ENVIRONMENTAL GEOCHEMISTRY

Geochemical Survey of Missouri
Plans and progress for sixth six-month period
(January - June, 1972)

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Preface

This is the sixth in a series of progress reports assembled for the Environmental Health Surveillance Center of the University of Missouri. Each report describes the activities and current results of our reconnaissance geochemical survey of the State of Missouri. The survey is directed at the rocks, soils, plants and waters of the State and is designed to provide epidemiologists of the Environmental Health Center with data on the variability of the geochemical environment throughout the State. Emphasis is on the natural environment although a few studies of artificial pollution have been undertaken.

A considerable volume of geochemical data in the form of summary statistics and maps appeared in the last (fifth) progress report. To a large extent, this sixth report comprises a companion volume to the fifth in that many of the remaining element summaries appear herein. The principal research areas for which laboratory results or data analysis are as yet incomplete are studies of the surficial geologic deposits, the surface waters, the agricultural crops, and the role of parent material composition in pedogenesis.

With this report, we have finished our third year of effort in the geochemical survey of Missouri. Field work on the major aspects of the survey is nearly complete, a large amount of data has been analyzed, and some initial work has been undertaken on compilation of the final reports. Our current plans call for submittal of all final reports in the program by July 1, 1973, and consequently, administrative termination of this survey on that date.

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INTRODUCTION AND SUMMARY

This is the sixth in a series of reports issued at six-month intervals describing current results of a reconnaissance geochemical survey of the State of Missouri. The survey was begun in July, 1969 and is intended primarily to provide epidemiologists of the Environmental Health Surveillance Center of the University of Missouri with geochemical information in support of their studies on the role of environmental factors underlying human and animal health. Secondarily, the survey is regarded as a pilot venture in the area of environmental geochemistry of large and geologically diverse regions.

In the first section of this report, Drs. Ebens and Connor explain at some length the difficulties involved in preparing geochemical maps of the geologic units of Missouri. These difficulties arise from the fact that the geologic phase of the geochemical survey of Missouri is in fact a conglomeration of many independent studies, each focusing on a distinct broad-scale geologic entity. Because some entities or rock bodies are intimate mixtures of chemically distinct rocks, it is impossible to unequivocally predict the expected concentration or range of an element at a specific geographic locality without first ascertaining what variety of rock underlies that locality. This is particularly true of northern and western Missouri where the bedrock unit, which is called Pennsylvanian, is in fact largely a mixture of shale, limestone, and locally sandstone, each of which has its own distinct chemistry. Until such time as detailed mapping provides a picture of geographic distribution of these rock varieties, geochemical maps of the bedrock units in Missouri must be used in conjunction with field examinations to determine the specific rock types present.

Another aspect of map patterns in rock chemistry which is peculiar to the bedrock study is that of assessing the chemical distinctiveness of rocks of similar composition but occurring in different rock units. Calcareous rocks, for example, are quantitatively the most important rock type in the geologic units of Missouri. Calcareous rocks are composed predominantly of the carbonate minerals calcite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$, and are generally low in trace elements, when compared to siliceous or argillaceous rocks. Nevertheless, the various geologic conditions under which calcareous rocks originate can permit distinctive chemical differences to arise. In making a geochemical map of an element, it is important to know whether or not such compositionally similar rocks are distinct enough to show separately or are so similar as to merge them into a single map unit.

Conventionally, an assessment of this kind is undertaken with a suitable statistical test, such as Duncan's Multiple Range. The decision early in the program to treat each rock unit as a unique study and the use of different hierarchical sampling designs in each appears to preclude such standard statistical tests of mean differences among units, and Drs. Ebens and Connor have described a slightly different approach based on a modification of Mahalonobis' D^2 (a "generalized distance statistic"). This approach purports to assess the practical distinction between two geochemical populations, instead of distinguishing among means like Duncan's Multiple Range test, and is in effect simply an attempt to quantify visual assessments of differences among histograms. In general, this procedure suggests that the carbonate bedrock units are not really very distinct in their geochemical properties, but that among the siliceous bedrock units, sandstones of the Roubidoux Formation are markedly different from both Pennsylvanian shale and the Precambrian granitic rocks.

In the second section of this report, Dr. Tidball presents 32 additional maps showing the distribution of elements in the agricultural soils of Missouri. All of these maps, except the map of iodine, are based on analysis of 1,140 specimens of agricultural soils. Together with the nine maps given previously (U.S. Geol. Survey, 1972, p. 44-52), a total of 41 such maps have now been produced.

In a detailed analysis of the reliability of any obvious or suspected patterns appearing in these maps, Dr. Tidball points out that the more localized the pattern, the greater the risk that it reflects chance fluctuations rather than meaningful geographic variation. Moreover, a comparison of one small area (for example, a county) with another by averaging all available data in both areas appears, on the whole, to be inappropriate.

It seems that the expected variation of an average value for a localized area is large when compared to the expected difference between that average and any other average in a similarly small area. Under such conditions, more precise (that is, more reliable) averages may be gotten by increasing the number of specimens collected in each area. For the agricultural soil study, however, Dr. Tidball points out that any immediate use of the data precludes additional sampling, and the only way to increase reliability in compositional averages is by increasing the area for which the average is computed. By so doing, of course, additional specimens are included in the average. He concludes that, in general, the minimum area to be used in computing compositional averages of high reliability is an area approximately equal to a one-degree quadrangle, or an area about 70 miles across.

Because the county is a convenient epidemiologic unit, the desire to use compositional averages based on counties is strong. Dr. Tidball's analysis, however, demonstrates that the risk of obtaining meaningless averages for a geographic unit of this size is large. However, because counties in Missouri tend to be rather uniform in size (at about 25-30 miles across), a block of any four contiguous counties should approach an acceptable minimum area for averaging.

In the third section of this report, Drs. Shacklette and Erdman and Mr. Keith give distribution maps of arsenic and fluorine in the uncultivated soils of the State. This brings the number of such maps to 34, including the 32 published in U.S. Geological Survey (1972).

In addition, they have begun some preliminary studies on the possible role of soil chemistry in determining trace element concentrations in plant tissue. Although uncultivated B-horizon soil from the soil vegetation-type areas of the State show marked differences in nearly all elements (U.S. Geol. Survey, 1971, p. 30), only seven of 19 elements measured in ash of sumac show similarly strong differences among vegetation-type area. Moreover, a comparison of geographic patterns in soil and plant tissue shows little correspondence for any of these seven elements. This suggests that the natural compositional variation of the B-horizon of undisturbed soils bears no simple relation to the trace metal content of sumac. Drs. Shacklette and Erdman and Mr. Keith conclude that the rather marked deficiency in some trace elements in ash of sumac collected from the Cedar Glades reflects the generally higher pH of the uncultivated soils from that region, rather than a general deficiency of these elements in the soil.

They further note that Q-mode factor analysis of the composition of the uncultivated soils across the State suggests that such soils belong to two major groups which are best described in terms of three end-member compositions. One group consists of soils from the Cedar Glades and the second group represents a more or less continuous spectrum of compositions between Glaciated Prairie soils and Oak-hickory-pine Forest soils. Floodplain Forest soils are the most heterogenous soils in the second group and probably reflect the fact that because they developed on Mississippi River alluvium, they reflect a multiple parentage.

In the last section of this report Mr. Feder discusses the advantage of using a 0.1-micrometer filter rather than the commonly-used 0.45-micrometer filter, in order to obtain more accurate measurements of trace elements in solution. Surface water always contains suspended material, and it is important, therefore, to differentiate the proportion of a trace element concentration that is carried in suspension from that carried in solution. Filtration of duplicate samples obtained at one site demonstrated that the 0.1-micrometer filter substantially reduced the quantity of suspended material in the filtrate; without this filtration, this suspended material would be considered as in solution.

Mr. Feder also notes that although sampling for the surface water study is as yet incomplete, some preliminary data suggest that the trace-element compositions of ground water and surface water in the same geohydrologic unit may be largely independent of one another. If so, the geochemical characterization of any geologically coherent region of the State takes on an added complexity in that cities may obtain their water supplies from either, or both, sources of water.

It is expected that these and previously reported results of the geochemical survey of Missouri will prove to be most useful in epidemiological work in providing realistic estimates of the norm, the background, or baseline geochemistry as it is variously called. Such baselines are needed for meaningful investigations into particular local situations of epidemiological interest. Geochemical anomalies, whether naturally occurring or arising from artificial pollution, cannot be identified and mapped unless a baseline or norm has been previously established for comparison with the anomalous area, and it is evident from the results of the survey so far that there is significant variation in the chemical character of the natural environment throughout the State.

A number of localized areas have been identified as geochemically unusual or possibly unusual during the three years of work on this survey. The first area to be intensively studied as geochemically anomalous was the roadside environment near Centerville, Missouri, in the southeastern part of the State. This work is described in detail in U.S. Geological Survey (1969, p. 10-18) and in Connor, Shacklette and Erdman (1971). Following detailed examinations of the area, the extraordinarily high concentrations of lead and associated metals, noted in roadside soils and cedar trees, were attributed to contamination of the roadside environment by the continual escape of fine-grained particulate lead-bearing cargo from by-passing ore trucks.

Another, and only recently completed, study of a geochemically unusual area was undertaken in a small watershed in Callaway County where metabolic disorders in cattle have been observed by veterinarians of the University of Missouri. This study is described in detail in Ebens and others (1972), and concludes that the local geochemical environment of the watershed has been altered by the presence, near the head of the watershed, of an abandoned claypit and its associated pile of mined debris. The changes in the local environment include unusually high levels of a number of trace elements, including aluminum, beryllium, cobalt, copper, molybdenum, and nickel, in alluvium, water and vegetation. The veterinarians suspect that the altered conditions are causally related to the poor health of the cattle.

A third, and as yet unfinished, study of a geochemically unusual situation in the municipal water supply of the city of Sedalia, Missouri has been undertaken. Exploratory studies (U.S. Geol. Survey, 1972, p. 143) by Mr. Feder suggest that one of the city's three water sources may, at least on occasion, contain unusually high concentrations of selenium.

Other investigations relating to unusual geochemical environments include a preliminary study of high lead concentrations in some agricultural soils developed on the Big River flood plain in southeastern Missouri. Dr. Tidball, in this report, tentatively concludes that the downstream valley soils are affected by material derived from upslope mine debris.

Recent work by Drs. Shacklette, Erdman and Mr. Keith, described in this volume, indicates that ash in sumac from southeast Missouri, through the general area of the Old Lead Belt, is noticeably high in lead. They provisionally attribute this to generally elevated levels of airborne lead during the life of the plants. The three scientists also suggest that the B-horizon of uncultivated soils in Howell County may be unusually high in molybdenum and arsenic. Although no additional work has yet been done in that area, there seems to be no visibly obvious reason why soil there should be compositionally different from similar soils in adjacent areas.

A very important aspect of environmental geochemistry is the cycling of elements through the various parts of the environment. The simplest and perhaps most widely held view of such cycling is based on the assumption that a high element concentration in a substrate material will generally be reflected by a high concentration in a daughter or derivative material. That is, if a rock unit is higher than average in a given element, the soil developed on that unit, and the plants growing in those soils, as well as water coming in contact with the unit, would be expected to exhibit higher than average amounts of that element also.

While it is clear that bedrock units constitute the ultimate source of elements in the environment, element cycling in the natural materials of Missouri is obviously much more complicated than the simplistic model above would indicate. The bedrock units in Missouri, in a very generalized way, consist largely of shaley and trace element-rich rocks in the northwestern half of the State and largely of calcareous and trace element-poor rocks in the southeastern half. Mr. Feder, in the present volume, notes that the marked compositional difference in the rocks of these two areas is reflected also in a marked compositional difference in the ground water of the two areas, although the relation is not apparently linear, and for some elements (like Zn), it may even be an inverse one. He further states that this apparent correspondence between trace element-rich rocks and trace element-rich ground water undoubtedly reflects a more complicated physico-chemical system than simple solution in proportion to amount present. The effects of pH, Eh, residence time and presence of complex ions in ground water appear to be the primary controls on trace element content of Missouri ground water.

The compositional relations of trace elements in soils to trace elements in bedrock in Missouri, is even more complicated in that the State is extensively blanketed by deposits of thick surficial materials, part of which are not necessarily genetically related to the bedrock at a given locality. Much of southern Missouri is blanketed by a residual accumulation of red clay (carbonate residuum) which is the product of prolonged and intense weathering of the underlying carbonate rock. Although it is believed that trace element differences among parts of the residuum directly reflect similar but largely obscured differences in the parent bedrock, it is also apparent that the processes of weathering have greatly concentrated some elements in residuum compared to the parent, particularly silicon, iron, and aluminum and the transition elements, and have largely removed others, particularly the alkaline earth elements (U.S. Geol. Survey, 1972, p. 40). Paralleling the compositional relation between bedrock and ground water, the compositional relation between carbonate parent and derivative residuum may be positive for some elements and negative for others, and need not be linear for any.

In northern Missouri and in the major river valleys, the surficial materials are a mixture of locally and distantly derived materials in glacial, eolian, and alluvial deposits. Hence, compositional variation in much of the surficial material of northern and southeasternmost Missouri need not necessarily be related to the underlying bedrock composition, except where the surficial material is largely derived from a local bedrock source.

These considerations suggest that the compositional variation in residual soils in Missouri may well reflect bedrock compositions in southern Missouri, where the surficial deposits are themselves largely derived from local bedrock. The compositional variation in these soils may not reflect bedrock compositions in northern Missouri, or may only partly reflect bedrock compositions. Thus, although bedrock compositional patterns may tend to reflect a rough northeasterly subdivision of the State, with trace element-rich materials occurring to the northwest, soil compositional patterns may be subdivided along a more easterly line (at roughly the Missouri River) reflecting the distribution of the surficial deposits. The first (and strongest) pattern described by Dr. Tidball in this report is essentially that of the distribution of the surficial geologic materials.

Again, however, the relation between substrate and derivative material is far from straightforward in that many trace elements in the agricultural soils exhibit little or no broad-scale patterns. Moreover, patterns in the B-horizon of the uncultivated soils include distributions both similar and dissimilar to the surficial materials distribution. Finally, as Drs. Shacklette and Erdman and Mr. Keith note, soil pH seems to be a much more important control on trace element content of native plant tissue than is the element concentration in the soil.

GEOCHEMICAL SURVEY OF GEOLOGIC UNITS

by R. J. Ebens and J. J. Connor

Present status.--Work on this phase of the Missouri studies consisted of a three-week sampling trip in mid-spring and continued analysis of geochemical data on the geologic units of the State. In addition, two talks were presented at the meeting of the North-central Section of the Geological Society of America held at DeKalb, Illinois, May 11-12, 1972, which were based in part on studies of rock geochemistry in Missouri. Abstracts of these talks are given in Connor and Ebens (1972) and Ebens and others (1972).

Additional sampling of surficial units.--Results of first-stage sampling in the geologic units of Missouri (U.S. Geol. Survey, 1972, p. 35) indicated that for all units, except the carbonate residuum and sandstone of Pennsylvanian age, geochemical variation over distances greater than about 50 miles within each unit is practically non-existent. In contrast, nearly every element detected in the residuum exhibited statistically significant amounts of variation over large distances, that is, variation between parent areas. This variation would be most conveniently presented on maps as differences in the average level of element concentration in each parent area. But the first stage of sampling involved only six specimens from each parent area and because the residuum is believed to be the most heterogenous of all units studied, differences among parent-area averages, each of which is based on only six specimens, may be unreliable.

The stability of differences among averages may be assessed by comparing the variation among parent-area means to the imprecision in estimating those means. Tidball (U.S. Geol. Survey, 1970, p. 20-22) discusses by means of an example the use of such comparisons in determining the requirements of a second stage of sampling. A similar analysis of our first-stage results for carbonate residuum indicates that a reliable comparison of element averages in residuum from the different parent areas in southern Missouri requires up to 24 specimens from each parent area. Moreover, these 24 specimens must be collected from six random sampling localities of about 2-3 miles diameter in each parent area; two random specimens from each of two random sites in each locality are required. Twenty-four specimens from each of seven parent areas (areas underlain by Meramec, Osage, Jefferson City, Roubidoux, Gasconade, Potosi-Eminence, and Bonneterre rocks) results in a total sample load of 168 samples. Three weeks were spent in the field in May collecting these specimens.

At the same time, a preliminary investigation was undertaken to assess the compositional variability of loess away from the bluffs near the Missouri River. Loess sampling in Missouri has concentrated on examining compositional variation in the bluffs along the Missouri and Mississippi Rivers, primarily because loess is better developed (thicker) and better exposed in these bluffs than elsewhere. Results of these studies indicated that loess is compositionally a very homogeneous unit in comparison to the other geologic units studied (U.S. Geol. Survey, 1972, p. 31).

In order to examine compositional variation with distance away from the bluffs, specimens of loess were taken in three traverses eastward from the Missouri River--a northern traverse eastward from Rockport along U.S. Route 136, a central traverse eastward from St. Joseph along U.S. Route 36, and a southern traverse eastward from Lisbon along State Route 124. Sample localities were spaced at geometric intervals of 1/2, 1, 2, 4, 8, etc., miles from the edge of the Missouri River flood plain. Each sample locality consisted of a stratigraphic section of the thickest exposure in the immediate vicinity. Three random specimens were taken vertically in each section for a total of 72 specimens. The locality farthest from the river was one at 128 miles along the central traverse. We were assisted in this sampling by Mr. J. R. Keith.

Geochemical comparison of geologic units.--One of the goals of the geochemical survey of Missouri has been to produce maps of the State showing broad-scale patterns of chemical variability, if they exist, in the different natural materials of the State. Insofar as the rocks are concerned, it was pointed out at the beginning of the work (U.S. Geol. Survey, 1969, p. 5) that because strong mineralogic contrasts are known to exist among many of the major geologic units, and because these units tend to underlie mutually exclusive areas of the State, it was reasonable to expect strong statewide geochemical patterns in the geologic units.

The summary statistical data and accompanying maps given in the previous six-month progress report (table 14 and figs. 3 and 4, U.S. Geol. Survey, 1972) constitute the raw data with which geochemical maps of geologic materials in Missouri can be made. Such maps would be similar in appearance to those of Shacklette, Erdman, and Keith (U.S. Geol. Survey, 1972, p. 59-91) and Feder and Miesch (U.S. Geol. Survey, 1972, p. 105-137). The greatest risk in interpreting such maps for the geologic materials lies in the fact that the major geologic units, while generally characterized by a dominant mineralogic (chemical) rock type, also contain minor interbeds of chemically diverse material. Thus, to chemically characterize a large part of the State in terms of the major rock type underlying that part would be misleading for the rare localities of that part which are in fact underlain by locally unusual rocks.

In order to assess the "normalness" or "unusualness" of a given rock specimen from a particular locality, the chemical composition of the specimen must be compared to the expected composition and the expected range of mineralogically similar rocks. For example, the bedrock in much of northwestern Missouri consists of interbedded limestone and shale of Pennsylvanian age. The expected concentration of Cu in Pennsylvanian limestone is 3.5 parts per million (ppm) and the expected range is .77-16 ppm (U.S. Geol. Survey, 1972, p. 36). For shale, the expected Cu concentration is 23 ppm and the expected range is 3.4-160 ppm. In addition, northwestern Missouri is overlain by extensive deposits of loess, whose expected Cu concentration is 18 ppm and whose expected range is 11-31 ppm. Suppose a rock specimen is collected from a locality of epidemiological interest in northwesternmost Missouri and the Cu concentration is measured as 50 ppm. Whether or not this rock is to be viewed as unusual or "anomalous" in its Cu concentration depends on whether it is a sample of limestone, shale, or loess. If the sample is limestone or loess, it is anomalously high in its Cu content; if the sample is shale, it is quite ordinary in its Cu content.

Another aspect in making statewide geochemical maps of geologic materials concerns the problem of assessing the importance of observed differences among means of an element in mineralogically similar rocks from the different major units. For example, carbonate rocks are the dominant material in both the Cambro-Ordovician unit of southern Missouri and the Mississippian unit in southwesternmost and northeasternmost Missouri; they also form an important part of the Pennsylvanian unit of northwestern Missouri. Carbonate rocks, predominantly composed of calcite and dolomite, are characteristically low in most trace elements, and the chemical difference between carbonates in these different units may or may not be of importance in determining statewide geochemical patterns. If the carbonate rocks in two different units are distinct in one or more trace elements, any resulting statewide geochemical maps should show that distinction; conversely, if they are not distinct, any resulting geochemical maps should merge the two units into a single one.

The problem of assessing the importance of observed differences among units can be a difficult one. Shacklette, Erdman, and Keith (U.S. Geol. Survey, 1972, table 15) and Feder and Miesch (U.S. Geol. Survey, 1972, table 17) made statistical inferences as to the significance of observed chemical differences among uncultivated soils and ground waters, respectively, using Duncan's Multiple Range Test. This test, and similar ones, requires an estimate of the standard error of the means being tested. In contrast to the studies in the soils, plants, and waters of Missouri, where the use of a single hierarchical sample design permits estimation of a single,pooled standard error, the geologic studies were based on different hierarchical designs for each major unit of study. Thus, an independent estimate of the standard error of the mean of any given element is obtained for each unit. Any comparison between the means of two or more units requires pooling of their standard errors. Procedures exist for such pooling, but they require a knowledge of $\underline{n}$, defined as the number of independent specimens on which each error variance is based. Unfortunately, the use of hierarchical designs obscures not only the value of $\underline{n}$, because all specimens are not independent, but, also, the degrees of freedom (computed as a function of $\underline{n}$) needed to test for the significance of any comparisons.

A somewhat different approach to geochemical comparison, which circumvents the need for a pooled standard error, but which still precludes a formal test of significance, has been tentatively applied to the rock studies in Missouri. This approach is based on the magnitude of the pooled error variance rather than on the magnitude of the pooled standard errors, and is illustrated in figure 1. Two overlapping hypothetical populations of normal form and equal variance are shown in figure 1A. The Student's $\underline{t}$ test for this hypothetical comparison would assess the difference in means (d) in terms of the standard error about each mean (reflected in the dashed lines). The ability to reject the null hypothesis of equal means is a function of the "tightness" with which the standard error of the means bounds each mean and the difference, d, between the two means.

As pointed out above, the studies of rock chemistry in Missouri are such that an assessment of d in this manner seems impossible. Nevertheless, it seems intuitive that inasmuch as the size of d reflects the degree of separation or distinctiveness of the two groups, it should be a useful guide in judging whether or not to merge the two populations into one single group. However, a simple ratio of means may be inadequate in making this judgment as may be seen in the comparison of figure 1B with figure 1A. The difference, d, in figure 1B is identical to that in 1A, but clearly there is a greater distinction between the populations in 1A than in 1B, even though the ratios of the means in the two cases are the same. Obviously, a more realistic comparison of the means will result if all data in both hypothetical cases are cast into standard measure (units of the pooled standard deviation) so that the difference measurement reflects not only the difference in means but the average scatter or variance as well.

A standardized measure of the difference, D, may be obtained from:

$$D = \frac{d}{\sqrt{\frac{1}{n}\sum_{i}^{n} S_i^2}} \qquad (1)$$

where d is the raw difference between the means of two populations, S_i^2 is the variance of the ith population and n is the number of populations being compared. A prerequisite assumption for pooling the variances in (1) would seem to be only that of homoscedasticity (homogeneous variance). Each variance could be viewed as an independent and unbiased estimate of the true, but unknown, population variance. Of course, a simple average of the observed variance ignores the fact that each variance may have associated with it a different confidence band.

Separations of hypothetical populations based on D = 1, 2, and 4 standard deviations are visually compared in figure 1C. Separations where D = 2 reflect fairly distinct populations, and separations where D = 4 or more reflect almost completely separated populations. Equation (1), if

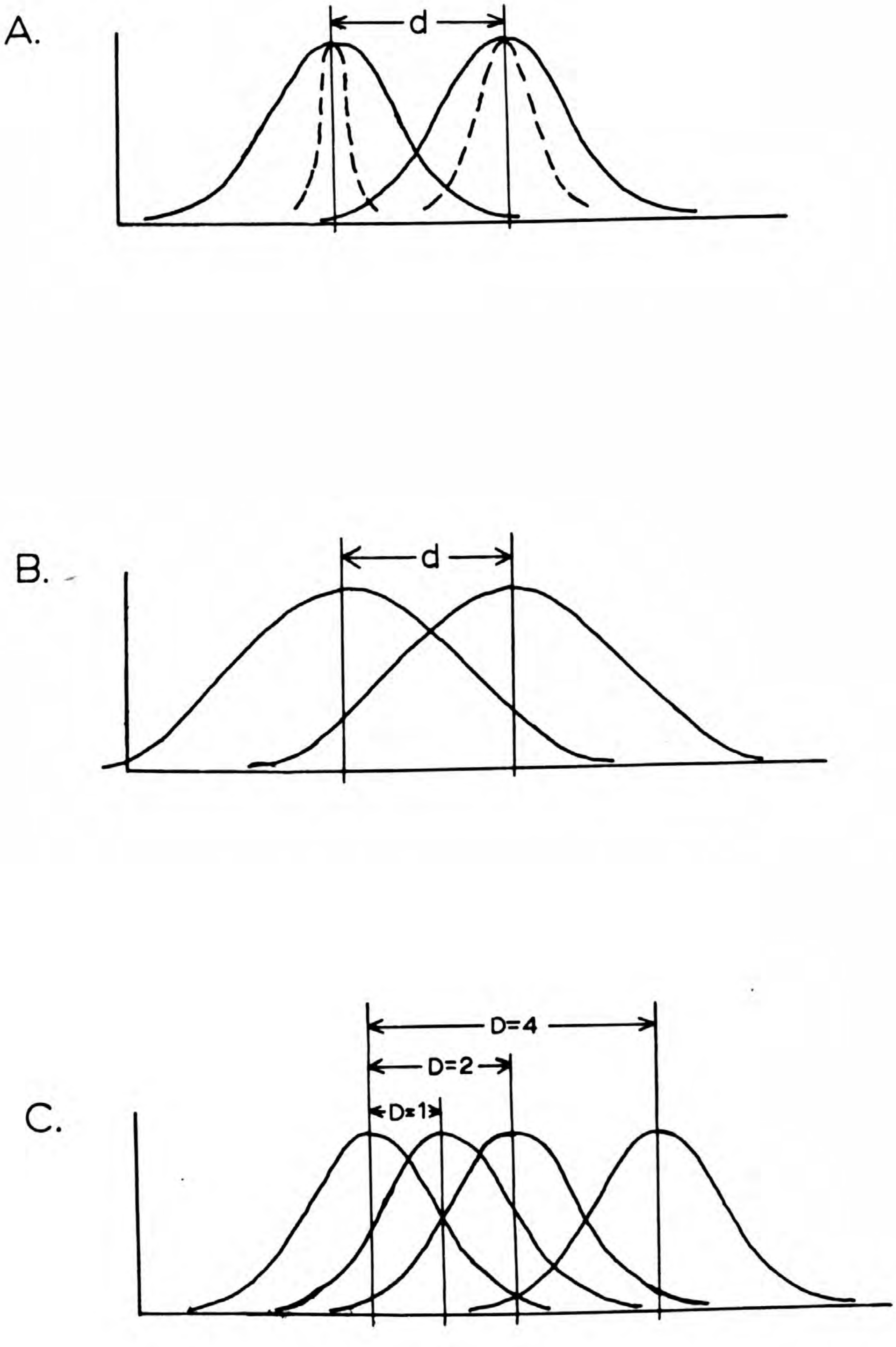


Figure 1. Visual comparison of multiple hypothetical populations. A. Two hypothetical populations of normal form and equal variance. "d" is the difference in means of two populations. Dashed lines reflect the standard errors of the two means. B. Two hypothetical populations of normal form and equal variance. "d" is the same as in A but the population variance is larger. C. Four hypothetical populations of normal form and equal variance. Separations between population means are equal to 1, 2, and 4 standard deviations. D is defined by equation (1) in text.

squared, is analogous to Mahalanobis' multivariate D^2 or "generalized distance" measure and, except for the pooling procedure, constitutes a univariate adaptation of a multivariate measure. Moreover, the statistical testing implied by (1) is quite distinct from that implied by Student's *t*. The *t* test strives to demonstrate a real difference in means regardless of how distinct the parent populations may be. A *t* failing of significance indicates only that additional sampling is needed before one can declare with any degree of confidence that the means are truly unequal. The D in (1), and Mahalanobis' D^2, strives to quantify the degree of separation between populations and could well result in a conclusion that the subject populations are not really very distinct in a practical sense even if a *t* should demonstrate that the means are distinguishable.

This approach is illustrated for the bedrock units of Missouri using the estimated geometric means and geometric deviations for barium listed in figure 2. These data are taken from table 14 of Ebens and Connor (U.S. Geol. Survey, 1972) and are a reasonably complete description of barium in the bedrock units of Missouri. Data on quantitatively minor units (sandstones of Pennsylvanian age) or environmentally inert materials (chert of Mississippian age) are excluded here as playing only an insignificant role in the broad-scale description of barium.

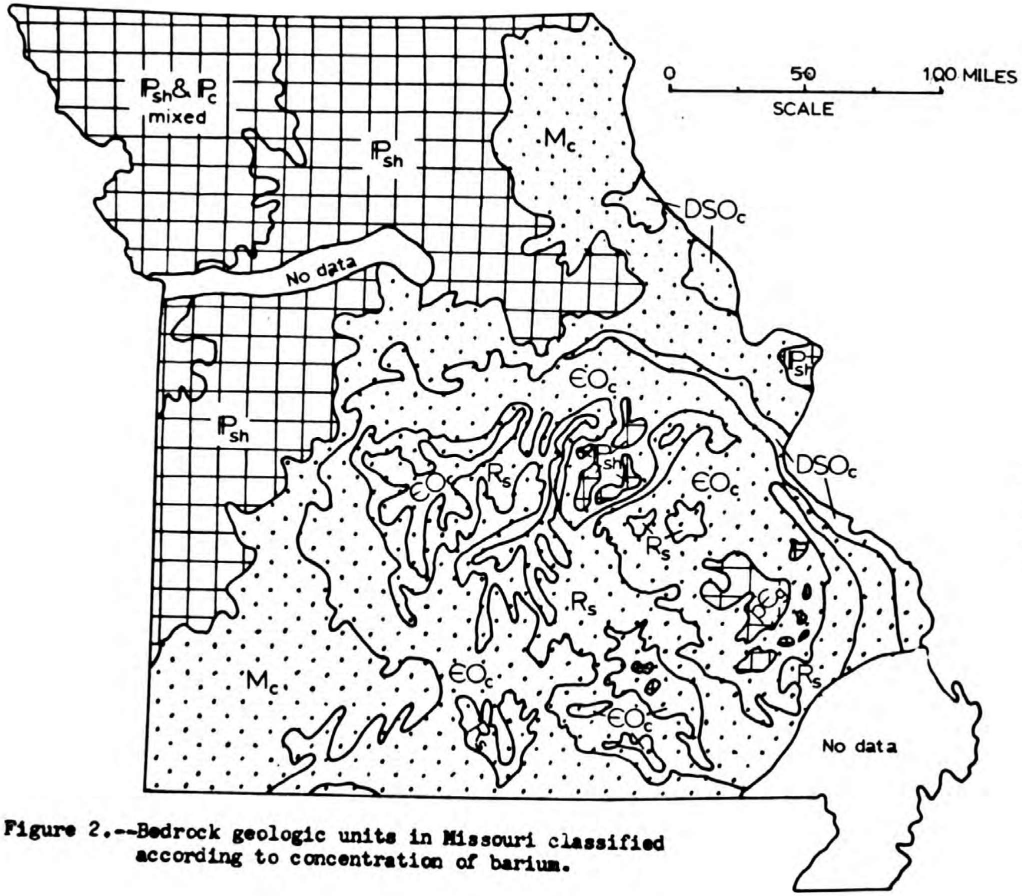
The expected level of barium in these units ranges from a low of 5.8 ppm in the Ordovician, Silurian, and Devonian carbonate rocks to a high of 600 ppm in the Precambrian granitic rocks. The magnitude of variation of barium, as seen in the geometric deviations, is dependent on whether the unit is composed of calcareous rocks or siliceous rocks. The barium concentrations appear to be consistently more uniform in the siliceous rocks than in the carbonate rocks. Because of this, it seems best to compute an average (pooled) variance for each compositional type.

D^2 in the carbonate rocks is computed as:

$$D^2_{ij} = \frac{(\bar{x}_i - \bar{x}_j)^2}{\frac{1}{4}(S^2_c + S^2_o + S^2_m + S^2_p)} \qquad (2)$$

where D^2_{ij} is the square of the "distance" between the ith and jth rock units. Because trace element concentrations tend to be lognormally distributed, or nearly so, $\bar{x}_i$ and $\bar{x}_j$ are the logarithmic means (equal to the logs of the geometric means) of the ith and jth units, and S^2_c, S^2_o, S^2_m, and S^2_p are the logarithmic variances (equal to the squares of the logs of the geometric deviations) of the Cambro-Ordovician, Ordovician-Silurian-Devonian, Mississippian, and Pennsylvanian units, respectively. For example, D^2 for barium in the Mississippian and Pennsylvanian carbonate units is:

$$D^2_{\mathrm{I\!P}M} = \frac{(1.6435-.8195)^2}{\frac{1}{4}(.2960+.5007+.6931+.2276)} = 1.58 \qquad (3)$$



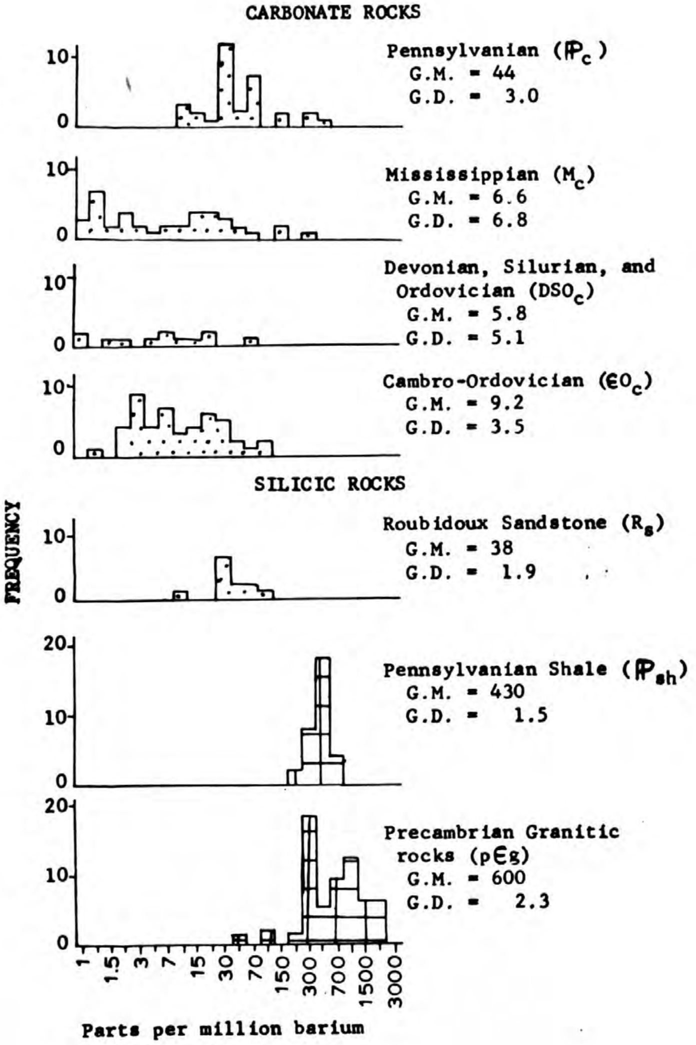


Figure 2.--Bedrock geologic units in Missouri classified according to concentration of barium.

thus, D is equal to 1.3 (the square root of 1.58), and we conclude, from inspection of figure 1C, that the separation between these two populations for barium is not really very large.

