MOLYBDENUM TRACE ANALYSIS
OF CERTAIN PHREATOPHYTES
AS A BIOGEOCHEMICAL PROSPECTING METHOD
IN THE SEDIMENTARY BASINS OF SOUTHERN ARIZONA

by

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ABSTRACT

The problem of detecting dispersion trains of molybdenum in basin sediments within Arizona's basin and range province was explored biogeochemically by analyzing twigs from three phreatophytes native to the area. Molybdeniferous deposits are located in the highlands above the basins or under the buried pediment. Molybdenum is dispersed as a part of the alluvium or as solute in ground-water. The three plants used were mesquite (Prosopis juliflora var. velutina (Woot.) Sarg.), blue palo verde (Cercidium floridum Benth.), and white thorn acacia (Acacia constricta Benth.). Soil and plant samples were analyzed for molybdenum. Soil samples showed much less contrast with background molybdenum values than did plant samples. Three areas were sampled. A molybdenum gradient was detected on the bajada of the Sierrita Mountains near Tucson from ore bodies on the exposed pediment and mountains. The buried Sacaton deposit near Casa Grande was not revealed by biogeochemical sampling. Dispersion from Copper Creek district was detected in trees along the stream draining the district and in trees several miles away along the San Pedro River flood-plain. Dispersion in the Sierritas is believed to be from bajada forming processes. Anomalous trees along the San Pedro River probably gleaned molybdenum from a ground-water source.

INTRODUCTION

The physiography of southern Arizona is typically basin and range. The landforms making up the basins and ranges today are believed to be largely the result of block faulting and an arid weathering cycle. As seen today the arid climate prevalent throughout most of the area has generally produced predictable erosional and depositional features such as mountainous regions, pediments, alluvial fans, bajadas, and lacustrine and river deposits. Each of these erosional and depositional features is in various stages of dissection or burial as the equilibrium conditions that produced them change because of local variations and alterations in base level, climate, or rock type.

A question commonly asked by those exploring for ore deposits in the basin and range province is how the alluvium (including alluvial fans and bajadas) of the intermontane basins may be wisely used to indicate undiscovered deposits in bedrock areas either exposed above the basin alluvium or buried by it. One neglected but potentially useful method is a biogeochemical one; the analysis of plant material growing on the alluvium to indicate certain desired elements either in the alluvial sediments, in the bedrock below the alluvium, or in the ground-water within them. Such elements can be considered as dispersion trains from a source in the higher mountains or pediment or from the pediment surface beneath the alluvium.

In this study an investigation was made into the possibility of using trace amounts of molybdenum found in certain perennials that grow on alluvial sediments to indicate the presence of anomalous molybdenum zones on bedrock surfaces adjacent to or under the alluvium. Emphasis was put on the use of the technique for reconnaissance work to indicate the anomalous presence of molybdenum and to point to an ore body district rather than to delimit the shape, size, and exact position of an ore body.

The experimental areas biogeochemically sampled were all in south-central Arizona around ore deposits that contain greater than trace amounts of molybdenum. The area most intensely studied was around the Pima and Twin Buttes mining districts in Pima County south of Tucson (figure 1 in pocket). These districts contain the Pima-Mission, Twin Buttes, and Sierrita-Esperanza open pit operations and numerous smaller, mostly inactive mines. Molybdenum is found in all of the open pit ore bodies and in several of the smaller underground mines. The second area studied was the molybdenum dispersion from the Copper Creek mining district near Mammoth in Pinal County (figure 2 in pocket). A third area sampled was at the Sacaton ore body now being developed near Casa Grande in Pinal County.(figure 3 in pocket). Each of these areas contains somewhat unique geomorphological relations of the ore bodies to the alluvium. Different interpretative problems for the biogeochemical results were thus presented in each situation.

One important advantage of biogeochemistry over soil sampling should be considered. "Plants are the only part of the prospecting prism which extends through several layers simultaneously" (Brooks 1972, p. 23). The ability of a plant to translocate mineral components from its roots to its surface structure can be put to good advantage. The subsurface area sampled by plant leaves or stems is the total volume of the absorbant root system rather than the small volume taken in a soil sample. The shape and extent of a root system varies from species to species of plant. Types of plants should be used that have the root characteristics desired for the depth of regolith to be sampled. For this study to glean a composite shallow and deep sample of the alluvium, plants with a deep root system, likely to be phreatophytes, were used in preference to shallow rooted xerophytes such as cacti or creosote bush.

Due to the nature of alluviation, surface soil samples may not indicate everything of interest about the molybdenum distribution in the drainage area. If there is a molybdenum anomaly within the area of the mountains or exposed pediment currently undergoing erosion, it might be detected by surface soil sampling of either the modern stream alluvium or the older alluvium of the interfluves. Plants can also indicate this anomaly, however. If the molybdenum anomaly is present on a pediment buried unconformably by younger alluvium, little sign of it will show at the surface because weathering of the anomalous surface is not visible at the air-clastic interface. Ore bodies which exemplify such a situation are the Twin Buttes and Sacaton porphyry copper deposits. They were found by the fortuitous presence of altered inselbergs rising above the bajada surface. The Pima-Mission porphyry copper deposit was buried completely under 200 feet of alluvium and was discovered by geophysical means and physical exploration, but its presence might have been inferred through biogeochemical techniques.

The problem of detecting molybdeniferous ore deposits under the alluvium by biogeochemical techniques was first seriously investigated by Lyman Huff (Huff and Marranzino 1961) in the early 1960's. Huff studied the bajada and pediment around the Pima-Mission copper mine which is under the buried pediment northeast of Sierrita Mountains, some 15 miles south of Tucson, Arizona. He analyzed ground-water, soil, and mesquite twigs for copper and molybdenum and found little molybdenum in the soil but some good correlation between values of molybdenum in ground-water from wells and in mesquite trees growing in the vicinity. Also he found signs that copper was mobilized across the unconformity and up into the alluvium close to the ore body. He assumed that molybdenum could move in the same way. The conclusion one can draw from his work is that molybdenum from the ore body dissolved in ground-water, then moved down-gradient in that medium to the Santa Cruz River sediments several miles away. Phreatophytes, such as mesquite, growing on the bajada tapped this ground-water and took up molybdenum into their tissues. Thus the presence of the ore body was revealed at the surface several miles away. The present study was designed, in part, to test some of Huff's concepts. In addition, I made studies into phreatophyte-water relations to aid in predicting what the plant is actually sampling; ground-water, alluvium, or both.

I chose molybdenum to study based on some of its chemical and biological properties and its economic importance. It is an essential micronutrient for plants and therefore it is actively taken up by them. On the average, plants rarely need more than 2 or 3 ppm (dry weight) molybdenum for good health. Different plants vary greatly in their capacity to absorb molybdenum. Potato and tomato plants of the Nyctaginaceae (nightshade family) are very sensitive to above average amounts present in the soil and readily show toxicity symptoms (Stiles 1961). Members of the Leguminosae (bean family), however, tend to absorb more than non-legumes when they are grown in soils with high soluble molybdenum and can concentrate many times the amount required without apparent harm (Barshad 1948).

This particular ability of the legumes can cause molybdenosis or "teart", a disease caused by excess molybdenum in animal tissue, in certain ruminants that graze on those plants (Robinson and Edgington 1948). The plants selected for sampling in this study are members of the Leguminosae.

The solubility of molybdenum as a molybdate is increased at neutral to alkaline pH and, so rendered, it is more soluble in arid environs where soil and water pH is generally high (Bloom 1966). This is an important factor in choosing molybdenum rather than other pertinent plant nutrients such as copper, zinc, and manganese for biogeochemical prospecting in dry southern Arizona. The latter elements are less soluble in alkaline conditions, more so at low, acidic pH. Thus molybdenum is more available for plant uptake over a wide area, and plants can readily reflect changes in molybdenum concentrations in their growing medium. Also, because of its greater solubility, more molybdenum can be transported greater distances in ground-water and in slightly basic surface runoff than the other elements mentioned. This fact makes it a good candidate for use in broad reconnaissance prospecting.

Molybdenum is partly chalcophile and is commonly found in molybdenite in many sulfide ore deposits (Bloom 1966). Its presence in many porphyry copper deposits can increase the value of marginal ore to a mineable grade. Secondary wulfenite is a less frequent form associated with lead concentrations. Powellite occurs as a primary mineral and also secondarily from the alteration of molybdenite. It also occurs as a secondary mineral in soils. Tiny amounts of molybdenum can be held in the crystal lattices of feldspars and micas and would be added to the soil by the weathering of those minerals. Its presence in greater than trace amounts in an ore body usually adds an anomalous amount to a regolith weathering above it because of the minute background abundances normally encountered. On the average, one ppm of the earth's crust is molybdenum as compared with 45 ppm for copper (Mason 1958). Normal mineral soils average between one to five ppm molybdenum (Hawkes and Webb 1962). A porphyry copper deposit containing only 100 to 200 ppm could readily disperse amounts of molybdenum around it that would be well above background levels.

METHODS

Phreatophyte Problems

As was mentioned in the introduction, one of the primary goals of biogeochemical prospecting on the alluvium is to try to locate anomalous zones on the pediment under a shallow alluvial cover. The medium for dispersal of molybdenum from the buried pediment surface to the plant roots is ground-water. Plants would have to tap the free watertable to absorb this molybdenum. Huff's conclusions from his study of dispersion around the Pima ore deposit were based on this assumption. As my field work progressed, it became apparent to me that some phreatophytes were more adaptable to scarce water conditions than others. This observation prompted the following study on the species of plants to be sampled in order to establish the relationship between the plant and the water conditions enabling it to survive. This would give the geologist some way to determine whether the plant is giving a reflection of the molybdenum conditions in the alluvium, permanent ground-water, or both. Correspondingly, he would have some idea as to how reliable these phreatophytes are in detecting molybdenum dispersion in ground-water from a buried ore zone.

