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GEOLOGICAL SURVEY BULLETIN 1278-D

Geochemical Exploration Techniques Based on Distribution of Selected Elements in Rocks, Soils, and Plants, Mineral Butte Copper Deposit, Pinal County, Arizona

By MAURICE A. CHAFFEE

CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

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A comparison and evaluation of some different types of samples that may be useful for geochemical prospecting for copper in the semiarid environment

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SYSTEM OF MEASUREMENT UNITS

This report uses both the metric and English systems of units. In the text the metric units are given first and the equivalent measurement in English units is given in parentheses. The units are frequently abbreviated using the notations shown below. The metric units were converted to English units by multiplying by the factors given in the following list:

Metric unit *To Convert*	*Multiply by*	*English unit* *To obtain*
Centimetres (cm)	0.3937	Inches (in.).
Metres (m)	3.28	Feet (ft).
Kilometres (km)	.62	Miles (mi).

Conversions of temperature from degrees Celsius (°C) to degrees Farenheit (°F) were taken from a table in Weast, R. C., ed., 1967, Handbook of Chemistry and Physics; Cleveland, Ohio, The Chemical Rubber Co., p. F100–F101.

CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

GEOCHEMICAL EXPLORATION TECHNIQUES BASED ON DISTRIBUTION OF SELECTED ELEMENTS IN ROCKS, SOILS, AND PLANTS, MINERAL BUTTE COPPER DEPOSIT, PINAL COUNTY, ARIZONA

By Maurice A. Chaffee

ABSTRACT

A geochemical study was made of rock, soil, and plant samples collected in the vicinity of the Mineral Butte copper deposit in Pinal County, Ariz. This deposit is in a Precambrian granite host rock near its contact with a small Upper Cretaceous biotite quartz monzonite stock. Of the potentially economic minerals only secondary copper minerals are present in bedrock exposures.

Bedrock and residual-soil samples were collected on a 150-metre (500-foot) grid. Two soil fractions were separated for analysis: a 1-2 millimetre coarse fraction and a <0.063 millimetre fine fraction. Leaf and stem samples from four plant species (mesquite, catclaw acacia, blue paloverde, and ironwood) were collected from plants growing in stream channels in the area of the deposit.

The rock and soil samples were analyzed for 39 elements. The soil samples were also analyzed for soil pH. The analyses of 31 elements did not provide sufficient information, and these were not evaluated further. Eight elements provided sufficient useful analyses; cobalt, fluorine, gold, lead, molybdenum, silver, and zinc are thought to be geochemically associated with copper and are discussed in this report.

Anomalously low pH values were found in soil samples collected near the Mineral Butte deposit. The areal extent of these low values seems to be related to areas of silicified Precambrian granite. This distribution of low values might also represent a halo around the copper-rich area, thereby providing a larger exploration target than that of the copper geochemical anomaly.

The distributions of concentrations of cobalt, copper, gold, molybdenum, silver, and zinc in bedrock samples yield positive anomalies. The areal extent of the cobalt anomaly most closely matches that of copper. The distributions of concentrations of

fluorine and lead in bedrock samples yield what appear to be negative anomalies that also coincide closely with the copper anomaly. Another interpretation of the fluorine and lead data suggests that these two elements show a positive aureole around the copper anomaly. A more regional geochemical sampling program is needed in order to interpret better the anomalies of these two elements.

In contrast to many other copper districts, there does not seem to be a close association between the distributions of copper and molybdenum in the Mineral Butte area.

The distributions of anomalies of cobalt and gold in soil samples most closely match the known copper anomaly. For copper, cobalt, gold, and molybdenum, samples of the fine-soil fraction provide more widespread and (or) more easily interpreted anomalies than do samples of either rock or the coarse-soil fraction. For these elements, at least, a regional reconnaissance sampling program using a fine-soil fraction should be considered.

Physical and chemical data from this study indicate that eolian contamination of soil samples is not a serious problem to consider in anomaly interpretation in the Mineral Butte area.

Ash from the leaves and stems of the four plant species was analyzed for 38 elements. The analyses of most of these elements did not provide sufficient information. This report describes the results for copper, zinc, and molybdenum. Examination of the geochemical data for these three elements indicates that the concentrations of these elements in plant ash vary according to the particular species and plant part sampled. Those plant-element populations that produced the greatest spread of analytical values also produced the most useful vegetation maps.

Of the three elements studied in samples of plant ash, copper clearly provided the most consistent and meaningful information for locating the known deposit. Molybdenum was not as useful. No spatial correlation was found between zinc anomalies in rock and soil samples and zinc anomalies in the ash of any of the plant species studied.

The copper deposit was best located using analyses of mesquite samples. Those of blue paloverde and catclaw acacia were almost as effective. In general, those samples that contain anomalous metal concentrations in both plant parts, rather than in just one part, are likely to represent the most significant anomalies.

Deep-rooted plants can be an effective regional reconnaissance sample medium for geochemical surveys in arid lands, especially in the search for metal deposits buried under a thin layer of overburden.

INTRODUCTION AND ACKNOWLEDGMENTS

A geochemical study has been made of rock, soil, and plant samples collected in the vicinity of the Mineral Butte copper deposit, Pinal County, Ariz. This study has a threefold purpose. The first is to provide basic information on the abundances of many elements in a variety of sample types collected in the vicinity of a known copper deposit. The second is to determine, by evaluation and comparison of the different sample types, the optimum type(s) to use. The third is to identify those elements in the different sample types that would be most useful in the search for copper deposits in similar environments. Emphasis in this investigation has been to determine in different sample media what elements, if any, would characterize the copper deposit as well as, or better than, would copper itself. No attempt has been made to study the trends in concentrations of the selected elements on a truly regional scale.

The Mineral Butte copper deposit is located in the Blackwater mining district, Pinal County, Ariz., about 13 km (8 mi) northwest of the town of Coolidge (fig. 1). Elevations in the study area range from 581 m (1,907 ft) to 411 m (1,350 ft).

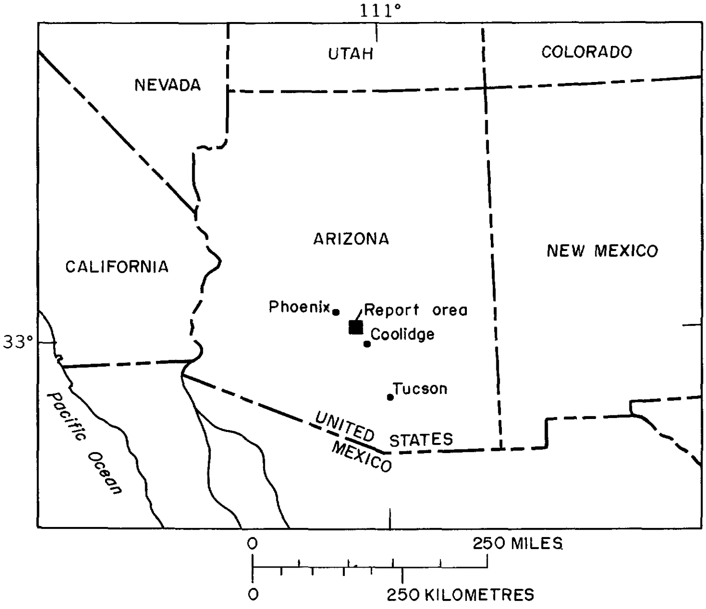

FIGURE 1. — Location of the report area.

The climate and flora in the vicinity of the study area are typical of the semiarid lower Sonoran Desert of Arizona. The weather station nearest Mineral Butte is at Casa Grande National Monument, just to the north of Coolidge, about 13 km (8 mi) southeast of the study area. The mean annual precipitation at that station for the years 1908 through 1957 was 22.0 cm (8.74 in.). The mean daily maximum and minimum temperatures were approximately 31°C (about 87°F) and 10°C (about 51°F), respectively (Green and Sellers, 1964). The Mineral Butte area supports a large variety of herbs, shrubs, and trees. Many trees growing in or near the active stream channels reach heights of 10 m (about 33 ft) or more. The plant species selected for this investigation are among those that commonly grow in the stream channels of the region.

The area of the Mineral Butte deposit was selected for this geochemical study for several reasons. First, the surface has not been greatly disturbed by man's activities. Wilson (1969) noted that the area was originally prospected for copper, silver, and gold, although mining activity to date has been restricted to a few small shafts and pits. Second, the area is geologically simple. Only three geologic units of major importance crop out in the area, and one of these comprises from 80 to 90 percent of the total surface exposures. Premineralization-age bedrock is exposed throughout much of the study area and overall relief is low, allowing a comparison of bedrock geochemical data with corresponding residual-soil data. Finally, although all streams in the area have only intermittent flow, the chemistry of water crossing this deposit and continuing downstream toward the Gila River can be studied indirectly by analyzing the plants growing in the one main channel that crosses directly over the deposit. These analyses can then be compared to those from samples of plants growing in other nearby stream channels that do not cross the deposit to determine how well and how far from any outcrop the analyses from the plant samples would indicate the known deposit.

The Mineral Butte copper deposit is on land leased from the Gila River Indians by the Duval Corporation. The assistance and cooperation of the staff of this corporation, especially Mr. R. A. Metz, are gratefully acknowledged.

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In addition, appreciation is extended to Mr. A. A. M. A. Gayayel of the Geological Survey of Egypt, who assisted the author in the field while working for the U.S. Geological Survey as a United Nations Special Fund Fellow.

GEOLOGIC SETTING

Six different geologic units have been mapped in the Mineral Butte area (fig. 2). Exposures in this area of the oldest unit, the Pinal Schist of Precambrian X age[1] (Drewes, 1972, 1975), are gneiss rather than schist. The Pinal Schist was intruded by a coarse-grained, equigranular Precambrian granite, which is thought to be equivalent to the Oracle Granite north of Tucson (Balla, 1972). The Oracle Granite has been dated as 1,420 m.y. (million years) (Damon, 1968, p. 38). This granite is the most extensive of the six

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[1] An interim scheme for subdivision of Precambrian time recently adopted by the U.S. Geological Survey assigns Precambrian X time to the interval 1,600-2,500 m.y. ago and Precambrian Y time to the interval 800-1,600 m.y. ago.

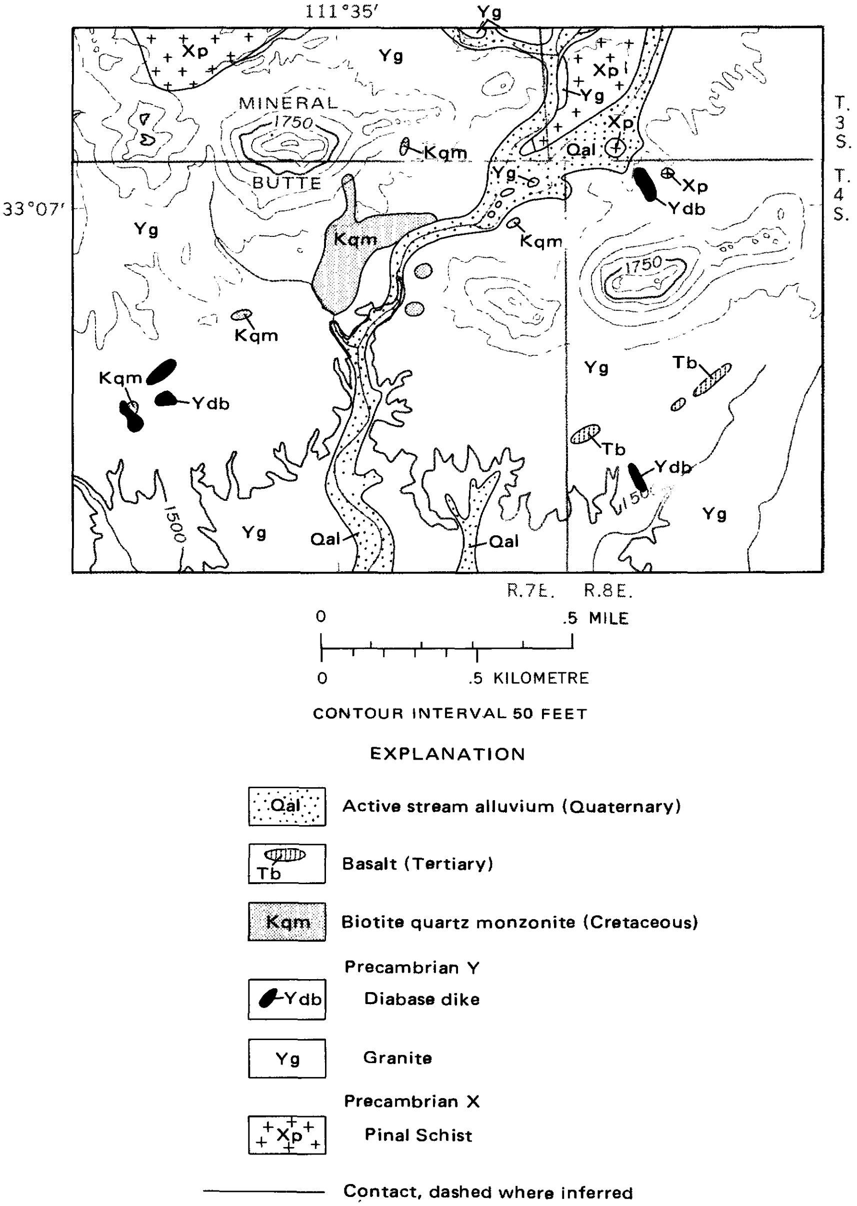

FIGURE 2. — Geology of the Mineral Butte area.

units exposed in the study area and is the host rock for most of the copper minerals. Topographic relief in the granite suggests that at least 120 m (400 ft) of granite may have been eroded from the top of the present surface of the copper deposit. A few dikes of diabase cut the granite. This diabase is similar in appearance to, and, therefore, probably the same age as, the extensive diabases which intrude the Precambrian Y[1] Apache Group and other Precambrian formations throughout central Arizona.

The granite was intruded during the Late Cretaceous by a stock of variable mineralogical composition which is predominately biotite quartz monzonite. This stock has been dated at 70 m.y. (Balla, 1972). Field mapping indicates that this intrusive is present at or near the surface of much of the central part of the study area.

Tertiary basalt flows and possibly some fluvial deposits may have covered much of the area of figure 2. Today, only a few basalt remnants remain and no fluvial deposits are present. Fluvial deposits consisting of unconsolidated river silt with varying amounts of sand and gravel occur south of the area of figure 2. Stream sediments of Holocene age are present in the major stream channels of the area.

The deposition of copper minerals was probably associated in time and space with the intrusion of the biotite quartz monzonite. Most of the copper minerals are concentrated in the granite near the granite-quartz monzonite contact. Nearly all of the copper minerals — both at the surface and at depth as seen in drill hole cuttings — are secondary, although pyrite and minor chalcopyrite are present in the cuttings (R. A. Metz, oral commun., 1972). Both fresh pyrite and limonite pseudomorphs after pyrite are locally present in surface exposures. From a geochemical standpoint, the environment of the copper deposit can be described as being near the contact of an intrusion of intermediate composition and its more felsic, relatively nonreactive wallrock (the Precambrian granite).

Soil horizons in the region are typically poorly developed, as might be expected of desert soils. Soil thicknesses usually do not exceed about 20 cm (8 in.). Field examination of soil and bedrock colors reveals a close correlation between the color of the parent rock and the color of the immediately overlying soil. This observation, together with geochemical evidence to be discussed later, suggests that most of the soil immediately above bedrock is probably residual.

PROCEDURES FOR COLLECTING, PREPARING, AND ANALYZING SAMPLES

Samples of bedrock, residual soil, and vegetation were collected and were analyzed for this report. The rock and soil samples were

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[1] See footnote 1 on page D4.

collected to find the distribution of selected trace elements relative to the distribution of copper and to determine which, if any, of the different elements and sample media would best define the deposit. The vegetation samples were collected to determine (1) whether analyses of plant samples would indicate the presence of the known copper deposit, and (2) just how far beyond any outcrop the analytical data would be useful for indicating the presence of the deposit.

BEDROCK AND RESIDUAL SOIL

Samples were collected over the known copper deposit on a 150-m (500-ft) grid. At each site on the grid a sample of bedrock and one of residual soil were collected. The rock sample was hand cobbed to remove any obviously weathered surface material and then was crushed and was pulverized for analysis. The soil sample was collected at the soil-bedrock interface after the overlying portion of soil and any associated organic debris were first removed. Two size splits were obtained from each soil sample — a 1-2 mm fraction and a <0.063-mm fraction. The 1-2 mm fraction was pulverized; the <0.063-mm fraction was used without further treatment.

The samples were analyzed for 30 elements by a six-step semi-quantitative emission spectrographic method (Grimes and Marranzino, 1968). In addition, copper, gold, lithium, mercury, potassium, silver, sodium, and zinc were determined by atomic absorption spectrophotometry (Ward and others, 1969). Fluorine (fluoride-ion concentration) was determined by specific-ion electrode potentiometry (Ficklin, 1970). All told, 39 elements were determined by the various methods; several of the elements were analyzed by more than one method.

