RADIUM ANALYSES OF MARINE SEDIMENTS IN NORTHERN PACIFIC AND ADJACENT WATERS

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Although systematic soundings of the ocean bottom were initiated approximately 100 years ago, and although the United States Coast and Geodetic Survey took hundreds of ocean bottom samples beginning about 75 years ago, it was not until the ship Carnegie collected a number of bottom samples at great depths that information began to be available on the radioactive properties of deep ocean sediments. An analysis of some of the Carnegie bottom samples by Joly (6) showed that they had a considerable range of radium content and that some of them contained from 16 to 20 times as much radium per gram of material as was found in land rocks. This relatively high concentration of radium in deep sea sediment was also found by Pettersson (7) in analyses of samples collected by the Princess Alice II.

These early results, verified later (8, p. 229), showed that deep ocean sediments have a radium content as high as $22 \cdot 10^{-12}$ g of radium per gram of material. Undoubtedly this high value was an important incentive for further investigation, since continental granites have only about $1.6 \cdot 10^{-12}$ g of radium per gram of material. The basic igneous land rocks and the sedimentary igneous land rocks have even less.

Sea water from various localities and depths have been analyzed. The measurements of Evans, *et al.* (3, p. 247), which were made on 13 samples, yielded an average of $0.8 \cdot 10^{-16}$ g of radium per cc of water. These samples from the Pacific, Lat. 32° 32′ N., Long. 117° 22′ W., were obtained at depths which varied from the surface to 1,300 meters. Also, Foyn, *et al.* (4, p. 27) found for 23 samples an average value of $0.86 \cdot 10^{-16}$ g of radium per cc of water.

A systematic survey of the radium content of sediments in the waters of Vancouver Island were made by Utterback and Sanderman (13, p. 187). These samples were from locations such that one would conclude that they were deposited by drainage from Vancouver Island and the coast of British Columbia. This territory is composed largely of schist and quartzite with a small amount of dolorite. The average

radium content of samples from 11 stations was $0.24 \cdot 10^{-12}$ g of radium per gram. In Puget Sound, samples from five stations showed an average content of $0.37 \cdot 10^{-12}$ g of radium per gram. The surrounding territory is made up largely of glacial drift with a radium content comparable with the average of the five stations.

Sanderman and Utterback (10, pp. 132, 137), in a more extensive survey, obtained many samples of sediments from the Arctic Ocean, Norton Sound, Bering Sea, the Alaska Peninsula, southern Alaska, the Canadian Coast, and Queen Charlotte Islands. The concentration in these samples varied from $0.24 \cdot 10^{-12}$ to $1.57 \cdot 10^{-12}$ g of radium per gram, several samples showing relatively high values. Those of high radium concentration were all taken from glacier-fed inlets, and the average was $1.31 \cdot 10^{-12}$ g of radium per gram. Several samples taken from the region of the mouth of the Skeena River showed an average of $0.63 \cdot 10^{-12}$ g of radium per gram, while representative rocks furnished by the Chief Geologist of the Department of Mines and Resources of Canada had an average radium content of $0.64 \cdot 10^{-12}$ g of radium per gram. Obviously this does not permit of a general conclusion, but it seems to indicate a radium content of sediments comparable to that of adjacent land areas or drainage areas. In this study the highest average was from the region of the southern Alaska Coast where most of the rivers rise from the glacial slopes of the near-by granitic mountains. The lowest average is from the volcanic Alaska Peninsula.

The bottom samples referred to above were collected by means of a clam shell sampler or a short length of pipe. But in any case the bottom was sampled to a depth of a few centimeters. The results are in confirmation of the hypothesis that the radium content of inshore and nearshore bottom samples is due to the deposition from the surrounding land areas.

