

RADIOACTIVITY OF OCEAN SEDIMENTS. V. CONCENTRATIONS OF THE RADIO- ELEMENTS AND THEIR SIGNIFI- CANCE IN RED CLAY.

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ABSTRACT. The relationship between the radio-elements, uranium, ionium, and radium, in those deep-sea deposits known as "Red clay" is similar to that previously described for the calcareous sediments of the ocean. The Red clay, represented here by a core 246 cm. long, is distinguished from the calcareous sediments by a very rapid decrease in the radium content just below the surface of the ocean bottom, and the attainment of the final equilibrium between the above three radio-elements in the bottom quarter of the core, which signifies a very slow deposition compared with that of the calcareous deposits. The radium content at equilibrium with the uranium is only seven per cent of that near the surface of this Red clay deposit. The high surface concentrations of radium and ionium, particularly in Red clay, are therefore only transient phenomena, produced by some unknown mechanism which concentrates these elements, relative to the uranium content, during the deposition of the sediment.

INTRODUCTION.

THE radioactivity of those deep-sea sediments named Red clay by Murray and Renard in their standard work on Deep-Sea Deposits¹ is particularly interesting. Radium analyses of several types of ocean sediments demonstrate that the surface of the ocean bottom is much richer in radium than are the rocks of the continents.² The results of Joly³ and of Pettersson⁴ show a consistently higher radium content in the Red clays than in the Terrigenous muds and Globigerina oozes. Piggot's determinations of the radium content of 28 of the specimens secured by the *Carnegie* on her last cruise confirm this relation.⁵ A comparison of all the results is given in Table I. Dr. Roger Revelle has recently communicated to us his classification of these samples collected by the *Carnegie* on this cruise. This classification was not available at the time of publication of the first paper of this series,⁵ and the designations used were those furnished the author. The new classification indicates that the highest radium concentrations are in radiolarian ooze, which is in agreement with Joly's results.

The geophysical significance of this relation and an explanation of the difference between the radium content of continental rocks and the various types of ocean sediments necessitated an

investigation of the radioactive properties of these sediments below the immediate surface of the ocean bottom. Measurements of the radium content at various depths in ocean sediments, consisting of Blue mud and Globigerina ooze,⁶ have demonstrated that the high radium concentration is not maintained below the surface, and it has been concluded that the ionium concentration controls the decrease of the radium content until ultimately equilibrium is established with the small amount of uranium present.⁷

These results are of importance in a study of the thermal history of the ocean basins and the manner of transport of material from the land areas to the ocean deeps. The relations existing between the radio-elements, uranium, ionium, and radium, in the sediments provide an objective method of determining the rate of deposition of the ocean bottom and the changes of this rate which vary with both time and locality.^{8, 9}

TABLE I.

Ratio of the Average Radium Content of Various Types of Sediment to that of Red Clay for Surface Specimens of the Ocean Bottom.

Type of Sediment	Joly	Pettersson	Piggot ^b
Terrigenous muds	0.1 (1) ^a	..	0.3 (2)
Diatom ooze	0.6 (3)
Globigerina ooze	0.25 (5)	0.25 (4)	0.6 (12)
Radiolaria ooze	1.3 (2)	0.9 (2)	1.6 (3)
Red clay	1.0 (3)	1.0 (14)	1.0 (7)

^a The number of individual results.

^b Based on the final classification of the *Carnegie* samples by Dr. Roger Revelle at the Scripps Institution of Oceanography.

A similar examination of Red clay is interesting because of its phenomenal radium content and slow accumulation. Moreover, Red clay probably constitutes the foundation material of the pelagic deposits formed in deep water and remote from land. The various types of these deposits differ only in the admixture of varying quantities of calcareous material (Globigerina and Pteropods) or siliceous deposits (Diatoms and Radiolaria), and the oozes are classified according to the predominance of the remains of one or the other of these organisms.¹⁰

The collection of core samples of the ocean bottom obtained with the coring apparatus of this Laboratory^{11, 12} is confined to the Atlantic Ocean, Caribbean Sea, and Gulf of Mexico, and

contains no sample of Red clay. The examination of a Red-clay core was made possible by the coöperation of Dr. Roger Revelle of the Scripps Institution of Oceanography, La Jolla, California, who supplied the samples and the mechanical and chemical data.

