A STUDY OF THE Io/Th (Th^{230}/Th^{232}) CHRONOLOGY OF SOME

MARINE SEDIMENTS USING SOLID-STATE DETECTORS

A THESIS SUBMITTED TO THE GRAUDATE DIVISION OF THE

UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN CHEMISTRY

JANUARY 1967

By

Hatsuo Taira

Thesis Committee:

John J. Naughton, Chairman
Robert A. Duce
John C. Belshe

We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Chemistry.

THESIS COMMITTEE

_____
Chairman

_____

_____

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

A. Historical

The chemical and mineralogical composition of marine sediments provide important records of geological processes in the ocean. The separation of the radioactive elements carried out in the sediment via chemical processes, and the analysis of these elements, allow the determination of the ages of the sediment samples corresponding to the time interval during which deposition occurred to the point of sampling.

The common techniques used for the determination of the age of marine sediment samples have been the radiocarbon-14 and the ionium-radium methods. These methods have suffered from certain inherent limitations. The C^{14} method developed by Libby[1] is restricted to a maximum age of 40,000 years. The second is based on the fact that ionium (Th^{230}) produced by the decay of uranium dissolved in sea-water is selectively precipitated together with the sediment.[2] The subsequent growth of radium from this parent ionium in the sea sediment is measured to determine the age. Attempts have been made to use the vertical distribution of radium in deep-sea sediments for dating back to 350,000 years.[3] This method, however, has produced some questionable results due perhaps to the non-uniform deposition of ionium with time or to migration of daughter radium out of the system.[4]

In 1954, Picciotto and Wilgain[5] first reported on the use of the ionium/thorium (Th^{230}/Th^{232}) method for dating sediments, which depends only on a single elemental ratio. The method based on this ratio should be free from the difficulties of the ionium-radium method since both substances involved are isotopes of the same element, thorium, and act

the same chemically. Also since the ratio of the isotopes is measured, errors due to the assumption of a uniform sedimentation rate of ionium and to the separation of two different elements by chemical processes would be eliminated.

In 1958, Goldberg and Koide[6] reported the use of an alpha-ray spectrometric method for the simultaneous measurement of the alpha activity and for the determination of ionium and thorium separately through their respective alpha-decay energies. Measurements were made on the thorium chemically separated from deep-sea deposits, by the use of a grid-type ionization chamber as a detector, coupled to a pulse height analyzer as an energy spectrometer.

The introduction of semiconductor solid-state detectors for alpha counting,[7] with inherent better resolution and low background, has made the low level measurements more accurate and simpler. They prove particularly useful in measurements of deep-sea sediment samples in which simultaneous identification of several radionuclides is necessary.

Th^{230} decays by alpha emission according to the exponential law of radioactive decay. The ionium/thorium (Th^{230}/Th^{232}) ratio is obtained directly from the alpha energy spectrum of the sample and theoretically should decrease exponentially with depth in the sediment sample (Th^{232}; $t\frac{1}{2} = 1.4 \times 10^{10}$ y, Th^{230}; $t\frac{1}{2} = 76,000$ y). Goldberg and Koide[6], [8] have verified this exponential decrease in the ionium/thorium (Th^{230}/Th^{232}) ratio with depth in marine deposits. This indicates that ionium may not be redistributed after deposition, thus showing that this possible source of error is not important.

According to Goldberg, et al.[6], the ionium/thorium (Th^{230}/Th^{232}) ratios measured at the top or surface of the sediment in the Eastern

Pacific clays fall into two distinct groups; a set in the region between the Aleutian Islands and Hawaii with the value of the ratio of about 15, and a second group in the region around the equator between 120° and 140° W and lat. 40° N, with a ratio varying around 35.

B. Purpose of the Investigation

The ionium-thorium method has been actively applied to the determination of the age of marine sediment samples throughout the Pacific. It was the plan of this work to compare measurements on similar core samples from the Pacific Ocean made with modifications in the chemistry of thorium separation, and with the use of semiconductor solid-state detectors with low background for alpha counting. The techniques were then applied to the measurement of the ages of different levels in a sediment core from the Arctic Ocean. A check of procedures and measurements were obtained from comparisons with data obtained by other investigators on cores from the Pacific Ocean.

C. Principles of the Method

The ionium-thorium method is based on the simultaneous removal of two isotopes of thorium by the sediment: Thorium-232, naturally occurring thorium with a half life of 1.4×10^{10} years, and thorium-230 which has been produced from the decay of uranium-238, with a half life of 76,000 years. Since thorium is less soluble than uranium in water, ionium is precipitated in freshly deposited sediment in excess of the amount expected from the decay of uranium-238. Thorium-232 remains practically constant in concentration, while ionium decays with its shorter half life. The constant deposition of ionium then makes it possible to obtain a time function dependent upon the thorium isotopic

ratio. To this end, several assumptions are made in the application of the method. Goldberg and Koide summarized these as follows:

1. The ionium/thorium (Th^{230}/Th^{232}) ratio has remained constant in a given water mass over the dating interval for the last half-million years.

2. Ionium and thorium have the same chemical speciation in sea-water. This means that both ionium and thorium have the same chemical form in sea-water and they should have been chemically precipitated from sea-water, not carried in mineral residue.

3. The sample materials do not contain detrital minerals of continental or volcanic origin with a significant distribution of ionium and thorium.

4. There is no migration of thorium in the sediment.

With fulfillment of these assumptions the ionium/thorium (Th^{230}/Th^{232}) ratio should decrease exponentially with depth in the sediment column and should depend only on the time elapsed since the deposition occurred. The age index at any level can be computed by comparison with surface values utilizing the 76,000 years half life of ionium. The age index R is,

$$R = (Ioa - Iou)/Th = (Ios)t/Th$$

where Ioa and Th are the content of total ionium and thorium in the sediment and Iou is ionium content produced from the decay of uranium-238 in the sediment after deposition. (Ios)t is then the content of ionium precipitated with sediment from sea-water via chemical processes only. If the thorium isotopes are assumed to be in secular equilibrium with their parents, the disintegration rate of ionium derived from uranium-238 in the solid phase, (Iou), becomes equal to the disintegra-

tion rate of thorium-234. Since thorium-232 is also in secular equilibrium with its short-lived daughter thorium-228, the disintegration rate of thorium-232 should be equal to the disintegration rate of thorium-228 in freshly separated samples. Then,

$$R = Ioa/Th - Th^{234}/Th^{228} = (Ios)t/Th$$

or

$$R = Ioa/Th - Th^{234}/(\text{beta daughter of } Th^{228}) = (Ios)t/Th$$

If Ro is the surface value of this ratio, then

$$R/Ro = \frac{(Ios)t/Th}{(Ios)o/Th} = (Ios)o\ e^{-\lambda t}/(Ios)o = e^{-\lambda t}$$

where λ is the decay constant of ionium and t is the age of the sediment sample at a given depth in the core.

The Ioa/Th ratio can be determined directly from an alpha energy spectrum and the Th^{234}/(beta daughter of Th^{228}) from a beta energy spectrum, using their respective peaks. It is noted here that the correction factor, using the Th^{234}/(beta daughter of Th^{228}) in this way, can be applied only if the age of the sediment at a given depth is greater than the order of 10^5 years. For younger ages it is a maximum correction, since equilibrium between uranium-238 and ionium has not yet been attained for this age range. Goldberg and Koide,[8] however, pointed out that such corrections only become significant in times in the orders of several half-lives of ionium. From this point of view, and also since thorium-234 was added into sample solutions to study chemical yields in the separation of the thorium isotopes, the correction factors for ionium derived from uranium-238 were not applied in results of the experiments reported here.

EXPERIMENTAL

A. The Source of Sample Materials

The method was applied in detail to an Arctic sediment sample,
No. SI - 13A Phleger Core, collected by the ship USS Staten Island
(AGB-5) during August in 1959. The general location of the sample is
from the entrance of Dolphin and Union Straits, specifically at lat. 69°
01.3' N and long. 116°46.6' W. For the purpose of checking the method
by comparison with independent determinations run in another laboratory,
a few samples from adjacent areas in the Pacific Ocean in the region
between the Aleutian Islands and Hawaii were also analyzed. The
relative location of these samples are shown in Figure 1.

B. Methods of Chemical Separation of the Thorium Isotopes

To minimize the errors due to the separation of two different
elements by chemical processes and to simplify sample preparations, the
isotopes of a single element, thorium, were isolated from the sediment
sample. In order to minimize the energy loss by sample self-absorption,
the thorium isotopes were then electroplated onto a 2 cm. platinum disk
as a very thin cource—a technique necessary in alpha counting.

The majority of the separations of the thorium isotopes from sedi-
ment samples have been carried out using the extraction technique
reported by Goldberg and Koide.[8] In addition an ion-exchange separation
technique described by Y. Miyake and Y. Sugimura[9] was tried.

