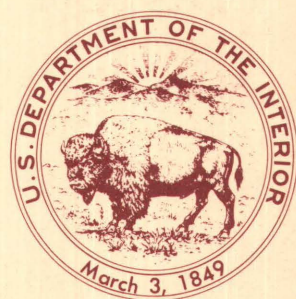


Biogeochemistry of a Highly Serpentinized,
Chromite-Rich Ultramafic Area, Tehama
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ERRATA SHEET

This table replaces table 2 in USGS Bulletin 1901.

Table 2. Summary statistics for element concentrations in leaf and stem material of whiteleaf manzanita and needles of digger pine

[Prior to calculation, data were converted to logarithms; data expressed as ppm, dry weight base, except where noted; site replicated samples (12 and 9, manzanita and pine, respectively) and duplicate analyses (12 for each species) were averaged prior to calculations; ratio, proportion of the number of analyses having values above the lower limit of determination to the total number of analyses; GM and GD, geometric mean and deviation, respectively; leaders (--), no data available]

Element or ash yield	Manzanita				Digger pine			
	Ratio	GM	GD	Observed range	Ratio	GM	GD	Observed range
Ash%	112:112	3.6	1.20	2.0 - 5.8	91:91	2.3	1.20	1.5 - 3.5
Al	112:112	20	1.40	11 - 68	91:91	73	1.56	21 - 170
As	8:112	--	--	<1.2 - 2.6	1:91	--	--	<0.85 - 0.88
Ba	112:112	8.9	1.67	1.2 - 30	91:91	0.84	1.49	0.30 - 1.9
Ca%	112:112	0.67	1.41	0.18 - 1.6	91:91	0.27	1.60	0.086 - 0.80
Cd	44:112	--	--	<0.03 - 0.17	11:91	--	--	<0.026 - 0.075
Cr	112:112	1.4	2.13	0.29 - 7.5	91:91	1.1	1.80	0.42 - 7.5
Cu	112:112	4.3	1.43	1.4 - 9.0	91:91	4.2	1.34	1.9 - 9.1
Fe	112:112	28	1.39	13 - 59	91:91	91	1.62	16 - 220
Mg%	112:112	0.34	1.12	0.10 - 0.6	91:91	0.24	1.31	0.12 - 0.46
Mn	112:112	29	1.75	8.0 - 130	91:91	73	1.81	7.8 - 210
Nb	95:112	0.25	1.36	<0.15 - 0.48	41:91	--	--	<0.12 - 0.23
Ni	112:112	2.6	1.94	0.56 - 13	91:91	4.2	1.82	0.70 - 13
P%	112:112	0.052	1.52	0.015 - 0.17	91:91	0.12	1.32	0.057 - 0.25
Pb	2:112	--	--	<0.24 - 0.41	77:91	0.52	1.80	<0.24 - 2.2
Sr	112:112	14	1.54	3.4 - 34	91:91	2.4	1.88	0.59 - 15
Ti	112:112	1.3	1.49	0.60 - 3.2	91:91	3.6	1.73	0.73 - 10
V	7:112	--	--	<0.04 - 0.08	91:91	0.14	1.77	0.024 - 0.37
Y	36:112	--	--	<0.007 - 0.036	18:91	--	--	<0.006 - 0.01
Zn	112:112	30	1.25	14 - 50	91:91	20	1.49	5.3 - 54

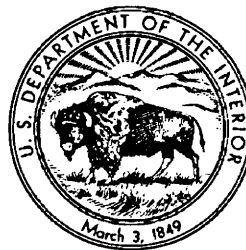
Biogeochemistry of a Highly Serpentinized, Chromite-Rich Ultramafic Area, Tehama County, California

By L. P. GOUGH, G. R. MEADOWS, L. L. JACKSON,
and S. DUDKA

Biogeochemical processes in a chaparral-zone, serpentinized ultramafic area are investigated as they relate to geochemistry and element concentration patterns in manzanita and pine tissue

U.S. GEOLOGICAL SURVEY BULLETIN 1901

DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, JR., Secretary



U.S. GEOLOGICAL SURVEY
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CIP

CONTENTS

Abstract	1
Introduction	1
Purpose of study	1
Description of the study area	2
Location	2
Geology	2
Country rock	3
Alteration	3
Physiography and vegetation	4
Chromium resource assessments	4
Sample collection, preparation, and analytical methods	4
Gridded sampling design for plants	4
Excavated manzanita shrub	6
Vertical traverse sampling design for soils	6
Surface water collections	6
Statistical analysis of data	7
Results and discussion	8
Biogeochemical summaries, gridded study area	8
Powder X-ray analysis of plant ash	8
Summary statistics	8
Results of the analysis of variance	8
Description of biogeochemical patterns	9
Interpretation of univariate element associations	9
Interpretation of multivariate element associations	11
Vertical element trends in the soil profile	16
Uptake and translocation of elements by manzanita	17
Biogeochemical exploration for chromium	21
References cited	23

FIGURES

1. Map showing topography, past mining sites, and surface water sampling sites in Elder Creek study area 2
2. Photograph of Elder Creek study area 3
3. Map showing biogeochemical and geochemical sampling sites in gridded study area 5
4. Three-dimensional diagrams showing areal concentration patterns for six selected elements and ash yield in manzanita shrub stem and leaf material and digger pine needles 12
5. Graphs showing soil physical and chemical variables for soil profiles 08I and 07G 18

- 6-7. Diagrams showing:
 6. Relative position of sampled materials and concentration of selected elements from whiteleaf manzanita shrub **21**
 7. Relation between distance from the basal burl of an excavated manzanita shrub and concentrations of Ca, Mg, and ash yield, and Cr, Fe, Mn, and Ni in samples of roots, stems, and leaves **22**

TABLES

1. Methodology for analyses of sampled materials **7**
2. Summary statistics for element concentrations in leaf and stem material of whiteleaf manzanita and needles of digger pine **9**
- 3-4. Distribution of element concentration variation in samples of:
 3. Whiteleaf manzanita leaf and stem material **10**
 4. Digger pine needles **10**
- 5-6. Results of R-mode factor analysis for:
 5. Manzanita stem and leaves showing relative loadings of element concentrations on four factors derived by varimax rotation **16**
 6. Digger pine needles showing relative loadings of element concentrations on four factors derived by varimax rotation **16**

Biogeochemistry of a Highly Serpentinized, Chromite-Rich Ultramafic Area, Tehama County, California

By L.P. Gough, G.R. Meadows, L.L. Jackson, and S. Dudka

Abstract

The processes that influence Cr mobility and its uptake by plants were studied in a serpentinized, chromite-rich ultramafic area of the Coast Range, northern California. Areal element concentration trends in the stem and leaf material of *Arctostaphylos viscida* (whiteleaf manzanita) and in the needles of *Pinus sabiniana* (digger pine) are related to geological and biological processes that control or influence these trends.

Plants were collected from a gridded rectangular area of about 0.25 km²; 44 m separates the sampling sites. Both manzanita and pine were collected, where found, at 116 accessible sites. Based on the results of element concentration patterns in plant materials, soils were collected in excavated pits at eight sites; both dry- and wet-season collections were made.

Results of a one-way, three-level analysis of variance show that, in general, differences in concentrations of most elements in manzanita shrubs and pine trees separated by 44 m or more are greater than those separated by less than about 3 m. Very similar areal patterns between the two plant species were found for Ni concentrations and to a lesser degree for Cr, Al, Fe, and P.

Associations for 14 and 15 elements (and ash yield) within manzanita and pine, respectively, were examined using R-mode factor analysis. A four-factor varimax solution explains almost two-thirds of the total variance for manzanita. Similarly, four almost identical factors explain almost three-fourths of the total variance for pine. Factor 1 (for manzanita) and factor 2 (for pine) are mainly associated with the alkaline-earth metals and account for 25 and 21 percent of the total variance, respectively. All four factors demonstrate the importance of intrinsic and possibly extrinsic processes that influence the chemistry of these plants.

The uptake of Cr by manzanita and its translocation within the shrub was found to be regulated. Chromium concentrations were five times greater in some root tissue samples than in stem material. Nevertheless, areal Cr

patterns were found to vary greatly and, in general, show high Cr concentrations on the western side of the study area in a highly dissected ridge and gully region near two abandoned chromite mines. Additional scattered high Cr concentrations throughout the study area are suspected to reflect areas where the availability of Cr is greatest due to topographical and chemical influences.

In general, the uptake of Cr by manzanita and pine in these serpentinized soils probably involves both the physical dissemination of chromite and the oxidation of Cr(III) to Cr(VI).

The use of biogeochemistry to differentiate the occurrence of concealed chromite deposits is not yet clearly defined. It would seem, however, that in regions where dispersion of chromite aggregates (pods) has occurred (resulting in increased chromite-grain surface area) and where the potential for Cr oxidation exists, biogeochemistry may be a useful tool with which to locate new exploration targets.

INTRODUCTION

Purpose of Study

Chromium is considered a strategic "mineral" by the U.S. Government, but of the 51 major Cr deposits and districts identified worldwide, none are in the U.S. (DeYoung and others, 1984). Ninety-five percent of the world's known Cr reserves are in South Africa and Zimbabwe, and because the U.S. currently imports all of the Cr it uses and because world supplies are precarious, it is important to assess less conventional methods with which to find domestic Cr deposits.

This study was initiated as part of the U.S. Geological Survey's CUSMAP (Contiguous U.S. Mineral Assessment Program) project of the Redding, Calif., 1°×2° quadrangle. We report the results of investigations designed to define areal element concentration trends in plant material, and we suggest

geochemical and biogeochemical processes that may control or influence these trends. A better understanding of the mechanisms of Cr mobility in serpentinized ultramafic soils and of element uptake by plants growing in ultramafic areas containing chromite deposits is necessary if biogeochemical methods of chromite prospecting are to be effective.

Although chromite is a refractory mineral, vegetation growing in ultramafic areas typically contains large and variable Cr concentrations. In order for Cr uptake to occur, hexavalent forms of Cr apparently must be present; however, the mechanisms by which Cr(VI) is formed in soil or absorbed by vegetation is not known. The use of Cr concentrations in vegetation as an exploration tool has also not been determined.

An increase in our knowledge of the biogeochemistry of Cr and related elements is applicable not only to exploration efforts but also to environmental and toxicological concerns because Cr (particularly as Cr(VI)) can be both phyto- and zoo-toxic.

Description of the Study Area

Location

The study area is in the southeast corner of the Redding 1° × 2° quadrangle, Tehama County, northern California, in the southeast-quarter of sec. 16, T. 25 N., R. 7 W. (Raglin Ridge, Calif., 1:24,000 quadrangle) (fig. 1). It encompasses an area of slightly less than 0.25 km² in rugged, highly serpentinized, ultramafic terrain south of the North Fork of Elder Creek.

The elevation of the Elder Creek study area ranges from about 450 to 670 m. The topography of the area is varied; for purposes of discussion, we divided the region into four landscape units (fig. 2): (1) a region of steep ridges and gullies, (2) a gently sloping (< 5 percent) low bench region, (3) a moderately sloping (> 5 percent) high bench region, and (4) a high, moderately dissected ridge. The ridge and gully region is deeply cut by highly eroded incised drainages.

Geology

The study area is at the northern tip of a north-trending, tabular peridotite body of the Coast Range ophiolite suite (Strand, 1962; Irwin, 1964) near the junction of three major geologic provinces, the Klamath Mountains, the Coast Range, and the Great Valley (Irwin, 1966). Although Bayer (1983) mapped the area as part of the Franciscan Complex of the Coast Range, Blake and others (1982) associated it with the pre-Cenozoic rocks of the Great Valley.