D^2 for barium in the siliceous rock units is computed as:

$$D^2_{ij} = \frac{(\bar{x}_i-\bar{x}_j)^2}{1/3(S_p^2+S_r^2+S_{p\epsilon}^2)} \qquad (4)$$

where S_p^2, S_r^2, and $S_{p\epsilon}^2$ are the logarithmic variances of the Pennsylvanian shale, Roubidoux sandstone, and Precambrian granitic units, respectively. A comparison of barium between the Precambrian granitic rocks and Roubidoux sandstones is:

$$D^2_{p\epsilon-R} = \frac{(2.7782-1.5798)^2}{1/3(.0310+.0777+.1308)} = 17.98 \qquad (5)$$

Thus, D for this comparison is 4.2 and inspection of figure 1C suggests that these two units are quite distinct in their concentration of barium.

D^2 (and D) for the six comparisons among the carbonate units and the three comparisons among the siliceous units are listed in table 1. The only comparisons for which D is close to 4 are those of the Roubidoux sandstones with the Pennsylvanian shales and the Roubidoux sandstones with the Precambrian granitic rocks.

A provisional map of barium in the bedrock units is shown in figure 2. Although no quantitative comparison of silicic rock units with the carbonate rock units has been made, it seems obvious from inspection of the histograms in figure 2 that the Pennsylvanian shale and Precambrian granitic rocks are distinctly high in barium compared to the remaining units. Moreover, there is little difference between the Pennsylvanian shale and Precambrian rocks (D = 0.51), and we conclude that barium in the bedrock units of Missouri may be mapped using two gross units, one consisting of the Precambrian granitic rocks combined with Pennsylvanian shale and the other consisting of the remaining five units.

Although the preceding description of how one might go about making a geochemical map of the bedrock units is thought to be valid, there are, nevertheless, important shortcomings to this or other related procedures. The most serious has to do with the aforementioned mixing of rock types in the field. In the barium map, for example, northwestern Missouri is patterned as a high-barium area, and this has been done because the dominant bedrock type is shale. However, carbonate rock is locally prominent in this general area and parts of northwestern Missouri underlain by carbonate rock are not represented in this map. And, of course, it seems improper to quantify a comparison in the face of heterogenous variance, as exists for a comparison of barium in a carbonate rock with barium in a silicic rock. It is also conceivable that the form of the parent frequency distributions could change from one rock type to another, which would further complicate an already weak procedure for comparison.

Table 1.--Geochemical comparison of barium concentration in selected bedrock units in Missouri. Values of D calculated using equation (1).

Geologic units compared		D^2	D
Carbonate rocks			
Cambrian-Ordovician	vs. Devonian, Silurian and Ordovician	0.09	0.3
-------- Do. -------	Mississippian	.05	.2
-------- Do. -------	Pennsylvanian	1.08	1.0
Devonian, Silurian, and Ordovician	Mississippian	.01	.1
-------- Do. -------	Pennsylvanian	1.80	1.3
Mississippian	----- Do. --------	1.58	1.3
Silicic rocks			
Precambrian granitic rocks	Roubidoux sandstone	17.98	4.2
-------- Do. -------	Pennsylvanian shale	.26	.5
Roubidoux sandstone	----- Do. --------	13.90	3.7

Finally, for many elements, the best estimate of the expected concentration in one or more geologic units can only be presented as "less than" some upper boundary, usually the limit of analytical detection. No procedures will permit quantitative evaluation of differences involving expected concentrations given in this form, although a minimum value of D may be computed. For many such comparisons, however, visual inspection of the two histograms is the only realistic alternative. This is illustrated in figure 3, which shows the expected boron concentration in the bedrock units of Missouri. The expected level of boron in Pennsylvanian shale is 72 ppm but in all other units is less than 20 ppm. It is obvious from inspection of the histograms in figure 3 that boron is distinctly high in Pennsylvanian shale compared to the other rock units. However, it is not possible to assess differences in the boron concentrations among the other rock units without using a more sensitive analytical method.

In order to aid the reader in assessing geochemical differences among the major bedrock units of the State, D values for 26 elements are listed in table 2. In general, the carbonate rock units are not very distinctive in their geochemical properties. In a comparison of Pennsylvanian carbonates with carbonates of Devonian, Silurian, and Ordovician age, only iron and manganese exhibit a D value of 2.0 or larger. Pennsylvanian carbonates are also moderately distinct in their magnesium, manganese, and strontium content when compared to Cambro-Ordovician carbonates. The Mississippian and Cambro-Ordovician carbonates are also moderately distinct in terms of magnesium. A comparison of the silicic rocks indicates that sandstones of the Roubidoux Formation are in general markedly distinct from both shale of Pennsylvanian age and the granitic rocks of Precambrian age, particularly in aluminum, barium, iron, gallium, potassium, yttrium, ytterbium, zirconium, and probably strontium and titanium. Pennsylvanian shales and the Precambrian granitic rocks are less distinct except in chromium and perhaps copper, yttrium, and ytterbium.

Some of the problems encountered in sampling rocks in environmental studies, and in presenting the results in a way that will be useful to epidemiologists, have been discussed recently by Miesch (1972).

Table 2.--D values for geochemical comparisons of selected bedrock units in Missouri.

D values calculated using equation 1 (see text). Data used in calculation obtained from table 14 (U.S. Geol. Survey, 1972).

CC, carbonate carbon; OC, organic carbon; --, no computation.

Geologic units compared		Elements																															
		Al	B	Ba	Be	CC	OC	Ca	Co	Cr	Cu	Fe	Ga	Hg	K	La	Li	Mg	Mn	Na	Nb	Nd	Ni	P	Pb	Si	Se	Sc	Sr	Ti	V	Y	Yb	Zn	Zr
		Carbonate rocks																															
Pennsylvanian	Mississippian	--	--	1.3	--	0	0.5	0	--	0.5	1.4	1.6	--	0	0.2	--	--	0.1	1.8	1.1	--	--	--	--	--	0.5	0.5	--	1.2	0.8	0.8	--	--	0.3	--
----- Do. ------	Devonian, Silurian and Ordovician	--	--	1.3	--	0	.7	0	--	1.8	> 1.6	2.0	--	.4	.1	--	--	.4	2.2	1.6	--	--	--	--	--	.6	.8	--	1.0	.9	> 1.2	--	--	1.1	--
----- Do. ------	Cambro-Ordovician	--	--	1.0	--	.5	.1	1.3	--	1.5	.6	1.6	--	.1	.2	--	--	2.0	2.5	.6	--	--	--	--	--	.4	.6	--	2.2	.9	1.0	--	--	> 1.4	--
Mississippian	Devonian, Silurian, and Ordovician	--	--	.1	--	0	.2	0	--	1.2	> .2	.4	--	.4	.2	--	--	.5	.4	.4	--	--	--	--	--	.1	.3	--	.3	0	> .4	--	--	.8	--
----- Do. ------	Cambro-Ordovician	--	--	.2	--	.5	.5	1.4	--	1	.7	0	--	.1	.5	--	--	2.1	.7	.5	--	--	--	--	--	.2	.1	--	1.0	0	.3	--	--	> 1.1	--
Devonian, Silurian, and Ordovician	Cambro-Ordovician	--	--	.3	--	.5	.7	1.4	--	.2	> .9	.3	--	.3	.3	--	--	1.6	.3	.9	--	--	--	--	--	.2	.1	--	1.2	0	> .1	--	--	> .3	--
		Silicic rocks																															
Pennsylvanian shale	Roubidoux sandstone	> 18	--	3.7	> 1.6	--	.2	> 1.8	--	5.5	3.4	> 9.9	> 5.7	> 1.9	> 13	> 1.3	--	1.0	1.8	4.9	--	--	--	> 1.7	> 1.0	1.9	> 1.6	> 2.7	3.8	3.7	--	> 3.6	> 3.6	--	3.3
----- Do. ------	Precambrian "granitic" rocks	1.6	--	.5	0	--	--	.7	--	> 6.1	3.0	1.8	.1	1.4	1.9	.4	--	--	.6	--	--	--	--	.9	.2	1.3	1.5	1.6	1.4	1.1	--	2.0	2.2	--	.9
Roubidoux sandstone	Precambrian "granitic" rocks	> 16	--	4.2	> 1.6	--	--	> 1.0	--	> .6	.4	> 8.0	> 5.6	> .5	> 15	> 1.7	--	--	2.5	--	--	--	--	> .8	> 1.2	.6	> .1	> 1.2	2.4	2.6	--	> 5.6	> 5.8	--	4.1

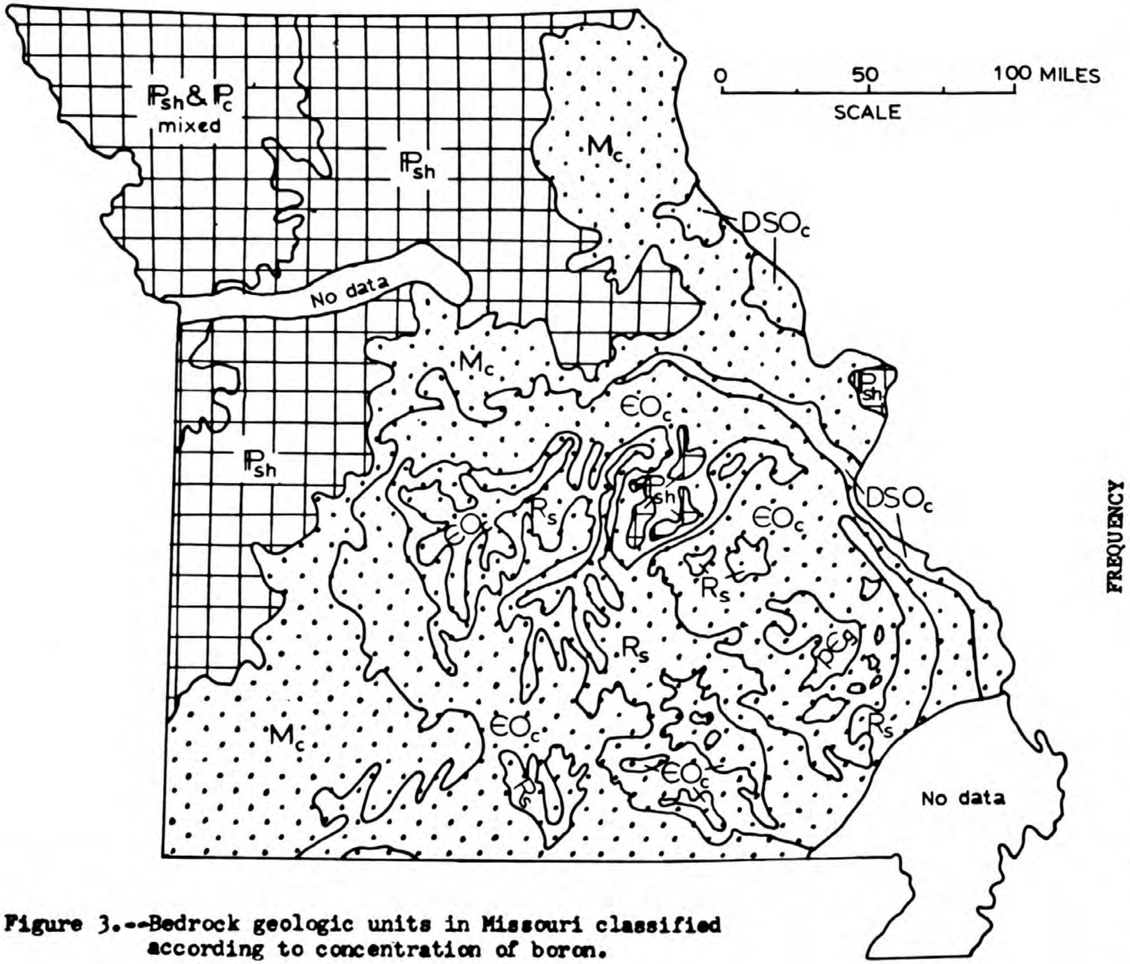
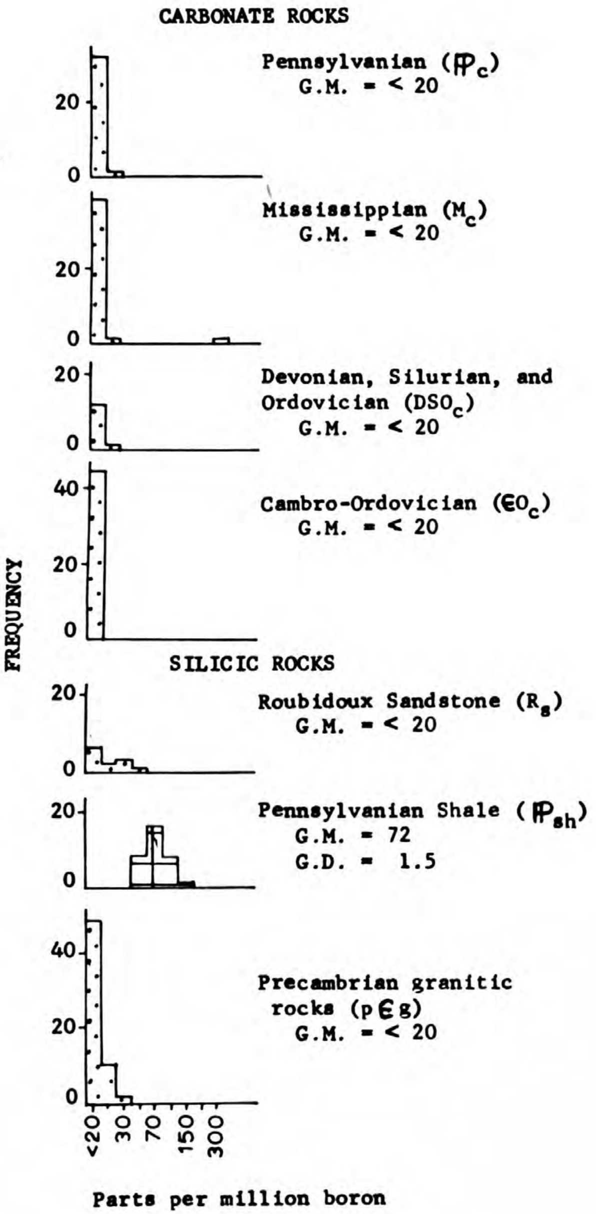


Figure 3.--Bedrock geologic units in Missouri classified according to concentration of boron.



Geochemical survey of soils

by R. R. Tidball

Present status.--No field work was done during the report period, nor is any further field work anticipated for the remainder of the project. The soils project is currently subdivided into three studies: (1) soil parent material, (2) Big River flood plain, and (3) agricultural soils. The soil parent material study was described elsewhere (U.S. Geol. Survey, 1970, p. 16; 1972, p. 41). The Big River floodplain study is a small special interest study initiated to investigate the occurrence of a few unusually high lead values in specimens of agricultural soil collected from the flood plain of Big River in southeastern Missouri. Additional specimens of soil have been collected from this area. Big River commences in northern Iron County and flows northeasterly through Washington, St. Francois, and Jefferson Counties, and joins the Meramac River near St. Louis. Big River flows through the old Missouri Lead Belt and locally flows past the base of mine tailing piles in the vicinity of Bonne Terre, Flat River, and Leadwood. Lead production has been nearly continuous in this area since the first discovery in 1701. The hypothesis that downstream valley soils are affected by materials resulting from upstream mining activity is to be tested. Analytical work for both the Big River flood plain and the soil parent material studies is as yet incomplete.

Agricultural soils.--The analytical results of 1,140 specimens of agricultural soils are now complete except for two elements--arsenic and fluorine. The results for nine elements were reported earlier (U.S. Geol. Survey, 1972, p. 41-55). The results for an additional 32 elements, most of them trace elements, are given here as distribution maps in figures 4-35. Each map is a gray-level density diagram, except as noted below, consisting of a combination of the following symbols: 1, (lowest concentrations) horizontal bar "-"; 2, vertical bar "|"; 3, plus sign "+"; 4, double plus "‡"; 5, (highest concentrations) number sign "#". Distribution maps for cadmium, molybdenum, silver, and tin are shown with the reported concentrations plotted rather than symbols because most of the concentrations lie below the limits of analytical detection. The plus (+) symbols on these maps indicate the location of the sampling site, rather than a range of concentration. The map for iodine shows only 114 symbols. Because of the expense of the iodine analytical method (neutron activation), only one randomly selected specimen (of 10 available) per county was submitted for analysis.

Because trace element data tend to be lognormally distributed, or approximately so, the histogram accompanying each map is based on a logarithmic scale. The boundaries of the frequency classes corresponding to each map symbol are also given. An attempt was made to subdivide the range of concentration of each element into approximately five (in some cases, three) equal geometric classes with about 20 (or 33) percent of the specimens in each class. The geometric mean, geometric deviation, and the percentage of the total observed variance due to analytical error are given with each histogram. In general, the class represented by the plus (+) contains the geometric mean concentration, except for barium where it falls into the next higher class (‡), and beryllium, cerium, lead, neodymium, and niobium where it falls into the next lower class (|).

The overall reliability of patterns in any map can be assessed in terms of the proportion of the total variation in that map attributable to (1) analytical variation and to (2) actual geographic variation. The variance attributable to analytical error (more accurately, laboratory procedures) is given below each histogram and is expressed as a percentage of the total observed variance. This portion of the variance, if excessive, can easily obscure geographic patterns. Elements particularly affected by a large analytical variance include barium (42 percent of the total observed variance), carbonate carbon (64 percent), chromium (41 percent), lanthanum (48 percent), mercury (52 percent), titanium (45 percent), ytterbium (71 percent), yttrium (57 percent), and zirconium (49 percent). The portion of the variance in cerium attributable to analytical imprecision was not determined because most of the concentrations were below the limit of analytical detection. There is no way of subtracting the effects of such error from each analytical value, but because the 1,140 specimens were analyzed in a randomized sequence, there is little possibility that any patterns seen in the maps reflect systematic laboratory error.

In general, the smaller the proportion of analytical variance, the greater the confidence that a given map symbol truly reflects the element concentration of the analyzed specimen. However, insofar as map patterns are concerned, even under conditions of perfect analysis spurious or misleading patterns can arise in localized areas of the map. Soils tend to be naturally heterogenous in composition and a specimen collected at a given point may differ markedly from another one collected only a few feet away. Thus, although a map symbol can truly reflect the composition of the analyzed specimen, it may at the same time inaccurately reflect the composition of the general area from which the specimen was collected. Chance fluctuations due to small-scale compositional diversity may produce small-scale (detailed) patterns that are not reproducible.

Nevertheless, the primary goal of the study is to provide the user with maps of element variability with which he may legitimately attempt to interpret epidemiologic or other geographically-oriented data. Because potential relations between soil chemistry and epidemiologic data in localized areas of the State are investigated using compositional averages, it becomes vitally important to know just how reliable the mean soil composition of those localized areas are. The general problem can be stated in another way: for a given element and with the available specimens, how large must a localized area of the State be if we are to have confidence that a mean computed for that area will be distinctly different from means computed for other, similarly-sized, areas? This question was examined by subdividing the total variance into several components by analysis of variance techniques. A nested design based on several quadrangles of diminishing size was established by sorting the entire sample set according to location into appropriate quadrangles as follows: One-degree quadrangles, 30-minute quadrangles within each one-degree quadrangle, 15-minute quadrangles within each 30-minute quadrangle, and 7½-minute quadrangles within each 15-minute quadrangle. This process permits calculation of the minimum number of randomly selected specimens that are required within the several quadrangle areas to obtain a reliable estimate of the quadrangle mean with a high degree of confidence. These values, shown in table 3, may be compared to the average number of specimens already collected within each quadrangle area as follows: One-degree quadrangles, 58; 30-minute quadrangles, 15; 15-minute quadrangles, 4; and 7½-minute quadrangles, 2. If the required number of specimens is equal to or greater than the number already collected, then the existing data may be used to calculate a reliable estimate of the quadrangle mean; if not, additional specimens are needed.

As an example of applying the procedures described above, stable or reliable means for the element aluminum will result if subareas are chosen to be at least as large as a one-degree quadrangle--that is, an area about 70 miles across. A minimum of five specimens is required to estimate the mean of a one-degree quadrangle with a probability of 0.05. The question may arise as to why a one-degree quadrangle can be adequately characterized by five specimens, whereas a 30-minute quadrangle, only one-fourth as large, requires 29 specimens (table 3). The reason is that the variation <u>among</u> one-degree quadrangles is much larger than that <u>among</u> 30-minute quadrangles. The larger number of specimens required for the 30-minute areas is the price to be paid for a more detailed final map--one which will allow the description of the finer features of the geochemical pattern of variation. The lower number of specimens for the larger 1-degree areas is acceptable because the objective is less ambitious.

Therefore, to compare means in smaller areas is to risk seeing differences among means that may not actually exist. If one is willing to accept a higher risk (say P=0.2) of chance fluctuations, then the smallest quadrangle area in which the mean of aluminum can be estimated with existing specimens is the 30-minute quadrangle where there are 15 specimens on hand but only a minimum of 9 is required.

In general, the minimum area for which stable means may be computed for the agricultural soil data with a high degree of confidence appears to be that of a one-degree quadrangle (note in table 3 under the column labeled "one-degree quadrangle," that nearly all of the values shown for P=0.05, are less than 58). The exceptions are carbonate carbon, cobalt, lanthanum, mercury, and yttrium which require areas larger than the one-degree quadrangle. Sodium may be averaged with a high degree of confidence in areas as small as a 30-minute quadrangle.

Table 3.--Estimates of the minimum number of soil specimens required in order to estimate mean element concentrations with reliability that is sufficient to distinguish between quadrangles at the 0.05 and 0.2 probability levels.

[>, greater than the number given.]

Element	Size of quadrangles, and number of specimens on hand							
	1-degree, 58		30-minute, 15		15-minute, 4		7½-minute, 2	
	Probability levels							
	0.05	0.2	0.05	0.2	0.05	0.2	0.05	0.2
Al	5	2	29	9	>60	>60	26	9
B	50	17	>60	>60	>60	25	>60	>60
Ba	13	4	50	17	31	11	>60	>60
C (total)	15	5	33	12	33	12	>60	>60
C (organic)	14	5	32	12	30	10	>60	>60
C (carbonate)	>60	>60	>60	>60	>60	31	>60	>60
Ca	7	2	22	8	30	10	>60	>60
Co	>60	>60	38	14	41	15	>60	29
Cr	23	8	32	11	50	19	>60	>60
Cu	33	12	>60	26	37	13	>60	>60
Fe	11	4	>60	26	44	16	22	8
Ga	7	2	31	17	>60	37	51	19
Hg	>60	>60	>60	22	>60	37	25	9
K	7	2	23	8	21	7	27	9
La	>60	40	57	20	>60	37	>60	>60
Li	13	4	51	19	>60	26	>60	25
Mg	6	2	32	11	41	15	>60	>60
Mn	33	12	33	12	27	9	22	8
Na	4	1	12	4	14	5	>60	>60
Ni	11	3	32	11	18	6	>60	>60
P	29	9	>60	>60	21	7	>60	>60
Pb	29	9	>60	24	19	7	27	9
Sc	13	4	51	19	>60	26	>60	37
Se	25	8	58	21	>60	>60	>60	>60
Si	8	3	49	19	>60	>60	>60	>60
Sr	4	1	25	8	36	13	41	15
Ti	45	16	59	22	>60	24	27	9
V	10	3	45	16	51	19	24	8
Y	>60	22	31	11	>60	>60	16	5
Yb	43	16	>60	27	43	16	14	4
Zn	16	5	60	22	25	9	16	5
Zr	28	9	56	21	36	13	45	16

These conclusions do not mean that reliable averages cannot be computed for smaller areas; but in order to introduce any reasonable amount of stability in averages based on smaller areas, *more specimens within such areas are needed*. Given the sampling distribution as it now exists for the agricultural soil study, any given compositional average may be misleading if based on an area less than about 70 or so miles across. These results are of the utmost importance, of course, in terms of use of the geochemical maps. The county appears to be a very convenient, or at least a very much used, geographic unit in epidemiological work. Missouri counties tend to be rather uniform in size, measuring some 25-30 miles across. The results listed in table 3 strongly suggest, however, that a county average based on existing agricultural soils data, will result in an unreliable estimate of element concentration, except perhaps for sodium.

Under ideal conditions of sampling, the significance of the difference between compositional means of any two localized areas (counties or otherwise) could be assessed by Student's *t*. However, the conditions of sampling were not ideal in the study of the agricultural soils, mainly because unknown amounts of personal sampling bias entered into the collection of all specimens. Therefore, such a test seems limited in its application. If *t* is not significant, the two areas in question cannot be considered different; but even if *t* is significant, it might simply be reflecting a personal bias in sampling. Because the consequences of a wrong conclusion about compositional differences might be substantial, it behooves us to continually assess the reliability of existing data. For the available data on the agricultural soils, we recommend that averages not be computed for areas smaller than about four contiguous counties, which over much of Missouri will comprise an area from 50 to 60 miles across.

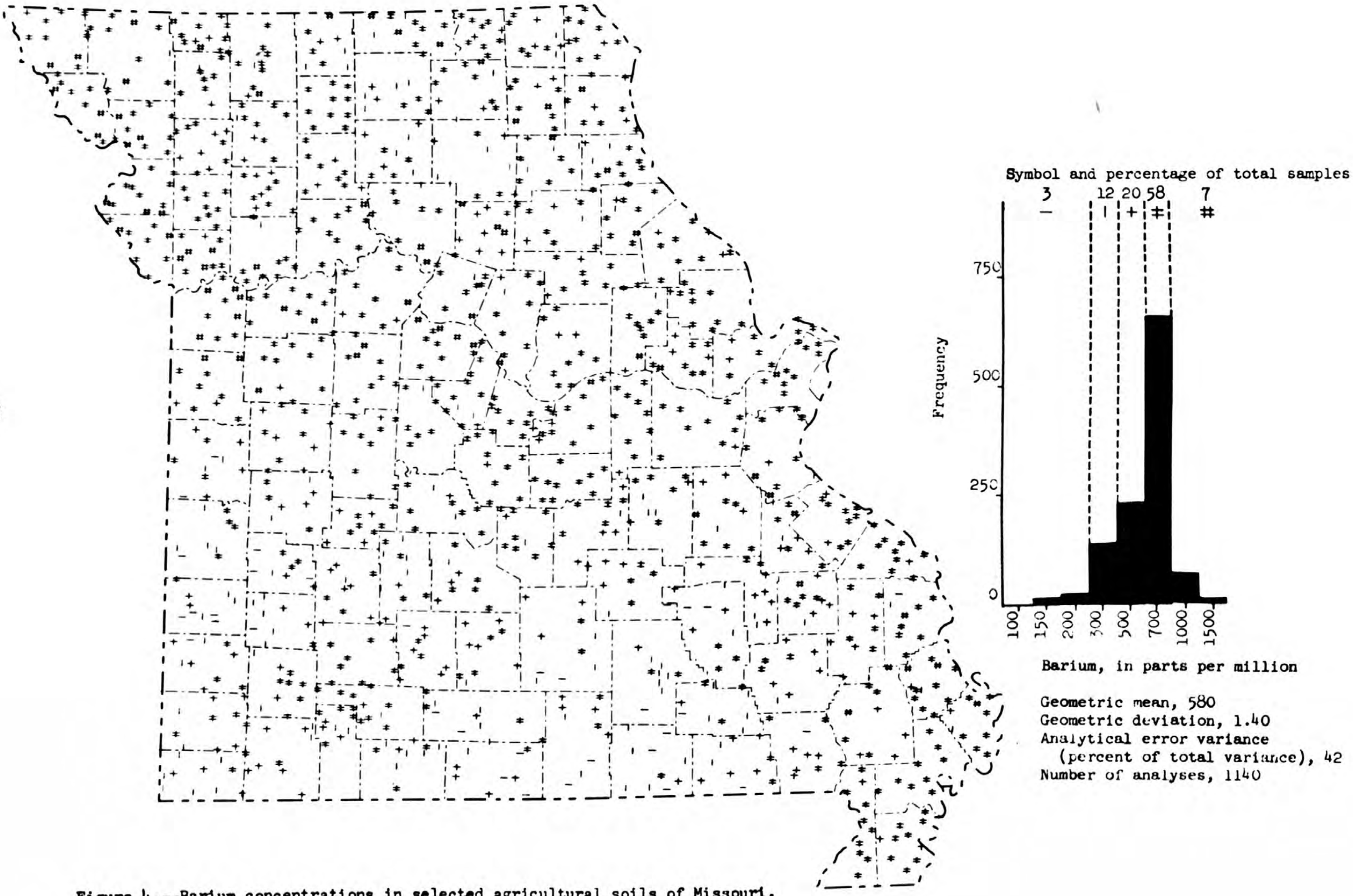
Although the difficulties in assessing detailed patterns appear insuperable (without additional sampling), there appear to be four basic broad-scale distribution patterns for the agricultural soils of Missouri. The first pattern, typified by sodium (U.S. Geol. Survey, 1972, p. 52), includes most of the other major elements as well--aluminum, calcium, magnesium, potassium, and strontium. These elements generally exhibit above-average concentrations in specimens collected in the northern part of the State, and below-average concentrations in specimens from the southern part of the State. In addition, a rather abrupt boundary exists between these two areas. Furthermore, within the southern part of the State, the southeast-central area exhibits exceptionally low concentrations for these elements. Their general distribution appears to be related to the occurrence of at least three major geologic materials, 1) glacial and glacially-related materials, including till, loess and alluvium, 2) rocks of Precambrian, Mississippian and Pennsylvanian age, and 3) carbonate rocks of Cambro-Ordovician age.

A second pattern, similar to the first but less well developed, is typified by lithium (fig. 18). It can also be seen in the distribution of copper, gallium, iron, nickel, scandium, vanadium and zinc. For these elements, the boundary between above-average concentrations to the north and below-average concentrations to the south is less distinct than it was in the first pattern, although the suggestion of a parent material control on soil composition is still apparent.

A third pattern may in reality be best defined as a nearly total lack of broad-scale variation. The elements included here are barium, beryllium, boron, carbonate carbon, cerium, chromium, cobalt, lanthanum, mercury, neodymium, phosphorus, selenium and titanium. Phosphorus may be weakly related to the distribution of the deeper loess deposits in that above-average concentrations appear to be concentrated in a wide northwest-trending belt across the State. Cerium, lanthanum and neodymium appear to be unusually low in the Delta region to the southeast. Because carbonate carbon, chromium, lanthanum, mercury and titanium were previously noted to exhibit large amounts of analytical error, and carbonate carbon, cobalt, mercury and lanthanum were previously noted to generally require areas greater than a one-degree quadrangle for useful averaging, any broad-scale patterns seen in the agricultural soil maps for these elements should be viewed cautiously.

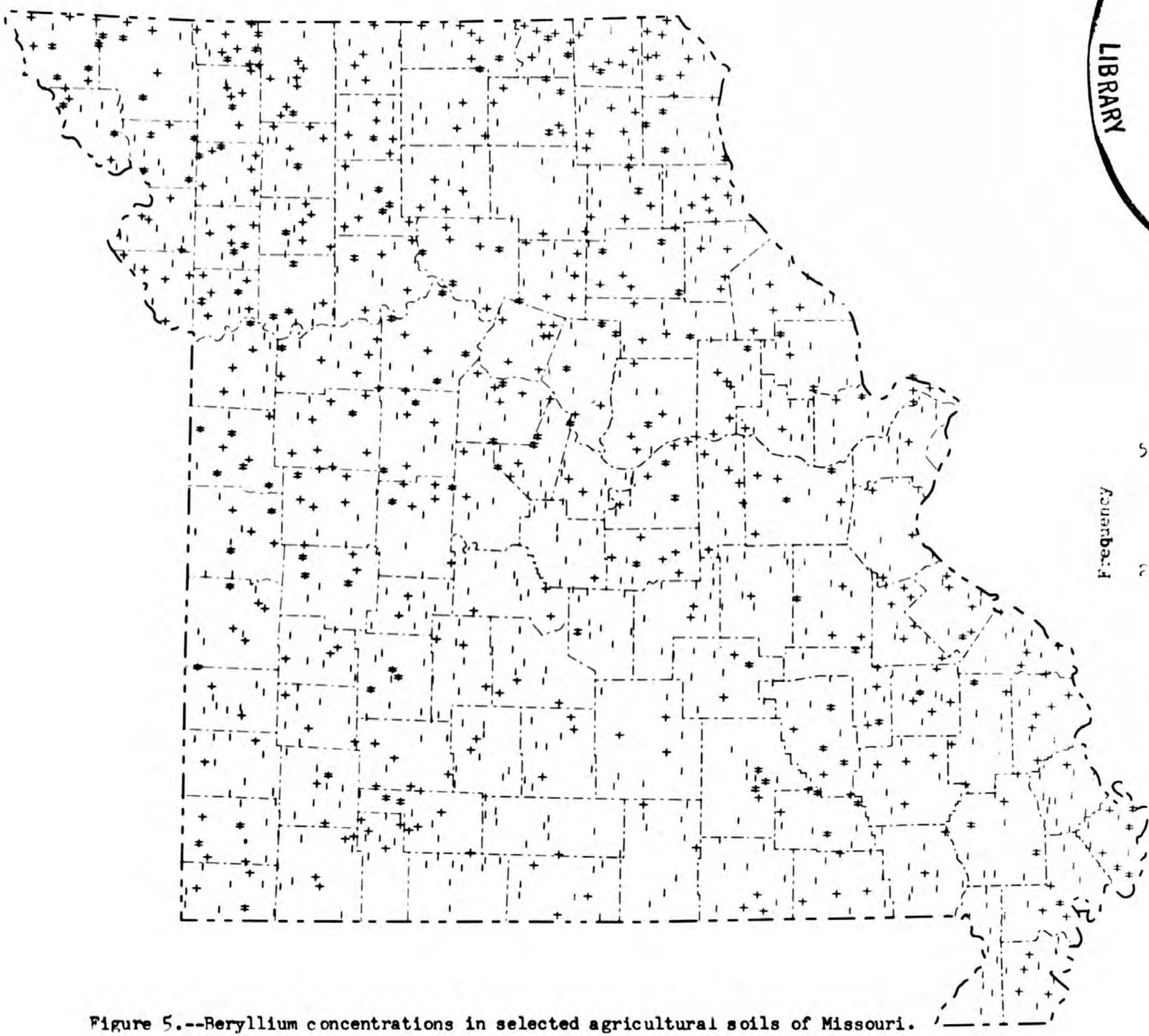
A fourth pattern is typified by silicon (U.S. Geol. Survey, 1972, p. 47) and appears to be complementary to the first two patterns. The elements in this pattern tend to be below-average in specimens from the northern half of the State, and above-average in specimens from the southern half, particularly in the southwest. Other elements with this pattern are manganese, niobium, ytterbium, yttrium and zirconium. As with the second pattern, the boundary between these two regions is indistinct.