The extraction technique used for the separation of the thorium
isotopes reported by Goldberg, et al., can be summarized as follows:
One to two grams of dry core sample is leached with concentrated
hydroxide by adding lanthanum nitrate and by passing NH_3 gas into the
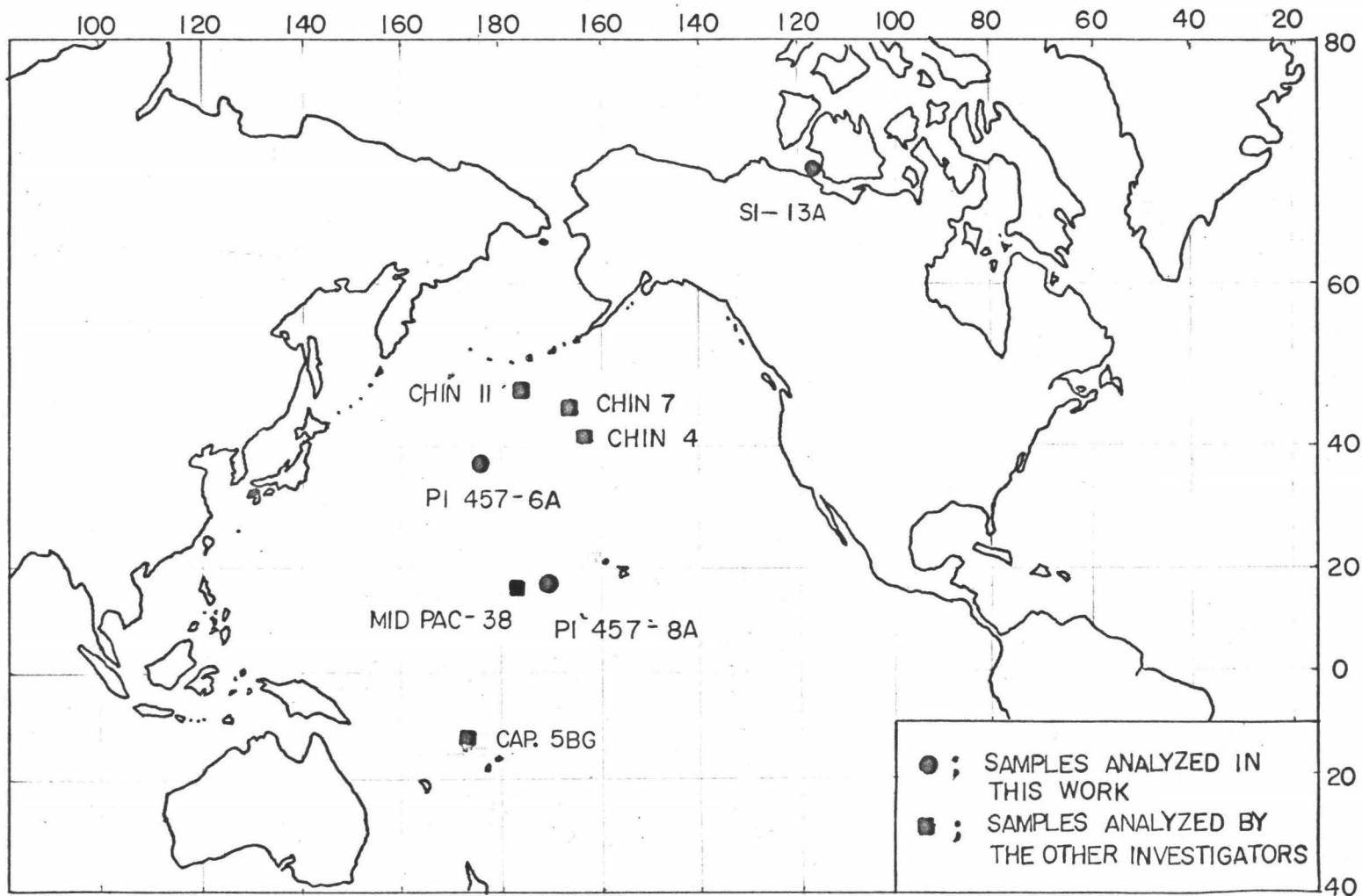
FIGURE 1. GEOGRAPHICAL LOCATION OF SAMPLE MATERIALS

solution. The hydroxides are converted to fluorides by the addition of concentrated hydrofluoric acid. The LaF_3 precipitate is converted to nitrate. The thorium isotopes are extracted with mesityle oxide and stripped into distilled water and are again extracted with TTA solution (0.25 M alpha-thenoyltrifluoroacetone in benzene) by adjusting the pH to 2. The thorium isotopes are then stripped with 2 N HNO_3, and the acid solution is evaporated to dryness. To provide a thin source for alpha counting the thorium isotopes are plated onto a 2 cm platinum disk.

By means of yield studies it was found that the use of the ion-exchange resin for the isolation of the thorium isotopes was superior to the extraction technique from the viewpoint of the simplicity and recovery. The ion-exchange technique used in this work can be summarized as follows:

(1) Take one to two grams of dried sediment sample and dissolve in 15 ml of a mixture of hydrochloric acid and perchloric acid on a sand bath for a half hour in 125 ml Erlenmeyer flask.

(2) To the solution add a Th^{234}-tracer solution of several hundred counts per minute as assayed under an end window G-M counter.

(3) Separate the liquid phase from residual solid-phase by centrifugation in a 50 ml Teflon centrifuge tube. Repeat the leaching. Wash the solid-phase with water, stir, centrifuge and combine supernatant in a 50 ml beaker.

(4) Place the solution on a sand bath and take nearly to dryness.

(5) Dissolve the precipitate in 10 ml of 3 N hydrochloric acid and remove silica by filtration.

(6) Pass the solution through a cation exchange column (4 mm x 10 mm, packed with Dowex 50-x8, 200-400 mesh resin) previously washed with 3 N

hydrochloric acid.

(7) Carefully wash the side of glass wall with four 2 ml portions of 4 N hydrochloric acid and 5 ml of water.

(8) Elute the thorium isotopes with 6 ml of 0.5 M oxalic acid.

(9) To the eluate, add 2 ml of concentrated perchloric acid and take to dryness to decompose any organic matter. No visible residue should remain.

(10) Add 5 ml of 2 M ammonium chloride, having previously adjusted the pH to 2, while the beaker was still hot.

(11) Place the solution in an electroplating unit. The thorium isotopes are plated onto a 2 cm diameter platinum disk for 40 minutes at a voltage of 6 volts and a current of 1 ampere, using constant voltage electroplating equipment.

(12) A Th^{234}-tracer solution, equal to that introduced into the sediment samples, is plated in the same manner. Its activity assayed under an end window G-M counter is compared with Th^{234} recovered from the sample to determine the yield of the analysis.

The Th^{234} solution which serves as a yield monitor is separated from uranyl nitrate by means of a cation exchange separation technique modified by Goldberg and Koide.[8]

C. Equipment

1. Electroplating System

In order to prevent self-absorption of alpha radiation and attenuation of the radiation energy which would produce broadening of the lines in the alpha-particle spectrum, the thorium isotopes were plated onto a 2 cm platinum disk as an extremely thin uniform coating. The electro-

deposition was carried out for 40 minutes, using constant voltage electrolysis equipment adjusted to 6 volts. Deposition was from 2 M ammonium chloride solution which was adjusted to a pH of 2.

A platinum disk is used as a support for the thorium source and is made the cathode in an electrolysis cell such as that shown in Figure 2. With a current density of about 1 ampere per cm^2 of cathode surface, the rapid discharge of hydrogen ions to form hydrogen gas at the cathode surface produces a layer of solution depleted in hydrogen ions and therefore of very high hydroxide ion concentration. Insoluble thorium hydroxide is therefore precipitated. The violent stirring due to the gas formation brings all parts of the solution to the cathode surface layer where the source material is deposited. Before the current is turned off, the electrolyte is made basic by the addition of a few drops of concentrated ammonium hydroxide solution. If this step is omitted, the collapse of the cathode basic layer when the current is turned off causes the deposited hydroxide to redissolve immediately in the solution. Then, the cathode is removed, and is washed free of ammonium chloride. It is then heated to redness in air to form ThO_2. The sample is counted under an end window G-M counter for yield and subsequently submitted to alpha assay.

2. Semiconductor detector

Detection of full-load energies emitted from radioactive species makes it possible to identify an individual isotope. Detection of the energy of an alpha radiation is one of the ways used to identify the emitting isotope. For this purpose, various kinds of alpha detectors are now commercially available. However, for low level measurements a variety of radiation detectors and accessory equipment are used to
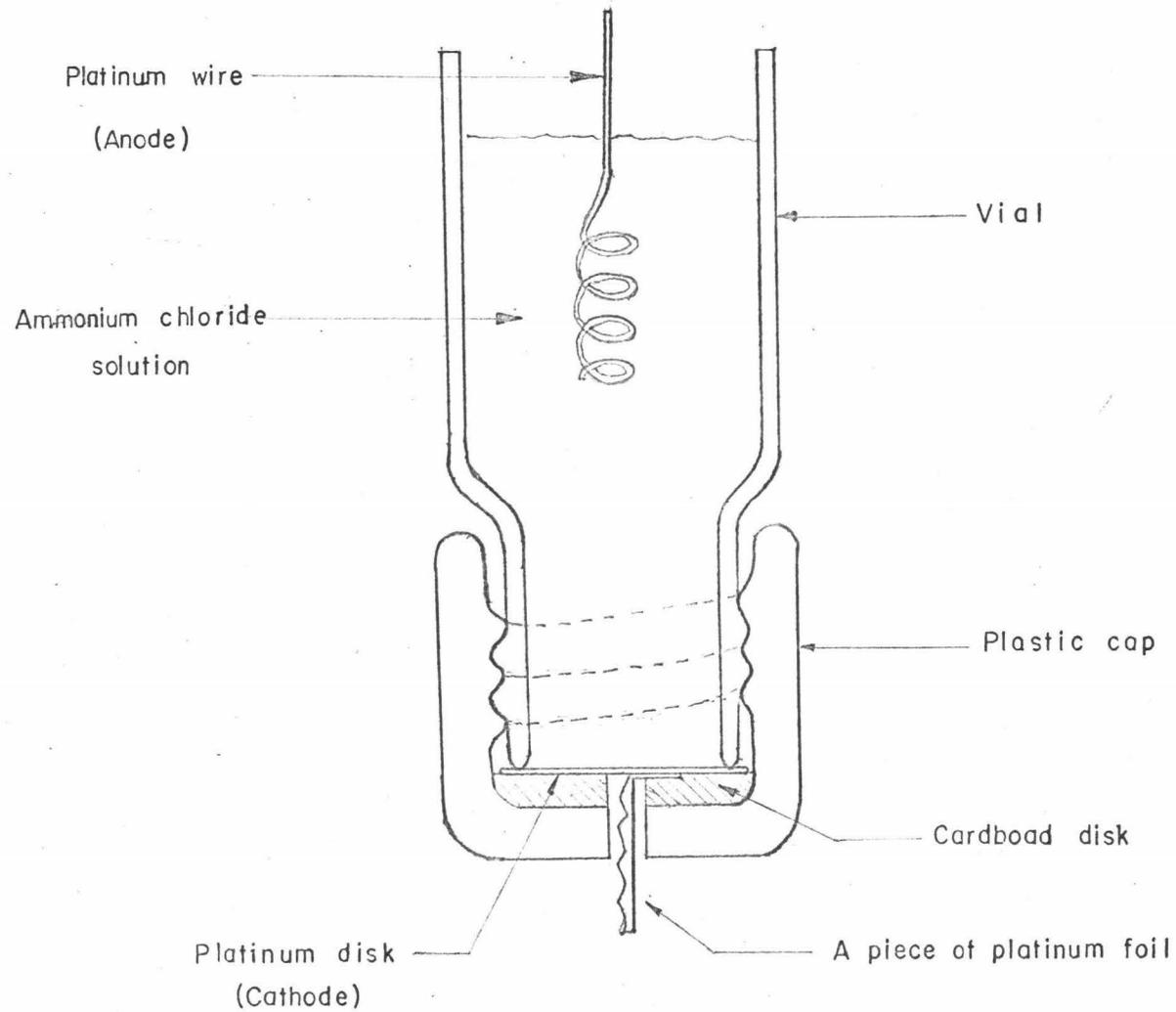
FIGURE 2. ELECTROPLATING CELL

reduce the background enough to make significant sample measurements possible.

