Further Studies of the Distribution of Uranium in Rich Phosphate Beds of the Phosphoria Formation

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A CONTRIBUTION TO THE GEOLOGY OF URANIUM

FURTHER STUDIES OF THE DISTRIBUTION OF URANIUM IN RICH PHOSPHATE BEDS OF THE PHOSPHORIA FORMATION

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ABSTRACT

Five sets of "close" samples (narrow and contiguous samples across a lithologic unit) from beds of high phosphate content of the Phosphoria formation in Idaho, Utah, and Wyoming were analyzed chemically for F and CO_2. Very good correlations between F, CO_2, and P_2O_5 were found in several of the samples.

The size of phosphate pellets was measured in thin sections of two sets of close samples. Frequency histograms and cumulative curves were plotted from these size measurements, but when compared with uranium concentration for each sample, no significant correlation between size and uranium concentration was discovered.

Analyses of these samples for P_2O_5, CaO, organic matter, and equivalent uranium are presented in a previous report by this writer (U. S. Geol. Survey Bull. 988–D). In two sets of samples a good correlation was found between equivalent uranium and each of the other components. The samples in these two sets have a uranium content that is relatively high for the Phosphoria formation, and they show considerable range in P_2O_5 content.

INTRODUCTION

In connection with the Geological Survey's work on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission, a study was made of the distribution of uranium in rich phosphate beds of the Phosphoria formation of Permian age in the Northwestern United States. This study is described in a previous report.[1] The present report concerns a further investigation of the problem.

In the previous investigation, a study was made of special "close" samples from the rich phosphate beds. A "close" sample is defined as one of a set of small, contiguous samples taken across a stratigraphic unit, the set being representative of the entire unit. Sets of close samples, with from 12 to 31 samples to a set, were taken across a layer of the phosphate-rich rock. The thickness of the layers that were sampled ranged from 0.5 foot to 1.2 feet, and the thickness of the individual samples was on the order of half an inch. Chemical analyses of the groups of close samples for U, CaO, P_2O_5, organic matter, and loss on ignition, radiometric analyses for equivalent uranium, and Rosiwal

[1] Thompson, M. E., 1953, Distribution of uranium in rich phosphate beds of the Phosphoria formation: U. S. Geol. Survey Bull. 988-D.

analyses of some of the samples for mineral content are given in the previous report. Comparisons were made between the proportions of the various components, and positive correlations were found between P_2O_5 and uranium content in the groups of close samples whose uranium content was higher than average. A positive correlation between uranium and organic matter was obtained in the group of close samples with the lowest average uranium content. Negative correlations were found between uranium and organic matter in three groups of close samples whose uranium content was higher than average.

In the present report, the problem has been pursued along two lines, as follows:

1. Analyses of F and CO_2 (table 1) were made in order to determine if the concentration of uranium is related to the nature of the apatite in the phosphate rock.

TABLE 1.—*Chemical and radiometric analyses, in percent, of close samples from phosphate rock of the Phosphoria formation in Idaho, Utah, and Wyoming*

[Analyses of F and CO_2 by Harry Levine, David Deibler, and Henry Mela, Jr.]

Sample no.		F	CO_2	eU	P_2O_5
Brazer Canyon, Utah					
WT-604	30	1.38	1.44	0.014	10.85
	29	3.10	1.92	.014	23.36
	28	1.56	1.60	.011	12.30
	27	1.74	1.20	.011	14.00
	26	3.38	2.04	.010	29.51
	25	3.62	1.78	.010	32.77
	24	3.66	1.62	.014	33.58
	23	3.58	1.62	.015	32.09
	22	3.64	1.48	.017	32.76
	21	3.77	1.74	.029	33.70
	20	3.48	1.62	.014	31.21
	19	3.22	1.60	.015	30.78
	18	3.55	2.08	.013	31.31
	17	3.57	1.40	.011	32.91
	16	1.88	1.40	.012	15.59
	15	1.84	1.12	.010	14.96
	14	3.14	1.84	.023	26.73
	13	2.88	1.84	.015	24.37
	12	2.58	1.58	.011	21.89
	11	2.68	1.42	.012	23.86
	10	2.66	1.60	.010	23.05
	9	2.90	1.56	.010	23.37
	8	3.28	1.67	.008	29.04
	7	3.22	1.72	.010	28.50
	6	3.24	1.78	.010	29.50
	5	3.36	2.12	.009	29.91
	4	3.30	2.10	.010	28.88
WT-605	3	3.36	2.04	.009	28.47
	2	3.14	2.04	.010	27.57
	1	3.55	2.04	.014	32.15
WT-603	24	3.95	2.30	------	------
	23	3.77	2.34	------	------
	22	3.69	2.74	------	------
	21	3.73	2.42	------	------
	20	3.42	2.08	------	------
	19	3.71	2.48	------	------
	18	3.39	2.70	------	------
	17	3.95	2.32	------	------
	16	3.93	2.58	------	------

TABLE 1.—*Chemical and radiometric analyses, in percent, of close samples from phosphate rock of the Phosphoria formation in Idaho, Utah, and Wyoming*—Con.