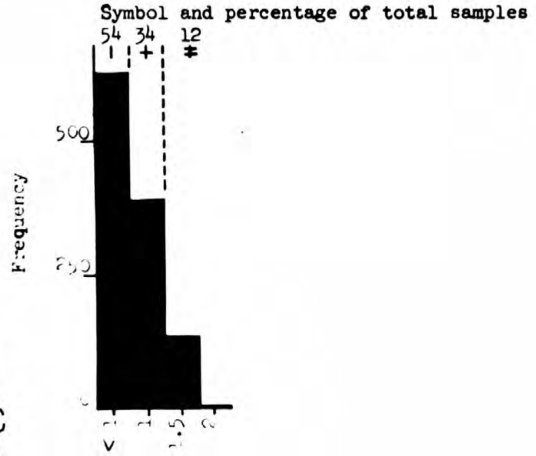
Earlier studies (Tidball, 1971, p. 15-25) have shown that the composition of Missouri soils is not strongly related to any conventional soil taxonomic grouping. It is not surprising, therefore, to find little similarity between element distributions in figures 4-35 and the Statewide soil maps (Missouri University, 1931; Scrivner, Baker, and Miller, 1966). Although it is suspected that, in Missouri at least, soil compositions are probably strongly controlled by parent material composition, definitive conclusions with regard to parent material control on trace elements in the agricultural soils are not possible because of a lack of specific information about the parent material of each specimen. This can only be inferred from the general location of the sampling site, and commonly, the local landscape is a mosaic of soils derived from two or more parent material types. The mapping units on both soil and geology maps tend to portray the predominant material for a given locality, and minor inclusions of other material may or may not be described. A truly random selection of specimens would result in a sample suite containing approximately the same proportion of soils and their corresponding parent materials as appears in the original populations. It is known from the manner in which the agricultural soil specimens were selected that the sample set is not truly random, although the deviations from true randomness may be of little practical concern in evaluating broad-scale patterns over the State. Nevertheless, the possibility remains for a personal bias in collecting. This could result from a desire, for example, to have the "best" soils of a county represented in the sample set at the expense of either some minor soil type, or agriculturally unimportant soils. A case in point is Shannon County. Insofar as can be reconstructed from location information, the apparent compositional anomaly described for this county in the U.S. Geological Survey (1972, p. 55) report results from the collection of most of the county specimens from soils developed from an outlying exposure of rocks of Cambrian and Precambrian age, even though at least three-fourths of the county is underlain by rocks of Ordovician age.



Geometric mean, 580
Geometric deviation, 1.40
Analytical error variance
(percent of total variance), 42
Number of analyses, 1140

Figure 4.--Barium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

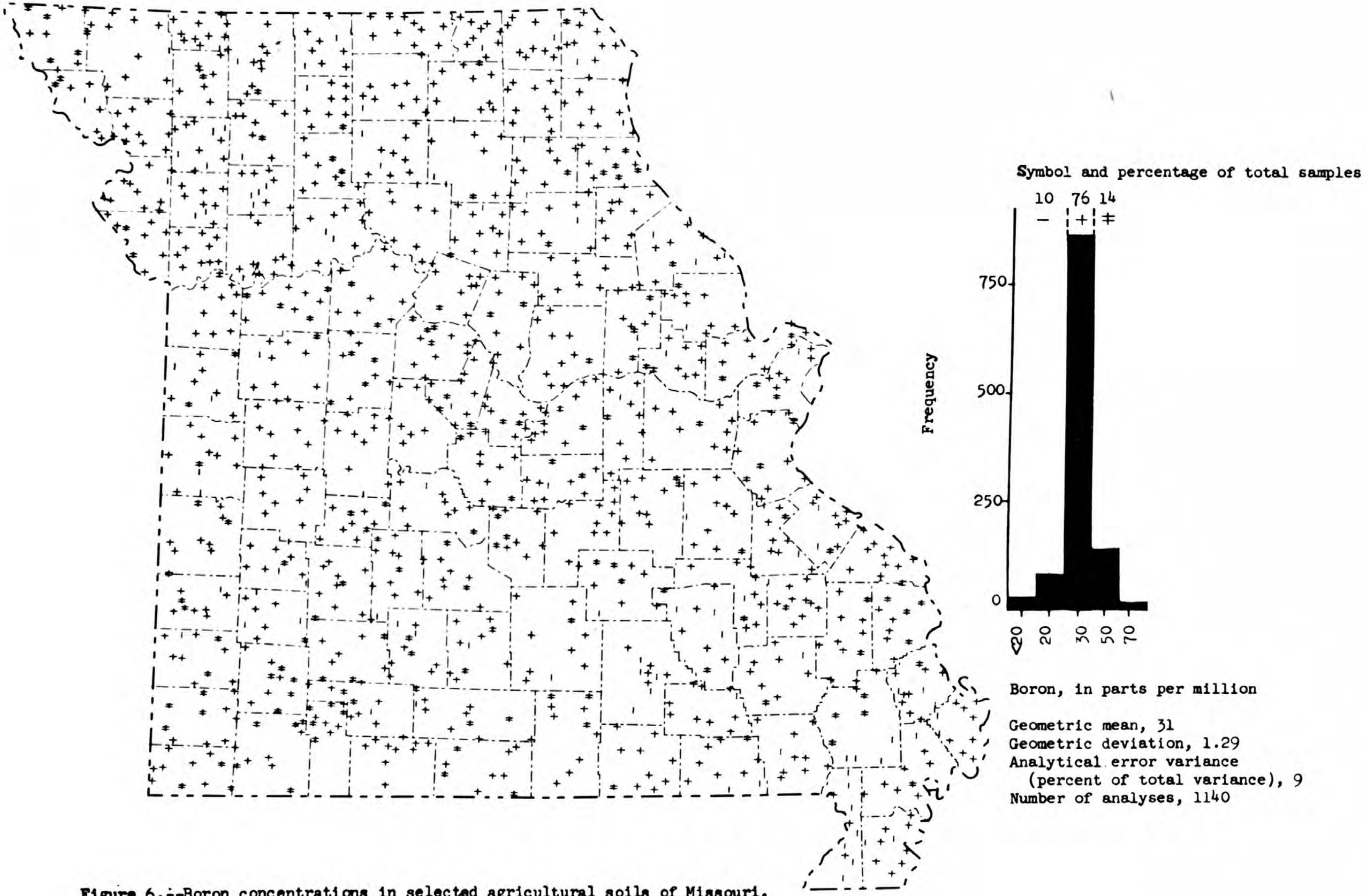




Beryllium, in parts per million

Geometric mean, 0.8
Geometric deviation, 1.43
Analytical error variance
(percent of total variance), 17
Number of analyses, 1140

Figure 5.--Beryllium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 31
Geometric deviation, 1.29
Analytical error variance
(percent of total variance), 9
Number of analyses, 1140

Figure 6.--Boron concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

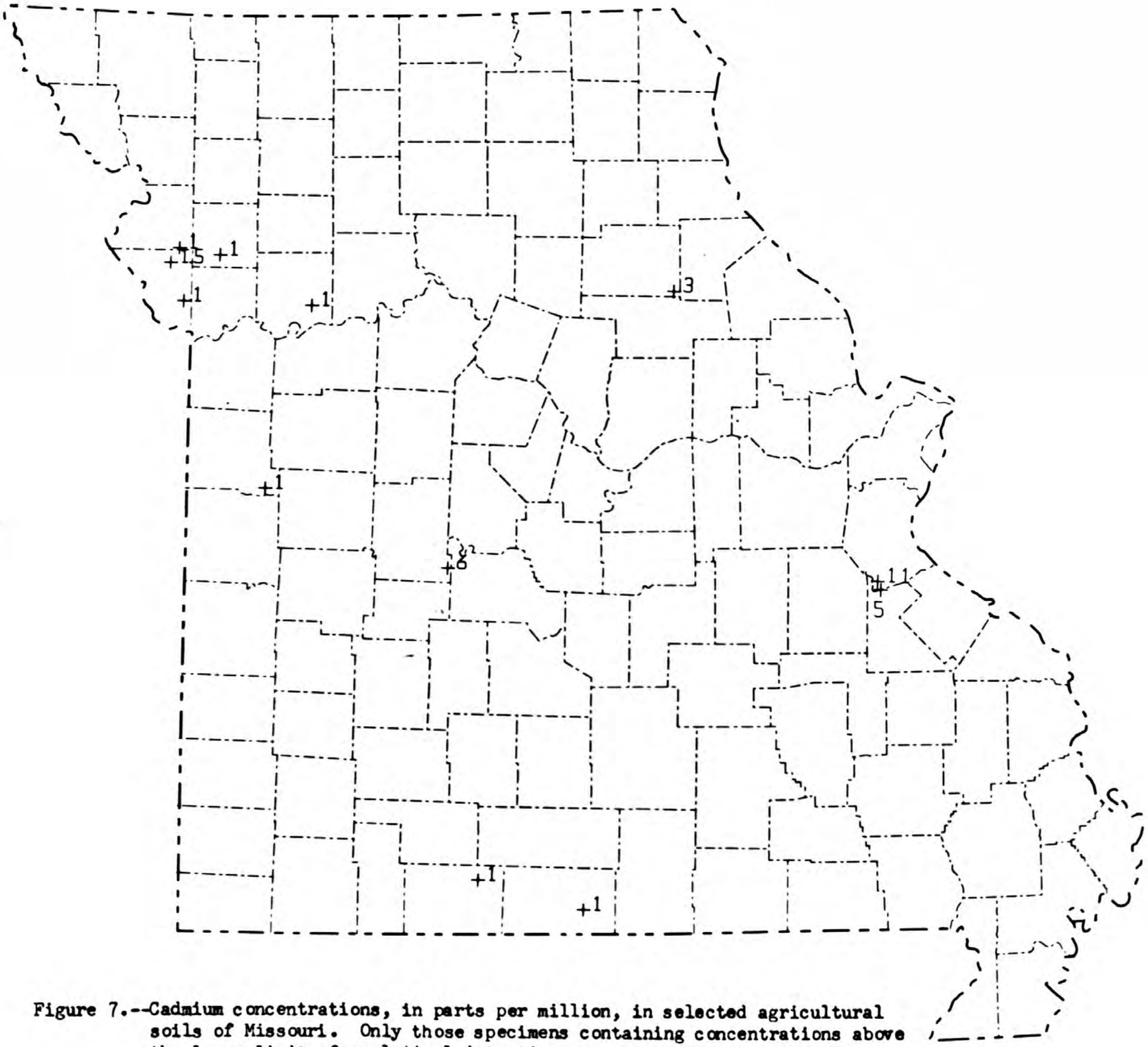
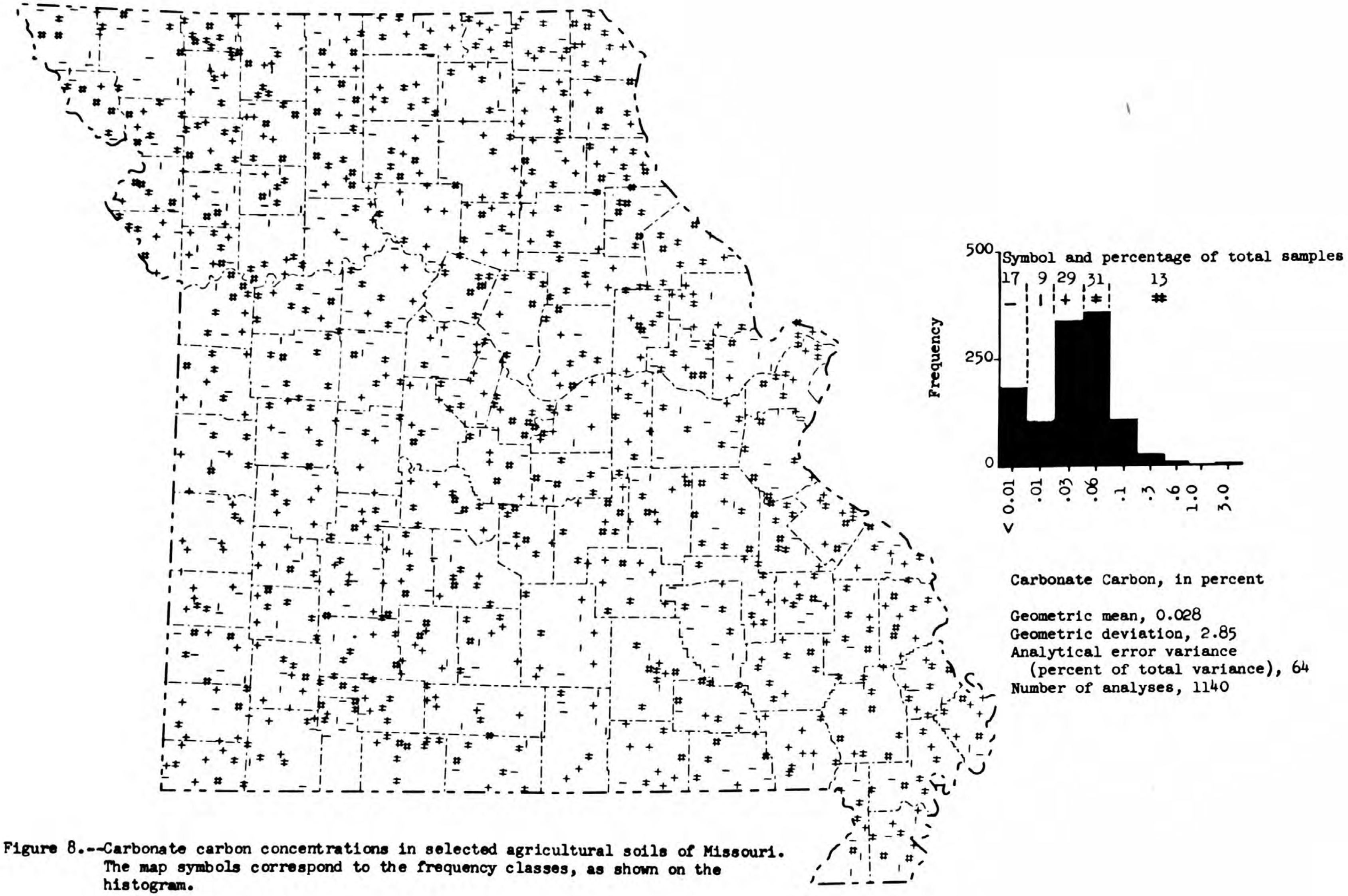


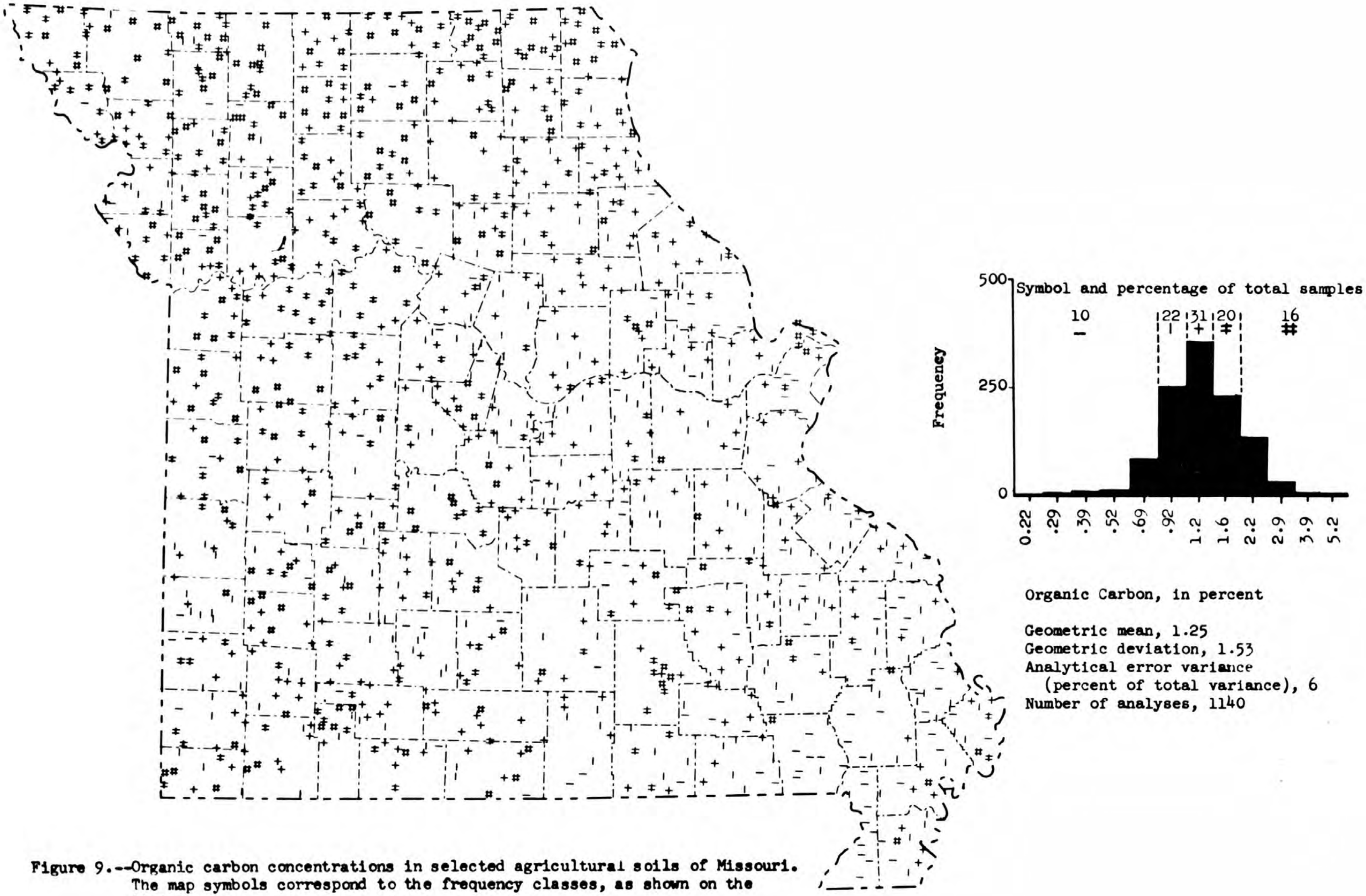
Figure 7.--Cadmium concentrations, in parts per million, in selected agricultural soils of Missouri. Only those specimens containing concentrations above the lower limit of analytical detection are shown; the plus symbol indicates the location of the sampling site.



Carbonate Carbon, in percent

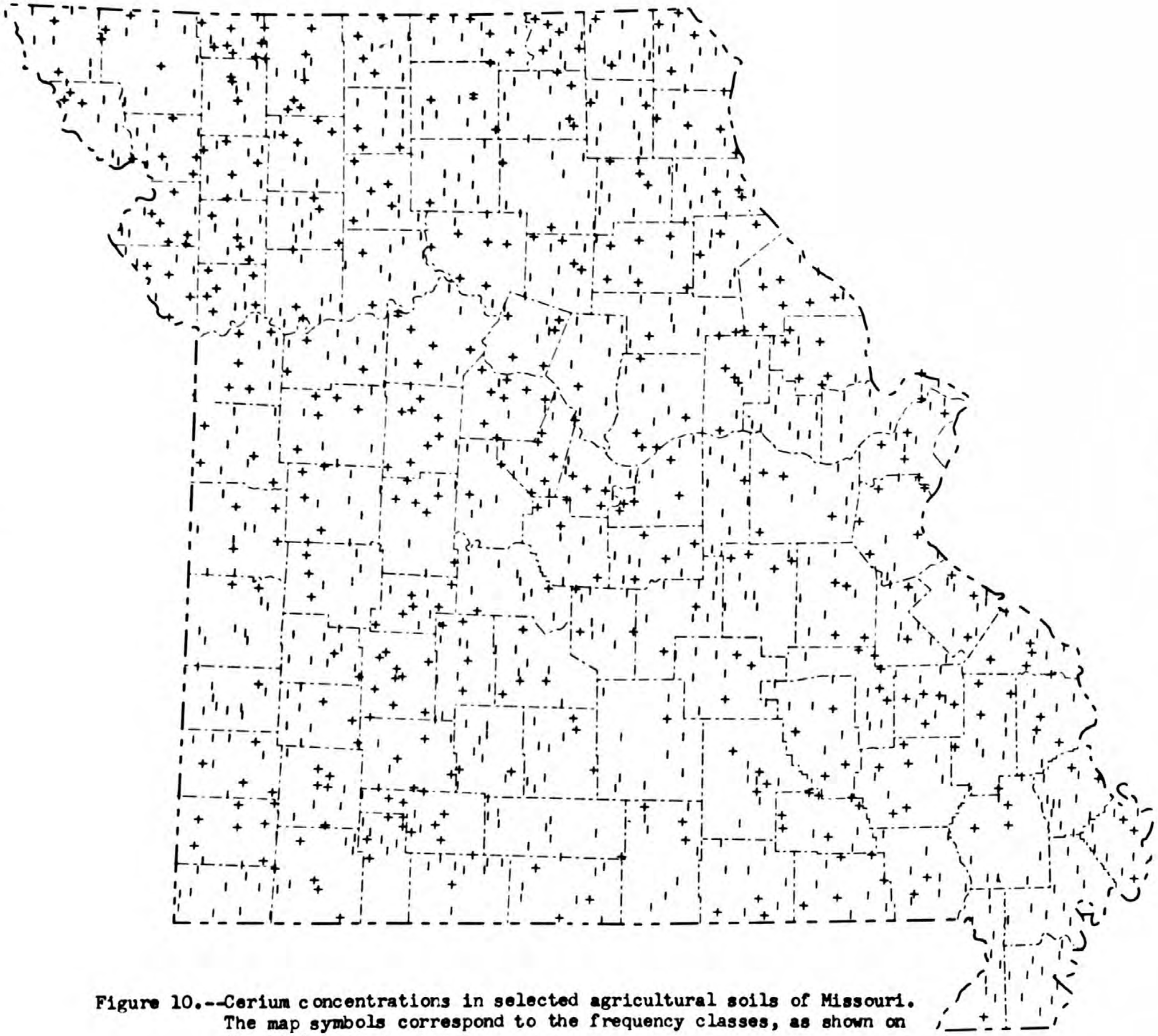
Geometric mean, 0.028
Geometric deviation, 2.85
Analytical error variance
(percent of total variance), 64
Number of analyses, 1140

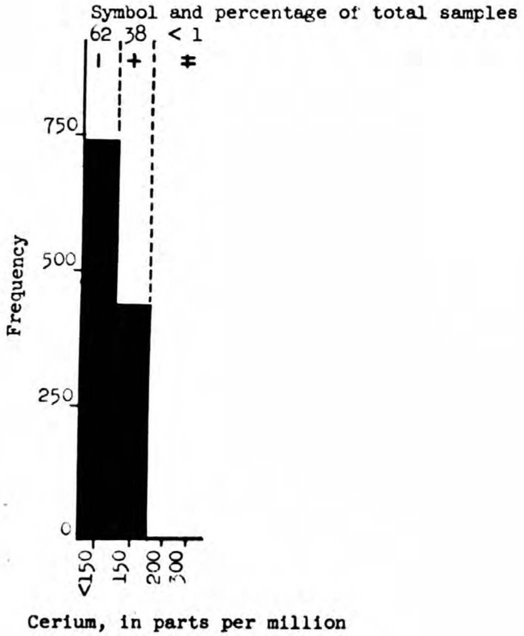
Figure 8.--Carbonate carbon concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 1.25
Geometric deviation, 1.53
Analytical error variance
(percent of total variance), 6
Number of analyses, 1140

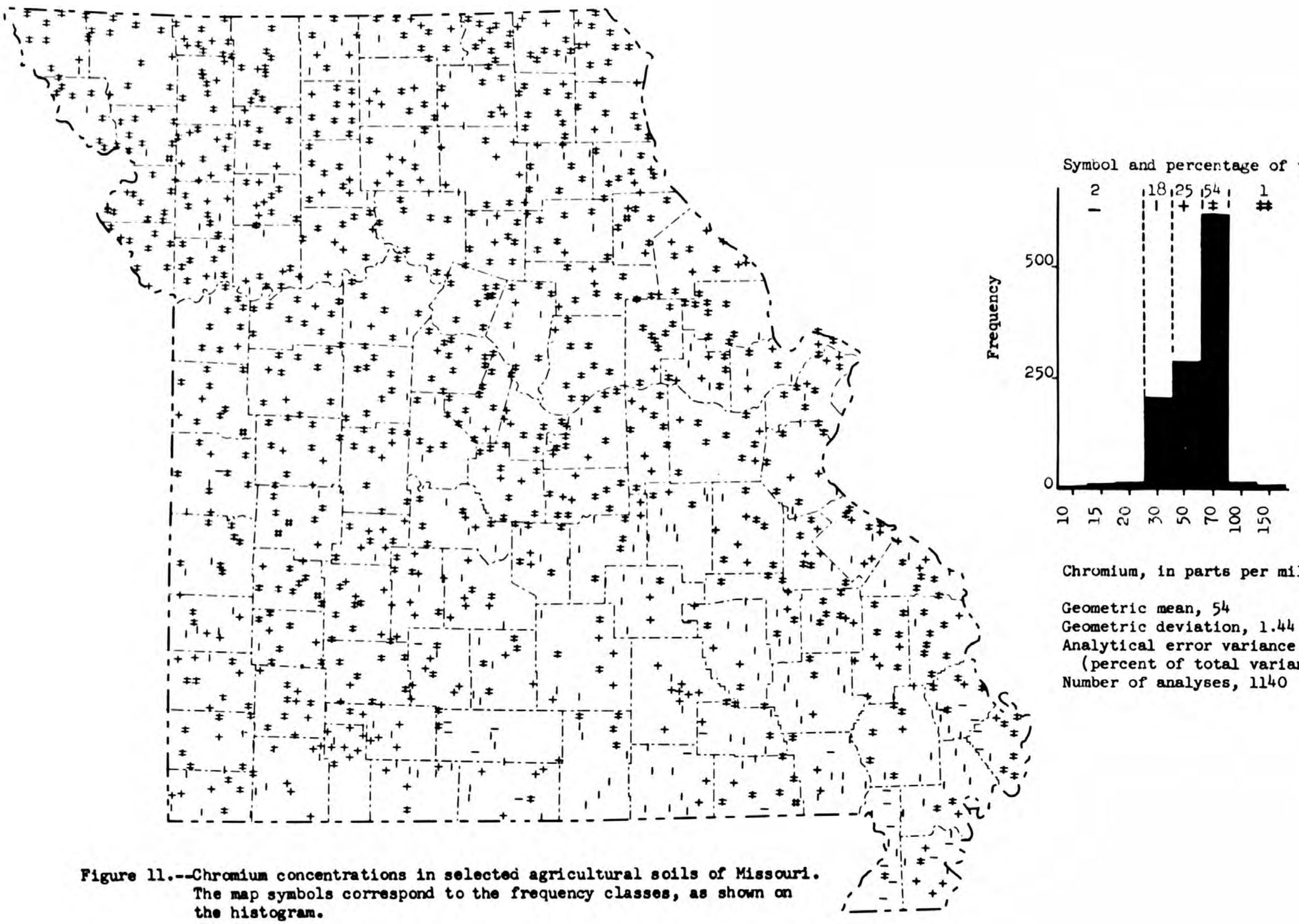
Figure 9.--Organic carbon concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.





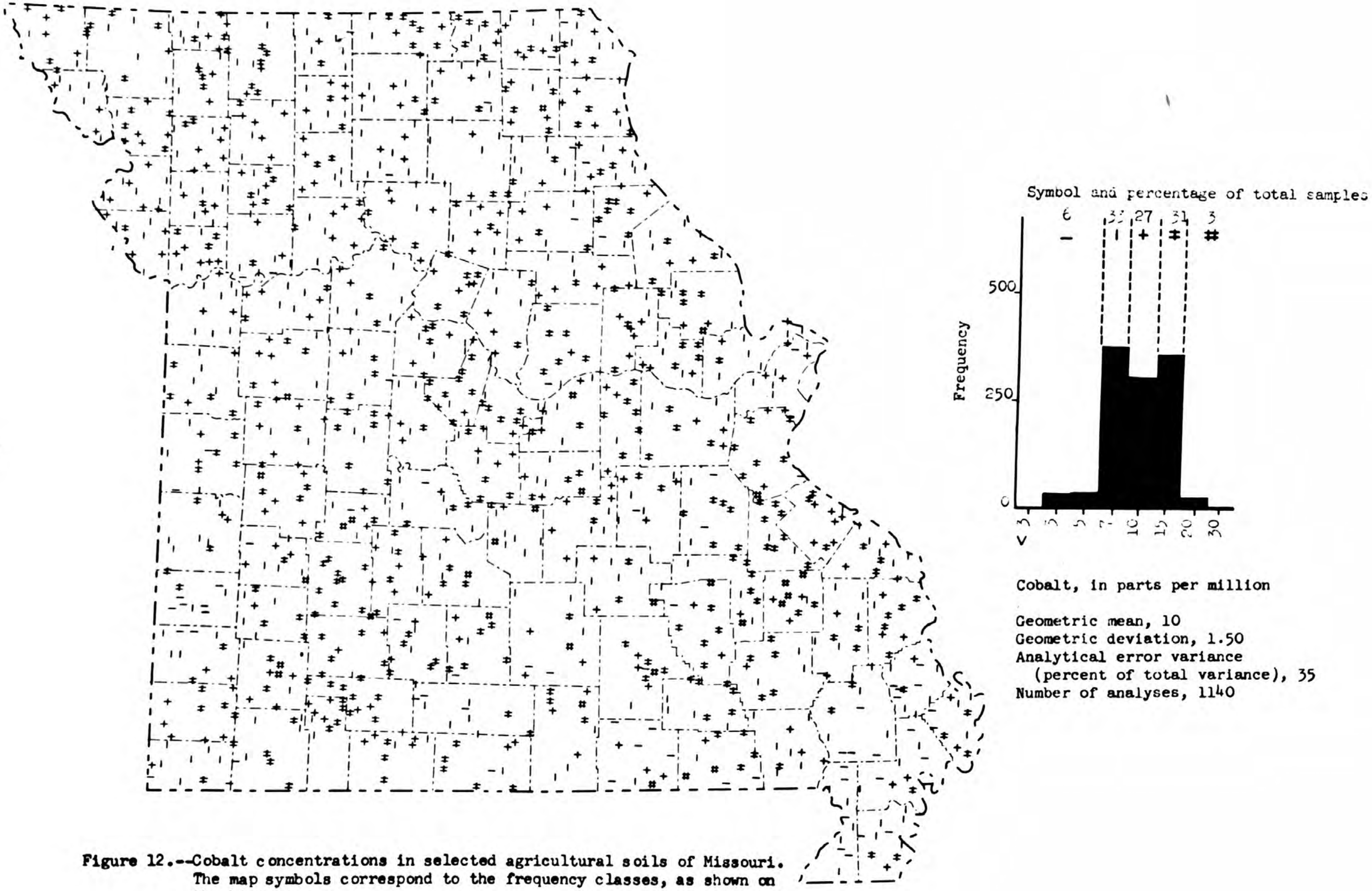
Geometric mean, 115
Geometric deviation, 1.27
Analytical error variance
(percent of total variance), not determined
Number of analyses, 1140

Figure 10.--Cerium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 54
Geometric deviation, 1.44
Analytical error variance
(percent of total variance), 41
Number of analyses, 1140

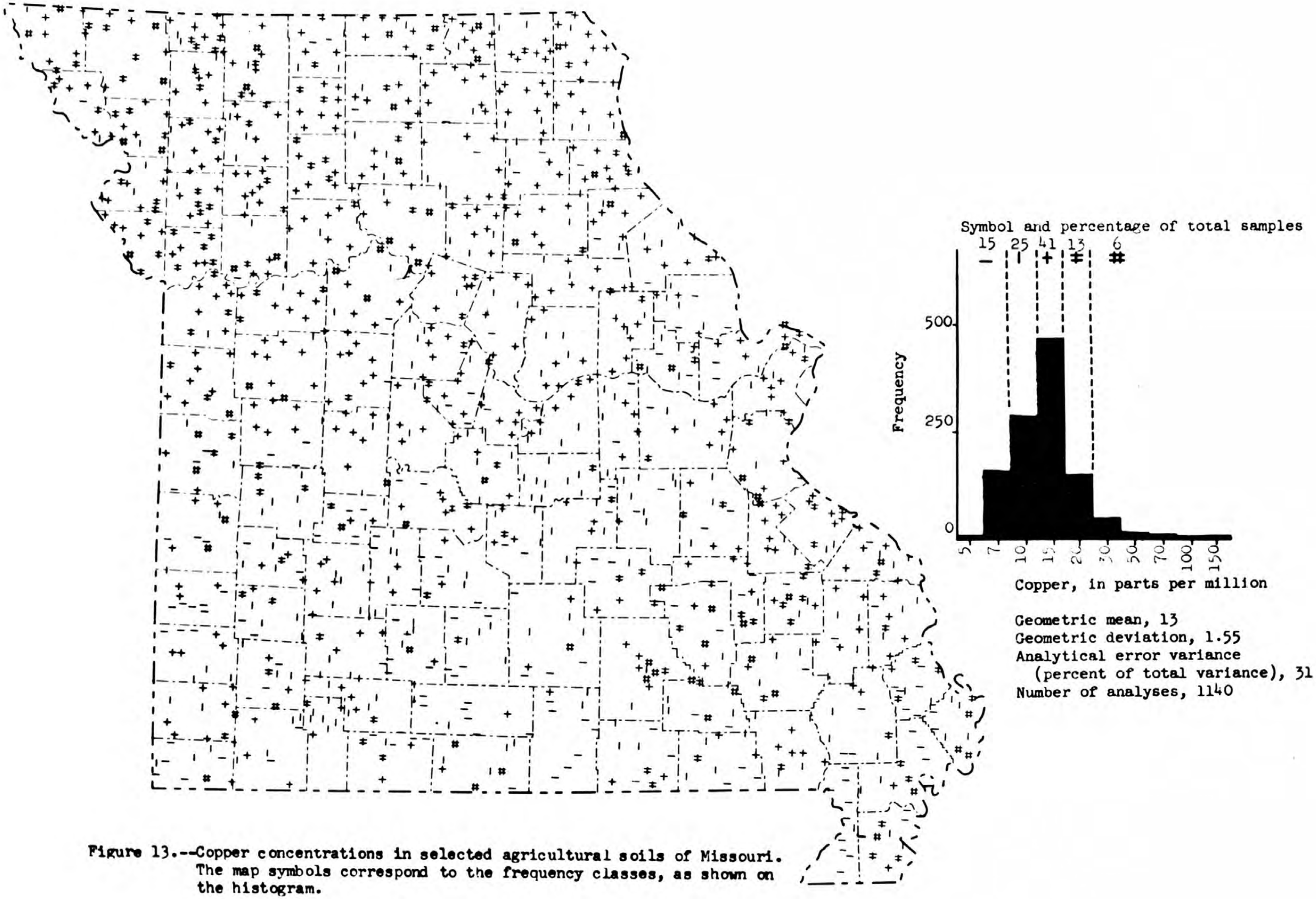
Figure 11.--Chromium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Cobalt, in parts per million