The usual method used to make measurements in the low level counting range for alpha radiation was a Frisch screen-grid ionization chamber with an energy resolution of $\sim 3\%$ and background of about 1-2 cpm. Since naturally occurring alpha-emitting isotopes have energy levels of 3-9 MeV, one must have at least $\sim 10\%$ energy resolution to separate the energy levels efficiently by this counter.

Recently developed semiconductor detectors have several advantages over gas-filled counters. An inherent better energy resolution (0.5% compared to 3%) and the low background (0.008 cpm compared to 1-2 cpm) lead to higher accuracy and greater simplicity in use for low level measurements.

The semiconductor radiation detector is analogous to the gas ionization chamber except that the charge is carried by electrons and electron holes in a solid instead of electrons and positive ions in the gas of the ionization chamber. The sensitive layer of the solid can be very thin and yet possess a high stopping power. Low values for an average energy for electron-hole production (3.5 eV in Si) and the energy gap between the highest filled band and conduction band (1.1 eV for Si) lead to smaller statistical fluctuations. Therefore, the semi-conduction detector has potentially good energy resolution.

When an electric field is applied across the semiconductor, a leakage current passes through it. In order to use a semiconductor as a radiation detector, one must apply the electric field without such leakage current. The use of reverse-biased diodes is one of the ways to reduce this leakage current. Schematic diagram for a reverse bias type

detector is shown in Figure 3.

A thin layer (0.1 μ) of n-type silicon (with an excess of positive hole charge carriers) is prepared by diffusion of phosphorus into p-type silicon (which has an excess of negative electron charge carriers). On the opposite face a thin layer of aluminum is evaporated to facilitate electrical contact. The edge is protected by painting with Apiezon W dissolved in trichloroethylene to reduce surface current leakage. Then, a reverse bias is applied in the order of 10^3 volts per centimeter. The positive holes in the p-type base material with a very small concentration of free charge carriers.

When ionizing radiation, such as an alpha particle, enters the p-n junction side, the depletion layer serves as the sensitive volume, and electron-hole pairs are produced. They will quickly be collected as an electric pulse.

The surface barrier detector is made by evaporation of a thin layer of gold (100 μg/cm^3) on the surface of n-type silicon to form a conducting layer. Electrical connection to this layer is made by pressure contact to the top of the face of the epoxy disk and the ohmic contact, at the back side of n-type silicon, is made by soldering to a surface which has been nickel-plated. The surface barrier detectors operate in essentially the same way as the p-n type discussed above, although the mechanism of the surface barrier junction is not well understood. In this work, an "Ortec" surface barrier detector with an active surface of 100 mm^2 was used.

3. Amplifier

The signal from a radiation detector is produced by delivering an amount of charge (q) onto an input capacitance (C). Since signals from
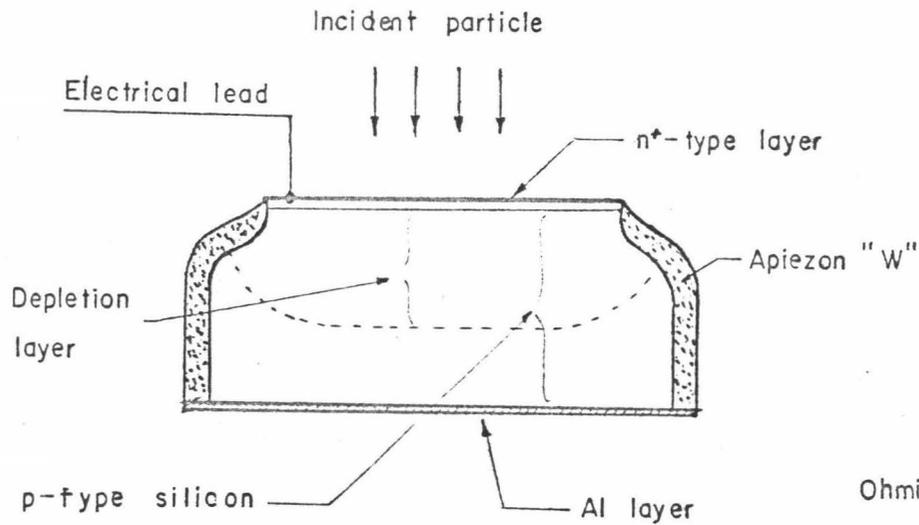
(a) Junction detector   (b) Surface barrier detector
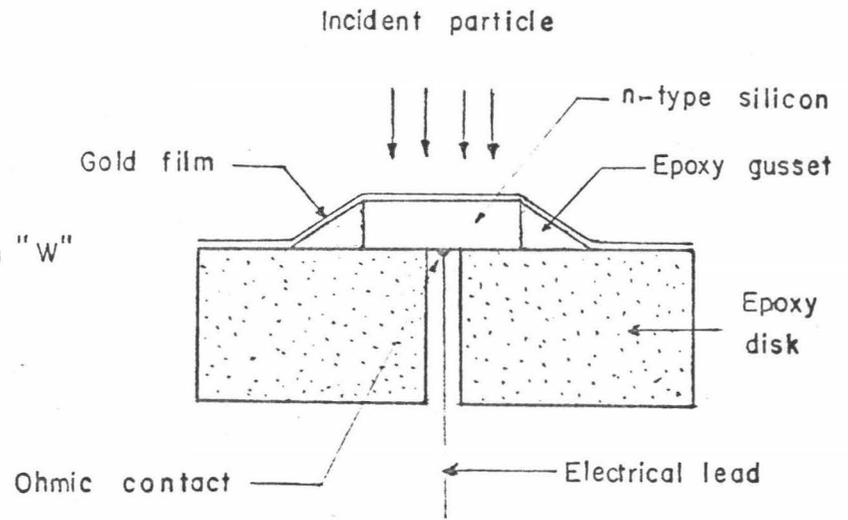
FIGURE 3. SCHEMATIC DIAGRAM OF SEMICONDUCTOR DETECTOR

the detector are of such low voltage magnitude (0-25 mv for a Si detector), an amplifier is needed between the detector and the measuring apparatus to make pulse height measurement possible.

Most conventional amplifiers are of the voltage-sensitive type, where the output pulse height is proportional to q/C. However, it is not desirable to couple the detector to a voltage-sensitive amplifier since it will reflect any variation in input capacitance resulting from variation in the barrier properties.

An alternate is the use of a charge-sensitive amplifier, where the pulse height does not vary with input capacitance since the output is essentially proportional to charge alone. Thus one will be able to alter the input circuit without changing the gain calibration significantly. Although the output pulse height of a charge-sensitive amplifier is essentially independent of the input capacitance, it exhibits nearly the same noise contribution as a voltage-sensitive amplifier, if the input capacitance is the same. Since the noise level increases with input capacitance, a long connecting cable between detector and amplifier will significantly affect the pulse height measurements at the output of an amplifier. The use of a preamplifier mounted on or near the detector makes it possible to provide the shortest possible detector leads. A preamplifier usually has a gain of 1-30, and should have as its output stage a cathode follower cable of low impedance.

Practically, however, it is not necessary to amplify the pulses for the energy range starting from zero. Some way of shifting the amplifier threshhold is needed. This is accomplished by first amplifying the pulses in the usual way, and then cutting off a certain amount of height from each pulse by changing the bias voltage. The resulting pulses are

then amplified to the required size. This type of amplifier is known as a post amplifier. The "Ortec" 101-201 low noise amplifer system is a good example including a convenient post amplifier arrangement.

4. Pulse-height Analyzer

The height of pulses produced in a detector depend on the energy deposited within the detector's sensitive area. If these energy-dependent pulses can be stored according to their heights, an energy spectrum can be obtained. Such a device, which can perform this sorting, is called a pulse-height analyzer.

A series of pulses from a detector is viewed very much as it would appear as a voltage-time waveform on a oscilloscope. In order to separate the pulses according to their heights, pulse-height selector units, which trigger certain pulses by the bias supply, are used. When a pulse-height selector is biased on a pulse of height E, the pulses lower than this height do not have sufficient amplitude to trigger the pulse height selector presenting output signals. If another pulse height selector is biased to $E + \Delta E$ units, the pulses above this $E + \Delta E$ height will be accepted by this upper pulse height selector; i.e., only the pulse-heights falling within the ΔE window will present output signals. This kind of device is called a single channel analyzer.

As a result of developments in radioactivation analysis, construction of a multichannel analyzer was desired which could measure short-lived nuclides with high sensitivity. The most obvious approach to the design of a multichannel analyzer is to construct a number of pulse-height selectors, whose bias levels are progressively increased. A stacked-discriminator type of 20-channel analyzer (a series of single channel analyzers) was first constructed, but the expense was high.

