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THE RADIUM AND RADON CONTENT OF PACIFIC OCEAN WATER, LIFE, AND SEDIMENTS.

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ABSTRACT.

We have measured the radium content of sea water from the Pacific and Atlantic coasts of the United States. In all cases the results are several orders of magnitude lower than those obtained by previous workers. Instrumental reasons are given for regarding the lower results (ca. 10^{-16} g Ra per cc) as correct. A large increase in radium concentration with depth in the ocean has been found at several stations. This suggests that radium is being continuously precipitated out of the ocean. The bottom mud in quiet deep water shows a high radium content, mainly due to high radioactivity of the finest particles in the sediment. These fine particles are possibly organic, and as further evidence that biochemical precipitation processes play an important rôle in ocean chemistry, the radium content of a few marine plants and animals is shown to be the order of 100 times that of the water in which they live. The oceans must be more widely sampled and many more analyses must be made before the problems of oceanic radium chemistry may be completely solved, but the general character of the results is becoming clearer.

I. INTRODUCTION.

The quantitative study of the radium content of ordinary materials has already led to significant new results in the geological and cosmological sciences. Radium occurs in minute amounts as a contaminant in substantially every type of material found in, on, or above the earth. It is well established that ordinary igneous rocks contain on the average, the order of 1×10^{-12} grams of radium per gram. Ocean-bottom sediments, however, usually contain several times this amount of radium. The average values for terrestrial and ocean-bottom sediments are sufficiently different to leave no doubt regarding the reality of the higher average radium content shown by the deep-ocean sediments.

Between 1907 and 1911 knowledge of the radium content of ocean water was sought in an effort to explain the penetrating radiation observed in ionization chambers operated on ships at sea. The radium analyses of ocean water by Eve,[1] Joly,[2] and Satterly[3] and the emanation analyses by Knoche[4] gave sufficiently low values to show clearly that the penetrating radiation at sea is too large to be due to oceanic radioactivity. The subsequent discovery of cosmic rays provided a satisfactory explanation of the ionization over the sea, and little further[5] experimental work on the radium content of sea water was undertaken as the World War closed down such research programs.

In recent years the oceanographic problems of radium precipitation have attracted new interest. The solution of the radium problem must bring with it new light on other phases of oceanic chemistry. During the summer of 1930 Devaputra, Thompson, and Utterback[6] carried out radium analyses on 74 sea-water specimens, mostly from the Pacific Ocean. All the early workers had found considerable variation in the radium content of ocean-water samples drawn from various parts of the Atlantic, Mediterranean, and Indian Oceans. Table I summarizes briefly the results of these investigations. Devaputra, Thompson, and Utterback are in general agreement with Joly in assigning a high radium content to the oceans, while Eve and Satterly obtained values which are about an order of magnitude lower. There is very little spread in the Devaputra-Thompson-Utterback data, suggesting that something beside the sea-water specimens contributed heavily to the observed electroscope currents.

Strutt,[7] Eve,[8] Mialock,[9] and Hewlett[10] examined salts, obtained by the evaporation of sea water, for radium, usually by the carbonate-fusion-emanation technique. These results are included in Table I.

The general conclusions regarding the radium content of the seas to be drawn from all these analyses are the following:

1. Variations due to ocean currents, depths, proximity to land, etc., probably exist.
2. The concentration of radium in ocean water is very low.
3. Because of this low concentration, the absolute magnitude of the radium concentration is difficult to determine, and hence the activities reported for similar specimens seem to depend less on their origin than on the analytical technique employed in the radium analyses.

TABLE I.

Radium Content of Ocean Water and Sea Salts, Reported by Various Observers.

Sea Water

Author and Date	General Locality	No. of specimens	Radium, in 10^{-16} g per cc	
			Range	Mean
Eve (1907)	N. Atlantic	1	6.	6.
Joly (1908)	England Arabia Mediterranean	11	20. to 390.	255.
Eve (1909)	N. Atlantic	6	5. to 15.	9.
Joly (1909)	Ireland Atlantic Mediterranean Black Sea Indian Ocean	25	20. to 340.	255.
Satterly (1911)	S. E. England	4	2. to 16.	10.
Lloyd (1915)	Gulf of Mexico	1	17.	17.
Devaputra, Thompson, and Utterback (1932)	Pacific	58	33. to 69.	50.
Devaputra, Thompson, and Utterback (1932)	Atlantic Hudson Bay	16	380. to 470.	450.
Evans, Kip, and Moberg (1937)	Pacific Atlantic	14	0.0 to 3.2	0.8

Sea Salt

			Radium, in 10^{-14} g per g
Strutt (1906)	?	1	7.5*
Eve (1907)	?	1	2.04
Mialock (1916)	Atlantic Pacific	20	150.
Hewlett (1917)	Atlantic Pacific	15	Less than 10.

