Distribution of Radioactivity in Pelagic Clays[1]

By GUSTAF ARRHENIUS and EDWARD D. GOLDBERG

Scripps Institution of Oceanography, La Jolla, California and California Institute of Technology, Pasadena, California

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Abstract

An attempt is made to study the localization of radioelements in different mineral phases of pelagic clay sediments. The results so far obtained indicate that the ionium supported radium is redistributed by diffusion through the interstitial solution and that the authigenic zeolite phillipsite plays an important role as a scavenger of radioelements within the deposit. The mechanism of transfer of radioelements from the ocean to pelagic deposits is discussed, and points of uncertainty in the interpretation of the distribution of gross beta-activity are indicated.

The distribution of radioelements in marine sediments has been extensively studied, primarily for use as a geochronological tool. However, serious shortcomings in dating pelagic sediments have arisen in the cases where uranium and its daughter products have been utilized (a summary of the present situation is given by KRÖLL, 1954). Much of the difficulty in the interpretation of the distribution of uranium, ionium and radium in pelagic sediments stems from a lack of knowledge of the chemical behavior of these elements in marine waters as well as in the sediments.

The purpose of the present investigation was to obtain a deeper insight into the chemistry of the natural radioactive elements in marine deposits through the study of the radioactivity in different components of the pelagic clays.

Experimental

The gross beta-activity of clay samples was determined with a windowless flow counter (Nuclear Instrument and Chemical Model

Table 1. Pelagic sediment samples used for the investigation

Sample	Expedition	Core	Latitude	Longitude	Depth	Description
A	Capricorn	33 BG	12° 46′ S	143° 33′ W	4375 m	Mixed material mainly from the lower part of the 128 cm core
B	»	49 BP	9° 17′ N	124° 09′ W	4400	0—24 cm
C	»	21—25 HG + 33 BG	16.5°—17° S	159°—163° W	4375—5150	Mixed material
D	»	31 BG	17° 29′ S	158° 40′ W	4900	4—12 cm
E	»	31 BG	17° 29′ S	158° 40′ W	4900	Mixed material
F	Yo—Yo	7 P	20° 50′ N	125° 11′ W	4520	0—30 cm
	Capricorn	23 HG	16° 59′ S	161° 35′ W	5150	Entire core. Each sample integrating vertically over 4 cm
G	»	39 BG	15° 02′ S	113° 49′ W	2940	Top 4 cm

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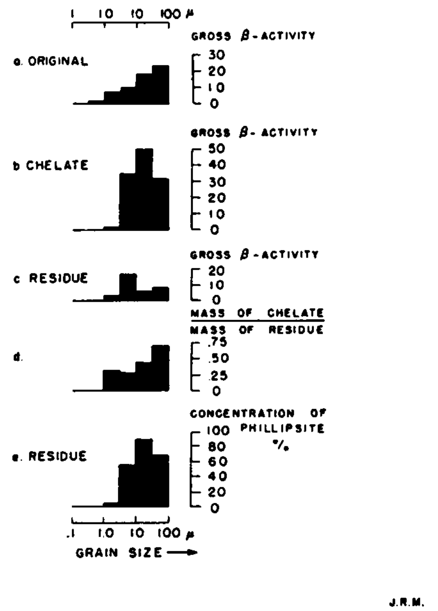

Fig. 1. Distribution of properties in sample A.

D-46 A), in the Geiger region. The powdered sample was compressed into an aluminum planchet with a diameter of 3.1 cm and a depth of 0.2 cm giving 0.1—0.2 g of solid per cm^2 of sample surface. For small samples equally deep planchets were employed with diameters of 1.5 and 1.0 cm and the corresponding net count was multiplied by the appropriate surface factors. The gross beta-activity is mainly due to the decay products of radium and to a minor extent to UX, potassium-40 (about 3 counts per minute), and beta emitters of the thorium family. Loss of emanation would thus markedly influence the results.

The gross beta-activity of the different size fractions of a ferruginous pelagic clay from the South Pacific (Sample A, see Table 1) demonstrated that the coarse fractions are considerably more active han the fine fractions (Fig. 1a and table 2). Since the zeolite phillipsite displayed a similar size distribution (figure 1e), it appeared possible that the activity was associated with this mineral.

