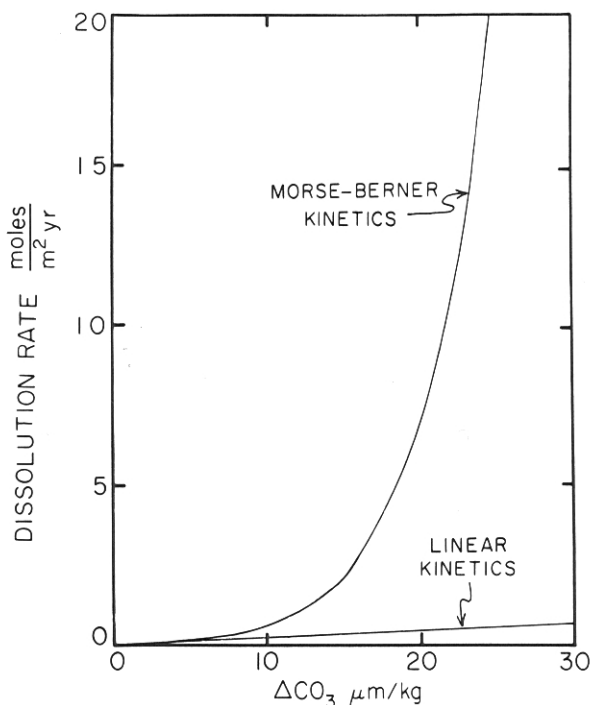


Fig. 7. Comparison of the dissolution rates for the linear kinetic model as calibrated using the Holocene CaCO₃ distribution with that for the exponential kinetic model as calibrated using the Holocene CaCO₃ distribution. The assumptions of these models are outlined by *Takahashi and Broecker (1977)*.

A MODEL FOR THE DISSOLUTION OF SEDIMENT IN THE WESTERN BASIN OF THE ATLANTIC OCEAN

Since the NADW ventilation time is small compared to that for the deep Pacific Ocean, events in the Atlantic Ocean will dominate during the next hundred or so years. The deep mixing model selected here is designed with this fact in mind.

The radiocarbon data from the GEOSECS Program show that the water in the western basin of the central deep Atlantic Ocean is replaced on a time scale of about 200 years (*Stuiver, 1976*). Furthermore the "age" of the water does not show any strong dependence on depth or latitude. Thus, in modeling it is appropriate to assume that throughout the western basin the NADW component is being replaced at the rate of one part in 200 each year. The water exiting the western basin of the central Atlantic Ocean is assumed to pass

in part directly to the Antarctic and in part to the eastern basin of the Atlantic Ocean.

The water below the ridge crests in the Atlantic Ocean is a mixture of NADW and Antarctic Bottom Water (AABW). The salinity section (Figure 8) through the western basin shows the geographic and depth dependence of the composition of these mixtures. The end members have salinities of 34.93‰ (NADW) and 34.67‰ (AABW). The 34.80 isohaline thus marks a 50-50 mixture of the two end members.

As AABW contains a large component of recirculated Deep Pacific Ocean Water which has not reequilibrated with the atmosphere, its $\text{CO}_3^{=}$ content will be slow to change. The time scale for its alteration will be many hundreds of years. Thus, for the calculations to be carried out here, the $\text{CO}_3^{=}$ content of AABW will be assumed to remain unchanged. Therefore, as the mixture is renewed, only the NADW component will change in $\text{CO}_3^{=}$ content (at least during the next hundred or so years).

Plots of $\text{CO}_3^{=}$ content for deep waters in the northern and southern parts of the central Atlantic Ocean are shown in Figure 9 along with the critical carbonate ion curve (i.e., the $\text{CO}_3^{=}$ content at which the dissolution rate becomes geologically significant). In the northern western basin where NADW dominates the deep water column, the present day crossover depth (i.e., depth where the *in situ* $\text{CO}_3^{=}$ content becomes less than the critical $\text{CO}_3^{=}$ content) is about 4700 meters. In the western basin of the South Atlantic Ocean, where AABW underrides and mixes upward into the NADW, the crossover is at a shallower depth (~4000 meters).