* Corrected for revised U : Ra ratio; see Eve and McIntosh, Phil. Mag., 14, 231, 1907.

II. ANALYTICAL TECHNIQUE.

In the present experiments about 50 radon analyses have been made on 31 different samples of ocean water, life, and sediments. The radium content of ocean water was found to be considerably lower than the values reported by previous workers. Accordingly, a number of special experiments were performed to make sure of the quantitative accuracy of the analyses as well as to locate the sources of errors which had led previous workers to report what seem to be fictitiously high radium concentrations.

The analytical technique developed for these measurements has been fully described by one of us.[11] The method completely excludes the effects of all radioactive substances except radon and radium, hence the uncertainty voiced by Clark[22] cannot arise here. It remains only to point out the particular difficulties encountered in precise analyses of the radium content of sea water.

Many of the water specimens were collected during the spring and summer of 1934 under the direction of Moberg, using a small boat sent out on one-day cruises for this sole purpose from the Scripps Institution at La Jolla, California. Clear, new, ground-glass-stoppered, one-liter glass bottles, specially cleaned and dried were used, together with the standard oceanographic technique for obtaining water samples for dissolved gas analysis. Two bottles were used for each sample, both being completely filled except for a few cc of air at the neck to allow for subsequent temperature changes. The boat schedule was arranged to meet the evening train, the samples being put aboard and delivered to the laboratory at Berkeley the following morning. Here the glass stopper on each bottle was replaced with an identical stopper previously drilled axially, and 1,600 cc of each sample were transferred by siphon into the evacuated radon apparatus shown in Fig. 2 of reference 11. In this way all the radon present in the water sample was available for the analysis which was immediately carried out.

This analysis, when corrected for the subsequently determined true radium content, and for the decay of free radon after bottling the sample at sea, gives the excess radon content, that is, the free radon which had been absorbed by the sea water from its environs, particularly the atmosphere and the bottom muds. This excess radon is not due to radium in the seas. The sample then remained sealed in the apparatus for

about eight days, during which time the radium in the specimen rebuilds the radon to about three-quarters of its equilibrium value. This radon is then boiled off as before, and its analysis leads to the value for the true radium content of the sample. The radium measurement can of course be repeated as many times as desired at intervals of about one week, the sample having been in contact with the atmosphere at no time since it left the ocean. These precautions are necessary because the radon content of air near land masses is the order of 10^{-16} curie per cc; thus a given volume of terrestrial air contains more radon than the same volume of sea water, and the transfer of the water sample by pouring might introduce appreciable errors. The radon content of the laboratory air was $0.7 \pm 0.1 \times 10^{-16}$ curie per cc on May 24, 1934 near the middle of the present experiments.

The possibility of contamination of the sample is completely circumvented by this technique, which avoids the concentration of the sample by boiling in an open dish in the laboratory, the addition of talc and hydrochloric acid, and similar procedures used by most of the previous workers. The sample flask on the radon apparatus is cleaned between specimens by boiling HCl and $BaCl_2$ in it, and rinsing with distilled water, all of which are previously analyzed for radium and found to contain negligible amounts for the quantities used.

Several control tests were run to determine whether or not all of the radon in the water sample is released by the reflux-boiling and nitrogen-agitating methods used. It was found that the 20 minute boiling technique, which is adequate for 250 cc samples, was not sufficient, but that a one hour boiling program removed all the radon in the 1,600 cc sample. Two hours of additional boiling then failed to yield any more radon. Secondly, a method of internal standardization was employed. To an analyzed 1,600 cc sea-water sample (No. 8493, Table V) was added 0.786×10^{-12} gm of radium from a standard solution previously compared with the International Radium Standard.[11] Repeated analysis of this water standard ($[5.0 \pm 0.2] \times 10^{-16}$ g Ra per cc) showed that the one hour boiling technique does in fact completely de-emanate the sample, and that after standing for a month no radium is precipitated in such a way as to make its radon inaccessible to further analyses. The absolute values obtained are further confirmed by the agreement between this sea water standard, the 19.66×10^{-12} gram radium standard usually employed for calibration, and the

theoretical calibration[12] based only on apparatus geometry, and the decay constants and ranges of the alpha rays of radon and its decay products.