Sample no.	F	CO_2	eU	P_2O_5
Brazer Canyon, Utah—Continued				
WT-603 15	3.73	2.32		
14	3.81	2.26		
13	3.81	2.24		
12	3.77	2.42		
11	3.81	2.18		
10	3.65	2.54		
9	2.02	1.56		
8	1.98	.98		
7	1.16	.36		
6	1.34	.42		
5	1.46	.70		
4	2.78	1.20		
3	3.14	1.68		
2	1.64	1.12		
1	.72	.50		
Trail Canyon, Utah				
[Entries marked with asterisks are determinations of U, not eU]				
WT-365 26	3.43	1.66	.018	33.9
25	3.24	1.83	.017	29.8
24	3.42	1.66	.014	32.6
23	3.34	1.50	.017	32.4
22	3.35	1.76	.009	32.9
21	3.35	2.94	.011	32.8
20	3.35	2.12	.006	32.2
19	3.14	1.56	.005	33.5
18	2.98	2.08	.004	31.1
17	2.80	4.32	.006	27.5
16	2.94	2.74	.005	29.1
15	2.76	1.63	.005	27.3
14	2.96	1.74	.005	28.8
13	2.76	1.78	.005	27.2
12	2.82	2.10	.005	29.3
11	2.84	1.76	.007	27.0
10	2.60		.007	24.1
9	2.76	2.02	.009	27.7
8	2.98	1.90	*.007	29.3
7	2.56	1.66	*.012	26.2
6	2.16	1.42	*.009	20.8
5	2.06	1.00	*.010	19.9
4	3.42	2.66	*.006	33.0
3	3.58	2.16	*.008	35.1
2	3.36	2.86	*.006	32.9
1	3.30	2.14	*.006	30.7
Coal Canyon, Wyoming				
WT-700 12	3.34	1.70	0.039	31.45
11	3.79	1.60	.044	32.71
10	3.85	1.58	.045	34.35
9	3.73	1.58	.040	33.55
8	3.59	1.58	.048	33.15
7	3.58	1.46	.065	31.37
6	1.24	.42	.021	7.64
5	1.52	.70	.022	9.50
4	1.92	1.06	.025	16.21
3	.50	.20	.006	.83
2	.56	.08	.006	.73
1	.88	.42	.011	3.71

TABLE 1.—*Chemical and radiometric analyses, in percent, of close samples from phosphate rock of the Phosphoria formation in Idaho, Utah, and Wyoming*—Con.

Sample no.	F	CO_2	eU	P_2O_5
Reservoir Mountain, Idaho				
WT-910 31	3.61	2.76	0.007	33.60
30	3.81	2.62	.008	35.48
29	3.65	2.52	.008	34.32
28	3.79	2.58	.007	35.46
27	3.63	2.50	.008	34.62
26	3.75	2.56	.011	34.79
25	3.73	2.72	.011	34.32
24	3.71	2.32	.008	35.61
23	3.71	2.44	.009	35.49
22	3.65	2.38	.010	32.81
21	3.63	2.72	.022	33.38
20	3.63	2.34	.019	33.57
19	3.65	2.36	.017	34.09
18	3.63	2.26	.017	35.30
17	3.79	2.44	.015	35.22
16	3.63	2.36	.012	34.42
15	3.67	2.38	.016	33.32
14	3.85	2.44	.021	34.41
13	3.67	2.74	.023	32.81
12	3.73	2.34	.025	33.29
11	3.81	2.18	.030	35.80
10	3.73	2.00	.030	34.72
9	3.75	2.28	.026	34.47
8	3.85	1.96	.023	34.71
7	3.59	2.56	.022	32.58
6	3.69	2.26	.018	33.78
5	3.67	2.10	.013	33.23
4	3.77	2.26	.013	33.06
3	3.73	2.30	.013	31.14
2	3.85	2.32	.019	31.89
1	3.77	2.22	.022	32.05
Laketown Canyon, Utah				
WT-509 25			0.012	36.20
24			.012	34.80
23			.009	34.40
22			.008	33.80
21			.009	32.10
20			.008	33.80
19			.012	35.20
18			.017	33.80
17			.014	34.60
16			.011	34.80
15			.003	10.6
14			.006	24.00
13			.010	35.20
12			.013	35.20
11			.017	34.80
10			.013	35.20
9			.009	35.00
8			.009	35.00
7			.009	35.40
6			.008	36.20
5			.007	33.80
4			.010	34.80
3			.009	34.60
2			.010	35.20
1			.005	29.50

2. Because the rich phosphate beds of the Phosphoria formation have a typically oolitic or pelletal texture, the size of the pellets in thin sections of two sets of close samples was measured for comparison with uranium content. It was hoped that the significance of variations of pellet size might be more easily discovered in these samples, because a number of chemical analyses had already been obtained on these or similar samples with the intention of making comparisons of uranium content with other components.

As in the earlier report, the order of correlation of the various components was expressed numerically by means of the correlation coefficient. The formula used is that given by Snedecor,[2]

$$r=\frac{\Sigma x_1 x_2}{\sqrt{(\Sigma x_1^2)\,(\Sigma x_2^2)}},$$

where x_1 and x_2 are individual values of the two components being compared. The following is summarized from Snedecor: The expression

$$\frac{\Sigma x_1 x_2}{\sqrt{(\Sigma x_1^2)\,(\Sigma x_2^2)}}$$

is designed to vary between minus 1 and plus 1, according to the closeness of the relationship of the two components. Where there is a direct correlation between two sets of values, the points plotted on a scatter diagram tend to lie in a band extending from lower left to upper right and are not scattered randomly over the whole field. These points are confined to an elliptical area with the major axis inclined toward the right. Negative values of r indicate an inclination of the ellipse of points downward toward the right, large values of one variate being associated with small values of the other. The thinness of the ellipse of points exhibits the magnitude of r, and the inclination of the axis to the right or left shows its sign. A good correlation, either positive or negative, is fairly obvious from a graph. If the number of samples is small, a single point can make a great difference. Judgment about the degree of correlation should be made in the light of other correlations in the same field.

From the point of view of a statistician, the number of samples used in this investigation was probably too small to give dependable results. Therefore, only the strongest correlations should be regarded as significant: those where r is well over 0.5 or well under -0.5.

[2] Snedecor, G. W., 1946, Statistical methods applied to experiments in agriculture and biology, p. 138. Ames, Iowa State College Press.

THE PHOSPHATE MINERAL AND RELATION OF F AND CO_2 TO URANIUM CONTENT

The localities from which sets of close samples were collected are fully described in the earlier report. They are listed in table 2.

