Estimation of the Geologic Age of Radioactive Sediment Containing Radium Isotopes

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Introduction

The determination of the geologic age of sediment is one of the important and very difficult problems in geochemistry. Generally the complex conditions governing the sedimentation process present many difficulties for researchers.

So far as radioactive sediments are concerned, however, it is sometimes possible to estimate their geologic age. The ionium-radium method¹⁾ proposed for the determination of the geologic age of deep-sea sediments is the best known example of this. But this method is only applicable to appreciably old sediments of several hundred years. Recently, Koczy²⁾ estimated the sedimentation intensities³⁾ of some sorts of clay by statistical calculations using the content of radium, manganese and titanium in these samples. In this case, however, it is obvious that the degree of accuracy is limited by the number of samples analyzed.

When a fairly young sediment contains isotopes of radium which are not supported by their long-lived parents, the abundance ratios of these isotopes should vary with the age of the sediment. Based upon this relation, three new methods are proposed for the estimation of sedimentation rate and intensity of young sediments which are approximately one to two hundred years old.

Assumptions

In our methods, the following conditions are assumed to persist during the period of sedimentation.

(1) The abundance ratios of radium isotopes keep constant in the water precipitating sediments.

(2) There is no way for the elements once precipitated in the sediments to be lost by any process.

(3) Within the sediments, no migration of elements occurs.

(4) Sedimentation intensity of an element keeps constant and consequently the intensity is uniform at least in that part of the sediments which we examine.

The conditions (1) to (4) are necessary to develop the following methods (a) and (b), while in the method (c), the condition (3) is not necessary.

In this paper the following values are used as the decay constants of radioactive elements: 4.3×10^{-4}, 68.7, 3.1×10^{-2}, 0.10, 0.36 and 69.3 per year for Ra^{226}, Ra^{222}, Pb^{210}, Ra^{228}, Th^{228} and Ra^{224}, respectively. These values are calculated on the basis of nuclear data which appeared in the Table of Isotopes by Hollander, Perlman and Seaborg.

Principle of the Methods

(a) The Method Based on the Vertical Variation of the Ratios of Radium Isotopes. —Let us consider an infinitely thin layer in a sediment perpendicular to the direction of growth. The number of atoms of radium isotopes present in the layer at the time t

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1) C. S. Piggot and W. D. Urry, *Ameri. J. Sci.*, **240**, 1 and 93 (1942).

2) F. F. Koczy, *Geochim. et Cosmochim. Acta*, **1**, 73-85 (1951).

3) Sedimentation intensity means the sedimentation velocity in gram per unit area per unit time, see koczy loc. cit.

from the beginning ($t=0$) of sedimentation can be represented by the following equations.

$$[\mathrm{Ra}^{226}]^t=[\mathrm{Ra}^{226}]\,e^{-\lambda_1 t}, \tag{1}$$

$$[\mathrm{Ra}^{228}]^t=[\mathrm{Ra}^{218}]\,e^{-\lambda_2 t}, \tag{2}$$

$$[\mathrm{Ra}^{224}]^t=[\mathrm{Ra}^{224}]\,e^{-\lambda_4 t}+\lambda_2\lambda_3/\lambda_4(\lambda_3-\lambda_2), \\ [\mathrm{Ra}^{228}]\,(e^{-\lambda_2 t}-e^{-\lambda_3 t}), \tag{3}$$

where $[\mathrm{Ra}]'$ and $[\mathrm{Ra}]$ stand for the number of atoms of radium in the layer at $t=t$ and $t=0$, respectively, λ_1, λ_2, λ_3 and λ_4 being the decay constants of Ra^{226}, Ra^{228}, Th^{228} and Ra^{224}, respectively. Deriving the above equations the contributions by Th^{228} and other long-lived parents are neglected because, as will be given later, the Th^{228} content in the water precipitating the sediment is negligibly small and because the effect by other long-lived parents is also negligibly small so far as a short period of from 100 to 200 years is concerned. In addition, the first term of the equation (3) can be neglected if t is longer than about thirty days as in our samples described later.

