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

By
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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.

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 could be discovered.

Analyses of these samples for P_2O_5, CaO, organic matter, and equivalent uranium were presented in a previous report. 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 variation in P_2O_5 content.

GEOLOGY AND MINERALOGY

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

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INTRODUCTION

In connection with Geological Survey's work on behalf of the U. S. Atomic Energy Commission, a study was mde of special "close" 1/ samples from rich phosphate beds in the Phosphoria formation of the northwestern United States. This earlier work is described in a report entitled, "Distribution of uranium in rich phosphate beds of the Phosphoria formation," (U. S. Geol. Survey Bull. 988-D, in press). This report gave the results of chemical analyses of groups of close samples for U, CaO, P_2O_5, organic matter, and loss on ignition, of radiometric analyses for equivalent uranium, and of Rosiwal analyses of some of the samples for mineral content. 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 with higher-than-average uranium content. 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 with higher-than-average uranium content.

Work on this problem has now been continued along two lines: first, F and CO_2 analyses, by Geological Survey chemists Harry Levine, David Deibler, and Henry Mela, Jr., were made on the close samples to see if the nature of the apatite in the phosphate rock had a relation to the concentration of uranium. These analyses are given in table 1.

1/ A "close" sample is one of a large number of small, contiguous samples taken across a single stratigraphic unit, where all of the samples together represent the entire unit.

* This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

Table 1.--Results of chemical and radiometric analyses of close samples, in percent.

Sample no.		Locality	F	CO_2	eU	P_2O_5
WT-604	30	Brazer Canyon, Utah	1.38	1.44	0.014	10.85
	29		3.10	1.92	0.014	23.36
	28		1.56	1.60	0.011	12.30
	27		1.74	1.20	0.011	14.90
	26		3.38	2.04	0.010	29.51
	25		3.62	1.78	0.010	32.77
	24		3.66	1.62	0.014	33.58
	23		3.58	1.62	0.015	32.09
	22		3.64	1.48	0.017	32.76
	21		3.77	1.74	0.029	33.70
	20		3.48	1.62	0.014	31.21
	19		3.22	1.60	0.015	30.78
	18		3.55	2.08	0.013	31.31
	17		3.57	1.40	0.011	32.91
	16		1.88	1.40	0.012	15.59
	15		1.84	1.12	0.010	14.96
	14		3.14	1.84	0.023	26.73
	13		2.88	1.84	0.015	24.37
	12		2.58	1.58	0.011	21.89
	11		2.68	1.42	0.012	23.86
	10		2.66	1.60	0.010	23.05
	9		2.90	1.56	0.010	23.37
	8		3.28	1.67	0.008	29.04
	7		3.22	1.72	0.010	28.50
	6		3.24	1.78	0.010	29.50
	5		3.36	2.12	0.009	29.91
	4		3.30	2.10	0.010	28.88
WT-605	3	Brazer Canyon, Utah	3.36	2.04	0.009	28.47
	2		3.14	2.04	0.010	27.57
	1		3.55	2.04	0.014	32.15
WT-603	24	Brazer Canyon, Utah	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		

Table 1.--Continued

Sample no.	Locality	F	CO_2	eU	U	P_2O_5
WT-603 16	Brazer Canyon, Utah	3.93	2.58			
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	0.98			
7		1.16	0.36			
6		1.34	0.42			
5		1.46	0.70			
4		2.78	1.20			
3		3.14	1.68			
2		1.64	1.12			
1		0.72	0.50			
WT-365 26	Trail Canyon, Utah	3.43	1.66	0.018		33.9
25		3.24	1.83	0.017		29.8
24		3.42	1.66	0.014		32.6
23		3.34	1.50	0.017		32.4
22		3.35	1.76	0.009		32.9
21		3.35	2.94	0.011		32.8
20		3.35	2.12	0.006		32.2
19		3.14	1.56	0.005		33.5
18		2.98	2.08	0.004		31.1
17		2.80	4.32	0.006		27.5
16		2.94	2.74	0.005		29.1
15		2.76	1.62	0.005		27.3
14		2.96	1.74	0.005		28.8
13		2.76	1.78	0.005		27.2
12		2.82	2.10	0.005		29.3
11		2.84	1.76	0.007		27.0
10		2.60		0.007		24.1
9		2.76	2.02	0.009		27.7
8		2.98	1.90		0.007	29.3
7		2.56	1.66		0.012	26.2
6		2.16	1.42		0.009	20.8
5		2.06	1.00		0.010	19.9
4		3.42	2.66		0.006	33.0
3		3.58	2.16		0.008	35.1
2		3.36	2.86		0.006	32.9
1		3.30	2.14		0.006	30.7

Table 1.--Continued

Sample no.	Locality	F	CO_2	eU	P_2O_5
WT-700 12	Coal Canyon, Wyoming	3.34	1.70	0.039	31.45
11		3.79	1.60	0.044	32.71
10		3.85	1.58	0.045	34.35
9		3.73	1.58	0.040	33.55
8		3.59	1.58	0.048	33.15
7		3.58	1.46	0.065	31.37
6		1.24	0.42	0.021	7.64
5		1.52	0.70	0.022	9.50
4		1.92	1.06	0.025	16.21
3		0.50	0.20	0.006	0.83
2		0.56	0.08	0.006	0.73
1		0.88	0.42	0.011	3.71
WT-910 31	Reservoir Mountain, Idaho	3.61	2.76	0.007	33.60
30		3.81	2.62	0.008	35.48
29		3.65	2.52	0.008	34.32
28		3.79	2.58	0.007	35.46
27		3.63	2.50	0.008	34.62
26		3.75	2.56	0.011	34.79
25		3.73	2.72	0.011	34.32
24		3.71	2.32	0.008	35.61
23		3.71	2.44	0.009	35.49
22		3.65	2.38	0.010	32.81
21		3.63	2.72	0.022	33.38
20		3.63	2.34	0.019	33.57
19		3.65	2.36	0.017	34.09
18		3.63	2.26	0.017	35.30
17		3.79	2.44	0.015	35.22
16		3.63	2.36	0.012	34.42
15		3.67	2.38	0.016	33.32
14		3.85	2.44	0.021	34.41
13		3.67	2.74	0.023	32.81
12		3.73	2.34	0.025	33.29
11		3.81	2.18	0.030	35.80
10		3.73	2.00	0.030	34.72
9		3.75	2.28	0.026	34.47
8		3.85	1.96	0.023	34.71
7		3.59	2.56	0.022	32.58
6		3.69	2.26	0.018	33.78
5		3.67	2.10	0.013	33.23
4		3.77	2.26	0.013	33.06
3		3.73	2.30	0.013	31.14

Table 1.--Continued

Sample no.	Locality	F	CO_2	eU	P_2O_5
WT-910 2	Reservoir Moun-	3.85	2.32	0.019	31.89
1	tain, Idaho	3.77	2.22	0.022	32.05
WT-509 25	Laketown Canyon,			0.012	36.20
24	Utah			0.012	34.80
23				0.009	34.40
22				0.008	33.80
21				0.009	32.10
20				0.008	33.80
19				0.012	35.20
18				0.017	33.80
17				0.014	34.60
16				0.011	34.80
15				0.003	10.6
14				0.006	24.00
13				0.010	35.20
12				0.013	35.20
11				0.017	34.80
10				0.013	35.20
9				0.009	35.00
8				0.009	35.00
7				0.009	35.40
6				0.008	36.20
5				0.007	33.80
4				0.010	34.80
3				0.009	34.60
2				0.010	35.20
1				0.005	29.50

The rich phosphate beds of the Phosphoria formation have a typically "oolitic" or pelletal texture. Secondly, therefore, the size of the pellets was measured in thin sections of two sets of close samples 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

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

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

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

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, 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. In small numbers of samples a single point can make a great deal of difference. Judgment about the size of a correlation should be made in the light of similar correlations in the same field.

