Utilization of Mull (Forest Humus Layer) in Geochemical Exploration in the Empire District, Clear Creek County, Colorado

GEOLOGICAL SURVEY BULLETIN 1278-B





# Utilization of Mull (Forest Humus Layer) in Geochemical Exploration in the Empire District, Clear Creek County, Colorado

By GARY C. CURTIN, HUBERT W. LAKIN, ARTHUR E. HUBERT, E. L. MOSIER and K. C. WATTS

CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

GEOLOGICAL SURVEY BULLETIN 1278-B

Sampling of the forest humus layer may be an effective geochemical tool in areas where the bedrock is covered by colluvium or glacial drift



# UNITED STATES DEPARTMENT OF THE INTERIOR ROGERS C. B. MORTON, Secretary

**GEOLOGICAL SURVEY** 

W. A. Radlinski, Acting Director

(Library of Congress catalog-card No. 75-170292)

# CONTENTS

			Page
Abstract			<b>B</b> 1
			1
Ack	nowl	edgments	3
		ing	4
Geochen	nical	investigations	7
	erial	s sampled	7
	Con	tamination of mull samples	8
Ana	lytic	al procedures	8
Dist	ribut	tion of geochemical anomalies	8
	Gold	d-copper-bismuth anomalies	9
		er-lead-zinc-molybdenum anomalies	10
	Tun	gsten-tin anomalies	10
		nganese anomalies	10
		urium-mercury anomalies	10
		richment in mull ash	10
Met	al co	ntent of ash of pine and aspen trees in the Empire district	12
Cor	relati	on analysis	13
			15
Reference	es ci	ted	16
Erann	,	To do not consider the Class Court Court of the Court of	Page
FIGURE	1.	Index maps showing location of Clear Creek County and Empire district	<b>B2</b>
	2.	Geologic map of the north half of the Empire district	4
	3.	Map of the north half of the Empire district showing sample localities	6
4	-21.	Geochemical maps and histograms of—	
		4. Gold in mull ash	18
		5. Gold in soil.	19
		6. Copper in mull ash	20
		7. Copper in soil	21
		8. Bismuth in mull ash	22
		9. Bismuth in soil	23
		10. Silver in mull ash	24
		11. Silver in soil	25
		12. Lead in mull ash	26
		13. Lead in soil	27
		14. Zinc in mull ash	28
		15. Zinc in soil	29
		16. Molybdenum in mull ash	30

# CONTENTS

		Page
FIGURES 4-21.	Geochemical maps and histograms of—Continued	
17.	Molybdenum in soil	B31
18.		32
19.		33
20.	Tungsten in mull ash	34
21.	Tungsten in soil	35
22.	<del>-</del>	36
23.	Histograms of manganese in mull ash and soil	37
24.	Geochemical map of tellurium in soil	38
25.	Geochemical map of mercury in soil	39
	TABLES	
		Page
TABLE 1.	Metal content in the ash of pine and aspen trees that grow in the Empire district compared with that of various plants that grow elsewhere	B12
2.	Matrix showing correlation of selected metals in mull ash with each other and with percent ash	14
3.	Matrix showing correlation of selected metals in soil with each other	14

# CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

# UTILIZATION OF MULL (FOREST HUMUS LAYER) IN GEOCHEMICAL EXPLORATION IN THE EMPIRE DISTRICT, CLEAR CREEK COUNTY, COLORADO

By Gary C. Curtin, Hubert W. Lakin, Arthur E. Hubert, E. L. Mosier, and K. C. Watts

#### ABSTRACT

Results of geochemical studies in the Empire district, Clear Creek County, Colo., show that the distribution of anomalously high amounts of gold, copper, and bismuth in mull reflects the known distribution of these metals in bedrock beneath an extensive cover of colluvium and glacial drift; but their distribution in the transported soil that underlies the mull poorly delineates the distribution of the known metal deposits.

High anomalies of silver, lead, zinc, and molybdenum in the mull encircle the principal anomalies of gold, copper, and bismuth and may reflect enrichment of silver, lead, zinc, and molybdenum in the bedrock beneath the colluvial and morainal cover.

The high anomalous concentrations of gold, copper, bismuth, silver, lead, zinc, molybdenum, tin, and tungsten detected in the mull ash and the detection of these metals (except tungsten) in the ash of pine and aspen trees may reflect a geochemical cycle in which these metals are leached from the bedrock, are absorbed by the trees, and then in part deposited in the leaves and needles; they are finally concentrated in the mull as the leaves and needles decay.

Some areas anomalously high in certain metals in mull are not related to known mineralization and merit further investigation.

#### INTRODUCTION

The Empire district, which has an area of approximately 6 square miles, is located in the southern part of the Empire 7½-minute quadrangle, Clear Creek County, Colo., about 37 miles west of Denver in the Front Range of the Rocky Mountains (fig. 1). Altitudes in the district range from 9,000 to 11,000 feet. The U.S. Geological Survey has made geochemical investigations of the north half of the district as part of its investigation of the geochemistry of gold in the zone of weathering.

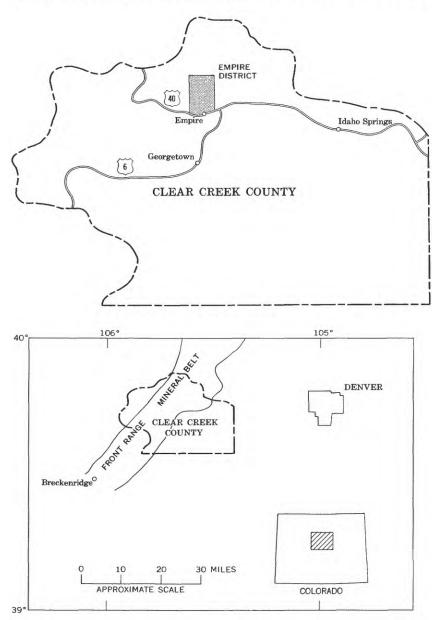


FIGURE 1.—Index maps showing location of Clear Creek County and Empire district.

Mining began in the district in 1862 (Spurr and Garrey, 1908, p. 401) with the discovery of gold in the oxidized and decomposed rock of the Silver Mountain ore zone (fig. 2). This rock was washed in sluices and yielded approximately \$2 million in gold during 1862–65 (Harrison, 1964,

p. 93). These placer operations decreased in economic importance in the 1870's, but they continued on a small scale for many years.

Lode mining was conducted intermittently from the 1860's to 1943. Some of the more important mines in the north half of the district are the Minnesota, the Silver Mountain, and the Conqueror (fig. 3). During 1933–43 more than 90,000 ounces of gold was produced from lode deposits in the district, mostly from the Minnesota. Small amounts of copper and silver have been produced from time to time.

The geology of the Empire district has been described by S. H. Ball (in Spurr and Garrey, 1908), Lovering and Goddard (1950), and Braddock (1969). The ore deposits have been described by Spurr and Garrey (1908) and Lovering and Goddard (1950).

This investigation includes a study of the distribution and association of gold, silver, copper, bismuth, lead, zinc, molybdenum, tin, tungsten, and manganese in mull (forest humus layer) and in the underlying soil (6- to 12-inch depth), and of tellurium and mercury in the soil. Mull is defined by the U.S. Department of Agriculture (1951, p. 245) as "a humusrich layer consisting of mixed organic and mineral matter, generally with a gradational boundary to the underlying mineral horizon." Results of the geochemical studies show that the distribution of anomalously high amounts of gold, copper, and bismuth in mull reflects the known distribution of these metals in the bedrock beneath a cover of colluvium and glacial drift; but their distribution in the transported soil that underlies the mull poorly delineates the known metal deposits. The distribution of anomalously high amounts of silver, lead, zinc, molybdenum, tungsten, and tin in mull may also reflect enrichment of these metals in bedrock beneath a cover of glacial drift. In general the geochemical data on mull ash (figs. 4-17) show that a central zone containing the principal high anomalies of gold, copper, and bismuth is encircled by a peripheral zone containing the principal high anomalies of silver, lead, zinc, and molybdenum.