Figure 10 illustrates what the situation will be when the ion content of NADW has dropped by $17 \mu\text{m}/\text{kg}$. The crossover depth at this time will have risen to about 3700 meters throughout the Atlantic Ocean. The sediments in the transition zone between the pre-industrial lysocline and the compensation depths will be subjected at that time to much more vigorous dissolution than during the pre-industrial era. Superlysocline sediments will also become subject to attack by the acidified deep water.

In the sections that follow, an attempt will be made to model the attack of the sediments in the western basin of the Atlantic Ocean by the progressively acidified NADW. A simple box model approach is used. The NADW component of waters below 3000 meters in the western basin of the Atlantic Ocean is assumed to be well mixed. Three processes tend to change the ΣCO_2 content and $\text{CO}_3^{=}$ content of this water.

1) The input of new NADW progressively enriched in total dissolved inorganic carbon: The volume of water in the western basin of the Atlantic Ocean beneath 3000 meters between 30°S and 40°N is $32 \times 10^{15} \text{ m}^3$. Of this about 75% is NADW. If this water is to be replaced once every 200 years, the flux of new NADW must be $1.2 \times 10^{14} \text{ m}^3/\text{yr}$ (i.e., about 4 Sverdrups). The $\text{CO}_3^{=}$ content of this input is calculated as follows.

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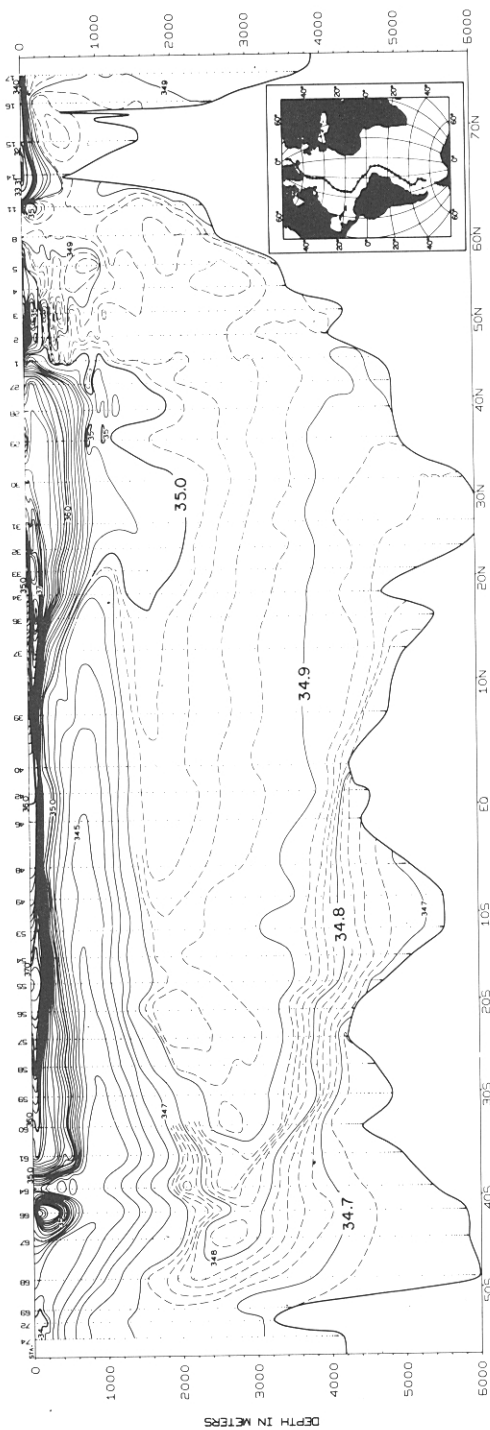


Fig. 8. Salinity section along the GEOSECS track in the western basin of the Atlantic Ocean. The mixing zone of interest to the $CaCO_3$ dissolution problem is that below 3 kilometers where AABW water ($S = 34.670/00$) mixes up into NADW water ($S > 34.900/00$).

