Relationship of uranium and other trace elements to post-Cretaceous vulcanism

By R. R. Coats, 1910-

Trace Elements Investigations Report 159

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RELATIONSHIP OF URANIUM AND OTHER TRACE ELEMENTS TO POST-CRETACEOUS VULCANISM*

By

Robert R. Coats

June 1955

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RELATIONSHIP OF URANIUM AND OTHER TRACE ELEMENTS TO POST-CRETACEOUS VULCANISM

By Robert R. Coats

ABSTRACT

A regional study of the distribution of uranium, boron, tin, beryllium, niobium, lanthanum, lead, zirconium, lithium, and fluorine in 112 samples of Cenozoic volcanic rocks of predominantly rhyolitic and dacitic composition has shown that the content of uranium has a significantly high positive correlation with that of niobium, beryllium, and fluorine, a lower but still significant positive correlation with lithium and tin, a significant negative correlation with boron and lanthanum, and no significant correlation with zirconium and lead. A study of the relation of content of the several elements to the geographic provenance shows significant variation with provenance for all these elements, except tin and lanthanum. On the basis of these variations and on patterns of consistency, five comagmatic provinces, one of which is subdivided into three sub-provinces, have been delimited, in part, on a map of the western United States. The pattern of distribution of boron is significantly different from that of the other elements. The regional differences are perhaps best explained by structural control of the effectiveness of vertical transport.

INTRODUCTION

The observational background for the investigation here reported upon was the close relationship between the distribution of structurally controlled uranium deposits in the Cordilleran region, and the distribution of post-Cretaceous volcanic rocks (Kaiser and Page, 1952). It was also apparent from this report that, although very few uranium deposits were remote from surficial manifestations of Cenozoic volcanic activity, broad areas of volcanic rocks such as the Columbia Plateau, the Sierra Nevada, and the Cascade Mountains, were completely lacking in known uranium deposits.

Two questions are posed by these observations: 1.) is the lack of known uranium deposits in these areas the result of scarcity of uranium-bearing outcrops and inadequate prospecting, or 2.) is it because of a real scarcity of uranium deposits? The answers to these questions would point the way to economies in prospecting activity in some areas, and lead to the concentration of activity in other more favorable areas, and thus increase the likelihood of the discovery of new deposits.

Basic concepts

Two basic concepts are involved in planning this investigation. The first concept is the well-known one of the petrographic province, which briefly defined, is the idea that there exist, within definite areas, igneous rocks of a limited age range, which display certain petrographic and chemical characters in common. Fersmann (1929, p. 5) pointed out the existence of certain element associations in certain geographical zones. A zone so defined he proposed to call a geochemical province.

The second basic concept is that of the metallogenetic province, which applies the provincial concept to the resemblances between ore deposits of a limited age range within a limited geographic area. The hypothesis is that, for ore deposits of magmatic origin, there is a genetic connection, direct or indirect, between the comagmatic (Washington, 1906, p. 5) or petrographic province, and the metallogenetic province, where these are founded in part on the same element.

The idea that there are uraniferous metallogenetic provinces has been supported by several investigators; Rankama and Sahama (1950, p. 395) point out the contrast in uranium content of ore deposits in the Canadian and Fenno-Scandian Precambrian areas. Adams (1952, p. 1229) has stated that the idea of uraniferous provinces has been confirmed by his analytical results, and that the uranium content of volcanic rocks seems to be governed, first, by the general uranium content of the province and second, by the silica content of the rock type.

The rocks analyzed cover a range of composition with respect to the major elements. Percentagewise this range, however, is much less than the range in content of the minor elements studied. When sufficient analyses of the major elements become available, it is planned to study this factor. The report was prepared before any of the thin sections of the rocks analyzed were available for study; some of the rocks may have been altered, and some of the analyses may have been affected thereby, although effort has been made, in the collection of samples, to minimize this possibility.

Plan of investigation

Field work

Methods

Because it was not feasible to investigate all volcanic rocks within the Cordilleran region, the study was restricted to rhyolites and dacites, particularly to the wholly or partly glassy rhyolites and dacites. The reasons for this restricted choice of rock types will be discussed in another place. In the beginning, field measurements of radioactivity with scintillation counters were attempted, partly in order to have a guide to the collection of samples that these might represent as wide a range as possible of uranium content, and also to attempt to determine in the field any geologic controls governing differences in uranium content from one body of igneous rocks to another, and from one part of a body to another. An effort was made to get as wide and nearly uniform a coverage as possible; so it is believed that there is very little bias in the direction of too high a uranium content.

Choice of rock types sampled

Rhyolites as residual magmas.--Because of the low concentration of most of the elements sought in the average igneous rock, it was thought desirable to determine the distribution of these elements in the type of igneous rock in which they are present in the highest concentration. It was already known that certain lithophile elements (Mason, 1952, p. 118) such as B, Be, W, Nb, Ta, Sn, Th, U, Cs, rare earths,

Li, and Rb, tend to be concentrated in residual magmas and finally in pegmatites. Bowen (1937, p. 20) has already shown that the salic portions of many rhyolites, trachytes, and phonolites fall in the low-temperature trough in the system SiO_2-$KAlSiO_4$-$NaAlSiO_4$ and that these therefore represent residual magma, and hence should be especially rich in the elements listed above. In addition to these, it is known that zirconium (Hevesy and Würstlin, 1934) and lead (Rankama and Sahama, 1950, p. 733) are more highly concentrated in granite than in most calc-alkalic igneous rocks. Lead is known to enter potash feldspar structures, but as the residual fluids are enriched in potash, they should likewise be enriched in lead. Adams (1952, p. 1229) has correlated uranium with silica content.

Glasses as samples.--At the beginning of this investigation, it was not known whether the crystallization of volcanic rocks resulted in loss of any trace elements from the solidifying lava. A priori, however, it seemed likely that some of the more volatile constituents, particularly those that do not form stable minerals under low pressure conditions, such as boron compounds, might escape, and the possibility that volatile compounds of the other elements also might escape was suggested by the known occurrence of heavy metals in fumarolic incrustations. It seemed desirable to concentrate the field efforts on glassy, or partly glassy rocks, but not to the entire exclusion of hypocrystalline or holocrystalline volcanics, and, where gradations from glassy to crystalline phases could be found in the same rock body, to endeavor to determine the possible differences in trace element concentration. This has been possible in but few places. The nature of the differences found will be discussed later. An additional reason for preferring glassy and partly glassy rocks lies in the widespread alteration, in part hydrothermal and in part deuteric, which volcanic rocks in many parts of the west have undergone. The effects of this alteration could be discounted by careful petrographic work, but it was thought that much time and effort might be spent on the collection and analysis of unsuitable rocks before thin sections became available for petrographic study, time and effort that could better be spent on rocks that could be confidently regarded as unaltered.

Spectrographic and chemical work

The samples were analyzed for equivalent uranium by analysis of radioactivity, uranium by fluorimetric methods, and many other elements by quantitative spectrographic analysis. The earliest request for spectrographic work included the elements Mn, B, Be, La, Li, Nb, Sn, Ta, Th, and W. Subsequently, when Pb, Zr, Zn, and Ge were looked for in a selected group of the same fifty samples, Zn and Ge were not found to be present above the limit of detectability, but Pb and Zr were ultimately determined in all fifty. Mn, as determined in the 1952 samples, proved to range rather erratically and showed no evident relationship to any other element; it was therefore not sought in the analyses of the 1953 samples. Inasmuch as Ta, Th, and W had proved to be present below the limit of detectability in the 1952 samples, they, as well as Zn and Ge, were not looked for in any of the 1953 samples. The possibility remains that Zn, Ge, Ta, Th, and W may have been present above the limit of detectability in all of the 1953 samples, and Ge and Zn in a number, not known to me, of the 1952 samples. The probability of this being true is considered to be rather small, and it appears almost certain that the mean content of all of these elements in most of the rocks sampled is less than the lower limit of detectability.

The lower limits of detectability by the method used, so far as these are known to me, is shown in table 1 below in parts per million (Myers, A. T., 1953, written communication).

Table 1.--Threshold values for spectrographic method

Element	Ppm	Element	Ppm
Mn	3	Nb	2
B	10	Sn	4
Be	1	Ta	300
La	40	Th	300
Li	1	W	70
Pb	7	Zn	300
Zr	7	Ge	3

Acknowledgments

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The laboratory work performed has been done by the following persons in the Denver laboratories of the Geological Survey. The great extent to which this paper is based on their work will be obvious to the reader.

Year submitted	Report no.	Type of work	Analyst (s)
1952	TDS-418	Spectrographic	P. R. Barnett
1952	TDS-536	Spectrographic	P. R. Barnett
1952	TDC-2647	Radiometric	S. P. Furman
1952	TDC-2647	Fluorimetric Chemical	W. Mountjoy J. Meadows
1953	TDS-627	Spectrographic	P. R. Barnett
1953	TDS-645	Spectrographic	P. R. Barnett N. M. Conklin
1953	TDS-646	Spectrographic	P. R. Barnett N. M. Conklin
1953	TDP-418	Radiometric	S. P. Furman
	TDP-426	Radiometric	S. P. Furman
1953	TDC-3746	Fluorimetric Radiometric Chemical (F)	J. Meadows S. P. Furman L. F. Rader, Jr.
1953	TDC-3812	Chemical (F) Fluorimetric	J. Meadows W. Mountjoy
1953	TDC-3814	Chemical (F) Fluorimetric	J. Meadows W. Mountjoy

I wish to thank Dr. Howel Williams and Dr. Garniss Curtis of the University of California and Donald Kupfer of the Geological Survey for specimens of glassy rocks, and Dr. W. H. Youden of the Bureau of Standards for advice on the treatment of the statistical data.

Possibilities of bias and error

Certain possible sources of bias and error ought to be listed, evaluated as far as possible, and the methods taken to avoid them explained. The preference for glassy rocks over crystalline may have introduced some bias, as it is not known whether rhyolitic glasses are representative of rhyolites in general. This preference for glasses might introduce a bias in several different ways. One of these is the possible effect of some constituents on crystallinity, which is known to be a factor in the crystallization of artificial glasses; glasses might then be expected to be lower in such constituents than rhyolites in general. Another possible source of bias is the known tendency of glasses to devitrify with age; hence rhyolitic glasses are probably younger than rhyolites in general; being younger, they may represent a more extreme stage of differentiation, and hence greater concentrations of those elements that tend to be enriched in the residual magma. The number of latities or andesites included is probably small enough so that the averages are not appreciably affected, more particularly because most evidence shows that the intermediate rocks are also intermediate in content of the elements sought. The ranges in analysis shown far exceed the standard deviation of a set of spectrographic analyses of a single sample. Unfortunately, none of these determinations was replicated, but it is believed the smaller dispersion of the values found for rocks of a single series, within a small geographic area, indicates the reality of the major differences found.

To a certain extent, the differences in trace element content between the provinces may be a reflection of the differences in gross chemical composition of the glassy rocks available for sampling, which may, in turn, be in part a function of the degree to which differentiation has proceeded. In other words, it is certain that, since the gross chemical compositions are not known, comparisions are being made among rocks belonging to a range of levels of differentiation, rather than of rocks all at the same level. It is possible that, when sufficient analyses of major constituents are available, this effect may be factored out. In so far as the rocks are completely or almost completely glassy, indices of refraction may serve to give a rough indication of the composition.

Examples of the range of variation within geographically coherent groups of rocks are given below.

Another possible source of error is the non-homogeneity of the rock masses sampled, so that the sample is not representative of the mass. None of the samples is a channel sample, but an effort was made to include a number of chips from different points on the mass. A small sample should be adequate, unless large-scale inhomogeneity is present, because of the fine grain of most of the rocks. The groups of analyses in table 2 suggest that some variation is present, in groups of samples taken from different rock masses; it seems reasonable to expect that the variation within a single rock mass should not exceed that between different rock masses closely associated in space and time, and presumably derived from the same or closely related magma chambers.

Table 2.--Minor-element content in three sets of closely-related rocks, in parts per million.

Sample no.	B	Be	La	Nb	Sn	Pb	Zr	U
Three rhyolitic obsidians, Medicine Lake, Modoc County, Calif.								
52C40	30	4	50	8	5	10	200	2
52C41	30	3	40	10	5	10	200	2
52C43	30	3	50	6	4	10	200	<1
Two obsidians and a perlite, south of Mono Lake, Mono County, Calif.								
52C69	30	2	40	6	Tr.	20	100	3
52C70	30	3	--	5	4	20	90	6
52C71	30	2	80	9	5	20	200	6
One obsidian, one perlite and two perlitic vitrophyres, Yellowstone Park, Wyoming.								
53C45	10	6	80	30	10	40	100	7
53C50	10	5	100	40	30	80	200	5
53C51	10	5	100	40	10	20	200	6
53C52	10	6	100	40	10	20	200	5

OBSERVATIONAL RESULTS

Levels of concentration

Analytical results on 116 samples collected in 1952 and 1953 were used for the computation of means and correlation coefficients. Of these, 112 were attributed to particular provinces and were used in calculating the statistical significance of the variations among the provinces.

Some of these means, for the 1952 collections, table 3, differ significantly from those arrived at by averaging the results of the 1953 collections together with the 1952 collections. For the elements plotted, it does not appear likely that these differences are due to any difference in the analyst or the analytical method, but it is impossible to exclude these sources of error without the inclusion of a substantial number of duplicate samples in the batches analyzed at different times. In a few areas, collections were made in both years; and it is upon the lack of significant difference between the results for the two years in these areas that the conclusion rests that there were no significant differences between analysts or in analytical method from one year to the next.

The differences between the averages for 1952 and those for the two years together is attributed to the effects of provincial differences and to differences in the distribution of the samples, by provinces, in the two years.

Correlations between uranium content and that of other elements

The values for some of the elements determined correlate well with each other, while others correlate poorly. Because the correlation between uranium and the other elements was the most important relationship to be investigated, correlation coefficients, table 4 based on the set of 116 analyses of the rocks collected in 1952 and 1953, were computed for uranium with niobium, tin, beryllium, lead, boron, lanthanum, lithium, fluorine, and zirconium. For the 1952 collection, coefficients were computed for uranium with manganese and equivalent uranium with niobium. The correlation of equivalent uranium with niobium was less than that for uranium with niobium. In general, because of the number of factors that

Table 3.--Mean minor element content in rhyolitic and dacitic rocks (ppm)

Element	1952 (48 analyses)	1952 and 1953 (116 analyses)
U	4	5
B	40	33
Be	4	5
Nb	15	21
La	30	40
Pb	21	24
Sn	3	5
Mn	350	
Zr	129	138
F	538	654
Li	528	456

may influence the equivalent value in these rocks of low radioactivity, equivalent uranium is much less useful than uranium, determined by fluorimetric methods. The coefficients were calculated according to the formula $r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{(x - \bar{x})^2 (y - \bar{y})^2}}$

which reduces to $r = \frac{\Sigma xy - \frac{\Sigma x \Sigma y}{n}}{\sqrt{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{n}\right]\left[\Sigma y^2 - \frac{(\Sigma y)^2}{n}\right]}}$

where x = values of one variate

y = values of other variate

$\bar{x}$ = mean of all x's

$\bar{y}$ = mean of all y's

n = number of pairs of analyses

The following values resulted:

Table 4.--Correlation coefficients of uranium with some minor elements in 116 analyses of Cenozoic rhyolitic and dacitic rocks of the Cordilleran region.

	Nb	Sn	Be	Pb	B	Zr	Li	F	La
U	+0.447	+ 0.364	+ 0.445	+ 0.159	- 0.178	+ 0.01	+ 0.317	+ 0.55	- 0.412

For 48 analyses on 1952 samples, the correlation of equivalent uranium with niobium is + 0.34, and of uranium with manganese is - 0.085.

Of the values given above, those for niobium, tin, beryllium, lithium, fluorine, and lanthanum reach or exceed the 0.1 percent level of significance (Davies, 1947, p. 276). This means that there is a probability of less than 0.001 that a correlation coefficient this high could be the result of chance variation. The correlation coefficient for boron of 0.178 is about that of the 5 percent level of significance, that is, the probability of a coefficient that high occurring by chance is about 1 in 20.

Possible explanations of observed relationships

It is noteworthy that the best correlations for uranium are with niobium, beryllium, and fluorine, of which the first two are elements characteristically found in granitic pegmatites. Uranium correlates less well with tin, which is found both in pegmatites and hydrothermal deposits, as well as in scattered deposits in rhyolite that resemble fumarolic deposits, and still less well with lead, which is typical of hydrothermal deposits, and occurs in some fumaroles, but is much less conspicuous in pegmatites, where it may be concealed in the lattice of potash minerals. The high correlation coefficient of uranium with fluorine is very suggestive in connection with the known occurrence of uranium in many fluorite deposits in the Cordilleran region, and its occurrence in fluorite deposits in Wolsendorf, in Bavaria, and in the well-known uranium deposits of the Saxon and Bohemian Erzgebirge. In view of the many occurrences of uranium without fluorite, and of fluorite without uranium, the co-existence in a few deposits may reflect an uncommonly high concentration of both elements in the magmas of a given area; the high correlation between the two suggests concentration by the same processes in the course of differentiation.