#### ACKNOWLEDGMENTS

We thank Mr. H. C. Nelson, Mr. C. P. Clifford of the Minnesota Mines, Inc., Mrs. H. M. Stoner, Mr. Harrison Bristol, and Mr. E. J. Woodriff for permission to publish data on samples collected on their properties. Mr. Nelson was especially helpful in aiding us in the proper identification of abandoned mines and mill sites and in supplying other relevant information not available in published reports. The following members of the U.S. Geological Survey assisted us in both the field investigations and the analytical work: M. A. Chaffee, H. D. King, C. W. Gale, J. G. Frisken, K. E. Espelie, R. C. Humphrey, K. R. Murphy, and O. J. Roman.

## **GEOLOGIC SETTING**

The Empire district is underlain by igneous and metamorphic rocks of Precambrian age which have been intruded by porphyries of Tertiary age (fig. 2). The Precambrian rocks are biotite gneiss and microcline gneiss that have been intruded by large, partly concordant bodies of Boulder Creek Granite and relatively small bodies of Silver Plume Granite. A small stock of hornblende granodiorite porphyry, a small stock of leucocratic monzonite, and dikes of granodiorite porphyry, hornblende granodiorite porphyry, biotite granodiorite porphyry, biotite quartz monzonite porphyry, and bostonite porphyry, all of Tertiary age, intrude the Precambrian rocks. Bedrock in most of the area is covered either by

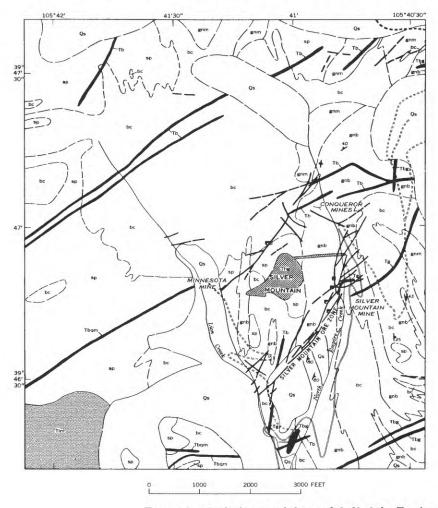
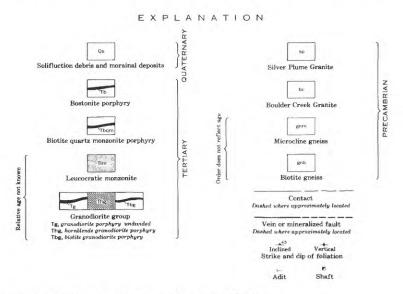


FIGURE 2.—Geologic map of the north half of the Empire

Quaternary colluvium or by Quaternary glacial drift which ranges in total thickness from about 3 feet to 40 feet. The Quaternary deposits shown in figure 2, which were not subdivided during mapping (Braddock, 1969, p. 45), consist only of glacial drift and solifluction debris (water-saturated colluvium).

The ore deposits of the north half of the Empire district are fissure fillings, placers, and disseminated deposits of auriferous pyrite (Lovering and Goddard, 1950, p. 156, 158). Principal vein minerals are pyrite, chalcopyrite, and quartz. Gold content increases with chalcopyrite content, and silver content of the ore generally is only a few ounces to the ton (Lovering and Goddard, 1950, p. 158). A small quantity of native bismuth was reported from the Silver Mountain ore zone (S. H. Ball, in Spurr and Garrey, 1908, p. 399).

The veins of the Minnesota mine and the Silver Mountain ore zone are the two principal vein systems in the area studied (fig. 2). The Minnesota mine is composed of one primary vein and several discrete secondary veins which either coalesce into or are parallel to the primary vein, whereas the Silver Mountain ore zone is a strong zone of fracturing and alteration as much as several hundred feet wide in places. Individual ore bodies occur as irregular shoots along the veins and range from a few feet to 100 feet in height, and from less than 1 foot to 20 feet in width, and from a few feet to 1,800 feet in length. The vein system shown on the geologic map and the geochemical maps (figs. 2, 4–25) was compiled in part from field mapping during the summer of 1967 and in part from



district. Geology modified from Braddock (1969).

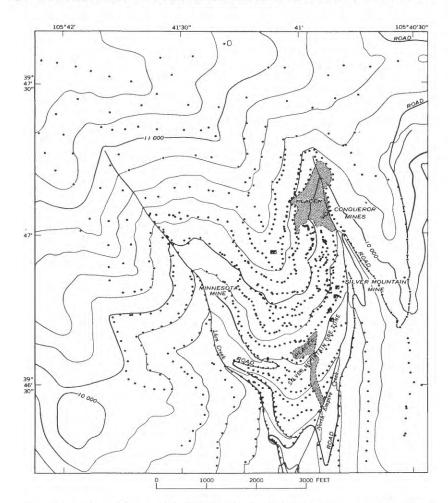


FIGURE 3.—Map of the north half of the Empire district showing sample localities (small dots). Contour interval, 200 feet.

previous maps by Braddock (1969), Lovering and Goddard (1950, fig. 59, p. 157, pl. 13), and Spurr and Garrey (1908, pl. 81).

A small stock of hornblende granodiorite porphyry is located in the area between the Minnesota mine and the Silver Mountain ore zone. Lovering and Goddard (1950, p. 156) suggested that the vein systems were formed by the stresses related to the intrusion of the stock and subsequent collapse of the roof when some of the underlying magma was withdrawn after late-stage consolidation of the stock.

Although argillic alteration is relatively widespread in the Precambrian rocks surrounding the hornblende granodiorite porphyry stock, it is confined to narrow zones in the wallrocks of veins in the peripheral zone of the area. Both iron and manganese oxide stains were observed on the fracture surfaces of the altered rock.

#### GEOCHEMICAL INVESTIGATIONS

The purpose of this study was to determine if the distribution of gold and associated ore metals in vegetation, forest humus, and soil reflects the distribution of these metals in the underlying bedrock. The Empire district was chosen for the study after G. J. Neuerburg (unpub. data) in 1965 and 1966 showed the presence of anomalously high amounts of gold and other metals in the soil of the north half of the district.

The present study showed that gold and associated ore metals generally are enriched in the forest humus layer relative to the underlying soil.

Results of the geochemical investigations are summarized in the geochemical maps of the distribution in mull ash and soil of gold, copper, bismuth, silver, lead, zinc, molybdenum, tin, tungsten (figs. 4–21), the distribution of manganese in mull ash (figs. 22, 23), and the distribution of tellurium and mercury in soil (figs. 24, 25). Analytical data from the mull ash and soil samples were treated statistically in the U.S. Geological Survey IBM 360/65 computer with card input using the STATPAC statistical evaluation library. The output included histograms (figs. 4–23) and the linear correlation coefficients between pairs of logarithms of variables (tables 2 and 3).

#### MATERIAL SAMPLED

Samples of mull and soil that were used in this study were collected at 894 localities (fig. 3). Mull only was collected at 35 localities, soil only was collected at 78 localities, and both soil and mull were collected at 781 localities.

The forest cover of the Empire district is chiefly lodgepole pine (*Pinus contorta*), but limber pine (*Pinus flexilis*) and groves of aspen (*Populus tremuloides*) are present locally. Samples of roots, trunks, branches, needles, and leaves of pine and aspen trees were collected at nine localities where the mull contained gold.

Pine mull is present as pads, 1–3 inches thick, beneath individual trees. The burrowing of rodents and the action of downslope wash have resulted in the addition of varying quantities of mineral matter to these pads. Aspen mull is present as a diffuse layer rarely more than 1 inch thick. Mull samples were collected beneath pine trees where possible, but about 100 samples of aspen mull were collected at localities where pine trees were absent.