From the point of view of a statistician, a very small number of samples was used in this investigation, probably too few to show dependable results. Therefore, attention should be paid only to the strongest correlations, those where r is well over 0.5 or well under -0.5.

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

Figures 1 through 5 (pp. 18-22) 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 2 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.

The localities from which the samples were collected were fully described in the earlier report and will be but briefly indicated here. The 26 samples in WT-365 were taken from field unit no. RAH-184-47 in the Trail Canyon trench in Caribou County, Idaho. The 31 samples in WT-910 were taken from field unit no. DFD-4769 in the trench at Reservoir Mountain, Caribou County, Idaho. The 12 samples in WT-700 were taken from field unit no. 3061 in the Coal Canyon trench in Lincoln County, Wyoming. The 3 samples in WT-605, 27 samples in WT-604, and 24 samples in WT-603 were taken from field unit nos. RAH-105, 106, and 107 in the trench at Brazer Canyon, Rich County, Utah.

Table 2.--Correlation coefficients relating various components, and average percent eU in four sets of close samples

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	0.020	+ 0.8	+ 0.93	+ 0.99
WT-604, 605	0.013	+ 0.2	+ 0.52	+ 0.98
WT-365	0.008	+ 0.1	+ 0.29	+ 0.95

All of these samples were taken from units of phosphate rocks in the Phosphoria formation and are, in general, moderately to finely oolitic. The oolites might be more properly described as pellets, as none of those examined show evidence of concentric structure. 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 the pelletal phosphate or "collophane"; 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 some clays and calcite.

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 no fluorite was 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 present but not as a second mineral phase.

X-ray studies 4/ in this laboratory 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.

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.

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

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

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

1. The samples with higher percentages of equivalent uranium show much 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 some direct relation to the concentration of uranium in the rock. Arguments have been proposed that the size of a pellet might reflect the length of time during which the pellet "grew", or that the size of a pellet might indicate the conditions under which it was formed. As a corollary to the above, it has been suggested that the longer a pellet "grew" or was in contact with ocean waters, the more uranium it might have absorbed from the sea water.

The size of pellets was measured, by means of a micrometer ocular, in two sets of twenty-four thin sections each, in order to compare the pellet size in each sample with the percentage equivalent uranium in that sample, and to determine whether there was any correlation between uranium content and size of the phosphate pellets.

These thin sections were cut normal to the bedding of the rock, and showed a pronounced flattening of the pellets in the plane of the bedding. Both the longest and the shortest dimension of each pellet as seen in thin section was measured. There was little variation in the length of the shortest dimension of the pellets.

These two sets of thin sections were chosen because neither set of samples had a large amount of obscuring organic matter.

One group of thin sections was made from a set of close samples, WT-509 from Laketown Canyon, Utah. These samples have not been referred to in the previous report. The lowest sample was taken from 2 feet above the Wells formation in the phosphatic shale member of the Phosphoria formation at Laketown Canyon. The samples cover a stratigraphic thickness of 1 foot and were numbered 1 to 25, from the lowest to the highest sample stratigraphically.

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 earlier chemical and radiometric analyses of the other samples are presented in table 1.

Traverses were made across each thin section of the Laketown (WT-509) and Trail Canyon (WT-365) samples, and all grains passing under one line on the micrometer ocular were measured until 100 grains had been measured in each thin section.

No correction was 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 wanted and not the absolute size.

The measurements of the long diameters (that is, 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 6 shows a typical frequency histogram and the related cumulative curve. The 1st and 3d 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 any significant correlation being discovered. Figures 7 and 8 are scatter diagrams showing the comparison of various properties of the size measurements with uranium content. The coefficients of correlation that were obtained are summarized below.

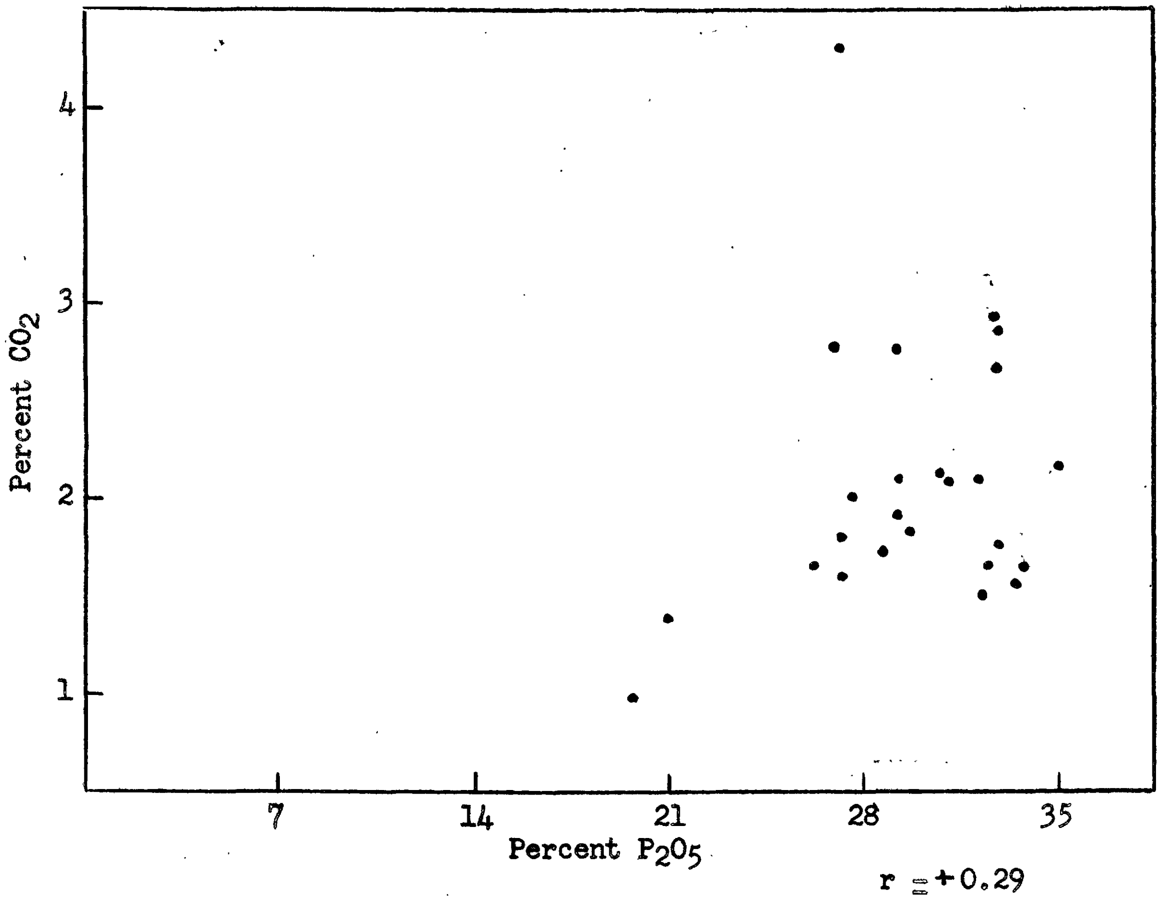
Correlation coefficients of variation in uranium contents with variation of the following size measurement properties