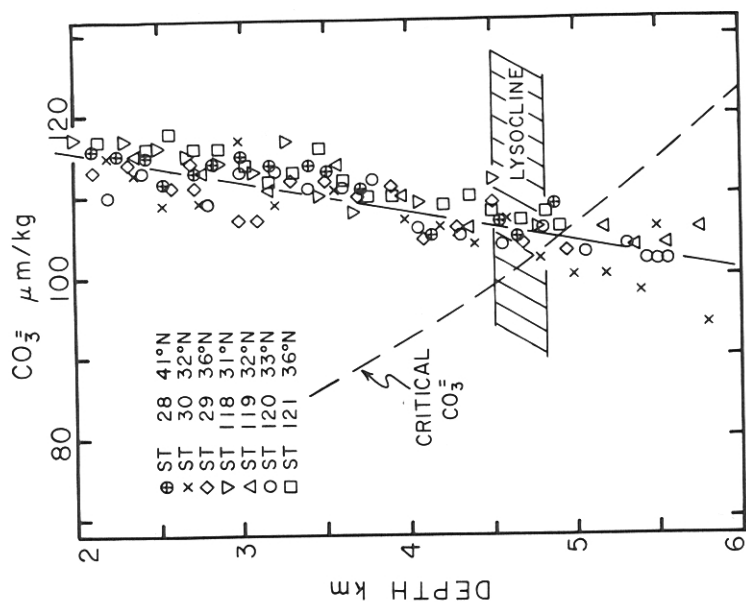


Fig. 9a. Carbonate ion content versus depth in the western North Atlantic Ocean as calculated from the GEOSECS titration data using the constants adopted by *Takahashi et al.* (in press). The lysocline depth is based on the data of *Kipp* (1976). The critical carbonate ion content curve is that of *Broecker and Takahashi* (in press).

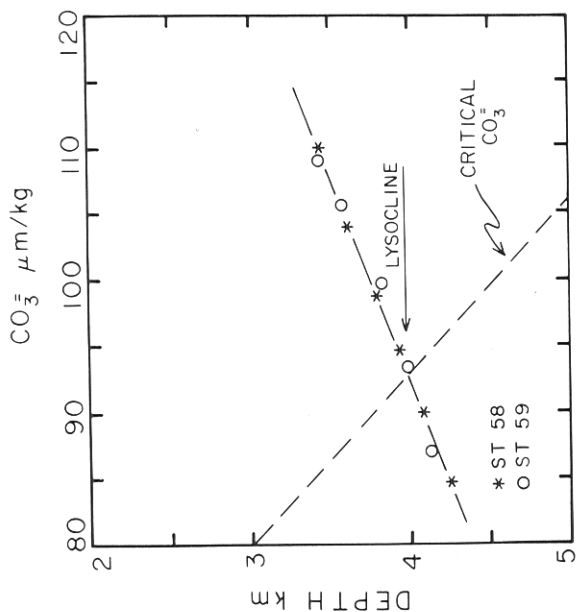


Fig. 9b. Carbonate ion content in the basal NADW-AABW mixing zone of the western South Atlantic as calculated from potential temperature using the relationship given by *Broecker and Takahashi* (in press). The critical carbonate ion content curve is given for reference.

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the basal NADW-AABW mixing zone of the western South Atlantic as calculated from potential temperature using the relationship given by Broecker and Takahashi (in press). The critical carbonate ion content curve is given for reference.

in the western North Atlantic Ocean as calculated from the GEOSECS titration data using the constants adopted by Takahashi *et al.* (in press). The lysocline depth is based on the data of Kipp (1976). The critical carbonate ion content curve is that of Broecker and Takahashi (in press).