Blake and others (1982) suggested that the peridotite and associated sedimentary rocks were

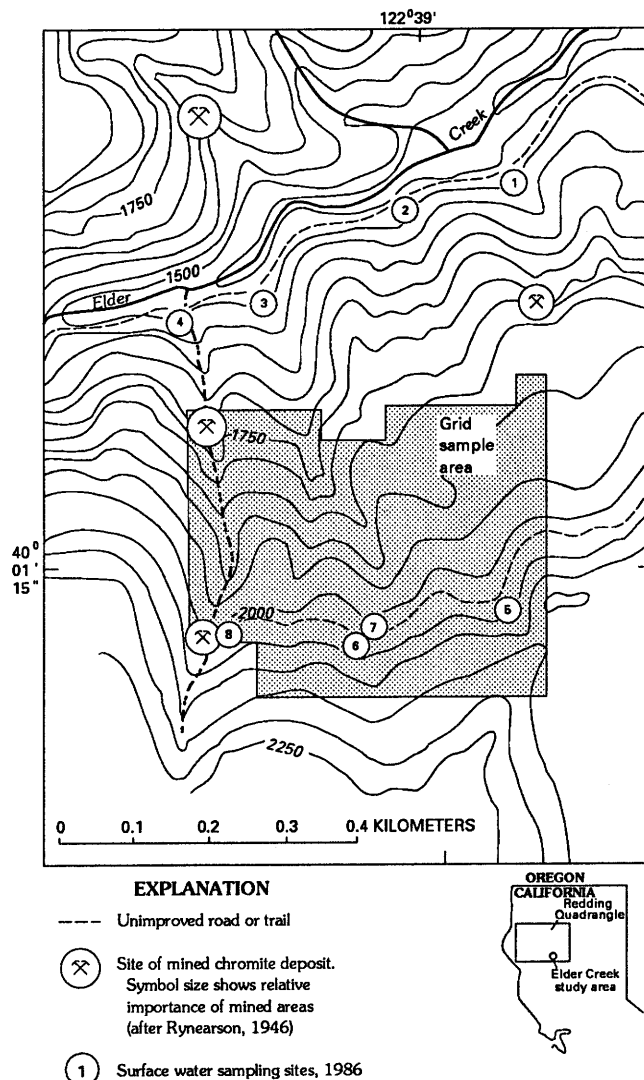


Figure 1. Topography, past mining sites, and surface water sampling sites in the Elder Creek study area. Contour interval 50 ft. Grid sample area is in SE/4 sec. 16, T. 25 N., R. 7 W.

obducted onto a Late Jurassic age volcanic arc, sometime between Late Jurassic and Early Cretaceous time. This ophiolite sequence and the overlying sedimentary rocks have been identified as the Elder Creek terrain (Blake and others, 1984).

The chromite deposits within the peridotite have been classified as alpine-type (podiform), rather than stratiform-type deposits (Wells and others, 1946; Thayer, 1966; Page and Johnson, 1977) based on tectonic origin and chemistry. Podiform-type deposits occur within island arcs or mobile mountain belts, whereas stratiform deposits are associated with stable cratons of Precambrian age (Hutchison, 1983). Cr/Al ratios of podiform-type deposits vary greatly with respect to relatively constant Mg/Fe ratios (LeBlanc and Violette, 1983).



Figure 2. View of the Elder Creek study area looking south. The ravine of the North Fork of Elder Creek is in the foreground, and four landscape units are identified (see text for discussion).

Although the formation of podiform-type chromite deposits is not completely understood, the geologic processes involved are agreed upon by most researchers. Partial melting of oceanic, upper mantle rock produces a dunitelike residuum in which segregation and crystal settling occur to form cumulate layers of chromite within the dunite. Later tectonic forces may give the chromite layers their tabular, podiform shapes (Dickey, 1975; Hutchison, 1983). These deposits are then obducted at some later time as part of an ophiolite sequence.

Shearing and serpentinization were probably the dominant geologic forces within the area. The tectonic origin of the steep gullies that cut the area is made obvious by the associated altered and brecciated rocks. Ephemeral streams, active during the wet, rainy season from November to March, have deepened and emphasized the shear zones. The gullies trend north. Two major gullies dominate the topography of the "steep ridges and gullies" section of the western half of the study area (fig. 1). Shearing and subsequent erosion have resulted in the physical transport of large volumes of chromite downslope.

Country Rock

The peridotite in the Elder Creek study area is composed mostly of dunite, with small amounts of saxinite, diorite, and rodingite (Rynearson, 1946). At least one diorite dike cuts the study area; it strikes east-west, normal to the shear zones. The dike is composed of very fresh, unaltered rock to highly altered rock that can be identified only by a relict intrusive texture seen in thin section. No outcrops of pyroxenite were observed in the area, and rodingite was noted at only one locality, in one of the shear zones. A small sample of a micaceous, lavender rock was tentatively identified as kammerite. Chemical analysis shows it contains only 1.2 percent Cr, however, and it has subsequently been classified as a chromium chlorite.

Alteration

Serpentine is omnipresent in the study area and serpentinization is by far the most common form of alteration. The serpentine usually has a black, glossy

appearance, though it may be present in the soil as a fine, medium-green, earthy material.

The second most common type of alteration is a complex of magnesitelike carbonate minerals. This type of alteration is most commonly found in the shear-zone gullies and smaller erosion gullies. The magnesite may take several forms, from dense white rocklike material, to pisolitic nodules, to a white powderlike substance that forms the matrix of highly altered, breccialike rocks. Pisolitic nodules were also found on a vertical wall formed downslope of the study area, where mining operations have cut the toe from a slope. These nodules appear to have formed recently—they are soft and clayey during the wet season and more dense and dry during hot, dry periods—and some of the carbonate may be derived from weathering activity. The dense, white magnesite thus would be derived from the flushing of mobile magnesium by the weathering of peridotites (Wildman and others, 1968).

Physiography and Vegetation

Kruckeberg (1984, p. 9) described the physiography of the northern Coast Range region, which includes the area of the Redding quadrangle, as follows:

From the arid foothills bordering the western edge of the Sacramento Valley to the fog belt of the coastal redwood region, serpentines outcrop with great frequency. The Klamath-Siskiyou mountains to the north have the largest ultramafic outcrops in the state, indeed in North America. From arid to mesic, from low elevation * * * to the highest peaks * * * there is an ultramafic outcrop (either igneous or metamorphic) for nearly every kind of terrain and exposure in northwestern California.

The vegetation of the Elder Creek study area has been defined as serpentine chaparral (Kruckeberg, 1984). The ecology of serpentine areas is complex and is characterized by: (1) soils imbalanced in macronutrients (very high in Fe and very low Ca/Mg ratios) and having low levels of N and P, (2) soils containing unusually high (often toxic) levels of Cr, Ni, and sometimes Co, (3) sparsely vegetated areas (the term "serpentine barren" refers to areas completely lacking vegetative cover), (4) areas of open-tree and shrub canopies and high surface soil temperatures, and (5) unstable soils usually low in surface soil moisture (Walker, 1954). Kruckeberg (1984) quoted Hanes' (1977) description of California serpentine chaparral as follows:

Serpentine chaparral is an open, low type associated with serpentine soils from San Luis Obispo Co. northward through the Coast Ranges and foothills of the northern Sierra Nevada. The shrubs are characterized by apparent "xeromorphism"***and dwarfed stature resulting from reduced productivity and growth***The dominant shrubs are *Adenostoma fasciculatum****and *Heteromeles arbutifolia****, but noteworthy are several localized endemic shrub species, *Arctostaphylos viscida* and *Ceanothus jepsonii*.

Cupressus sargentii, *Garrya congdonii*, and *Quercus durata* are unmistakable "indicator species" because of their

typical restriction to, and numerical dominance on, serpentine soils ***Serpentine chaparral may be associated with foothill woodland (*Pinus sabiniana* ***) or montane coniferous forest (*P. jeffreyi****, *P. ponderosa*****P. attenuata****, and *Pseudotsuga menziesii*) as an understory***The thousands of hectares of serpentine chaparral in the north Coast Ranges are easily distinguished from the oak-grasslands on hills of non-serpentine origin***

The dominance of whiteleaf manzanita (*Arctostaphylos viscida* Parry) is evident in the photograph of the area (fig. 2). Manzanita shrubs generally are smaller and more crowded in the low bench region (northeast) and larger and more widely spaced in the high bench region (southwest). Individual digger pine trees (*Pinus sabiniana* Dougl.) are scattered about but are apparently most common on the small ridge crests, particularly in the steep ridge and gully region.

Chromium Resource Assessments

Only a very few Cr resource assessment studies of the Elder Creek area are available (Diller and others, 1921; Rynearson, 1946; Wells and Hawkes, 1965). These studies are quite dated and were made when Cr production in the area was near its maximum. Most of the mining in the Elder Creek area of Tehama County occurred between 1890 and the late 1940's (Rynearson, 1946).

Reports on U.S. and world Cr production, the past and future development of Cr as an essential industrial commodity, and the status of the Cr industry in general have been reviewed by Thayer (1966, 1973), Morning (1978), Thayer and Lipin (1978), Lipin and Thayer (1980), Papp (1983), and DeYoung and others (1984).

Acknowledgments.—We especially thank Joanne Danielson, Shasta College, Redding, Calif., for her field observations and for bringing to our attention the geological role of the shear zones. Examination of dry plant material and ash by powder X-ray diffraction was provided by Steve Sutley and Jerry Gaccetta. Chemical analyses were performed by the authors and by Paul H. Briggs.

SAMPLE COLLECTION, PREPARATION, AND ANALYTICAL METHODS

Gridded Sampling Design for Plants

In June 1984, a grid of approximately 440 m by 500 m was positioned over an area of known chromite