"Phreatophytes are plants that depend for their water supply upon ground-water that lies within reach of their roots" (Robinson 1958, p. 4). They are gleaners of water and nutrients below the soil horizon and survive in desert regions only because of this ability. In contrast, xerophytes are shallow rooted and depend upon infiltrating vadose water from the infrequent desert rains. More than 70 species of plants in the western United States are considered phreatophytes.

The depth to a ground-water source is probably the most important limiting factor for the growth of a phreatophyte. Some phreatophytes such as cottonwood (*Populus fremontii* S. Wats.), willow (*Salix exigua* Nutt.), and Arizona sycamore (*Platanus wrightii* S. Wats.) are very sensitive to ground-water depth. The willow seems unable to survive where the free watertable is below 15 feet, and the limit for cottonwood is about 30 feet. These plants are usually restricted to the flood-plains of permanent or intermittent trunk streams draining a basin where there is a major amount of recharge and a relatively shallow watertable. Tamarisk (*Tamarix gallica* L.) roots can reach 100 feet to the watertable, but they are also typically limited to flood-plain areas (Robinson 1958). Perhaps this is due to edaphic factors or the need for large volumes of water.

These phreatophytes were not used for biogeochemical prospecting because of their restricted ecological range. They are not commonly found on alluvial fans or bajadas. Also flood-plain phreatophyte growth would tend not to be a reliable indicator of a molybdenum anomaly in the adjacent hills. Once runoff and ground-water from a particular alluvial area joins the ground-water in the flood-plain sediments of the main trunk stream, any molybdenum in it becomes very much diluted by waters from other sources. Note figure 1 which indicates that the mesquite samples taken on the Santa Cruz River flood-plain show very spotty values if 20 ppm molybdenum in the plant ash is the cutoff for the anomalous condition. The values from mesquite growing on the eastern toe of the adjacent bajada more consistently show the anomalous condition. Similar circumstances exist along the San Pedro River in the Copper Creek area (see figure 3). Soil values on the flood-plain also tend to fall off from those on the alluvium. Dilution from upstream sediments could be a contributing factor.

Three other plants that have a more widespread habitat in southern Arizona are listed by Robinson as phreatophytes. They are mesquite (Prosopis juliflora (Swartz) D.C. var. velutina (Woot.) Sarg.), blue palo verde (Cercidium floridum Benth.) and white thorn acacia (Acacia constricta Benth.) (Kearney and Peebles 1951). These perennials are present on the flood-plains of trunk streams and on the adjacent bajadas and pediment. Each seems to have varying degrees of success growing in the latter areas. Frequently one or the other is absent from one area of the bajada and is proliferating in another. They are often found growing as members of the same plant association and also entirely separate from one another. Much of their geographic growth pattern could relate to their different tolerances to water scarcity. They all have or are suspected of having deep tap roots as well as a diffuse root system (Robinson, 1958, Meinzer 1927, Cannon 1911). Maximum root depths are not well known, but a probable mesquite root was found 175 feet below the surface during the stripping operations for the Pima Mine (Huff 1970). Presumably, some mesquite could tap the watertable at this depth. There is evidence that these three plants do not everywhere have to tap the free watertable in order to survive, although they would if the water is available. Robinson mentions in his definition of phreatophytes that they merely require a ground-water source, not particularly a free watertable. As will be further pointed out, the watertable in much of the area with mesquite, acacia, and blue palo verde growth is too deep for roots to penetrate.

The alluvial material making up the fans and bajadas is of a highly heterogeneous character. There is poorly sorted, rudely stratified, slightly consolidated material ranging from boulders to clay-sized particles and lenses of well sorted sands, gravels, and clays. Also observed in stream and road cuts were numerous buried caliche layers. Water percolating down through the alluvial sediments can become trapped above relatively impermeable local caliche layers forming saturated or unsaturated moisture pockets in sands or gravel. The water can also be adsorbed by clay layers or perched over them and thus be prevented from descending any further (Heindl and DeCook 1952). These water pockets can exist in local aquifers at any level in the alluvium. This type of water supply would not be likely to have a direct link with the perennial water supply and its dissolved molybdenum. These perched zones are available on a limited basis to those plants that are hardy enough to grow on the poor soils of the alluvium; that have a deep, extensive rooting system, that can survive on small, intermittent amounts of ground-water; and that can resist drought for a period of time when these pockets occasionally dry up.

Knowledge of ground-water conditions on most bajadas is scanty because of the few wells on them. Figure 1 is a map of the eatern half of the Sierrita area with some static watertable depths. Many of the watertable levels are greater than 200 feet below the surface. It is improbable that many phreatophyte roots are tapping water below 200 feet. Yet, in most areas, mesquite and one of the other experimental plants were growing in the vicinity in numerous amounts. The Pima-Mission mining operation removed over 200 feet of alluvium before reaching the pediment and no watertable was encountered (Huff 1970). The Twin Buttes Mine removed from 450 to 550 feet of alluvium without intersecting a watertable. The watertable in this place was finally reached 100 feet below the pediment surface. In each locale, mesquite, blue palo verde, and white thorn acacia were growing on the bajada surface over the ore body and are presently growing near the pits. These plants quite probably did not tap a free watertable but had an alternative water source. Since the mine stripping operations were dry, this water source was probably unsaturated moisture pockets and percolating rain water. These plants, then, cannot be depended upon to indicate molybdenum dissolved in the permanent ground-water in every instance.

The water relations of the three plants will be considered individually in the following descriptions.

Mesquite

Most of the samples taken in this study were from this plant. It is a common tree or shrub along washes draining the bajadas of southern Arizona and also occurs on the interfluves in many areas. The most successful mesquite growth is on the flood-plains of trunk streams where they often form dense forests. On the divides of the bajadas, the density is much lower.

Mesquite is an aggressive, tenacious plant partly because of its extensive root system which both fans out laterally and has one or more deep tap roots (see figure 4) (Robinson 1958). This enables it to obtain a supply of water from moisture present in a large volume of soil and

Figure 4. Mesquite trees with tap roots and diffuse roots exposed along the bank of the Santa Cruz River. The vertical escarpments are about 10 feet high.

sediments. Thus the plant is excellent for sampling through large depths of the alluvium.

Studies relating mesquite to ground-water conditions have been numerous (Meinzer 1927). Most observations have related foliar growth, tree density, and size to the depth to the watertable. Water consumption by the plants is inversely related to watertable depth (Davis and DeWiest 1966). Most investigators expect the most luxuriant mesquite growth where the watertable is between 15 and 35 feet, although one study gave a maximum figure of 60 feet. As water depths increase from 35 feet, plant density diminishes and the trees carry fewer leaves and are more stunted (figures 5 and 6). The study areas in which those observations were made are diverse. Climate, soil, and rock type could also have influenced the disparate growth patterns observed.

Observations in the Sierrita area were, in general, similar to those above. Old mesquite trees on the Santa Cruz River flood-plain are often large, with dense leaves, and have a single, well defined bole (figure 5). Since 1947, when reliable water records begin, the watertable in this area has dropped from between 30 to 50 feet to over 100 feet in most wells (Matlock and Davis 1972). The roots of many of the older, larger trees could have followed the slowly lowering watertable. Younger trees growing away from the influence of infiltrating irrigation water often show a more stunted condition indicating that possibly they are

Figure 5. Two large mesquite trees growing on the Santa Cruz River flood-plain near Tucson. Trees of this size indicate good water and soil conditions.

Figure 6. A small shrub-like mesquite on the Sierrita bajada. Mesquite on the bajada are typically of this size and shape.

not tapping the watertable. On the bajadas the trees are smaller, with numerous main stems and fewer leaves. They become more shrub-like. Their stunted condition could result from an unreachable watertable or from lean water yields from perched moisture pockets and rainfall. On the exposed pediment near the mountain front, there were commonly larger, well foliated trees interspersed with smaller ones. Here the phreatic zone can be as shallow as 20 feet. Water supplies are local and are contained in fractures in bedrock. Trees growing on the pediment and bajada demonstrated a more dramatic increase in foliage in response to late summer rains than did those on the Santa Cruz River flood-plain which suggests that these trees depend more on infiltrating vadose water than those enjoying the better ground-water conditions of the flood-plain.

It was thought that measurement of transpiration rates could indicate the water conditions around the plant roots. Possibly those mesquite trees growing where the ground-water supplies were scarce have a lower transpiration rate through a given area of leaf. An Enis Rate Hygrometer was used to measure transpiration rates on trees in good water conditions along the Santa Cruz River and on trees growing where water levels were below 200 feet on the Sierrita bajada. No essential rate differences could be discerned between them. The plant apparently compensates for a lack of water to transpire by producing fewer leaves (table 1).

In controlled laboratory experiments, spine lengths on mesquite were correlated with moisture content in the soil and temperature (Karpiscak 1973). I noticed that spine length sizes on mesquite in the field could vary greatly from plant to plant and even from branch to branch. On some branches thorns were extremely diminutive, barely seen; on others the lengths exceeded three inches. Other studies have correlated large spines with browsing intensity (A. M. Solomon, oral communication, 1974). I attempted to note spine lengths and location of trees and correlate them with possible water conditions. Observations were made while sampling in the Sierrita area. No such correlation was evident from the data, probably because many other factors than moisture influence spine length. Browsing by cattle is prevalent throughout most of the area (table 2).