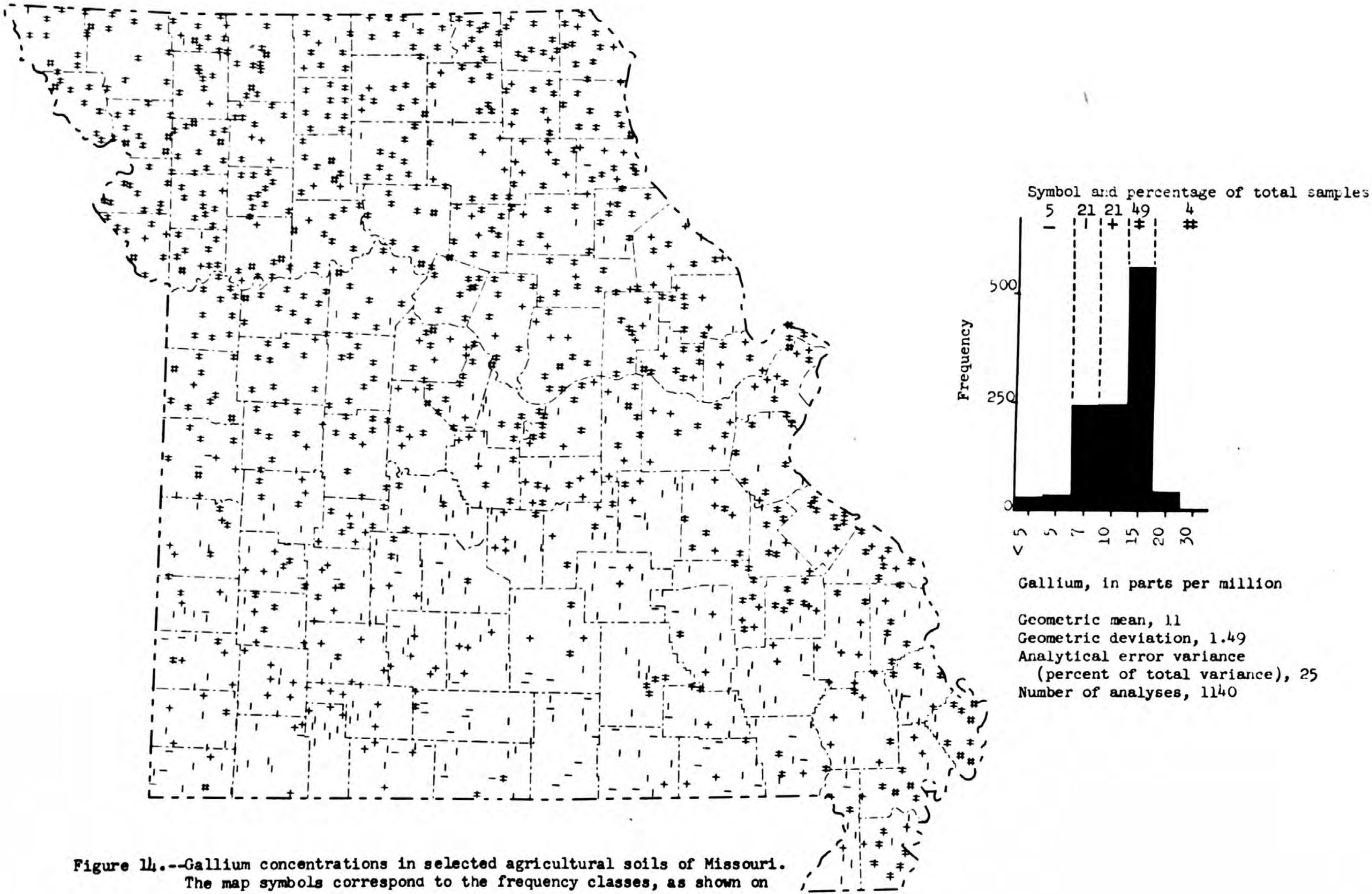
Geometric mean, 10
Geometric deviation, 1.50
Analytical error variance
(percent of total variance), 35
Number of analyses, 1140

Figure 12.--Cobalt concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



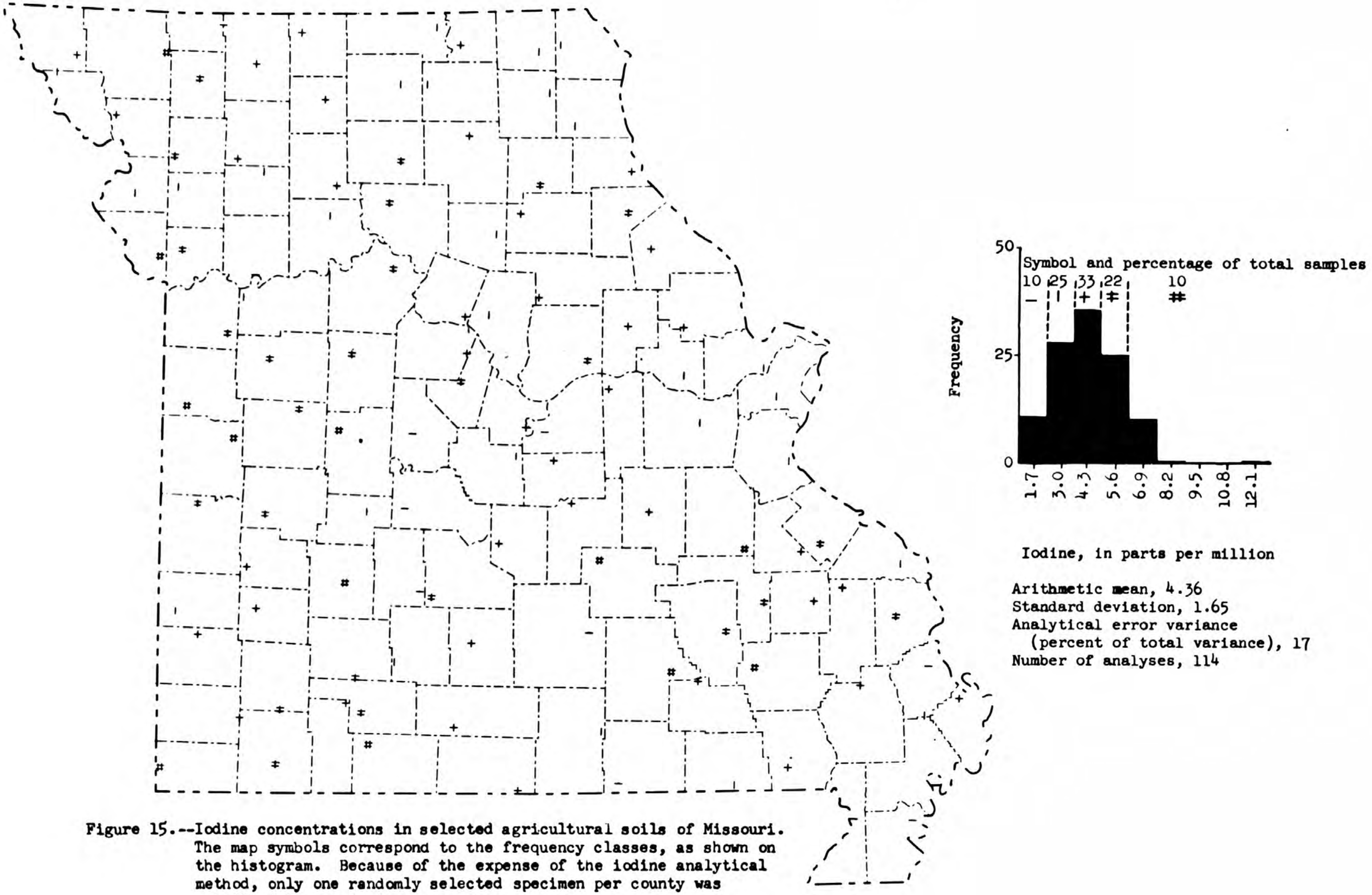
Geometric mean, 13
Geometric deviation, 1.55
Analytical error variance
(percent of total variance), 31
Number of analyses, 1140

Figure 13.--Copper concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



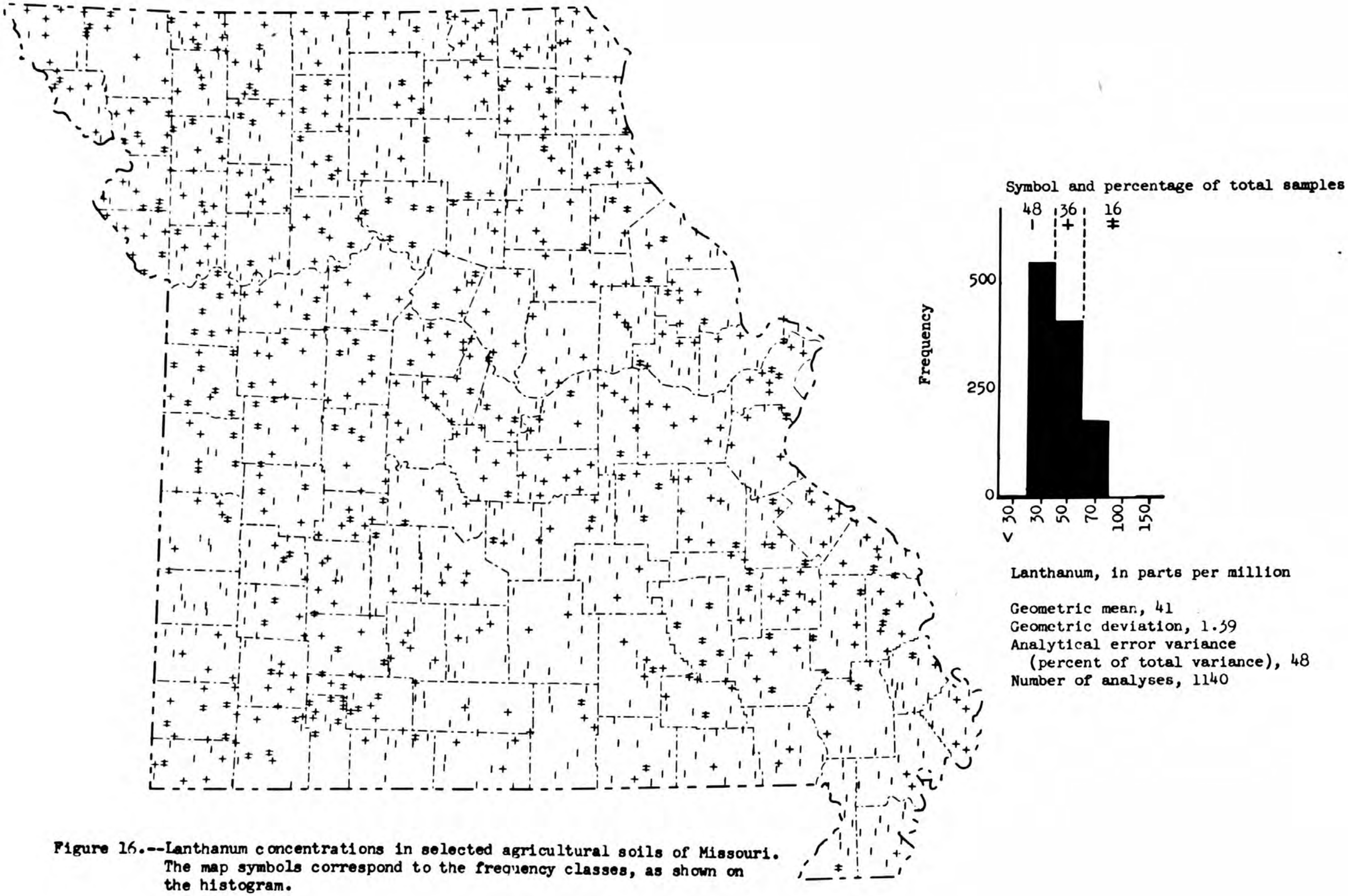
Geometric mean, 11
Geometric deviation, 1.49
Analytical error variance
(percent of total variance), 25
Number of analyses, 1140

Figure 14.--Gallium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



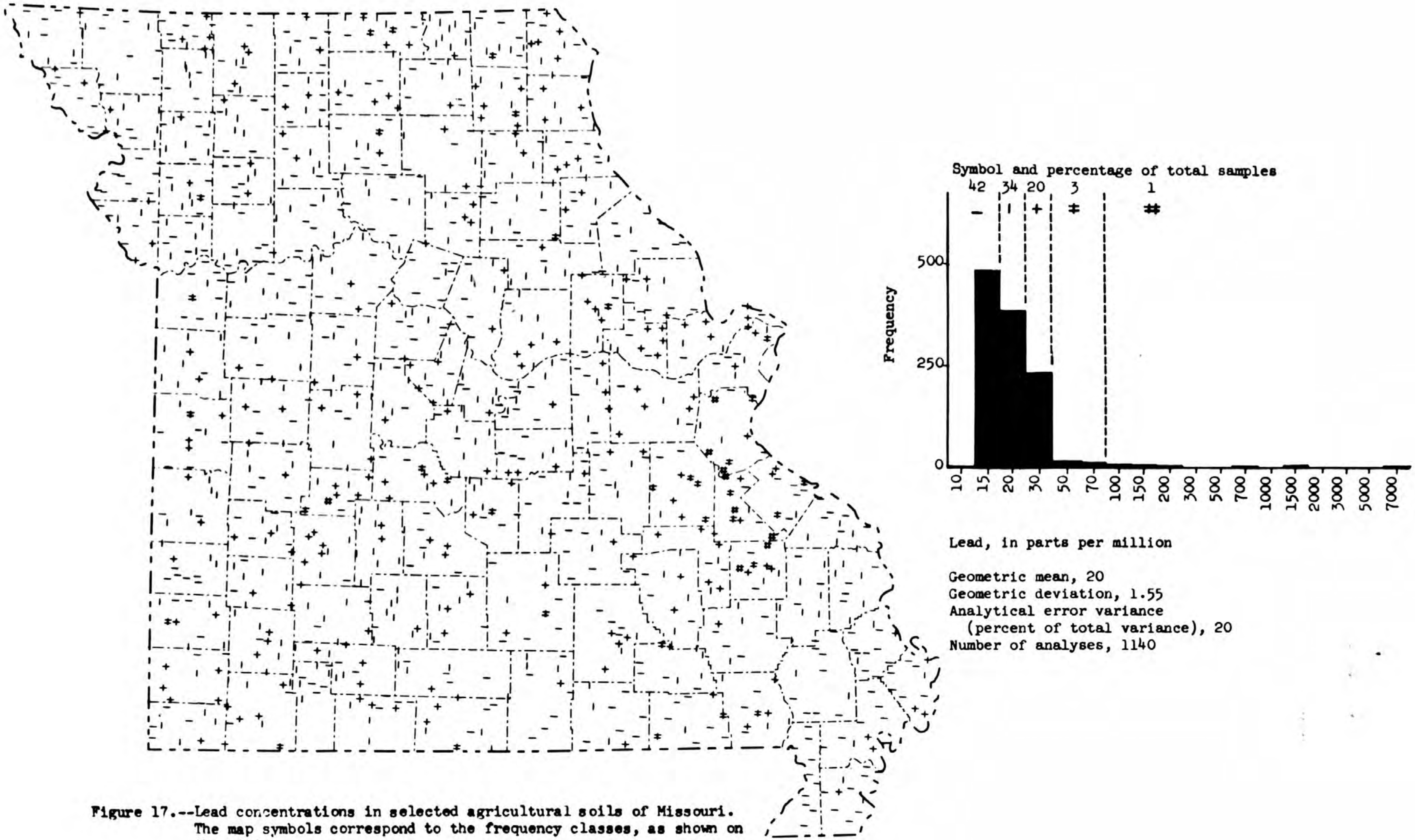
Arithmetic mean, 4.36
Standard deviation, 1.65
Analytical error variance
(percent of total variance), 17
Number of analyses, 114

Figure 15.--Iodine concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram. Because of the expense of the iodine analytical method, only one randomly selected specimen per county was submitted for analysis.



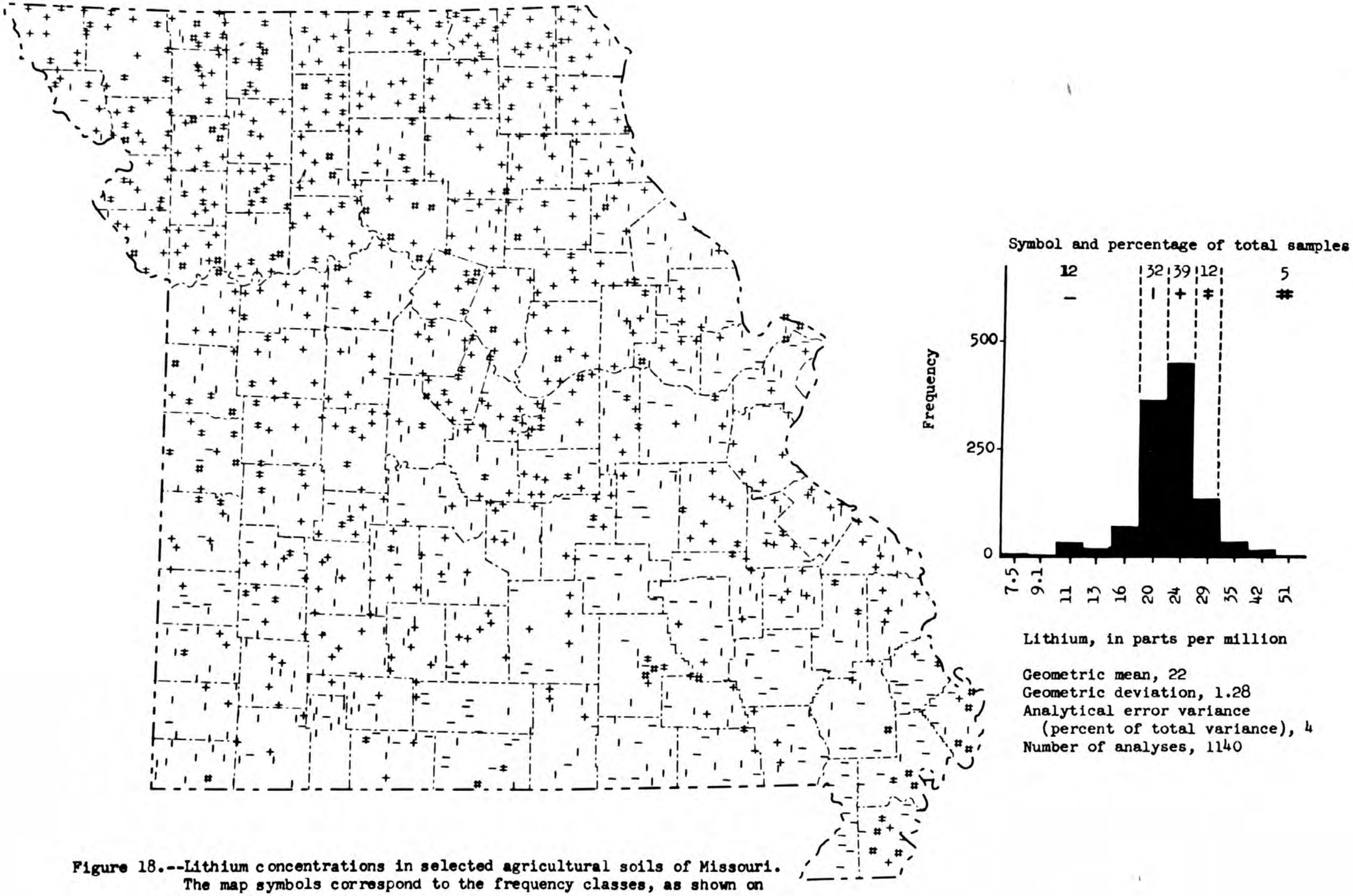
Geometric mean, 41
Geometric deviation, 1.59
Analytical error variance
  (percent of total variance), 48
Number of analyses, 1140

Figure 16.--Lanthanum concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



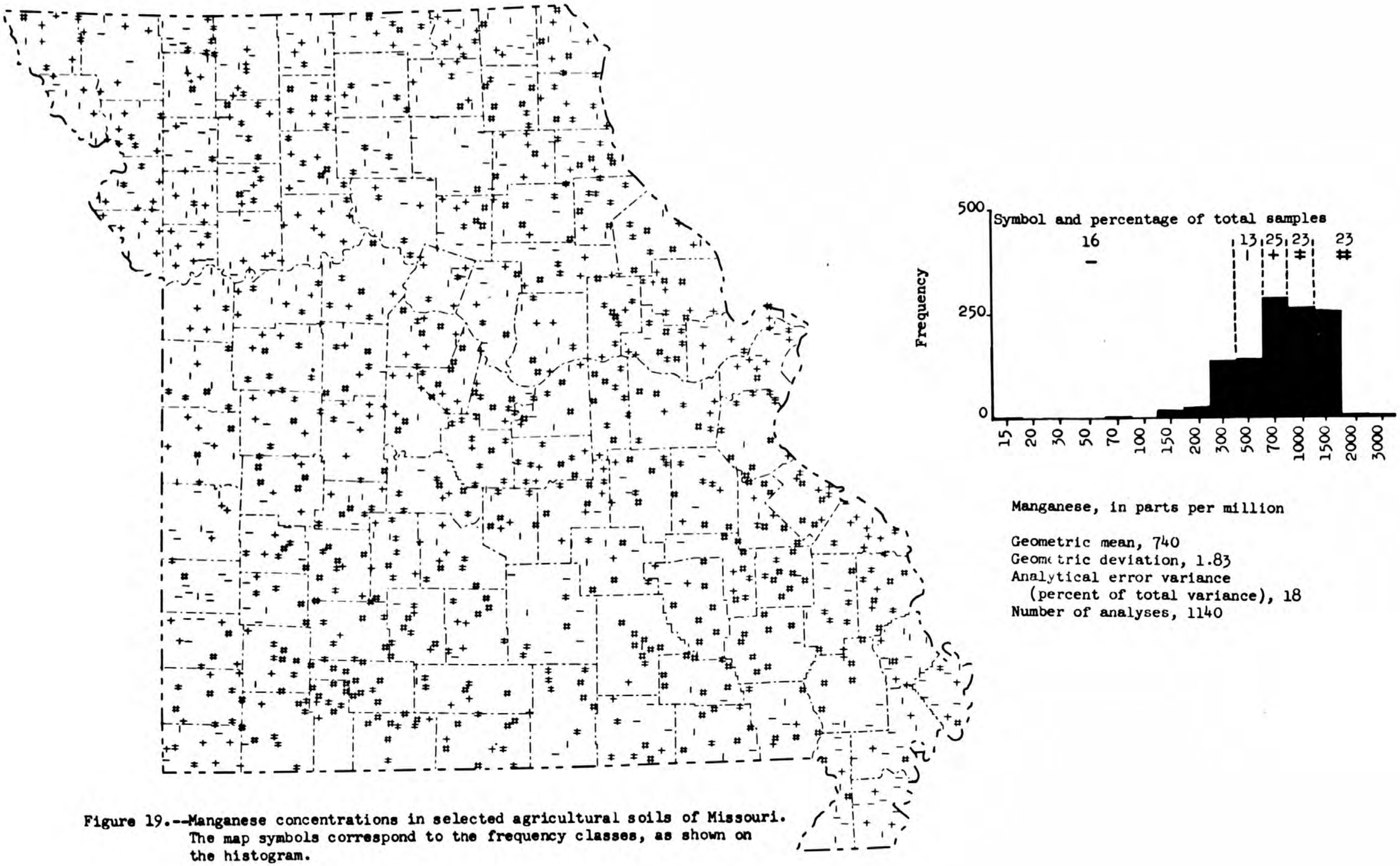
Geometric mean, 20
Geometric deviation, 1.55
Analytical error variance
(percent of total variance), 20
Number of analyses, 1140

Figure 17.--Lead concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 22
Geometric deviation, 1.28
Analytical error variance
(percent of total variance), 4
Number of analyses, 1140

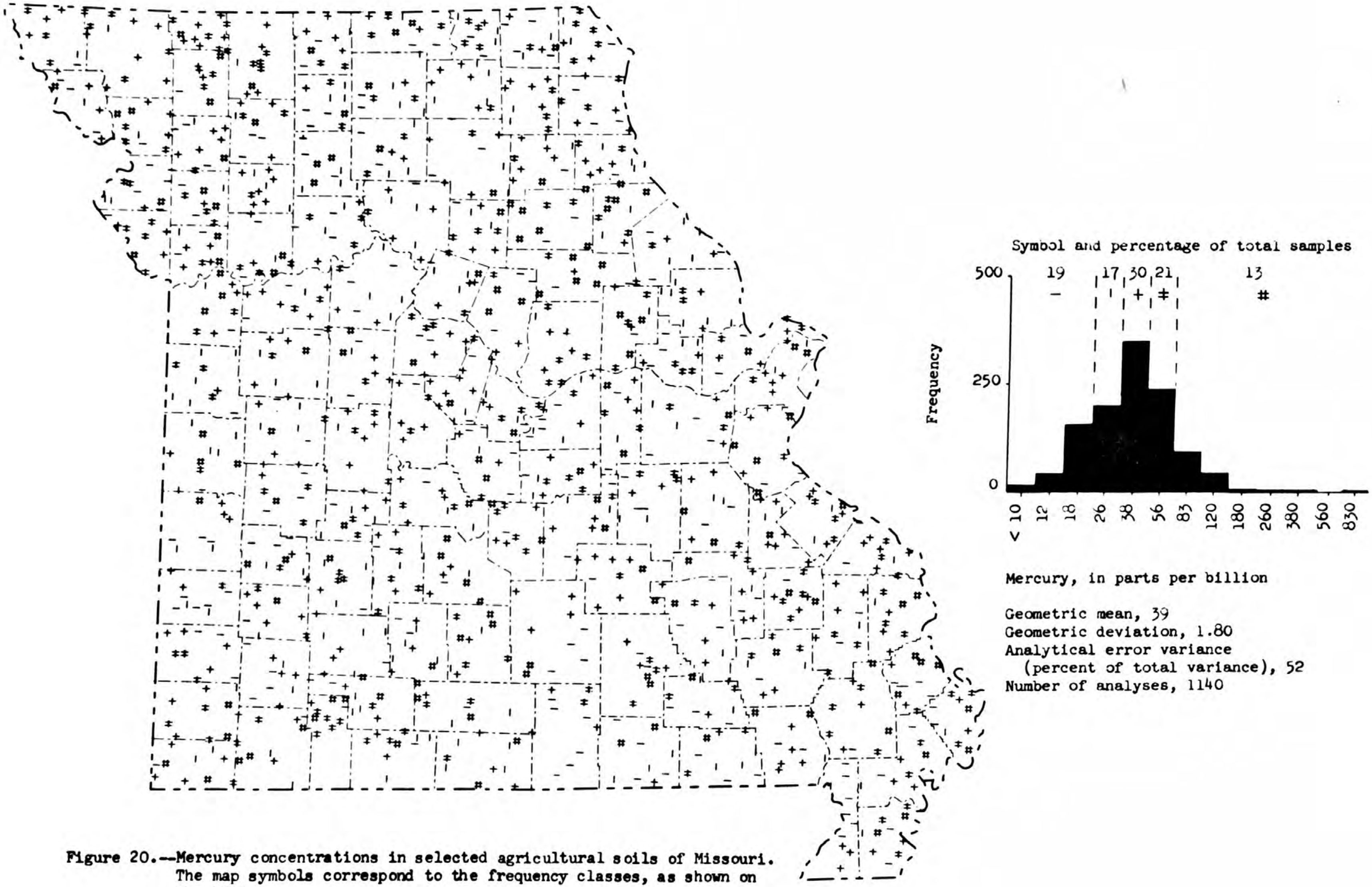
Figure 18.--Lithium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Manganese, in parts per million

Geometric mean, 740
Geometric deviation, 1.83
Analytical error variance
(percent of total variance), 18
Number of analyses, 1140

Figure 19.--Manganese concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 39
Geometric deviation, 1.80
Analytical error variance
(percent of total variance), 52
Number of analyses, 1140

Figure 20.--Mercury concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

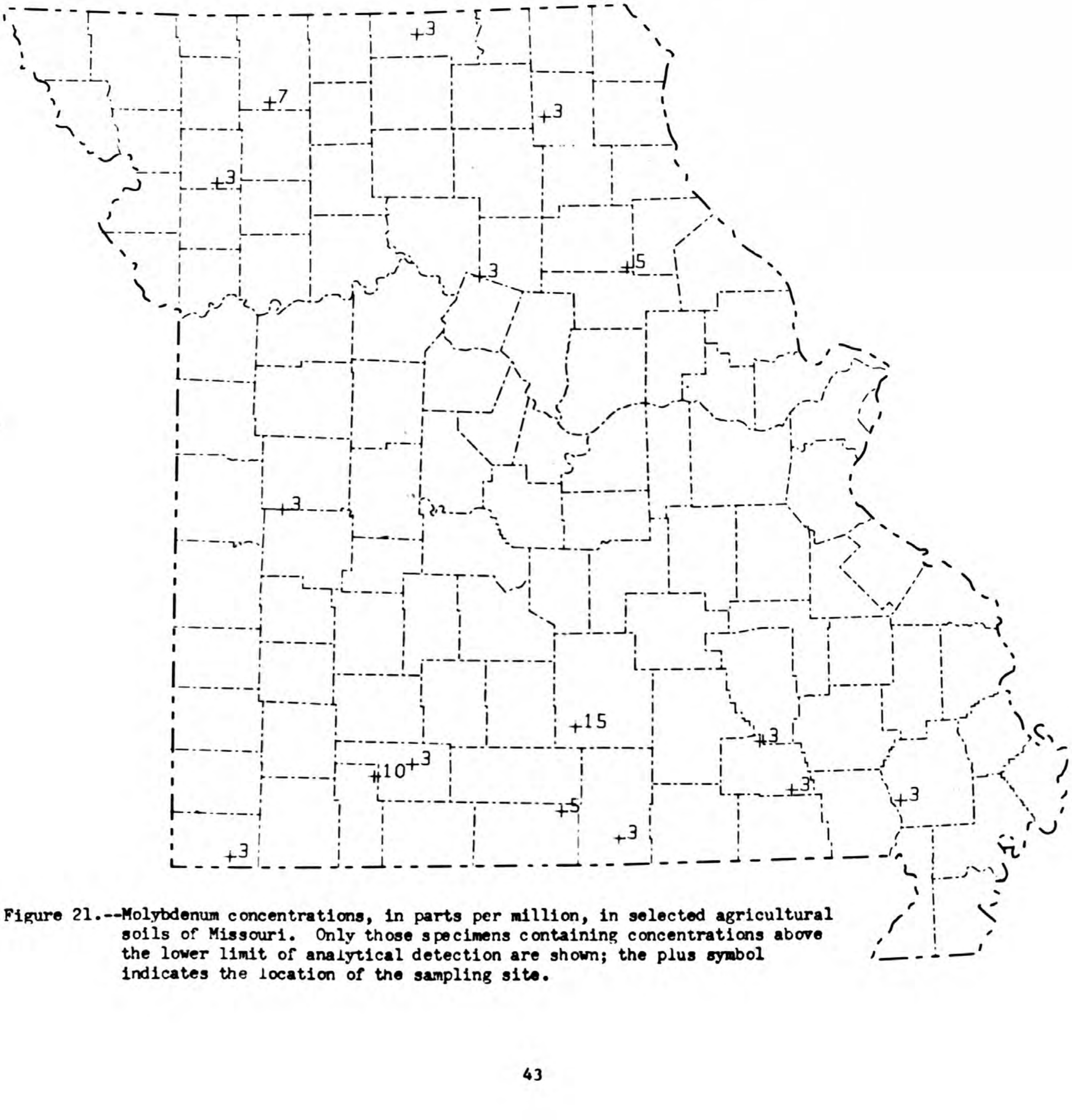
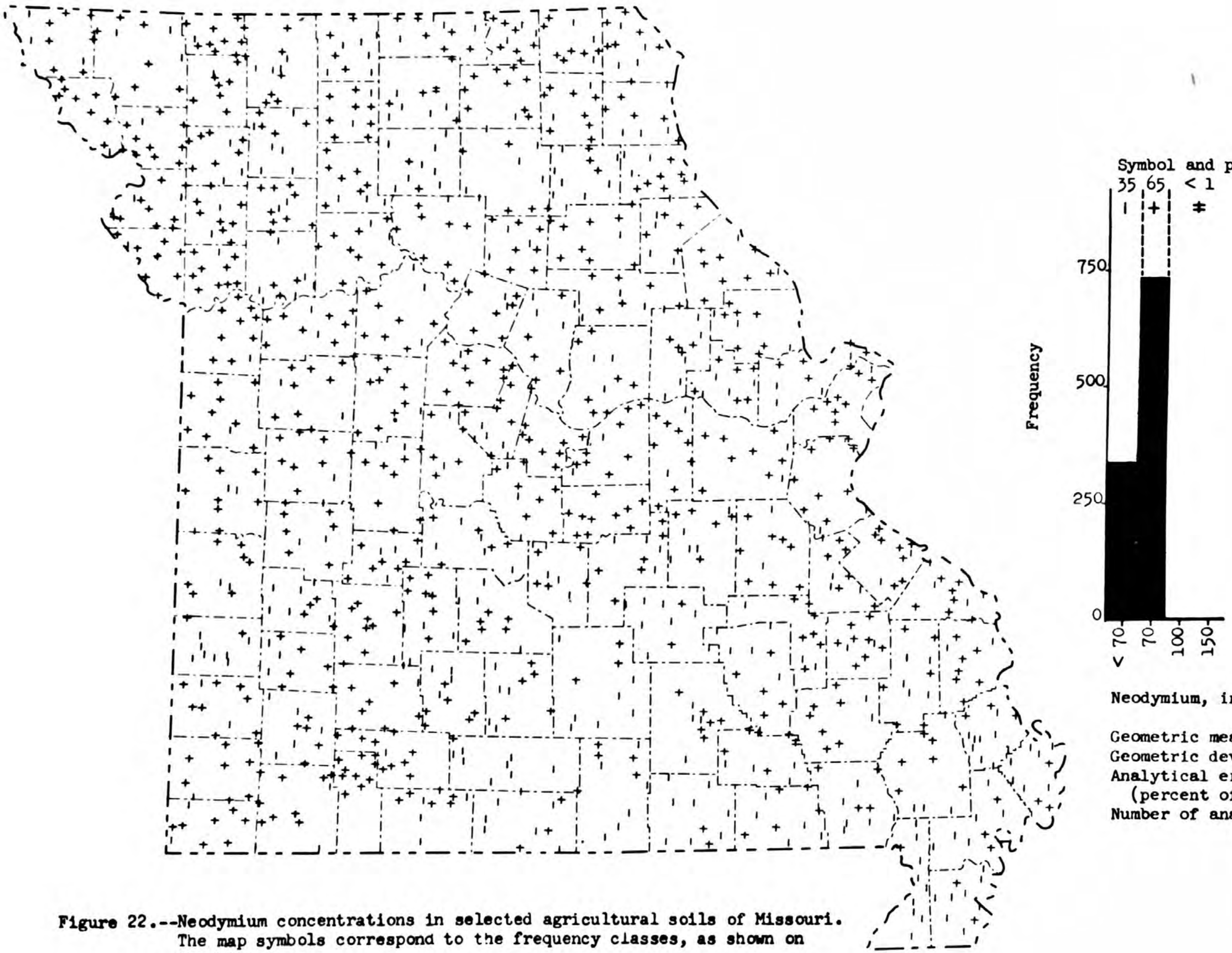


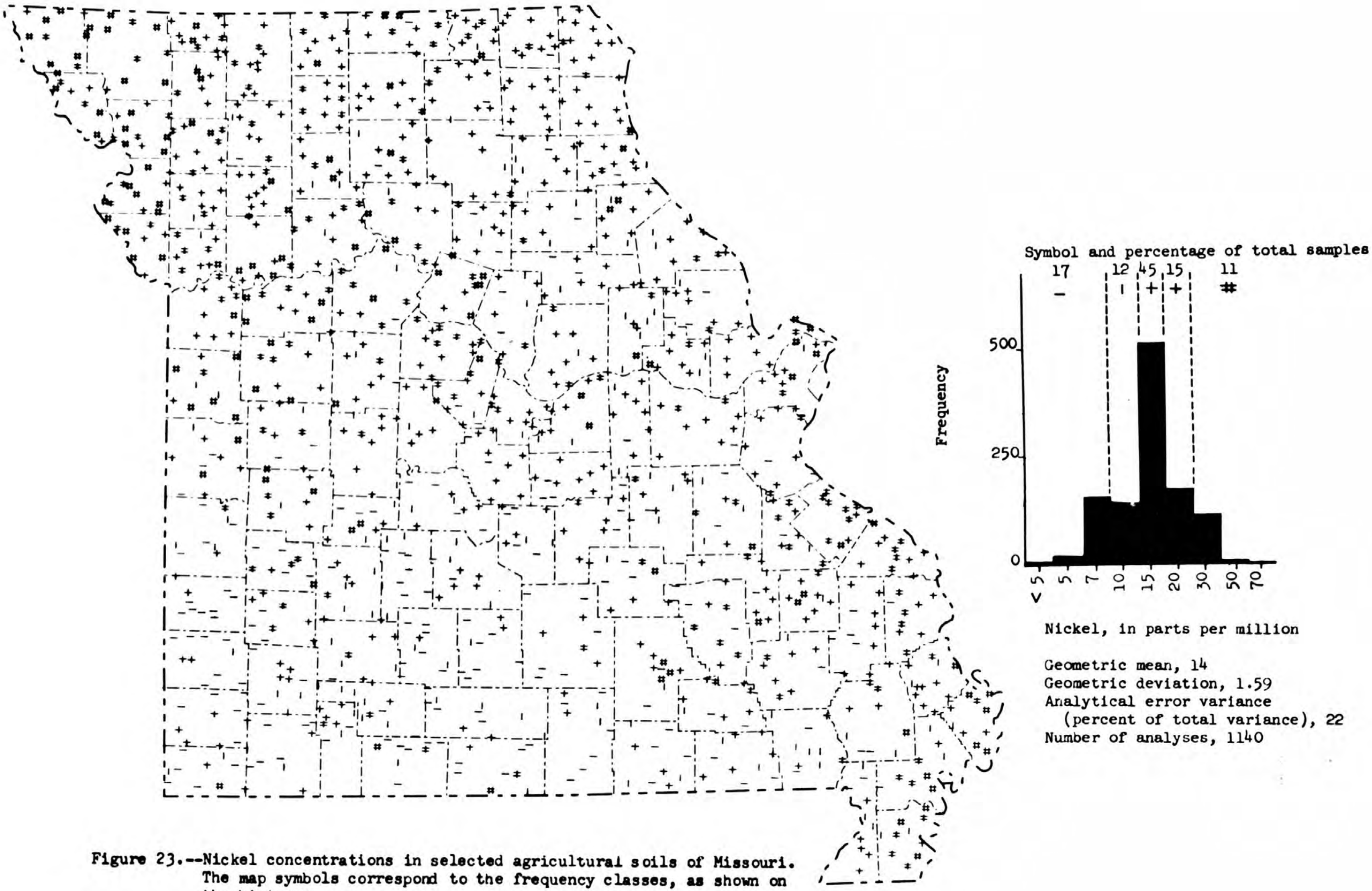
Figure 21.--Molybdenum concentrations, in parts per million, in selected agricultural soils of Missouri. Only those specimens containing concentrations above the lower limit of analytical detection are shown; the plus symbol indicates the location of the sampling site.



