A Geochemical Study of Alluvium-Covered Copper Deposits in Pima County, Arizona

By LYMAN C. HUFF

With a section on ANALYTICAL METHODS

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CONTRIBUTIONS TO ECONOMIC GEOLOGY

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A GEOCHEMICAL STUDY OF ALLUVIUM-COVERED COPPER DEPOSITS IN PIMA COUNTY, ARIZONA

By Lyman C. Huff

ABSTRACT

The dispersion pattern of the ore metals around the covered copper deposits in the Pima district of southern Arizona was studied to find out if any geochemical prospecting techniques could be used in the search for other deposits concealed beneath alluvium. Materials sampled include the 200-foot-thick Pleistocene(?) alluvial gravels overlying the ore, soils developed on the Pleistocene(?) alluvium, modern alluvium, ground water from wells, and vegetation. These samples were analyzed colorimetrically for copper and for molybdenum, and some were analyzed spectrographically for associated elements.

The soil and alluvium samples generally were found to contain from 25 to 100 ppm (parts per million) copper. Most of this copper appears to have been derived from scattered ore deposits several miles distant. Analysis of samples from the Pima Mining Co. open pit suggests that the deeper alluvium has a similarly low copper content except at its base, where, just above bedrock, carbonate-cemented alluvium contains more than 4,000 ppm copper. This high concentration, apparently the result of deposition by copper-rich ground water, was traced in drill holes 1.5 miles northeast of known ore deposits.

The alluvium and soils contain little molybdenum. Near the ore deposits, the ground water contains as much as 250 ppb (parts per billion) molybdenum, and in areas distant from ore deposits it contains from 4 to 6 ppb. Anomalous concentrations of molybdenum, apparently derived from the buried ore deposits, were detected in ground water 8 miles northeast of the deposits. Thus, the anomalous concentrations of molybdenum can be traced much farther than those of copper.

The molybdenum content of plant ash ranges from about 4 to 220 ppm. Among the species compared, mesquite, a deep-rooted phreatophyte, contains the most molybdenum. The greatest molybdenum concentrations were found in the same general area where ground water has a high molybdenum content, which suggests that most of the molybdenum in this mesquite is derived from the ground water rather than from the alluvium.

Tracing the dissolved metals in ground water appears to be the most promising geochemical prospecting technique for finding similar hidden deposits. In the Sonoran Desert, the molybdenum content of ground water and phreatophytes apparently can be used to locate large areas in which the molybdenum content is anomalously high. Within these areas, widely spaced core drilling and analysis of the basal conglomerate for copper may provide useful local guides for the location of buried ore.

INTRODUCTION

The study of hidden ore deposits is of ever-increasing interest in mineral exploration. Exposed ore deposits are comparatively easy to find, and most were found long ago. New deposits are becoming more and more difficult to find. Recent ore discoveries include an increasingly high proportion that are hidden beneath a barren cover of lava, sedimentary rock, or alluvium. To assure a future source of mineral resources, we must study these covered ore deposits and develop geochemical exploration techniques and other scientific prospecting methods for finding more.

The vast areas of unexplored bedrock under alluvial cover in the Basin and Range physiographic province are particularly favorable for future ore discovery. The ore deposits yet to be found in this province, as suggested by Nolan (1950), may exceed in number the many that have been found to date, and many of the hidden deposits undoubtedly occur at a practical mining depth on thinly covered bedrock pediments.

The first notable discovery of this type was made in the Pima mining district of southern Arizona in 1951. The author conducted geochemical investigations there to determine how far from known ore deposits abnormal concentrations of the ore metals copper and molybdenum can be detected and what geochemical techniques are best for finding similar ore bodies both in this district and elsewhere. A previous report briefly describes some of the data obtained for molybdenum (Huff and Marranzino, 1961).

The materials sampled were selected to investigate the secondary or supergene dispersion of the ore metals. Part of the dispersion of the ore was by mechanical removal from outcrops and incorporation in alluvium, part was by solution in surface runoff or ground water, and part was the result of geochemical cycling by plants. Thus, soil, alluvium, water, and plants were selected for sampling.

GEOGRAPHY

The Pima mining district is in Pima County, Ariz., about 15 miles southwest of Tucson and is included in the Twin Buttes and San Xavier Mission quadrangles. About 6 miles to the southwest lies the main mass of the Sierrita Mountains (fig. 1). This low, maturely dissected range is bounded on all sides by the very extensive Sierrita pediment, which extends from the foot of Samaniego Peak, 8 miles southwest of Mineral Hill, to the Santa Cruz River and the city limits of Tucson, about 11 miles northeast of Mineral Hill (fig. 1). Close to the mountains, the pediment is a surface of low relief cut on granodiorite, and at its distal margin, near the Santa Cruz River, it is covered by gravelly alluvium several hundred feet thick. This alluvium covers much of the Pima mining district and obscures geologic details in the bedrock (Cooper, 1960, pl. 1).

Within the district several small hills, such as Mineral Hill, Helmet Peak, and Twin Buttes, rise above the pediment surface much like islands above a sea.

Altitudes in the area range from 5,991 feet at Samaniego Peak in the northern Sierritas, to 4,400 feet at the head of the pediment, to 3,300 feet at the Pima mine, and to 2,600 feet along the bank of the Santa Cruz River near Tucson. Precipitation in this part of the Sonoran Desert averages 10 inches per year, and the vegetation consists of saguaro, palo verde, cholla, prickly pear, mesquite, and other desert plants.

ACKNOWLEDGMENTS

The writer is very much indebted to the local mining companies and to various individuals who have provided chemical and geologic data and samples or permission to sample, thereby facilitating this investigation. Special acknowledgment is due the American Smelting and Refining Co., the Banner Mining Co., the Bear Creek Mining Co., the Duval Corp., the Pima Mining Co., and R. C. Cribbs and H. A. Schmitt of Tucson, Ariz. John Baldessari of the U.S. Geological Sur-

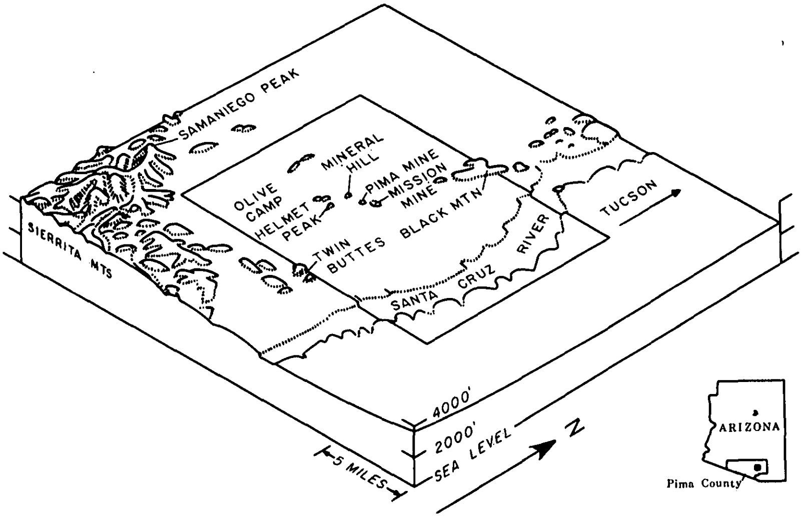

FIGURE 1.—Block diagram showing the setting of the Pima mining district and vicinity.

vey, and Juan Aspilcueta, Hector de la Iglesia, Abraham Jutoran, Akgun Mertdogan, Rudoljub Novacovic, and Raul Sister, participants in the program of the Agency for International Development, assisted in the fieldwork. A. P. Marranzino, H. M. Nakagawa, Uteana Oda, and C. E. Thompson, U.S. Geological Survey chemists, made the chemical analyses and also assisted in the fieldwork.