These studies on mesquite-water relations were adduced to stress that some caution should be used in concluding where an anomaly might be when revealed by molybdenum values in mesquite trees growing on the bajada. A few wells on the bajada can reveal something as to the nature of the watertable and the possibility of mesquite roots tapping it. If no wells are available, perhaps a comparison with another known area with similar weather conditions, alluvial cover, geomorphology, and vegetation can be an aid in estimating ground-water conditions. This coupled with an observation of the physical condition of the

Table 1. Transpiration Rates of Mesquite Leaves in Seconds per Square Centimeter

Trees on Santa Cruz River flood-plain:			
12	14	13	18
9	9	11	12
17	22	25	
Trees on Sierrita bajada:			
14	13	13	13
9	8	8	20
20	20	17	16

Table 2. Thorn Lengths in Inches on Mesquite Growing in Good and Lean Water Condition

Lengths on trees along Santa Cruz and San Pedro River flood-plains:			
2 1/2	1	1/4	1/8
1/8	1/8	1/2	1/4
1 1/4	3	3 1/4	1 1/2
1/8	3/4	3/4	
Lengths on trees on Sierrita bajada:			
1/4	1/4	3	3
1/8	1/8	1/4	3/4
1	1 3/4	2	3 1/4
2 3/4	1/8	1/8	

trees can lead one to a reasonable guess at what the roots are sampling.

Blue Palo Verde

Of the three plants sampled, the blue palo verde is probably the most xerophytic (see figure 7). The small leaves on specimens growing on the bajada are absent much of the time. Rainfall stimulated marked leaf growth. There are no records as to root depth, but most likely they do not extend as far as mesquite. I noticed on uprooted specimens and at root zones exposed along stream cuts that a predominant tap root often could not be distinguished. Tap roots are especially noticeable on mesquite. Rather, palo verde roots of almost equal size radiate out from a base and are seen at shallow depths where the surface is bulldozed (see figure 8). Blue palo verde are more plentiful in predominantly xerophytic communities than are mesquite and white thorn acacia. They are also seen growing on flood-plains of major streams where water supplies are more plentiful.

The yellow or foothill palo verde (Cercidium microphyllum (Torr.) Rose & Johnst.) is more closely associated with xerophytic conditions and is not considered a phreatophyte by Robinson (1958). It was not sampled.

Figure 7. Blue palo verde trees on the Sierrita bajada.

Figure 8. An uprooted blue palo verde showing the disposition of its root system.

White Thorn Acacia

Of the several species of _Acacia_ growing in southeastern Arizona, _Acacia constricta_ was the species most commonly found on the Sierrita bajada (figure 9). When found with mesquite they occupy similar ecological niches along washes and on the interfluves, although the white thorn acacia has a greater tendency to concentrate along washes and gullies.

One important reason for sampling _Acacia_ is that as a genus it is common in arid parts of Africa, Australia, and Asia. The species are either trees or shrubs and often stand out as the only large plants for miles around. They have been successfully used in prospecting for copper, zinc, nickel, lead, and cobalt in Africa (El Shazly et al. 1971). Since they are legumes, it is possible that they could be used equally well for molybdenum indication.

Root depth data for _Acacia constricta_ are lacking. It is smaller and more shrub-like than mesquite and has more xerophytic characteristics. Root depths for this species of _Acacia_ are probably not as extensive as mesquite.

Plant-Molybdenum Relations

When doing biogeochemical prospecting, the geologist can be aided by a knowledge of the relation between the element considered and the plant. Such familiarization can help in deciding whether the element is readily available to the vegetation of the particular area.

Figure 9. A white thorn acacia bush on the Sierrita bajada.

So far as is known, the primary function of molybdenum in plant growth is to aid in reducing absorbed nitrate to ammonia (Sauchelli 1969, Chatt 1974). Without molybdenum, this function is severely impaired, and nitrate can build up in the tissues to toxic levels or the plant can suffer from nitrogen deficiency. Molybdenum is found in plant tissues that have the greatest amount of metabolic activity. Thus, on the average, it is mostly concentrated in the phloem, cambium, and vascular parenchyma; in lesser amounts in the cortex and epidermis; and is negligible in the xylem. Certain stains were applied to different plant tissues where the color intensity of the stain varied directly with the reducing activity of molybdenum in the tissue (Hewitt and Agarwala 1952). I thought that perhaps such a staining technique could be used for a quick field test for anomalous molybdenum quantities in plant tissues. Unfortunately, reduction activity increases up to a maximum quantity, then stops. More molybdenum is excess and apparently has no function in the plant. The functional molybdenum boundary is below the amount needed for biogeochemical prospecting.

Molybdenum also is a necessary agent in nitrogen fixing bacteria to aid in reducing atmospheric diatomic nitrogen to ammonia in the root nodules of certain plants such as members of the Leguminosae (Barshad 1948). Many legumes are extremely tolerant to large amounts of molybdenum in their tissues, possibly because of this relationship. One mesquite tree analyzed had over 600 ppm (ash weight) in its twigs and showed no apparent toxicity symptoms.

Soil and water pH effects plant molybdenum uptake. Studies have indicated that the optimum pH for molybdenum uptake is between 7.0 and 7.5 (Barshad 1951). Below pH 7, molybdate becomes progressively less soluble. Above pH 7.5, roots are likely to absorb less molybdenum due to mechanisms within the plant. On the alluvium of the areas studied, the soil pH ranged from 6.6 to 8.4 (Gelderman 1972). Groundwater pH in the Sierrita and Sacaton areas averaged between 7.0 and 7.6. Responses of plants to molybdenum uptake in this study indicated that these pH ranges probably did not seriously hinder favorable results for exploration purposes.

Of obvious importance to biogeochemical prospecting are the plant parts most likely to contain molybdenum and reflect available molybdenum quantities in the growing medium. As with plant tissues, the plant parts most likely to have high amounts of molybdenum are those with high metabolic activity (Barshad 1948). Young roots usually have the highest molybdenum but are impractical for sampling. Leaves, twigs, axillary buds, and apical buds have the highest molybdenum content of the subareal elements. The seeds, their pods, and other parts of fruits in general have lower molybdenum values. For example, the twigs of a blue palo verde had 9 ppm, whereas the seeds and pods measured 4 and 2 ppm, respectively. Leaves and twigs are the most easily sampled.

In eleven comparison tests of twigs and the leaves growing on them, the twigs were consistently higher beyond the 99% confidence level (table 3). Huff's determinations showed the reverse condition (1970). Twigs were used in this study because of my data and also Huff's use of twigs. They are also readily available for sampling during any season.

The presence of other plant nutrients can effect the amount of molybdenum absorbed by the plant and thus possibly obscure an anomalous content in the alluvium. Experiments by Bolle-Jones (1956) and others revealed that molybdenum tends to accumulate in sulfur deficient leaves, that there is a distinct molybdenum depression in leaves with phosphate deficiency, and a similar depression in some nitrogen and boron deficient leaves. Molybdenum depression can also occur with the presence of significant amounts of other heavy metals in the soil solution such as copper, manganese, zinc, and nickel (Sauchelli 1969). These metals might pose problems to biogeochemical detection of molybdenum anomalies in acidic soil and water environments.

Methods of Analysis

The thiocyanate method was used for analyzing total molybdenum in plant material and soil. The procedure was modified from that described by Ward, Lakin and Canney (1963). Several changes were

Table 3. Molybdenum Values in ppm (Ash Weight) of Eleven Twigs and the Leaves Pruned from them

Twigs	Leaves
31 ppm	27 ppm
30	18
33	21
21	18
21	18
15	14
40	23
30	26
37	24
30	23
37	29

found helpful. Instead of adjusting the pH of the sample solution by using 0.6 ml of concentrated hydrochloric acid, only 0.5 ml was used because the thiocyanate solution was unstable using the former amount. Two drops of 0.01 N ferric chloride and 0.5 ml of 10% solution of potassium nitrate were added to both standard and sample solutions after they were neutralized. These additions increase the color intensity and the stability of the colored organic complex (Barshad 1949). Without the addition of ferric iron to the standard solution, an error of nearly 50% may result. Each sample solution was analyzed in a Bausch and Lomb Spectronic 20 colorimeter. The increase in color intensity was beneficial when using the colorimeter because of the increase in color range. The quantity of ether was also changed from 1 ml to 2.5 ml in order to have a sufficient amount for the transmissivity measurement. The increase in color intensity also compensated for the dilution effect of the additional ether.

Values for soil samples were acquired by visually comparing the sample solutions with standards.

Elements that commonly interfere in the thiocyanate test are iron, tungsten, rhenium, titanium, vanadium, and platinum (Reisenauer 1965). Most are not found in quantities sufficient to seriously interfere with the effectiveness of the test in determining molybdenum anomalies. Iron is reduced and rendered colorless by stannous chloride.

Tungsten is known to be taken up by plants and substituted for molybdenum to form certain reductase analogues which are not functional (Notton and Hewitt 1974). In several duplicate plant analyses, citrate was added to the acid solution to remove any tungsten from the color complex. No color difference was discerned. Thus, tungsten was not present in appreciable quantities. Rhenium is present in amounts up to 780 ppm in the molybdenite as mined (Bloom 1966). The effectiveness of the test for biogeochemical prospecting would not be curbed by these quantities of rhenium.

Unless otherwise specified, parts per million molybdenum refers to the ash weight of the plant material. All plant material was burned to a white ash in preparation for analysis.

Sampling Procedures

Routine vegetation samples were taken with emphasis on consistency and expeditiousness. From 10 to 12 twigs were pruned from around the outside perimeter of each tree or shrub and cut into one inch sections. About 6 or 7 grams were needed for an adequate amount of ash. Mesquite twigs collected were less than 3/8 inch thick, no more than two growing seasons old, from 6 to 12 inches long, slightly woody, and living. Blue palo verde twigs were living and up to 6 inches long. The most slender, dead twigs of acacia were taken. The living twigs of acacia were difficult to handle and prepare in the field and laboratory because of their thorns. Leaves in each case were removed and discarded unless desired for a sample. From 5 to 6 grams of leaf material was sufficient. All plants sampled were the larger representatives of those growing in the area. Sampling began in June, 1974 and was concluded in mid-December.

