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Further Studies in the Rare Gases. III. The Helium–Neon Content of the Ocean Waters

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An extensive study of the variation of the oxygen content of ocean waters with locality and depth has been conducted by the Woods Hole Oceanographic Institution. Dr. N. W. Rakestraw of Brown University kindly supplied me with forty sealed samples from four stations visited by the "Atlantis" during the summer of 1933. The initial interest in the specimens was to determine the average helium–neon content of ocean waters, but during the course of the determinations it was observed that the helium–neon values might well form a convenient method of fixing a base line for the oxygen values, that is, the amount of oxygen taken up when the gases were originally absorbed. By comparison with the oxygen values experimentally determined, such a base line would afford an aid in tracing the later history of the oxygen or the water masses involved.

The methods employed in the measurement of small quantities of helium and neon as developed by Paneth and his co-workers have been outlined in Parts I and II of these studies.[1,2]

If the solubility ratio of the helium–neon to oxygen absorbed from air in sea water is known, it follows that one can calculate the oxygen absorbed from a knowledge of the helium–neon content. For the present purpose, differences in ocean water salinity are disregarded as being within the experimental error. In Table I the saturation oxygen values at 760 mm. for Cl equal to 19 g. per kg. were taken from Fox's Tables.[3]

Owing to lack of data in the literature, the saturation values for helium–neon were determined. These values have been read from a smoothed curve. It was almost impossible to determine whether any true change in the solubility occurred but a small trend accounts for the slight decrease in solubility with temperature recorded in Table I. On the other hand, the temperature coefficient of the solubility of oxygen is large and thus the ratio increases rapidly with temperature. It was also established that the helium–neon to oxygen ratio at any given temperature is independent of the degree of saturation, at least down to half-saturation values and within a liberal estimate of an accuracy of 7%.

TABLE I

VARIATION OF THE HELIUM–NEON TO OXYGEN RATIO WITH TEMPERATURE

Temp., °C.	Gas content at saturation He–Ne, cc./cc.	Gas content at saturation O_2, cc./cc.	Ratio (He–Ne)/O_2
0	16.2×10^{-8}	8.16×10^{-3}	1.99×10^{-5}
5	16.1	7.15	2.25
10	16.0	6.44	2.48
15	16.0	5.86	2.73
20	15.9	5.39	2.95
25	15.9	4.95	3.21
30	15.8	4.52	3.50

Figure 1 refers to station 1730 where soundings went to a depth of 2000 meters and Fig. 2 to station 1734 with soundings to 4500 meters. Curves I show the variation of the helium–neon content with depth, Curves II the calculated oxygen content and Curves III the measured values of the oxygen content. The limits of the experimental errors are given on all the curves by the horizontal lines through the recorded points. The complete data including two further stations are given in Table II.

The rate of diffusion of gases in liquids is too low to account for any of the phenomena observed,[4] especially in the region of currents where the masses of water are changing comparatively quickly and where the deviations are mostly observed. An exception to this may be at greater depth where the oxidation of matter on the ocean bottom may produce a downward migration of oxygen in the comparatively stable deeper waters.

To account for the deviations of the measured oxygen values from the calculated base line, there are four possibilities. (1) The air from which the gases were absorbed differs appreciably in com-

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(1) THIS JOURNAL, **54**, 3887 (1932); **55**, 3242 (1933). A complete list of references will be found in Part I.

(2) Since the helium–neon content is of the order of 10^{-7} cc. per cc. of water, 60 to 100 cc. was the usual amount taken.

(3) C. J. J. Fox, "On the Coefficients of Absorption of the Atmospheric Gases in Sea Water and Distilled Water," Publ. de Circonstance, No. 41, Copenhagen, 1907.

(4) The effect of hydrostatic pressure on the solution (gas phase absent) can also be calculated to be negligible.

position from the present day. (2) There is an actual deficiency or surplus of oxygen less than or over and above the absorbed amount. (3) There is an actual deficiency or excess of helium–neon. (4) The mass of water under consideration absorbed its gases at some other temperature than that at which it exists at the time of sampling, and hence the ratio for the recorded temperature would not hold. If this is applied to deviations where the absorption temperature must have been lower, in no case is the subsequent warming up sufficient to produce supersaturation.