Neodymium, in parts per million

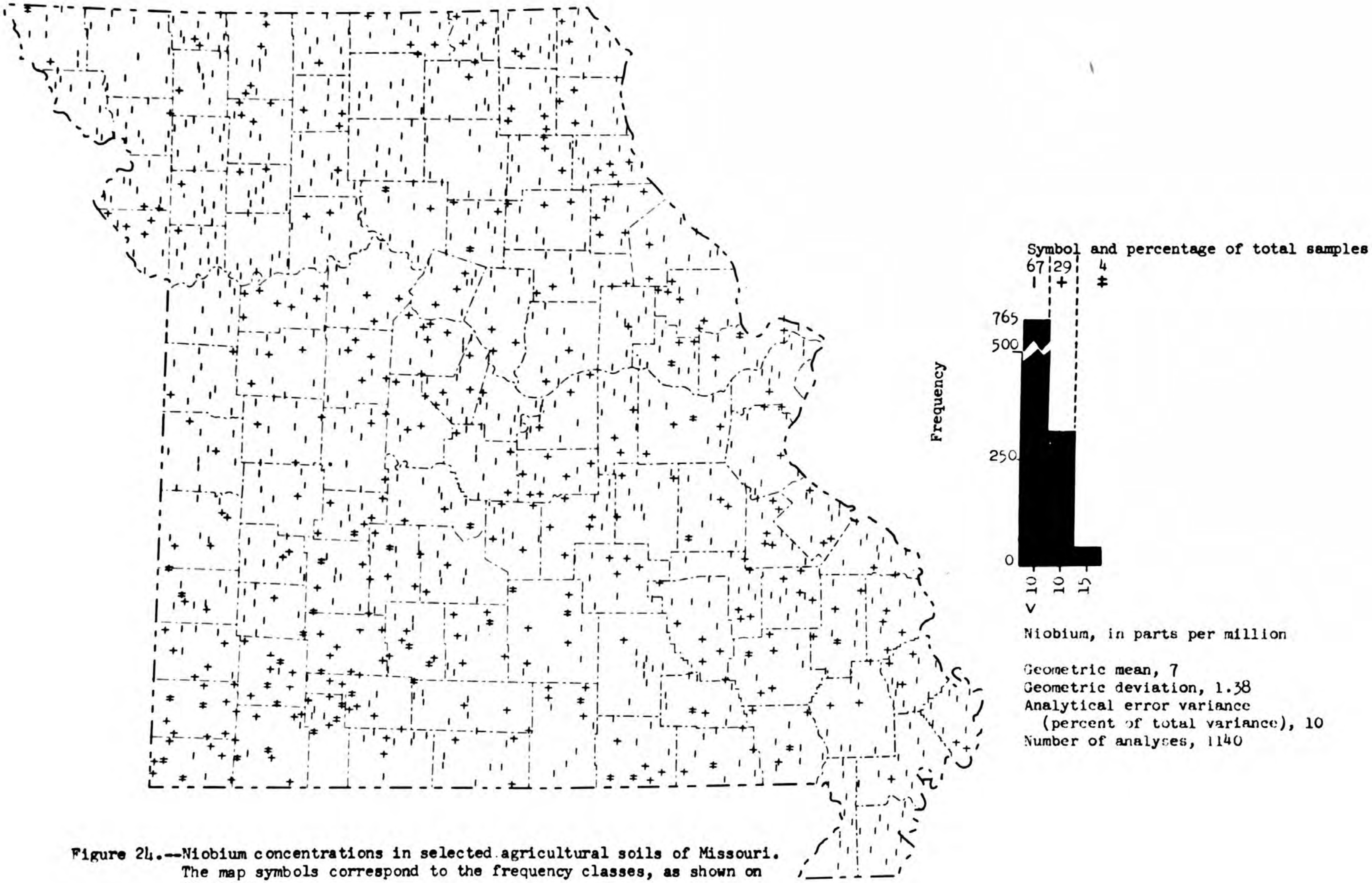
Geometric mean, 63
Geometric deviation, 1.17
Analytical error variance
(percent of total variance), 0
Number of analyses, 1140

Figure 22.--Neodymium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



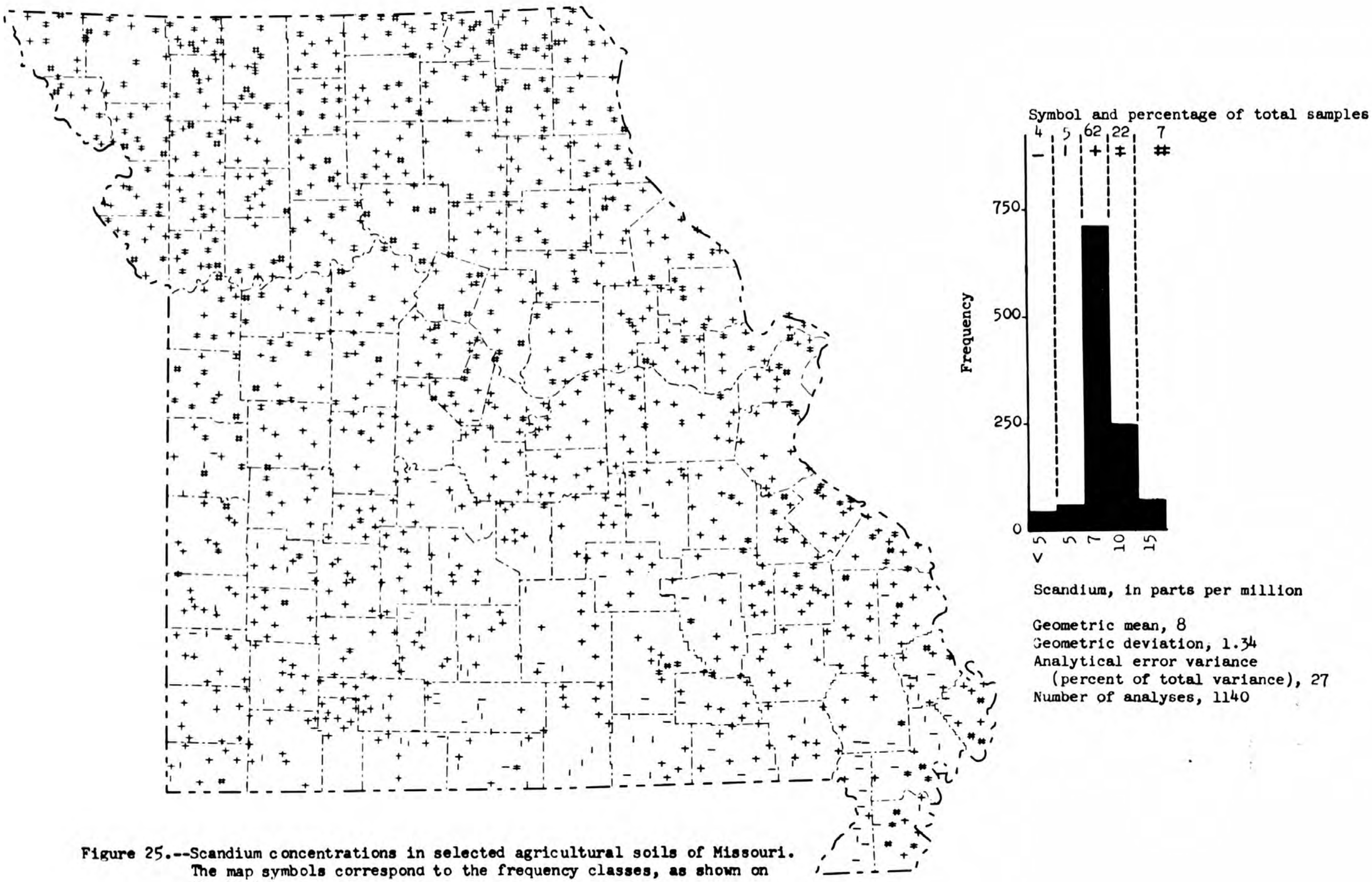
Geometric mean, 14
Geometric deviation, 1.59
Analytical error variance
(percent of total variance), 22
Number of analyses, 1140

Figure 23.--Nickel concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 7
Geometric deviation, 1.38
Analytical error variance
(percent of total variance), 10
Number of analyses, 1140

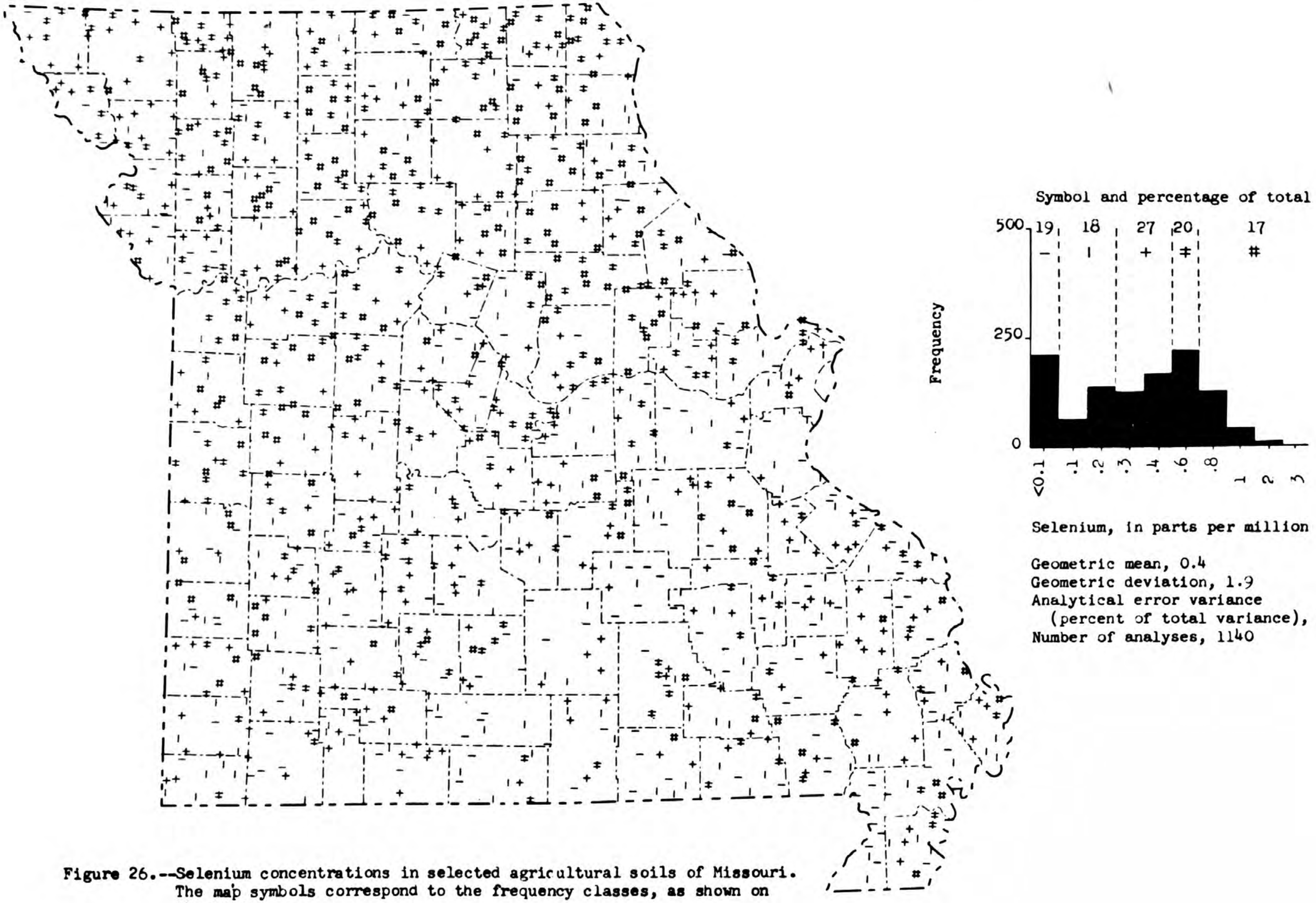
Figure 24.--Niobium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Scandium, in parts per million

Geometric mean, 8
Geometric deviation, 1.34
Analytical error variance
(percent of total variance), 27
Number of analyses, 1140

Figure 25.--Scandium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 0.4
Geometric deviation, 1.9
Analytical error variance
(percent of total variance), 30
Number of analyses, 1140

Figure 26.--Selenium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

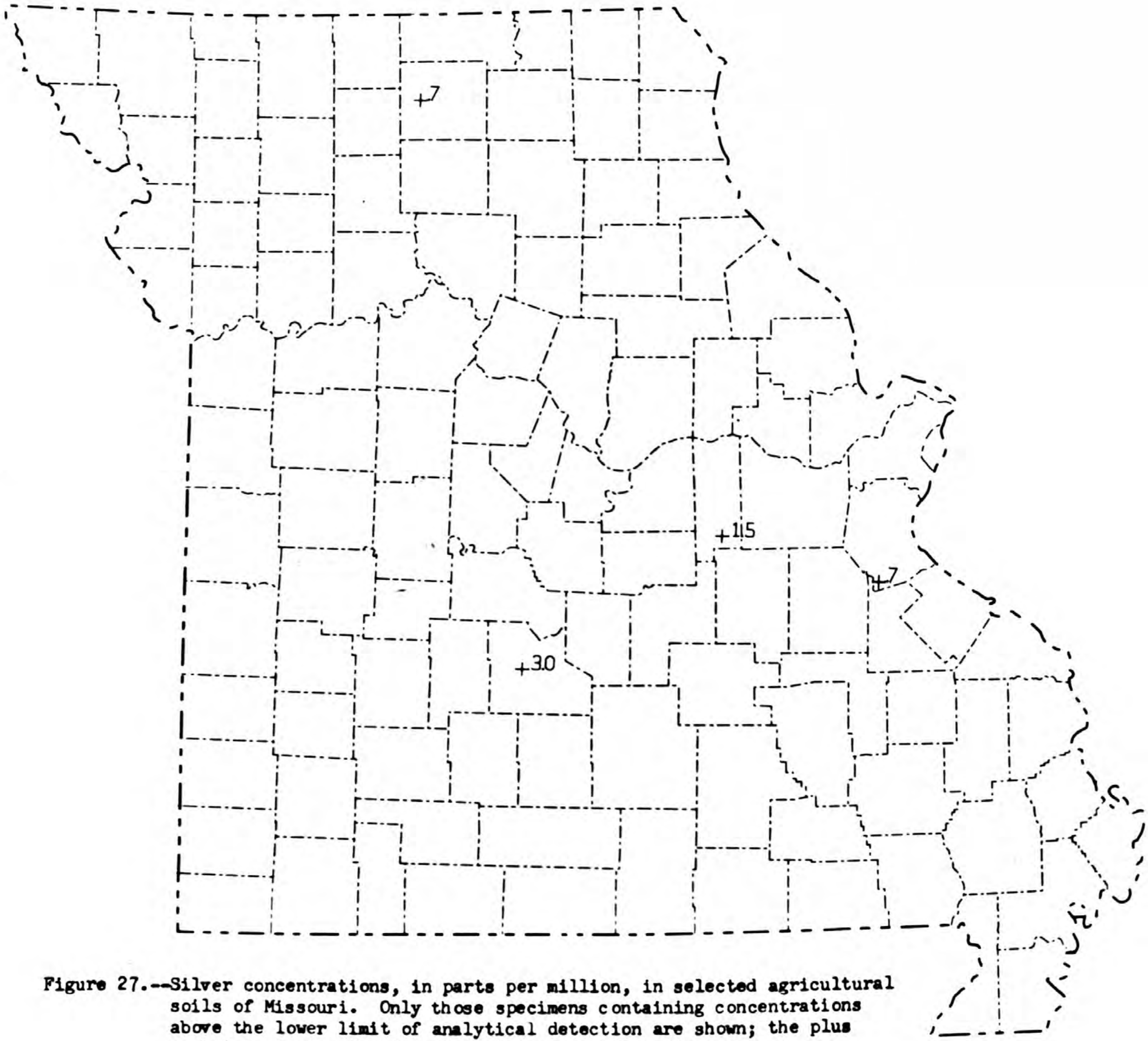
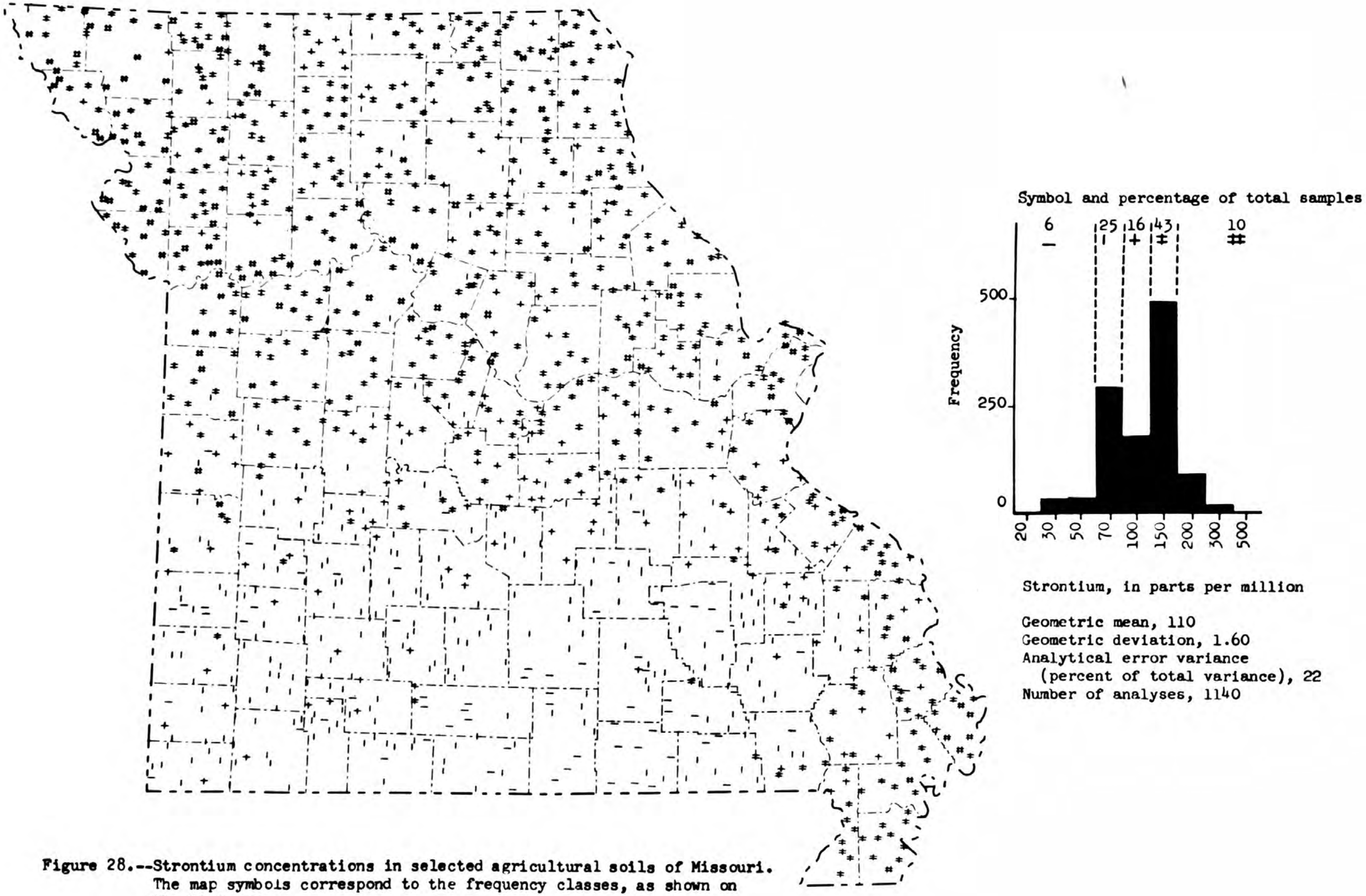


Figure 27.--Silver concentrations, in parts per million, in selected agricultural soils of Missouri. Only those specimens containing concentrations above the lower limit of analytical detection are shown; the plus symbol indicates the location of the sampling site.



Geometric mean, 110
Geometric deviation, 1.60
Analytical error variance
(percent of total variance), 22
Number of analyses, 1140

Figure 28.--Strontium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

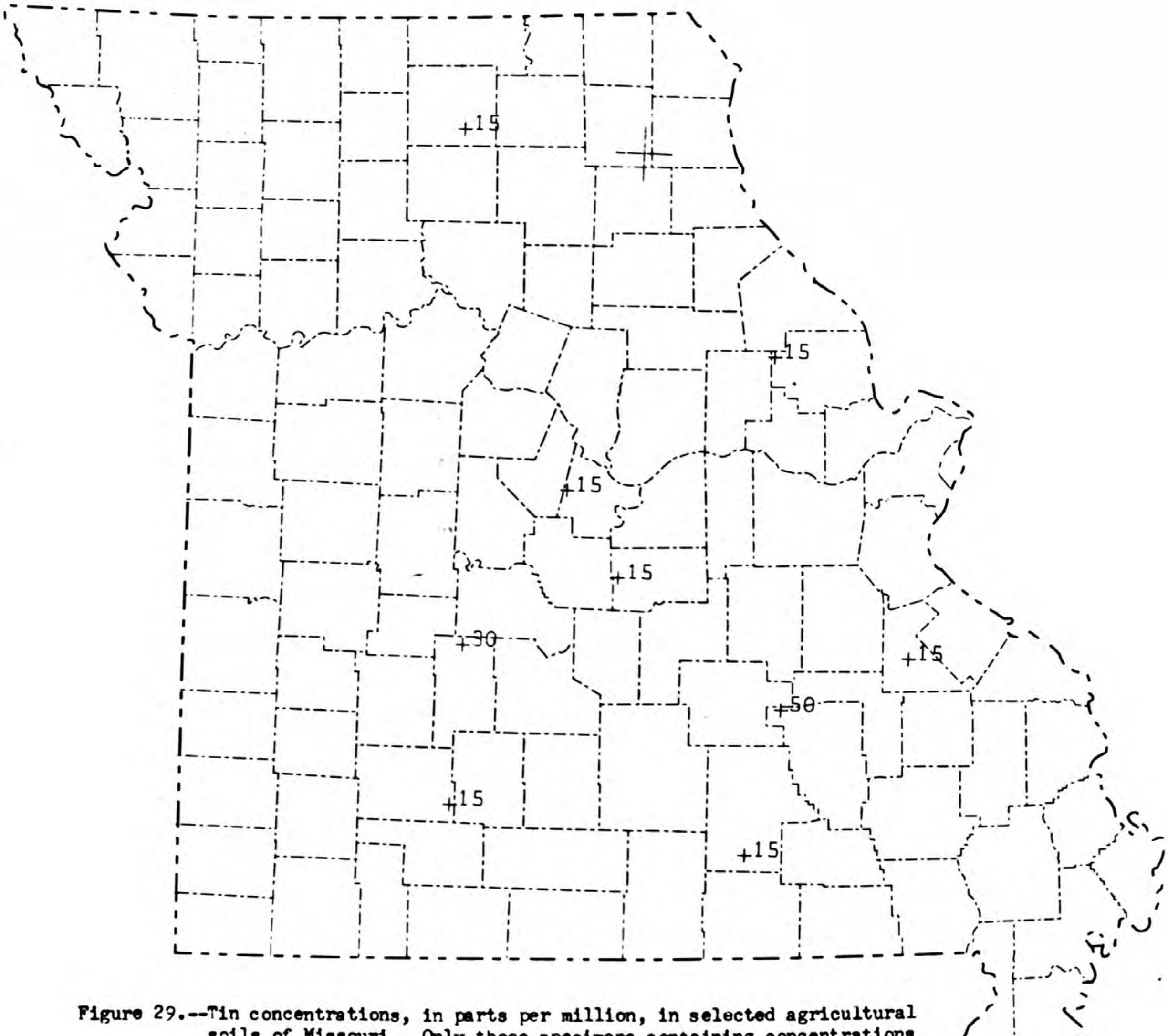
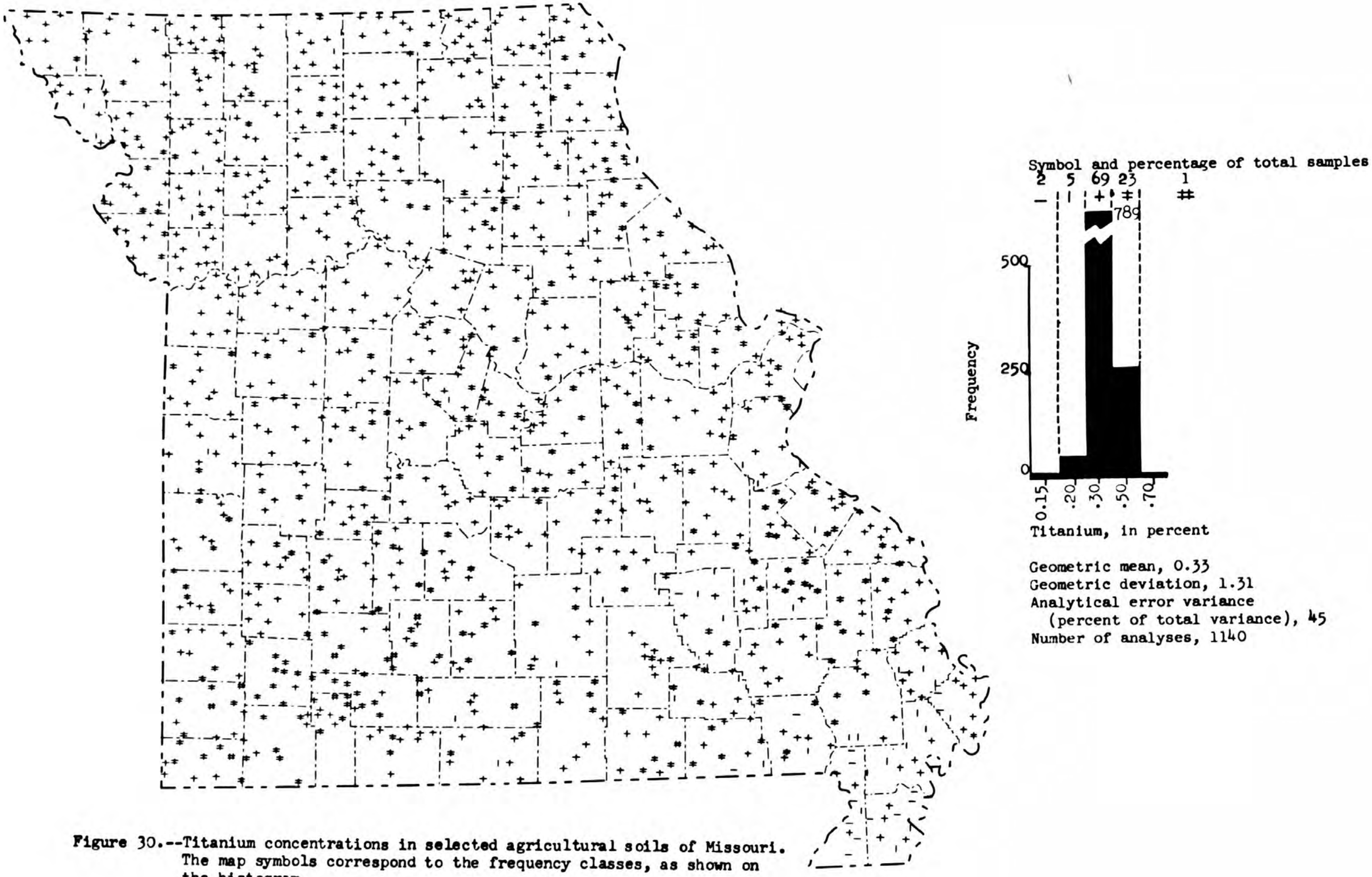
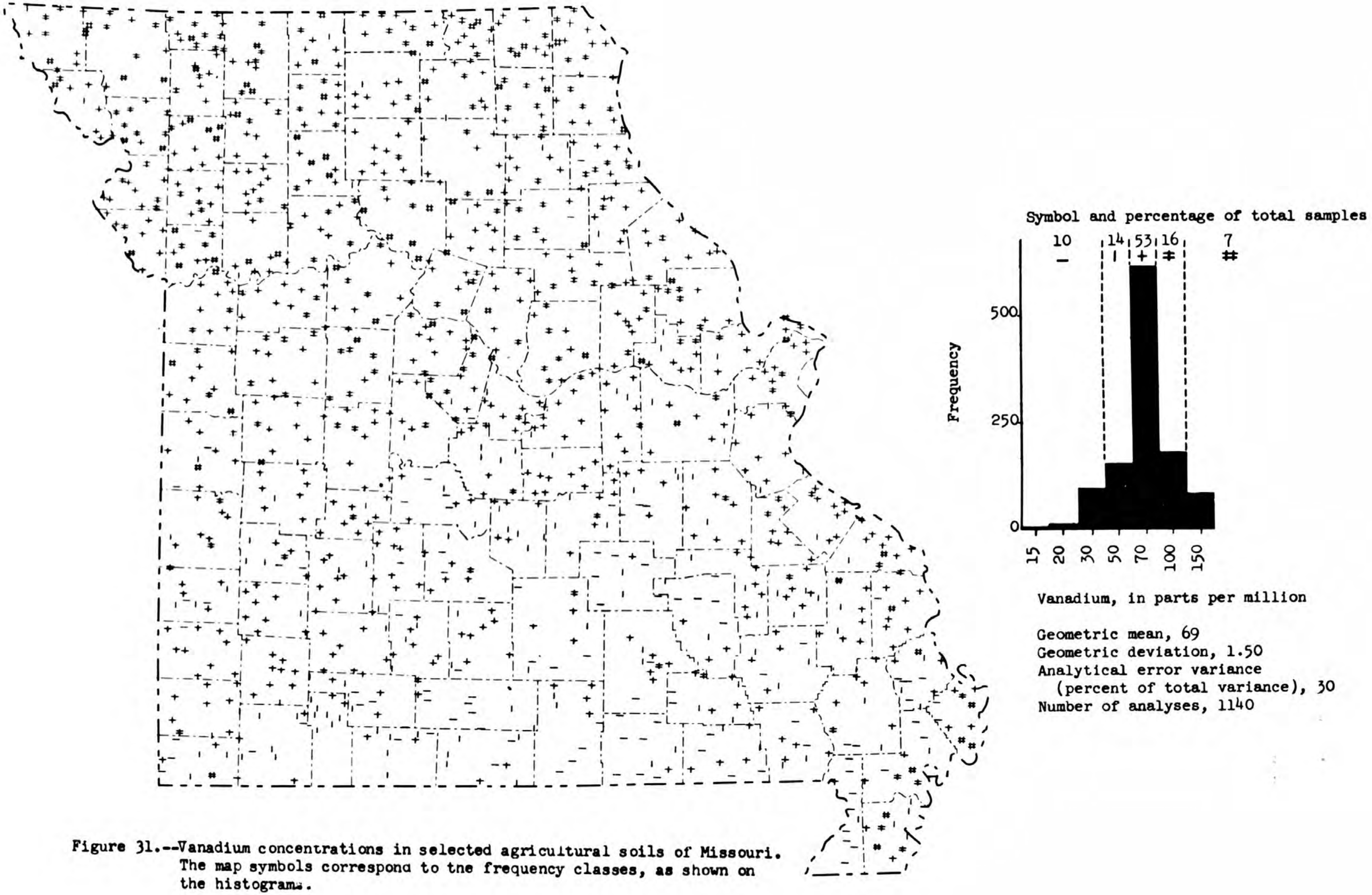


Figure 29.--Tin concentrations, in parts per million, in selected agricultural soils of Missouri. Only those specimens containing concentrations above the lower limit of analytical detection are shown; the plus symbol indicates the location of the sampling site.



