ON ASSESSING THE AGE OF DEEP OCEANIC WATER BY CARBON-14

By L. H. N. Cooper, D.Sc.

The Plymouth Laboratory

(Text-fig. 1)

The rate of circulation and age of the deep water of the oceans is of much interest. Worthington (1955) has suggested an age of 100–160 years for northern North Atlantic water which has reached the Carribean and Cayman Seas. I (in part, Cooper, 1955, 1956) have suspected that the rate of circulation of much of the North Atlantic deep water may be even faster than Worthington's results suggest. Provisional direct observations by G. Wüst & G. Dietrich (private communication) also suggest that the deep circulation is quite rapid.

In strong contrast, Kulp (1952, 1953*a*, *b*) and Carr & Kulp (1954) have attributed ages of 1600 to 1950 years to seawater samples drawn from various depths in the North Atlantic (Table I, nos. 6-9a).

The discrepancy is not real, but arises from tacit assumptions as to the nature and age of a water mass which are incompatible and from peculiarities of the cycle of ${}^{12}\text{CO}_2$ and ${}^{14}\text{CO}_2$ in nature.

Kulp (1952) wrote: 'Although atmospheric carbon dioxide is in equilibrium with the carbonate in surface ocean water, the submergence of such water cuts it off from its supply of carbon 14 as effectively as does death in the case of a plant or animal.' The first clause requires proof by observation. It would be better to replace 'is in equilibrium' by 'approaches equilibrium'.

He went on: 'Since ocean water sinks in the polar regions and moves along the bottom towards the equator, the rate and direction of movement can be measured by determining the time since a unit of water left the polar surface.'...'The carbon 14 measurements of several water samples taken from the ocean floor at about the latitude of Newfoundland on either side of the Mid-Atlantic Ridge are shown in Table 4' (included here as Table I, nos. 5-9a). 'The data suggest that it takes about 1500 years for the water to reach this latitude from the Arctic. Thus the time of the turnover of the oceans must be thought of in terms of several thousand years.'

In a way the whole of this statement is true; but it is a way of no value to an oceanographer seeking a better understanding of oceanic circulation. This approach may be compared with that of a man who would measure the strength of currents in the North Sea with drift bottles, not knowing that between putting out the bottles and their stranding on a shore they had many times circled the northern North Sea Great Eddy (Tait, 1937). His results

22-2

Reference Kulp		Location	Sea area	Depth*		Apparent age
				ft.	m.	(years)
I.	1953 a	13° 35' N., 66° 35' W.	Caribbean	Surface		Recent
2.	1953 a	19° 24' N., 78° 33' W.	South of Cuba	Surface		Recent
3.	1953 a	41° 00' N., 54° 35' W.	West North Atlantic, south of Newfoundland	Surface	—	Recent
3 a.	1953 b	54° 35' N., 41° W.	West North Atlantic	Surface		Recent
4.	1953 a	63° 46' N., 00° 26' W.	Norwegian Sea	10,440	3182	500 ± 200
5.	1953 a	38° 42' N., 67° 54' W.	North-west North Atlantic	13,500	4115	450 ± 150
6.	1953 a	35° 46' N., 69° 05' W.	North-west North Atlantic	15,300	4663	1950 ± 200
7.	1953 a	34° 56' N., 68° 14' W.	North-west North Atlantic	16,560	5047	1550 ± 300
8.	1953 <i>a</i> , 1953 <i>b</i>	58° 19' N., 32° 57' W.	Reykjanes Ridge, Western Slope	6,000	1829	1600 ± 130
9.	1953 b	53° 53' N., 21° 06' W.	Southern tip of Rockall Bank	9,000	2743	1750 ± 150
9a.	1953 a	53° 53' N., 21° 06' W.	Southern tip of Rockall Bank	9,100	2774	1900 ± 150

TABLE I. AGE OF OCEANIC WATER ACCORDING TO J. L. KULP

* Roman figures give depths reported by Kulp: italic figures conversions by the writer.

would suggest a much more sluggish circulation than would measurements made with current meters.

To appreciate what is involved, a number of separate points in the physical chemistry and oceanography of carbon dioxide have to be examined and then synthesized into a complete whole. The material for such a study has been provided by Buch (1942, *inter alia*).