From equations (1) and (3), equation (4)′ is obtained.

$$[\mathrm{Ra}^{224}/\mathrm{Ra}^{226}]^t=[\mathrm{Ra}^{224}/\mathrm{Ra}^{226}]\,e^{(\lambda_1-\lambda_2)t} \\ +\lambda_2\lambda_3/\lambda_4(\lambda_3-\lambda_2)[\mathrm{Ra}^{228}/\mathrm{Ra}^{226}]\,(e^{-\lambda_2 t} \\ -e^{-\lambda_3 t})/e^{-\lambda_1 t} \tag{4$'$}$$

where the first term can be neglected because it is much smaller than other terms when t is longer than about thirty days. Then by introducing numerical values for constants, equation (4) is obtained.

$$[\mathrm{Ra}^{224}/\mathrm{Ra}^{226}]^t=2\times10^{-3}[\mathrm{Ra}^{228}/\mathrm{Ra}^{226}]' \\ (e^{-0.10t}-e^{-0.36t})/e^{-0.43\times10^{-4-4t}} \tag{4}$$

Here, according to condition (1), the ratio $[\mathrm{Ra}^{228}/\mathrm{Ra}^{266}]'$ can be represented by the corresponding ratio in the water at the present time, which can be determined experimentally. Also the ratio $\mathrm{Ra}^{224}/\mathrm{Ra}^{226}$ in the layer now in qnestion can be determined. Thus the time elapsed after the layer was formed and consequently the rate of sedimentation for the sediment laying above the layer are calculated.

(b) The Method Based on the Vertical Variation of the Beta-activity of the Daughter Nuclides from Radium Isotopes.—The equation for the beta-activity in the same layer as considered in the method (a) can be similarly derived. Here, the contributions by short-lived nuclides originally precipitated from the water are neglected, and only the secondarily produced activities from Ra^{226}, Pb^{210} and Ra^{228} are taken into consideration. The activity due to beta particles from Pb^{210} can also be neglected because of their extremely low maximum energy. Then the beta activity of a layer is given by the following equations at the time t,

$$[\Sigma\mathrm{Ra}^{226}]^t=3\lambda_1[\mathrm{Ra}^{226}]'e^{-\lambda_1 t}+(\lambda_5[\mathrm{Pb}^{210}]' \\ -\lambda_1[\mathrm{Ra}^{226}]')^{-\lambda_5 t}$$

$$[\Sigma\mathrm{Ra}^{228}]^t=\lambda_2[\mathrm{Ra}^{228}]\,\{(1+2/(\lambda_3-\lambda_2))e^{-\lambda_2 t} \\ -1/(\lambda_3-\lambda_2)\cdot e^{-\lambda_3 t},$$

where $[\Sigma\mathrm{Ra}^{226}]^t$ and $[\Sigma\mathrm{Ra}^{228}]^t$ stand for the beta-activity of Ra^{226}-series and of Ra^{228}-series, respectively, and λ_5 expresses the decay constant of Pb^{210}. Then by the summation of the two equations the total beta-activity of the layer, A_β^t, is obtained as follows:

$$\mathrm{A}_\beta^t=4.3\times10^{-4}[\mathrm{Ra}^{226}]'\{3-(1-q)e^{-3.1\times10^{-2}t} \\ +8.7pe^{-0.10t}-3.9pe^{-0.36t} \tag{5}$$

where $p=\lambda_2[\mathrm{Ra}^{228}]'/\lambda_1[\mathrm{Ra}^{226}]'$ and
$q=\lambda_5[\mathrm{Pb}^{210}]'/\lambda_1[\mathrm{Ra}^{226}]'$.

By the same consideration as in the method (a) we can calculate the geologic age of a layer by measuring the total beta-activity of the layer, assuming q is also constant during the period of sedimentation.

(c) The Method Based on the Total Time Variation of the Abundance Ratios of Radium Isotopes in Sediments.—Let us consider a column parallel to the direction of growth of the sediment. The concentration of a radium is controlled by two factors, an increase of the isotope by sedimentation and a decrease by radioactive decay.

When dk and $d[\mathrm{Ra}]^t$ express the increase of an isotope of radium by sedimentation and the total change of the isotope in the column, respectively, in a small time, dt, at $t=t$, the increase of the amount of the isotope at $t=t$ can be written by the following equation:

$$d(\mathrm{Ra})^t=dk-\lambda(\mathrm{Ra})^t\,dt,$$

where $(\mathrm{Ra})^t$ stands for the total amount of an isotope of radium in the column at $t=t$.