Some experiments were conducted on comparative molybdenum quantities in different morphological parts of mesquite. These samples were taken primarily from a group of trees on the Sierrita bajada in section 26, T16S, R13E, just east of the Pima Mine Road and I-19 junction.

Total numbers of vegetation samples taken in the Sierrita area are: mesquite, 236; blue palo verde 16; white thorn acacia, 22. In the Sacaton area, 34 mesquite and 9 blue palo verde samples were collected. In the Copper Creek area, 38 mesquite samples were collected.

Soil samples were sieved through a nylon screen (approximately 60 mesh) and the fines analyzed. A 1/2 cm layer of the surface soil was removed in order to eliminate any molybdenum rich dust from nearby mining operations. Total numbers of soil samples were: Sierrita area, 43; Sacaton area, 7; Copper Creek, 4.

Sampling and Analytical Errors

Reproducibility of the plant analysis was tested by replicate determinations on splits of the same sample. Forty-eight pairs of samples yielded a coefficient of variation of 0.08 (Huff et al. 1961) (Table 4). According to Huff (1970), this is an acceptable error for a biogeochemical technique. The average span of error was ±2.4 ppm molybdenum in ash samples having 1 to 95 ppm total molybdenum. The span of error increases as molybdenum values increase. The maximum difference was 9 ppm. Much of the difference could be due to a 4% possible error when weighing the plant ash. Because of the time consumed in weighing, each 0.025 gram sample was only weighed to ±0.5 milligram.

The span of error for replicate soil samples was estimated to be less than 1 ppm with values less than 5 ppm and 3 ppm for higher amounts. The difficulty in visually estimating small differences in color values limits a more precise determination.

Sampling error was determined by taking double samples at many of the sample sites. Fourteen pairs of mesquite twig analyses yielded an average coefficient of variation of 0.10 which is only slightly higher than the analytical error and cannot be considered significantly different to distinguish the two errors (see table 5).

Table 4. Replicate Analysis of Ash Samples Produced an Average Coefficient of Variation of 0.08

Analysis 1	Analysis 2	Analysis 1	Analysis 2
12 ppm	14 ppm	18 ppm	14 ppm
18	23	57	61
29	23	28	37
6	9	25	32
13	12	62	64
15	15	89	95
1	3	31	26
5	5	89	98
32	29	25	23
30	32	34	35
17	19	3	2
8	10	35	36
62	59	45	37
6	6	17	13
6	6	30	27
20	20	11	12
35	35	67	67
29	30	11	10
95	89	34	34
68	65	52	51
35	34	27	31
53	57	42	40
13	13	18	18
68	68	23	22

Table 5. Duplicate Samples Produced an Average Coefficient of Variation 0.10

Sample 1	Sample 2
11 ppm	10 ppm
6	6
31	29
19	17
29	34
53	59
63	65
13	12
51	78
72	52
29	34
74	67
22	22
11	13

However, two of the sample pairs had a much greater range than was ever encountered as analytical error. One sample pair had values of 51 and 78 ppm; another pair ran 92 and 52 ppm. Huff had a coefficient of variation of 0.35 for his double samples. This is an objectionably high error and he attributed it to sampling procedure.

Several studies were made to determine some of the sources of sampling error. Nodes of mesquite twigs averaged over four times the molybdenum content of the internodes by dry weight and over three times the amount by ash weight (see table 6). I observed that many twigs had different node spacings. Random selection of twigs could result in some samples containing fewer nodes because of long internodes. In figure 10 are two sets of twigs pruned from the same tree. The set with the large internodes had 16 ppm, the other had 21 ppm. One value would have been interesting biogeochemically, the other not. It is recommended that nodes be included on most of the sections of twigs to be ashed or that only nodes be sampled. Even the tiny nodes on white thorn acacia had greater molybdenum values than the internodes, but it would not be practical to separate the two on this plant.

Twigs of different ages were compared to see if significant differences occur (see table 7). A comparison was made of mesquite twigs less than two growing seasons old and older twigs. The average for the younger samples

Table 6. A Comparison of Molybdenum Values in Mesquite Ash from the Nodes and Internodes of the Same Tree

Nodes	Internodes	Whole Twig*
55 ppm	13 ppm	
68	16	
59	20	
67	11	37 ppm
65	13	40
46	12	30
18	9	
16	9	
18	12	
12	4	

* The three whole twig values were from branches next to those sampled for node-internode analysis.

Figure 10. Mesquite twigs compared. The lower twig has internodes half again as long as the other two. All are from the same tree. The middle and lower twigs were ashed for analysis.

Table 7. Age Relations of Twigs*

1 season	1-2 seasons	2 seasons	dead
38	40	52	103
30	30	39	41
38	37	33	100
23	27	55	62
32	30	29	72

*The twigs on each line were pruned from the same mesquite. Values, in general, go up as the twig grows beyond 2 seasons in age.

was 33 ppm and for the older, 42 ppm. The older twigs contain greater molybdenum concentrations significant beyond the 99% confidence level. Another comparison was made of twig growth less than one season old and those older than one but less than two seasons old. They were not significantly different. Dead twigs of indeterminate age were also compared with the living twigs described. They averaged 75 ppm. Dead twigs consistently had the highest molybdenum values per ash weight and dry weight. This may be largely due to the fact that as the twig gets older, the ash weight to dry weight ratio becomes smaller and after death it is the least. Molybdenum quantities increase inversely with this ratio. Older leaf laminae also can have higher molybdenum contents than younger leaves as a study of rubber tree laminae showed (Bolle-Jones 1957). Consistent use of similar aged material is necessary if one is to meaningfully relate samples with one another and to the background.

Different main branches of the same mesquite tree were separately sampled to see if molybdenum varied among them. Most of the trees had similar values for all main branches. Two did not, however. Since variations due to age needed to be eliminated in this test, young leaves were sampled and compared rather than twigs. One tree yielded 17, 31, and 36 ppm for its three main branches; another measured 21, 21, 21, and 31 ppm. Reasons for these differences are speculative. It is known that one part of the root system can effect one portion of the plant's subareal growth (T. C. Tucker, oral communication, 1974). Perhaps the molybdenum could differ around the root zone. Also, molybdenum quantities are the greatest in foliage that has the highest water content (Bertrand 1940). Portions of the plant's foliage could have a higher water content because of their advantageous root positions or root health factors. When sampling around a tree, some care should be taken to glean similar amounts of twigs from each main branch, especially when collecting multiple samples.

Cognizance of these variations of molybdenum values in plants and the attending sampling errors that can result can help insure that proper precautions be taken and that the values obtained reliably reflect the molybdenum contents of the growing medium.

Plant Comparisons and Background Sampling

In order to compare the effectiveness of the three plants for biogeochemical prospecting, blue palo verde and white thorn acacia were sampled as companion plants of a number of mesquite trees. The companion plants chosen grew close to the mesquite on the same geomorphic surface (old alluvium, modern alluvium, flood-plain, etc.). The three plants were also sampled for background values in a non-anomalous area.

Background values of whole mesquite twigs ran as high as 14 ppm molybdenum. One sample of nodes had 18 ppm. Huff used 18 ppm as a cutoff from an anomalous condition. The overall average for plant ash in general is 13 ppm (Cannon 1960). The choice of a critical value reflecting an anomalous condition is somewhat arbitrary and depends mostly on the geologist's feeling for the factors influencing molybdenum availability in the area being studied. In this study, 16 ppm or less was regarded as background, from 17 to 19 as threshold, and 20 and above as anomalous. Samples taken for background values were from the alluvial slopes flanking the south side of the Santa Catalina Mountains, just north of Tucson. Soil values here were less than 2.5 ppm molybdenum. There is no known ore body containing more than a trace of molybdenum which contributes material to that alluvium. With the exception of minerals common to ore deposits, the mineralogy of the Santa Catalinas is somewhat similar to the mountains adjacent to the experimental areas.

Sixteen pairs of blue palo verde and mesquite samples were collected from the central and northeast portion of the Sierrita bajada (see figure 1). The Student's T Test on their values established that molybdenum values in the blue palo verde are significantly lower than those of the mesquite at the 99% confidence level. The highest background counts for blue palo verde were 6 ppm.

Several of the mesquite trees carrying anomalous values did not have corresponding anomalous values in their companion blue palo verde trees. I conclude that blue palo verde is not as reliable an indicator of molybdenum content in alluvium as mesquite. Since its roots are likely to be more shallow than mesquite, it should be restricted for use in detecting molybdenum values to the first few feet of alluvium at best.

Twenty-two pairs of white thorn acacia and mesquite were sampled from the central and southeast portion of the Sierrita bajada (see figure 1). The dead twigs of acacia carried higher values than the living mesquite twigs in almost every case. The Student's T Test rates acacia values significantly higher at the 99% confidence level. The highest background count for dead acacia growth was 12 ppm. Mesquite-acacia pairs consistently gave compatable results in anomalous and non-anomalous situations. Acacia is at least as good as mesquite in reflecting molybdenum values in shallow alluvial sediments and soils.

RESULTS AND DISCUSSION

The Sierrita Area

The main mass of the Sierrita Mountains is a low, maturely dissected range located about 20 miles southwest of the city of Tucson. The range is bounded on all sides by the extensive Sierrita pediment and bajada. The slope of the bajada is from 2½ to 4 degrees and extends for as much as 12 miles. Altitudes in the area range from 5,991 feet at Samaniego Peak, to 4,400 feet at the head of the pediment, to 2,600 feet along the Santa Cruz River. The alluvial apron may begin at the mountain front or as far as five miles away.