TABLE 2.—*Location of analyzed samples of phosphate rock of the Phosphoria formation*

Name of section	County and State	Field unit no.	Laboratory nos.	Thickness (feet)
Trail Canyon	Caribou County, Idaho.	RAH-183-47 [1]	WT-365-1—WT-365-26	0.8
		RAH-184-47 [1]		
Reservoir Mountain.	Caribou County, Idaho.	4769-DFD [2]	WT-910-1—WT-910-31	1.0
Coal Canyon	Lincoln County, Wyo.	2061 [3]	WT-700-1—WT-700-12	.5
Brazer Canyon	Rich County, Utah	RAH-105-47 [4]	WT-605-1—WT-605-3	.1
		RAH-106-47 [4]	WT-604-3—WT-604-30	1.0
		RAH-107-47 [4]	WT-603-1—WT-603-24	1.2
Laketown Canyon	Rich County, Utah	Equivalent to RWG-3827. [5]	WT-509-1—WT-509-25	1.0

[1] McKelvey, V. E., Armstrong, F. C., Gulbrandsen, R. A., and Campbell, R. M., 1953, Stratigraphic sections of the Phosphoria formation in Idaho, 1947-48, part 2: U. S. Geol. Survey Circ. 301.
[2] Davidson, D. F., Smart, R. A., Peirce, H. W., and Weiser, J. D., 1953, Stratigraphic sections of the Phosphoria formation in Idaho, 1949, part 2: U. S. Geol. Survey Circ. 305.
[3] McKelvey, V. E., Smith, L. E., Hoppin, R. A., and Armstrong, F. C., 1953, Stratigraphic sections of the Phosphoria formation in Wyoming, 1947-48: U. S. Geol. Survey Circ. 210.
[4] Smith, L. E., Hosford, G. F., Sears, R. S., Sprouse, D. P., and Stewart, M. D., 1952, Stratigraphic sections of the Phosphoria formation in Utah, 1947-48: U. S. Geol. Survey Circ. 211.
[5] Cheney, T. M., Smart, R. A., Waring, R. G., and Warner, M. A., 1953, Stratigraphic sections of the Phosphoria formation in Utah, 1949-51: U. S. Geol. Survey Circ. 306.

Figures 9 through 13 are scatter diagrams in which F and CO_2 are plotted against P_2O_5 for each set of close samples. The correlation coefficients relating equivalent uranium and P_2O_5 that were given in the earlier report are repeated in table 3 together with correlation coefficients relating CO_2 and F with P_2O_5 and with equivalent uranium. Correlation coefficients for the set of samples from Reservoir Mountain were not calculated because of the small variation in P_2O_5 content.

TABLE 3.—*Correlation coefficients relating various components and average percent eU in four sets of close samples from phosphate rock of the Phosphoria formation*

Sample No.	Average percent eU	Correlation coefficients		
		U/P_2O_5	CO_2/P_2O_5	F/P_2O_5
WT-700	0.031	+0.9	+0.98	+0.99
WT-603	.020	+.8	+.93	+.99
WT-604, 605	.013	+.2	+.52	+.98
WT-365	.008	+.1	+.29	+.95

Although material from the Phosphoria formation has been described as oolitic, these samples are more properly referred to as pelletal in view of the absence of concentric structures in the pellets. The rocks are dark brown to black, except for the samples from the Reservoir Mountain trench which contain less organic material. The phosphatic material in these samples is chiefly pelletal phosphate

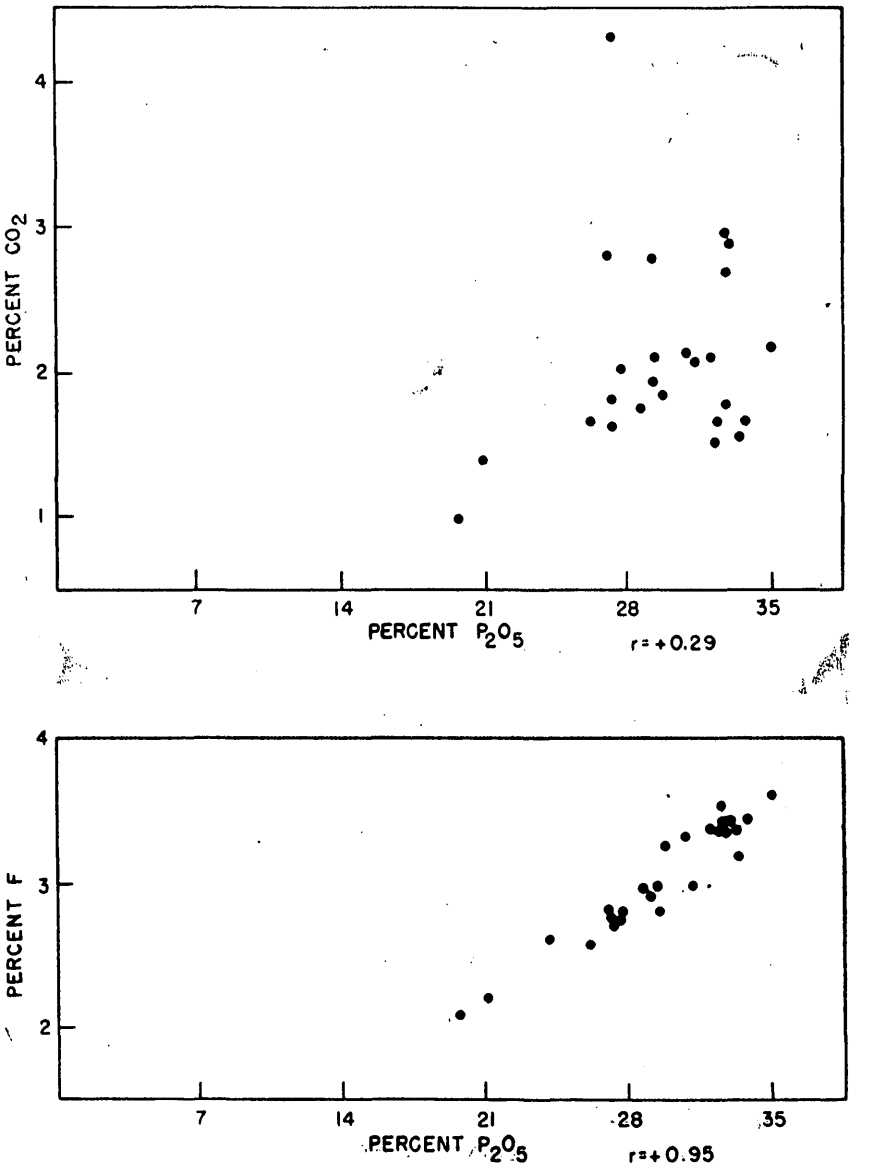

FIGURE 9.—Scatter diagrams of Trail Canyon samples WT-365.

of the type referred to in the older literature as collophane, but more properly designated carbonate-fluorapatite. Where thin sections of the samples were made and examined, most of the pellet material was found to be nearly isotropic, and very little of the secondary or recrystallized variety (francolite) was seen. The accessory minerals in the samples are chiefly quartz and mica, with clays and calcite.