An evaluation of the analyses and areal distributions of the elements resulted in the conclusion that eight elements are of interest from the standpoint of this study. These elements are copper, cobalt, fluorine, gold, lead,molybdenum, silver, and zinc. The other 31 elements[2] were rejected for inclusion in this report for various reasons. For many of the rejected elements there were not enough valid analytical values to produce meaningful maps. For such elements, most or all of the samples contained the given elements in concentrations less than the lower detection limits of the analytical methods used for those elements. For some of the

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[2] The following elements (with lower detection limits in parts per million shown in parentheses) were analyzed by emission spectography and results are not included in this report for reasons outlined in subsequent paragraphs: As (200), Au (10), B (10), Ba (20), Be (1), Bi (10), Ca (500), Cd (20), Cr (10), Cu (5), Fe (500), La (20), Mg (200), Mn (10), Nb (20), Ni (5), Sb (100), Sc (5), Sn (10), Sr (100), Ti (20), V (10), W (50), Y (10), Zn (200), and Zr (10). Other elements rejected (Ag (0.5), Hg (0.02), K (100), Li (5), and Na (100))were analyzed by atomic absorption spectrophotometry.

elements there were sufficient valid values available, but there were only two or three different concentration levels reported; consequently, no concentration trends could be established on geochemical maps for such elements. Several of the rejected elements had sufficient valid analytical values and adequate analytical variation, but plots of the values did not show any concentration trends that could be associated spatially with the known copper deposit.

VEGETATION

Plant samples from four species were collected at irregular intervals along the stream channels crossing the region around the copper deposit. Three of the four species are generally considered to be phreatophytes — that is, they are species known to have deep, extensive root systems that may reach the permanent ground-water table where it is present within about 30 m (100 ft) or less of the surface. The three phreatophyte species are mesquite (*Prosopis juliflora* var. *velutina* (Wooten) Sarg.), catclaw acacia (*Acacia greggii* A. Gray), and blue paloverde (*Cercidium floridum* Benth. *ex* A. Gray) (Shreve and Wiggins, 1964). The fourth species sampled was ironwood (*Olneya tesota* A. Gray) (Shreve and Wiggins, 1964), which, while not considered to be a phreatophyte, sometimes seems to behave like one. Ironwood normally occurs as large trees, and specimens reach their largest size and also their greatest root development in stream channels where ground water is commonly available throughout the growing season.

Sampling experience gained during an earlier study (Chaffee and Hessin, 1971) indicated that leaves and young stems are the easiest materials to collect and that these materials also provide meaningful geochemical information. For this study a leaf-stem pair of samples was collected from one plant of a particular species at each sample site. Leaves and stems were analyzed as two separate samples for two reasons. First, analyses of the two plant parts provide basic chemical-abundance data. Second, for physiological reasons the metal concentrations of the two parts of the plants selected for this study should theoretically vary sympathetically; consequently, analyses of the two plant parts should provide an independent analytical check for each plant at each sample site. Sample material for all four species was taken completely around the given plant at a height of about 1 to 1.5 m (3 to 5 ft). Only 1- and 2-year-old stems of mesquite, catclaw acacia, and ironwood were collected; new growth was rejected wherever possible. For samples of blue paloverde the age of the stems could not be determined; consequently, the outer 10-20 cm (4-8 in.) of live material was collected.

Plant samples were air dried and then chopped in a Wiley mill after the leaves and stems were separated. The chopped material was then ashed for approximately 22 hours at temperatures that reached a maximum of about 450°C (about 840°F).

Previous studies near several copper deposits (Chaffee and Hessin, 1971; L. C. Huff, oral commun., 1972) indicated that only a very few chemical elements are generally useful in biogeochemical surveys searching for porphyry copper deposits in the arid Southwest. The plant samples collected for the present study were initially analyzed by atomic absorption spectrophotometry (Ward and others, 1969; Ward, 1975) for copper, molybdenum, and zinc because these elements proved useful in an earlier survey (Chaffee and Hessin, 1971). In an effort to discover other useful elements, the plant samples were also analyzed for 35 elements using a six-step semiquantitative emission spectrographic method (Mosier, 1972). Plots of the spectrographic analyses did not reveal any new elements that would have helped to locate the known deposit; consequently, only the atomic absorption analyses have been used in this report.[3]

SOIL pH

Soil pH was measured in a Denver laboratory of the U.S. Geological Survey for the < 0.063-mm fraction from each site using the method described in U.S. Dept. Agriculture Handbook 18 (Soil Survey Staff, 1951, p. 237). Preliminary study of sieved soil fractions indicated that there was very little variation in pH among size fractions less than 2.0 mm in diameter; consequently, the pH value of the fine-soil fraction is assumed to represent any size fraction of soil material less than 2.0 mm in diameter.

STATISTICAL TREATMENT OF GEOCHEMICAL ANALYSES

For each type of sample the analyses for each selected element and for pH were separated into concentration classes, and cumulative frequency curves were constructed according to the method of Lepeltier (1969). The interpretation of these curves, especially for the analyses of samples of bedrock and residual soil, was purposely biased because most of the samples were collected

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[3] The following elements (with lower detection limits in parts per million shown in parentheses) were analyzed by emission spectrography and results are not included in this report for reasons outlined previously for the rock and soil samples: Ag (0.1), As (200), Au (2), B (5), Ba (20), Be (1), Bi (1), Cd (2), Co (10), Cr (5), Cu (1), Fe (500), Ga (2), Ge (2), In (2), La (20), Li (200), Mg (200), Mn (10), Mo (2), Na (100), Nb (50), Ni (5), Pb (1), Sb (50), Sc (5), Sn (5), Sr (100), Ti (20), Tl (2), V (10), W (50), Y (10), Zn (100), and Zr (10).

over or near a known mineral deposit. Consequently, as many as 30 percent of the samples in any one sample population might be anomalous. In a more "normal" population probably less than 5 percent of the samples would be expected to be anomalous.

The cumulative frequency curves were used in combination with visual inspections of maps illustrating the distributions of concentrations of the selected elements in order to determine the minimum anomalous value, or threshold value, to be used for each of the geochemical maps. In every case the 50th percentile (median) value was used for the background value. The concentrations for each element and the values for pH were plotted on base maps and the values were contoured using the threshold value as the contour level.

ANALYTICAL RESULTS OF BEDROCK AND RESIDUAL SOIL SAMPLES

A total of 101 rock samples and 100 soil samples were collected for this study. A summary of information concerning the eight selected elements and soil pH is given in table 1.

The Precambrian Pinal Schist and granite and the Cretaceous biotite quartz monzonite were sampled for this report. Approximately 95 percent of the samples were collected from granite outcrops and their superjacent soil. The 5 percent of the samples collected from the other two units did not show any strong chemical bias in the selected elements that could be attributed solely to differences in rock type; consequently, the differences in lithology have been ignored in computing the information presented in table 1.

DISTRIBUTION OF SOIL pH

Soil-pH values as low as 5.0 were determined in the fine-soil fractions (table 1). Acid soil-pH values in desert soils are unusual; most desert soils are alkaline. The background (median) pH value of 7.2 indicates that most of the soil samples in the study area are normal desert soils.

The lowest soil-pH values at Mineral Butte are generally found in those areas that are topographically high (fig. 3). Field investigation indicates that these higher areas have been silicified and that the surrounding rock has not. Because of the presence of silica, the silicified areas have been more resistant to weathering than the surrounding unsilicified rock and, therefore, are higher topographically than those areas that have not been silicified. In these silicified, topographically high areas, pyrite is occasionally found in outcrops. Possibly this pyrite, which has been differential-

TABLE 1. — *Statistical data for soil pH and selected elements in samples of bedrock and residual soil, Mineral Butte area, Pinal County, Ariz.*

[All values in parts per million except for pH. L means detected but at concentrations below the limit of detection shown in parenthesis; N means not detected at the limit of detection shown in parenthesis; leaders (...) indicate no data]

	Sample type	Range of values	Background (median) value	Threshold value	Anomaly contrast value	Average low-calcium granite[1]
pH	<0.063 mm soil fraction	5.0-8.2	7.2	7.0	......	......
Copper	Bedrock	5-23,000	45	120	2.67	10
	1-2 mm soil fraction	20-7,500	60	130	2.17	......
	<0.063 mm soil fraction	5-3,000	100	150	1.50	......
Cobalt	Bedrock	N(5)-70	L(5)	7	>1.40	1.0
	1-2 mm soil fraction	L(5)-30	7	10	1.43	......
	<0.063 mm soil fraction	5-70	15	20	1.33	......
Fluorine	Bedrock	60-1,360	400	200	.50	850
	1-2 mm soil fraction	90-950	350	230	.66	......
	<0.063 mm soil fraction	200-1,600	450	350	.78	......
Gold	Bedrock	L(.02)-.10	L(.02)	.02	......	.004
	1-2 mm soil fraction	L(.02)-.28	L(.02)	.02	......	......
	<0.063 mm soil fraction	L(.02)-.15	L(.02)	.02	......	......
Lead	Bedrock	N(10)-300	20	10	.50	19
	1-2 mm soil fraction	10-100	30	20	.66	......
	<0.063 mm soil fraction	15-100	40	30	.75	......
Molybdenum	Bedrock	N(5)-100	L(5)	5	......	1.3
	1-2 mm soil fraction	N(5)-50	L(5)	5	......	......
	<0.063 mm soil fraction	N(5)-50	L(5)	5	......	......
Silver	Bedrock	N(.5)-20	N(.5)	.5	......	.037
	1-2 mm soil fraction	N(.5)-2.0	N(.5)	.5	......	......
	<0.063 mm soil fraction	N(.5)-1.5	N(.5)	.5	......	......
Zinc	Bedrock	.5-300	5	10	2.00	39
	1-2 mm soil fraction	5-130	20	40	2.00	......
	<0.063 mm soil fraction	30-140	50	70	1.40	......

[1] Data from Turekian and Wedepohl (1961).

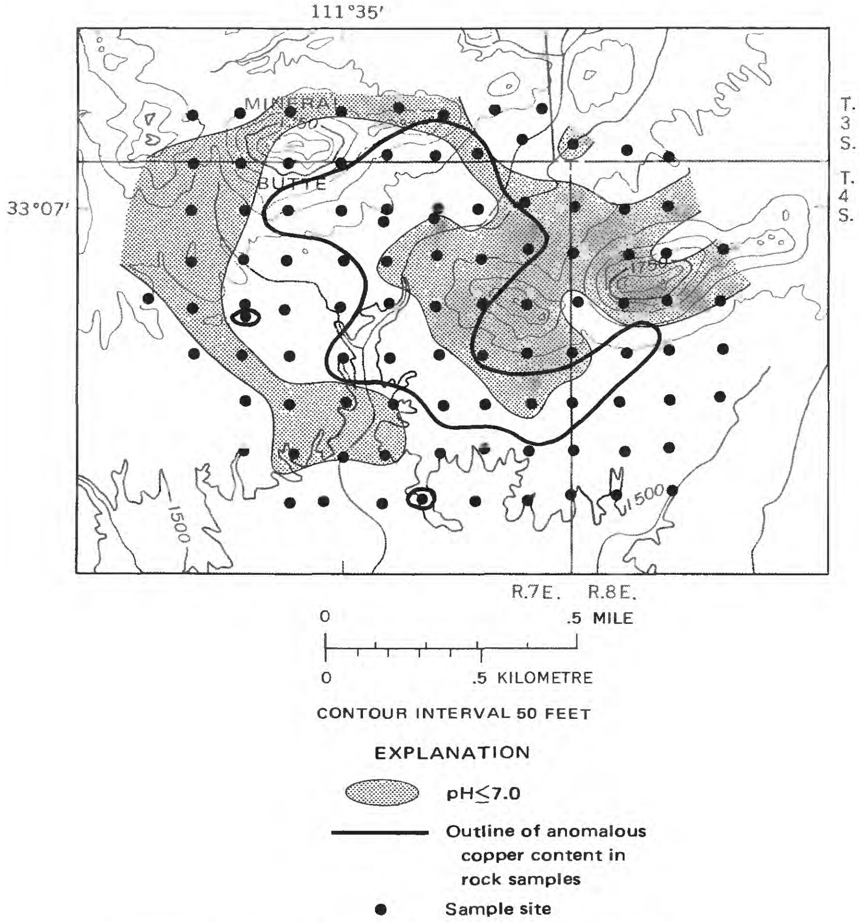

FIGURE 3. — Distribution of pH values, Mineral Butte area.

ly protected from weathering by the silica, is now slowly oxidizing and producing acidic soil conditions.

In the immediate area of the copper deposit, no sulfide minerals remain near the surface; therefore, no acid of any consequence is being formed to produce soil-pH values below 7. A comparison of the distribution of soil-pH values with the distribution of the main copper anomaly based on bedrock samples (fig. 3) indicates that the copper-rich area is generally associated with normal desert soil-pH values. The distributions of anomalous copper in bedrock samples and unoxidized sulfides in bedrock exposures at Mineral Butte do not coincide; thus, the distribution of soil-pH values in this district is apparently an indicator of the distribution of unoxidized sulfide and is not a good direct indicator of the distribution of anomalous concentrations of copper. An examination of figure 3 suggests, however, that the distribution of low soil-pH values might represent a crude halo around the copper-rich area. If this relationship were more clearly pronounced, the distribution of anomalously low soil-pH values might be useful in identifying target areas that are favorable for copper exploration. Sampling on a more regional basis would be necessary to prove or disprove the value of routine soil-pH analysis as an exploration tool in similar environments.

DISTRIBUTIONS OF SELECTED ELEMENTS

Copper. — Copper (table 1) shows the widest range of values of any of the elements studied. The background (median) value for copper in bedrock samples collected at Mineral Butte is much higher than the average value given by Turekian and Wedepohl (1961) for copper in low-calcium granites (table 1). The high background value determined for copper in this study reflects biased sampling, a fact already established because all samples were collected over or near a copper-rich area in which a high regional background for copper exists.

On the basis of background and threshold values, there is an enrichment of copper in the fine-soil (<0.063-mm) fraction relative to the coarse (1-2 mm) fraction and the bedrock samples (table 1). A comparison of the copper concentrations in the pairs of soil fractions from each site indicates that 98 percent of the pairs have a higher concentration of copper in the fine fraction; only 2 percent of the pairs have a higher copper concentration in the coarse fraction. This enrichment of copper in the silt-clay soil fraction suggests that much of the copper is in a finely disseminated form, perhaps in clay minerals.

The anomaly contrast values for copper (in this report the ratio of threshold value to background value) are highest for the rock samples and lowest for samples of the fine-soil fraction (table 1). Normally, the sample medium with the highest contrast would be expected to most clearly identify the anomalies present; however, in this case the differences in areal extent of the anomalies produced by samples of the two soil fractions and of bedrock are slight (figs. 4*A*, 4*B*).

The copper deposit as defined by subsurface drilling is essentially contained within the anomalies of the three sample types (figs. 4*A*, 4*B*). The distribution of fine-soil anomalies is slightly larger than are those of the other soil fraction and the rock samples. The close coincidence of the distributions of copper anomalies in

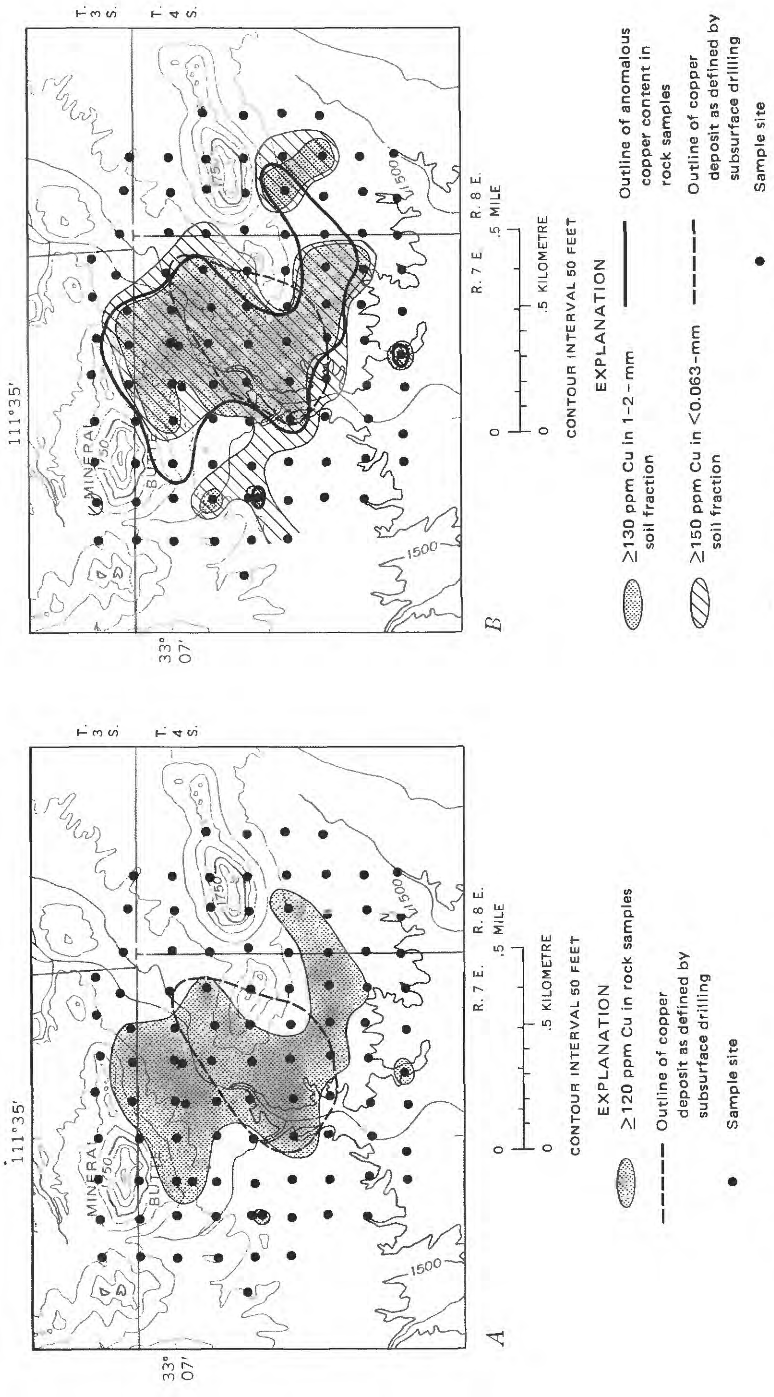

FIGURE 4. — Distributions of copper in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

bedrock (primary dispersion) and of copper anomalies in the soil fractions (secondary dispersion) would indicate, however, that the migration of copper during soil formulation was limited.