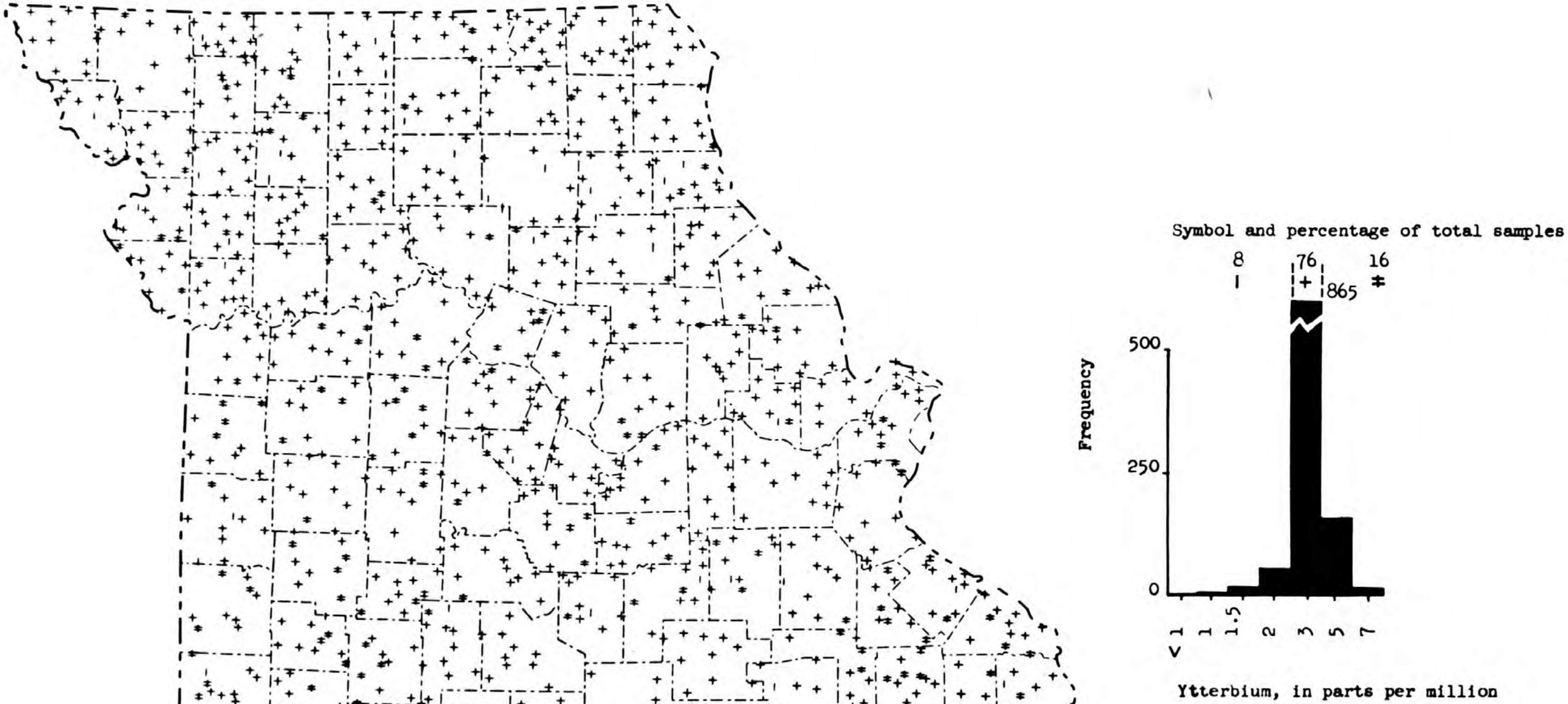
Geometric mean, 0.33
Geometric deviation, 1.31
Analytical error variance
(percent of total variance), 45
Number of analyses, 1140

Figure 30.--Titanium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



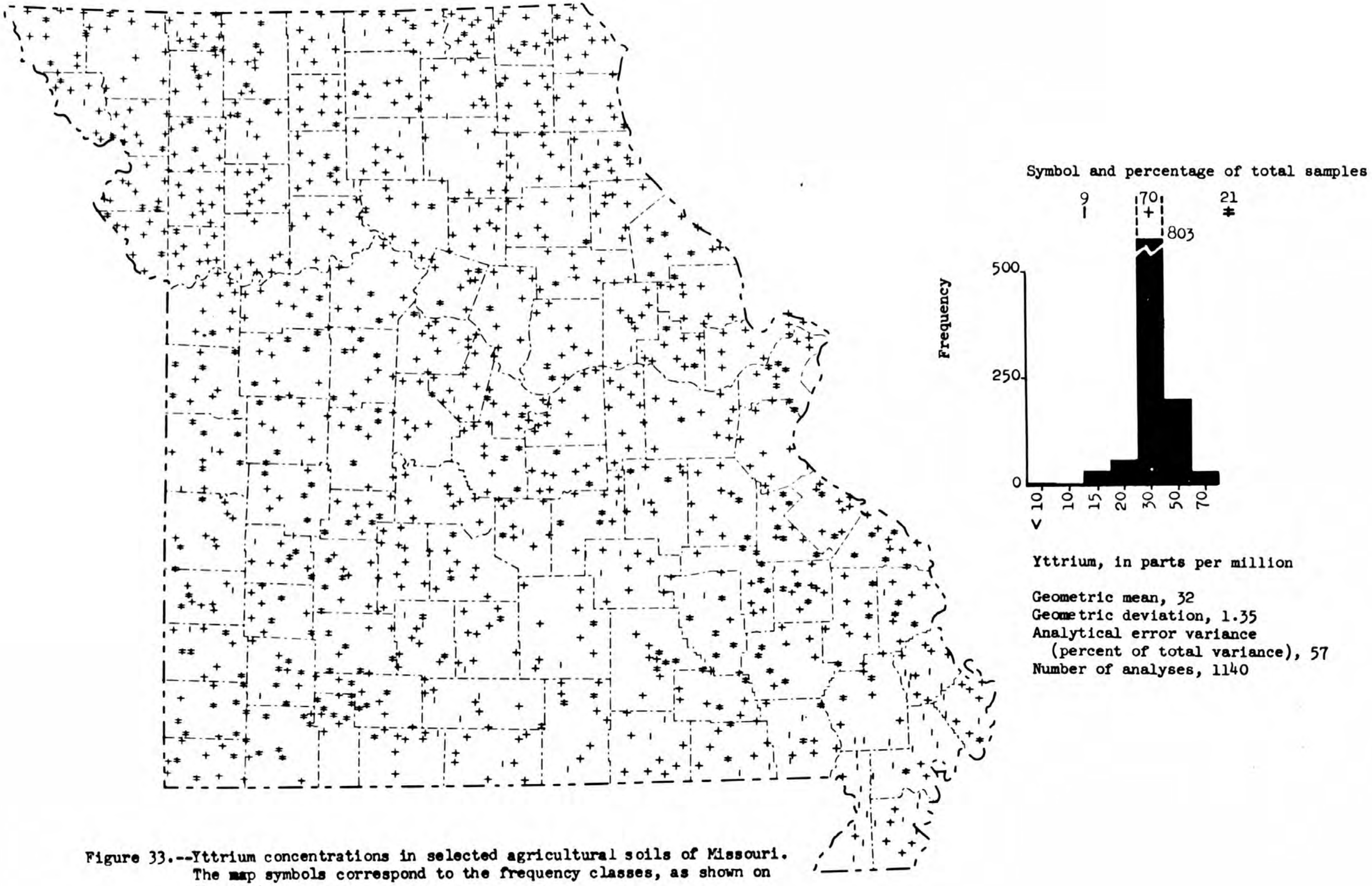
Geometric mean, 69
Geometric deviation, 1.50
Analytical error variance
(percent of total variance), 30
Number of analyses, 1140

Figure 31.--Vanadium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histograms.



Geometric mean, 3
Geometric deviation, 1.31
Analytical error variance
  (percent of total variance), 71
Number of analyses, 1140

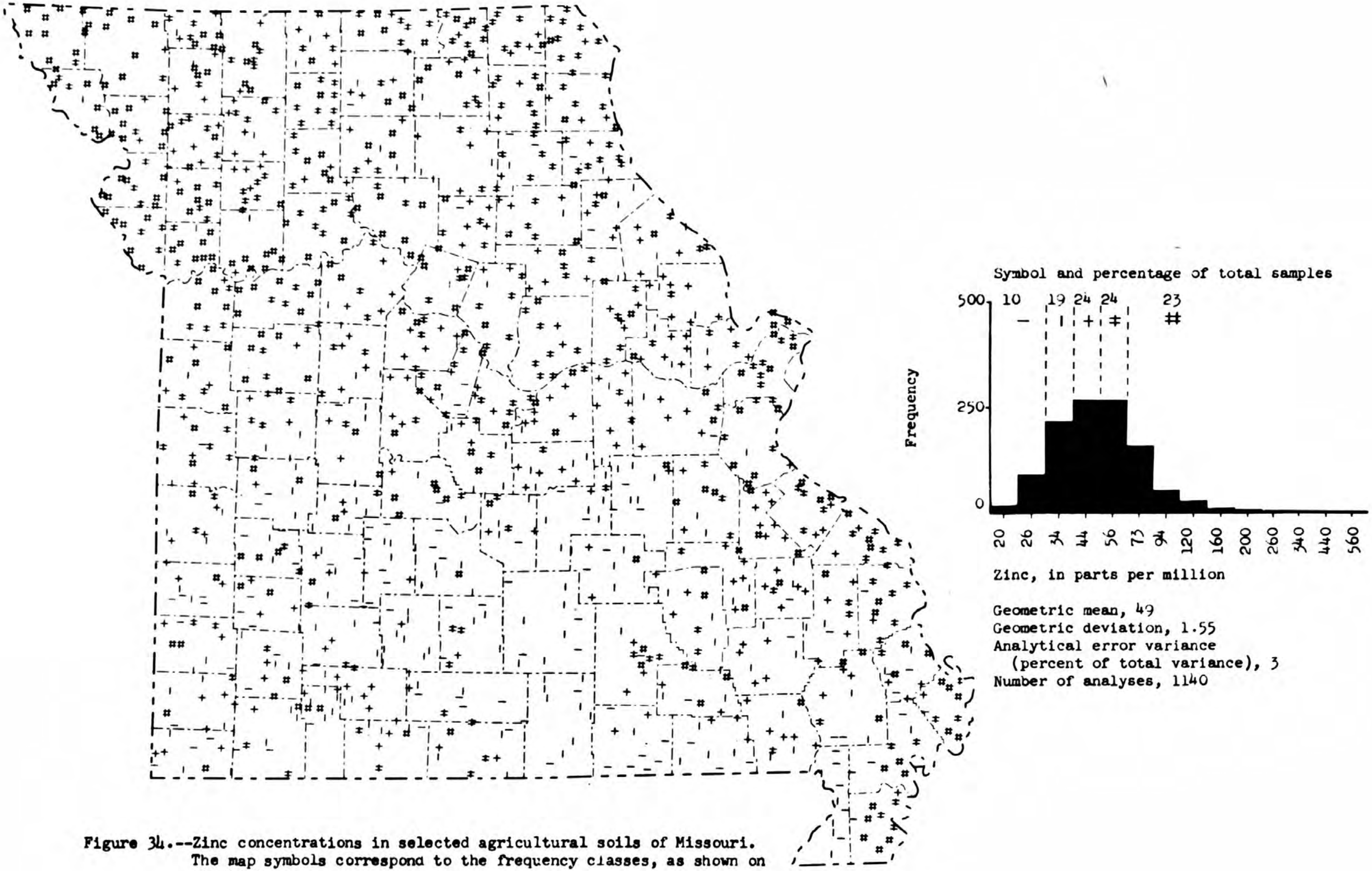
Figure 32.--Ytterbium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Yttrium, in parts per million

Geometric mean, 32
Geometric deviation, 1.35
Analytical error variance
(percent of total variance), 57
Number of analyses, 1140

Figure 33.--Yttrium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.



Geometric mean, 49
Geometric deviation, 1.55
Analytical error variance
(percent of total variance), 3
Number of analyses, 1140

Figure 34.--Zinc concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

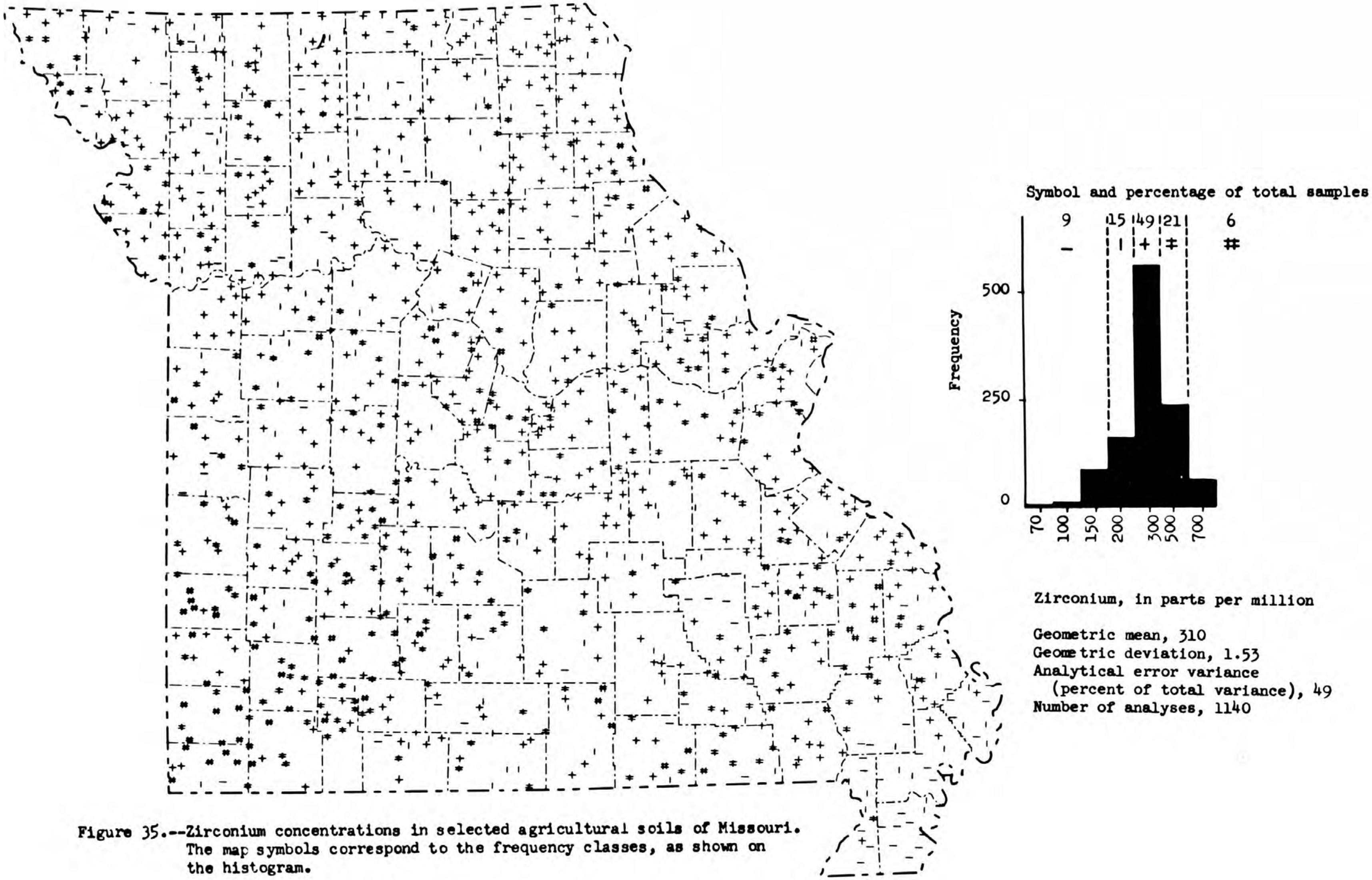


Figure 35.--Zirconium concentrations in selected agricultural soils of Missouri. The map symbols correspond to the frequency classes, as shown on the histogram.

Zirconium, in parts per million

Geometric mean, 310
Geometric deviation, 1.53
Analytical error variance
(percent of total variance), 49
Number of analyses, 1140

GEOCHEMICAL SURVEY OF VEGETATION

by H. T. Shacklette, J. A. Erdman, and J. R. Keith

Present status.--Reduction of the uncultivated soils data to tabular and graphical forms has been completed with the exception of a small refinement of the multivariate analysis described herein. Statistical analysis of the plant data, for the most part, is still pending. We are able, however, to give some results on the analyses of smooth sumac that we have sampled throughout the State. After the plant data are analyzed statistically, we intend to apply the appropriate univariate and multivariate correlation techniques between the element concentrations in plant ash and the element concentrations in specimens of the underlying soils. The resulting information should present a measure of the capacity of plants to reflect the geochemical system in which they grow.

Specimens of cultivated soils from crop sampling sites have been analyzed spectrographically, but analyses by other methods have not been completed. The specimens of crop plants (corn, soybeans, and pasture grasses) have not yet been analyzed.

Chemical composition of uncultivated soils in the six vegetation-type areas.--Distribution of arsenic and fluorine in uncultivated B-horizon soil samples is summarized and displayed in figures 36 and 37. These data were analyzed using moment statistics, analysis of variance, and the Duncan Multiple Range test. The generally high concentrations of these two elements in specimens from the prairie region fits one of the principal patterns already established for both uncultivated and agricultural soils in the State (U.S. Geol. Survey, 1972, p. 54 and 98).

Unusually high values for arsenic and molybdenum have been observed in specimens of uncultivated soils collected in Howell County in the south-central part of Missouri. The average arsenic content of five specimens collected in the Pottersville area (Cureall Quadrangle) is 26 ppm, considerably above that of other quadrangle averages shown in figure 36. The five specimens from this quadrangle contain 59, 51, 7, 21 and 28 ppm arsenic. With but one exception, these values far exceed the 8 ppm characteristic for soils from that general area (the Oak-hickory Forest). Three of the specimens contain arsenic concentrations that exceed the central 95-percent range of 2-27 ppm. These values also appear to be exceptionally high when compared to some preliminary data on arsenic in the carbonate residuum (Connor, oral commun., 1972) which is the parent to the soil in this area. If these preliminary data are valid, the residuum (soil parent) has an expected concentration of about 18 ppm and an expected range of about 10-34 ppm. Thus, the high arsenic in these samples is not easily explained as simply representing material below the intended sampling horizon. Furthermore, the two specimens highest in arsenic also appear to be high in molybdenum--they contain 30 and 7 ppm and are the only soil specimens collected in the Oak-hickory Forest found to contain detectable molybdenum. A followup reconnaissance of the general area by the geologists (Connor and Ebens) concluded that there are no obvious geologic differences between this area and adjacent areas.

The chemical data for the 300 uncultivated soil specimens from Missouri were subjected to Q-mode factor analysis, a multivariate classification technique used previously on the ground-water data by Feder and Miesch (U.S. Geol. Survey, 1972, p. 104). This analysis, although preliminary, suggests that the uncultivated soils from the six vegetation-type areas in Missouri can be viewed as consisting of two major composition groups whose variability can be described in terms of three end members (fig. 38). Soils from the Cedar Glades in the south-central part of the State form a clearcut group composed of soils that are slightly alkaline, organically rich, and high in calcium-magnesium carbonate which reflects the dolomitic parent material. The Glaciated Prairie and the Oak-hickory-pine Forest includes the Unglaciated Prairie, Oak-hickory Forest, and in part Flood-plain Forest soils. Soils from both prairie types and from the Flood-plain Forest are typically rich in aluminum, iron, sodium, and many trace elements. In contrast, soils from the Oak-hickory Forest and the Oak-hickory-pine Forest are generally depleted in most elements, except silicon and zirconium--probably because of their long history of weathering. Within this three-component model, the soils from the Flood-plain Forest strongly reflect an influence from both ends of the Glaciated Prairie and Oak-hickory-pine Forest continuum, and less strongly reflect an influence from the Cedar Glades. Because Flood-plain Forest soils are developed on Mississippi River alluvium, which is a heterogenous mixture of both soil and parent material from a wide area of North America, it is not unreasonable to expect its composition to reflect multiple sources.

The average chemical compositions of the specimens from the end-member quadrangles represented on the triangular diagram (fig. 38) are listed in table 4.

Chemical composition of smooth sumac (Rhus glabra) in the six vegetation-type areas.--Results of the spectrographic analyses of ash of smooth sumac stems that were sampled from the six vegetation types in Missouri, expressed as geometric mean concentrations, geometric deviations, and detection ratios for each element, are given in table 5. Where extreme mean concentrations were demonstrated by analysis of variance to be significantly different, the highest and lowest means are underscored. Of the 19 elements for which summary data are given, only seven--barium, lead, magnesium, manganese, nickel, strontium, and titanium--have concentrations in the stem tissue that are different among the vegetation-type areas. The following maps (figs. 39-45) enable one to compare the concentrations of these elements in the ash of smooth sumac specimens with the concentrations in specimens of the underlying soils.

There appears to be little correspondence between the element concentrations in soils and in the ash of smooth sumacs that have grown in them. However, the ash of smooth sumac from the Cedar Glade area contains the lowest concentrations of many of the elements (table 5). This suggests that because the pH of the soils from the cedar glades is significantly higher than the pH of soils collected from the other areas in the State (U.S. Geol. Survey, 1972, p. 91), soil acidity may be one of the leading factors controlling the availability of some trace elements to plants. Further evidence that the alkaline nature (pH typically 7.3) of the Cedar Glade soils may strongly control the element availability to the plants can be seen in the molybdenum levels (table 5). The detection ratios for molybdenum in smooth sumac are very low for all vegetation types excepting the Cedar Glade type. Because of these low ratios, only three geometric means could be estimated using the technique of Cohen (1959). The mean for the Cedar Glade type--3.3 parts per million--appears to be appreciably higher than the other two means given. Because molybdenum concentrations in the soils do not appear to differ to any great extent among vegetation-type areas (U.S. Geol. Survey, 1971, table 8, p. 31), we believe the higher molybdenum concentrations in sumac specimens from the cedar glades reflects the higher soil pH. This conclusion is consistent with conclusions in the published literature (Sauchelli, 1969).

The distribution of lead in uncultivated soils and sumac ash (fig. 40) is interesting in view of the fact that lead is probably the best known of the metal air pollutants. Lead concentrations in sumac ash from the Oak-hickory-pine area are significantly higher than lead levels in sumac ash from elsewhere in Missouri; yet lead concentrations in the soils from this same area are the lowest of any of the six vegetation-type areas. Moreover, the slight indication of a bimodal frequency distribution for lead in smooth sumac (fig. 40b), in addition to the fact that the sumac with the higher lead concentrations in ash were collected from areas near mining activities, points to airborne contamination of these plants with lead.

Table 4.--Mean chemical properties of the three end members in the Q-mode factor model for B-horizon soils from six vegetation-type areas in Missouri. Values are arithmetic means based on five samples from each of three quadrangles.

Oxide, element, or pH	Quadrangles and associated vegetation types		
	Unionville West (Glaciated Prairie)	Garber (Cedar Glades)	Van Buren (Oak-hickory-pine Forest)
		Percent	
SiO_2	69	53	91
Al_2O_3	11	5.6	2.8
Total Fe as Fe_2O_3	5.9	2.3	1.5
MgO	.96	3.1	.13
CaO	.48	12	.082
Na_2O	.59	.14	.23
K_2O	1.8	1.8	.56
P_2O_5	.066	.22	.096
Ti	.34	.16	.28
F	.056	.046	.012
C, Total	.72	5.9	1.2
C, Carbonate	.066	3.4	.056
C, Organic	.66	2.6	1.1
		Parts per million	
As	13	5.8	5.1
B	28	24	32
Ba	600	170	164
Co	12	9.4	9.8
Cr	70	40	23
Cu	30	14	7.8
Ga	21	11	4.6
Hg	.060	.17	.036
La	38	38	26
Li	33	19	12
Mn	520	1200	830
Ni	23	27	7.6
Pb	18	17	17
Se	1.4	.23	.21
Sr	130	72	23
V	130	56	24
Y	28	34	18
Yb	2.8	2.2	1.8
Zn	75	56	26
Zr	170	92	210
		Standard units	
pH	4.96	7.36	5.10

Table 5.--Mean chemical composition and chemical variation in the ash of smooth sumac stems from six vegetation-type areas in Missouri

[Analyses performed by a semiquantitative spectrographic method. GM, geometric mean; GD, geometric deviation; Ratio, number of samples in which detected:total number of samples; - - -, no data available. Geometric means for certain elements were tested, using analysis of variance, for significant differences among the samples from the six areas. Significant differences at the 0.05 probability level were found among these means for barium, magnesium, manganese, nickel, lead, strontium, and titanium in the plant ash; the highest and lowest mean concentrations of these elements, by vegetation-type area, are shown in **boldface** and *italic*, respectively. Significant differences in concentrations of aluminum, boron, copper, and iron among areas were not demonstrated at the 0.05 probability level. Because of insufficient data, analysis of variance could not be applied to concentrations of the remaining elements.]

Element	Vegetation type																	
	Floodplain Forest			Glaciated Prairie			Unglaciated Prairie			Cedar Glade			Oak-hickory Forest			Oak-hickory-pine Forest		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
	Percent																	
Al-----	0.11	2.55	48:48	0.13	2.09	50:50	0.11	2.29	49:49	0.10	1.92	49:49	0.12	2.11	50:50	0.13	1.99	49:49
Fe-----	.11	1.98	48:48	.13	1.57	50:50	.13	1.74	49:49	.10	1.68	49:49	.11	1.89	50:50	.12	1.66	49:49
Mg-----	**2.9**	1.48	48:48	2.2	1.54	50:50	2.3	1.40	49:49	2.2	1.69	49:49	2.0	1.43	50:50	*2.0*	1.50	49:49
Ti-----	.0098	2.54	48:48	.012	1.65	50:50	.012	1.99	49:49	*.0094*	1.77	49:49	.013	2.15	50:50	**.017**	1.89	49:49
	Parts per million																	
Ag-----	- - -	- - -	1:48	- - -	- - -	0:50	- - -	- - -	0:49	- - -	- - -	0:49	- - -	- - -	0:50	- - -	- - -	0:49
B------	230	1.31	48:48	230	1.44	50:50	230	1.33	49:49	220	1.37	49:49	200	1.26	50:50	220	1.38	49:49
Ba-----	3500	1.84	48:48	2600	1.60	50:50	2600	1.78	49:49	*270*	2.35	49:49	3400	2.33	50:50	**4500**	2.00	49:49
Be-----	- - -	- - -	1:48	- - -	- - -	0:50	- - -	- - -	0:49	- - -	- - -	0:49	- - -	- - -	0:50	- - -	- - -	0:49
Cr-----	- - -	- - -	37:48	- - -	- - -	40:50	- - -	- - -	36:49	2.2	2.05	31:49	2.7	1.95	40:50	3.1	1.87	43:49
Cu-----	110	1.40	48:48	110	1.41	50:50	100	1.46	49:49	86	1.58	49:49	89	1.43	50:50	97	1.51	49:49
La-----	- - -	- - -	1:48	- - -	- - -	0:50	- - -	- - -	0:49	- - -	- - -	0:49	- - -	- - -	0:50	- - -	- - -	1:49
Mn-----	760	1.74	48:48	560	1.68	50:50	640	1.62	49:49	*470*	1.62	49:49	700	1.60	50:50	**770**	1.58	49:49
Mo-----	.91	3.38	6:48	.76	4.27	7:50	- - -	- - -	3:49	3.3	2.80	21:49	- - -	- - -	3:50	- - -	- - -	4:49
Ni-----	**17**	2.51	46:48	11	2.15	48:50	11	1.93	47:49	*.81*	3.56	13:49	4.0	2.82	36:50	3.9	2.68	35:49
Pb-----	*26*	2.28	34:48	32	1.82	42:50	28	2.11	38:49	42	2.17	43:49	30	2.36	37:50	**61**	2.23	46:49
Sr-----	3400	1.62	48:48	3500	1.49	50:50	**3700**	1.46	49:49	*400*	1.72	49:49	2700	2.19	50:50	3100	1.79	49:49
V------	- - -	- - -	2:48	- - -	- - -	1:50	- - -	- - -	2:49	- - -	- - -	0:49	- - -	- - -	3:50	- - -	- - -	1:49
Y------	- - -	- - -	1:48	- - -	- - -	0:50	- - -	- - -	0:49	- - -	- - -	0:49	- - -	- - -	0:50	- - -	- - -	1:49
Zr-----	4.1	3.49	6:48	- - -	- - -	4:50	- - -	- - -	4:49	- - -	- - -	4:49	11	1.85	11:50	- - -	- - -	13:49

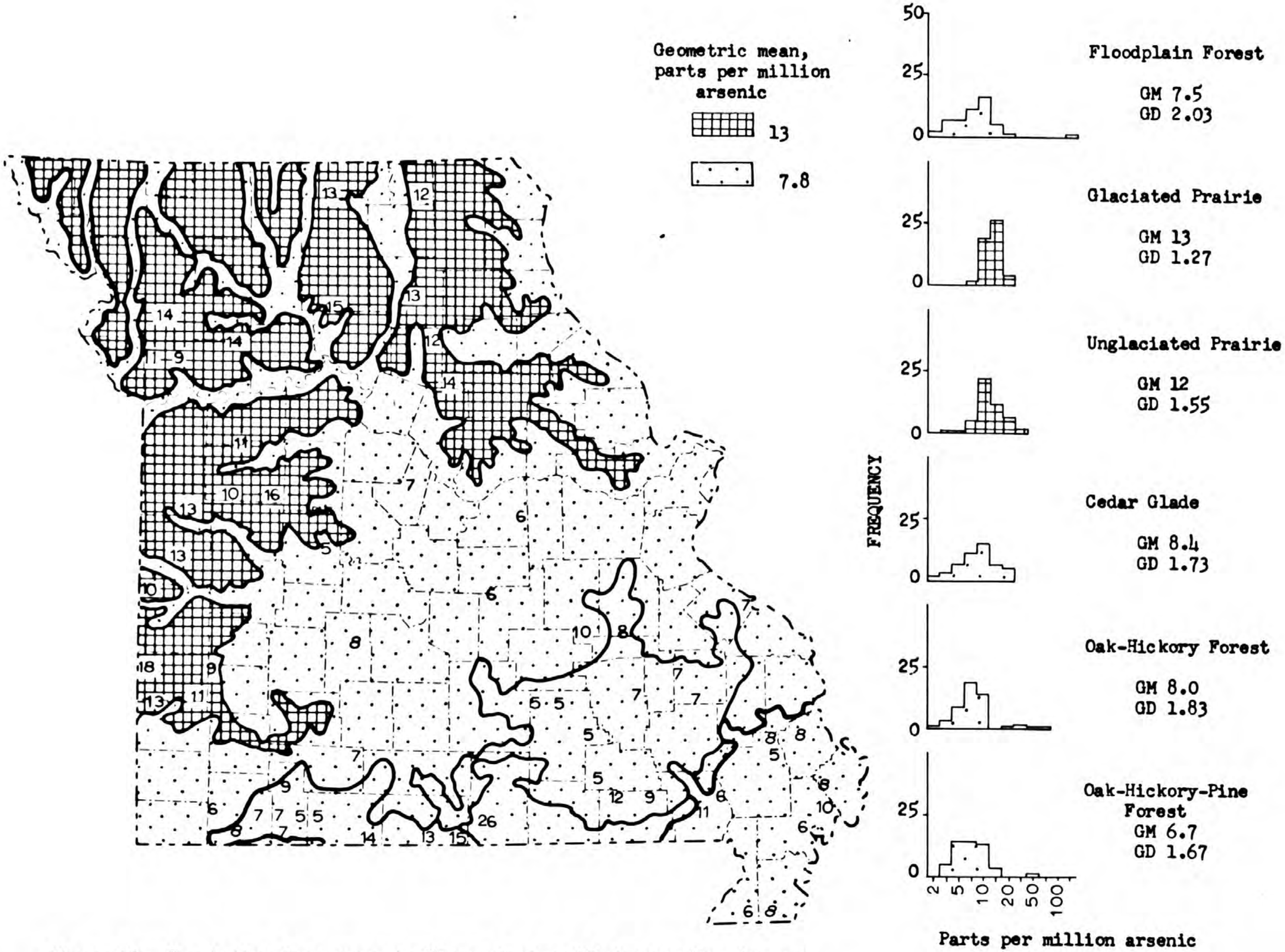


Figure 36.—Vegetation-type areas in Missouri classified according to mean concentration of arsenic in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of arsenic in five samples from a 7½-minute quadrangle.

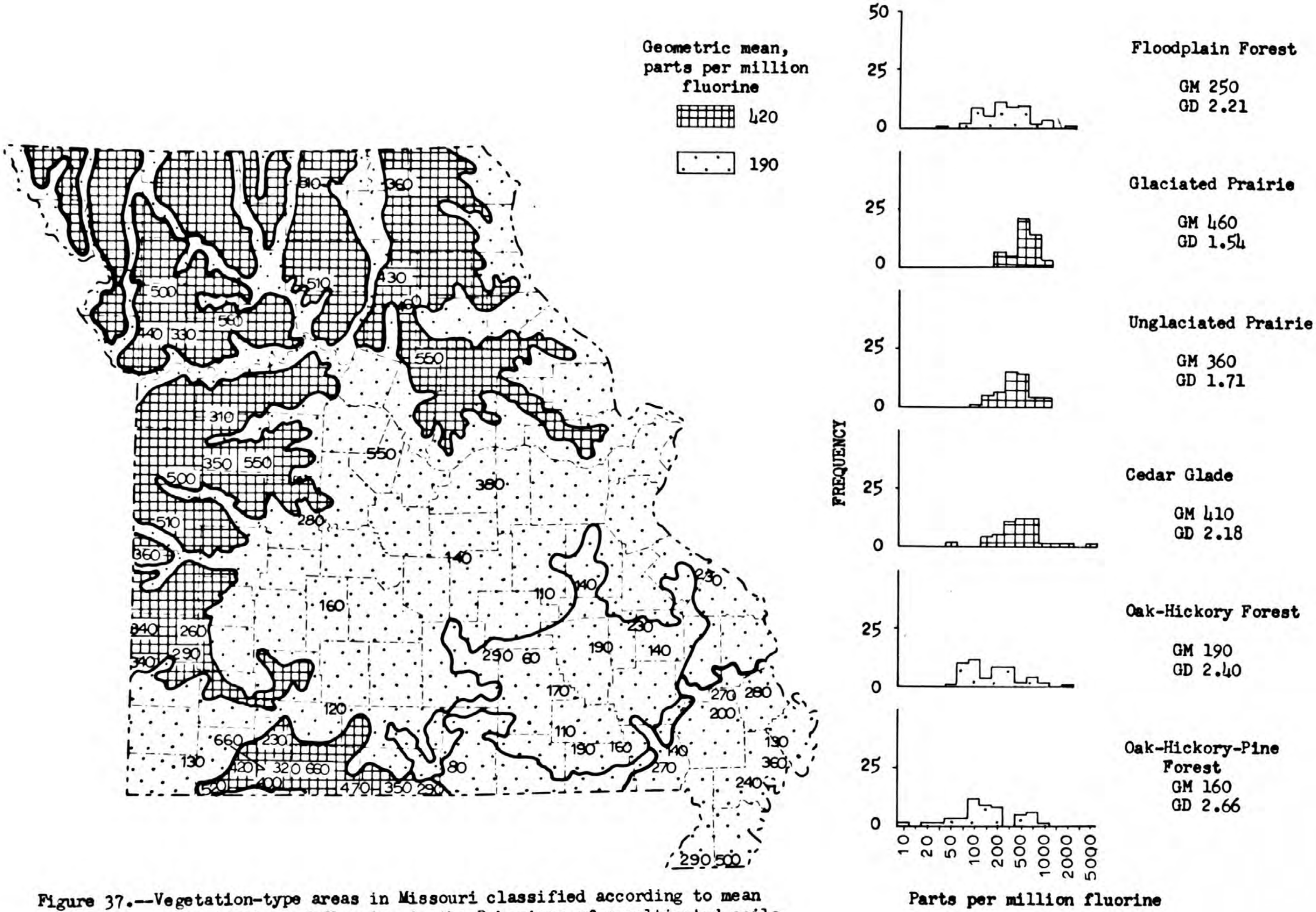


Figure 37.--Vegetation-type areas in Missouri classified according to mean concentration of fluorine in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of fluorine in five samples from a 7½-minute quadrangle.

