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RADIOACTIVITY OF OCEAN SEDIMENTS. III.*

RADIOACTIVE RELATIONS IN OCEAN WATER AND BOTTOM SEDIMENT.†

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ABSTRACT. Since its beginning, the ocean has been the repository of materials removed from the continents. All but radioactive atoms have a continuous existence and may go into and out of the ocean many times. Because radioactive substances change with time their presence in the ocean is transitory and of peculiar interest.

There is much less radium in the ocean water and much more in the bottom sediment than is appropriate to the uranium present in each place. Studies of core samples of deep ocean sediments, several meters long, reveal that some mechanism exists which removes radium, and its immediate parent ionium, from the water and leaves most of the uranium behind. The ionium produces more radium, and the excess of these two elements, unsupported by uranium, eventually disappears, leaving an equilibrium based on the small uranium content—which is of the same order of magnitude as is found in ordinary sedimentary rocks. It is now apparent that the high radium content of the ocean sediments is transitory and of no great geophysical significance. Several mechanisms for this separation and concentration are discussed.

INTRODUCTION.

PRESUMABLY the ocean came into being as soon as the Earth cooled below the condensation point of water, and it has been receiving substances leached and eroded from the continents ever since. Many of these substances have made the journey from continent to ocean and back again several times and may continue to do so. But the radioactive substances are unique in their ability to put a limit to this sort of thing, by simply ceasing to exist after a time.

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Ordinary sediments may come and go, but radium does not go on forever, and its presence in the ocean is therefore a transitory thing, possessing an essential association with the concept called time. This is true of all the radio-elements whether possessed of long or short life spans.

Shortly after the discovery of radium, its presence in all manner of rocks and soils was demonstrated by various investigators, particularly Strutt and Joly.[1, 2] Joly, having access to the Challenger Collection, tested samples brought up from the bottom of the ocean and was the first to learn that this material possesses an extraordinarily high radium content.[3] These early results have been confirmed by Pettersson[4] and others,[5, 6] so that it is now quite conclusively demonstrated that the sediments lying below about 3000 meters, and far enough from land to be beyond the range of immediate detrital material, contain a greater concentration of radium than that existing in the granites, basalts, and other original igneous rocks from which it or its progenitors must have come.

If we assign a value of 1.0 to what seems to be the average for granitic rocks (granitic rocks are highest in radium content), we find ocean-bottom sediments containing concentrations of four, six, and even ten on this scale.

RADIUM IN THE SEDIMENTS.

The higher concentrations are usually found under very deep water, or at locations remote from land masses. This leads to the assumption that the radio-elements—uranium, ionium, and radium, in particular—are each separating from the sea water at a more or less uniform rate, and that the deposit thus created is diluted, here and there, by detrital material from the land. It has been found that those samples of sediment obtained from nearer the shore tended to approach the content of coastal material,[2, 7] thereby supporting the hypothesis that the ocean water is a great, more or less uniform solution, so far as radioactivity is concerned.

The greatest concentrations reported have been found in so-called red clay, an exceedingly fine material found underlying very deep water. This material seems to contain no coarse sand or detrital material at all, and no minute shells (as of foraminifera) or even diatoms (the siliceous skeletons of minute surface plants) both of which apparently are dissolved before they reach the more profound deeps. It may be that red clay

is composed of materials formed from the sea water at these quiet, cold, and very remote regions.

A comparison between the radium content of continental rocks and of various ocean sediments is shown in Table I.

TABLE I.

Radium in Rocks and Ocean-bottom Sediments in 10^{-12} gram per gram.

Continental Rocks		Ocean-bottom Sediments	
Granites	0.2 to 5.0	Red clay	3 to 22
Basalts	0.1 to 1.0	Globigerina ooze	3 to 7
Sedimentary	0.05 to 0.5	Blue mud	1 to 3

27 Red clay samples average: 12.1.
13 Globigerina ooze samples average: 4.1.

Whatever this "red clay" may be, its high radium content is a challenge to our knowledge of the chemistry and physics of deep-ocean waters. A conclusive explanation of why these concentrations exist in ocean-bottom sediments, but not in any sedimentary rocks so far tested, has yet to be provided. Some evidence of how it comes about is offered here.

It is not uranium that is coming out of the water and into the sediment to build up, ultimately, an appropriate equilibrium amount of radium, for the surface materials have not been in place long enough for this to occur, and recent analyses have indicated that this equilibrium is attained only in sediments lying below the surface of the ocean bottom at a depth that obviously depends upon the rate of sedimentation, which varies greatly from place to place.

On the contrary, recent determinations of the uranium content of bottom sediments reveal that it is nowhere near the amount necessary to maintain the high radium concentration found in and near the surface of these sediments. In some cases, the high radium content in the surface material appears to be due to the deposition of an excess of ionium, which is the immediate parent of radium. Even in such cases, however, a considerable fraction of the radium in the surface materials must have been removed from the ocean water as radium *per se*.

