pCO_2 in Sea Water and its Effect on the Movement of CO_2 in Nature[1, 2]

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Abstract

A method is described for measuring pCO_2 in sea water. A gas phase is analyzed continuously by infrared absorption for CO_2 while it is equilibrated gently with the water in a countercurrent column. It has been used to determine the changes in pCO_2 produced by variations of temperature and total CO_2. Partial pressure shows large changes for small increments in these two independant variables. These properties of sea water are useful in estimating the movement of CO_2 between the atmosphere and oceans. It appears, for instance, that most of the fossil fuel CO_2 released by man has been effective in increasing the percentage of this gas in air.

Such diverse problems as biological productivity, climatic change, and carbon dating are linked to an understanding of the movement of carbon dioxide in nature. Pertinent to all of these is a knowledge of the concentration of this gas in air and its exchange between the oceans and the atmosphere.

Transport within the atmosphere and oceans is chiefly by mixing processes. But the movement of CO_2 across the sea surface depends on diffusion. Since tension or partial pressure is the driving force of diffusion, an understanding of air-ocean exchange of CO_2 must include a quantitative knowledge of the factors such as temperature and total CO_2 which effect the tension of this gas in the sea.

When CO_2 from the atmosphere dissolves in sea water it enters the following chain of reactions:

$$\begin{matrix}\downarrow\uparrow\\ \downarrow\uparrow\end{matrix}\ \begin{matrix}CO_2\\ CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- \rightleftarrows CO_3^=\end{matrix}$$

The sums of these forms will be called total CO_2 in this paper. The partial pressure or tension exerted by the physically dissolved CO_2 is denoted by pCO_2. HARVEY (1955) has reviewed the considerable work of Buch and others that has been done on the chemistry of the CO_2 system in sea water. The amounts present as bicarbonate and carbonate ions can be found from pH, temperature, and salinity with the aid of the apparent dissociation constants for carbonic acid determined by Buch in sea water. Henries law is not valid for the relationship between pCO_2 and total CO_2 since only that component present as a physically dissolved gas is responsible for the tension.

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Buch has computed a series of tables in which pCO_2 and total CO_2 can be determined from pH, temperature, and salinity. The agreement between pCO_2 computed from these tables and that measured directly has been rather poor if one considers the limited range of surface sea water (BUCH 1939, DEACON 1940). Part of the cause is due to the inability to measure pH with sufficient precision. An error of .02 pH units will change the estimated partial pressure by 10 percent. Direct tension measurements may be equally inaccurate due to the difficulties of measuring a component that makes up only 1 part in 3000 of a gas mixture. Buch's tables are, in addition, inconvenient for deriving the relationship of pCO_2 and total CO_2 and also the effect of temperature on pCO_2 when total CO_2 remains unchanged. This is due to the pH changes that occur. It was the need for these two relationships that resulted in the present work.

There is an additional reason for directly measuring the CO_2 partial pressure properties. Buch defined apparent dissociation constants, K'1 and K'2 for the carbonic acid system in sea water using concentrations of ions rather than activities. When a comparison is made with the known dissociation constants it is found that the carbonate ions exert an activity equal to only 2 percent of their measured chemical concentration, (The Oceans, page 205). Some recent work of GARRELLS et al (1960) shows that this is due to complexing of CO_3 ions, primarily with Mg and Na. Thus the actual situation in sea water can be considered:

$$CO_2 + H_2O \underset{}{\overset{}{\rightleftarrows}} H_2CO_3 \overset{K_1'}{\rightleftarrows} HCO_3^- \overset{K_2'}{\rightleftarrows}$$

$$CO_3^{=} + Mg \overset{K_3'}{\rightleftarrows} MgCO_3 + Na^+ \overset{K_4'}{\rightleftarrows} NaCO_3^-$$

Other cations have only a minor effect. There is a small amount of complexing involving the bicarbonate ion.