BEDROCK AND ORE DEPOSITS

The bedrock of the Pima mining district has been studied extensively (Ransome, 1922; Lacy, 1959; Cooper, 1960; Lacy and Titley, 1962; Kinnison, 1966) and will be reviewed only briefly here. A granodiorite batholith of Cretaceous or Tertiary age forms the core of the nearby Sierrita Mountains. Along the northeast margin of the batholith, Precambrian granite and Paleozoic and Mesozoic sedimentary rocks have been folded, faulted, and intruded by small bodies of diorite, andesite, granodiorite, and quartz monzonite porphyry. In this belt are the islandlike hills, such as Mineral Hill and Helmet Peak, which are composed of steeply dipping Paleozoic sedimentary rock. Black Mountain (fig. 1), which is north of the Pima district but within the area of geochemical study, is composed of unmetamorphosed and little-disturbed upper Tertiary basalt and andesite (Heindl, 1959).

The structural geology of the district is complicated and has been only partly deciphered. In the Mineral Hill–Helmet Peak area, the Paleozoic and Mesozoic rocks form the upper plate of the low-angle San Xavier thrust fault. Granodiorite of the batholith underlies the fault at a depth of about 800 feet. Ore mineralization postdated some faulting and the deposition of the Tertiary (Miocene) Helmet Fanglomerate but apparently predated movement along the San Xavier thrust. The ore deposits probably are genetically related to the porphyry intrusives along the northeast margin of the batholith (Cooper, 1960, p. 66).

Small high-grade ore deposits were discovered in this district prior to 1880 and have been mined intermittently by underground methods. The deposits include the Olive Camp group, mined chiefly for gold and silver but containing some accessory copper, lead, and zinc; the San Xavier deposit, mined chiefly for lead and zinc; and the Mineral Hill deposit, mined chiefly for copper. These deposits are mostly fissure fillings and replacement bodies along faults and breccia zones. At Olive Camp and Mineral Hill, they are characterized by an abundance of malachite and chrysocolla where they crop out at the surface and by a lack of supergene enrichment at depth. The alluvium in washes draining these deposits contains scattered pebbles of oxidized copper ore derived from mineralized outcrops and old mine dumps. During weathering and erosion of these deposits, much of the copper is dispersed in the washes by mechanical transport of copper-rich sediment.

The Pima copper deposit was discovered in 1951 by geophysical methods and exploratory drilling through about 200 feet of alluvium (Thurmond and others, 1955). This deposit and the similar Mission copper deposit discovered later (Richard and Courtright, 1959) contain large tonnages of disseminated ore and are being mined in large open pits (fig. 2). These deposits consist of copper and molybdenum minerals disseminated in porphyry intrusives and in metasedimentary wallrock.

Chalcopyrite is the dominant copper mineral in the disseminated copper deposits at the Pima and Mission mines. The sulfide ore also contains pyrite and some molybdenite. Supergene copper minerals—malachite, chrysocolla, and a little chalcocite—occur in a thin layer overlying the sulfide ore just beneath the pediment gravel (Richard and Courtright, 1959, fig. 1), suggesting that there has been some local movement of copper dissolved in ground water. Some copper must have been mechanically dispersed as well, because ore was exposed to erosion when the basal beds of the pediment gravel were deposited.

FIGURE 2.—Pima open pit mine, showing the 200-foot-thick overburden of alluvium sampled during the geochemical study.

SURFICIAL DEPOSITS

The surficial deposits were studied in somewhat greater detail than they had been before to better guide the direction of geochemical study of these deposits. The age of the deposits is somewhat in doubt. They are classified here as Pleistocene(?) and Holocene(?).

PLEISTOCENE(?) DEPOSITS

CARBONATE-CEMENTED CONGLOMERATE

At the base of the surficial sequence is a distinctive zone of conglomerate firmly cemented with calcium carbonate. In the open pit mines, it must be drilled and blasted before it can be removed, and it limits the depth to which scrapers can be used. Its local name, caliche, will not be used here because of uncertainty concerning its origin.

The carbonate-cemented conglomerate varies considerably in thickness. Measurements made by planetable and alidade in the Pima mine showed that it rests upon an irregular bedrock surface and ranges in thickness from 5 to 70 feet. It is thickest in valleys cut into the bedrock surface.

The conglomerate ranges from light yellowish gray (5*Y* 8/2) to moderate reddish orange (10*R* 6/6) (Goddard and others, 1948); most of the reddish-orange color is in the matrix. Component fragments range from boulders more than 1 m (meter) across to coarse sand grains 1–2 mm (millimeter) in diameter. About one-third of the fragments are pebbles, 4–32 mm across. The pebbles are angular and fairly well sorted but closely packed and well cemented by the matrix.

At the Pima mines the fragments consist of andesite and andesitic tuff, quartz monzonite porphyry, granite, quartzite, quartzitic siltstone, and silicified limestone. Also present are pebbles of gray, yellow, and white limestone and others of clear crystalline vein quartz. The pebbles and cobbles of granite are more highly rounded than the other fragments. Many fragments of porphyry are silicified, contain disseminated sulfied minerals, and are stained with limonite. Sand grains and granules in the conglomerate are chiefly quartz and feldspar fragments. The cement consists mostly of white crystalline calcite with thin seams of pinkish plastic clay.

Bedding in the conglomerate is indistinct. The contact with the overlying alluvium transects the bedding and is defined by the upper limit of the cemented zone. The contact with the underlying bedrock is sharp. Some fragments at the base of the conglomerate are composed of rock identical with the underlying bedrock and apparently were moved only a few feet prior to deposition. In most exposures in the Pima mine, the conglomerate rests upon oxidized ore stained with greenish malachite or chrysocolla, although none of these minerals were found in the conglomerate itself.

The preceding description generally applies also to exposures of conglomerate at localities other than the Pima mine (fig. 3). Outside the mine, the conglomerate ranges in thickness from a few inches to about 10 feet. Wherever found, it is at the base of the alluvium; no conglomerate was found overlying unconsolidated gravel.

According to some local geologists, the carbonate cement was deposited at the same time as the gravel or shortly thereafter. For this reason they call it caliche. The author found many etched and partly dissolved pebbles of limestone in the alluvium that overlies the conglomerate. Thus, it seems likely that some of the carbonate cement originated by deposition from downward-percolating calcium bicarbonate-laden waters after most of the overlying alluvium was deposited. If so, the conglomerate is unlike most soil caliche in origin.

FIGURE 3.—Carbonate-cemented basal conglomerate overlying bedrock as exposed in wash near Helmet Peak.

OLDER UNCONSOLIDATED ALLUVIUM

The unconsolidated alluvium above the basal conglomerate is a mixture of silt, sand, pebbles, and a few cobbles and boulders. The pebbles are similar to those of the conglomerate below, except that limestone pebbles are absent from the uppermost beds, and they are etched and partly dissolved in the middle beds. In the Pima mine, individual gravel lenses range in thickness from about 1 to 5 feet and in length from 10 to 50 feet. They lie approximately parallel to the pediment surface. Internal cross-stratification in the gravel beds is simple and dips gently. Much of the gravel is well sorted; interstices are only partly filled with sand and silt. Massive beds of silt are interbedded with gravel lenses. The contacts are gradational at the top of the gravel beds but sharp at the bottom. Many gravel lenses occupy shallow channels cut in the silty beds. In the open pit mines, where the thickness of the unconsolidated alluvium averages about 150 feet, the proportion of silty beds increases irregularly upward. The silty beds are locally colored white by a thin caliche coating, but they contain no noteworthy buried soils.

The lithology of pebbles in the unconsolidated alluvium across the Sierrita pediment reflects the rocks from which the pebbles were derived. Near the open pit mines and to the south, the pebbles consist largely of sandstone, arkose, rhyolite, and porphyry; granite pebbles are scarce. North and northwest of the mines, all the pebbles are igneous rock; most are granite and a few are pegmatite and vein quartz. The average size decreases markedly away from the mountains. Near the Santa Cruz River, the older alluvium consists mostly of sand with only a few scattered pebbles.

OLDER SOIL

The alluvium is covered by remnants of an old soil along the low divides between the modern washes. One prominent horizon in this soil is a caliche-cemented layer about 3 feet thick which is commonly within 3 feet of the surface. A red clay horizon with a maximum thickness of 1 foot occurs just above the caliche. This old soil appears to have developed on the original surface of the Pleistocene(?) alluvium. Dissection of this surface to a depth of about 10 feet has exposed these horizons and removed most of the red clay horizon. In areas where the caliche zone is exposed, its top surface is highly irregular and, somewhat like a miniature karst topography, shows the effect of late leaching.

