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ISOTOPIC THORIUM AND ISOTOPIC URANIUM COMPOSITIONS
OF MODERN AND FOSSIL MARINE MOLLUSCAN SHELLS

by

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A dissertation presented to the
Graduate School of Arts and Sciences
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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1. INTRODUCTION¹

The slow decay of naturally occurring radioactive elements in the earth's crust has ticked off the seconds with unalterable precision since the earth was born. Thus by measuring the amount of the elements' decay we can determine the age of the material of which they are a part.

More than a dozen long-lived natural radioisotopes have been discovered. However, we are interested only in the uranium, actino-uranium and thorium series in this study. Table 1 shows the members and the transformation of these three series.

In undisturbed samples of very old materials the members of these three radioactive series will be in secular equilibrium. However, the loss or gain, by natural processes, of the parent or daughter elements in the material causes disequilibria within the decay series. Normally such natural processes are slow and consequently disruption of equilibrium in the radioactive families will be noticeable only if the separation or enrichment processes involve nuclides with relatively long half-lives.

The disequilibria that one may expect to observe in the three naturally occurring radioactive families usually arise because of gain or loss of one or more of the following nuclides (half-lives given in parentheses):

¹This dissertation was prepared under the direction of Professor Herbert A. Potratz.

Table I

Uranium, Actino-uranium and Thorium Decay Series

1. Uranium series

U^{238} (4.5×10^9 y.), U^{234} (2.48×10^5 y.), Th^{230} (75,200 y.),
 Ra^{226} (1,620 y.), Pb^{210} (22 y.), Po^{210} (138 days).

2. Actino-uranium series

U^{235} (7.1×10^8 y.), Pa^{231} (3.4×10^4 y.), Ac^{227} (22 y.).

3. Thorium series

Th^{232} (1.4×10^{10} y.), Ra^{228} (6.7 y.), Th^{228} (1.9 y.).

The other short-lived daughter elements are expected to be in equilibrium with their long-lived parents.

When uranium is incorporated into a marine carbonate without its following products, the increase of the daughter elements can be used for age determination if there is no gain or loss of uranium and the daughter elements. The first attempt to date carbonates by this method was made on marine corals by Barnes, Lang and Potratz, who found that coral limestone cuttings taken over the first two hundred feet in drilling on Elugelab Island in the Eniwetok Atoll exhibited an irregular increase of ionium to uranium with increasing depth which presumably was a direct consequence of the Th^{230} to U^{238} disequilibrium in the ocean water.²

This discovery gave rise to the possibility of determining absolute age for marine carbonates in the range from approximately 5,000 years B. P. to 300,000 years B. P., partially filling the gap between the C^{14} and the U-Pb, K-Ar, and Rb-Sr methods of dating.* In 1958 Sackett published Th^{230}/U^{238} ratios for coral limestone cuttings from Parry Island, Eniwetok

²J. W. Barnes, E. J. Lang and H. A. Potratz, Science, 124, 175 (1956).

*B. P. is the abbreviated form of Before Present.

Atoll and for other calcium carbonate materials.³

Three basic conditions must be fulfilled for the $\text{Th}^{230}\text{-U}^{238}$ dating method to be valid. (1) The original marine-deposited calcium carbonate must contain a measurable amount of uranium; (2) it must be initially free of Th^{230} or contain this nuclide at a low and predictable concentration; and (3) the specimen must, during aging, behave as a closed system.

Blanchard made an intensive study on thirty modern marine mollusks from fourteen geographic locations and on corals and ancient shells from a number of well defined marine horizons. He also set up several criteria by which one could select samples which would probably yield reliable $\text{Th}^{230}/\text{U}^{238}$ ages. Where these criteria were fulfilled, the ages corresponded rather well with age estimates based on stratigraphic considerations or C^{14} analyses.⁴

From the work of Sackett and Blanchard, the following conclusions were made:

(1) Marine calcium carbonates were found to contain uranium in a measurable quantity. The amount present was usually in the range 0.1 to 5 ppm. This satisfies the first condition for dating calcium carbonates by the $\text{Th}^{230}\text{-U}^{238}$ method. Both Blanchard and Broecker reported that living marine mollusks have less uranium than their fossil counterparts.^{4,5} Two possible explanations were given for this difference. Either the oceans

³W. M. Sackett, PhD Thesis, Washington University, St. Louis, Mo. (1958)

⁴R. L. Blanchard, PhD Thesis, Washington University, St. Louis, Mo. (1963).

⁵W. S. Broecker, J. Geophys. Res. 68, 2817 (1963).

contained more uranium during the years these fossil shells were developing, or all of the fossil shells were contaminated with uranium after the organism's death and deposition.

(2) The initial Th^{230} concentration was very nearly zero. This satisfies the second condition specified above.

(3) Whether or not a marine carbonate fulfills the third condition, the closed system condition, was uncertain.

Blanchard has shown that ages based on $\text{Th}^{230}/\text{U}^{238}$ in a number of well preserved fossil marine mollusk specimens are in agreement with age estimates of those specimens based on stratigraphic considerations. However, the agreement between the $\text{Th}^{230}/\text{U}^{238}$ and the stratigraphic age can not be taken as good evidence that the age obtained is correct. Additional evidence must be sought to support the assumption that closed system conditions have prevailed in the specimen since the time of its deposition.

The first purpose of the work reported in this thesis was to seek additional criteria which may be applied to fossil marine mollusks as tests of closed system conditions. The second purpose was to apply these criteria to two series of well preserved fossil marine mollusks.

A series of stratigraphically equivalent samples from marine terraces on the California coast ^{was} ~~were~~ chosen for part of this investigation. It is assumed that these specimens were deposited at a time in the past when the sea stood approximately 100 feet above its present level.⁶ A second series of samples came from Russia. They were collected from deposits associated with Anzhu II transgression, the Karginian transgression, the Kazantsevan transgression and the Sanchugovian transgression with estimated

⁶W. C. Bradley, Bull. Geol. Soc. Amer., 67, 675 (1956)

geologic ages of 22-45,000 years B. P., 22-45,000 years B. P., 70-100,000 years B. P., and 110-180,000 years B. P. respectively.⁷

⁷Personal communication from V. A. Zubakov to Thor Karlstrom, U. S. Geological Survey.

II. THEORY OF URANIUM DECAY SERIES METHODS FOR DATING MARINE MOLLUSCAN SHELLS

1. GENERAL GROWTH AND DECAY EQUATION

In a radioactive series $N_1 \xrightarrow{\lambda_1} N_2 \xrightarrow{\lambda_2} N_3 \xrightarrow{\lambda_3} N_4 \dots$

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \quad \text{and} \quad N_1 = N_1^0 e^{-\lambda_1 t}$$

where N_1 is the number of unchanged atoms of N_1 at time t , N_1^0 is the number present at $t=0$ and λ_1 is a decay constant characteristic of the species N_1 . The second species is formed at the rate at which the first decays, $\lambda_1 N_1$, and itself decays at the rate $\lambda_2 N_2$. Thus,

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

This linear differential equation is solved with the condition $N_2 = N_2^0$

at $t=0$, and we obtain the solution for N_2 .

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t}$$

N_3 may be found by solving the new differential equation:

$$\frac{dN_3}{dt} = \lambda_2 N_2 - \lambda_3 N_3$$

The solution for N_n with $n \geq 3$ are more complicated. Bateman⁸ has given solution for a series of n members with the special assumption that at $t=0$ the parent substance alone is present, that is, $N_2^0 = N_3^0 = \dots = N_n^0 = 0$.

This solution is,

$$N_n = c_1 e^{-\lambda_1 t} + \dots + c_n e^{-\lambda_n t}$$

$$c_1 = \frac{\lambda_1 \lambda_2 \dots \lambda_{n-1}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \dots (\lambda_n - \lambda_1)} N_1^0$$

⁸H. Bateman, Proc. Cambridge Phil. Soc., 15, 423 (1910)

$$C_2 = \frac{\lambda_1 \lambda_2 \dots \lambda_{n-1}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2) \dots (\lambda_n - \lambda_2)} N_1^0, \text{ etc.}$$

If we do require a solution to the more general case with $N_2^0, N_3^0, \dots$, $N_n^0 \neq 0$, we may construct it as follows. Add to the Bateman solution for N_n in an n -membered series, a Bateman solution for N_n in an $(n-1)$ -membered series with substance 2 as the parent, and, therefore, $N_2 = N_2^0$ at $t=0$. Next add a Bateman solution for N_n in an $(n-2)$ -membered series, and so on.

2. $\text{Th}^{230}/\text{U}^{234}$ METHOD*

This method as has already been pointed out is based on the assumptions that, the initial Th^{230} activity is equal to zero, that U^{238} and U^{234} at time zero are in secular equilibrium, and that the sample acts as a closed system with respect to thorium and uranium. From these assumptions it follows that

$$N_{\text{Th}^{230}} = N_{\text{U}^{238}} \frac{\lambda_{\text{U}^{238}}}{\lambda_{\text{Th}^{230}} - \lambda_{\text{U}^{238}}} (e^{-\lambda_{\text{U}^{238}} t} - e^{-\lambda_{\text{Th}^{230}} t})$$

Since $\lambda_{\text{U}^{238}} \ll \lambda_{\text{Th}^{230}}$ and $N_{\text{U}^{238}} = N_{\text{U}^{238}} e^{\lambda_{\text{U}^{238}} t}$ and since for time interval under consideration $t \ll 1/\lambda_{\text{U}^{238}}$ the equation may be approximated as follows:

$$N_{\text{Th}^{230}} = N_{\text{U}^{238}} \frac{\lambda_{\text{U}^{238}}}{\lambda_{\text{Th}^{230}}} (1 - e^{-\lambda_{\text{Th}^{230}} t})$$

which gives the formula,

$$t = - \frac{1}{\lambda_{\text{Th}^{230}}} \ln \left(1 - \frac{A_{\text{Th}^{230}}}{A_{\text{U}^{238}}} \right)$$

However, Cherdyntsev and his co-workers⁹ discovered radioactive disequilibrium in nature between U^{234} and its parent U^{238} . Thurber¹⁰ confirmed this anomaly and showed that dissolved uranium in sea water is enriched in U^{234} activity by 15 percent over that of its parent U^{238} . These

* The method is also frequently called the Th^{230} growth or the $\text{Th}^{230}/\text{U}^{238}$ method.

⁹ V. V. Cherdyntsev, P. I. Chalov and G. Z. Khaidarox, Izv. Akad. Nauk SSSR, Moscow, P. 175 (1955)

¹⁰ D. L. Thurber, J. Geophys. Res. 67, 4518 (1962).

discoveries not only required a revision of previous age estimates but also opened the possibility of an independent age method based on the decay of the excess U^{234} .

Bearing in mind that the Th^{230} activity arises from the growth toward equilibrium with U^{238} and its equilibrium amount of U^{234} and the growth toward transient equilibrium with the excess U^{234} we write

$$A_{Th^{230}} = \left[(1 - e^{-\lambda_{Th^{230}} t}) A_{U^{238}} \right] + \left[(R - 1) A_{U^{238}} \frac{\lambda_{Th^{230}}}{\lambda_{Th^{230}} - \lambda_{U^{234}}} (e^{-\lambda_{U^{234}} t} - e^{-\lambda_{Th^{230}} t}) \right]$$

$$\text{and } \frac{A_{Th^{230}}}{A_{U^{238}}} = \left[1 - e^{-\lambda_{Th^{230}} t} \right] + \left[(R - 1) \frac{\lambda_{Th^{230}}}{\lambda_{Th^{230}} - \lambda_{U^{234}}} (e^{-\lambda_{U^{234}} t} - e^{-\lambda_{Th^{230}} t}) \right]$$

where R is the initial activity ratio of U^{234} to U^{238} . Substituting the values $2.79 \times 10^{-6} \text{ year}^{-1}$ and $9.21 \times 10^{-6} \text{ year}^{-1}$ for the decay constants of U^{234} and Th^{230} respectively, the equation becomes;

$$\frac{A_{Th^{230}}}{A_{U^{238}}} = 1 - e^{-9.21 \times 10^{-6} t} + (1.43) (R - 1) (e^{-2.79 \times 10^{-6} t} - e^{-9.21 \times 10^{-6} t})$$

Table 2 lists data for $A_{Th^{230}}/A_{U^{238}}$ versus time for various values of R where initial $A_{Th^{230}}$ is zero.

Since Th^{230} is the immediate decay product of U^{234} , the age may be expressed in terms of $A_{Th^{230}}/A_{U^{234}}$. To calculate the Th^{230}/U^{234} age on the basis of $A_{U^{234}}/A_{U^{238}} \neq 1.00$, the following relationship may be used.

$$\frac{A_{Th^{230}}}{A_{U^{234}}} = \frac{A_{U^{238}}}{A_{U^{234}}} (1 - e^{-\lambda_{Th^{230}} t}) + \frac{A_{U^{238}}}{A_{U^{234}}} (R - 1) \frac{\lambda_{Th^{230}}}{\lambda_{Th^{230}} - \lambda_{U^{234}}} (e^{-\lambda_{U^{234}} t} - e^{-\lambda_{Th^{230}} t})$$

$$\text{Since } \frac{A_{U^{238}}}{A_{U^{234}}} = \frac{1}{1 + (R - 1)e^{-\lambda_{U^{234}} t}} \quad (\text{see } U^{234}/U^{238} \text{ method described later}),$$

the equation becomes

$$\frac{A_{Th^{230}}}{A_{U^{234}}} = \frac{1 - e^{-\lambda_{Th^{230}} t}}{1 + (R - 1)e^{-\lambda_{U^{234}} t}} + \frac{R - 1}{1 + (R - 1)e^{-\lambda_{U^{234}} t}} \frac{\lambda_{Th^{230}}}{\lambda_{Th^{230}} - \lambda_{U^{234}}} (e^{-\lambda_{U^{234}} t} - e^{-\lambda_{Th^{230}} t})$$

Table 3 lists data for A_{Th230}/A_{U234} vs. time for various values of R where initial A_{Th230} is zero.