A layer of gray, ash-textured material (2–4 in. thick) that contains abundant small roots is present beneath the mull layer. Below this layer is a mixture of weathered cobbles and yellow to yellow-brown coarse to fine sand, of colluvial or morainal origin, that does not visibly change in

mineralogic composition or texture downward to bedrock. Soil samples were collected at a depth of 6–12 inches.

#### CONTAMINATION OF MULL SAMPLES

Locally the mull is contaminated. Detrital pyrite was observed in the heavy-mineral fractions (that fraction composed of minerals having a specific gravity of 3 or more) of six mull samples collected near mine dumps. As much as 52 percent of the total gold was in the heavy-mineral fractions of nine samples collected near large dumps. The gold in the heavy-mineral fractions of these samples could have been contributed principally by windblown auriferous pyrite. Even in these contaminated samples the organic fractions contained as much as 26 percent of the total gold.

Most of the samples that contain high contents of gold and other metals were collected at localities relatively remote from sources of contamination, however, and one of these samples that was studied in detail contained no observable pyrite or other contamination. The organic fractions of this sample contained 72 percent of the total gold. The presence of appreciable gold in the interior wood of pine and aspen trees (table 1) and in the organic fractions of the mull substantiates the biogeochemical origin of most of the high gold anomalies found in the area studied.

#### ANALYTICAL PROCEDURES

Samples were analyzed by several procedures. Gold was determined by atomic absorption (Thompson and others, 1968), tellurium by a wet chemical method (Lakin and Thompson, 1963), and mercury by an atomic absorption method (Vaughn and McCarthy, 1964); and the other metals were determined by a semiquantitative spectrographic field method (Grimes and Marranzino, 1968). Most of the analyses were made in mobile field laboratories. Soil samples were sieved and the minus 2-millimeter fraction was ground and pulverized before it was analyzed. Mull samples were sieved and the minus 2-millimeter fraction was ashed and analyzed. The ash of the mull, as used in this report, is the sum of the admixed mineral matter and the ash of the organic matter. The metal content of the mull samples is reported on an ash-weight basis.

Vegetation samples were air dried, weighed, and ashed at 450°C in a thermostatically controlled furnace and the metal content was reported on an ash-weight basis. The bark and outer wood layer were shaved from the trunks and large roots of the pine and aspen trees. The interior wood, free from contamination, was analyzed.

#### DISTRIBUTION OF GEOCHEMICAL ANOMALIES

The areas of anomalous concentrations of metals in mull ash and soil are shown in figures 4–25. An area rich in gold, copper, and bismuth is shown

in figures 4, 6, and 8, and an area rich in silver, lead, zinc, and molybdenum is shown in figures 10, 12, 14, and 16. The geographic distribution of tin and tungsten in mull ash (figs. 18, 20), does not correspond well with either of the above-mentioned two groups, but tin and tungsten roughly correspond with each other.

The central part of the mapped area—that area bounded on the west by Lion Creek and on the east by North Empire Creek—contains most of the high gold, bismuth, and copper anomalies in mull ash (figs. 4, 6, 8). Areas of anomalously high silver, lead, zinc, and molybdenum in mull ash (figs. 10, 12, 14, 16) form an encircling zone—more prominent on the west than on the east—around the gold, bismuth, copper area.

This zoning pattern is similar to the zoning pattern in the Central City district (Sims and others, 1963, p. 38–41; Lovering and Goddard, 1950, p. 170, 173, pl. 9).

#### GOLD-COPPER-BISMUTH ANOMALIES

In mull ash the geographic distribution of gold is so pervasive at a minimum concentration level of 0.2 ppm (parts per million) (fig. 4) that the known vein systems are not delineated. This pattern of distribution suggests that gold is dispersed in the zone of weathering, possibly by inclusion of vein material in colluvium, by the biogeochemical cycle (described on p. 11) or by windblown material from mine dumps. The geographic distribution of gold in mull ash at a minimum concentration level of 0.6 ppm (fig. 4), however, appears to delineate the known gold deposits as well as additional areas that merit further investigation.

Copper distribution in mull ash at a minimum concentration of 150 ppm (fig. 6) generally corresponds with the distribution of gold in mull ash at a minimum concentration of 0.6 ppm (fig. 4). The association of gold and copper in the ash of the mull layer reflects the increase in tenor of gold with chalcopyrite in the veins (Lovering and Goddard, 1950, p. 158; S. H. Ball, in Spurr and Garrey, 1908, p. 399).

Bismuth distribution in mull ash at a minimum concentration of 15 ppm (fig. 8) roughly corresponds with high gold and copper anomalies (figs. 4, 6). However, bismuth is also associated to a lesser extent with the silver-lead-zinc-molybdenum group. Anomalously high bismuth in mull ash generally ranges from 10 to 30 ppm, and increases to 200 ppm in places on the eastern periphery of the district. Three samples of mull ash collected at localities on the first ridge east of North Empire Creek contain 70, 150, and 200 ppm bismuth. The mull ash sample that contains 200 ppm bismuth was collected over a gold-bismuth-silver vein. The gossan of this vein contains 1.5 percent bismuth.

In soil, in contrast to mull ash, the distribution of metals (figs. 5, 7, 9) is erratic High metal values in many of the soil samples in areas without known gold deposits may be due chiefly to the inclusion of vein material

in otherwise barren colluvial or morainal cover. However, some areas of high gold, copper, and bismuth (figs. 5, 7, 9) in soil coincide with known gold deposits in bedrock, and these may reflect metal enrichment in the soil by the biogeochemical cycle.

#### SILVER-LEAD-ZINC-MOLYBDENUM ANOMALIES

The prominent high silver-lead-zinc-molybdenum anomaly in the ash of the mull layer west of Lion Creek and near the south edge of the mapped area (figs. 10, 12, 14, 16) is in an area where the bedrock is hidden by a cover of glacial drift (fig. 2). This anomalous area, which is remote from a source of contamination, may reflect mineralized bedrock and, therefore, it merits further investigation. The widespread lead anomaly in mull ash and scattered isolated anomalies of silver and zinc in the northwest corner of the mapped area also warrant further exploration.

## TUNGSTEN-TIN ANOMALIES

The distribution patterns of tungsten and tin roughly correspond with each other and in part with several of the extensive high gold, copper, and bismuth anomalies (figs. 4, 6, 8). The most significant high tungsten anomaly in mull ash is on Lion Creek near the west edge of the Silver Mountain ore zone (fig. 20) where tungsten values of 100–500 ppm correspond to a widespread high gold anomaly (fig. 4). This tungsten anomaly may reflect mineralized rock at depth and should be investigated further.

#### MANGANESE ANOMALIES

The distribution of manganese in mull ash at concentrations of 5,000 ppm or more (fig. 22) forms anomalies that partly encircle the extensive area of high gold-copper-bismuth anomalies. These manganese anomalies correspond rather well with the silver-lead-zinc-molybdenum group of high anomalies.

Most of the low manganese values in mull ash (1,500 ppm or less) are in the central part of the area (fig. 22). They partly correspond with the gold-copper-bismuth group of high anomalies and the principal high tungsten anomaly.

#### TELLURIUM-MERCURY ANOMALIES

Owing to lack of adequate methods for the analysis of tellurium and mercury in mull ash, data on these elements in mull ash are not available. However, the scattered high tellurium-mercury anomalies in soil (figs 24, 25) are within the general area occupied by the high gold-copper-bismuth anomalies in mull ash and soil.