DESCRIPTION OF THE CORE

A core of brownish-red clay, 246 cm. long, was obtained from a depth of 4080 meters on August 2, 1938, by the research vessel *E. W. Scripps* at about 220 miles west of San Diego, California. The vessel was under the direction of Dr. F. P. Shepard, and a gravity coring apparatus devised by K. O. Emery and R. S. Dietz^{20,21} was employed. The mechanical and chemical analyses of this core (FPS-186, our number P-259) as furnished us by Doctor Revelle are partially reproduced in Table II. The very low percentage of CaCO_3 and of material greater than 50 microns in size, and the high percentage of

TABLE II.
A Portion of the Mechanical and Chemical Data on
Core FPS-186 (P-259).

(Reproduced by permission of Dr. Roger Revelle).

Depth in core cm.	% sand (\geq 50 microns)	% silt (5-50 microns)	% clay (1-5 microns)	% colloid ($<$ 1 micron)	% organic nitrogen ^a	% CaCO_3	% Cl ^b	% H_2O of wet weight ^c
2.5- 7.6	0.5	21.4	33.7	44.4	0.058	0.46	2.55	57.3
28-33	1.3	21.7	29.8	47.3	.068	..	2.44	56.0
48-53	0.9	22.6	32.4	44.1	.068	..	2.45	56.0
68.5-73.5	0.6	23.0	31.6	44.8	.056	..	2.30	54.5
89-94	1.0	20.7	31.7	46.6	..	0.10	2.26	53.7
130-135	1.2	21.7	32.1	45.0	.056	..	2.16	52.9
170-175	0.3	20.6	32.7	46.4	.056	..	2.33	54.9
216-221	2.3	28.2	33.7	35.8	.058	0.55	2.50	56.7
236-241	57.3
241-246	0.4	25.6	32.7	41.3	.052

^a % of air-dried sample.

^b % of sample dried at 105° C.

^c Calculated from the % Cl in the preceding column. The water content has been determined also by the usual method of dehydration. The values are in general agreement with those quoted here but are subject to error which is due to an evaporation of the water prior to analysis. The % H_2O by the "chloride method" may be subject to error by a constant factor, but only the values relative to one another are required for this discussion.

material less than 1 micron in size, suggest that this clay may be representative of the residuum of the various pelagic deposits, as suggested by Murray and Hjort.¹⁰ The analyses show that the core is uniform in composition throughout its length so that the radioactive relations are not complicated by differences in the type of deposit.

Chemical analyses of Red clays as a class are numerous,¹³ but offer little evidence of the mode of their formation. A sequence of chemical events in the production of Red clay has been suggested by Murray and Hjort.¹⁰ No complete chemical analysis exists for this core.

RADIUM MEASUREMENTS.

The samples, which were removed from the core at various depths and sent to this Laboratory in small vials, contained between 10 and 35 per cent of water at the time of analysis, because they had partially dried by exposure to the atmosphere. They were dehydrated at 105°C. to constant weight, powdered, and well mixed. The radium was determined by the technique previously described^a by the authors in the AMERICAN JOURNAL OF SCIENCE.¹⁴

Table III shows the experimentally determined values of the radium content per gram, Ra , of dry-weight sediment. For an analysis of these results, to determine the rates of deposition, it is necessary to express the content on a volume basis.⁶ This requires a knowledge of the weight of dry material, ρ , in a centimeter cube of the wet sediment, which has been determined for this core by a different method from that previously used for the Piggot cores.⁶

If a is the fractional water content by wet weight of sediment given in Table II, and d_g the mean grain density of the particles, then

$$\rho = \frac{d_g(1-a)}{ad_g + (1-a)} \dots \dots \dots (1)$$

The mean grain density d_g is not accurately known. Between $d_g = 2.5$ and 2.7 only the absolute values of ρ are changed. For the present discussion the values relative to one another are sufficient. In Table III, ρ is calculated for $d_g = 2.50$.

^a The results in Table III are based on a calibration of the apparatus with a standard radium solution containing 10^{-11} g. Ra prepared by the National Bureau of Standards.

The radium content per centimeter cube R is calculated from

$$R = Ra \times \rho \dots \dots \dots (2)$$

The shape of the curve in Fig. 1, where the radium content in grams per gram of dry sample is plotted against the depth in the core, is altered inappreciably by the conversion of units tabulated in the final column of Table III.

TABLE III.

Radium Content of a Red Clay Core from the Pacific Ocean.

Core No. P-259 (FPS-186). Depth of Water 4080 meters.

Latitude $30^{\circ} 41' N$. Longitude $121^{\circ} 46' W$.

