

THORIUM-TO-URANIUM RATIOS AS INDICATORS OF SEDIMENTARY PROCESSES: EXAMPLE OF CONCEPT OF GEO-CHEMICAL FACIES¹

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ABSTRACT

Because of analytical difficulties, few data are available on the thorium and uranium contents of sedimentary rocks. More than 200 new thorium and uranium determinations have been made by a gamma-ray spectral technique and by an alpha activity-fluorometric uranium technique. Together these two independent techniques can be used as an experimental test of secular radioactive equilibrium. Only rarely in this study have fresh samples of ancient sedimentary rocks been found out of radioactive equilibrium. The accuracy of the thorium-to-uranium ratio determinations is more than sufficient for many geologic studies.

The thorium-to-uranium ratios in sedimentary rocks range from less than 0.02 to more than 21. Ratios in many oxidized continental deposits are above 7, whereas most marine deposits have ratios much below 7. Thus, the thorium-to-uranium ratio varies with sedimentary processing and depositional environment. A cyclothem and several other sedimentary sequences illustrate the use of this ratio to distinguish environments and processes. The thorium content of shales varies much less than the uranium content. By mineral and trace-element analysis an attempt has been made to evaluate the residate, hydrolyzate, clay, and precipitate (evaporite) contributions to the thorium and uranium contents of sedimentary rocks. These data also provide some insight into the details of the mobilization, transportation, and fixation of thorium and uranium in the sedimentary cycle.

Field tests indicate that quantitative potassium, uranium, and thorium determinations can be made with a spectral gamma-ray logging instrument. Logs obtained with such instruments may provide an important additional means for subsurface interpretations.

INTRODUCTION

This study was undertaken to test and to extend several fundamental geochemical hypotheses regarding the thorium and uranium contents of sedimentary rocks. Thorium and uranium are of particular interest for the following reasons. 1. Their indicated distribution suggests that Th/U ratios may reflect sedimentary processing and products. 2. A better understanding of the distribution of thorium and uranium in sedimentary rocks should provide a basis for more detailed interpretation of gamma-ray logs and of spectral gamma-ray logs obtained with newly developed borehole instruments that measure separately the gamma rays from the thorium series, the uranium series, and potassium-40. In addition to providing all the information obtainable from a conventional gamma-ray log, the spec-

¹ Publication No. 148, Shell Development Company, Exploration and Production Research Division. Read before the Society of Economic Paleontologists and Mineralogists at St. Louis, April, 1957. Manuscript received, August 28, 1957.

² Department of Geology, The Rice Institute. The part of this work done at The Rice Institute was supported by Grant No. C-009 from the Robert A. Welch Foundation.

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The writers gratefully acknowledge the indispensable help provided by their colleagues in obtaining samples and discussing the geologic environment of various samples. J. M. Parks and R. J. Dunham of the Shell Development Company and G. S. Hamill and K. Richardson of The Rice Institute were particularly helpful in providing samples. R. A. Rowland and others read the manuscript critically. Any errors in the text are the sole responsibility of the writers. The work at The Rice Institute was carried out solely through the generous financial support of the Robert A. Welch Foundation under Grant C-009.

tral gamma-ray logs provide opportunities for subsurface interpretations based on the relative and absolute concentrations of thorium, uranium, and potassium. In particular, correlations were sought between Th/U ratios and (1) rock type and mineralogy, (2) thoroughness of oxidation and weathering, and (3) position in the basin of deposition (distance from the shore). This study was made possible by the recent development of laboratory techniques for determining thorium, uranium, and Th/U ratios in large numbers of rocks. By use of these new techniques, the number of sedimentary rock analyses available for consideration has been greatly increased.

PREVIOUS WORK

Although many details were lacking, certain outstanding aspects of the geochemistry of thorium and uranium have been known for some years (McKelvey, Everhart, and Garrels, 1955). Pliler (1956) gave a summary of the published data regarding the general distribution of thorium and uranium during weathering, erosion, and deposition. Much of the published data consists of analyses on aggregates, or composites, made up of a number of individual rocks. The published data on igneous rocks are relatively the most complete (438 analyses on 1,919 samples). At the beginning of the present study, the data on clastic rocks were much less complete (about 60 analyses on 200 samples), although Pliler and Adams (Pliler, 1956; and Adams and Pliler, 1956) had recently established the general range of values. The published data on chemical precipitates, particularly carbonate rocks, were very few; an unpublished study by Adams, Saunders, and Zeller provides information on the general range of uranium in carbonate rocks (analyses on 26 composite samples composed of 516 rocks). Near the close of the experimental work of this study, a paper with a large number of data on the thorium and uranium content of sediments of the Russian Platform (Baranov, Ronov, and Kunashova, 1956) became available. Their data are restricted to analyses on aggregate samples of many rocks and are valuable for average concentrations in the shales and carbonate rocks of the Russian Platform. However, the use of aggregate samples provides little information on the range of the Th/U ratios and the range of thorium and uranium concentration in individual rock formations.

In general, sedimentary rocks appear to have a much greater range in thorium and uranium concentration and in Th/U ratios than is the case with common primary igneous rocks. The separation of thorium and uranium in sedimentary processes is strikingly evidenced by the extremely low Th/U ratio of 0.0002 found in solution in sea water (Koczy, 1956). Considering that the uranium inventory in the oceans can be replaced completely with uranium brought in by streams in less than 100,000 years (Koczy, 1954), a significant amount of uranium in solution, accompanied by very little thorium, has moved to the oceans and been fixed in sedimentary rocks. This marked separation of thorium and uranium is due to the fact that (1) uranium can be oxidized to the very soluble uranyl form,

but thorium has no comparable state under surface or near-surface conditions, and (2) thorium can be concentrated in placers and residual deposits such as bauxite. Thus, since oxidizing conditions are rare in the cosmos, the cosmic and general terrestrial Th/U ratio is about 3 or 4. Under plutonic, more reducing conditions, thorium and uranium are both in the tetravalent state and behave almost like isotopes of the same element due to the great chemical similarities within the actinide series of which they are members (Seaborg and Katz, 1954). It is only in contact with the oxygen of the earth's atmosphere or in unusual, late magmatic differentiations that thorium and uranium are separated to any extent. On a global basis, the published data indicate that oxidation during weathering is the major mechanism for separating thorium and uranium.

With the data and theories outlined, several previous workers have suggested that thorium and uranium concentrations or Th/U ratios might serve as sensitive indicators of sedimentary processes or environments. Koczy (1949) suggested on the basis of a few analyses that the Th/U ratio should decrease as the distance from the shore increased. Hurley (1956) states: "The U/Th ratios in many shales are known to be related to the distance offshore of the depositional site," but it is not clear whether he is following Koczy or whether Hurley has unpublished data on the Th/U ratio in shales. Baranov, Ronov, and Kunashova (1956) report that high thorium concentration and high Th/U ratios in their aggregate shale and aggregate carbonate samples correlated with nearness to shore or rapid uplift during the time of deposition. Adams (1954) on the basis of a study on extrusive rocks concluded:

Finally, the Th/U ratio may be very useful in discriminating between those volcanic and plutonic rocks derived in part from sediments and those volcanics containing iron and uranium that have never been oxidized. . . . Thus, one might expect the Th/U ratio in oxidized sediments to be much higher than the same ratios in rocks that have never been oxidized. However, the present state of the art of thorium analysis does not permit a test of this hypothesis.

The testing of these and other related hypotheses, as well as the correction of some unreliable data based on inadequate analytical methods (beta activity versus Th/U; Beers and Goodman, 1944), had to await the development of more suitable analytical techniques such as those described in the next section.

SAMPLING AND ANALYTICAL TECHNIQUES

The analytical techniques used in this work for determining Th/U ratios are fully described by Adams, Richardson, and Templeton (to be published). One technique for determining thorium, uranium, and potassium involves the spectral analysis of gamma radiation from the rock sample; usually more than 800 grams of sample is required for these measurements, but less than 100 grams of unusually radioactive rock may suffice. The systematic errors in this technique depend on the concentrations of thorium, uranium, and potassium, and on the Th/U and Th/K ratios. With most of the sedimentary rocks studied to date, the Th/U ratio can be determined to within less than ± 10 per cent by gamma-ray spectral analysis. Larger errors are found with extreme Th/U ratios (less than

0.10 or more than 20) and with concentrations of less than 1 ppm thorium and less than 1 ppm uranium.

A second technique used for determining Th/U ratios involves the measurement of total alpha activity of the powdered rock sample together with a chemical (fluorometric) determination of uranium. This technique is more widely applicable because only a gram or so of sample is required. The main errors in this technique are due to emanation effects in the alpha counting and heterogeneity in the samples. The over-all error is estimated to be less than ± 20 per cent of the Th/U ratio where that ratio is more than 0.5 and there is more than 0.3 ppm uranium and more than 0.3 ppm thorium. Below these limits the errors are considerably larger.

Both the spectral gamma-ray technique and the alpha activity-fluorometric uranium technique are valid only where secular radioactive equilibrium exists in the sample measured. Breger (1955) showed experimentally that the eight ancient sedimentary rocks studied by him were in secular radioactive equilibrium. The two techniques described can also be used to determine if secular radioactive equilibrium exists. Thus, if both techniques are used on the same sample and identical uranium concentrations and identical Th/U ratios are found to be within experimental error, the sample must be in secular radioactive equilibrium. This follows because the alpha activity-fluorometric uranium technique requires equilibrium between all the alpha-emitting nuclides in the thorium and uranium series, whereas the gamma-ray technique requires equilibrium between certain gamma-ray-emitting daughters and the parent thorium or uranium. A comparison of the two techniques on 22 samples is given in Table I and Figure 1. In Figure 1 it can be seen that 20 of these 22 samples are in secular radioactive equilibrium or close enough to it for the application of these techniques. One sample, number 15, is deficient of an equilibrium amount of uranium (fluorometric uranium is less than that determined by gamma-ray analysis); it is believed that this outcrop sample is slightly weathered and some of the original uranium has been leached, leaving the gamma-ray-emitting daughters behind. The other major deviation, number 16, in Figure 1, is believed to be due to lack of homogeneity. In this entire study, involving the analysis of more than 200 samples, the data from only 9 samples were rejected because of lack of radioactive equilibrium.

In evaluating the limits of error cited, one must consider the end use of the data obtained. The data listed here show that the Th/U ratio in sedimentary rocks varies from less than 0.02 to more than 21. The analytical errors permit this more than 1,000-fold range to be divided into more than 20 distinct categories. It is not certain that there are many geologic conditions where greater analytical accuracy is necessary. A direct determination of thorium would be desirable because (1) it might reduce the errors; (2) there would be no necessity for secular radioactive equilibrium as required in the two radiometric methods; and (3) as a consequence of (2) it would be possible to work with the most recent sediments. It may finally develop that the most critical analytical errors will be those of the

TABLE I. DATA FOR CALIBRATION CURVE

Sample Number	Formation	Rock Type	Gamma-Ray Spectral Analysis			Fluorometric Uranium in ppm	Alpha Counts Per Hour	Ratio Th_0/U_0	Ratio $acph/U_0$
			U_0 in ppm	Th_0 in ppm	K_0 in %				
1	AEC Standard	Pitchblende in dunite ^c	10 ^a	0 ^b	—	10 ^a	110	0.0	11
2	AEC Standard #5	Carnotite	780	0 ^d	—	930 ^a	9,340	0.0	10
3	AEC Standard #1	Phosphate Rock	240	4	1.1	250 ^a	2,200	0.02	8.8
4	Chattanooga	Black Shale	80 79	5.2 6.5	2.7 2.8	67 72 65 74	575	0.07 0.08	8.3
5	Winchell	Limestone	4.1	0.6	0.04	3.6	38	0.15	11
6	Heebner	Black Shale	32	9.8	2.2	27 26 29 24	238	0.31	8.8
7	Morrow	Limestone	1.4	1.1	0.4	1.3 1.4	16	0.79	13
8	Marble Falls	Limestone	(3.3) ^e <u>3.1^f</u>	(2.2) ^e <u>2.7^f</u>	(0.5) ^e <u>0.5^f</u>	(12.3) ^e <u>2.7^f</u>	(141) ^e <u>48^f</u>	(10.6) ^e <u>0.87^f</u>	(18) ^e <u>18^f</u>
9	Austin Chalk	Limestone	1.7	1.6	0.3	1.8 1.8 1.8	27	0.94	15
10	Austin Chalk	Limestone	(11.2) ^e <u>1.3^f</u>	(2.0) ^e <u>1.4^f</u>	(0.5) ^e <u>0.5^f</u>	(11.0) ^e <u>1.1^f</u>	(17) ^e <u>25^f</u>	(1.7) ^e <u>1.1^f</u>	(17) ^e <u>22^f</u>
11	Austin Chalk	Limestone	2.4	5.1	1.7	2.1	49	—	23
12	Lawrence	Underclay	4.2	13	2.4	2.4 ^g	101	3.1	42
13	Lawrence	Shale	4.0	13	2.0	3.8	103	3.3	27
14	Smithwick	Shale	2.4	8.7	1.6	2.4 2.3 2.4 2.0 2.4	80	3.6	35
15	Loe	Sandy Shale	3.7	14	2.5	1.9 ^g 2.2 ^g 2.1 ^g	143	3.8	68
16	Del Rio	Shale	(1.2) ^e <u>1.0^f</u>	(1.1) ^e <u>1.2^f</u>	(2.0) ^e <u>2.0^f</u>	(1.0) ^e (2.6) ^h <u>(3.0)^h</u>	(54) ^e 182 ^h <u>196^h</u>	(9.2) ^e <u>6.7^f</u>	(54) ^e (59) ^e <u>(32)^h</u>
17	Point Peak	Shale	1.9	13	8.5	1.9 2.0 2.1	93	6.8	49
18	Lawrence	Red Shale	1.6	13	2.9	1.6	95	8.1	59
19	Oak Hall	Bentonite	4.0	34	3.8	4.3	303	8.5	71
20	Arkansas	Bauxite	6.4	96	0.3	6.4	745	15	116
21	Surinam	Bauxite	6.1	132	0.5	6.0	1,088	21.6	181
22	AEC Standard	Monazite in dunite ^c	0.4 ^a	10 ^a	—	0.4 ^a	73	25 ^a	182

NOTES:

(After Adams, Richardson, and Templeton)

^aCertificate value for standard.

^bNo thorium detected in this pitchblende.

^cStandards made at New Brunswick Laboratory, AEC, by diluting NBS Standards No. 2670 (pitchblende) and No. 2601 (monazite) with dunite.

^dNone detected.

^eValue rejected because of poor homogeneity.

^fValue accepted after thorough mixing.

^gSample may be weathered and deficient of an equilibrium amount of uranium.

^hValue plotted in Figure 2, but homogenization probably not adequate.