#### METAL ENRICHMENT IN MULL ASH

The distribution and abundance of metals shown on the geochemical maps (figs. 4-25) demonstrate the enrichment of metals in mull ash

relative to soil. Enrichment of certain elements in humus (a major constituent of mull) has been reported by Goldschmidt (1937), Cox and Hollister (1955), and Boyle and Dass (1967). Goldschmidt (p. 670) found that the uppermost humus layer of a very old forest of beech and oak in central Germany was enriched in gold, thallium, beryllium, cobalt, nickel, zinc, germanium, arsenic, cadmium, tin, lead, and silver. Goldschmidt (1954, p. 204), in a discussion of the geochemistry of gold, concluded that the enrichment of gold in humus was convincing evidence for the circulation of gold in living plants; he stated "It is possible that this observation may be used as an indication of the occurrence of gold in the lower levels of the soil." Cox and Hollister (p. 939) reported zinc enrichment in humusrich soil over a zinc deposit covered by glacial till in Stevens County, Wash. Boyle and Dass (p. 274) found that in areas of deciduous tree cover near Cobalt, Ontario, the A horizon (organic-rich) of the soil was enriched in lead, zinc, copper, arsenic, antimony, molybdenum, silver, cobalt, manganese, and mercury relative to the B horizon (organic-poor); and they suggested that the A horizon becomes enriched in metals as the leaves decay.

The anomalously high concentrations of gold, bismuth, silver, lead, zinc, molybdenum, and tin detected in mull ash (see histograms, figs. 4–23) probably are caused by a geochemical cycle in which these metals are leached from bedrock, are absorbed by the pine and aspen trees, and then are deposited in the leaves, needles, cones, woody material, and bark. The metals are finally concentrated in the mull as the leaves, needles, and other parts of the trees decay. Tree roots have been observed in the Empire district in fractures in bedrock at mine workings, sample pits, and trenches. In one of the mine workings tree roots were observed 50 feet below the surface.

The histograms (percent frequency distributions) of metal content in mull ash and soil (figs. 4–21, 23) show that in the Empire district mull ash is significantly enriched in lead (sixfold), manganese (fourfold), gold, silver, bismuth, zinc, molybdenum, and tin relative to the soil. The amount of enrichment of gold, bismuth, silver, zinc, molybdenum, and tin in mull ash relative to soil cannot be determined because the histograms (figs. 4, 8, 10, 14, 16, 18) are truncated at the concentration determined by the lower limits of analytical detection. The enrichment of these metals in mull ash relative to the underlying soil, however, is shown.

Mull ash is only slightly enriched in copper and tungsten. The enrichment of mull ash in metals such as gold, bismuth, silver, zinc, and lead relative to soil suggests that mull may be a useful sample medium in delineating the distribution of these metals in the bedrock beneath a transported overburden.

#### METAL CONTENT OF ASH OF PINE AND ASPEN TREES IN THE EMPIRE DISTRICT

The anomalously high metal content of the mull ash suggests that the pine and aspen trees from which the mull is formed should also contain high amounts of metal. Samples of roots, trunks, branches, needles, and leaves of pine and aspen trees were collected and analyzed in order to test this possibility. The samples were collected at nine localities where the mull ash contains high amounts of gold and bismuth or gold, silver, and bismuth and only moderate to minor amounts of molybdenum, lead, zinc, tin, and tungsten. In table 1 the maximum and minimum metal contents (in ppm) in the ash of pine and aspen trees that grow in the studied area are compared with the average metal content in the ash of more than 1,000 species of plants that grow in unmineralized ground (Cannon, 1960, p. 596), with the ash of conifer needles from trees growing on silicic rocks in Finland (Lounamaa, 1967, p. 310), and with the ash of 1,501 samples of vascular plants (Shacklette, 1965, p. D14).

The gold, silver, and lead content of the ash of pine and aspen trees collected in the Empire district generally is anomalously high relative to the gold, silver, and lead content of the ash of vegetation reported in the literature cited in table 1. The presence of bismuth in the ash of pine trees collected in the Empire district (table 1) and the presence of tin in both pine and aspen trees in the district (table 1) may be anomalous because bismuth and tin were detected in only 2.8 and 1.9 percent, respectively, of the 1,501 vascular plant samples (table 1) reported in the literature.

The copper, molybdenum, and zinc content in the pine and aspen trees, however, ranges from slightly less to slightly more than the average copper, molybdenum, and zinc content of the ash of vegetation reported in the literature cited in table 1.

Table 1.—Metal content, in parts per million, in the ash of pine and aspen trees that [N, not detected at values shown in parentheses. \_\_\_\_\_, no data given in published source. Empire no tungsten

				E	mpire dis	trict				
			Aspen							
Root interior (1 sample				Branch interior (5 samples)		Needles (12 samples)		Root interior (1 sample)	Trunk interior (7 samples)	
Metal		Min	Max	Min	Max	Min	Max		Min	Max
Au Cu Bi Mo Pb Zn Ag Sn	3 200 10 10 700 1,000 30 10	0.5 150 N(10) 5 300 300 1.5 N(10)	500 10 10 2,000 1,000 100 15	0.2 100 <10 <5 150 700 N(0.5)	500 50 10 1,000 2,000 100 N(10)	0.04 100 <10 <5 100 500	0.7 200 10 15 1,000 1,500 3 N(10)	0.2 200 N(10) 20 300 300 7 N(10)	0.7 100 N(10) N(5) 50 500 N(0.5) N(10)	1.6 1,000 <10 15 700 1,000 20 10

Values from Lounamaa (1967).
 Values from Cannon (1960).
 Values from Shacklette (1965), based on 1,501 plant samples.

The relatively high content of gold, silver, bismuth, and lead and the average content of copper, molybdenum, and zinc in the ash of pine and aspen trees collected in the Empire district is congruent with the metal content of both the ash of the underlying mull and the oxidized zone of the underlying mineralized bedrock. The presence of metals in the pine and aspen trees substantiates the biogeochemical origin of the metal content of the mull.

#### CORRELATION ANALYSIS

The product moment coefficient of correlation was calculated for every pair of elements in soils and mull ash in order to indicate the degrees of association among the elements in these media. Arbitrary constants were assigned to values reported as not detected, to values less than the lower limit of detection, and to volumes greater than the upper limit of detection. The analytical data were transformed to logarithms for correlation analysis because the correlation coefficients of the logarithms of the metal content are less subject to the effects of extremely high or low values than are the correlation coefficients of the untransformed metal content. Correlation matrices of the logarithmic concentrations of elements in soils and mull ash are shown in tables 2 and 3. Elemental components of the soil sample correlation matrix are gold, copper, bismuth, silver, lead, zinc, molybdenum, tin, tungsten, iron, manganese, tellurium, and mercury. Elemental components of the mull ash correlation matrix are gold, copper, bismuth, silver, lead, zinc, molybdenum, tin, tungsten, iron, manganese, and percent ash of the mull. A correlation coefficient of 0.3 or greater is classified as significant, a correlation coefficient of 0.2 to 0.3 is classified as slight (noticeable linear relationship, but not significant), and a correlation coefficient of less than 0.2 is classified as insignificant.

grow in the Empire district compared with that of various plants that grow elsewhere district samples: gold analyses by A. E. Hubert; all other analyses by E. L. Mosier and K. C. Watts; detected]

Empi	re distric	et—Contir	ued	Areas other than Empire district						
A	spen—(	Continued								
Branch Leaves				Averag	Average metal content of—					
(5 samples)		(9 samples)		Deciduous trees and	Conifer needles 1	1,000+ species of	Vascular plants 3	vascular plants in which metal		
Min	Max	Min	Max	shrubs 1	needles -	plants 2	plants	found		
< 0.04	1.		0,1			< 0.007				
300	500	50	150	150	240	183	112	99.9		
N(10)	<10	N(10)	<10				30	2.8		
N(5)	_ 5	N(5)	. 5	.5	2	13	25	4.7		
70	500	_30	300	16	38	70	111	88		
1,000	2,000	700	1,000	2,100	1,500	1,400	1,010	99.9		
2	15	N(0.5)	2			<1	5	1.5		
	N(10)		N(10)				68	1.9		

