DIRECT OBSERVATION OF THE OCEANIC CO_2 INCREASE

Peter G. Brewer

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

Abstract. The increase in atmospheric CO_2 of approximately 50 ppm from the mid-nineteenth century to 1972 has led to a corresponding increase in the pCO_2 of sea water. The record of this increase is present in the oceanic water masses, though the signal is obscured. By observing the alkalinity and total CO_2 concentration within a water mass, and stripping off the perturbations of the CO_2 system due to respiration, carbonate dissolution and nitrate addition, the original atmospheric equilibration signal may be recovered. The application of these calculations to GEOSECS (1972) data from the core of the Antarctic Intermediate water reveals propagation of the atmospheric CO_2 signal northwards.

Introduction

The well-documented increase in atmospheric CO_2 content, due to fossil fuel burning, cement production and terrestrial biosphere changes over the past century, has been the subject of intense investigation. The first report by Callendar (1938) admirably described the problem. He calculated the effect of the increased CO_2 on the global radiation balance and estimated that about three quarters of the fossil fuel CO_2 produced had remained in the atmosphere, the remainder dissolving in sea water. Using approximate oceanic circulation times, and pCO_2 and alkalinity data, he attempted to predict future atmospheric CO_2 levels and recognized their dependence upon equilibration rates with the ocean. Box models, such as those used by Revelle and Suess (1957) and Craig (1957), and the recent box diffusion model of Oeschger et al. (1975) have been widely used in attempts to understand the oceanic CO_2 sink and to describe exchange processes. Most of these models use the observed distribution of both natural and bomb-produced ^{14}C to derive exchange coefficients and to predict the fate of fossil fuel CO_2. The use of ^{14}C as a tracer is not without problems, and a direct measurement of the oceanic CO_2 increase would be most desirable. Recently, Takahashi et al. (1978) have reported an increase in the oceanic pCO_2 observed in the western Atlantic between the I.G.Y. (1957-58) and GEOSECS (1972) cruise tracks which is consistent with the observed atmospheric increase. It is the purpose of this paper to show that the oceanic CO_2 concentration is indeed increasing with time, that this increase can be measured directly, and that the record of this increase is written in the interleaved structure of oceanic water masses.
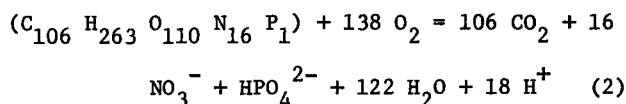
The Dissolved CO_2 System

Consider an element of sea water in equilibrium with the atmosphere. A complete description

of its CO_2 system may be achieved by measurement of any two of the four properties: pH, pCO_2, alkalinity and total CO_2. Once this element of water sinks below the euphotic zone, its CO_2 system is modified by respiration, which consumes O_2 and produces CO_2. Its alkalinity is also changed both by carbonate dissolution and nitrate production (Brewer et al. 1975). If these changes can be measured precisely and stripped from the observed CO_2 properties at any place in the ocean, then the original atmospheric CO_2 equilibration signal may be recovered. The alkalinity and total CO_2 pair are well-suited for this purpose, being temperature and pressure independent. The atmospheric CO_2 increase has had no effect on alkalinity. Taking the salinity and alkalinity at the time of atmospheric equilibration as reference points, the deviations from this condition are given by:

$$\Delta \text{ Alkalinity} = \text{Alkalinity}_{obs.} - \left[\frac{\text{Alkalinity}_{ref.}}{\text{Salinity}_{ref.}} \times \text{Salinity}_{obs.} \right] \quad (1)$$

For addition of CO_2 by respiration, the well-known relationship

$$(C_{106} H_{263} O_{110} N_{16} P_1) + 138 \ O_2 = 106 \ CO_2 + 16$$
$$NO_3^- + HPO_4^{2-} + 122 \ H_2O + 18 \ H^+ \quad (2)$$

holds. The change in alkalinity due to $CaCO_3$ dissolution (Δ Alkalinity $CaCO_3$) is then

$$\Delta \text{ Alkalinity}_{CaCO_3} = \Delta \text{ Alkalinity} + \Delta \text{ NO}_3 \quad (3)$$

Thus the change in total CO_2 is given by $\quad (4)$

$$\Delta \Sigma CO_2 = [\Delta O_2 \times 0.768] + [\Delta \text{ Alkalinity}_{CaCO_3} \times 0.5]$$