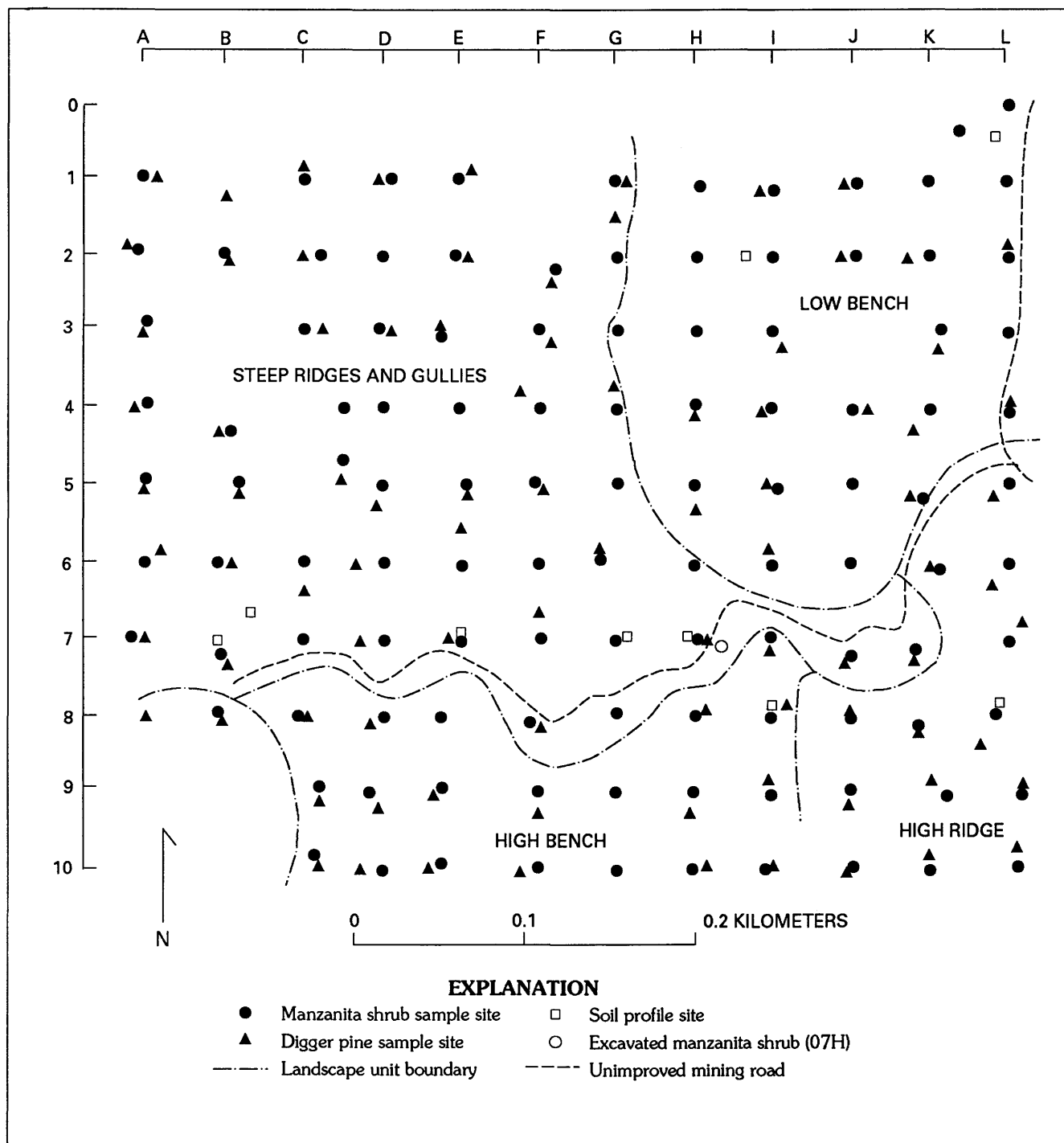


Figure 3. Biogeochemical and geochemical sampling sites in the gridded study area (fig. 1).

mineralization (figs. 1, 3). The grid design allowed us to evaluate areal biogeochemical data for the purpose of mapping individual element concentration trends. In the less than 0.25-km² area, there are 120 sampling sites with

centers separated by 44 m. Because of impassible terrain, however, six sites were not sampled (fig. 3); two additional sites were added in the northeast corner, making a total of 116 accessible sites.

At each site, plant material collected included stems and leaves (current year's growth, usually the terminal 5–8 cm) of the shrub whiteleaf manzanita (*A. viscida*) and two-year-old needles (needles from the second whorl) of the tree digger pine (*P. sabiniana*). Because element concentrations in leaf samples can vary depending on where on the plant the sample is taken (Brooks, 1984), each sample consists of about 20 g of material collected from around the perimeter of a single individual shrub or tree located as close as possible to the measured grid point. All manzanita samples were collected at about 1.5 m above the ground using stainless steel shears. Pine needles were stripped by hand from the lowest accessible branches; these usually were 3–5 m above ground and had to be obtained using extension pruning shears.

Manzanita was found at 112 of the 116 sampling sites and digger pine at 91 (fig. 3). About 10 percent of the sites for each species were chosen randomly for replication and another 10 percent for duplicate sample analysis. At each replicated site a shrub (or tree) adjacent to the original sample was chosen for sampling. The analytically duplicated samples were made after the dry material was ground in the laboratory.

Plant samples were stored in Hubco cloth bags. In the laboratory the samples were dried in a forced-air oven at about 38 °C for 24 hours. Samples were then ground in a Wiley mill to pass a 1.3-mm screen. Ten percent of each of sample was then split and submitted for duplicate chemical analysis.

Excavated Manzanita Shrub

In August 1985, a single manzanita shrub at the crest of an old road cut near site 07H (fig. 3) was excavated. The purpose of this collection was to evaluate the relative concentrations of elements among regions of the plant and to assess the possible partitioning of absorbed elements between root and shoot tissue. Major roots were traced laterally along the road cut for about 7 m and vertically for about 2 m. Samples include: (1) root cortex and stele (epidermis peeled and removed) at about 1-m intervals away from the basal manzanita burl, (2) basal burl wood (composite of cross section, bark peeled and removed), (3) main stem wood 1 m above burl (composite of cross section, bark peeled and removed), (4) primary branches off main stem (outer bark was peeled and removed), (5) secondary branches off primary branches, and (6) small stems with leaves. As above, all samples were ground in a Wiley mill after being dried in an oven. Prior to grinding the wood samples were first cut into small pieces using a bandsaw.

Vertical Traverse Sampling Design for Soils

In August 1985, eight pits were excavated through the highly weathered soil and rock profile (fig. 3) at sites judged to be different biogeochemically as determined by evaluation of the manzanita and digger pine chemistry. The purpose of the soil collections was to examine soil chemical and physical properties that might help to define trace metal mobility in ultramafic terrains.

The pits were located adjacent to the manzanita shrub (or shrubs) that was sampled as part of the gridded biogeochemical study. Pits were excavated to a depth of about 100 cm and samples were collected at five depths: 0–5 cm (surface litter having been scraped away), 10, 20, 40, and 80 cm. At each depth, paired samples, separated by about 20 cm, were sieved through a 1-cm screen and then placed in 1-L polyethylene acid-washed bottles. The bottles were sealed in order to prevent moisture loss. Rocks were collected from the bottom of each pit for chemical analysis and thin section examination.

In the laboratory, part of the collected soil was allowed to dry at ambient temperature and part was kept in plastic bottles. About 50 g of undried material was removed, and pH, moisture percentage, and the presence of Cr(VI) were measured; mineralogical determinations using X-ray diffraction were conducted for selected samples. In addition, 25 g of bulk material was placed in 65-mL screw-cap bottles, the material was rewetted with 25 mL of distilled water, and the samples were allowed to stand for 6 months after which they were again tested for the presence of Cr(VI). One hundred grams of soil was ground to –100 mesh and used for bulk chemical determinations of total and inorganic C (organic C was calculated as the difference between the two measured C values) and other major and trace elements as described in table 1.

Surface Water Collections

The study area is cut by several north-trending gullies, all of which drain into Elder Creek (fig. 1). Surface water is present in these gullies for only a relatively short time during the wet season each spring.

In late March 1986, we collected water samples from four different gullies, at both the top of the slope containing the field area and the bottom of the slope before the streams drained into Elder Creek (fig. 1). The samples were placed in acid-rinsed 500-mL polyethylene bottles. The bottles were capped and refrigerated. Measurements were made of pH, conductivity, and the colorimetric test for the presence of hexavalent Cr.

Table 1. Methodology for analyses of sampled materials

[Study: A, soil pit geochemical; B, plant grid biogeochemical; C, excavated shrub biogeochemical; D, intermittent stream chemical]

Variable	Method	Study	Reference or notes
Total concentrations of B, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sc, Ti, V, Y, Zn, and Zr	ICP ¹ on dry soils sintered with Na ₂ O ₂	A	Lichte and others, 1988
Total concentrations of Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Nb, Ni, P, Pb, Sr, Ti, V, Y, and Zn	ICP ¹ on acid-digested ash of plant material	B	Church and others (1987)
Total concentrations of Ca, Cu, Cr, Fe, Mg, Mn, and Ni	Atomic absorption spectrometry on acid-digested ash of manzanita leaves, stems, and leaves and stems together	C	Harms (1976)
Percent total C, organic C, and carbonate C	Combustion infrared photometry, difference, and coulometric titration, respectively, on dry soil	A	Jackson and others (1988)
Soil moisture	Gravimetric	A	Loss of weight after 24 hrs at 105 °C
Ash yield	Gravimetric on plant dry material	B	Ashed at 500 °C
Plant ash and soil mineralogy	Powder X-ray diffraction	A, B	Starkey and others (1984)
pH	Glass electrode, 1:1 water:soil (<2-mm fraction) slurry, and stream water	A, D	Peech (1965)
Cr(VI) presence in water and field soils	Qualitative colorimetric test with s-diphenyl carbazide	A, D	Modified from Bartlett and James (1979)

¹Inductively coupled argon plasma optical emission spectrometry.

STATISTICAL ANALYSIS OF DATA

All chemical data summarized and interpreted in this report are listed in Meadows and others (1988). Data reported by the analyst for plant material on an ash-weight basis were converted to dry-weight equivalents and then transformed to logarithms prior to statistical analysis. Summary statistics are reported as the geometric mean (GM) and geometric deviation (GD). For those elements having normal frequency distributions but for which there were censored values at the left or low end of the distribution (values below the lower limit of analytical determination, LLD), the geometric mean and deviation were estimated using the technique of Cohen (1959). For those elements not censored, the geometric mean was calculated as the antilogarithm of the mean of the logarithmic values, and the geometric deviation was calculated as the antilogarithm of the square root of the total variation as estimated by analysis of variance. The latter calculation accounts for the effects on the total variability of the nested analysis of variance design.

Because ash yield varies, the conversion from an ash-weight base to a dry-weight base produces variable LLD values for elements with censoring. The mean and

deviation estimation technique of Cohen (1959), however, cannot handle variable LLD values. A single LLD was created using an algorithm devised by A.T. Miesch (oral commun., 1986, U.S. Geological Survey, retired) which adjusts the variable LLD values to a common value based on a procedure that produces the fewest overall changes in the data in order to make that adjustment.

Detailed discussions of the application of the unbalanced, nested, analysis of variance design are given by Tidball (1976), Tidball and Ebens (1976), and Severson and Tidball (1979) for geochemical studies and by Erdman and others (1976) and Erdman and Gough (1977) for biogeochemical studies. In the present study three analysis of variance levels were employed. The design allowed us to estimate how the element content of both plant and soil materials varies geographically and with sample preparation and analysis.

The analysis of variance requires completely numeric data sets; therefore, all censored data were substituted with a real value equal to 0.7 times the LLD in ash. This multiplier is an acceptable fraction of the LLD as used in these types of studies (see Miesch, 1976). We assumed that this substitution would result in valid

analysis of variance results as long as censoring did not exceed about one-third of the total number of values. If an element was more than one-third censored, it was dropped from the study.

Fourteen uncensored elements in manzanita and fifteen elements (one with censoring) in pine were used in R-mode factor analysis. This nonstatistical multivariate technique is used to examine groupings of elements and is based on the correlation coefficients between elements within a species. A varimax rotation of the principal components was performed on the element concentration data (variables), and loadings of the variables were calculated for each factor (see McNeal and others, 1985; Davis, 1986). A loading is equivalent to the correlation between the variable and the factor score. Statistical analysis of the data was performed using the U.S. Geological Survey's STATPAC library (VanTrump and Miesch, 1977).

For three-dimensional surface plots, irregularly spaced x, y, and z data were gridded by using an interpolation method based on an inverse distance-squared weighted-power algorithm (Golden Software, GRID and SURF gridding and plotting programs, version 3.0). Cubic-spline smoothing was employed in the calculation of the grid lines and x, y, z plots were generated that have exaggerated height/width ratios.