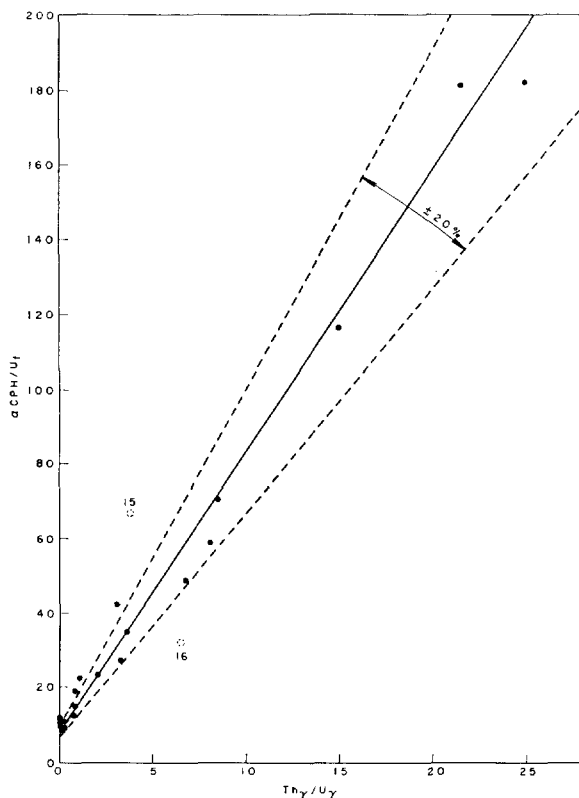


FIG. 1.—Calibration curve: $\alpha\text{cpH}/U_f$ versus $\text{Th}\gamma/U_\gamma$ (Adams, Richardson, and Templeton—to be published).

borehole logging tool, because the Th/U ratios measured in the hole may well be those of greatest application (see subsequent section on Applications). The limits of error discussed are based on the more systematic errors, e.g., the total number of radioactive events counted, the signal-to-background ratio, the extraction efficiency in chemical uranium procedures, etc. Unsystematic errors, particularly heterogeneity in the samples, were the source of much difficulty during the earlier phases of this work.

The selection and treatment of the samples are of great importance for Th/U ratio determinations, because they can be the source of large unsystematic analytical errors. First of all, secular radioactive equilibrium is a prerequisite in the sample. Breger's data previously cited and the data in Table I indicate that most ancient sedimentary rocks are in secular radioactive equilibrium if they are fairly well consolidated, have not been weathered at all, and do not have great amounts of pore water than can dissolve oxygen and emanation.

A greater problem arises in homogenizing the sample. Homogenization is of

great importance because widely different sample weights are used; thus, less than 0.2 gram of sample contributes to the alpha-activity measurement; 0.050 to 0.50 gram of sample is used for the fluorometric determination of uranium; more than 800 grams of sample is needed in the spectral gamma-ray analysis. Many disagreements between the Th/U ratios measured by different methods early in the present work were due to lack of representative samples. Thus, Th/U ratios measured in the borehole can not be compared directly with measurements made on small sidewall cores, because the borehole logging instrument measures the Th/U ratio in a large volume of rock weighing many kilograms, whereas the sidewall core represents only a fraction of a kilogram. The measurements on the two samples will agree only where the formation is several feet thick and very homogeneous. By thorough mechanical mixing of the finely ground (—100-mesh) sample and by taking care to avoid bias of the sample (e.g., shaking and tamping the sample bottle so that zircons and other dense, radioactive minerals concentrate in the bottom), representative samples can be obtained and the unsystematic errors reduced to insignificance compared with the systematic errors discussed.

TABULATION OF DATA

Table II (pages 394–400) contains a compilation of 319 uranium and thorium determinations, representing 11,411 sedimentary rocks. Of these determinations, 236, representing 242 rocks, are new; the rest are taken from the literature. The samples have been grouped into eight major subdivisions: (1) carbonate rocks, (2) chemical precipitates (other than carbonate rocks), (3) gray and green shales, (4) black shales, (5) red and yellow shales and residual clays, (6) bentonites, (7) sandstones, and (8) accessory minerals. Within each subdivision the samples are listed in order of decreasing Th/U ratio.

The Th/U ratio in the rock samples ranges from less than 0.02 to more than 21. The uranium values range from less than 0.1 to 250 ppm and the thorium from less than 0.1 to 132 ppm. Table III summarizes the thorium, uranium, and Th/U values for limestones and shales. Certain carbonate rocks and certain chemical precipitates have the lowest thorium content and lowest Th/U ratio; certain bauxites have the highest thorium content and highest Th/U ratio. Figures 2, 3, and 4 contain histograms for each of the major groups, showing the range together with the mean and median values. Some interpretations of these distributions follow.

TABLE II. TABULATION OF DATA

Carbonate Rocks											
Geol. Age	Name, Location	ppm U _x	ppm U _y	ppm Th _x	Th/U	acph	Min.	% Residue	% C	ppm Zr	Env.
Dev.	Duperow, N. Dak.	0.1		0.6	6.0	5	Cal. III.	1.7			Marine
Dev.	Lyle, N. Dak.	1.3		4.7	3.6	46	Dol. Chl.				
Penn.	Toronto, Kans.	0.6		2.2	3.6	21	Cal.	11		260	Cont.
Prec.	Ocoee, N. C.	1.6		5.2	3.3	52	Dol. III.	54		340	Marine
Dev.	Duperow, N. Dak.	0.5		1.5	2.9	15	Cal. III.	2.6			
Dev.	——, W. Tex.	2.3		6.5	2.8	67	Dol. Cal.	44			Marine
Camb.	Morgan Creek, C. Tex.	0.3		0.7	2.3	7.5	Glauc.				Marine
Dev.	Duperow, N. Dak.	2.4		5.5	2.3	60	Dol. Anh.				Marine
Penn.	Toronto, Kans.	0.6		1.4	2.3	15	Cal.	12		180	Marine
Miss.	——, Sask.	1.1		2.4	2.2	27	Dol. III.	2			Marine
Prec.	Agg. (7), Pac. ¹	0.65		1.4	2.2	16		20			Marine
Cret.	Austin Chalk, C. Tex.	2.1	2.4	5.1*	2.1	49	Cal. Mont.	38			Marine
Miss.	——, Sask.	1.4		2.5	1.8	30	Dol. III.	22			
Dev.	Sakken, N. Dak.	1.4		2.5	1.8	30	Dol. III.	20	0.25		Marine
Miss.	——, Sask.	0.2		0.3	1.7	4.3	Cal. III.	5			Marine
Ord.	Agg. (9), Pac. ¹	0.75		1.2	1.6	15		9.9			Marine
Dev.	Duperow, N. Dak.	0.6		1.0	1.6	12	Cal. M. L.	4.6			Marine
Dev.	Duperow, N. Dak.	0.9		1.4	1.5	17	Cal.	1.2			Marine
Dev.	Agg. (18), Atl. ¹	1.6		2.4	1.5	31	Cal.	6.1			
Perm.	——, N. Mex.		2.4	3.3*	1.4		Cal. M. L.	42			Marine
Dev.	Duperow, N. Dak.	1.3		1.7	1.3	23	Dol. III.				Marine
Miss.	——, Sask.	1.3		1.7	1.3	23	Cal. Dol.	8.5			Marine
Miss.	Agg. (20), Mid. Cont. ¹	1.3		1.5	1.2	22	Cal.	3.2			Marine
Miss.	——, Sask.	0.6		0.7	1.2	10	Cal.	1.3		20	Marine
Dev.	Agg. (5), Pac. ¹	0.8		0.9	1.1	13	Cal.	1.6			Marine
Cret.	Austin Chalk, C. Tex.	1.1	1.3	1.4*	1.1	24	Cal. Mont.	12			Marine
Paleoz. through Quat.	5475 Samples, Russian Platform ²		2.1	2.4	1.1			11.7			
Miss.	——, Sask.	2.3		2.5	1.1	37	Dol. III.	19			
Miss.	——, N. Tex.		3.5	3.9*	1.1		III.				
Tri.	Agg. (9), Pac. ¹	1.1		1.0	1.0	17		10			Marine
Cret.	Austin Chalk (16), Tex. ³	2.8		2.8	1.0						Marine
Dev.	Duperow, N. Dak.	0.7		0.7	1.0	11	Cal. III.	2.5			Marine
	Average 5 Ls. ⁴	1.3		1.1	0.9						
Miss.	Chapell, Tex.		5.3	4.9*	0.9		Cal. III.		0.05		Marine
Miss.	Chapell, Tex.		0.8	0.7*	0.9		Cal. M. L.	0.4			Marine
Cret.	Austin Chalk, C. Tex.	1.8	1.7	1.6*	0.9	27	Cal. Mont.	11			Marine
Penn.	Marble Falls, C. Tex.	2.5	3.1	2.7*	0.9	48	Cal. Chert	50			Marine
Penn.	Leavenworth, Kans.	1.2		1.0	0.85	17	Cal.	5.1		150	Marine

*Determined by gamma-ray spectral analysis.

1. Adams, Saunders, and Zeller (unpublished data).
2. Baranov, Ronov, and Kunashova (1956); radiometric method.
3. Breger (1955); emanation method.
4. Evans and Goodman (1941); emanation method.

TABLE II (continued)

Carbonate Rocks (continued)

Geol. Age	Name, Location	ppm U _F	ppm U _Y	ppm Th _F	Th/U	acph	Min.	% Residue	% C	ppm Zr	Env.
Cret.	Austin Chalk, C. Tex.		3.6	2.9*	0.8		Cal. Mont.	22			Marine.
Penn.	Magdalena, W. Tex.	1.3	1.4	1.1*	0.8	16	Cal. M. L.	7			Marine
Ord.	Agg. (91), Mid. Cont. ¹	1.4		0.9	0.7	18		5			Marine
Miss.	——, Sask.	0.5		0.3	0.7	7	Cal. Dol.	0.7		20	Marine
Cret.	Selma Chalk (331) ²	3.08		2.0	0.65						Marine
Perm.	——, N. Mex.		1.2	0.7*	0.6		Cal. Chert	10			
Perm.	——, N. Mex.		1.8	1.1*	0.6		Cal. Chert	39			
Perm.	——, N. Mex.		3.4	1.9*	0.6		Cal. Ill.	8			Marine
Cret.	Austin Chalk, C. Tex.		3.1	1.9*	0.6		Cal. Mont.	18			Marine
Tert.	Agg. (3), Pac. ¹	1.3		0.7	0.6	16		1			Marine
Miss.	Agg. (45), Pac. ¹	0.80		0.5	0.6	10	Dol. Cal.	2			Marine
Miss.	——, Sask.	1.3		0.8	0.6	16	Dol. Ill.	8			
Miss.	——, Sask.	3.0		1.5	0.5	35	Cal. Dol. Ill.	12			
Jur.	Agg. (4), Pac. ¹	2.1		1.0	0.5	25	Cal.	10			Marine
Sil.	——, Pac. Coast ¹	1.2		0.6	0.5	14		5			Marine
Cret.	Agg. (3), Mid. Cont. ¹	3.6		1.8	0.5	42	Cal.	15			Marine
Penn.	Agg. (208), Mid. Cont. ¹	2.8		1.4	0.5	32	Cal.	9			Marine
Dev.	Duperow, Sask.	1.2		0.6	0.5	14	Cal.	0.5			
Miss.	——, Sask.	0.7		0.3	0.4	7.5	Dol. Anh.	6			
Tert.	Agg. (2), Mid. Cont. ¹	3.3		1.3	0.4	36		18			Marine
Dev.	Agg. (8), Mid. Cont. ¹	3.3		1.3	0.4	36		5			Marine
Sil.	Agg. (12), Mid. Cont. ¹	1.8		0.7	0.4	19	Cal. Dol.	5			Marine
Miss.	——, Sask.	0.1		0.04	0.4	1	Cal. Anh.	22			
Camb.	Agg. (10), Pac. ¹	0.82		0.2	0.3	8.5	Cal.	3			Marine
Tri.	——, Atl. Coast ¹	18		5	0.3	182	Cal.	5			Marine
Cret.	Agg. (7), Pac. ¹	2.0		0.6	0.3	20		4			Marine
Penn.	Toronto, Kans.	1.3		0.4	0.3	13					Marine
Penn.	Magdalena, W. Tex.	1.5		0.4	0.25	15					
Perm.	Agg. (34), Pac. ¹	6.4		1.5	0.2	54	Cal. Dol.	15			Marine
Penn.	Agg. (26), Pac. ¹	2.5		0.5	0.2	23	Cal. Dol.	17			Marine
Prec.	Agg. (4), Mid. Cont. ¹	8.8		2.0	0.2	62		18			Marine
Penn.	Winchell, C. Tex.	3.6	4.1	0.6*	0.15	38	Cal. Ill.	4			Marine
Perm.	——, N. Mex.		6.6	0.9*	0.14		Ill.	0.1			Marine
Miss.	Fayetteville, Ark.		3.6	0.5*	0.14		Cal. M. L.	2			Marine
Miss.	——, Sask.	1.5		?	< 0.1	8	Cal. Ill.	0.8		40	Marine
Camb.	——, Atl. Coast ¹	2.0		< 0.2	< 0.1	12		9			Marine
Penn.	Toronto, Kans.	2.2		0	< 0.1	15	Cal. Ill.	10		150	Marine
Sil.	Agg. (2), Atl. ¹	1.1		0	< 0.1	8		2			Marine
Ord.	Agg. (17), Atl. ¹	0.75		0	< 0.1	6	Cal.	6.5			Marine
Miss.	——, Sask.	1.1		< 0.1	< 0.1	7	Cal. Ill.	0.1			Marine
Perm.	——, N. Mex.		4.8	0.3*	0.06		Mont.	0.2			
Perm.	——, N. Mex.		6.0	0.3*	0.05		Cal. Ill.	< 0.05			Marine

*Determined by gamma-ray spectral analysis.