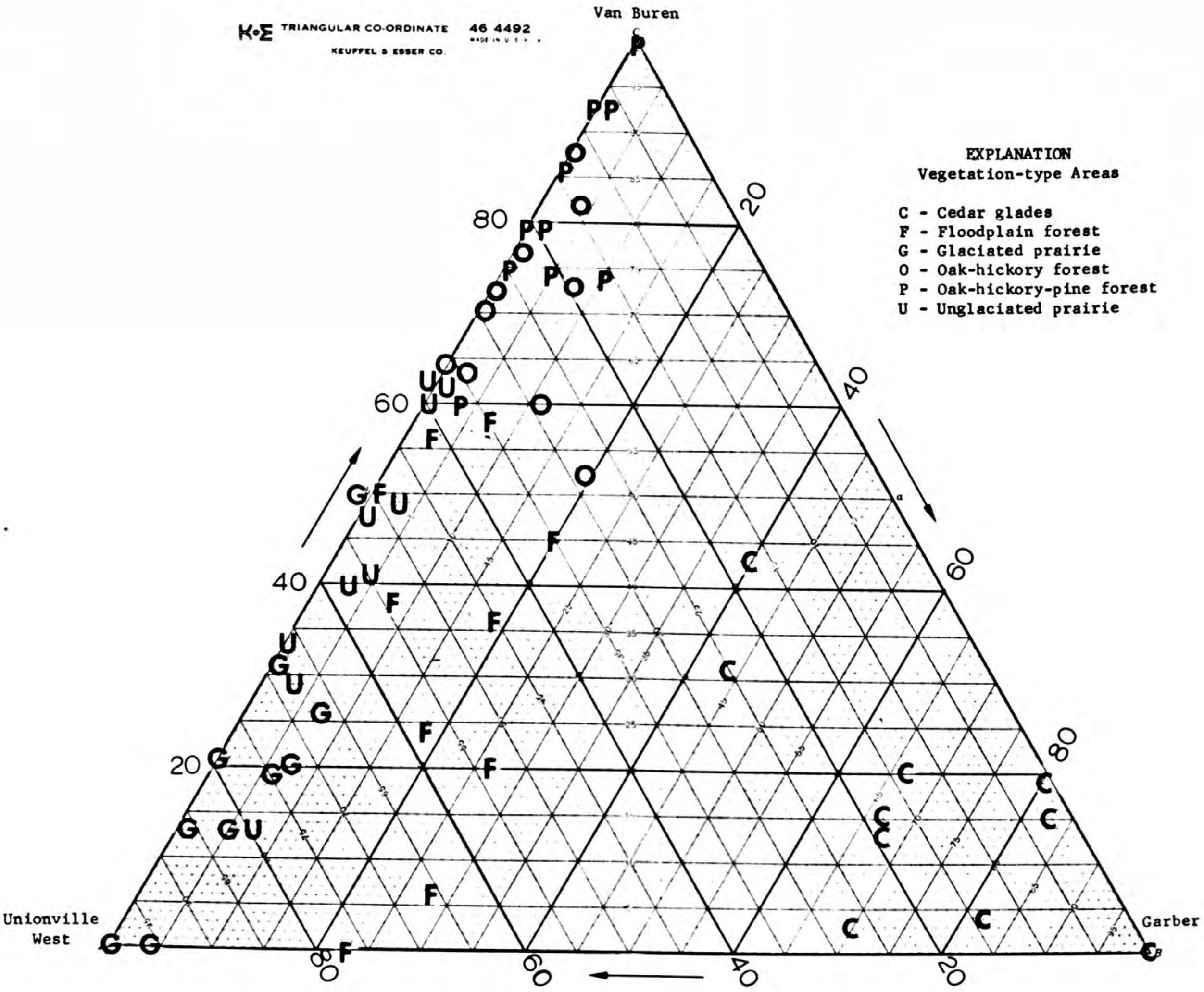


Figure 38.--Trilinear plot of the results of a Q-mode factor analysis of chemical data on B-horizon uncultivated soil samples from six vegetation-type areas in Missouri. Each letter represents a quadrangle sampled; the end-member quadrangles are named.

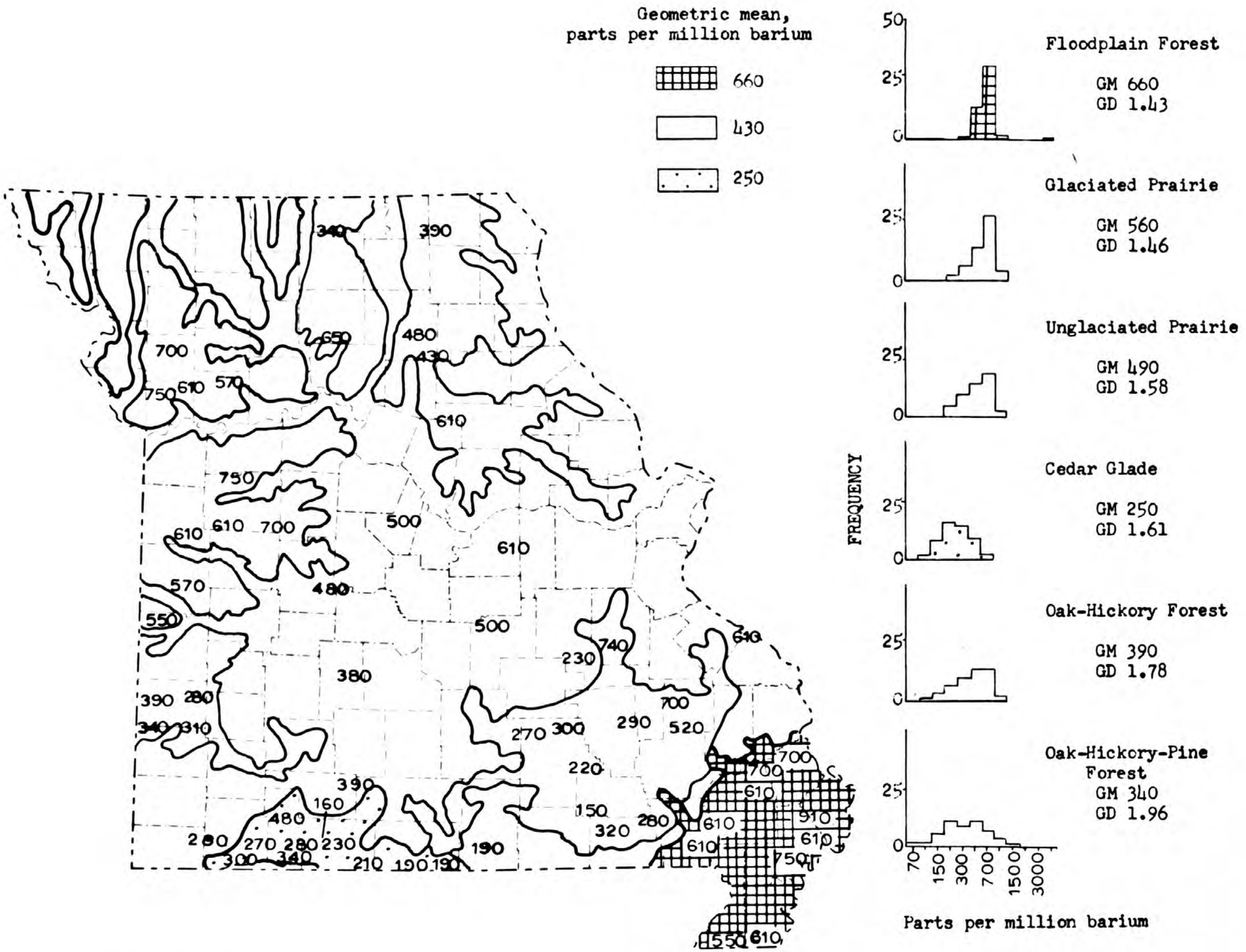


Figure 39a.--Vegetation-type areas in Missouri classified according to mean concentration of barium in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of barium in five samples from a 7½-minute quadrangle.

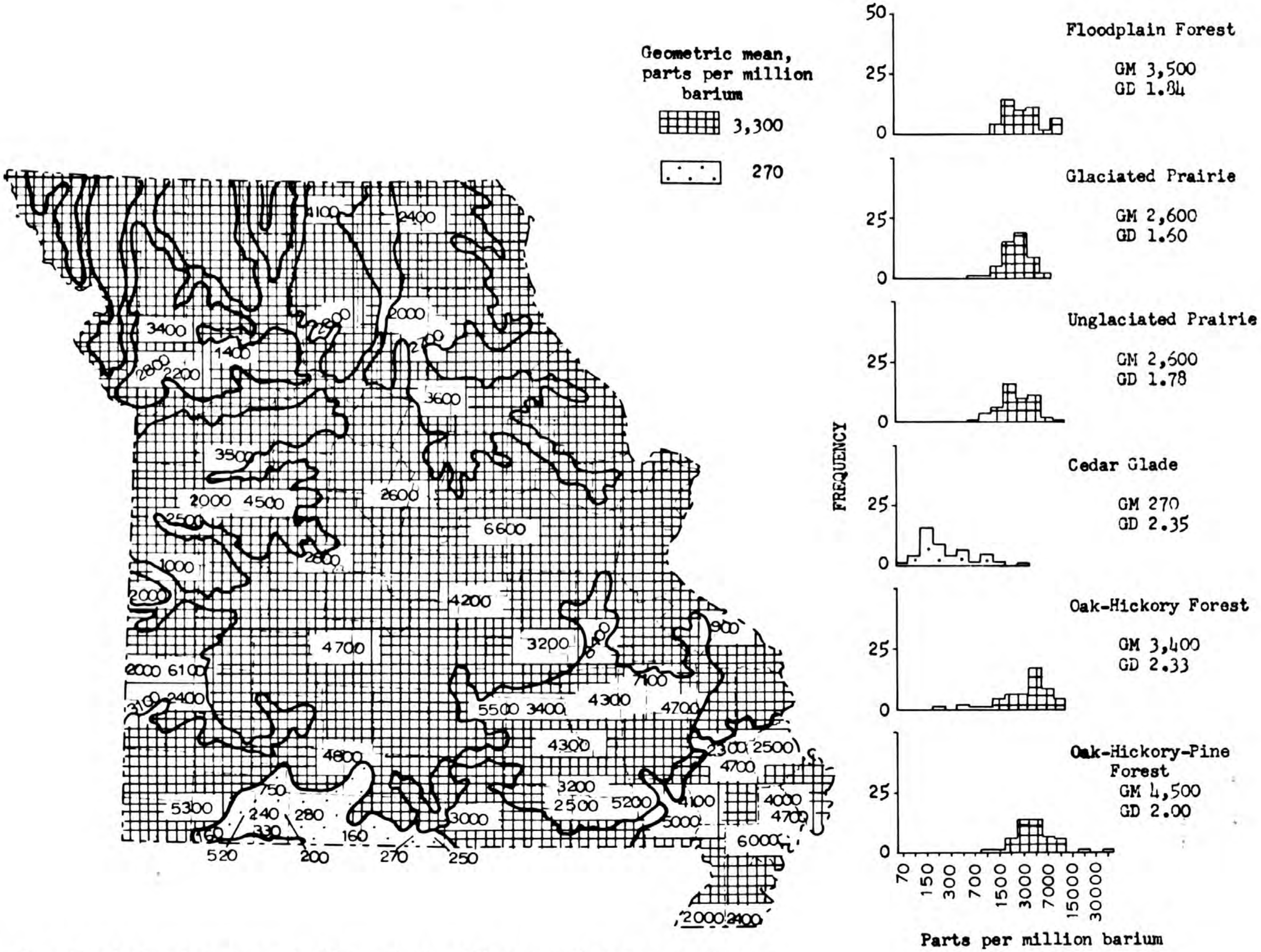


Figure 39b.--Vegetation-type areas in Missouri classified according to mean concentration of barium in stems of smooth sumac. Each number on the map is the geometric mean concentration of barium in generally five samples from a 7½-minute quadrangle.

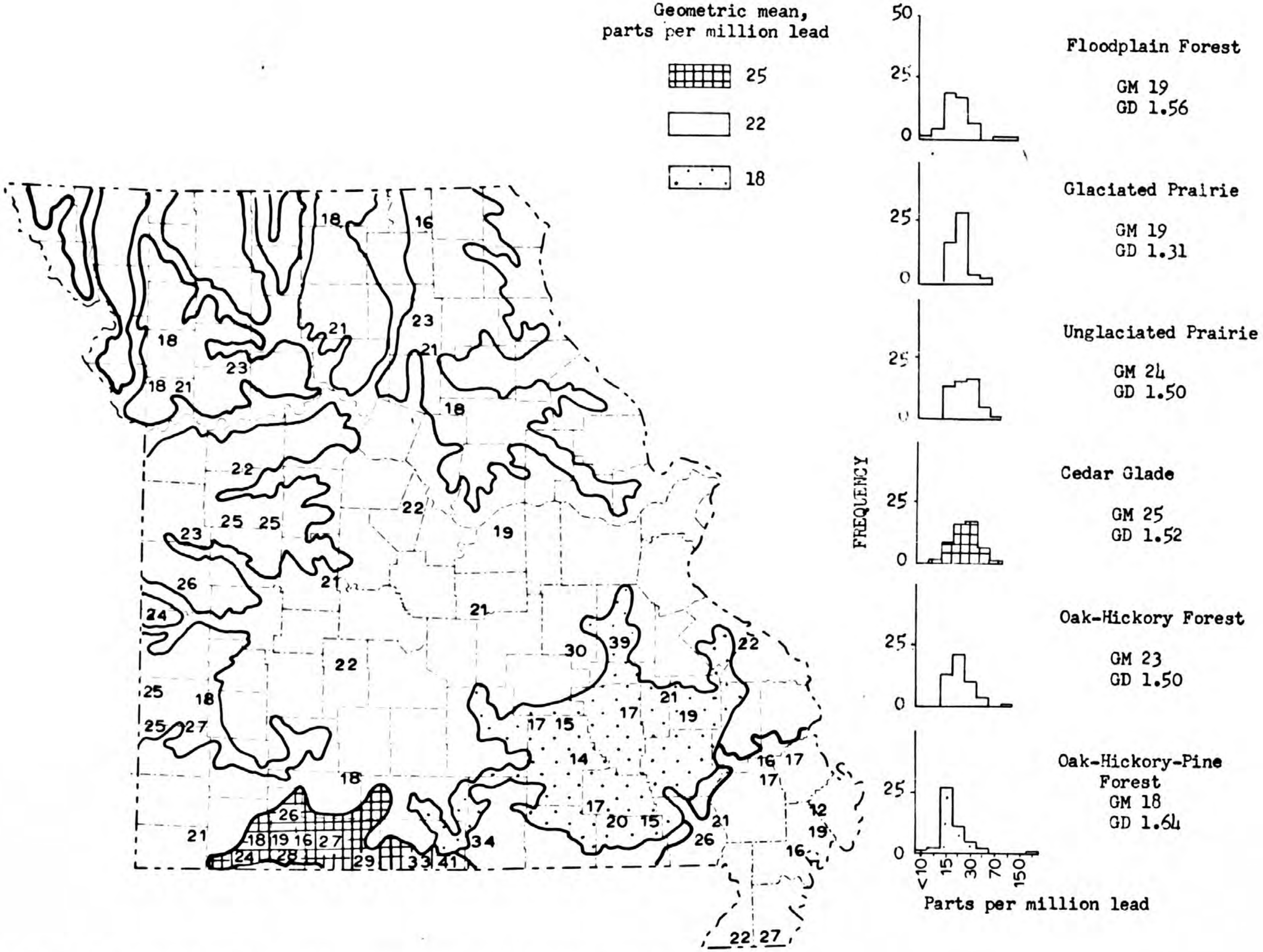


Figure 40a.--Vegetation-type areas in Missouri classified according to mean concentration of lead in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of lead in five samples from a 7½-minute quadrangle.

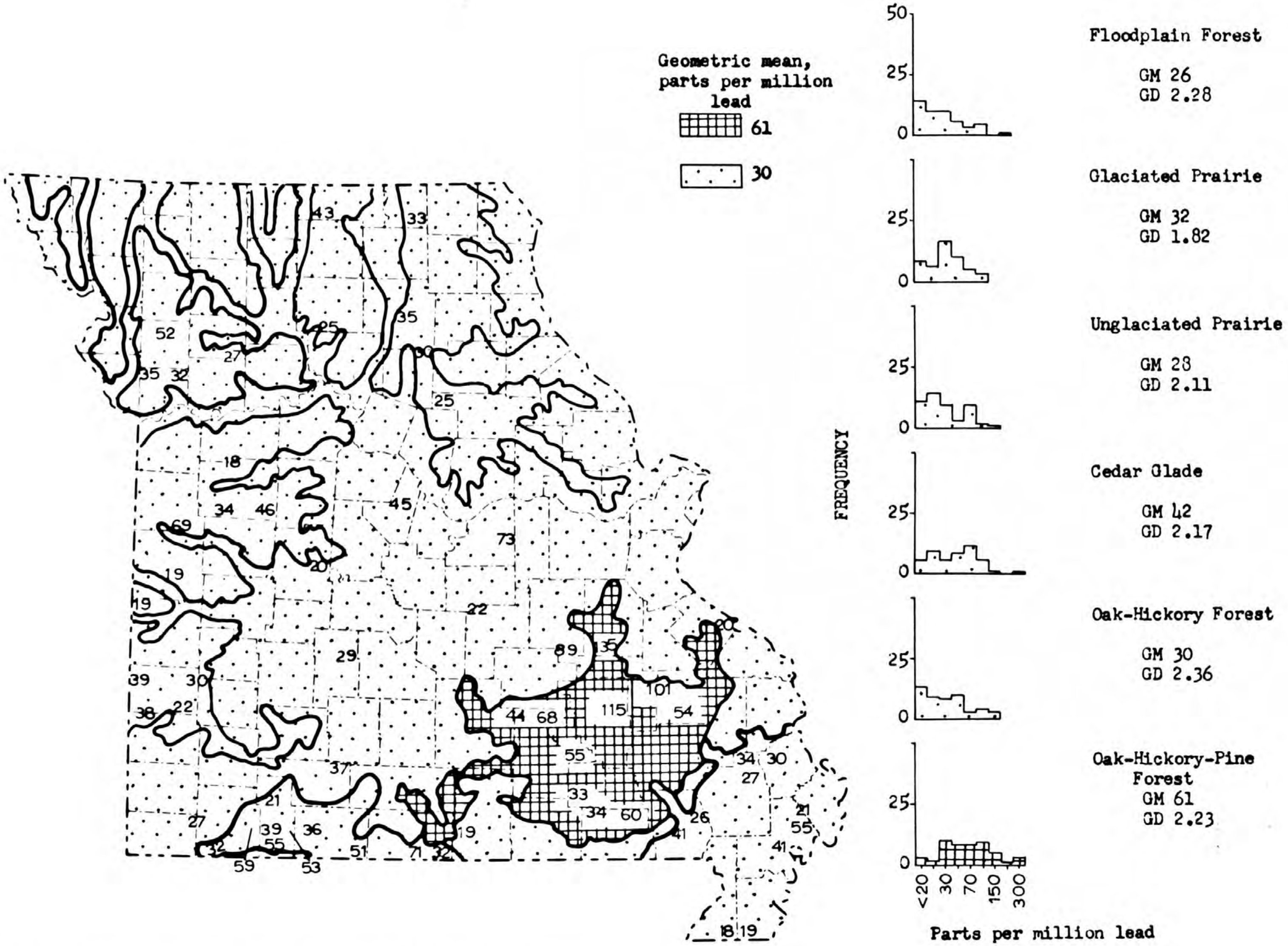


Figure 40b.--Vegetation-type areas in Missouri classified according to mean concentration of lead in stems of smooth sumac. Each number on the map is the geometric mean concentration of lead in generally five samples from a 7½-minute quadrangle.

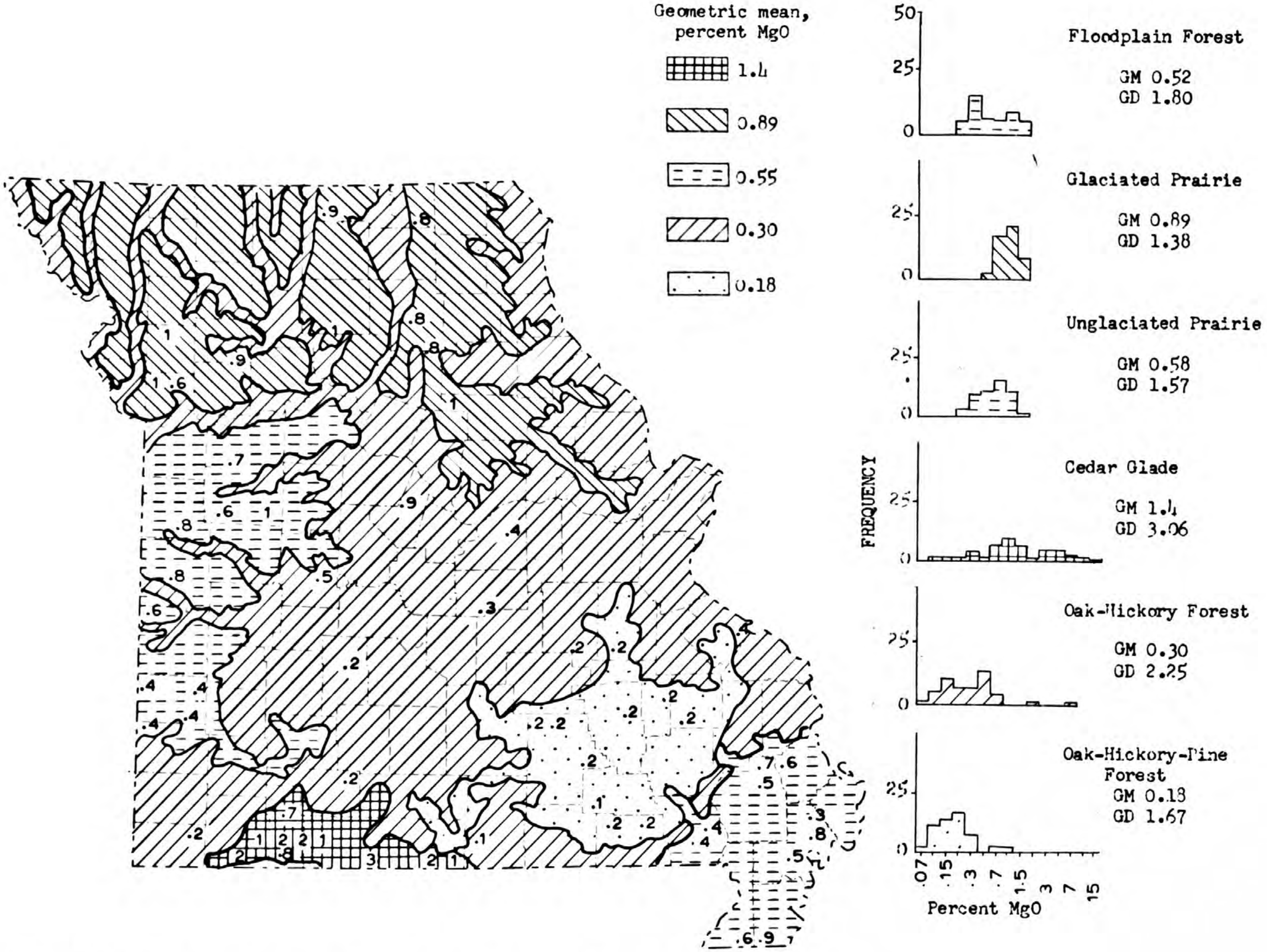


Figure 41a.--Vegetation-type areas in Missouri classified according to mean concentration of magnesium in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of magnesium in five samples from a 7½-minute quadrangle.

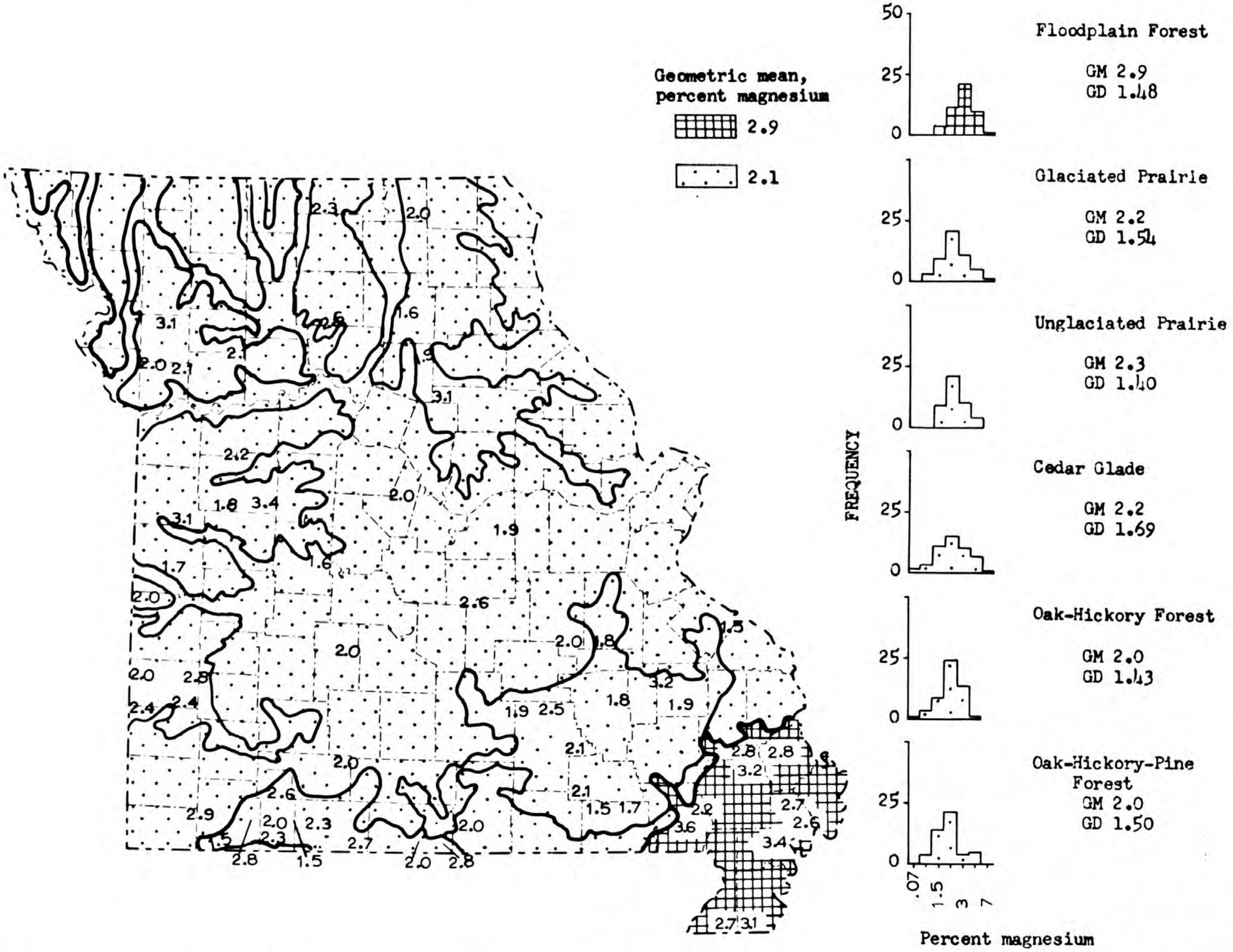


Figure 41b.--Vegetation-type areas in Missouri classified according to mean concentration of magnesium in stems of smooth sumac. Each number on the map is the geometric mean concentration of magnesium in generally five samples from a 7½-minute quadrangle.

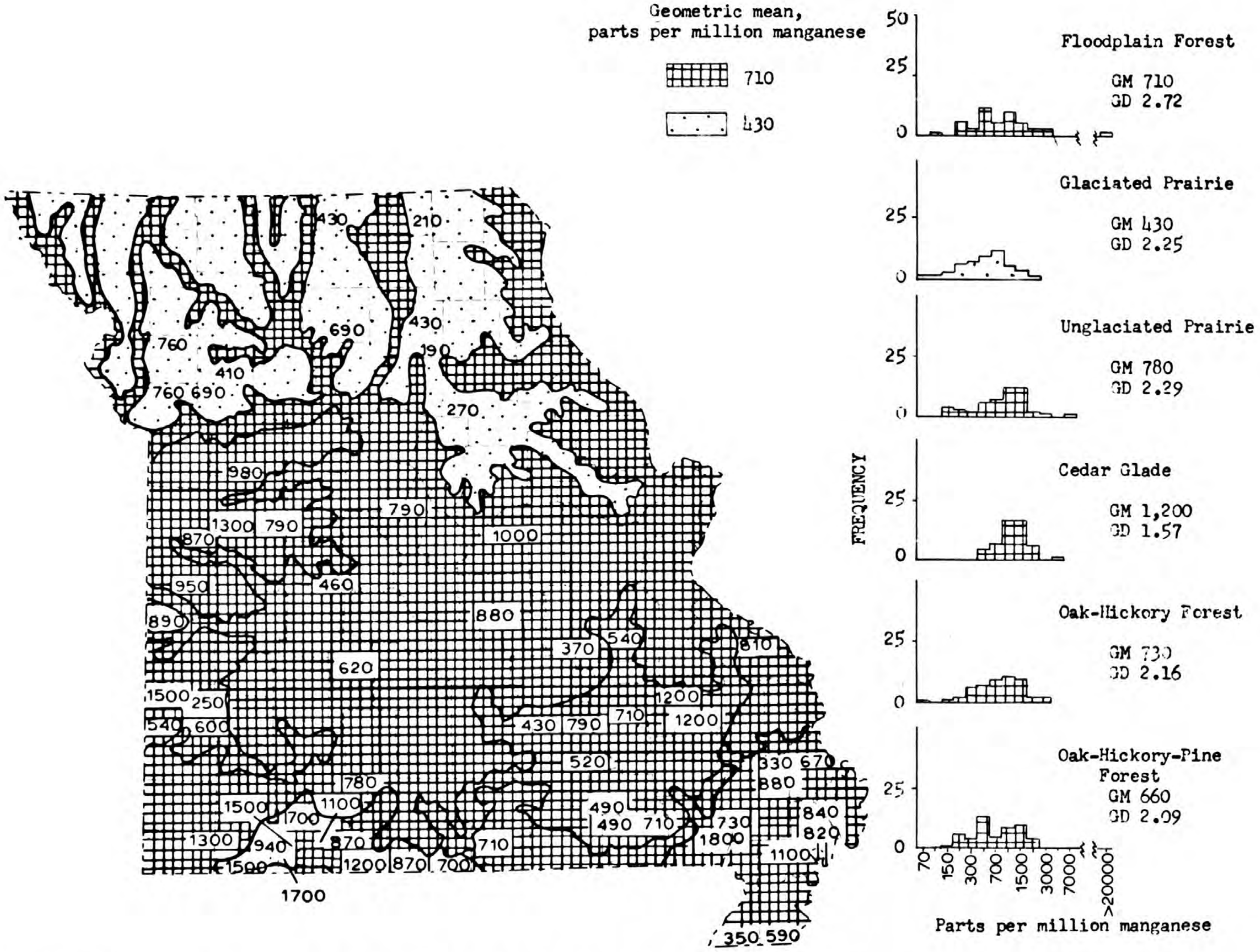


Figure 42a.--Vegetation-type areas in Missouri classified according to mean concentration of manganese in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of manganese in five samples from a 7½-minute quadrangle.

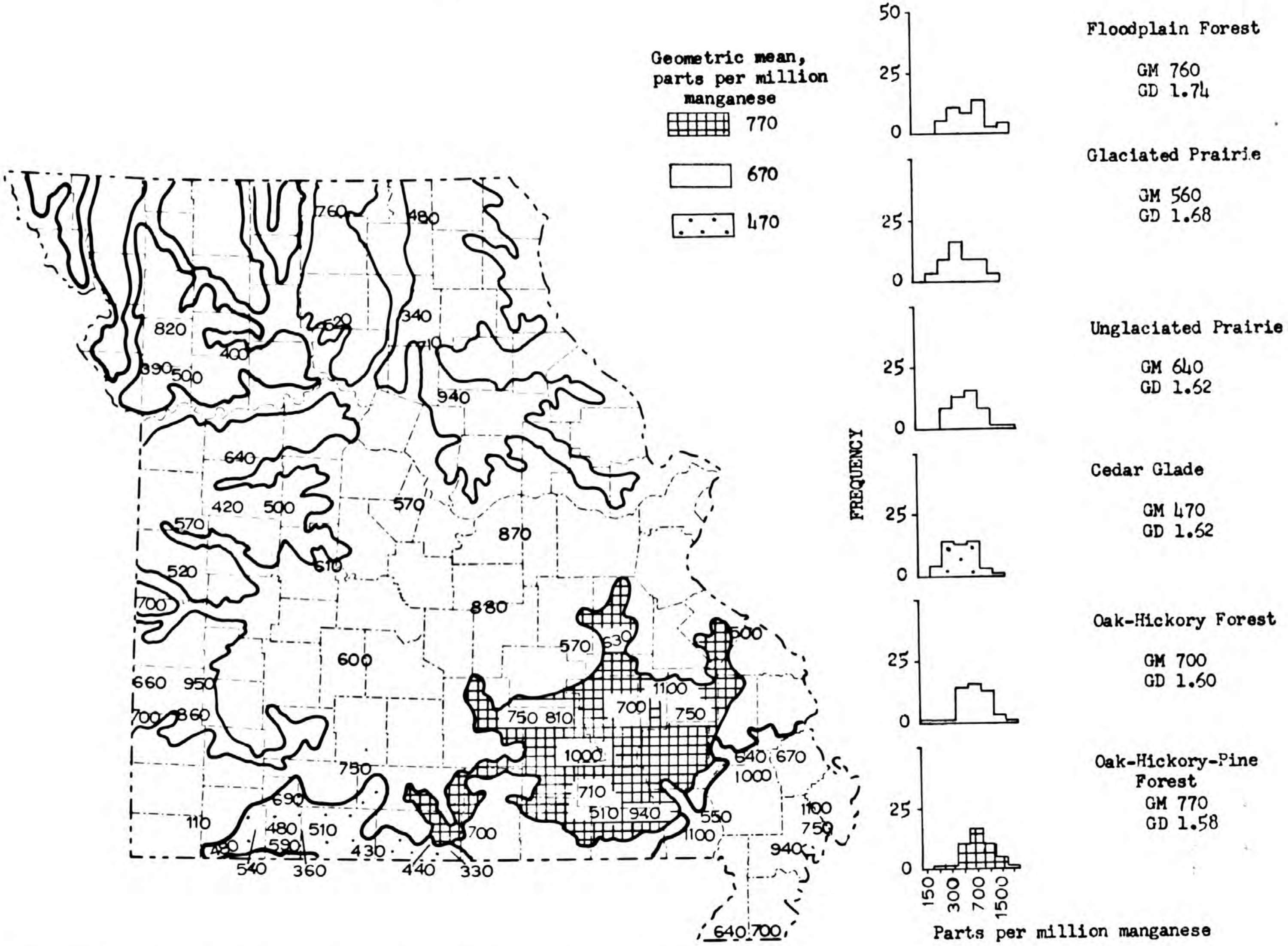


Figure 42b.--Vegetation-type areas in Missouri classified according to mean concentration of manganese in stems of smooth sumac. Each number on the map is the geometric mean concentration of mangenese in generally five samples from a 7½-minute quadrangle.