Specimen No.	Depth cm.	Ra		ρ g./cm. ³	R
		Radium content in 10^{-12} g./g.			Radium content in 10^{-12} g./cm. ³
P-259-0	2.5-7.6	10.79 \pm 0.13		0.574	6.19
P-259-28	28-33	4.40	0.06	0.598	2.63
P-259-48	48-53	3.96	0.04	0.598	2.37
P-259-68	68.5-73.5	3.26	0.05	0.626	2.04
P-259-89	89-94	2.70	0.03	0.641	1.73
P-259-129	130-135	1.43	0.03	0.656	0.94
P-259-170	170-175	0.82	0.02	0.618	0.51
P-259-216	216-221	0.70	0.01	0.585	0.41
P-259-241	241-246	0.76	0.01	0.574	0.44

DISCUSSION.

Sampling. The individual samples represent about 5 cm. of core-length, which is longer than desirable, particularly near the surface of the sediment, where the radium content is changing rapidly, as shown in Fig. 1. The results demonstrate the importance of the first few centimeters of such a sediment.

Interpretation. It has been demonstrated that the radium content with respect to depth in Globigerina ooze is controlled by the ionium concentration.^{2,6} The existence of a maximum radium concentration at a certain distance below the surface in such sediments, and in others since examined, substantiates this interpretation. The attainment of a maximum radium content is due to the fact that in any given time the radium deposited with the sediment is less than the amount appropriate to equilibrium with the ionium that is also precipitated. This Red-clay core shows no maximum, because the radium deposited was in excess of the amount appropriate to equilibrium with the ionium.

The ultimate attainment of a constant radium content with increasing depth has been predicted,² because one consequence of the interpretation is that the radium and ionium must finally reach equilibrium with the uranium present. In the lowest

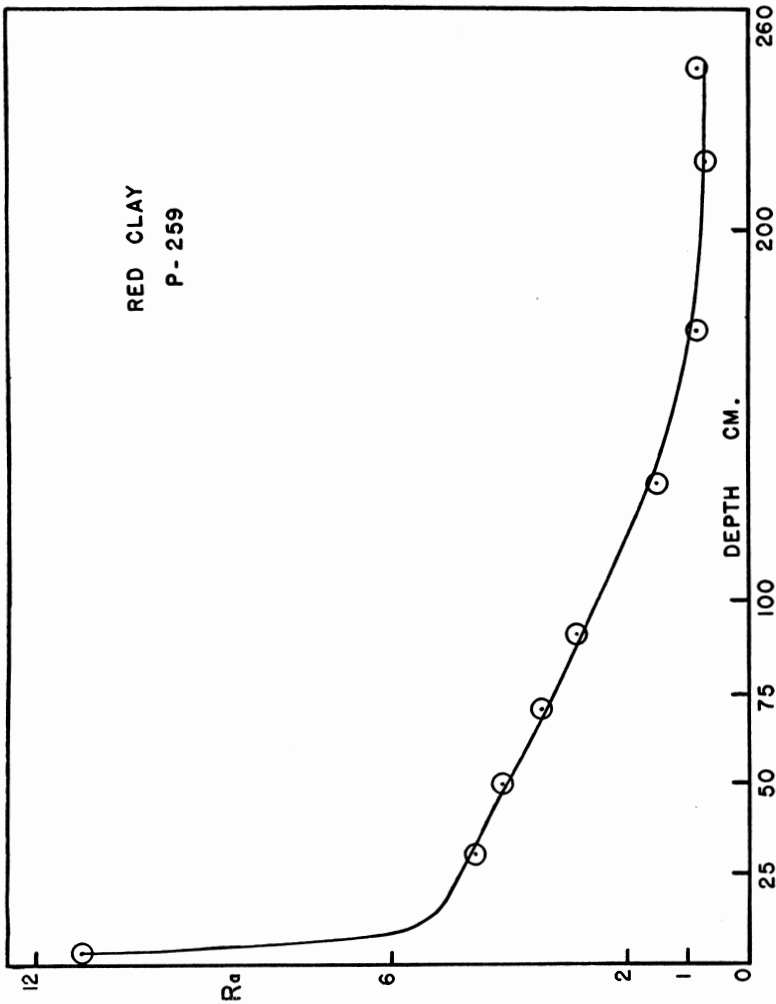


Fig. 1. The variation of the radium content of a deep-sea Red clay with the depth in the core. The radium is expressed in 10^{-12} g. per g. of dry sample. The radium values plotted here are 4.1 per cent higher than will be found in Table III. This represents the difference between our laboratory radium standard and the new standard prepared by the National Bureau of Standards.