However, improvements in detectors, and the growing need for more automated data recording, created a need for multichannel analyzers with a very large number of channels. The introduction of techniques developed for digital computers made it possible to construct multichannel analyzers having thousands of channels.

The most important part of the analyzer is the analog-to-digital converter, which converts the pulse height to a train of pulses. The number of pulses produced determines the channel number in which the pulse is to be stored. These address pulses are counted by the address scaler.

The information is stored in a ferrite-core memory unit. Once the address scaler has selected a channel number, the number of counts are already stored in the memory at that address is read out into a add-one scaler. Then, the store command is given, the scaler increases the old number by one, and the new number is written back into the memory.

The information stored in the memoray unit can be read out in many ways. The decimal number can be recorded by using a teletypewriter. The binary-coded decimal information can be recorded in computer format on punched paper tape and digital information can be converted to analog voltage to drive an X-Y recorder. The "Nuclear Data" model ND-180 FM Analysis System is a good example of a multichannel analyzer, and includes all of these readout arrangements.

In the experiment reported here, the apparatus was modified in the following ways. Instead of using a Frisch screen-grid ionization chamber, an "Ortec" surface barrier detector with an active surface of 100 mm^2 with an "Ortec" 101-201 low noise amplifier system was used (Oak Ridge Technical Enterprises Corp., Oak Ridge, Tenn.). The pulse

signals were then introduced to a "Nuclear Data" 512 channel pulse height analyzer (Nuclear Data Inc., Palatine, Illinois). The surface barrier detector was biased at 30 volts and the measured alpha resolution (FWHM) varied between 35 and 49.5 KeV. The functional block diagram for the alpha counting system, which was introduced in this work, is shown in Figure 4, and the spectra obtained through the system are pictured in Figures 5, 6, 7 and 8.