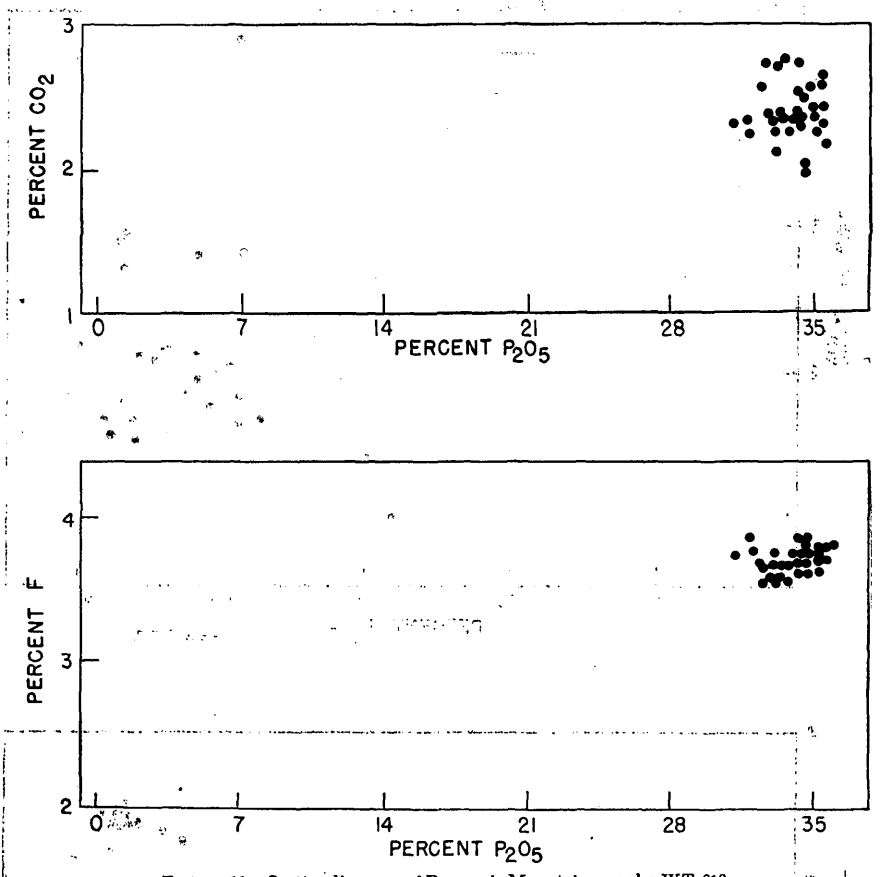

FIGURE 10.—Scatter diagrams of Reservoir Mountain samples WT-910.

The predominant phosphate mineral in the Phosphoria formation is a fluorine-bearing apatite. Therefore, it is not surprising that all of the sets of samples show a strong correlation between F and P_2O_5. The analyses of all the samples show, however, an excess of F over the amount required by the fluorapatite formula $Ca_{10}(PO_4)_6F_2$ computed on the basis of P_2O_5 content.

Fluorite is not an uncommon mineral in the Phosphoria formation, but it was not observed in the rock layers from which these samples were taken, and examination of a number of thin sections made from the samples failed to reveal the presence of any visible fluorite.

There has been much discussion as to the exact nature of the phosphate mineral in the Phosphoria formation. According to K. D. Jacob,[3] it is an apatite with excess fluorine and with a small amount of carbonate.

[3] Jacob, K. D., and others, 1933, The composition and distribution of phosphate rock with special reference to the United States: U. S. Dept. Agriculture Tech. Bull. 364, p. 72-75.