The older soil and the underlying alluvium on the Sierrita pediment are probably Pleistocene in age. An artifact and a turtle shell which were found between depths of 150 and 175 feet in the Pima mine are of Pleistocene age (John Journay, Pima Mining Co., oral commun., 1962). All the alluvium must be considerably younger than the folded Helmet Fanglomerate of Miocene age (Cooper, 1960) and the latest diastrophic tilting of the Sierritas, because there is no evidence of significant diastrophic changes of the Sierrita pediment or of its alluvial cover.

HOLOCENE(?) DEPOSITS

SOIL

A light-brown loam composed of silt, sand, and scattered pebbles covers most of the land surface. This material is about half a foot thick and, like other desert sierozems, lacks organic material. Locally this soil covers the red clay layer of the older soil, but in places it rests upon the caliche horizon of the older soil. The uniformly brown color and high silty content, even where it rests upon materials lacking silt, suggest that much of this modern soil is loessial in origin. In fact, fresh accumulations of silt around grass clumps and larger plants indicate some present-day deposition of windblown material.

ALLUVIUM

The Holocene(?) or modern alluvium is a clean well-sorted sand or sandy gravel which covers the beds of the present-day washes (fig. 4). Typically the washes are 20–100 feet wide and 2–10 feet lower than the general alluvial surface. This modern alluvium is probably nowhere more than 10 feet thick. A few chrysocolla-coated pebbles derived from mineralized outcrops, mine workings, and mine dumps occur locally in the alluvium. As a result of the incorporation of metal-rich material from mine dumps and tailings, the copper content of the alluvium in many present-day washes is probably greater than it was before mining started.

Remnants of the Pleistocene(?) soil on the divides show that these areas have not been crossed by modern streams. Thus, the drainage divides on the pediment, though very low, appear to have been long established, and the possible source area of any particular sample of this modern alluvium can be determined from the location of these divides.

GEOCHEMICAL INVESTIGATIONS

Most of the materials sampled for the geochemical study were surficial deposits directly overlying or near the hidden ore bodies. These included residual soil, modern alluvium, older alluvium, carbonate-cemented conglomerate, ground water, and plants.

Samples of modern soil were collected and sieved at the site with an 80-mesh stainless steel and aluminum sieve; the fine fraction was stored in a paper envelope and the coarse fraction discarded. Samples

FIGURE 4.—Alluvium in modern wash on Sierrita pediment. Soil-covered older alluvium in background.

were taken at a depth of 2 inches to minimize the effect of possible contamination by metal-rich dust from mine dumps. In many places, samples of the underlying red clay and caliche horizons of the old or Pleistocene(?) soil were collected also.

The modern alluvium was sampled by compositing grab samples from five or six places along the channel of the wash and sieving to the minus-80-mesh fraction at the sample site. Previous work has shown that in an arid climate most of the detrital copper is in the fine fraction of the alluvium (Lovering and others, 1950); thus, screening concentrates the copper.

Most ground-water samples were collected from pumping wells. To minimize compositional changes, they were stored in polyethylene bottles from 1 to 4 liters in size and were analyzed within a few days after collection.

Most plant samples were twigs of mesquite three-eighths of an inch or less in diameter. The twigs were clipped into segments from ½ to 1 inch in length and stored in half-pint cardboard cartons. Two plants were sampled at many sample sites to investigate sampling errors. At other sites leaves as well as twigs were collected.

ANALYTICAL METHODS

By A. P. Marranzino and H. M. Nakagawa

Both geochemical prospecting tests (colorimetric analyses) and spectrographic analyses were made. Most of the geochemical prospecting tests were made in a temporary laboratory set up in a Tucson motel kitchen, and the spectrographic analyses were made in Tucson in a truck-mounted spectrographic laboratory. To check these field values, many of the samples were reanalyzed by the same methods in the Denver laboratory of the U.S. Geological Survey. Details are given here for only the geochemical prospecting tests which depart from published descriptions.

SAMPLE PREPARATION

The minus-80-mesh fraction of the soil and alluvial samples required no preliminary treatment before analysis. Plant samples were ashed before analysis in unglazed alundum crucibles heated in a portable electric muffle furnace to 500° C for 1 hour. Portions of the ash for analysis were weighed using a simple spring balance (Huff, 1962) after it was learned that scooping of the fluffy ash gave erroneous results.

GEOCHEMICAL PROSPECTING TESTS FOR COPPER

The geochemical prospecting test for copper is the biquinoline method of Almond (1955) with slight modifications. The test for copper in water is as follows:

1. Pour 50 ml (milliliters) of the water sample into a 100-ml glass-stoppered cylinder.
2. Add 2 ml of copper buffer and 2 ml of the isoamyl alcohol solution of biquinoline, and shake cylinder for 30 seconds.
3. Compare the resulting pink color produced in the organic phase with standards similarly prepared.

The test for copper in soil or alluvium is as follows:

1. Transfer 0.1 g (gram) of the sample to a test tube.
2. Add 1.0 ml of 6 M hydrochloric acid and heat in a boiling water bath for 30 minutes.
3. Dilute contents of tube with metal-free water to 10 ml, and shake to mix.
4. Transfer an aliquot of 2 ml to a 22 × 150-mm test tube.
5. Add 10 ml of copper buffer and 2 ml of biquinoline reagent, and shake tube for 30 seconds.
6. Compare resulting pink color produced in organic phase with standards similarly prepared.

GEOCHEMICAL PROSPECTING TESTS FOR MOLYBDENUM

Molybdenum in water was determined by the thiocyanate method (Nakagawa and Ward, 1960), but without concentration on an ion-exchange resin. To eliminate the time-consuming task of preparing fresh reagent solutions daily in the field, the potassum thiocyanate solution and the stannous chloride solutions were placed in glass ampoules, which were sealed to prevent oxidation and decomposition. These solutions have been checked over a 6-month period and found to be stable.

The procedures for preparing the solutions in ampoule form are as follows:

Potassium thiocyanate solution, 10 percent

1. Dissolve 30 g of a potassium thiocyanate crystals in 300 ml of metal-free water.
2. Transfer of 3 ml of solution to each of 100 3-ml ampoules.
3. Seal the ampoule and store in a dark place.

The procedure for determining the content of molybdenum in water is as follows:

Stannous chloride solution, 10 percent

1. Dissolve 30 g of stannous chloride crystals in a 400-ml beaker containing 50 ml of concentrated hydrochloric acid and 250 ml of metal-free water.
2. Transfer 3 ml of solution to each of 100 3-ml ampoules.
3. Seal the ampoule and store in a dark place.

The procedure for determining the content of molybdenum in water is as follows:

1. Transfer 50 ml of the water sample to a 125-ml separatory funnel.
2. Add 5.5 ml of concentrated hydrochloric acid and 1 ml of a 1-percent solution of ferric ammonium sulfate.
3. Add the contents of an ampoule of potassium thiocyanate and mix.
4. Add the contents of an ampoule of stannous chloride solution and mix.
5. Add 1.25 ml isopropyl ether and shake funnel and contents for 30 seconds.
6. Let the phases separate.
7. Drain the aqueous phase until 10 ml remains in the funnel.
8. Transfer remaining aqueous phase and organic phase to a 16×150-mm test tube.
9. Compare the amber color in organic phase with standards for 1, 2, and 4 mg (milligrams) of molybdenum similarly prepared.

Molybdenum in plants was determined on the ash by using the thiocyanate method of Reichen and Ward (1951), slightly modified. The potassium thiocyanate and stannous chloride solutions are the same as those previously described. The plant ashes were free of carbonaceous material and required no fusion with lithium nitrate. The procedure is as follows:

1. To 50 mg of plant ash in a test tube add 5 ml of 6-percent hydrochloric acid and heat gently.
2. Add 1 ml of 10-percent potassium nitrate solution, 0.3 ml of 5-percent potassum thiocyanate solution, 0.5 ml of 10-percent stannous chloride solution, and 0.5 ml of isopropyl ether.
3. Cork and shake tube for 30 seconds.
4. Compare the amber color with standards for 0.5, 1, and 2 mg of molybdenum similarly prepared.