According to the condition (4), dk or $dk/dt=K$ in this equation is constant and we can solve the differential equation obtaining the total amount of the isotope in the column at $t=t$. Thus for Ra^{226} and Ra^{228} the following equations can be given:

$$(\mathrm{Ra}^{226})^t=K_1(1-e^{-\lambda_1 t})/\lambda_1 \tag{6}$$

$$(\mathrm{Ra}^{228})^t=K_2(1-e^{-\lambda_2 t})/\lambda_2 \tag{7}$$

When the determination is carried out at a

TABLE I

CONTENTS AND RATIOS OF RADIUM ISOTOPES IN THE SPRING WATERS

Date	Content of Ra^{226}	The Atomic Ratio		Content of Th^{228}
		Ra^{224}/Ra^{226}	Ra^{228}/Ra^{226}	
October '53	2.0×10^{-11} g./l.	5.9×10^{-5}	ca. 5×10^{-2}	ca. 0
July '54	1.4 „	5.0 „	—	ca. 0

time t' after sample has been collected and when the time t' is sufficiently large in comparison with the half-life of Ra^{224} so that the sedimented Ra^{224} has completely decayed off at the time of determination, the total amount of Ra^{224} at this time will be obtained by integrating the equation (3) from t' to $t+t'$ giving the equation (8).

$$(Ra^{224})^{t+t'}=\{K_2/\lambda_4(\lambda_3-\lambda_2)\}$$
$$\{\alpha(\lambda_3-\lambda_2-\lambda_3e^{-\lambda_2t}+\lambda_2e^{-\lambda_3t})+\beta\lambda_3$$
$$(1-e^{-\lambda_3t})\}, \tag{8}$$

where $\alpha=e^{-\lambda_3t'}$, and $\beta=e^{-\lambda_2t'}-e^{-\lambda_3t'}$, respectively.

From the equation, (6) and (8), the total variation of the ratio, Ra^{224} to Ra^{226}, v.s. time in the column is represented by the following equation when we insert numerical values for constants:

$$(Ra^{224}/Ra^{22}{}_{9})^{t+t'}=(K_2/18K_1)$$
$$\{\alpha(0.26-0.36e^{-0.10t}+0.10e^{-0.36t}\}$$
$$+0.36\beta(1-e^{-0.36t})\}/t+t' \tag{9}$$

where $e^{-\lambda_1}(t+t')$ is approximated to $1-\lambda_1(t+t')$.

In this equation K_2/K_1 is considered to be equal to the abundance ratio of the two isotopes in the water. Then the geologic age of the sediment as well as the mean rate of sedimentation can be estimated by measuring the ratio, Ra^{224} to Ra^{226}, in the total mass of the columnar sample.

The Rough Estimation of the Sedimentation Rate as well as the Sedimentation Intensity of Hokutolite.

Hokutolite is one of the radioactive sinter deposits from hot springs[4,5] and is being precipitated from spring waters at temperatures ranging from 98°C to 40°C. In most cases, it is growing layer by layer on the surface of the base rock, andesite and is considered to be the most suitable sample for our methods.

The content and the ratios of radium isotopes in the spring water are shown in Table I. Pb^{210} is also supposed to be present, but the content in the water has not yet been determined. In Table II are shown the mean content of Ra^{226} and ratio, Ra^{224} to Ra^{226}, in the two samples, Hokutolite A and Hokutolite B. The Hokutolite A is of a thickness of eleven millimeters and is grow-

TABLE II

CONTENT AND RATIO OF RADIUM ISOTOPES IN HOKUTOLITE

Sample	Age observed	Content of Ra^{226}	The Atom Ratio Ra^{224}/Ra^{226}
Hok.—A	unknow	1.0×10^{-9} g./g.	1.0 0.2
Hok.—B	5 yr.	1.6 „	4.0 0.2

TABLE III

VERTICAL CHANGE OF RADIOACTIVE PROPERTIES IN HOKUTOLITE A

Nos. of pieces	Depth from the Surface (mm.)	Cont. of Ra^{226} (10^{-9}g./g.)	Atom. Ratio Ra^{224}/Ra^{226} (10^{-5})	Specific—Activity (c.p.m./g.)
1		1.9	6.0	6010
2		0.8	6.0	3500
3		1.9	3.5	2400
4		0.9	2.7	1480
5		1.8	0.87	960
6		—	—	820
7		1.5	0.10	555
8	3	—	—	—
9		1.4	0	—
10	4	1.1	0	—
11		—	—	710
13		0.9	0	—
14	6	—	—	350
16		0.7	0	—
17		—	—	330
19		0.8	0	—
20		—	—	455
23		—	—	460
25		0.8	0	—
26	9	—	—	410
29		—	—	—
32		0.8	0	310
33	11	1.5	0	405

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[4] R. Ohashi, Mineralogical Mag., 19, 73 (1920); I. Suganuma, Bull. Chem. Soc. Japan, 3, 69 (1928); E. Minami, Kobutsugaku *Zasshi* (J. Mineralogical Soc. Japan), 2, 1 (1954).