RADIUM IN THE WATER.

Many measurements of the radium content of ocean water have been made since the investigations of Eve[8, 9, 10, 11] in 1907, but the recent measurements of Pettersson[12] in Sweden, and

of Evans[13] in this country, and their associates, seem to demonstrate that previous determinations of the radium in ocean waters have erred on the high side. Both groups of investigators offer independent confirmation of this point, and their determinations are in good agreement when one considers the very different sources of the samples and the different techniques.

Thus the average of 12 samples of Pacific-Ocean water at various depths plus one composite sample of Atlantic water as determined by the Evans group is 0.8×10^{-16} gram Ra per cc., compared with an average of 0.87×10^{-16} gram Ra per gram as determined by Pettersson's group for 23 samples of sea water around the Swedish coast.* As shown in Table II, the sea water, weight for weight, is more than 10,000 times poorer in radium than the igneous rocks and 1,000 times poorer than the sedimentary rocks. Still more striking is the difference in the radium content between the sea water and the ocean sediments; a ratio of one to 170,000 for the average value of surface specimens of Red clay and one to 60,000 for the average value of the Globigerina oozes. The mechanism which is concentrating the radium in the ocean sediments, whatever it may be, is truly efficient.

TABLE II.

Ratio of the Radium Content of Ocean Water to that of other Materials.

Ocean water	1
Sedimentary rocks	1,000
Igneous rocks	10,000
Globigerina ooze	60,000
Red clay	170,000

RELATION OF RADIUM TO URANIUM IN THE WATER AND SEDIMENTS.

Measurements mentioned below indicate a deficiency of uranium in the surface of the ocean sediments, compared with that concentration which is necessary to maintain the radium content. Is this uranium held in solution, or in some other manner, in the water above?

* Evans, Kip, and Moberg infer from their measurements that an increase of radium content with depth exists. This conclusion is worthy of further experimental verification. The average radium content of the ocean water is sufficient for the present discussion. The average of the measurements of Pettersson and Rona is quoted here, but they prefer to give their earlier results less weight and suggest a value of 0.7×10^{-16} gram Ra per gram. A round figure of 0.8×10^{-16} gram Ra per gram will be used.

Hernegger and Karlik[14] have determined the uranium content of sea water by a method which is independent of the radium measurement. Their results demonstrate a relationship with salinity. Excluding specimens showing a salinity of less than 34 per mille, e.g. those from fjords and the Baltic Sea, the average uranium content is 1.3×10^{-9} gram per gram. The ratio of radium to uranium in equilibrium being 3.40×10^{-7}, the sea water requires 0.24×10^{-9} gram uranium per gram ($0.8 \times 10^{-16}/3.4 \times 10^{-7}$) to maintain its radium content. There is, therefore, more than five times as much uranium in the ocean water as is required to maintain its radium content.

To return to a consideration of the bottom sediments, it will be remembered that the surface of the sediments is deficient in uranium compared with the radium content. Qualitatively, then, the two parts of the ocean fit together. The water has too much, and the bottom too little uranium for the amount of radium in each. By means of a method which differs from that employed by previous investigators,[14, 15, 16] preliminary measurements have been made by Urry[17] of the uranium content of samples from a core taken from the Cayman Trough near Jamaica. The activity of uranium to radium at the top of this core averages 0.24, which indicates that the uranium content of the surface sediment is only one-fourth of that required to maintain the radium content.

Therefore the excess of uranium in the water has an approximately quantitative counterpart in the deficiency of uranium in the surface sediments.

These data are too meager to warrant further elaboration at this time, but the significance of this situation is that the ocean is a reservoir for most of the uranium that is poured into it, while the ocean bottom is the repository for the transient radium. The ocean-bottom sediments should therefore reveal some interesting relations, and they do.

THE RELATION OF RADIUM TO IONIUM IN THE SEDIMENTS.

During the past few years a number of radium determinations have been completed on samples from deep-sea cores of ocean-bottom sediments by a method which was briefly outlined in a presentation of the preliminary results.[18] We shall consider two examples, representing two classes of cores. All the other cores so far examined fall, without exception, into these two classes.