Seeking further to establish instrumental reasons for the high values reported by previous workers, we were able to reproduce fictitiously large electrometer readings by eliminating the insulation drying trays in the ionization chambers. It was definitely established that the ordinary phosphorus pentoxide drying tube in the gas line leading from the reflux condensers to the ionization chambers is insufficient to dry the gases adequately. The internal dryer located inside the ionization chamber and near the amber insulation is absolutely essential in preventing leakage currents from falsifying the electrometer readings. The absence of an internal dryer in the Lind ionization chamber used by Devaputra, Thompson, and Utterback, together with the rapidity with which their measurements had to be made, and possible under-estimates of the important effects of cosmic rays in these ionization measurements, may explain the high and uniform values they obtained.

In the present experiments the radon ionization current was usually observed for a period of 10 to 15 hours for each analysis, with an equivalent length of background interdigitated between specimens. Such long observations are made possible by the fully automatic calibrating and continuous photographic recording[11] features of the detection apparatus. They are necessary in order that the large statistical fluctuations in the emission of the alpha rays of radon and its decay products may be averaged out. Observations of a few minutes or even an hour's duration, such as characterized the visual observations of the earlier investigators, cannot disclose the magnitude of these statistical errors. Much of the non-reproducibility of the early measurements must arise from such fluctuations.

Each sample yields the order of 10^{-13} curie of radon, and therefore gives about 25 alpha rays per hour for the ionization of the gas in the ionization chamber. Since the natural and unavoidable radioactivity of the brass walls of the chamber gives about 200 alpha rays per hour, it is clear that the Poisson Law fluctuations in the resultant ionization are very appreciable. The probable errors assigned to the various results in the following section have been determined in the manner described earlier for this apparatus.[11, 13] Most of this uncertainty arises from the statistical fluctuations in the background ionization.

III. RESULTS ON OCEAN WATER AND MUDS.

A. Variation of radium concentration with depth.

The first set of ocean-water samples tested was collected February 6, 1934 at a station 13 nautical miles from Point Loma, California, the nearest point on the mainland, and nine miles north of Coronado Island, Lat. 32° 32′N, Long. 117° 22′W. Using the sampling technique described in the previous section, water samples were collected from just below the surface, from 600 meters depth, and from 1,300 meters, the last being the ocean bottom. The determination of the excess radon in the surface sample was the first analysis undertaken and its result is more uncertain than the others because only a 600 cc sample was used in view of the optimistic predictions of the previous literature. The initial radium measurements were repeated after an interval of over five months. The second values (Table II) in every case are in perfectly satisfactory agreement with the first analyses, and suggest that the probable errors assigned on a basis of the observed statistical fluctuations in ionization are essentially correct, and that no errors are present of the type assigned by Joly to sulphate precipitation.

TABLE II.

Scripps Ocean Water and Mud Specimens, February 6, 1934.
Lat. 32° 32′ N., Long. 117° 22′ W.

The second analyses indicated for the water specimens were made five months after the first runs.

Sample	Depth in Meters	Radium in 10^{-16} g Ra per cc water	Excess Radon in 10^{-16} curie per cc water
8491	0	$\left\{\begin{matrix}0.3 \pm 0.1\\0.5 \pm 0.2\end{matrix}\right.$	$4. \pm 2.$
8490	600	$\left\{\begin{matrix}1.5 \pm 0.1\\1.3 \pm 0.3\end{matrix}\right.$	0.0 ± 0.1
8489	1300 (bottom)	$\left\{\begin{matrix}3.2 \pm 0.2\\2.6 \pm 0.3\end{matrix}\right.$	22.0 ± 0.8
8489 (Mud)	1300	$3.00 \pm 0.05 \times 10^{-12}$ gm Ra per gm mud 3.17 ± 0.05	

The radium concentrations show a marked increase with water depth, amounting to nearly a factor of ten over the entire 1,300 meters, and a factor of about four over the first 600 meters.