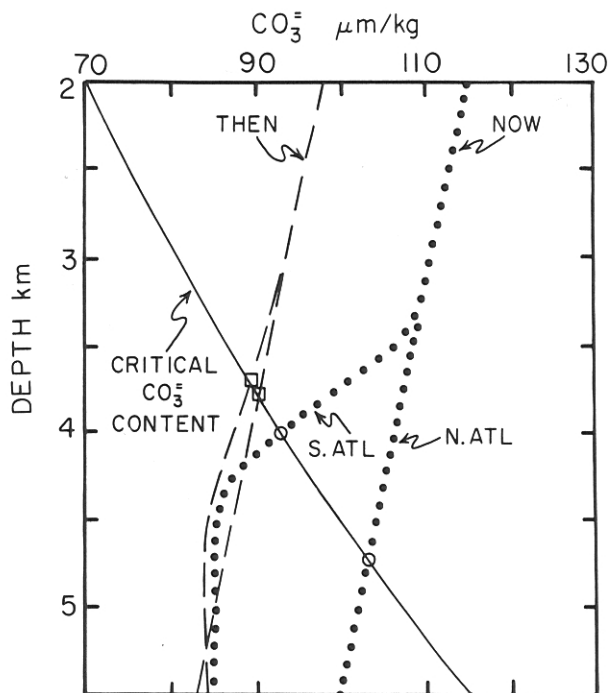


Fig. 10. $CO_3^{=}$ versus depth curves for the western basin of the Atlantic Ocean (dotted curves) prior to the introduction of fossil fuel CO_2 and after fossil fuel CO_2 introduction has reduced carbonate ion content of the NADW component of the mixing zone water by $17 \mu m/kg$ (dashed curves). The circles represent the present depths at which the *in situ* $CO_3^{=}$ content currently cross the critical value and the squares the depths at which these crossover will lie after the NADW has been "acidified" to the level where its $CO_3^{=}$ ion content has dropped $17 \mu m/kg$.

$$[CO_3^{=}]_{INPUT}^t = \frac{[CO_3^{=}]_{INPUT NADW}^{1850}}{[CO_3^{=}]_{INPUT NADW}} [CO_3^{=}]_{NADW}^{1850} \quad (5)$$

The ratio $\frac{[CO_3^{=}]_{INPUT NADW}^t}{[CO_3^{=}]_{INPUT NADW}^{1850}}$ is that given in

Figure 6. In order to eliminate the subsurface processes taking place in the natural (i.e., pre-industrial) system, the actual input

value is taken to be the pre-industrial mean $\text{CO}_3^{=}$ content of *in situ* NADW (i.e., $115 \mu\text{m}/\text{kg}$) times this ratio. This assumes that the natural respiration processes and the natural dissolution processes continue at the same rate as in pre-industrial time. Since these processes are limited by the availability of NO_3^- and $\text{PO}_4^{=}$, rather than by CO_2 , this assumption is likely valid. As the alkalinity of the incoming water should remain unchanged, the carbonate system is uniquely defined by assigning the carbonate ion content of the input water.

2) Loss of excess industrial CO_2 by outflow from the western basin to the eastern basin and to the Antarctic: The excess CO_2 concentration in the exiting water is assumed to be equal to the mean excess for the water mass itself.

3) Addition of Ca^{++} and $\text{CO}_3^{=}$ to the deep water through excess dissolution of deep sea sediments (the natural dissolution has been taken care of through our handling of the input concentrations): For sediments below the lysocline the rate of excess dissolution at any point on the sea floor depends on the decrease in the $\text{CO}_3^{=}$ content of the water from its pre-industrial value. In a separate paper (Broecker and Takahashi, in prep.) it will be shown that for sediments moderately rich in CaCO_3 (i.e., >40%), dissolution proceeds at a rate of $.025 \text{ moles}/\text{m}^2 \text{ yr}$ per $\mu\text{m}/\text{kg}$ decrease in the $\text{CO}_3^{=}$ content below the critical carbonate ion content. It will be assumed that for each additional decrease of $1 \mu\text{m}/\text{kg}$ in $\text{CO}_3^{=}$ content the rate of dissolution of these carbonate-rich sediments will rise by $0.025 \text{ moles}/\text{m}^2 \text{ year}$ (i.e., linear kinetics). For sediments above the natural lysocline, no dissolution will take place until the $\text{CO}_3^{=}$ content of the water reaches the critical carbonate ion value. Once it drops below this value the same dissolution rate versus $\Delta\text{CO}_3^{=}$ relationship is used as for the sub-natural lysocline sediment. In the North Atlantic Ocean the lysocline will rise 100 meters per $1.7 \mu\text{m}/\text{kg}$ drop in the $\text{CO}_3^{=}$ content of NADW. Thus as the $\text{CO}_3^{=}$ content drops, both the area of sediment exposed to excess dissolution and the rate of the excess dissolution at any given depth will increase.