These corrections to the observed data permit calculation of the original atmospheric equilibration signal. The error in measurement of total CO_2 ($\pm$ 10 μmoles/kg) and in alkalinity ($\pm$ 3 μ equivalents/kg) correspond to an error of ca. $\pm$ 15 x 10^{-6} atm. in pCO_2. Since the atmospheric increase is now > 50 x 10^{-6} atm., the data are precise enough to permit observation of this change. As an example, I use GEOSECS data from Antarctic Intermediate Water to demonstrate advection of fossil fuel CO_2 along an isopycnal surface. The apparent dissociation constants of Mehrbach et al. (1973) were used in all calculations. The solubility of CO_2 gas in sea water was taken from Weiss (1974) and the apparent dissociation constant of boric acid from Lyman (1953).
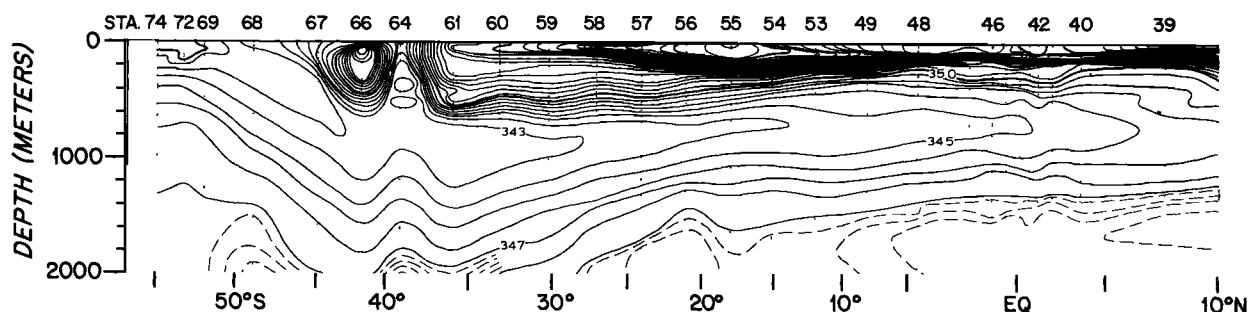
Fig. 1. The GEOSECS salinity section in the western south Atlantic Ocean showing the tongue of low salinity Antarctic Intermediate Water.

Antarctic Intermediate Water

In Table 1, I present data from GEOSECS (1972) Atlantic Station 67-48, covering a range of latitude of 45°S to 4°S. At each station, points were taken at the salinity minimum at the core of the Antarctic Intermediate Water. This water is shown in Figure 1, as a tongue of low salinity water extending northwards at depths of 500-1000 meters. The salinity minimum is coincident with the 27.18 $\sigma\theta$ isopycnal surface which intersects with the sea surface near 50°S in the southern winter (Reid et al., 1977). The December, 1972, oceanic pCO_2 values at 50°S were 270-300 x 10^{-6} atm., with the most intense gradients existing east of the Falkland Islands. (Takahashi, et al. 1978). Since the mean 1972 atmospheric pCO_2 values were 320 x 10^{-6} atm., the region is a well-defined oceanic CO_2 sink. The choice of reference values for the initial salinity and alkalinity of the source water is somewhat subjective, but can be constrained by careful observation. For the purposes of this paper, I select 34.100°/°° and 2300 μ equivalents/kg which are close to the observed values at 50°S in December, 1972. As this water mass sinks and propagates northwards to the equator, the dissolved oxygen concentration drops from an atmospheric equilibrium value of 320 μm/kg to 150 μm/kg, salinity increases to 34.46°/°° through mixing with adjacent waters, and temperature increases from 4.0 to 4.6°C. Corrections for these changes are large (Δ ΣCO_2 = ca. 120 μmoles /kg), but can be made with an accuracy of ca. ±5 μmoles/kg. The application of the NO_3 correction for waters of Antarctic origin requires particular care. Surface waters south of 50°S have significant quantities of nitrate due to upwelling (GEOSECS Sta. 74 at 55°S has 24 μm NO_3/kg at 8 m). I have applied the NO_3 correction from a knowledge of the oxygen deficiency (Broecker, 1974) as $-\Delta O_2 = 9 \, \Delta \, NO_3$.