A COMPARISON BETWEEN THE RATES OF EXCHANGE OF O_2 , ${}^{12}CO_2$ and ${}^{14}CO_2$ between Air and Sea

Let P_0 , V_0 = the partial pressure and volume of a gas in the surface water of the sea when in equilibrium with the atmosphere under specified conditions.

P, V = the partial pressure and volume of a gas when not in equilibrium.

 $\gamma =$ an exchange coefficient, assumed to be the same for all three gases.

t = time.

On integration

Then

$$\frac{P}{P_0} = \frac{V}{V_0}.$$

Also, the rate of invasion or evasion of a gas from the atmosphere into the sea, or vice versa, may be written

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \gamma (P_0 - P) = \frac{\gamma P_0}{V_0} (V_0 - V),$$
$$\mathrm{d}t = \frac{V_0}{\gamma P_0} \frac{\mathrm{d}V}{V_0 - V}.$$

or

$$t = \int_{V=V_2}^{V=V_2} dt = \frac{V_0}{\gamma P_0} \log_e \frac{V_0 - V_1}{V_0 - V_2}.$$

AGE OF DEEP WATER

Let us now consider a litre of water from which 2x ml. of O₂ and 2x ml. of $^{12}CO_2$ have been removed, and then compute the ratio of the times required to reabsorb x ml. of each gas. For both gases:

$$\log_e \frac{V_0 - V_1}{V_0 - V_2} = \log_e \frac{2x}{x} = \log_e 2.$$

Consequently

 $\frac{t_{\text{carbon-12 dioxide}}}{t_{\text{oxygen}}} = \frac{V_0, \text{ carbon-12 dioxide}}{V_0, \text{ oxygen}} \cdot \frac{P_0, \text{ oxygen}}{P_0, \text{ carbon-12 dioxide}}.$

Let us now compute this ratio (Table II) for moist air conditions in the Norwegian Sea and in the tropical Atlantic, using the tables of Truesdale, Downing & Lowden (1955) for oxygen, and of Buch (1933) for carbon dioxide.

TABLE II. RELATIVE TIMES REQUIRED BY CARBON-12 DIOXIDE AND BY OXYGEN TO APPROACH EQUILIBRIUM WITH THE ATMOSPHERE WHEN UNDER-SATURATED OR SUPERSATURATED TO THE SAME EXTENT

	Norwegian Sea	Tropical Atlantic
Temperature (° C)	0	25
$V_0, \Sigma^{12}CO_2 (ml./l.)$	49.5	47.5
$P_0 O_2(\text{atm.})$ $P_0, 1^2 CO_2(\text{atm.})$	0.209	0.203
Ratio of times, $t_{12}CO_2/t_{O_2}$	3880	6244

Thus, when ${}^{12}\text{CO}_2$ and O_2 are displaced from their equilibrium values by the same amount, then ${}^{12}\text{CO}_2$ requires between 4000 and 6000 days (between 10 and 17 years) to achieve an approach towards an equilibrium which oxygen may attain in 1 day.

This is a general conclusion, independent of the storminess of the sea and the actual rates of transfer. It is equally true whichever side of equilibrium the departure may be made. Whenever oxygen is not in equilibrium, it is highly unlikely that carbon-12 dioxide will be so.

When ${}^{14}\text{CO}_2$ is at an overall equilibrium state in air and water, its partial pressure and its volume will both bear the same ratio to the partial pressure and volume of ${}^{12}\text{CO}_2$. The ratio V_0/P_0 will be essentially the same for both isotopes so that the above calculation applies.

In general, however, due to radio-active decay, the volume and partial pressure of ${}^{14}\text{CO}_2$ in the water will tend to diminish. Consequently, ${}^{14}\text{CO}_2$ may require even longer to approach towards equilibrium than does ${}^{12}\text{CO}_2$.

On the Concentration Gradient of Carbon Dioxide between the Equator and the Poles

Kulp (1953a) has said that 'the C¹⁴ concentration in air at widely different geographic positions is essentially constant and is independent of time of day, rainfall, altitude and temperature'.

This apparently straightforward statement may mean either (a) the concentration of ¹⁴C per litre of air at N.T.P. is constant; or (b) that the ¹⁴C concentration per unit volume of carbon dioxide (${}^{12}CO_2 + {}^{13}CO_2 + {}^{14}CO_2$) is constant.

The alternatives are not closely related. Interpretation (a) is probably the one intended. However, in the same paragraph he stated that 'about two dozen living trees from all over the world gave the same carbon-14 concentration within about 10%'. This implies that the carbon-14 content is proportional to the amount of carbon dioxide assimilated and supports interpretation (b).