To check this assumption, phillipsite in mixed material from the cores *Capricorn 21—25 HG* and *33 BG* was isolated from other minerals by repeated centrifugation of the grains larger than 80 μ in an ethylene tetrabromide-diethyl phthalate mixture with a density of 2.16. The lighter fraction consisted entirely of phillipsite, mostly in the form of single lathes. An intermediate fraction of density 2.16—2.28 contained approximately 95 % of this mineral in the form of crossed twins and spherolithic aggregates, approximately 3 % of manganese micronodules and the rest fossil fragments and unidentified minerals. The heavy fraction with a density greater than 2.50, constituting about 40 % of the size fraction used, consisted mainly of manganese micronodules, with subordinate amounts of feldspar, quartz, phosphatic fossil fragments, fish teeth, foraminiferal tests and 6 % phillipsite. The net activity of the light, intermediate and heavy fractions were 32, 42 and 16 counts per minute respectively.

Radioautographs were prepared of the light (pure phillipsite) and the heavy (phillipsite-poor) fraction by spraying a thin coating of lacquer over a glass slide, distributing the grains over the sticky surface and coating them with another thin spray of lacquer. After drying the specimens, a piece of Eastman No-Screen X-ray film was brought in contact with the mount and exposed for seven weeks. In the light fraction all grains (439) were active enough to give an autograph. In the heavy fraction 130 out of 3,200 grains or 4 % of the sample produced darkening of the film. This is in reasonable agreement with the phillipsite content of 6 %.

Additional autographs were prepared by evaporating suspensions of the light and the heavy fraction of sample D on glass slides, covering the mounts with Kodak liquid

Table 2. β-activity of the size fractions of sample A.

Size Fraction μ	Net β-activity counts/minute	Wt % of total sample	Concentration of phillipsite %
> 32	23.7	6,5	63
10—32	18.9	9.2	89
3.2—10	10.3	12.3	51
1.0—3.2	5.6	22	4
< 1.0	1.8	50	not measured

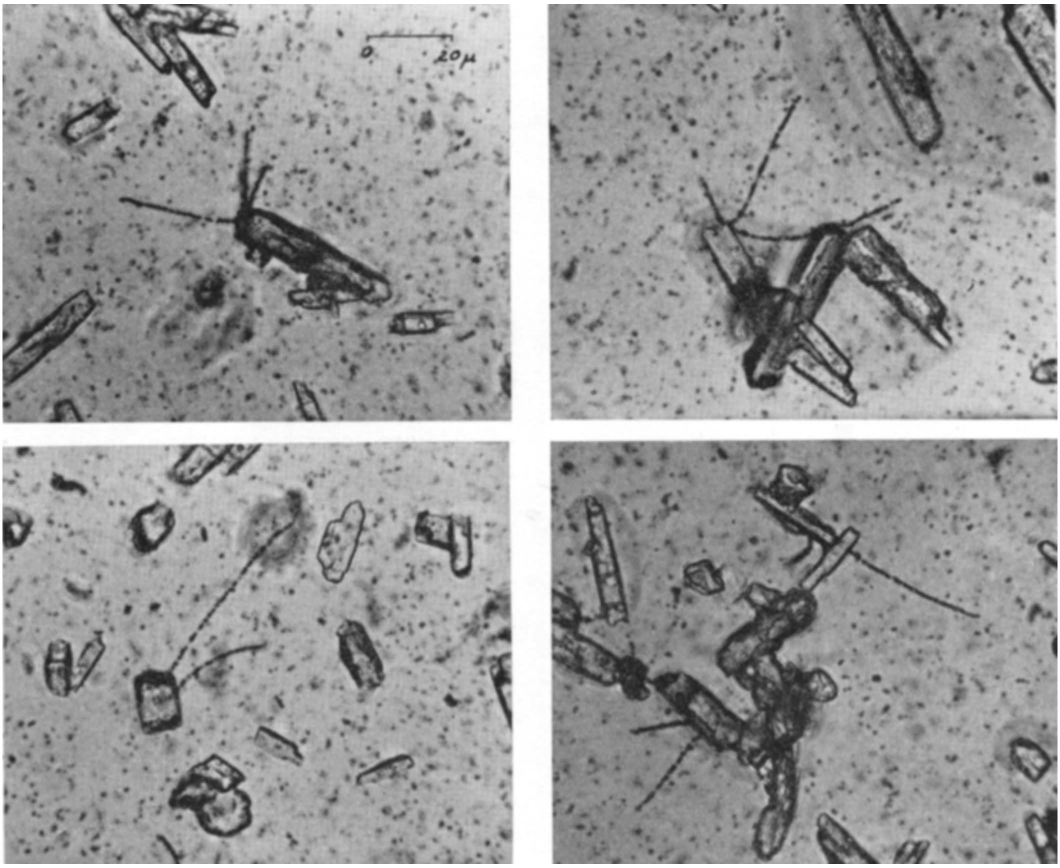

Fig. 2. Radioautographs of alpha particles emitted from phillipsite crystals (sample D) embedded in nuclear track emulsion.

nuclar track emulsion, drying, and exposing for ten days.