[5] Hokutolite is composed of the mixed crystal of barium sulfate and lead sulfate, and was found first at the Hokuto springs in Formosa and then at the Tamagawa Springs (formerly called Shibukuro Springs) in Akita perfecture in Japan. The molecular ratio, lead sulfate to barium sulfate, in Hokutolite from Tamagawa is found to fluctuate between 0.2 and 0.02. The spring waters of Tamagawa contain radioactive elements of both uranium- and thorium-series which make the mineral distincly radioactive. The main constituents of the water are Al^{+++}, Fe^{++}, and Cl^{-}, with smaller quantities of SO_4^{--}, F^{-} and Fe^{+++}. Barium and lead are also contained in the water but their concentrations are in the order of p.p.m.

ing on the large base rock. It is deposited from the flowing water with a temperature as high as 45°C. A small column is made carefully from this sample, and is cut, layer by layer, into thirty-three pieces from the surface to the bottom. The measurements of the content and the ratio of radium isotopes as well as the specific beta activity are performed on each of these pieces and the results are summarized in Table III.

Hokutolite B is, on the other hand, about 0.75 mm. thick and is known to be about five years old. This sample is growing on a small andesite block on which the spring water, with a temperature of 75°C, splashes vigorously.

The content and the ratio of radium isotopes of the water are determined by the following method. One hundred milligrams of barium are added to the sample water as barium chloride and barium sulfate is precipitated by the usual method. Barium chloride method reported by Ames et al[5] is employed in order to eliminate other radioactive elements coprecipitated with radium. The alpha-activity of the barium sulfate is measured continuously by a Lauritsen type electroscope and the variation with time of the activity is plotted on a graph paper. The content of Ra^{226} and the ratio, Ra^{224} to Ra^{226}, are easily calculated from the curve, but the calculation of the ratio, Ra^{228} to Ra^{226}, is not so easy because of the somewhat long half-life of Ra^{228}. As described later, the ratio, Ra^{228} to Ra^{226}, in the spring water, is evaluated by the more convenient way. In the determination of these values in Hokutolite, the same method is employed but barium chloride need not be added to the sample in this case.

(1) The Estimation of the Rate of Growth Near the Surface of Hokutolite.—From the equations, (4) and (5), it is calculated that the ratio, Ra^{224} to Ra^{226}, or the total beta-activity of a layer becomes zero or constant when about fifty years has passed since its precipitation. From Table III, it is shown that in the case of Hokutolite A this time corresponds to the period of sedimentation of the layer about 3 mm. thick. The mean rate of growth above this layer is then calculated to be about 6×10^{-2} mm. per year.

This fact is more clearly shown in Fig. 1 and Fig. 2, which are constructed on the basis of the following considerations: the experimentally determined ratio of radium isotopes as well as beta-activity for each piece shown in Table III are not the values for infinitely thin layers, but the mean values for the layers with some thickness. Considering the above estimated rate of growth, the thickness of each layer seems to correspond to about seven years sedimentation. To compare these facts with theoretical data, therefore, we must use mean "theoretical" values for every seven years. The ratio, Ra^{228} to Ra^{226}, in the water is evaluated by equalizing the mean theoretical ratio, Ra^{224} to Ra^{226}, for the first seven years to the observed ratio and this gives 8×10^{-2} for the value. This value is considered to be more reliable than the one experimentally determined in Table I and will be used in the following discussion.