The correlations with manganese and zirconium are not significant. Manganese is an element that tends to proxy for magnesium and iron, and is therefore removed in early stages in ferromagnesian minerals; zirconium, because of the low solubility of the mineral zircon, mostly begins to separate from granitic magma early, but may or may not be removed. Some highly alkalic rocks are rich in zirconium. Boron, because of its volatility, is a fumarolic element, and may be subject to vapor-phase transportation, in addition to the transportation in pegmatitic residual fluids. It is difficult to avoid the impression that the concentration of uranium, niobium, beryllium, lithium, and fluorine in rhyolites and similar rocks is governed in large part by the same laws; presumably these also govern the concentration of the rare elements in pegmatites.

If there is a genetic relationship between the occurence of uranium in these rhyolitic rocks and in ore deposits of the typical hydrothermal type, it must be an indirect one, because the elements that typically accompany pitchblende in hydrothermal ore deposits are lead, zinc, copper, iron, and sulfur, in most of the Cordilleran region. Cobalt, nickel, and silver, common elsewhere, are much less prevalent here. This observation serves to reinforce one that has been made many times, that pegmatites are seldom observed to grade into normal hydrothermal sulfide-bearing quartz veins, and that the elements most prominent in one are less common in the other. An inference favored by many is that hydrothermal ore deposits and pegmatites are not derived from the same phase, changing continuously in composition over the interval between the conditions under which pegmatites are formed and those under which hydrothermal ore deposits are formed. Turner and Verhoogen (1951, p. 333) suggest that the formation of a vapor phase may result in the splitting of the rare constituents of a magma into those which occur in pegmatites and those which are more commonly found in hydrothermal veins.

Geographic distribution of the several elements

Method of displaying analytical results

The positions of the analyzed samples were plotted on a 1: 5,000,000 scale map of the western states, and overlays then prepared for each of the elements plotted. The analytical values were not grouped by value for plotting purposes, with the exception of those for fluorine, and a few of the lowest values for some of the elements. When all the values for each of the elements had been plotted, the area in which most of the analyzed rocks occurred was subdivided into provinces (pl. 1), the boundaries being drawn at the positions that would produce the greatest average contrast in value between sets of analyses belonging to adjacent provinces. Although the exact position of the boundaries was decided on the basis of the analytical values plotted, the decision as to the existence of certain sets of provinces may have been influenced by pre-conceived ideas concerning the existence of petrographic provinces in the West. Because of the lack of analyzed material, or in some places, of material suitable for analysis, the provinces are not completely bounded. It should be emphasized that provincial boundaries are not based on the analytical results for any single element, but on the combined values for all the elements. Equal weight has not been given to all the elements; those elements that showed the best correlation with uranium were given most weight.

The comagmatic provinces

Five comagmatic provinces have been tentatively delimited, in whole or in part, on plate 1. One of these, the Ute, has been further subdivided into three subprovinces. The five principal provinces are: Cascade, Shahaptin, Shoshone, Coastal, and Ute. The subprovinces of the Ute province are in the Mountain Border, the Mohave, and the Yuma. Further work will undoubtedly result in the shifting of some boundaries and perhaps in the deletion of others. It is also possible that more intensive sampling may permit the subdivision of some of these provinces, perhaps down to the scale of a district.

PLATE I

COMAGMATIC PROVINCES IN THE CORDILLERAN REGION

BASED ON TRACE ELEMENT RELATIONSHIPS IN CENOZOIC RHYOLITIC AND DACITIC ROCKS

In an investigation of Aleutian volcanoes (Coats, 1952, p. 510), substantial differences in the content of some trace elements were found in the rocks of volcanoes of the same age, but a few miles apart. The emphasis in that study was on the differences between rocks of different volcanic centers in the same province, and on the resemblances between rocks of the same volcanic center. In the present study, the attempt has been made to discern consistency within provinces, and differences between provinces.

Table 4âa shows the distribution by provinces, of probability levels for each of the elements. In this connection, the term "probability level" means the probability, expressed as a percentage, that the number of samples that give an analytical value above a given level (approximately the arithmetic mean) for that element and that province (or subprovince) , could be obtained by a random selection of a number of analytical values equal to the total for the province (or subprovince), from the whole group of 112 analytical values. This value was arrived at by applying the chi-squared test to the statistics set forth in the tables, under each element (tables 4a to 13, inclusive). A high figure means a correspondingly high probability that the observed distribution could be a matter of chance, a low figure a correspondingly low probability that the observed distribution could be a matter of chance. As can be seen from the table, the Shoshone province is most sharply marked out from its neighbors; the table does not indicate that the deviations in the case of the Shoshone province are nearly all positive, those of the Shahaptin province, nearly all negative. Two subprovinces do not have a probability reaching the 8 percent level of significance for a single element. It is possible that the effort to separate the Ute province into subprovinces is not justified, and all these subprovinces should be grouped in the statistics. If this were done, the Ute province would still be distinguished from its neighbors by its average character.

Distribution of individual elements, by provinces

Uranium

The distribution of the several analytical values for uranium is shown in figure 1. The highest uranium content appears to be found in the rocks of the Shoshone province, with smaller values in the Ute and Coastal provinces. The distribution of the uranium, with respect to province and content, is shown for

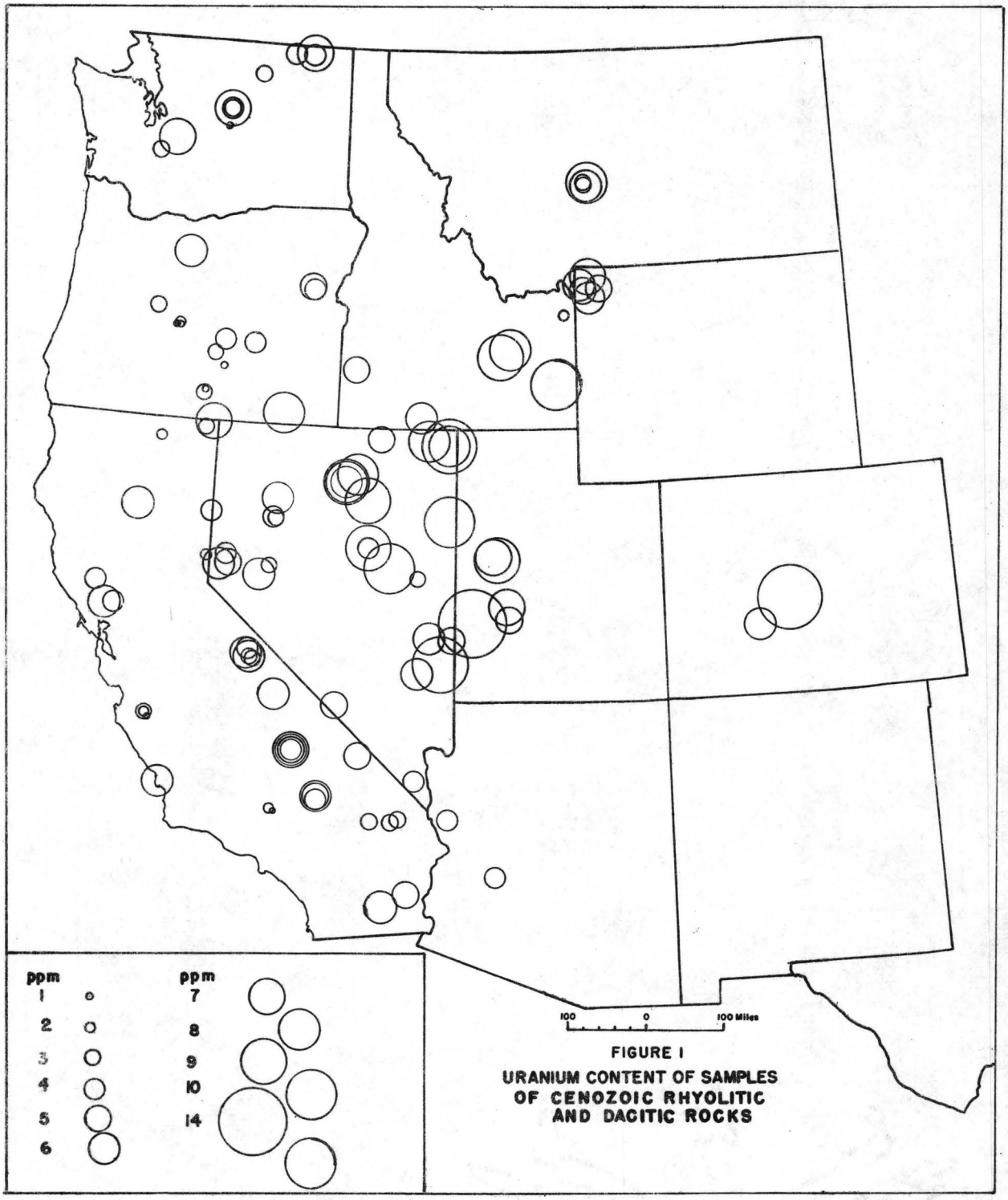


FIGURE 1

URANIUM CONTENT OF SAMPLES OF CENOZOIC RHYOLITIC AND DACITIC ROCKS

Table 4aa.--Probability levels, in percentages, derived by applying chi-squared test to analytical value distributions shown in tables 4a to 13, inclusive.

	PROVINCE					
Element	Ute (Mohave)	Ute (Yuma)	Ute (Mountain Border)	Cascade	Coastal	Shahaptin	Shoshone
Uranium				7.5			0.6
Boron					2.3		
Tin						7.5	
Beryllium				3.8		2.5	0.25
Niobium						7.5	<0.1
Lanthanum						8	
Lead						4.2	0.1
Zirconium	7.7			1.6		6.4	
Lithium	7					5.5	4.7
Fluorine				6			0.8

112 of the rocks, in table 4a. Because this table is typical of all the tables used to show the distribution of each of the several elements, by province and content, its arrangement will be explained here, once for all.

In the table, the column headed "content" lists the values reported in the rocks analyzed, which range from zero, or a trace, to 30 ppm. The columns headed by provincial names show, for each of the values, the number of analyses corresponding to that value, for the rocks sampled from that province. The column headed "sum" carries the sums, computed across, of the number of analyses having each value. The column headed "product" lists the respective products of the number of analyses by the corresponding contents of uranium. The total of the "product" column, divided by the number of analyses, gives the mean value for the number of analyses reported.

Table 4a.--Distribution of uranium, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
	Ute			Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
0				1		1		2	0
1			1	3	1	2		7	7
2			1	4	1		1	7	14
3	3		2	5	1	2	6	19	57
4	2	1	2	4	2	3	4	18	72
5	3	1	2			2	5	13	65
6	1	1	5		2	1	10	20	120
7			1	3			4	8	56
8							7	7	56
9							5	5	45
10							2	2	20
11	1						1	2	22
12									
13									
14							1	1	14
30							1	1	30
Sum	10	3	14	20	7	11	47	112	578
Number above 5 ppm	2	1	6	3	2	1	31	46	
Expected:	4.1	1.23	5.75	8.2	2.87	4.51	19.25	46	
Deviation:	-2.1	-.23	.25	-5.2	-.87	-3.51	11.75	0	
Contribution to χ^2	1.07	.04	.01	3.29	.26	2.74	7.67	15.08	
P				7.5%		10%	0.6%		

The entries at the bottom of the table list the total number of rocks analyzed from each province. In the row below these totals is listed the total number above the mean value of 5 ppm. The next row lists the number to be expected above this value, assuming that the distributions of analyses, by value, are the same for all provinces. The row beneath this, headed "deviation", gives the deviations, positive or negative, of the actual numbers found, compared with the numbers expected. (The number expected, will in general, not be a whole number.) The row next following gives the calculated contribution to chi-squared, arrived at by the formula $\chi^2 = \frac{(\text{Deviation})^2}{\text{Expectation}}$ (Davies, 1946, p. 180).

The last row shows the probabilities (P), in terms of percentages, that the number of analyses above the mean, within the several provinces, might be obtained by a chance drawing of the number of analyses appropriate to the province, from the total number of analyses. A high probability means that the distribution might readily be obtained by chance; a probability of 5 percent means that there is one chance in twenty that the number of analyses above the given level in the particular province could be obtained by a chance drawing from the total number of analyses. It is thus a measure of the significance of the variation shown. A value of more than 10 percent is considered (Davies, 1947, p. 53) not significant; one between 10 and 5 percent possibly significant, one between 5 and 1 percent as significant, and one of less than 1 percent highly significant. The values for the several provinces indicate that the deviation shown by the values for the Shoshone province is highly significant; and for the Cascade Province is possibly significant. Other deviations are insignificant. It should be noted that the levels of significance determined by this test are influenced somewhat by the choice of the value used as a cut off; e. g., if 4 ppm were used instead of 5 ppm, then the probability of chance deviations as great as the deviation shown by the Cascade province drops from 7.5 percent to 2.4 percent and becomes significant, whereas that shown by the Shoshone Province rises from 0.6 percent to 2.4 percent, a value that is still significant. In short, border-line evaluations of significance can be changed by the choice of the cut-off level, but probability levels based on larger numbers of analyses are changed little.

The statistical study of the distribution suggests strongly that the Shoshone province is relatively a uraniferous province, or part of a larger uraniferous province, at the levels of concentration measured by the analyses used herewith. The boundaries as indicated on the map (pl. 1) are of course tentative, and the province may well be regarded as part of the larger uraniferous province that includes the Colorado Plateau and the Colorado Front Range. Delimitation of boundaries on the basis of the silicic volcanic rocks alone has the disadvantage that the distribution of the volcanic rocks of the type sought is not a uniform one, and, where evidence is lacking, the boundaries may be drawn short of the positions they would have if nature had provided an adequate number of samples of Cenozoic extrusive rocks. If the Shoshone province is a part of the larger province that has been recognized by many previous workers, then this uraniferous province is larger than previously recognized. On the negative side, a rational explanation for the relative scarcity of uranium deposits over the large areas of other provinces is thus offered. Of the other provinces, the Cascade and Shahaptin are apparently the least favorable, although the deviation for the Shahaptin province barely approaches significance.

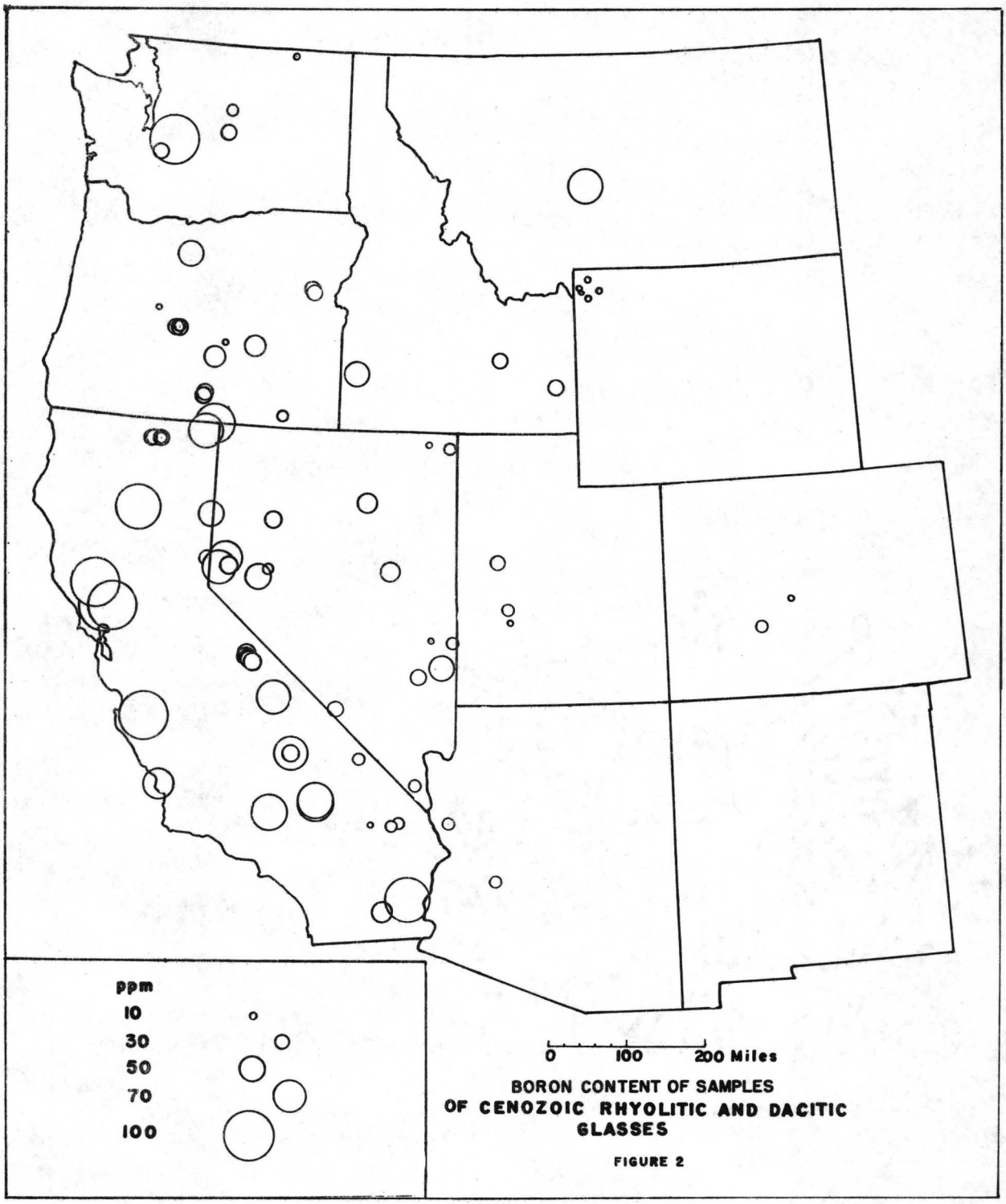
Boron

The negative correlation coefficient of uranium with boron suggests that there are considerable contrasts in the distribution of these two elements, and the map showing the distribution of boron* (fig. 2) when

*It will be noted that the rocks plotted in figure 2 are wholly or partly glassy rocks, rather than the rhyolitic or dacitic rocks in general. The reason for doing this was the fact that some evidence suggests that crystallization of the rock results in loss of boron. The clearest example available is the following pair of analyses, of a rhyolite and a perlite respectively, from different parts of the same intrusive, in San Benito County, Calif.:

	52C49 (rhyolite)	52C50 (perlite)
Boron (ppm)	30	100

compared with figure 1, shows that this is the case. The distribution of boron is unlike that of any other



BORON CONTENT OF SAMPLES
OF CENOZOIC RHYOLITIC AND DACITIC
GLASSES

FIGURE 2

of the elements studied. The highest values are found in the Coastal province, and the next highest in the Mountain Border sub-province, with intermediate values in the Shoshone and Shahaptin provinces, and relatively low values in the Mohave subprovince, and in the Cascade province. The distribution of boron in the rocks of the several provinces is indicated in table 5. Only the values found in the Coastal province are indicated, by the chi-squared test, to be significantly above the general average.