TABLE II (continued)

Chemical Precipitates (Other than Carbonate Rocks)

Geol. Age	Name, Location	ppm U _f	ppm U _γ	ppm Th _f	Th/U	αcpH	Min.	% Residue	% C	ppm Zr	Env.
	Salt Dome, La.		0.08	0.5*	< 5		Hal.				Marine
	Salt Dome, La.		0.1	0.4*	< 4		Hal.				Marine
	Salt Dome, La.		0.2	0.4*	< 1		Hal.				Marine
Dev.	Duperow, N. Dak.	0.1		0.15	1.5	2	Anh.				Marine
Dev.	Caballos, W. Tex.	1.9		1.6	0.85	27	Chert		0.97		Marine
Plio.	Phosphate Rock Bone Valley, Fla.	250	240	3.9*	< 0.02	2200	Apat.				Marine
Dev.	Novaculite, Ark.	3.3		0.03	< 0.01	2.5	Chert		0.01		Marine

Shales: Black (With One Coal)

Cret.	Cantuar, Alta.	2.0		24	12.0	201	Kaol.		3.50		Cont.
Jur.	Fernie, Alta.	1.4		12	8.5	101	M. L.				Marine
Cret.	Tuscaloosa, Ala.	1.5		11	7.6	98	Chl. Ill.				Cont.
Eoc.	——, Calif.	2.7		16	5.8	140	Mont.			580	
Cret.	Dakota, Colo.	3.6		19	5.2	170	M. L.		1.35		Cont. Marine
Cret.	Dakota, Colo.	4.8		21	4.3	193	M. L. Kaol.		2.75		Cont. Marine
Dev.	——, W. Tex.	6.9		28	4.1	266	Sty.		0.22		
Cret.	——, Calif.	4.2		9.5	2.2	104	Mont.		0.14		
Penn.	Stanley, Okla.	2.9		6	2.1	69	Ill.				Tuff. Marine
Cret.	Cantuar, Alta.	14		28	2.0	307	Kaol.		1.15	1200	Marine
Miss.	Barnett, C. Tex.	9.9		13	1.3	177	M. L.		2.2		Marine
Mio.	——, Calif.		22	16*	0.75		Mont.				
Penn.	Toronto, Kans.	2.8		1.6	0.7	36			62.2		Coal
Miss.	Barnett, C. Tex.	8.8		5.2	0.6	108	Ill.		3		Marine
Penn.	Heebner, Kans.	27.0	32	9.8*	0.3	238	Ill.		10.8		Marine
Mio.	Nod. 11351, Calif. ³	14.4		3.6	0.25						Marine
Dev.	Antrim (2001, Mich. ³)	17.5		2.8	0.16						Marine
Miss.	Woodford, C. Tex.		65	7.4*	0.11		Ill.		11.7		Marine
Miss.	Chattanooga, Tenn.	69	80	6.0*	0.07	575	Ill.		20		Marine

Agg.	Aggregate sample. Number of individual samples given in ()	M. L.	Mixed layer clay
αcpH	Alpha counts per hour per 20.2 cm. ²	Mont.	Montmorillonite
Anh.	Anhydrite	Pac.	Western United States
Apat.	Apatite	ppm	Parts per million by weight = grams per metric ton
Ark.	Arkose	Peg.	Pegmatite
Atl.	Eastern United States	Prec.	Precambrian
Cal.	Calcite	Sph.	Sphene
Dol.	Dolomite	Sty.	Styolite
Glauc.	Glauconite	Th _f	Thorium determined by alpha activity-fluorometric uranium method
Gran.	Granite	Th _γ	Thorium determined by gamma-ray spectral analysis
Hal.	Halite	U _f	Uranium determined by fluorometric method
Ill.	Illite	U _γ	Uranium determined by gamma-ray spectral analysis
Kaol.	Kaolinite		
% K	Weight per cent of potassium calculated as the metal		
Mid. Cont.	Mid-continental United States	Zir.	Zircon
Min.	Mineralogy		

TABLE II (continued)

Shales: Red, Yellow, and Residual, Including Bauxites

Geol. Age	Name, Location	ppm U ₂	ppm U _y	ppm Th ₂	Th/U	αcpH	Min.	% Residue	% C	ppm Zr	Env.
	Bauxite, Arkansas		3.1	91.2*	29.4	567					
	Bauxite, Surinam	6.0	6.1	132 *	21.6	1088					Cont.
	Bauxite, Surinam		3.6	74.2*	20.9						
	Bauxite, Surinam		3.7	73 *	19.8						Cont.
	Bauxite, Arkansas	6.4	6.4	96 *	15.0	745					Cont.
Penn.	Winchell, C. Texas		1.8	17 *	9.4		III. Chl.				Cont.
Penn.	Winchell, C. Texas		1.9	16 *	8.4		III. Chl.				Cont.
	Bauxite, Bintan		7.1	58.7*	8.3						
	East Indies		1.6	13 *	8.1	95	M.L. III.				Cont.
	Lawrence, Kansas		5.0	40.2*	8.0						
	Bauxite, Brit. Guiana										
	Bauxite, Gold Coast, Africa		2.7	21.2*	7.9						
	Bauxite, Greece		7.5	59.2*	7.9						
Cret.	Tuscaloosa	1.8		13	7.5	116	III. Chl.				Cont.
Mio.	Venezuela	1.7		12.5	7.4	108	III. Chl. Kaol. M.L.			570	Cont.
	Bauxite, Istria, Yugoslavia		6.5	47.3*	7.3						
Cret.	Tuscaloosa	1.6		11	6.7	93	III. Chl.				Cont.
Cret.	Cantuar, Alta.	2.4		16	6.5	136	Kaol. M.L.			340	Cont.
Cret.	Kaolin, Georgia	1.7		11	6.3	94	Kaol.				Cont.
	Bauxite, Italy		8.3	51.5*	6.2						
	Bauxite, Miss.		5.9	36.3*	6.2						
	Bauxite, French Guinea		24.1	127.4*	5.3						
	Bauxite, Dalmatia, Yugoslavia		8.4	43.8*	5.2						
Cret.	Tuscaloosa	1.9		9.9	5.2	89	III. Chl.				Cont.
	Bauxite, France		12.4	55.6*	4.5						
	Bauxite, Dominican Republic		8.1	34.8*	4.3						
	Bauxite, Oregon		4.5	19.3*	4.3						
	Diaspore clay, Missouri			13.0	56.0*						
	Kaolin, La.	10.8		46	4.3	435	Kaol.				Cont.
	Bauxite, Jamaica		12	45 *	3.8						Cont.
	Bauxite, India		6.5	23.2*	3.6						
	Bauxite, Brazil		15.7	54.3*	3.5						
	Bauxite, Georgia		13.5	46.9*	3.5						
Mio.	Venezuela	2.5		7.0	2.8	73	Kaol. M.L.			510	Cont.
	Bauxite, Jamaica		17.0	42.0*	2.5						
	Bauxite, Georgia		15.4	34.6*	2.2						
	Bauxite, Jamaica		26.7	46.5*	1.7						
	Bauxite, Palau Is., Pacific		3.3	5.0*	1.5						
Mio.	Venezuela	9.5		9.0	0.95	142	Kaol. M.L.				Marine

*Determined by gamma-ray spectral analysis.

TABLE II (continued)

Notes: Gray and Green

Geol. Age	Name, Location	ppm U _f	ppm U _y	ppm Th _f	Th/U	αcpb	Min.	% Residue	% C	ppm Zr	Env.
Mio.	Soda Lake, Calif.	1.1		12	11	100	Kaol. III.				Marine Cont.
Eoc.	——, Calif.	2.2		24	11	195	M. L.			440	
Cret.	Austin Chalk, W. Tex.		2.6	28*	10.8		Mont. Cal.				Marine
Cret.	Del Rio, W. Tex.		1.6	17*	10.6		III. Kaol.				Marine
Mio.	Soda Lake, Calif.	1.3		11	8.8	97	Mont.			220	Marine
Jur.	Rierdon, Alta.	2.6		22	8.5	187	Mont.			490	Marine
Cret.	Tuscaloosa	1.8		15	8.1	124	III. Kaol.				Marine
Jur.	Morrison, Alta.	1.6		13	8.0	109	III. Kaol.				Marine
Prec.	Ocoee, N. C.	1.9		15	8.0	130	III.				
Penn.	Brownwood, C. Tex.		2.3	17*	7.4		III. Chl.				Marine Cont.
Camb.	Point Peak, C. Tex.	1.9	1.9	13*	6.8	93	III.				
Cret.	Del Rio, C. Tex.	3.0	1.8	12*	6.7	96	III. M. L.		0.3		Marine
Penn.	Winchell, C. Tex.		2.4	16*	6.7		III. Cal.				
Cret.	Tuscaloosa	1.6		10	6.4	90	III. Chl.				Marine
Cret.	Cantuar, Alta.	3.2		18	5.7	163	III. Kaol.				Cont.
Penn.	Winchell, C. Tex.		2.7	15*	5.6		III. M. L.				
Eoc.	——, Calif.	3.2		17	5.2	150	Mont.				
Jur.	Rierdon, Alta.	1.9		9.7	5.1	89	Mont. Cal.				Marine
Cret.	Dakota, Colo.	3.9		20	5.1	180	Mont.				Marine
Penn.	Smithwick, C. Tex.	1.7		8.5	5.0	78	III. M. L.				Marine
Mio.	Soda Lake, Calif.	3.3		16	4.9	148	Chl. M. L.				Marine
Penn.	Morrow, Okla.	1.9		9	4.9	88	III. M. L.		0.45		Marine Cont.
Penn.	Winchell, C. Tex.		3.5	17*	4.9		III. Kaol.				
Mio.	——, S. Tex.	2.7		13	4.8	120	M. L. III.				Marine
Penn.	Winchell, C. Tex.		3.5	16*	4.6		III. M. L.				
Penn.	Average 11 Samples, W. Tex.		3.3	15*	4.5		III. Chl.				Marine Cont.
Penn.	Winchell, C. Tex.		3.0	13*	4.3		M. L. Cal.				Marine
Mio.	——, S. Tex.	2.4		10	4.1	94	Mont.				Marine
Cret.	Dakota, Colo.	12		47	3.9	444	Kaol.			950	Cont.
Penn.	Toronto, Kans.	2.1	3.7	14*	3.8	143	III. Chl.				
Eoc.	Green River, Utah	2.9		11	3.8	105	III.				Cont.
Mio.	——, S. Tex.	2.8		10	3.7	100	M. L. III.				Marine
Penn.	Smithwick, C. Tex.	2.3	2.4	8.7*	3.6	80	III. M. L.				Marine
Eoc.	Juncal, Calif.		2.3	8.0*	3.5						
	Vicksburg, S. Tex.		4.0	13.7*	3.4						
Plio.	Pico, Calif.		4.1	13.7*	3.3						
Cret.	Cantuar, Alta.	4.0		13	3.3	130	Mont.				Marine Cont.
Penn.	Lawrence, Kans.	3.8	4.0	13*	3.3	103	M. L. III.				
Mio.	——, S. Tex.	2.9		9.5	3.3	95	Mont. III.				Marine
Plio.	Repetto, Calif.		3.9	12.8*	3.3						
Penn.	Lawrence, Kans.	2.4	4.2	13*	3.1	101	M. L. III.				

*Determined by gamma-ray spectral analysis.

TABLE II (continued)

Shales: Gray and Green (continued)

Geol. Age	Name, Location	ppm U _L	ppm U _y	ppm Th _L	Th/U	αcpb	Min.	% Residue	% C	ppm Zr	Env.
Eoc.	——, Calif.	2.8		8.5	3.0	85	Mont. Kaol.			170	
Jur.	Vicksburg, S. Tex.		3.4	10.2*	3.0						
Prec. through Quat.	Swift, Alta.	2.0		5.7	2.9	59	Mont.			450	Marine
	4795 Shales of Various Types, Russian Platform ^a		4.1	11.0	2.7						
Mio.	——, La.	2.0		5.3	2.7	56	Mont. Ill.				Marine
Mio.	——, La.	1.9		5.0	2.6	52	M. L. Ill.				Marine
Mio.	——, Venezuela	3.8		6	1.6	76	Kaol. M. L.				
Mio.	Soda Lake, Calif.		12.0	16.3*	1.4						
Plio.	Repetto, Calif.		8.4	11.1*	1.3						
Eoc.	Green River, Utah	2.5		1.6	0.75	33	Ill. Dol.			20	Cont.
Cret.	Tuscaloosa (55) ^a	2.8		0.2	0.7						
Eoc.	Green River, Utah	4.5		0	< 0.1	32					

Sandstones

Mio.	Zion Canyon, Utah ^a	0.86		5.4	6.3		Ss.				
Penn.	Similar, Calif.	0.9		4.5	5.1	42	Ark.				
Cret.	Brownwood, C. Tex.		3.5	14.4*	4.1		Sh. Ss.				
Cret.	Cantuar, Alta.	0.3		1.0	3.3	10	Qtz.				
Cret.	Cantuar, Alta.	1.2		3.0	2.6	33	Gray.				

Accessory Minerals

	Wards	5		115	23	890	Apat.				
	Uncompahgre Gran., Colo. ^c	12.4		130	10.5		Apat.				
	Various Local.				1.3-10. ^d		Apat.				
	Haliburton, Ont. ^e	2650		2180	0.82		Zir.				
	Acc. Min. of Gran., E. Mass.		1433*	673*, ^b	0.46 ^c		Zir.				
	5 Various Local.				0.2-0.6 ^d		Zir. from Gran.				
	Capetown, S. Africa ^e	1060		177	0.17		Zir.				
	5 Various Local.				0.1-5.0 ^d		Zir. from Peg.				
	Various Local.				0.1-5.0 ^d		Sph.				
	AEC Standard No. 3		2.94%	0.1*	0.03		Pitch.				
	AEC Standard No. 5	930	780	0	0	9340	Carn.				

*Determined by gamma-ray spectral analysis.

^aAverage of 21 zircons, range 405-2765 ppm. Webber, Hurley, Fairbairn (1956).

^bAverage of 21 zircons, range 130-1890 ppm. Webber, Hurley, Fairbairn (1956).

^cAverage of 21 zircons, range 0.31-0.74. Webber, Hurley, Fairbairn (1956).

^dHurley and Fairbairn (1956).

^eCited in *Nuclear Geology* (1964).

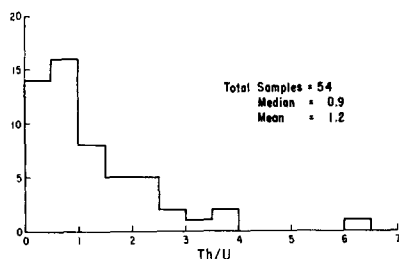
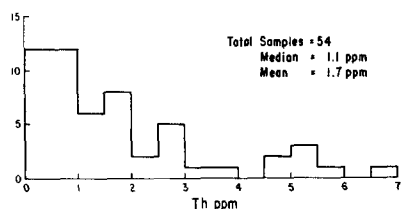
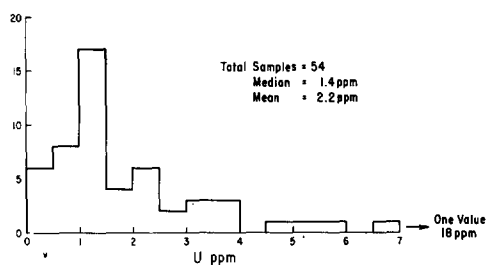
TABLE II (continued)