Cobalt. — The background (median) value for cobalt in the Mineral Butte rocks is close to the value given by Turekian and Wedepohl (1961) for cobalt in low-calcium granites (table 1). On the basis of background and threshold values, the progressive enrichment of cobalt with decrease in size of sample material from rock to fine soil is similar to the pattern shown by copper. Comparison of cobalt concentrations in pairs of coarse- and fine-soil fractions from each sample site shows that 88 percent of the pairs have a higher concentration of cobalt in the fine fraction. Nine percent of the pairs have equal concentrations for both fractions; only 3 percent of the pairs have a higher concentration in the coarse fraction. The lack of significant differences between the background and threshold values for cobalt in the three sample types (table 1) makes comparisons of the anomaly contrasts among the three sample types difficult; however, the anomaly contrast value for the bedrock samples is evidently slightly higher than that of either of the soil-sample fractions, suggesting that the analyses of bedrock samples should provide the most useful geochemical map.

Cobalt, and many of the other elements described in this study, may be more enriched in the fine-soil fraction because the primary mineral or minerals containing cobalt occur as extremely small particles that are released during soil formation. However, on the basis of the presence in outcrops of secondary rather than primary copper minerals, it seems probable that cobalt is present in the soil mostly in fine-grained secondary minerals.

The distributions of anomalous cobalt in bedrock and coarse soil samples (figs. 5*A*, 5*B*) are similar to the distribution of anomalous copper in bedrock samples. The anomalies of cobalt in fine soils (fig. 5*B*), however, are more widespread than are the anomalies of the other two sample types. In terms of identifying the target area, then, it appears that analyses of samples of the fine-soil fraction are superior to those of samples of the bedrock, notwithstanding the anomaly contrast values.

Fluorine. — The background (median) value for fluorine (fluoride ion) in Mineral Butte rocks is roughly half that given by Turekian and Wedepohl (1961) for fluorine in low-calcium granites (table 1). Comparison of fluorine concentrations in the pairs of coarse-soil and fine-soil fractions from each site shows that 79 percent of the pairs have a higher concentration of fluorine in the fine fraction. Twelve percent of the pairs have a higher concentration of fluorine

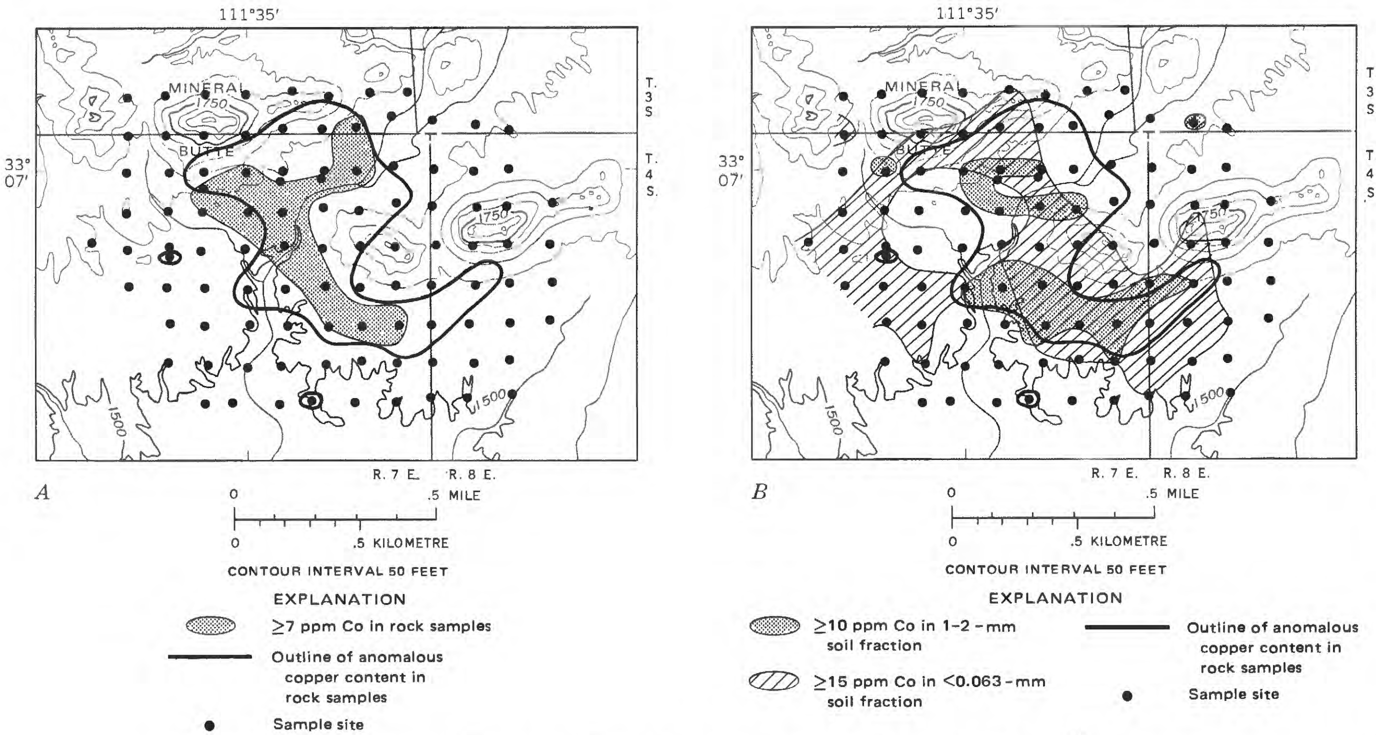

FIGURE 5. — Distributions of cobalt in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

in the coarse fraction, and 8 percent of the pairs have the same concentration of fluorine in both fractions.

In comparison to the copper and cobalt values, the highest anomaly contrast value for fluorine is for the samples from the fine-soil fraction, and the lowest contrast value is for the samples of bedrock (table 1). The map illustrating the distribution of fluorine anomalies in bedrock samples (fig. 6*A*) shows an apparent negative fluorine anomaly that covers much of the same area as the positive copper anomaly for bedrock samples. Both the direct reversal in the ranking of anomaly contrast values for fluorine and contrast values that are numerically less than one are the result of dealing with sample populations based on predominantly negative rather than positive anomalies. The lowest anomaly contrast value, then, should indicate the most useful sample type in cases where negative anomalies are present. Accordingly, the map showing fluorine anomalies in bedrock (fig. 6*A*) should be the most useful. Examination of the maps for the rock and soil samples (figs. 6*A*, 6*B*) seems to corroborate this conclusion for fluorine.

This apparent negative fluorine anomaly can be interpreted in two different ways. First, there may truly be a negative anomaly, as shown best in the map for fluorine anomalies in rock samples (fig. 6*A*). Second, there may actually be a positive fluorine anomaly in an aureole around the positive copper anomaly. In this case the apparent negative fluorine anomaly may only represent an area of background fluorine concentrations. The map illustrating fluorine anomalies in the two soil fractions (fig. 6*B*) suggests this concept best. Further sampling of the Precambrian granite on a regional basis would be necessary to interpret the observed fluorine anomalies unequivocally.

On the basis of figures 6*A* and 6*B* it can be stated, empirically at least, that there appears to be an area of relatively low fluorine concentrations directly over the copper anomaly surrounded by an area of relatively higher fluorine concentrations. This distribution of fluorine concentrations should in itself be a useful concept applicable in the search for new copper deposits in similar environments.

Gold. — Gold is one of the three selected elements for which the lower detection limit for the method of analysis used (0.02 ppm) is higher than the expected background value. Because this value is probably somewhere near that of 0.004 ppm given by Turekian and Wedepohl (1961) for gold in low-calcium granite (table 1), any amount of gold detected at or above the 0.02 ppm analytical lower limit is here considered to be anomalous. Because of analytical

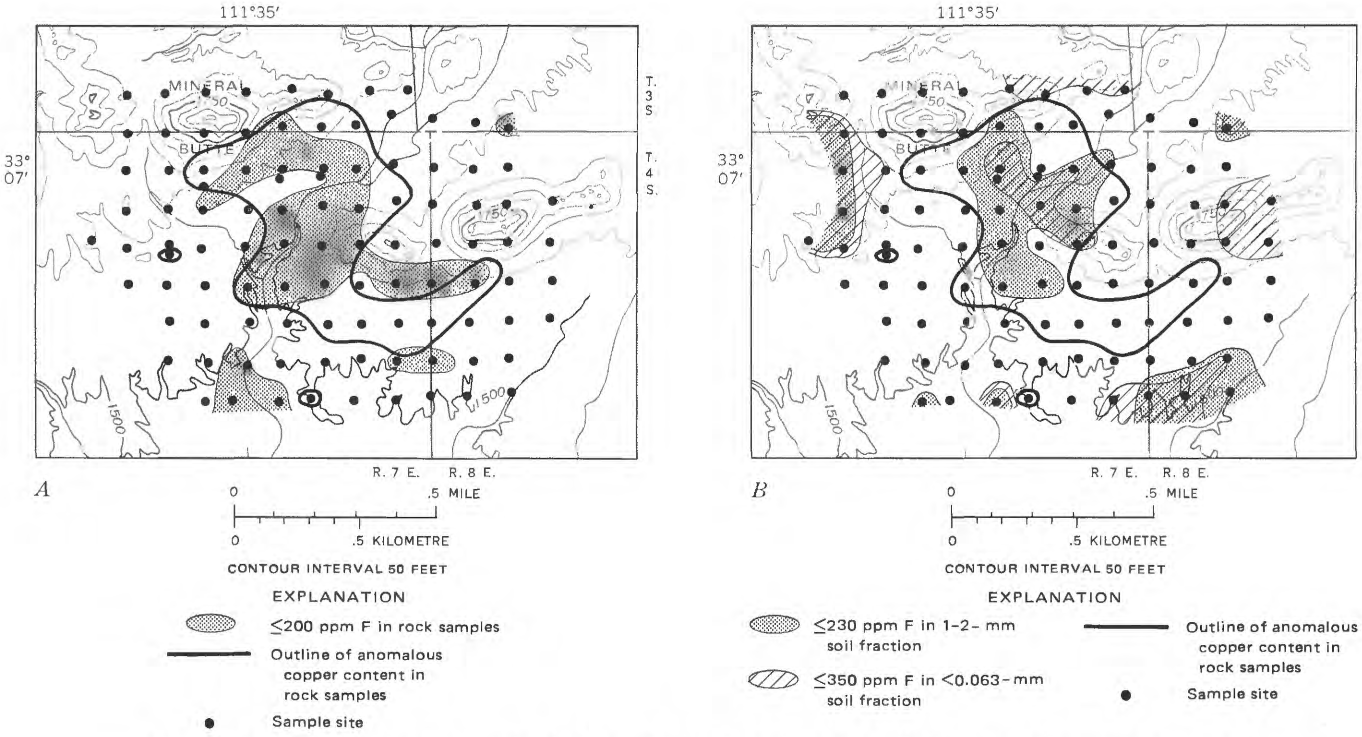

FIGURE 6. — Distributions of fluorine in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

variation to be expected in a semiquantitative method near the limit of sensitivity, the low levels of reported concentrations for gold introduce the possibility of analytical "noise" into the data.

The background and threshold values for gold are the same for all three sample types (table 1); therefore, no anomaly contrast values can be computed for gold and no conclusion can be drawn as to which type of sample should produce the most useful geochemical map for gold. The low levels of gold concentration relative to the lower detection limit for gold also make it impossible to establish trends of gold enrichment that can be related to the size of sample material; no trends for gold are evident in table 1. A study of the soil pairs for each site indicates that 19 percent of the pairs have a higher concentration of gold in the fine fraction; only 8 percent have a higher gold concentration in the coarse fraction. Seventy-three percent of the pairs had no differences in gold content, mainly because neither sample of the pair had gold concentrations exceeding the 0.02 ppm lower detection limit. On the basis of the preceding information it seems that gold could be preferentially concentrated in finer material either because of weathering processes or because the primary gold was deposited predominantly as very fine grained material.

The map illustrating the distribution of anomalous gold in rock samples (fig. 7*A*) shows only a few areas of anomalous gold. The lower analytical detection limit for gold apparently is not low enough to reveal the real extent in bedrock samples of the gold anomalies thought to be associated with the copper anomaly. In contrast, the map illustrating the distributions of anomalous gold in soils (fig. 7*B*) shows a widespread gold anomaly for both soil fractions. The extent of the anomalies of the two soil fractions is almost identical; those of the fine fraction are just slightly larger.

The possibility that the progressive increase in anomaly size with the corresponding decrease in the size of sample material together with (1) the tendency of the fine fraction of the soil pairs to have the higher gold content and (2) the presence of oxidized copper suggests that, in the environment found at Mineral Butte, gold may have migrated and(or) have been concentrated by weathering processes.

Lead. — The background (median) concentration of lead in the Mineral Butte rocks is very close to that found by Turekian and Wedepohl (1961) for lead in low-calcium granites (table 1). The background and threshold values in this table indicate that lead is progressively enriched in finer material. This latter conclusion is confirmed by the distribution of lead in the soil pairs. Sixty-three percent of the pairs have a higher concentration of lead in the fine

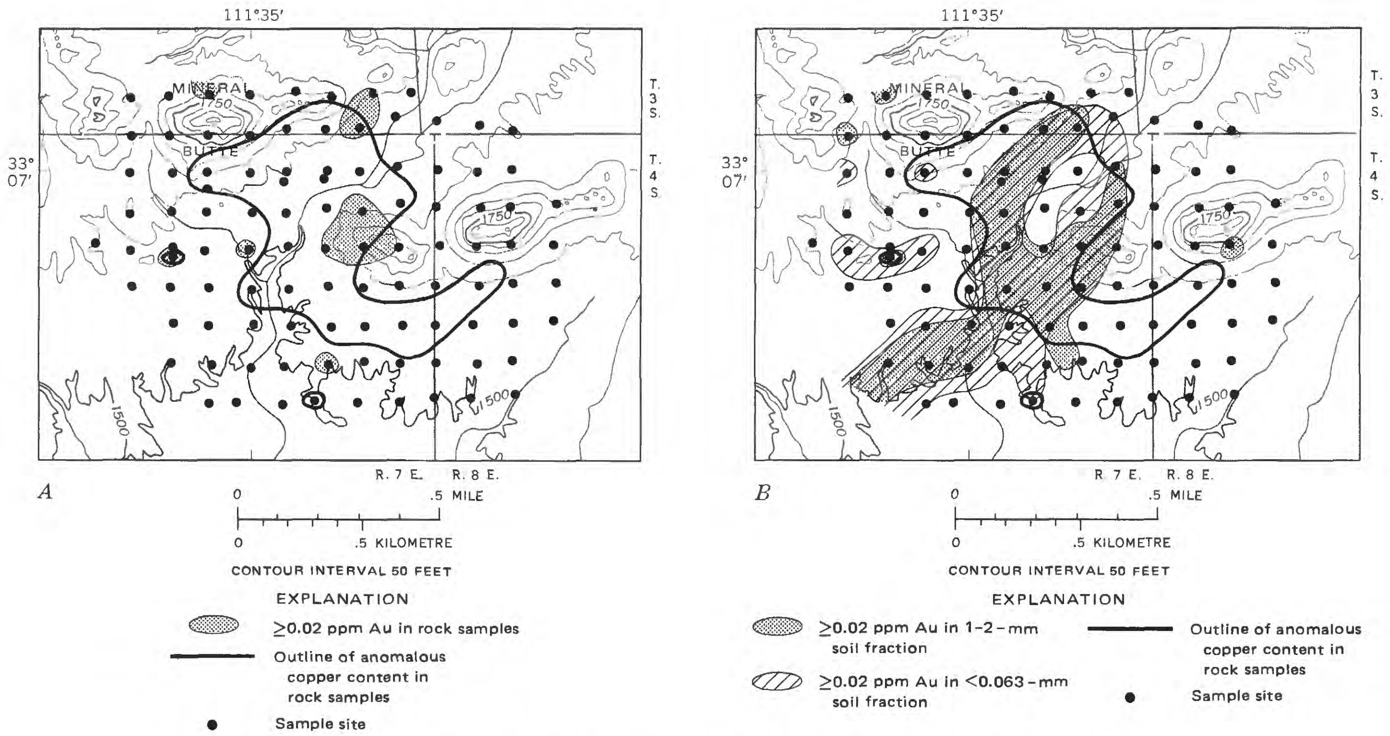

FIGURE 7. — Distributions of gold in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

fraction; only 12 percent have a higher concentration in the coarse fraction. The lead concentration is the same in 25 percent of the pairs.