(WT-365)	
modes of longest dimensions of pellets	0.53
means of longest dimensions of pellets	0.45
arithmetic quartile deviations of longest dimensions of pellets	0.17
geometric quartile deviations of longest dimensions of pellets	0.007
(WT-509)	
modes of longest dimensions of pellets	0.22
means of longest dimensions of pellets	0.004

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 there was no relation between uranium concentration and these properties.

Figures 9 and 10 show some of the variously shaped histograms that were obtained from samples with the same percentage equivalent uranium.

The original size and shape of the phosphate pellets may have been considerably changed since the time of their formation, and perhaps these two sets of samples are not typical of the pelletal phosphate of the Phosphoria formation, but the measurements made in this investigation show little if any relation between the concentration of uranium and pellet size, and they present little reason for believing that pellet size has, or reflects, any influence upon the concentration of uranium in phosphate rock.



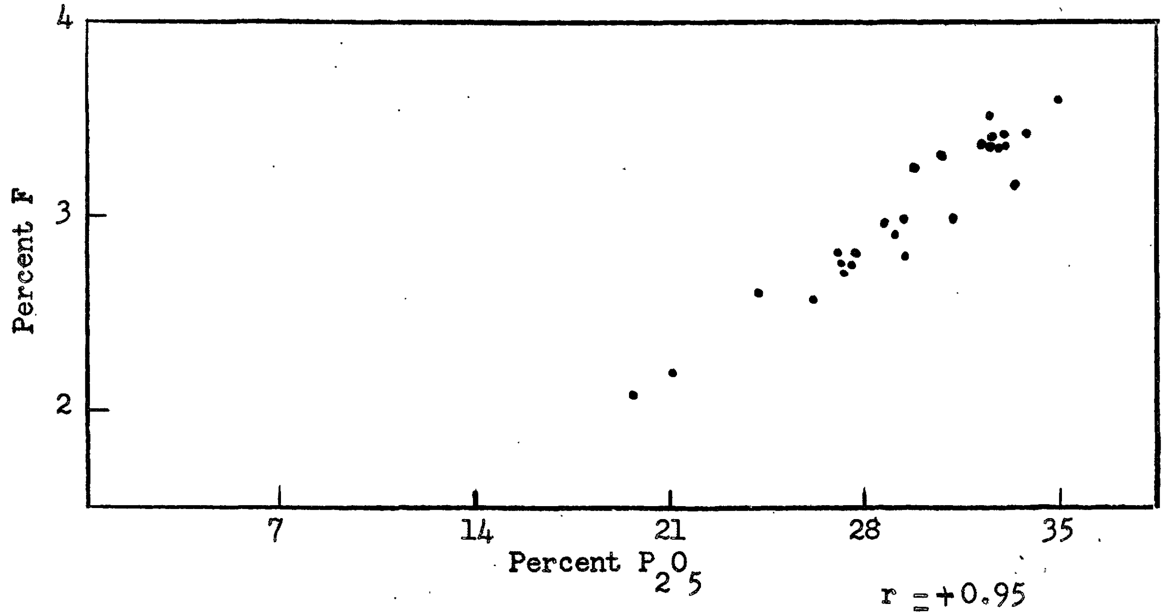
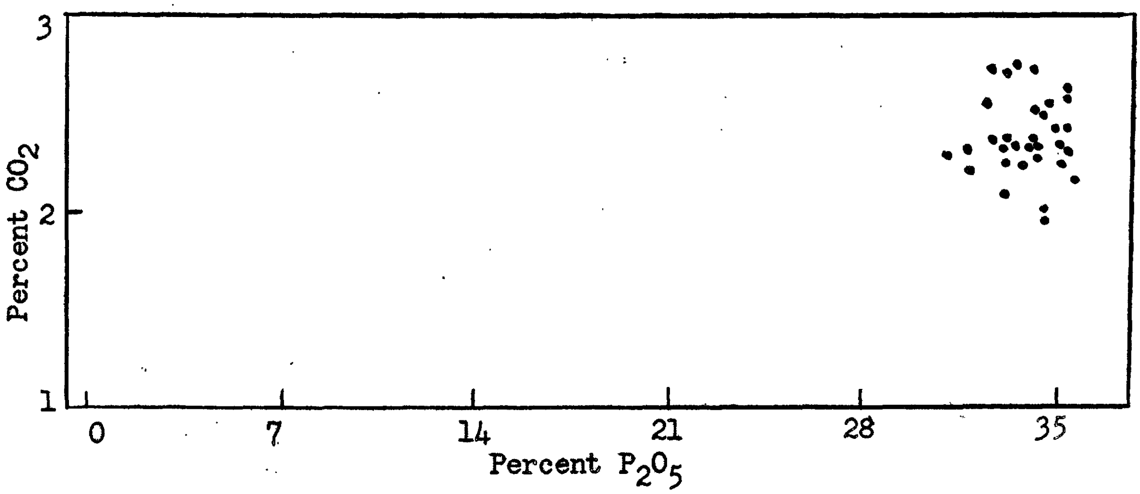