There is no indication of extremely long periods of stability of these lower masses of water although movements may be comparatively slow. Hence the first possibility may be ruled out rather definitely.

The second possibility is quite plausible although a surplus of oxygen would probably be confined to the photosynthetic zone above the first hundred meters.

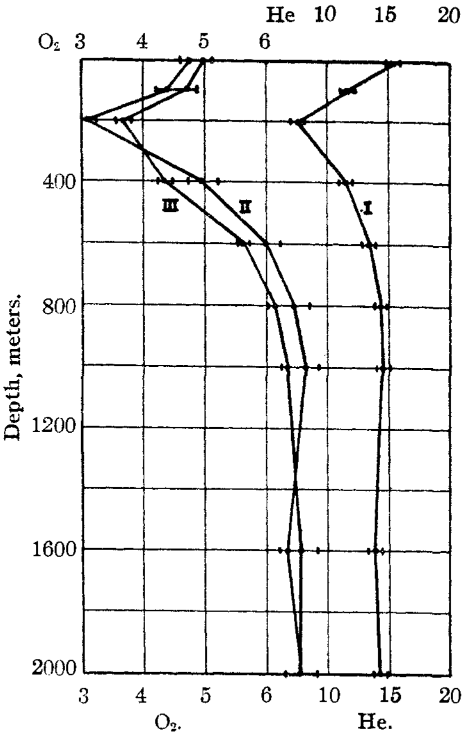

Fig. 1.

TABLE II

ALL SEA WATER SAMPLES WERE COLLECTED JULY 25–31, 1933

Depth, meters	Recorded temp., °C.	He–Ne content, cc./cc.	(He–Ne)/O_2 for recorded temperature	O_2 content calcd. cc./cc.	O_2 content measured, cc./cc.
		Station 1729. 39° 25′ N 69° 40′ W			
0	19	15.1×10^{-8}	..	..	..
100	12.8	13.3	..	..	..
300	8.1	14.1	..	..	..
		Station 1739. 40° 20′ N 70° 20′ W			
1	19.7	9.5×10^{-8}	..	..	..
20	11.5	9.6	..	..	..
50	9.4	12.4	..	..	..
75	9.9	16.5	..	..	..
		Station 1730. 38° 47′ N 69° 11′ W			
1	25.4	15.5×10^{-8}	3.24×10^{-5}	4.75×10^{-3}	4.95×10^{-3}
100	12.9	11.5	2.62	4.39	4.69
200	(10)	7.5	2.48	3.02	3.66
400	6.7	11.5	2.32	4.96	4.36
600	5.0	13.4	2.23	6.01	5.66
800	4.5	14.3	2.21	6.47	6.16
1000	4.2	14.6	2.19	6.67	6.36
1600	3.8	13.8	2.18	6.38	6.58
2000	3.5	14.2	2.16	6.57	6.56
		Station 1734. 36° 27′ N 68° 38′ W			
1	25.6	.. $\times 10^{-8}$	3.25×10^{-5}	.. $\times 10^{-3}$	4.69×10^{-3}
22	24.0	16.2	3.18	5.10	4.94
87	19.8	..	2.96	..	5.09
693	14.6	11.5	2.70	4.26	3.90
866	10.4	10.0	2.49	4.02	3.36
1000	7.0	..	2.33	..	..
1400	5.1	14.7	2.24	6.56	5.48
2000	3.9	14.9	2.18	6.83	6.33
3000	3.0	15.3	2.13	7.18	6.13
4000	2.7	15.3	2.11	7.25	5.96
4500	2.7	15.5	2.11	7.35	..