In applying this equation we use as R the ratio A_{U234}/A_{U238} in present day sea water and living marine organisms. Analyses by Thurber, Goldberg, Blanchard, Osmond and others give values of R in the range 1.07 to 1.27.¹¹⁻¹⁶

Osmond et al. applied this method to date corals from the Pleistocene Key Largo limestone (a fossil coral reef) and Pleistocene Miami oolites.¹⁷

The Th^{230}/U^{234} method of dating corals and oolites has been evaluated in detail for reliability and various criteria have been established by Thurber et al.¹⁸ The method was found to give apparently reliable results to about 200,000 years B.P.¹⁹

Fanale and Schaeffer made a comparison of He/U ages with the

¹¹D. L. Thurber, ibid.

¹²W. S. Broecker and D. L. Thurber, Science, 149, 58 (1965)

¹³M. Koide and E. D. Goldberg, Progress in Oceanography, Vol. 3, p. 173 (1965)

¹⁴R. L. Blanchard, J. Geophys. Res., 70, 4055 (1965)

¹⁵J. K. Osmond, J. R. Carpenter, and H. L. Windom, J. Geophys. Res., 70, 1843 (1965)

¹⁶M. H. Cheng, this thesis, p.

¹⁷J. K. Osmond, J. R. Carpenter, and H. L. Windom, op. cit.

¹⁸D. L. Thurber, W. S. Broecker, R. L. Blanchard and H. A. Potratz, Science 149, 55 (1965)

¹⁹W. S. Broecker and D. L. Thurber, Science 149, 58 (1965)

Th²³⁰/U²³⁴ ages for selected Pleistocene and Tertiary shells and corals and found that the ages are in good agreement except for those fossils for which independent criteria indicate a chemically open system.²⁰

Thurber extended the study of this method to marine terraces and Pleistocene beach formations and concluded that Th²³⁰/U²³⁴ ages for mollusks are more difficult to evaluate than those obtained for coral and oolite.²¹ Stearns and Thurber have determined apparent Th²³⁰/U²³⁴ ages of fossil mollusks from the Mediterranean and Moroccan littorals.²² They believe these apparent ages show sufficient internal consistency and agreement with other estimates of age to justify further exploration of their usefulness.

3. U²³⁴/U²³⁸ METHOD

This method is based on the decay of the 15% excess U²³⁴ activity to secular equilibrium with its parent U²³⁸. To calculate the U²³⁴/U²³⁸ age on the basis of $A_{U^{234}}^0/A_{U^{238}}^0 = 1.15$, an equation can be obtained as follows:

$$N_{U^{234}} = N_{U^{238}}^0 \frac{\lambda_{U^{238}}}{\lambda_{U^{234}} - \lambda_{U^{238}}} (e^{-\lambda_{U^{238}} t} - e^{-\lambda_{U^{234}} t}) + N_{U^{234}}^0 e^{-\lambda_{U^{234}} t}$$

since $\lambda_{U^{238}} \ll \lambda_{U^{234}}$ and $N_{U^{238}}^0 = N_{U^{238}} e^{\lambda_{U^{238}} t}$

the equation may be approximated for $t \ll 1/\lambda_{U^{238}}$ as follows:

$$\frac{A_{U^{234}}}{A_{U^{238}}} = 1 - e^{-\lambda_{U^{234}} t} + R e^{-\lambda_{U^{234}} t} = 1 + (R-1) e^{-\lambda_{U^{234}} t}$$

²⁰F. P. Fanale and O. A. Schaeffer, Science 149, 312 (1965)

²¹D. L. Thurber, Symposium on Marine Geochemistry, Narragansett Marine Laboratory, University of Rhode Island, Occasional Publication No. 3, 1 (1965).

²²C. E. Stearns and D. L. Thurber, Quaternaria, VII, Roma, 29 (1965).

$$\frac{A_{U^{234}}}{A_{U^{238}}} = 1 + 0.15 e^{-2.79 \times 10^{-6}t}$$

Table 4 lists data for $A_{U^{234}}/A_{U^{238}}$ as a function of time for various values of R.

The U^{234}/U^{238} method is based on the following assumptions:

- (1) $A_{U^{234}}^0/A_{U^{238}}^0 = 1.15$
- (2) The sample has remained a chemically closed system.

Application of the U^{234}/U^{238} method to the dating of deep sea sediments has been investigated by Ku.²³ It has been concluded that the sediments do not form a closed system and that post-depositional migration of U^{234} in the sedimentary column takes place.

The possible usefulness of the U^{234}/U^{238} method for dating other materials remains to be demonstrated.

²³T. L. Ku, J. Geophys. Res. 70, 3457 (1965)

Table 2

Data for A_{Th}^{230}/A_U^{238} vs. Time for Various Values of R

t (yrs.)	A_{Th}^{230}/A_U^{238}		
	(R = 1.15)	(R = 1.20)	(R = 1.30)
0	0.00	0.00	0.00
10,000	0.10	0.11	0.11
20,000	0.19	0.20	0.22
40,000	0.35	0.37	0.40
60,000	0.48	0.50	0.54
80,000	0.59	0.61	0.66
100,000	0.68	0.70	0.76
120,000	0.75	0.78	0.83
140,000	0.81	0.84	0.90
160,000	0.86	0.89	0.95
180,000	0.90	0.93	0.99
200,000	0.93	0.96	1.02
250,000	0.99	1.01	1.07
300,000	1.02	1.04	1.10
350,000	1.03	1.06	1.10
400,000	1.04	1.06	1.10
450,000	1.04	1.06	1.10
500,000	1.04	1.06	1.10

Table 3

Data for A_{Th}^{230}/A_U^{234} vs. Time for Various Values of R

t (yrs.)	A_{Th}^{230}/A_U^{234}		
	(R = 1.15)*	(R = 1.20)	(R = 1.30)
0	0.00	0.00	0.00
10,000	0.09	0.09	0.09
20,000	0.17	0.17	0.17
40,000	0.31	0.31	0.31
60,000	0.43	0.43	0.43
80,000	0.53	0.53	0.53
100,000	0.61	0.61	0.62
120,000	0.68	0.68	0.69
140,000	0.74	0.74	0.75
160,000	0.78	0.79	0.80
180,000	0.82	0.83	0.84
200,000	0.86	0.86	0.87
250,000	0.92	0.92	0.93
300,000	0.95	0.96	0.97
350,000	0.98	0.98	0.99
400,000	0.99	1.00	1.00
450,000	1.00	1.00	1.01
500,000	1.00	1.00	1.02

*The graphical representation of these data for R = 1.15 is given in Figure 1.

Table 4

Data for $A_{U^{234}}/A_{U^{238}}$ vs. Time for Various Values of R

t (yrs.)	$A_{U^{234}}/A_{U^{238}}$		
	(R = 1.15)*	(R = 1.20)	(R = 1.30)
0	1.15	1.20	1.30
50,000	1.13	1.17	1.26
100,000	1.11	1.15	1.23
150,000	1.10	1.13	1.20
200,000	1.09	1.11	1.17
250,000	1.07	1.10	1.15
300,000	1.06	1.09	1.13
350,000	1.06	1.08	1.11
400,000	1.05	1.07	1.10
450,000	1.04	1.06	1.09
500,000	1.04	1.05	1.07

*The graphical representation of these data for R = 1.15 is given in Figure 1.

Figure 1. Theoretical Decay and Growth Curves for U²³⁴ and Th²³⁰ in a Fossil Marine Mollusk (R = 1.15).

III. ISOTOPIC THORIUM AND URANIUM COMPOSITIONS OF MODERN AND FOSSIL MARINE MOLLUSCAN SHELLS

1. INTRODUCTION

The samples analyzed fall into the following categories:

(1) A limestone standard designated as MLS # 1.

(2) A fossil marine shell sample which shows clear evidence of open system conditions. This is designated as Alas.-F-D-1116.

(3) A series of well preserved marine shells from the first marine terrace on the California coast near Santa Cruz. These samples are designated Cal.-M-1, Cal.-F-1, etc., where "M" indicates "modern" and "F" indicates "fossil". The fossil shells in this series are stratigraphically equivalent.

(4) A series of well preserved fossil marine shells from Russia designated USSR-F-1, USSR-F-2, etc. The stratigraphic age estimates on these shells range from 22,000 to 180,000 years B.P.

(5) A sample from Greenland collected near the source of sample, 61Ahp-453 and 61Ahp-456, which Blanchard had analyzed and had shown to have $\text{Th}^{230}/\text{U}^{234}$ ages in good agreement with the estimated age of the geologic unit from which they were collected.²⁴

The shell samples were thoroughly cleaned, as described in Appendix I, before analyzing. Total uranium and isotopic thorium and uranium were determined by the methods described in Appendix II. Mineralogy of the samples were determined by the x-ray diffraction method given in Appendix III. A detailed description of each sample is given in Appendix IV.

²⁴R. L. Blanchard, Thesis, op. cit., p. 93.

2. ISOTOPIC THORIUM AND URANIUM COMPOSITIONS

In order to check the validity of the analytical procedure, the Mississippian limestone standard was analyzed for isotopic thorium and uranium content. The results are given in Table 18 (P, 83). These results show good agreement with those obtained by other workers in this and other laboratories as can be seen from the table. Blank analyses on reagents were made but no alpha activity was found. The chemical yields for thorium analyses were usually in the range of 80 to 100 percent. For uranium analyses the yields were in the range of 50 to 90 percent. The results of isotopic thorium and uranium analyses for all the sample are given in Table 5.

Table 5
Isotopic Thorium and Uranium Compositions of Modern
and Fossil Marine Molluscan Shells

Sample Designation	A _U 238 (d/m/g)	A _U 234 (d/m/g)	A _{Th} 232 (d/m/g)	A _{Th} 230 (d/m/g)	A _{Th} 228 (d/m/g)
Cal.-M-1	0.26 (±0.01)	0.33 (±0.02)	≤0.002	≤0.007	≤0.06
Cal.-F-1	1.04 (±0.15)	1.31 (±0.20)	0.018 (±0.003)	0.67 (±0.04)	0.14 (±0.02)
Cal.-F-2	0.10 (±0.01)	0.11 (±0.01)	0.010 (±0.002)	0.052 (±0.006)	0.025 (±0.004)
Cal.-F-3	1.18 (±0.10)	1.49 (±0.13)	0.018 (±0.002)	0.69 (±0.04)	0.093 (±0.007)
Cal.-F-4	0.49 (±0.04)	0.56 (±0.06)	0.007 (±0.002)	0.076 (±0.009)	0.033 (±0.007)
USSR-F-1	0.16 (±0.01)	0.29 (±0.02)	0.063 (±0.004)	0.45 (±0.02)	0.10 (±0.01)
USSR-F-2	0.10 (±0.01)	0.15 (±0.01)	0.033 (±0.004)	0.15 (±0.01)	0.05 (±0.01)
USSR-F-3	1.01 (±0.09)	1.23 (±0.12)	0.074 (±0.008)	0.31 (±0.03)	0.09 (±0.01)
USSR-F-4	0.23 (±0.01)	0.26 (±0.01)	0.024 (±0.003)	0.20 (±0.02)	0.025 (±0.003)
USSR-F-5	0.54 (±0.02)	0.72 (±0.05)	0.059 (±0.006)	0.30 (±0.02)	0.11 (±0.01)
USSR-F-6	0.26 (±0.01)	0.37 (±0.03)	0.054 (±0.006)	0.25 (±0.02)	0.057 (±0.006)
Greenld.-F -62AMh24	0.07 (±0.01)	0.09 (±0.01)	0.074 (±0.004)	0.077 (±0.005)	0.17 (±0.01)
Alas.-F- D-1116	1.92 (±0.07)	4.90 (±0.26)	-	-	-
MLS #1	0.73 (±0.03)	0.74 (±0.05)	0.030 (±0.006)	0.76 (±0.05)	0.032 (±0.006)

IV. CRITERIA TO BE APPLIED IN EVALUATING RESULTS

For the uranium decay series methods of dating molluscan shells to be valid the specimen, must during aging, behave as a closed system. Such a specimen would be expected to meet the following criteria.²⁵⁻²⁷

1. State of Preservation. The sample should show no evidence of recrystallization.
2. Uranium Content. The uranium content of the fossil should not differ greatly from that of its modern counterpart.
3. Thorium-232 Content. The thorium-232 content of the fossil should not differ greatly from that of its modern counterpart.
4. Th²²⁸/Th²³² Activity Ratio. This ratio should be 1.0.
5. U²³⁴/U²³⁸ Activity Ratio. This ratio, corrected for decay of the excess U²³⁴, should fall within the range of U²³⁴/U²³⁸ ratios in modern marine shells.
6. Consistency. Th²³⁰/U²³⁴ ages should be consistent with stratigraphic data.

²⁵R. L. Blanchard, Thesis, op. cit.

²⁶D. L. Thurber, W. S. Broecker, R. L. Blanchard, and H. A. Potratz, Science, 149, 55 (1965)

²⁷C. E. Stearns and D. L. Thurber, op. cit.

V. DISCUSSION OF RESULTS

The results obtained in this work will be discussed in their relationship to the criteria cited in the foregoing section. While failure to meet these criteria can be taken as evidence of open system conditions it can not be argued that a specimen that satisfies all these conditions necessarily represents a closed system.

1. STATE OF PRESERVATION (MINERALOGY)

The two most important calcium carbonate polymorphs composing marine molluscan shells are calcite and aragonite. Calcite is rhombohedral and aragonite, the more dense of the two, is orthorhombic. Under atmospheric conditions, calcite is thermodynamically stable with respect to aragonite. The standard free energy change of the aragonite to calcite transition is -237 calories per mole.²⁸ However, certain marine organisms precipitate aragonite which remains unaltered for thousands of years afterwards. Geologic evidence implies that aragonite at low temperature and pressure will remain unaltered for long periods of time when in contact with solutions similar to those from which the aragonite was precipitated or when dry sealed.²⁹ In addition, the aragonite to calcite transition is a reconstructive phase transformation which helps to explain the persistence of the aragonite structure. It has also been suggested that the presence of foreign ions, such as Pb^{++} and Sr^{++} , might stabilize aragonite with respect to calcite at earth surface conditions.