The atmospheric circulation over the North Atlantic according to Bjerknes and the distribution of carbon dioxide (${}^{12}CO_2$) according to Buch are shown schematically in Fig. 1 (Buch, 1942).

In temperate latitudes the partial pressure of carbon dioxide in the air and in surface water in equilibrium with the air is usually about $3 \cdot 1 \times 10^{-4}$ atm. In summer, in extensive areas of the Arctic, this partial pressure may sink as low as 1.5×10^{-4} atm. Polar regions in summer are the site of much solution in the sea of atmospheric carbon dioxide both as ${}^{12}CO_2$ and ${}^{14}CO_2$. There are no winter observations in the Arctic.

In the Antarctic south of 57° S. lat. in winter (Deacon, 1940) the partial pressure in surface water is about $3 \cdot 3 \times 10^{-4}$ atm. If this figure applies in the central Norwegian Sea where deep water is formed, we may reasonably assume that in winter the water sinks with the properties shown in Table III.

If a parcel of this water, sealed against gain or loss of everything except heat, were transported to the tropics and warmed to 25° C, the equilibria of the carbonate system would be strongly displaced. The partial pressure and pH would acquire the values also shown in Table III, calculated from Buch (1933). The increase in partial pressure of CO₂ is a purely physico-chemical effect. Living organisms and solution or deposition of calcium carbonate have nothing to do with it. Failure to appreciate this effect of temperature change has led to much loose thinking about decay processes in the sea. Since partial pressure of CO₂ and pH may be so misleading, only from the total concentration of CO₂ may sound conclusions be drawn about regeneration processes.

This is essentially a thermodynamic argument, so that the history of the parcel of water between sinking near the poles and upwelling by some means in the tropics is immaterial. The conclusion is that, in an azoic world, upwelling water in the tropics must have a partial pressure of ¹²CO₂, greatly in excess of the 'equilibrium value' in the tropical atmosphere. In upwelling areas the over-

lying air must be locally enriched. To balance this circulation of ${}^{12}\text{CO}_2$ in the oceans between poles and tropics a considerable concentration gradient of carbon dioxide is imposed upon the atmosphere between tropics and poles. This is what Buch found.





TABLE III

Temperature (° C)	- I to - I.8	25
Salinity (‰)	34.92	34.92
Chlorinity (‰)	19.33	19.33
Partial pressure of CO_2 (atm.)	3.3×10^{-4}	8.6×10^{-4}
ΣCO_2 (m-mole/l.)	2.20	2.20
pH	8.10	7.84

From every point of view this upwelled water is 'old' so that the ratio ${}^{14}\text{CO}_2/{}^{12}\text{CO}_2$ must be low; so must the ratio in the gas which has there escaped to the atmosphere.

The equilibrium state between air and water is not static but dynamic, and means only that in unit time as many molecules of ${}^{12}\text{CO}_2$ or ${}^{14}\text{CO}_2$ enter the

water as leave it. For the two isotopic molecular species, the balance may everywhere be struck differently. Often a tropical surface water may gain ${}^{14}\text{CO}_2$ from the air whilst losing ${}^{12}\text{CO}_2$.

If the air has arrived over an area of upwelling with an 'equilibrium' concentration of ${}^{14}CO_2$, referred either to the volume of air or to the volume of ${}^{12}CO_2$ in it, then addition of CO_2 , poor in ${}^{14}CO_2$, must displace this equilibrium. It is clear that the total concentration of CO_2 in the air and the ratio of ${}^{14}CO_2$ to ${}^{12}CO_2$ should be subject to many changes in the course of a single cycle between tropics and poles and back. Either of the interpretations (*a*) and (*b*) on p. 344 may be true, but not both.

ISOTOPIC PARTITION FUNCTIONS

Partition functions of the reactions:

$${}^{12}\text{CO}_2 + \text{H}^{14}\text{CO}'_3 \rightleftharpoons {}^{14}\text{CO}_2 + \text{H}^{12}\text{CO}'_3, \\ \text{H}^{12}\text{CO}'_3 + {}^{14}\text{CO}''_3 \rightleftharpoons \text{H}^{14}\text{CO}'_3 + {}^{12}\text{CO}''_3,$$

depend on temperature (Stranks & Harris, 1953). Between 0 and 28° the partition function of the first reaction changes from 0.957 to 0.965. At the higher temperature relatively more ¹⁴C is free as ¹⁴CO₂ and can escape. The difference lies within present limits of error of the counting technique on carbon-14.