The map showing the distribution of lead anomalies in rock samples (fig. 8*A*) reveals a negative lead anomaly that is similar to the apparent negative anomaly for fluorine in rock samples (fig. 6*A*). This lead anomaly also covers much of the same area as the positive copper anomaly based on analyses of rock samples. As was the case for the anomaly contrast values for fluorine, the reversal in ranking of these values for lead (table 1) and their values of less than unity are the result of dealing with sample populations based on predominantly negative rather than predominantly positive anomalies. By analogy with the fluorine example, then, the map showing anomalous lead in rock samples should provide the best information. Examination of figures 8*A* and 8*B* suggest that this conclusion is correct.

The lead anomalies can be interpreted as were those of fluorine. Specifically, either there is truly a negative lead anomaly associated with the positive copper anomaly (best illustrated by the bedrock map, fig. 8*A*), or there is a positive lead aureole around the copper anomaly (best illustrated by the soil-fraction map, fig. 8*B*). Again, regional sampling of the Precambrian granite would be necessary to interpret the lead anomalies unequivocally. There seems to be, empirically at least, an area of relatively low lead concentrations directly over the copper anomaly surrounded by an area of relatively higher lead concentrations. This distribution of lead may be a useful relationship applicable in the search for copper deposits in similar environments.

Molybdenum. — Molybdenum is another of the three elements for which the lower detection limit for the method of analysis used (5 ppm) is higher than the expected background value, which is probably somewhere near the value of 1.3 ppm given by Turekian and Wedepohl (1961) for molybdenum in low-calcium granite (table 1). As was the case for gold, any amount of molybdenum detected at or above the 5 ppm lower limit is here considered to be anomalous. The low levels of reported concentrations for molybdenum again introduce the possibility of analytical "noise" into the data. Interpretations of molybdenum distributions were made with this possibility in mind.

The background and threshold values for molybdenum are the same for all three sample types (table 1); thus, no anomaly contrast values can be computed for molybdenum. Therefore, anomaly contrast values cannot be used to select the sample type that should provide the most useful geochemical map for molybdenum.

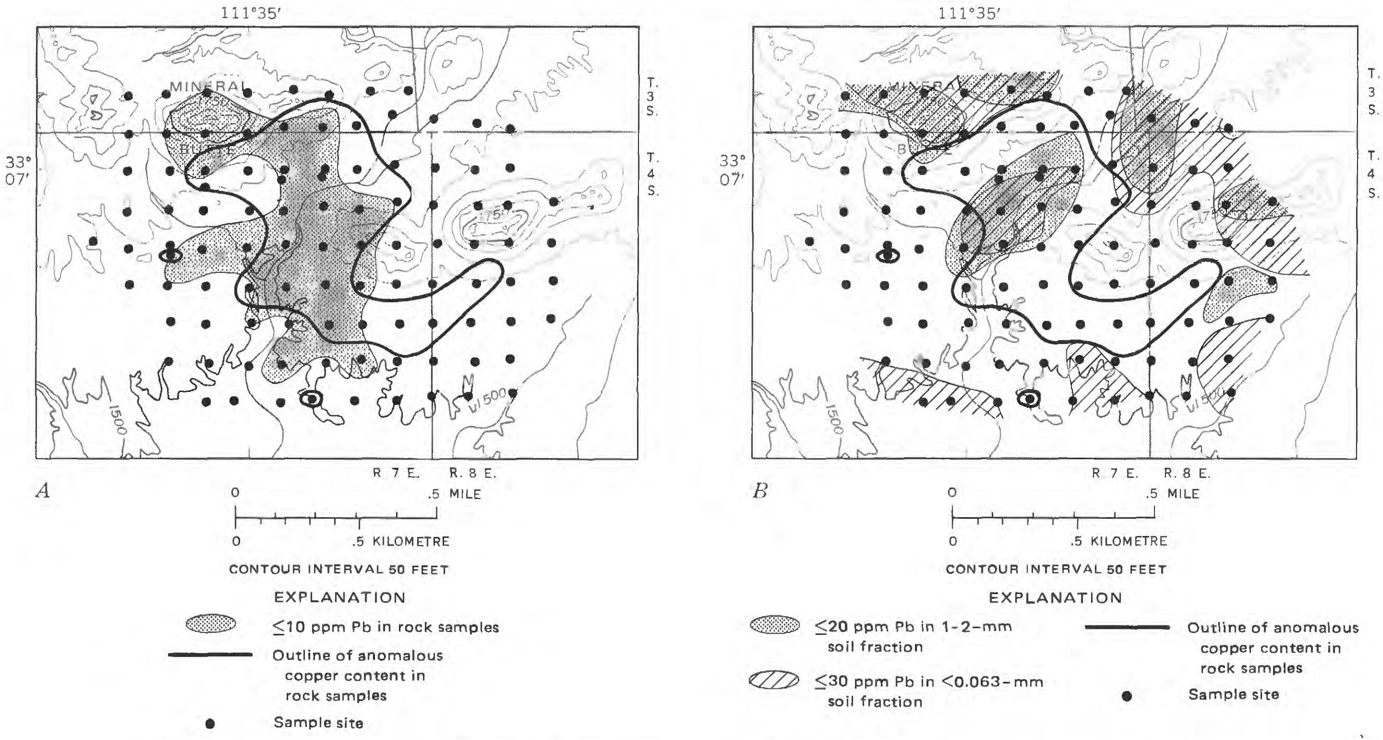

FIGURE 8. — Distributions of lead in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

Because of the low levels of molybdenum concentrations relative to the lower detection limit (table 1), there is no way to establish a trend of molybdenum enrichment in relation to sample particle size. Only 15 percent of the soil pairs show a higher concentration of molybdenum in the fine fraction. On the other hand, 33 percent of the pairs show higher molybdenum concentrations in the coarse fraction. A majority (52 percent) of the pairs have the same molybdenum concentration for each size fraction. In most of these pairs molybdenum was not detected in either fraction.

In contrast to the distributions of anomalies of the other selected elements, the anomalies of molybdenum for all three types of samples seem to be offset to the northeast of the area in which rock samples contain anomalous copper (figs. 9*A*, 9*B*). The reason for this offset is not known. Possibly, the areas enriched in molybdenum might be part of some sort of crude zoning of elements around the copper-enriched area. Balla (1972) has described a regional contact between the Precambrian granite and the Pinal Schist in the vicinity of the Mineral Butte deposit. The molybdenum anomalies might also be related to this contact. In summary, sampling on a more regional basis is needed to understand better the spatial relation of molybdenum to copper.

The distributions of anomalous molybdenum in both soil fractions are more widespread than is the distribution of anomalous molybdenum in bedrock samples; however, because the spatial relationship of molybdenum anomalies to those of copper at Mineral Butte is not obvious, the advantage of using either of the soil geochemical maps for molybdenum rather than the bedrock geochemical map is not clear.

Silver. — Silver is the third of the three elements described in this report for which the lower detection limit for the method of analysis used (0.5 ppm) is higher than the expected background value, which is probably somewhere near the value of 0.037 ppm given by Turekian and Wedepohl (1961) for silver in low-calcium granite (table 1). Again, any silver detected is anomalous. Analytical "noise" was once more considered in interpreting the silver analyses.

As was the case for gold and molybdenum, the background and threshold values for silver are the same for all three sample types (table 1). Thus, because no anomaly contrast values can be computed for silver, such values cannot be used to select the sample type that should provide the most useful geochemical map for silver.

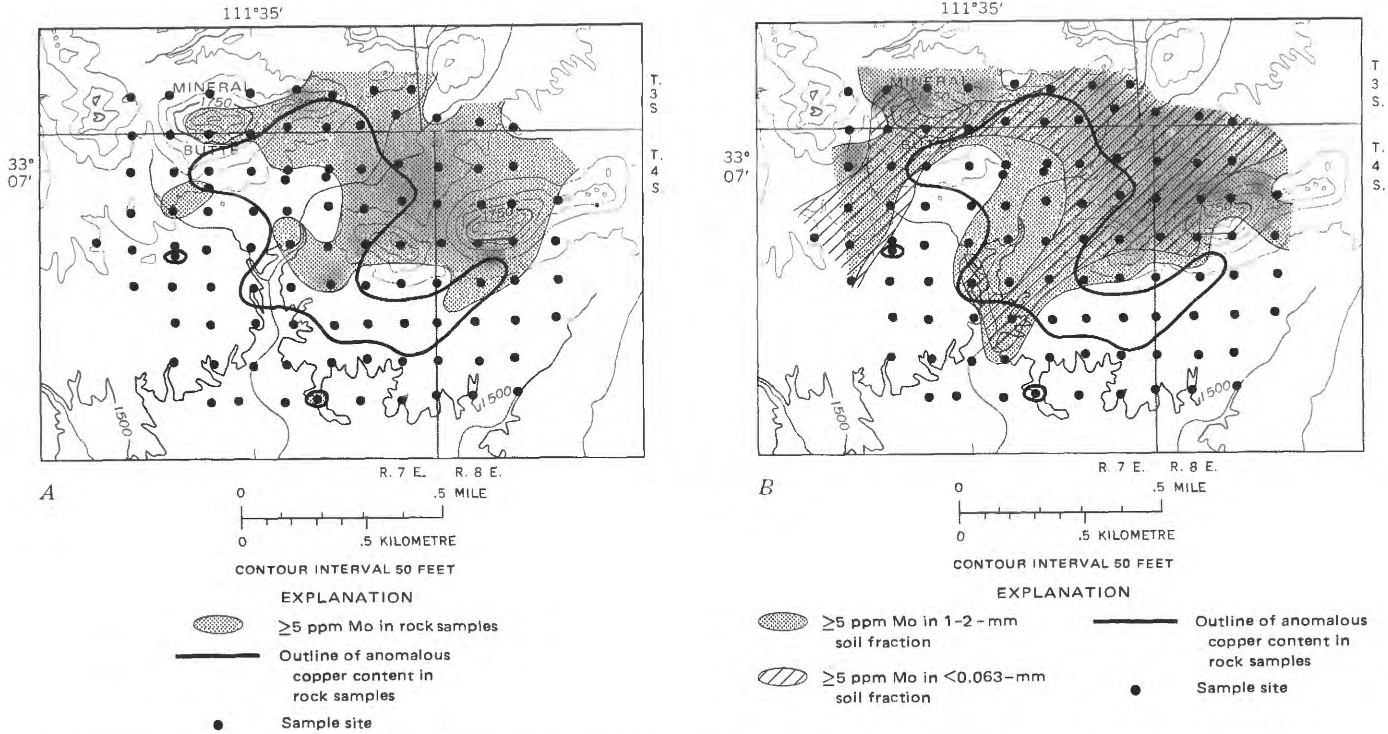

FIGURE 9. — Distributions of molybdenum in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

Table 1 provides no insight as to where silver may be preferentially concentrated among the three sample types. Unfortunately, the study of soil pairs provides no clear-cut evidence either, mainly because of the high number of pairs with equal values. In 14 percent of the soil pairs the silver concentration is higher in the fine fraction. In 19 percent of the pairs it is higher in the coarse fraction. Sixty-seven percent of the pairs have the same silver value reported for each fraction. In most of these pairs, silver was not detected in either fraction.

The map illustrating the distribution of anomalous silver in bedrock samples (fig. 10*A*) shows a fairly close coincidence of the silver and copper anomalies, although the silver anomaly is locally more widespread. The map showing the distributions of silver anomalies in the two soil fractions (fig. 10*B*) does not indicate a very close spatial relationship between these silver anomalies and the anomaly for copper in rock samples. The silver anomalies could, therefore, be interpreted as being mostly analytical "noise." A more sensitive analytical method might provide more conclusive geochemical information for silver in soil samples.

Zinc. — Zinc, like copper, shows a very wide range of values for all three sample types. The background (median) value of zinc in Mineral Butte rocks is below the value given by Turekian and Wedepohl (1961) for zinc in low-calcium granites (table 1). The low background concentration for zinc at Mineral Butte might result from the Precambrian granite being deficient in primary zinc within the area studied or might result from the granite being leached. The anomaly contrast values for zinc for the three sample types (table 1) show the same value for the samples of rock and coarse soil but show a lower value for the samples of fine soil as compared to the other two sample types. These values suggest that coarser material, probably rock samples, should provide the best geochemical map for zinc.

The background and threshold values for zinc (table 1) indicate a progressive concentration of zinc in finer material. This concentration change is clearly reflected in the progressive changes in background and threshold values for each sample type.

Comparison of zinc concentrations in pairs of coarse-soil and fine-soil fractions from each site shows that 98 percent of the pairs have a higher concentration of zinc in the fine fraction. Only 2 percent of the pairs have a higher concentration in the coarse fraction. Of the selected elements, only copper shows this same strong tendency for enrichment in the finer fraction.

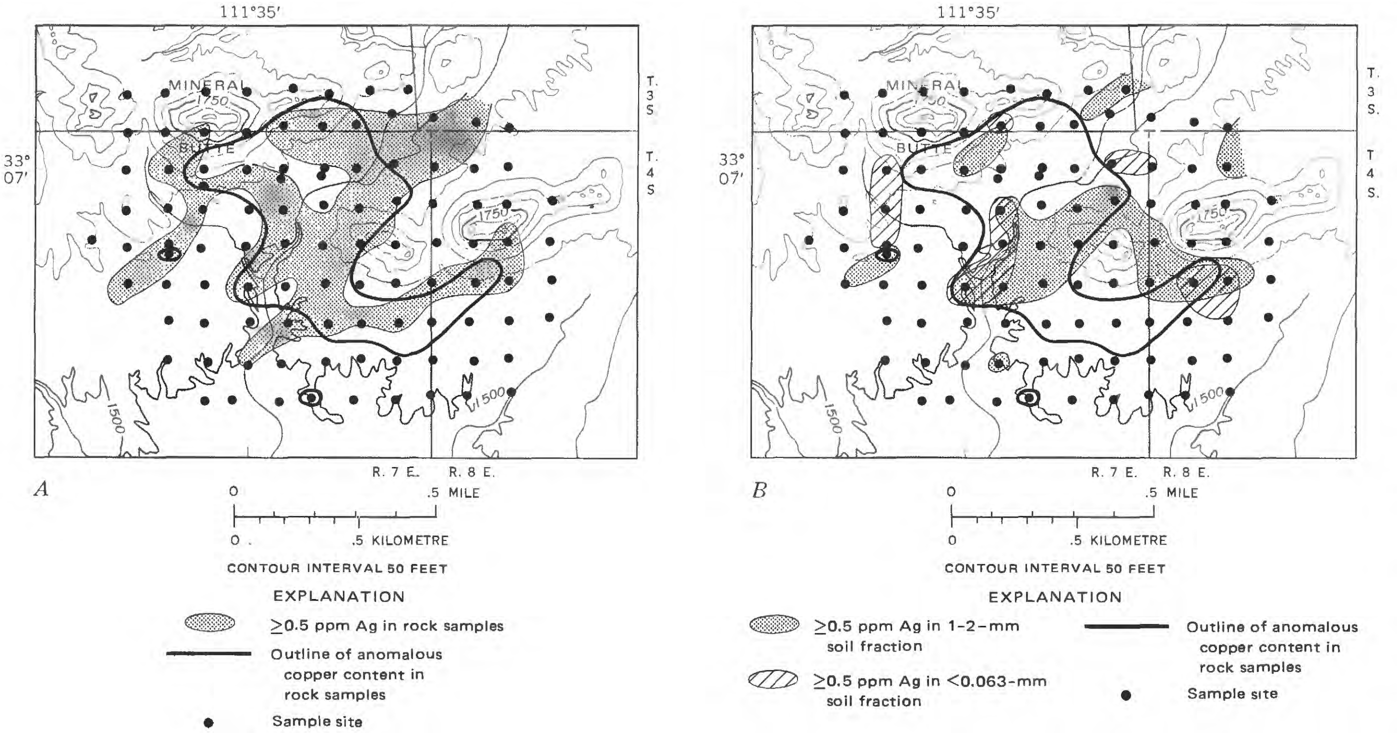

FIGURE 10. — Distributions of silver in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

The distribution of anomalous concentrations of zinc in rock samples (fig. 11*A*) shows an anomaly that not only includes much of the copper anomaly based on analyses of bedrock samples but also extends generally south and east from the copper anomaly. The highest zinc concentrations fall within the copper anomaly. The distributions of zinc anomalies in the two soil fractions (fig. 11*B*) are more restricted than is the main bedrock anomaly and do not coincide very well with the copper anomaly based on analyses of bedrock samples.

There seems to be a close correlation between the areas containing anomalous zinc in all three sample types (figs. 11*A*, 11*B*) and the area of high soil-pH values (fig. 3). This correlation suggests the possibility that zinc has been leached from areas of low soil-pH values and has migrated to, and precipitated in, the areas of high soil-pH values. It should be emphasized that the anomalies of zinc in rock samples also reflect this correlation with soil-pH values; consequently, if the zinc has indeed been leached and has migrated, then the rock material that was sampled has also been affected.

Zinc- and copper-enriched zones do not normally coincide at most Arizona copper deposits; consequently, the zinc geochemical patterns at Mineral Butte might be the result of zinc variations originally present in the granite host rock, or the patterns might represent the addition of hydrothermal zinc, or perhaps mobilized secondary zinc, to zinc originally present in the granite host rock.

ANALYTICAL RESULTS OF VEGETATION SAMPLES

This section describes the distributions of copper, zinc, and molybdenum in the ash of leaves and stems of four different plant species that commonly grow along stream channels. These species, with the number of samples collected for each species shown in parentheses, are mesquite (41), catclaw acacia (45), blue paloverde (27), and ironwood (36). A summary of information concerning the analyses used in preparing the biogeochemical maps is given in table 2.