REPRODUCIBILITY OF RESULTS

The reproducibility of the geochemical prospecting tests was investigated by collecting two identical samples at many of the sample sites and analyzing them separately. Reproducibility was measured by calculating the coefficient of variation of each pair of analyses. In some experiments, two different kinds of samples from the same sample site were compared. For these, an increase of the coefficient of variation measures the bias introduced by using different kinds of samples.

The geochemical prospecting test used for copper in alluvium yielded an average coefficient of variation of 0.24 for 26 pairs of samples. Laboratory analysis of the same samples yielded a coefficient of variation of 0.28. These coefficients are somewhat higher than the 0.17 obtained using essentially the same test on residual soil (Huff and others, 1961) but are in the satisfactory range. The geochemical prospecting test for molybdenum in 24 pairs of mesquite twig samples yielded a coefficient of variaton of 0.35, indicating an objectionably high error of measurement and a need for better techniques.

In an effort to obtain more accurate results, the same 24 pairs of samples were reanalyzed by a standard laboratory method utilizing a complete digestion process and a photometric color measurement. However, the results of the standard laboratory method yielded a coefficient of variation of 0.31, which is only a slight improvement. It was concluded that the analytical refinements did not improve these tests appreciably. Large sampling errors very probably are the principal limitation upon reproducibility of measuring the molybdenum content of mesquite.

After it was concluded that most of the error of measurement was in the sampling, rather than in the analysis, several additional experiments were made to investigate sampling errors.

Samples contaminated by dust from the mines have an excessively high metal content. Such contamination of alluvium on the sides of the Pima open pit was evaluated by collecting at each of 32 sample sites one sample coated with copper-bearing(?) dust from the pit and a second sample of uncontaminated alluvium several inches beneath the surface. These pairs show a strong bias (coefficient of variation of 0.52); in fact, some sample pairs in this set show that such contamination may amount to as much as 100 ppm (parts per million) of copper, but, on the average, the difference is about 50 ppm.

The surface soil in the Pima district is subject to a similar contamination by dust from the mines and tailings ponds. The extent of airborne contamination was checked by sampling at 50 sites the surface (possibly contaminated) soil and subsurface (uncontaminated) soil at a depth of 2–3 inches. The coefficient of variation of these pairs was found to be 0.33, indicating some bias due to contamination. In 30 out of 50 sample pairs, the surface sample has more copper than the subsurface, and in four pairs the surface sample has less. As might be anticipated, the soil samples showing the greatest effects of contamination are those collected closest to the tailings ponds, which are apparently the major source of copper-bearing dust. The greatest contrast was measured in a pair of samples collected only 300 feet east of the tailings pond from the Pima mine. In this pair, the surface sample contains 150 ppm and the subsurface 30 ppm. Between this sample site and the tailings pond, the soil has a coat of powdery gray tailings, obvious evidence of windborne dust from the tailings pond. The movement of dust is readily observable in this area on dry windy days. A mile or more from the mines, the amount of such contamination is apparently less than 20 ppm. To avoid such contamination, all other soil samples were collected at a depth of about 3 inches.

The plants, especially the leaves with their large surface area, are also subject to contamination by dust from the mines. Paired samples of leaves and twigs from the same plants analyzed for molybdenum gave an average coefficient of variation of 0.55. Out of the 63 pairs compared, the leaves in 62 pairs have a higher molybdenum content than the twigs.

On the average, leaves contain from 20–30 ppm more molybdenum than twigs from the same plant. This difference may be due, in part, to a natural tendency for leaves to take up more molybdenum than twigs, but part of the difference is probably due to contamination of leaves by airborne metal-bearing dust. One series of samples was collected of leaves and twigs from trees growing within several miles of the tailings pond of the Pima mine. Almost all the leaves in this series contain more copper and molybdenum than the twigs (table 1).

The difference is greatest for the samples collected closest to the tailings pond. The amount of contamination in leaves appears to be large enough to obscure natural variations of metal content in the mesquite.

TABLE 1.—*Comparison of the copper and molybdenum content of leaves and twigs of mesquite collected near the Pima Mining Co. tailings pond*

Distance (miles) from tailings pond	Copper (ppm)		Molybdenum (ppm)	
	Leaves	Twigs	Leaves	Twigs
0.1 east	300	150	60	8
0.5 east	150	120	24	8
1.0 east	120	60	30	6
1.5 east	150	120	30	6
2.0 east	150	80	44	6
2.5 east	120	120	30	12
3.0 east	120	60	30	6
0.5 west	220	120	60	12
1.0 west	220	80	30	12
1.5 west	120	120	24	12
2.1 west	150	120	30	12

The molybdenum content of twigs from large mesquite trees was compared with that of twigs from small trees to investigate a possible bias. The larger trees probably have deeper roots and therefore might accumulate more molybdenum from ground water than the shallow-rooted smaller plants. However, the coefficient of variation of 53 such pairs was bound to be 0.34, or almost equal to the 0.35 obtained for replicate sampling. Thus, small mesquite plants apparently contain just as much molybdenum as large ones.

These experiments indicated what kinds of samples should be taken to avoid contamination and what reliance could be placed on their analysis. They led to the practice of using twigs rather than leaves and of collecting samples from two different trees at each sample site so that values shown on the map (pl. 5) would represent the average of two analyses.

STUDIES OF A THIN ALLUVIAL COVER

The Pima ore deposit is unsatisfactory in several respects for studies of dispersion of ore metals through an alluvial cover. The thickness of the cover (200 ft), the tightly cemeted conglomerate, the presence in the overlying alluvium of detrital fragments of ore minerals derived from distant outcrops, and the mining activities all might tend to limit or obscure the detection of geochemical anomalies. For these reasons, a search was made for an area where the effects of diffusion through a thin alluvial cover might be detected.

A series of samples was collected around a small mineralized hill (fig. 5), referred to herein as "Prospect hill," on the San Xavier Reservation about 2½ miles northwest of the Pima mine. Cretaceous meta-arkose (Heindl, 1959) containing partly leached copper minerals crops out on this hill. The surrounding alluvium is derived entirely from

FIGURE 5.—Small hill of mineralized rock selected for geochemical study of a thin alluvial cover. Black Mountain in background. Vegetation is typical of study area.

granite and is free of carbonate minerals. Residual soil developed on bedrock was sampled at 14 sites on the hill (table 2); of these, 6 contain 100 ppm or more of copper and 10 contain more than 50 ppm copper. The soil on the alluvium around the foot of the hill contains from 10 to 20 ppm copper, markedly less than soil on the hill and not enough to indicate any dispersion of copper upward through this thin alluvial cover.

Table 3 gives representative spectrographic analyses of six samples of residual soil overlying mineralized rock on Prospect hill. In this group, only the copper ranging from 100 to 300 ppm appears to be significantly above background amounts. Table 3 also gives representative spectrographic analyses of soil and the thin layer of alluvium overlying mineralized rock. In this set, both copper and molybdenum, as well as all the accessory elements, are in the background ranges.