Figure 1.--Scatter diagrams of Trail Canyon samples WT-365



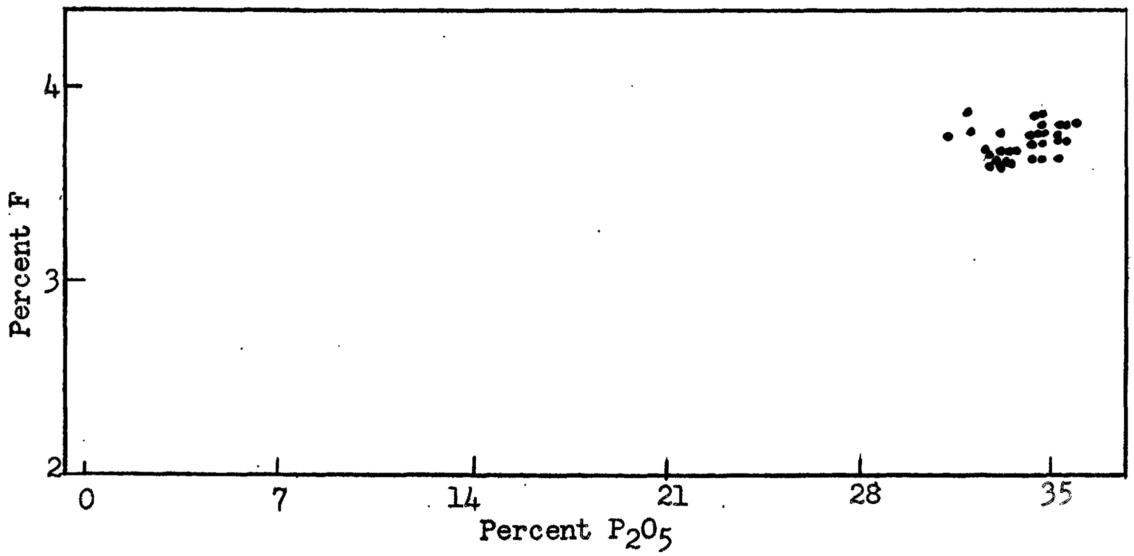


Figure 2.--Scatter diagrams of Reservoir Mountain samples WT-910

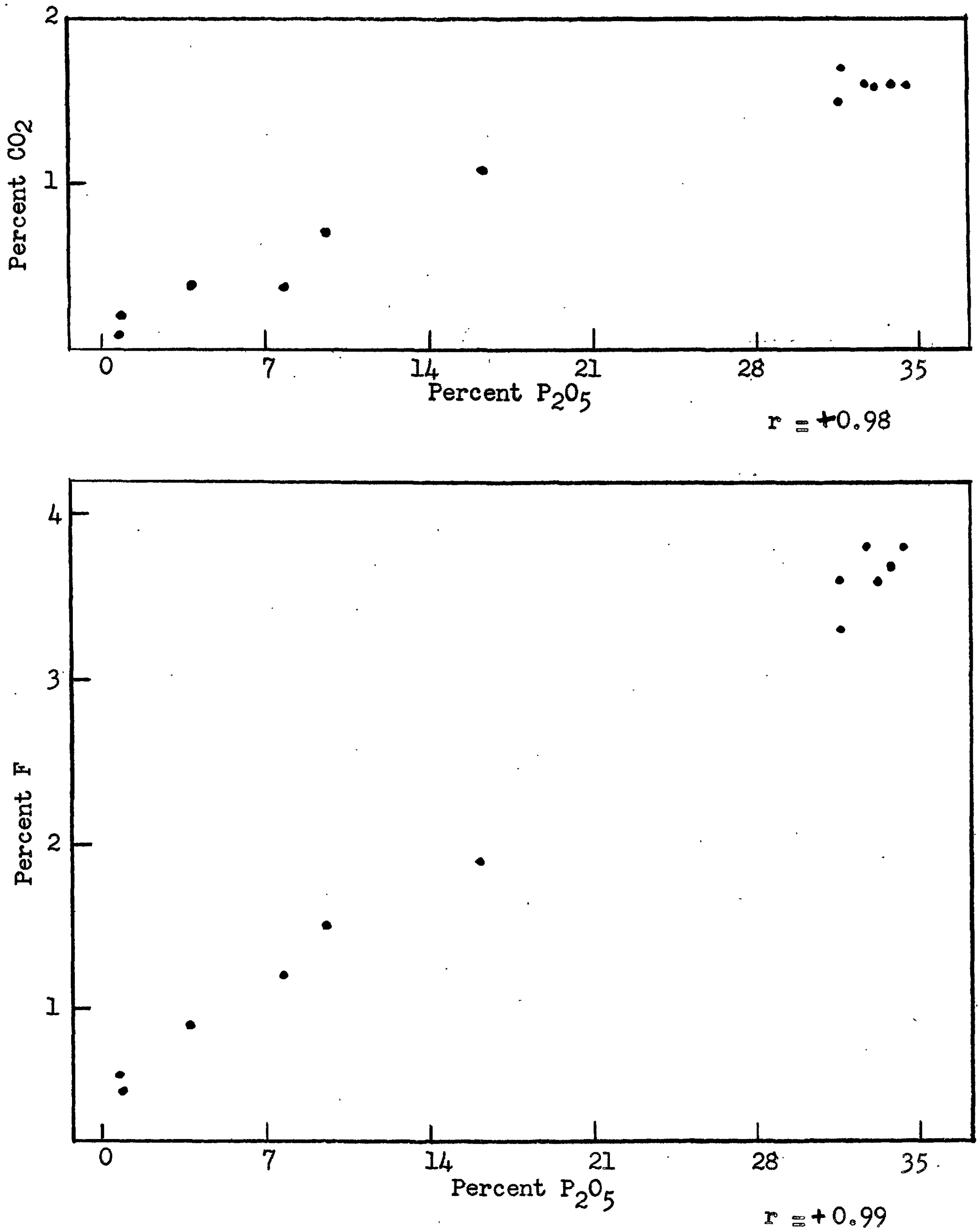
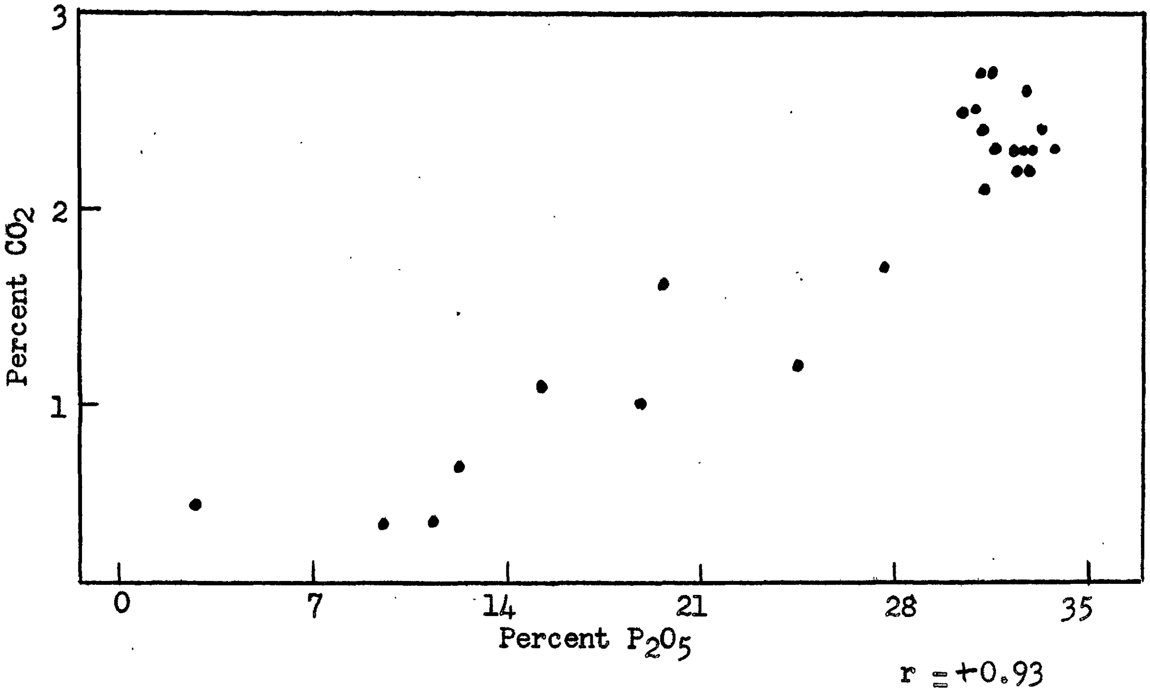