Within the observational uncertainty of the measurements the increase is approximately linear with depth. These results suggested that some radium precipitating mechanism is active.

Fortunately the field sample bottles containing the 1,300 meter specimen each contained a few grams of very fine gray mud, which had been collected with the bottom specimens and had simply been allowed to stand in the bottom of the bottles when the water samples were siphoned into the emanation apparatus. This mud was removed, dried, weighed (8.679 g) and, as its reaction to HCl showed the presence of carbonates, the sample was baked three hours at 1,000° C to destroy the carbonates. The loss of weight on baking was 21 per cent, and the sample became pink in color. The resulting 6.884 g of material was divided into two specimens which were sealed in pyrex tubing for a month to permit the radon to come back to equilibrium with the radium. Subsequent analysis using the direct fusion furnace technique[11] gave 3.00 ± 0.05 and $3.17 \pm 0.05 \times 10^{-12}$ g Ra per gram of fresh dry mud, or an average of $3.1 \pm 0.1 \times 10^{-12}$ g Ra per g.

The radium content of this bottom mud is therefore about three or more times higher than average terrestrial formations, and this high radium concentration seems to have a rather direct correlation with the concentration gradient observed in the sea water lying over it. Also it explains the large amount of free radon shown in Table II for the bottom water. This excess radon is supplied to the water by the radium in the fine bottom mud. As might be expected, the water at the middle depth of 600 meters shows no excess radon; that is, the fresh sample contained radium and radon in their radioactive equilibrium proportions. The surface water again exhibits an excess of radon, which may be absorbed from the atmosphere.

Further studies of the variation of the radium and radon concentration with depth were made on samples collected for the purpose by R. L. Bolin, of the Hopkins Marine Station at a station (Lat. 36° 44′N, Long. 122° 01′W) 7.5 miles NW of Point of Pines on July 24, 1934. Table III summarizes the data on three specimens taken at depths of 0, 450, and 900 meters, the latter being an undetermined distance (1 to 400 m) above the bottom.

These results again display an increase of radium concentration as the depth of the water increases. An excess of radon at the

TABLE III.

Hopkins Ocean Water Specimens, July 24, 1934.
Lat. 36° 44′ N., Long. 122° 01′ W.

Sample	Depth in Meters	Chlorinity 0/00	Temperature	Radium in 10^{-16} g Ra per cc	Excess Radon in 10^{-16} curie per cc
H1	0	19.381	13.4° C.	0.4 ± 0.1	0.9 ± 0.3
H2	450	19.765	6.5° C.	0.8 ± 0.2	-0.2 ± 0.3
H3	900	19.967	4.2° C.	0.9 ± 0.3	0.0 ± 0.3

surface is again evident, while the deeper samples exhibit radioactive equilibrium between radon and radium. The deepest specimen was too far from the bottom to contain free excess radon. The lower salinity of this surface specimen suggests that it contains an appreciable amount of fresh water. River and well water usually contain an excess of free radon, which they absorb from rocks and this may be the origin of most of the excess radon observed in this surface specimen.

The same general picture (see Table IV) was given by two specimens taken June 7, 1934, from the Scripps Institution Boat, at Lat. 32° 52′5N, Long. 117° 16′8W, where the water is only 276 meters deep. Analysis of a specimen of the ocean floor material at this station is given in the next section.

TABLE IV.

Scripps Ocean Water Specimens, June 7, 1934.
Lat. 32° 52′5 N., Long. 117° 16′8 W.

Sample	Depth in Meters	Temperature	Radium in 10^{-16} g Ra per cc	Excess Radon 10^{-16} curie per cc
8497	0	19.6° C.	0.3 ± 0.3	0.7 ± 0.5
8498	137	13.4° C.	0.8 ± 0.3	0.1 ± 0.3

Measurements of the total active deposit from atmospheric thoron and radon were made by Simpson and Wright.[16] Their results show that near land areas, particularly during an offshore breeze, the ocean air differs little from that over land.