TABLE 2.—*Copper and molybdenum content of soils and plants collected on or near Prospect hill*

[All values are in parts per million]

Sample description	Samples collected on hill		Samples collected on alluvium 20–200 feet from foot of hill	
	Copper	Molybdenum	Copper	Molybdenum
Soil	40, 40, 40, 40, 60, 60, 60, 80, 100, 120, 120, 100, 300, 400.	1, 1, 1, 1, 1, 1, 1, 1, 1, 2, 2, 2, 2, 5.	10, 10, 10, 10, 15, 15, 15, 15, 15, 15, 15, 15, 15, 20, 20.	1, 1, 1, 1, 1, 1, 1, 1, 1, 2, 2, 2, 2, 2, 5.
Plants (after ashing):				
Mesquite, leaves	300, 450, 600.	30, 30, 45.	60, 80, 120, 120.	14, 15, 20, 30.
Mesquite, twigs	120, 120, 150.	8, 10, 15.	80, 80, 120, 120.	6, 6, 10, 14.
Palo verde	50, 70, 100.	2, 3, 6.	20, 30, 50.	2, 2, 6.
Grass	50, 100.	5, 6.	30, 50.	5, 8.
Jumping cholla	30, 70.	2, 2.	30, 30.	1, 3.
Prickly pear	15, 30.	1, 1.	10, 15.	1, 2.
White thorn	20, 70.	3, 4.	20, 30.	3, 8.
Ocotillo	300.	8.	------	------

On this hill, as elsewhere in the Sonoran Desert, the vegetation is of two physiologic types. The xerophytes, such as the cacti, are shallow rooted and depend for their water supply upon absorbing water quickly during rainy weather and hoarding it during the long dry periods. The phreatophytes, like palo verde and mesquite, have long, deeply penetrating roots which enable these plants to tap ground water beneath the permanent ground-water table (fig. 6). Mesquite roots may extend to depths of more than 60 feet (Robinson, 1958, p. 38), and live roots, probably from mesquite, have been collected in the Mission mine at a depth of 175 feet, about 65 feet above the water table. This is the deepest known penetration of any kind of plant roots on record (Phillips, 1963).

TABLE 3.—*Chemical analyses of representative samples*

[Semiquantitative spectrographic analyses by E. F. Cooley and Uteana Oda; wet chemical analyses by H. M. Nakagawa. ..., no determination. Results for Si, Fe, and Mg are in percent; results for other elements are in parts per million]

Sample	Semiquantitative spectrographic analyses																					Wet chemical analyses			Sample description
	Si	Fe	Mg	Ti	Mn	Ag	B	Ba	Be	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sr	V	Y	Zn	Zr	Cu	Zn	Mo	
												Samples from Prospect hill														
650	-----	2	0.5	2,000	300	<1	20	700	1	10	50	100	20	<50	<2	10	30	200	50	20	<100	300	80	50	1	Residual soil overlying mineralized rock.
651	-----	1.5	.3	2,000	200	<1	20	500	1	10	30	100	20	<50	<2	7	20	200	50	20	<100	200	120	-----	-----	Do.
652	-----	1.5	.3	3,000	300	<1	20	500	1	10	30	100	20	<50	<2	7	30	200	70	20	<100	300	120	30	<1	Do.
653	-----	2	.5	3,000	300	<1	30	700	1	10	30	100	20	<50	<2	15	30	300	70	20	<100	700	40	30	<1	Do.
722	-----	2	.3	2,000	300	<1	20	500	1	10	30	100	15	<50	<2	10	30	150	50	20	<100	500	60	30	<1	Do.
723	-----	2	.5	1,500	300	<1	20	500	2	10	30	300	20	<50	<2	15	30	150	70	15	<100	300	400	30	1	Do.
656	-----	2	.7	3,000	300	<1	30	700	2	10	30	10	20	<50	<2	10	30	500	70	20	<100	700	15	40	<1	Alluvial soil near foot of hill.
657	-----	2	.7	2,000	500	<1	30	700	2	15	30	15	20	<50	<2	15	30	500	100	20	<100	700	15	40	<1	Do.
658	-----	1.5	.5	2,000	300	<1	20	500	1	10	20	15	20	<50	<2	5	20	300	50	15	<100	300	15	40	<1	Do.
660	-----	3	.7	2,000	500	<1	30	500	2	20	30	15	20	<50	2	20	30	300	100	20	<100	300	15	40	<1	Do.
724	-----	3	.5	2,000	300	<1	30	300	2	10	50	15	20	150	2	15	30	200	150	30	<100	500	20	30	<1	Do.
725	-----	3	.5	2,000	500	<1	20	500	2	10	30	15	15	150	2	10	30	300	100	20	<100	500	20	40	<1	Do.
												Holocene(?) alluvium near ore deposits														
304	-----	7	1	5,000	1,500	<1	15	700	3	20	20	200	15	<50	20	7	70	300	70	20	<200	700	200	310	11	Mineral Hill wash.
470	-----	10	.7	7,000	700	<1	15	700	2	10	30	50	15	100	5	7	70	300	200	30	<200	700	40	70	1	Unnamed wash.
473	-----	10	.7	5,000	700	<1	15	700	<2	15	30	20	15	50	<5	7	50	300	200	20	<200	700	20	90	<1	Do.
474	-----	5	.7	5,000	700	<1	10	700	<2	<10	20	70	15	<50	<5	5	70	300	70	20	<200	700	60	130	<1	Pima wash.
475	-----	7	.7	5,000	700	<1	10	700	<2	10	50	70	15	<50	<5	5	70	200	150	10	<200	1,000	60	100	<1	Do.
478	-----	2	.5	3,000	500	<1	10	700	<2	<10	<10	50	10	<50	<5	5	70	300	30	<10	<200	300	60	80	<1	Mission wash.

Carbonate-cemented basal conglomerate

522	20		2	1.5	2,000	700	<1	10	500	<1	<10	20	150	<20	<50	<10	10	100	150	70	30	500	200		150	210	<1	Pima mine, 23 ft above contact.
521	20		3	1	2,000	700	<1	10	500	<1	<10	30	200	<20	50	<10	10	30	200	70	20	500	150		250	190	<1	Pima mine, 20 ft above contact.
520	20		5	1.5	3,000	1,500	<1	20	700	1	10	20	700	<20	50	<10	15	150	150	100	30	700	200		300	260	1	Pima mine, 17 ft above contact.
519	15		2	1	2,000	1,000	<1	10	500	<1	<10	20	500	<20	100	<10	10	70	150	50	30	200	200		250	140	1	Pima mine, 16 ft above contact.
518	15		2	1	1,500	700	<1	10	300	<1	<10	15	700	<20	<50	<10	7	50	100	50	20	500	200		200	220	1	Pima mine, 12 ft above contact.
517	15		3	1	2,000	1,000	<1	10	300	<1	<10	20	1,000	<20	<50	<10	10	100	100	70	20	700	200		800	220	<1	Pima mine, 8 ft above contact.
516	15		5	.7	2,000	1,000	1	10	300	<1	<10	20	1,500	<20	<50	<10	10	50	100	70	20	300	200		1,500	190	1	Pima mine, 4 ft above contact.
515	20		5	2	2,000	1,000	1	20	300	<1	10	20	5,000	<20	<50	<10	15	100	100	70	20	700	150		>4,000	420	1	Pima mine, 2 ft above contact.
514	20		5	2	2,000	1,000	1	15	500	<1	<10	15	5,000	<20	<50	<10	15	50	100	50	20	700	200		>4,000	400	1	Pima mine, 1 ft above contact.