Figure 3.--Scatter diagrams of Coal Canyon samples WT-700



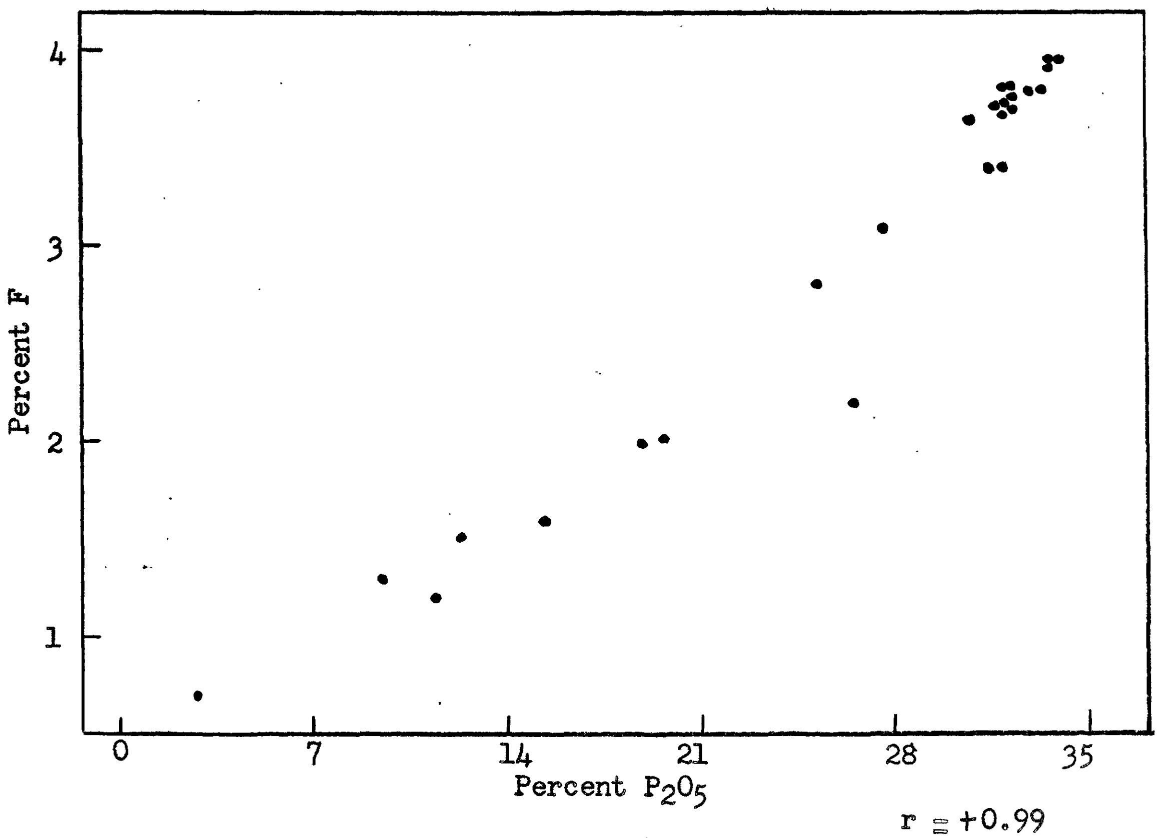


Figure 4.—Scatter diagrams of Brazer Canyon samples WT-603

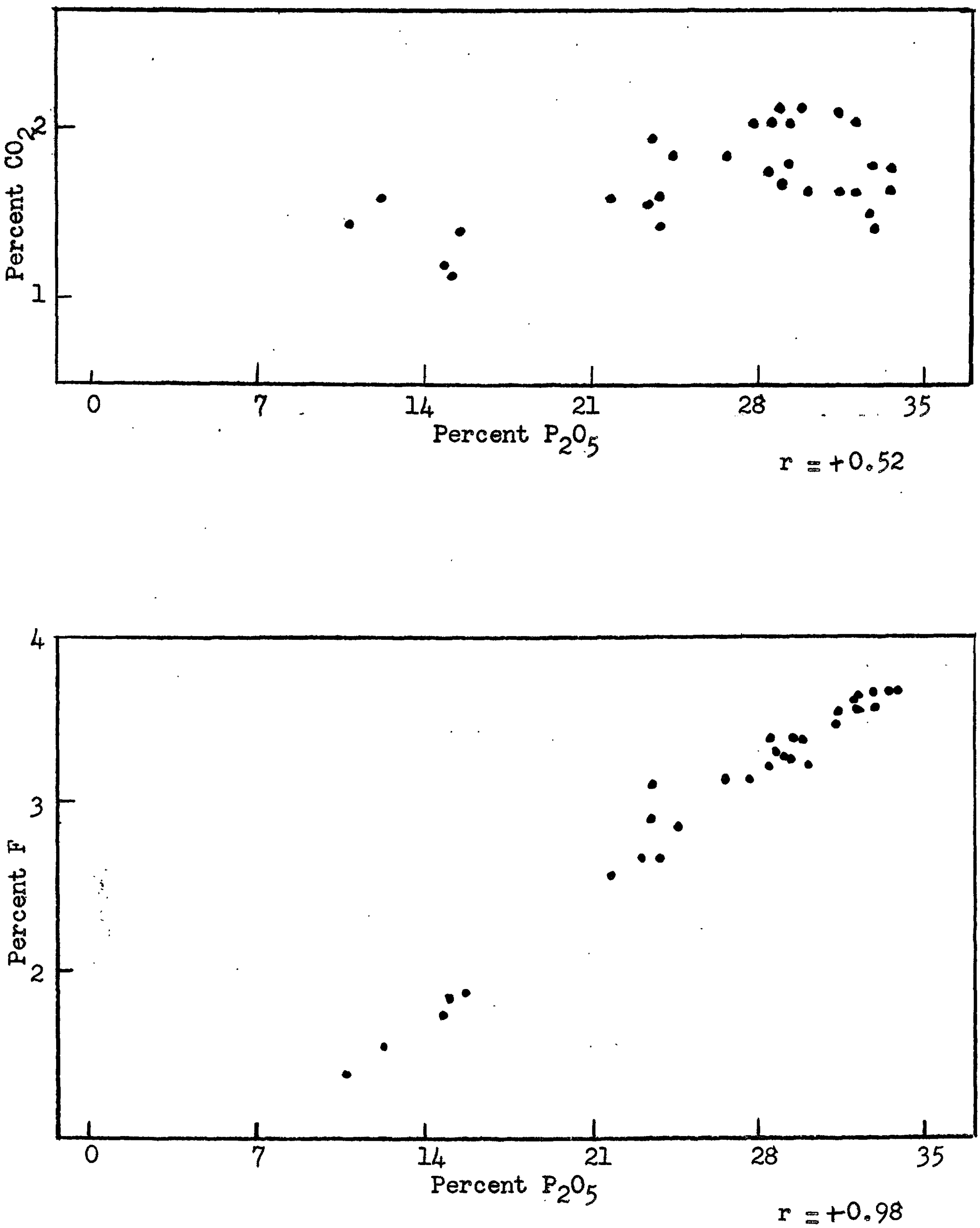