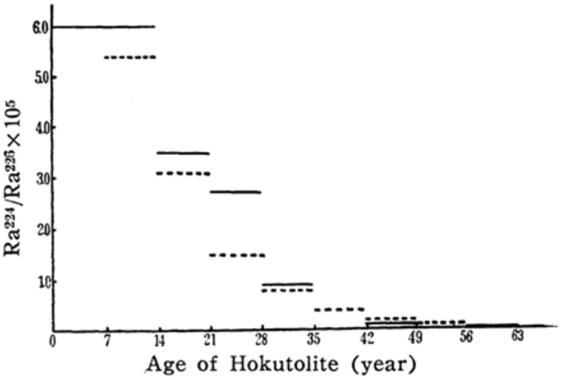

Fig. 1. Vertical change of the ratio, Ra^{224}/Ra^{226}, in Hokutolite-A.

Solid lines: Observed ratio, Ra^{224}/Ra^{226}, in each piece of Hokutolite-A up to No. 9 in Table III.

Dotted lines: Theoretical mean ratio for every seven years. Theoretical. value for first seven years is equalized to the observed one.

From Fig. 1 and Fig. 2, it is concluded that the rate of growth estimated above is approximately valid near the surface of the sample.

(2) The Estimation of the Mean Rate and Intensity of Sedimentation of Hokutolite for the Past One to Two Hundred Years.— From the above discussion the value for K_2/K_1 in the equation (9) is 8×10^{-2} and the time t', is known as 0.25 years for Hokutolite A and Hokutolite B, respectively. Using these data the theoretical time variation of the ratio, Ra^{224} to Ra^{226}, in the total mass of the deposit is plotted in Fig. 3 in a solid line. Comparison of the data in Table II with the curve in Fig. 3 gives the age and

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[6] D.P. Ames, J. Sedlet, H.H. Anderson and T.P. Kohman, The Transuranium Elements, (Natl. Nuclear Energy Series IV-14B) p. 1700 (1949).

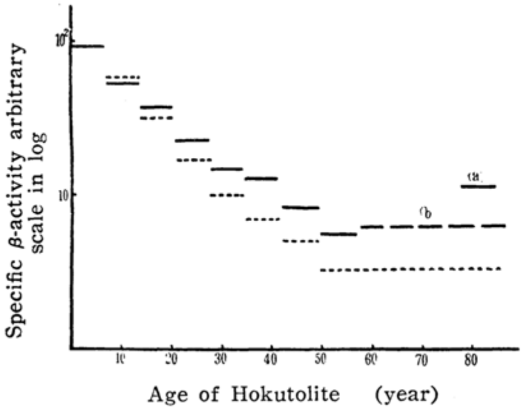

Fig. 2. The Vertical change of β-activity of Hokutolite.

Solid lines: Observed specific β-activiteis of each pieces of Hokutolite-A up to No. 11 in Table III.

Dotted lines: Theoretical mean β-activities for evry seven years. Pb^{210} is assumed to be in equilibrium with Ra^{226} in the water and the value for the first seven years is equalized to the observed one.

(a): observed value for No. 11, exceptionally high.

(b): observed mean value from No. 14 to No. 33.

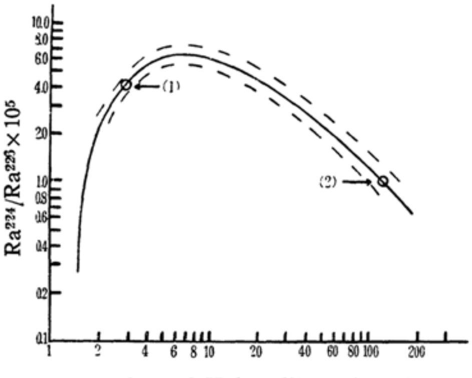

Fig. 3. The variation with time of the mean ratio, Ra^{224}/Ra^{226}, in total mass of Hokutolite.

Solid line: $K_2/K_1=8\times 10^{-2}$

Dotted lines: above $K_2/K_1=9\times 10^{-2}$, below $K_2/K_1=7\times 10^{-2}$

(1) and (2): observed values for Hokutolite-B and-A, respectively.

the mean rate of sedimentation. Combining these results with the content of each element in Hokutolite and weight of the sample, the sedimentation intensity of each element can be estimated. Here the sedimentation intensities of radium and of Hokutolite as a whole are given. In the calculation of the sedimentation intensity of Hokutolite, the water content in the sediment is neglected. The reason is that the weight of Hokutolite A is approximately 4.5 gr./cm³ while the specific gravity of Hokutolite is 4.5. These results are summarized in Table IV.