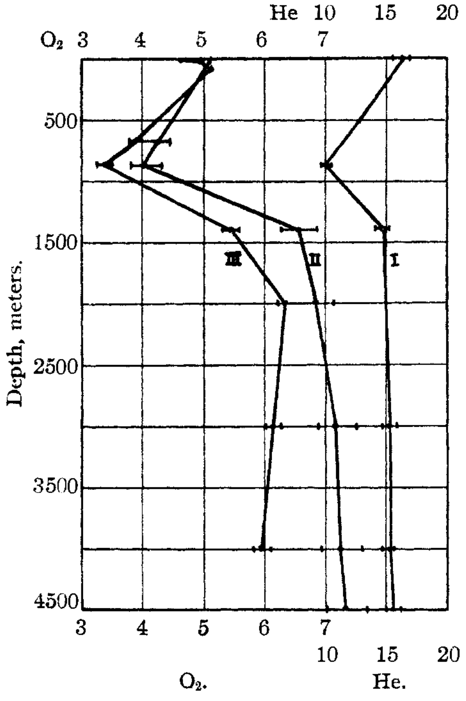

Fig. 2.

The third possibility is unlikely. Helium and neon are unadsorbed on solid matter at the temperatures in question. Unlike the case of oxygen there are no chemical reactions possible to fix these two gases. The radioactive content of ocean waters is too low to cause any enrichment of the helium approaching anywhere near to the proportion in the mixture. Leaching of radioactive helium from the bottom and subsequent diffusion also plays no role unless unreasonably long geological periods are considered. From rough spectroscopic tests the deep waters show about the same composition for the helium–neon mixtures as those at the surface—probably a slight excess of neon compared with the atmospheric composition.

The present data are insufficient to differentiate between the two feasible possibilities 2 and 4. Both factors probably play a part and a distinction between a deficiency or excess of oxygen and an absorption of gases at some other temperature than that recorded must be left to routine oceanographic work. Certain selection rules, however, may be formulated. Thus at station 1730 (Fig. 1) there are two depths at which the measured and base line oxygen values do not fall together within the limits of error. At 200 meters there is an apparent surplus of oxygen. The calculated and measured oxygen values would fall together on the supposition of an absorption temperature of about 1.3° (lower ratio) and subsequent heating up to the recorded temperature of about 10°, which would appear to fit the facts better at 200 meters than the assumption of an actual excess of oxygen. Such a mass of water may have come from icebergs having regard to the location and the time of the year. Some support for this is found in the fact that the water at this depth is a little under half-saturated having been in contact with the air for only a short while. At 400 meters there would appear to be a deficiency of oxygen. Here there is no selection principle to decide whether such is the case or whether the water was saturated at 13.4° and subsequently cooled to 6.7°, although subsequent cooling to such an extent is improbable.

At station 1734 an apparent deficiency of oxygen between about 700 and 1800 meters is shown (Fig. 2). On the other hand, this apparent deficiency could be accounted for if this mass of water took up its gases at about 20°. The proximity of the Gulf Stream may here provide a means of differentiating between the two possibilities. The deficiency of oxygen at 3000 and 4000 meters must be real since in order that the calculated and measured values coincide, absorption temperatures of about 10.5° would be necessary compared to between 2.7 and 3.0° recorded. These deeper polar waters, however, must be warming up with a warmer earth below and warmer water above and any considerable cooling after establishing gas equilibrium seems improbable. The correlation of biological oxidation with depth is as yet incomplete. There is a striking significance between the oxygen minima and other factors such as nitrate and phosphate content.

The foregoing discussion is not intended as a final analysis of the two cases investigated but only to illustrate the applicability of the inert gas analyses in determining a base line for the oxygen content. Since the helium–neon saturation values are almost independent of temperature within a likely range of absorption (0–30°), the ratio of helium–neon by analysis to a mean saturation value (16.0×10^{-8} cc. per cc.) gives the degree of saturation independent of the temperature conditions under which the original absorption took place. It is significant that the minima in the helium–neon content occur at the same depth as the minima in the measured oxygen content. Although it is possible to account for a deficiency of oxygen to some extent by biological oxidation it would appear that certain masses of water may not have become saturated on taking up the atmospheric gases originally.

I wish to express my thanks to Dr. Rakestraw and the Woods Hole Oceanographic Institution for kindly furnishing the specimens and the required data of depth, temperature and oxygen content.

Summary

1. The variation of the helium–neon content of ocean waters has been measured.

2. It is shown how such data may be used in fixing a base line for the oxygen content, and by comparison with the measured oxygen and recorded temperatures, how this base line may be used in tracing the history of the present oxygen or the water masses involved.

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