Figure 5.--Scatter diagrams of Brazer Canyon samples WT-604, 605

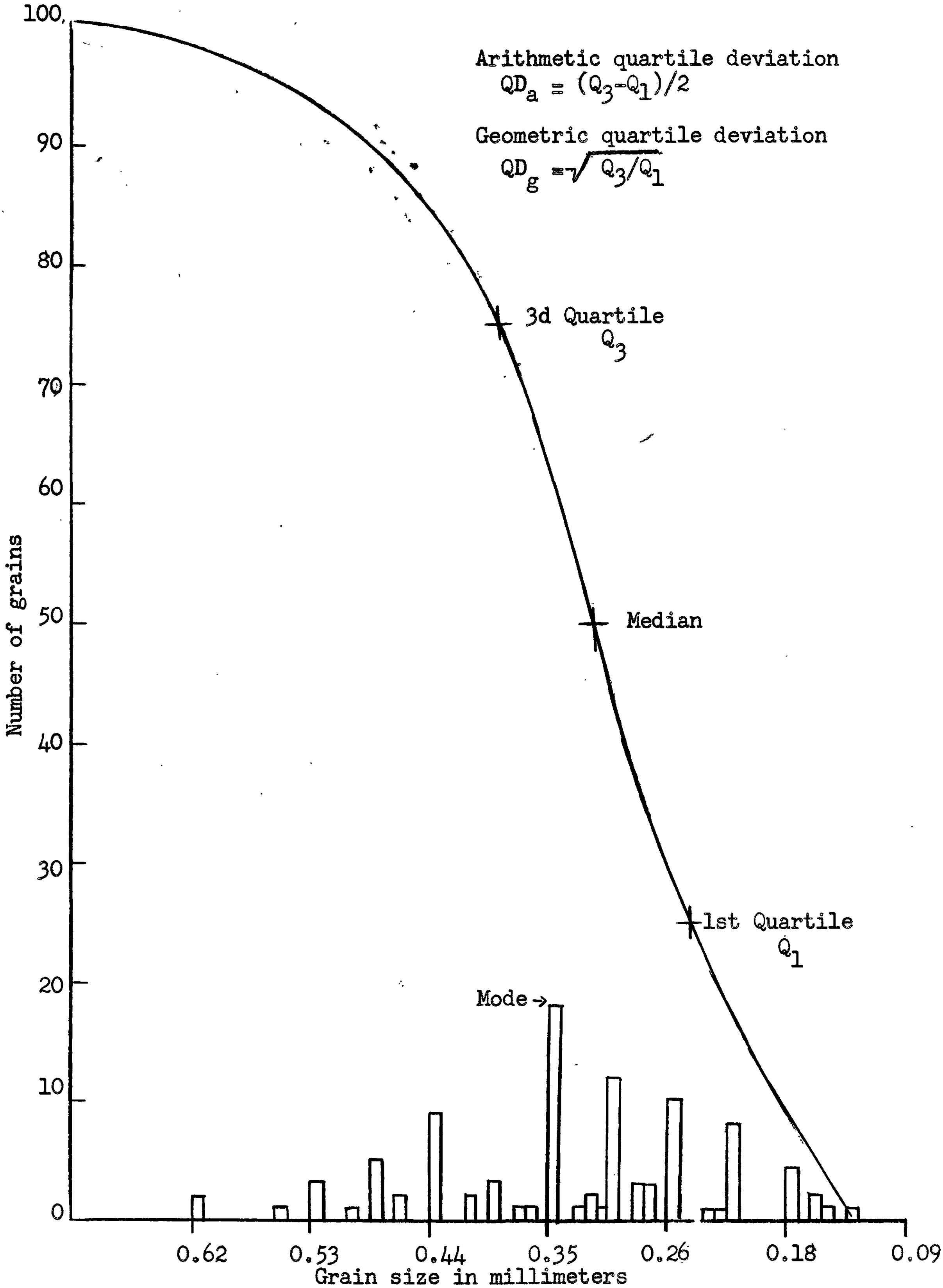


Figure 6.--A typical frequency histogram and cumulative curve showing 1st and 3d quartiles, the median, and the mode

(Sample no. WT 365-7 eU = 0.012 percent)