In the attempt to understand the basic factors influencing the

²⁸W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, p. 320 (1959)

²⁹P. E. Cloud, Geochim. et Cosmochim. Acta 26, 867-884 (1962)

precipitation of calcium carbonate by marine organisms, investigators turned to controlled laboratory experimentation. These experiments show that the formation of aragonitic calcium carbonate is favored by high temperature, a low concentration of precipitating ions, CO_3^{--} and Ca^{++} ³⁰, high pH³¹, and particularly by the presence of divalent cations with an ionic radius larger than that of calcium ion.³²⁻³⁵

The mineralogy of the calcium carbonate deposited by a marine organism is not genetically fixed. Lowenstam noted compositions varying from 100 percent calcite to 100 percent aragonite in the same species, in going from latitudes 59° 40' N. to 7° 19' N.³⁵ An increased temperature results in a loss of CO_2 , with an attendant rise in pH and a reduction of bicarbonate ion, carbonic acid and carbonate ion concentrations. The laboratory investigation mentioned above indicated that all three of these effect, i.e., increase in temperature, increase in pH and decrease in carbonate ion concentration, favor the formation of the aragonite form of calcium carbonate.

When divalent ions larger than calcium ion are incorporated into the crystal lattice the formation of aragonite is favored. Thompson and Chow³⁶

³⁰J. L. Wray and F. Daniels, J. Amer. Chem. Soc. 79, 2031-2034 (1957)

³¹E. J. Zeller and J. L. Wray, Bull. Amer. Ass. Petrol. Geol. 40, 140-152 (1956)

³²W. L. Bragg, Atomic Structure of Minerals, p. 114 (1937)

³³T. G. Thompson and T. J. Chow, Papers in Marine Biology and Oceanography, Suppl. to Vol. 3 of Deep Sea Research, 20-39 (1955)

³⁴F. Daniels, Geochim. et Cosmochim. Acta 22, 65-74 (1961)

³⁵H. A. Lowenstam, Proc. Nat. Acad. Sci. 40, 39-48 (1954)

³⁶T. G. Thompson and T. J. Chow, op. cit.

and Kulp, Turekian and Boyd³⁷ have reported that aragonitic calcium carbonate deposited by marine organisms contains many times more strontium than does organically deposited calcitic calcium carbonate.

The salinity of the ocean water also appears to have an effect in determining the mineralogy of a marine shell. Lowenstam³⁸ found that low salinities tend to raise the aragonitic fraction synthesized and that fluctuation in composition might be due in part to fluctuations in salinity.

The aragonite-calcite ratios of the modern and fossil shells are determined by x-ray diffraction analysis. If the analysis shows calcite to be absent one may conclude that there has been no recrystallization. The presence of calcite, however, cannot be taken as proof that recrystallization has occurred, because some organisms deposit a mixture of calcite and aragonite. The recrystallization process is likely to lead to violation of the closed system assumption.

The results of x-ray diffraction analysis are listed in Table 17 (P. 78). In 91 percent of the samples analyzed, calcite was below the limit of detection (1-2% calcite), an observation which we take as evidence that little or no recrystallization has occurred in these samples.

2. URANIUM CONTENT

For the dating methods based on the uranium-decay series to be useful, the carbonate samples must contain a measurable amount of uranium.

There are several factors which may influence the uranium content of marine deposited calcium carbonates. One factor is the concentration

³⁷J. L. Kulp, K. Turekian and D. N. Boyd, Bull. Geol. Soc. Amer. 63, 701-706 (1952)

³⁸H. S. Lowenstam, op. cit.

of uranium in the ocean waters from which the calcium carbonates have been deposited. During the time span for which the ionium-uranium and uranium-uranium ratio might be useful, the uranium concentration in the ocean has probably changed very little. Holland and Kuip have estimated that the uranium concentration has changed less than 20 percent in 10^7 year.³⁹ For very old carbonates, other factors such as the recrystallization of the calcium carbonate are more important in determining their present uranium content.⁴⁰

The concentration of calcium in ocean water is 0.4 g./l.⁴¹ Taking the concentration of uranium in ocean water as 3.0×10^{-6} g./l., one may calculate the atomic ratio of U/Ca to be 1.2×10^{-6} .⁴² This is approximately the U/Ca ratio one finds in living and fossil aragonitic corals but is much greater than the U/Ca ratio in living mollusks. This difference may be related to the very porous nature of coral resulting in a large surface area. If the uranium were incorporated after the material was deposited by the exchange of the ionic species in the ocean water and in the solid, the resulting exchange would probably be much more rapid in a material such as coral than in a very hard and compact material such as a shell.

³⁹H. D. Holland and J. L. Kuip, *Geochim. et cosmochim. Acta* 5, 197 (1954)

⁴⁰R. L. Blanchard, Thesis, op. cit.

⁴¹K. Rankama and T. G. Sahama, *Geochemistry*, p. 287 (1950)

⁴²M. Nakanishi, *Bull. Chem. Soc. Japan* 24, 36 (1951)

Table 6

The Uranium Content of Modern and Fossil Marine Mollusks

Sample Designation	Uranium (ppm)	Sample Designation	Uranium (ppm)
Cal.-M-1	0.35 $\pm$ 0.01	USSR-F-1	0.22 $\pm$ 0.01
Cal.-M-3	0.58 $\pm$ 0.04	USSR-F-2	0.14 $\pm$ 0.01
Cal.-F-1	1.41 $\pm$ 0.20	USSR-F-3	1.37 $\pm$ 0.12
Cal.-F-2	0.13 $\pm$ 0.01	USSR-F-4	0.31 $\pm$ 0.01
Cal.-F-3	1.60 $\pm$ 0.14	USSR-F-5	0.74 $\pm$ 0.03
Cal.-F-4	0.66 $\pm$ 0.06	USSR-F-6	0.35 $\pm$ 0.02
		Greenld. -F-62AMh24	0.10 $\pm$ 0.01
		Atas.-F-D-1116	2.62 $\pm$ 0.10

Uranium contents of the shells are listed in Table 6. Fossil mollusks Cal.-F-1 and Cal.-F-3 contain appreciably more uranium than their contemporary counterparts Cal.-M-1 and Cal.-M-3. Both Blanchard⁴⁴ and Broecker⁴³ reported that fossil mollusks have higher uranium concentrations than living mollusks. This relationship is clearly demonstrated by the histogram in Figure 2 which is obtained by combining the results of Broecker,⁴³ Blanchard,⁴⁵ Stearns and Thurber,⁴⁶ and the data in Table 6. Two possible explanations are given for this difference.^{43,44} Either the ocean contained more uranium during the years these fossil

⁴³W. S. Broecker, op. cit.

⁴⁴R. L. Blanchard, Thesis, op. cit.

⁴⁵R. L. Blanchard, J. Geophys. Res. 70, 4055 (1965)

⁴⁶C. E. Stearns and D. L. Thurber, op. cit.

shells were developing, contrary to the estimates of Holland and Kulp, or the excess uranium was added after death of the organism. Stearns and Thurber commenting on the results of Broecker and Blanchard have pointed out that 50% of the living organism shells that were analyzed contained <0.06 ppm U^{238} , but that fossil shells both within the range of radiocarbon dating and beyond ($>25,000$ years B.P.) contained significant amounts of U^{238} (65% of the fossil shells tested contained between 0.25 and 2.0 ppm U^{238}). Moreover, fossils less than 20,000 years old do not, in general contain less U^{238} than fossils greater than 20,000 years old. They conclude, therefore, that uranium is fixed rapidly by some process such as the degradation of organic material, and that the event dated by Th^{230}/U^{234} ratios is close in time to the death of the organism.⁴⁷

Certainly the origin of the uranium in mollusks must be better understood before the usefulness of these materials for inequilibrium dating can be evaluated.

Another interesting observation from Table 6 is the relatively high uranium concentrations in certain fossil shells collected from the California Coast, (Cal.-F-1 and Cal.-F-3), from Russia, (USSR-F-3), and from Alaska, (Alas.-F-D-1116). Following the arguments of Stearns and Thurber one might assume that this excess uranium entered the shell soon after death of the organism. Some evidence to be considered later, however, indicates that this is probably not the case.

Sample Alas.-F-D-1116 has been subjected to extreme and unusual conditions for thousands of years as described on page 41 of this dissertation. During this time physical and chemical changes in the shell material could have occurred. It is not unreasonable to assume that the

⁴⁷C. E. Stearns and D. L. Thurber, ibid.

Figure 2. Histogram of Uranium Concentrations in Modern and Fossil Marine Molluscan Shells.

trace element composition of these shells may have been considerably altered by the prolonged contact with circulating ground waters and possibly also by the recent exposure to direct weathering.

Sample USSR-F-3 contains no detectable calcite; so one may conclude that there has been little or no recrystallization. There was not sufficient sample to permit a check on the possibility of surface contamination by uranium. Such a check was however made on another fossil sample that was high in uranium content, Cal.-F-3. This was done by dissolving the outer and the inner half of the whole shell separately with HNO_3 , and determining the concentration of uranium in each fraction by the method given in the appendix. The results obtained were as follows:

BFMC-3 Inside fraction 1.60 ± 0.13 ppm

Outside fraction 1.36 ± 0.16 ppm

The uranium difference between fractions was within the limit of experimental error, indicating uniform distribution.

Blanchard has observed that modern marine shells collected from the California Coast average somewhat higher in uranium content than do modern marine shells from other localities.⁴⁸ The results here reported, samples Cal.-M-1 and Cal.-M-3, Table 6 and Figure 2, confirm this. Whether this variation in uranium content of the shells is related to the variation in uranium content of the coastal waters have not been determined.

⁴⁸ R. L. Blanchard, Thesis, op. cit., p. 29.

3. THORIUM-232 CONTENT

Because of the very low concentration of Th^{232} in ocean water, appreciable quantities of this isotope would not be expected in marine shells. Blanchard looked for Th^{232} in 30 modern marine shell specimens collected from 14 locations. In all specimens Th^{232} was below his limit of detection which was generally about 0.005 d/m/g.⁴⁹ The data for Cal.-M-1 (Table 7) support Blanchard's observation. The Th^{232} content of this shell is less than 0.002 d/m/g.

Further examination of the data in Table 7 reveals that the fossil marine mollusks unlike their modern counterparts contain a considerable amount of Th^{232} , an amount such that $A_{\text{Th}^{232}}$ approaches $A_{\text{Th}^{230}}$ in some specimens. It seems reasonable to assume that this Th^{232} must have entered the shell after death of the organism. If Th^{230} entered along with Th^{232} , and it seems likely that this would be the case, then the $\text{Th}^{230}/\text{U}^{234}$ ratio can not serve as an age measure.

Tatsumoto and Goldberg have suggested that the concentration of Th^{232} might provide a means for evaluation of the extraneous Th^{230} content of the sample.⁵⁰ However, the $\text{Th}^{230}/\text{Th}^{232}$ activity ratio commonly varies between 1 and 4 in surface water (Thurber, unpublished) and between 6 and 30 in sea water.^{51,52} Therefore, it is difficult to predict in what proportions these two thorium isotopes would be added to the shell.

This problem of contamination by thorium apparently does not arise or at least appears to be much less serious in corals that have been de-

⁴⁹ R. L. Blanchard, Thesis, op cit., p. 78.

⁵⁰ M. Tatsumoto and E. D. Goldberg, *Geochim. et Cosmochim. Acta*, 17, 201 (1959)

⁵¹ E. D. Goldberg and M. Koide, *Science*, 128, 175 (1958)

⁵² W. S. Moore and W. M. Sackett, *J. Geophys. Res.*, 69, 5401 (1964)

Table 7

Thorium Content of Modern and Fossil Shells

Sample Designation	A_{Th232} (d/m/g)	A_{Th230} (d/m/g)	$\frac{A_{Th230}}{A_{Th232}}$
Cal.-M-1	≤ 0.002	≤ 0.007	≤ 9
Cal.-F-1	0.018 ± 0.003	0.67 ± 0.04	37 ± 7
Cal.-F-2	0.010 ± 0.002	0.052 ± 0.006	5 ± 1
Cal.-F-3	0.018 ± 0.002	0.69 ± 0.04	38 ± 5
Cal.-F-4	0.007 ± 0.002	0.08 ± 0.01	11 ± 3
USSR-F-1	0.063 ± 0.004	0.45 ± 0.02	7 ± 1
USSR-F-2	0.033 ± 0.004	0.15 ± 0.01	5 ± 1
USSR-F-3	0.074 ± 0.008	0.31 ± 0.03	4 ± 1
USSR-F-4	0.024 ± 0.003	0.20 ± 0.02	8 ± 1
USSR-F-5	0.059 ± 0.006	0.30 ± 0.02	5 ± 1
USSR-F-6	0.054 ± 0.006	0.25 ± 0.02	5 ± 1
Greenld.-F-62AMh24	0.074 ± 0.004	0.077 ± 0.005	1 ± 0.1
Alas.-F-D-1116	- - -	- - -	139 ± 57
MLS # 1	0.030 ± 0.006	0.76 ± 0.05	25 ± 5

posited and remain in a marine environment as illustrated by the data in Table 8.

In this Table modern and fossil mollusk specimens with $\text{Th}^{230}/\text{U}^{234}$ activity ratios over the range 0.00 to 1.00 are paired with modern and fossil coral specimens of similar $\text{Th}^{230}/\text{U}^{234}$ activity ratios. One observes that unlike the mollusks, the fossil corals show no evidence of Th^{232} uptake. The average Th^{232} content in the fossils is no different than in the modern specimen. Also, as indicated by the $\text{Th}^{230}/\text{Th}^{232}$ activity ratios, $A_{\text{Th}^{230}}$ in the fossil corals is usually several hundred times $A_{\text{Th}^{232}}$.

4. $\text{Th}^{228}/\text{Th}^{232}$

In fossil shells Th^{228} , with a half-life of 1.90 years, should be in radioactive equilibrium with its parent Th^{232} , i.e., $\text{Th}^{228}/\text{Th}^{232}$ activity ratio should be equal to one. Any excess Th^{228} would indicate recent contamination of the shell with thorium and/or Ra^{228} which is the parent of Th^{228} .