Before launching out on the model calculation, one basic assumption needs justification. Are the products of the dissolution well distributed in the deep water column? As the volume of water per unit of area of sediment contacted decreases with each depth slice down the water column, if vertical mixing does not occur then the impact of the dissolution process will increase strongly with water depth.

Whether or not the products of calcite dissolution are mixed throughout the water column can be best tested by considering the natural steady state. In the northern western basin nearly all the carbonate falling below about 5100 meters dissolves. In the southern western basin the corresponding depth is 4400 meters. The area of sediment nearly free of CaCO_3 in the western basin is about $10 \times 10^{12} \text{ m}^2$. If the mean rain rate of CaCO_3 is taken to be 0.8

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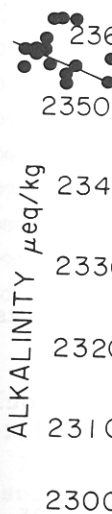


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$gm/cm^2 \cdot 10^3$ yrs (i.e., 8×10^{-6} moles/cm² yr) and if the products of this dissolution are assumed to have been confined to the volume below the top of the dissolution zone (volume of 6×10^{15} m³) then during its residence time of 200 years the water would increase in alkalinity by $55 \mu eq/kg$. There would, of course, then be no alkalinity increase for waters above the dissolution zone. The observed increase is on the order of only $10 \mu eq/kg$ (see Figure 11) and shows no strong correlation with depth or geographic location. On the other hand, if the dissolution products are mixed upward to a depth of 3000 meters (volume of 32×10^{15} m³), then the expected alkalinity increase would be only $10 \mu eq/kg$ -- a value roughly consistent with the GEOSECS results. The near uniformity of the alkalinity increase throughout the mixing zone beneath the Two Degree Discontinuity (TDD) suggests that the products of dissolution are not confined to the level from which they were released, but rather that they are mixed well up into the water column. Mixing along isopycnal surfaces (i.e., along the isohalines in Figure 8) could produce the observed distribution.

The model calculation is begun in the year 1900. Since the amount of CO₂ added to the NADW mass up to this time was quite small, it will be assumed that the NADW was still at its steady