In addition to the samples mentioned above, five grab samples from the Northeast Pacific are reported by Piggott (8, p. 231) to have an average radium content of $7.6 \cdot 10^{-12}$ g of radium per gram. A sample taken from the bottom of water intermediate between the deep ocean and the near land was collected off the coast of California. It was analyzed by Evans (2) and was found to have $3.2 \cdot 10^{-12}$ g of radium per gram. Piggott (9, p. 675) obtained eleven cores between the Grand Banks of Newfoundland and the Continental Shelf southwest of Ireland. In these cores the red clay varied from $3 \cdot 10^{-12}$ to $22 \cdot 10^{-12}$ g of radium per gram, the globigerina ooze from $3 \cdot 10^{-12}$ to $7 \cdot 10^{-12}$ g of radium per gram, and the blue mud from $1 \cdot 10^{-12}$ to $3 \cdot 10^{-12}$ g of radium per gram. The higher concentrations were in samples taken at locations far from land masses and under deep water.

The high concentration of radium in deep sea deposits has led to some speculation about the process by which radium is deposited. Four possible processes have been considered. These are chemical precipitation, biological concentration, absorption of radium from settling particles, and submarine volcanic activity. However, the mode of deposition of radium in ocean water is not known, probably because the biological, chemical, and physical processes and changes in the deep ocean waters have not been determined with sufficient completeness.

Experimental data are available to test some of the processes suggested to account for the high radium content of deep sea sediment.

It is well known that marine organisms are capable of concentrating some of the constituents of ocean water. Berget (1) suggests that perhaps the radium content of deep sea sediments is due to organic accumulation. Evans, *et al.* (3, p. 256) determined the radium content of samples of plankton taken near La Jolla, and samples of kelp from Mission Beach, California. Using the weight of the samples before they were reduced to ash, they concluded that the radium concentration in living plankton and kelp is about 100 times as great as that of the water in which they live. However, when these samples were reduced to ash, the plankton had a concentration of $0.46 \cdot 10^{-12}$ g of radium per gram, and the kelp a concentration of $0.21 \cdot 10^{-12}$ g of radium per gram.

There is some evidence relative to the possible chemical extraction of radium. Foyn, *et al.* (4, p. 31) have compared the effect of calcium extraction by marine organisms and have compared the radium to calcium ratio in calcareous shells. They concluded that the rate of extraction of radium is no greater than the rate of extraction of calcium from sea water. Since the rate of extraction of calcium changes the calcium content of water but little, then any large rate of extraction of radium must be of some other source. However, since the precipitation of iron hydroxide is a method for precipitating ionium from dilute solutions, such a process might conceivably occur. It has been observed by Thompson, *et al.* (11, p. 288) that the concentration of ferric iron in ocean water is less than it should be if all the iron received were held in solution. The precipitation of uranium would be inhibited by the presence of the carbonate ion. This could contribute to the means by which the ionium-uranium unbalance in the sea water and sediment occurs. However, the question arose as to whether the extraction process concerned radium or a parent substance. Tests were made on the uranium content of sea water and on samples of high radium concentration. Hernegger and Karlik (5) found that sea water had an average of $1.3 \cdot 10^{-9}$ g of uranium per

gram of water, but the average of many observers in many determinations is $0.8 \cdot 10^{-16}$ g of radium per gram of water. If these averages are assumed to be correct, then the average amount of radium per gram of water could be supported by $0.24 \cdot 10^{-9}$ g of uranium per gram of water, so the sea water would contain five times as much uranium as necessary to maintain the radium content. It was found by Urry (12, pp. 199–203) that a bottom sample of high radium content had about one-fourth as much uranium as necessary to support its radium content. However, the uranium concentration in these bottom samples would not be the determining factor in the radium concentration. As Correns (1a) has estimated, the rate of deposition in the deep ocean is about one centimeter per 1,000 years, and therefore the uranium and radium may not be in equilibrium. Whatever the process, it must be efficient, since high concentration bottom samples contain tens of thousands of times as much radium per unit weight as does the ocean water.

The experimental data and the analyses up to 1941 show a definite pattern of radium concentration in ocean sediments. The concentrations varied with high values under deep water far from land, lower values in the samples taken off the coast, and concentrations comparable with surrounding land rocks in samples taken under inshore waters. In view of the fact that a systematic survey had been made of the radium contents of bottom samples from the surface of the bottom in the region extending from the northern tip of Alaska to the southern end of Puget Sound, it seemed desirable in this new survey over the same area to obtain samples of the sediment to as great a depth as possible below the ocean floor. To this end, a core sampler designed by Piggott (9, p. 675) was provided, and with it a number of cores up to ten feet in length were obtained in selected regions in the inshore waters of Puget Sound and the San Juan Archipelago. While the analyses of the cores have not been completed (because of interruption during the war), some positive evidence has been obtained concerning the radium concentration of sediments under the inshore water.