In addition, the first dissociation constant, K'_1, is defined using the total unionized CO_2 for the undissociated carbonic acid. Actually only about 1/1000 of this is H_2CO_3, so K'_1 is 1,000 times smaller than the true K_1. It seemed possible that these approximations could have an effect on the dynamics of the CO_2 system in sea water.

Since this work has been finished a paper by Bolin and Eriksson has appeared that treats theoretically much of what I have done experimentally. The agreement with my measured values is rather good which indicates that the possible effects mentioned above are not drastic. Their work will be referred to further.

Method: A method has been developed for the continuous recording of CO_2 partial pressure in sea water. The apparatus is shown in Figure 1. A Fernbach flask containing about

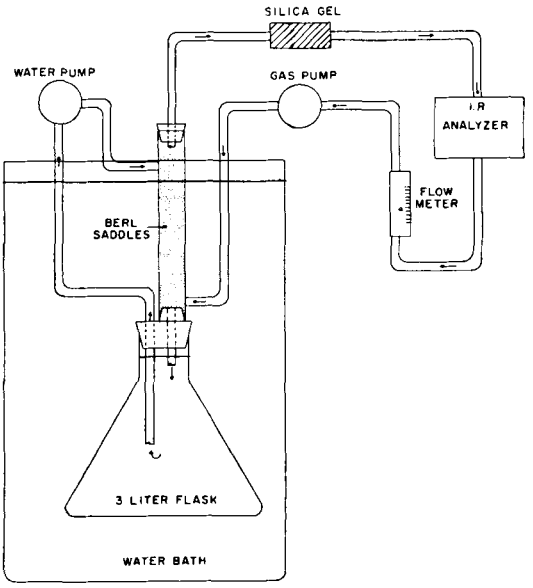

Fig. 1. Diagram of apparatus for pCO_2 determination.

3 liters of sea water is surmounted by a gas equilibrating column. Water is pumped from the flask to the top of the column where it flows down by gravity over a packing of Berl saddles and re-enters the flask. The air stream enters at the bottom of the column and leaves at the top. Both countercurrent flow and a large surface facilitate tension equilibration between the air and the gases in solution. The entire apparatus is placed in a temperature bath.

A closed 500 ml. volume of air continuously circulates through the column, a drying tube, infra red CO_2 analyzer, and pump. Since the ratio of sea water to air volume is 6:1, very little CO_2 must be supplied by the water to bring the air into equilibration at the normally occurring values of pCO_2. The three liters of

sea water contain about 135 ml. of total CO_2. The amount in the air at 300 ppm is only .1 percent of this. A correction has been computed at the higher tensions.

The analyzer is a dual path type with a CO_2 filled pneumatic detector, (model 200, Mine Safety Appliances Co.) The beam chopper is quartz which does not absorb appreciably in the infrared until 4u. Thus only the longer wave length absorption bands are effective. This results in a 2,000 to 1 differentiation against water vapor. In spite of this the gas stream must be dried. If it were not, that amount of water vapor in 20° C saturated air would appear as a 20 ppm CO_2 signal. The infrared principle offers a 10 to 100 times increase in sensitivity over previous methods in determining CO_2 in gaseous mixtures.

It is necessary to frequently calibrate the analyzer with gas mixtures of known CO_2 content. These are made by volumetrically diluting 100 percent CO_2 with nitrogen in a 20 liter stainless steel spirometer. The CO_2 is injected from a syringe. If pure gases are used the accuracy depends primarily on measurement of volume, with some errors introduced by temperature differences at which the volumes are determined. Given values could be repeated to within 1 percent.

The amount of total CO_2 in the sea water has been varied in different ways. Distilled water was saturated with 1 atmosphere of CO_2 gas at a known temperature to produce a solution of known concentration. This was checked by measuring its electrical conductivity. Small amounts of the solution were titrated into the 3 liters of sea water from a syringe, while pCO_2 was continuously recorded. Introduction of equivalent amounts of CO_2 free water caused no pCO_2 shift.