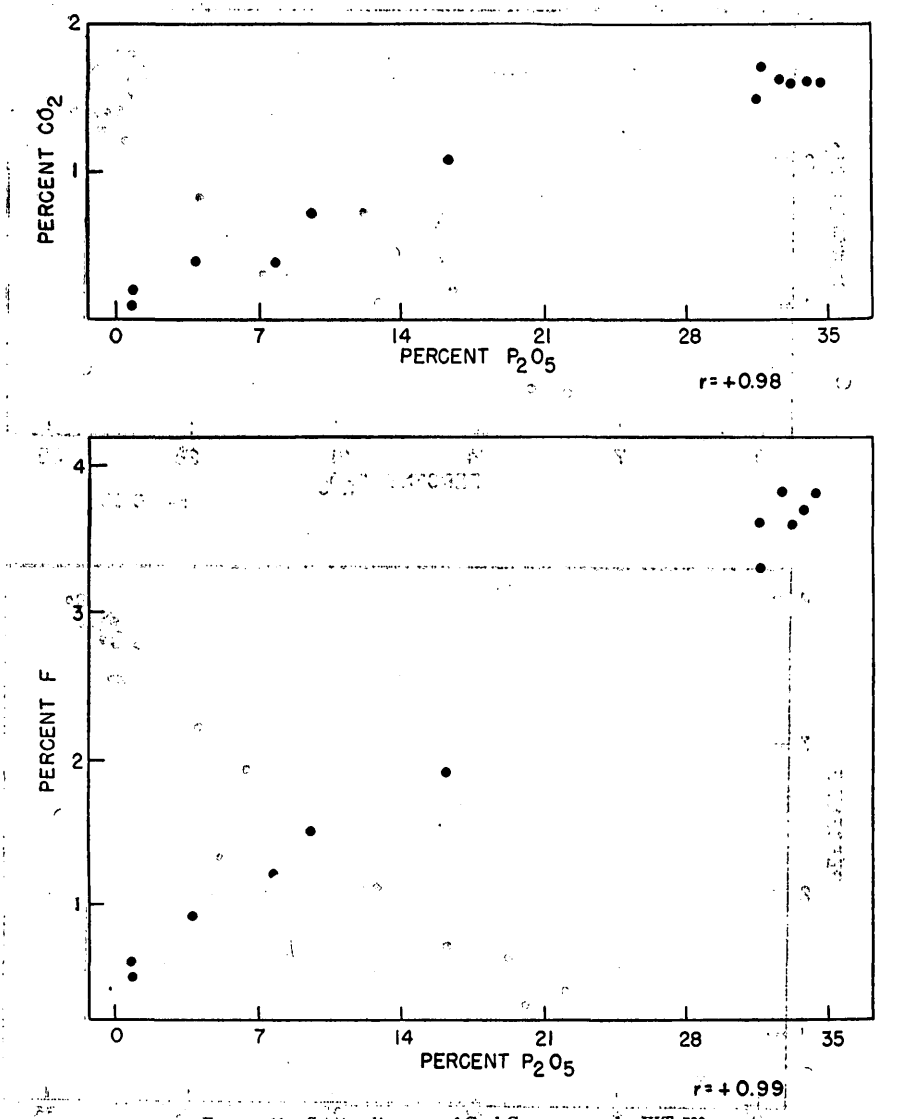

FIGURE 11.—Scatter diagrams of Coal Canyon samples WT-700.

X-ray studies [4] of a number of carbonate-bearing fluorapatites have shown that they are a structurally distinct variety, different from either fluorapatite or hydroxylapatite. X-ray powder patterns of phosphatic material from the Phosphoria formation match the type pattern of the carbonate-bearing fluorapatites; that is, they show the same difference from fluorapatite or hydroxylapatite as do the carbonate-bearing fluorapatites.

[4] Altschuler, Z. S., and Cisney, E. A., 1952, X-ray evidence of the nature of carbonate-apatite (abs.): Geol. Soc. America Bull., v. 63, no. 12, pt. 2,

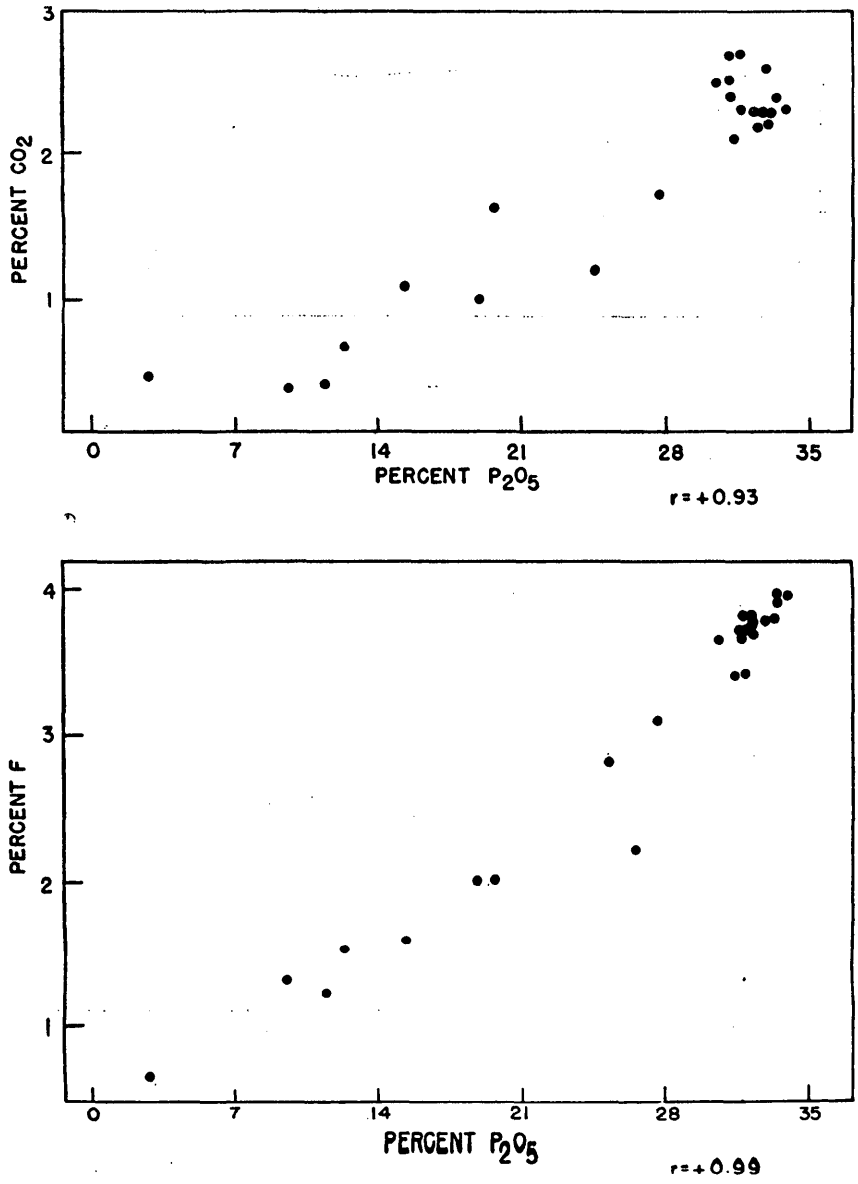

FIGURE 12.—Scatter diagrams of Brazer Canyon samples WT-603.

In two sets of close samples there is a very good correlation between CO_2 and P_2O_5, and it seems probable that the phosphate-bearing mineral in these samples is a carbonate-bearing fluorapatite.