Table 5.--Distribution of boron, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
		Ute		Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
0-9				5			3	8	15
10	1					1	16	18	180
20	6	1		4		1	13	25	500
30	2		8	8	2	5	6	31	930
40		1				2	2	5	200
50	1			1		2	1	5	250
60									
70			6	1			5	12	840
80							1	1	80
90		1			1			2	180
100				1	4			5	500
Sum	10	3	14	20	7	11	47	112	3675
Mean									32.8
No. above mean	1	2	6	3	5	4	9	30	
Expectation:	2.68	0.8	3.75	5.35	1.87	2.94	12.58	30	
Deviation:	-1.68	+1.2	+2.25	-2.35	+3.13	+1.06	-3.58		
Contribution to χ^2	1.06	1.8	1.37	1.04	5.23	.383	1.04		
P			25%		2.3%				

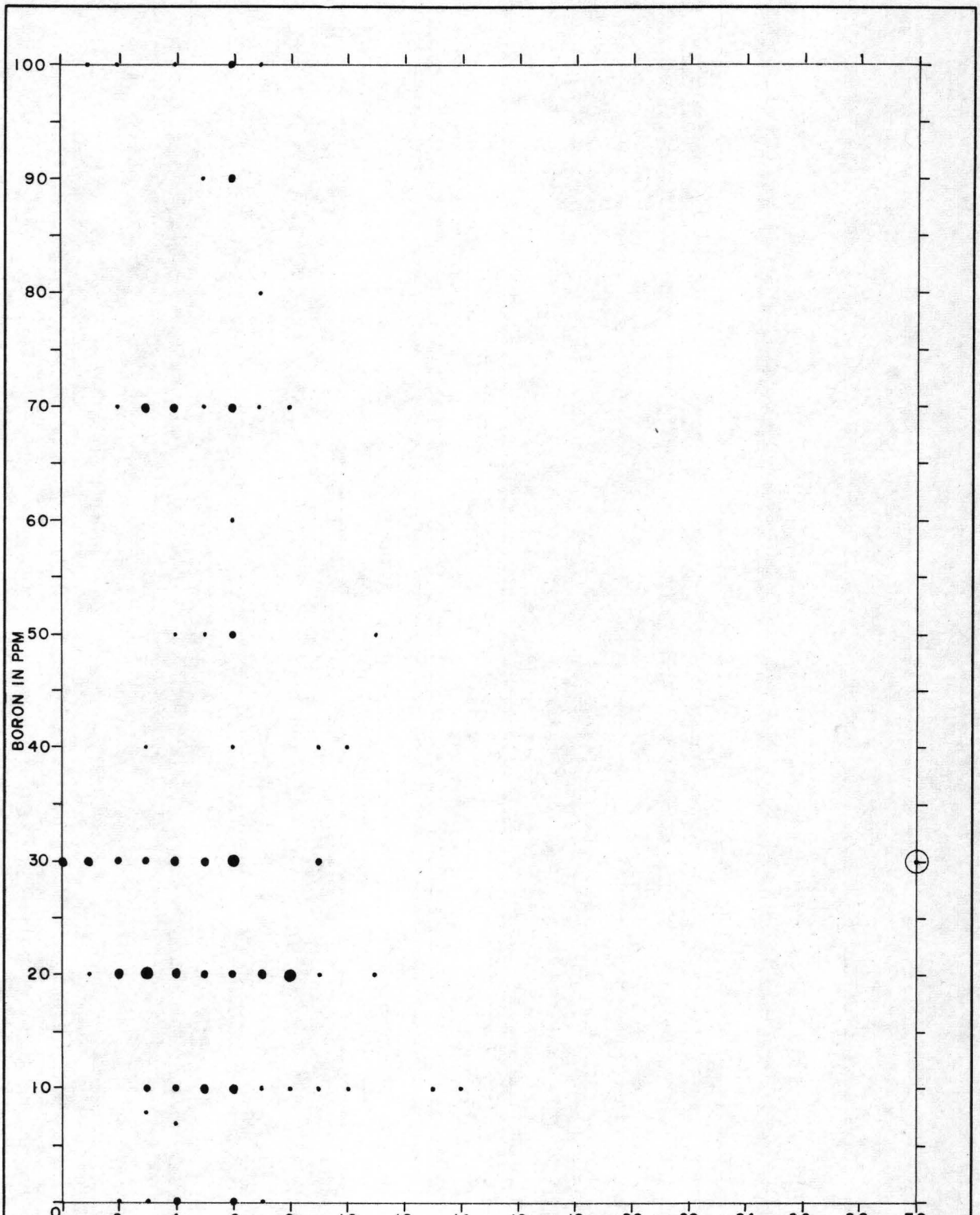
The values reported here seem to be considerably less, on the average, than those found by Wasserstein (1961) in South African granites. Wasserstein found from 0 to 500 ppm in granites, with the younger granites generally having a higher content, probably because they have been transected by erosion at higher levels, where the rocks are enriched in boron. The younger Cape granites averaged, in Wasserstein's work, 150 ppm. It is not yet clear whether the difference between rhyolites and granites reflects escape of boron from the extrusive magmas, or a regional difference.

The relation of the uranium and boron contents of the analyzed rocks is indicated by the distribution of points in figure 2a.

Tin

The distribution of tin, as shown on figure 3, resembles that of uranium and beryllium, but the correlation of tin with uranium is not as good as that of beryllium with uranium. The greater dispersion of the results may in part, at least, be a reflection of the fact that a much greater proportion of the results for tin are reported as being below the lower limit of sensitivity (4 ppm) than is true of the results for beryllium, for which the lower limit of sensitivity is 1 ppm. The Shoshone province shows the greatest dispersion and the highest mode and mean, followed by the Coastal province, and then by the Cascade province and Mountain Border subprovince. The distribution of the various analytical values, by provinces, is shown in table 6.

The interval that most nearly approaches the mean is indicated in table 6 by a line between 5 and 6 ppm; when the chi-squared test is applied to the provinces on the basis of the relative proportions of analyses above this level, only the contribution to chi-squared for the Shahaptin province, which approaches the 7 percent level of significance, is possibly significant. The conclusion is that the variations in tin content are not statistically significant, although the correlation coefficients show that tin contents trend in the same direction as the uranium, niobium and beryllium contents. The distribution of tin with respect to uranium is indicated by the values plotted in figure 3a.



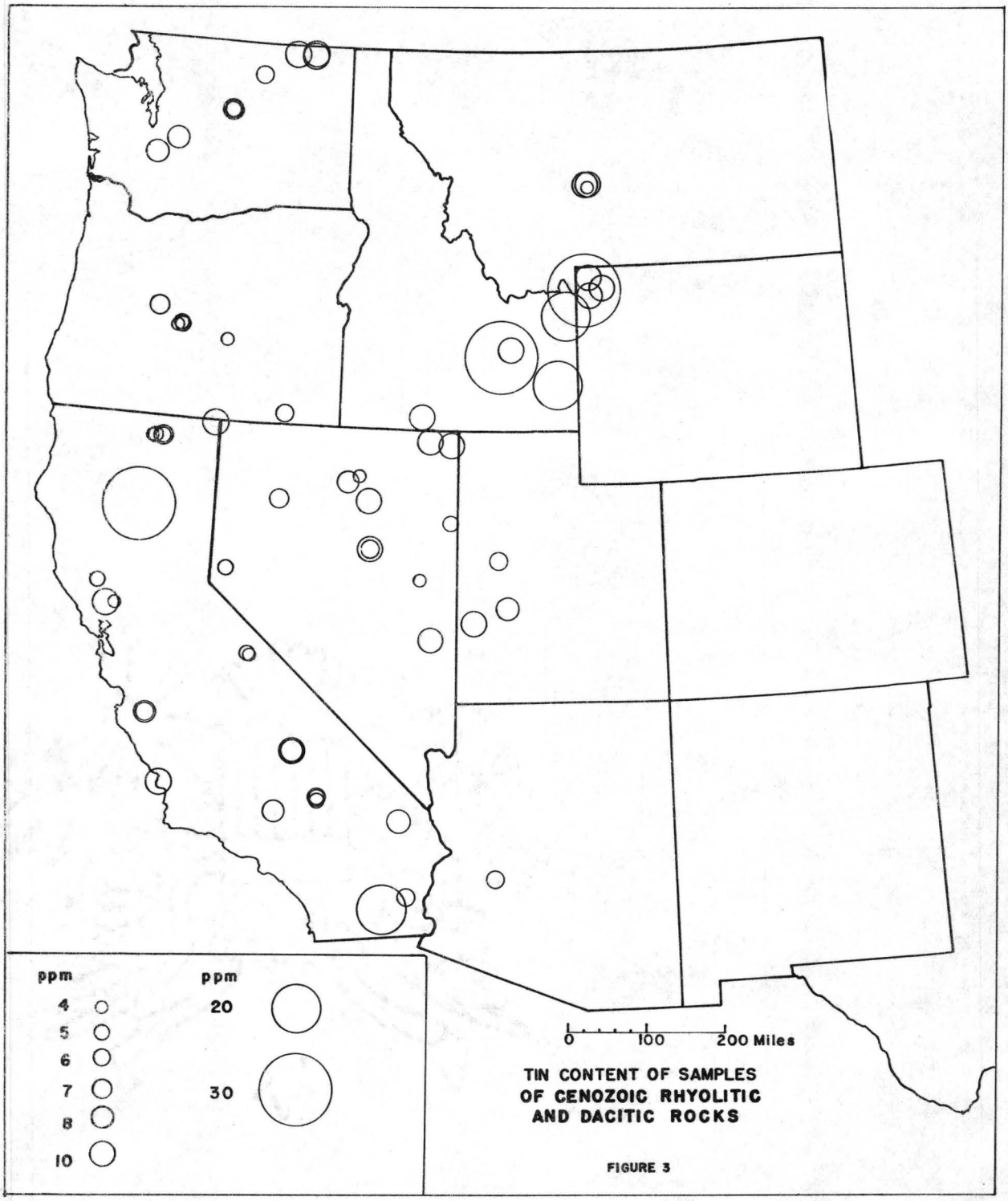
SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND BORON CONTENT

$r = -0.178$

Relative size of spots indicates number of coincident pairs of values for the several points.

FIGURE 2a

GPO 837925

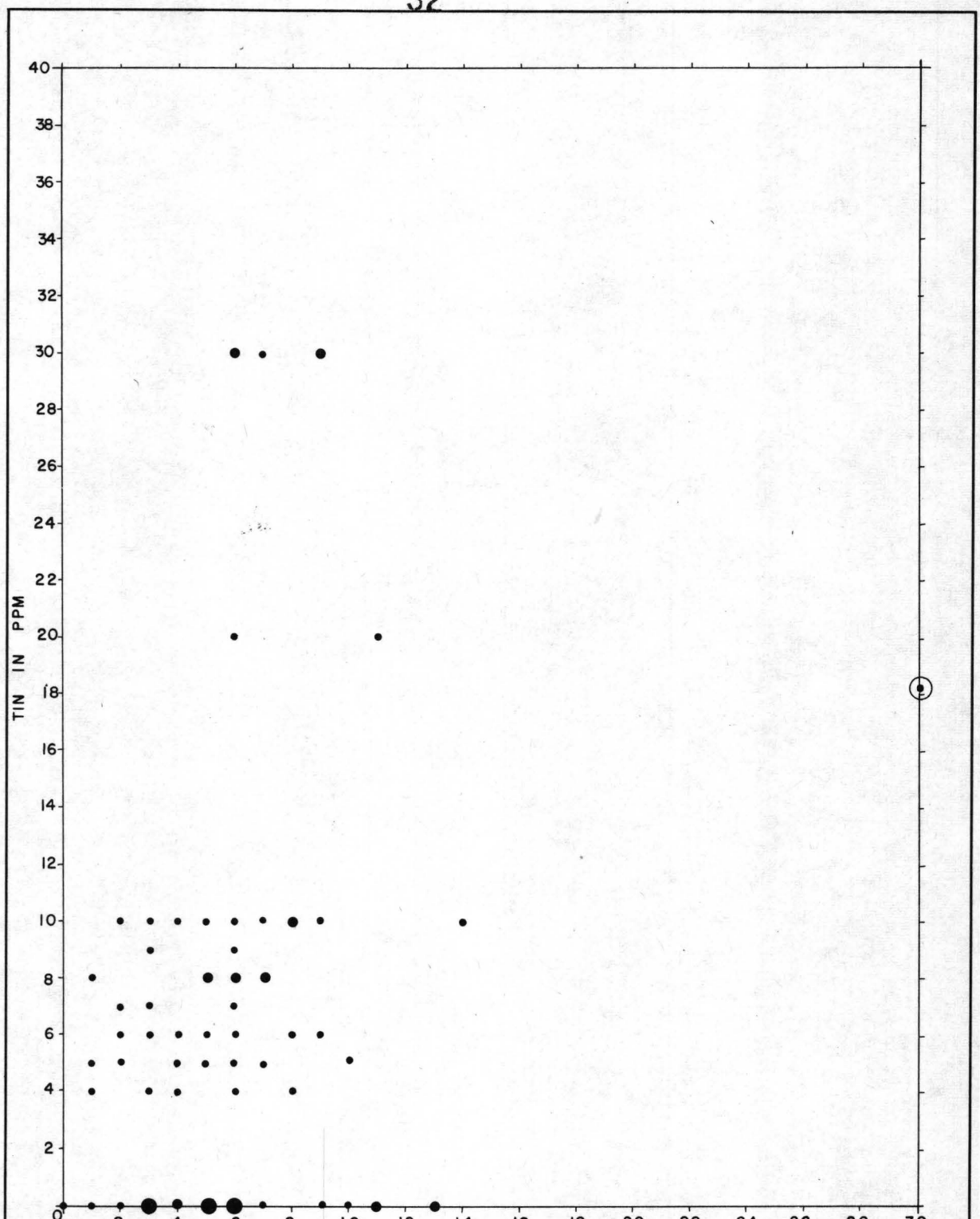


TIN CONTENT OF SAMPLES
OF CENOZOIC RHYOLITIC
AND DACITIC ROCKS

FIGURE 3

Table 6.--Distribution of tin, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
	Ute			Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
0	9		5	3		9	15	41	0
4			1	2	1	1	2	7	28
5			3	5	1		2	11	55
6		2	1	2	2		4	11	66
7				4			1	5	35
8			2	1	1		3	7	56
9	1					1		2	18
10			2	3	1		14	20	200
20		1					3	4	80
30					1		2	3	90
40							1	1	40
Sum	10	3	14	20	7	11	47	112	658
Mean									5.87
No. above mean	1	3	5	10	5	1	28	53	
Expectation:	4.73	1.42	6.6	9.5	3.32	5.2	22.2		
Deviation:	-3.73	+1.58	-1.6	+0.5	+1.68	-4.2	+5.8		
Contribution to χ^2	2.21	1.76	0.39	0.03	0.85	3.38	1.5	10.1	
P	16%					7%			



SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN URANIUM AND TIN CONTENT

$r = +0.364$

Relative size of spots indicates number of coincident pairs of values for the several points.