One of the regions included the area from the mouth of the Skagit River through Skagit Bay; the material brought down by the river is deposited along the length of the Bay. Another was Hood Canal, which is a long narrow body of water extending from Puget Sound into the Olympic Peninsula. The third region was East Sound in the San Juan Archipelago; this was selected because it is especially rich in plankton.

SKAGIT BAY

The region drained by the Skagit River and its tributaries lies east of Puget Sound and extends into the Cascade mountains. A geological report by Weaver (14) describes most of the region, the greater part of which is composed of sandstone, slate, and shale. One broad granitic area extends from Mt. Shukson on the west to the north-south stretch of the Skagit River on the east. A small region of basic andesitic lavas is found in the Mt. Baker district and also in the higher peaks of the Cascades. Skagit Bay is very shallow at the mouth of the river and deepens to about 75 fathoms down the Bay. Four stations were occupied and cores taken at each.

Station I was just off the river mouth where the water was 10 fathoms deep. The analysis of this core showed a radium content in grams of radium per gram of $0.60 \cdot 10^{-12}$ in the top three inches, $0.58 \cdot 10^{-12}$ in a sample from a depth of 27 inches in the core, $0.71 \cdot 10^{-12}$ from 51 inches, and $0.67 \cdot 10^{-12}$ from 60 inches.

Another core in Skagit Bay was obtained at Station II where the water was 15 fathoms deep and in a region where the water began to deepen rapidly. At distances down the core of 11, 35, 59, and 83 inches, the radium content was in grams of radium per gram $0.58 \cdot 10^{-12}$, $0.58 \cdot 10^{-12}$, $0.64 \cdot 10^{-12}$, and $0.55 \cdot 10^{-12}$ respectively.

The third core was from further down the Bay at Station III where the depth of water was 45 fathoms. At depths in the core of 3, 27, 51, and 75 inches, the radium concentration in grams of radium per gram was $0.52 \cdot 10^{-12}$, $0.50 \cdot 10^{-12}$, $0.60 \cdot 10^{-12}$, and $0.57 \cdot 10^{-12}$.

At Station IV the water was 75 fathoms and the core was nine feet in length. While the variation in radium concentration (with respect to depth in the core) was about the same for the first three stations, it differed considerably at the fourth station. In the cores mentioned above, the maximum radium concentration was found at about five feet below the surface of the core, after which it decreased. At the fourth station the concentration rose from a value of $0.35 \cdot 10^{-12}$ g of radium per gram at 3 inches to a value of $0.62 \cdot 10^{-12}$ g of radium per gram at 27 inches. The concentration was quite constant to about 60 inches, then rose to a maximum of $0.71 \cdot 10^{-12}$ g of radium per gram at 75 inches and gradually decreased to $0.43 \cdot 10^{-12}$ g of radium per gram at 106 inches.

Station II was 3 miles from Station I, Station III 5 miles further, and Station IV 7.5 miles further down the Bay, making a total distance of 15.5 miles from the flat at the mouth of the river. The average of 23 samples from four cores was $0.6 \cdot 10^{-12}$ g of radium per gram.

Although the results of the analyses show that the radium content rises to a maximum at some depth below the surface of the core, further analyses will be necessary to attempt an explanation of the rate of deposition of radium which will account for the experimental results.

In so far as the analyses have proceeded, a consideration of the average radium content of the cores and the nature of the drainage area constitutes further evidence that the radium concentration of inshore sediments, even at considerable depths, is due to a deposition of sediment from the surrounding land areas.

HOOD CANAL

The second region selected was Hood Canal, which is a narrow body of water whose total length is approximately 60 miles. It empties into Puget Sound at the north end, while the south end, which extends into the Olympic Peninsula, is closed. There are numerous rivers and streams flowing in from the Olympic mountains on the west and a few streams from the land area on the east. The stations selected for sampling, numbered from I to V inclusive, are located, with respect to the junction of the Canal with Puget Sound, at distances of 24, 29, 45, 49, and 53 miles respectively. The respective water depths were 74, 79, 74, 64, and 41 fathoms.