MESQUITE

Figures 12–14 show the distributions of copper, zinc, and molybdenum anomalies, respectively, in the ash of mesquite leaves and stems.

Copper. — A comparison of the concentration of copper in the ash of mesquite leaves to that in mesquite stems for the pair of samples from each of the 41 sample sites shows that the copper

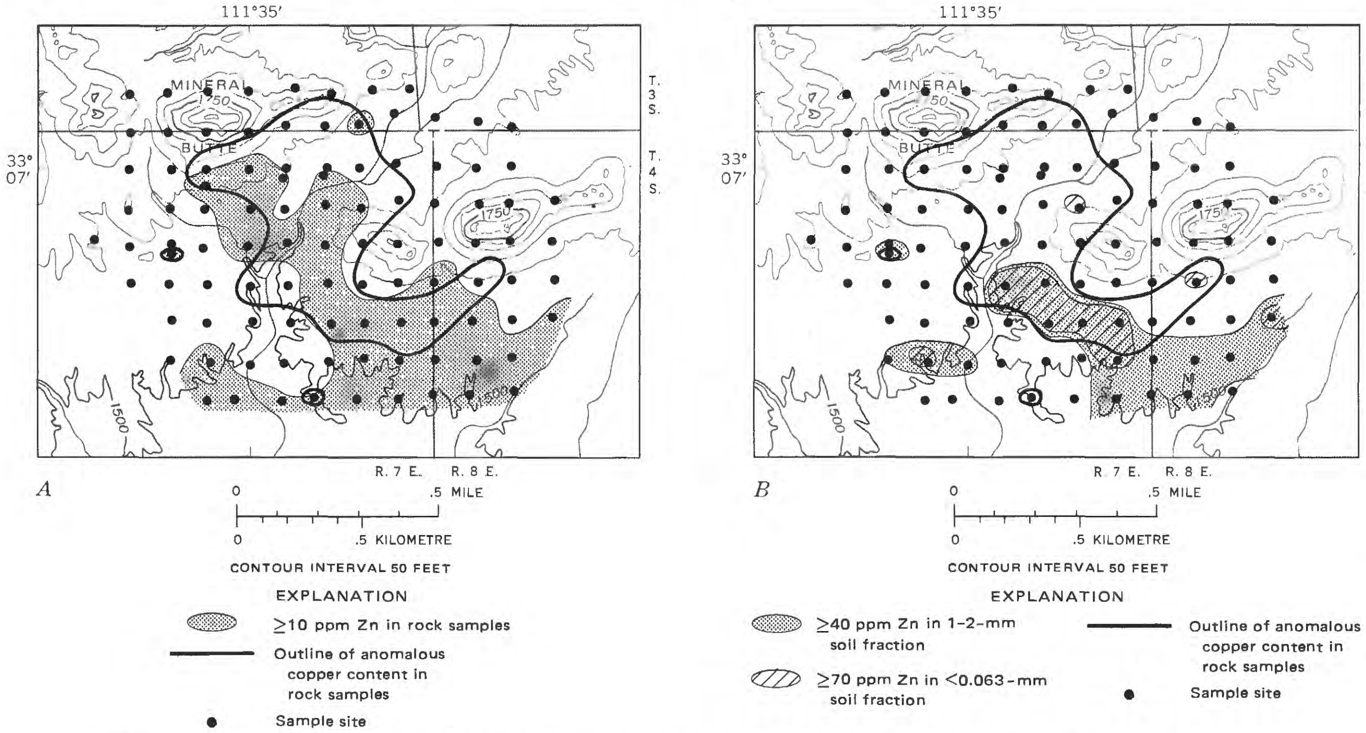

FIGURE 11. — Distributions of zinc in (*A*) rock samples and in (*B*) soil fractions, Mineral Butte area.

TABLE 2.—*Statistical data for copper, zinc, and molybdenum in plant ash, Mineral Butte copper deposit, Pinal County, Ariz.*

[All values in parts per million]

Sample description	Range of values			Background (median) value			Threshold value		
	Cu	Zn	Mo	Cu	Zn	Mo	Cu	Zn	Mo
Mesquite leaves	90-735	190-670	3-44	220	375	15	250	450	22
Mesquite stems	70-280	200-770	5-42	170	400	12	200	500	20
Catclaw acacia leaves	60-700	90-700	5-21	150	250	10	180	350	14
Catclaw acacia stems	100-340	170-700	5-28	160	450	9	200	550	12
Blue paloverde leaves	70-260	210-940	.6-11.9	130	400	3.0	150	550	4.4
Blue paloverde stems	70-170	300-800	.8-7.8	110	450	2.4	130	600	3.0
Ironwood leaves	45-190	170-650	3-24	80	250	8	90	350	12
Ironwood stems	50-200	260-1,900	2-49	90	400	13	100	550	16

content is higher in the leaf ash in 85 percent of the pairs. The concentration of copper in the stem ash is higher in 13 percent of the pairs, and 2 percent of the pairs have the same concentration of copper in the ash of both parts. The background and threshold values for copper in mesquite ash (table 2) also indicate that copper is more concentrated in the leaf ash than in the stem ash.

Relative to the known copper deposit, the distribution of anomalous copper in the ash of both leaves and stems of mesquite is impressive (fig. 12). The samples containing anomalous copper are mostly from sites clustered along the main stream channel that crosses the copper deposit. Anomalous copper in both leaves and stems was detected in samples collected at least 0.8 km (0.5 mi) downstream from the deposit. Two other samples of mesquite leaves (but not stems) collected farther down this same channel also contain anomalous concentrations of copper.

Mesquite samples collected upstream from the copper deposit also contain anomalous concentrations of copper. The reason for these samples being anomalous is not clearly understood. A group of soil samples collected near the stream channels in this area showed only background copper concentrations. No obvious copper staining is present in outcrops in this area; however, rocks of this area are extensively iron stained, similar to those around the known copper deposit, suggesting that copper could be present at depth.

The generally close areal relationship of anomalous concentrations of copper in mesquite ash to the copper anomalies seen in the bedrock and soil-sample maps indicates that sampling for copper in mesquite ash should readily detect copper-rich areas if the sample site is no more than about 0.8 km (0.5 mi) downstream from copper-rich outcrops.

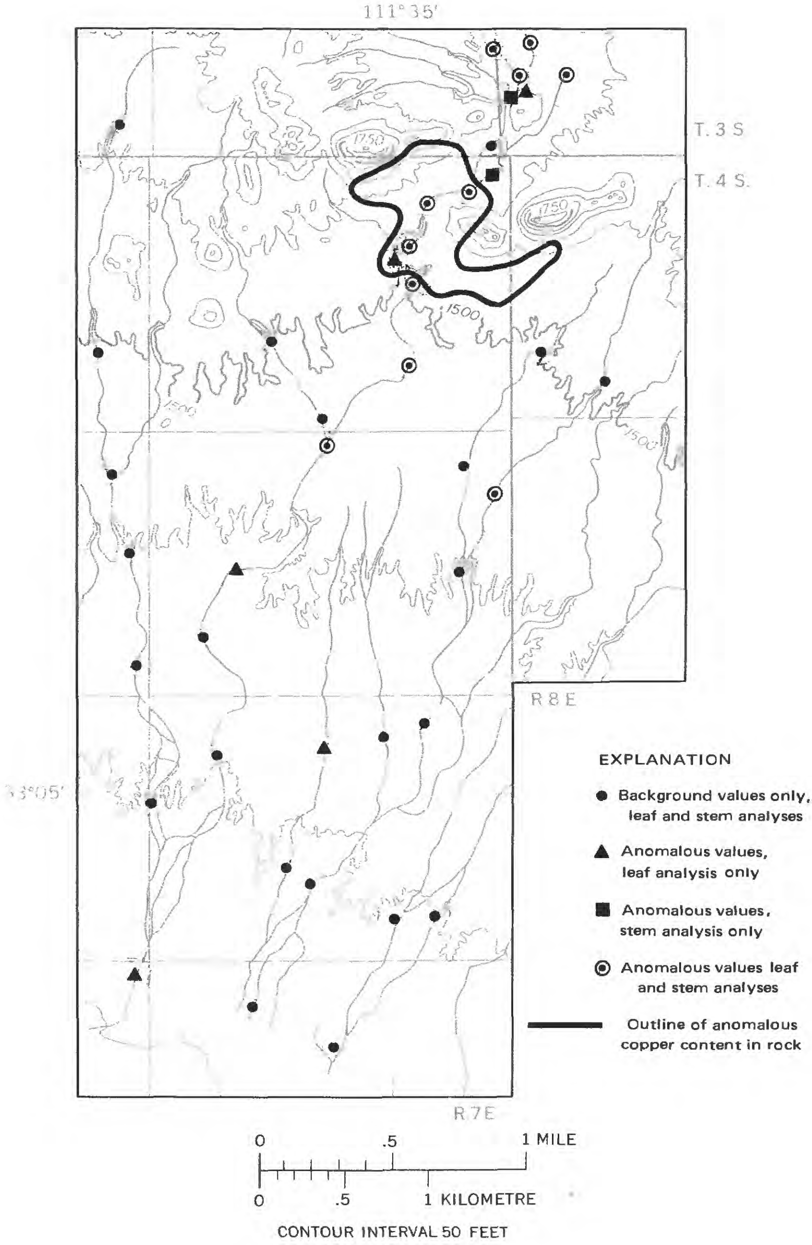

FIGURE 12. — Distribution of copper in mesquite leaf and stem ash, Mineral Butte area.

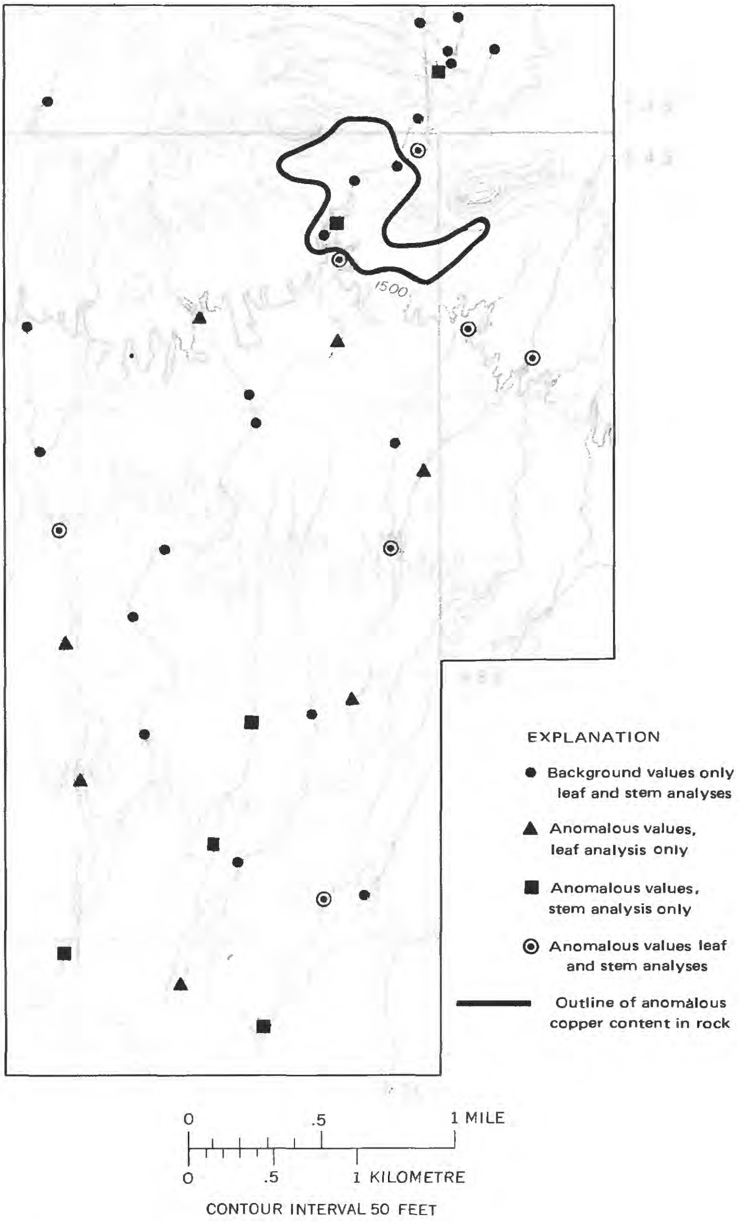

FIGURE 13. — Distribution of zinc in mesquite leaf and stem ash, Mineral Butte area.

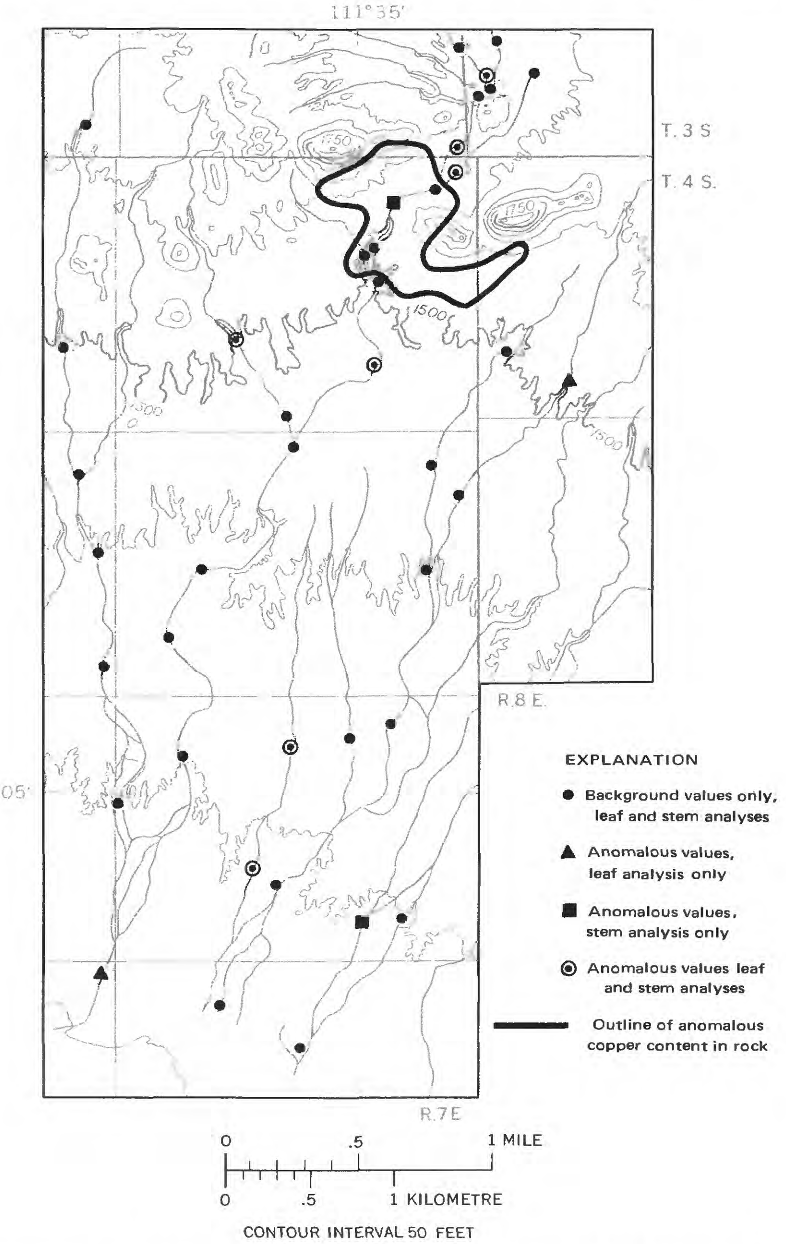

FIGURE 14. — Distribution of molybdenum in mesquite leaf and stem ash, Mineral Butte area.

Zinc. — Zinc does not seem to be preferentially enriched in the ash of either plant part relative to the other. Forty-eight percent of the leaf-stem pairs have a higher concentration of zinc in the stem ash, 42 percent of the pairs have a higher concentration of zinc in the leaf ash, and 10 percent of the pairs contain equal concentrations of zinc in both parts. Background and threshold values for zinc (table 2) indicate that zinc is slightly more abundant in the ash of mesquite stems. Because of normally expected analytical variation, however, this difference may not be statistically significant.

Concentrations of zinc in both leaf and stem ash are considerably higher than those of copper (table 2), as is normally the case for most plant species, in spite of the fact that the rocks and soils at Mineral Butte have higher concentrations of copper than they have of zinc.

The map illustrating the distribution of zinc anomalies in the ash of mesquite leaves and stems (fig. 13) is disappointing from an exploration standpoint because it does not show any pattern that can be clearly related to the Mineral Butte copper deposit. Analyses of ashed samples of leaves and stems of mesquite and of the other three species discussed in this report collected in a zinc-rich area show a good spatial correlation of zinc anomalies in rocks and soils and of zinc anomalies in the ash of the plants. This correlation indicates that mesquite and the other species can be used to locate areas that are enriched in zinc. It seems, therefore, that in the Mineral Butte area the concentration levels of zinc available to the mesquite are simply not high enough to create anomalous zinc concentrations in the plant ash and thereby do not reflect any anomalous zinc concentrations in the soil or rock close to the plant. The zinc anomalies in mesquite ash seem to occur at random, suggesting that none of them is a significant anomaly related to the known copper deposit. Probably the variations in zinc concentrations in the ash of mesquite samples simply represent normal natural variations of zinc in the plant parts. The absence of high zinc concentrations in the ash of samples from plants growing near the areas containing anomalous concentrations of zinc in bedrock and soil samples indicates that for the Mineral Butte area the zinc content in mesquite ash is independent of the zinc content of the material in which the plant is rooted.