#### B14 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

Table 2.—Matrix showing correlation of selected metals in mull ash with each other and with percent ash

[Numbers are linear correlation coefficients calculated after logarithmic transformation. Boldface figures indicate significant positive correlation; italic figures indicate slight positive correlation; roman figures indicate insignificant correlation; and boldface italic figures indicate slight to significant negative correlation]

Cu	.45										
Bi	.22	.37									
Ag	02	.27	.21								
Pb	17	. 19	.18	.55							
Zn	06	.18	-08	. 48	.46						
Mo	08	.13	.05	. 35	.31	.29					
Sn	.26	. 37	. 33	.28	.31	.19	.25	l	_		
W	.25	.21	.15	.03	11	01	.24	.27			
Fe	.27	.42	.02	.09	.10	.14	.04	.13	.12		
Mn	26	.20	.31	. 33	. 58	.34	.21	.11	12	.08	
Percent ash	. 17	03	08	32	37	27	19	06	.15	.04	30
	Au	Cu	Bi	Ag	Pb	Zn	Mo	Sn	W	Fe	Mn

Table 3.—Matrix showing correlation of selected metals in soil with each other

[Numbers are linear correlation coefficients calculated after logarithmic transformation. Boldface figures indicate significant positive correlation; italic figures indicate slight positive correlation; and roman figures indicate insignificant correlation.

Cu	.27	Ì										
Bi	.34	.31										
Ag Pb	.12	.12	.16									
Pb	03	.19	.09	.17								
Zn	02	.10	09	. 17	.03							
Mo	02	.14	.04	.13	.07	.007						
Sn	.20	. 26	.25	. 13	.09	.002	.11					
w	.25	.19	.22	.17	.10	03	. 13	.37				
Fe	.15	. 46	.22	08	.14	.11	.04	. 12	.12			
Mn	.02	. 34	.02	06	. 30	.26	.09	03	04	. 52		
Te	.18	.03	.05	.03	03	.05	.01	.06	.17	06	11	
Hg	.23	. 32	.17	.16	.11	. 15	001	.10	.14	.29	.25	.09
	Au	Cu	Bi	Ag	Pb	Zn	Mo	Sn	w	Fe	Mn	Te

Gold, copper, and bismuth show either significant or slight positive correlations with each other in both the mull ash and the underlying soil.

Silver, lead, zinc, molybdenum, and manganese show significant positive correlations with each other in mull ash with the exception of the zinc-molybdenum pair (slight positive correlation), but all these metals show only slight to insignificant correlations with each other in the underlying soil. The significant positive correlations among silver, lead, zinc, molybdenum, and manganese in mull ash and the absence of significant correlations among these metals in the transported soil suggest that the metals in the mull reflect mineralized bedrock, particularly in the absence of any known source of contamination. The percentage of mull ash is an inverse function of the amount of organic matter in the mull (see definition, p. 3). The inverse relation of silver and lead with percentage of mull ash indicates a direct relation of silver and lead with the organic matter in the

mull. Therefore, the biogeochemical origin of silver and lead in the mull is demonstrated by the significant negative correlation that percentage of mull ash shows with the silver and lead.

Although tin values are relatively low (fig. 18), the widespread distribution of tin in mull ash is suggested by the significant to slight positive correlation that tin shows with copper, bismuth, lead, silver, tungsten, gold, and molybdenum in mull ash. Tin shows a significant positive correlation with tungsten and a slight positive correlation with gold, copper, and bismuth in soil.

#### SUMMARY

In the Empire district, gold deposits in bedrock beneath the colluvial and glacial cover are best delineated by the gold and, to a lesser extent, by the copper and bismuth content of the mull ash. The distribution of anomalously high amounts of these metals in the soil below the mull corresponds to the gold deposits in bedrock only in places, and many of the high anomalies in soil probably reflect the inclusion of vein material in otherwise barren colluvial or morainal cover.

Zoning of the metals into two principal groups (gold-copper-bismuth and silver-lead-zinc-molybdenum-manganese) is shown in the geochemical maps and is substantiated by the correlation analysis. In general, the central part of the mapped area—that area bounded on the west by Lion Creek and on the east by North Empire Creek—contains the principal high gold-copper-bismuth anomalies. High silver-lead-zinc-molybdenum-manganese anomalies encircle—more prominently on the west than on the east—the central zone. Tungsten and tin correspond with each other and in part with the high gold-copper-bismuth anomalies to form a rather extensive high anomaly on Lion Creek at the west end of the Silver Mountain ore zone.

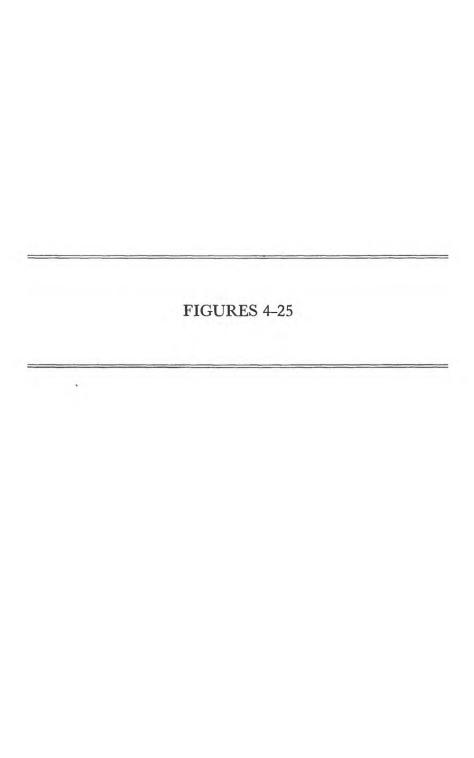
The histograms show that the mull ash is appreciably enriched in gold, silver, bismuth, lead, zinc, molybdenum, and tin relative to soil, whereas the mull ash is moderately enriched in copper and is only slightly enriched in tungsten relative to soil.

The accumulation of gold, silver, and other metals by trees is demonstrated by the presence of these metals in the interior of roots, trunks, and branches and in pine needles and aspen leaves. This accumulation probably accounts for most of the metal content of the mull.

The results obtained in the Empire district suggest that mull may be an effective geochemical sampling medium for gold, silver, bismuth, lead, and zinc in forested areas blanketed by colluvium or glacial drift where the transported material offers no clue to the nature of the underlying bedrock.