FIGURE 3a

GPO 837925

Beryllium

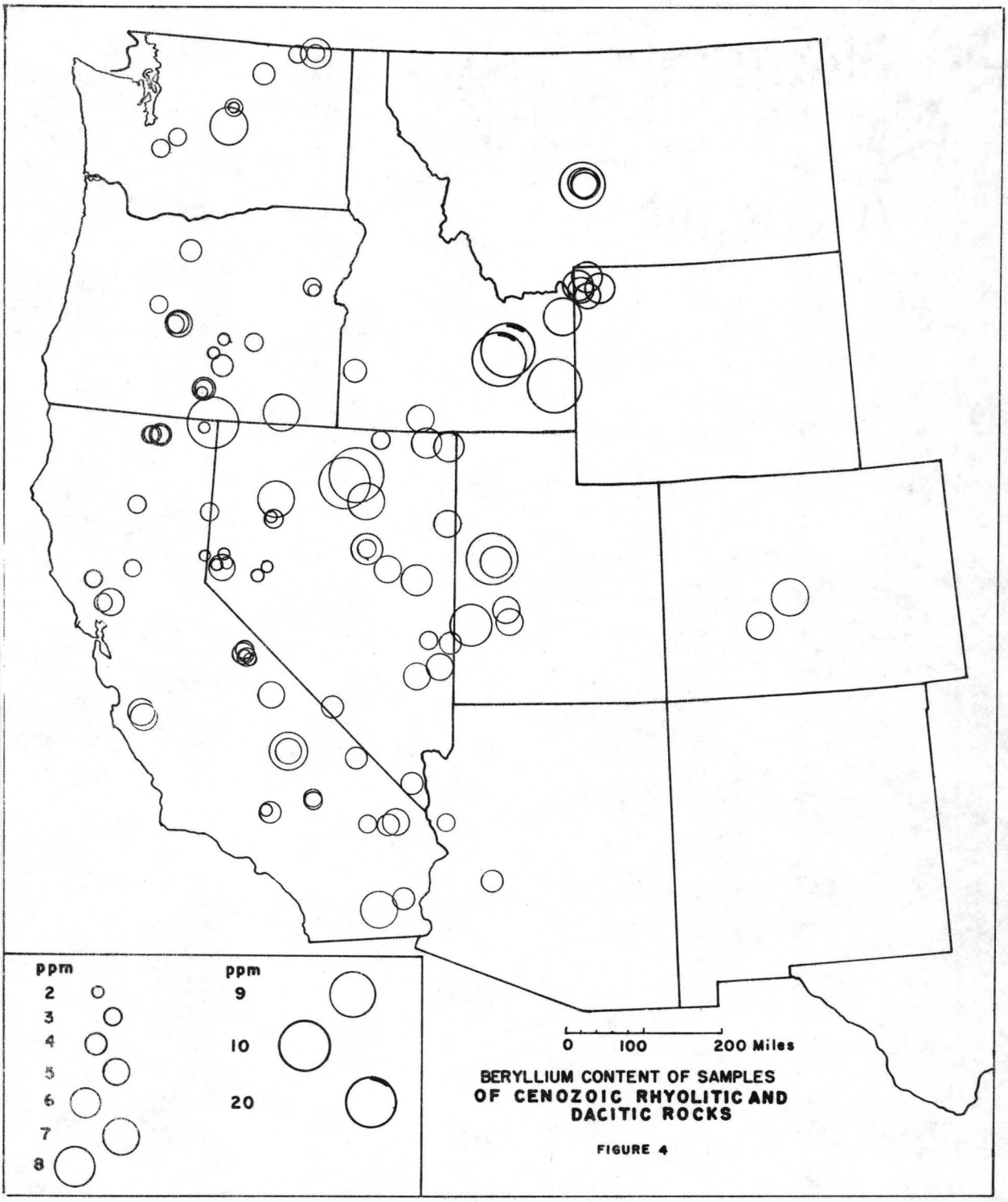
The distribution of beryllium is similar in pattern to that of uranium. The highest values, and the greatest dispersion of values, are found in the Shoshone province, where values as high as 20 ppm are found. Smaller ranges and lower means are found in the Mohave subprovince, and a slightly greater range, coupled with somewhat lower mode, in the Mountain Border subprovince and Cascade province. The lowest mean is found in the Shahaptin province. The distribution of the various analytical values, by provinces, is shown in table 7. The P levels, shown in the last row of the table, indicate that the contribution to chi-squared made by the Shoshone province is highly significant, and that the contributions of the Cascade and Shahaptin provinces are significant. The distributions for the other provinces do not differ significantly from the distribution of the whole group of analyses.

The distribution of the analyzed rocks and the beryllium values found are indicated on figure 4. The distribution of the beryllium analytical values, with respect to those for uranium from the same rocks, is shown in figure 4a.

The average beryllium content (4.5 ppm) found in the course of this investigation corresponds closely with that found by Sandell (1952, p. 211-216) in granitic rocks--an average of 3 ppm with a range from 2.4 to 5.5. The range found in this investigation is considerably greater--almost one-third of the total have more than 5 ppm. It is noteworthy that a sample of obsidian from Yellowstone Park was reported by Sandell to carry 5.5 ppm. Obsidian from Obsidian Cliff, in Yellowstone Park, presumably from the same exposure, carried 6 ppm, and the average of four glassy or partly glassy rhyolitic rocks from Yellowstone Park was 5.5 ppm in this investigation. Sandell comments on the fact that Goldschmidt reports 35 ppm of beryllium on a sample from the same locality (presumably, Obsidian Cliff). The averages found in this investigation are somewhat less than those reported by Holser and others (1951, p. 1450), which were 20 ppm of BeO for granitic and 7 ppm for intermediate rocks. Goldschmidt (1954, p. 207) reports a range of 4 to 40 ppm of beryllium in obsidianites.

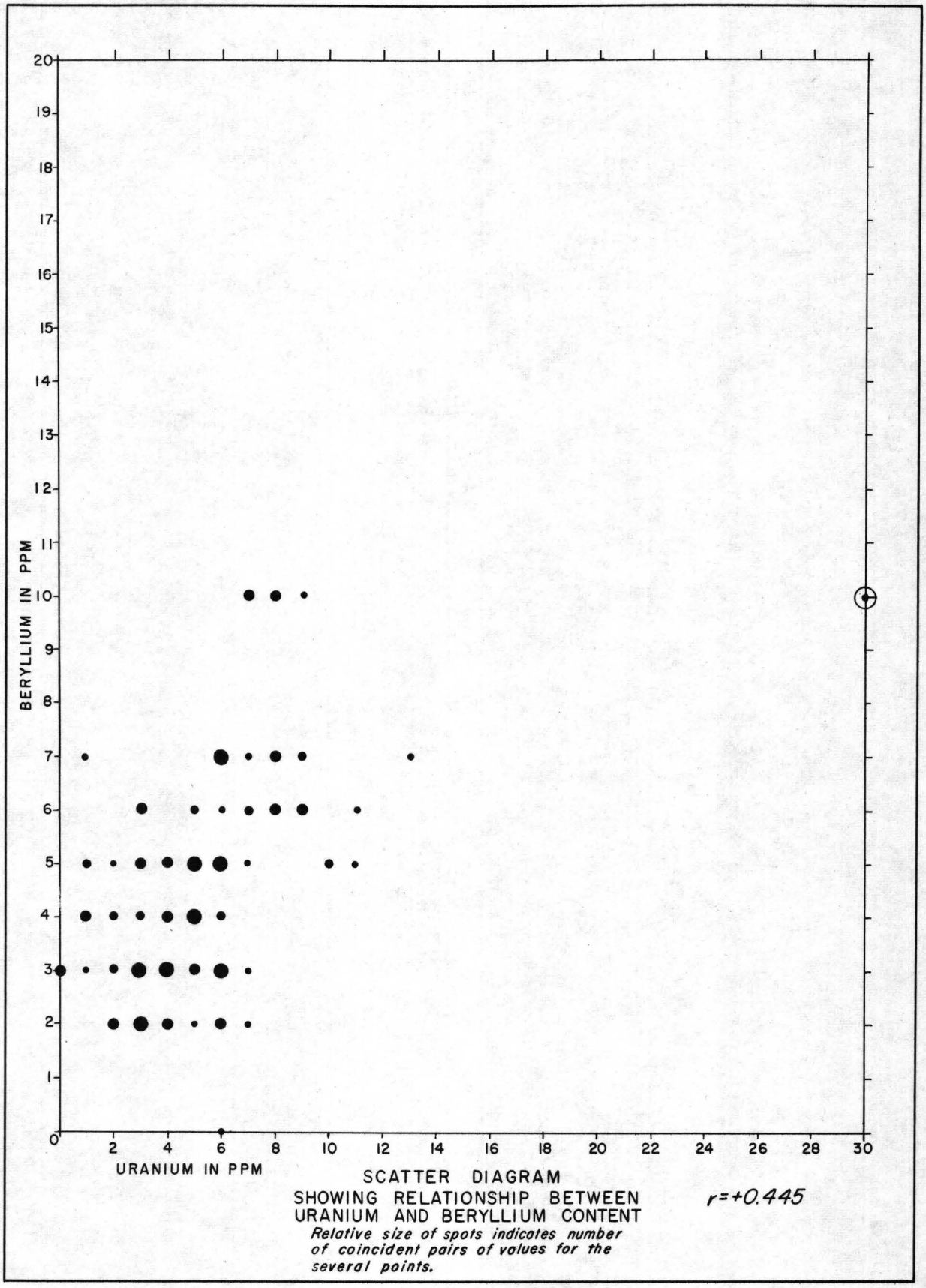
Table 7.--Distribution of beryllium, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
		Ute		Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
2			3	2		4	6	15	30
3	2		4	12	3	3	4	28	84
4	5	2	2	3		4	1	17	68
5	3		2	1	4		9	19	95
6			1	1			12	14	84
7		1	2	1			4	8	56
8							1	1	8
9							2	2	18
10							6	6	60
20							2	2	40
Sum	10	3	14	20	7	11	47	112	543
Mean									4.52
No. above mean	3	1	5	3	4	0	36	52	
Expectation:	4.63	1.39	6.5	9.28	3.25	5.1	21.8	52	
Deviation:	-1.63	-0.39	-1.5	-6.28	+.75	-5.1	+14.2	0	
Contribution to χ^2	0.57	0.11	0.34	4.25	0.18	5.1	9.4	19.95	
P				3.8%		2.5%	0.25%		



BERYLLIUM CONTENT OF SAMPLES OF CENOZOIC RHYOLITIC AND DACITIC ROCKS

FIGURE 4



SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND BERYLLIUM CONTENT

Relative size of spots indicates number of coincident pairs of values for the several points.

$r = +0.445$

FIGURE 4a

GPO 837925

Niobium

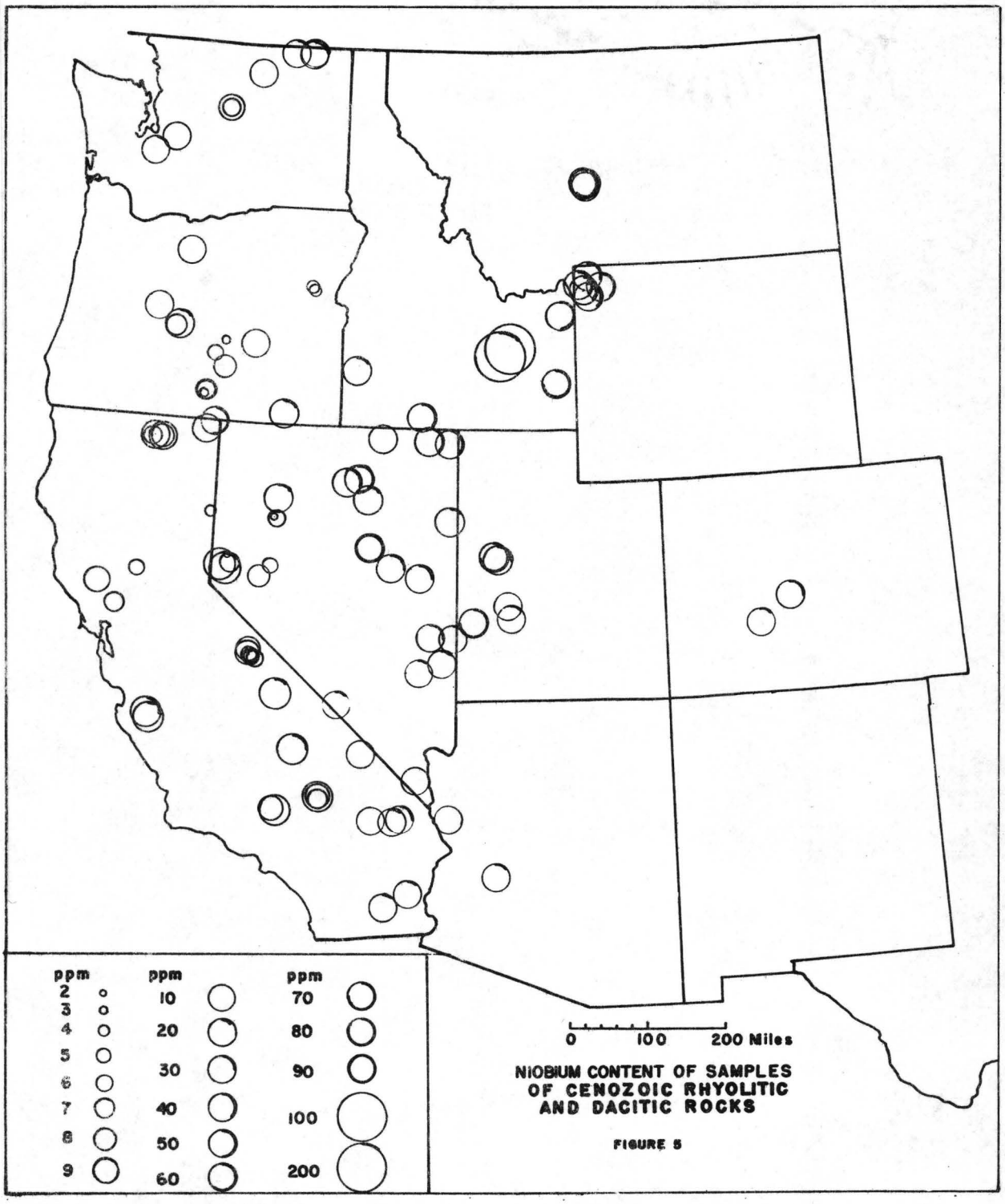
The distribution of niobium resembles that of uranium, as is suggested by the relatively high correlation coefficient. The highest values, and greatest dispersion of values, are found in the Shoshone province, where one value as high as 200 ppm was found. This highest value was found in an obsidian from Big Butte, Butte County, Idaho. The next highest value, 100 ppm, was found in a rhyolite from East Butte, Bingham County, Idaho, a few miles east of the rock with the highest niobium content. These rocks were regarded by Stearns (1938, p. 35) as of Miocene (?) age. The lowest mean and maximum are found in the Shahaptin province. The Cascade and Coastal provinces and Mountain Border subprovince are rather similar; the Mohave subprovince appears to have a slightly higher mean, and relatively small dispersion, but the number of analyses available for study is too few to be certain of this. The positions of the various analyzed samples, and the values found, are indicated in figure 5, and the distribution of the various analytical values, by provinces, is shown in table 8. The proportion of analyses that are above the mean differs significantly from the proportion of the total number that are above the mean only for the Shoshone province, which has a higher number. The Shahaptin province has less than the average number of analyses below the level of the mean, but the difference only approaches statistical significance.

The arithmetic mean (20.95) found above is closely comparable to that determined by Rankama (1948, p. 13) of 20 ppm in granites, and less than the 30 ppm reported by Goldschmidt (1937, p. 655) from granites. Both authors found far more niobium in nepheline syenites than in granites.

The relationship of uranium to niobium is indicated by the distribution of the points plotted in figure 5a.