In Figure 5, the first peak around channel 185 corresponds to thorium-232 and the second, around channel 250, to ionium (Th^{230}). The third around channel 320 is a peak for thorium-228 and the rest of the peaks resulted from the short-lived daughters of thorium-228, which were produced by the decay of thorium-228 after the separation of the thorium isotopes (radium-224, radon-220, bithmuth-212, and polonium-216). The spectra shown here are used in Figure 9 to give depth profiles of the ionium/thorium (Th^{230}/Th^{232}) ratio for the Pacific and the Artic Ocean sediment samples.
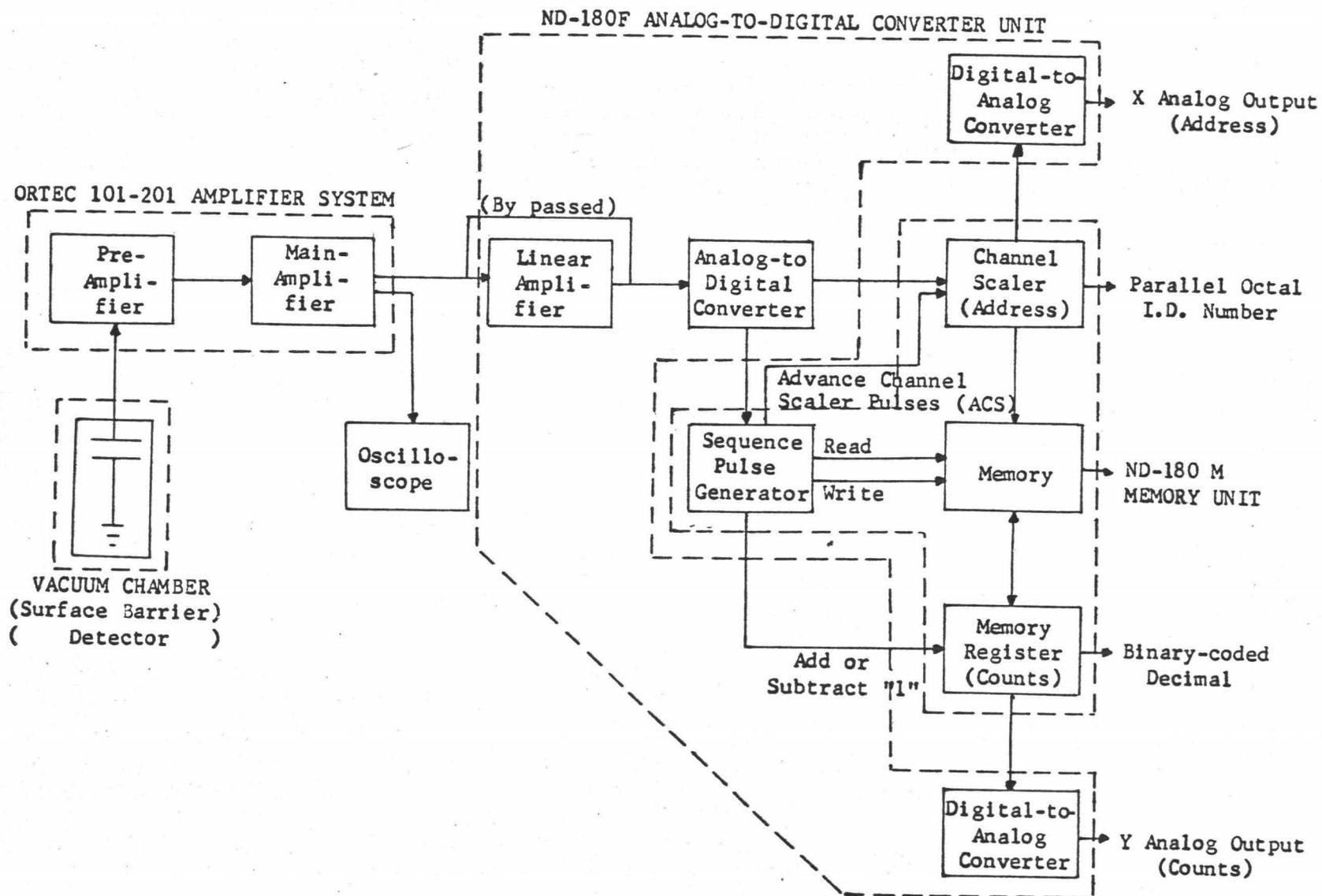
FIGURE 4. FUNCTIONAL BLOCK DIAGRAM FOR ALPHA-PARTICLE MEASUREMENT SYSTEM
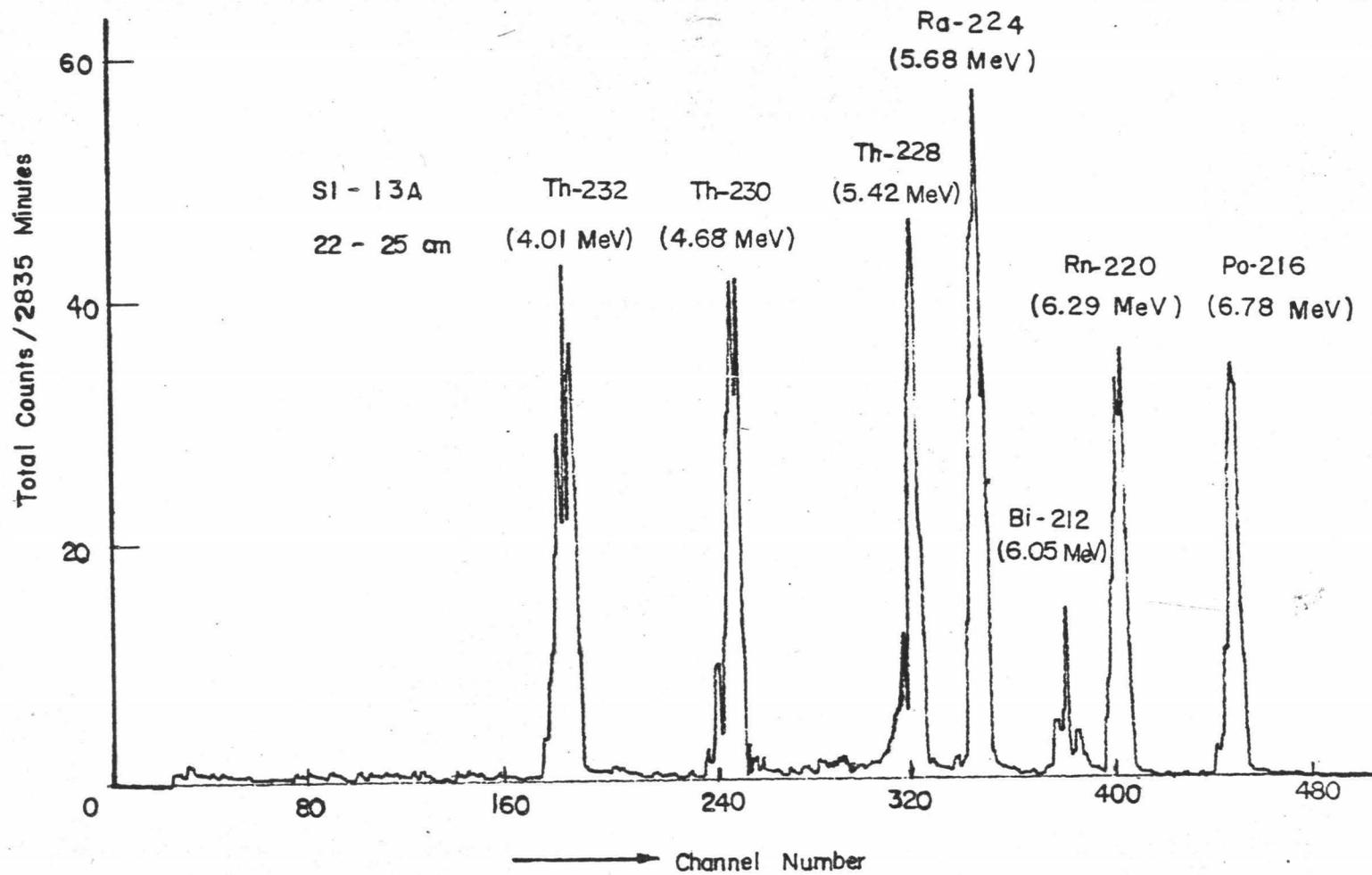
FIGURE 5. THE ALPHA-SPECTRUM OF THORIUM ISOTOPES ISOLATED FROM ARCTIC OCEAN CORE
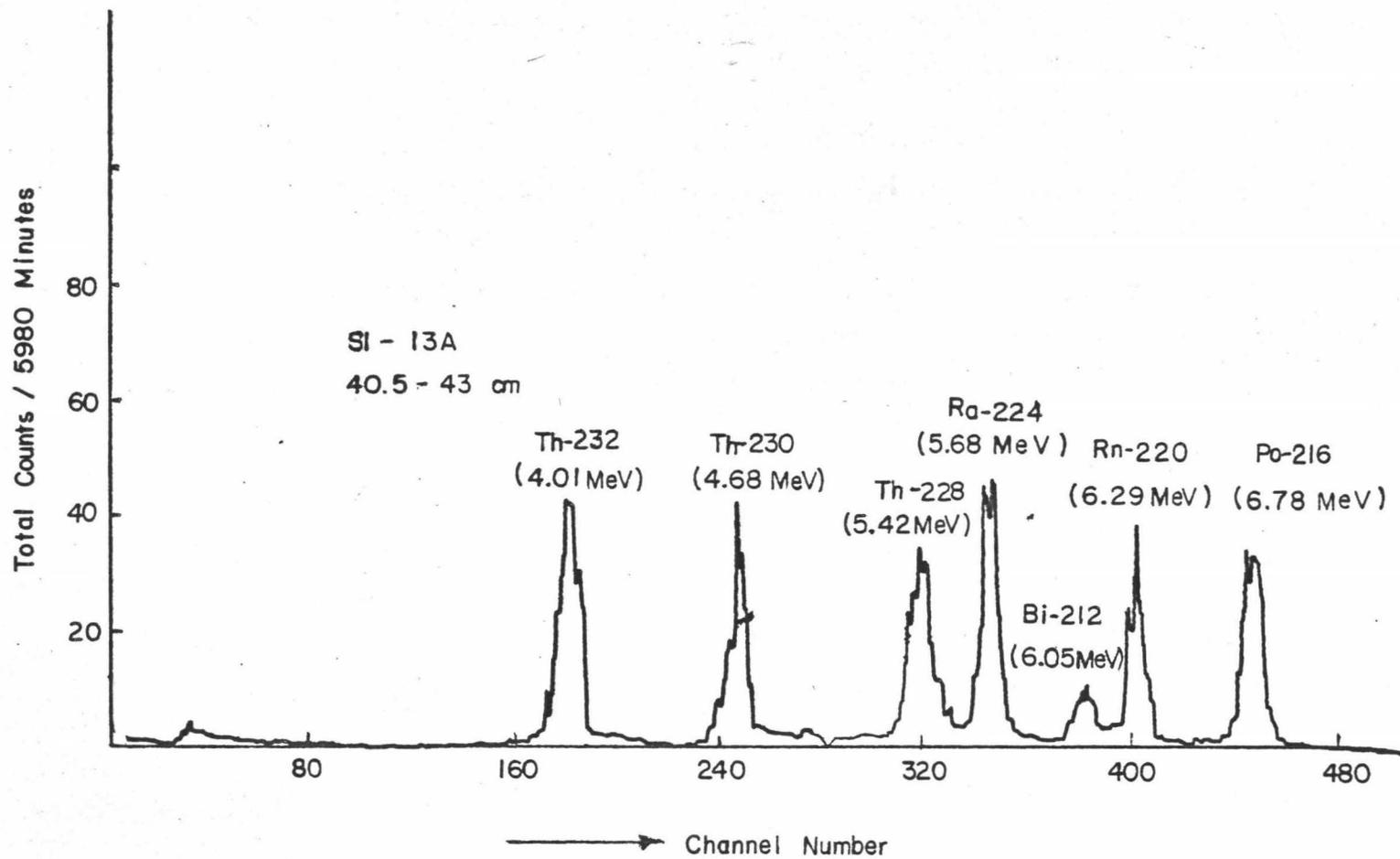
FIGURE 6. THE ALPHA-SPECTRUM OF THORIUM ISOTOPES ISOLATED FROM ARCTIC OCEAN CORE
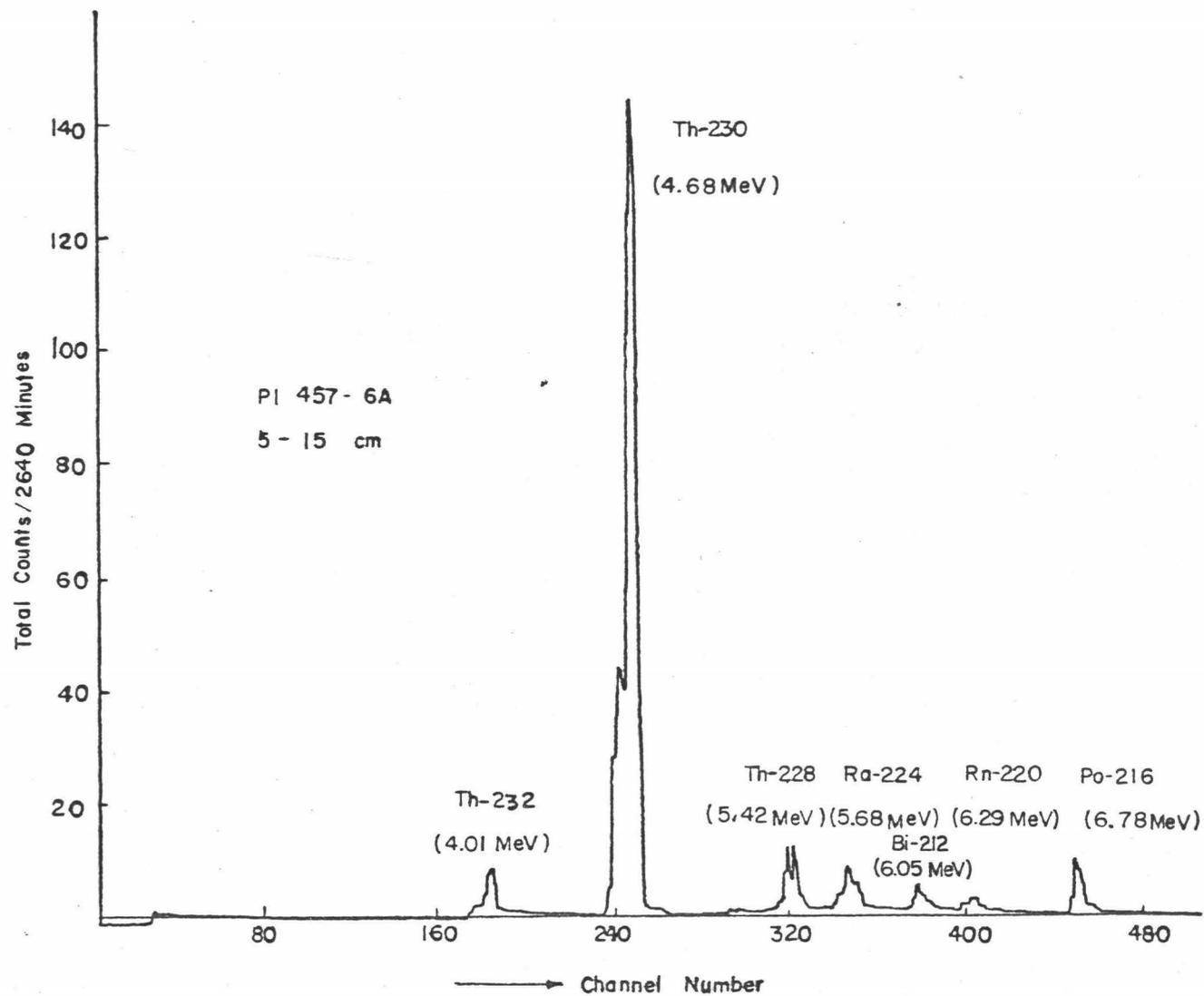
FIGURE 7. THE ALPHA-SPECTRUM OF THORIUM ISOTOPES ISOLATED FROM PACIFIC OCEAN CORE