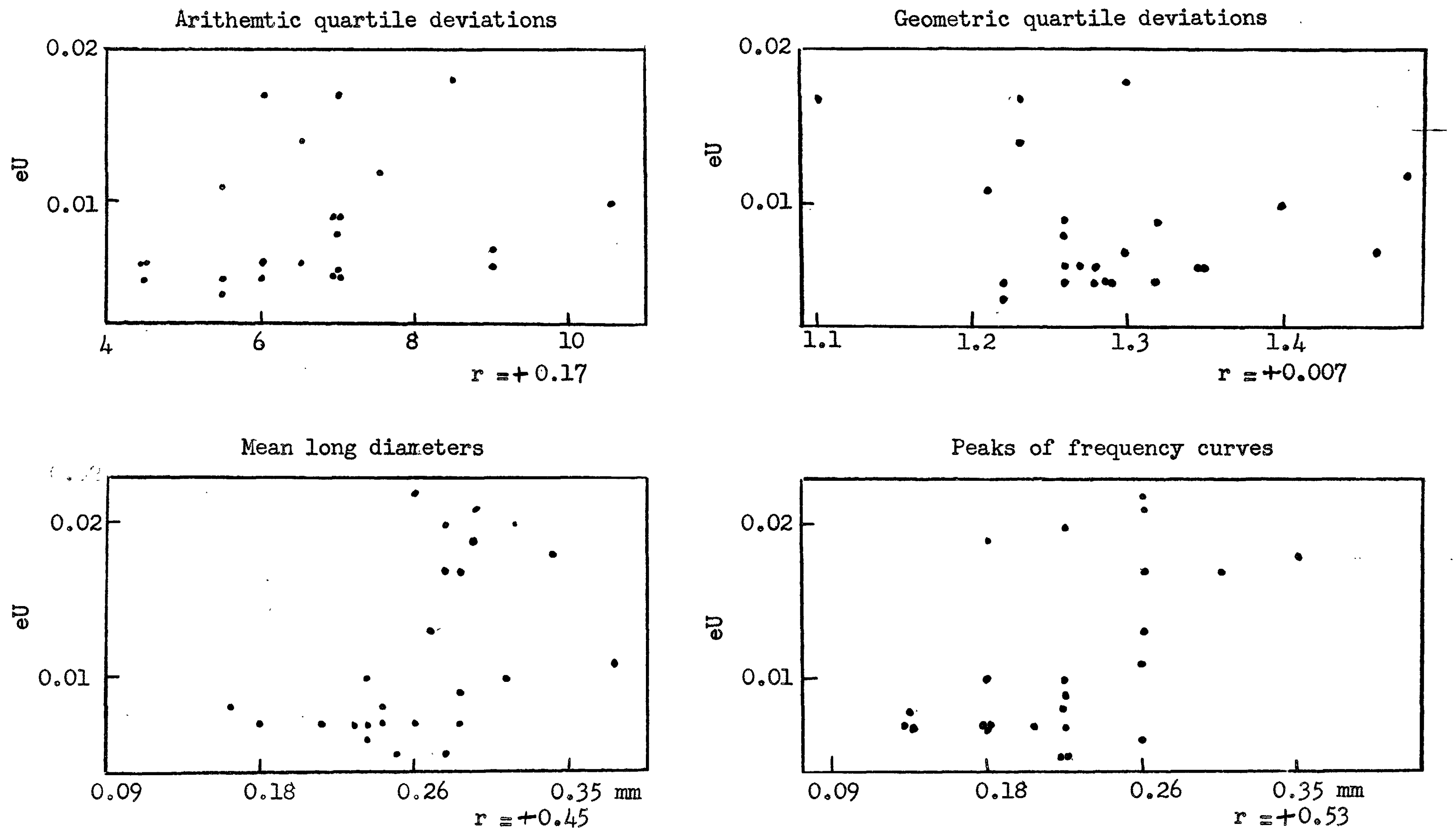


Figure 7.--Scatter diagrams showing comparison of various size measurements with uranium content, Trail Canyon samples WT-365

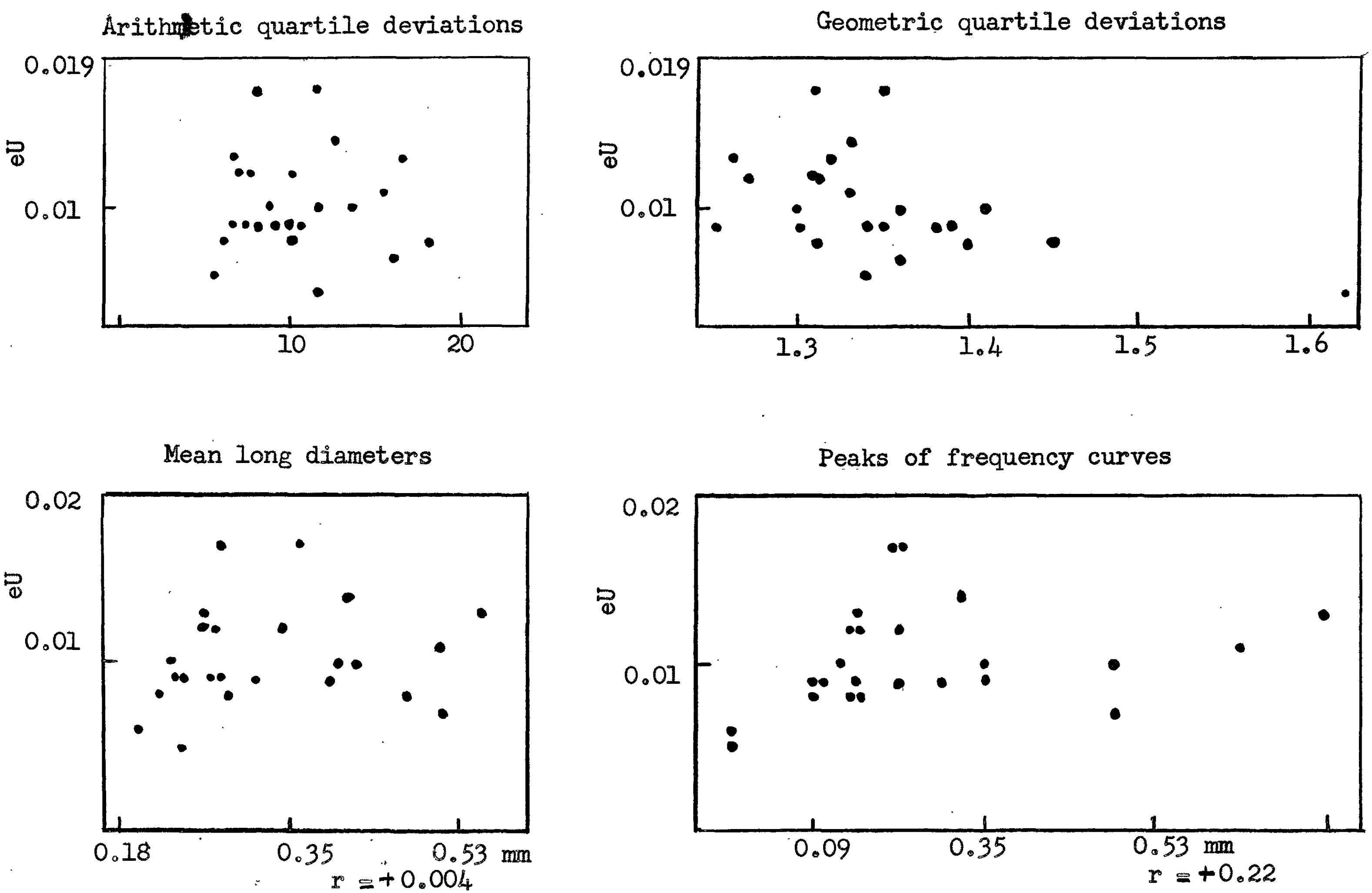


Figure 8.--Scatter diagrams showing comparisons of various size measurements with uranium content, Laketown Canyon samples WT-509