$\text{Th}^{228}/\text{Th}^{232}$ activity ratios for the modern and fossil shells are listed in Table 9. The results show that in most of the fossil shells this activity ratio is greater than one. This is good evidence that the system is open or has been open very recently.

Koczy, Picciotto, Poulaert, and Wilgain have observed an excess of Ra^{228} in coastal waters and have suggested a redissolution of Ra^{228} from near shore bottom sediments or its introduction from rivers.⁵³ Thurber⁵⁴ has shown that river waters contain unsupported Th^{228} . Modern shells are known to contain more Ra^{226} than can be supported by the uranium present.^{55,56}

⁵³F. F. Koczy, E. Picciotto, G. Poulaert and S. Wilgain, *Geochim. et Cosmochim. Acta*, 11, 103 (1957)

⁵⁴D. L. Thurber, unpublished data

⁵⁵R. L. Blanchard, Thesis, *op. cit.*, p. 32

⁵⁶W. S. Broecker, *op. cit.*

Table 8

Comparison of Thorium and Uranium Activities in Mollusks and
Typical Pacific Coral Samples*

Sample	A_{U234} (d/m/g)	A_{Th232} (d/m/g)	A_{Th230}/A_{U234}	A_{Th230}/A_{Th232}
Cal. -M-1 - (Modern mollusk)	0.33	≤ 0.002	≤ 0.02	≤ 9
Loc. 15 (Modern Coral)	2.76	0.007	0.004	1.5
Cal. -F-1 (Fossil mollusk)	1.31	0.018	0.51	37
Mu 7-13 (Fossil coral)	2.34	0.002	0.58	660
USSR-F-6 (Fossil mollusk)	0.37	0.054	0.69	5
Mu 7-23 (Fossil Coral)	2.18	0.004	0.68	340
USSR-F-4 (Fossil mollusk)	0.26	0.024	0.76	8
Mu 7-34 (Fossil coral)	1.96	0.006	0.79	300
Grnld.-F-62AMh24 (Fossil mollusk)	0.09	0.074	0.86	1
K-1-16 (Fossil coral)	2.74	0.005	0.87	435
USSR-F-2 (Fossil mollusk)	0.15	0.033	1.03	5
F-1 (Fossil coral)	1.56	0.010	1.00	140

* Data on coral samples are from Thurber, Broecker, Blanchard and Potratz, Science, 149, 56 (1965)

Table 9
 $\text{Th}^{228}/\text{Th}^{232}$ Activity Ratios in Modern and Fossil Shells

Sample Designation	$A_{\text{Th}^{228}}$ (d/m/g)	$\frac{A_{\text{Th}^{228}}}{A_{\text{Th}^{232}}}$
Cal.-M-1	≤ 0.06	≤ 65
Cal.-F-1	0.14 ± 0.02	8 ± 2
Cal.-F-2	0.025 ± 0.004	2.5 ± 0.4
Cal.-F-3	0.10 ± 0.01	5 ± 1
Cal.-F-4	0.033 ± 0.007	5 ± 2
USSR-F-1	0.10 ± 0.01	1.6 ± 0.1
USSR-F-2	0.05 ± 0.01	1.5 ± 0.2
USSR-F-3	0.09 ± 0.01	1.3 ± 0.1
USSR-F-4	0.025 ± 0.003	1.0 ± 0.2
USSR-F-5	0.11 ± 0.01	1.9 ± 0.2
USSR-F-6	0.06 ± 0.01	1.0 ± 0.1
Greenld.-F-62AMh24	0.17 ± 0.01	2.4 ± 0.1
Alas.-F-D-1116	- - -	5 ± 2
MLS # 1	0.032 ± 0.006	1.1 ± 0.3

Moore and Sackett have confirmed the presence of excess Ra^{228} in coastal waters.⁵⁷ Considering the relatively high mobility of radium compared to thorium, these observations lead one to suspect that the excess Th^{228} in fossil shells may arise from decay of Ra^{228} which has come into the specimen from ground waters. However we have no data to confirm this.

5. $\text{U}^{234}/\text{U}^{238}$ ACTIVITY RATIO

Radioactive disequilibrium between U^{234} and U^{238} in minerals and rocks was initially observed by Cherdyntsev and co-workers.^{58,59} The fractionation of these two isotopes is attributed to a hot-atom effect. In minerals the products of U^{238} decay are displaced by recoil into different sites of the crystalline lattice, where they reside in the form of foreign, generally weakly bound, inclusions. During the interaction of weathering solutions with minerals, the radioactive-decay product U^{234} passes into solution to a greater extent than does U^{238} . Rosholt et al⁶⁰ showed that U^{234} preferentially leached at one locality may be subsequently deposited at another, thus giving rise to a deficiency at one location and an excess at another, as compared with the equilibrium amount.

Figure 3 shows the variation of the $\text{U}^{234}/\text{U}^{238}$ activity ratios in some natural waters - deep ocean water,⁶¹ river waters⁶² and coastal waters.⁶³

⁵⁷W. S. Moore and W. M. Sackett, J. Geophys. Res., 69, 5401 (1964)

⁵⁸V. V. Cherdyntsev, D. P. Orlov, E. A. Isabaev and V. I. Ivanov, Geochemistry USSR (English Transl.) No. 10, 927 (1961)

⁵⁹V. V. Cherdyntsev, Abundance of Chemical Elements, p. 107, Univ. of Chicago Press, Chicago (1961)

⁶⁰J. N. Rosholt, W. R. Shields, and E. L. Garner, Science, 139, 224 (1963)

⁶¹M. Koide and E. D. Goldberg, Progress in Oceanography, vol. 3, p. 173 (1965)

⁶²D. L. Thurber, unpublished data

⁶³R. L. Blanchard, J. Geophys. Res., 70, 4055 (1965)

Figure 3. Variation of A_{234}/A_{238} in Natural Waters.

As can be seen from the figure the average ratio for river water is far higher than that of deep ocean water.

If closed system conditions have prevailed, the U^{234}/U^{238} activity ratio in a fossil marine shell, corrected for decay of the excess U^{234} , should not differ from the U^{234}/U^{238} ratio in a modern marine shell. Two assumptions are implicit in this statement. Namely, the U^{234}/U^{238} ratio in all modern marine shells is the same and the U^{234}/U^{238} ratio in living marine shells is the same now as it was in the fossil shells at the time of their formation. The latter assumption seems reasonable but is not subject to direct proof. The assumption that all modern marine shells have identical or nearly identical U^{234}/U^{238} activity ratios may be correct. However, too few modern specimens have been analyzed to permit a definite conclusion. Coastal surface waters in some locations may have relatively high U^{234}/U^{238} activity ratios. One would expect this might be the case near a river mouth if the U^{234}/U^{238} activity ratio in the river water is high, as it is known to be in some rivers. The U^{234}/U^{238} activity ratio in the coastal water should be reflected in the U^{234}/U^{238} ratio in the marine organism living in this water.

The U^{234}/U^{238} activity ratios of the marine carbonate samples are listed in Table 10. The ratio for the modern shell, Cal.-M-1, is 1.27 ± 0.06 which is somewhat higher than the ratio in ocean water. Whether this relates to a relatively high U^{234}/U^{238} ratio in the coastal water from which this sample was collected has not been determined. Blanchard⁶⁴ has analyzed some modern molluscan shells collected at seven locations on the seacoast of the United States and found U^{234}/U^{238} activity ratios that fall within the range of 1.07 to 1.17. Relatively few modern shells and

⁶⁴R. L. Blanchard, ibid.

Table 10. $^{234}\text{U}/^{238}\text{U}$ Activity Ratios in Modern and Fossil Specimens

Sample Designation	$A_{\text{U}234}$ (d/m/g)	$A_{\text{U}238}$ (d/m/g)	$\left(\frac{A_{\text{U}234}}{A_{\text{U}238}}\right)$ observed	$\left(\frac{A_{\text{U}234}}{A_{\text{U}238}}\right)$ calc.
Cal.-M-1	0.33 ± 0.02	0.26 ± 0.01	1.27 ± 0.06	
Cal.-F-1	0.31 ± 0.20	1.04 ± 0.15	1.26 ± 0.05	≤ 1.13
Cal.-F-2	0.11 ± 0.01	0.10 ± 0.01	1.18 ± 0.09	
Cal.-F-3	1.49 ± 0.13	1.18 ± 0.10	1.26 ± 0.04	
Cal.-F-4	0.56 ± 0.06	0.49 ± 0.04	1.16 ± 0.05	
USSR-F-1	0.29 ± 0.02	0.16 ± 0.01	1.76 ± 0.11	≤ 1.16
USSR-F-2	0.15 ± 0.01	0.10 ± 0.01	1.42 ± 0.08	
USSR-F-3	1.23 ± 0.12	1.01 ± 0.09	1.22 ± 0.04	≤ 1.14
USSR-F-4	0.26 ± 0.01	0.23 ± 0.01	1.13 ± 0.05	
USSR-F-5	0.72 ± 0.05	0.54 ± 0.02	1.32 ± 0.08	≤ 1.13
USSR-F-6	0.37 ± 0.03	0.26 ± 0.01	1.42 ± 0.06	≤ 1.12
Greenld.-F-62AMh24	0.09 ± 0.01	0.07 ± 0.01	1.21 ± 0.10	≤ 1.12
Alas.-F-D-1116	4.90 ± 0.26	1.92 ± 0.07	2.56 ± 0.12	1.00
MLS # 1	0.74 ± 0.05	0.73 ± 0.03	1.02 ± 0.05	1.00

$\left(\frac{A_{\text{U}234}}{A_{\text{U}238}}\right)$ calc. = activity ratio based on estimated stratigraphic age and on assumption that closed system conditions hold and that $A_{\text{U}234}/A_{\text{U}238}^0 = 1.17 \pm 0.10$.

(Estimated stratigraphic ages of samples are given in Table 11).

even fewer coastal water samples have been analyzed for U^{234}/U^{238} , therefore, it is rather difficult to specify a U^{234}/U^{238} ratio for modern marine shells. From the limited number of results we will tentatively set a ratio of 1.17 ± 0.10 for modern marine mollusks.

The U^{234}/U^{238} activity ratio in fossil mollusks then should always be lower than 1.27 and should approach 1.00 in the oldest samples if closed system conditions are met. In Table 10 observed U^{234}/U^{238} activity ratios are compared with U^{234}/U^{238} activity ratios calculated from the estimated stratigraphic ages of the samples on the assumption that closed system conditions hold and that $A_{U^{234}}^0/A_{U^{238}}^0 = 1.17 \pm 0.10$.

In the shells of the Cal.-F series the U^{234}/U^{238} ratios, within limits of experimental error are identical. The disagreement with the calculated U^{234}/U^{238} ratio is not significant because of the uncertainty in the stratigraphic age estimate for these samples (see Table 11).

Most of the samples in the USSR series have U^{234}/U^{238} ratios significantly higher than the calculated ratios. Contamination by ground waters, a subject to be discussed later, may be the explanation. This also is assumed to account for the high U^{234}/U^{238} ratio in sample Alas.-F-D-1116 (see page 40).

6. Th^{230}/U^{234} AGES SHOULD BE CONSISTENT WITH STRATIGRAPHIC DATA

The fossil samples from the California coast are stratigraphically equivalent, and if preconditions for the Th^{230}/U^{234} dating are satisfied the Th^{230}/U^{234} ratios in these specimens should be identical. As can be seen by reference to Table 11, this is not the case. The fact that the stratigraphic age estimate on these shells may be in error is irrelevant.

The samples in the USSR series also lack internal consistency; samples from the same stratum differ widely in observed Th^{230}/U^{234}

Table 11

$^{230}\text{Th}/^{234}\text{U}$ Ratios and Estimated Geological Ages of Fossil Shells

Sample Designation	$\left(\frac{A_{\text{Th}230}}{A_{\text{U}234}}\right)_{\text{obs.}}$	Estimated Stratigraphic Ages $\times 10^{-3}$ yrs.	$\left(\frac{A_{\text{Th}230}}{A_{\text{U}234}}\right)_{\text{calc.}}$
Cal.-F-1	0.51 ± 0.08	50-100*	0.50
Cal.-F-2	0.46 ± 0.07		
Cal.-F-3	0.46 ± 0.05		
Cal.-F-4	0.14 ± 0.02		
USSR-F-1	1.56 ± 0.13	22-45	0.27
USSR-F-2	1.03 ± 0.11	22-45	
USSR-F-3	0.25 ± 0.03	70-100	0.55
USSR-F-4	0.76 ± 0.07	70-100	
USSR-F-5	0.41 ± 0.04	110-150	0.71
USSR-F-6	0.69 ± 0.07	140-180	0.79
Greenld.-F-62AMh24	0.86 ± 0.12	130-175	0.77
MLS # 1	1.03 ± 0.10	3×10^5	1.00

$\left(\frac{A_{\text{Th}230}}{A_{\text{U}234}}\right)_{\text{calc.}}$ = activity ratio calculated from stratigraphic age estimate assuming closed system conditions, $A_{\text{Th}230}^0 = 0$ and $A_{\text{U}234}^0/A_{\text{U}238}^0 = 1.17$.

* The samples in the Cal.-F series are stratigraphically equivalent.

activity ratios. These ratios, moreover, are completely out of line with stratigraphic age estimates. Note, for example, that the shells from the most recent stratum have the highest $\text{Th}^{230}/\text{U}^{234}$ activity ratios. The stratigraphic age estimates may well be correct. The fact that the $\text{Th}^{230}/\text{U}^{234}$ ratios in these shells lack internal consistency rules out any possibility of calculating absolute ages from these ratios.

To account for these results we assume that the original trace element compositions including the thorium and uranium contents of these shells have been altered by contact with ground waters.

Excess Th^{230} in a shell (USSR-F-1) in which there is no evidence of recrystallization seems surprising but has been observed before (see, for example, sample Alas.-F-D-1116, Table 12) and has been discussed in some detail by Blanchard who comments as follows:⁶⁵

"The following hypothesis is offered as an explanation for the presence of excess Th^{230} Acidic ground waters (rain water, etc.) percolating through -- silt dissolve uranium and thorium. These waters then react with the shells (CaCO_3). The reaction leads to precipitation of thorium, and possibly uranium. Assuming that the uranium in the ground waters is in the + 6 oxidation state the reaction with CaCO_3 favors precipitation of thorium over uranium, thus increasing the Th - U ratio in the shell."