TABLE 3.—*Chemical analyses of representative samples*—Continued

Sample	Semiquantitative spectrographic analyses																						Wet chemical analyses			Sample description
	Si	Fe	Mg	Ti	Mn	Ag	B	Ba	Be	Co	Cr	Cu	Ga	La	Mo	Ni	Pb	Sr	V	Y	Zn	Zr	Cu	Zn	Mo	
Water residues																										
9	------	<0.01	5	10	50	<1	70	20	<2	<10	<10	20	<10	<50	50	<5	<10	1,500	<10	<10	<200	<10	20	-----	100	Well water associated with ore deposits.
40	0.2	<.01	.5	<10	15	<1	200	<10	<1	<10	<10	<5	<20	<50	15	<5	<10	200	<10	<10	<200	<10	<1	-----	90	Do.
36	1.5	.01	2	<10	<10	<1	300	200	<1	<10	30	20	<20	<50	150	<5	<10	2,000	50	<10	<200	<10	13	-----	150	Do.
39	2	.015	3	<10	<10	<1	300	70	<1	<10	150	<5	<20	<50	700	5	<10	2,000	50	<10	<200	<10	<10	-----	230	Do.
51	1.5	<.01	2	<10	<10	<1	150	150	<1	<10	10	<5	<20	<50	200	<5	<10	3,000	50	<10	<200	<10	<10	-----	460	Do.
43	1.5	.015	5	<10	<10	<1	100	500	<1	<10	70	200	<20	<50	10	5	<10	3,000	20	<10	<200	<10	83	-----	20	Do.
10	1	.015	3	<10	<10	<1	100	150	<1	<10	50	<5	<20	<50	10	5	<10	1,500	15	<10	<200	<10	<10	-----	12	Well water from barren ground.
17	1	<.01	2	<10	<10	<1	100	150	<1	<10	10	<5	<20	<50	<10	<5	<10	1,000	15	<10	<200	<10	<10	-----	8	Do.
19	1	<.01	2	<10	<10	<1	100	100	<1	<10	<10	<5	<20	<50	10	<5	<10	1,000	15	<10	<200	<10	<12	-----	12	Do.
29	1.5	.015	3	<10	<10	<1	200	200	<1	<10	50	10	<20	<50	15	<5	20	1,500	20	<10	<200	<10	<15	-----	14	Do.
33	2	.015	3	<10	<10	<1	300	200	<1	<10	70	5	<20	<50	30	5	<10	1,500	30	<10	<200	<10	<10	-----	80	Do.
53	2	.015	2	<10	<10	<1	200	200	<1	<10	70	20	<20	<50	70	5	<10	3,000	50	<10	<200	10	9	-----	40	Do.
Ash from mesquite twigs																										
4	------	------	------	100	200	<1	200	500	<1	<10	<10	100	<5	<50	10	<5	20	2,000	10	<10	<200	<10	120	-----	11	Plants growing near ore deposits.
48	------	------	------	150	200	<1	100	1,500	<1	<10	<10	50	<5	<50	5	<5	<10	7,000	<10	<10	<200	<10	------	-----	11	Do.
55	------	------	------	200	300	<1	100	1,500	<1	<10	<10	70	<5	<50	20	10	10	7,000	<10	<10	<200	<10	------	-----	16	Do.
60	------	------	------	200	150	<1	100	1,500	<1	<10	<10	50	<5	<50	10	10	10	3,000	<10	<10	<200	<10	------	-----	7	Do.
65	------	------	------	150	70	<1	100	100	<1	<10	<10	70	<5	<50	10	10	10	500	10	<10	<200	<10	120	-----	9	Do.
103	------	------	------	100	200	<1	100	300	<1	<10	<10	50	<5	<50	7	10	<10	3,000	<10	<10	<200	<10	------	-----	17	Do.
22	------	------	------	150	200	1	150	3,000	<1	<10	10	50	<5	<50	2	<5	10	10,000	10	<10	<200	<10	------	-----	6	Plants growing on barren ground.
31	------	------	------	100	300	<1	150	500	<1	<10	<10	30	<5	<50	5	<5	10	3,000	10	<10	<200	<10	80	-----	10	Do.
33	------	------	------	150	300	<1	200	300	<1	<10	<10	30	<5	<50	2	<5	<10	2,000	10	10	<200	<10	60	-----	6	Do.
35	------	------	------	200	500	<1	200	2,000	<1	<10	10	70	<5	<50	10	20	10	7,000	10	<10	<200	<10	120	-----	3	Do.
37	------	------	------	200	300	<1	200	500	<1	<10	<10	70	<5	<50	7	<5	10	7,000	<10	10	<200	<10	80	-----	8	Do.
95	------	------	------	200	300	<1	100	3,000	<1	<10	<10	30	<5	<50	7	<5	50	7,000	<10	<10	<200	<10	------	-----	11	Do.

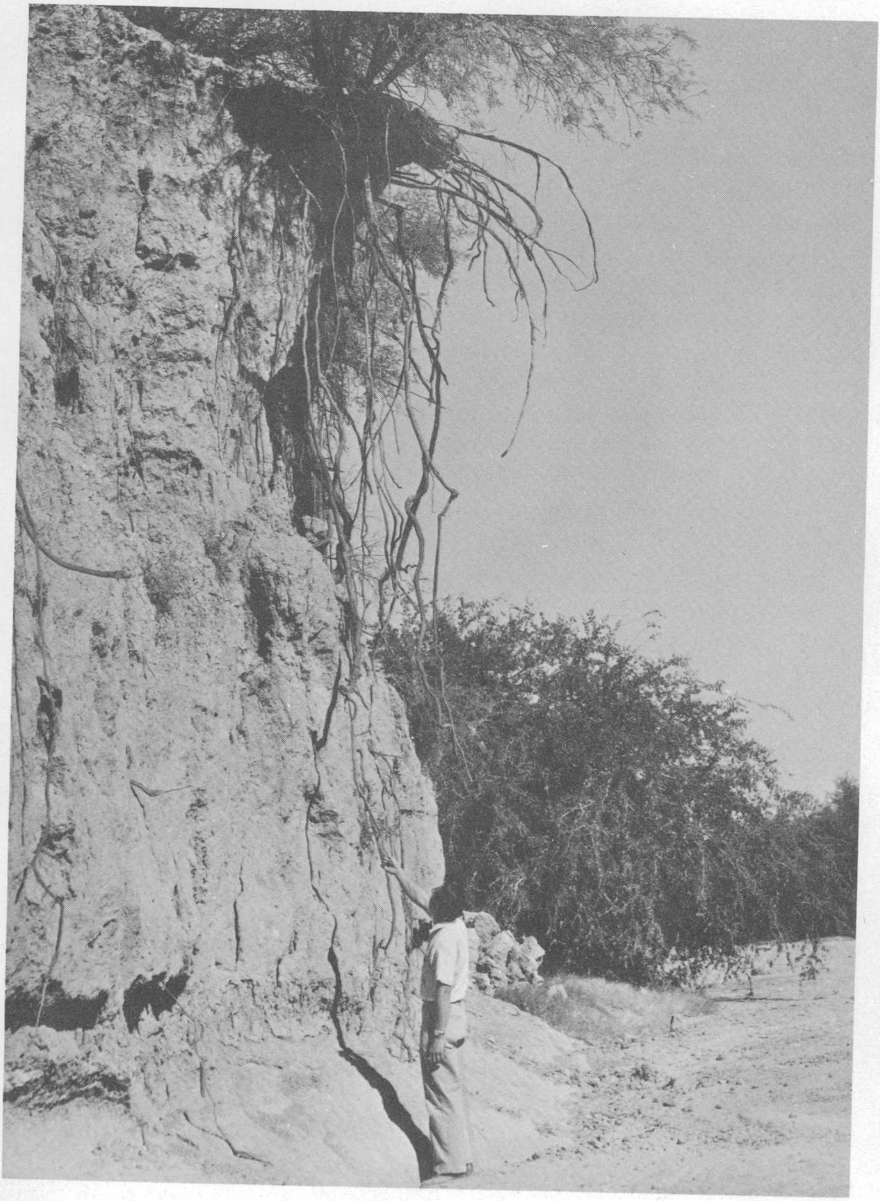

FIGURE 6.—Mesquite trees with roots exposed by erosion to a depth of 25 feet.

Various types of plants and the soil in which they grow were compared to see which have the highest concentrations of copper. The copper content of mesquite was found to be highest of all (table 2); the ash of six samples of mesquite collected on Prospect hill all contain anomalous amounts of copper (120–450 ppm), which is on the average about three times as much copper as in the associated residual soil. Mesquite growing on the alluvium near the hill contains 60–120 ppm of copper (after ashing), about six times more than the soil (10–20 ppm). Thus, copper tends to accumulate in plants, particularly mesquite.

Mesquite also contains more molybdenum than the other species it was compared with, and more molybdenum than the soil in which it grows. The soil, both on and off the hill, contains only about 2 ppm of molybdenum, but mesquite ash contains from 6 to 30 ppm molybdenum (table 2). The molybdenum content of the mesquite on the hill averages 23 ppm, or about 12 times as much as the soil. Mesquite growing on the alluvium averages 14 ppm or about seven times the molybdenum content of the soil.

The high copper and molybdenum contents in mesquite may be due to absorption of the metals through the plant's deep roots. Thus, analysis of mesquite growing on barren alluvium may yield some indication of the metal content of the underlying concealed bedrock.

These preliminary data suggested that analysis of mesquite from other parts of the district might give a better indication of buried ore than analysis of soil and alluvium. For this reason, mesquite plants (as well as soil and alluvium) around the Pima and other known ore deposits were sampled and analyzed. (See p. C26–C28.)