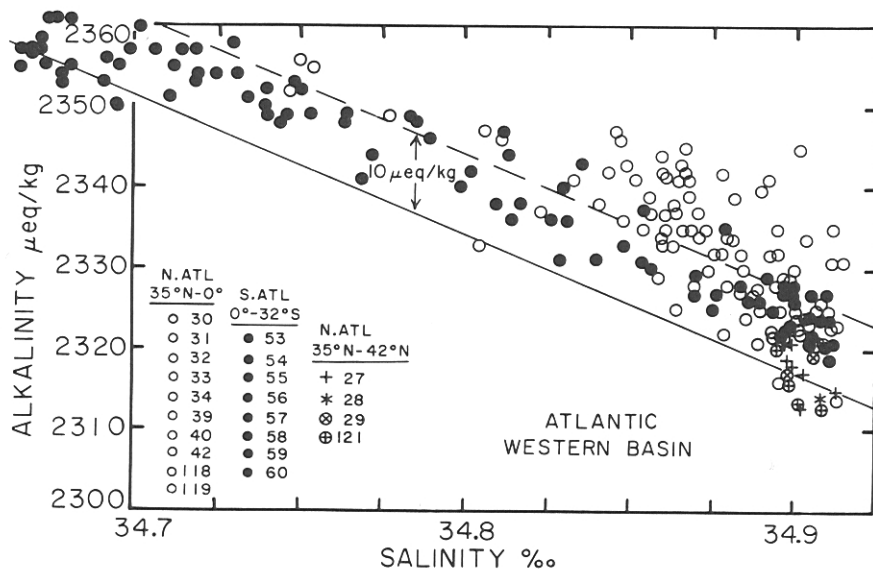


Fig. 11. Alkalinity versus salinity in the mixing zone between AABW and basal NADW. The lower solid line represents the values expected if there were no CaCO₃ dissolution in this mixing zone. The upper solid line represents the alkalinity expected if the products of natural CaCO₃ dissolution were spread uniformly through this mixing zone.

state $\text{CO}_3^{=}$ content (i.e., 115 $\mu\text{m}/\text{kg}$) and at its mean alkalinity (2330 $\mu\text{eq}/\text{kg}$). The calculation is carried out in 10 year increments. The CO_2 pressure in the atmosphere and the composition of the input water are taken to be those for the mid-point of the decade over which the calculation is being carried out. The $\text{CO}_3^{=}$ content of the NADW reservoir used in the dissolution and outflow calculations is taken to be that calculated for the end of the preceding decade. At the end of each decade the net change in the ΣCO_2 content and in the alkalinity of the NADW is recomputed. The $\text{CO}_3^{=}$ content obtained from these values is used for the next decade.

The area of sediment in the western basin of the Atlantic Ocean lying between the lysocline and the compensation depth is about $7 \times 10^{12} \text{ m}^2$. These sediments are assumed to yield 0.025 moles of excess CaCO_3 dissolution per square meter year for each $\mu\text{m}/\text{kg}$ drop in the $\text{CO}_3^{=}$ ion content of NADW. The sediments beneath the compensation depth are assumed to contribute nothing. The area of sediment above the natural lysocline contributing to the excess dissolution is taken to be $0.4 \times 10^{12} \text{ m}^2$ per $\mu\text{m}/\text{kg}$ drop in $\text{CO}_3^{=}$ content of the NADW reservoir. As the difference between the critical carbonate ion content and the *in situ* carbonate ion content for this depth interval averages one half the drop in carbonate content of the NADW, a factor of 1/2 must be introduced to account for this gradient in $\Delta\text{CO}_3^{=}$ in the superlysocline region. Thus the dissolution rate, R , is calculated as follows:

$$R = \Delta\text{CO}_3^{=} (A_{L-C} + \frac{1}{2} A_{<L}) b \quad (6)$$

where

$$\Delta\text{CO}_3^{=} = \text{CO}_3^{=} \text{ INITIAL} - \text{CO}_3^{=} \text{ } t \\ \text{NADW} \quad \text{NADW}$$

A_{L-C} = area of sediments between the natural lysocline and natural compensation depth

$A_{<L}$ = area of sediment above the natural lysocline which has come under attack (i.e., $0.4 \times 10^{12} \times \Delta\text{CO}_3^{=}$)

b = coefficient of dissolution (i.e., 0.025 moles/ m^2 yr per $\mu\text{m}/\text{kg}$)

The results of this calculation for the period between 1900 and 2105 are given in Table 8. This is the period where the rate of the CO_2 content increase for the atmosphere is assumed to rise

1900-1910

1910-1920

1920-1930

1930-1940

1940-1950

1950-1960

1960-1970

1970-1980

1980-1990

1990-2000

2000-2010

2010-2020

2020-2030

2030-2040

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TABLE 8. Western Basin Atlantic Model Calculation Carried Out Over the Period During Which the Atmospheric CO₂ Rise Rate is Assumed to be Increasing by 2% per Year