The calculated initial pCO_2 at the core of the Antarctic Intermediate Water is shown plotted versus latitude in Figure 2. The error bars are ±15 x 10^{-6} atm. Stations 67-64 from 40°-50°S plainly have pCO_2 values of ca. 300 x 10^{-6} atm., close to that observed for the present day southern ocean at 50°S 45'W (Takahashi et al., 1978). Stations 56-48 from 20°S to the equator show initial pCO_2 values of ca. 250 x 10^{-6}atm. The difference of ca. 50 x 10^{-6} atm. is consistent with both the estimated mean atmospheric increase since the last century, and with the present day observed oceanic disequilibrium of minus 20 - 40

x 10^{-6} atm. with atmospheric CO_2 at 50°S. It should be noted that latitude is not simply related to time. Both Reid et al. (1977) and Buscaglia (1971) have shown that direct northward flow of this water mass from its source extends only to about 40°S. The flow then tends eastward in the subtropical anticyclonic gyre, not returning to the coast of South America again until 30°S. The low initial pCO_2 values for Stations 61-59 are consistent with this scheme. These conclusions are also consistent with the ^{14}C data of Stuiver (1978) who showed that bomb ^{14}C had not penetrated to these depths north of 30°S. The possibility that the pCO_2 gradient observed here is not due to the atmospheric increase, but is simply the result of mixing of Antarctic Intermediate Water with waters of northern origin, which are markedly out of atmospheric equilibrium, must be considered. Surface waters in the Norwegian and Greenland Seas have a pCO_2 of -100 x 10^{-6} atm. with respect to the atmosphere (Takahashi et al., 1978). The salinity minimum signal of the Antarctic Intermediate Water (34.10°/°° at its source) is eroded by mixing from above and below until the water mass is no longer recognizable as the salinity at the remnants of the core approaches 34.90°/°° in the Sargasso Sea. Thus, water at Station 60 is approximately 20% diluted, and at station 54 is 45% diluted, from its source properties. The calculated property of initial pCO_2 (Table 1) cannot be used in diffusive or mixing calculations. Oxygen concentrations decrease along the core of the
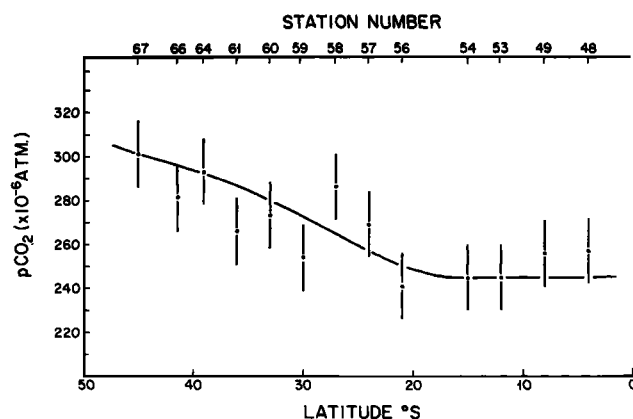

Fig. 2. The calculated initial pCO_2 of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

TABLE 1. Observed properties and calculated initial pCO_2 along the core of the Antarctic Intermediate Water from the 1972 GEOSECS Atlantic Expedition.

Station	Position	Depth (m)	S°/°°	θ C°	Alkalinity eq/kg	ΣCO_2 μmoles /kg	O_2 μmoles /kg	Calculated Initial pCO_2 x 10^{-6} atm.
67	44°58'S, 51°00'W	445	34.178	4.100	2285	2145	273	301
66	41°33'S, 50°52'W	976	34.206	3.720	2295	2153	262	281
64	39°11'S, 48°35'W	515	34.191	4.010	2281	2144	268	293
61	36°00'S, 45°00'W	996	34.224	3.776	2296	2153	251	266
60	32°58'S, 42°30'W	828	34.263	4.536	2300	2152	247	273
59	30°12'S, 39°18'W	942	34.276	3.899	2307	2164	234	254
58	27°00'S, 37°00'W	874	34.334	3.967	2317	2202	214	286
57	23°59'S, 35°00'W	792	34.333	4.406	2309	2186	214	269
56	21°00'S, 33°00'W	793	34.374	4.189	2308	2183	195	241
54	15°04'S, 29°31'W	689	34.395	4.306	2313	2195	187	245
53	12°00'S, 28°01'W	895	34.447	4.000	2315	2210	174	245
49	07°55'S, 28°15'W	810	34.466	4.562	2312	2231	150	256
48	04°00'S, 29°00'W	681	34.460	4.659	2317	2228	156	257

salinity minimum, and total CO_2 concentrations increase, principally by mixing and partly by in situ biological activity. Waters of lower oxygen content, and higher CO_2 content, occur both above and below the core. The warmer waters above the core must have equilibrated with the atmosphere at lower latitudes and thus should have high initial pCO_2 signals (Keeling, 1968; Takahashi et al., 1978). The colder waters below the core are made up principally of Antarctic Circumpolar Water (Reid et al., 1977). The initial pCO_2 values of ca. 250×10^{-6} atm. calculated for Stations 56-48 thus represent the mean signal from a complex mixture of waters added by diffusion to this intrusive sheet of low salinity water.