Bentonites

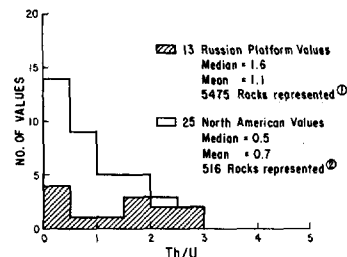
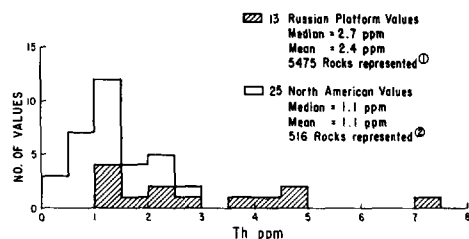
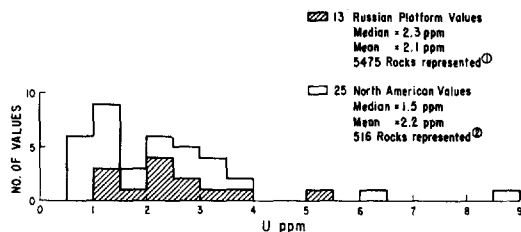
Geol. Age	Sample Number	Location	ppm U_f	ppm U_y	ppm Th_y	Th/U	acph	% K
Ord.	GH-11	Tenn.		1.2	25.0	20.8		5.2
Ord.	GH-2	Ala.		1.4	17.9	12.8		4.0
Ord.	GH-27	Tenn.		1.3	16.2	12.5		6.0
Ord.	GH-24	Tenn.		2.6	30.6	11.8		4.4
Ord.	GH-71	Penn.		3.4	36.1	10.6		4.4
Ord.	GH-19	Tenn.		2.1	20.2	9.6		5.3
Ord.		Penn.	4.3	4.0	34.0	8.5	303	3.8
Ord.	GH-47	Va.		3.1	25.9	8.4		4.6
Ord.	GH-6	Ala.		3.5	28.9	8.3		4.8
Ord.	GH-73	Penn.		2.9	22.7	7.8		2.8
Ord.	GH-60	Penn.		4.4	33.4	7.6		4.8
Ord.	GH-69	Penn.		2.1	15.7	7.5		3.9
Ord.	GH-78	Penn.		4.0	29.1	7.3		3.6
Ord.	GH-38	Va.		3.5	25.1	7.2		4.2
Ord.	GH-54	Va.		4.1	29.0	7.1		4.6
Ord.	GH-41	Va.		3.0	21.2	7.1		2.9
Ord.	GH-68	Penn.		1.8	12.4	6.9		2.4
Ord.	GH-51	Va.		5.0	33.9	6.8		4.3
Ord.	GH-45	Va.		5.2	34.8	6.7		5.3
Ord.	GH-15	Tenn.		4.0	25.5	6.4		4.7
Ord.	GH-12	Tenn.		3.6	24.1	6.3		4.4
Ord.	GH-64	Penn.		6.2	38.0	6.1		3.9
Ord.	GH-61	Penn.		4.2	25.8	6.1		5.6
Ord.	GH-52	Va.		4.6	27.6	6.0		3.7
Ord.	GH-14	Tenn.		3.6	21.1	5.9		3.6
Cret.		Wyo.	4.5		25.5*	5.9	240	
Ord.	GH-76	Penn.		4.5	26.3	5.8		5.4
Ord.	GH-49	Va.		5.2	29.6	5.7		5.0
Ord.	GH-63	Penn.		5.3	29.0	5.5		5.4
Ord.	GH-48	Va.		3.5	19.3	5.5		3.1
Ord.	GH-75	Penn.		4.5	24.8	5.5		6.0
Ord.	GH-10	Tenn.		4.0	21.9	5.5		3.5
Ord.	GH-20	Tenn.		3.1	16.7	5.4		4.4
Ord.	GH-22	Tenn.		2.7	14.6	5.4		4.8
Ord.	GH-13	Tenn.		4.7	25.3	5.4		4.5
Cret.		Wyo.	3.9		21*	5.3	188	
Ord.	GH-9	Tenn.		3.7	19.3	5.2		2.1
Cret.		Wyo.	6.2		42.0*	5.1	379	
Ord.	GH-46	Va.		5.2	26.3	5.1		5.6
Ord.	GH-50	Va.		5.5	27.6	5.0		4.9
Ord.	GH-77	Penn.		6.8	33.4	4.9		3.8
Ord.	GH-36	Va.		5.4	25.6	4.7		2.7
Ord.	GH-55	Penn.		4.7	22.3	4.7		3.9
Ord.	GH-56	Penn.		6.1	28.4	4.7		4.5
Ord.	GH-39	Va.		4.5	21.3	4.7		2.2
Ord.	GH-35	Va.		4.7	21.8	4.6		3.3
Ord.	GH-31	Va.		4.4	19.8	4.5		3.9
Ord.	GH-8	Tenn.		6.3	27.6	4.4		3.5
Ord.	GH-1	Ala.		2.9	12.8	4.4		4.7
Ord.	GH-21	Tenn.		4.6	20.3	4.4		3.6
Ord.	GH-40	Va.		6.1	25.8	4.2		2.5
Ord.	GH-72	Penn.		3.7	15.2	4.1		4.7
Ord.	GH-26	Tenn.		4.1	16.7	4.1		5.7
Ord.	GH-33	Va.		5.9	22.4	3.8		4.2
Dev.	GH-79	N. Y.		4.9	18.2	3.7		6.2
Ord.	GH-23	Tenn.		4.1	15.3	3.7		6.2
Cret.		Wyo.		12.0	42.0	3.5		0.5
Ord.	GH-34	Va.		5.6	18.9	3.4		2.7
Ord.	GH-7	Tenn.		6.6	22.4	3.4		2.8
Ord.	GH-29	Ky.		5.7	18.0	3.2		6.4
Ord.	GH-30	Ky.		5.8	18.8	3.2		6.7
Cret.		Wyo.	7.1		22.0*	3.1	224	
Cret.		Wyo.	10.0		29.0*	2.9	299	
Cret.		Wyo.	11.0	15.0	41.0	2.7		0.5
Ord.	GH-59	Penn.		5.5	14.0	2.5		5.3
Ord.	GH-65	Penn.		5.6	14.1	2.5		4.1
Ord.	GH-17	Tenn.		3.4	7.2	2.1		7.9
Dev.	GH-25	Tenn.		10.5	18.9	1.8		5.6
Dev.	GH-16	Tenn.		20.9	19.7	0.94		6.0

*Determined by alpha activity-fluorometric uranium method.

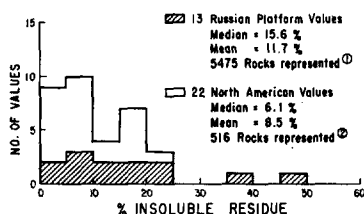
INDIVIDUAL CARBONATE ROCKS



AGGREGATE CARBONATE ROCKS



AGGREGATE CARBONATE ROCKS



NOTE:

- ① From Baranov, Ronov, and Kunashova (1956).
② See Table I for literature references.

FIG. 2.—Histograms of data on carbonate rocks.

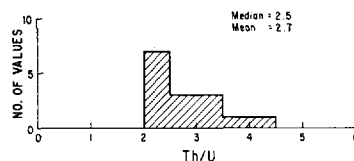
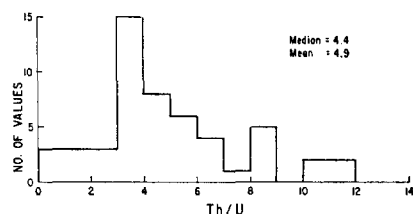
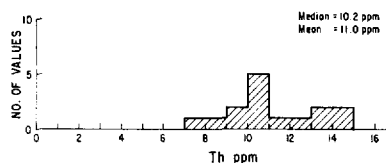
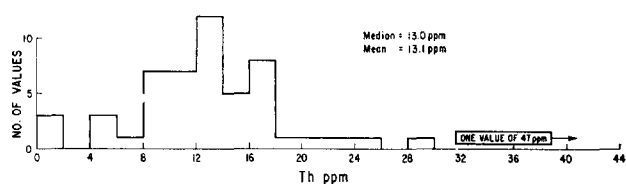
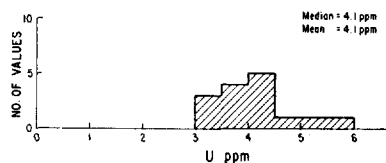
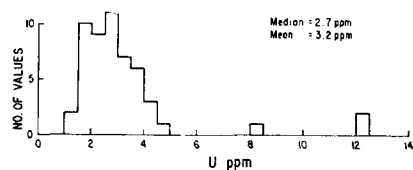
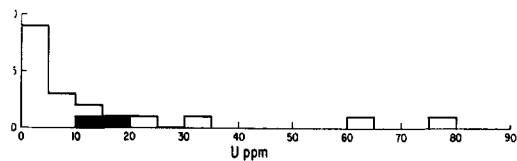
52 ANALYSES
GRAY & GREEN SHALESAGGREGATE SHALES OF RUSSIAN PLATFO
15 VALUES REPRESENTING 4795 ROCK
(Baranov, Ronov, Kunashova 1956)

FIG. 3.—Histograms of data on shales.

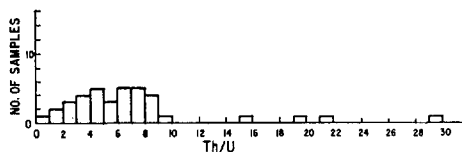
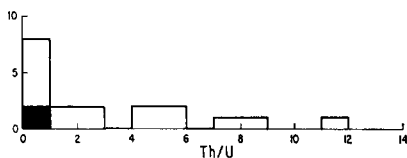
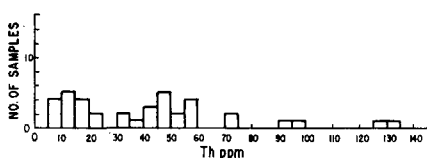
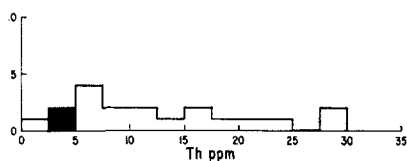
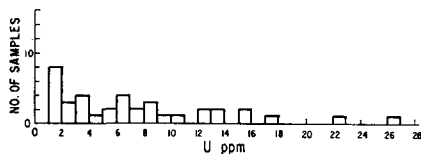
TABLE III. SUMMARY OF DATA ON LIMESTONES AND SHALES

	Thorium in ppm		Uranium in ppm		Th/U		% Insoluble Residues
	Mean	Median	Mean	Median	Mean	Median	Mean
Limestones							
North American individual samples (54)	1.7	1.1	2.2	1.4	1.2	0.9	—
25 North American aggregates (516)	1.1	1.1	2.2	1.5	0.7	0.5	8.5
13 Russian Platform aggregates (5 475)	2.4	2.7	2.1	2.3	1.1	1.0	11.7
Shales							
American gray-green (52)	13.1	13	3.2	2.7	4.9	4.4	
15 Russian Platform aggregates (4,795)	11	10.2	4.1	4.1	2.7	2.5	
North American bentonites (60)	24.0	22.7	5.0	4.5	5.8	5.4	
Estimates for average shale	12 ± 1		3.7 ± 0.5		3.8 ± 1.1		

SHALES (BLACK WITH ONE COAL)



RED & YELLOW SHALES, RESIDUAL CLAYS & BAUXITES



LEGEND:
 □ 19 Values
 ■ 2 Values representing 336 Rocks (Bregger 1955)

FIG. 3 (continued).—Histograms of data on shales.

INTERPRETATION OF DATA

It is obvious from the data in Figures 2, 3, and 4 that there are general and distinct groupings of the Th/U values. In order to determine the reasons for these groupings it is necessary to determine as well as possible the nature of the occurrence of thorium and uranium in these samples. Uranium and thorium can occur in several ways: (1) in detrital heavy minerals such as zircon, monazite, apatite, and xenotime; (2) in common detrital minerals; (3) in minerals precipitated from sea water, e.g., calcite; (4) adsorbed on iron and aluminum oxides or hydroxides; (5) adsorbed on clay minerals (McKee and Adams, to be pub-

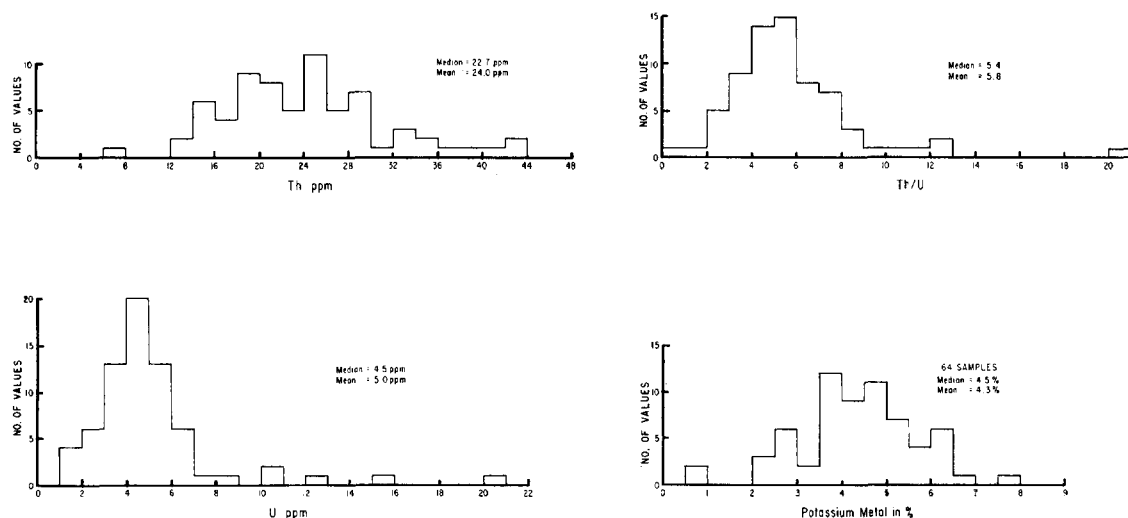


FIG. 4.—Histograms of data on bentonites.

lished) or organic matter; and (6) possibly adsorbed on the surfaces of carbonate and other minerals. Some discrimination between these various possibilities can be made by analysis of different fractions of the rock, by leaching and adsorption experiments, and by correlations with zirconium, carbon, and other elements geochemically related to uranium or thorium.

LIMESTONES, DOLOMITES, PHOSPHATE ROCK, EVAPORITES, AND CHERT

These rocks are derived in large part from material that was previously in solution in sea water and it is of genetic importance to determine how much thorium and uranium was derived from solution in sea water and how much was carried to the site of deposition in or on detrital material.

An estimate of the relative importance of precipitated and detrital material in carbonate rocks can be based on the data in Figure 5 where the ppm thorium is plotted against the per cent insoluble residue for the limestones and dolomites listed in Table II. The ppm uranium and Th/U ratio show a random distribution; however, there is a rather good linear relationship between the thorium content and the per cent insoluble residue. Because some of the residues consist of anhydrite and chert and because the thorium concentration in the insoluble residue can be expected to show some range, a close relation is not to be expected between thorium and insoluble residue. However, the slope of the line (drawn by inspection) in Figure 5 indicates that the insoluble residues generally contain about 13 ppm thorium, which is very near the mean concentration found in shales.