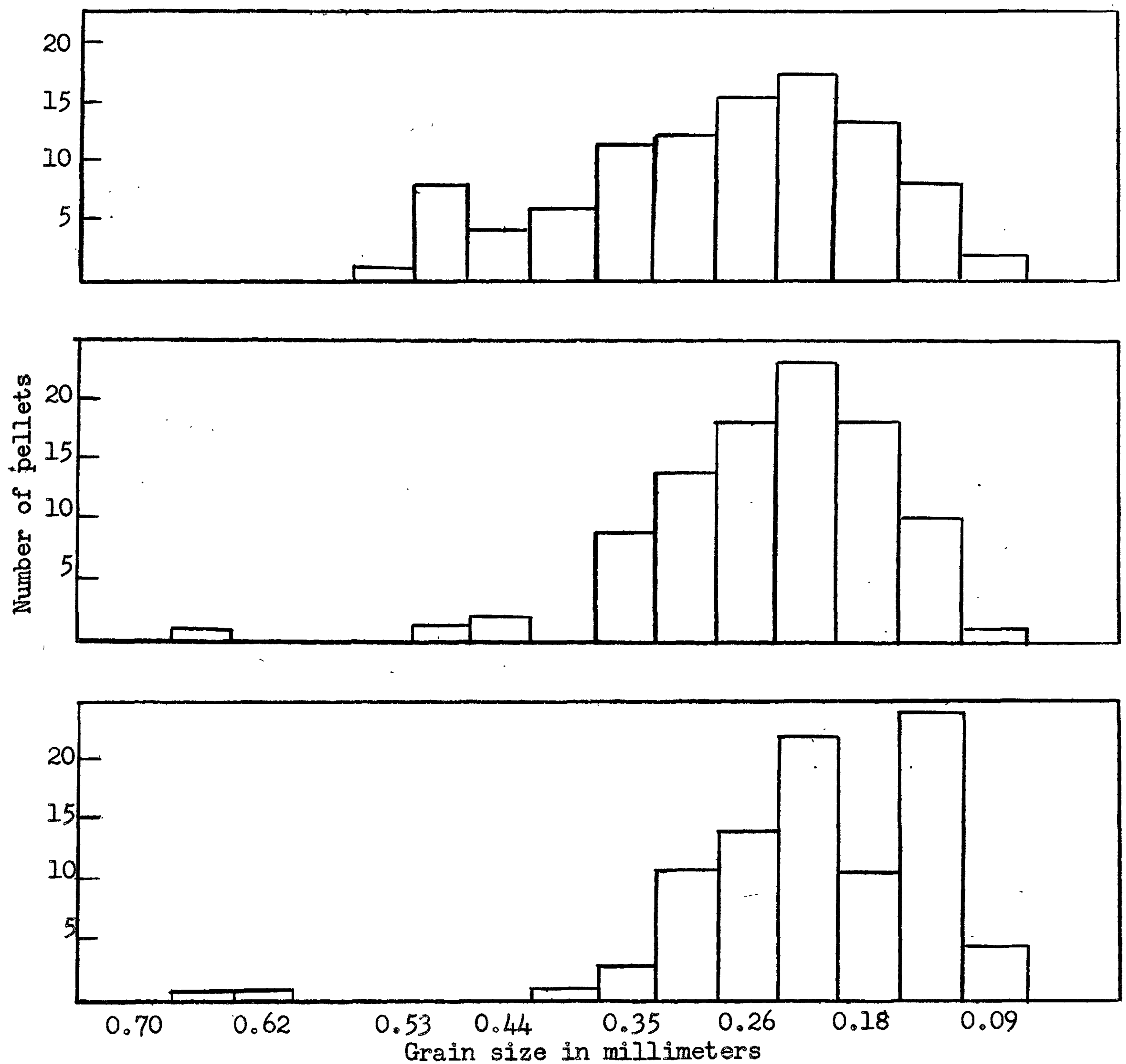


Figure 9.--Various frequency distribution curves obtained from samples with the same percent quivalent uranium. From bottom to top, the samples are WT-365-4, 17, 20, Trail Canyon

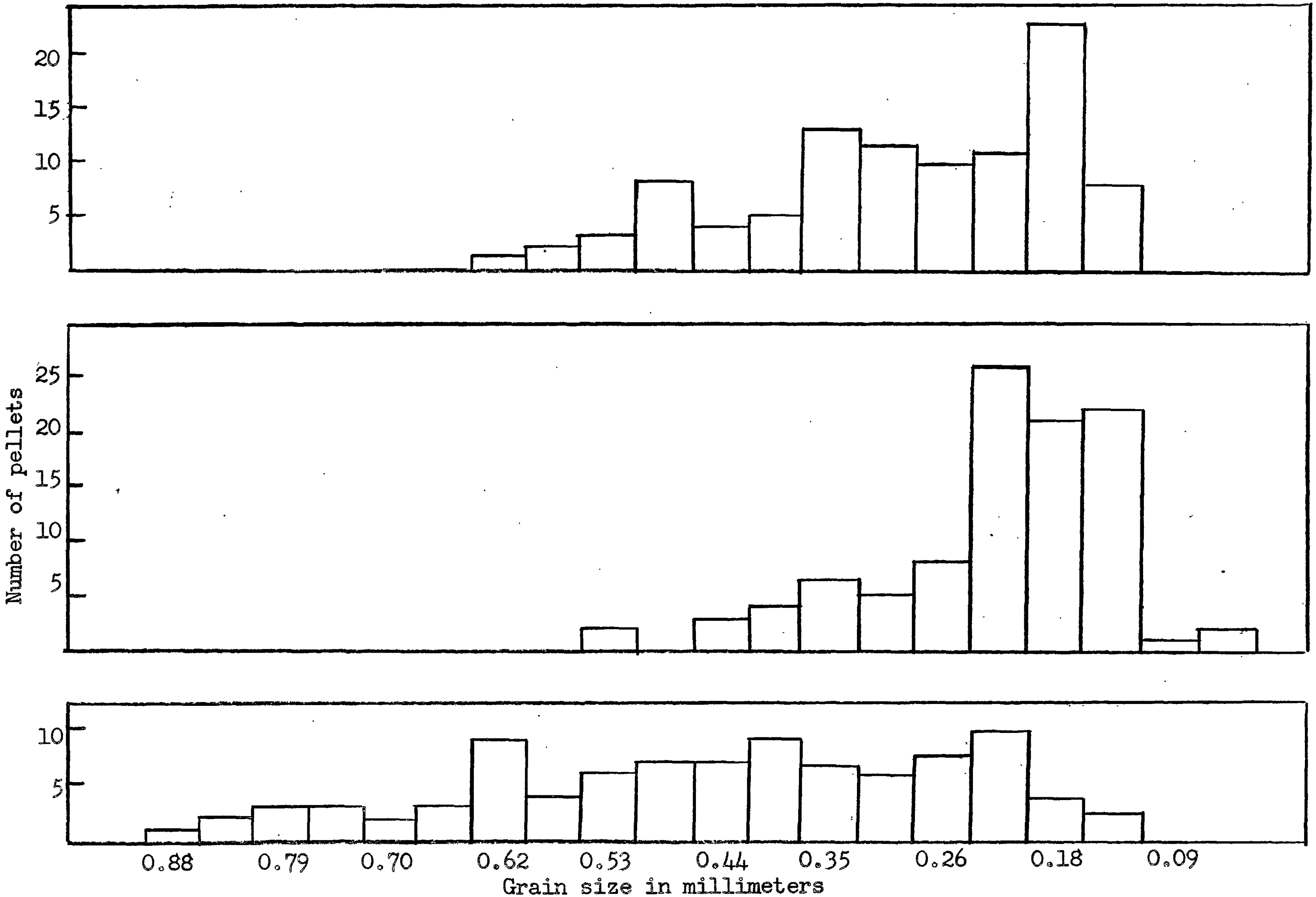


Figure 10.--Various frequency distribution curves obtained from samples with the same percent equivalent uranium. From bottom to top, the samples are WT-509-6, 20, 22, Laketown Canyon