Biological material, fish and sea weeds, were also used to introduce known amounts of CO_2. Their CO_2 output rate was initially determined by enclosing them in a container and using gas analysis. The material was then introduced into the sea water for varying lengths of time to provide the desired CO_2 increase. Photosynthesis of sea weeds, measured by oxygen increase, was used to remove known amounts of CO_2.

The increase in CO_2 from biological activity and the normal gas exchange of a stored sample require that the water for pCO_2 determinations be immediately at hand if the value is to represent that which occurred in the ocean. For this reason, I have been able to make measurements only on water from Woods Hole Harbor. This has a salinity of about 31.5 ‰. The buffering capacity of sea water for CO_2 will increase in proportion to salinity so the data given can be extrapolated.

Results

Figure 2 shows the large changes in pCO_2 that result when the temperature of a single water sample is varied. The total CO_2 remains

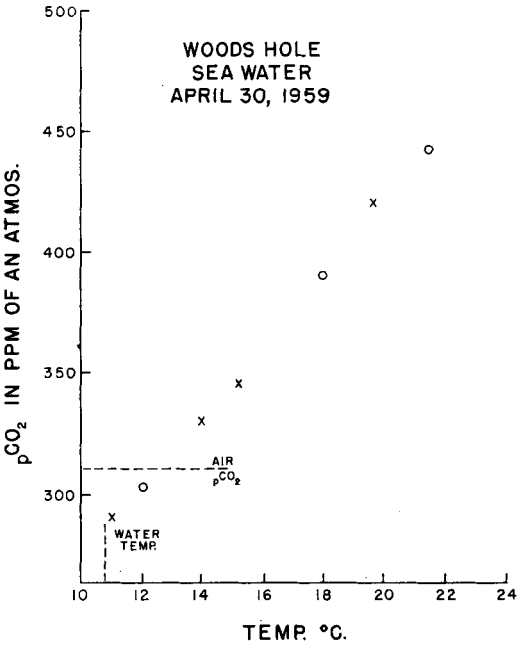

Fig. 2. Effect of temperature on pCO_2 in a local water sample. The cross points were taken with increasing temperature and the circles with decreasing to show that the effect is reversible.

unchanged during a run since the system is sealed and the biological activity in the water sample is negligable. The CO_2 partial pressure at the sea temperature at the time of this run was 285 ppm. The air at this time had a concentration of 315 ppm. The sea was distinctly undersaturated with reference to the atmosphere.

The tension increases about $4\,^1/_2\,\%/°$ C. HARVEY (1955 pg. 6) states that pCO_2, increases 1 %/°C and this is what one finds from Buchs tables at constant pH. However, with constant total CO_2, pH decreases about. .01 units for each °C increase. It is this pH change and its resulting effect on the various equilibria of the carbonate system that accounts for the larger observed sensitivity of pCO_2 with temperature. It is unnatural to speak of temperature variation with constant pH since this can only happen if the normal temperature induced pH change is buffered with the addition of acid or base. This latter is in effect a change in alkalinity which has been shown not to occur to any extent in sea water. Revelle and Suess arrived at a 7 percent change per °C in some undescribed manner. BOLIN and ERICSSON unfortunately did not include the effect of temperature in their theortical analysis of the CO_2 system.