7. CLOSED SYSTEM VERSUS OPEN SYSTEM CONDITIONS

From the data presented thus far it is evident that the fossil mollusks that were analyzed generally fail to satisfy the criteria that have been set as tests of closed system conditions. As has already been indicated (Table 8), fossil coral samples come closer to obeying these criteria.⁶⁶

⁶⁵R. L. Blanchard, Thesis, op. cit., p. 56

⁶⁶D. L. Thurber, W. S. Broecker, R. L. Blanchard, H. A. Potratz, op. cit.

In Table 12 data on a typical coral sample, Mu-7-34, which shows no evidence of open system conditions, are compared with data for a fossil mollusk, Alas.-F-D-1116, which fails to meet any of the criteria and is obviously an open system.

These mollusk shells, collected from the Intermediate Beach near Nome, Alaska and submitted by D. M. Hopkins, U. S. Geological Survey, consisted of a mixture of small and large sea shells, all showing evidence of weathering. The deposit from which these shells were collected is presumed to have been laid down during the Aftonian interglacial interval. These shells were exposed from 14 to 24 years on a "tailings-pile" of a placer-gold mine prior to collection in 1959. The pre-mining history of the shell sample is described by D. M. Hopkins as follows:⁶⁷

"The sediments beneath the coastal plain at Nome are generally perennially frozen to bedrock, but in some places a layer of sediment resting immediately upon bedrock is thawed and contains circulating ground water. Evidence in the region indicates that the perennially frozen ground probably thawed out completely during the last (Sanamon) interglacial cycle. Thus, specimen D-1116 probably has been subjected to thawing temperatures for at least a few tens of thousands of years of its history and will have been in contact with circulating ground water during that interval."

It is not unreasonable to assume that the trace element composition of these shells may have been considerably altered by the prolonged contact with circulating waters and possibly also by the recent exposure to direct weathering.

The other sample in Table 12, sample MLS # 1, is from a Mississippi Lime Company mine near Ste. Genevieve, Missouri. The oolitic portion of the Spergen formation from which this sample was taken lies about 160 feet

⁶⁷D. M. Hopkins, personal communication (1962)

Table 12. Closed System versus Open System Conditions in Fossil Marine Carbonates

Sample	Calcite (%)	A_{U238} (ppm)	A_{Th232} (d/m/g)	$\frac{A_{Th228}}{A_{Th232}}$	$\frac{A_{U234}}{A_{U238}}$	$\frac{A_{Th230}}{A_{U234}}$	Stratigraphic age estimate (yrs.)
	Crite- rion 1	Crit. 2	Crit. 3	Crit. 4	Crit. 5	Crit. 6	Crit. 6
Mu-7-34* Fossil Coral	< 2	2.5	0.006	-	1.09 (+0.01)	0.79	Pleistocene < 10^6
MLS # 1 Mississippian Limestone	-	0.99 (+0.04)	0.030 (+0.006)	1.1 (+0.3)	1.02 (+0.05)	1.03 (+0.10)	Mississippian > 3×10^8
Alas.-F-D-1116 Fossil Mollusk	> 2	2.62 (+0.10)	0.03**	5 (+2)	2.56 (+0.12)	4.6**	Aftonian Interglacial 10^6

* Data on this coral sample are from Thurber, Broecker, Blanchard and Potratz, Science 149, 56 (1965).

** Calculated from data in Blanchard's thesis ($A_{Th228} + A_{Th232}$ and A_{Th230}/A_{U238}) using our measured values of A_{U234}/A_{U238} and A_{Th228}/A_{Th232} for this sample.

below the surface. Above it lies gray Spargen limestone and above this a stratum of St. Louis limestone about 100 feet in thickness.⁶⁸

Early in the geologic history of this material while original marine carbonate was being consolidated into limestone the system was probably open, and though the mineralogy of this sample has not been investigated it is not unreasonable to assume that the material is mainly calcite.⁶⁹ During Pleistocene and recent times, however, it seems likely that closed system conditions have prevailed. The U^{234}/U^{238} , Th^{228}/Th^{232} and Th^{230}/U^{234} activity ratios bear out this assumption.

⁶⁸J. M. Weller and S. St. Clair, Mo. Bureau of Geology and Mines, Vol. 22, 2nd Series (1928)

⁶⁹J. K. Osmond, J. R. Carpenter, and H. L. Windom, op. cit.

VI. SUMMARY

Work previously reported indicates that the extent of disequilibrium between Th^{230} and U^{234} may be used as a measure of age of corals and oolites that have formed and remain in a marine environment. The information obtained is, however, of limited use because of the limited distribution of these materials and because of the difficulty of collecting many significant samples. The present work relates to an attempt to extend the scope of the $\text{Th}^{230}/\text{U}^{234}$ dating method by applying it to marine mollusks collected from terrestrial environments.

If reliable absolute ages are to be obtained from $\text{Th}^{230}/\text{U}^{234}$ ratios three conditions must be satisfied. (1) the original marine-deposited calcium carbonate must contain a measurable amount of uranium; (2) it must be initially free of Th^{230} ; and (3) the specimen must, during aging, behave as a closed system.

Earlier work has shown that the first two conditions are satisfied in shells of living marine mollusks and in marine shells that have been deposited during recent times. It is not unreasonable to assume that fossil marine shells also were originally free of Th^{230} . Whether or not closed system conditions have prevailed in a fossil specimen during its entire history can probably never be established with certainty. One may, however, set criteria which are consistent with closed system conditions and reject all specimens which fail to meet these criteria. In judging the reliability of $\text{Th}^{230}/\text{U}^{234}$ ages of fossil marine mollusks the following criteria were used.

- (1) The sample should show no evidence of recrystallization.
- (2) The uranium content of the fossil should not differ greatly from that of its modern counterpart.

- (3) The Th^{232} content of the fossil should not differ greatly from that of its modern counterpart.
- (4) The $\text{Th}^{228}/\text{Th}^{232}$ activity ratio should be 1.0.
- (5) The $\text{U}^{234}/\text{U}^{238}$ activity ratio, corrected for decay of the excess U^{234} , should fall within the range of $\text{U}^{234}/\text{U}^{238}$ activity ratios in modern marine shells.
- (6) $\text{Th}^{230}/\text{U}^{234}$ ages should be consistent with stratigraphic data.

From the results obtained in this work one may conclude that age determination of fossil marine carbonates by uranium decay series disequilibrium measurements, while apparently applicable, in certain instances, to fossil corals and possibly other fossil marine carbonates that have formed and have remained in a marine environment, does not yield consistent results when applied to fossil marine mollusks collected from terrestrial environments. Data obtained in isotopic uranium and thorium analyses indicate open system conditions in these fossil mollusks. Stratigraphically equivalent samples collected from a marine terrace near Santa Cruz, California gave varying $\text{Th}^{230}/\text{U}^{234}$ activity ratios in the range 0.14 to 0.51. $\text{Th}^{230}/\text{U}^{234}$ ratios in fossil shells from deposits associated with Anzhu II, Karginian, Kazantsevian and Sanchugovian transgressions in the USSR are not consistent with stratigraphic age estimates. Fossil mollusks contain more Th^{232} than do modern mollusks indicating that this nuclide, presumably accompanied by unknown amounts of Th^{230} entered the shells after they were deposited. $\text{Th}^{228}/\text{Th}^{232}$ activity ratios greater than 1.0 observed in most of the fossil specimens indicate open system conditions. The U^{238} concentration in many fossil mollusks is higher than in modern shells and $\text{U}^{234}/\text{U}^{238}$ ratios in some fossil specimens as compared to $\text{U}^{234}/\text{U}^{238}$ ratios in modern shells also indicate open system conditions.

in the fossils.

Table 13 summarizes experimental data that were obtained on fossil shells from California, Russia and Greenland. These data are compared with data based on criteria for closed system conditions. Only one sample (USSR-F-4) comes close to meeting all criteria. In this sample the absolute age calculated from the $\text{Th}^{230}/\text{U}^{234}$ ratio agrees with the stratigraphic age estimate. The agreement may well be fortuitous.

Table 13 - Summary

Sample	State of Preservation	U (ppm)		A _{Th} 232 (d/m/g)		A _{Th} 228/A _{Th} 232		A _U 234/A _U 238		A _{Th} 230/A _U 234		
		Crit.1	Found	Crit.2	Found	Crit.3	Found	Crit.4	Found	Crit.5	Found	Crit.6*
Cal.-F-1	S***		1.41 (+0.20)	<~0.7	0.018 (+0.003)	<~0.005	8 ± 2	1.0	1.26 (+0.05)	**	0.51 (+0.08)	0.50
Cal.-F-2	S		0.13 (+0.01)	<~0.7	0.010 (+0.002)	<~0.005	2.5±0.4	1.0	1.18 (+0.09)	**	0.46 (+0.07)	0.50
Cal.-F-3	S		1.60 (+0.14)	<~0.7	0.018 (+0.002)	<~0.005	5 ± 1	1.0	1.26 (+0.04)	**	0.46 (+0.05)	0.50
Cal.-F-4	S		0.66 (+0.06)	<~0.7	0.007 (+0.002)	<~0.005	5 ± 2	1.0	1.16 (+0.05)	**	0.14 (+0.02)	0.50
USSR-F-1	S		0.22 (+0.01)	<~0.7	0.063 (+0.004)	<~0.005	1.6±0.1	1.0	1.76 (+0.11)	**	1.56 (+0.13)	0.27
USSR-F-2	S		0.14 (+0.01)	<~0.7	0.033 (+0.004)	<~0.005	1.5±0.2	1.0	1.42 (+0.08)	**	1.03 (+0.11)	0.27
USSR-F-3	S		1.37 (+0.12)	<~0.7	0.074 (+0.008)	<~0.005	1.3±0.1	1.0	1.22 (+0.04)	**	0.25 (+0.03)	0.55
USSR-F-4	S		0.31 (+0.01)	<~0.7	0.024 (+0.003)	<~0.005	1.0±0.2	1.0	1.13 (+0.05)	**	0.76 (+0.07)	0.55
USSR-F-5	S		0.74 (+0.03)	<~0.7	0.059 (+0.006)	<~0.005	1.9±0.2	1.0	1.32 (+0.08)	**	0.41 (+0.04)	0.71
USSR-F-6	Q*****		0.35 (+0.02)	<~0.7	0.054 (+0.006)	<~0.005	1.0±0.1	1.0	1.42 (+0.06)	**	0.69 (+0.07)	0.79
Greenld.-F 62Amh24	Unknown		0.10 (+0.01)	<~0.7	0.074 (+0.004)	<~0.005	2.4±0.1	1.0	1.21 (+0.10)	**	0.86 (+0.12)	0.77

* The $\text{Th}^{230}/\text{U}^{232}$ activity ratios listed under criterion 6 were calculated from stratigraphic age estimates assuming closed system conditions, $A_{\text{Th}^{230}} = 0$, and $A_{\text{U}^{234}}/A_{\text{U}^{238}} = 1.17$.

** This ratio should be in the range 1.00 - 1.27.

*** S = satisfactory.

**** Q = questionable.

APPENDIX I - PREPARATION OF SAMPLES

1. CLEANING PROCESS

The shells are first scrubbed with a hard bristle brush and distilled water to remove silt and clay and then cleaned with detergent solution and distilled water in a supersonic cleaner.* After the shells are thoroughly cleaned, they are dried and crushed to a fine powder.

2. DISSOLVING PROCESS

100.0 gram of the sample is dissolved by adding concentrated HNO_3 dropwise until no further foaming is observed. Fifty milliliters of concentrated HNO_3 is added and the solution is heated to fumes and digested for two hours to oxidize the organic material present. The solution is then diluted to 500 ml. with 2M HNO_3 in a 500 ml. volumetric flask.

*SONOGEN Automatic Cleaner, Cole-Parmer Instrument & Equipment Co., Chicago, Ill.

APPENDIX II - PROCEDURES

1. ISOTOPIC THORIUM AND URANIUM ANALYSIS

Alpha spectrometry is used for the isotopic analysis of thorium and uranium.

For this work it is important to have very thin sources in order to get a good peak resolution. The electrodeposition technique is used for preparing these sources.

It is also important to separate thorium from uranium because of the similarity in energy of the alpha particles emitted by Th^{230} (4.69 Mev.) to those emitted by U^{234} (4.72 Mev., 4.77 Mev.).

The anion exchange technique is used for the separation of thorium from uranium. Rather thorough investigations have been made on the adsorption of elements on anion exchange resins. Some results of these studies have been published and are reproduced here. Figure 4 is for a chloride system,⁷⁰ and Figure 5 for a nitrate system.⁷¹ The failure of thorium to form anionic chloride complexes to an appreciable extent, can be utilized to separate it from uranium. The separation procedure is summarized as follows:

⁷⁰K. A. Kraus and F. Nelson, Proc. First Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 7, 113-125 (1955)

⁷¹R. F. Buchanan and J. P. Faris, Proc. Int. Atomic Energy Agency, Copenhagen, September (1960); or Radioisotopes in the Physical Sciences and Industry, Vol. 11, 361 (1962)

Figure 4. Adsorption of the Elements from HCl on Strongly Basic Anion Exchange Resin

Figure 5. Adsorption of the Elements from HNO_3 on Strongly Basic Anion Exchange Resin

A. Separation of Thorium and Uranium

Step 1. Pipette an aliquot of sample solution (an amount equal to 20 to 50 gm. of sample) into a beaker. Add tracers in known amounts (approximately 300 counts per minute of Th^{234} and 20 counts per minute of U^{232}). Add 1 mg. of Fe^{+++} and 1/4 mg. of Al^{+++} carriers per gram sample. Dilute the solution to a volume of 20 ml. per gram sample. Boil the solution for ten minutes and make up to the volume with distilled water. (Note 1)

Step 2. Allow the solution to cool. Add carbonate-free NH_4OH dropwise until $\text{pH}=8$. Digest the mixture for ten minutes. Let the $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ precipitates stand for an hour, centrifuge in a 250 ml. centrifuge bottle and decant. (Note 2)

Step 3. Dissolve the hydroxide precipitates in 1 ml. of 8N HCl per gram sample and transfer quantitatively into a 90 ml. centrifuge tube. Add carbonate-free NH_4OH dropwise until $\text{pH}=8$. Put the centrifuge tube in a Temp-Block module heater* and digest the mixture for 10 minutes or until the precipitate floats on the surface. Cool, centrifuge and decant.