Discussion

The accuracy of the values calculated depends largely on the validity of assumptions first proposed. Among them assumption (4) is the most unlikely. A remarkable discrepancy between the values for the growth rate of Hokutolite A, between the values by the first two methods and the value by the third method, is evidently due to this. The fact that most of the Hokutolite samples consist of alternating white and brown layers suggests that sedimentation has proceeded not uniformly. Really it was shown by Mr. Sasaki[7] in our laboratory using the nuclear emulsion method that white layers are richer in radio-active elements than brown layers.

From these observations it is probable that the mean rate of growth of Hokutolite is smaller in recent years than in the older period.

On the other hand, the difference of the rate of growth between the sample A and sample B is considered mainly due to the difference of the conditions governing the sedimentation process. Some of them are shown in the beginning of this chapter. In addition, the content of Ra^{226} in the water precipitating Hokutolite A is about one-half of that in the water near Hokutolite B. The contents of barium and lead are probably decreased by the same proportion as radium though not yet assured.

As for the first assumption, that is, the constancy of the abundance ratio of radium

TABLE IV

THE SEDIMENTATION RATE AND INTENSITY OF HOKUTOLITE

Sample	Age calcd by the Method (c) yr.	Sedimentation Rate by the Method (a) & (b) mm./yr.	Sedimentation Rate by the Method (c) mm./yr.	Sedimentation Intensity by the Method (c) of Ra 10^{-11} g./cm²/yr.	Sedimentation Intensity by the Method (c) of Hokutolite 10^{-2} g./cm²/yr.
Hok.－A	120±20	0.06	0.09±0.015	4±0.7	4±0.7
Hok.—B	3± 0.2	—	0.25±0.03	18±1	11±0.7

The Density of Hok.－B is assumed to be 4.5.

Experimental error in the determination of the ratio Ra^{224} to Ra^{226}, is only considered here.

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[7] Symposium on Geochemistry held in Fukuoka October, 1954.

isotopes, its validity cannot be ascertained experimentally within a short period. If radium isotopes are introduced into the spring water from the same mother rocks, sudden and appreciable change of their ratios would not take place in such a short period as one or two hundred years. In this case, however, the steady increase or decrease of the ratios, probably in both directions, may occur to some extent. In Fig. 3, the limit of the error is shown in two dotted lines as the ratio, Ra^{228} to Ra^{226}, in the water varies from 7×10^{-2} to 9×10^{-2}.

Uncertainties arising from other assumptions may be minimized by taking samples near the center of gross sediment.

The determination of the ratio, Ra^{224} to Ra^{226}, is done by the rather inconvenient method described before. The error is estimated to be about fifteen per cent when the ratio is less than 1×10^{-5}, while it decreases to about five per cent as the ratio increases. In our purpose, however, the uncertainty of this order could be allowed if one considers non-validities of the conditions assumed.

In the methods, (a) and (b), another important error is introduced by the crystalization of Hokutolite. The surface of Hokutolite becomes uneven as the crystalization takes place and it is very difficult to measure accurately the depth of a layer from the surface. This error is considered to amount to about ten per cent at the depth of 3 mm.

Comparing three methods with each other, (a) ond (b) are better than (c) in that the assumption for the uniform growth is not necessary to them and the time t is obtained rather distinctly, when the ratio, Ra^{224} to Ra^{226}, or the total beta activity becomes zero or constant. In the method (b), however, the uncertainty from the ratio, Pb^{210} to Ra^{226}, must be taken into consideration. In the case of the method (c), on the other hand, it is possible to estimate the mean rate of growth in the period ranging from a few years to one or two hundred years, while the first two methods can estimate the value only for about sixty years.

From these discussions it can be concluded that compared to the observed rate of growth, 0.15 mm./year the calculated rate for Hokutolite B, 0.25 mm./year, is fairly satisfactory. Perhaps, the value for Hokutolite A is also satisfactory with good approximation.

Summary

Under some assumptions, three methods for the estimation of sedimentation rate as well as sedimentation intensity of radioactive sediments are proposed. These methods are based on the time variation of the abundance ratios of radium isotopes in the sediments. The rate of sedimentation of a radioactive sediment, Hokutolite, is estimated for two samples by these methods. The result is 0.25 mm./year for one sample for which the observed value is known to be 0.15 mm./year. For the other sample of unknown age, the rate is estimated to be 0.09 mm./year.

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