Figure 3 is a plot of the temperature variation of pCO_2 with varying amounts of total CO_2. The parallel straight lines on a logarithmic

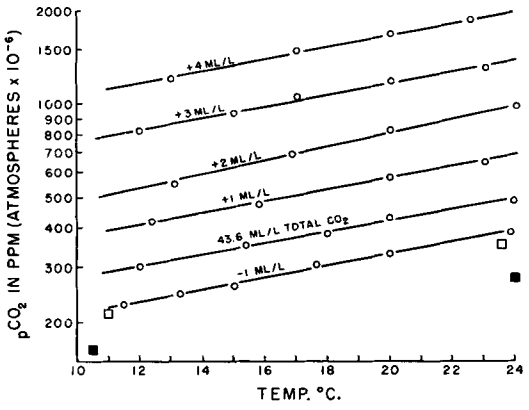

Fig. 3. Temperature variation of pCO_2 with different amounts of total CO_2.

plot show that the effect of temperature is constant in percent per degree regardless of the initial tension. The meaning of these curves is clear. If one is to measure pCO_2 meaningfully to 1 percent then the temperature must be regulated to .2° C and this must be related with equal accuracy to the sea temperature.

The variation of pCO_2 with changes in total CO_2 is shown in Figure 4. It is readily apparent

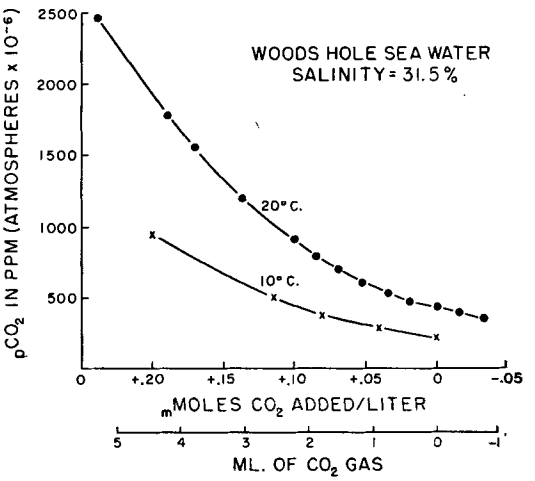

Fig. 4. Variation of pCO_2 with changes in total CO_2. The 10° C values were taken on the same water sample after the 20.

that sea water undergoes large changes in pCO_2 from the variations in CO_2 that are regularly produced by biological and physical processes. This increase in tension must be due to the increase in the physically dissolved component of the carbonate system. It can be computed (using the solubility of CO_2) that about a $^1/_{13}$ of any CO_2 added to sea water stays as a physically dissolved gas. Fresh waters low in alkalinity should show at least 10 times as great a tension change since most of the CO_2 stays in solution. My determinations on distilled water have confirmed this.

Discussion:

The measured CO_2 partial pressure properties of sea water can be applied to some considerations of the movement of CO_2 in nature. The curves in Figures 3 and 4 can be used in estimating, for example, the amount of CO_2 that must enter or leave a water mass to keep pCO_2 constant when the temperature is varied. The important point to consider is the large sensitivity of tension to changes in both temperature and total CO_2.

Different levels in the oceans show large variations in CO_2 partial pressure. Intermediate ocean depths are typically low in O_2 due to biological activity and are thus high in CO_2. These layers may be nearly anaerobic in the

tropical Pacific and Atlantic and the partial pressure will therefore be as high as 2,000 to 3,500 ppm. I measured a pCO_2 of 3,000 ppm in the nearly anaerobic bottom layer of a polluted harbor at Woods Hole. The presence of such high values is probably of little significance to the air-ocean mixing of CO_2 since waters of this type rarely reach the surface. The high pCO_2 layer is separated from the mixed surface layer by a temperature produced density difference which inhibits vertical mixing. As small amounts do mix across this thermocline they are diluted into the mixed layer with relatively little effect. Since the higher CO_2 is accompanied by nutrient salts it may be largely fixed by photosynthesis before the elevated tension can be relieved by CO_2 diffusing into the air. This general argument may be valid for all cold bottom water formed at high latitudes which moves at depth to the tropics.

The surface water does show more limited variations in pCO_2 which are unrelated to mixing or to temperature change. COOPER (1937) found that these changes in the English Channel accompany the seasonal variations in photosynthesis and respiration of marine organisms. I have found such changes in the coastal water at Woods Hole. The partial pressure is below atmospheric during a plankton bloom when photosynthesis is fixing CO_2, and is higher than the air when the organic material is decaying. One might expect the largest excursions in Artic waters during the long hours of daylight. Buch has found a pCO_2 of 150 ppm in the summer near Spitzbergen.