Out of 886 phillipsite crystals counted, twenty-five displayed alpha tracks, whereof eight single, nine double, and seven three-branched tracks. In one case eight tracks emerged from one single phillipsite crystal. Microphotographs of some of the active crystals are shown in Fig. 2.

As only the upper side of the mount was coated with emulsion, the recording geometry is approximately 50 %. Most of the single and double tracks observed may therefore be expected to correspond to three-branched stars with one or two of the alpha particles emitted into the glass slide. The high proportion of three-branched stars indicates that the activity is mainly due to an intercept of a disintegration series containing two short-lived alpha emitters. This leaves as the only possibility radium, radon and radium A as the elements responsible. As only in one case a two-branched star was observed in the emulsion without connection to a mineral grain it is probable that the phillipsite retains the emanaftion in an efficient way.

In the heavy (phillipsite-poor fraction) mounted and exposed in the same way as the light fraction, only three mineral grains out of 3,640 counted, displayed alpha tracks, confirming that the radium of the grain size fraction above 5 μ is practically entirely bound to phillipsite.

Most of the activity could be removed by chelation for ½ hour at 100° C. with the neutral ammonium salt of ethylene diamine tetra-acetic acid (Figures 1b – c and Table 3) and by cation exchange using 1N ammonium

Table 3. Chelation of β-active components in sample A.

Size fraction μ	Net β-activity, counts/min	
	Chelate, ashed	Residue
> 32	—	8.2
10—32	30.9	4.7
3.2—10	49.3	14.1
1—3.2	34.4	3.5
< 1	1.5	—

acetate (Table 4). The active constituent occurring in the phillipsite is therefore believed to be sorbed in the pores of the zeolite structure.

The salt from the interstitial solution generally displays a low beta activity which can partly be accounted for by potassium-40 (approx. 3 counts/min). An exception is the interstitial salt from the highly active surface layer of core *Capricorn 31 BG* (Sample D, Table 4 and 5), possibly indicating that in this case a considerable fraction of the radioactive elements are dissolved and not yet in sorption equilibrium with the solid phases.

Sample D displays the highest gross beta activity found in any material so far investigated by the present authors. In contrast to the conditions in the samples A and C, the almost phillipsite-free (4 %) clay fraction displays the same high activity as the pure phillipsite fraction ($> 5\,\mu$, $\varrho < 2.25$) (Table 5).

In order to test the correlation between the stratigraphically abnormal activity and the concentration of phillipsite in the sedimentary sequence, a core was selected (*Capricorn 23 HG*) which displayed in the upper part the type of activity distribution, expected as a result of decay, and in the lower part a marked secondary activity maximum (Fig. 3). All samples from this sequence were analyzed for their phillipsite concentration, using the intensity above background of the X-ray radiation diffracted by planes with the spacing $d_{hkl} = 3.175$ Å. A North American Philips Norelco X-ray diffractometer was used, employing Mn-filtered Fe $K\alpha$ radiation. The intensities were measured by the time required to accumulate 3,200 counts (40—180 seconds) and the experimental error is approximately ± 3 % of the concentration. The results, shown in Figure 3 indicate that the stratum 44—68 cm, carrying an abnormally high activity, is also characterized by a high content of phillipsite.

Table 4. Net β-activity of salt from interstitial solution, and of sorbed ions exchanged with 1N ammonium acetate.

Sample	Net β-activity counts/min.
B salt.........	4.2
B sorbate......	67
D salt.........	65
E salt.........	6.5
E sorbate......	126
F salt.........	9.4
F sorbate......	34

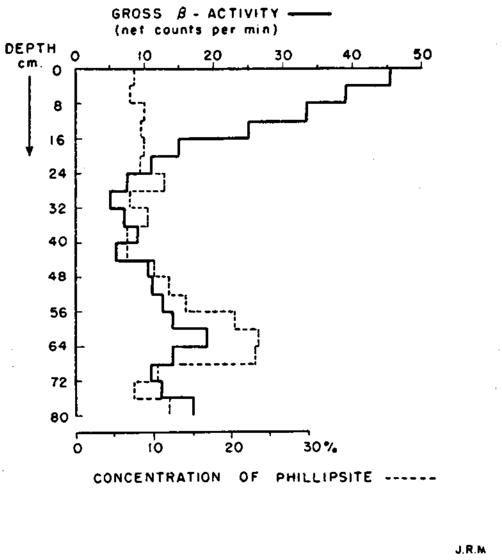

Fig. 3. Vertical distribution of gross beta-activity and phillipsite in core *Capricorn 23 HG.*

The above related results can be summarized in the following way: The beta-active con-

Table 5. Net β-activity of sample D.