Two general statements may be made concerning the distribution of uranium in these samples:

1. The samples with high percent of equivalent uranium show much

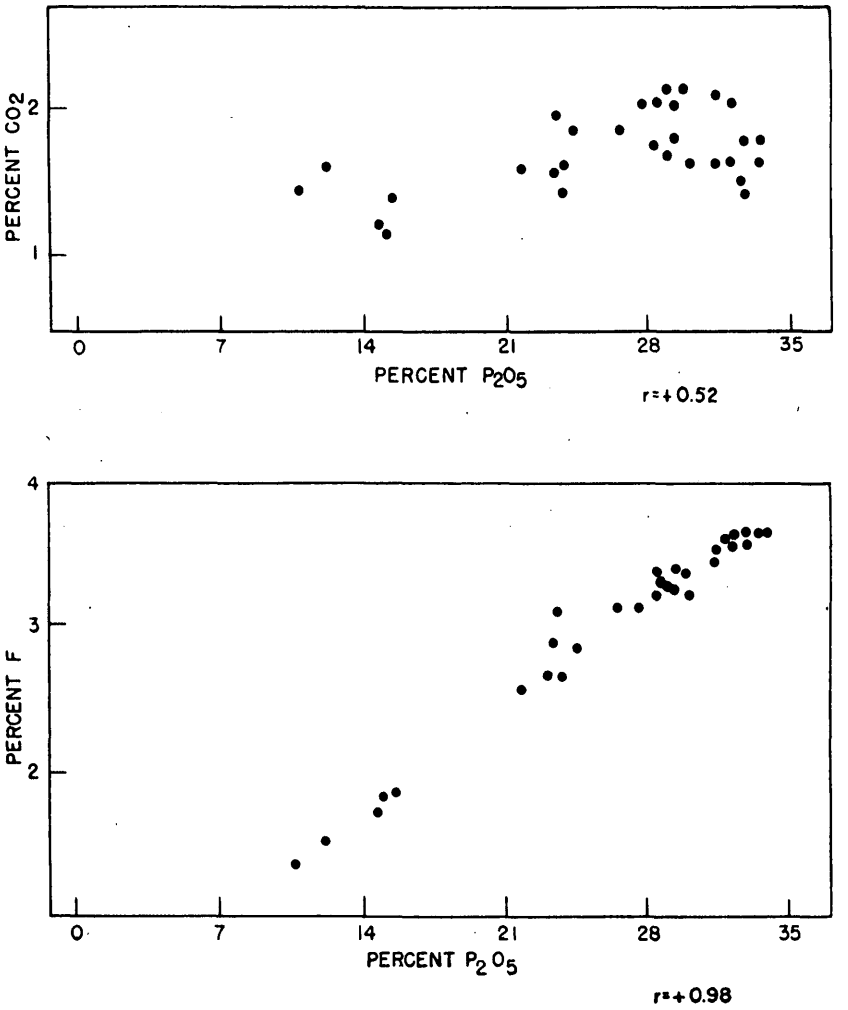

FIGURE 13.—Scatter diagrams of Brazer Canyon samples WT-604 and WT-605.

better correlation of equivalent uranium and P_2O_5 (WT–700, WT–603).

2. The samples that show good correlation of equivalent uranium and P_2O_5 show better correlation of CO_2 with P_2O_5 (WT–700, WT–603).

PELLET SIZE AND URANIUM CONTENT

It has been suggested that the size of the pellets in phosphate rock might have a direct relation to the concentration of uranium in the rock and that the size of a pellet might also reflect either the length of time required for the pellet to form or the conditions under which it formed. As a corollary to the above, it has been suggested that the longer the period required for a pellet to form, or the longer it was

in contact with ocean waters, the more uranium it might have absorbed from the sea water.

To determine if a correlation exists between pellet size and uranium content, the size of pellets was measured in thin sections of two sets of samples. One set was from Laketown Canyon, Utah (WT–509), and the other was from Trail Canyon, Idaho (WT–365). These particular sets were chosen because neither contained enough organic matter to obscure the pellets. Twenty-four thin sections, which were cut normal to the bedding of the rock, were prepared for each set. It was observed that the pellets were distinctly flattened in the bedding plane. By means of a micrometer ocular, the longest and shortest observed dimensions of each pellet were measured. There was little variation of the measurements of the shortest dimension of the pellets.

The 25 samples from Laketown Canyon, Utah, which were not referred to in the previous report, were taken from the phosphatic shale member of the Phosphoria formation. They cover a thickness of 1 foot and are numbered from lowest to highest stratigraphically. The lowest sample, no. 1, was taken 2 feet above the Wells formation. This group of samples was analyzed for P_2O_5 and equivalent uranium. The results of these analyses, together with the results of some of the chemical and radiometric analyses of samples that were taken earlier, are presented in table 1.

Traverses were made across each thin section of the Laketown Canyon and Trail Canyon samples, and all grains passing under one line on the micrometer ocular were measured until 100 grains had been measured in each thin section. A correction was not made for the fact that the grains were measured in thin sections of indurated rock, because only the variation in size of the pellets was needed, not the absolute size. Measurements of the longest dimensions of the pellets were plotted in frequency histograms, and the related cumulative curves were plotted. The arithmetic and geometric quartile deviations of the measurements for each sample were obtained from the graphs of the cumulative curves. Figure 14 shows a typical frequency histogram and the related cumulative curve. The first and third quartiles are indicated on the figure.