Most of the zinc anomalies in mesquite ash (fig. 13) are in samples of either leaves or stems, but not in both parts. The lack of corroboration of anomalies for both plant parts at a given site and the random locations of the sites with zinc anomalies are considered to be unfavorable factors for using this plant-element combination in geochemical exploration for copper deposits occurring in geochemical environments similar to the one at Mineral Butte.

Molybdenum. — Molybdenum is clearly more concentrated in the ash of mesquite leaves than in the corresponding stem ash; fully 68 percent of the sample pairs contain more molybdenum in the leaf ash. Only 22 percent of the pairs have higher molybdenum concentrations in the stems; 10 percent have the same concentrations in both plant parts. Background and threshold values (table 2) also indicate that, for mesquite, molybdenum is more abundant in the leaf ash than in the stem ash. Concentrations of molybdenum in the leaf and stem ash of mesquite are one to two magnitudes less than the concentrations of copper and zinc in the same samples (table 2). These concentration differences, which are also present for the other three species studied, are normally observed in most plant species.

Figure 14 illustrates the distribution of molybdenum anomalies in the ash of mesquite leaves and stems. Molybdenum anomalies are clustered along the major stream channel crossing the deposit but in a less consistent pattern than is seen for copper (fig. 12). The clustering suggests a general concentration of molybdenum upstream from the Mineral Butte deposit, as well as over the deposit, and as much as 0.4 km (0.25 mi) downstream from the deposit. The two anomalous samples from adjacent sites near the bottom of the area of figure 14 are more than 1.6 km (1 mi) downstream from any outcrops. The meaning, if any, of this second cluster is not known.

As is the case for copper in mesquite ash, the Mineral Butte deposit could probably be best identified using only those sites that are anomalous for molybdenum in both plant parts rather than those anomalous for either part alone.

In terms of exploration potential in areas similar to Mineral Butte, molybdenum in mesquite ash is better than zinc, but neither element is as discriminating as copper. In a study of the distribution of molybdenum in mesquite ash in the Pima mining district, Pima County, Ariz., Huff (1970) reported a widespread area of anomalous molybdenum around and downstream from the large copper-molybdenum deposits of that district. He did not report copper or zinc analyses for his samples. The molybdenum concentrations shown in his figure 5 (Huff, 1970) are considerably higher overall than the concentrations obtained in the present study. Mineral deposits in the Pima district contain considerably greater concentrations of molybdenum than are found in the Mineral Butte area. As previously noted for zinc, the differences in molybdenum concentrations in the two districts suggest that there may be some minimum concentration of molybdenum below which biogeochemical sampling for the element will not be effective.

CATCLAW ACACIA

Figures 15-17 show the distributions of copper, zinc, and molybdenum anomalies, respectively, in the ash of catclaw acacia leaves and stems.

Copper. — The analyses of leaf-stem pairs for copper in the ashed samples of catclaw acacia indicate that slightly greater concentrations of copper are present in the stem ash. Fifty-three percent of the pairs have a higher copper concentration in the stem ash. Forty percent of the pairs have a higher concentration in the leaf ash, 7 percent of the pairs have the same content of copper in both parts. Background and threshold copper values (table 2) also indicate a slightly higher concentration of copper in the stem ash; however, because of normally expected analytical variation, this difference may not be statistically significant. Copper anomalies in samples of both the leaf and stem ash of catclaw acacia (fig. 15) are confined to the main stream channel that crosses the Mineral Butte copper deposit. Samples of the plant from other channels are only anomalous for either leaves or stems, but not for both. As was the case for mesquite, copper anomalies in the ash of samples of catclaw acacia are present upstream from the known deposit.

The relatively limited range of values for copper in ashed samples of catclaw acacia stems (table 2) makes it difficult to differentiate between background and anomalous samples. This difficulty is reflected in the map illustrating the distribution of copper anomalies in the leaf and stem ash (fig. 15), where it is apparent that the sampling of only catclaw acacia leaves would have provided a somewhat more meaningful distribution of copper anomalies than would have the sampling of only stems. In spite of this problem, those sites where samples of both leaf and stem ash are anomalous locate the known copper deposit better than do those sites where only one plant part is anomalous. The distribution of copper in catclaw acacia ash should be nearly as useful as that of copper in mesquite ash in locating deposits similar to that at Mineral Butte.

Zinc. — The study of leaf-stem pairs indicates that zinc is clearly more concentrated in the ash of catclaw acacia stems than it is in the ash of the leaves. Fully 93 percent of the sample pairs have a higher content of zinc in the leaf ash. The background and

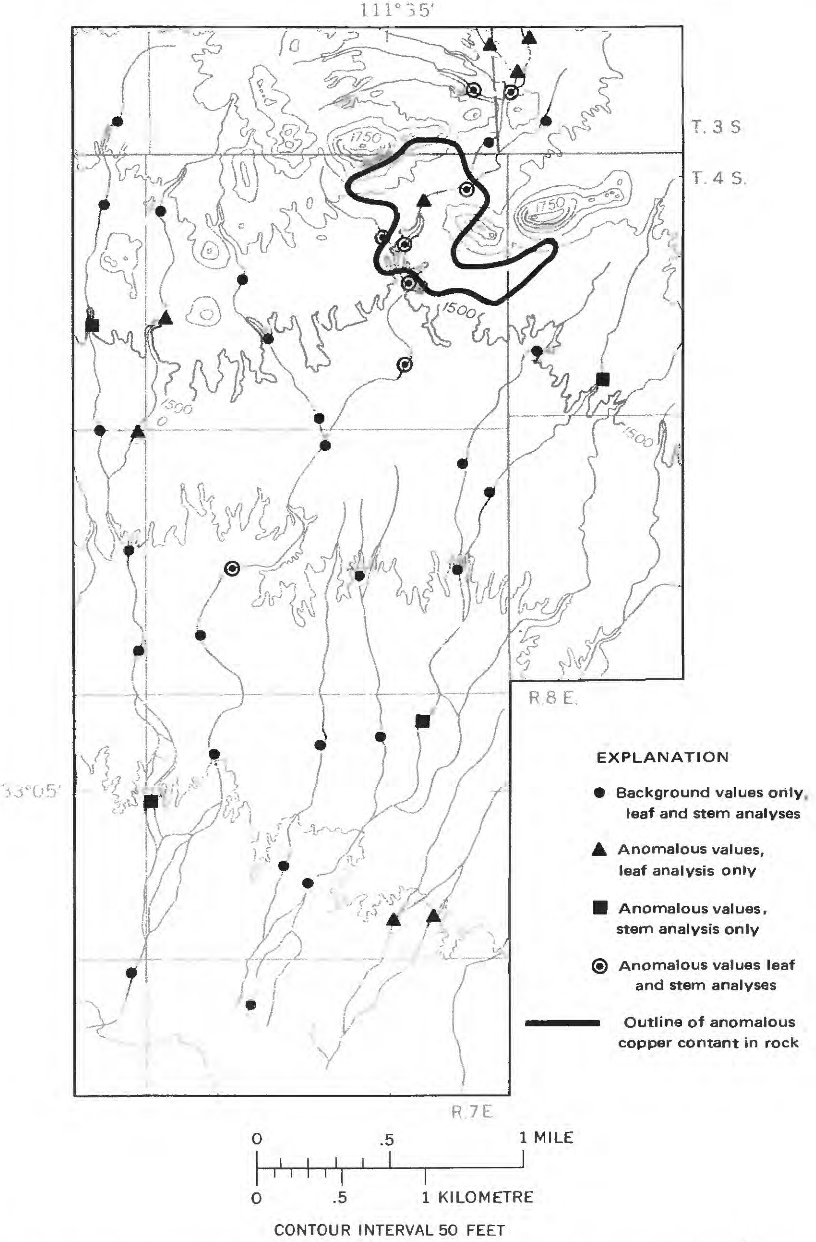

FIGURE 15. — Distribution of copper in catclaw acacia leaf and stem ash, Mineral Butte area.

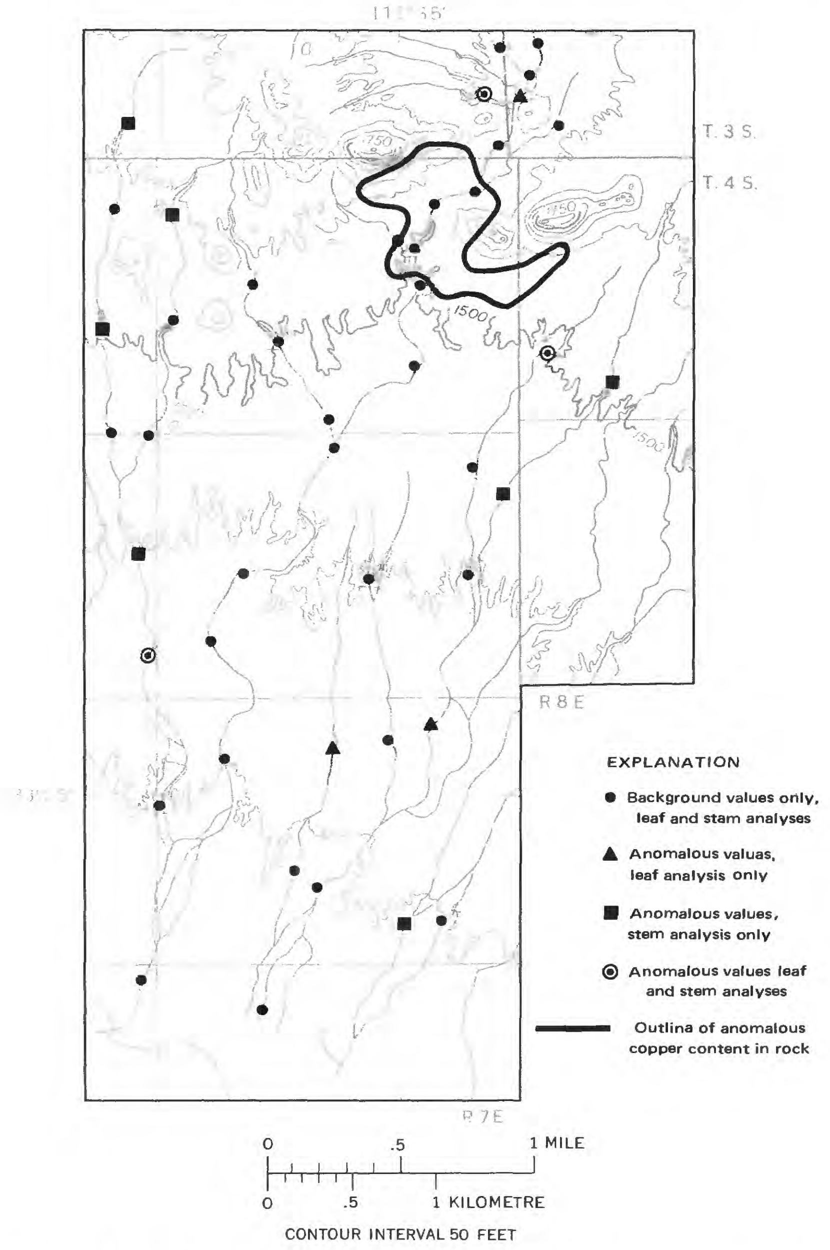

FIGURE 16. — Distribution of zinc in catclaw acacia leaf and stem ash, Mineral Butte area.

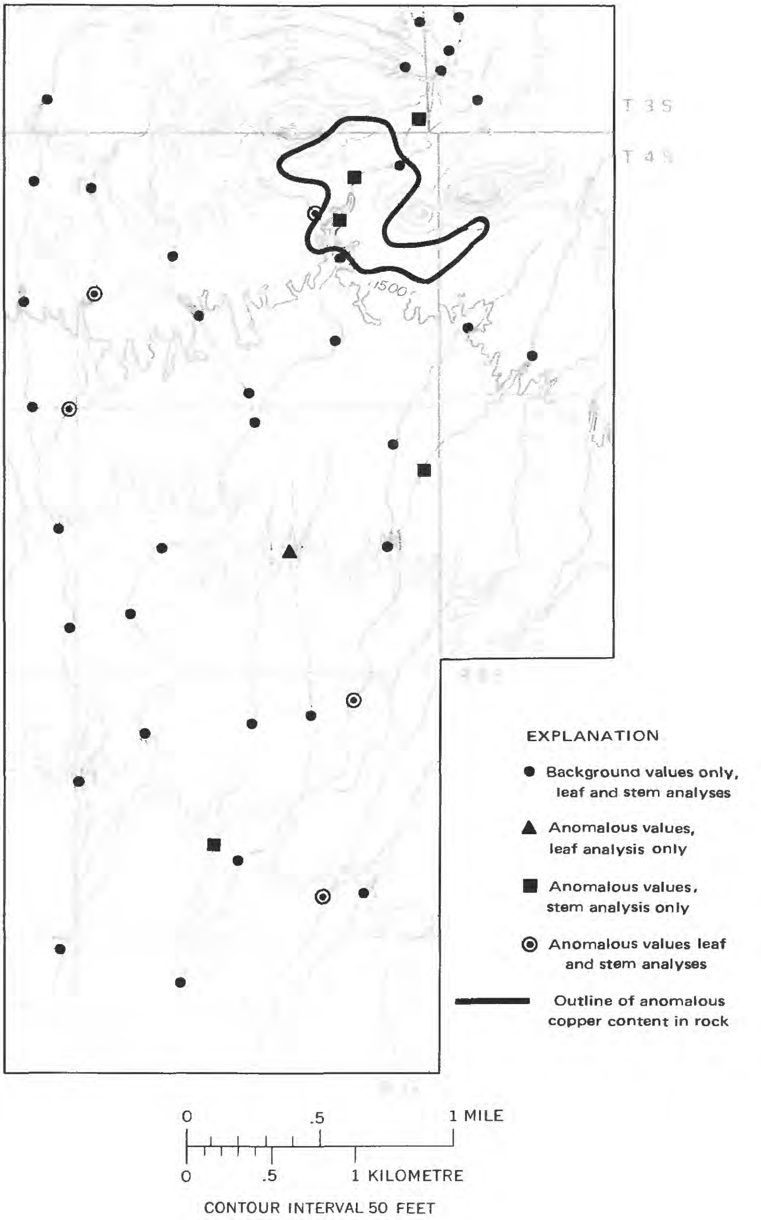

FIGURE 17. — Distribution of molybdenum in catclaw acacia leaf and stem ash, Mineral Butte area.

threshold values for zinc in catclaw acacia ash (table 2) also show much higher zinc concentrations in the stem ash.

The map illustrating the distribution of zinc anomalies in the ash of catclaw acacia leaves and stems (fig. 16) shows no pattern that would indicate the presence of the copper deposit or even the presence of the anomalous zinc concentrations in bedrock and soil samples. The poor response for zinc in catclaw acacia ash is probably the result of the generally low zinc concentrations in the rocks and soils of the area, as mentioned previously for zinc in mesquite ash.

The distribution of zinc anomalies in catclaw ash suggests a crude zinc halo around the copper deposit and around the main stream channel crossing the deposit; however, this distribution of anomalies is entirely fortuitous for at least two reasons. First, most of the anomalies are based on high concentrations of zinc in either leaves or stems but not in both parts. Second, none of the other three plant species examined in this study shows a similar pattern. As was the case for zinc in mesquite ash, the zinc-catclaw acacia combination seems to be of little value in biogeochemical prospecting for deposits similar in nature to the Mineral Butte deposit.

Molybdenum. — In contrast to the distributions of copper and zinc, the molybdenum concentrations in the ash of catclaw acacia leaf-stem pairs are slightly higher in the leaves than in the stems. Compilation of the analyses for leaf-stem pairs indicates that molybdenum is more concentrated in the leaf ash of 42 percent of the pairs. Thirty-one percent of the pairs have higher concentrations of molybdenum in the stem ash. Twenty-seven percent of the pairs have equal concentrations of molybdenum in both plant parts. The background and threshold values (table 2) also suggest that molybdenum is slightly more abundant in catclaw acacia leaf ash; however, the difference in values for the two parts may not be statistically significant.

The relatively restricted ranges of values for molybdenum in the ash of both catclaw acacia parts (table 2) make it difficult to pick a meaningful threshold value for either of these two parts. This difficulty is reflected in the map showing the distribution of molybdenum anomalies in catclaw acacia leaf and stem ash (fig. 17). On this map it can be seen that some of the samples from sites near the copper deposit are anomalous, especially if only the stem analyses are considered; however, some samples from sites near the deposit are not anomalous for either plant part. Samples that are anomalous for both plant parts seem to occur completely at random, producing several nonsignificant anomalies. The resulting overall picture is disappointing from an exploration standpoint because, objectively, one cannot discriminate the significant anomalies associated with known copper enrichment from the nonsignificant anomalies that exist for no known reason. Thus, this particular plant-element combination probably has little value for biogeochemical prospecting in areas that are geochemically comparable to the Mineral Butte area.

BLUE PALOVERDE

Figures 18-20 show the distributions of copper, zinc, and molybdenum anomalies, respectively, in the ash of blue paloverde leaves and stems.

Copper. — Analyses of copper in the ash of blue paloverde leaf-stem pairs indicate that copper is more abundant in the leaf ash in 69 percent of the pairs. Copper is more abundant in the stem ash in only 19 percent of the pairs, and 12 percent of the pairs have equal concentrations of copper in the ash of both plant parts. The background and threshold values (table 2) also suggest that copper is slightly more abundant in the leaf ash of blue paloverde samples; however, the differences in values for the two parts may not be statistically significant.