ON CIRCULATION AND RECIRCULATION OF CARBON DIOXIDE IN THE ATLANTIC

Kulp's definition (quoted above) of the age of a water mass implies that there are bodies of water which make long journeys in the ocean whilst retaining all or nearly all their properties unchanged. No oceanographer who has studied the deep sea holds this view, but all are responsible in some measure for propagating it. The trouble starts when names such as 'North Atlantic deep water' or 'Antarctic bottom water' have to be devised to make complex concepts comprehensible. Because some dominant property may be traced for thousands of miles it is only too easy to assume that most of the water that accompanies the property has made the same journey in the same way at the same time. This is rarely so. There is no such thing as a pure-bred water mass. Attribution of a zero oceanographic age, therefore, implies some arbitrary selection of a time and place of birth and an understanding of subsequent mixing processes.

None the less 'water mass' is a useful and fruitful concept. Sometimes changes are so abrupt that it is possible to say that a new water mass has been born from well-defined parent water masses. More often exchanging and mixing processes are formless.

346

AGE OF DEEP WATER

Thought is clarified by conceiving dominant characters of water masses. By a dominant character is meant one by which a water mass may be recognized after it has been mixed with a large proportion of other waters with poorer diagnostic characters. In this sense in the eastern North Atlantic, around 1000 m. depth, Mediterranean water is dominant after it has become mixed with many times its volume of North Atlantic Central water. The dominant characters are salinity, temperature-salinity relationship and the nitratephosphate ratio. In this case the characters of the North Atlantic Central water are all masked except for one—phosphate.

SINKING SOUTH-EAST AND SOUTH-WEST OF GREENLAND

This is the area where Helland-Hansen & Nansen (1909), Defant, Böhnecke & Wattenberg (1936), Smith, Soule & Mosby (1937), Wattenberg (1938) and Wust (1943) have considered that much deep water is formed. It is unquestionably an area where an enormous mass of water with markedly homogeneous properties is created. The mixing pot is at least 2000 m deep. Most oceanographers would consider this a good place to ascribe zero age to a water mass. If it is to have zero-age on the ¹⁴C scale, the whole of this enormous volume of water would need to be completely equilibrated with the atmosphere for O_2 , ¹²CO₂ and ¹⁴CO₂. An intensely vigorous process of exchange through the sea surface and of vertical circulation would be needed to achieve this. In fact it is not achieved, not even for oxygen.

Two of the most representative stations were Meteor stations nos. 121 and 122 (56° 37' N., 44° 55' W. and 55° 03' N., 44° 46' W.) worked on 9 March 1935 (Defant *et al.* 1936). Here, between 300 and 2000 m, oxygen lay between 90.8 and 96.2% saturated and averaged 93.0%.¹ Equilibrium with the atmosphere was not attained. It is certain that equilibrium could have been attained neither by ¹²CO₂ nor by ¹⁴CO₂. Consequently, if ¹⁴C is to be a useful tool, its concentration in a newborn water mass such as this needs to be established empirically.

ON THE ¹⁴CO₂ CONTENT OF NORTH ATLANTIC DEEP WATER

Wattenberg (1938) and Wust (1943) have critically discussed the origin of the North Atlantic deep water and the Subarctic bottom current. They suggest that, from time to time, a pulse ('Einschübe') of Norwegian Sea water through the Denmark Strait may contribute to the deep water, but is not very important. The writer believes not only that such pulses are frequent, but that they dominate much of the oceanography of the North Atlantic. The evidence is being prepared for publication. Meanwhile, for the carbon-14 problem the following summary must suffice.

 1 Recomputed from the oxygen saturation tables of Truesdale *et al.* (1955); the range is 92·1–98 % and average 94·6 %.

The North Atlantic deep water would seem to arise, not at any one place, but by a continuing process all the way from Jan Mayen to Labrador (Cooper, 1956). Many waters with varying contents of ${}^{14}CO_2$ will contribute to it.

Let us first consider the North Atlantic Drift and the Norwegian Sea.