#### REFERENCES CITED

- Boyle, R. W., and Dass, A. S., 1967, Geochemical prospecting—Use of the A horizon in soil surveys: Econ. Geology, v. 62, no. 2, p. 274-276.
- Braddock, W. A., 1969, Geology of the Empire quadrangle, Grand, Gilpin, and Clear Creek Counties, Colorado: U.S. Geol. Survey Prof. Paper 616, 56 p.
- Cannon, H. L., 1960, Botanical prospecting for ore deposits: Science, v. 132, no. 3427, p. 591-598.
- Cox, M. W., and Hollister, V. F., 1955, The Chollet project, Stevens County, Washington: Mining Eng., v. 7, no. 10, p. 937-940.
- Goldschmidt, V. M., 1937, The principles of distribution of chemical elements in minerals and rocks: Chem. Soc. [London] Jour., January-June, p. 655-673.
- ——— 1954, Geochemistry: Oxford, Clarendon Press, 730 p.
- Grimes, D. J., and Marranzino, A. P., 1968, Direct-current arc and alternating-current spark emission spectrographic field methods for the semiquantitative analysis of geologic materials: U.S. Geol. Survey Circ. 591, 6 p.
- Harrison, L. C., 1964, Empire and the Berthoud Pass: Denver, Big Mountain Press, 482 p.
- Kvalheim, Aslak, ed., 1967, Geochemical prospecting in Fennoscandia: New York, Interscience Publishers, 350 p.
- Lakin, H. W., and Thompson, C. E., 1963, Tellurium—A new sensitive test: Science, v. 141, no. 3575, p. 42-43.
- Lovering, T. S., and Goddard, E. N., 1950, Geology and ore deposits of the Front Range, Colorado: U.S. Geol. Survey Prof. Paper 223, 319 p. [1951].
- Lounamaa, J., 1967, Trace elements in trees and shrubs growing on different rocks in Finland, in Kvalheim, Aslak, ed., Geochemical prospecting in Fennoscandia: New York, Interscience Publishers, p. 287-317.
- Shacklette, H. T., 1965, Element content of bryophytes: U.S. Geol. Survey Bull. 1198-D, 21 p.
- Sims, P. K., Drake, A. A., Jr., and Tooker, E. W., 1963, Economic geology of the Central City district, Gilpin County, Colorado: U.S. Geol. Survey Prof. Paper 359, 231 p.
- Spurr, J. E., and Garrey, G. H., 1908, Economic geology of the Georgetown quadrangle (together with the Empire district), Colorado, *with* General geology, by S. H. Ball: U.S. Geol. Survey Prof. Paper 63, 422 p.
- Thompson, C. E., Nakagawa, H. M., and VanSickle, G. H., 1968, Rapid analysis for gold in geologic materials, in Geological Survey research 1968: U.S. Geol. Survey Prof. Paper 600–B, p. B130–B132.
- U.S. Department of Agriculture, 1951, Soil survey manual: U.S. Dept. Agriculture Handbook 18, 503 p.
- Vaughn, W. W., and McCarthy, J. H., Jr., 1964, An instrumental technique for the determination of submicrogram concentrations of mercury in soils, rocks, and gas, in Geological Survey research 1964: U.S. Geol. Survey Prof. Paper 501-D, p. D123-D127.



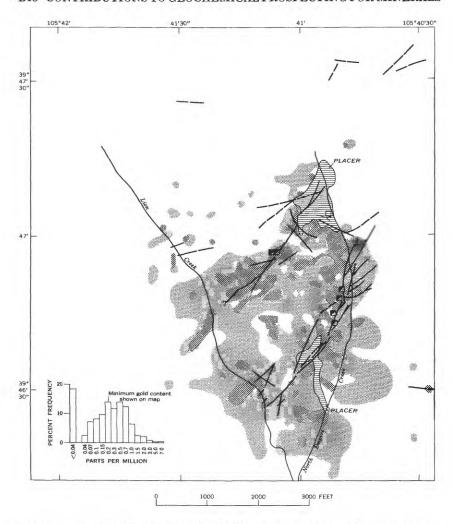


FIGURE 4.—Gold distribution in mull ash. Light stipple, ash contains 0.2-0.59 ppm gold; heavy stipple, ash contains at least 0.6 ppm gold. Heavy lines are veins. Analyses by A. E. Hubert.

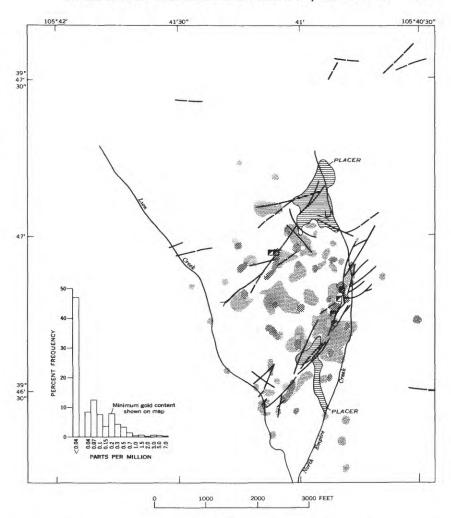


FIGURE 5.—Gold distribution in soil (6– to 12–inch depth). Light stipple, soil contains 0.2–0.59 ppm gold; heavy stipple, soil contains at least 0.6 ppm gold. Heavy lines are veins. Analyses by A. E. Hubert.

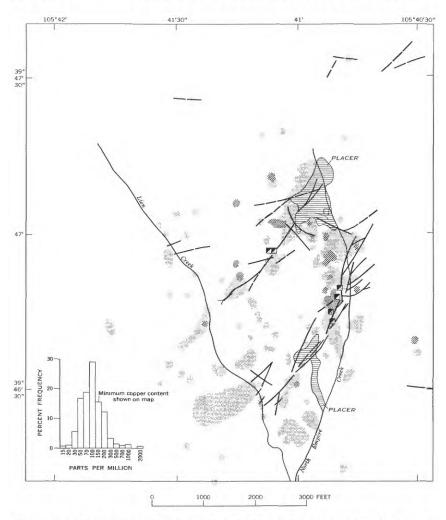


Figure 6.—Copper distribution in mull ash. Light stipple, ash contains 150-299 ppm copper; heavy stipple, ash contains at least 300 ppm copper. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

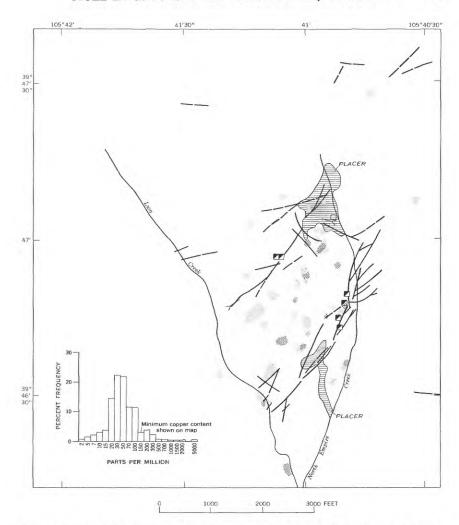


FIGURE 7.—Copper distribution in soil (6- to 12-inch depth). Light stipple, soil contains 150-299 ppm copper; heavy stipple, soil contains at least 300 ppm copper. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

#### B22 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

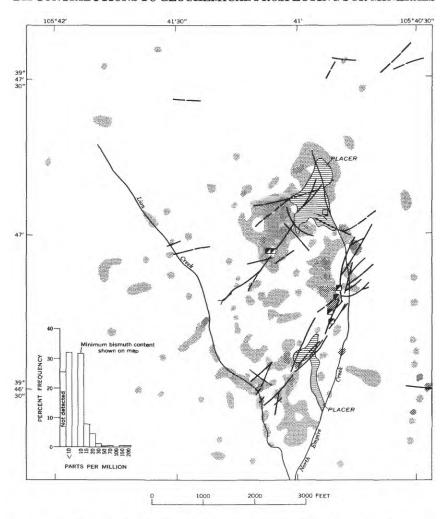


FIGURE 8.—Bismuth distribution in mull ash. Light stipple, ash contains 10–19 ppm bismuth; heavy stipple, ash contains at least 20 ppm bismuth. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

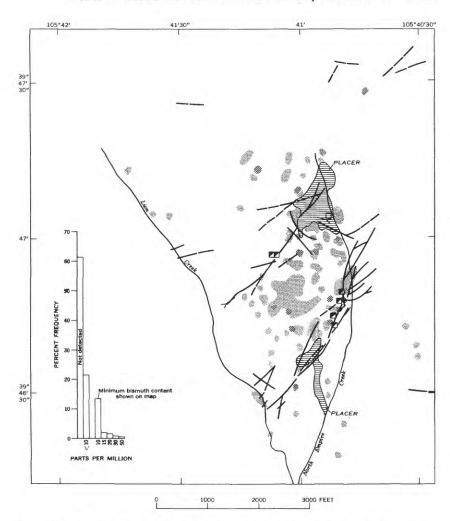


FIGURE 9.—Bismuth distribution in soil (6- to 12-inch depth). Light stipple, soil contains 10-19 ppm bismuth; heavy stipple, soil contains at least 20 ppm bismuth. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