The ranges of values for copper in the ash of both blue paloverde plant parts (table 2) are not large and may only represent variations to be expected from any natural sample population of this species. Thus, this plant-element combination is another that is difficult to evaluate with respect to its ability to locate the known copper deposit.

Figure 18 shows the distribution of copper anomalies in the ash of blue paloverde leaves and stems. Most of these anomalies are confined to the major stream channel crossing the Mineral Butte deposit. However, both plant parts are anomalous at only four sample sites in this main channel. If the sample sites along the main channel that show either part to be anomalous were all considered to represent significant anomalies, then this plant-element combination should be useful in biogeochemical surveys. Given a choice, however, it seems that mesquite (or possibly catclaw acacia) is a better species to use than blue paloverde.

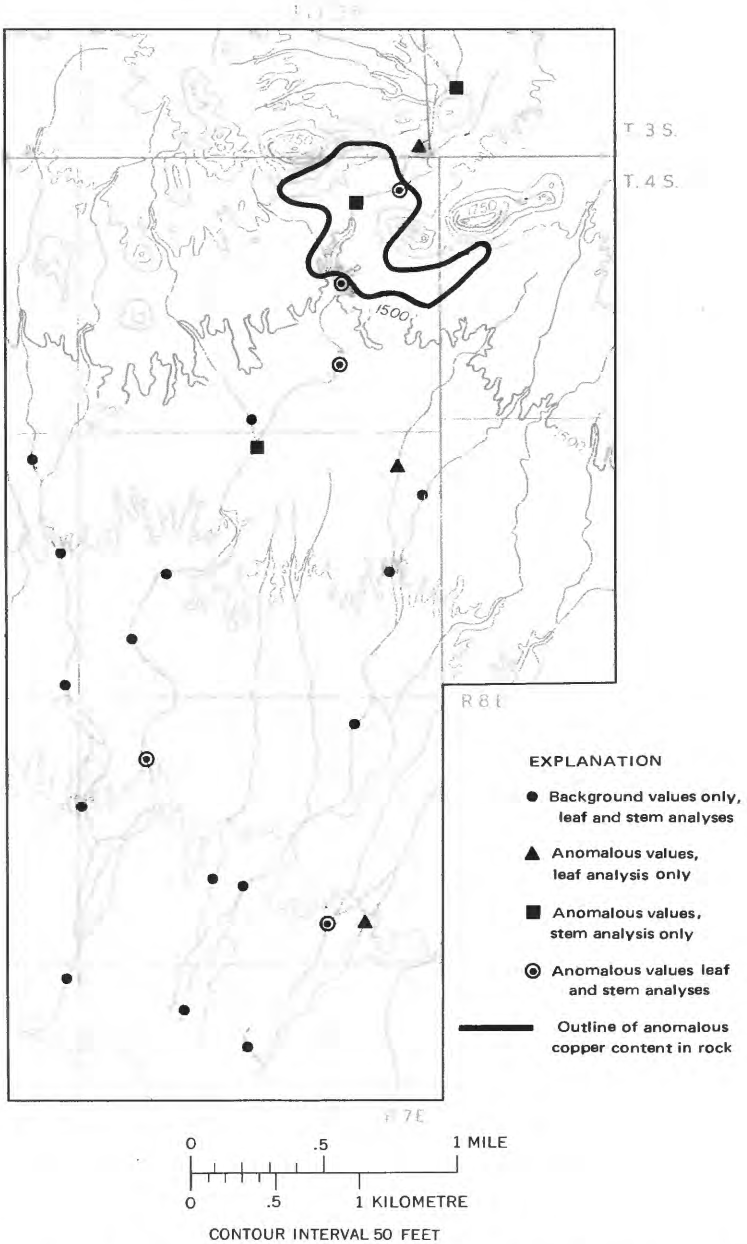

FIGURE 18. — Distribution of copper in blue paloverde leaf and stem ash, Mineral Butte area.

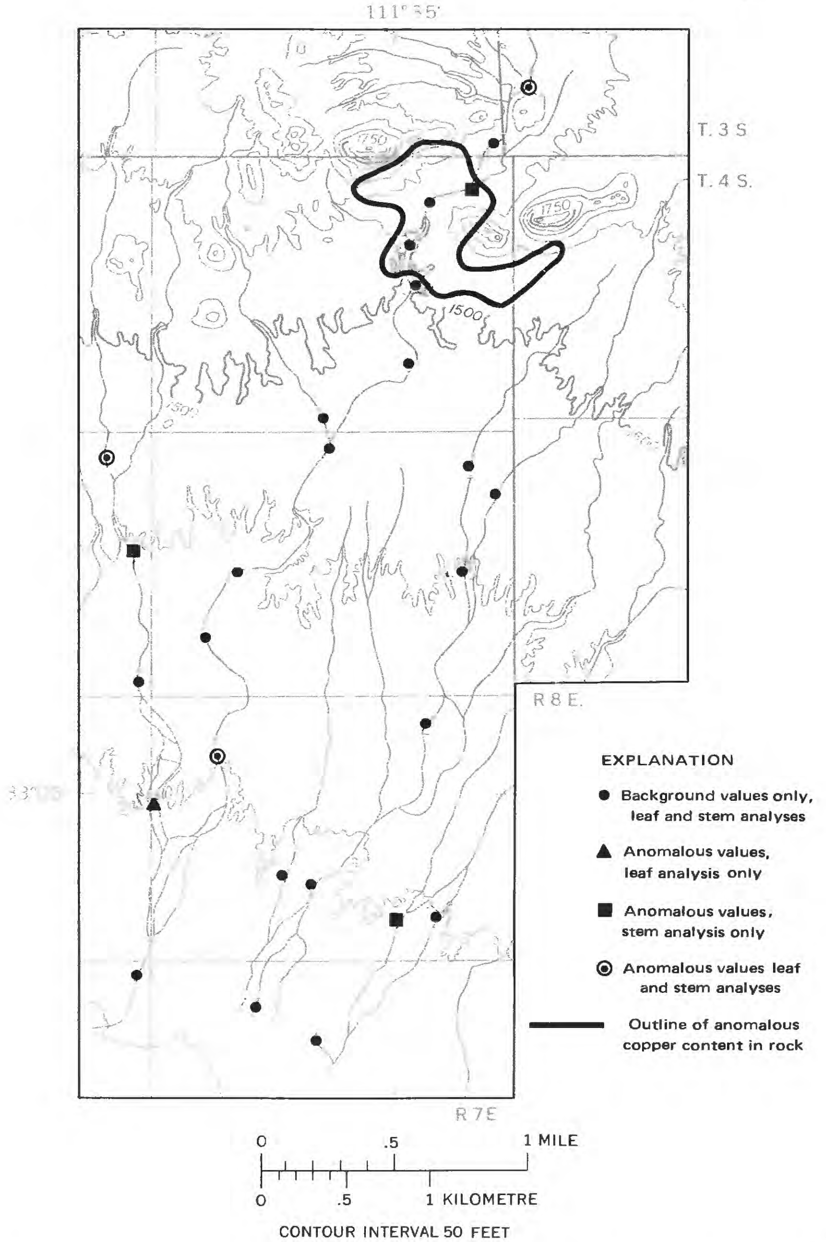

FIGURE 19. — Distribution of zinc in blue paloverde leaf and stem ash, Mineral Butte area.

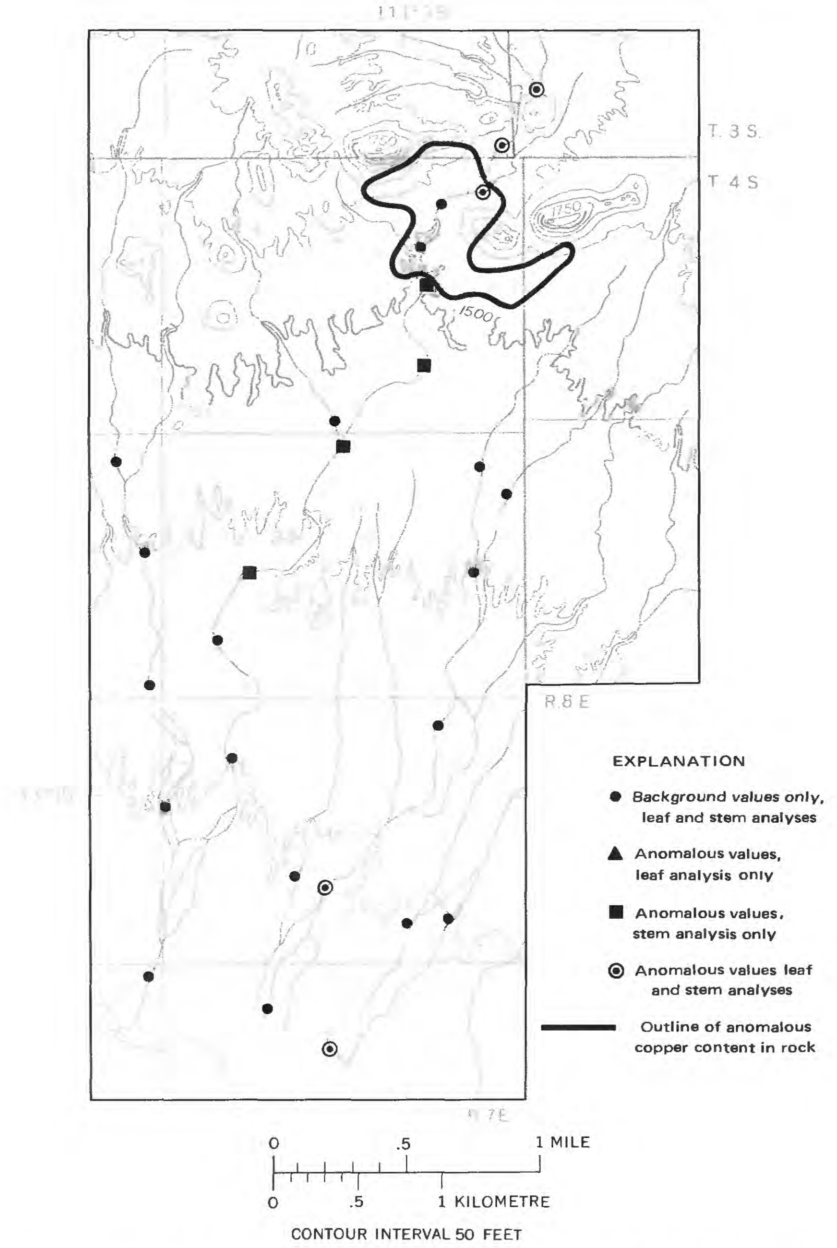

FIGURE 20. — Distribution of molybdenum in blue paloverde leaf and stem ash, Mineral Butte area.

Zinc. — The relative abundances of zinc in the leaf-stem pairs for blue paloverde ash are the reverse of those for copper and molybdenum. Sixty-one percent of the pairs have a higher concentration of zinc in the stem ash. The leaf ash contains more zinc in 31 percent of the pairs, and 8 percent of the pairs have the same amount of zinc in both plant parts. The background and threshold values (table 2) agree with these relative abundances of zinc in the ash of the two plant parts; although, once again, the differences in values for the two parts may not be statistically significant.

As in the cases of zinc in mesquite and catclaw acacia ash, the ranges of values for zinc in blue paloverde leaf and stem ash are relatively restricted and may only represent the variation to be expected in a natural sample population. Because of the same reasons described in the preceding section on mesquite, this plant-element combination is another that is difficult to evaluate with respect to any association of the plant anomalies with the known copper deposit.

Figure 19 shows the distribution of zinc anomalies in the ash of blue paloverde leaves and stems. The distribution of zinc anomalies again seems to be random, an observation expected from the preceding discussion. Biogeochemical prospecting using zinc in blue paloverde ash would not be successful in locating the Mineral Butte copper deposit.

Molybdenum. — The analyses of the leaf-stem pairs indicate that the molybdenum concentrations in the ash of blue paloverde are higher in the leaves, the same distribution as was seen for copper. Molybdenum is more concentrated in the leaf ash in 77 percent of the pairs. The stem ash contains more molybdenum in 15 percent of the pairs, and both plant parts have the same concentration in 8 percent of the pairs. The background and threshold values (table 2) show a similar distribution pattern in the leaf and stem ash. It is noteworthy that molybdenum is significantly less abundant in the ash of blue paloverde leaves and stems than it is in the ash of either part of the other three plant species studied (table 2). This marked abundance difference has been seen in other areas and is apparently a pecularity of blue paloverde.

Figure 20 illustrates the distribution of molybdenum anomalies in blue paloverde leaf and stem ash. With two exceptions the anomalous samples are confined to sample sites in the main stream channel crossing the copper deposit. The distribution of sites for samples with anomalous molybdenum in the stems shows a pattern extending about 1.6 km (1 mi) downstream from the deposit. The leaf analyses do not show this same downstream anomaly pattern; thus, because of lack of corroboration of data for the two plant parts, one cannot be completely sure that the entire anomaly is significant. Nevertheless, it seems that molybdenum in blue paloverde ash may be a useful plant-element combination for biogeochemical exploration, particularly when other species such as mesquite are not available.

IRONWOOD

Figures 21-23 show the distributions of copper, zinc, and molybdenum anomalies, respectively, in the ash of ironwood leaves and stems.

Copper. — A study of analyses of individual leaf-stem pairs indicates that copper is more abundant in the stem ash of 75 percent of the pairs. Only 17 percent of the pairs have a higher copper content in both plant parts; 8 percent of the pairs have the same copper content in both plant parts. The background and threshold values (table 2) also show higher concentrations of copper in ironwood leaf ash, although, as in other cases, the differences in values are probably not statistically significant.

The ranges of values for copper in ironwood leaf and stem ash (table 2) are relatively restricted, thereby limiting the usefulness of this plant-element combination as is the case for some other combinations. The difficulty in evaluating the copper anomalies in ash is clearly seen by studying figure 21. Most of the anomalies on this map are for samples that are anomalous for both plant parts, normally a favorable situation. Unfortunately, although there are many anomalies from samples collected in the stream channel crossing the copper deposit, there are also anomalies in other drainages. Objectively, it is impossible to separate the significant and nonsignificant anomalies; as a consequence, it would be difficult to locate the deposit using copper in ironwood ash as the only plant-element sample type. From the same line of reasoning it should be difficult to select one plant part over the other as being the best sample type for this plant-element combination.

It is noteworthy that all the ironwood anomalies are in the upper parts of the stream channels, a distribution not found in the other three plant species. There are at least two possible explanations for the common locations for these anomalies. First, the area of anomalous copper in ironwood ash is generally that in which bedrock is exposed or only covered by just a few metres of sediment. All the downstream sample sites are located where bedrock is buried under increasing but varying thicknesses of postmineralization-age unconsolidated sediment of Tertiary or

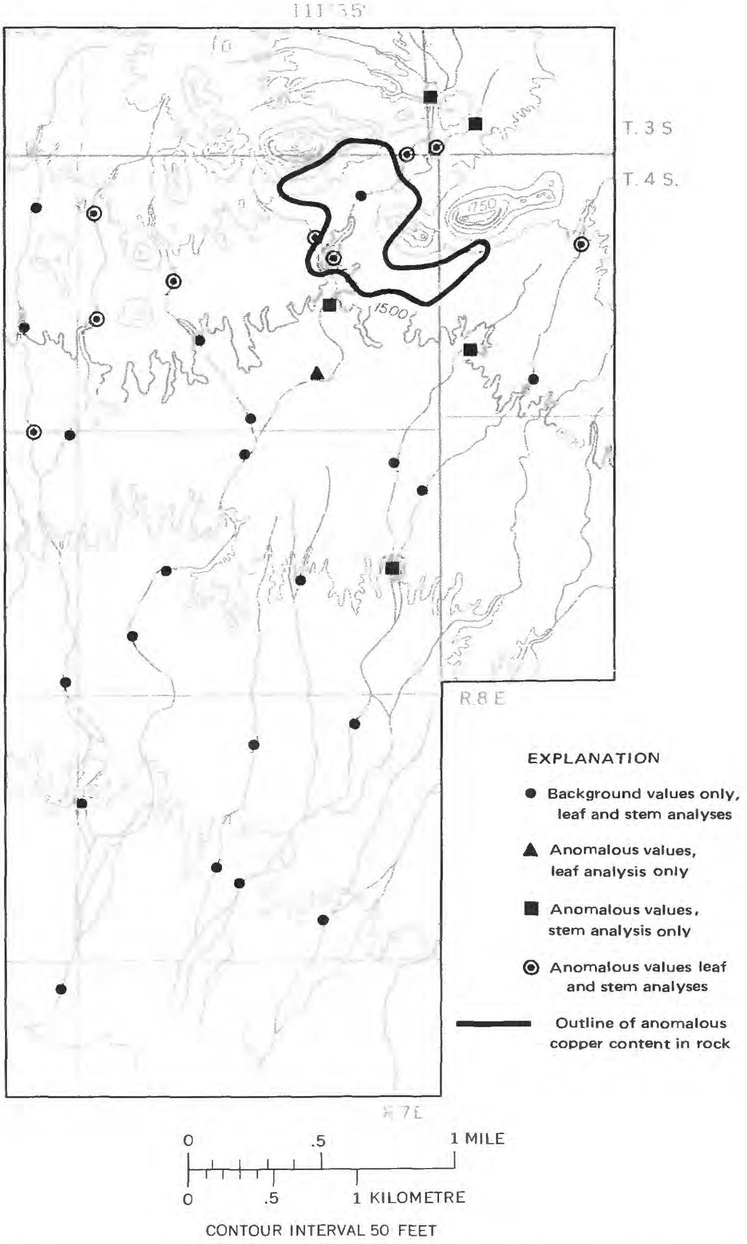

FIGURE 21. — Distribution of copper in ironwood leaf and stem ash, Mineral Butte area.