Step 4. Reprecipitate $\text{Fe}(\text{OH})_3$ as in Step 3. Wash precipitate once with distilled water. Dissolve the precipitate with 0.5 ml. of concentrated HCl and rinse down the sides of the centrifuge tube with 8N HCl. At this point if there is any insoluble residue present, heat the residue in three successive portions of 1 ml. of 6N HCl with a centrifugation between each heating and combine the supernatants with the solution obtained above. (Note 3)

Step 5. Transfer the 8N HCl solution quantitatively to the top of

*Temp-Block Module Heater, Lab-Line Instruments, Inc., Melrose Park, Illinois.

a 4 mm. x 7 cm., Dowex 1-X8, 200-400 mesh, conditioned, anion exchange column and allow the solution to flow through under atmospheric pressure. (Note 4)

Step 6. When the liquid level reaches the resin, wash the column with three 2 ml. portions of 8N HCl, then flush with 5 ml. of 8N HCl. Uranium and iron are adsorbed on the column and thorium and aluminum are in the effluent. Thorium and uranium are purified by the following procedures.

B. Purification and Electrodeposition of Thorium

Step 1. To the thorium-bearing 8N HCl effluent of the anion exchange column add 5 mg of Fe^{+++} carrier. Heat the solution for ten minutes and add NH_4OH dropwise to precipitate aluminum and iron hydroxides and coprecipitate thorium. Put the centrifuge tube in a Temp-Block module heater and digest the mixture for ten minutes. Cool, centrifuge and decant.

Step 2. Dissolve the precipitate in 10 ml. of 7M HNO_3 and reprecipitate the hydroxides as above. Wash precipitate once with distilled water. (Note 5)

Step 3. Dissolve the precipitate in 1/2 ml. of conc. HNO_3 and rinse down the sides of the centrifuge tube with 7M HNO_3 . Transfer the 7M HNO_3 solution to the top of a 3 mm. x 4 cm., Dowex 1-X8, 200-400 mesh, nitrate-form, conditioned, anion-exchange column and allow the solution to flow through under atmospheric pressure. (Note 6)

Step 4. When the liquid level reaches the resin, wash the column with three 2 ml. portions of 7M HNO_3 , then flush with 3 ml. of 7M HNO_3 . Aluminum and iron are in the effluent and thorium is adsorbed on the column.

Step 5. Elute thorium from the column with 7 ml. of 1N HCl. Collect the effluent in a 30 ml. beaker. Evaporate the solution to near dryness

several times with concentrated HCl.

Step 6. Take up the residue in 1 ml. of 1N HCl and transfer it quantitatively into an electroplating cell with 6 ml. of saturated NH_4Cl solution. (Note 7)

Step 7. Electroplate thorium isotopes onto a one inch diameter platinum planchet (cathode) at 3.5-4.0 v., 0.3 amp. for two hours. Adjust the pH to 2 every thirty minutes with a few drops of NH_4OH . At the end of electroplating, add several drops of NH_4OH to make the solution basic. While the voltage is still on, pipette out half the solution from the cell, add distilled water to full. Repeat this process several times until the current is zero. (Note 8)

Step 8. Turn off the current and remove the platinum planchet from the electroplating cell. Peel off the rubber cement and wash the planchet with water. Dry under a heat lamp and heat the planchet to redness over a Bunsen burner.

Step 9. Count the alpha and the beta activities of thorium isotopes on the planchet by proportional counters and analyze the alpha particle energies by alpha spectrometry.

C. Purification and Electrodeposition of Uranium

Step 1. Elute uranium from the uranium-bearing anion exchange column with 10 ml. of 0.1N HCl. Collect the effluent in a 30 ml. beaker and evaporate the solution to dryness.

Step 2. Take up residue in 8N HCl and transfer the solution quantitatively into a 50 ml. graduated test tube with 10 ml. of 8N HCl. Add 10 ml. of isopropyl ether, cap the test tube tightly with a polyethylene stopper, mix the two phases with a Vortex mixer for three minutes

and centrifuge. Discard the ether layer. Repeat the isopropyl ether extraction of iron twice. In the second or the third ether extraction, if the yellow color of iron is not extracted into the ether layer add a few drops of concentrated HCl and shake the mixture again. After the third ether layer is discarded, transfer the aqueous layer quantitatively into a 30 ml. beaker and evaporate to almost dryness. Fume with concentrated HNO_3 several times until all the chloride is converted to nitrate. (Note 9)

Step 3. Take up the residue in 2 ml. of 0.1N HNO_3 and transfer the solution quantitatively into an electroplating cell with 5 ml. of 4M NaNO_3 . (Note 7)

Step 4. Electroplate uranium isotopes onto a one inch diameter stainless steel planchet (cathode) at 6.0-6.5 v., 1.5 amp. for two hours. Adjust the pH to 2 every fifteen minutes with a few drops of 4N HNO_3 . After the completion of electroplating, pipette out half the solution from the cell and add distilled water to full. Repeat this process several times until the current is zero (Note 8)

Step 5. Turn off the current and remove the stainless steel planchet from the electroplating cell. Peel off the rubber cement and wash the planchet with distilled water. Dry the planchet under a heat lamp.

Step 6. Count the alpha activity of uranium isotopes on the planchet with a proportional counter and analyze the alpha particle energies by alpha spectrometry. (Note 10)

D. Counting and Alpha Spectrometry of Thorium and Uranium Isotopes

The instruments used for the measurement of gross alpha and beta activities are:

- A) Nuclear Measurements Corp. decade scaler Model DS - 1A.
- B) Nuclear Measurements Corp. windowless gas-flow proportional counter Model PCC-11A (lead shield) for beta measurements and Model PCC-10A (no lead shield) for alpha measurements. P-10 counter gas which consists of 90% argon and 10% methane is used.

The instruments used for alpha pulse height analysis are:

- A) Oak Ridge Technical Enterprises Corp. Model 101-201 low noise amplifier system.
- B) Oak Ridge Technical Enterprises Corp. silicon surface barrier semiconductor radiation detector.
- C) Nuclear Diode vacuum chamber.
- D) RIDL Model 34-12 400 channel pulse height analyzer.

The source is placed approximately 5 mm below the detector. The chamber is then evacuated. Alpha particles impinging on the detector generate electrical pulses proportional to their energy. The pulses are amplified and fed into a multi-channel analyzer which records the number of pulses received in each energy interval. The data stored by the analyzer are read out by using an IBM typewriter modified for this purpose. Energy calibration of the analyzer is accomplished by the use of alpha standards. A block diagram of the circuit used for alpha spectrometry is shown in Figure 6.

Figure 6. Block Diagram of the Circuit Used for Alpha Spectrometry.

E. Calculation of Isotopic Thorium and Uranium Contents

A) Thorium Spectra

Table 14 gives the energy values of the alpha particles of the naturally occurring thorium alpha emitters and those emitted by the daughters of Th^{228} .

Figure 7 shows the alpha-spectrum of thorium isotopes isolated from sample USSR-F-3. The peaks beyond channel number 170 are the peaks of Th^{228} daughters which have grown in. The alpha particles from the small amount of Th^{227} activity present are not resolved but contribute to the counts under the Bi^{212} and Ra^{224} peaks.

The yield of thorium is calculated from the recovery of the beta emitting Th^{234} tracer.

$$\% \text{ yield Th} = \frac{\left(\frac{\text{c/m } \beta^- \text{ of Th}^{234}}{\text{recovered}} \right)}{\left(\text{c/m } \beta^- \text{ of Th}^{234} \text{ tracer added} \right) + \left(\frac{\text{c/m } \beta^- \text{ of Th}^{234} \text{ contributed}}{\text{by the sample}} \right) + (\text{Blank})}$$

Counts per minute beta of Th^{234} contributed by the sample is calculated from the activity of U^{238} by assuming U^{238} and Th^{234} in the sample are in secular equilibrium. This correction is rather small, on the order of less than one percent. The correction for the blank is even smaller.

The sums for Th^{232} , Th^{230} and Th^{228} peaks are computed and the following corrections are made:

- 1) The correction for background.
- 2) The correction for blank.
- 3) The correction for the Ra^{224} which appears in the Th^{228} region. From Table 14 we see that 4.9 per cent of Ra^{224} alphas are emitted with an amount of energy such that they are registered under the Th^{228} peak. Therefore, the counts under the Ra^{224} peak are summed up and 4.9/95.1 times this sum is subtracted from the Th^{228} peak sum. After the

Table 14

The Nuclear Characteristics of Certain Thorium Isotopes
and Daughters of Th²²⁸

Isotope	Half-life	Alpha Particle Energy (Mev.) ⁷²
Th ²³²	1.41 x 10 ¹⁰ yrs.	4.01
Th ²³⁰	75,200 yrs. ⁷³	4.615 (24.0%) 4.682 (76.0%)
Th ²²⁸	1.91 Yrs.	5.137 (0.03%) 5.173 (0.20%) 5.208 (0.40%) 5.338 (28.0%) 5.421 (71.0%)
Th ²²⁷	18.17 days	5.755 (21 %) 5.976 (24 %) 6.036 (23 %) others
Ra ²²⁴	3.64 days	5.445 (4.9%) 5.681 (95.1%)
Bi ²¹²	60.6 min.	5.481 (0.02%) 5.603 (1.1 %) 5.622 (0.15%) 5.765 (1.7 %) 6.047 (69.9%) 6.086 (27.2%)
Rn ²²⁰	56 sec.	5.74 (0.3%) 6.29 (99.7%)
Po ²¹⁶	0.15 sec.	6.78
Po ²¹²	0.30 μ sec.	8.78 (others to 10.53)

⁷²D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. of Mod. Phys. 30, 788-818 (1958)

⁷³R. W. Attree et al., Canadian J. Phys., 40, 194 (1962)

Figure 7. The Alpha-Spectrum of Thorium Isotopes Isolated from Sample USSR-F-3.

corrections are made, the net number of counts of each thorium peak is obtained and the percent it represents of the total number of counts under all the peaks in the spectrum can be calculated. If the total alpha activity of the thorium source in disintegrations per minute per gram of sample, at the time of alpha pulse height analysis is represented by A and the activity of a thorium isotope by A_i , then

$$A_i \text{ (d/m/g)} = A \times \frac{\text{(the percent of the total alpha activity contributed by the isotope)}}{\text{(the percent yield of thorium)}}$$

An example of the calculation of isotopic thorium compositions is given below:

Weight of sample (USSR-F-3) = 12.17 gm.

Uranium content of the sample = 1.37 ± 0.12 ppm.

$A_{U238} = 1.37 \times 12.17 \times 0.735 = 12.2$ dis./min.

c/m β^- of Th^{234} recovered = 509 ± 5

c/m β^- of Th^{234} tracer added = $(620 \pm 6) \times 0.8011^*$

c/m β^- of a blank run = 1.5

c/m alpha at the time of alpha pulse height analysis = 4.0 ± 0.3

Geometry of the proportional counter = 0.50 ± 0.01

Alpha spectrum of the sample -- see Figure 7.

Total Counts under	Bkgd.	Blank	Correction for Ra-224	Net counts of
Th^{232} region 188	0	0	-	Th^{232} 188
Th^{230} " 786	0	0	-	Th^{230} 786
Th^{228} " 268	26	0	5.4**	Th^{228} 237
Ra^{224} " 134	28	0	-	Ra^{224} 106
All the peaks 1786	109	3	-	All the peaks 1674

* 0.8011 is the correction factor for Th^{234} decay⁷⁴

** 5.4 = $106 \times 4.9/95.1$

⁷⁴H. W. Kirby, Anal. Chem., 26, 1063-1072 (1954)

$$\% \text{ yield Th} = \frac{509}{(620 \times 0.8011) + (12.2 \times 0.50) \times (1.5)} = 101 \pm 2\%$$

The percent of the total activity contributed by each thorium isotope is,

$$\text{Th}^{232} = 188/1674 = 11.2 \pm 0.9\%$$

$$\text{Th}^{230} = 786/1674 = 47.1 \pm 2.0\%$$

$$\text{Th}^{228} = 236/1674 = 14.1 \pm 1.0\%$$

A = total alpha activity at the time of alpha pulse height analysis
 $= 2 \times 4.0/12.17 = 0.66 \pm 0.05 \text{ d/m/g}$. Therefore the activities of each thorium isotope are:

$$A_{\text{Th}^{232}} = 0.66 \times 0.112/1.00 = 0.074 \pm 0.008 \text{ d/m/g}$$

$$A_{\text{Th}^{230}} = 0.66 \times 0.471/1.00 = 0.31 \pm 0.03 \text{ d/m/g}$$

$$A_{\text{Th}^{228}} = 0.66 \times 0.141/1.00 = 0.093 \pm 0.009 \text{ d/m/g}$$

B) Uranium Spectra

Table 15 gives the energy values of the alpha particles emitted by certain uranium isotopes.

Table 15

The Nuclear Characteristics of Some Uranium Isotopes

Isotope	Half-life	Alpha Particle Energy (Mev)
U^{238}	$4.51 \times 10^9 \text{ yrs.}$	4.19
U^{235}	$7.13 \times 10^8 \text{ yrs.}$	4.12 (5.8 %)
		4.32 (8.0 %)
		4.33 (14.0 %)
		4.35 (35.0 %)
		4.37 (25.0 %)
		4.52 (2.7 %)
U^{234}	$2.48 \times 10^5 \text{ yrs.}$	4.56 (6.7 %)
		4.72 (28.0 %)
U^{232}	72 yrs.	4.77 (72.0 %)
		5.13 (0.32%)
		5.26 (32.0 %)
		5.32 (68.0 %)

Figure 8. The Alpha-Spectrum of Uranium Isotopes Isolated from Sample Cal.-F-4.