RESULTS AND DISCUSSION

Biogeochemical Summaries, Gridded Study Area

Powder X-ray Analysis of Plant Ash

Dry, ground plant material and plant ash were analyzed mineralogically using powder X-ray diffraction. The ash consists of calcite and fairchildite (a potassium calcium carbonate) or natro-fairchildite. These minerals are pyrogenically derived from an organic-Ca mineral (identified as the calcium oxalate hydrate mineral whewellite) in the dry-ground manzanita leaf material. This type of conversion has been reported previously (Milton and Axelrod, 1947; Erdman and others, 1977). Geometric mean Ca concentrations are 0.67 and 0.27 percent of the dry material for manzanita and pine, respectively (table 2). The X-ray analysis provides no information on the possible contribution of any Mg-carbonate minerals (for example, magnesite), even though Mg concentrations average 0.34 and 0.24 percent of the dry material in manzanita and pine, respectively.

Summary Statistics

The concentrations of Cr, Cu, Mg, Nb, Ni, and Zn in manzanita and pine are similar (different by less than a factor of two)(table 2). Although concentrations of Cr, Mg, and Ni are usually high in ultramafic soils, their areal patterns are very dissimilar across the study area (discussed later). Concentrations of the alkaline-earth metals (Ba, Ca, and Sr) are much higher in manzanita than in pine (by factors of two to ten). Barium and Sr substitute for Ca in plant cell walls. Because the manzanita samples consist of some woody material, their higher alkaline earth concentrations seems logical. The manzanita and pine samples possess low ash yields typical of vegetation samples free of dust; microscopic examination of both types of material showed very little surficial contamination.

Data for Ca, Mg, Cr, and Ni in both species compare closely with element levels in similar plant materials from other serpentine areas in California (Koenigs and others, 1982; Wallace and others, 1982). The Ca levels in both species are also similar to Ca levels in plant materials from nonserpentine areas (Ebens and Shacklette, 1982; Kabata-Pendias and Pendias, 1984). In general, however, concentrations of Cr, Mg, Ni, and Ti are elevated as compared to plant materials from nonserpentine areas, whereas concentrations of Al, Fe, P, Pb, and Sr are very much lower (from a factor of about two for Fe and P to about eight to ten for Al and Sr). Elevated levels of Cr, Mg, and Ni in plant tissue reflect the elevated levels of these same elements in the soil, which is derived from ultramafic parent material; however, soils of the study area are also very high in Fe, a trend not reflected in the plants.

Results of the Analysis of Variance

The one-way analysis of variance design segregated the total variance for each element (in either manzanita or pine) between the following sources: (1) among the gridded sites, (2) between replicated shrubs or trees at a site, and (3) between duplicate analyses of the same sample (tables 3, 4).

Of the elements tested, only Ca concentrations in manzanita had an important proportion of their variance attributed to the analytical level; 46 percent of the variability in these data result from analytical imprecision. Except for Ca, therefore, interpretation of areal element concentration patterns is possible. Analysis of variance was not performed for those elements having more than one-third of their values below the lower limit of analytical determination.

Fifteen of sixteen and fifteen of nineteen elements in manzanita and pine, respectively, showed a significant proportion of their variability among sites; 8 of 16 and 12

Table 2. Summary statistics for element concentrations in leaf and stem material of whiteleaf manzanita and needles of digger pine

[Prior to calculation, data were converted to logarithms; data expressed as ppm, dry-weight base, except where noted; site-replicated samples (12 and 9, manzanita and pine, respectively) and duplicate analyses (12 for each species) were averaged prior to calculations; ratio, proportion of the number of analyses having values above the lower limit of determination to the total number of analyses; GM and GD, geometric mean and deviation, respectively; leaders (--), no data available]

Element or ash yield	Manzanita				Digger pine			
	Ratio	GM	GD	Observed range	Ratio	GM	GD	Observed range
Ash %	112:112	30.6	10.20	20.0 - 50.8	91:91	20.3	10.20	10.5 - 30.5
Al	112:112	20	10.40	11 - 68	91:91	73	10.56	21 - 170
As	8:112	--	--	<10.2 - 20.6	1:91	--	--	<0.85 - 88
Ba	112:112	80.9	10.67	10.2 - 30	91:91	0.84	10.49	0.30 - 10.9
Ca %	112:112	0.67	10.41	0.18 - 10.6	91:91	0.27	10.60	0.086 - 0.80
Cd	44:112	--	--	<0.03 - 0.17	11:91	--	--	<0.026 - 0.075
Cr	112:112	10.4	20.13	0.29 - 70.5	91:91	10.1	10.80	0.42 - 70.5
Cu	112:112	40.3	10.43	10.4 - 90.0	91:91	40.2	10.34	10.9 - 90.1
Fe	112:112	28	10.39	13 - 59	91:91	91	10.62	16 - 220
Mg %	112:112	0.34	10.12	0.10 - 0.6	91:91	0.24	10.31	0.12 - 0.46
Mn	112:112	29	10.75	80.0 - 130	91:91	73	10.81	70.8 - 210
Nb	95:112	0.25	10.36	<0.15 - 0.48	41:91	---	--	<0.12 - 0.23
Ni	112:112	20.6	10.94	0.56 - 13	91:91	40.2	10.82	0.70 - 13
P %	112:112	0.052	10.52	0.015 - 0.17	91:91	0.12	10.32	0.057 - 0.25
Pb	2:112	--	--	<0.24 - 0.41	77:91	0.52	10.80	<0.24 - 20.2
Sr	112:112	14	10.54	30.4 - 34	91:91	20.4	10.88	0.59 - 15
Ti	112:112	10.3	10.49	0.60 - 30.2	91:91	30.6	10.73	0.73 - 10
V	7:112	--	--	<0.04 - 0.08	91:91	0.14	10.77	0.024 - 0.37
Y	36:112	--	--	<0.007 - 0.036	18:91	--	--	<0.006 - 0.01
Zn	112:112	30	10.25	14 - 50	91:91	20	10.49	50.3 - 54

of 19, respectively, show significance between replicated samples at a site. For most elements, therefore, the variability in the data has a strong regional component across the study area, as well as a site-specific component. Exceptions include the concentrations of Cu, Nb, and Pb in pine, which show significant proportions of their variance as between neighboring individuals (table 4). Regional trends for these elements in pine therefore do not occur. The chemistry of manzanita shrubs and pine trees separated by 44 m or more should be more important, in general, than that of those separated by less than about 3 m.

The strong regional component supports a general growth-form characteristic of both species. We observed that the lateral root system of an excavated manzanita extended 7 m away from the basal burl. At one location, where a hillside was truncated by a small stream, the roots of a moderately large manzanita were observed to extend vertically for more than 5 m through deeply weathered serpentinite. Morov (1967) reported that on stony soils digger pine characteristically has a well-developed, deep-penetrating tap root and extensive, spreading root laterals. Our observations support this same general trend for pines growing over serpentinite. The chemistry of the aerial portions of both manzanita

and pine, therefore, should represent an integration of a very large area. By sampling at 44-m intervals, we had hoped to minimize root-area overlap, and the results of the analysis of variance support this supposition.

Description of Biogeochemical Patterns

Interpretation of Univariate Element Associations

Results of the analysis of variance show that regional differences exist in the chemistry of manzanita and pine but cannot be used to discern areal patterns. Figure 4 graphically depicts the concentration patterns for six selected elements and ash yield in manzanita shrub stems and leaves and digger pine needles. Except for P in pine needles, large proportions of the total variance of these six elements occur at a regional scale (> 44 m; tables 3, 4).

The following is a list of the simple correlation coefficients (*r*) between concentrations of the same component in manzanita and pine. Correlations were calculated between samples taken at 88 sites where both species were collected (probability levels and significant

Table 3. Distribution of element concentration variation in samples of whiteleaf manzanita leaf and stem material [Unbalanced nested variance analysis based on 137 samples except where noted; asterisk (*) indicates variance component tested significant at the 0.05 probability level; ratio represents proportion of the number of analyses having values above the lower limit of determination to the total number of analyses]

		Analysis of variance			
		Percentage of total variance			
Element or ash yield	Ratio	Total log ₁₀ variance	Among sites (113) ¹	Between shrubs at a site (12) ¹	Between duplicate analyses (12) ¹
Ash	137:137	0.0064	89*	10*	<1
Al	137:137	0.0217	78*	18*	4
Ba	137:137	0.0494	78*	16*	6
Ca	137:137	0.0222	21	33	46
Cr	137:137	0.1083	91*	8*	1
Cu	137:137	0.0237	66*	17	17
Fe	137:137	0.0205	88*	7	5
Mg	137:137	0.0224	94*	4*	2
Mn	137:137	0.0592	92*	7*	<1
Nb ²	120:137	0.0510	62*	12	26
Ni	137:137	0.0830	97*	2*	1
P	137:137	0.0331	84*	12*	4
Sr	137:137	0.0352	95*	3	2
Ti	137:137	0.0301	82*	<1	18
Zn	137:137	0.0092	83*	8	9

¹Number of samples representing ANOV level.

²Data reported as below the lower limit of analytical determination were replaced with a value equal to 0.7 times the limit value.

correlation coefficients follow, $P_{.05} \approx 0.21$, indicated by *, and $P_{.01} \approx 0.27$, indicated by **):

Al	0.332**	Cr	0.413**
Ash yield	0.211*	Cu	0.063
Ba	0.098	Fe	0.308**
Ca	0.178	Mg	0.026
Mn	0.160	Sr	0.247*
Ni	0.750**	Ti	0.207
P	0.512**	Zn	-0.131

These data indicate that the distribution patterns for elements having significant positive correlation coefficients tend to be similar for both manzanita and pine; the larger r , the more similar the pattern. The patterns for Ni in manzanita and pine are very similar, concentrations are low on the west side of the study area and progressively higher toward the east and northeast. Aluminum, Cr, Fe, and P have r values between manzanita and pine greater than 0.3 but less than 0.52 and show similar areal concentration patterns (fig. 4). Ash yield and Sr patterns ($r = 0.211$ and 0.247 , respectively) are less similar. These data indicate that manzanita and pine

Table 4. Distribution of element concentration variation in samples of digger pine needles [Unbalanced nested variance analysis based on 112 samples except where noted; asterisk (*) indicates variance component tested significant at the 0.05 probability level; ratio represents proportion of the number of analyses having values above the lower limit of determination to the total number of analyses]

		Analysis of variance			
		Percentage of total variance			
Element or ash yield	Ratio	Total log ₁₀ variance	Among sites (91) ¹	Between shrubs at a site (9) ¹	Between duplicate analyses (12) ¹
Ash	112:112	0.0065	90*	9*	<1
Al	112:112	0.0368	87*	12*	1
Ba	112:112	0.0304	88*	4	8
Be ²	82:112	0.0416	70*	11	19
Ca	112:112	0.0429	83*	14*	3
Cr	112:112	0.0651	95*	2	3
Cu	112:112	0.0164	21	65*	14
Fe	112:112	0.0435	83*	11*	6
Mg	112:112	0.0136	79*	11	10
Mn	112:112	0.0665	89*	8*	3
Nb ²	85:112	0.0294	17	72*	11
Ni	112:112	0.0676	92*	<1	8
P	112:112	0.0147	51	38*	11
Pb ²	100:112	0.0782	27	56*	17
Sr	112:112	0.0757	92*	8*	<1
Ti	112:112	0.0567	82*	10	8
V	112:112	0.0611	84*	8	8
Zn	112:112	0.0300	73*	24*	3

¹Number of samples representing ANOV level.

²Data reported as below the lower limit of analytical determination were replaced with a value equal to 0.7 times the limit value.

may have somewhat similar uptake, translocation, and accumulation physiological abilities for Al, Cr, Ni, P, and Fe.