Figures 6, 7, and 8 contain graphs which show the relation between uranium, thorium, Th/U ratio, and insoluble residue for three separate formations. Within each formation the composition of the insoluble residues is quite similar: quartz, feldspar, and illite (Fig. 6); quartz, feldspar, illite (Fig. 7); quartz and montmorillonite (Fig. 8). In Figure 6, where the insoluble residues are less than 5

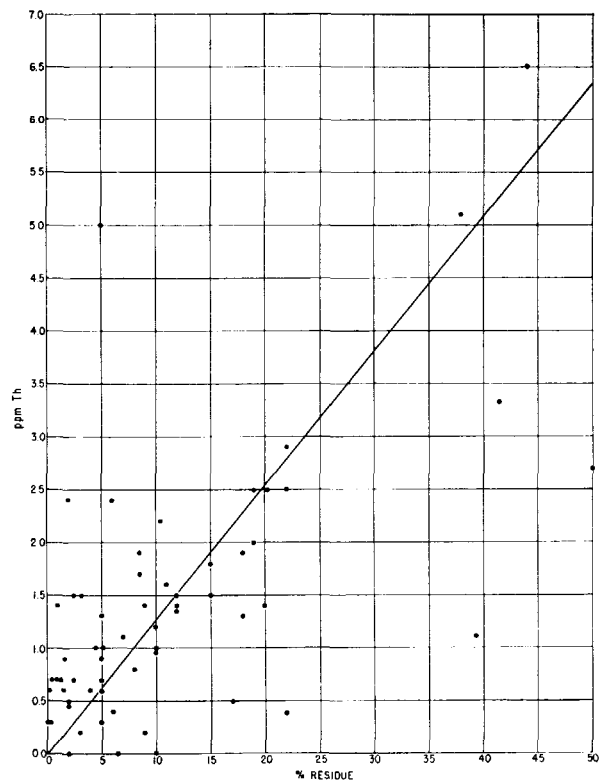


FIG. 5.—Insoluble residues in carbonate rocks versus thorium.

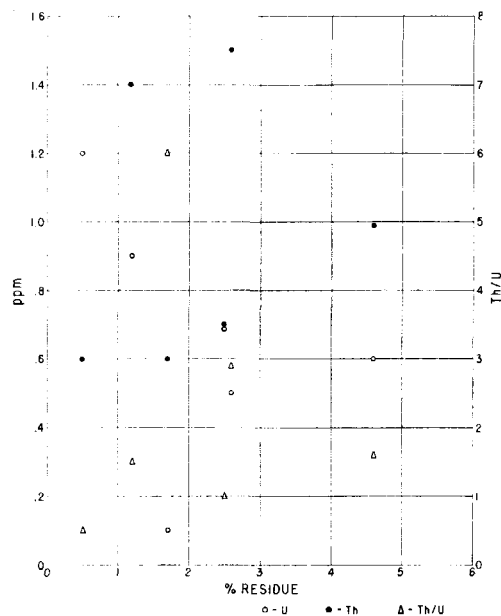


FIG. 6.—Insoluble residues in carbonate formation versus uranium, thorium, and Th/U ratio.

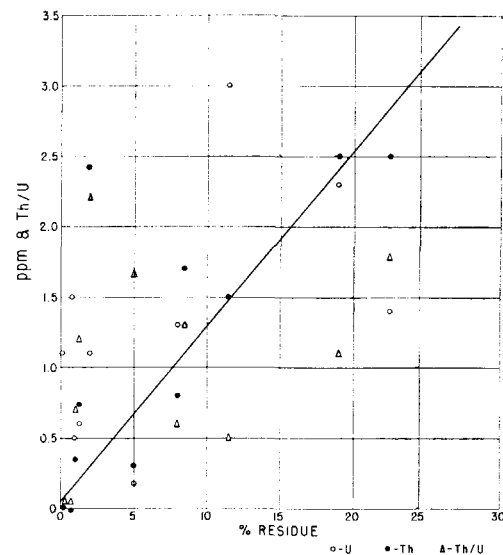


FIG. 7.—Insoluble residues in carbonate formation versus uranium, thorium, and Th/U ratio.

per cent, the data show a random distribution. In Figures 7 and 8, where the residues range from 0.2 to 23.5 per cent and from 11 to 38 per cent, respectively, there is again a good linear relation between the ppm thorium and the per cent residue. The slopes of the lines for both graphs are similar to each other and to the line in the graph containing all the carbonate samples (Fig. 5). Thus, these data indicate that most of the thorium in limestones is contained in the detrital, insoluble residue fraction; this conclusion fully substantiates the observations of Baranov, Ronov, and Kunashova (1956).

The uranium in the acid-soluble fraction and the acid-insoluble fraction of the limestones was determined for 32 samples. The per cent of the uranium in the acid-soluble fraction ranged from 50 to 100 per cent, averaging about 80 per cent. The relation between per cent soluble uranium and the per cent insoluble residue is very poor, but there is a suggestion that as the per cent insoluble residue increases, the per cent soluble uranium decreases. There is a fair direct relation between the ppm uranium in the insoluble residue and the per cent insoluble residue

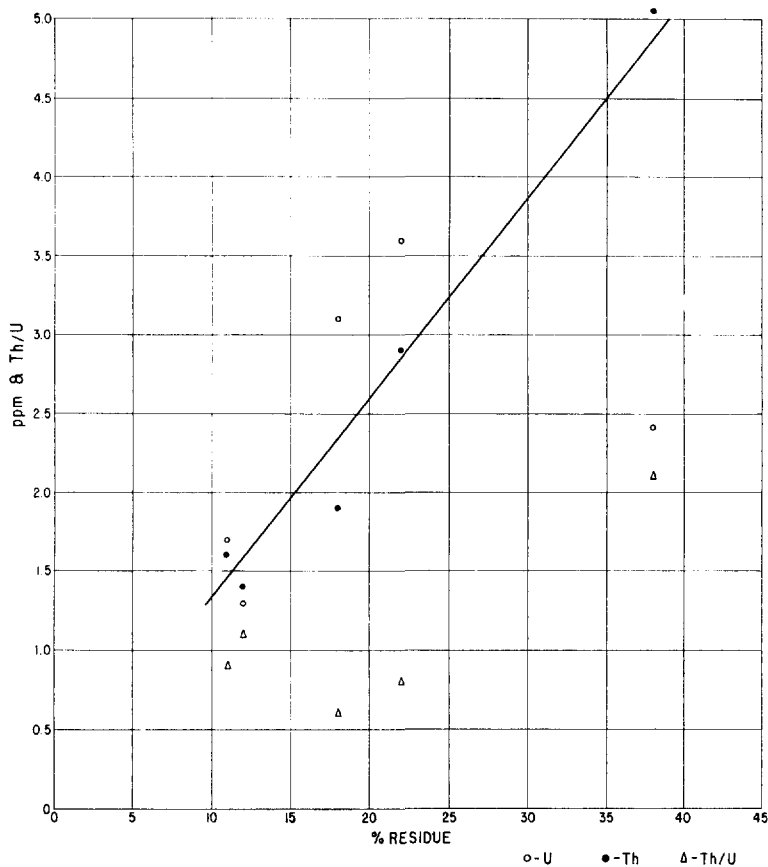


FIG. 8.—Insoluble residues in carbonate formation versus uranium, thorium, and Th/U ratio.

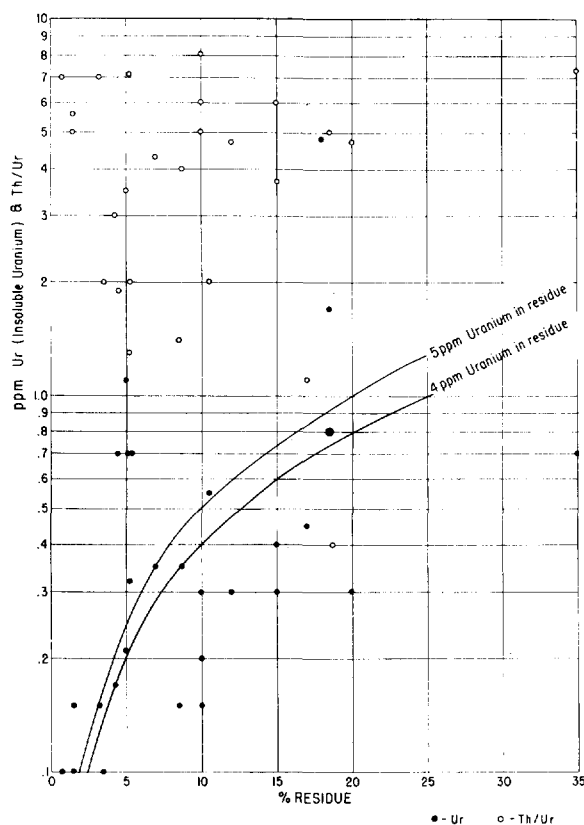


FIG. 9.—Total uranium and Th/U ratio in insoluble residue versus per cent insoluble residue.

(Fig. 9). The slope of the line in Figure 9 indicates that the insoluble residues generally contain approximately 4.5 ppm uranium. This value, like the calculated thorium value, is also close to the mean concentration found in shales.

In order to estimate how much of the uranium may have been leached from the detrital, acid-insoluble residue fraction by the hydrochloric acid treatment, illite, montmorillonite, and kaolinite shale samples were digested in hydrochloric acid heated to 80°–100°C. for 24 hours and washed with warm hydrochloric acid. The results are shown in Table IV.

These limited data indicate that the uranium in these gray, illitic, and mont-

TABLE IV. AMOUNT OF URANIUM LEACHABLE FROM CLAYS

Shale Sample	% of Shale Dissolved	% of U Dissolved	ppm U in Original Shale
Illite	10	0	1.9
Montmorillonite	10	10	3.9
Kaolinite	20	60	1.1

morillonitic shales is held in a relatively insoluble form (illite and montmorillonite are the most abundant clays in limestones). The high value for the dissolved uranium in the kaolinite sample may indicate that the uranium was associated with iron or aluminum oxides.

From the foregoing, it is concluded that most of the thorium and approximately 20 per cent of the uranium in limestones and dolomites occur in the detrital, acid-insoluble fraction. The insoluble fraction generally has a thorium and uranium content and Th/U ratio comparable with that of shales (Fig. 9). The acid-soluble portion of the limestone contains on the average about 80 per cent of the total uranium found. This uranium was probably fixed in the acid-soluble carbonate minerals by occlusion or co-precipitation. The fact that carbonate rocks contain about a thousand times more uranium than modern sea water and the great stability of the uranyl-tricarbonate complex in solution might favor coprecipitation. The possibility that uranium is also adsorbed on the surfaces of carbonate grains can not be eliminated at present.

The histograms in Figure 2 summarize the published and new data on carbonate rocks and provide comparisons between three main groups of data: (1) 54 individual North American rocks from various ages and basins, (2) 25 North American aggregate samples, representing 516 rocks from various ages and basins, and (3) 13 Russian Platform aggregates representing 5,475 rocks of various ages. In each of the three groups, the mean uranium concentration is about 2.2 (2.2, 2.1, 2.2). More than 90 per cent of the uranium values are less than 4.0 ppm. (Three of the seven values more than 4.0 ppm are associated with high porosity and insoluble residues below one per cent; see Example 2, Permian Limestone, New Mexico.) The determination of the acid-soluble uranium indicates that an average of about 80 per cent of the uranium in carbonate rocks is in or on the carbonate grains; thus, a detrital-free carbonate rock could be expected to have an average of about 1.8 ppm uranium with very few cases of uranium contents above 4.0 ppm (Table II).

As can be seen in the histograms in Figure 2, the higher residue Russian samples have a higher thorium content of 2.4 ppm compared with 1.1 ppm in the lower insoluble residue American rocks. No value is more than 7.0 ppm. All this evidence indicates that the thorium content of carbonate rocks is largely a function of the amount of insoluble residue and the concentration of thorium-rich resistates such as zircon, monazite, and xenotime in the insoluble residues. A detrital-free carbonate rock could be expected to have a thorium content of about 0.1 ppm or less (Table II).

The histograms in Figure 2 indicate that the Th/U ratio in carbonate rocks seldom exceeds 3 and that 80 per cent of the values are below 2. Because the major portion of the thorium is believed to be associated with the detrital material, detrital-free carbonate rock could be expected to have a Th/U ratio of 0.1 or less and in some cases may even approach the 0.0002 value found in modern sea water (Table II).

The Florida phosphate rock (Bone Valley formation) sample provides an

analogous case to the carbonate rocks. The thorium content is 3.9 ppm, presumably a detrital contribution for the most part. The uranium content, 250 ppm, is located in the apatite. As Baes (1956) has shown experimentally, uranyl ion can be reduced by ferrous ion provided that enough phosphate ion is available to complex the tetravalent uranium; this mechanism may account for the marked extraction and fixation of uranium observed. It is hypothesized that the phosphate-tetravalent uranium complex can be considerably more effective than the uranyl-tricarbonate complex in extracting and fixing uranium from sea water.

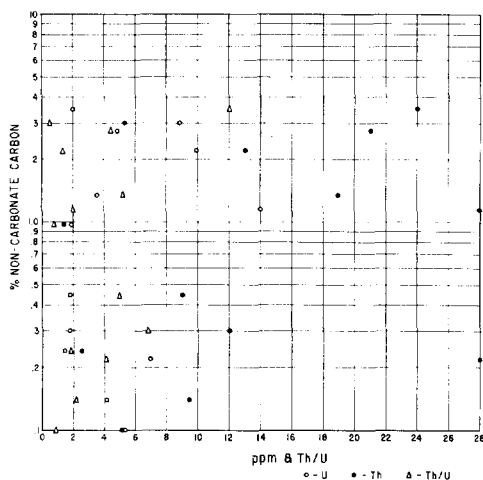


FIG. 10.—Per cent non-carbonate carbon versus uranium, thorium, and Th/U ratios in shales and carbonate rocks.

The data on halite, anhydrite, and anhydrite-rich carbonate rocks are scanty (Table II, Chemical Precipitates), and their very low thorium and uranium contents are difficult to measure accurately. In most cases listed in Table II only a minimum Th/U ratio can be calculated. In considering the size, charge, and chemistry of thorium and uranium ions there are no known reasons to expect the thorium and uranium concentration to be any higher than that observed. In other words, with halite and anhydrite there are no known complexes or mechanisms for fixing uranium comparable with those discussed in connection with the carbonate rocks and phosphate rock. It is hypothesized that the high minimum Th/U ratios found in two of the halite samples may be due to detrital, particularly eolian, material, which would be well oxidized and leached of uranium. The two chert samples suggest that these materials, during their deposition, were about as effective as carbonate rocks in extracting and fixing uranium from sea water.

The per cent non-carbonate carbon was determined for 13 limestone, shale, and chert samples (Table II; Fig. 10 excludes the coal and Chattanooga shale samples). If the per cent carbon is plotted against thorium and uranium, there is only a vague relation. Bates (1954), Beers and Goodman (1944), and others have

indicated that such a relationship does exist; however, their analyses were restricted to shales having a high percentage of organic matter and to a few specific formations. As can be seen from Figure 10, where the amount of carbon is small, the scatter is great. This does not necessarily mean that there is no relation between organic content and uranium content, but that where the organic content is low, the uranium present in other materials is sufficiently large to mask the relationship.

Even among shales with a relatively high carbon content there is little relation to the amount of uranium present (Fig. 3). However, when these black shales are divided into marine shales and continental shales a better relation is found. The organic-rich marine shales have relatively high uranium values, but the continental or near-continental organic-rich shales have values as low as, or lower than, those found in gray and green shales. This suggests that although reducing conditions existed during the deposition of these shales and the organic matter was preserved, deposition was too rapid for a build-up of the uranium concentration, or post-depositional leaching removed much of the uranium. Probably all of these factors are in part responsible and some of the continental black shales may have been deposited under essentially oxidizing conditions with slow removal rather than accumulation of organic material.