Figure 8 shows the alpha spectrum of uranium isotopes isolated from sample Cal-F-4. The dashed-line peak is at the position of U^{232} . This peak appears when U^{232} tracer is added to the sample.

The sum for each uranium peak is computed and the following corrections are made.

- 1) The correction for background
- 2) The correction for blank.
- 3) The correction for U^{235} which appears in the U^{238} peak. From Table - 15 we see that 5.8 per cent of U^{235} alphas are emitted with an amount of energy such that they are recorded in the U^{238} peak. Therefore, 5.8% of the theoretical U^{235} is subtracted from the U^{238} peak sum. The theoretical U^{235} count is found by using the value of 21.96 as the ratio of specific activities of U^{238} to U^{235} and dividing this figure into the U^{238} peak count.
- 4) The correction for the tailing of U^{234} alphas into the U^{235} peak. The theoretical value of U^{235} as found above is always slightly lower than the experimentally ascertained U^{235} activity. The difference is ascribed to tailing of the U^{234} and is added to the U^{234} activity.

When U^{232} is run alone it shows a peak only in the U^{232} region, so no correction need be made for impurities in the U^{232} tracer.

If the total count under each peak in the U^{238} , U^{235} , U^{234} and U^{232} regions are represented by A, B, C, and D respectively, then

$$\text{Net count of } U^{238} = (A - \text{Bkgd.} - \text{Blank}) - (5.8\% \text{ of the theoretical } U^{235} \text{ counts})$$

----- (1)

$$\text{the theoretical } U^{235} \text{ count} = (\text{net count of } U^{238}) / 21.96$$

----- (2)

substitute (2) into (1) we obtain,

$$\begin{aligned} \text{U}^{234} \text{ tailing} &= (B - \text{Bkgd.} - \text{Blank}) - \left[(\text{net. count of U}^{238}) / 21.96 \right] \cdot [0.942] \\ &= (B - \text{Bkgd.} - \text{Blank}) - \left[(A - \text{Bkgd.} - \text{Blank}) / 22.02 \right] \cdot [0.942] \end{aligned}$$

substitute (3) into (4) we obtain,

$$\text{Net Count of U}^{232} = (D - \text{Bkgd.} - \text{Blank})$$

From these corrected values, the activity ratios U^{234}/U^{238} , U^{238}/U^{232} and U^{234}/U^{232} are computed. By multiplying the last two ratios by disintegration per minute U^{232} added, the dpm of U^{238} and U^{234} in the sample are obtained. The specific activities are calculated as follows:

$$A_{U^{234}} \text{ (d/m/g)} = \frac{(\text{dpm } U^{232} \text{ added}) (\text{net count of } U^{234})}{(\text{wt. of sample}) (\text{net count of } U^{232})}$$

$$A_{U^{238}} \text{ (d/m/g)} = \frac{(\text{dpm } U^{232} \text{ added}) (\text{net count of } U^{238})}{(\text{wt. of sample}) (\text{net count of } U^{232})}$$

Since 1 μ g of uranium of normal isotope abundance gives 0.735 disintegration per minutes of U^{238} , $A_{U^{238}}$ ^{238}U : ^{235}U : ^{234}U = 100 : 138 : 4

$$\frac{A_{U^{238}}}{0.735} = \text{ppm } U^{238} \text{ in the sample.}$$

F. Nótes

Note 1. (a) Th^{234} tracer is prepared by periodically "milking" the same uranyl perchlorate- HClO_4 solution. Mallinckrodt A. R. uranyl nitrate hexa-hydrate is used for the preparation of the uranyl perchlorate solution. The uranyl perchlorate solution is transferred to the top of a Dowex-50-X4, 200-400 mesh cation exchange column and is allowed to flow through under atmospheric pressure. When the liquid level reaches the resin the inside of the tube is washed down with several 1 ml. portions of 3N HCl until the yellow color has completely disappeared from the effluent. 3 ml. of 0.5M oxalic acid is added to the column and the effluent

is collected in a 30 ml. beaker. 5 ml. of concentrated HNO_3 is added to the beaker and the solution is heated to fumes until approximately 2 ml. of solution remains. The solution is cooled and 2 ml. of 72% HClO_4 is added. The solution is heated to fumes of HClO_4 and evaporated to a volume of 1 ml. After the solution has cooled 1 ml. of concentrated HCl and 2 ml. of distilled water are added. The perchlorate solution is passed through a second Dowex-50-X4 column identical to the first. When the liquid level reaches the resin, the inside of the tube is washed down with eight 1/2 ml. portions of 3N HCl . The Th^{234} on the column is eluted with 3 ml. of 0.5M oxalic acid and the effluent is collected in a 30 ml. beaker. To the beaker 5 ml. of concentrated HNO_3 is added, and the solution is heated to fumes and evaporated to a volume of approximately 2 ml. The solution is cooled; 2 ml. of 72% HClO_4 is added. The solution is evaporated to dryness and the residue is taken up in 3M HNO_3 . The final solution is diluted to the desired Th^{234} activity with 3M HNO_3 . Two 100 lambda tracer aliquots are mounted on platinum planchets - one by evaporation and flaming, and the other by electrodeposition. The mounted sources are counted with a proportional counter. 621 ± 6 count/min./100 lambda is obtained for the evaporated source, and 618 ± 6 count/min./100 lambda for the electroplated source. The difference between these two counts is within the limit of counting statistics. The average of these two activities is compared with the Th^{234} activity recovered from the sample to determine the yield of the thorium analysis.

(b) U^{232} tracer solution is prepared from U^{232} that was obtained from the Argonne National Laboratory. The tracer solution is in 4N HNO_3 .

(c) The solution is diluted because precipitates formed from a very concentrated solution are often in the form of extremely fine crystals with colloidal properties.

(d) The solution is boiled to expel CO_2 and to promote exchange between the thorium, uranium in the tracer and the thorium, uranium in the sample.

Note 2. Carbonate free concentrated NH_4OH is used to insure complete precipitation of uranium, since uranyl carbonate complexes are highly soluble. The mixture is digested, and is allowed to stand to help the flocculation of the precipitates.

Note 3. Reprecipitation removes calcium and magnesium from the precipitate.

Note 4. This column is prepared as follows. Dowex-1-X8 Cl^- form 200-400 mesh resin is washed once with distilled water. The water resin slurry is added to water filled column until the resin fills the column to the desired length. The column is then washed with 5 ml. H_2O and 5 ml. 8N HCl alternately three times. Just before the sample is passed through the column, the column is washed once more with 5 ml. of 8N HCl .

Note 5. Sometimes peptization occurs when the precipitate is washed with pure water. When this happens the mixture is brought to near boiling to coagulate the precipitates.

Note 6. This column is prepared as follows. Dowex-1-X8 Cl^- form 200-400 mesh resin is washed once with distilled water. The water resin slurry is added to the water filled column until the resin fills the column to the desired length. In order to free the resin from impurities, the column is cleaned by expanding and contracting the resin bed by changing to various anion forms. The column is washed with 5 ml. of 1N HCl and 5 ml. of H_2O alternately three times. It is then converted to NO_3^- form by passing 20 ml. of 2M NaNO_3 through it. The conversion to the nitrate form is insured by testing the effluent for Cl^- with 0.1M

AgNO_3 solution. After it is converted to NO_3^- form, the column is washed with 5 ml. of H_2O and 5 ml. of 7M HNO_3 alternately three times. Just before the sample is passed through the column, the column is washed once more with 2 ml. of 7M HNO_3 .

Note 7. The electrodeposition cell is shown in Figure 9. The Sargent-Slomin Electrolytic Analyzer is used for electroplating. A clean coiled platinum electrode inserted into the stainless steel chuck on the motor bracket of the analyzer is used as a revolving anode. A platinum planchet or a stainless steel planchet forms a cathode and is held in place on the bottom of the glass cell by applying Carter's rubber cement between the contact surfaces. The distance between the electrodes is about 0.5 centimeters.

Note 8. The platinum planchets and the stainless steel planchets are cleaned and degreased by treating with concentrated nitric acid and carbon tetrachloride. Platinum disks are heated to dull red before and after mounting the source in order to improve the resolution in the alpha spectrum.

Note 9. Sometimes a third liquid phase appears in the extraction of ferric chloride by isopropyl ether. When this happens, distilled water is added to the graduated test tube and the mixture is shaken over again. This is repeated until the system is back to a two-phase system. Possible explanations for the formation of the third phase are given by Nachtrieb et al.⁷⁵ and Laurene et al.⁷⁶

Note 10. It is possible that Pa^{231} is present with the uranium isotopes on the planchet. As protactinium is strongly adsorbed on Dowex-1 anion exchange column from 8N HCl it may be eluted from the column with 0.1N HCl and electrodeposited onto the stainless steel planchet, along

⁷⁵N. H. Nachtrieb, et al., J. A. C. S., 74, 897 (1952)

⁷⁶A. H. Laurene, et al., J. Phys. Chem., 60, 901 (1956)

Figure 9. Electrodeposition Cell

with uranium. This is not certain for the tendency of protactinium to deposit on the walls of glass vessels is well-publicized. The exact amount of Pa^{231} present is not known, however, one can estimate the maximum amount which may be present.

Pa^{231} , a 32480-year alpha emitter, is a decay product of U^{235} . Fifteen percent of Pa^{231} alpha particles have energies such that they appear in the U^{234} peak region.

The deficiency of Pa^{231} in ocean water leads one to expect that Pa^{231} in modern marine molluscan shells is nearly zero.^{77,78} The maximum activity of Pa^{231} in fossil shells is determined by assuming that Pa^{231} is in secular equilibrium with U^{235} . The maximum activity of Pa^{231} which may appear in the energy range of U^{234} is calculated to be 0.7% of U^{234} activity by assuming the activity ratio of U^{234} to U^{238} to be 1.0 in fossil shells, and by using the value of 21.96 as the ratio of specific activities of U^{238} to U^{235} . This is smaller than the uncertainty from counting statistics. If Pa^{231} is present, 85% of its alphas should appear between the U^{234} and U^{232} peaks. No peak was observed in this region so no correction for Pa^{231} was made.

2. TOTAL URANIUM ANALYSIS

A. Fluorimetric Method

The very low uranium content of naturally occurring calcium carbonates, 0.01 to 5 ppm, makes it necessary to use a sensitive method for the uranium determinations. Exposure of certain uranyl salts to ultraviolet light of wavelength 3400-3650 Å results in fluorescence bands in the range of 4500-6500 Å with a maximum at 5500 Å. This reaction of uranyl ions, in the wavelength region stated, is specific for uranium

⁷⁷W. M. Sackett, Science, 132, 1761 (1960)

⁷⁸W. S. Moore and W. M. Sackett, J. Geophys. Res., 69, 5401 (1964)

and permits the determination of uranium in amounts as low as 10^{-11} g. The fluorescence output is a linear function of the uranium content of the sample. The fluorescence is markedly enhanced by fusion of the sample with sodium fluoride, lithium fluoride, or a mixture of alkali fluorides with alkali carbonates.

A number of elements and compounds are known to quench the uranium fluorescence with the degree of quenching action depending on their concentration. Ag, Au, Ca, Ce, Co, Cr, Cu, Fe, HNO_3 , H_3PO_4 , Ir, Mg, Mn, Ni, Pb, Pt, Pu, Si, Th and Zn are the materials possessing possible quenching action.

Two basic techniques can be used to minimize the effect of quenching agents. Where the uranium content of the sample is sufficiently high, dilution of the solution may overcome quenching difficulties. The other technique consists of spiking aliquots of the sample solution with various known amounts of standard uranium solution.

The following procedure is a modification of one described by Grimaldi and Levine.⁷⁹

A) Uranium Extraction Procedure

Step 1. Pipette an aliquot of sample solution equivalent to 2 to 3 grams of solid sample into a 30 ml. beaker. Heat and swirl beneath heat lamp until a thick paste is obtained. Dissolve the paste in 0.35 ml. of concentrated HNO_3 and wash quantitatively with distilled water into a 50 ml. graduated test tube. Make the volume to 5 ml. either by adding distilled water or by evaporating beneath a heat lamp. (Note 1.)

Step 2. Add 7.0 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, A. R. grade to the 5 ml. of solution. Heat gently over a low flame until the aluminum nitrate

⁷⁹F. S. Grimaldi and H. Levine, Geol. Survey Bull., 1006, 43 (1954)

is completely dissolved. Allow the solution to cool to room temperature.

Step 3. Add 10 ml. of A. R. grade ethyl acetate to the solution, cap tightly with a polyethylene stopper, shake with a Vortex mixer for three minutes and centrifuge for about 30 seconds at 750 rpm. Transfer the ethyl acetate layer quantitatively through a funnel fitted with a dry No. 2 Whatman paper into a 30 ml. beaker. (Note 2.)

Step 4. Repeat the ethyl acetate extraction twice using 10 ml. of ethyl acetate each time, and filtering through the same filter paper and into the same 30 ml. beaker. After the third extraction wash the filter paper with 5 ml. of ethyl acetate and evaporate the combined extracts to dryness under a heat lamp. (Note 3.)

Step 5. Dissolve the residue in 1 ml. of concentrated HNO_3 transfer quantitatively to a 5 ml. volumetric flask and make up to volume with distilled water.

B) Spiking and Fusion Procedure

Step 1. To three of six clean gold dishes add an appropriate aliquot of a standard uranium solution. This is normally 100 μ l of a 1 microgram/ml. uranium solution. Evaporate to dryness beneath a heat lamp. (Note 4.)

Step 2. To all six dishes add an appropriate aliquot of the sample solution (normally 0.1 ml. for samples containing 0.1 to 1.0 ppm. uranium) and take to dryness beneath a heat lamp. (Note 5.)

Step 3. Add 300 $\pm$ 2 mg. of flux to each dish, also, to a seventh clean dish to be employed as a blank. Fuse between 625 and 650 degrees centigrade for 15 minutes in a muffle furnace. Remove and allow to cool in a dessicator for 20 minutes. Read the fluorescence of each dish.