Streams draining the piedmont are ephemeral and form a radial drainage pattern around the mountain mass. These washes drain into the Santa Cruz River in the north and east and Sopori wash in the south. Most of the modern alluvium in the washes is shallow (less than 10 feet), and stream divides are low. Streams have not deeply dissected the pediment and alluvial surfaces. Local relief averages from 10 to 30 feet. Pleistocene soil remnants on the interfluves testify that these surfaces are old and have not been crossed by modern streams (Huff 1970).

Alluvial cover varies from zero over much of the exposed pediment to hundreds of feet near the Santa Cruz River.

Depth to the watertable increases upslope on the bajada. On the Santa Cruz flood-plain, the watertable was between 100 and 150 feet in 1974, but it was only 20 to 30 feet before pumping began years ago (Matlock and Davis 1972). None of the pit operations encountered water while stripping the alluvium to uncover the pediment surface. Water of any note was only encountered well below the pediment surface. Water under the exposed pediment is often very shallow (less than 20 feet) and confined to fractures in the bedrock. Because of this, quantities are not usually great and are sporadically distributed.

Numerous mines, mining prospects, and mineralized outcrops are scattered throughout the eastern Sierrita Mountains and pediment in the Pima and Twin Buttes mining districts. Mining operations began in the 1850's and have continued sporadically ever since (Kinnison 1966, Lynch 1967). Most of the early operations mined copper, lead, and zinc sulfides and silver in vein or replacement deposits. These mines are presently (1974) inactive. The Mineral Hill and San Xavier mines in the Pima mining district and several of the old mines in the Twin Buttes district contain molybdenum in minor amounts. The paucity of information and lack of molybdenum assays reported in many of the other operations makes one wonder about them. Most of the old mines are located on the exposed pediment or on inselbergs rising above the bajada. Since 1951, four large pit operations have begun in porphyry copper ore bodies. The ore deposits of the Pima-Mission and Twin Buttes operations are located on the buried pediment under a minimum of 200 and 450 feet of alluvium, respectively. The Duval excavations are just within the Sierrita Mountains at higher elevations than the other three. These large deposits contain an average of 0.025% molybdenum. All the ore deposits are suspected of being related temporally and geologically to the intrusion of a quartz monzonite porphyry stock of early Tertiary age (age of quartz monzonite - 57 million years BP, Marvin et al. 1973).

Several factors made the eastern Sierrita bajada somewhat unsatisfactory to test dispersion of molybdenum from an anomalous pediment surface through an alluvial cover. The presence of molybdeniferous ore bodies on the exposed pediment and in the mountain mass can obscure the detection of dispersion from under the alluvium. Dispersion trains from the Sierrita-Esperanza orebody, San Xavier, Mineral Hill, and the old Twin Buttes ore bodies and the numerous mineralized outcrops can effectively flood the bajada with molybdenum. Indeed, the bajada is partly made up of material from these ore bodies. Detrital material of ore derived from distant outcrops was found in modern alluvial materal. The heavy mining activity could also contribute to spurious results. However, molybdenite in the dust from recent mining activity should not drastically effect molybdenum values in plants since the MoS_2 must be oxidized to molybdate before becoming available for plant uptake. Soil molybdenum values are also much higher than average near the Duval ore bodies and in the Pima mining district (see figure 1). Values fall off with distance from these deposits, but they still remain higher than average throughout much of the eastern Sierrita piedmont. The lack of a watertable reachable by roots over much of the alluvium made the detection of molybdenum dispersion by phreatophytes rather dubious. Yet, with all its drawbacks, the area still had the advantage of Huff's study of the Pima mining district to use as a check before sampling new territory adjacent to it.

Vegetation associations varied greatly on the Sierrita piedmont, but mesquite was ubiquitous in most of the area. Mesquite grew on the interfluves of the bajada as well as along washes.

Biogeochemical Responses in the Sierrita Area

A number of samples in this study were taken throughout Huff's experimental area to test for compatibility (refer to figure 1). In general, most of the sampling north of the Pima-Mission Mine in Townships 15 and 16 south compared favorably. The anomalous and non-anomalous areas of Huff's study were fairly well confirmed by my samples. Differences did arise, however, in samples from around the

San Xavier and Olive Mining Camps. Huff's samples were low, reflecting a non-anomalous condition; whereas mine were generally higher than 30 ppm. It does not seem likely that even Huff's large sampling error of 0.35 could account for these disparities. All the mines in the camps are abandoned, and the area has been undisturbed for years other than for some small house construction. The Pima-Mission pit is two miles away. It does not seem likely that dust could have effected such large changes in plant molybdenum values, especially since the molybdenum is in sulfide form, and the small amounts of MoS_2 present in the dust from the mines would be greatly diluted as it spread around the area. Also, these camps are in the opposite direction from the prevailing winds in the area. Soil values from the two samples collected in the Olive Camp area have 20 ppm total molybdenum which is large enough to account for my values, considering soil background counts average less than 5 ppm. It is possible that analytical errors may account for the differences since Huff does not mention the additions of nitrate and ferric iron to his analysis procedure as suggested by Barshad (1949). Other than speculation, no satisfactory explanation can be given for these differences.

As can be seen on figure 1, the mesquite of the eastern Sierrita piedmont show a widespread molybdenum anomaly. The isoconcentration lines show the source area of much of the dispersion is around the Sierrita-Esperanza ore body, possibly from bedrock pediment in sections 1 and 2, T18S, R12E, and from around the San Xavier and Olive Camp mines. The Twin Buttes and Pima-Mission ore bodies seem not to have effected molybdenum in mesquite growing near them. The isoconcentration lines are not influenced by those areas.

Soil values themselves are anomalous throughout most of the bajada and pediment. High soil values correspond roughly with high values in mesquite. This is again contrary to Huff who reported very little molybdenum in the soil and alluvium.

In one area near the northeast corner of the Twin Buttes mine dumps, soil samples yielded only 1 to 2 ppm molybdenum while a mesquite had 49 ppm and an acacia had 44 ppm. A series of 6 soil samples were taken under these two plants and at a distance from them to ascertain whether the high molybdenum in the plant detritus influenced the amount of molybdenum in the soil under the plant. Soil values at the perimeter and under the mesquite and acacia had 1 to 2 ppm molybdenum but the soil values clear of the tree had less than 1 ppm.

It is commonly assumed by some that vegetation sampling will show nothing more than soil sampling would. The above example and others yet to be mentioned in the Copper Creek area serve to illustrate the fallacy of this idea.

The top three inches of soil contained the most molybdenum. Soil samples were taken through a vertical column in a stream cut in section 13, T18S, R13E, in a quarry in section 11, T18S, R12E, and from a hole in section 21, T18S, R13E. Results were as follows:

Section 13	
surface 3 inches	40 ppm
1 foot beneath surface	10 ppm
4 feet beneath surface	8 ppm
8 feet beneath surface	8 ppm
Section 11	
surface 3 inches	40 ppm
1 foot beneath surface	8 ppm
2 feet beneath surface	10 ppm
Section 21	
surface 3 inches	10 ppm
1 foot beneath surface	5 ppm

The high soil values obscure possible uptake from ground-water supplies. It is possible that the anomalous condition in trees located along the eastern toe of the bajada and on the Santa Cruz River flood-plain, especially east and southeast of Black Mountain, resulted from tapping the permanent water supply. Here, from Huff's data, molybdenum values in ground-water are high and the watertable shallow enough for mesquite roots to reach. However, soil values are slightly higher than background, between 5 and 10 ppm.

A dozen pairs of mesquite samples were taken on the bajada to detect any significant differences between trees growing on the old and modern alluvium (see table 8).

Table 8. Molybdenum Values from Mesquite Tree Pairs Growing on Old and Modern Alluvium

Old Alluvium	Modern Alluvium
22	20
31	19
23	32
36	22
82	28
30	28
41	33
45	51
34	30
77	74
36	8
28	20

In each locality, one tree grew on the old alluvium of the interfluves, the other nearby in a riparian environment on a modern floodplain or wash. The latter trees are commonly more lushly foliated because of the better water supply to their roots, the washes being better infiltration zones for vadose water. The trees on the old alluvium had significantly higher molybdenum values beyond the 0.95% confidence level. The divides are old surfaces. The old alluvium was derived from bajada forming processes which dispersed materials from mineralized zones over a wide area. Many of the modern washes do not drain a mineralized area on the pediment or in the mountains, nor do many of them even reach the pediment. Much of the modern alluvium is from a non-anomalous area or is reworked old alluvium. Molybdenum values would tend to be poorer in it. Also, mesquite in the washes could be using their diffuse root system to take up precipitation runoff and therefore very little molybdenum. When prospecting on a degrading bajada, it is recommended that trees growing on the two types of surfaces be distinguished from one another.

The distances to which molybdenum can be dispersed in anomalous quantities is striking on the Sierrita bajada. The mesquite samples along the Sopori Wash are anomalous 12 miles from the nearest known molybdenum source (the Duval Company mines). Note that trees on the south side of the Sopori Wash on the bajada of the Tumacacori Mountains are not anomalous. This demonstrates the influence that Sopori Wash drainage has had in effectively separating dispersion trains of elements from the two mountain ranges.

There is no way of discriminating in the Sierritas whether molybdenum values in trees are from a ground-water source or from within the sediments. But given the water-table levels throughout most of the area, it must be concluded that trees are primarily picking up molybdenum that was dispersed overland within clastic fragments or as a dissolved fraction of the sediment load during alluviation. The molybdenum anomaly in the mesquite, however, is more extensive than the soil anomaly.