	P _{CO₂} 10 ⁻⁶ atm	[CO ₃ ⁼] Input to NADW μm/kg	ΔΣCO ₂ Input to NADW μm/kg	[CO ₃ ⁼] NADW μm/kg	ΔΣCO ₂ NADW μm/kg	ΔCO ₃ ⁼ NADW μm/kg	Increase ΣCO ₂ via inflow 10 ¹¹ moles/yr	Increase ΣCO ₂ via dissolution 10 ¹¹ moles/yr
1900-1910	294	109	5	115	0.0	0.0	6.0	0.0
1910-1920	297	108	6	115	0.2	0.1	7.2	0.2
1920-1930	300	107	8	115	0.4	0.2	9.6	0.4
1930-1940	303	106	10	115	0.7	0.3	12.0	0.5
1940-1950	308	105	13	115	1.1	0.5	15.6	0.9
1950-1960	313	104	16	114	1.6	0.7	19.2	1.3
1960-1970	320	102	19	114	2.1	1.0	22.8	1.8
1970-1980	328	101	23	114	2.8	1.3	27.6	2.3
1980-1990	338	99	27	113	3.6	1.6	32.4	2.9
1990-2000	350	97	32	113	4.6	2.0	38.4	4.0
2000-2010	365	94	38	113	5.8	2.4	45.6	4.8
2010-2020	383	91	46	112	7.1	3.0	55.2	6.0
2020-2030	405	86	55	111	8.8	3.6	66.0	7.2
2030-2040	432	82	65	111	10.8	4.4	78.0	8.8
2040-2050	465	77	75	110	13.1	5.3	90.0	10.6
2050-2060	506	72	86	109	15.8	6.3	103.2	12.6
2060-2070	555	67	97	108	18.8	7.4	116.4	16.3
2070-2080	615	61	110	106	21.9	8.5	132.0	18.7
2080-2090	689	55	125	105	25.8	9.8	150.0	21.6
2090-2100	779	49	139	104	30.2	11.3	166.8	24.9
2100-2110	888	44	157	101	35.1	13.0	188.4	28.6

by 2% per year.* The yearly increase rate goes from 0.22 ppm/yr in 1905 to 0.90 ppm per year in 1975 to 12.1 ppm in 2105. The results for the period 2105 to 2205, during which the atmospheric CO₂ content is held constant, are shown in Table 9. At the end of this period the dissolution rate of CaCO₃ from deep Atlantic Ocean sediment becomes about one third the input rate of excess CO₂.

* If, as well may be the case, the acceleration of fossil fuel use is stemmed before the end of the next century, then the carbon ion content of NADW will not drop as fast as indicated by these calculations.

TABLE 9. Western Basin Atlantic Model for Period During Which the Atmospheric CO_2 Content is Assumed to Remain Constant

	$CO_3^{=}$	$\Delta\Sigma CO_2$	$\Delta CO_3^{=}$	ΣCO_2 In	ΣCO_2 Out	ΣCO_2 Dis	ΣCO_2 Net
	$\mu m/kg$			10^{11} moles/yr			
2100-2110	101	35	13.0	188	-42	29	175
2110-2120	100	41	14.8	188	-49	33	172
2120-2130	99	46	16.4	188	-55	36	169
2130-2140	97	51	18.0	188	-61	40	167
2140-2150	96	56	19.4	188	-67	46	167
2150-2160	94	62	20.6	188	-74	50	164
2160-2170	93	67	21.6	188	-80	52	160
2170-2180	93	72	22.4	188	-86	54	156
2180-2190	92	77	23.2	188	-92	56	152
2190-2200	91	82	23.8	188	-98	58	147
2200-2210	91	86	24.3	188	-102	60	146

$$P_{CO_2}^{atm} = 888 \text{ ppm}$$

$$\Sigma CO_2 \text{ input} = 2282 \mu m/kg$$

$$\Sigma CO_2 \text{ pre-ind. NADW} = 2125 \mu m/kg$$

$$ALK \text{ input} = 2290 \mu eq/kg$$

$$ALK \text{ pre-ind. NADW} = 2290 \mu m/kg$$

$$CO_3^{=} \text{ input} = 44 \mu m/kg$$

$$CO_3^{=} \text{ pre-ind. NADW} = 115 \mu m/kg$$

At steady state (i.e., when the NADW has come to equilibrium with this new atmospheric CO_2 content) about half of the incoming excess will be neutralized within the Atlantic Ocean. Table 10 summarizes the change in chemical composition of the input water to the NADW and of the mean NADW itself over this period. Table 11 compares the fluxes of excess CO_2 into the NADW and of $CaCO_3$ dissolution of sediments in contact with NADW with the flux of CO_2 into the atmosphere.