Lanthanum

The distribution of lanthanum appears, at first glance at the map, figure 6, to be one characterized by a wide dispersion of the values. The mode is somewhat higher in the Shoshone province than in the others, and perhaps slightly lower in the Cascade province. The Mountain Border subprovince and Shahaptin province appear to have slightly greater percentage of rocks with lanthanum contents below the threshold

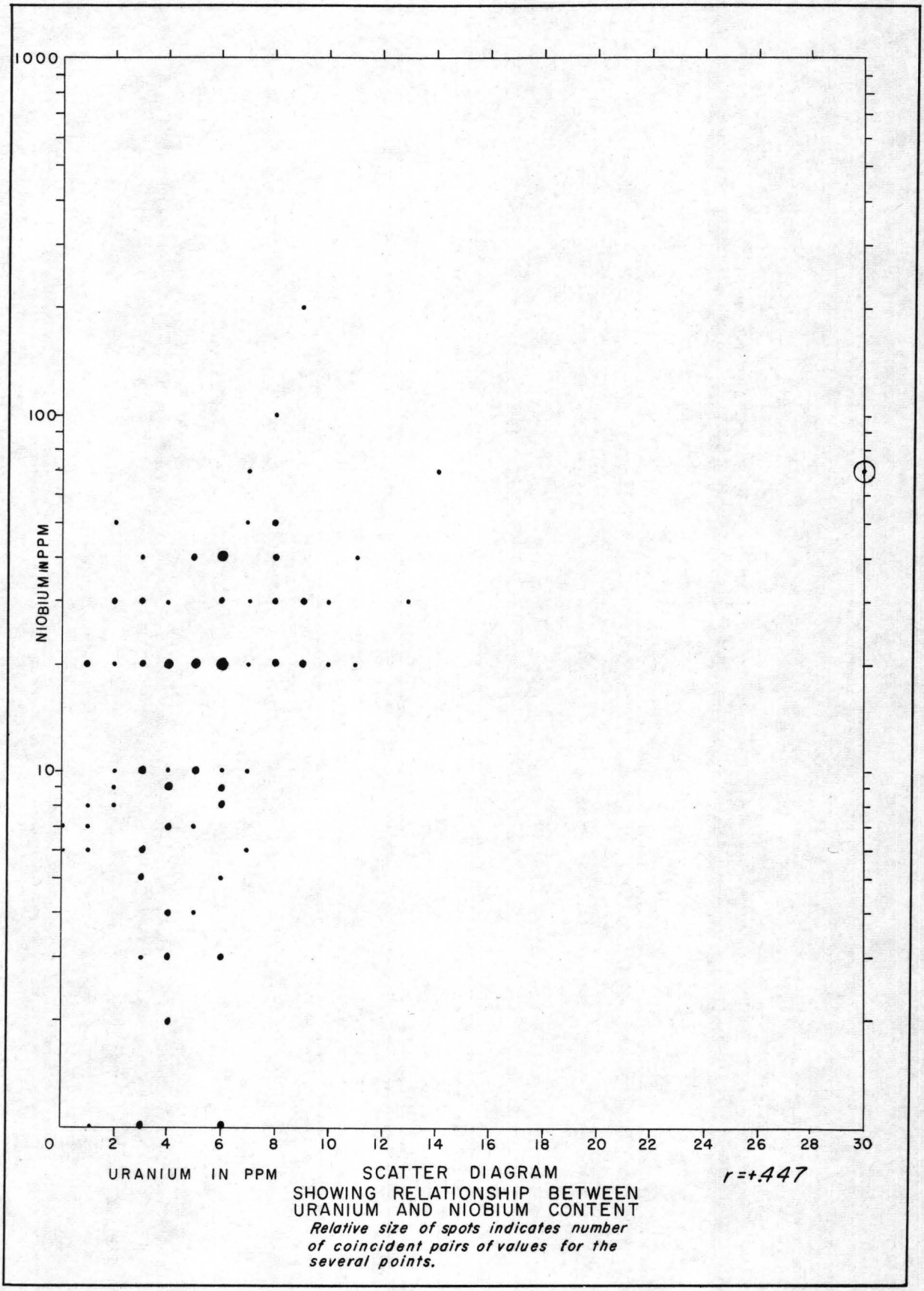


NIOBIUM CONTENT OF SAMPLES OF CENOZOIC RHYOLITIC AND DACITIC ROCKS

FIGURE 5

Table 8. --Distribution of niobium, with respect to province and content, in 112 rhyolitic and dacitic rocks.

Content (ppm)	PROVINCE: Ute (Mohave)	Ute (Yuma)	Ute (Mountain Border)	Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
0				2	2			4	
2							2	2	4
3			1			2		3	9
4				1		2		3	12
5			1			1	1	3	15
6			2	2		1	1	6	36
7			1	1	1	1	1	5	35
8				1		1	1	3	24
9			4	1	1		1	7	63
10	4		1	6		2	2	15	150
20	5	3	3	4	2	1	9	27	540
30	1		1	2	1		9	14	420
40							11	11	440
50							4	4	200
60									
70							3	3	210
80									
90									
100							1	1	100
200							1	1	200
Sum	10	3	14	20	7	11	47	112	2458
Mean									20.95
No. above mean	1	0	1	2	1	0	29	34	

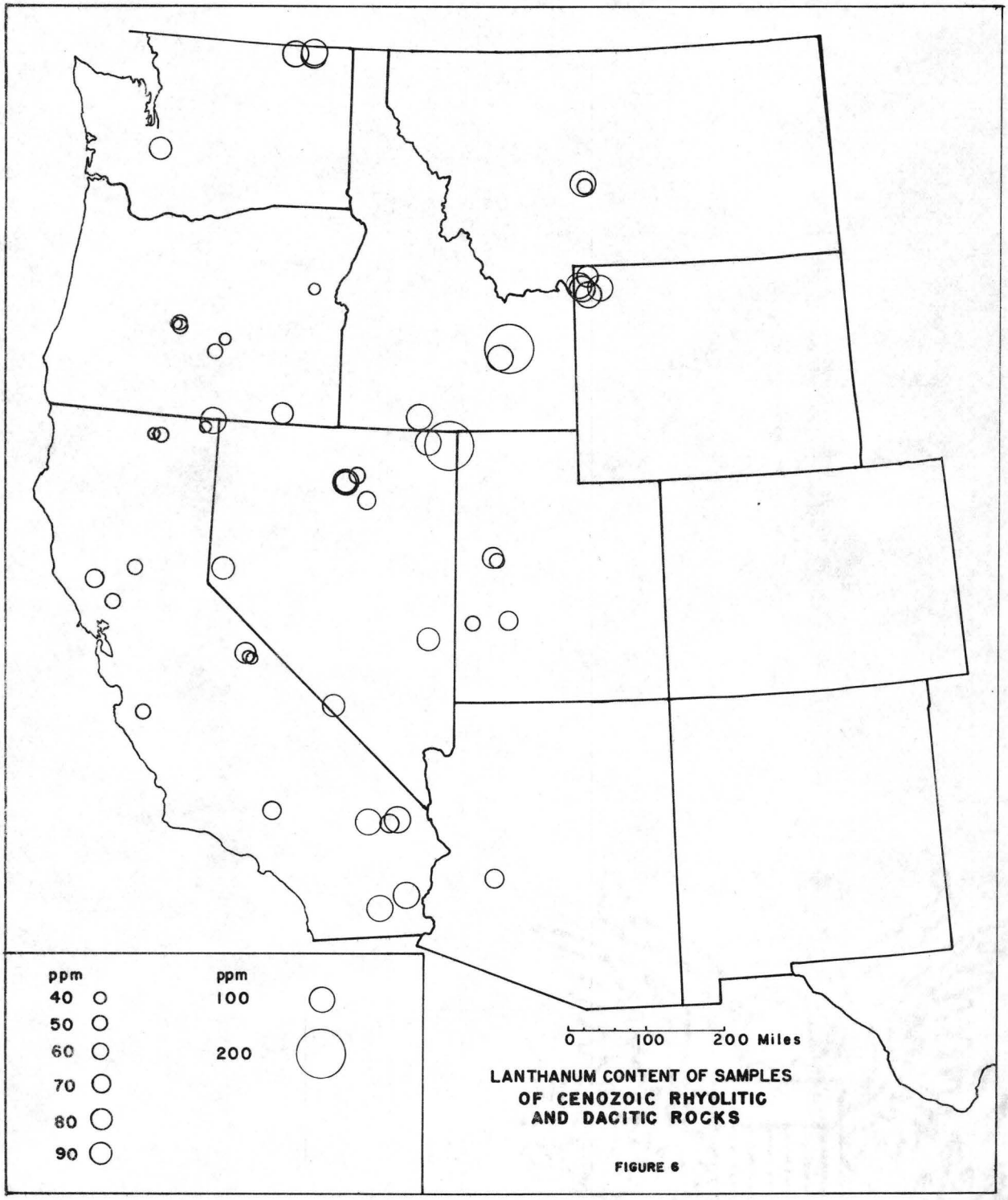


SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND NIOBIUM CONTENT

Relative size of spots indicates number of coincident pairs of values for the several points.

FIGURE 5a

GPO 837925



LANTHANUM CONTENT OF SAMPLES
OF CENOZOIC RHYOLITIC
AND DACITIC ROCKS

FIGURE 6

of sensitivity. It might be noted that while the mean of the values found, for 112 determinations, is 41.2 ppm, the mean, if a value of 20 ppm were assigned to each of the 55 determinations that are below the threshold, would be 51 ppm. This last is believed to be closer to the true value. The distribution of the various analytical values, by provinces, is shown in table 9. As indicated by the last line, only the values for the Shahaptin province even approach significance. The relationship between uranium and lanthanum is indicated by the distribution of points in figure 6a.

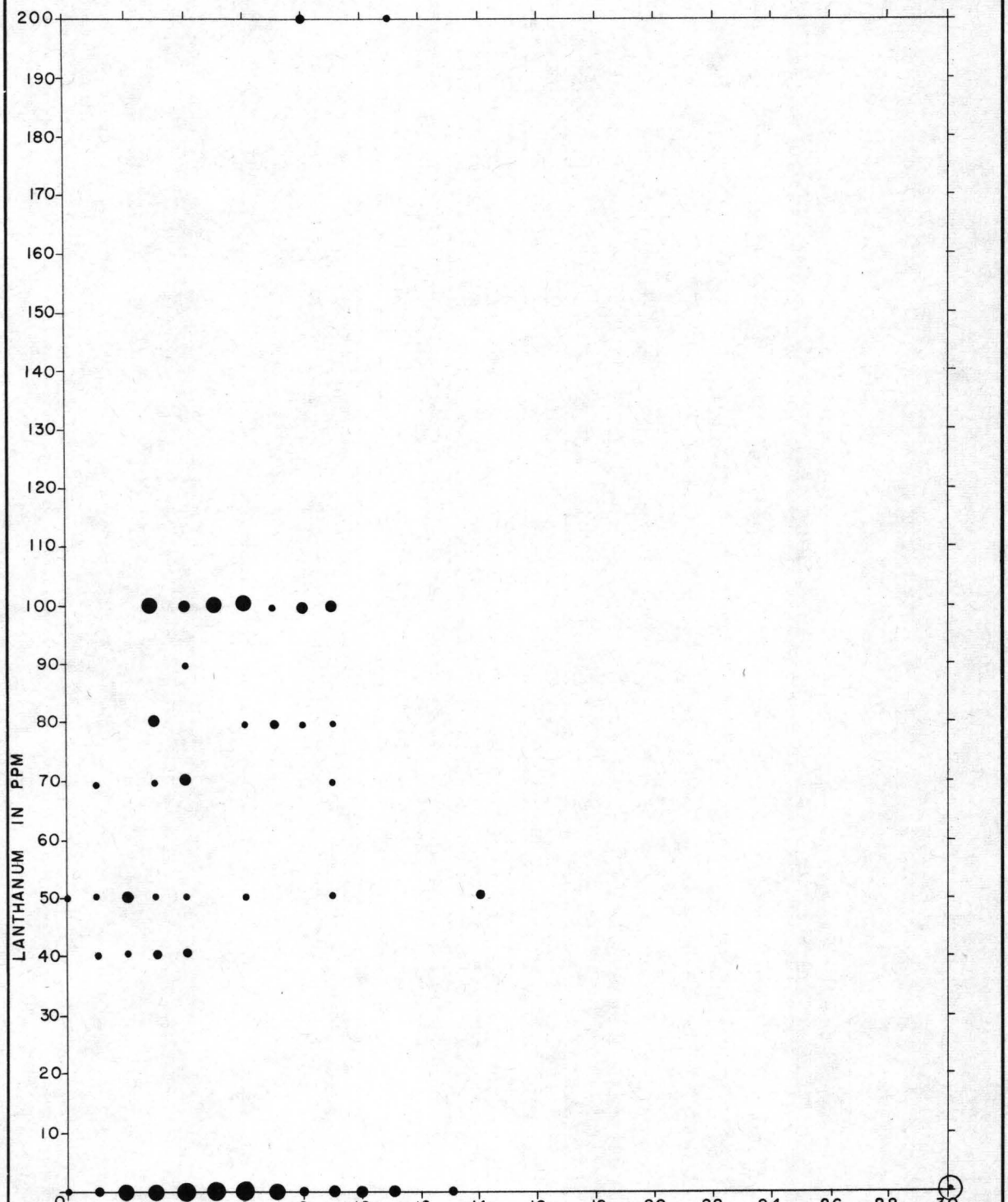
The distribution of lanthanum is explained by Rankama and Sahama (1950, p. 525) in part as a result of the separation of La^{3-} by the incorporation of that ion in the lattice of potash feldspar. They report (Rankama and Sahama, 1950, p. 528) a range of 43 to 60 ppm of lanthanum in granites, and 430 ppm in nepheline syenites. The mean content of lanthanum (41.2 ppm) found in this investigation is comparable with the means reported for granitic rocks by Rankama and Sahama. Somewhat higher amounts of lanthanum were found in granophyre associated with basic rocks by Wager and Mitchell (1951, p. 129-208).

Lead

Lead, as is well known, readily substitutes for potassium in the potash feldspar lattice. Inasmuch as most of the potash is relegated to the residual magma, and hence is higher in rhyolites and syenites than in more basic members of a differentiation series, it is to be expected that lead, since it is not readily accepted the lattices of the earlier-formed minerals, would also be relegated to the residual magma and would be as much concentrated in rhyolites and dacites as in granites and granodiorites. Although the values for lead show relatively little dispersion, apparently there are significant provincial differences, which are expressed by the distribution of symbols on figure 7, and also by the distribution of the several values in table 10. Of the several provinces, the Shoshone province, as shown by the chi-squared test, is the only one in which the percentage of analyses above the level of the mean (24.4 ppm) is significantly different from that for the whole group of analyses. The values for the Shahaptin province are significantly below those for the whole group of analyses.

Table 9.--Distribution of lanthanum, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
	Ute			Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
0	6		10	8	4	8	19	55	
40			2	3		2		7	280
50				5	2	1	3	11	550
60							1	1	60
70	1	1	1		1		2	6	420
80	1		1	1			5	8	640
90							3	3	270
100	2	2		3			11	18	1800
200							3	3	600
Sum	10	3	14	20	7	11	47	112	4620
Mean									41.2
No. above mean	4	3	2	9	3	1	28	50	
Expectation:	4.46	1.34	6.25	8.93	3.12	4.91	21		
Deviation:	-.46	+1.66	-4.25	+.07	-.12	-3.91	+7.0		
Contribution to χ^2	0.05	2.05	2.88	0.0005	0.004	3.1	2.33		
P						8%			



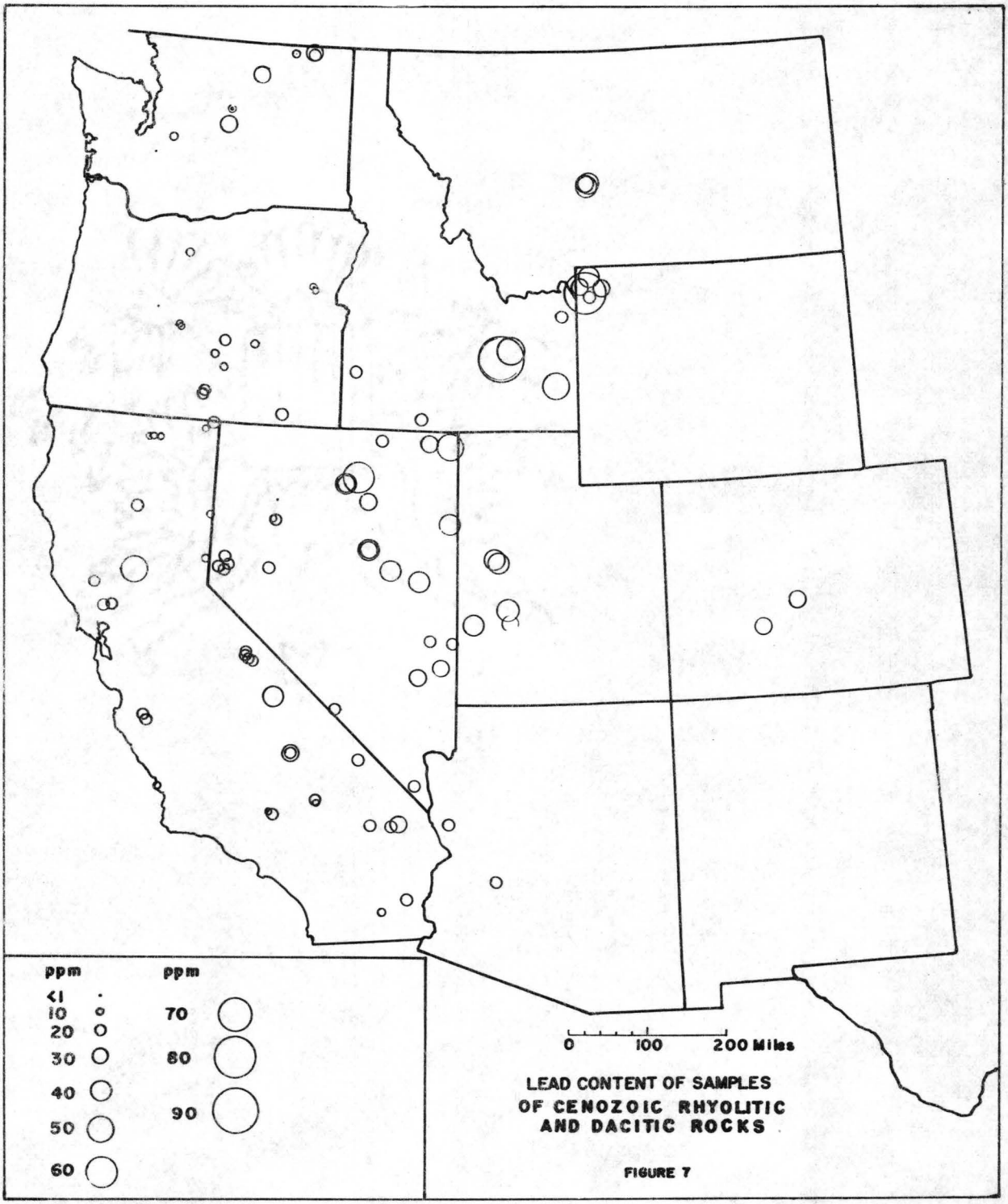
SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND LANTHANUM CONTENT

Relative size of spots indicates number of coincident pairs of values for the several points.