Collecting the active deposit on a long negatively charged wire, and using the arbitrary activity unit of Elster and Geitel, Simpson and Wright found values between 1 and 21, with a mean of 6, for oceanic air on the voyage of Scott's Antarctic Ship "Terra Nova" from England to New Zealand. These are the order of five per cent of typical land values, which have a mean of about 124 and a range of 52 to 256. Messerschmidt[17] made an extensive series of measurements of the radon content of the air at Halle, obtaining an average of 3×10^{-16} curie per cc, which is in qualitative agreement with unpublished measurements made by one of us at Pasadena and Berkeley, California, and Cambridge, Massachusetts, and is certainly correct in order of magnitude. The Henry's law coefficient for the distribution of radon between sea water[14, 15] at 18° C. and air is about 0.16 that is, the volumetric concentration of radon in the sea water should be about 16 per cent of the concentration of radon in the air if the two phases are in equilibrium. Assuming that the relative proportions of radon and thoron are about the same over land and ocean, that the radon content of ocean air far from land is derived from the radium in the sea, and that equilibrium is present between the radon in the water and in the air, the radium content of deep sea surface water might be expected to be about $0.16 \times (6/124) \times 3 \times 10^{-16} = 0.02 \times 10^{-16}$ g Ra per cc of sea water. It is difficult to see where this independent estimate of the mean oceanic radium concentration can be in error by a factor of 10^4, as would be required if Joly's radium results were accepted. On the other hand, the present observations are in qualitative agreement with this low estimate and in disagreement with all other previous work.

Swann's[27] measurements of the emanation content of sea air, during cruise IV of the *Carnegie,* led to values between 0.000 and 0.08×10^{-16} curie Rn per cc of air. Assuming equilibrium between sea water and air, this would suggest a radium content of the order of 0.01×10^{-16} g Ra per cc of sea water, contradicting the high oceanic radium concentrations of previous observers. (Table I.)

B. Radium and radon content of other surface water specimens.

Tests of the overall reproducibility of the sampling, transporting, and analytical techniques were undertaken on three

duplicate samples taken by the Scripps Institution boat on May 21, 1934, five miles off shore from the Institution at Lat. 32° 55′5W, Long. 117° 21′W. The water temperature at this station was 19.7° C. and the salinity 33.49 0/00. The low activity of the water and the unavoidable delays incident to completing the radon analyses on each specimen in its turn result in a high probable error for the excess radon in the samples analyzed last. In spite of this there are a few conclusions which may be drawn from these data. (Table V.) It seems rather definite that the radium concentration at this station cannot have greatly exceeded 0.5 x 10^{-16} g Ra per cc nor the excess radon have been much more than 1 x 10^{-16} curie per cc. This station, however, is very close, both in position and season, to that from which Devaputra, Thompson, and Utterback examined ten specimens taken at depths of 0 to 600 meters in June 1930 at Lat. 32° 52′W, Long. 117° 21′W. Their results range from 37. to 46. x 10^{-16} g Ra per cc, or more than a hundred times the values obtained in our experiments, and they show no clear variation with depth. In the previous section an explanation for these differences was proposed.

TABLE V.

Scripps Ocean Water Specimens, May 21, 1934.
Lat. 32° 53′5 N., Long. 117° 21′ W.

Sample	Depth	Radium in 10^{-16} g Ra per cc	Excess Radon in 10^{-16} curie per cc
8493	Surface	0.2 ± 0.2	0.4 ± 0.3
8494	Surface	0.3 ± 0.3	1.1 ± 0.6
8495	Surface	0.0 ± 0.3	1.8 ± 0.7

A surface specimen (8499) taken June 7, 1934 from the deep end of the Scripps Institution pier (water temperature 20.8° C.) showed 0.4 ± 0.4 x 10^{-16} g Ra per cc and 0.8 ± 0.6 x 10^{-16} curie excess radon per cc, in entire qualitative agreement with the low values found at all the off shore stations.

Through the kindness of Prof. C. L. Utterback, Mr. L. A. Sanderman of the Friday Harbor Oceanographic Laboratories of the University of Washington collected for us four one-liter specimens of surface water July 18, 1934 from off Yellow

Island, in the middle of the San Juan Channel. The station was at Lat. 48° 35′N, Long. 123° 3′W and is essentially the same as that from which Devaputra, Thompson, and Utterback analyzed specimens in the summer of 1930, reporting 47. x 10^{-16} g Ra per cc for surface water. The train trip from Seattle to Berkeley is too lengthy to prevent appreciable decay of excess radon during the shipment of the specimens. Consequently we examined the specimen for radium only, finding 0.6 ± 0.2 x 10^{-16} g Ra per cc, in good agreement with our other results on Pacific waters.