COPPER

COPPER IN MODERN ALLUVIUM

The alluvium of the present-day washes of the area studied contains from 5 to 20 ppm copper, except in the vicinity of the Pima and Mission pits, where the range generally is from 50 to 400 ppm (pl. 1). Microscopic examination of a sample from the head of Mineral Hill wash that contains 400 ppm copper showed it to be rich in sulfides, which were apparently derived from the Banner Minning Co. tailings pond upstream at Mineral Hill. Similarly, copper contents of 50 ppm and more in short washes between Mission wash and Helmet wash very probably reflect contamination from the Pima Mining Co. tailings pond. Concentrations of 50 ppm and more along Mineral Hill wash and Pima wash were traced upstream beyond the Pima and Mission ore bodies to mines at San Xavier and Olive Camp where copper ore is exposed. Similar concentrations occur in washes south of Helmet Peak that drain Olive Camp.

To compare chemical with visual prospecting guides, a search was made at each sample site for float stained with chrysocolla or any other easily recognized copper mineral. Most, but not all, of the samples containing 50 ppm or more of copper were found to be associated with copper-rich float, as were a few samples containing less than 50 ppm copper (pl. 1). Evidently, much of the copper in the modern alluvium was eroded mechanically from the exposed deposits and was not derived from the hidden Pima and Mission ore bodies.

COPPER IN SOIL

Only a few samples of modern soil collected in the Pima mine area contain more than 50 ppm copper (pl. 2). Soils with high copper contents occur on or near mineralized bedrock at Prospect hill and Olive Camp. Among samples of soil on alluvium, only one has a higher than average copper content (150 ppm). It was collected about 1,000 feet west of the Mission mine. Samples collected closer to the Mission mine contain 20, 30, and 40 ppm. The 150-ppm concentration may represent copper derived from Mineral Hill. All samples of the clay and caliche horizons of the older or Pleistocene soil also have low copper contents.

These results are similar to those obtained by Canney (1963), who concluded that slightly anomalous concentrations in soil directly overlying the Mission ore body resulted chiefly from copper transported mechanically from ore deposits exposed in the Mineral Hill–Helmet Peak areas. Because surface alluvium and soil have low copper contents, it seems unlikely that analysis of them could have led to the discovery of the Pima and Mission deposits and other nearby concealed ore bodies.

COPPER IN PLEISTOCENE(?) ALLUVIUM

The distribution of copper at various depths in the unconsolidated Pleistocene(?) alluvium was determined by sampling at the Pima mine. The copper content was found to increase irregularly from 5 ppm near the land surface to 250 ppm near the base of the unconsolidated alluvium (table 4). The presence in the alluvium of some pebbles containing oxidized copper minerals suggests that this copper is detrital and that it could not have been derived from the Pima ore body underneath.

The copper concentrations at the base of the carbonate-cemented conglomerate are much greater than those in any of the materials above. Close to its base, where it lies just above ore, the conglomerate contains about 4,000 ppm copper. The copper content decreases to 250 ppm about 20 feet above. Spectrographic analyses of samples of carbonate-cemented conglomerate from the northeast side of the Pima pit confirm the high copper content and show that copper is the only ele-

TABLE 4.—*Distribution of copper with depth in alluvium at Pima Mining Co. open pit*

[Underlying bedrock is low-grade copper ore, which was not sampled]

Description	Southwest side of pit		Northeast side of pit	
	Distance above bedrock (ft.)	Copper content (ppm)	Distance above bedrock (ft.)	Copper content (ppm)
Land surface	196 (alt 3,362)		186 (alt. 3,311)	
Unconsolidated alluvium	187	20	184	5
	181	25	178	20
	176	15	172	5
	170	10	167	20
	165	20	161	35
	159	10	156	20
	153	15	150	20
	148	20	145	20
	81	200	97	75
	75	40	86	10
	70	60	75	40
	65	30	64	150
	59	125	53	50
	54	80	48	40
	47	70	42	150
	41	150	31	125
	37	250	26	50
Carbonate-cemented conglomerate	30	110		
	26	80	23	150
	22	150	20	250
	18	150	17	300
	14	600	16	250
	10	600	12	200
	6	900	8	800
	4	1,500	4	1,500
	2	2,200	2	4,000
	1	3,500	1	4,000

ment present in abnormal concentrations (table 3). These high concentrations in the carbonate-cemented conglomerate were predicted by R. C. Cribbs (Am. Smelting and Refining Co., oral commun., 1958) on the basis of his earlier geochemical studies in the area.

Copper minerals, as such, could not be identified in the pebbles of the basal conglomerate. Because the copper is dissolved when the rock is digested in acid, the copper was suspected to be in the carbonate cement. The copper content of the cement was investigated by concentrating and analyzing the cement separately and by staining rock sections with a copper-sensitive reagent.

Rough crushing and sieving of the conglomerate to obtain the minus-80-mesh fraction partly concentrates the carbonate matrix, which crushes more readily than the rock fragments. A comparison of copper content of the minus-80- and the plus-80-mesh fraction of crushed rock shows clearly that most of the copper is in the carbonate matrix (table 5).

The rock sections were stained by applying rubeanic acid to a flat surface after exposing the surface to hydrochloric acid fumes. The dark copper rubeanate that formed showed that the copper is fairly evenly distributed throughout the carbonate matrix; thus, it is probably a chemical precipitate and not detrital.

The copper in the conglomerate must have been deposited by copper-bearing ground water. As described in the next section of this report, the present-day ground water contains very little copper. At some former time, ground water flowing northeast down the water-table gradient was probably slightly acidic and contained copper after flowing through the ore deposits. When this water came in contact with the calcium carbonate of the conglomerate, it was neutralized and the copper precipitated. This precipitation took place at or very close to the base of the conglomerate, and the upper part of the conglomerate was unaffected.

TABLE 5.—*Copper content of the carbonate-cemented conglomerate after crushing*

Conglomerate, 1 foot above bedrock	Percent by weight	Copper content (ppm)
Southwest side of Pima pit:		
Minus-80-mesh fraction	24	3, 500
Plus-80-mesh fraction	76	1, 500
Northeast side of Pima pit:		
Minus-80-mesh fraction	12	4, 000
Plus-80-mesh fraction	88	600

The carbonate-cemented conglomerate was sampled wherever possible throughout the area to investigate spatial relations between its copper content and the alluvium-covered ore bodies. Samples were obtained from outcrops along the base of the alluvial cover. Other samples were obtained of core from American Smelting and Refining Co. exploratory drill holes. The copper content of these samples is shown on plate 3. Where more than one sample was collected at a site, the maximum value is shown. At every site, the greatest concentration was found at the base of the conglomerate. Anomalous copper concentrations occur near the concealed ore bodes and up to 1.5 miles away from them. Conglomerate from a drill hole 1.5 miles northeast of the Mission mine contains 1,000 ppm copper and overlies rock devoid of copper.

COPPER IN GROUND WATER

Representative samples of ground water were analyzed for copper without detecting significant amounts. In the pH range of 7.1 to 7.6, which characterizes ground water throughout the district, copper has only a limited solubility (Bloom, 1966, p. 112). Table 3 gives spectrographic data on the metal content of 12 water residues from mineralized and unmineralized areas. Additional data on the composition of eight of these samples (and four others) are given in table 6. Only one sample was found to contain an abnormal concentration of copper; thus, the present-day solubility of copper in the surficial environment of this district is much lower than it was when copper was being deposited in the conglomerate. The distribution of copper in ground water was not mapped.

COPPER IN PLANTS

Desert plants near some copper deposits have been shown to have a high copper content (Clarke, 1953; Warren and others, 1951). Mesquite ash from the Pima district contains from 50 to 700 ppm copper and commonly is richer in copper than the soil or ground water. However, plants with high copper contents are distributed erratically throughout the district and do not appear to be spatially related to the ore deposits. The distribution is not shown here.

MOLYBDENUM

Representative samples of soil, alluvium, and basal conglomerate generally contain less than 10 ppm of molybdenum (tables 2, 3). Because this concentration is in the background range, the study of molybdenum dispersion was based chiefly on samples of ground water and plants (many of which are highly anomalous).