$r = -.412$

FIGURE 6a

GPO 837925



LEAD CONTENT OF SAMPLES
OF CENOZOIC RHYOLITIC
AND DACITIC ROCKS

FIGURE 7

Table 10.--Distribution of lead, with respect to province and content, in 112 rhyolitic and dacitic rocks.

	PROVINCE								
	Ute			Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
Content (ppm)	(Mohave)	(Yuma)	(Mountain Border)						
2				1				1	2
4							1	1	4
8				1				1	8
9				3				3	27
10		1	2	11		6	1	21	210
20	6	2	9	1	7	5	13	43	860
30	4		2	3			11	20	600
40			1				15	16	640
50							3	3	150
60							1	1	60
70									
80							1	1	80
90							1	1	90
Sum	10	3	14	20	7	11	47	112	2731
Mean									24.4
No. above mean	4	0	3	3	0	0	32	42	
Expectation:	3.75	1.12	5.25	7.5	2.62	4.13	17.6	42	
Deviation:	+.25	-1.12	-2.25	-4.5	-2.62	-4.13	+14.4	0	
Contribution to X^2	0.02	1.12	0.96	2.69	2.63	4.13	11.9		
P						4.2%	<0.1%		

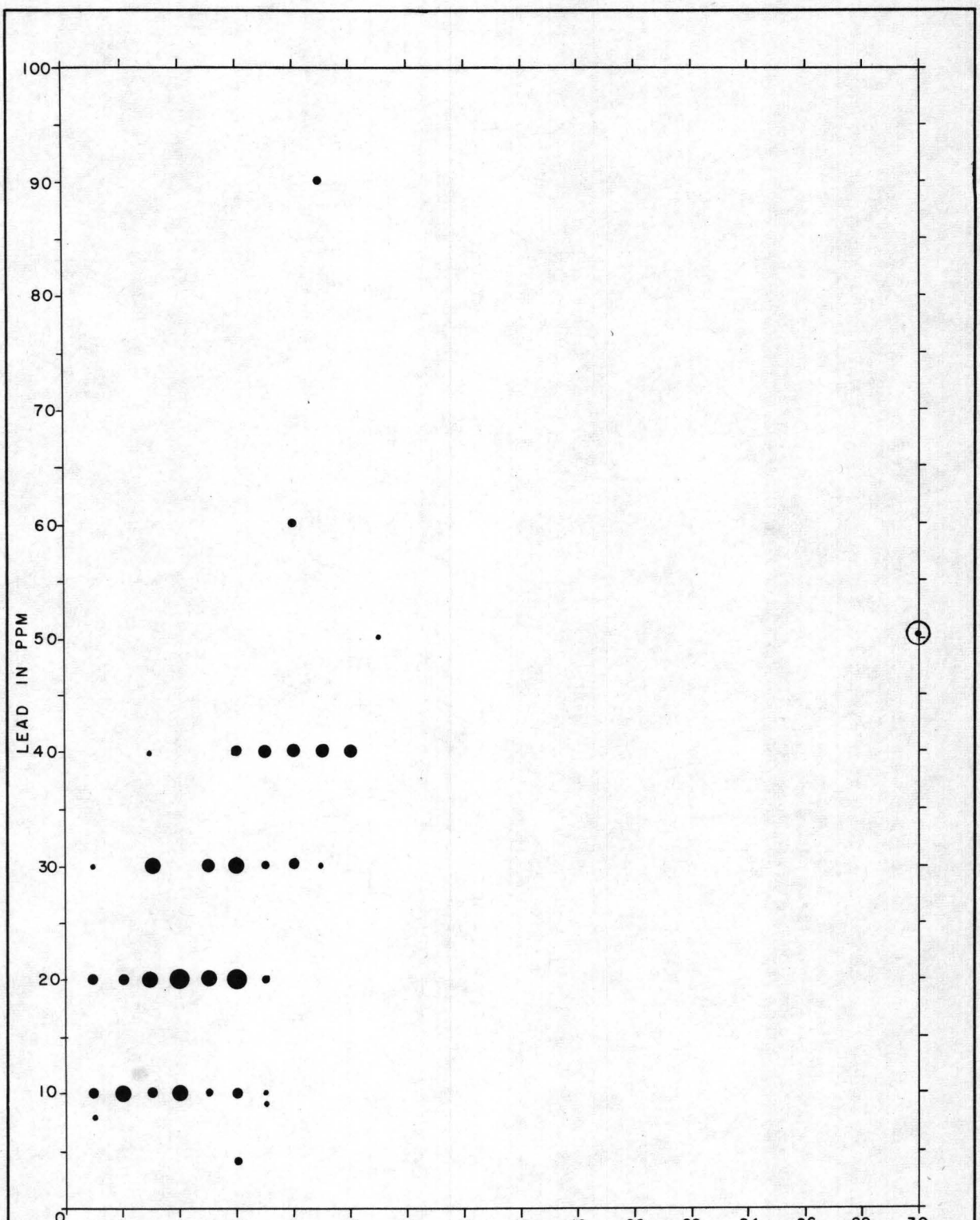
The relation between the uranium and lead values for the analyzed rocks is indicated by the distribution of points in figure 7a.

As indicated by the table, the highest mean and the highest individual values are found in the Shoshone province. The next highest mode is apparently in the Mountain Border subprovince, though the differences between this subprovince, on the one hand, and the Coastal province and the Mohave subprovince, on the other, are perhaps not significant. The Shahaptin province is apparently somewhat below these, and the Cascade province probably the lowest of all in lead content.

The arithmetic mean found in this investigation is comparable with that (30 ppm) found in granitic rocks (Hevesy, Hobbie, and Holmes, 1931, p. 1038). Sahama (1945) found lead ranging from 9 to 27 ppm in the granitic rocks of southern Finnish Lappland. Sandell and Goldich (1943) found an average of 19 ppm in some American granitic rocks. The results reported here suggest that these means, if computed from analyses made on rocks from widely separated localities, may serve to conceal important provincial differences.

Zirconium

The content of zirconium found in the analyses reported herewith ranges from 20 to 700 ppm. The regional distribution, as shown by the map (fig. 8), resembles that for niobium and beryllium, with certain differences. The greatest range is shown by the Shoshone province, followed closely by the Cascade. The highest mean, however, is that of the Cascade province (201 ppm) followed closely by the Yuma subprovince (197 ppm--probably not significant, because of the small number of samples) and the Shoshone (162). The lowest values for the mean are those of the Mountain Border subprovince (73.8), the Shahaptin (76.4), and Mohave (83). The overall mean, as shown in table 11, is 140 ppm. Of all the values shown, only the Cascade province has a number of analyses above the level of the mean which differs very significantly, as shown by the chi-squared test, from that of the group of analyses as a whole. The number of analyses above the mean from the Mohave sub-province and the Shahaptin province is less than that for the whole group of analyses by amounts which approach the 5 percent level of significance.



SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND LEAD CONTENT

$r = .159$

Relative size of spots indicates number of coincident pairs of values for the several points.

FIGURE 7a

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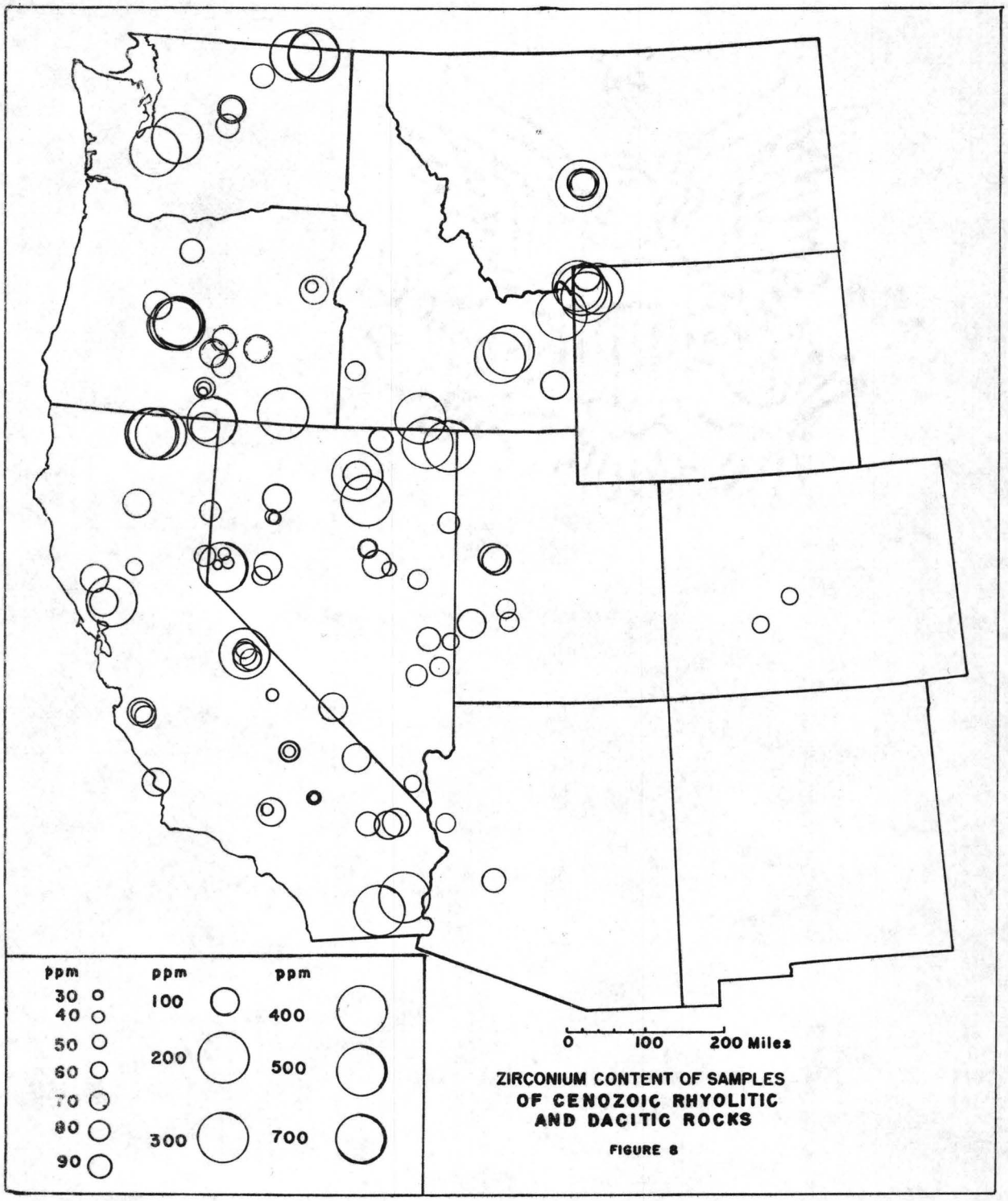


ZIRCONIUM CONTENT OF SAMPLES
OF CENOZOIC RHYOLITIC
AND DACITIC ROCKS

FIGURE 8

Table 11.--Distribution of zirconium, with respect to province and content, in 112 rhyolitic and dacitic rocks.

Content (ppm)	Ute (Mohave)	Ute (Yuma)	Ute (Mountain Border)	Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
20									
30			1			1	1	3	90
40			4			1	3	8	320
50			1			1	2	4	200
60	2			1			1	4	240
70	2		2			1	5	10	700
80	1		2	1	2	1	1	8	640
90	1	1	1	2		3	2	10	900
100	4		2	4	4	3	12	29	2900
200		1	1	9	1		13	25	5000
300		1					1	2	600
400				2			4	6	2400
500							2	2	1000
600									
700				1				1	700
Sum	10	3	14	20	7	11	47	112	15690
Mean									140
No. above mean	0	2	1	12	1	0	20	36	
Expectation:	3.22	0.97	4.5	6.43	2.25	3.54	15.1	36	
Deviation:	-3.22	+1.03	-3.5	+5.57	-1.25	-3.54	+4.9	0	
Contribution to χ^2_P	3.22	1.09	2.72	4.82	0.69	3.54	1.59		
	7.7%			1.6%		6.4%			

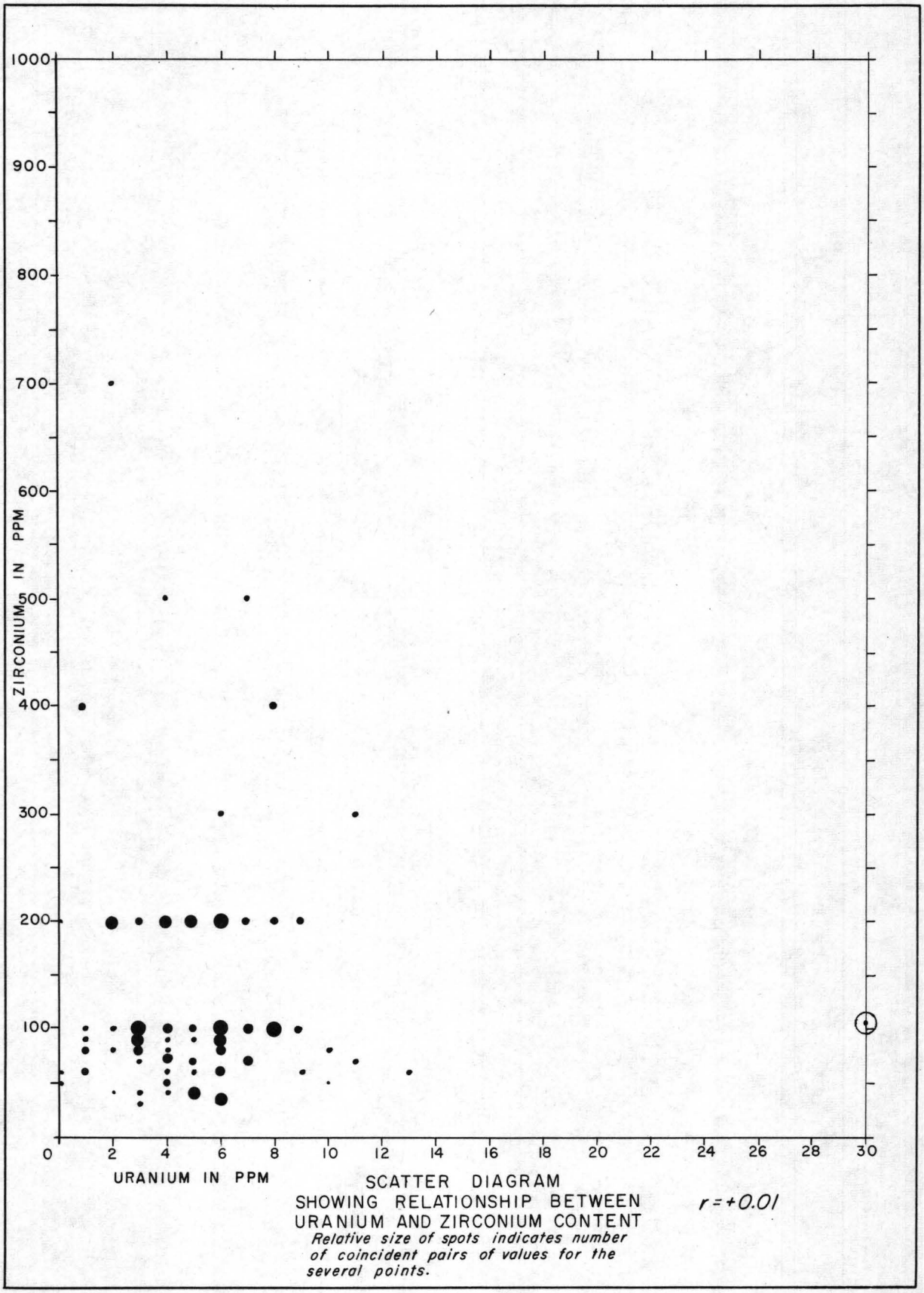
The relationship of zirconium to uranium is indicated by the distribution of points in figure 8a. The correlation coefficient is surprisingly low, considering the known association of zirconium with granitic rocks, and the relatively high uranium content of granitic zircon.