No obvious relationship was found between the concentration of uranium and the size measurements. Different properties of the frequency histograms and cumulative curves for each sample were compared with the concentration of uranium without discovering a significant correlation. Figures 15 and 16 are scatter diagrams showing the comparison of various properties of the size measurements with uranium content. The coefficients of correlation that were obtained for the two sets of samples are summarized as follows:

Size measurement properties	Coefficients of correlation WT-365	WT-509
Modes of longest dimensions of pellets	0. 53	0. 22
Means of longest dimensions of pellets	. 45	. 004
Arithmetic quartile deviations of longest dimensions of pellets	. 17	
Geometric quartile deviations of longest dimensions of pellets	. 007	

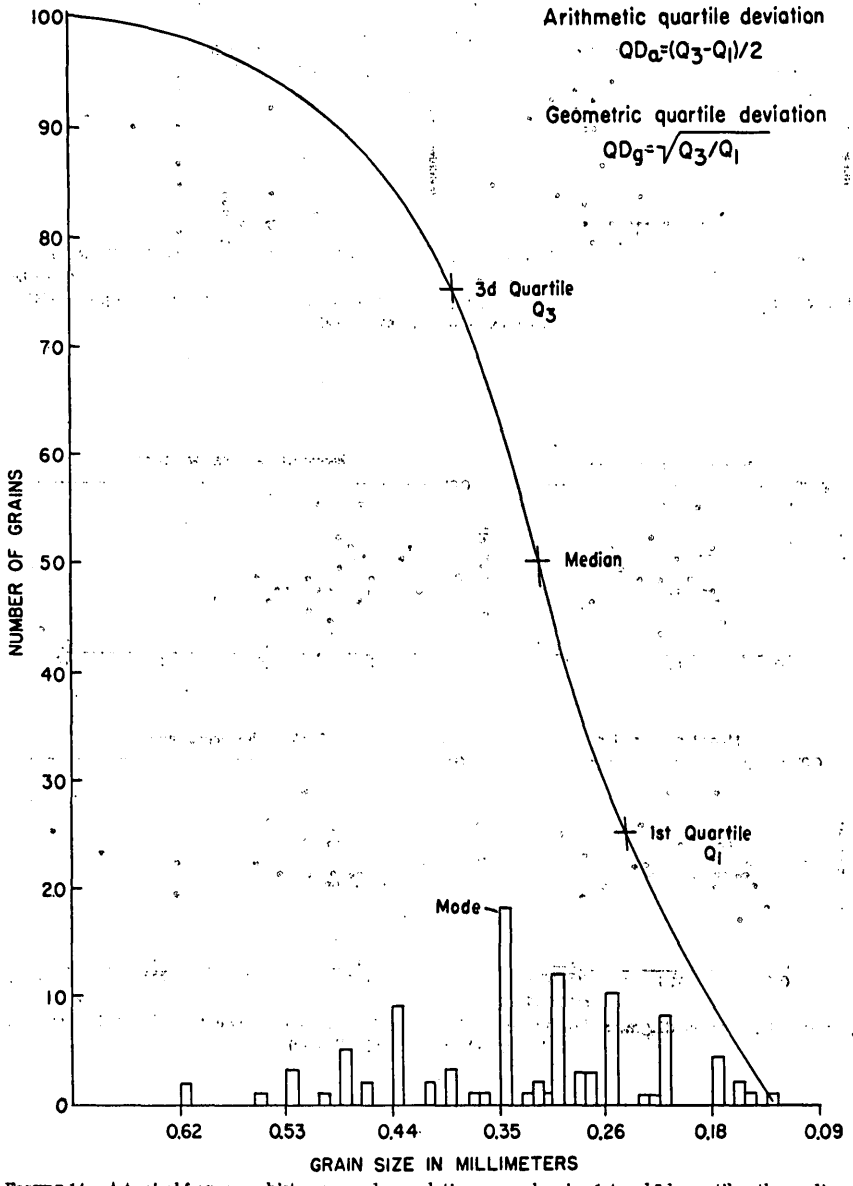

FIGURE 14.—A typical frequency histogram and cumulative curve showing 1st and 3d quartiles, the median and the mode. Sample WT-365-7; 0.012 percent eU.

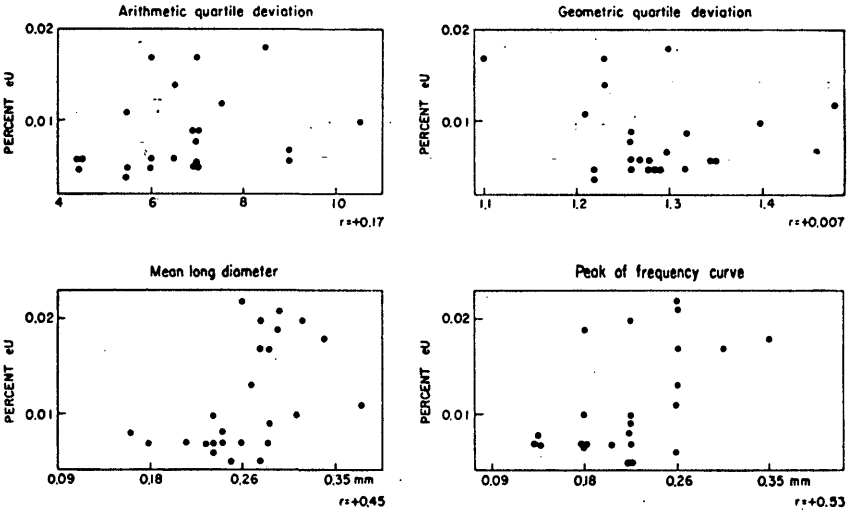

FIGURE 15.—Scatter diagrams showing comparison of various size measurements with uranium content, Trail Canyon samples WT-365.

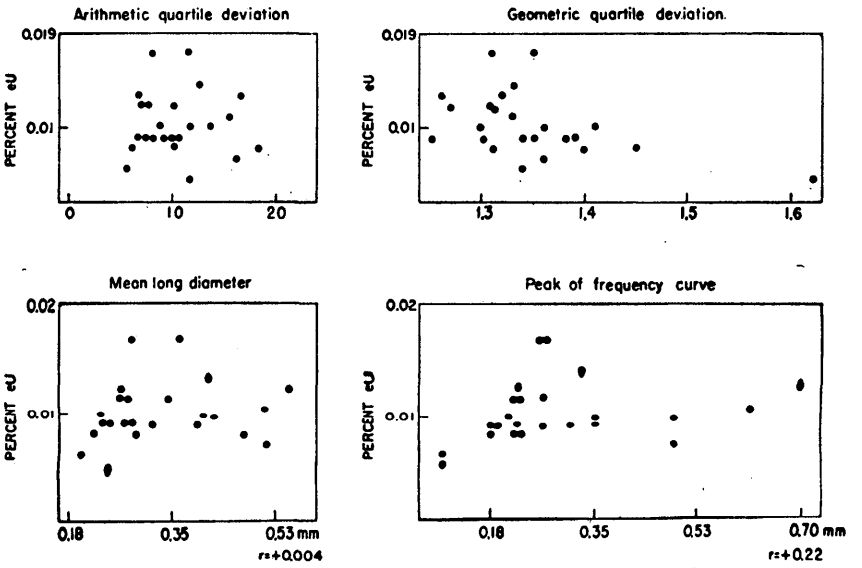

FIGURE 16.—Scatter diagrams showing comparison of various size measurements with uranium content, Laketown Canyon samples WT-509.