Devaputra, Thompson, and Utterback had also studied seawater specimens from the north Atlantic, approximately 100 miles off shore from Ocean City, Maryland. For these and their Hudson Bay specimens they obtained about ten times the radium concentration of their Pacific samples. Dr. H. B. Bigelow of the Woods Hole Oceanographic Institution generously supplied us with four liters of surface water made up from several stations in the central part of the Gulf of Maine, about 100 miles off shore from Boston. The chlorinity of the mixture was 17.925 0/00. Our radium analyses showed 1.5 ± 0.4 x 10^{-16} g Ra per cc, which is somewhat higher than our Pacific Ocean results, but again is less than one per cent of the concentration reported by Devaputra, Thompson, and Utterback.

IV. DISTRIBUTION OF RADIUM IN BOTTOM SEDIMENTS.

The high radium content of the fine mud associated with the water specimen 8489 (Table II), from a depth of 1,300 meters, and the suggestion from Table II that this is due in part to the precipitation of radium from the overlying water, led to the following experiment on the radium concentration in the coarse- and fine-grained fractions of a typical bottom mud.

With the small Scripps Institution boat and a pipe dredge, about one kilogram of bottom mud was collected at the station of Table IV where the water is only 276 meters deep.* The dredge brought up about one liter of water with the mud, and as this contained some of the finer sediments in suspension, the entire sample was dried at water-bath temperatures.

* The Pacific Ocean shipping strike had prevented making alterations on the large Scripps Institution boat which would have made it possible to collect a large sample of the mud from the deep station of Table II.

Thus the salt from about a liter of water was in the mud. About an eighth of this dried material was removed and radium measurements, carried out on it by the usual direct fusion furnace technique[11], gave $0.57 \pm 0.02 \times 10^{-12}$ g Ra per g.

The remainder of the sample was suspended in distilled water and, after partly settling, filtered through a Berkefeld filter. The wash water (2 liters) contained only $0.9 \pm 0.3 \times 10^{-16}$ g Ra per cc; hence no significant amount of radium was leached out of the material. The sediment remaining on the filter was added to the rest of the mud samples. More distilled water was added and the material sieved to obtain fractions one and two (Table VI). The remainder of the sample was suspended in distilled water and further separated by settling as described in Table VI. All the samples were then dried on a water bath, then for several hours in an oven at 110° C. The two liters of wash water from fractions one to six contained $0.7 \pm 0.2 \times 10^{-16}$ g Ra per cc, which is probably somewhat less than normal sea water at this station and depth, and the total radium involved is negligible in comparison with the radium found in the solid fractions.

About three grams of each of the fractions were weighed out, heated for three to five hours at about 1,000° C. to break down the carbonates, sealed in glass tubes for a month, and then analyzed for radium by the direct fusion furnace technique.[11] The right-hand column of Table VI shows that all the radium found in the analyses of the bulk sample is exactly accounted for in the analyses of the seven graded fractions. Doubtless fraction three, which makes up 80 per cent of the bottom deposit and is mainly sand, is representative of terrigenous materials washed to this near-shore area by ocean currents and tides. Its low radium content is in entire general accord with the radium content of various terrestrial materials[18, 19] measured with the same apparatus and techniques.

The main concentration of radium is found in those fractions containing the fine material of a few microns diameter. This finding supports the view that the high radium content of deep-sea sediments is mainly due to fine particles which have settled down from the overlying water.

If, as at least one author[20] has suggested, the radium in the ocean were due to radium dissolved out of the bottom sediments, then a concentration gradient similar to that found in section III might be expected. In this case, however, the original source of the radium in the bottom sediments would

TABLE VI.

Distribution of Radium in Mud Sample 8496 from 276 Meters Depth, Lat. 32° 52′5 N., Long. 117° 16′8 W. after Mechanical Analysis.