The first class is illustrated (Fig. 1, A) by the results from a core of Globigerina ooze that supplied the samples for the uranium determinations. The radium content is plotted against the depth below the surface of the ocean bottom. We may consider this curve as reflecting the progress, with time, of the radium content of any particular sample. There is some radium being deposited from the ocean, and also more ionium than is necessary to uphold this radium concentration, and much less uranium than is required to uphold this ionium concentration. The radium content therefore begins at a figure representing

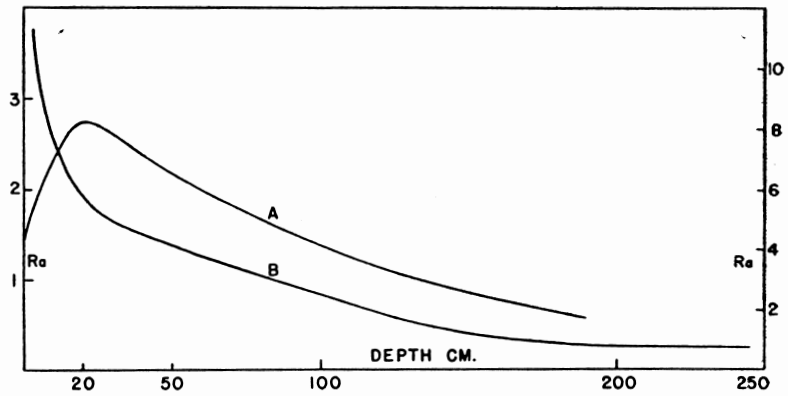

Fig. 1. The radium content of deep-sea cores plotted as a function of depth below the surface of the sediment.

A. Cores of Class I. Radium in units of 10^{-12} gram per gram—left-hand ordinate.

B. Cores of Class II. Radium in units of 10^{-12} gram per gram—right-hand ordinate.

the deposition of radium *per se*, and then increases as it acquires that which is produced by the ionium, and eventually it attains equilibrium with the ionium. It then decreases, as the ionium decreases, until the ionium content reaches that value fixed by equilibrium with the uranium content, which in this case must occur at a considerable depth below the bottom of the core. The radium content would then be approximately 0.35×10^{-12} gram radium per gram and it would remain practically constant from this point on down into the sediments, that is, over long periods of geological time. Such a value is in good agreement with the radium content of sedimentary rocks (see Table I). We are now attempting to obtain cores

of greater length and from the more remote depths of the ocean where the deposition may be considerably slower. It is hoped that some of these cores will reveal the attainment of the final equilibrium between the uranium, ionium, and radium in their lower portions.

The second class, in which we have so far only one example, is illustrated (Fig 1, B) by the results from a single Red-clay core, kindly furnished us by Doctor Revelle of the Scripps Institution of Oceanography. Unfortunately, it was not possible to obtain a number of small, closely spaced samples near the top of this core, but from other considerations it is reasonably well established that the initial steep gradient is due to the disintegration of unsupported radium. Whether or not the ionium in this particular sediment is deposited in excess of the concentration required to uphold the radium content, that is to say, whether or not there is a peak value, can be calculated from these available data. This particular Red clay runs true to character in having a high radium content, i.e., 11×10^{-12} gram radium per gram for the average of the top seven centimeters. At the bottom, 246 cm. below the surface, the radium content has decreased to only 0.8×10^{-12} gram radium per gram. Moreover, towards the bottom the radium content appears to be close to that nearly constant value which is attained when the ionium content has fallen to the value in equilibrium with the uranium. The uranium content of this core has not yet been measured.

Most of the interesting features of these curves, such as might be obtained in the first few centimeters, are lost by the destruction of the stratification which occurs in the older method of sampling with the telegraph snapper.[19, 20, 21]

There are obvious possibilities of determining the rate of deposition of ocean-bottom sediments from these ascertainable radioactive relations, but there are a number of assumptions which must be removed or substantiated before such rates can be determined with confidence.

THE MODE OF DISTRIBUTION BETWEEN THE WATER AND SEDIMENTS.

The distribution of the radio-elements between the ocean and its sediments is established with reasonable certainty. How and why such a distribution occurs is a challenge to our knowledge of the chemicophysical properties of ocean water.

We may classify the various mechanisms that have been proposed as follows:

1. Biological extraction.
2. A specific example of biological extraction, namely the possibility of concentrating radium in the bottom through the deposition of calcareous skeletons which constitute a large portion of many ocean sediments.
3. Chemical precipitation.
4. Physical processes, such as adsorption or base exchange.
5. Submarine volcanic eruptions with consequent extreme chemical reactions.

1. *Biological Extraction.* Several investigators[12, 13, 22] have found that a variety of aquatic animals and plants have the property of concentrating radium in their structure so that they contain concentrations which are, weight for weight, much greater than that of the water in which they live. This is true in particular of the planktons. Nevertheless, an inspection of the quantitative aspect of their rôle as carriers of radium to the ocean bottom reveals that they can remove no more than a few per cent of the radium from their habitats each year.[12] Moreover, it is known that their remains mostly dissolve before reaching any profound depth. Therefore it seems improbable that the planktons play any major rôle in producing the high radium concentrations in the surface of the sediments. Even an increasing radium content of ocean water with depth, as has been reported,[13] is difficult to explain by such an inefficient process when one considers the comparatively rapid vertical circulation of the water in the ocean.