22
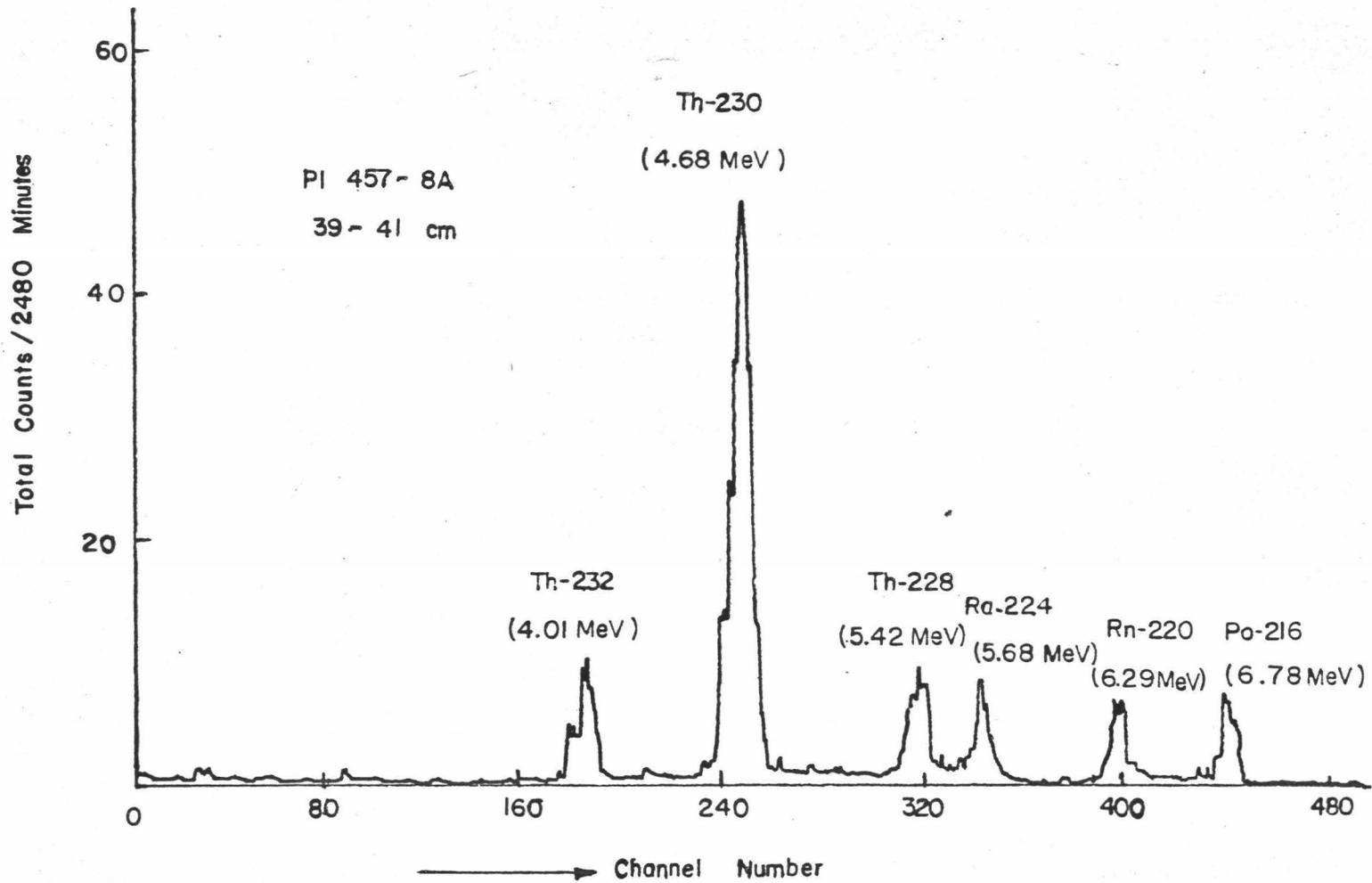
FIGURE 8. THE ALPHA-SPECTRUM OF THORIUM ISOLATED FROM PACIFIC OCEAN CORE

RESULTS AND CALCULATIONS

A. Calculations

Ages of various strata of the sample can be computed using the equation shown before.

$$R/Ro = e^{-\lambda t}$$

where R and Ro are the values of the ionium/thorium (Th^{230}/Th^{232}) ratio at a given depth and at the surface in the sediment sample, respectively, λ is the decay constant of ionium and t is the age of the sample corresponding to the depth in the sediment. If numerical values are substituted in the above equation, then

$$-\lambda t = \ln R/Ro$$

$$t = 1/\lambda \ \ln Ro/R = (t\tfrac{1}{2})/0.693 \ \ln Ro/R$$

$$= 76,000/0.693 \ \ln Ro/R \ \text{years}$$

$$t = 109.7 \ \ln Ro/R \times 10^3 \ \text{years}$$

The ionium/thorium (Th^{230}/Th^{232}) ratio, R, can be obtained directly from an alpha spectrum of the thorium isotopes. In this work, the ratios were obtained as activity ratios of counts of thorium-230 to thorium-232 under the respective peaks, rather than the measured areas. The surface value of the ionium/thorium (Th^{230}/Th^{232}) ratio, Ro, can be obtained as an intercept on the Y-axis from a plot of the ionium/thorium (Th^{230}/Th^{232}) ratio on a logarithmic scale as the Y-axis, and depth in the sample on an X-axis in linear scale (see Figure 9).

B. Chemical Yield of the Thorium Isotopes

Both extraction and ion-exchange separation techniques were used on the same core samples from the Pacific Ocean, with trace thorium isotope added, to compare the chemical yield of the thorium isotopes. The

results of tracer experiments gave a yield ranging from 22.6 to 76 per cent for both techniques. For the ion-exchange separation technique, the yield varied between 34 and 76 per cent while for the extraction technique it varied between 22.6 to 70 per cent.

Table 1 gives a comparison of the chemical yields of the thorium isotopes and ionium/thorium (Th^{230}/Th^{232}) ratios obtained through the use of both separation techniques.

According to Goldberg, et al.,[8] the leaching process, which used concentrated hydrochloric acid, removes nearly 70 per cent of the thorium in the sample. The treatment of the samples with a hot mixture of concentrated hydrochloric and perchloric acids would be expected to cause an additional release of the thorium isotopes from the undecomposed portions of the mineral which would remain from the less drastic hydrochloric acid leaching process. Moreover, the rather complicated procedure used in the extraction technique probably would result in lower yields than an ion-exchange technique due to greater manipulative losses.

C. Depth Profiles of the Ionium/Thorium (Th^{230}/Th^{232}) Ratios

1. Pacific Ocean Samples

For the purpose of checking the techniques applied, measurements were made on deep-sea sediments from the Pacific Ocean which also had been measured by other investigators using cores from adjacent areas. To this end, the sample PI 457-6A (lat., 39° 39.2' N, long., 178° 34.6' E, 5600 M) and PI 457-8A (lat., 19° 48.8' N, long., 170° 51' W, 3060 M), which were collected during June of 1965, were analyzed. The results of the analyses for the ionium/thorium (Th^{230}/Th^{232}) ratios are shown

TABLE 1.   CHEMICAL YIELDS OF THORIUM ISOTOPES

Sample	Extraction		Ion-exchange	
	Yield (%)	Io/Th	Yield (%)	Io/Th
PI 457-6A (5-15 cm)	22.6	11.9	34.0	11.5
PI 457-8A (0-2 cm)	22.9	54.4	76.0	51.6
PI 457-8A (4-6 cm)	70.0	87.5	75.0	88.0
PI 457-8A (14-16 cm)	37.7	26.0	70.0	26.7

partially in Table 1 and more extensive analyses for sample PI 457-8A
on deeper strata are shown in Table 2-(a). The ratios are then compiled
as a profile in Figure 9-(a).

Measurement of the ionium/thorium (Th^{230}/Th^{232}) ratio was made for
the different strata of sample PI 457-8A from the Mid Pacific. In a
plot of the ionium/thorium (Th^{230}/Th^{232}) activity ratio versus depth in
the sediment, the surface intercept had a value of 150. The rate of
accumulation on a gross basis was thus obtained as 0.8 mm/10^3 years with
surface disturbance occurring to a depth of about 5 cm. The ionium/
thorium (Th^{230}/Th^{232}) ratio in sample PI 457-6A from the mid-central
North Pacific, at a depth of 5-15 cm, was found to be 11.7. These
results are compared with the data reported by the other investigators
on cores from the adjacent area in the discussion.

2. Arctic Ocean Sample

Table 2 gives the depth variation of the ionium/thorium ($Th^{230}/$
Th^{232}) ratios. The ratios show a geographic dependence in the sediment
sample. A surface disturbance in the sediment seems to take place to a
depth of about 20 cm. From the surface intercept and the slope of
Figure 9-(b), an accumulation rate of 9.2 mm/10^3 years was obtained on
a gross basis.

DISCUSSION

A. Comparison of the Method

The ionium/thorium (Th^{230}/Th^{232}) ratio in sample PI 457-6A is
compared with the ratios for samples from adjacent areas, which were
analyzed by Goldberg, et al.;[8] i.e., Chinook 4, Chinook 7 and Chinook
11. They reported the ratios varying between 6 and 21 at a depth of