The patterns shown in figure 4 have almost opposite surface trends for Cr as compared to Ni and possibly Fe. Nickel concentrations, and to a lesser degree Fe concentrations, increase from the steep ridges and gullies on the west side of the study area to the less dissected, more gently sloping low benches of the northeast (fig. 3). Chromium, however, shows several scattered areas of high concentration; concentrations on the west side in the steep ridges and gullies region are generally higher.

The following table of correlation coefficients helps quantify these observed relations. The comparisons are made between elements within a species, not among species, and involve 112 samples of manzanita and 91 samples of digger pine. Because a large proportion of the variability for these elements in each species occurs among sites, each sample is considered independently; a

value greater than about 0.21 is statistically significant but may have only limited importance.

		Manzanita			
		Cr	Fe	Mn	Ni
Digger pine	Cr		0.172	0.009	-0.390
	Fe	0.260		-0.003	-0.174
	Mn	-0.304	0.076		0.300
	Ni	-0.355	0.089	0.713	

These data show that for both species Cr has a large, negative correlation with Ni. Strong positive correlations occur between Ni and Mn. These data support the observed areal trends discussed above and shown in figure 4.

Interpretation of Multivariate Element Associations

In order to better quantify the multivariate nature of the relations discussed in the previous section and to interpret the mechanism for the element concentration patterns, R-mode factor analysis was used to interpret the plant chemistry (tables 5, 6). Factor analysis relates variables (concentrations of elements) to factors based on the correlation coefficients among the variables (Davis, 1986). In this study a factor consists of an association of elements. The association can often be interpreted to indicate a common controlling process that may be chemical, physical, or physiological in nature. A loading is equivalent to the correlation between the variable and the factor score; consequently, the larger the loading, the stronger the relation. The composition of each factor is shown according to the order of loading on that factor. Significance values for loadings do not exist. Although the total composition of each factor includes all of the variables, we list only the more important ones—that is, those having loadings greater than 0.3 (explains more than 9 percent of the total variance of the variable).

A four-factor model was chosen as optimum; factors were extracted until simple structure was obtained (Joreskog and others, 1976). For manzanita, the four factors explain a total of 62 percent of the total variance in the data. The remaining 38 percent of the variance is not appreciably explained by increasing the number of factors to a maximum of ten.

For manzanita, factor 1 (table 5) explains 25 percent of the total variance. In factor 1, ash yield is associated with the alkaline-earth metals, Zn, and to a lesser degree, Cu, Ni, and Mn. This factor demonstrates the physiological correlation between ash yield and Ca.

Calcium is a major nutrient element and Ba and Sr commonly substitute for Ca in plant cell walls.

A four-factor model was also optimum for pine and explains a greater proportion (72 percent) of the total variability than for manzanita. Like manzanita, ash yield (factor 2, table 6) is identified with the alkaline-earth metals; also present are P, Mn, and Mg. Twenty-one percent of the variability in the pine data is explained by factor 2.

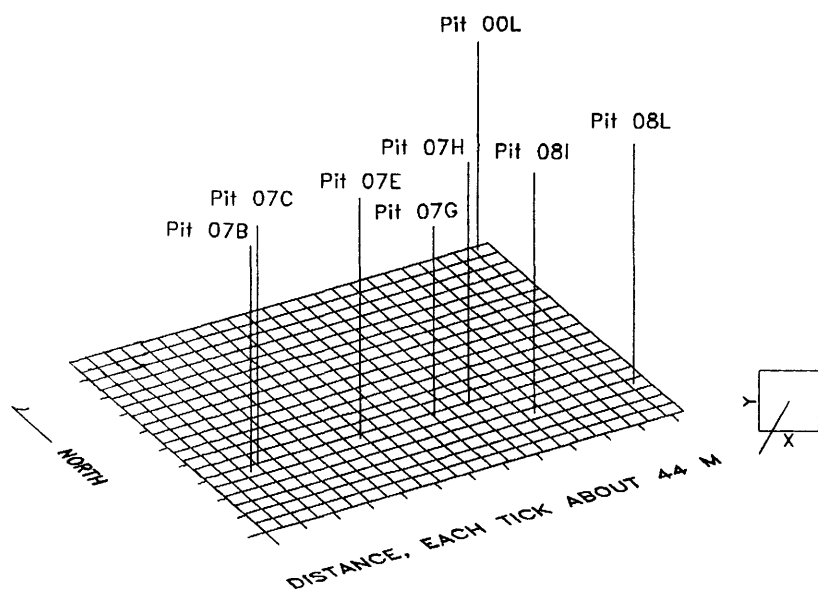
Both manzanita and pine have an Al, Fe, and Ti factor (factor 2, table 5, and factor 1, table 6, respectively). As with all peridotite soils, Fe is present in great abundance (about 4–14 percent), and because the soils are almost neutral (pH from about 6.8 to 7.4), a proportion of the Fe would be mobile. Titanium and Al, however, are not expected to be readily available for uptake. Fe/Ti and Al/Ti ratios for plant analyses versus soil analyses are dissimilar and suggest that this factor does not reflect the external presence of dust (clay):

	Approximate ratios	
	Fe/Ti	Al/Ti
Manzanita	22	15
Pine	25	20
A-horizon soil	103	6.8
B-horizon soil	115	6.6

Both manzanita and pine possess a factor dominated by Cr and Ni (factor 3, tables 5, 6). Although this factor makes up only 10 and 12 percent of the total variance for manzanita and pine, respectively, the inverse association of these two metals is clear. Chromium and Ni are not essential elements but are abundant in peridotite environments, the former in large concentrations in chromite and olivine and the latter in olivine and Mg-pyroxene. An important conclusion is that both species are responding in a physiologically similar manner to the incorporation of Cr and Ni into tissue. This conclusion may mean that soils high in Cr do not occur in the same location as those high in Ni.

The composition of factor 4 (tables 5, 6) varies greatly and has no readily apparent explanation. This factor explains only 10 and 8 percent of the total variability in the data. Phosphorus is usually deficient as a micronutrient in serpentine soils, not only because of its paucity in peridotite minerals, but also because in alkaline environments it tends to react with carbonates and is rendered unavailable for absorption. Copper is found as a substitution element in pyroxene; however, its

Soil pit locations



Ash Yield, Manzanita

Ash Yield, Digger Pine

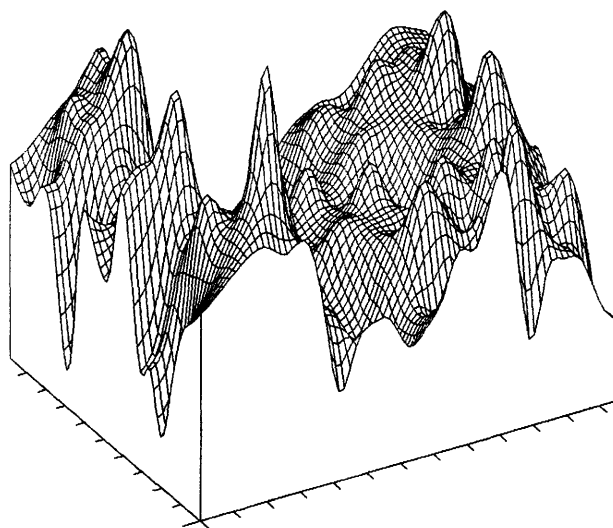
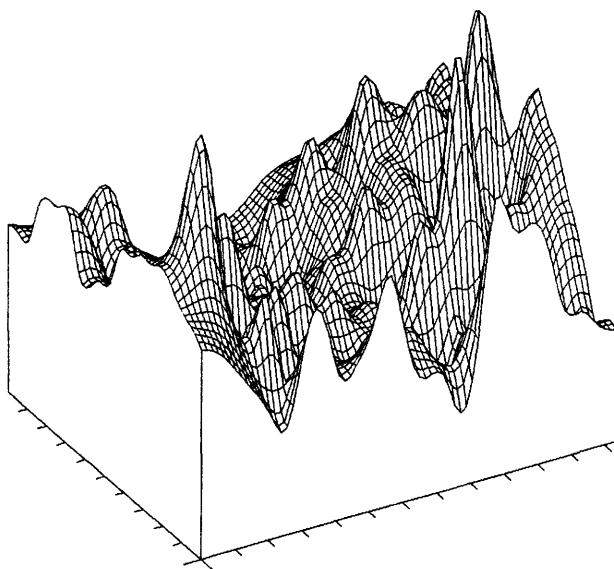


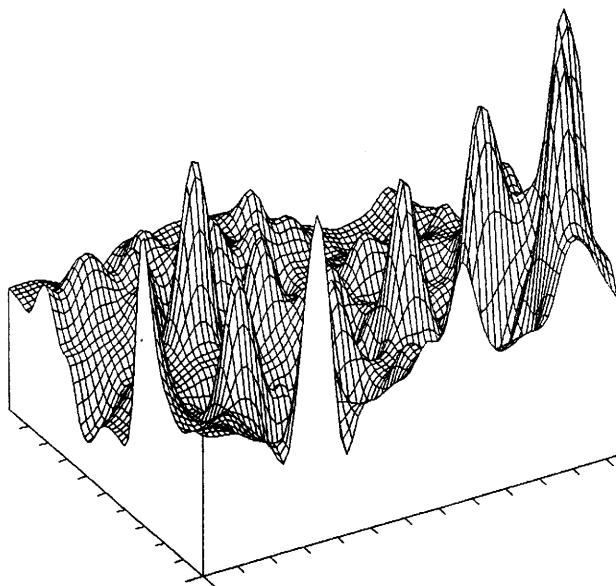
Figure 4 (above and following pages). Areal concentration patterns for six selected elements and ash yield in manzanita shrub stem and leaf material and digger pine needles within the Elder Creek study area. Reference plot shows viewing angle, general plot orientation, approximate position of grid lines (tick marks), and position of excavated soil profile sites.

mobility probably is not great in these soils. Copper, like P, is essential for plant growth and if available will be absorbed.

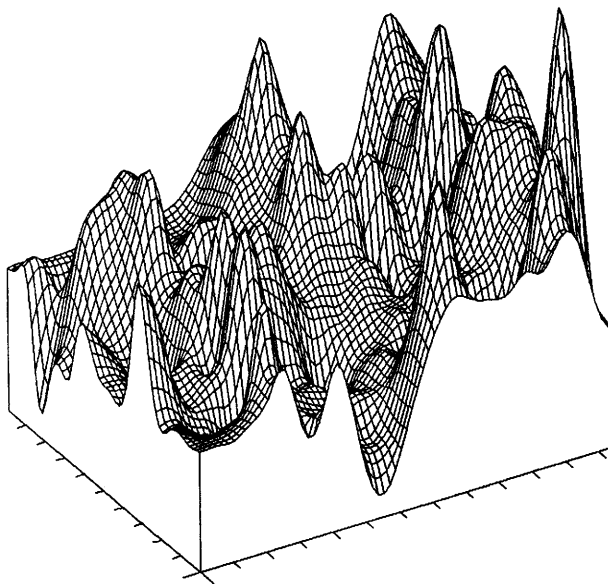
Magnesium loads more strongly on factor 4 for manzanita than for pine (45 and 10 percent, respectively). Once it has weathered free from peridotite, it can react with soil carbonate, and we have identified hydromagnesite as the dominant carbonate mineral in

soils of the study area. Hydromagnesite was also observed as an evaporite among the serpentine cleavages and along headwalls where ground water emerges from fractures in the ultramafic bedrock. Although Mg levels in these soils are high (typically 10–21 percent) and although the presence of evaporites suggests that the magnesium is mobile, its uptake by manzanita and pine is not great.