Other evidence raises questions concerning the role of organic matter in extracting uranium. For instance, the Arkansas novaculite, containing 0.01 per cent carbon, has nearly twice the uranium content of a black chert sample which contains 1 per cent carbon.

SHALES, RESIDUAL CLAYS, AND BAUXITES

The genetic interpretation of the observed distributions of thorium and uranium in the finer-grained clastics can well be discussed in terms of two opposite extremes of sedimentary conditions: (1) strongly reducing (low Eh) conditions with a very slow rate of deposition as in certain marine black shales, and (2) well oxidized (high Eh), well leached conditions of weathering characteristic of many bauxites, laterites, and residual clays. The great majority of shales and fine-grained clastics lies between these two extremes in regard to their thorium and uranium content.

The products of an environment characterized by strongly reducing (low Eh) conditions and a slow rate of deposition are exemplified by several marine black shale samples (Fig. 3 and Table II). It is hypothesized that the organic matter and other reductants in the environment reduce uranyl ion in solution to tetravalent uranium, which in turn can be fixed in several ways: (1) in organic complexes, (2) adsorbed on organic material, and (3) adsorbed on clay. As a result, the uranium is readily leachable and very dispersed (Bates *et al.*, 1954). In many undisputed marine black shales the uranium content is more than 10 ppm and may approach 100 ppm with the Th/U less than about 2. The thorium content of marine black shales has about the same range as common gray and green shales

(Fig. 3, and Table II). One of the exceptions to the limits just quoted is the Fernie shale (Table II); it is assumed that the low uranium (1.4 ppm) content of this and similar samples is a result of leaching during exposure to atmospheric oxygen at some time in the samples' history. The low thorium, uranium, and Th/U values for the Toronto coal (Table II) are interpreted as being the result of a strongly reducing condition causing the fixation of uranium from a relatively small volume of surface waters; the volume of water contacted with a given volume of coal was restricted by the relatively rapid accumulation of the low-thorium organic matter. In other words, a centimeter thickness of the Toronto coal represents a much shorter time of contact with sea or fresh water than does a centimeter thickness of the Chattanooga shale. Black shales deposited under continental and high-Eh conditions are believed to reflect uranium leaching, not uranium accumulation, by tending to have uranium contents less than about 2 ppm and high Th/U ratios of 7 or more (Table II); however, the oxidation was only intense enough to facilitate the leaching of the uranium and not intense enough to destroy all of the metastable organic matter.

By contrast with the marine black shales, bauxites and residual clays represent the products of intense oxidation and leaching of uranium resulting in high thorium concentrations and Th/U ratios of more than 20 in some cases. In none of the bauxites or residual clays is the uranium found to be less than 1 or more than 10 ppm. Two explanations are offered for the lack of a more drastic lowering of the uranium concentration. 1. Uranium is known to be co-precipitated with the hydroxides of iron and aluminum; thus, as the concentration of these hydroxides builds up there would be an increasing possibility of retention or even some extraction and fixation of uranium. 2. The resistates such as zircon will persist in the most oxidizing environments, retaining their uranium; thus, in the case of the Surinam bauxite samples, if it is assumed that zircons contained one-third of the uranium in the original granite, and that half of the total weight of zircon was dissolved while five-sixths of the total weight of granite was dissolved, then the uranium concentration of the resultant bauxite would be equal to that of the original granite, whereas the thorium concentration would be six times greater, assuming no loss of thorium.

It is obvious that if a rock had all of its thorium and uranium contained in a resistate such as zircon, the most intense weathering would greatly raise the thorium and uranium concentration without altering the Th/U ratio very much.

Among the bauxites analyzed, the Jamaican and several other samples are noteworthy in regard to low Th/U ratio and high uranium content (Table II). The geologic evidence indicates that the Jamaican bauxite was derived from the White limestone (Hartman, 1955). If this limestone had the mean limestone Th/U ratio of about 1.0 (Fig. 2), then the bauxite derived from it has a Th/U ratio three or four times higher, which is comparable with the shift in Th/U ratio when an igneous rock is converted to a bauxite (3 or 4 to more than 15). In general, the available evidence indicates that most of the other low-ratio

bauxites were derived from carbonate rocks or basic igneous rocks. However, the effects of original rock type, resistates, and provenance on the thorium and uranium content of bauxites need further elucidation.

One of the Venezuelan samples represents residual clay material deposited under marine conditions (Table II). This single sample is noteworthy for its high uranium content (9.5 ppm) and low Th/U ratio (0.95). It is hypothesized that the residual clay material had the opportunity to extract and fix uranium, perhaps by adsorption and co-precipitation on iron and aluminum hydroxides. If this hypothesis is correct, it may be possible to differentiate certain marine

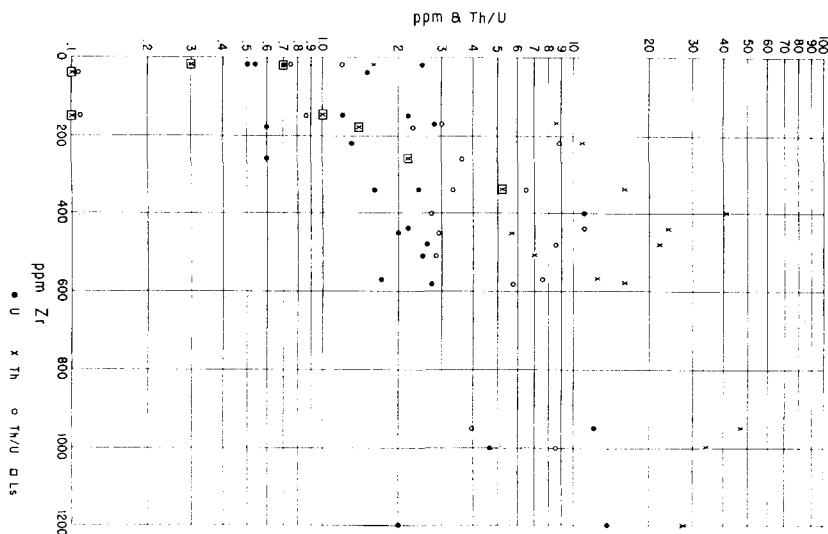


FIG. 11.—Zirconium versus uranium, thorium, Th/U ratio in shales and carbonate rocks.

red and yellow shales by means of their low Th/U ratio; conversely, many continental red and yellow shales would be expected to have much higher ratios of 6.0 or more.

As can be seen in Figure 3, many of the very common gray and green shales have thorium, uranium, and Th/U values but slightly different from those found in primary igneous rocks. In many of these shales rapid erosion and deposition prevented any significant leaching of uranium or fixation of uranium as in the two extreme cases just discussed. However, these shales as a whole constitute a continuum from the Arkansas bauxites to the Chattanooga black shale (Fig. 3), with the great majority of them in an intermediate range.

Despite the wide range of thorium, uranium, and Th/U values in the shales, it is of interest for later geochemical calculations to determine the mean for each of these three values. The data of Baranov, Ronov, and Kunashova provide 15

analyses on aggregates representing 4,795 shales of undesignated type from the Russian Platform. Their data are plotted in Figure 3 where they may be compared with the data on the individual American shales of various types. The Russian Platform aggregates average more uranium, lower thorium, and lower Th/U ratios than do the 52 gray and green American shales (Fig. 3). These differences are interpreted as indications of generally less thorough weathering and slower rates of deposition with fixation of uranium from sea water during the deposition of the Russian Platform shales. Although the Russian shales represent a section from Precambrian to Recent, they are restricted to one general basin and it is difficult to decide whether the Russian shales or the 52 gray and green shales are more representative of all shales. Certainly the data on marine black shales and bauxites need not be given much weight in calculating a mean, because their abundance is not very great and the bauxites and marine black shales would complement and to some extent cancel each other. The following estimates, covering the means of both the Russian samples and the 52 gray and green shales, are given for the average shale: 3.7 ± 0.5 ppm uranium; 12 ± 1 ppm thorium; 3.8 ± 1.1 for the Th/U ratio.

SANDSTONES AND THE ROLE OF RESISTATES

At present there are very few data on the thorium and uranium content of sandstones. Aside from the five analyses in Table II, it is known that high concentrations of thorium are present in placer beach sands and placers (United Nations, 1956). Some of these placers are commercial sources of monazite, which is the main carrier of the thorium; in many, zircon is also recovered commercially. The uranium content of most of these commercial placers is seldom reported. Most monazite specimens have Th/U ratios of 15 or more (Dana, 7th ed.). Despite the lack of direct data, tentative conclusions and calculations can be made concerning the distribution of thorium and uranium in sandstones.

For present purposes, sandstones may be divided into two groups—graywackes and orthoquartzites. The graywackes are mainly composed of material that has been eroded and deposited relatively rapidly. In this respect they are similar to many of the gray and green shales, and it is expected that the thorium and uranium contents and the Th/U ratios of graywackes will be much like those found in primary igneous rocks with ranges in the graywackes similar to those found in gray and green shales (Fig. 3).

In contrast to the graywackes, the purer orthoquartzites are generally the products of complete weathering and thorough sorting. It is expected that their thorium and uranium contents and Th/U ratios will range from those in primary igneous rocks to the very high thorium concentration and high Th/U ratio found in the placer beach sands previously mentioned. An estimate of the mean thorium, uranium, and Th/U values in sandstones can be calculated by the following geochemical material balances.

For Thorium:

$$\begin{array}{lcl} \text{Igneous rock} = \text{shales (46\%)} & (12 \pm 1 \text{ ppm}) & \\ (13.5 \pm 1.5 \text{ ppm}) & + \text{ sandstones (32\%)} & (X \text{ ppm}) \\ & + \text{ limestones (22\%)} & (1.7 \pm 0.7 \text{ ppm}) \end{array} \quad \text{Eq. 1}$$

For Uranium:

$$\begin{array}{lcl} \text{Igneous rock} = \text{shales (46\%)} & (3.7 \pm 0.5 \text{ ppm}) & \\ (3.5 \pm 0.5 \text{ ppm}) & + \text{ sandstones (32\%)} & (X \text{ ppm}) \\ & + \text{ limestones (22\%)} & (2.2 \pm 0.1 \text{ ppm}) \end{array} \quad \text{Eq. 2}$$

In equation 1, the 13.5 ppm thorium in all the igneous rock that has been weathered and eroded is distributed into shale, sandstone, and limestone. The relative proportions of these three sediments are difficult to assess (Pettijohn, 1949) and relative proportions as measured are used. Taking the average thorium content of shales and limestones from Table III, it is possible to calculate the mean thorium content of sandstones as being 24 ± 7 ppm (for maximum deviations). A similar calculation in equation 2 gives the uranium content of average sandstone as 4.1 ± 1.5 ppm; it follows that the Th/U ratio would be about 6 with a minimum limit of 3.0 and a maximum limit of 11.5. The biggest errors in this calculation lie in the relative proportions of the three sediments; there is also some possibility that residual clays and bauxites might be in sufficient quantity to raise the thorium content of the average shale slightly. Only analysis of many more sandstones will determine the validity of the calculation (Murray and Adams, to be published).

There is considerable evidence from leaching studies (Hurley, 1950, and many others) and from autoradiographic studies (Picciotto, 1950, and many others) that the thorium and uranium in many granites occur in the mineral interstices and fractures or in accessory minerals such as zircon, allanite, monazite, xenotime, apatite, and sphene. Therefore, a high Th/U ratio in orthoquartzites may mean that high thorium, high Th/U-ratio resistates such as monazite are relatively more important than low Th/U-ratio resistates such as zircons. This may well be the case because (1) the Th/U ratio in monazite is usually more than 15 and the thorium content several per cent; (2) the thorium and uranium content of zircons is usually only a few hundredths of a per cent; and (3) monazite has been reported in many sandstones examined by Pettijohn (1941).

The zirconium contents of 22 shale and carbonate rock samples were determined to see if there were any relationship between the zircon content and the uranium and the thorium content (Fig. 12). It is believed that most of the zirconium in these samples is present as zircon, ZrSiO_4 . The uranium, thorium, and Th/U ratio all tend to increase as the amount of zirconium increases, but the thorium increases at a much greater rate, indicating that the Th/U ratio of the zircons and associated resistate minerals may be greater than 1. Hurley and Fairbairn (1955) and others (Faul, 1954) report individual zircon samples with Th/U ratios ranging from 0.2 to 5.0 (Table II). Thus, it is possible that zircons from many sources might have Th/U ratios greater than 1 and contain a substantial

portion of the thorium in the rock. It is more likely, however, that an important quantity of thorium is adsorbed on the clays or present in other resistates, particularly monazite and xenotime.

CONCEPT OF GEOCHEMICAL FACIES

On the basis of the foregoing data and interpretations, thorium and uranium may be considered as forming geochemical or elemental facies in sedimentary rocks. These geochemical facies offer some promise as aids in geologic interpretation in favorable cases; however, like paleontological facies, it is not to be expected that helpful and unambiguous geochemical facies will be in evidence in every sedimentary rock. It is hypothesized that the geochemical facies will vary with the tectonic and basin conditions. Three major facies are proposed: (1) the low (below 2) Th/U facies, (2) the high (over 7) Th/U facies, and (3) the intermediate (2 to 7) Th/U facies. Considering analytical errors and the number of data available, the limits proposed for each geochemical facies are only tentative.

The low (below 2) Th/U facies develops in conditions where extraction from sea or fresh water is the major mechanism for the fixation of uranium in the sediment. Many marine black shales and phosphate rocks belong to this facies and their uranium content is commonly more than 10 ppm and may reach 100 ppm. Carbonate rocks with little admixed detrital silicates also belong to this facies; their uranium content seldom exceeds 3 ppm. Many cherts and anhydrites may be members of this facies (Table II and Figs. 2 and 3).

The high (over 7) Th/U facies may develop in at least two ways: (1) the concentration of high-Th/U resistates such as monazites in beach sands and placers, and (2) the removal of uranium by thorough weathering and leaching, leaving the relatively insoluble thorium behind in high concentrations. Many placers and bauxites belong to this facies and their thorium contents may approach or exceed 50 ppm. Residual clays, continental shales, and deeply weathered soils may also belong to this facies; their thorium content may be nominal, 10 ppm or so, but in many cases it exceeds 20 ppm (Table II and Fig. 3).

The intermediate (2 to 7) Th/U-ratio facies is thought to reflect poor weathering and rapid deposition of igneous rock detritus, or it may arise from mixtures of material from both low-ratio and high-ratio situations. Many gray and green shales and graywackes are thought to belong to this intermediate-ratio facies.

Some uses of these facies in geologic interpretation have been discussed. It has been shown how continental red shales could be differentiated from marine red shales in favorable cases. The similar distinction between low-ratio marine black shales and high-ratio continental black shales has also been discussed. It should also be noted that with spectral gamma-ray logs one may add potassium as a third member of these facies. To illustrate further some of the possible uses of these geochemical facies, the following examples are given.