## B24 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

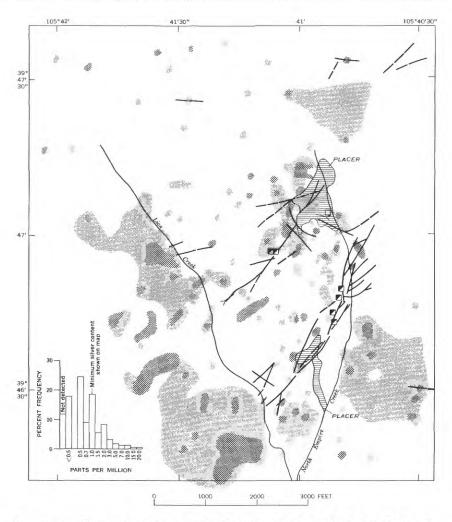


FIGURE 10.—Silver distribution in mull ash (6- to 12-inch depth). Light stipple, ash contains 1-1.9 ppm silver; heavy stipple, ash contains at least 2 ppm silver. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

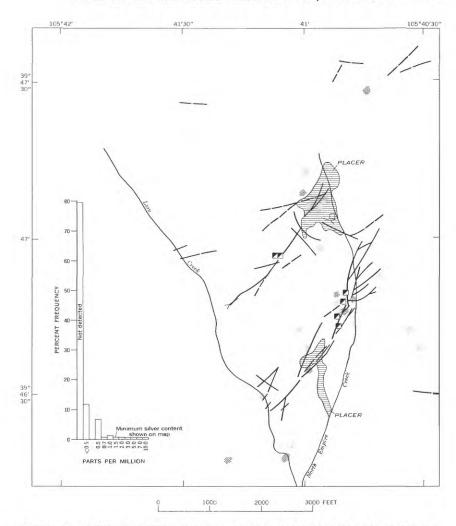


Figure 11.—Silver distribution in soil (6- to 12-inch depth). Light stipple, soil contains 1-1.9 ppm silver; heavy stipple, soil contains at least 2 ppm silver. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

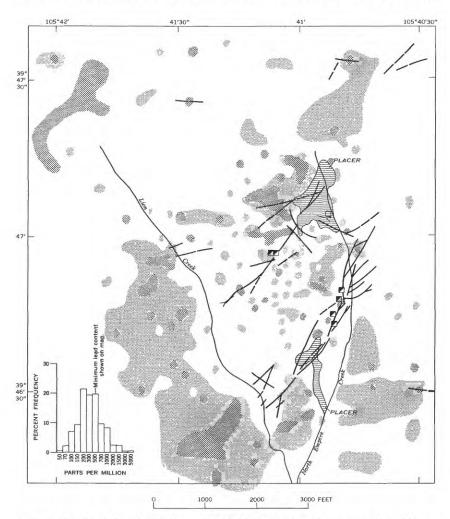


FIGURE 12.—Lead distribution in mull ash. Light stipple, ash contains 500-999 ppm lead; heavy stipple, ash contains at least 1,000 ppm lead. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

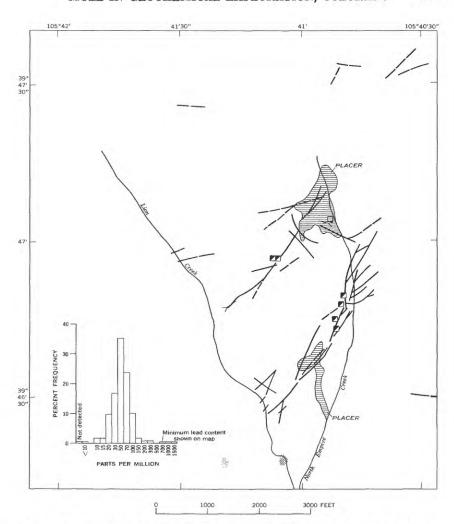


FIGURE 13.—Lead distribution in soil (6- to 12-inch depth). Light stipple, soil contains 500-999 ppm lead; heavy stipple, soil contains at least 1,000 ppm lead. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

## B28 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

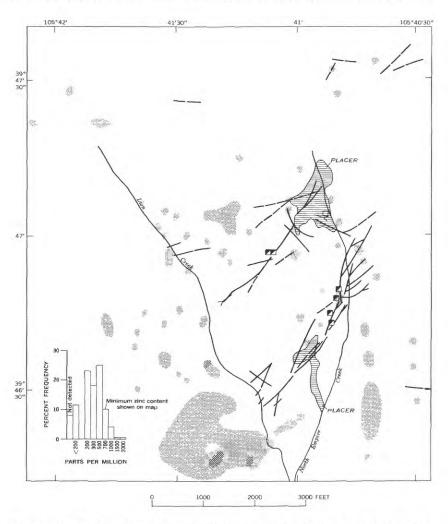


Figure 14.—Zinc distribution in mull ash. Light stipple, ash contains 700–1,499 ppm zinc; heavy stipple, ash contains at least 1,500 ppm zinc. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

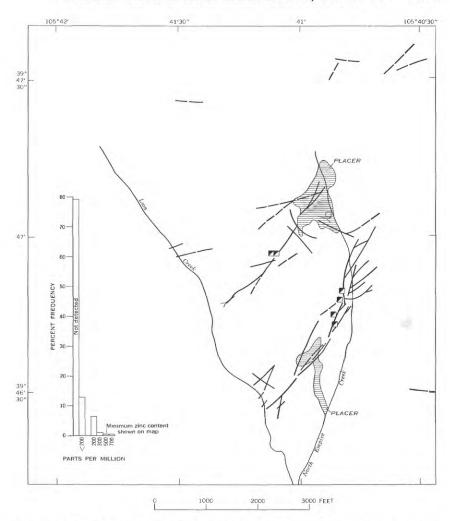


FIGURE 15.—Zinc distribution in soil (6- to 12-inch depth). Stipple area, soil contains 700-999 ppm zinc. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

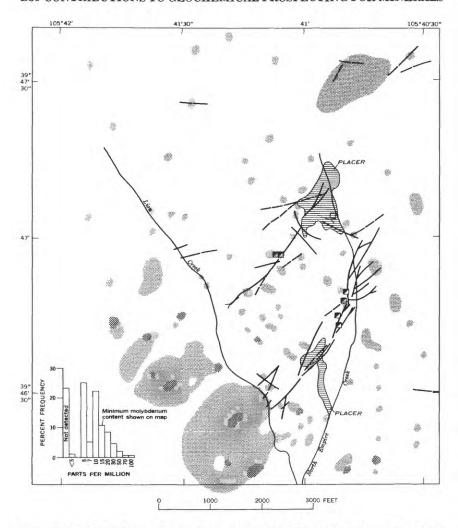


FIGURE 16.—Molybdenum distribution in mull ash. Light stipple, ash contains 15–49 ppm molybdenum; heavy stipple, ash contains at least 50 ppm molybdenum. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

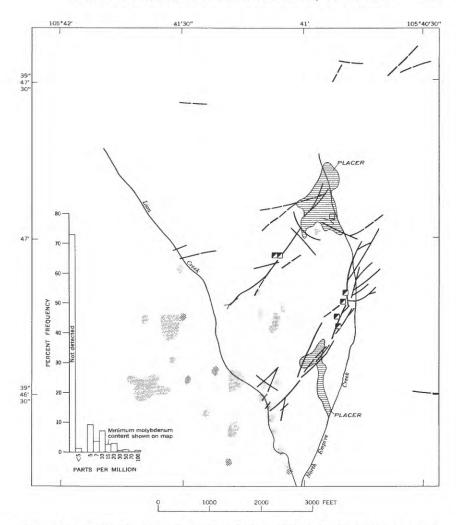


Figure 17.—Molybdenum distribution in soil (6- to 12-inch depth). Light stipple, soil contains 15-49 ppm molybdenum; heavy stipple, soil contains at least 50 ppm molybdenum. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