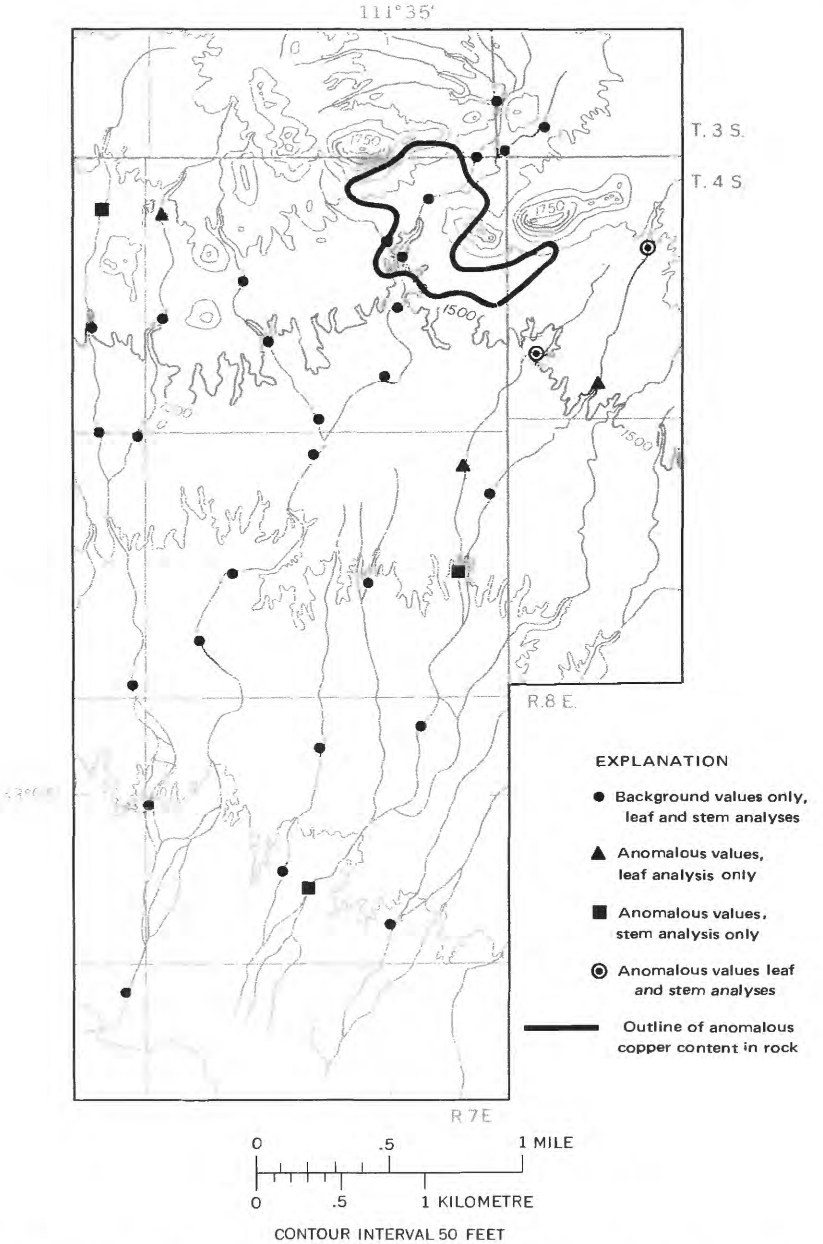

FIGURE 22. — Distribution of zinc in ironwood leaf and stem ash, Mineral Butte area.

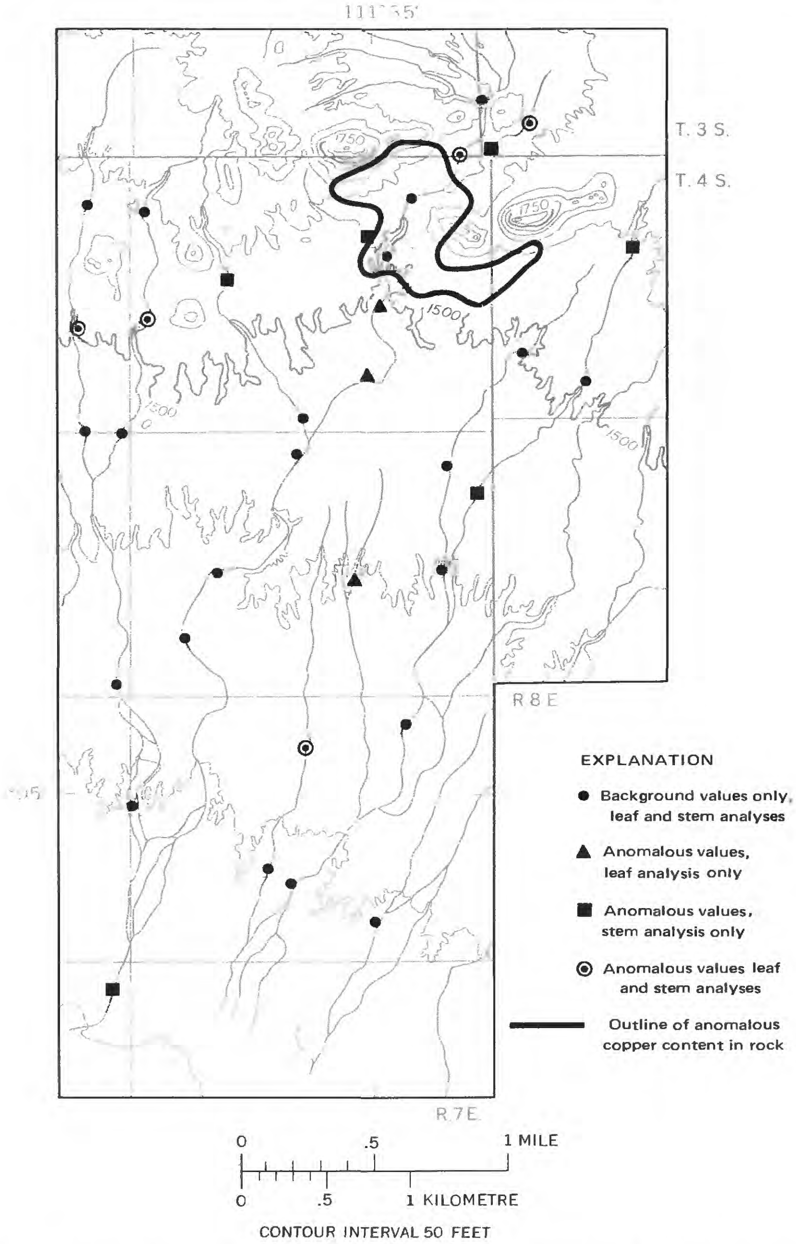

FIGURE 23. — Distribution of molybdenum in ironwood leaf and stem ash, Mineral Butte area.

Quaternary age. Probably, the presence or absence of exposed bedrock does not have a strong influence on the copper content of ironwood samples because none of the other three species displays this peculiar upstream distribution of anomalies. A second and more likely explanation for the distribution is that it is a function of the physiology of only this particular plant species. As noted earlier, ironwood is not a true phreatophyte; consequently, this species probably relies for its water needs more on intermittent infiltrating surface water than on the more or less constantly available circulating ground water that true phreatophytes can utilize. Possibly the higher copper uptake of ironwood in this upstream area is somehow related to the lower volume of water available at any given time in the stream channels in this area as compared to the higher water volume in the larger channels farther downstream.

Regardless of the cause of the upstream clustering of copper anomalies, this plant-element combination does not appear to be very useful in locating copper deposits similar to the one at Mineral Butte.

Zinc. — A study of the distribution of zinc in the ash of ironwood leaf-stem pairs indicates that zinc is more concentrated in the stem ash in 86 percent of the pairs. Zinc is more concentrated in leaf ash in only 11 percent of the pairs, and 3 percent of the pairs have equal concentrations of zinc in the ash of both plant parts. The background and threshold values (table 2) agree with this distribution of abundances between the plant parts. As was the case for zinc in the ash of all the other species, the ranges of values for zinc in ironwood leaf and stem ash (table 2) are probably not greater than what would be expected for a natural sample population.

The distribution of zinc anomalies in ironwood leaf and stem ash is illustrated in figure 22. A study of the known locations of copper and zinc anomalies in bedrock and soil samples indicates that none of the zinc anomalies in ironwood ash represent a significant anomaly. As was the case for the other three plant species, the zinc anomalies in ironwood ash show no spatial relationship to the Mineral Butte deposit or to known zinc anomalies in rock and soil samples. Therefore, biogeochemical sampling using analyses of zinc in ironwood ash is not an effective prospecting method in this district.

Molybdenum. — The molybdenum concentrations in the ash of ironwood leaf-stem pairs are higher in the stems of 75 percent of the pairs. Only 17 percent of the pairs have higher molybdenum concentrations in the leaf ash, and 8 percent of the pairs have equal concentrations in both plant parts. The background and threshold values (table 2) also indicate that molybdenum is more abundant in ironwood stem ash. It is interesting to note that ironwood is the only one of the four plant species studied in which all three of the elements determined are more concentrated in the same plant part (table 2).

Figure 23 illustrates the distribution of molybdenum anomalies in ironwood leaf and stem ash. As was the case for copper (fig. 21), most of the anomalies are confined to the area of bedrock in the northern part of the map. It is difficult to locate the copper deposit using the analyses of molybdenum in ironwood ash, however, because there are many nonsignificant anomalies. Furthermore, two of the samples collected directly over the copper deposit are not anomalous. Neither plant part seems to be significantly better than the other in locating the known deposit.

SUMMARY AND CONCLUSIONS

ROCK AND SOIL SAMPLING

Rock and soil samples were analyzed for 39 elements, including several elements that were determined by more than one method. Of these 39 elements, only 7 elements seem to have any spatial relationship of their anomalies with those of copper. Measurements of soil pH were also made on the fine fraction of the soil sample collected at each sample site. The following conclusions are based on the rock and soil analyses:

1. Anomalously low soil-pH values are present near the Mineral Butte deposit. The areal extent of these low values seems to be related to areas of silicified Precambrian granite. This distribution of low values might also represent a halo around the copper-rich area, thereby providing a larger exploration target than that of the copper geochemical anomaly.
2. The best material to select as a rock or soil-sampling medium may well depend on the element or elements sought. The results of this study indicate that no one medium works best for all elements.
3. The positive cobalt anomaly for rock samples probably coincides with the anomaly for copper in rock samples better than do anomalies of any of the other selected elements. The areal extents of the apparent negative anomalies for fluorine and lead in rock samples also coincide closely with the copper anomaly.
4. Geochemical studies in other copper districts of the Southwestern United States indicate that zinc, and often some other elements, form aureoles around the main copper deposit.

Within the area sampled at Mineral Butte, none of the selected elements (and none of the other elements analyzed but not further discussed in this report) appears to form an obvious aureole around the copper anomaly; however, it may be possible to interpret the distributions of fluorine and lead concentrations as producing such an aureole. Sampling on a more regional basis would be necessary to determine unequivocally whether any aureoles of pathfinder elements exist.

5. The anomaly contrast values and ranges of values for the selected element populations suggest that the coarsest sample material (rock) should provide the most meaningful data for anomaly interpretation; however, geochemical maps for copper, cobalt, gold, and molybdenum based on the analysis of the fine-soil fraction seem to provide more widespread and (or) more easily interpreted anomalies than do the respective maps based on use of the rock samples or the coarse-soil fraction. Where they can be used, samples of the fine-soil fraction have the additional advantage of eliminating the pulverizing step in sample preparation; thus, this sample medium should be considered for use in regional reconnaissance geochemical exploration programs in place of the routinely used -80 mesh fraction.
6. Although copper and molybdenum are closely associated spatially in many copper districts of the Southwestern United States, these two elements do not seem to show this intimate association in the Mineral Butte deposit.
7. The apparent increase in the size of anomalies with corresponding decrease in sample material size from rock to coarse soil to fine soil can be seen for some of the selected elements. This increase can be interpreted as being (1) the result of enrichment in place caused by the leaching of major constituents or (2) the result of migration of the elements caused by weathering processes. The presence of secondary copper minerals indicates that chemical weathering has taken place and suggests that this process may be the most important one influencing the increase in the sizes of positive anomalies with decrease in sample-particle size.
8. For some elements analyses of the fine-soil fraction yield the most widespread anomalies. For these elements this sample type should be superior to the other two types for use in regional reconnaissance geochemical surveys in spite of probable lower anomaly contrast values.
9. Most of any windborne soil material should be present in the fine-soil fraction of the samples collected for this study. Thus, one would expect that distributions of anomalies in this type of sample material would vary significantly from those of coarser

soil material if the finer material were mostly transported from outside the mineralized area. However, in most cases, the areal extents of the anomalies for each of the selected elements are similar for the two soil types. Furthermore, some of the selected elements (copper and zinc are two good examples) are greatly enriched in the samples of the fine-soil fraction as compared to the samples of the coarse-soil fraction taken from the same field sample. Lastly, the color and texture of the soil samples has been observed to be almost always closely related to the characteristics of the adjacent parent source rock. These facts suggest that eolian contamination of soil samples is not a serious problem to consider in anomaly interpretation in the Mineral Butte area.

VEGETATION SAMPLING

Leaves and stems of four plant species were collected along stream channels in the vicinity of the Mineral Butte deposit. Samples of leaves and stems were analyzed for 38 elements. The results for copper, zinc, and molybdenum are described. A study of the analyses for each plant part and of the spatial relationship of plant anomalies of the three metals to the known copper deposit yields the following conclusions:

1. The relative abundances of copper, zinc, and molybdenum in the rocks and soils of the study area, as expressed by median values, for example, in the respective sample populations, are not directly reflected by plants growing in the same materials. For example, the ash of plant samples is highly enriched in zinc compared to the corresponding samples of rocks and soils. The enrichments of copper and molybdenum in plant ash are much lower than that of zinc.
2. The concentration of a given element varies with the plant species and plant part sampled.
3. All elements are not necessarily enriched in the same part of a given plant species.
4. Samples that contain anomalous concentrations of an element in the ash of both leaves and stems of a plant species are generally more reliable indicators of significant anomalies than are samples containing anomalous concentrations in only one part of the plant.
5. Sites for collecting vegetation samples are limited by the availability or distribution of any one plant species; therefore, to insure an adequate sample density for a biogeochemical survey, more than one plant species may be needed to study an area.
6. The complete lack of any spatial correlation between zinc

anomalies in rock and soil samples and zinc anomalies in plant ash samples of any of the species studied suggests that there might be some critical concentration level for this element (and probably for some other elements as well) in the associated soils. Below this critical concentration a given plant will take up only normal but varying amounts of zinc necessary to sustain itself; above this concentration the plant will accumulate anomalous concentrations of the metal in the leaves and stems in approximately direct proportion to the concentration of zinc in the associated soils.

7. The Mineral Butte copper deposit was best located in the biogeochemical survey using the distribution of copper anomalies in plant ash. In contrast to other biogeochemical studies, molybdenum analyses obtained in this investigation proved to be more limited in value than copper analyses. For reasons previously stated, zinc analyses provided no useful information that could be applied to biogeochemical prospecting for copper deposits similar to the one at Mineral Butte.
8. The copper deposit was best located using analyses from mesquite samples. Catclaw acacia analyses were almost as effective; blue paloverde analyses may also be useful. Analyses from ironwood, the only one of the four species that is not a true phreatophyte, were much less effective in locating the deposit.
9. A number of the vegetation maps in this report show metal anomalies upstream from the known copper deposit. The cause of these anomalies is not known but does not seem to be related to the chemistry of the surface materials. Further study of this upstream area is suggested.
10. The range of analytical values for a given type of plant is an important factor to consider in determining whether the plant will yield information that can be relatively easily interpreted. For example, of the species studied for this report, none of the zinc maps show any useful relationship of zinc to the known copper deposit or even to zinc anomalies in the rock and soil samples. The same situation has been noted for other plant-element combinations not discussed in this report. Ideally, if plant analyses are to be useful, there should be about one magnitude of difference between the highest and lowest concentrations in the sample population.
11. The Mineral Butte deposit is well exposed at the surface; thus, this deposit can best be evaluated by using readily obtainable samples of bedrock and residual soil. Other copper deposits similar in nature, however, might occur in areas covered by a thin (less than, perhaps, 30 m (98 ft)) layer of postmineralization-

age overburden. In such a situation the deposit might best be detected by collecting samples of the deep-rooted plants growing along the stream channels developed in the overburden. Chemical analysis of the ash of these plants should reflect the chemistry of the ground water circulating over and through the buried deposit. Therefore, on the basis of the survey conducted at Mineral Butte, sampling of plants along stream channels at about 0.4-km (0.25-mi) intervals should be adequate to detect a similar thinly buried copper deposit. Nearly all of the stream channels sampled for the present study could be negotiated with a four-wheel-drive vehicle; similar conditions exist throughout many parts of the Southwestern United States. Consequently, biogeochemical sampling should be a quick and easy way to make reconnaissance geochemical surveys in areas covered with thin overburden.

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