The superficial waters of the North Atlantic Drift, subjected to intensive vertical mixing in winter but the site of intense photosynthesis in spring and summer, offer opportunity for equilibration of O_2 , ${}^{12}CO_2$ and ${}^{14}CO_2$ between sea and atmosphere. Much of this water enters the Norwegian Sea and, with the drainage from North-western and Northern Europe, contributes to the surface water of the Norwegian Sea. This alone may be said to have zero age on both an oceanographic and a carbon-14 time scale. In old polar ice, which also contributes by melting, the ratio ${}^{14}CO_2/{}^{12}CO_2$ may be slightly low.

In the area of sinking of Norwegian sea water to form deep water the physical equilibrium becomes neutral so that equilibrium of O_2 and ${}^{12}CO_2$ between air and water might well be maintained to great depths; ${}^{14}CO_2$ is, however, constantly decaying. If the vertical mixing is so vigorous that all the water is equilibrated with ${}^{14}CO_2$ within a score or so of years then all of it may be said to have zero ${}^{14}C$ age. Since such vigour is unlikely, Norwegian Sea deep water at the time and place of sinking should have a positive ${}^{14}C$ age compared with North Atlantic drift surface water.

Over much of the polar basin there is an ice seal, complete in winter and broken by leads of brackish water in summer. Over the whole of the ice-covered seas exchange of gases between air and deeper Norwegian Sea water is prohibited. The ¹⁴C age of this deeper water must be steadily increasing. Similarly, the cover of ice and brackish waters in the East Greenland Current provides a complete seal. Consequently, the water between 200 and 500 m depth in the Norwegian or Greenland Sea which is being sucked towards the passes into the Atlantic must have acquired a ¹⁴C age measured in scores or, maybe, centuries of years.

This water undergoes mixing with other waters, few of which have been near the surface for a very long time. In the confined area of the Denmark Strait, the relatively warm and saline north-bound Irminger current is adjacent to the outgoing cold bottom current. It may contain some water which has equilibrated with the atmosphere fairly recently and also deeper more mature water which has recently been upwardly displaced. By turbulent, lateral mixing some of this deeper water of the Irminger current should become incorporated in the outwardly flowing cold, heavy bottom current. On a smaller scale similar events should have occurred over the Iceland-Faeroe Rise (Cooper, 1955).

The dominant characters of the waters which result are their high density, low temperature and low content of silicate.

After passage through the Denmark Strait the temperature of the Norwegian Sea water, though remaining relatively low, increased by more than 1° C. This has come about by admixture with other deep waters. Some of this is Iceland-Faeroe water which has navigated the eastern slope of the Reykjanes Ridge and turned into the western basin in 50–52° N. latitude. This is comparatively young, though itself subjected to mixing with older water during its journey. However, much of the admixing water will already have circumnavigated the deep North-western and North-eastern Atlantic Basins in an anticlockwise sense at least once. All of these contribute to the water which comes to underlie the enormous homogeneous mass of water around Southern Greenland already discussed. It should have acquired an apparent carbon-14 age likely to be measured in centuries; this although its dominant component had been calved only a few years earlier in the Denmark Strait or Iceland-Faeroe Channel.

On this view there is constant and considerable recycling of water around the deep basins of the North Atlantic. On each cycle the waters are rejuvenated by a proportion of relatively young Norwegian Sea water but the process is never complete. This eddying or recycling involves water which is getting ever older. The currents which may be measured either directly or by dynamical calculations are the sum of movements of water which has newly sunk and of water which is being recycled. Moreover, all three dimensions of space have to be considered.

In the course of this circulation of the deep North Atlantic, deep water from south of the Equator will become incorporated. In its turn the South Atlantic deep water will have acquired parcels of water from Antarctic, Pacific and Indian Oceans. The simplest interpretation of the world distribution of nutrients suggests that these other oceans have a much more lethargic deep circulation than the Atlantic, and that their carbon-14 age will prove to be much higher.

Analyses of carbon-14, therefore, present the oceanographer with a very powerful weapon for attacking this complex problem.

THE PUBLISHED DATA FOR ¹⁴CO₂ IN THE NORTH ATLANTIC

Let us now examine the data (Table I) published by Kulp (1953 *a*, *b*). That the four surface waters are recent is to be expected. The first three are far from regions of sinking. The fourth is about 300 miles south-east of Cape Farewell, Greenland. However, the nearby 'General Greene' station 1994 worked by Soule & Graves (1937) on 3 August 1935 at 54° 47' N., 41° 52' W. does not suggest that the region is one of sinking deeper than 1000 m at most. None, therefore, gives a clue as to what composes the North Atlantic deep water at its places of origin.