Fraction	Description	Wgt. Grams	Fractional Weight	Radium in 10^{-12} g Ra per g	Radium Concentration x Fractional Weight
1	Particles more than 1 mm diameter, mostly shells.	3.7	0.0043	0.18 ± 0.02	0.0008 x 10^{-12}
2	1.0 to 0.5 mm diam.	0.2	0.0002	.....	.....
3	0.5 to 0.05 mm sand, settled in about 1.5 minutes.	690.	0.80	0.43 ± 0.01	0.340
4	50 to 7 microns, coarse silt, settled in about 30 minutes.	86	0.0996	1.05 ± 0.02	0.105
5	7 to 3 microns, fine silt and coarse clay, settled in 2 to 3 hours.	40	0.0464	1.11 ± 0.02	0.0515
6	3 to 1 microns, clay and colloid, settled in 3 days.	23	0.0266	1.31 ± 0.02	0.0348
7	Less than 1 micron. Colloid. 18 g remained in suspension more than 3 days when water removed by evaporation. 1.4 g obtained by filtration of water used in separating fractions 1 to 6.	19.4	0.0235	1.11 ± 0.03	0.026
TOTALS		862.	1.000		0.56
BULK MATERIAL			1.00	0.57 ± 0.02	

be obscure, and it seems much more likely that the radium in the ocean has its origin in the rocks of the land areas, and is leached out by rain and ground water and carried to the ocean by the rivers.[21] Moreover, if radium were being dissolved from the bottom sediments more rapidly than it is being precipitated, the fine-grained portions of the bottom sediments might be expected to be poorer in radium than the large-grained material. The precipitation mechanism is supported by the observation of the highest radium concentration in the finer fractions of the bottom mud.

V. RADIUM CONTENT OF MARINE LIFE.

The evidence of sections III and IV suggest that radium is being continually precipitated out of the ocean. The mechanisms might be strictly chemical, depending on the dissolved oxygen content of the water and other factors, or they might involve biochemical processes as well. If only ordinary chemical precipitation were present, fraction seven of Table VI would probably have been much more active than the others.

Shelled animals are known to conduct a very efficient calcium-accumulating process, withdrawing this element from the water and carrying it toward the bottom with them when they die.[22] Marine plants are effective in concentrating iodine and potassium, and the marine alga *Fucus vesiculosus* is reported[23] to concentrate barium so that its Ba concentration is several hundred times that (0.02 per cent) of the ocean water in which it lives. A similar process in the case of radium might go far to explain the results of sections III and IV. It is therefore of interest to examine the radium content of various forms of marine life, particularly plants and small animals since these have the greatest surface area per unit volume. A few tests of this type were carried out on kelp and plankton, both of which exhibit radium concentrations of about one hundred times that of the water in which they live.

Samples of kelp and plankton were prepared at the Scripps Institution laboratories and analyzed for radium at Berkeley employing the direct fusion furnace technique.[11] Kelp was found difficult to prepare. An unweighed quantity of fairly dry kelp was heated to between 650° and 700° C. for about seven hours a day for more than a week. In addition to removing the carbon by combustion this technique fused some of the

salts, probably of magnesium, and the ash was broken up occasionally. The resulting ash had a radium content of $0.21 \pm 0.02 \times 10^{-12}$ g Ra per g.

Taking the industrially-determined weight ratio of living kelp to dry kelp of ten to one, and assuming that the weight ratio of dry kelp to its ash is as much as ten to one, there still remains a factor of 100 between the radium concentration in living kelp and its ocean water medium.

Further samples were prepared by taking about 50 g of this ash and extracting first the portion soluble in boiling distilled water, then the portion soluble in nitric acid. The original ash was extracted with boiling distilled water until a chloride-free insoluble residue remained. The dissolved salts were then recovered by evaporation of the water, following which they were heated to 500° C. These water-soluble salts had a radium content of $0.09 \pm 0.02 \times 10^{-12}$ g Ra per g.

The insoluble residue was heated with 100 ml of nitric acid and filtered. The filtrate, with 15 ml of hydrochloric acid added, was evaporated to dryness, and the salts incinerated at 650° C. These nitric acid soluble salts contained $0.73 \pm 0.02 \times 10^{-12}$ g Ra per g.

The insoluble residue from these two extractions, after being evaporated to dryness with hydrochloric acid and incinerated at 800°C., weighed 1.2. g, and had a radium concentration of $0.75 \pm 0.06 \times 10^{-12}$ g Ra per g. The significance of these kelp fractionations is not yet obvious. The results are recorded for the benefit of experimenters who may later investigate this problem.