MOLYBDENUM IN GROUND WATER

Water samples from all the wells near the ore deposits and from wells spaced every mile or so along the Santa Cruz Valley were collected and analyzed for molybdenum. Representative samples were analyzed spectrographically and by standard methods of water analysis to identify elements associated with the molybdenum (tables 3, 6). Some water samples that were high in molybdenum were also found to be high in sulfate.

The molybdenum concentration in ground water ranges from 4 ppb (parts per billion) along the Santa Cruz Valley to 250 ppb near the Pima and Mission deposits (pl. 4). Waters from two wells east of Black Mountain and 8 miles downslope from the Pima and Mission ore deposits contain 55 and 120 ppb molybdenum. Ground water flows from those ore deposits toward these wells.

As ground water northeast of and downslope from the Pima and Mission deposits contains more molybdenum than that southwest or upslope (pl. 4), most of the molybdenum in the ground water apparently is derived from the buried ore and associated mineralized rocks. Thus, the molybdenum content of the ground water appears to be a useful prospecting guide.

TABLE 6.—*Chemical analyses of representative water samples collected March 15–24, 1960, in the Pima mine area*

Sample	10	19	23	27	29	33	39	40	41	43	49	51
	Concentrations in parts per million											
Silica (SiO_2)	35	35	34	33	36	54	43	55	34	54	46	36
Calcium (Ca)	136	80	68	48	74	74	54	600	270	110	84	48
Magnesium (Mg)	19	20	11	11	11	11	12	10	14	14	20	7
Sodium (Na)	35	33	39	48	30	48	40	29	39	52	45	39
Potassium (K)	3.0	3.0	3.5	3.5	2.3	2.8	3.7	3.5	4.3	5.1	3.5	3.8
Bicarbonate (HCO_3)	244	196	206	164	212	186	176	62	198	414	420	158
Sulfate (SO_4)	134	90	66	64	71	121	67	1,750	550	23	24	73
Chloride (Cl)	42	25	18	24	11	15	11	14	31	20	20	12
Nitrate (NO_3)	22	12	2.2	1.1	4.7	2.2	1.8	.0	.4	3.3	3.3	.4
Dissolved solids, residue on evaporation	500	350	360	290	280	390	300	2,800	1,190	480	350	260
Hardness as $CaCO_3$:												
Ca and Mg	418	282	215	165	230	230	184	1,539	732	332	292	148
Noncarbonate	218	121	46	30	56	81	40	1,488	570	0	0	18
	Concentrations in parts per billion											
Copper (Cu)	<4	<4	<4	<4	<4	4	<4	<4	<4	90	<4	<4
Molybdenum (Mo)	6	4	4	30	4	30	70	250	16	8	40	120
Heavy metals (Cu, Zn, and Pb)	<10	<10	<10	400	<10	300	30	<10	----------	200	250	<10
Arsenic (As)	<20	<20	<20	<20	<20	<20	20	40	20	<20	20	<20
pH	7.1	7.4	7.3	7.7	7.3	7.6	7.6	7.2	7.7	7.6	7.4	7.1

10. Irrigation well, SE¼NW¼ sec. 29, T. 16 S., R. 14 E.
19. Irrigation well, SE¼NW¼ sec. 8, T. 17 S., R. 14 E.
23. Irrigation well, NW¼SW¼ sec. 25, T. 17 S., R. 13 E.
27. Farm well, NE¼NE¼ sec. 35, T. 16 S., R. 13 E.
29. Tucson Municipal well SC 1, SE¼NE¼ sec. 20, T. 16 S., R. 14 E.
33. Emmons Ranch well, NW¼NW¼ sec. 21, T. 17 S., R. 13 E.
39. American Smelting and Refining Co. well, NW¼NE¼ sec. 34, T. 16 S., R. 13 E.
40. Banner Mining Co. well near new shaft, NE¼NE¼ sec. 36, T. 16 S., R. 12 E.
41. San Xavier mine, SW¼SW¼ sec. 2, T. 17 S., R. 12 E.
43. Ranch well, NW¼SW¼ sec. 3, T. 17 S., R. 12 E.
49. Ruby Star Ranch well, NW¼NW¼ sec. 26, T. 17 S., R. 12 E.
51. Irrigation well, SW¼SW¼ sec. 35, T. 15 S., R. 13 E.

MOLYBDENUM IN PLANTS

Inasmuch as deep-rooted plants absorb chemical constituents from the ground water, they were investigated to find out if they contained abnormal amounts of molybdenum. Mesquite was used for this purpose because it had yielded promising results in the preliminary study at Prospect hill.

The ash of mesquite collected in the Pima district contains from 4 to 220 ppm molybdenum (pl. 5). West of Twin Buttes, where the mesquite is particularly rich in molybdenum, the water table is about 30 feet deep, shallow enough to be tapped easily by mesquite roots. (See fig. 6.) The mesquite ash and water residue there contain about the same amounts of molybdenum. East of Black Mountain, where the water table is about 60 feet deep (Schwalen and Shaw, 1957), mesquite ash contains only about half as much molybdenum as the water residue. Close to the ore deposits, where the water table is about 200 feet deep, mesquite ash contains only about one-eighth as much molybdenum as the water residue. Thus, the molybdenum content of the mesquite appears to depend upon both the molybdenum content of the ground water and the depth of the water table.

Molybdenum contents of mesquite ash are anomalous in two large areas. One of these is 1–3 miles wide and extends irregularly down the pediment from the Pima and Mission mines about 8 miles northeastward toward the Santa Cruz River (pl. 5). Ash from mesquite twigs contains from 20 to 57 ppm molybdenum in most of this area. Some or all of this molybdenum must have been contributed to the ground water by the Pima and Mission deposits and possibly other deposits as yet undiscovered.

The other area in which mesquite has anomalously high concentrations of molybdenum is south of the Pima mine, near Twin Buttes. Two samples from a short distance west of Twin Buttes each contain more than 100 ppm molybdenum. These high values can be interpreted as being partly the result of a shallow water table. In part, though, the anomaly must reflect a high molybdenum content in the rocks. Recently, several rich copper-molybdenum deposits have been discovered nearby.

APPLICATION TO GEOCHEMICAL EXPLORATION

The most significant geochemical anomalies related to hidden copper and molybdenum deposits appear to be those resulting from dispersion of these metals in ground water. Copper formerly was transported in ground water northeastward down the pediment, and much of it was precipitated in the carbonate-cemented conglomerate just above the bedrock. This created a geochemical anomaly about 1 mile wide which extends into the unmineralized area about 1.5 miles northeast of the concealed deposits. The copper content of the anomalous conglomerate averages about 1,000 ppm, which is very high in comparison with the copper content of the other surficial materials.

The low copper content of today's ground water indicates that the water is transporting little copper now. Most of the copper in the basal conglomerate was probably deposited during Pleistocene time, when rapidly oxidizing sulfides in the ore made the ground water sufficiently acid to dissolve and transport copper.

Unlike copper, molybdenum is soluble in today's ground water. Molybdenum from the ore deposits travels farther than copper and can be detected in water and plants at a considerable distance from ore. Similar extensive dispersion of molybdenum has been observed elsewhere (Bloom, 1966; Ginzberg, 1960, p. 204–205; Malyuga, 1959). In the Pima district, molybdenum derived from ore deposits is being transported in ground water to wells about 8 miles downslope from the Pima mine. Anomalous molybdenum concentrations in ground water range from 50 to 250 ppb and are readily detectable.

Mesquite growing in areas where ground water has a high molybdenum content also has a high molybdenum content, commonly from 20 to 40 ppm (in ash). Mesquite, which can tap ground water as deep as 175 feet, can therefore be sampled and analyzed to evaluate the dispersion of molybdenum in ground water in areas where there are no wells. However, the sampling and analysis of mesquite involves objectionably large errors, and additional investigation is needed to improve techniques.

A logical first step in the search for other concealed copper-molybdenum deposits is to locate by analysis of well water and phreatophytes other drainage basins where ground water is rich in molybdenum. Within these basins, widely spaced drilling for geologic data and for sampling of the alluvial cover for copper determinations should permit further definition of exploration targets.

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