The lengths of the cores were as follows: 7.5 feet at Station I, 8 feet at Station II, 10 feet at Stations III and IV, and 6 feet at Station V. The cores showed no stratification at Stations I and V, very little at Stations II and IV, but considerable stratification at Station III.

The core taken at Station I had a uniform radium concentration throughout its length with an average value of $0.58 \cdot 10^{-12}$ g of radium per gram. The core from Station II also showed a uniform distribution with an average value of $0.61 \cdot 10^{-12}$ g of radium per gram. The core from Station III had a concentration of $0.86 \cdot 10^{-12}$ g of radium per gram in the upper three inches of its length; in the next five feet the concentration was fairly constant at $0.79 \cdot 10^{-12}$ g of radium per gram; the concentration decreased to $0.38 \cdot 10^{-12}$ g of radium per gram at 6 feet 3 inches and remained fairly constant, with a value of $0.44 \cdot 10^{-12}$ g of radium per gram at the bottom of the core. The core from Station IV had constant concentration for the first 8 feet of its length with an average value of $0.58 \cdot 10^{-12}$ g of radium per gram, but the concentration at 9 feet 9 inches was $0.33 \cdot 10^{-12}$ g of radium per gram. The radium concentration along the core taken at Station V was nearly constant with an average value of $0.36 \cdot 10^{-12}$ g of radium per gram.

The study of the cores from Hood Canal is incomplete and provides but little data from which positive conclusions as to rate of deposition

of radium might be based. However, some conclusions from the preliminary results of analyses are suggested. The geological structure of the drainage areas of the rivers flowing into Hood Canal has been reported by Weaver (14). Most of the west side of the Canal is composed of basalts extending from the shore of the Canal into the Olympic mountains. Some sandstone appears along the west shore from the location of Station II to Station III. Extending from Station III to Station V is a band of glacial material covering the underlying basalt. The materials exposed on the east side of the Canal are glacial sand, gravel, and clay.

The analyses of the cores show a range in the radium concentration extending from $0.33 \cdot 10^{-12}$ to $0.86 \cdot 10^{-12}$ g of radium per gram. This range is quite comparable to the range extending from the mean value of basic igneous rock, such as basalt, to a value between that of the intermediate and acidic igeneous rock, such as hornblende and granite. For the most part the cores from Stations I, II, and IV had radium concentrations comparable to that of intermediate and sedimentary igneous rock.

It is obvious that the sediment in Hood Canal is well mixed by river and tidal currents on entering the Canal. The rivers from the west side of the Canal rise in the Olympics at elevations of approximately 5,000 feet. They reach the Canal with relatively high currents and have a greater effect on the distribution of the sedimentary material than do the small rivers entering the Canal from the east, which rise from elevations of about 1,000 feet and have relatively low currents. The number of rivers entering from the west is much greater than those entering from the east. Also, there is a mixing of the materials along the axis of the Canal by tidal action.

EAST SOUND

This Sound is a long narrow body of water nearly surrounded by Orcas Island, the largest island in the San Juan Archipelago. It is approximately seven and one-half miles long and one to one and one-half miles wide. This body of water is of particular interest in as much as it contains a high concentration of plankton.

A core nine feet long was obtained at a station four miles from the mouth of the Sound at a water depth of 18 fathoms. The radium concentration was determined at one-foot intervals beginning at the surface. The samples from the first seven feet of the core, with the exception of those at the two- and five-foot depths, had a radium concentration varying between the values of $0.66 \cdot 10^{-12}$ and $0.62 \cdot 10^{-12}$ g of radium per gram. The samples taken from the two- and five-foot depths had a radium concentration of $0.52 \cdot 10^{-12}$ and $0.53 \cdot 10^{-12}$ g

per gram respectively. The bottom foot of the core exhibited a decrease in radium concentration to an average value of $0.57 \cdot 10^{-12}$ g of radium per gram.