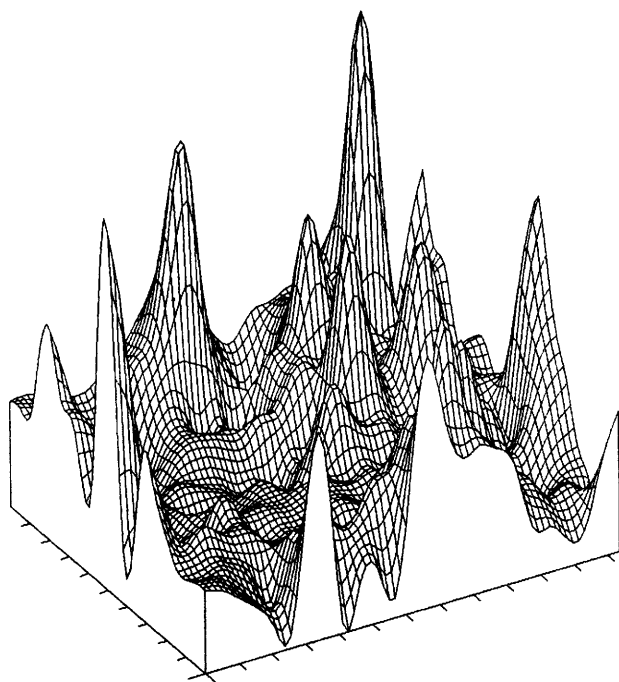
Iron, Manzanita



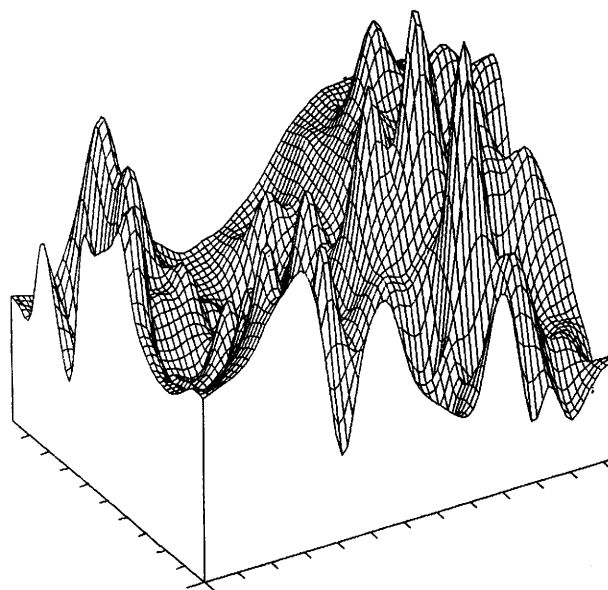
Iron, Digger Pine



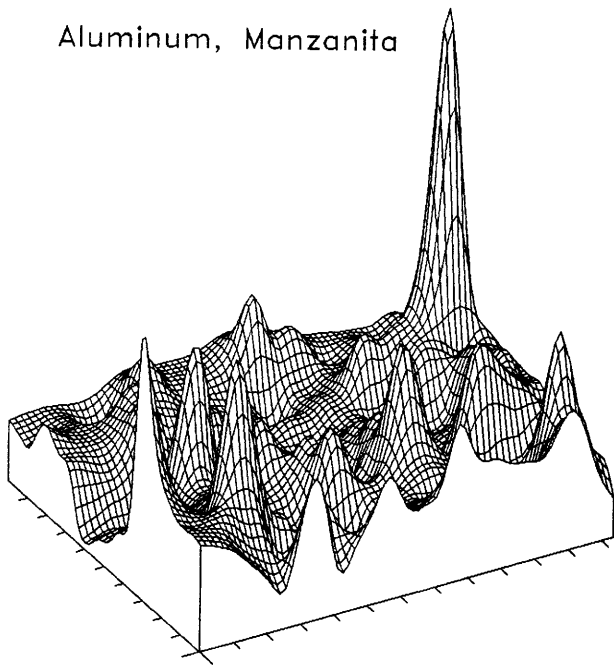
Manganese, Manzanita



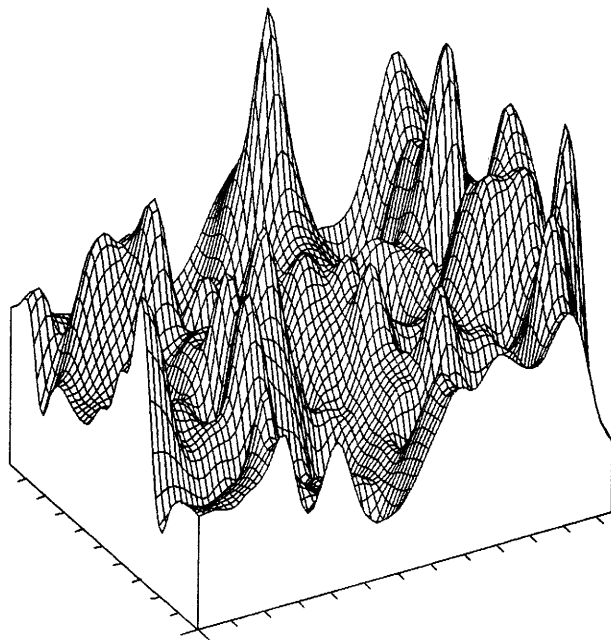
Manganese, Digger Pine



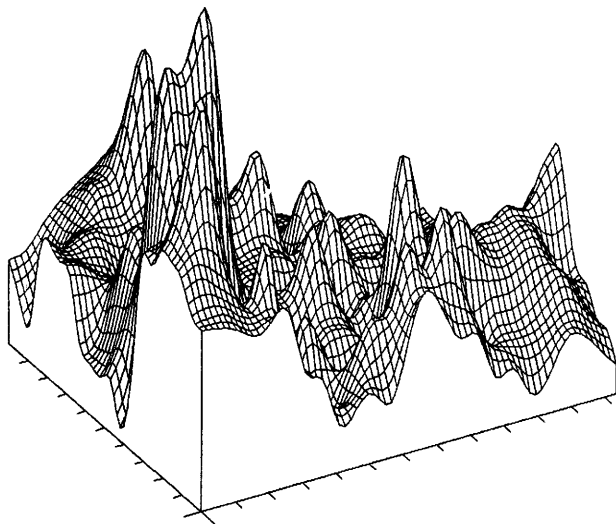
Aluminum, Manzanita



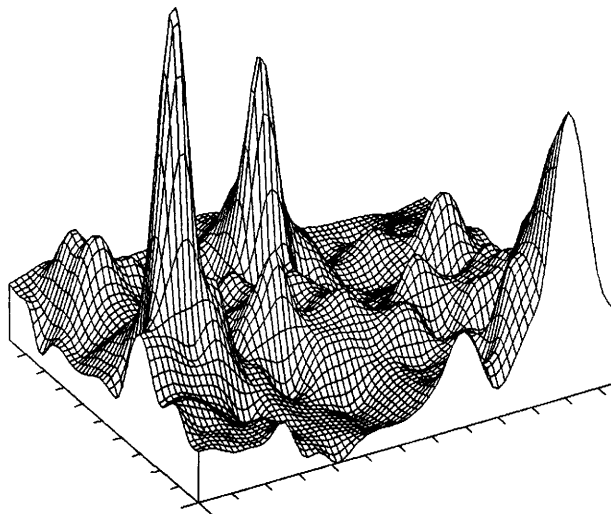
Aluminum, Digger Pine



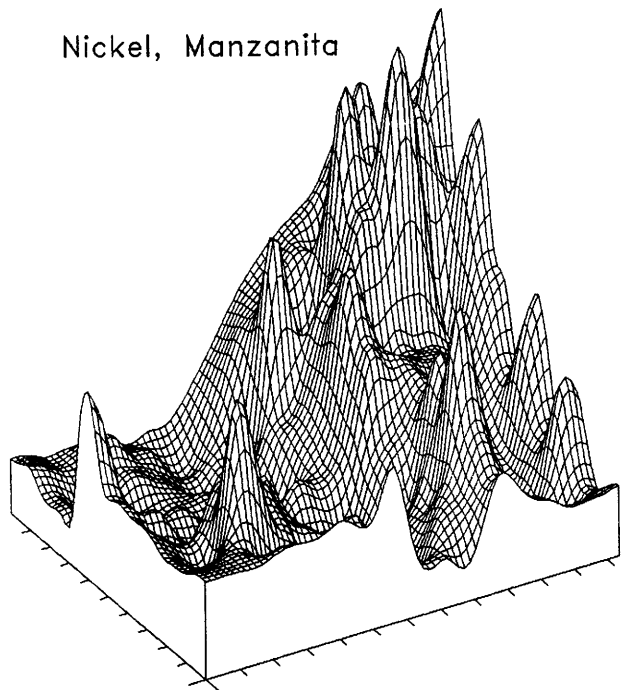
Chromium, Manzanita



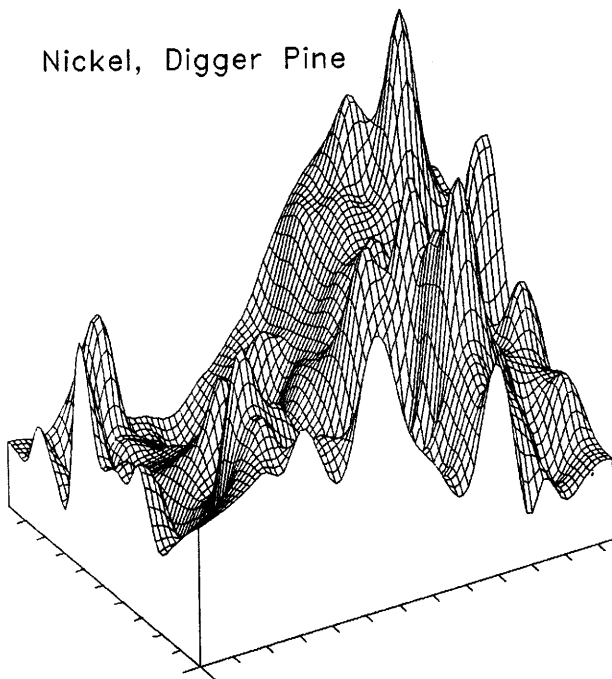
Chromium, Digger Pine



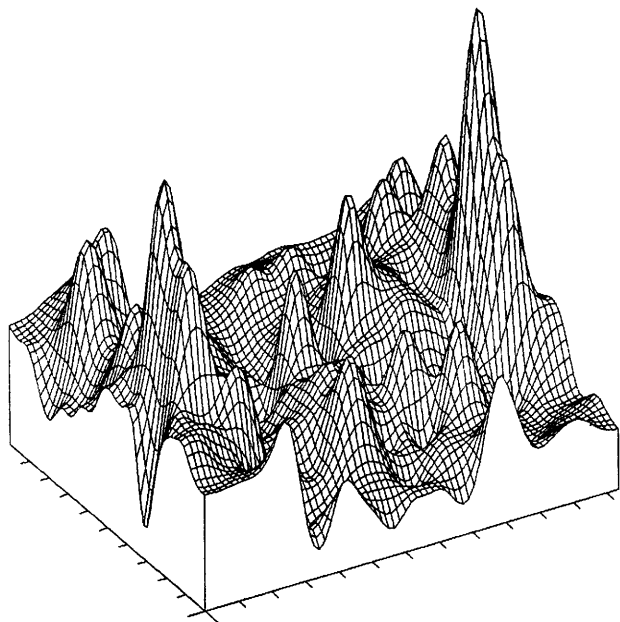
Nickel, Manzanita



Nickel, Digger Pine



Phosphorus, Manzanita



Phosphorus, Digger Pine

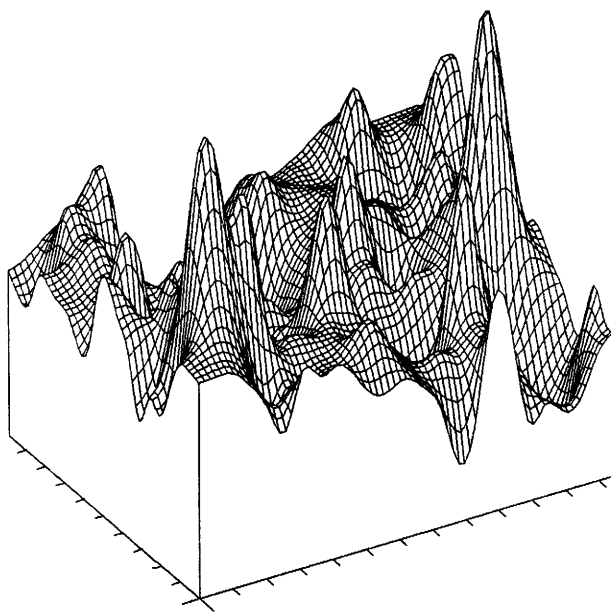


Table 5. Results of R-mode factor analysis for manzanita stems and leaves showing relative loadings of element concentrations on four factors derived by varimax rotation [Variables in the multivariate analysis include concentrations of Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, P, Sr, Ti, Zn, and ash yield]