(Note 6.)

C) Calculation of Uranium Content

As the fluorescence intensity is directly proportional to the amount of uranium present, a direct proportion can be set up which will give the uranium content of the final sample aliquot. Letting A equal the fluorescence reading, corrected for blank, of the sample aliquot, and A_s the fluorescence reading, corrected for blank, of the spiked sample aliquot, the micrograms of uranium in the final sample aliquot may be calculated:

$$\frac{A}{A_s - A} = \frac{\text{micrograms of uranium in final sample aliquot}}{\text{micrograms of uranium added in spike}}$$

Since the total sample volume is 5 ml., and the weight of the sample is known, the above value can easily be converted to ppm. of uranium in the sample.

D) Notes

Note 1. The amount of HNO_3 used gives a final concentration of about 7% HNO_3 by volume. At this HNO_3 concentration no appreciable change in ethyl acetate volume is observed during the extraction.

Note 2. The ethyl acetate is equilibrated with 7% HNO_3 to reduce the amount of aqueous phase dissolving into the organic phase. One hundred ml. of each are shaken together in a separatory funnel for three minutes and the aqueous phase is drained off.

A polyethylene stopper is used to cap the test tube since ethyl acetate dissolves rubber producing a gummy residue.

In the event aluminum nitrate separates out of solution, redissolve it, by warming, before commencing the next extraction.

Note 3. It will be necessary to evaporate part of the solution before the final extraction to allow sufficient volume in the 30 ml. beaker.

Note 4. A preliminary run of one aliquot of sample solution is made to determine the approximate uranium content. The aliquot of sample solution or the uranium standard solution is adjusted so the fluorescence of both can be read between 10 and 90 on the same sensitivity setting.

Note 5. The standard uranium solution is prepared by weighing 2.7080 mg. uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, on an Aloe gram electrobalance, dissolving in 7% HNO_3 and making up the volume to 1 liter with 7% HNO_3 . The solution contains 1.284 microgram uranium/ml.

Note 6. The flux is prepared by fusing 45.5 gm. K_2CO_3 , 45.5 gm. Na_2CO_3 and 9 gm. NaF in a large platinum dish and grinding the cooled flux to a fine powder.

If the fluorimetric readings for the triplicates are erratic, refuse for an additional 5 minutes. However, avoid exceeding 650 degrees centigrade as this will result in a sharp decrease in fluorescence. This may happen for only one or two dishes in the hot part of the furnace producing erratic results. The instrument used is a Jarrell Ash JA-2600 Galvanek-Morrison Fluorimeter.

The gold dishes, approximately 15 mm. in diameter and 4 mm. deep, are pressed from a 20 mil. gold sheet.

B. Alpha Pulse Height Analysis Method

The total uranium content of a sample can be obtained from the result of alpha pulse height analysis on the uranium isotopes isolated from the sample which is spiked with U^{232} .

The method is described on page 49 to 64 of this thesis. A comparison of some of the uranium results obtained by the fluorimetric method and the alpha pulse height analysis method is shown in Table 16.

Table 16

Comparison of Uranium Results

Sample	Uranium Result (ppm)	
	Fluorimetric	Alpha Pulse Height Analysis
BMMC-1 Cal.-M-1	0.35 ± 0.01	0.38 ± 0.02
BMMC-1 Cal.-F-1	1.41 ± 0.03	1.43 ± 0.14
BMMC-4 Cal.-F-4	0.66 ± 0.06	0.70 ± 0.08
Mississippian limestone standard # 1 (MLS # 1)	0.99 ± 0.04	1.06 ± 0.08

APPENDIX III DETERMINATION OF CALCIUM CARBONATE MINERALOGY
BY X-RAY DIFFRACTION*

The aragonite-calcite ratios in the calcium carbonate shells are determined by the method described by Davies and Hooper.⁸⁰ All samples are ground to pass a 170 mesh sieve and are caught on a 270 mesh sieve. The radiation from a copper target (Cu K_α radiation) is used with a Picker diffractometer. A nickel filter is inserted in front of the Geiger-Mueller tube to absorb the K_β radiations emitted from the copper target as their reflection interfered with the principal aragonite reflection. The lines used for the analysis are the 10 $\overline{1}$ 4 calcite line and the 111 and 021 aragonite lines combined (Figure 10).

The calibration curve is constructed by mixing pure calcite and pure aragonite in different proportions, measuring the $I_c/(I_c + I_a)$ ratio and plotting these values against weight percent calcite (Figure 11). Having constructed the calibration curve, the percent aragonite in the sample can be determined from the curve.

The lowest level of calcite detection is greater than 3% for randomly oriented samples. When compressed slightly, calcite orients on its cleavage face and can be easily detected at 3% but is not detectable at 1%. Table 17 shows the results obtained.

*Mineralogical analyses were made by M. W. Reams, Department of Earth Sciences, Washington University.

⁸⁰T. T. Davies, and P. R. Hooper, Mineralogical Magazine, 33, 608 (1963)

Figure 10. The X-Ray Spectrum of 90% Aragonite, Pure STROMBUS GIGAS, mixed with 10% Pure Calcite. (After Davies and Hooper).

Figure 11. Calcite: Aragonite Calibration Curve. (After Davies and Hooper).

Table 17
Mineralogy of the Molluscan Shell Samples

Sample Designation	General Location	Percent Calcite
Cal.-M-1	Calif., USA	N. D.*
Cal.-F-1	Calif., USA	N. D.
Cal.-F-2	Calif., USA	N. D.
Cal.-F-3	Calif., USA	N. D.
Cal.-F-4	Calif., USA	N. D.
USSR-F-1	Siberia, USSR	N. D.
USSR-F-2	Siberia, USSR	N. D.
USSR-F-3	Siberia, USSR	N. D.
USSR-F-4	Siberia, USSR	N. D.
USSR-F-5	Siberia, USSR	N. D.
USSR-F-6	Siberia, USSR	23 ± 5%

*N. D. = not detectable (less than 1-2%)

USSR-F-6 is the only sample containing a reliably detectable amount of calcite. It was noticed that one of the genera in this sample, Nuculana, had been preserved with its valves unseparated. This allowed mud to fill the cavity. Separate diffraction patterns of the Nuculana fraction and the other genera indicated that calcite was almost exclusively in the Nuculana fraction of the sample. Whether the mud filling the cavities of Nuculana was originally aragonite or calcite or a mixture of the two was not determined.

APPENDIX IV. DESCRIPTION OF SAMPLES

1. Samples received from W. C. Bradley* (collected by W. O. Addicott)--
-- United States Geological Survey

Sample designation	Description*
Cal.-M-1	Modern <u>Protothaca staminea</u> , a sand-dweller, was collected at Point Año Nuevo, California.
Cal.-M-3	Modern <u>Schizothaerus nuttalli</u> a sand-dweller, was collected from the intertidal zone at Point Año Nuevo, California.
Cal.-F-1	Pleistocene <u>Protothaca staminea</u> , a sand-dweller, was collected from the basal marine deposits on the first marine terrace at Santa Cruz, Calif., along West Cliff Drive. The deposits are about 15' thick at the collecting location.
Cal.-F-2	Pleistocene <u>Panitella penita</u> , a rock borer, was collected from holes in the bed rock platform of the first terrace on the north side of Point Año Nuevo, California.
Cal.-F-3	Pleistocene <u>Schizothaerus nuttalli</u> , a sand-dweller, was collected from the basal marine deposits on the first marine terrace at Santa Cruz, Calif., along West Cliff Drive. The deposits are about 15' thick at the collecting location.
Cal.-F-4	Pleistocene <u>Macoma inguinata</u> , a sand-sweller, was collected from the basal marine deposits of the first marine terrace along the south side of Año Nuevo Point, 20 miles north of Santa Cruz, California.

*W. C. Bradley, personal communication (1965)

2. Samples Received from D. M. Hopkins* (collected by D. S. McCulluch)
-- United States Geological Survey

Sample Designation

Description

Greenld.-F-
-62AMh24

The shells were collected in 1962 from Northeast shore of Baldwin Peninsula, Greenland (66°34'02" N. lat. and 161°56'25" W. long)

One hundred grams of firm, apparently well-preserved shells were picked out for analysis.

Alas.-F-D-1116

The shells were collected from the Intermediate Beach near Nome, Alaska and consisted of a mixture of small and large sea shells, all showing evidence of weathering. The deposit from which these shells were collected is presumed to have been laid down during the Aftonian interglacial interval (1,300,000 yrs. B.P.). The sediments beneath the coastal plain at Nome are generally perennially frozen to bedrock, but in some places a layer of sediment resting immediately upon bedrock is thawed and contains circulating ground water. Evidence in the region indicates that the perennially frozen ground probably thawed out completely during the last (Sangamon) interglacial cycle. Thus, specimen Alas.-F-D-1116 probably has been subjected to thawing temperatures for at least a few tens of thousands of years of its history and will have been in contact with circulating ground water during that interval.

*D. M. Hopkins, personal communication (1962)

3. Samples received from T. Karlstrom (collected by V. A. Zubakov)
 -- United States Geological Survey.
 Identifications of the Pelecypods are by H. L. Levin, Washington
 University, Department of Earth Sciences

Sample designation	Description
USSR-F-1	<u>Astarte and Yoldia</u> The Anzhu II Transgression, New Siberia Island, plus 20-40 m. Geol. Age: III _{3a} (Approx. 22-45,000 yrs. B. P.)
USSR-F-2	<u>Astarte</u> The Karginian Transgression N. Enisey District, 69°50' N. Lat., plus 22-30 m. Geol. Age: III ₃ Krg (Approx. 22-45,000 yrs. B. P.)
USSR-F-3	<u>Astarte</u> The Kazantsevia Transgression, N. Enisey District, Kazant, 70°N. Lat., plus 60-80 m. Geol. Age: III ₁ Kz (70-100,000 yrs. B. P.)
USSR-F-4	<u>Amiantis*</u> The Kazantsevia Transgression, R. Agapa, N. Enisey District, 70° N. Lat., plus 60-80 m. Geol. Age: III ₁ Kz (70-100,000 yrs. B. P.)
USSR-F-5	<u>Entodesma*</u> , <u>Macoma*</u> , and <u>Yoldia</u> The Sanchugovian Transgression, R. Bol. Kheta, N. Enisey District, 69° N. Lat., plus 100-150 m. Geol. Age: II ₄ s (110,000-150,000 yrs. B. P.)
USSR-F-6	<u>Nuculana</u> The Sanchugovian Transgression, River Enisey 65° N. Lat. Geol. Age: II ₄ s equals Eniseyan horizon (II ₄ e) (140-180,000 yrs. B. P.)

*The generic name of the shell is questioned because of the poor preservation which makes the identification difficult.

4. Mississippian limestone standard received from R. B. Martin --
Mississippi Lime Company, St. Genevieve, Missouri (Mississippian Limestone standard # 1)

The limestone is representative of the oolitic portion of the Spargen formation of the Mississippian age. The supplier furnished the following analytical data:

CaCO ₃	99.00%
MgCO ₃	0.46%
SiO ₂	0.31%
Al ₂ O ₃	0.09%
Fe ₂ O ₃	0.04%
Others	0.10%

The sample was placed in a large polyethylene bag and agitated manually for about ten minutes. Portions of the sample were then removed and sent to a number of laboratories for uranium analysis. The results which were reported are tabulated below:

<u>Method</u>	<u>Analyst</u>	<u>Report (ppm U)</u>
Fluorimetric	Alice Caemmerer U.S.G.S.	1.1 1.2
Fluorimetric	Edward J. Fennelly U.S.G.S.	0.8
Fluorimetric	William M. Sackett Washington University	1.02 (+0.05)
Fluorimetric	Mary M. H. Cheng Washington University	0.99 (+0.04)
Colorimetric	Mitsunobu Tatsumoto Scripps Institution of Oceanography	1.09 (+0.05)
Isotope Dilution	James Cobb Lamont Geological Observatory	1.04 (+0.06)
Neutron Activation	William M. Sackett Washington University	1.07 (+0.05)
Alpha Spectrometry	Mary M. H. Cheng Washington University	1.06 (+0.08)

Table 18

Uranium, Thorium and Radium Content of Mississippian Limestone Standard #1

$A_{U^{238}}$ (d/m/g)	$A_{Th^{230}}$ (d/m/g)	$A_{Ra^{226}}$ (d/m/g)	$A_{Th^{232}}$ (d/m/g)	$A_{Th^{228}}$ (d/m/g)	$A_{Th^{227}}$ (d/m/g)	$\frac{A_{Th^{230}}}{A_{U^{238}}}$	$\frac{A_{Ra^{226}}}{A_{U^{238}}}$	$\frac{A_{U^{234}}}{A_{U^{238}}}$	Analyst (Date)
0.75 (+0.04)	0.72 (+0.07)	-	0.035* (+0.003)	0.03 (+0.01)	-	0.96 (+0.10)	-	-	Sackett (1958)
-	0.79 (+0.08)	0.76 (+0.04)	0.035* (+0.003)	0.06 (+0.02)	0.01 (+0.03)	1.04 (+0.10)	1.01*** (+0.08)	1.01 (+0.02)	Blanchard (1963, 1965)
-	0.78 (+0.08)	0.76 (+0.04)	0.035* (+0.003)	0.04 (+0.02)	0.04 (+0.04)	1.03 (+0.10)	1.01*** (+0.08)	0.99 (+0.02)	Blanchard (1963, 1965)
0.76 (+0.03)	-	0.78 (+0.04)	-	-	-	-	1.03 (+0.07)	-	Broecker (1963)
0.73 (+0.04)	0.76 (+0.05)	-	0.030** (+0.006)	0.032 (+0.006)	-	1.04 (+0.09)	-	1.02 (+0.05)	Cheng (1966)
-	-	-	-	-	-	-	-	1.01 (+0.01)	Thurber (1962)

* Th^{232} determined by neutron activation - by H. A. Potratz.** Th^{232} determined by alpha spectrometry - by M. H. Cheng.

*** Calculated by using Blanchard's radium value and Sackett's uranium value.

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