It appears that biologically produced pCO_2 gradients at the sea surface are larger than those due to seasonal temperature changes. From the data presented here a 20° seasonal temperature shift requires about 1.5 ml/l difference in CO_2 to keep pCO_2 constant. The seasonal photosynthetically fixed CO_2 may be several times this. The two effects partly nullify each other since the water has more CO_2 made available from spring warming at the very time that photosynthesis is maximum. Unfortunately this reasoning depends largely on scanty data from coastal areas rather than the open sea.

In theory a knowledge of pCO_2 in space and time along with pertinent data on the physical state of the sea surface could be used to calculate net CO_2 fluxes. In practice this would be very difficult. However, surface pCO_2 does give qualitative information about where and in what direction the gas is diffusing. Isotope data provides an independent means of arriving at an average rate over a long period. CRAIG (1957) calculated that a given CO_2 molecule has an average residence time of 7 years in the atmosphere before diffusing into the ocean.

There has been considerable discussion of the effects and fate of the CO_2 that has been released by man's burning of fossil fuels. This has equaled more than 14 percent of the amount already in the atmosphere, (REVELL and SUESS 1957). BOLIN and ERIKSSON (1959) have presented a comprehensive discussion of the problem and have shown that most of the increase must still be in the atmosphere. The problem is essentially one of estimating how much of the potential increase has been buffered by the seas capacity to absorb CO_2. The pCO_2 properties presented here provide a basis for estimating this. BOLIN and ERIKSSON used a theoretically derived figure.

Any higher atmospheric pCO_2 must approach tension equilibrium with the seas and in the process some net CO_2 will pass into the water bringing its partial pressure up and lowering that of the air. Since the oceans contain some 60 times as much CO_2 as the air it would not be surprising if they had the ability to buffer out a large part of any atmospheric increase. We need consider here though only that portion of the oceans in touch with the sea surface, the mixed layer above the thermocline. Wooster (CRAIG 1957) has estimated from oceanographic data that the average depth of the thermocline is 75 meters, therefore less than 2 percent of the ocean water is in diffusion equilibrium with the atmosphere at one time. This contains only slightly more total CO_2 than is in the atmosphere. Referring to Figure 4, a 10 percent increase in partial pressure is produced by a .6 percent increase in the total CO_2. Thus one finds that less than 10 percent of any atmosperic increase would be removed by the amount of water in the mixed layer at one time. Since the same water does not remain in the mixed layer due to continual exchange with bottom water, some estimate of the rate of turnover of the mixed layer is needed. From oceanographic current data it seems unlikely that the mixed layer could have been renewed more than 2 to 5 times in the last 50 years. It is clear even

from these rough figures that any CO_2 released from burning fossil fuels has been largely effective in increasing the concentration of this gas in the atmosphere. Over longer periods of time, hundreds to thousands of years, all of the deep water will equilibrate at the surface and something like 90 percent of any atmospheric increase will be absorbed. However, man is burning fuel at an increasing rate so if one considers only the solubility effect described here, the CO_2 should continue to increase.

Bolin and Eriksson have presented a mathematically formalized version of this argument using the same two-layer model of the sea. They show that the amount of CO_2 increase is quite insensitive to a wide range of turnover rates for the deep ocean. This is a consequence of the small amount of water in the mixed layer aided by the poor buffering capacity for CO_2. Even if one assumes a short turnover time, which means the surface layer has been renewed many times, the total amount of water passing through it can absorb only a small part of any atmospheric CO_2 increase. CALLENDAR (1958) concluded from a consideration of actual measurements that there has been a 10 percent atmospheric increase. The above argument support this view.