At the time these analyses were being made, the water contained practically no plankton which could be caught in a tow net. A sample of plankton, collected earlier in Mission Bay, California, was therefore analyzed. The sample consisted mainly of small schizopod crustaceans and is not representative of typical oceanic plankton. From 16 grams of dry plankton, 1.40 g of ash were obtained by incineration. Radium analysis of the ash showed that the original dry material had a radium concentration of $0.040 \pm 0.003 \times 10^{-12}$ g Ra per g. Assuming the dry plankton represents only ten per cent of the weight of the living plankton, we see that the living organism contained more than 100 times the radium concentration of typical Pacific Ocean surface water.

Fragmentary as these results are, they do definitely indicate

the importance of biochemical processes in all considerations of radium chemistry in the sea. An extended investigation of these questions might bring many interesting matters to light.

VI. DISCUSSION.

These experiments have indicated that sea water is much poorer in radium than the results of earlier workers had suggested. Therefore, accurate analyses require much more refined technique and apparatus than that previously used. A 1,600 cc sample of sea water contains only the order of 10^{-13} g of radium, and less than 10^{-18} g of radon. This radon must be quantitatively removed from the specimen and placed in an ionization chamber, where it will produce only the order of 25 alpha rays per hour. The unavoidable radium content of the metal walls of the chamber produces some 200 alpha rays per hour, while cosmic rays and local gamma rays increase this background ionization even further. Ionization current observations of many hours' duration are therefore required and even at best the statistical fluctuations in the random emission of the alpha rays result in a fairly large probable error.

In every case the probable error r is given for each of the present measurements. From the theory of errors it follows that the probability that the true result lies outside the range $a \pm r$ is exactly one-half, while the chance that the measured value a, differs from the true value by more than $2\ r$ is 0.18, and the chance that a differs from the true value by more than $3\ r$ is only 0.044.

In section III a marked increase in the radium concentration of ocean water with depth is shown. Surface waters in the Pacific Ocean near the United States coast run about 0.2 to 0.3×10^{-16} g Ra per cc, while at a depth of 1,300 meters the water contains about ten times this concentration of radium. It seems probable that this is indicative of a continuous process of settling of radium in the sea, for the radium in bottom sediments is usually highest where the water is quiet and deep, and the finest particles in the bottom mud contain the highest radium concentration. Coarse material washed in from neighboring land areas is poorer in radium. Finally it appears probable that various forms of marine life concentrate radium, die, and settle to the bottom. It should be remarked, however, that in very deep waters the zone of abundant life may represent

only a thin surface layer in the whole ocean depth, hence biochemical concentration is probably aided by other mechanisms.

Radium itself has a half-life period of some 1690 years, and it is of great importance, in connection with any studies of the rates of oceanic processes, to know whether radium in the ocean and in deep-sea sediments is in equilibrium with its radioactive parent, uranium. Hernegger and Karlik[24] have recently succeeded in measuring spectroscopically the uranium content of a few specimens of sea water, collected near Sweden, by means of the ultra-violet fluorescence supported by the uranium after it has been chemically concentrated into a small sodium fluoride bead. Their present values range from 0.36 to 2.3 x 10^{-9} g uranium per cc of water. This amount of uranium would support from 1.2 to 8 x 10^{-16} g radium per cc if radioactive equilibrium were present. The radium content of their water specimens has not been measured.

Finally Botset[25] has published radium analyses of connate waters, which are probably derived from ancient seas and are now held stationary in deeply buried rocks. These waters may contain several times the salt content of modern seas, and usually show a low concentration of sulphates. Botset's radium values range between 5 and 19 x 10^{-13} g radium per cc, which seems very high and may be partly due to radium dissolved out of neighboring soft rocks.[26]

Unambiguous answers to many of the oceanographic questions concerning the radioactivity of ocean waters, life, and sediments cannot yet be given because too minute a fraction of the ocean areas has been sampled. However, reliable analytical techniques are now available for extending the range of knowledge in these fields, and the general nature of the results to be expected is beginning to be understood. The radium content of the organic fraction of bottom muds should be accurately studied, because of its important bearing on the mechanism of biochemical precipitation processes.

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