Size fraction μ	Density fraction	Net β-activity counts/min.	Phillipsite conc. %
< 5	—	86	4
> 5	< 2.25	89	100
> 5	> 2.25	36	17

stituents are to a great extent sorbed by phillipsite both in the younger and older strata. The fraction of the deposit which is finer than 5 μ, and which largely consists of clay and hydroxide minerals, is highly beta active in the young sediment, but displays a low activity in the lower parts of the sequence, where significant amounts of unsupported ionium can be expected to be absent. In one case a high beta-activity has been observed in the interstitial salt from the top stratum of the sediment.

The alpha-activity has so far been investigated only in the grain size fraction $> 5\ \mu$ of the young sediment, and is in this to a large extent due to radium and its daughter elements radon and radium A, all bound practically entirely to phillipsite.

Discussion

To explain the distribution of the radioelements observed in marine sediments, the solid matter that accumulated or contained these elements, as well as the chemical reactivity of these elements in the sediments merit consideration (KURBATOV, 1936).

The *lithogenous* (GOLDBERG, 1954) contribution of radioactivity appears generally to be relatively unimportant in the pelagic sediments of the Pacific. This is indicated by the fact (PETTERSSON, 1938; PIGGOT and URRY, 1941) that most of the ionium is not uranium supported.

The accumulation of ionic ionium and radium in hydrogenous oxide-, clay- and zeolite minerals appears to be the quantitatively most important mechanism of transfer of radioelements to the pelagic sediments of the Pacific Ocean. This accumulation could be explained by coprecipitation (scavenging) of the radioelements by the solid phases in statu nascendi, and isomorphous replacement under the same conditions. Scavenging of ionium with ferric hydroxide (PETTERSSON 1953) and with manganese oxides (GOLDBERG 1954) have been suggested. As a considerable fraction of the pelagic clay minerals may be precipitated from dissolved aluminum and silica in the ocean (ARRHENIUS 1954), aluminosilicates may also have to be taken into account as scavengers for radioelements in sea water. The contribution of radioelements by the accumulation of *biogenous* material in the sediments is apparently of less importance than the hydrogenous contribution. EVANS, KIP and MOBERG (1938) found that the shell material in a Pacific mud sample contained but a minor amount of the total radium content of the sediment. Further, core *Capricorn 39 BG*, which has a calcium carbonate content of circa 70 %, shows a beta-activity, based upon its $CaCO_3$-free weight, equivalent to that of the carbonate-free clays in adjacent pelagic areas.

An indication of the minimum contribution of biogenous unsupported radium is given by the radium and barium contents of sea water and pelagic clays, assuming that both elements have similar geochemical paths through the biosphere (*i.e.* fixation in the skeletons and in the soft parts of marine organisms). The barium content of some Pacific pelagic clays attains values of more than 1 % and there is evidence for a biogenous origin of more than 95 % of the barium (GOLDBERG and ARRHENIUS, unpublished). The Ba/Ra ratio in sea water cannot be defined exactly inasmuch as only an upper limit for the Ba-concentration is known. Using the values of $Ra = 3 \cdot 10^{-11}$ mg/l and $Ba < 9 \cdot 10^{-2}$ mg/l, the ratio is $< 3 \cdot 10^{-9}$ and the expected concentration of biogenous, unsupported radium in sediments is $3 \cdot 10^{-12}$ g/g or greater. Since the concentration of Ra in the upper strata of the sediment is between 10 and 70×10^{-12} g/g, the Ba-concentration of sea water needs to be only a few times less than the reported upper limit to make biogenous Ra important as a possible guest element in marine organisms.

Attempts are made at the present time to investigate in detail the distribution of radioelements in stratigraphically surveyed pelagic sediment sequences. On the basis of the present results, and of previous work by HAHOFER and HECHT, KOCZY, KRÖLL, KURBATOV, PETTERSSON, PICCIOTTO and WILGAIN, PIGGOT and URRY, it appears most likely that the high activity of the clay- and hydroxide-mineral fraction at the present sediment surface is largely due to ionium-supported radium.

The abnormal activity of the old strata, originally observed by PETTERSSON (1953), KRÖLL (1954), BARANOV and KUZMINA (1954), may in some cases be due to displaced radium, sorbed by phillipsite from the interstitial solution. Other possibilities, which have to be investigated, are that the activity maxima in old strata are due to presence of excess uranium (as indicated by some of the results of HAHOFER and HECHT, 1954), high concentration of potassium, or to a high retension of radon in the phillipsite, as compared to other minerals present.

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