70 cm. of this Red-clay core, which probably represents a considerably greater depth of sediment, the radium content is approximately constant at a value of 0.76×10^{-12} g. per g. This is only 0.07 of the radium content near the surface of the sediment. The significance of this fact in geothermal studies

has been discussed.^{2,5} The attainment of equilibrium within this depth indicates a very slow rate of sedimentation.⁶

Uranium Content. The uranium content of the Red clay can now be calculated from the equilibrium state in the sediment which is represented by the lower portion of this core and is $0.76 \times 10^{-12} / 3.4 \times 10^{-7} = 2.2 \times 10^{-6}$ g. uranium per g. of dry sample. The uranium content of a Globigerina ooze (core P-137) from the Cayman Trough in the Caribbean Sea has been measured directly.⁷ Within the limits of the experimental uncertainty, the amount of uranium is the same in the surface of this Globigerina ooze, at the place of the maximum radium content (20 cm. below the surface), and in the bottom of the core where the radium has decreased to 0.2 of the maximum value.⁷ A mean value of 0.84×10^{-6} g. uranium per g. was found. If the calcium carbonate content of core P-137 is estimated to be 70 per cent of the dry material, a value of 2.8×10^{-6} g. uranium per g. on a calcium carbonate-free basis is obtained. Little significance can be attached to the agreement between the calculated uranium content of the Red clay and the measured value of the uranium in the Globigerina ooze reduced to a non-calcareous basis, because of too few results. It seems reasonable to assume, however, that the uranium content, calculated for the bottom of the Red-clay core, is fairly representative of the whole core.

The deficiency of uranium, compared with the radium, in the surface of the ocean sediments can best be illustrated by the activity ratio of uranium to radium ($\lambda_{UI}N_{UI}/\lambda_{Ra}N_{Ra}$) which is unity for equilibrium. The activity ratio in the surface of the Globigerina ooze (core P-137) is 0.24⁷ and is as low as 0.07 for this Red-clay core.

An approach to a part of the present problem, stimulated by the early speculation of one of us (C. S. P.)⁵ that a highly concentrated deposition of uranium may account for the high radium content of Red clay, was made by Evans and Kip¹⁵ without recourse to cores of ocean sediment. These authors compared their measurements of the radium content of the so-called fossil deep-sea Red clays from the vicinity of the Noil Tobee river in Timor¹⁶ with the earlier radium measurements in the Geophysical Laboratory on the Red-clay specimens from the surface of the bottom.⁵ The deep-sea origin of the clays from Timor has been questioned, but if one accepts this origin,

they represent material comparable in radioactive properties with the bottom of this Red-clay core. Comparison of the three radium results of Evans and Kip for the Noil Tobee clays with the average value of the radium content of 13 deep-sea Red clays (9.5×10^{-12} g. Ra per g.), gives activity ratios of uranium to radium in the surface of the deep-sea Red clays equal to 0.03, 0.06, and 0.37. It should be noted, however, that while this result is in qualitative agreement with the present analysis in demonstrating a deficiency of uranium in the surface of the sediments, the same result would have been obtained if almost any land formation had been sampled.^b Until the deep-sea origin for the Noil Tobee clays has been demonstrated the comparison is without significance, and the converse argument is equally invalid.

Ionium Content. It was impossible to derive any information concerning the approach to the equilibrium state in the fossil clays. From the present results for a Red-clay core and from the data for the Globigerina ooze and Blue mud⁶ and the examination of a number of North Atlantic cores, it is concluded that the deposition of ionium plays the dominant rôle in the radioactive relations existing between the surface of the sediments and the depth at which uranium, ionium, and radium are all in equilibrium. This conclusion is very important because it offers a method of approach to the chronology of ocean sediments. The half-life of ionium is 82,250 years, whereas that of radium is 1690 years. If the dominant rôle be played by radium, as proposed by Evans and Kip,¹⁵ and the ionium be present in an amount approximating that in equilibrium with the uranium, the attainment of equilibrium will be confined to a few centimeters of Red clay, as may be calculated from estimates of the rate of deposition of ocean sediments.¹⁷ On the other hand, the approach to the equilibrium between ionium and uranium, which is experimentally ascertained by the variation in radium content, provides a measure of time over a span of half a million years. This is sufficient to give a chronology for the greater part of this Red-clay core and the entire length of all the other cores so far examined.