2. *Calcium.* The Globigerina ooze—a very common type of ocean sediment—is composed largely of calcareous shells, chiefly the remains of foraminifera. It is plausible to reason that considerable amounts of radium may be extracted with the calcium by the living foraminifera in building their shells. It appears, however, that the ratio of radium to calcium in mollusc shells is not greatly different from the same ratio in sea water[12] and that the depletion of calcium in sea water due to the foraminifera is not more than a few per cent. Moreover, the Globigerina oozes of which the core from the Cayman Trough, previously discussed, is representative, do not have particularly high radium contents—in fact, the calcareous material seems to act as a diluent. This is demonstrated in

Table III. The pure Globigerina layers in these cores are composed almost entirely of shells, but these are usually filled with fine material of other character. When the carbonate shells are separated from their contents, it is expected that the dilution effect will be more evident. It would be interesting to have similar data for the diatom oozes which are siliceous rather than calcareous.

TABLE III.

Comparison of the Radium Content of nearly pure Globigerina with normal Globigerina Ooze.

Core	Depth	Radium Content in 10^{-12} g per g
P–136	5 cm. above the Globigerina stratum	2.38
	Globigerina stratum	1.14
	20 cm. below the Globigerina stratum	2.22
P–135	12 cm. above the Globigerina stratum	1.30
	Globigerina stratum	0.70
	9 cm. below the Globigerina stratum	1.29

3. *Chemical Precipitation.* Chemical precipitation has been alternately proposed and discarded in accounting for the high radium concentrations in ocean sediments. A few authors have suggested certain chemical sequences in discussing the uranium and ionium,[5, 12] but such discussion has been limited because the quantitative distribution of uranium and ionium between the water and sediments was not known. The distribution of uranium and ionium, as demonstrated, may be explained by the known chemical facts concerning these elements.

The concentration of ferric iron in ocean water is considerably lower than it should be if all the iron that the ocean receives were held in solution.[23, 24] It is known that iron and particularly ferric iron compounds are very unstable in sea water. The iron is probably precipitated as micelles of ferric hydrate, and this accounts for the relatively high iron content of that portion of the sediment which is not calcium carbonate. The deeper ocean waters are richer in iron than those of the surface.[23] The precipitation of iron hydroxide is a recognized method of precipitating thorium and therefore its isotope ionium, from dilute solutions. Furthermore, the precipitation of uranium is inhibited by the presence of the carbonate ion.

Proposed mechanisms for the chemical precipitation of ra-

dium fail, in so far as there is no suitable analog of radium other than calcium, in sufficient concentration in the sediment. The calcium is mostly, if not entirely, due to calcareous shells. This possible mode of precipitation has been dealt with already.

It has been proposed that the precipitation of ionium accounts for the lack of radium in the ocean compared with the uranium.[12] If this were true, the radium content in the immediate surface of the sediments would be extremely low, only building up to a high value at a distance below the surface appropriate to the build-up of radium from ionium. All the cores so far examined exhibit a radium content in the immediate surface such as can only be explained by a direct removal of radium from the water. The simultaneous precipitation of the ionium is, of course, a contributory factor in creating a low radium content in the water compared with the uranium content.

4. *Adsorption.* The phenomena of adsorption and base exchange, as assisting in the concentration of radium in ocean-bottom sediments, have not been given the consideration they deserve.

5. *Submarine Volcanic Eruption.* This explanation has been suggested and ably developed by Pettersson,[4, 12] whose investigations of radioactivity and oceanography are the classics in this field. Being a highly intermittent phenomenon, the effect of submarine vulcanism should be exhibited by one or more definite breaks in the curve of radium content plotted against depth below the ocean bottom. Moreover, the trend of the curve for this relation of radium against depth, in the case of the Red-clay core, is very difficult to explain if the high radium content in the surface is to be due to submarine eruption.

CONCLUSIONS.

Despite our fragmentary knowledge of the relative concentrations of the radio-elements in the upper strata of the ocean sediments we arrive at a conclusion of considerable importance. The high concentrations of radium in the ocean sediments are purely superficial and do not extend to any appreciable depth below the ocean bottom. At a point but a few meters down into what may be many meters of sediment, the radium content reaches the value in equilibrium with the uranium. This radium content is comparable with that of the sedimentary rocks, and apparently there is no greater generation of heat by radio-

activity in the ocean floor, to blanket the flow of heat from below, than there is in the continental rocks.[5] It would appear that the opposite may be true.

Our knowledge of the chemical, physical, and biological processes involved in the distribution of the radio-elements between the ocean and its floor is at present rather meager. More data concerning the distribution of these elements are essential to a better understanding of this problem.

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