Lithium

The content of lithium reported in the analyses listed in this report ranges from a trace to 300 ppm. The highest values are in analyses of rocks from the Shoshone and Coastal provinces, as indicated in table 12, but the chi-squared test, applied on the basis of the number of analyses above the level of the mean (45.2 ppm) indicates that only the difference shown by the Mohave subprovince approaches the 5 percent level of significance, and that there are about 7 chances in 100 that the number of analyses above the level of the mean found in that province could be reached by chance. The distribution of the various analyzed rocks, and the values found, are indicated in figure 9.

The relationship between lithium and uranium is shown by the distribution of the points in figure 9a. Although lithium is an element commonly thought of as concentrating in pegmatites, it has been shown (Goldschmidt, 1954, p. 129-130) that lithium will be admitted to positions occupied by Mg^2, Fe^2, Al^3, or Ti, in late crystallizates. According to Goldschmidt, this is accomplished by the concurrent substitution of Li^1 and Fe^3 for $2Mg^2$. This process might account for the removal, in the course of differentiation, of part of the lithium, in the mica and hornblende crystals, where conditions were such that crystallization differentiation could take place. Such a partial removal would explain a deviation of the behavior of lithium from that of niobium, beryllium and uranium.

The amounts of lithium found in the rocks collected for this project are considerably less than those found in a composite sample of 9 granites from Saxony, (Goldschmidt, 1954, p. 132), which were 1000 to 1500 ppm Li_2O. An average of 8 obsidians from various parts of the world gave 98 ppm, while 14 liparites from Italy, averaged 73 ppm. None of the provinces outlined in this report appears to be especially lithium-rich.



SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND ZIRCONIUM CONTENT
Relative size of spots indicates number of coincident pairs of values for the several points.

$r = +0.01$

FIGURE 8a

GPO 837925

Table 12.--Distribution of lithium, with respect to province and content, in 112 rhyolitic and dacitic rocks.

$\bar{X}$ = 45.2 ppm

Content (ppm)	PROVINCE: Ute (Mohave)	Ute (Yuma)	Ute (Mountain Border)	Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
0-Tr.						1		1	0
1							1	1	1
2				1				1	2
3							1	1	3
4				3				3	12
5		1		2			3	6	30
6							1	1	6
7				2	1			3	21
8						1		1	8
9								0	0
10	2		2	2			1	7	70
20	5		4	2		1	6	18	360
30	1	1		2		2	2	8	240
40	2		3	1	1	5	11	23	920
50		1	2	2			2	7	350
60				1	1	1	8	11	660
70			2	2			1	5	350
80			1		1		1	3	240
90							1	1	90
100					1		5	6	600
200					2		2	4	800
300							1	1	300
Sum	10	3	14	20	7	11	47	112	5063
No. above mean	0	1	5	5	5	1	21	38	
Expectation:	3.39	1.02	4.75	6.79	2.38	3.73	15.92	38	
Deviation:	-3.39	-0.02	+0.25	-1.79	+2.62	-2.73	+5.08	0	
Contribution to χ^2	3.39	0	0.01	0.472	2.96	2.0	1.58		
P	7%								

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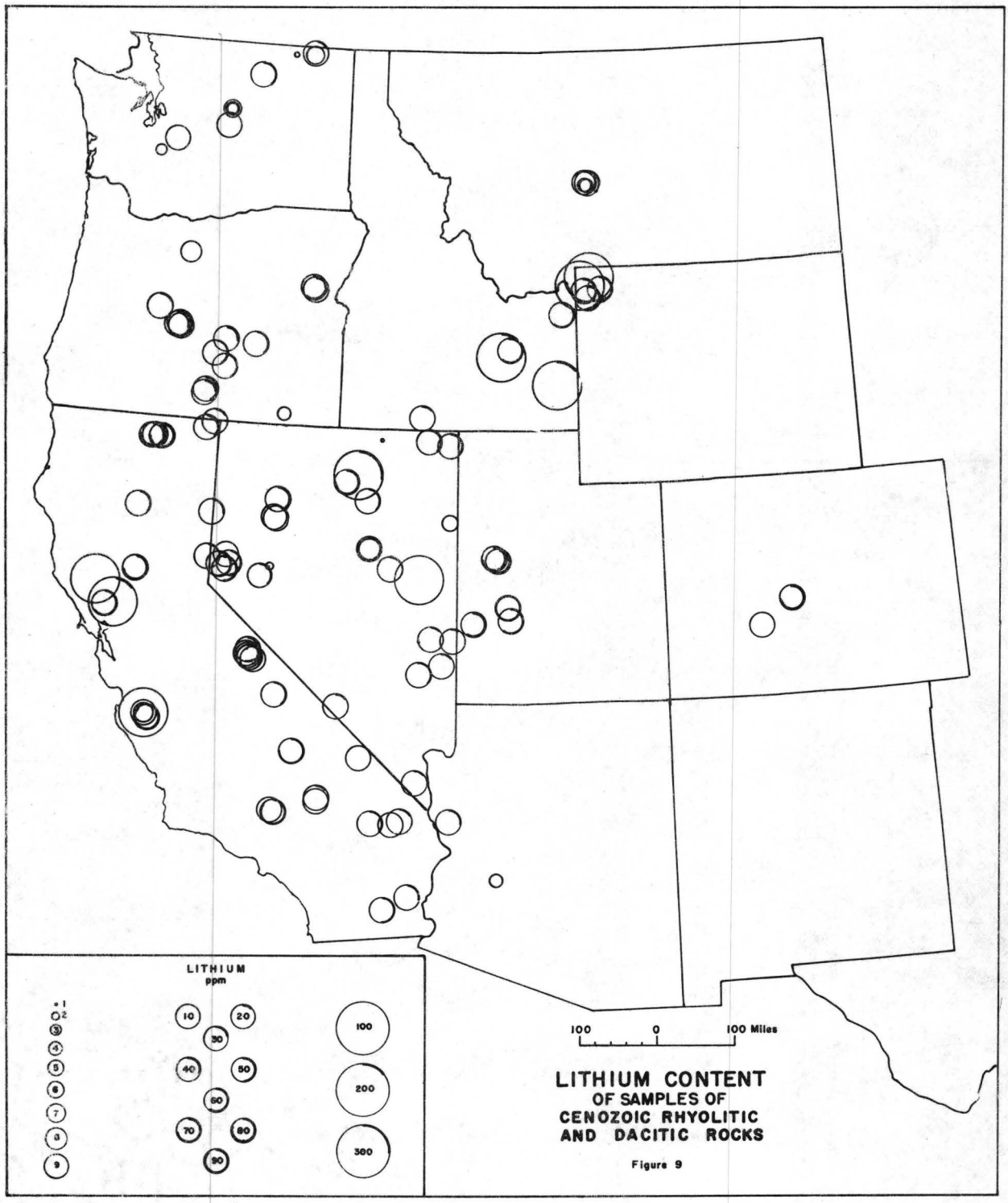
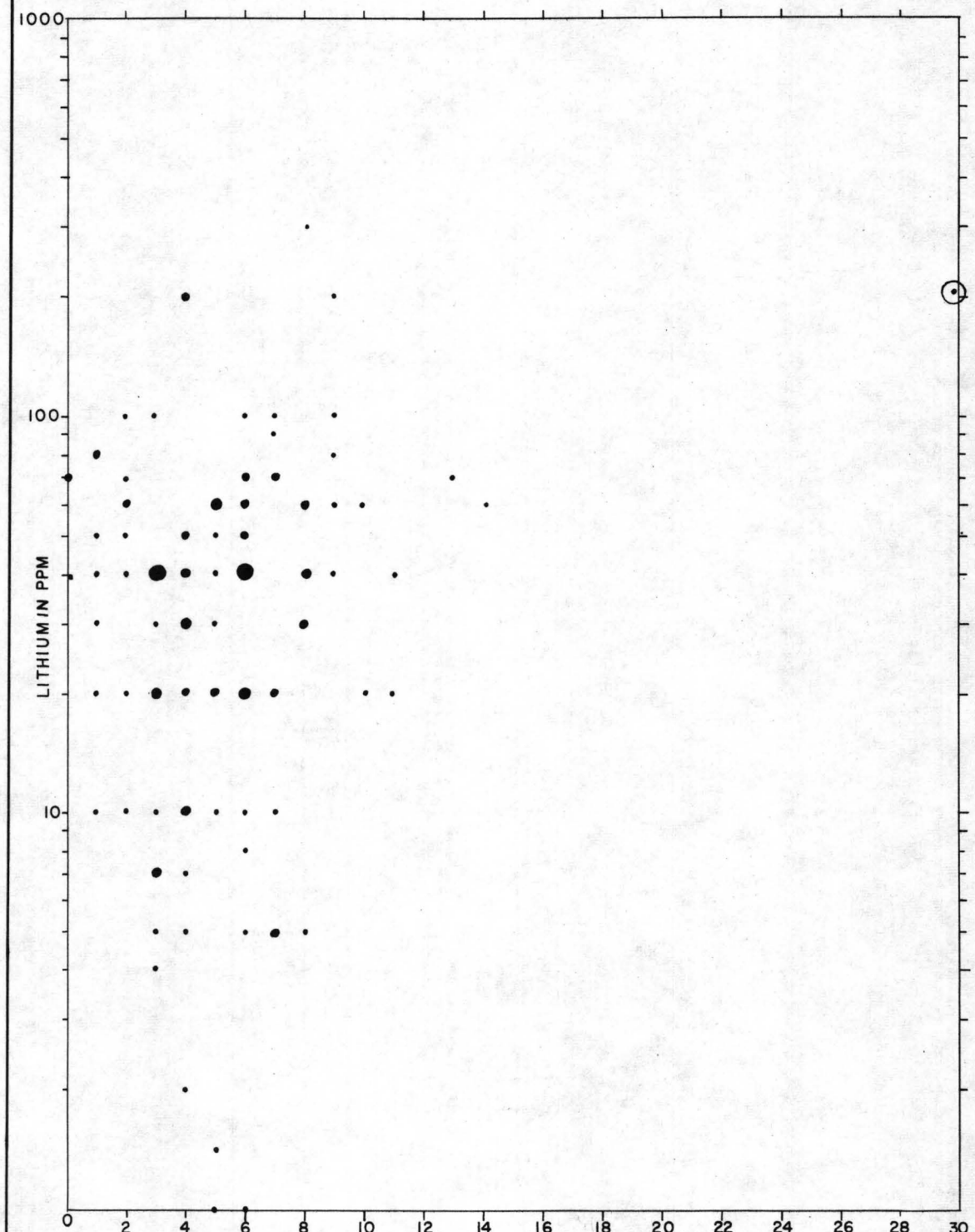


LITHIUM CONTENT
OF SAMPLES OF
CENOZOIC RHYOLITIC
AND DACITIC ROCKS

Figure 9



SCATTER DIAGRAM
SHOWING RELATIONSHIP BETWEEN
URANIUM AND LITHIUM CONTENT

Relative size of spots indicates number of coincident pairs of values for the several points.

$r = +.317$

FIGURE 9a

GPO 837925

Fluorine

The fluorine results, as shown by table 13, cover a wide range of values, from a minimum of about 5 parts per hundred thousand to a maximum of 430 parts per hundred thousand. All the values from 140 to 430 were confined to rocks from the Shoshone province. The distribution of the analyzed samples and the values found are indicated in figure 10. The relationship of the uranium to fluorine is shown in figure 10a. The correlation between uranium and fluorine is higher than that between uranium and any other element for which analyses were made. This is graphically expressed in figure 10a. The significance of the departures from the average proportion of anlyses above 690 ppm is shown by the probability levels of 0.8 percent for the Shoshone province, and 6 percent for the Cascade province. The fact that the pattern of distribution is rather similar to that for niobium and beryllium, as well as uranium, suggests that the fluorine is concentrated in residual fluids, which implies that it is not taken up in early-formed minerals. Koritnig (1951, p. 89-116) has recently shown that the attribution of all fluorine in igneous rocks to apatite is not valid, as much of the fluorine is in mica and hornblende, as well as in fluorite, and further (p. 94) that volcanic rocks seldom show enough fluorine-bearing minerals to account for all the fluorine, but the form in which the fluorine is present is not known. In a liparite from Eisenback, Hungary, Koritnig found 0.075 percent fluorine, and in the trachyte of the Drachenfels, 0.083 percent; in neither rock were sufficient fluorine-bearing minerals present to account for the fluorine. Glass was also absent.

POSSIBLE CAUSES OF NON-RANDOM VARIATIONS OF REGIONAL EXTENT

Types of regional variation

Two types of non-random variation of regional extent may be discerned in the distributions mapped. One of these may be described as consisting of apparently random fluctuations of minor-element content about a given value within broad areas that are relatively sharply delimited from neighboring areas, which are in turn characterized by rocks showing apparently random fluctuations about a different value of concentration. The other type of non-random variation consists of progressive, gradational changes in minor

Table 13. --Distribution of fluorine, with respect to province and content, in 112 dacitic and rhyolitic rocks.

Content Parts per 100,000	PROVINCE Ute (Mohave)	Ute (Yuma)	Ute (Mountain Border)	Cascade	Coastal	Shahaptin	Shoshone	Sum	Product
0-9						3		3	
10-19				3	2	2	6	13	
20-29	1	1	3	2		1	6	14	
30-39	1		2	4	2	2	5	16	
40-49	2		1	3		1	2	10	
50-59	5	1		4	3	2	3	18	
60-69			3	3			2	8	
70-79			1				2	3	
80-89			1				2	3	
90-99							5	5	
100-109		1						1	
110-119			1				3	4	
120-129			2	1			4	7	
130-139	1							1	
140-149							1	1	
190							1	1	
210							1	1	
250							1	1	
280							1	1	
290							1	1	
430							1	1	
Sum	10	3	14	20	7	11	47	112	7314
Mean									65.4
No. above 680	1	1	5	1	0	0	23	31	
Expectation:	2.77	0.8	3.08	5.54	1.94	3.05	13	31	
Deviation:	-1.77	+0.2	+1.12	-4.54	-1.74	-3.05	+10.0	0	
Contribution to χ^2	1.13	0.05	0.323	3.72	1.94	3.05	7.7		
P				6 %			0.3 %		

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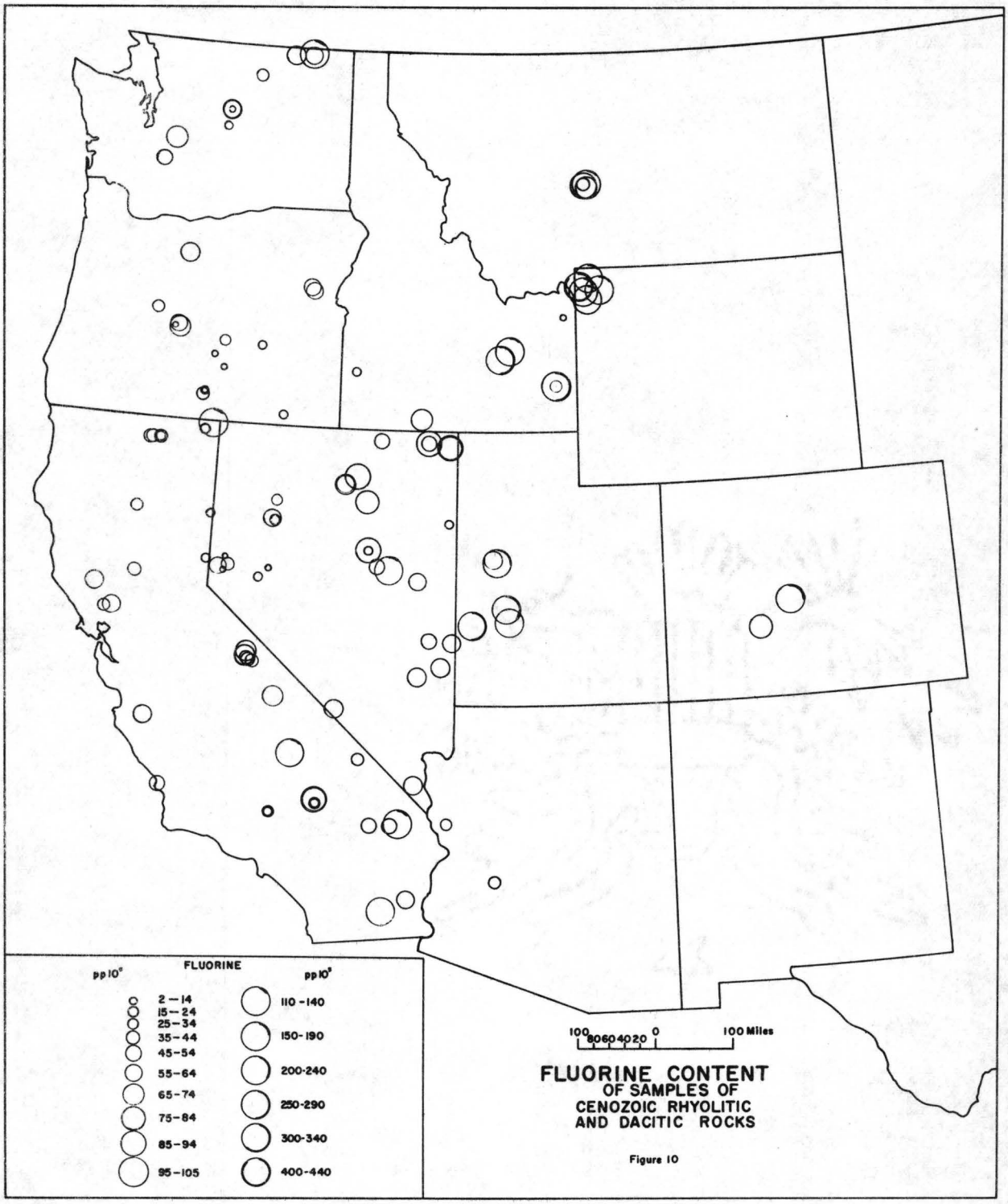