The deep sample from the Norwegian Sea is of much interest. Helland-Hansen & Nansen (1909) suspected that this deep water might be of great age, a view not supported by the high oxygen content. Kulp's result indicates that water at 3182 m north-east of the Faeroes cannot have an 'age' exceeding $500+200 \ (=700)$ years. It may well be very much less. Necessarily there must be an escape of water with density exceeding σ_{t} 28.0.

The sample at 58° 19' N., 32° 57' W. on the western slopes of the Reykjanes Ridge at 1800 m depth was well placed. The water thereabouts is composite in origin. The 'dominant' water which gives the water its salinity inversion is young and has come from the Iceland–Faeroe Ridge contouring around the slopes of the Reykjanes Ridge. From the results of the research vessels *Dana, Atlantis* and *Meteor*, especially from oxygen determinations, it is possible to conclude that there is also a slow deep drift of old, oxygen-poor water from the South Atlantic along the western slopes of the Mid-Atlantic Ridge. This takes place mostly at a depth considerably greater than 1800 m. Nevertheless, in the western basin north of 52° N., upward displacement and homogenization should be a very vigorous process at all depths, accounting for the large apparent age found for the 1800 m sample.

Water from this position continues to move northerly and then westerly until it is forced by the configuration of the sea bed to move south-west over and alongside the cold heavy water sinking from the Denmark Strait. Lateral and vertical mixing between the two very different parallel water masses must then occur. One result should be a rapid 'maturing' of the heavy water from the Denmark Strait on its way to form North Atlantic Deep Water.

The sample or samples from the southern tip of the Rockall Bank are not well placed. The water thereabouts has a highly characteristic temperatureoxygen relationship which suggests either a rapid increase in 'age' from a depth of about 2300 m towards the bottom or that the consumption of oxygen in the deep ocean is largely confined to the bottom and the water immediately above it. The organic carbon being oxidized by this process may have lain on the bottom for very many years. When transferred to the water by oxidation and upward mixing, it would be expected to impart a fictitiously high age to the water.

These several arguments suggest that whilst we are building up our knowledge of its distribution it may be wiser to report ${}^{14}\text{CO}_2$ in concentration units (per unit weight of carbon dioxide or per unit volume of water) which make no tacit assumptions about history.

Again, the significance of a determination of carbon-14 on a sample of sea water cannot be assessed unless the content of carbon-12 dioxide and everything else that has been discovered about the water is published. Date, depth, records of current, temperature, salinity, oxygen, nutrient salts and pH need to be reported or, alternatively, a reference to where these have been published and discussed should be given. No sound conclusions on age of water masses may yet be drawn.

AGE OF DEEP WATER

DEVELOPMENT

There is a strong case for directing effort to atmosphere and ocean in places and on occasions where conditions are likely to be extreme. Knowledge of extreme conditions should help evaluation of cases which are more average. Unfortunately, many of the places where extreme conditions may be expected are difficult of access.

The Atmosphere

Apart from places where coal and oil are burnt in large quantities, the highest concentrations of ${}^{12}CO_2$ are likely to occur over tropical areas of strong upwelling during quiet weather. Upwelling in the Pacific is likely to bring up more ${}^{12}CO_2$ than upwelling in the Atlantic. The upwelling waters off the desert coast of Peru are likely to produce the highest natural concentration of ${}^{12}CO_2$ in the air above to be found in the world. However, there is no reason to believe that ${}^{14}CO_2$ should there be exceptionally high. The ${}^{14}CO_2/{}^{12}CO_2$ ratio of air over upwelling water might be best determined during moderate south-easterly winds at a place on the coast of Peru in about 9° S. lat. The fetch of the air over upwelled water would then be several hundred miles.

Vegetation will assimilate all isotopes of carbon. The partition ratios for the several isotopes will be slightly different from the concentration ratios but within the limits of error of our present study, these differences may be ignored.

Areas of strong coastal upwelling are usually bordered by desert continental land. Even so the ratio of ¹⁴C to ¹²C in such vegetation as exists at places like Walvis Bay and the Peruvian guano zone is worthy of examination. To obtain samples it would be worth while to grow plants in pots. The ratio may be markedly lower than average. Moreover, in such places a strong seasonal variation in the isotopic ratio of the carbon assimilated may exist (cf. Currie, 1953), low at seasons of strong upwelling, average when upwelling is in abeyance.