REVELL and SUESS (1957) arrived at the much lower estimate of 3 to 6 percent for the atmospheric CO_2 increase due to fossil fuels. This difference is largely due to their using a model of the sea which assumes it is a well mixed reservoir. This is difficult to rationalize with our present oceanographic knowledge.

Fossil fuel CO_2 contains no C^{14} so its introduction decreases the specific activity of the atmospheric CO_2. The effect has been measured and found to be less than a few percent. This might at first seem incompatable with an atmospheric CO_2 increase of several times that. This can be explained by considering both the dynamic exchange and the tension equilibration taking place in the surface layer. It has already been mentioned that the water in the surface layer at one time can absorb less than $^1/_{10}$ of any atmospheric increase. But if diffusion back and forth across the sea surface is rapid enough, the surface layer CO_2 would completely mix with that in the air. The Suess effect decrease would be about 50 percent since these are nearly equal reservoirs. CRAIG'S (1957) estimate of 7 years as the average turnover rate of air CO_2 indicates this is nearly the case. His figure also demonstrates that tension equilibration with the atmosphere is nearly complete for water passing through the mixed surface layer. Isotope data only gives information on the size of the effective reservoir, independant of hydrographic considerations, with which the atmospheric CO_2 has been mixed.

The long term fate of the present or any other CO_2 increase is complicated. The solubility buffering described here will reduce the present increase to less than 3 percent. The slightly greater total CO_2 in the sea water will increase the solubility for $CaCO_3$. Sea water is in contact with this in bottom sediments and in animals such as corals. Bolin and Eriksson show that this increases by 3 times the capacity of sea water for CO_2. Thus the eventual increase left in the atmosphere will be less than $^1/_{10}$ of the original.

Further compensation of the greater amount of CO_2 may result from an increase in photosynthesis both on the land and in the sea. This would result in some of the newly released CO_2 being fixed as organic material. The increased Ca ion might concievably accelerate the formation of animal and plant $CaCO_3$. In the event of no further CO_2 disturbance these interdependant factors would eventually produce what we can consider the long time average value of atmospheric CO_2. The tendency towards equilibrium of carbonates with CO_2 (UREY, 1952) must be only one of many factors determining this value.

The regulatory mechanism just described would have a time constant of at least many centuries so oscillations of such periods might

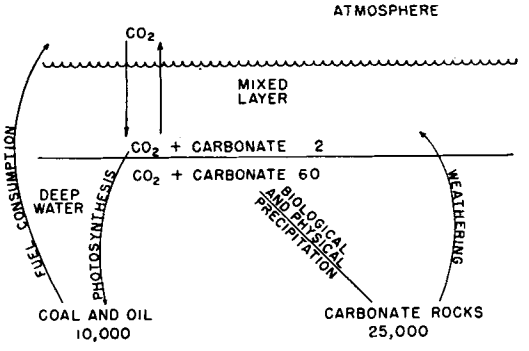

Fig. 5. Diagram abstracted from Redfield to show that large amounts of CO_2 have moved through the ocean-atmosphere system in geological time. The quantities are expressed on the basis of atmospheric CO_2 equals 1.

be expected. Figure 5 shows the amounts of carbon in different forms in nature expressed in units of atmospheric CO_2 (REDFIELD 1958). It is clear that in geological times large amounts of CO_2 have passed through the atmosphere-ocean pool. Since this flux has involved such cataclismic events as volcanic activity there must have been variations in the amount of CO_2 in transit.

PLASS (1959) and others feel that a rise in the earths surface temperature will result from more CO_2 in the air because of the increased absorption of thermal radiation which would otherwise be lost to space. It is tempting to attribute such things as climatic variations in historical and geological times to such a factor. The complicated atmospheric dynamics involved force one to view a cause and effect relationship of CO_2 and climate with caution. Fortunately man is providing his own experiment to test this hypothesis, (REVELLE and SUESS).

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