The coefficients of correlation of variation in uranium content with variation in the arithmetic and geometric quartile deviations of the longest dimensions of the pellets were not calculated for WT–509 samples, because it was obvious from inspection of scatter diagrams that no marked relationship exists.

Figures 17 and 18 show some of the variously shaped histograms that were obtained from samples with the same percent of equivalent uranium.

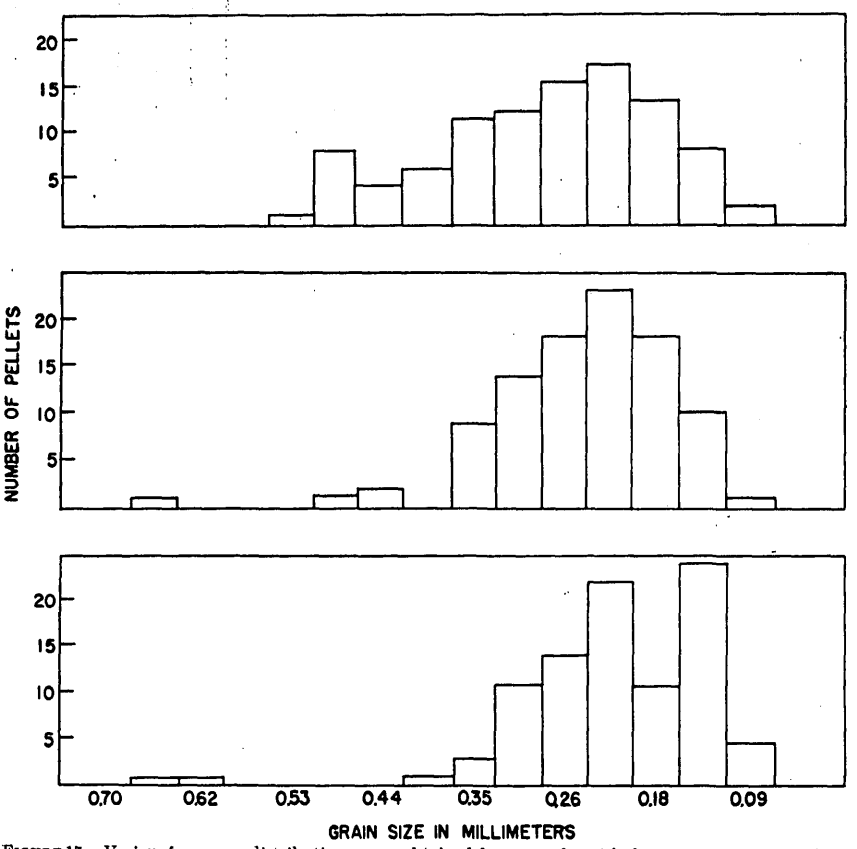

FIGURE 17.—Various frequency distribution curves obtained from samples with the same percent equivalent uranium. From bottom to top, the samples are WT–365–4, –17, –20, Trail Canyon.

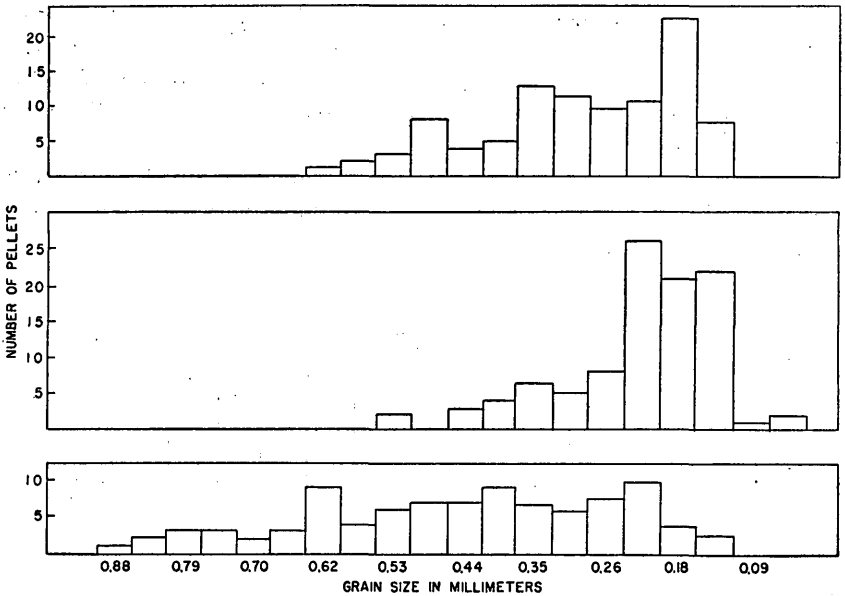

FIGURE 18.—Various frequency distribution curves obtained from samples with the same percent equivalent uranium. From bottom to top, the samples are WT-509-6, -20, -22, Laketown Canyon.

The original size and shape of the phosphate pellets may have been considerably changed since the time of their formation. Perhaps, also, the two sets of samples that were chosen are not typical of the pelletal phosphate of the Phosphoria formation. However, the measurements show little, if any, relation between the concentration of uranium and pellet size, and they give little reason for believing that pellet size has an influence upon, or reflects, the concentration of uranium in phosphate rock.

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