## B32 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

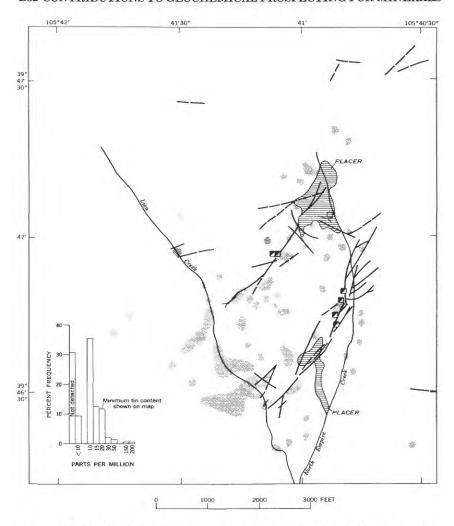


FIGURE 18.—Tin distribution in mull ash. Light stipple, ash contains 20-69 ppm tin; heavy stipple, ash contains at least 70 ppm tin. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

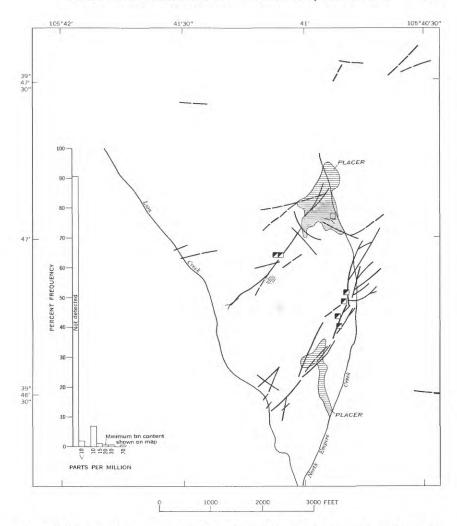


FIGURE 19.—Tin distribution in soil (6- to 12-inch depth). Light stipple, soil contains 20-69 ppm tin; heavy stipple, soil contains at least 70 ppm tin. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

## B34 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

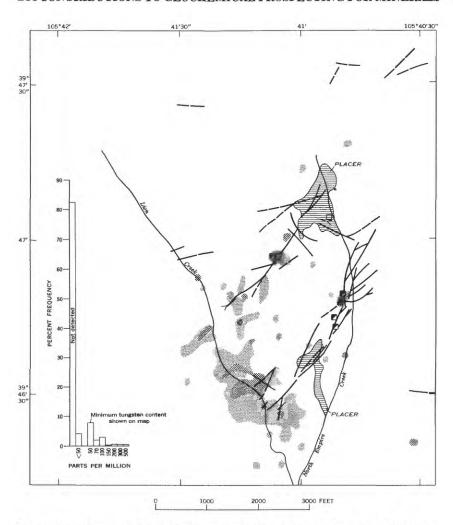


Figure 20.—Tungsten distribution in mull ash. Light stipple, ash contans 50-99 ppm tungsten; heavy stipple, ash contains at least 100 ppm tungsten. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

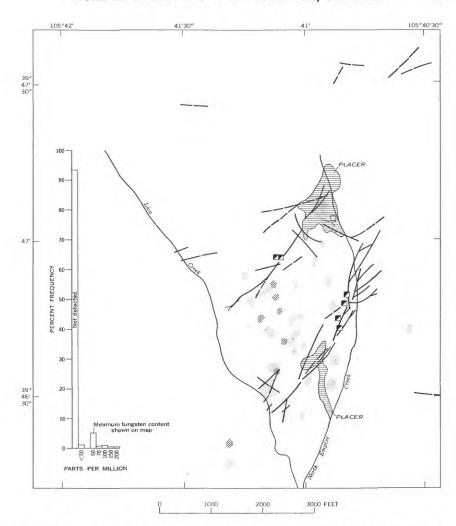


Figure 21.—Tungsten distribution in soil (6- to 12-inch depth). Light stipple, soil contains 50-99 ppm tungsten: heavy stipple, soil contains at least 100 ppm tungsten. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.

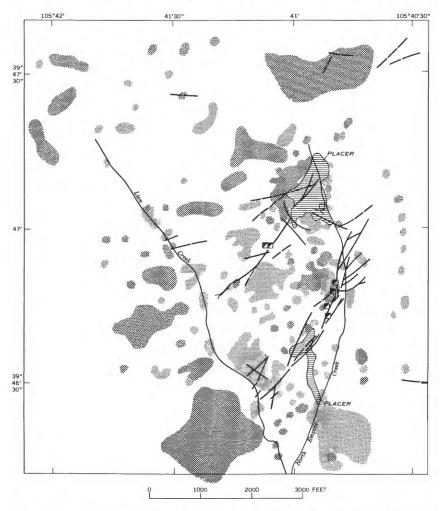
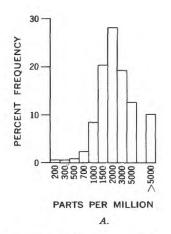


FIGURE 22.—Manganese distribution in mull ash. Light stipple indicates that ash contains 1,500 ppm or less manganese; heavy stipple, ash contains 5,000 ppm or more manganese. Heavy lines are veins. Analyses by E. L. Mosier and K. C. Watts.



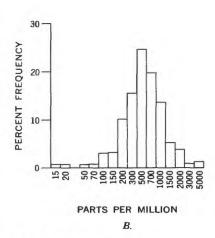


FIGURE 23.—Manganese distribution in mull ash (A) and in soil (B).

## B38 CONTRIBUTIONS TO GEOCHEMICAL PROSPECTING FOR MINERALS

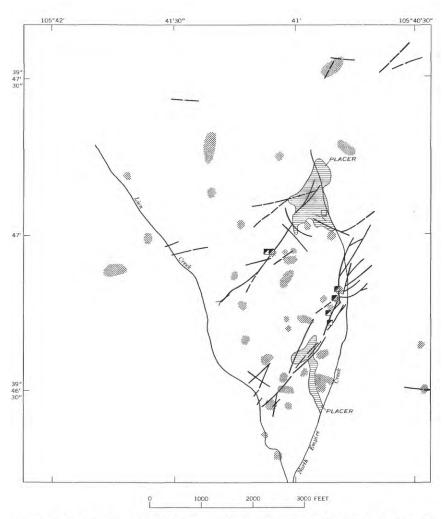


FIGURE 24.—Tellurium distribution in soil (6- to 12-inch depth). Stippled areas, soil contains at least 0.5 ppm tellurium. Heavy lines are veins. Analyses by R. L. Turner and J. R. Watterson.

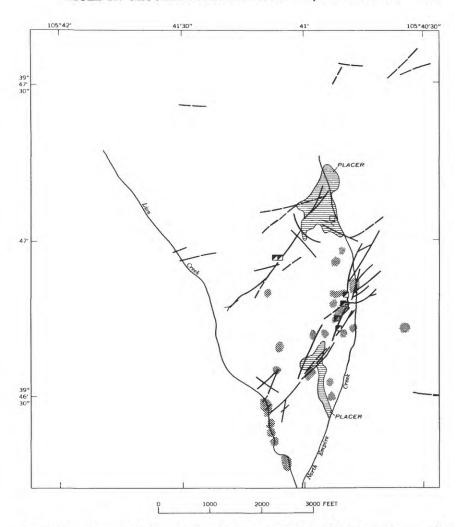


FIGURE 25.—Mercury distribution in soil (6- to 12-inch depth). Stippled areas, soil contains at least 0.1 ppm mercury. Heavy lines are veins. Analyses by W. W. Janes.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1971 0-423-560