The Sacaton Area

The Sacaton porphyry copper ore body is located under the buried pediment about one mile south of the Sacaton Mountain mass and some seven miles northwest of the town of Casa Grande.

The Sacaton Mountains are a small, low, deeply dissected range heavily laced with pediment passes, embayments, and cols. The range appears to be more of a loose collection of peaks and knolls than a mountain mass. The highest elevation is 2,800 feet on Sacaton Peak; the pediment usually begins at about 1,600 feet elevation; the Santa Cruz River is at 1,350 feet.

The pediment surface surrounding the mountains averages 1/2 mile in width and attains a maximum width of one mile. It is remarkably smooth in places, locally having a relief of less than one foot over many acres. Well drilling and mining activities show that the buried pediment has significant variability in depth over small distances; wells show alluvial thicknesses range from 150 to 400 feet within a small area (Tuan 1959). The minimum bedrock depth at the Sacaton ore body is 50 feet. However, the depth quickly increases in the northeast to over 1,000 feet within three-quarters of a mile because of a fault. Probably much of the alluvium over the latter depth is older material unrelated to bajada forming processes. The older alluvium has most likely been beveled itself.

The sediments of the bajada have a much larger fine grained fraction than those around the Sierrita Mountains. The inselbergs at the margin of the main mountain masses are completely surrounded by alluvium from the parent mountains rather than having their own fringe. The bajada has a slope of less than two degrees.

The bajada and pediment surfaces are undissected. The ephemeral streams barely cut into the surface and are often but trails of modern sand on the desert. Interfluves are flat. Local relief on the bajada is usually not more than three feet, in contrast to the Sierrita bajada. Even the Santa Cruz River is a spectre of its former self as it exists along the Sierritas. Its channel is much smaller and ill defined. The Sacaton Mountain area is often looked at as a good representative of the final stages in the degradation of a mountain range in an arid climate because of the fine grained alluvium, low slope, isolated residuals, and pediment passes (Tuan 1959).

Watertables have been descending in the area over the past 40 years because of intensive irrigation practices. In many wells, such as the main well for the Sacaton Mine, the watertable is over 200 feet below the surface. In wells drilled in the early 1950's, the watertable was usually between 80 and 150 feet deep. It was often noted, however, that small amounts of water were first detected at 30 to 50 feet (Halpenny 1952). During stripping of the alluvium for the pit over part of the Sacaton ore body, water was continually present with every drop cut. According to the mine staff, this water was not considered to be from the principal watertable. Present watertables in wells on the Sacaton bajada near the mine are usually more than 300 feet below the surface. Even near the Santa Cruz River, the watertable is below 200 feet (Babcock 1974). Water pH in the Sacaton Mine well is 7.2, ideal for molybdate solubility and the ore contains an appreciable amount of molybdenum, according the geologists at the Sacaton mine, 1974.

Mesquite trees are typically sparse or entirely lacking on the interfluves of the bajada. They are restricted to growing along stream courses and often are the only indication that a water course is there because the channels commonly become nonexistant. Tree growth is evidently largely dependent on the infiltration along these washes. Mesquite growth diminishes nearer the mountains and becomes nil between the mine and the mountain front. Blue palo verde and ironwood (Olneya tesota A. Gray) take over along the washes in that area. No mesquite forest marks the presence of the Santa Cruz River flood-plain. Mesquite and tamarisk only grow directly alongside the water course. No other phreatophytes were seen nearby.

The Sacaton ore body was discovered in 1961 because of the pervasive sericitic and argillic alteration on a granite inselberg. Stripping began in 1972 and economic mining in early 1974. The deposit is separated into two ore zones by the northwest trending, normal Sacaton fault. East of the Sacaton fault, the bedrock dropped between 1,000 and 1,800 feet. The east deposit is located on the downthrown block. Both deposits have chalcocite blankets that are between 100 and 600 feet thick. Primary sulfide mineralization is mainly chalcopyrite and pyrite. Molybdenum values average about 0.01%. Mineralization is probably related to the intrusion of a monzonite porphyry in the early Tertiary Period (Cummings 1974).

Alluvium covering the ore body appears to be of two types. The first is a conglomerate. It varies from zero to 600 feet thick over the upper, west ore body and from 700 to 1,500 feet over the east ore body. This conglomerate is probably related to post-faulting erosion and deposition. Overlying the conglomerate are the bajada sediments which are from 50 to 100 feet thick in the mineralized area. This material is derived from the processes of pedimentation and alluviation during the degradation of the Sacaton Mountains. The shallowest portion of the mineralized zone was about 50 feet below the surface on the crest of the upper fault block.

Biogeochemical Responses in the Sacaton Area

Of the three mineralized areas examined, the Sacaton ore body had several promising features that would lend to detecting molybdenum dispersion through an alluvial cover. Most important, there is no influence from source areas of molybdenum above the bajada surface. There are several, small mineralized zones containing copper on the eastern flanks of the mountains, and one in section 15, T5S, R5E, about 2½ miles northwest of the mine (Wilson 1969). None of these are reported to contain any molybdenum. Three blue palo verde were sampled in the dispersion path of the latter prospect and were not anomalous. Soil samples around the mine had only background amounts of molybdenum.

The rock of the discovery outcrop had only 10 ppm and its soil contains less than 1 ppm. As the area has only been disturbed for a short time by mining, the chances of contamination are small. Finally, ground-water is available for mesquite growth as indicated by wells and mine stripping operations. However, this water is probably perched and not connected to the principal phreatic zone below. Unfortunately, watertable depths preclude their being reached by most mesquite roots. This is the biggest single drawback to successful biogeochemical prospecting of the area and is believed to be responsible for the negative results obtained. Perhaps had this type of prospecting been done 40 years ago when the watertable was shallow enough to be tapped, results might have been different.

A total of 43 twig samples was taken around the Sacaton ore body (see figure 2). Mesquite twigs were used unless none could be found, then blue palo verde were sampled. Blue palo verde trees were only used north of the mine.

No sample had over 15 ppm molybdenum. No soil samples had over 2.5 ppm molybdenum. The area could well have been a study in background sampling as no reflection of the anomaly was detected at the air-land interface at any distance from the ore body.

Reasons for these results are somewhat speculative without a water analysis. The primary factor is the lack of a reachable watertable anywhere in the area. Even along the Santa Cruz River flood-plain, watertable depths were below mesquite root growth possibilities, as evidenced by the poor showing of trees in that area. It was thought that the perched, local water zones and moisture pockets nearer the surface might be suitable for molybdenum dispersion from the shallow parts of the ore body, but apparently they are not. The molybdenum content of the ore body itself might be a factor since it is lower than the other porphyry copper deposits examined.

The Copper Creek Area

The Copper Creek mining district lies within the Galiuro Mountains near their western edge, some 50 miles northeast of Tucson. Most of the mineralization is located in sections 10 and 11, T8S, R18E.

The trunk stream draining the western flanks of the Galiuro Mountains is the San Pedro River, a major stream in southern Arizona that flows most of the year. In the Copper Creek area, the San Pedro River is the principal drainage for the adjacent San Pedro Valley sediments of the Gila Group, the Santa Catalina and Black Mountains to the west, and the Galiuros to the east. Numerous ephemeral, tributary streams drain the basin sediments and mountains. Elevations range from 6,185 feet on Table Mountain near the Copper Creek Camp, to 5,000 feet where the first of the

Gila Group abuts on the flanks of the Galiuros, to 2,400 feet along the San Pedro River.

The San Pedro Valley is a large, northwest trending structural trough bounded by the tilted fault block mountains to the east and west (Heindl 1963). Following the depression of the trough, the sediments of the Gila Group were deposited in the basin probably beginning in the mid or late Tertiary Period and extending to the early Pleistocene. They have undergone a complex history of deposition and degradation. Three formations within the Gila Group have been distinguished in the Copper Creek area. The Quiburis formation is the dominant unit near Copper Creek district. The Copper Creek fault forms the contact between the Quiburis and the older rocks of the Galiuro Mountains. The lower Quiburis is composed of fine grained lacustrine deposits in the center of the valley grading to pebbly sandstone and conglomerate at the edges next to the mountain fronts. The lacustrine sediments are believed to have been deposited when volcanics dammed the ancestral Gila River system in the late Tertiary and early Quaternary Periods, and, as a consequence, large lakes were formed in the basins (Melton 1965). The upper unit is predominantly a pebbly to bouldery conglomerate. Fragments are mostly from volcanics and shallow intrusives. On the east side of the valley, the Quiburis is about 1,000 feet thick; along the river it attains local thicknesses of about 1,700 feet.

The Quiburis Formation is overlain in part by the Sacaton formation. This formation is composed predominantly of poorly consolidated sands and gravels. It lies disconformably on an erosion surface deeply cut in the Quiburis. The basal contact in the Copper Creek area is from 200 to 300 feet above the flood-plain of the San Pedro River. The formation attains a maximum thickness of 250 feet and thins out towards the mountains, never reaching them. Fragments of quartz monzonite and volcanics in the basal unit are characteristic of the Santa Catalina and Galiuro Mountains in the immediate vicinity. Also, there are fragments originating from upstream sources. The basal channel fill is generally parallel to the course of the river. Contacts between the Quiburis and Sacaton formations are generally conformable near the San Pedro River, but in some tributary washes a small, angular discordance was observed.

Late Pleistocene and Recent alluvial deposits consisting of channel fill, flood-plain, and terrace deposits occur along the inner valley of the San Pedro River and its larger tributaries. Some of the terraces are 30 feet above the surfaces of the modern channels. The terrace deposits are composed of a wide variety of materials and range from silty pebble sandstones to boulder conglomerates. The terraces probably represent changes in the degradational cycle in the late Quaternary Period. These deposits also lie on a Quiburis erosion surface.