FLUORINE CONTENT OF SAMPLES OF CENOZOIC RHYOLITIC AND DACITIC ROCKS

Figure 10

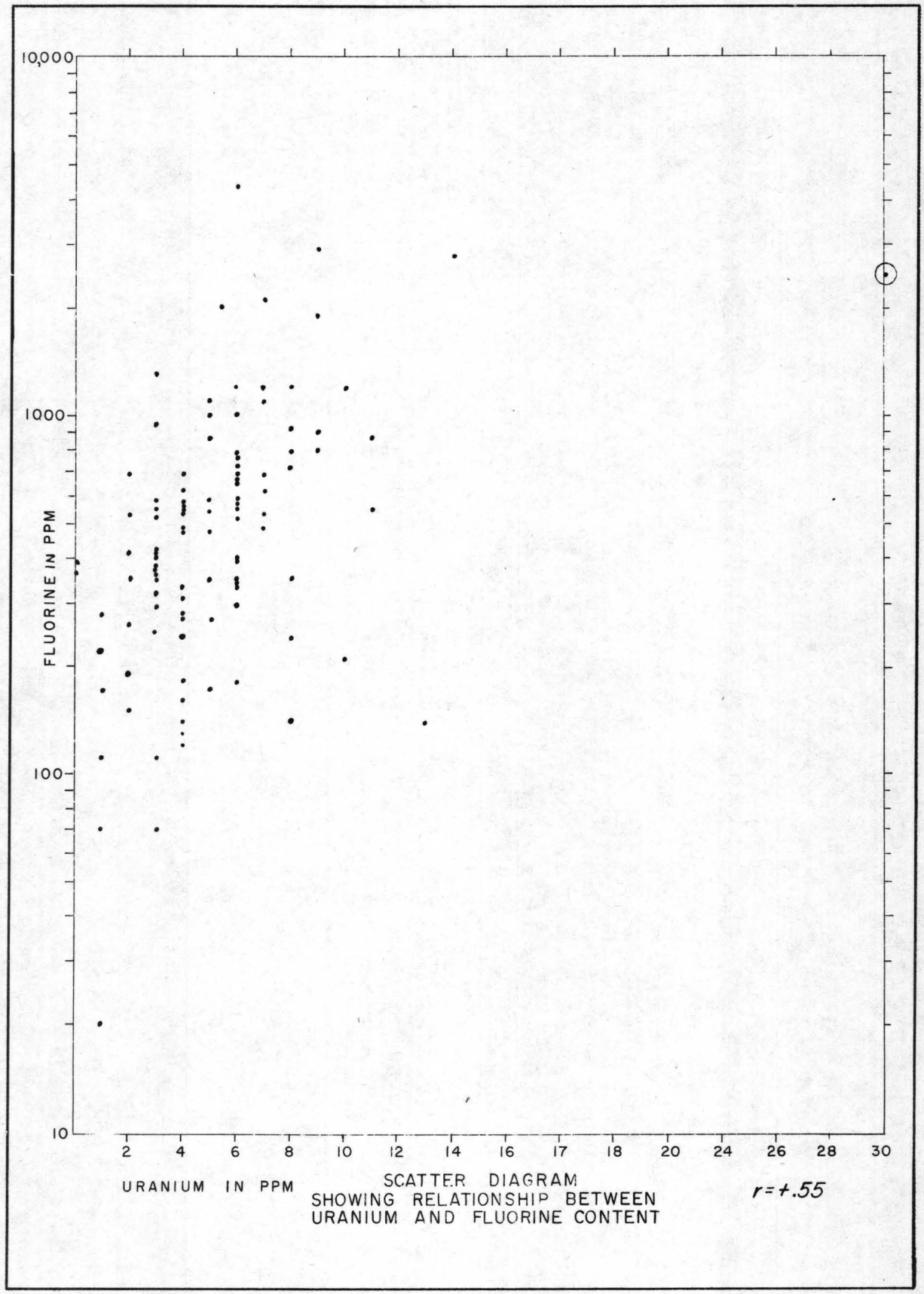

FIGURE 10a

GPO 837925

element content within a broad area. This latter is apparently what Pirsson called a "regional progression of types" (Iddings, 1913, p. 467). Both types of variation may be present in the Cordilleran area, some being effective for some elements, others for other elements. It should be noted that both types of variation may imply compositional gradients; samples may not be available, when the boundaries of provinces are delimited, to permit discrimination between provinces separated by a compositional discontinuity, and those separated by a relatively steep compositional gradient.

Origins of regional variation

In the discussion that follows, initial uniformity in the granitic shell of the earth will be assumed. It is true that regional differences, of either of the types discussed above, may have been present in the crust of the earth at the time of formation of the oldest observable rock. This possibility, if its truth were demonstrated, would still be some distance away from a demonstration of initial non-uniformity.

Subsequent lateral variation in the concentration of the rarer elements at accessible levels of the crust may arise in either of two ways: by lateral variation in the effectiveness of vertical transport, or by horizontal transport. Horizontal transport may be either endogene, operating within the crust, or exogene, operating surficially.

Exogene horizontal transport

Processes of this type are relatively familiar to us, because they are those of weathering, erosion, and sedimentation. Recently Cady, McKelvey, and Wells (1950, p. 1447) have pointed out the close relationship that exists between mineral deposits, particularly syngenetic deposits in sedimentary rocks, and the sedimentary facies and geotectonic environment in which the rock was deposited. A reasonable argument can be made out for attributing to this cause any particular example of horizontal variation, where it can be shown that the element in question is concentrated during the minor cycle, in sedimentary rocks characteristic of a particular facies, and that the area in which a particular element is concentrated coincides fairly closely with the distribution of the favorable sedimentary facies. In this study, the set of elements that seems most closely associated is characteristically a pegmatitic one, that is, the set of elements

characteristic of granitic rest magmas, rather than those characteristic of any particular sedimentary facies. The provincial boundaries that seem to express best the minor-element relationships are quite discordant with those of the major geosynclinal troughs of the Cordilleran region. To some extent, of course, this lack of accordance may be a reflection of the somewhat restricted distribution of Cenozoic rhyolitic and dacitic rocks, but the province with the most distinctive chemical characteristics and the best-defined boundary, the Shoshone province, is the one that shows the greatest discordance with past geosynclinal trends.

Endogene horizontal transport

Most of the geologists who have argued the efficacy of diffusion in the formation of igneous-appearing rocks have been content to apply the argument to movement of ions and molecules predominantly in the vertical sense. The many quantitative objections to the possible efficacy of diffusion through solid rocks, or even in the intergranular fluid, apply with much greater force to any argument for diffusion predominantly in the horizontal sense, over distances at least two orders of magnitude greater. Stress conditions in the crust apparently make any extensive lateral displacement of magma impossible. Recently, however, Gilluly (1952, p. 1330) has suggested subcrustal transport of sialic material as a possible explanation for the high altitude of the Colorado Plateau. If this explanation is a feasible one, it implies the possibility of differential transport, and the establishment of regional gradients in composition, because the remelting is almost sure to be, in part at least, differential. This mechanism seems to the writer to have the best chance of explaining progressive gradational changes in composition of the igneous rocks.

Lateral variation in effectiveness of vertical transport

Rankama (1946, p. 16) has adduced evidence that certain elements, viz., Li, Be, Rb, Cs, Ba, rare earths, Ta, and Pb, tend to be more highly concentrated in younger granites, at least within the area he studied. The evidence for a change in the last three is restricted to the contrasts within the group of Precambrian granites. There appears to be a greater change from the oldest Archean to the youngest Precambrian than in all subsequent time. Rankama attributes the change to the repeated "sweating out" and upward migration of palingenetic magmas, successively more and more enriched in the elements that

enter least readily into the earlier formed minerals. These are largely the elements for which regional differences in concentration have been found in this study. If the mechanism suggested by Rankama is an effective one, then there should be set up, within the sialic crust, a vertical concentration gradient in respect of the elements for which this process is effective, with the concentration of these elements being highest at that level in the crust, presumably a relatively high one, where transport is effectively halted. It is not necessary to envision precisely equal concentrations at equal depths in the crust; regions in which, because of tectonic conditions, migration upward is especially favored might be regions in which a higher level of concentration of the elements in question would be reached at a given depth than would be attained elsewhere at equal depths. Given such differences, then the eruption of silica-rich quasi-residual volcanic rocks that have been generated at loci within the crust having regionally delimited differences in minor element content should result in corresponding differences in the composition of the volcanic rocks. For the most part, it will be hard to obtain direct evidence that this proposed mechanism for the production of provincial differences in igneous rock composition is actually effective. Indirect evidence may be obtained by a study of the minor-metal content of granitic rocks exposed in extensive Precambrian terranes, with special reference to age and provincial distribution.

If the repeated generation and rise of granitic magmas in the crust are determined by large-scale tectonic features, then, to the extent that such major, through-going lineaments are reflected in the younger rocks, it may be possible to discern a relationship between the provincial boundaries and major lineaments. A comparison with the Tectonic Map of the United States (Am. Assoc. Petroleum Geologist, 1944) shows certain coincidences that may be genetically significant.

The northern boundary of the Shoshone province, as outlined on plate 1, follows the Snake River downwarp in a general southwesterly direction, and then coincides roughly with the southern edge of the Oregon fault-block mountains as far as the eastern edge of the Modoc Lava Plateau. The southern boundary of the Shoshone province includes most of the area in Nevada in which bodies of Tertiary intrusive rock are shown. The Cascade province, as drawn, includes almost all the High Cascade volcanoes of Washington and Oregon.

The extreme north-eastern portion differs somewhat in the distribution of minor elements and may well form part of a different province, but the data are too few and the evidence conflicting. The Mountain Border subprovince includes all the zone of Recent volcanics east and south of the Sierra Nevada.

A related but somewhat different mechanism may be suggested for certain of the constituents. In zones of active orogenesis, certain structures may act as conduits for fugitive and volatile constituents. Subsequent magma generation along these zones might be expected to result in assimilation of material especially high in the fugitive constituents, or the magmas could, to some extent, imbibe the volatiles directly. That some such mechanism may have operated in the case of boron is suggested by the close correlation between the distribution of high-boron glasses and the areas of faults active (?) in the Recent and late Pleistocene (Eardley, 1951, p. 454). Although many of the rocks whose analyses have been entered on this plot date back to the Miocene--e.g. the volcanic rocks of the San Benito quadrangle in California--yet, as Eardley has pointed out, activity on many of the faults began much earlier than the Pleistocene.

The contents of boron found in the extrusive rocks in this investigation, being much lower than those found in granites by Wasserstein (1951), as mentioned earlier, suggest either a regional difference, or perhaps a difference in cooling conditions. Tourmaline is a relatively common mineral in granite, but quite rare in rhyolite, nor does there appear to be any common rock-making mineral found in rhyolite in which the boron could be taken up. The contrast in boron content of rhyolite and equivalent perlite suggests that boron may be held more easily in glass than in rhyolite, but the amounts retained in granite may be greater than those held in glass. The high content of boron in saline deposits of many parts of the West may be related, in part, to the distribution of tectonic channelways, and also, and in large part, to the cooling of large amounts of magma under conditions such that boron could not be fixed in the rock, and the escaping volatile boron compounds were condensed and trapped in the closed basins characteristic of the area.

FURTHER LINES OF INVESTIGATION

The number of available analyses for the major constituents is too small to permit definite conclusions, but it is planned to study the relationships of certain selected samples and to extend the field work to eastern Arizona, New Mexico, and Texas, which will include parts of more highly uraniferous provinces.

CONCLUSIONS

The evidence presented suggests that there are significant differences in the content of uranium, boron, beryllium, niobium, lead, zirconium, lithium and fluorine in the Cenozoic rhyolitic and dacitic rocks of the Cordilleran region of the United States. It appears probable that these differences are related, directly or indirectly, to regional differences in the distribtuion of uranium, and possibly of some of the other elements, in the area concerned. If this is true, a rational explanation is available for the observed scarcity of uranium deposits in the Cascade region, and in the intermontane plateau north of Nevada. The distribution also suggests that the area shown as the Shoshone province is probably more favorable for the occurrence of deposits of uranium than other parts of the region studied thus far.

LITERATURE CITED

Adams, J. A. S., 1952, Some aspects of the geochemistry of uranium (abs.) : Geol. Soc. America Bull., v. 63, p. 1229.

American Association of Petroleum Geologists, 1944: Tectonic Map of the United States.

Bowen, N. L., 1937, Recent high-temperature research on silicates: Am. Jour. Sci., 5th ser., v. 33, p. 1-21.

Cady, W. M., McKelvey, V. E., and Wells, F. G., 1950, Geotectonic relations of mineral deposits (abs.) : Geol. Soc. America Bull., v. 61, p. 1447.

Coats, R. R., 1952, Magmatic differentiation in Tertiary and Quaternary volcanic rocks from Adak and Kanaga Islands, Aleutian Islands, Alaska: Geol. Soc. America Bull., v. 63, p. 485-514.

Davies, O. L., 1947, Statistical methods in research and production. London.

Eardley, A. H., 1951, Structural geology of North America: New York, Harper and Bros.

Fersmann, A. E., 1929, Geochemische Migration der Elemente usw., Teil 1, Abh. Prakt. Geol. Bergwirtsch. Bd. 18, p. 1-115.

Gilluly, James, 1952, Connection between orogeny and epeirogeny as deduced from the history of the Colorado Plateau and Great Basin (abs.): Bull. Geol. Soc. Am, v. 63, p. 1329-1330.

Goldschmidt, V. M., 1937, The principles of the distribution of the chemical elements in minerals and rocks: Jour. Chem. Soc., 1937, p. 655.

Goldschmidt, V. M., 1954, Geochemistry: London.

Hevesy, G. V., Hobbie, R., and Holmes, A., 1961, Lead content of rocks: Nature, v. 128, p. 1038.

Hevesy, G. V., and Würstlin, K., 1934, Die Häufigkeit des Zirkoniums: Zeitschr. anorg. allgem. Chem., v. 216, p. 305.

Holser, W. T., Warner, L. A., Wilmarth, V. R., and Cameron, E. N., 1951, Notes on the geochemistry of beryllium: Geol. Soc. America Bull., v. 62, p. 1450.

Iddings, J. P., 1913, Igneous rocks, Volume 1: New York, John Wiley and Sons.

Kaiser, E. P., and Page, L. R., 1952, Distribution of uranium deposits in the United States: U. S. Geol. Survey Circ. 220.

Koritnig, S., 1951, Ein Beitrag zur Geochemie des Fluors: Geochim. et Cosmochim. Acta., v. 1, p. 89-116.

Mason, B., 1952, Principles of geochemistry: New York, John Wiley and Sons.

Rankama, K., 1946, On the geochemical differentiation in the earth's crust: Comm. géol. Finland, Bull. 137.

Rankama, K., 1948, On the geochemistry of niobium: Anales Acad. Sci. Fennicae, A, v. 3, p. 13.

Rankama, K., and Sahama, Th. G., 1950, Geochemistry: Chicago, Univ. Chicago Press.

Sahama, Th. G., 1945, Spurenelemente der Gesteine im südlichen finnisch Lappland: Comm. géol. Finland Bull. 135, p. 9-27.

Sandell, E. B., 1952, The beryllium content of igneous rocks: Geochim. et Cosmochim. Acta, v. 2, p. 211-216.

Sandell, E. B. and Goldich, S. S., 1943, The rarer metallic constituents of some American igneous rocks: Jour. Geol., v. 51, pt. 1, p. 99-115; Pt. 2, p. 167-189.

Stearns, H. T., 1938, Geology and ground water resources of the Snake River Plain: U. S. Geol. Survey Water-Supply Paper 774.

Turner, F. W., and Verhoogen, J., 1951, Igneous and metamorphic petrology. New York, McGraw Hill.

Wager, L. R. and Mitchell, R. L., 1951, The distribution of trace elements during strong fractionation of basic magma; a further study of the Skaergaard intrusion, East Greenland: Geochimica et Cosmochimica Acta; v. 1, p. 129-208.

Washington, H. S., 1906, The Roman comagmatic region: Carnegie Inst. Washington Pub. 57.

Wasserstein, B., 1951, South African granites and their boron content: Geochim. et Cosmochim. Acta, v. 1, p. 329-338.