To contrast with such samples, others for analyses of ${}^{12}\text{CO}_2$ and ${}^{14}\text{CO}_2$ are needed from (*a*) the bitterly cold air which stagnates in winter over Siberia at places like Verkhoyansk, Oymyakon or Yakutsk. (Here is an area likely to be particularly favourable for transfer of ${}^{14}\text{CO}_2$ from stratosphere to troposphere), (*b*) air which has sojourned for some time over Antarctica or over the Arctic sea ice, (*c*) air from these sources and from temperate latitudes which has blown for hundreds of miles over areas of oceanic sinking.

The Ocean

The following are needed:

Samples of water from outstanding regions of upwelling such as the Peruvian coast, and from the thick fast currents which set away from these coasts under the influence of the trade winds. Samples from outstanding areas of sinking, such as the Norwegian Sea south of Jan Mayen, the oceanic area around Southern Greenland and the areas of formation of Antarctic bottom water.

Samples from precisely defined places where key processes in the circulation of the oceans are suspected of occurring. The Denmark Strait may be one such place and key positions are: (a) North of the Sill where the current at 200-500 m is flowing towards the south-west (say 68° 30' N., 24° 40' W.). (b) South-west of the sill crossing the meridian 27° 45' W. between 66° 10' and 66° 35' N. latitude where on occasion the bottom current is believed to run fast on the continental terrace and parallel to the coast for the next 70 miles (130 km). In some years this position is overlain by ice. A more accessible position some miles to the south-east is unlikely to sample the water in question. Since the outflow is likely to be intermittent, it would be essential to establish that the desired water was being sampled. The season from March to June would be most appropriate. (c) At 66° 10' N., 30° 30' W. in what appears to be a submarine canyon extending south-east from the fjord Kangerdlugssuak.

Living organisms

The ratio of $Ca^{14}CO_3$ to $Ca^{12}CO_3$ in shells and of ${}^{14}C/{}^{12}C$ in shore plants and animals from the special areas listed above should be of interest. There should be a considerable difference between shells and organisms from, say, Spitzbergen or Jan Mayen on the one hand, and Peru or South-west Africa on the other.

SUMMARY

The carbon-14 method for determining the age of deep oceanic water gives ages much higher than are suggested by physical and chemical oceanographic observations. The discrepancy arises from tacit assumptions as to the age and nature of water masses and from peculiarities of the cycles of ${}^{12}\text{CO}_2$ and ${}^{14}\text{CO}_2$ in nature. These are:

(1) When surface water is under or over saturated to the same extent with oxygen or ${}^{12}CO_2$ equilibrium between atmosphere and ocean is much more rapidly restored with oxygen. An approach towards equilibrium which oxygen may achieve in 1 day requires 10–17 years for carbon-12 dioxide. Carbon-14 dioxide should behave similarly to carbon-12 dioxide.

(2) When polar water is transported via the deep ocean to upwell in the tropics, heating causes the partial pressure of ${}^{12}\text{CO}_2$ to increase about three times. Upwelling water must, for physico-chemical reasons, be super-saturated with ${}^{12}\text{CO}_2$ with respect to the atmosphere. A compensating concentration gradient for ${}^{12}\text{CO}_2$ must therefore build up in the atmosphere between tropics and poles. The corresponding gradient for ${}^{14}\text{CO}_2$ should be different.

(3) Due to the vast masses of water in areas of oceanic sinking which have to be equilibrated for ${}^{14}CO_2$ with the atmosphere and the complexity of the processes, it is unlikely that a water mass which an oceanographer would consider newly born, will sink with a zero age on the present carbon-14 scale. The content of ${}^{14}CO_2$ in sinking waters needs to be determined empirically and used as the starting point of a carbon-14 time scale.

(4) In the deep North Atlantic basin there is much recycling of ever-ageing water. This is rejuvenated by descent of Norwegian Sea water from the sills of the Denmark Strait and the Iceland-Faeroe Rise.

The significance of existing measurements of carbon-14 on deep oceanic waters is discussed. No sound conclusions on age of water masses may yet be drawn from them. It may be wiser, for the present, to report ${}^{14}\text{CO}_2$ in concentration units which make no tacit assumptions about history. On any sample, submitted for carbon-14 analysis, all the standard oceanographic measurements need to be reported.