At present, streams emerge from deeply cut valleys in the Galiuros into deeply dissected valleys in the Gila Group. Some valleys in the basin sediments are over 500 feet deep and slopes are steep. The degree of dissection is in marked contrast to the Sierrita and Sacaton bajadas.

Vegetation associations range from thick mesquite forests on the flood-plain of the San Pedro River, to desert xerophytic growth on the lower portions of the Gila Group sediments, to grass lands on the higher hills near the mountains. Mesquite were locally scarce, especially in the predominantly xerophytic zone. Mesquite were most abundant along washes. Growth on the higher interfluves was light but sufficient for reconnaissance prospecting.

Molybdenite in the Copper Creek district is found in numerous breccia pipes. The breccia pipes are believed to be fault controlled and related to the emplacement of a granodiorite intrusion (Kuhn 1941). They can contain 1 to 8% molybdenum. Other economic minerals include lead, silver, and copper. Mining began for copper and silver in 1863. For years the district remained inactive, until recently, when a copper leaching plant went into operation. The only stream draining the mineralized area is Copper Creek which empties into the San Pedro River about 7 miles from the district. Mineralized rock could be seen in the modern alluvium of the wash several miles from its source.

Molybdenite is also present in the San Manuel ore body located several miles to the west of the San Pedro River near the town of Mammoth. Dispersion from this source is believed not to have interfered with the detection of the Copper Creek dispersion because of the lower values in trees on the San Pedro River flood-plain in contrast with those growing just east of it.

Watertable levels range from 13 to 25 feet on the flood-plain of the river (Babcock 1974). Farther up on the Gila Group sediments, about halfway between the river and the Galiuros, it is down to 318 feet. The latter depths preclude their being reached by roots. There are also numerous deep artesian wells along the river. The artesian aquifer is at least 600 feet deep. An impervious clay layer several hundred feet thick provides the confining cap (Heindl 1952).

Biogeochemical Responses in the Copper Creek Area

The principal question in the Copper Creek area was how the dispersion from the mineralized zone in the Galiuro Mountains was to manifest itself in the intermontane sediments not solely derived from adjacent mountains. The presence of lacustrine deposits including marl and gypsum layers shows that the Gila Group sediments are not simply alluvial rubble. Alluvial fan deposits are found only near the mountain fronts and are common in the San Manuel formation, the lowest formation of the Gila Group, but one that is deeply buried under the Quiburis formation near the Copper Creek district (Heindl 1963). As a result, dispersion trains of molybdenum might not be found radiating from the Copper Creek district across the piedmont to the trunk drainage below except in the modern alluvium of washes directly draining the area.

Sampling produced interesting results as to the dispersion characteristics across the basin sediments. The most striking feature is the absence of anomalous trees between the mountain front and the vicinity of the San Pedro River valley, and the sudden emergence of high molybdenum contents in trees growing proximally to the river valley (see figure 3). Many of the trees growing within a mile east of the San Pedro flood-plain, either on modern alluvium of tributary washes or on the Quiburis formation interfluves, show anomalous amounts of molybdenum. Such trees occur for at least 12 miles parallel to the river valley and as far as 11 miles from the Copper Creek district. The only tributary stream that shows a continuous molybdenum dispersion in trees along its course is Copper Creek itself and it drains the mineralized area. A soil sample from the modern alluvium taken near the confluence of Copper Creek and the San Pedro River flood-plain had 25 ppm molybdenum.

Mulberry Wash, draining an area in the Galiuros only one mile from the mines in the Copper Creek district has no anomaly at the mountain front nor several miles from it. Yet trees along Copper Creek at the mountain front have up to 495 ppm molybdenum. There is, then, marked discrimination in the character of molybdenum dispersion in the modern alluvium from wash to wash, and it is unlikely that dispersion is moving overland in modern material other than within the Copper Creek system.

Many of the stream systems with anomalous molybdenum in the trees growing along their reaches near the San Pedro flood-plain do not reach the Galiuros and, as a consequence, are only draining Gila Group sediments. A series of samples taken up two small washes near Copper Creek Road and along a small stream just north of Mulberry Wash bear anomalous trees for about a mile east of the flood-plain. The boundary between the anomalous and non-anomalous condition is just below the basal conglomerate of the Sacaton formation, above which no anomalous trees occur. Soil samples above and below the basal unit along one of the washes next to the road possess only background molybdenum quantities. Another sample taken in soil derived from the weathering of the basal conglomerate also contains only background amounts even though many of the fragments were derived from a nearby source in the Galiuros. If these few samples are indicative of the molybdenum values of the Quiburis and Sacaton formations, the anomalous trees are not gleaning their molybdenum from that element's primary content in those sediments. Vegetation sampling again reveals more than soil sampling.

The physiography and ground-water conditions may be important in helping to explain this phenomenon. The slope is steep from the margin of the San Pedro River flood-plain to the Sacaton formation contact, after which the Sacaton crops out in a gentler inclined, nearly flat terrace until its eastern contact with the Quiburis is reached where there is a marked increase in slope and dissection. There is almost 300 feet of relief from the San Pedro River to the basal unit of the Sacaton formation. Ground-water in the San Pedro River valley is shallow enough to support a dense growth of mesquite on the flood-plain. As mentioned before, farther up in the hills the watertable is probably too deep to be tapped by mesquite roots but tends to become shallower towards the river valley, possibly becoming shallow enough to be reached by roots near the fringe of the flood-plain. There is over 1,200 feet of relief between Copper Creek at the mountain front and its emergence at the San Pedro River. This slope gives the ground-water system an adequate head to keep water with its dissolved molybdenum moving towards the river from the ore bodies of the Copper Creek district. The numerous artesian wells in the valley testify to the effectiveness of the aquifer and the head of water.

Since the mesquite east of the Sacaton formation boundary and the soil samples reveal the low molybdenum content of both the Sacaton and Quiburis formations and the modern alluvium, the most probable explanation for the pattern of anomalous trees near the San Pedro River valley is that the trees are tapping a molybdeniferous ground-water source moving down-gradient from the Galiuros. Mesquite could tap this ground-water or its capillary fringe for a distance upslope until the watertable became too deep. The critical depth apparently occurs near the Sacaton-Quiburis boundary. Unfortunately, no wells are present on this slope and so there is no watertable data with which to further test this hypothesis. The more stunted condition of the mesquite growing on the hills and washes near the flood-plain could be due to the deeper watertable and poorer soil conditions. Trees growing farther up in the hills are tapping perched moisture sources which are not connected with the principal water-table. The lower values of trees growing on the San Pedro flood-plain precludes a backwash of molybdenum-laden ground-water originating from Copper Creek and moving up into tributary washes from the San Pedro flood-plain.

CONCLUSIONS AND RECOMMENDATIONS

Some generalizations can be made from this study as to the effectiveness of biogeochemical sampling for molybdenum-bearing ore bodies in the basins of southern Arizona and in similar physiographic and climatic areas.

When soil samples have higher than background amounts of molybdenum, mesquite trees always reflect this condition with anomalously high amounts of molybdenum in their twigs. White thorn acacia also reliably reflect high molybdenum in soil. Blue palo verde trees are the least responsive to anomalous soil values.

Some mesquites have anomalous amounts of molybdenum where the soil around them does not. This condition is seen in a sample located near the northeast corner of the Twin Buttes mine dumps and in several of the samples in the Copper Creek area. Mesquite, then, can indicate anomalous conditions in basin sediments in an area where soils do not have high molybdenum contents. Analysis of these soils would not prompt further exploration, nor would they be satisfactory in detecting dispersion trains for follow-up work. The high values in the trees may come either from buried molybdeniferous zones within the alluvium or from its presence in ground-water surrounding the root zone.

The above conclusions strongly suggest that mesquite sampling is more effective than soil sampling for reconnaissance prospecting for molybdenum dispersion in basin sediments of the southwest where the soil characteristics and soil and ground-water pH of the region are likely to be favorable for molybdenum availability to plants. Other deep-rooted plants that fix nitrogen probably can be used for similar purposes in other parts of the world. Biogeochemical prospecting could aid in eliminating or encouraging further interest in the exposed rocks adjacent to basins without the effort required to move physically in those areas. Since the molybdenum values of the plants varied in a roughly direct relationship to its content in the growing medium, the method is appropriate for sampling within the dispersion halo to locate the ultimate source of molybdenum.

The negative results around the Sacaton deposit indicate that analysis of phreatophytes for molybdenum cannot be relied upon everywhere to detect dispersion from a buried molybdeniferous ore zone. The dispersion can be effectively weakened by the excessive depth of the alluvium and the absence of a shallow watertable that can be tapped by phreatophyte roots. Dispersion trains from ore zones located above the basin sediments was readily detected by biogeochemical sampling.