Factor loading	Factor number and interpretation				Percent variance explained
	Factor 1 25 ¹	Factor 2 17 ¹	Factor 3 10 ¹	Factor 4 10 ¹	
1.0					100
					90
0.9		Ti			80
	Ash	Al			70
		Fe			
0.8	Ca				
			-Cr ²	-p ²	60
			Ni		
0.7	Ba				50
				Mg	40
0.6					
	Zn				30
0.5	Sr				
			Sr		20
0.4			Cu	Mn	
	Mn				
	Cu				
	Ni		Zn		10
0.3					

¹Percentage of total variance explained by factor and by all factors.

²Variable with a negative loading.

Vertical Element Trends in the Soil Profile

The explanation of the factors discussed above helps define the biogeochemical processes that produce particular element associations in plants. Additional geochemical information is needed, however, to further explain element mobility and uptake processes.

Based on the areal element concentration patterns observed for elements in plant tissue discussed above, in 1985 soil profiles were exposed at sites (fig. 1) where both manzanita and pine showed: (1) high levels of Cr and low levels of Ni and Mn (pits 07B, 07C, and 07H), (2) high levels of Ni and Mn and low levels of Cr (pits 08I and 00L), and (3) low levels of all three elements (pits 07E, 07G, 08L)(fig. 3). These areas were delimited using the general patterns shown in figure 4 and element concentration percentile maps.

As discussed in the methods section, paired soil samples were collected from the profiles at depths of 0–5, 10, 20, 40, and 80 cm. The consolidation of this material varies with depth, from truly loose soils, high in oxidized Fe (red), to friable, highly weathered peridotite (gray green). Mineralogical identification of parent material in

Table 6. Results of R-mode factor analysis for digger pine needles showing relative loadings of element concentrations on four factors derived by varimax rotation

[Variables in the multivariate analysis include concentrations of Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Ti, Zn, and ash yield; Pb is the only element included in the calculations that possesses censored values]

Factor loading	Factor number and interpretation				Percent variance explained
	Factor 1 31 ¹	Factor 2 21 ¹	Factor 3 12 ¹	Factor 4 8 ¹	
1.0					100
					90
0.9	Al				80
	Ti	Ca			70
	Fe				
0.8	Ba				
	Pb	Ash	Mn		
		Sr			
0.7					
			-Cr ²		50
		P			40
0.6					
					30
0.5					
			-Mg ²		20
0.4	Mg				
		Mn		Ash	
		Ba		Zn	
0.3	Cr		Ba	Mg	10
	Sr	Mg			

¹Percentage of total variance explained by factor and by all factors.

²Variable with a negative loading.

thin sections from each of the profiles was difficult because of extensive weathering and serpentinization; however, phenocrysts of unaltered pyroxene grains were observed. Parent material having a large number of these phenocrysts was classified as saxonite (Ryner, 1946) and parent material having no phenocrysts and remnant dunitelike textures was classified as dunite. The classification given to the parent material collected at the bottom of each soil profile is as follows:

Soil profile	Rock type
02I	Saxonite
07B	Dunite
07C	Dunite
07E	Saxonite
07G	(unknown)
07H	Dunite
08I	Saxonite
08L	Saxonite
00L	Dunite

Figure 5 shows the average value for variables measured in paired samples from two profiles, 08I and 07G; element concentrations represent total amounts.

Based on both physical setting and on element concentrations, these two profiles were selected as qualitatively representative end-member examples of the spectrum of differences in the nine profiles excavated. Profile 08I is typical of the gently sloping (<5 percent), bench regions within the study area (fig. 3). It seems to represent a higher degree of weathering relative to pits located in more steeply sloping terrain. The Mg/Fe ratio in the top 20 cm of profile 08I is considerably lower than that for profile 07G. This relative decrease in Mg and corresponding increase in Fe is due to Mg removal by ground waters and is usually considered to represent a high degree of weathering in serpentine-derived soils (Wildman and others, 1968).

Pit 08I is in an area where both manzanita and pine show relatively high levels of Ni and Mn and low levels of Cr. Pit 07G, typical of the steep ridges and gullies, is located where manzanita and pine show low levels of Cr, Ni, and Mn. This latter pit is on the side of a 15-percent slope that has deep, transported soil.

In general, profile 08I shows higher total concentrations of the elements selected than does profile 07G; Al is different by almost an order of magnitude, but, more commonly, a factor of only 2 or 3 separates the values in the two pits. Vertically, the profile in the gully having transported soil (07G) shows very uniform concentrations with depth; the variability in the profile on the nearly level bench (08I) is much greater. This latter profile shows decreases in Ca, Cr, and organic C with depth and an increase in soil moisture. Profile 07G shows only a major decrease in organic C with depth; soil moisture increases but, unlike 08I, only within the first 10 cm. The profile in the gully shows considerably higher pH values than profile 08I; pH does not appreciably vary with depth in either profile.

As determined through the use of element concentration percentile maps (mentioned above), profile 08I is in an area where both manzanita and pine show generally high levels of Ni and Mn and low levels of Cr; profile 07G is in an area where manzanita shows generally low levels of all three elements (pine was not collected here). Based solely on total soil chemistry, the soil samples from these profiles are directly related to this general plant-chemistry observation. In addition, because pH is lower in the soils from 08I, it follows that more mobile forms of the metal cations might be available to plants in this region.

Uptake and Translocation of Elements by Manzanita

A manzanita shrub was excavated near pit 07G (fig. 1) in an attempt to understand the importance of element uptake and translocation. Figure 6 shows the total concentration of six elements (ash-weight base) and ash

yield in manzanita root, basal burl, stem, and stem and leaf samples collected at eight locations along the excavated shrub. Soil contamination was minimal because of the very smooth and easily peeled nature of manzanita root epidermis.

The ratio of Ca to Mg in plant tissue increases from root tissue to stems (fig. 7, upper), as expected for a plant growing in a soil high in available Mg relative to Ca. This ratio then decreases in the terminal leaf tissue, where Mg plays a major role in photosynthesis. The Ca/Mg ratio of 2.8 in terminal leaf tissue is similar to a ratio of 2.2 reported by Wallace and others (1982) for a different species of California serpentine manzanita; the absolute concentrations are considerably different (Ca ~0.54 and Mg ~0.25 percent), probably because we included stem tissue in our samples. The ash yield increases from the small secondary roots to the larger primary roots, decreases at the basal burl, and then increases toward the stems and leaves. This pattern may result both from differences in tissue type and because the ground samples were not dried at temperatures greater than 40° C prior to analysis. By comparing element trends only on an ash-weight basis, however, problems due to differences in ash yield are avoided.

Figure 7 (lower) shows trends for Cr, Fe, Ni, and Mn with respect to distance from the basal burl. Chromium, Fe, and Ni behave similarly in that they decrease in concentration from the secondary to the primary roots and then greatly increase in the basal burl before continuing to decrease toward the stems and leaves. Although relatively little Cr, Fe, or Ni are translocated along the roots, the basal burl appears to accumulate these elements; at the very least, the burl is a central collecting point for root-translocated elements. Also, very little Cr, Fe, or Ni are translocated to the leaves.

Iron and Mn are essential elements and both are involved in respiration reactions, enzyme activation, and electron transport. Unlike Mn and other essential cations, however, Fe is relatively immobile within plant tissue. Figure 7 (lower) clearly shows that Mn, and not Fe, is readily translocated to the secondary stems and leaves where it is concentrated by an order of magnitude over what is in the burl.

We sampled only tissue associated with major lateral roots, not the mass of smaller, less readily traceable feeder rootlets, and our observations of metal translocation do not account for the activity of these rootlets. The soil pit excavations reveal that a great majority of manzanita and pine rootlets occur at depths of about 15 cm or less. The relative importance of metal uptake by the major deep laterals as compared to the shallow rootlets is unknown.