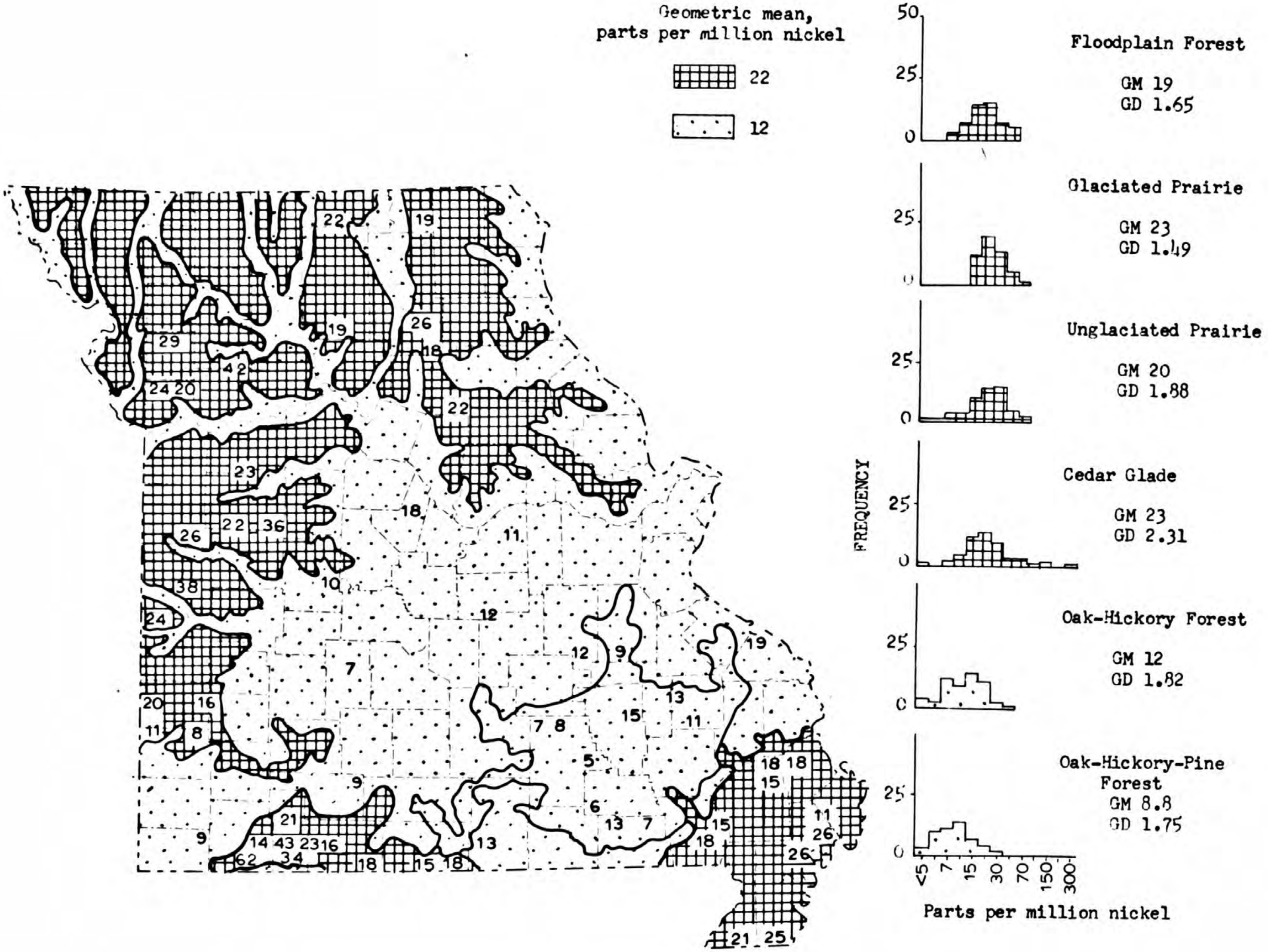


Figure 43a.--Vegetation-type areas in Missouri classified according to mean concentration of nickel in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of nickel in five samples from a 7½-minute quadrangle.

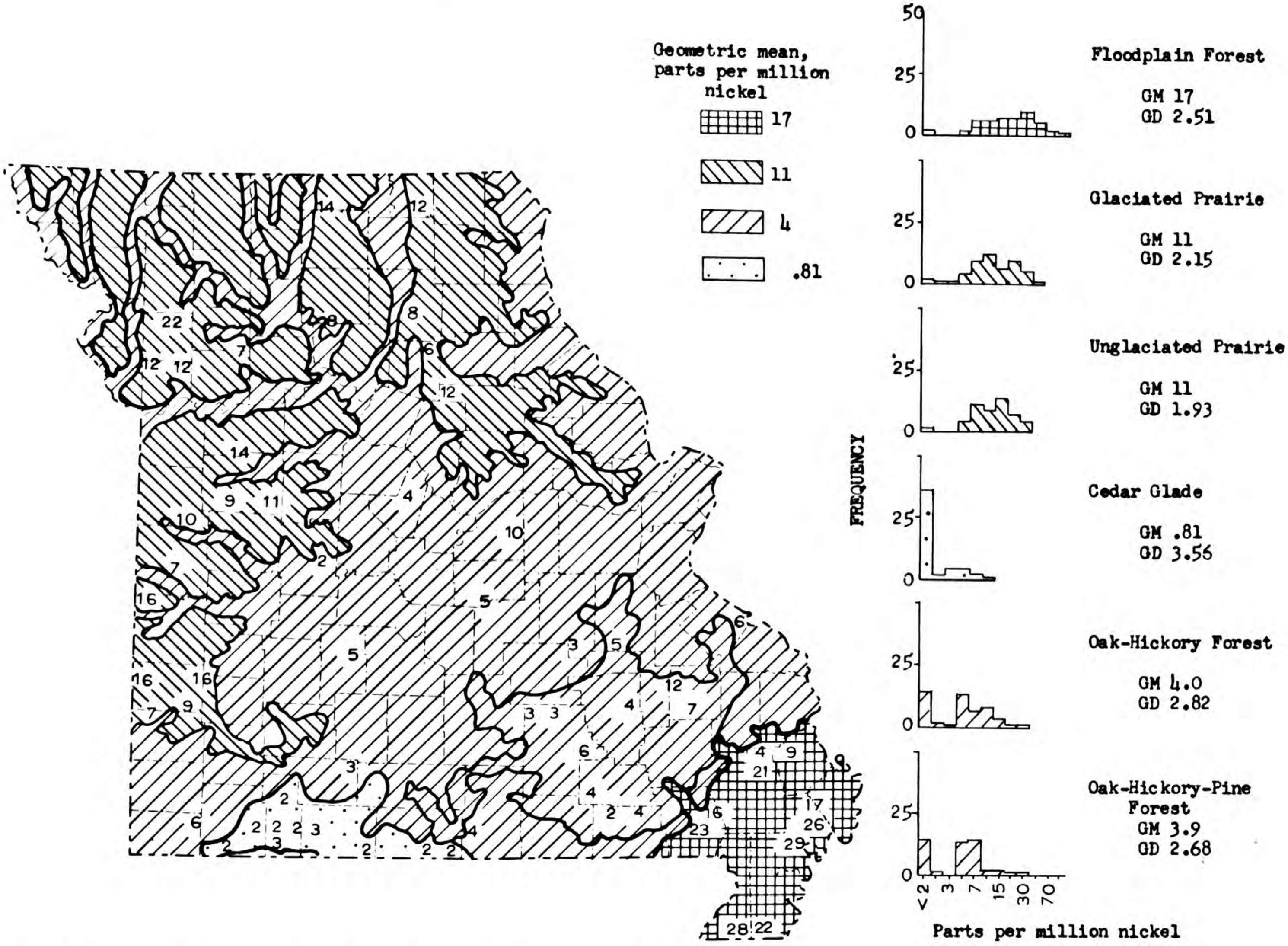


Figure 43b.--Vegetation-type areas in Missouri classified according to mean concentration of nickel in stems of smooth sumac. Each number on the map is the geometric mean concentration of nickel in generally five samples from a 7½-minute quadrangle.

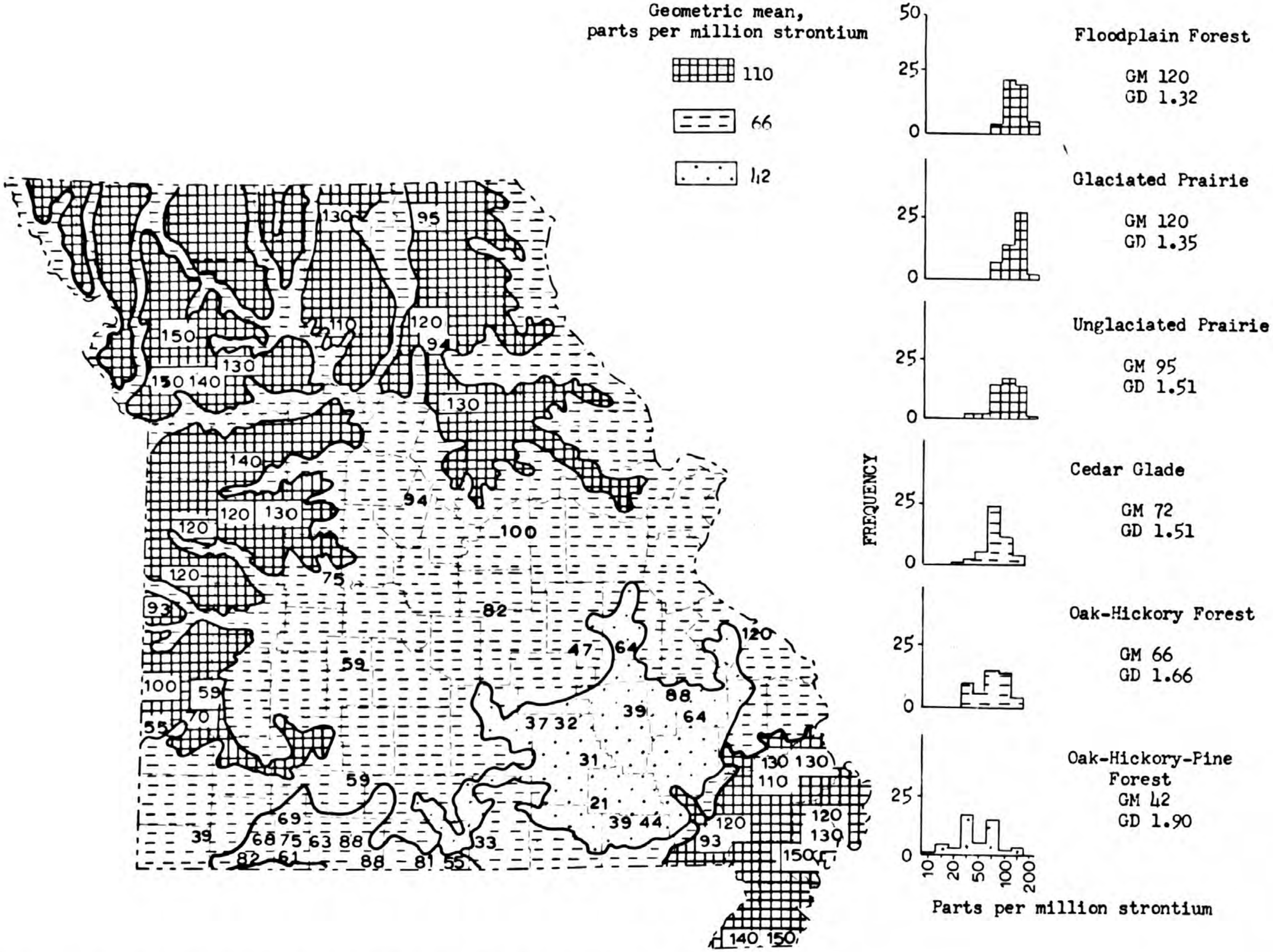


Figure 44a.--Vegetation-type areas in Missouri classified according to mean concentration of strontium in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of strontium in five samples from a 7½-minute quadrangle.

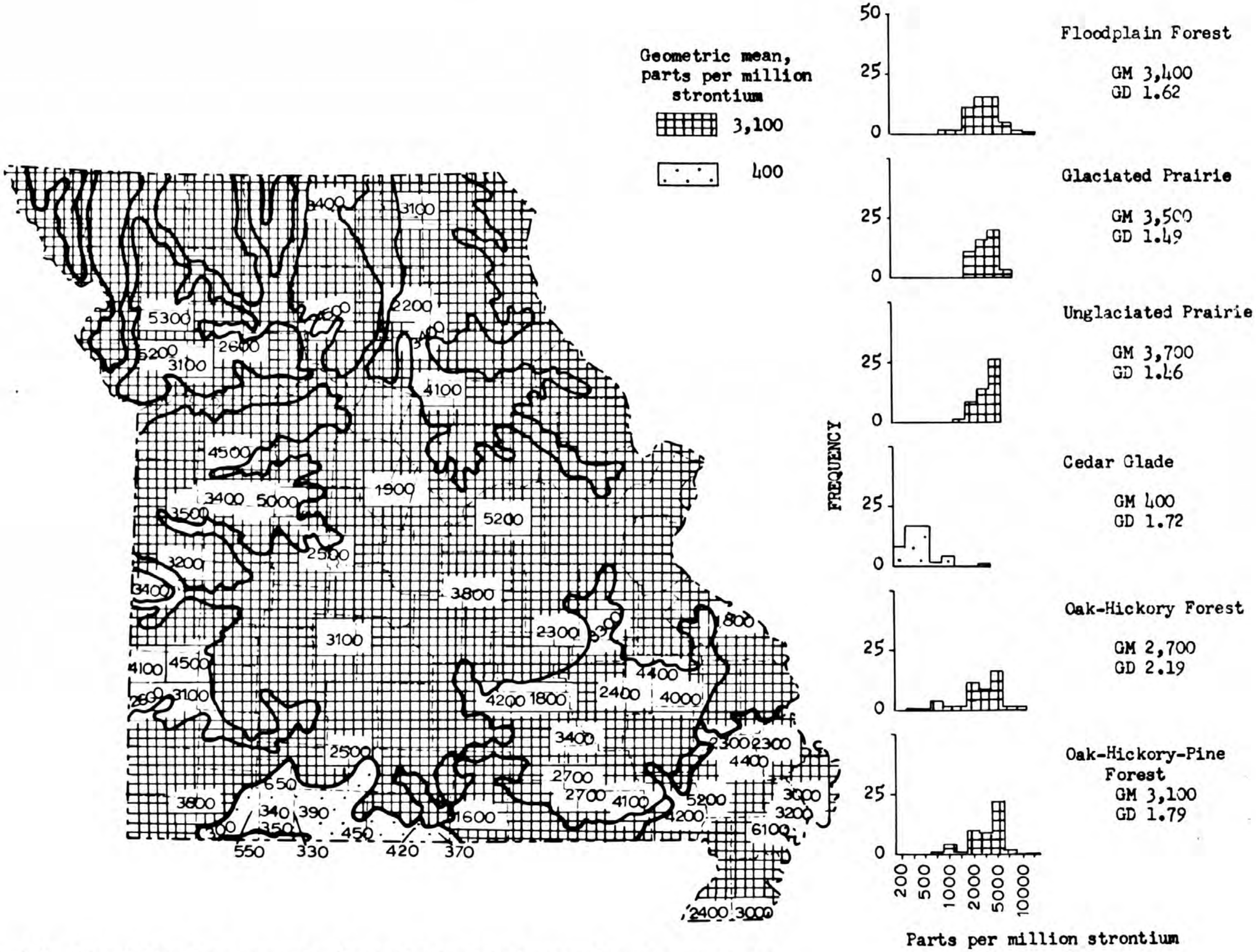


Figure 44b.--Vegetation-type areas in Missouri classified according to mean concentration of strontium in stems of smooth sumac. Each number on the map is the geometric mean concentration of strontium in generally five samples from a 7½-minute quadrangle.

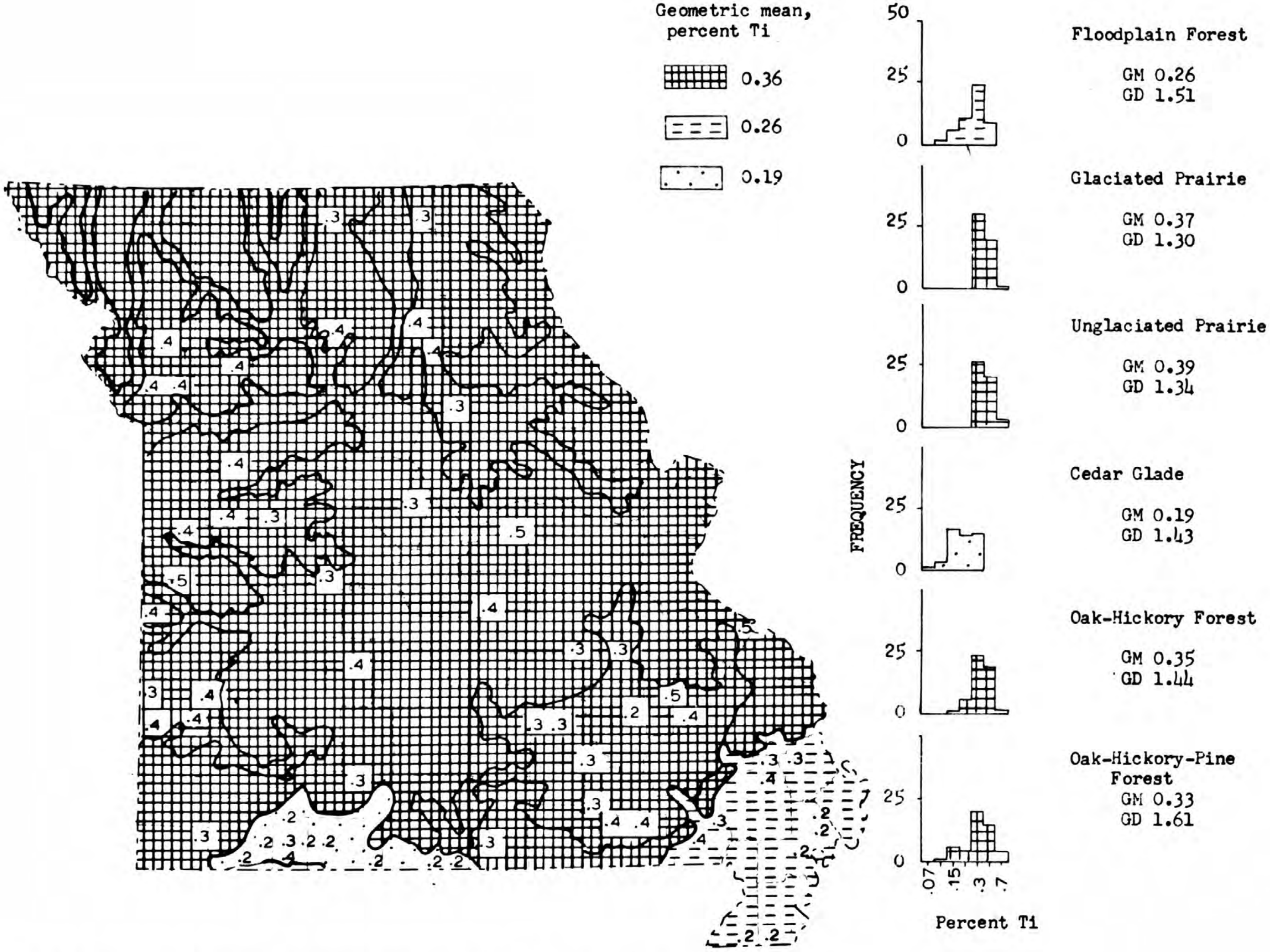


Figure 45a --Vegetation-type areas in Missouri classified according to mean concentration of titanium in the B horizon of uncultivated soils. Each number on the map is the geometric mean concentration of titanium in five samples from a 7½-minute quadrangle.

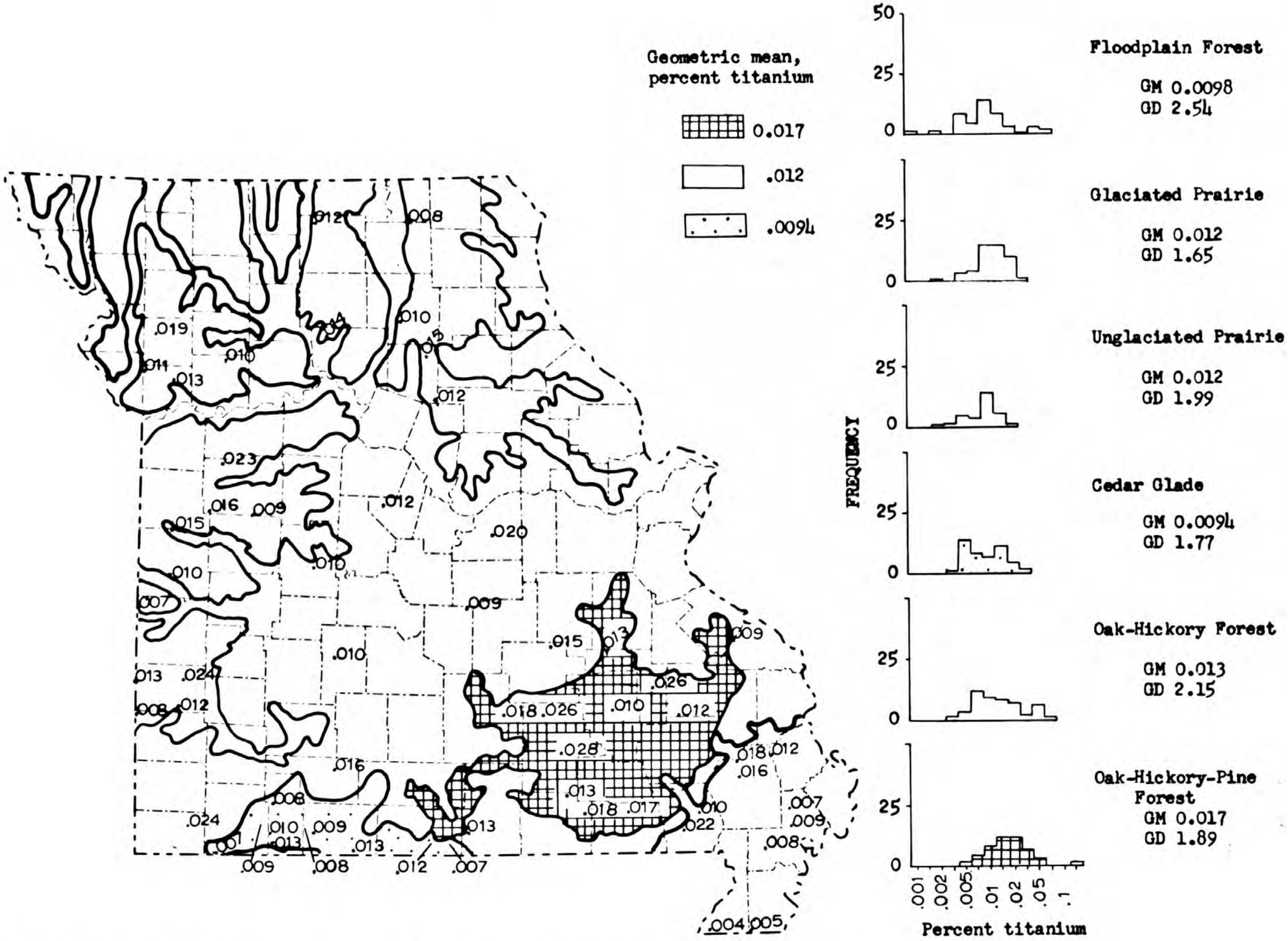


Figure 45b.--Vegetation-type areas in Missouri classified according to mean concentration of titanium in stems of smooth sumac. Each number on the map is the geometric mean concentration of titanium in generally five samples from a $7\frac{1}{2}$-minute quadrangle.

GEOCHEMICAL SURVEY OF WATER

by G. L. Feder

Present status.--During this phase of the work all laboratory analyses for the low-flow part of the surface-water sampling program were received. Due to an unusually dry spring season in Missouri, only four of eight sampling sites for high-water flows have yet been sampled. The laboratory analyses for the four sampled stations have been completed. The four remaining stations will be sampled as soon as intense rainfall returns to Missouri. Detailed statistical analysis of the surface-water data is awaiting completion of the sampling program.

Sampling methods.--Throughout the surface-water part of this phase of the Missouri study, a 0.1-micrometer filter was used in an attempt to separate the dissolved solids from the suspended solids. For most trace element work on surface waters a 0.45-micrometer filter is used. However, V. C. Kennedy (oral commun., 1971) suggested the use of a 0.1-micrometer filter in order to assure removal of very fine particulate material which could pass through a 0.45-micrometer filter. Any particulate material passing a filter, when analyzed, is reported as part of the dissolved solids. Even with a 0.1-micrometer filter the finest sediment and most colloidal material will be passed. A comparison of the relative efficiencies of a 0.1-micrometer and a 0.45-micrometer filter was undertaken by collecting water samples from a low-flow sampling site using filters of both sizes. The two filtered samples, along with an unfiltered sample, were analyzed spectrographically and the results are shown in table 6.

These data demonstrate that filtering does not necessarily alter the concentration for all elements. Strontium and copper, and perhaps barium and manganese, appear to occur, at least at the time of sampling, almost exclusively in solution or associated with colloidal material. The small differences noted between some determinations are probably within the limits of analytical precision. However, the results for aluminum, boron, iron, nickel, and titanium indicate that they occur in significant amounts in suspended solids. Apparently, iron occurs in large amounts in both the coarse and fine fractions of the suspended matter.

Some preliminary comparisons of low-flow surface-water data with ground-water data.--In spite of the fact that the surface-water sampling is incomplete, there is a growing indication that important differences in trace element composition exist between surface water and ground water within a geohydrologic unit. Significant differences were found between lithium concentrations in the ground water from the seven geohydrologic units (U.S. Geol. Survey, 1971). Ground water from the Pennsylvanian geohydrologic unit contains a geometric mean concentration of 68 μg/l lithium, while ground water from the Cambrian and Ordovician geohydrologic unit had a geometric mean concentration of 0.7 μg/l lithium. In contrast,

Table 6.--Comparison of effects of filter pore size on concentrations of selected elements in the filtrate. Samples collected from Cedar Creek at Pleasantville, Mo., on November 11, 1971.

[Values given in μg/l]

Element	Unfiltered	Filtered	
		0.45μ pore size	0.1μ pore size
Aluminum	310	77	57
Barium	90	87	80
Boron	31	16	17
Copper	2	1	2
Iron	740	240	49
Lithium	< 10	< 10	< 10
Manganese	200	170	160
Nickel	8	6	< 5
Strontium	67	73	70
Titanium	7	2	< 2

all the low-flow surface-water samples, whether filtered or unfiltered, from either unit had lithium concentrations below the detection limit of 10 µg/l. Ground water supplying the low-flow streams on the Pennsylvanian geohydrologic unit is probably quite limited and comes mostly from thoroughly leached near-surface aquifers and saturated residuum. The two streams sampled in this unit have drainage areas of 420 and 414 square miles, yet their median 7-day low flows are 0.7 and 0.2 cfs (cubic feet per second), respectively (Skelton, 1966). These flow rates contrast with those of the two streams sampled on the Cambrian and Ordovician geohydrologic unit, whose drainage areas of 404 square miles and 398 square miles are similar to the other areas, but whose median 7-day low flows of 27 and 122 cfs are considerably greater. This difference in yield of ground water to streams in the two geohydrologic units is caused by many factors but the most important is believed to be related to the permeability of the aquifers and the extent of connection between the aquifers and the surface streams. These factors may also be important in determining, within a geohydrologic unit, how closely the trace element content of surface waters during low flow reflects the trace element content of the ground water. Compositional differences, like the one for lithium, between surface water and ground water from the same geohydrologic units can only add to the complexity of attempting to describe the trace element characteristics of geologically coherent regions.

Some preliminary comparisons between lithologic and ground-water data.--The concentrations of many trace elements in ground water appear to be mostly a function of their abundances in the aquifer rocks. This relation is not a simple one, however, most likely because of the kinetics of solution and the rate of circulation of the ground water. For example, in table 7, where higher concentrations of barium, boron, and lithium in ground water correspond with higher concentrations in the aquifer rocks, the relation is clearly not linear.

A few trace elements, notably zinc, suggest the presence of an inverse relation between abundance in rock and abundance in ground water. As shown in table 7, even though the Pennsylvanian age strata have an appreciably higher concentration of zinc than strata of Cambrian and Ordovician age, the ground waters in the Pennsylvanian strata are lower in zinc. Evidently, the low Eh and the presence of H_2S in the ground water of the Pennsylvanian strata sharply reduces the solubility of zinc in comparison to its solubility in the relatively high Eh waters in the Cambrian and Ordovician strata.

Due to the generally low solubilities of sulfides of the transition metals, any aquifer containing fresh water (less than 1,000 mg/l dissolved solids) that has a significant concentration of H_2S will contain very low concentrations of these elements in solution even though they may be abundant in the aquifer rocks.

Table 7.--Summary of data on concentration of selected elements in rocks (U.S. Geol. Survey, 1972, p. 36) and ground water (U.S. Geol. Survey, 1971, p. 58) for three geohydrologic areas in Missouri. Values given represent the geometric mean (GM), and the geometric deviation (GD). Concentrations measured in parts per million (ppm) and micrograms per liter (µg/l).

Element	Strata of Pennsylvanian age								Strata of Mississippian age				Strata of Cambrian and Early Ordovician age			
	ROCK						WATER		ROCK Limestone		WATER		ROCK Dolomite		WATER	
	Sandstone		Limestone		Shale											
	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD
Ba ----	170 ppm	2.2	44 ppm	3.0	430 ppm	1.5	140 µg/l	2.2	6.6 ppm	6.8	53 µg/l	1.2	9.2 ppm	3.5	43 µg/l	1.3
B -----	37 ppm	2.0	< 20 ppm	-	72 ppm	1.3	200 µg/l	3.5	< 20 ppm	-	11 µg/l	1.5	< 20 ppm	-	11 µg/l	1.3
Li ----	17 ppm	2.3	< 5 ppm	-	79 ppm	1.5	68 µg/l	2.0	< 5 ppm	-	1.6 µg/l	5.8	< 5 ppm	-	0.66 µg/l	5.9
Zn ----	33 ppm	3.0	24 ppm	2.3	82 ppm	1.5	< 16 µg/l	-	20 ppm	1.7	< 28 µg/l	-	< 10 ppm	-	75 µg/l	2.9

Even though both relationships described above seem in agreement with known thermodynamic principles, the complexity of various hydrologic streams may result in large departures from thermodynamic equilibrium between aquifer rocks and ground water at the point of sample collection. Departures from equilibrium may be especially large where several water-bearing horizons of different chemistry yield water to a well, or where circulation in an aquifer is very rapid, as in many carbonate terranes.

REFERENCES CITED

Cohen, A. C., Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: Technometrics, v. 1, no. 3, p. 217-237.

Connor, J. J., Shacklette, H. T., and Erdman, J. A., 1971, Extraordinary trace-element accumulations in roadside cedars near Centerville, Missouri, in Geological Survey Research 1971: U.S. Geol. Survey Prof. Paper 750-B, p. B151-B156.

Connor, J. J., and Ebens, R. J., 1972, Geochemical variation in Pennsylvanian shale (abs.): Geol. Soc. of America, Abstracts with programs, v. 4, no. 5, p. 314-315.

Ebens, R. J., Erdman, J. A., and Feder, G. L., 1972, Geochemical anomalies in a claypit area, Callaway County, Missouri where metabolic disorders in cattle were reported (abs.): Geol. Soc. of America, Abstracts with programs, v. 4, no. 5, p. 319.

Ebens, R. J., Erdman, J. A., Feder, G. L., Case, A. A., and Selby, L. A., 1972, Geochemical anomalies of a claypit area, Callaway County, Missouri, and related metabolic imbalance in beef cattle: U.S. Geol. Survey open-file report, 69 p.

Miesch, A. T., 1972, Sampling problems in trace element investigations of rocks: Annals of the New York Acad. Sci., v. 199, p. 95-104.

Missouri University Agricultural Experiment Station, 1931, Reconnaissance survey soil map of Missouri, 1:750,000, 1 sheet.

Sauchelli, Vincent, 1969, Trace elements in agriculture: New York, Van Nostrand Reinhold Co., 248 p.

Scrivner, C. L., Baker, J. C., and Miller, B. J., 1966, Soils of Missouri: Circ. No. 823, Extension Div., Missouri Univ., Columbia, 47 p.

Skelton, John, 1966, Low-flow characteristics of Missouri streams: Water Resources Report 20, Missouri Geol. Survey and Water Resources, 47 p.

Tidball, R. R., 1971, Geochemical variation in Missouri soils, in Hemphill, D. D., ed., Trace substances in environmental health, Missouri Univ., 4th Ann. (1970) Conf., Proc., p. 15-25.

U.S. Geol. Survey, 1969, Geochemical survey of Missouri, plans and progress for first six-month period (July-December, 1969): U.S. Geol. Survey open-file report, 49 p.

REFERENCES CITED--Continued

U.S. Geol. Survey, 1970, Geochemical survey of Missouri, plans and progress for third six-month period (July-December, 1970): U.S. Geol. Survey open-file report, 33 p.

______ 1971, Geochemical survey of Missouri, plans and progress for fourth six-month period (January-June, 1971): U.S. Geol. Survey open-file report, 63 p.

______ 1972, Geochemical survey of Missouri, plans and progress for fifth six-month period (July-December, 1971): U.S. Geol. Survey open-file report, 145 p.