Since the average radium concentration of the East Sound core is essentially the same as that of the cores from the Hood Canal and Skagit regions which are not rich in plankton, it seems that the biological extraction of radium must not be of prime importance in the radium deposition process.

The above analyses and the conclusions from the data so far obtained constitute a preliminary report on the cores obtained in Skagit Bay, Hood Canal, and East Sound. The completion of the mineralogical and mechanical analyses of the cores may modify or supplement the above conclusions.

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SUMMARY

Several hundred samples of marine sediments from the surface of the ocean bottom have been analyzed for radium content. These bottom samples were from the region extending from the northern tip of Alaska to the southern end of Puget Sound, including the Arctic Ocean, Bering Sea, the Alaska Peninsula, southern Alaska, Queen Charlotte Islands, Vancouver Island, and the San Juan Archipelago. The radium content varied from $0.24 \cdot 10^{-12}$ to $1.57 \cdot 10^{-12}$ g of radium per gram. The samples of high radium content were all from glacier-fed inlets.

The analysis of 23 samples from four cores gave an average value of $0.6 \cdot 10^{-12}$ g of radium per gram. These cores were from selected stations in the Puget Sound area and in the San Juan Archipelago.

The data show a definite pattern of radium concentration in ocean sediments. The radium content of samples taken off the coast or from inshore waters is comparable to that of rocks in near-by land areas or of rocks in adjacent drainage areas.

BIBLIOGRAPHY

1. Berget, Alphonse
1930. Leçons d'océanographie physique. Ann. Inst. océanogr. Monaco, N. S. *9:* 1–352.

1a. Correns, C. W.
1937. Die Sedimente des äquatorialen Atlantischen Ozeans. D. Auswertung der Ergebnisse. I. Die Korngrössenvertielung. Wiss. Ergebn. "Meteor," 1925–27, Bd. *3*, Teil 3, Lief. 2: 191–204.

2. Evans, R. D.
1934. Improved technique for determination of radon and radium in liquids. Phys. Rev., (2) *46:* 328.
3. Evans, R. D., A. F. Kip and E. G. Moberg
1938. The radium and radon content of Pacific Ocean water, life, and sediments. Amer. J. Sci., *36:* 241–259.
4. Foyn, Ernst, Berta Karlik, Hans Pettersson and Elisabeth Rona
1939. The radioactivity of seawater. Göteborg. VetenskSamh. Handl., Femte Foljden, (B) *6* (12)*:* 1–44.
5. Hernegger, Friedrich and Berta Karlik
1935. Uranium in sea-water. Göteborg. VetenskSamh. Handl., (B) *4* (12)*:* 1–15.
6. Joly, J.
1908. On the radium-content of deep-sea sediments. Phil. Mag., (6) *16* (XCI): 190–197.
7. Pettersson, Hans
1930. Teneur en radium des dépôts de mer profonde. Résult. Camp. sci. Monaco, Fasc. 81: 1–50.
8. Piggot, C. S.
1933. Radium content of ocean-bottom sediments. Amer. J. Sci., (5) *25:* 229–238
9. 1936. Apparatus to secure core samples from the ocean-bottom. Bull. geol. Soc. Amer., *47:* 675–684.
10. Sanderman, L. A. and C. L. Utterback
1941. Radium content of ocean bottom sediments from the Arctic Ocean, Bering Sea, Alaska Peninsula, and the coasts of southern Alaska and western Canada. J. Mar. Res., *4* (2)*:* 132–141.
11. Thompson, T. G., R. W. Bremner and I. M. Jamieson
1932. Occurrence and determination of iron in sea water. Ind. Engng. Chem., Anal. Ed., *4* (1)*:* 288–290.
12. Urry, W. D.
1941. The radioactive determination of small amounts of uranium. Amer. J. Sci., *239* (3)*:* 191–203.
13. Utterback, C. L. and L. A. Sanderman
1938. Radium content of some inshore bottom samples in the Pacific Northwest. J. Mar. Res., *1* (3)*:* 187–191.
14. Weaver, C. E.
1937. Tertiary stratigraphy of western Washington and northwestern Oregon. Univ. Wash. Publ. Geol., *4:* 1–266.