TABLE 2.   DEPTH VARIATIONS OF THE IONIUM/THORIUM (Th^{230}/Th^{232}) RATIO

(a) Pacific Ocean   (b) Arctic Ocean

Pioneer 457-8A 3060 meters 19°48.4' N; 170°51' W			Phleger Core; SI-13A 89 meters 69°01.3' N; 116°46.6' W		
Depth (cm)	Io/Th	Technique Applied	Depth (cm)	Io/Th	Technique Applied
0-3	53.0	Extraction Ion-exchange	0-5	0.87	Extraction
			6-8	1.00	Extraction
4-6	88.0	Extraction Ion-exchange	12-14.5	0.98	Ion-exchange
14-16	26.4	Extraction Ion-exchange	17-20	0.87	Extraction
			22-25	0.92	Ion-exchange
19-21	14.9	Ion-exchange	26-29	0.89	Extraction
39-41	5.8	Ion-exchange	32-35	0.87	Ion-exchange
			40-43	0.83	Extraction
			46-49	0.73	Extraction
			56-59	0.66	Extraction
			67-70	0.61	Extraction
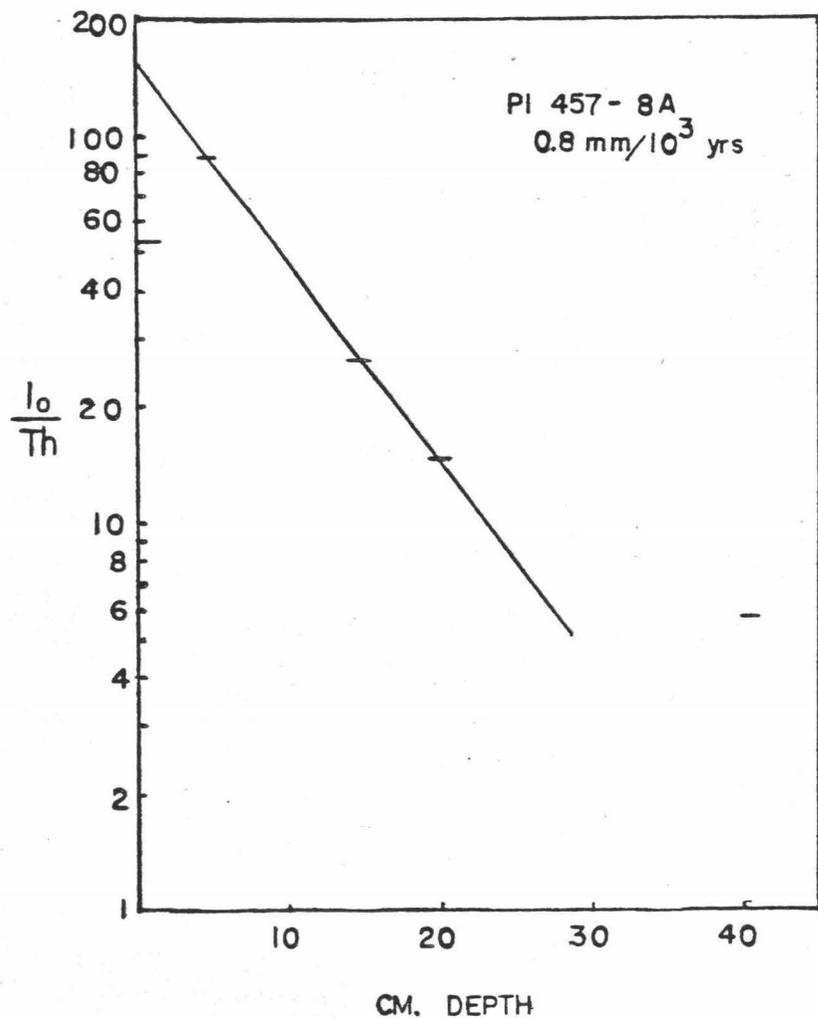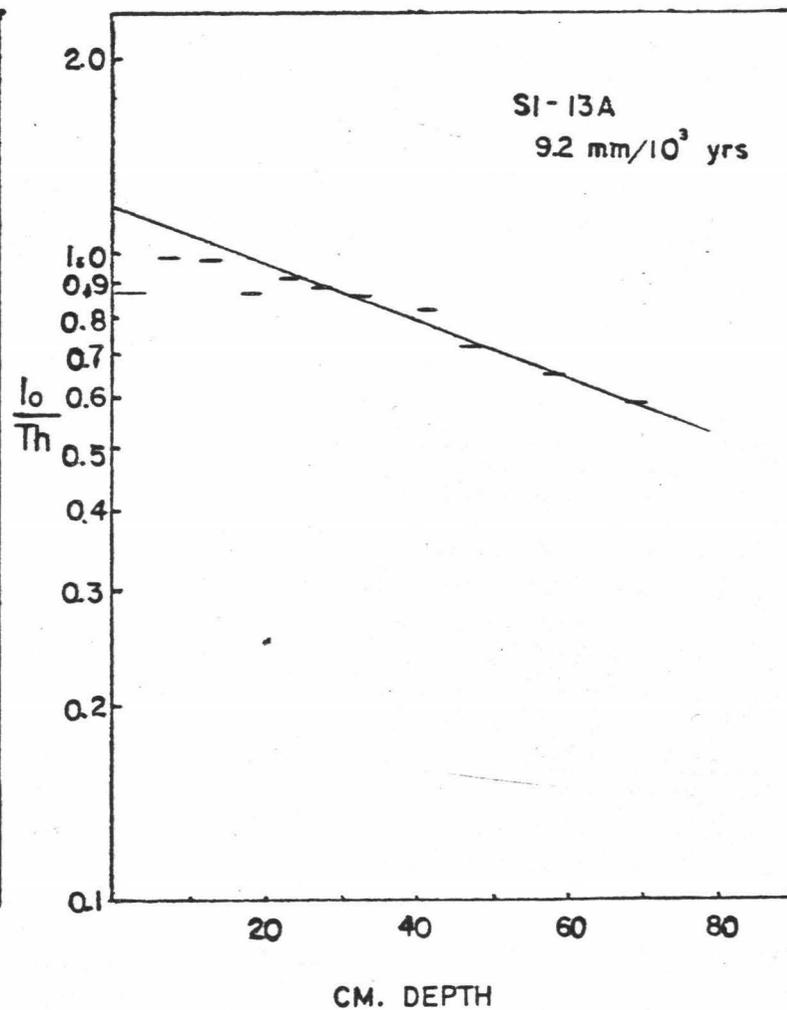
(a) PACIFIC OCEAN CORE   (b) ARCTIC OCEAN CORE

FIGURE 9. THE IONIUM/THORIUM RATIOS AS A FUNCTION OF DEPTH

5-15 cm, the ratios being 15-21 for Chinook 4, 8.1-10 for Chinook 7 and 6-20 for Chinook 11 (see Appendix and Figure 10). No disturbance in the sediment was observed at this depth in Chinook 11, while in Chinook 4 and 7 the ionium had been homogenized within this depth by the surface disturbance. The result obtained in this work for sample PI 457-6A for the same depth (11.7) closely agrees with the ratio in Chinook 11 (6-20). Considering the effect of surface disturbance on the sediments and the same sedimentary material, clay mineral, the ionium/thorium (Th^{230}/Th^{232}) ratios will most probably remain around 10 at a depth of 5-15 cm in the sediments from these adjacent areas.

Examining the sediment from the Mid-Pacific, disagreement is observed for the ionium/thorium (Th^{230}/Th^{232}) ratios between sample PI 457-8A, which was analyzed in this laboratory, and sample Mid-Pac. 38 (4774 M), which was reported by Goldberg, et al.[8] (see Appendix). Goldberg, et al., found that the ionium/thorium (Th^{230}/Th^{232}) ratios in Mid Pac. 38 remain almost the same to a depth of 15 cm, showing evidence of surface disturbance. Then, the ratios decrease rapidly corresponding to a rate of sedimentation of 0.4 mm/10^3 years on a gross basis. On the other hand, Almondovar[10] observed a sedimentation rate of 1 mm/10^3 years for the sediment from an adjacent area. However, the rate of accumulation in PI 457-8A was obtained in this laboratory as 0.8 mm/10^3 years on a gross basis with a surface disturbance occurring to a depth of 5 cm in the sediment. The surface value of the analyzed ratio was obtained as 53.0 and the intercept of the ratio was obtained as 150. These results closely agree with sample Capricorn 5BG (4960 M) from the South Pacific, which was also reported by Goldberg, et al. They obtained an average surface intercept of 149 with a range between 143

FIGURE 10. PROFILES OF THE IONIUM/THORIUM (Th^{230}/Th^{232}) RATIO

IN SEDIMENT SAMPLES FROM THE PACIFIC OCEAN[*]

(Heavy lines are data obtained in this work.)

CM DEPTH IN CORE

CM DEPTH IN CORE
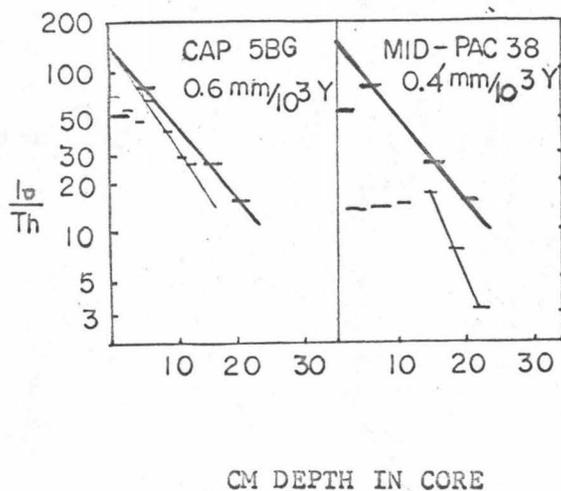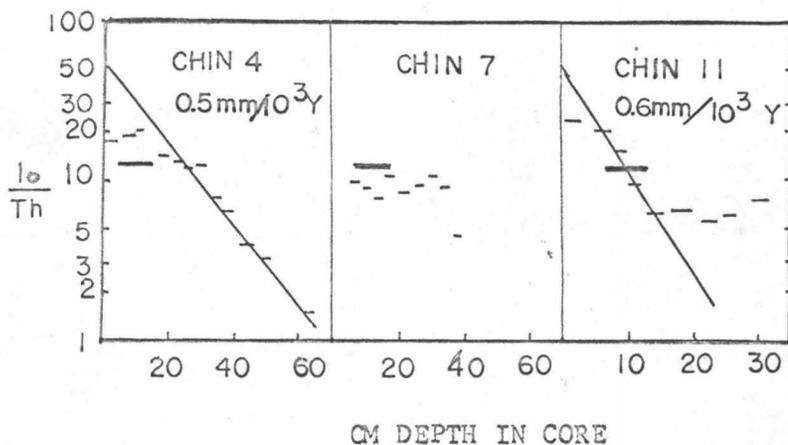
[*] Data were reproduced from Geochimica et Cosmo. Acta, 26, 430 (1962), Goldberg, E. D. and M. Koide.

and 158 for six analyzed sediment samples from the South Pacific, and .
thus showed quite uniform rates of accumulation of from 0.3-0.6 mm/10^3
years.

The disagreement on the ionium/thorium (Th^{230}/Th^{232}) ratios between
PI 457-8A and Mid-Pac. 38 may be accounted for as follows: Goldberg,
et al.,[11], [12] reported the relationship between the surface values of
the ionium/thorium (Th^{230}/Th^{232}) ratios and calcium carbonate contents
on the sediment samples from the Indian and Atlantic Oceans, showing
that the increase in the values of the ratio is complemented by
increased carbonate contents. The sample highest in $CaCO_3$ had the
highest intercept in a plot of the ratio as a function of depth in the
sediment. Since sample PI 457-8A is a carbonate material, the ionium/
thorium (Th^{230}/Th^{232}) ratios would be expected to be higher than in clay
minerals from the adjacent areas. Another probable explanation is that
the difference in the ratios could also arise from the difference of
the depth of the sediment in the ocean. Recent investigators suggested
that the highly reactive elements with short residence times in the
ocean, such as barium,[13] the rare earths,[14] lead-210[15] and mercury,[16]
conveyed from shallow to deeper water by inorganic and/or biochemical
processes. Therefore, the transfer of thorium-232 from surface to
deeper waters by the same mechanisms appears reasonable. If we assume
that the supply of thorium-232 into the open ocean from continents or
from volcanoes is very low and can be neglected, and since the rate of
production of thorium-230 is constant in the ocean regardless of depth
due to the uniform concentration of uranium-238 throughout the ocean
waters, then the ionium/thorium (Th^{230}/Th^{232}) ratio in surface waters
will be higher than that in deeper waters. Thus, the shallower a core

is in the open ocean, the higher will be its values for the ionium/thorium (Th^{230}/Th^{232}) ratio.