EXAMPLES

EXAMPLE 1. SASKATCHEWAN SECTION

Figure 12 shows the Th/U ratio of a section of Cretaceous continental and marine shales from Saskatchewan. The Th/U ratios of the two continental shales are 6 and 13. The leached goethitic soil zone has a Th/U ratio of 6. The marine shales have Th/U ratios between 2 and 3.5. Some shales reported as marine in this section have ratios as large as 8.5 and they have two to three times as much thorium as the other marine shales. The reasons for this high thorium anomaly are not known. It is likely that a Th/U log of this section should be helpful in delineating the unconformities and differentiating between the continental and marine shales.

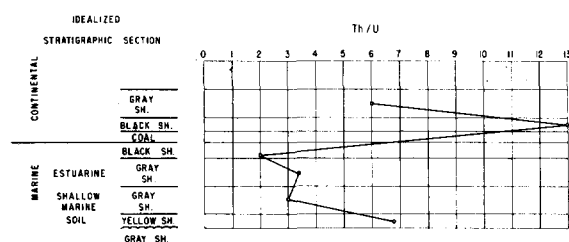


FIG. 12.—Variation of Th/U ratio in Saskatchewan section.

EXAMPLE 2. PERMIAN LIMESTONE, NEW MEXICO

The series of Permian limestone samples from 10,310 to 10,505 feet in the Shell's Townsend ETA well can be divided into three broad lithologic zones. The upper and lower zones, consisting of black, dense, argillaceous and cherty limestone, have insoluble residues ranging from 8 to 42 per cent. The middle zone contains tan, porous limestone with insoluble residues of less than 1 per cent (R. J. Dunham,⁴ personal communication, 1956). The thorium and uranium data for six samples from this section are given in Table V. On the basis of the ura-

TABLE V. TABULATION OF DATA ON THREE ZONES IN PERMIAN LIMESTONE, NEW MEXICO

Sample	% Residue	ppm U	ppm Th	Th/U	% K
10,314.6	42	2.4	3.3	1.4	0.6
10,332.0	8	3.4	1.9	0.6	0.3
10,378.5	0.1	6.6	0.9	0.14	0.12
10,412.4	0.05	6.0	0.3	0.05	0.00
10,438.3	0.2	4.8	0.3	0.06	0.005
10,482.0	39	1.8	1.1	0.6	0.1
10,493.0	10	1.2	0.7	0.6	0.04

⁴ Shell Development Company.

ratio of 3.8. A Th/U ratio of 3.8 is unusually high for a limestone (Fig. 2) and indicates rapid near-shore or fresh-water deposition with additions of well oxidized, low-uranium material from the land surfaces. No dolomite was detected by X-ray diffraction and the insoluble residue amounted to 10 per cent of the sample.

Gray shale.—This shale has thorium (13 ppm) and uranium (4.0 ppm) concentrations and a Th/U ratio (3.3) typical of marine shales, or a shale composed of slightly weathered material.

Underclay.—The underclay was probably much like the underlying gray shale until it was modified by the plants that formed the overlying coal. Its color is lighter than the gray shale, but it has essentially the same concentrations of thorium (13 ppm) and uranium (4.2 ppm). The reducing conditions that favored the accumulation of organic matter to form the overlying coal probably prevented any oxidation and leaching of the uranium from the underclay. Weathering on the outcrop has apparently caused some leaching of uranium and this sample is far out of secular radioactive equilibrium (fluorometric uranium less than that determined by the gamma-ray method).

Coal.—The coal is markedly different from the underlying formations, having a Th/U ratio of 0.66. It is believed that all of the thorium was brought in with the clastic material. On the other hand the bulk of the uranium was extracted from surface water, which has a very low Th/U ratio. The mechanism of extraction may have been reduction followed by adsorption.

Sandy shale.—This outcrop sample is one of the nine samples in this entire study that was found to be far out of secular radioactive equilibrium (fluorometric uranium less than that determined by the gamma-ray method). According to spectral gamma-ray analysis, the Th/U ratio is 3.8, slightly higher than the underlying shales. The higher Th/U may be due to more oxidizing conditions or to a higher concentration of radioactive heavy minerals such as zircon in the sand-size fraction.

Limestones 7 and 3.—These two subdivisions of the Toronto limestone have typical concentrations of thorium and uranium and a typical Th/U ratio for limestones (Fig. 2). The low Th/U ratio is due to the fact that much of the uranium was extracted from sea water. Practically all of the uranium in the Bed 7 sample can be brought into solution by treatment with nitric acid, indicating that very little of the total uranium is bound up in the quartz, feldspar, and kaolinite that form the 10 per cent insoluble residue. Bed 7 is about 15 per cent dolomite.

Limestone 1.—This bed is unusual for a limestone in that it has an abnormally high Th/U ratio of 2.3 and that the 10 per cent insoluble residue contains kaolinite and mixed-layer illite-montmorillonite. The presence of this mixed-layer clay suggests that altered volcanic material may be present. Thus, thorium may have been introduced into this limestone during a volcanic ash fall. Another explanation is suggested by the high kaolinite content and the oölitic-like texture which

suggest that this may be a very shallow-water limestone which was deposited rapidly and adsorbed a relatively small amount of uranium.

Limestone.—The Leavenworth limestone beneath the Heebner shale has a normal Th/U ratio (0.85) for limestones (Fig. 2). Nearly all the uranium can be brought into solution with nitric acid. The 5-per cent insoluble residue contains the usual quartz, feldspar, illite, and kaolinite. No dolomite was detected with X-ray diffraction. This thin bed may have been deposited closer to the shore than were beds 7 and 3.

Black shale.—The Heebner black shale at the top of the section is unique in several respects. The thorium content of 9.8 ppm is in the general range of

esized that this shale has more uranium than the coal in this section because the shale was deposited more slowly and thus came into contact with a larger volume of water from which it could extract uranium. (Sea water and fresh waters have essentially the same uranium concentration; Koczy, 1954.) According to this hypothesis, the Chattanooga shale with 80 ppm uranium may well represent still slower rates of deposition. The Heebner shale is very similar lithologically, environmentally, and in uranium content and geologic age to a black shale recently studied by Krumbein and Slack (1956). They found that the total alpha activity in this shale varied very little over distances of hundreds of miles. Their data indicate that the Th/U ratio in such a formation might be uniform for long distances.

In summary, this cyclothem illustrates most of the basic conclusions of this work regarding the distribution of thorium and uranium in sedimentary rocks. The red shale is typical of the high-ratio environment, which results from thorough oxidation and leaching of uranium. The four shales with Th/U ratios of 3 to 4 are typical of many marine shales, or shales composed of slightly weathered

however, the range of ratios is narrow and there appears to be no systematic relation between the Th/U ratios and environments in this suite of samples. The results suggest that where the source material remains relatively constant and sedimentation is rather rapid, there is little variation in Th/U ratios in the products of marine shale environments. It must also be borne in mind that these wet, unconsolidated Miocene shales may not be in secular radioactive equilibrium. Results from several other scattered Miocene shale samples were not included in the results (Table II), because alpha-activity measurements on these samples showed the very poorest reproducibility encountered in this study. It is hypothesized that in these fine-grained, unconsolidated sediments emanation (radon) can migrate at least short distances, giving rise to a lack of secular radioactive equilibrium, because the distribution of emanation (radon) and its daughters will tend to be uniform, whereas the distribution of the parent thorium and uranium may not be uniform. It is quite possible that the spectral gamma-ray logging tool will overcome this difficulty because of the considerably larger volume of rock being measured.

EXAMPLE 5. BENTONITES

The suite of bentonites listed in Table II was drawn largely from a collection made by Gilmor Hamill of The Rice Institute. The 69 samples have Th/U ratios from 0.94 to 20.8 with an average of 5.8 (Fig. 4). The thorium content averages 24 ppm and the uranium content 5.0 ppm. Thus, the bentonites exhibit almost the full range of Th/U ratios found in sedimentary rocks, but only a few are lower than the intermediate range. Their thorium content averages about twice that of normal marine shales or igneous rocks, with some samples having several times the concentration of common shales. Their average uranium content is also nearly twice that of normal marine shales. It is the high concentration of thorium and uranium combined with a high concentration of potassium that causes the high gamma-ray activity that bentonites have long been known to exhibit. Mineralogically, 59 of the 69 bentonites⁵ are largely mixed-layer clays with only 10 dominantly montmorillonite and kaolinite samples. The two samples with lowest ratios (0.94 and 1.8) are largely kaolinitic as regards clay minerals as are those listed in Table VII. These data on bentonites are interpreted in the following ways.

The following interpretations are a partial revision and substantial extension of Osmond's (1954) pioneer study on the thorium and uranium contents of bentonites. All of the bentonites studied are believed to have been formed from volcanic ash deposits. The original composition of these ashes was probably that of late, silicic magmatic differentiates. Their composition might have approached that of the 30 obsidians studied by Adams (1954). These obsidians, like most acid igneous rocks, have a Th/U ratio of between 3 and 4 and a thorium

⁵ Bentonite, as used here, is any clay material formed by alteration of volcanic ash.

content of about 12 to 24 ppm in most cases. The Th/U ratio found in the bentonite formed by alteration of these ash falls depended on the environment into which the ash fell. If the ash fell into a non-oxidizing environment, such as water of some hundreds of feet depth, little uranium would be oxidized and leached. Thus, the Th/U ratio would remain close to 3 or 4. In a non-oxidizing environment, however, the concentration of both the thorium and uranium would increase as the volcanic glass devitrified and sodium, the alkaline earths, and other soluble materials were dissolved. If the ash fell into an oxidizing environment, either shallow-water or continental, the uranium would be oxidized and leached, giving rise to higher and higher Th/U ratios as the process went to completion. If the ash fell into a strongly reducing, marine black-shale environment, with very slow deposition of detrital material, uranium may have been extracted from sea water by reduction, followed by adsorption on clay minerals. Two samples from the Chattanooga shale are believed to represent examples of this type. Their low Th/U ratios result from the addition of uranium. The presence of organic acids may account for the formation of kaolinite, which is found in these two bentonite samples. In each of the three cases just discussed, the concentration of the immobile thorium was raised by the removal of sodium, the alkaline earths, and other soluble material as the ash devitrified and was altered to bentonite.

Two additional factors, aside from the environment into which the ash fell, may affect the Th/U ratio found in bentonites. In a few obsidians Th/U ratios as high as 5.6 have been reported (Evans and Goodman, 1941; and Adams, 1954). These rare, higher ratios may result from the presence of some remelted, high-ratio sedimentary material in the obsidian or it may result from plutonic processes (Adams, 1954).

Another factor may be the mineralogic location of the uranium. In cases where most of the uranium is dissolved in the volcanic glass it will be very susceptible to leaching if the ash falls into an oxidizing environment. If, on the other hand, much of the uranium is carried in zircons and other resistates, it will be oxidized and leached very slowly, particularly where the resistates tend to coarser grain sizes and thus have minimal surface areas per unit weight. It is believed that much of the uranium in the high Th/U-ratio bentonites may be contained in resistate minerals. This last conclusion is based largely on the data in Table VI wherein are listed thorium, uranium, and zirconium determinations together with Th/U and Zr/U ratios of various fractions of a commercial Wyoming bentonite. The samples were obtained from a production plant of the Baroid Division of the National Lead Company. The bentonites had been processed through three successive continuous centrifuges in order to remove as much grit as possible. The zirconium determinations were made by an X-ray fluorescence technique that is believed to be accurate to the first significant figure. If the analytical errors are disregarded, there is little significant difference between any

of the various fractions, with the exception of the first underflow. The first underflow consists of the coarser grains of zircon, feldspar, and quartz with some clay aggregates. The fact that this underflow has considerably more uranium, more zirconium, a lower Th/U ratio, and a Zr/U ratio equal to the other fractions suggests that much of the uranium may be in the zircons. The Th/U ratio in the zircons would have to be less than 1.5, which agrees closely with the values that Hurley and Fairbairn (1955) report for the Th/U ratios in zircons.

TABLE VI. DETERMINATIONS ON COMMERCIAL WYOMING BENTONITE FRACTIONS

	<i>Thorium in ppm</i>	<i>Uranium in ppm</i>	<i>Zirconium in ppm</i>	<i>Th/U</i>	<i>Zr/U</i>
Feed material	29	10	250	2.9	25
First overflow	— ^a	9	290	— ^a	32
First underflow	55 ^b	36 ^b	810	1.5 ^b	22
Second overflow	31	9	230	3.4	26
Second underflow	44	13	330	3.4	25
Third overflow	— ^a	9	180	— ^a	20
Third underflow	45	15	320	2.8	21

^a No alpha-activity measurement made.

^b Determined by gamma-ray spectral analysis. Other thorium and uranium determinations made by alpha activity-fluorometric uranium method.

Determinations were also made of four highly kaolinitic bentonites that are approximate stratigraphic equivalents of the montmorillonitic Wyoming bentonite just discussed. The data are listed in Table VII. With one exception, sample 4-7, the Th/U ratio is markedly higher in these kaolinitic portions of the Wyoming bentonite. The thorium content is essentially the same in both the

TABLE VII. DETERMINATIONS ON KAOLINITIC WYOMING BENTONITES

<i>Sample Number</i>	<i>Mineralogy</i>	<i>Uranium in ppm</i>	<i>Thorium in ppm</i>	<i>Th/U</i>
1-17	Kaolinite (Diffuse X-ray lines)	4.5	25.5	5.9
1-22	Kaolinite	3.9	21	5.3
4-7	Kaolinite	7.1	22	3.1
4-11	Kaolinite (Sharp X-ray lines)	8.2	42	5.1

montmorillonitic and kaolinitic types, except for one kaolinitic sample, 4-11, where the thorium content is much higher. These four samples are believed to represent places where the original volcanic ash fell into shallower-water or continental environments, providing conditions where uranium was oxidized and leached and where kaolinite formed. Apparently the range in Th/U ratios is due to different rates in the leaching of uranium.

APPLICATIONS

GAMMA-RAY SPECTRAL LOG

The study of the distribution of thorium and uranium reported in the previous section grew in part out of an earlier interest in spectral gamma-ray well logging. It is of interest to note that with a 3-inch scintillation counter an equal weight of thorium in radioactive equilibrium produces approximately 1,300 times as many gamma rays as potassium-40. Under the same conditions uranium produces approximately 3,600 times as many gamma rays as potassium-40. These three elements are present in shales in amounts roughly inversely proportional to their gamma-ray activity. Thus, in the average shale, potassium-40 produces nearly half of the detected gamma activity, the thorium series produces a little less than one-third, and the uranium series produces a little less than one-fourth (Table VIII).

TABLE VIII. RELATIVE CONTRIBUTIONS TO GAMMA-RAY FLUX AS MEASURED WITH THREE-INCH SCINTILLATION COUNTER

	<i>K</i>	<i>Th</i>	<i>U</i>
Relative gamma-ray activity per unit weight of element	1	1,300	3,600
Relative abundance in average shale	7,300	3.8	1
Relative contribution to measured gamma-ray flux of average shale	2.0	1.2	1

Orr and Templeton (private communication) reported:

Scintillation spectroscopy depends on the ability of the scintillation counter and associated electronic equipment to discriminate between gamma rays on the basis of their energies. This method raised the possibility of a gamma-ray log corresponding to a single energy band, or a log with several traces, each corresponding with a separate energy band. In natural rocks the gamma-ray activities are low, and for rocks at least one million years old only three classes of radioactivity appear to be distinguishable: potassium-40; the uranium series in secular equilibrium; and the thorium series in secular equilibrium. Three peaks appear to be suitable for spectral purposes: 1.76 Mev from the uranium series; 1.47 Mev from potassium-40; and 2.62 Mev from the thorium series.