Attention is directed to places where the concentration of ${\rm ^{12}CO_2}$ and ${\rm ^{14}CO_2}$ in atmosphere and ocean are likely to be extreme. Determinations in such places should hasten the assessment of determinations where conditions are more average.

REFERENCES

BUCH, K., 1933. Der Borsäuregehalt des Meerwassers und seine Bedeutung bei der Berechnung des Kohlensäuressystems in Meerwasser. Rapp. Cons. Explor. Mer., Vol. 85, pp. 71–5.

— 1942. Kohlensäure in Atmosphäre und Meer. Ann. Hydrogr., Berl., Jahrg. 70, pp. 193–205.

CARR, D. R. & KULP, J. L., 1954. Dating with natural radioactive carbon. Trans. N.Y. Acad. Sci., Ser. 2, Vol. 16, pp. 175-81.

COOPER, L. H. N., 1955. Deep water movements in the North Atlantic as a link between climatic changes around Iceland and the biological productivity of the English Channel and Celtic Sea. *J. mar. Res.*, Convocation issue (in the Press).

— 1956. Hypotheses connecting fluctuations in Arctic climate with biological productivity in the English Channel. *Pap. mar. Biol. Oceanogr., Deep-Sea Res.* Suppl. to Vol. 3, pp. 212–23.

CURRIE, R., 1953. Upwelling in the Benguela current. Nature, Lond., Vol. 171, p. 497.

DEACON, G. E. R., 1940. Carbon dioxide in Arctic and Antarctic Seas. *Nature, Lond.*, Vol. 145, p. 250.

DEFANT, A., BÖHNECKE, G. & WATTENBERG, H., 1936. Die ozeanographischen Arbeiten des Vermessungsschiffes 'Meteor' in der Dänemarkstrasse und Irmingersee. I. Teil. Veröff. Inst. Meeresk. Univ. Berl. 2 N.F., A, Heft 32, pp. 1–152.

HELLAND-HANSEN, B. & NANSEN, F., 1909. The Norwegian Sea. Rep. Norweg. Fish. Invest., Vol. 2, No. 2, 390 pp.

KULP, J. L., 1952. The carbon 14 method of age determination. Sci. Mon. N.Y., Vol. 75, pp. 259-67.

— 1953a. Carbon-14 measurements on geological samples. Atomics, Vol. 4, pp. 96–8.

— 1953b. Dating with carbon 14. J. chem. Educ., Vol. 30, pp. 432-5.

L. H. N. COOPER

- SMITH, E. H., SOULE, F. M. & MOSBY, O., 1937. The Marion and General Greene Expeditions to Davis Strait and Labrador Sea. Sci. Res., Pt. 2, Physical Oceanography. Bull. U.S. Cst Guard, No. 19, 259 pp. (Coll. Pap. Woods Hole oceanogr. Instn, 1937, Pt. II.)
- SOULE, F. M. & GRAVES, G. VAN A., 1937. International ice observations and Ice Patrol Service in the North Atlantic Ocean. Season of 1935. Bull. U.S. Cst Guard, No. 25, 140 pp.
- STRANKS, D. R. & HARRIS, G. M., 1953. Predicted isotopic enrichment effects in some isotopic exchange equilibria involving carbon-14. J. Amer. chem. Soc., Vol. 75, pp. 2015–16.
- TAIT, J. B., 1937. The surface water drift in the northern and middle areas of the North Sea and in the Faroe-Shetland Channel. Part II, Section 3. Sci. Invest. Fish. Div. Scot., 1937, No. I, 60 pp.
- TRUESDALE, G. A., DOWNING, A. L. & LOWDEN, G. F., 1955. The solubility of oxygen in pure water and sea-water. J. appl. Chem., Lond., Vol. 5, pp. 53-62.
- WATTENBERG, H., 1938. Die Verteilung des Sauerstoffs und des Phosphats im Atlantischen Ozean. Wiss. Ergebn. dtsch. Atl. Exp. 'Meteor', Bd. 9, Lief. 1.
- WORTHINGTON, L. V., 1955. A new theory of Caribbean bottom-water formation. Deep-Sea Res., Vol. 3, pp. 82-7.
- WUST, G., 1943. Der subarktische Bodenstrom in der westatlantischen Mulde. Ann. Hydrogr., Berl., Jahrg. 71, pp. 249-55.

354