How long can this go on? At a $CO_3^{=}$ depletion of $20 \mu m/kg$, the rate of dissolution is $0.5 \text{ m/m}^2 \text{ yr}$ (i.e., 0.5 mm/decade). For sediment averaging 70% $CaCO_3$, the amount of available $CaCO_3$ is about 2000 moles/m^2 . Hence, the time constant for depletion is on the order of 4000 years. This is about threefold longer than the time constant for the replacement of deep Indian Ocean and Pacific Ocean waters.

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TABLE 10. Summary of Composition of Input Water to the NADW and of NADW Itself Over Period Covered by the Model Calculations

	← Input →			← NADW →		
	P _{CO₂}	CO ₃ ⁼	ΣCO ₂	CO ₃ ⁼	ΣCO ₂	ALK
1850	283	115	2125	115	2125	2290
1975	328	101	2148	114	2128	2290
2105	888	44	2282	101	2160	2300
2205	888	44	2282	91	2211	2325

TABLE 11. Summary of Fossil Fuel CO₂ Fluxes Contrasting the Total Flux into the System with that Leaving the Surface Ocean for the Deep North Atlantic and with that of Fossil Fuel Induced Dissolution of Western Basin Sediments

	10 ¹² moles/yr		
	Total CO ₂ Influx	Flux to NADW	Flux to NADW Sediments
1850	0	0	0.0
1975	177	3	0.2
2105	2140	19	2.9
2205	-	19	6.0

To be more realistic this model would have to include:

- 1) The dependence of dissolution rate on the CaCO_3 content of the sediment.
 - a) If the rate limiting step is a "stagnant boundary film" at the sediment-water interface then the dependence will be quite small until very low calcite contents are achieved.
 - b) If the rate limiting step is the resaturation time of the sediment pore waters then the rate of dissolution will vary with the square root of the fraction calcite.
- 2) The dependence of the dissolution rate on $\Delta\text{CO}_3^{=}$. If the rate limiting step for dissolution is the release of ions from the crystal surfaces, then as shown by the experiments of *Morse and Berner* (1972) an exponential rather than linear dependence on $\Delta\text{CO}_3^{=}$ would have to be used. If so, dissolution will occur about an order of magnitude faster.
- 3) The relative rates of burrowing and dissolution. At a dissolution rate of $0.5 \text{ m/m}^2 \text{ yr}$, in the absence of bioturbation an insoluble residue one characteristic diffusion length in thickness would be built up in a decade or so. Therefore, if burrowing occurs on the time scale of centuries, rather than years, it will quite soon become the rate limiting step.

CONCLUSIONS

The rate of deep sea sediment dissolution is certainly fast enough that this process will take place concurrently with the transfer of CO_2 from the atmosphere-shallow ocean reservoir to the deep sea reservoir. The amount of calcite "kinetically" available for dissolution is comparable to the amount of carbon locked up in recoverable fossil fuels. The major uncertainties remaining to be resolved before adequate modeling can be done are:

- 1) The identification of the rate limiting step for dissolution on the sea floor (i.e., a distinction between linear and exponential kinetics must be made).
- 2) The quantification of mixing rates of sediments on the sea floor (the mechanical eddy diffusivity as a function of depth in the sediment column must be determined).

ACKNOWLEDGEMENTS

Much of the $\text{CO}_3^{=}$, ΣCO_2 , $p\text{CO}_2$ and alkalinity data used in this paper was generated by the GEOSECS Program. Financial support for this work was provided by a grant to Lamont-Doherty Geological Observatory from the Energy Research and Development Administration (E(11-1)2185) and by a grant to CUNY from IDOE (OCE72-06419). Lamont-Doherty Geological Observatory Contribution No. 2513.

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