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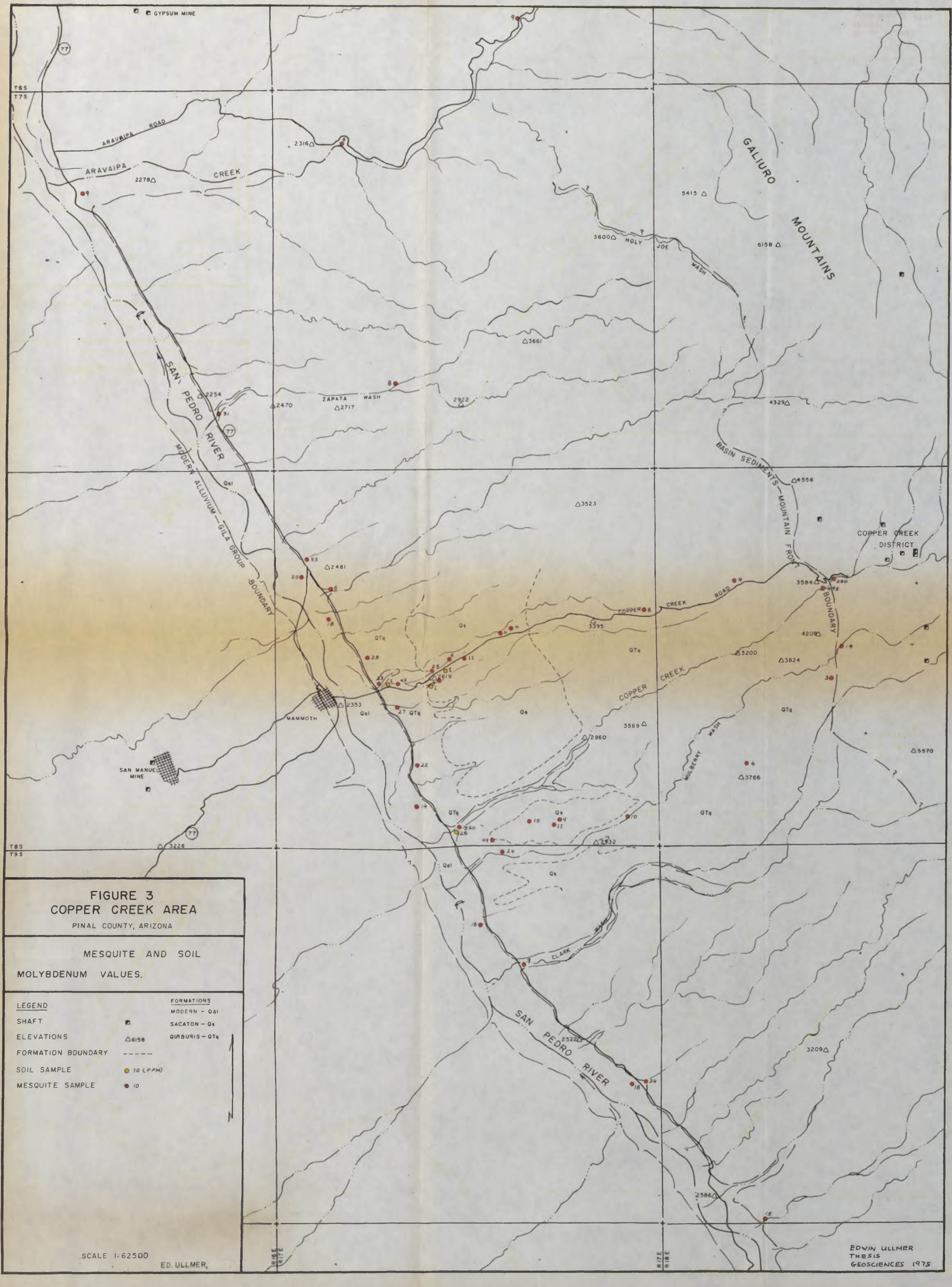

FIGURE 3
COPPER CREEK AREA
PINAL COUNTY, ARIZONA

MESQUITE AND SOIL
MOLYBDENUM VALUES.

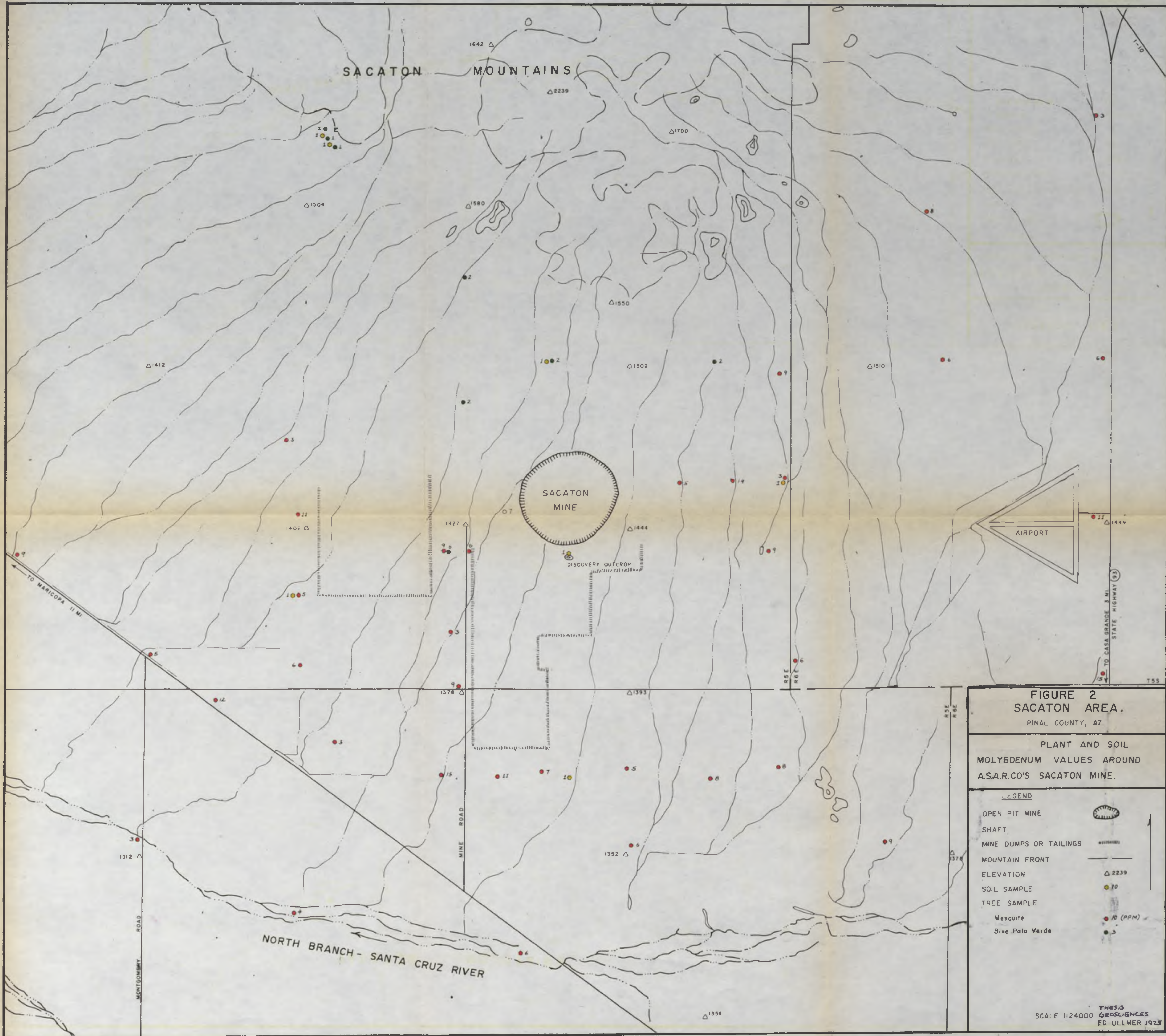
SACATON MOUNTAINS
SACATON MINE
DISCOVERY OUTCROP
AIRPORT
TO MARICOPA 11 MI
TO CASA GRANDE 5 MI. STATE HIGHWAY (93)
I-10
MINE ROAD
MONTGOMERY ROAD
NORTH BRANCH - SANTA CRUZ RIVER
R5E R6E
T5S
FIGURE 2
SACATON AREA.
PINAL COUNTY, AZ
PLANT AND SOIL
MOLYBDENUM VALUES AROUND
A.S.A.R.CO'S SACATON MINE.
LEGEND
OPEN PIT MINE
SHAFT
MINE DUMPS OR TAILINGS
MOUNTAIN FRONT
ELEVATION
SOIL SAMPLE
TREE SAMPLE
Mesquite
Blue Palo Verde
(PPM)
SCALE 1:24000
THESIS
GEOSCIENCES
ED. ULLMER 1975


FIGURE I
EASTERN SIERRITA AREA
PIMA COUNTY, ARIZONA
PLANT AND SOIL MOLYBDENUM VALUES, WATERTABLE DEPTHS ON THE SIERRITA BAJADA AND PEDIMENT.
LEGEND
OPEN PIT MINE
SHAFT
MINE DUMPS OR TAILINGS
PROSPECT
GEOMORPHIC BOUNDARY
ELEVATION 5991
TREE SAMPLES
Mesquite 20 (PPM)
Mesquite from Huff, 1970 20
Mesquite–Blue Palo Verde Pair 20,15
Mesquite–Acacia Pair 20,25
SOIL SAMPLE 8
WATERTABLE DEPTH 150
Mo ISOCONCENTRATION LINE 20
EXPOSED PEDIMENT & OUTLIERS
SCALE 1:62500
ED ULLMER 1975
THESIS
GEOSCIENCES
BLACK MOUNTAIN
TUCSON - 8 Miles
SANTA CRUZ RIVER
NOGALES HIGHWAY
SAHUARITA
PIMA MINE ROAD
MISSION
MINERAL HILL
PIMA MINE
SAN XAVIER
OLIVE CAMP
TWIN BUTTES
ANAMAX MINE
DUVAL MINE ROAD
GREEN VALLEY
SIERRITA
MOUNTAINS
McGEE RANCH
DEMETRIE WASH
SIERRITA
DUVAL MINES
ESPERANZA
ESPERANZA WASH
PEDIMENT–BAJADA BOUNDARY
APPROXIMATE MOUNTAIN FRONT–PEDIMENT BOUNDARY
BAJADA–FLOOD PLAIN BOUNDARY
APPROXIMATE
BATAMOTE WASH
SOPORI WASH
ARIVACA JUNCTION
CERRO COLORADO MTNS
T16S
T19S