On the basis of successful laboratory results, a field test was conducted during the summer of 1955 (W. R. Orr, R. G. Stevenson, C. C. Templeton, and C. E. Weaver). Five shallow holes (24 to 90 feet) were drilled in Cretaceous and Paleozoic rocks of central Texas. Figure 14 illustrates some of the types of gamma-ray spectra which were obtained during the logging of these holes. It can be seen from these spectra that it is possible to resolve the potassium, uranium, and thorium gamma rays in the subsurface. This field of investigation showed that semiquantitative analyses of potassium, uranium, and thorium could be obtained and that there was considerable variation in the relative abundance of these three elements in sediments; however, the voltage regulation, the film method of recording, and the calibration were not sufficiently constant to allow good comparison of data over any large interval of depth. These faults have

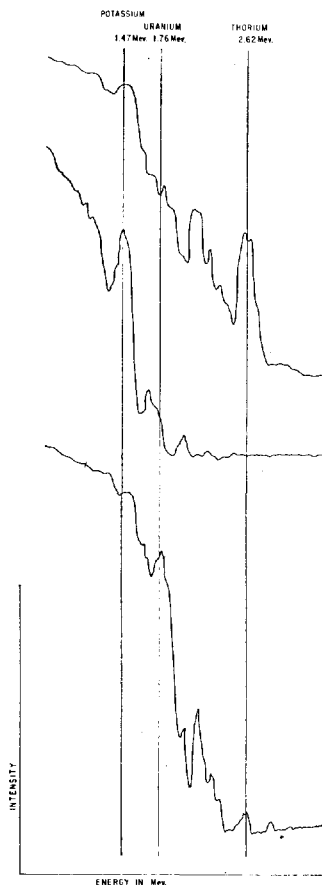


FIG. 14.—Gamma-ray spectra obtained in well logging.

since been corrected and with the present equipment it should be possible to obtain comparable quantitative potassium, uranium, and thorium analyses throughout a thick section and from well to well. It should be noted that with this equipment the Th/U ratio determined would be more accurate than any of the single-element determinations.

Figure 15 contains a plot of the relative gamma-ray activity of $K_{1.47}$, $U_{1.76}$, and $Th_{2.62}$ through a 61-foot section of Pennsylvanian shales and limestones. This is probably the best set of data obtained during the field investigations and it is likely that the data within this interval are comparable. The thorium and uranium data are based on the relative gamma activity of the 1.76-Mev line of the uranium spectrum ($U_{1.76}$) and the 2.62-Mev line of the thorium spectrum ($Th_{2.62}$). As the specific gamma-ray activity of the uranium daughter being measured is several times greater than that of the thorium daughter, it is neces-

sary to divide the uranium gamma count by a factor so that the gamma ray-determined $\text{Th}_{2.62}/\text{U}_{1.76}$ ratios are comparable with those obtained from chemical data. Figure 15 contains several Th/U ratios based on the absolute amounts of thorium and uranium as determined in the laboratory. In order to get comparable ratios from the gamma-ray data it is necessary to divide the relative uranium gamma-ray count by a factor of five.

The three limestone beds (Fig. 15) are readily identified by their relatively

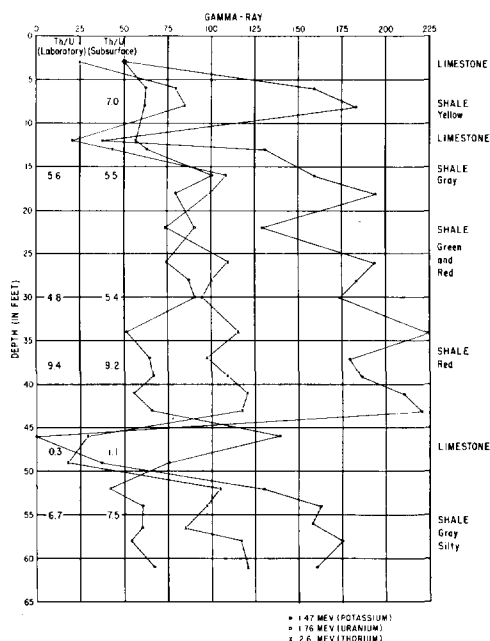


FIG. 15.—Potassium, uranium, and thorium logs through 61-foot Pennsylvanian section.

low thorium, potassium, and Th/U values and by their relatively high uranium values. The limestone bed in the 45–50-foot interval has the highest uranium value encountered in this section. As this is a fragmental, relatively porous limestone, it tends to corroborate the suggestion made previously that porous limestones might characteristically have a relatively higher uranium content. The shales in this section are colored yellow, red, green, and gray. The Th/U ratios of these shales, as determined from the gamma-ray log and by laboratory measurements, are similar to those reported in the previous section: for gray and green shales, relatively intermediate ratios ranging between 5.4 and 5.5, and for red and yellow shales, ratios ranging between 7.0 and 9.2.

Figure 16 is a plot of the $\text{Th}_{2.62}/\text{U}_{1.76}$ ratio based on the relative gamma-ray activity obtained by spectral logging through a Cretaceous limestone, shale,

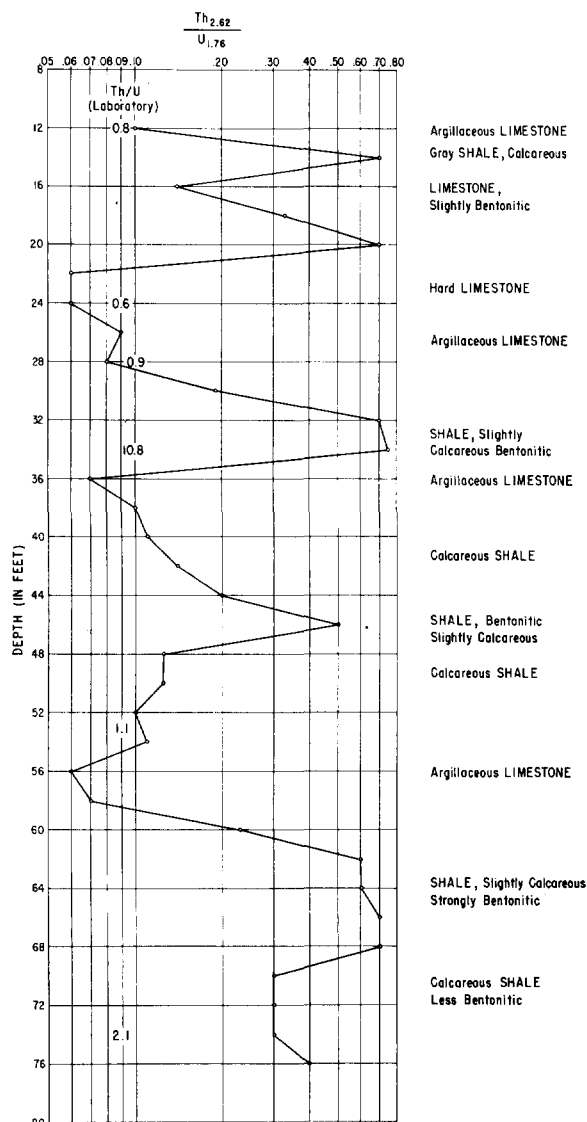


FIG. 16.—Spectral gamma-ray Th/U-ratio log of Cretaceous section.

shaly limestone, and calcareous shale section (near Austin, Texas). As can be seen from the lithologic description, the $\text{Th}_{2.62}/\text{U}_{1.76}$ ratio closely reflects the lithology. It should also be noted that there is a fairly linear relation between the absolute Th/U ratios determined in the laboratory and the relative ratios determined directly from the spectral gamma-ray log. Scattered insoluble-residue determinations indicate a fairly good relation between the per cent residue

and the Th/U ratio. Fairly accurate data of this type can probably be expected through intervals where the composition of the residue remains relatively constant as it does in this case. The $U_{1.76}/K_{1.47}$ and $K_{1.47}/U_{1.76}$ graph plotted in Figure 17 reflects to some extent the variations in clay mineralogy of the more argillaceous intervals. X-ray analyses indicate the intervals with the higher $K_{1.47}/U_{1.76}$ ratios tend to have more illitic clay than the intervals with higher $U_{1.76}/K_{1.47}$ ratios (these have relatively high montmorillonite content).

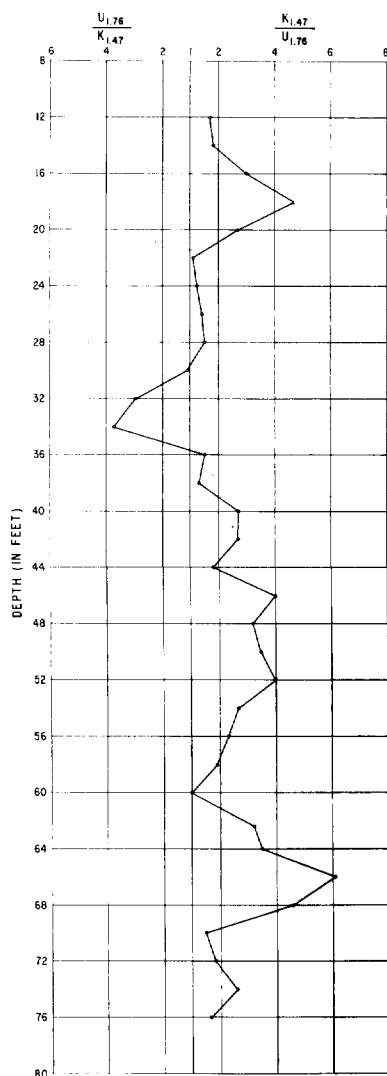


FIG. 17.—Spectral gamma-ray uranium and potassium log of Cretaceous section.

INTERPRETATION OF TOTAL GAMMA-RAY LOGS

Some preliminary tests were conducted to determine if a knowledge of the distribution of potassium, uranium, and thorium in a producing limestone-dolomite section could be of use in interpreting gamma-ray logs and electric logs or if they could provide more useful information than could be obtained by conventional logging instruments.

Eighteen limestone and dolomite samples from the Midale field in Saskatchewan (Table II) were examined to determine the origin of their radioactivity. All residues are similar in composition, containing approximately 85 per cent quartz, 10 per cent feldspar, and 5 per cent illite. Alpha counts, uranium, thorium, and the Th/U ratio were determined on 13 samples. The uranium content varies from 0.1 to 2.3 ppm, the thorium content from 0.01 to 2.5 ppm, and the Th/U ratio from 0.1 to 2.2. Studies of the radioactivity of limestones indicate that the uranium is obtained from solution and most of it is probably bound up in the calcite lattice. The great bulk of thorium is usually contained in the insoluble detrital fraction. In the Midale samples the rocks which show high gamma-ray activity and low self-potential generally have the highest thorium content; those with high gamma-ray activity and high self-potential have only about half as much thorium; those with both low gamma-ray activity and low self-potential have on an average about $\frac{1}{15}$ as much thorium. Also the samples with the highest thorium content are dolomites and contain the largest percentage of detrital-insoluble residue (excludes gypsum and anhydrite); those with intermediate thorium values are calcareous dolomites and have intermediate amounts of residue; those with the lowest thorium content are calcite limestones and contain the smallest amount of detrital residue. Much of this high thorium gamma activity could be associated with the zircons, monazite, and other resistates rather than clay minerals, and there need be no relation between high gamma activity and high self-potential. More detailed studies of this type should provide information on the methods of dolomitization and afford more accurate interpretation of gamma-ray and electric-log data.

The information obtained from this study and the study of the Permian limestone section from New Mexico suggest the spectral gamma-ray logging might be extremely useful for detailed petrophysical analyses of limestones as well as for general geologic interpretation.

CONCLUSIONS

1. The distribution of thorium and uranium in sedimentary rocks is largely determined by (a) the oxidation and leaching of uranium during weathering, with the immobile thorium left behind in resistates or adsorbed on clays and hydrolyzates, and (b) the distribution of resistate minerals containing a high concentration of thorium and uranium.

2. Products of the high Th/U-ratio (more than about 7) environment are

materials that are thoroughly weathered, oxidized, and leached, e.g., certain continental shales and bauxites.

3. Products of the low Th/U-ratio (less than about 2) environment have resulted where uranium was removed from sea or other surface waters and fixed, e.g., marine black shales (Chattanooga shale), limestones, and Florida phosphate rock.

4. Products of the intermediate Th/U-ratio (about 2 to about 7) are incompletely weathered and leached of uranium or are mixtures of materials from low- and high-ratio environments.

5. The general distribution of thorium and uranium in sedimentary rocks is summarized in Figure 18, where primary igneous rocks with a Th/U ratio of 3 to 4 and thorium contents of 10 to 15 ppm are fractionated upon complete

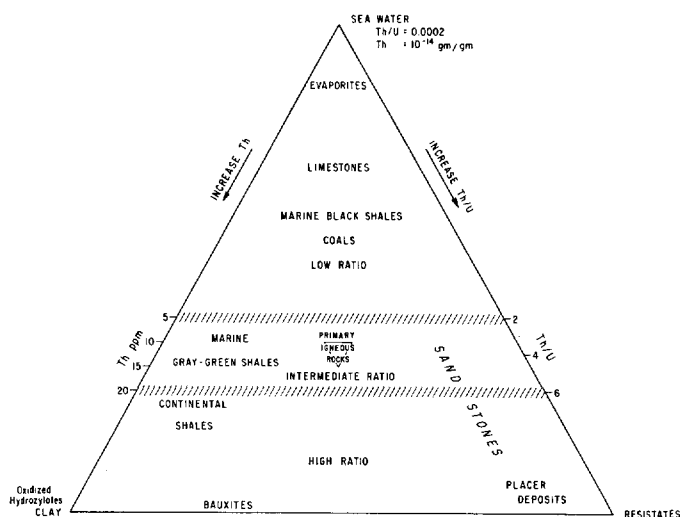


FIG. 18.—Distribution of thorium and uranium in sediments.

weathering in three directions: (a) to sea water with a very low Th/U ratio (0.0002), (b) to hydrolyzates and oxidized clays with high Th/U ratios and high thorium contents, and (c) to resistate minerals with high Th/U ratios and high thorium contents.

6. Th/U-ratio logs offer numerous possibilities as aids to subsurface interpretations, particularly in regard to the location of unconformities under which there are well weathered fossil soils, in distinguishing between marine and continental shales, possibly in recognizing porous zones, dolomitized zones, and high-residue zones in limestones, and in characterizing sedimentary sections for correlation.

7. The data and conclusions presented have been and should continue to be of great assistance in interpreting total gamma-ray logs and in interpreting gamma-

ray logs that separate the thorium, uranium, and potassium contributions to the gamma-ray flux.

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