Judging from the above comparison and discussion, agreement with other workers can be said to be satisfactory and the method is applicable for the determination of the ages of marine sediment samples which fulfill the assumptions involved (see also Figure 10).

B. Surface Values of the Ionium/Thorium (Th^{230}/Th^{232}) Ratios

The geographical dependence of the ionium/thorium (Th^{230}/Th^{232}) surface ratio in the marine sediments probably reflects variations in the ionium/thorium (Th^{230}/Th^{232}) ratio in the water adjacent to the deposits. Since ionium is produced from the uranium-238 in sea-water, and the latter is constant in sea-water, the ratio variation probably arises from differences in the concentration of thorium-232 in sea-water. As the residence time of thorium is very short (~ 350 y) compared to that of the uranium-238 ($\sim 500,000$ y), the concentration of thorium-232 relative to the concentration of ionium in the mixing layer of the coastal area of the ocean would be expected to be higher than that of deeper layers due to the input of land-derived thorium-232. Inasmuch as the analyzed sample (SI-13A) was collected from a depth of only 89 meters, which occurs within the mixing layer and in a coastal area, the lower value of the ionium/thorium (Th^{230}/Th^{232}) surface ratio in this sample would most probably be due to the above described speciation of the thorium in the region.

The surface disturbance of the sediment takes place through two mechanisms which results in a layer of homogenized deposit. (1) Bottom water currents which can carry the deposited solid phase into suspension

would provide a stirring mechanism for those top layers, causing a net flow of ionium from a richer to a poorer part of the deposit. This kind of stirring mechanism would be particularly effective in the sediments which occur within the mixing layer of the ocean (down to 100 meters in depth). (2) The other well known mechanism of surface disturbance is that of burrowing organisms, which cause a disturbance and a churning of the sediments at the water-sediment interface.

The surface disturbance of the completely analyzed sediment sample (SI-13A) would most probably be caused by the first mechanism since it would come under the action of the mixing layer of the ocean.

It is of interest to point out that Goldberg, et al., found the surface values of the ionium/thorium (Th^{230}/Th^{232}) ratios in sediment cores from the North Atlantic varying between 1.5 and 6, but were able to show no evident dependence on geography down to a depth of 30 cm.[8]

C. Precision and Accuracy of the Method

When considering the errors inherent in an analytical method it is convenient to distinguish between the precision (reproducibility), which contains the effect of random errors only, and the accuracy (approach to the truth), which also includes the effect of systematic errors.

1. Precision

Precision of the analytical method depends partially on the choice of methods for the determination of each constituent present in the sample and partially on the determinative methods available in a particular laboratory, as well as on one's own personal predilections for certain methods. The classical extraction technique, as well as the ion

exchange technique, has long been recognized as a useful means of sepa-
ration of minute amounts of radionuclides. The final determination of
these radioactive elements, preceded by the chemical separations, can
be achieved by the introduction of radiation detectors for the detection
of the specific radiation of the emitting element.

For the detection of alpha radiation from naturally occurring
radioactive elements with low-level activities, one must place stringent
restrictions on radiation detectors to reduce the background level
sufficient to make significant sample measurements with high standards
of precision. If the thorium isotopes were isolated with high precision
through different methods of separation, the precision of the method
will depend upon the counting statistics of the alpha radiation. In
this work, the ionium/thorium (Th^{230}/Th^{232}) ratios were calculated as
activity ratios from the alpha spectrum under their respective peaks.
The coefficient of the standard deviation varied between 7.4% and 16.9%,
being 9.6% and 12.4% for the Pacific sediments and 7.4% and 16.9% for
the Arctic Ocean sediment.

The separation of the thorium isotopes by both extraction and ion
exchange techniques was accomplished with good agreement on the measured
ionium/thorium (Th^{230}/Th^{232}) ratios. The variance in the ratios between
both techniques falls within the statistical errors of alpha counting
on the thorium separated samples.

2. Accuracy

The accuracy of the method depends upon the precision and also
includes the systematic errors of the chemical separation of the thorium
isotopes. The chemical errors in the method will arise mainly from
incomplete decomposition of the sample materials. The principal

detrital minerals in the sediments, not attacked in the leaching process, are quartz and feldspars.[8] Since the feldspars would possibly persist in the sediments over time periods of at least millions of years, the ionium would be in equilibrium with its parent uranium-238. The complete decomposition of sample material, such as in a fusion process, will thus tend to decrease the ionium/thorium (Th^{230}/Th^{232}) ratio, reflecting the dilution of the unsupported excess of the ionium relative to the thorium in the leachates. The precision and accuracy in the method will depend, therefore, very much on the method of decomposing the sample materials.

The accuracy will also depend on the sensitivity of the alpha counting instrument for low-level measurements. The introduction of recently developed semiconductor detectors has proved particularly useful for such low-level measurements. Inherently better resolution ($\sim 0.5\%$) and low background (0.008 cpm) lead to sharply defined energy peaks for the alpha spectra and greatly simplify the calculation of the ionium/thorium (Th^{230}/Th^{232}) ratios under their respective peaks.

SUMMARY

The exponential decrease in the ionium/thorium (Th^{230}/Th^{232}) ratios with depth indicates that the assumptions of the method are in conformity with nature. The utilization of both extraction and ion exchange techniques shows good agreement in the measured ionium/thorium (Th^{230}/Th^{232}) ratios but better recovery of the thorium isotopes is obtained for the ion exchange technique.

The ionium/thorium (Th^{230}/Th^{232}) ratios depend upon geographical locations and on sedimentary materials in the ocean. The surface values

of the ionium/thorium (Th^{230}/Th^{232}) ratios are smaller for those areas receiving large amounts of land derived solid phase, and higher for carbonate materials.

The rate of accumulation in the Mid-Pacific is 0.8 mm/10^3 years and in the Arctic Ocean is 9.2 mm/10^3 years on a gross basis. The deposits near coastal areas show a rapid accumulation rate due to the large amount of land-derived solid phase in these regions.

APPENDIX

Comparison of Ionium/Thorium (Th^{230}/Th^{232}) Ratios[*]

Depth (cm)	Io/Th	Depth (cm)	Io/Th
Chinook 4 (6132 meters) 42°29.9' N; 162°08.2' W		Chinook 7 (5050 meters) 47°10' N; 165°45' W	
0-5	17	0-5	18
5-10	19	5-10	10
10-12	21	10-12	9.1
12-16	12	12-16	8.1
16-20	15	16-20	11
20-24	14	20-24	8.9
24-28	12	24-28	9.6
28-32	13	29-32	11
32-36	9.8	32-36	9.3
36-40	6.6	36-40	4.6
40-44	4.1		
44-48	4.0		
48-52	3.3		
60-64	1.4		
Chinook 11 (4850 meters) 49°39.5 N; 177°39' W		Capricorn 5 BG (4960 meters) 9°03' S; 174°52' E	
0-4	23	0-2	72
4-8	20	2-4	59
8-10	15	4-6	47
10-12	9.3	6-8	65
12-16	6.0	8-10	43
16-20	6.3	10-12	29
20-24	5.4	12-14	26
24-28	5.9	20-22	27
28-32	7.5		
Mid-Pac. 38 4774 meters 19°02' N; 177°18' W			
0-4	12.9		
4-8	13.8		
8-12	14.4		
12-16	17.0		
16-20	8.0		
20-24	3.3		

[*] Data were reproduced from Geochimica et Cosmo. Acta, 26, 444 (1962), Goldberg, E.D. and Koide, M.

BIBLIOGRAPHY

1. Libby, W. F. "Radiocarbon Dating." 2nd ed., Univ. of Chicago Press, Chicago, 1955.

2. Isaac, N. and E. Picciotto. Nature, 171, 747 (1953).

3. Piggot, C. S. and W. D. Urry. Amer. J. Sci., 81, 239 (1941).

4. Droll, U. S. Deep-Sea Res., 1, 211 (1954).

5. Picciotto, E. and S. Wilgain. Nature, 173, 632 (1954).

6. Goldberg, E. D. and M. Koide. Science, 128, 1003 (1958).

7. Weiss, W. L. and E. M. Whatley. Nucleonics, 21, Sept. 66 (1963).

8. Goldberg, E. D. and M. Koide. Geochim. et Cosmo. Acta, 26, 417 (1962).

9. Miyake, Y. and Y. Sugimura. Science, 133, 1823 (1961).

10. Almodovar, I. Thorium isotopes method for dating marine sediments. Unpublished Thesis, (1960).

11. Goldberg, E. D. and M. Koide. Earth Sciences and Meteoritics. North-Holland Publ. Co., Amsterdam, 90 (1963).

12. Goldberg, E. D., M. Koide, J. J. Griffin and M. N. A. Peterson. Isotopic and Cosmic Chem. North-Holland Publ. Co., Amsterdam, 219 (1963).

13. Chow, T. J. and E. D. Goldberg. Geochim. et Cosmo. Acta, 20, 192 (1960).

14. Goldberg, E. D., M. Koide, R. A. Schmidt and R. H. Smith. J. Geophys. Res., 68, 4205 (1963).

15. Rama, M. Koide and E. D. Goldberg. Science, 134, 98 (1961).

16. Hosohara, K., R. Kuroda and H. Hanaguchi. Nippon Kagaku Zasshi, 82, 347 (1961).

ACKNOWLEDGMENT