Discussion. There are several approximations in the calculations given here. Firstly, the effects of a diffusion have been neglected. Secondly, the specific alkalinity of ocean surface water is not constant, but is a weak function of temperature (Edmond, 1974). This result will have very little effect on the Antarctic Intermediate Water calculations, but would have a greater effect on calculations on water masses where a greater temperature range is exhibited. Salinity is not a perfect conservative tracer, (Brewer and Bradshaw, 1975); moreover, the oceanic CO_2 increase will itself generate salinity (conductance) changes. An increase in dissolved CO_2 of 33 μmoles/kg produces a .001°/°° conductance salinity change. This approximately corresponds to the inferred surface water CO_2 increase over the last century.

The calculations given here are simple, but essentially correct. The results reveal direct observation of the oceanic CO_2 increase. This is currently at the limit of detection, however, the signal will be very much easier to observe in future years as atmospheric CO_2 inputs increase. A comparable calculation of the initial pCO_2 of northern Atlantic water masses is not easily made due to the lack of GEOSECS alkalinity and total CO_2 data in the Atlantic north of 40°N. The acquisition of this data from the important CO_2 sink in the far north Atlantic should be of high priority for oceanographers.

References

Brewer, P. G, G.T.F. Wong, M. P. Bacon and D. W. Spencer, An oceanic calcium problem?, Earth Planet. Sci. Lett., 26, 81-87, 1975.

Brewer, P. G. and A. Bradshaw, The effect of the non-ideal composition of sea water on salinity and density, J. Mar. Res., 33, 157-175, 1975.

Broecker, W. S., "NO", A conservative water-mass tracer, Earth Planet Sci. Lett., 23, 100-107, 1974.

Buscaglia, J. L., On the circulation of the Intermediate Water in the southeastern Atlantic Ocean, J. Mar. Res., 29, 245-255, 1971.

Callendar, G. S., The artificial production of carbon dioxide and its influence on temperature, Q. J. Roy. Meteorol. Soc., 64, 223-240, 1938.

Craig, H., The natural distribution of radiocarbon and the exchange time of carbon dioxide between atmosphere and sea, Tellus, 9, 1-17, 1957.

Edmond, J. M., On the dissolution of carbonate and silicate in the deep ocean, Deep-Sea Res., 21, 455-480, 1974.

Keeling, C. D., Carbon dioxide in surface ocean waters , Global distribution, J. Geophys. Res. 73, 4543-4553, 1968.

Lyman, J., Buffer mechanism of sea water, Ph.D. Thesis, Univ. of California, Los Angeles, Calif., 196 pp., 1956.

Mehrbach, C., C. H. Culberson, J. E. Hawley and

R. M. Pytkowicz, Measurement of the apparent
dissociation constants of carbonic acid in sea
water at atmospheric pressure, Limnol. Oceanogr.
18, 897-907, 1973.

Oeschger, H., U. Siegenthaler, U. Schatterer and
A. Gugelmann, A box diffusion model to study
the carbon dioxide exchange in nature, Tellus,
27, 168-191, 1975.

Reid, J. L., W. D. Nowlin and W. C. Patzert, On
the characteristics and circulation of the
southwestern Atlantic Ocean, J. Phys. Oceanogr.,
7, 62-91, 1977.

Revelle, R. and H. E. Suess, Carbon dioxide ex-
change between atmosphere and ocean and the
question of an increase of atmospheric CO_2 dur-
ing past decades, Tellus, 9, 18-27, 1957.

Stuiver, M., Atmospheric carbon dioxide and car-
bon reservoir changes, Science, 199, 253-258,
1978.

Takahashi, T., W. S. Broecker, and A. E.
Bainbridge, Carbon dioxide in the atmosphere
and the surface waters of the Atlantic and
Pacific Oceans, Earth and Planet. Sci. Letts.,
Submitted.

Weiss, R. F., Carbon dioxide in water and sea
water; the solubility of a non-ideal gas, Mar.
Chem., 2, 203-215, 1974.