Lateral Distribution of Radium. The geographical distri-

^b See Table 1, Radioactivity of Ocean Sediments, III. This table compares the radium content of the various types of rocks with that of the ocean sediments.

bution of radium in the surface of the ocean sediments has been given in the first of this series of papers.⁵ It is interesting to note a remarkable uniformity of the radium content of the surface sediments as represented by the samples from four *Carnegie* Stations, Nos. 132, 133, 136, 137. These stations lie approximately on a line, some 1500 nautical miles in length, extending from the position of the core here discussed towards the southernmost of the Hawaiian Islands. The radium varies within the narrow range of 9.0 to 10.4×10^{-12} g. per g.; values that are close to the radium content of 10.8×10^{-12} in the top sample of this Red-clay core. The significance of this constancy is not apparent, but it is mentioned to draw attention to the possibility of correlation with other oceanographic properties. The samples from four *Carnegie* Stations, 149, 151, 153, 156, on a course of comparable length, in a direction from the above line south towards Christmas Island, show marked fluctuations by comparison. The recent classification of the Carnegie samples by Revelle indicates that the four specimens Nos. 132 to 137 were correctly designated Red clay in the first paper of this series.⁵ The samples Nos. 149 to 156 originally designated Red clay are classified by Revelle as one Red clay (149), two Radiolarian oozes (151 and 153), and one siliceous Globigerina ooze (156). Thus the fluctuations in this group are explained.

Distortion. The problem of determining the distortion that occurs when the core sample is taken has been mentioned previously.⁶ From our experiments in the varved-clay pits near Hartford, Connecticut, it is obvious that successive equal increments of core represent increasingly longer increments of the sediment, as the coring-bit penetrates farther into the sediment. Moreover, the true depth to which the sediment is sampled is not the depth of instrument penetration in the case of the varved clays, but lies between the length of core obtained and the depth of instrument penetration. The penetration of the coring-bit taking this Red-clay core by a technique differing from that used by Piggot, was about 366 cm. for a core 246 cm. long. Knowledge of the exact corrections to be applied to the different types of sediments is lacking, although progress has been made in a qualitative manner.¹⁹ Experiments with the coring bit²¹ which was used to collect this Red-clay core indicate a very different type of distortion from that found by one of us.¹⁹ Dr. Revelle informs us that in cores taken with their instrument, the ratio of core length to penetration is constant.

Other Results. Four out of the six short cores analyzed for radium by Pettersson⁴ are designated as Red clay. At Station P. A. 2081 in Table IV, the gradient of the radium content against depth is very similar to that in Fig. 1. Core P. A. 2075 shows a smaller decrease of radium content with depth. Core P. A. 1160 contained 19 per cent of calcium carbonate, but Murray and Renard's¹ arbitrary lower limit of 30 per cent calcium carbonate for a calcareous ooze places this sediment in the class of Red clay. In both the absolute radium content and the increase just below the surface (14 cm.) it is more characteristic of our curves for Globigerina ooze.⁶ Only core P. A. 1169 shows a decided departure in principle from all Pettersson's results and those for the present Red-clay sediment. Thoulet's remarks on the chemical and mineralogical analysis of this material and its richness in "Volcanic Elements" may be pertinent.¹⁸

TABLE IV.

Radium Content of Red-Clay Cores Collected by the
Princess Alice II. (After Pettersson.)

Station	Latitude	Longitude	Depth of water meters	Depth in core cm.	Ra in 10 ⁻¹² g./g.	% CaCO ₃
PA 2081	26° 37' N.	36° 35' W.	5382	2	9.3	
				7	8.9	
				17	4.4	
PA 1160	14° 00' N.	30° 01' W.	5443	8	3.7	19
				14	4.3	19
PA 2075	25° 57' N.	35° 08' W.	5580	2	8.5	
				14.5	6.7	
PA 1169	12° 05' N.	33° 31' W.	6035	12.5	7.8	1
				18.5	30.3	1

CONCLUSIONS.

The variation of the radium content with depth below the surface of ocean deposits of Red clay is so typical of the approach, with time, to radioactive equilibrium in a mixture of radium, ionium, and uranium, introduced into a system in amounts quite unrelated to the equilibrium quantities, that it is difficult to formulate an interpretation for this variation other than that given above. It is supported by similar relations between the radio-elements in core samples from widely separated regions representing different classes of ocean sediments.

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