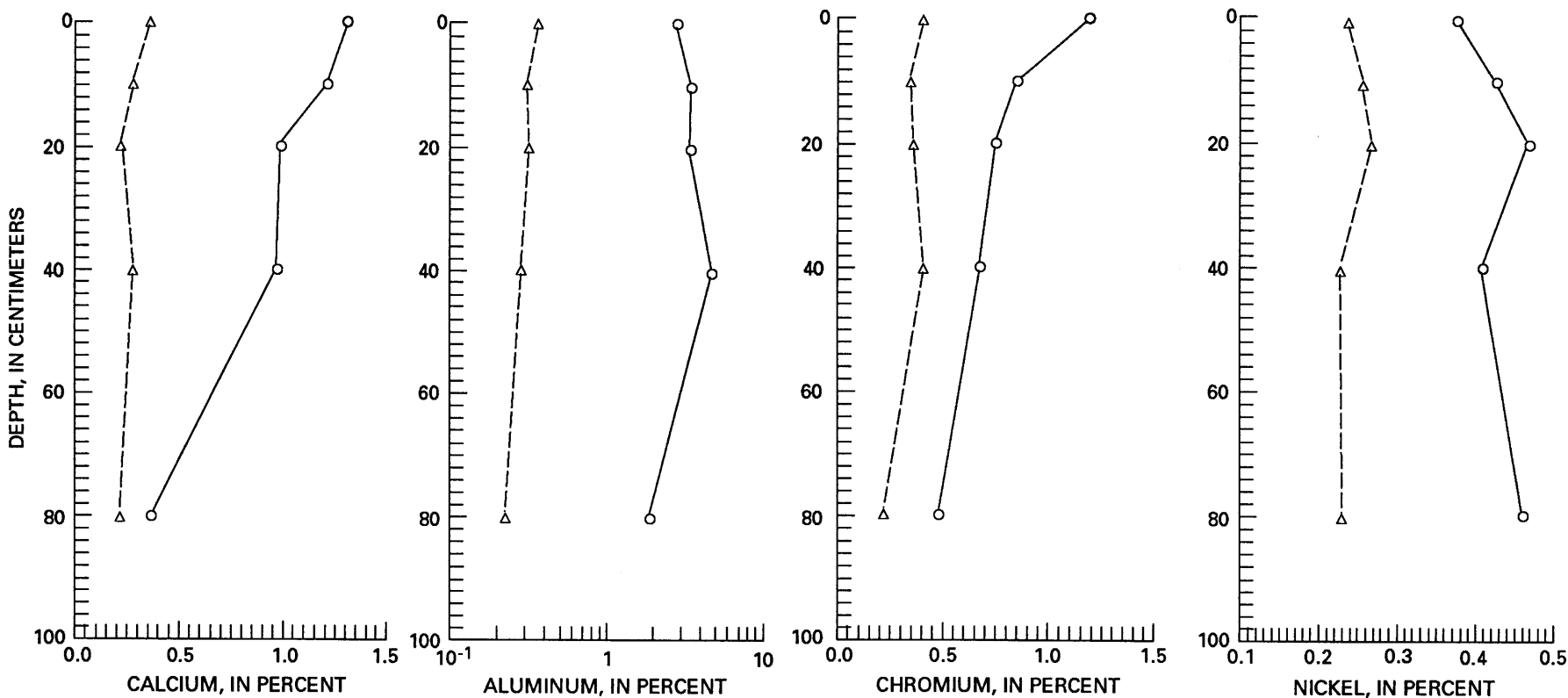
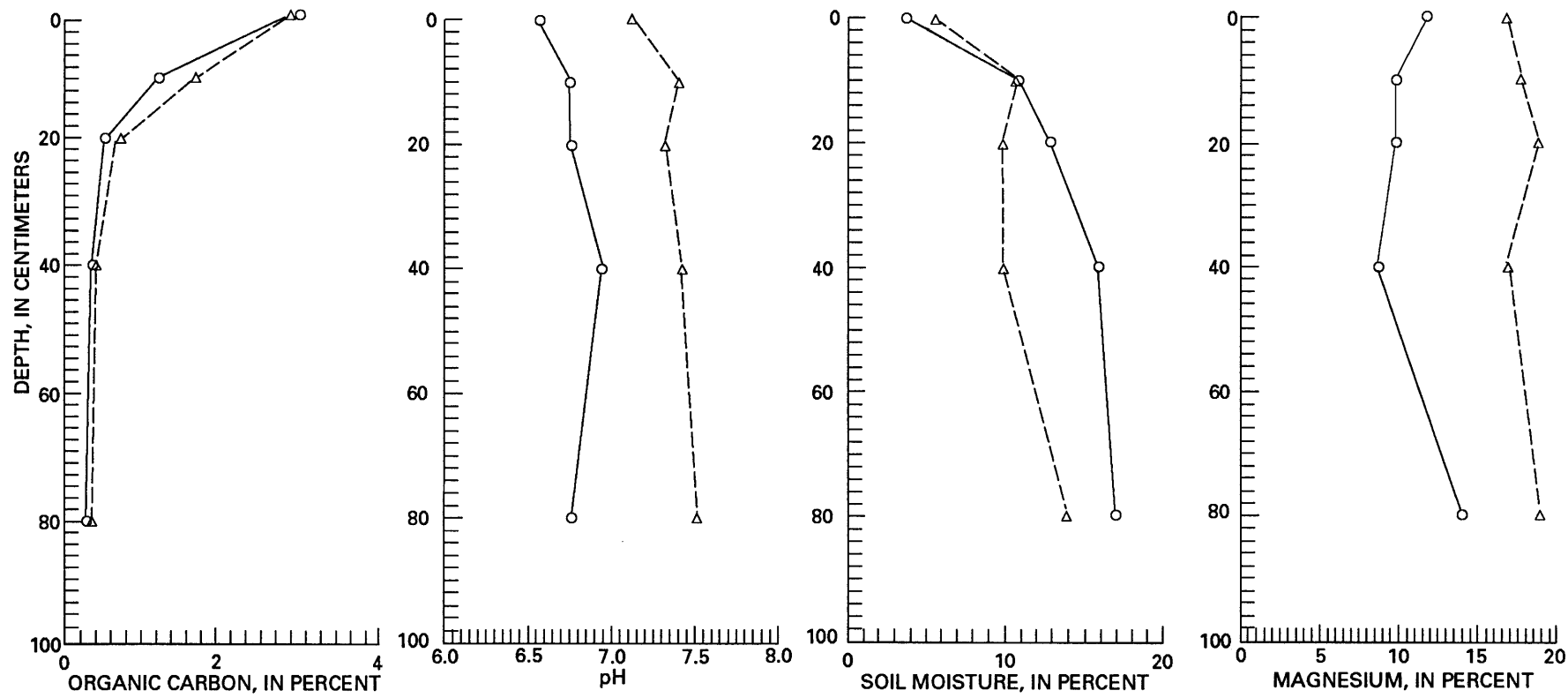
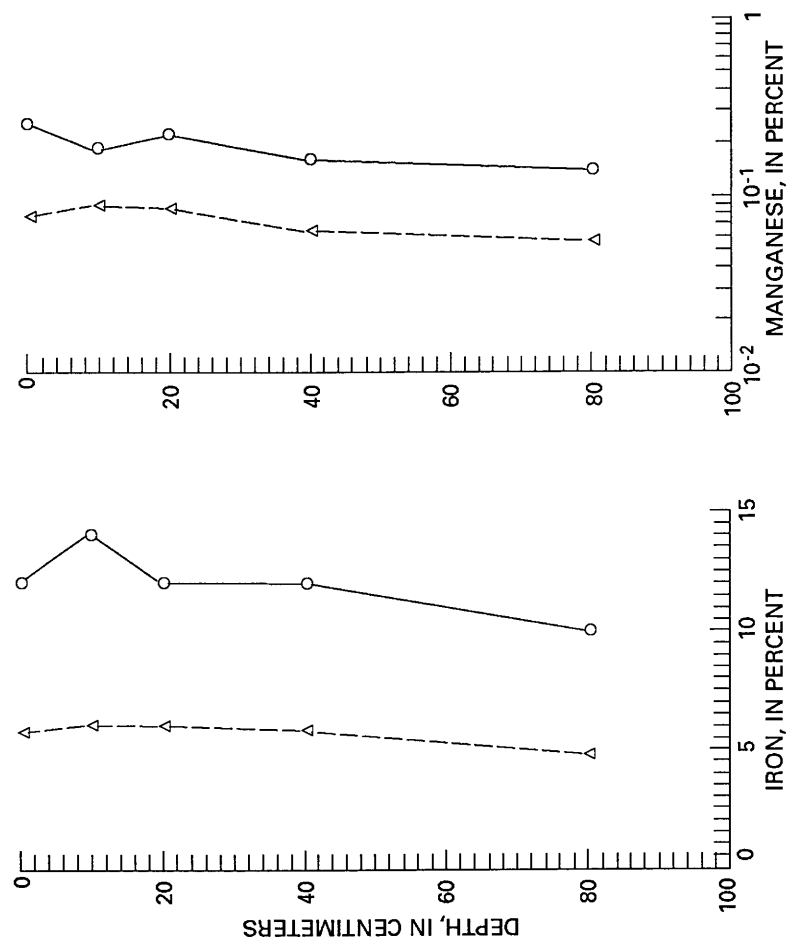


Figure 5 (above and following three pages). Soil physical and chemical variables for soil profiles 08I (circles) and 07G (triangles) plotted as a function of depth in excavated soil pits. Profile 08I was in the gently sloping, high bench area, which has moderate to good soil development; profile 07G was in the steep, eroded ridge and gully region, which has a moderate to deep layer of transported soil.





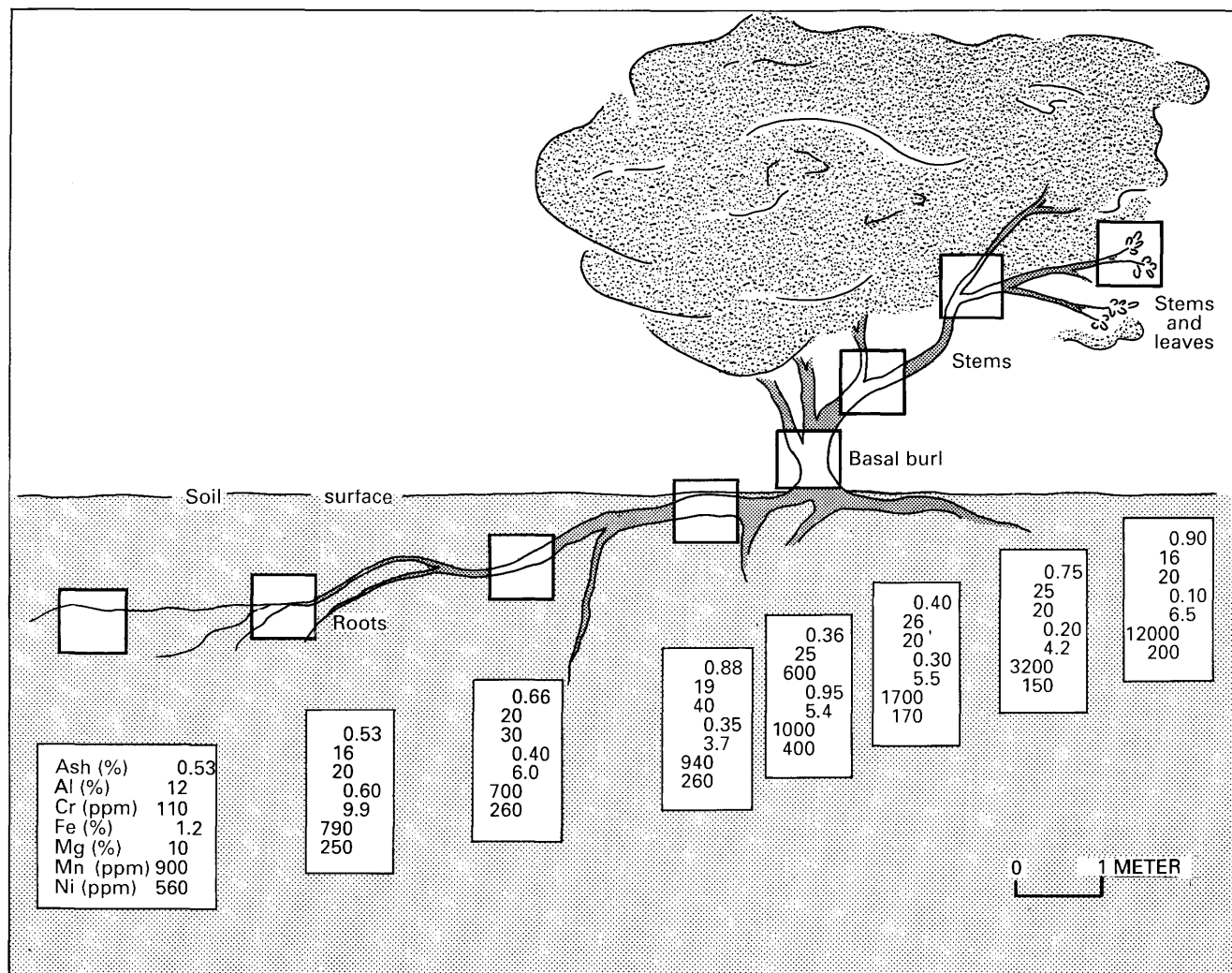


Figure 6. Relative position and the concentration of selected elements (ash-weight basis) in sampled materials from whiteleaf manzanita shrub.

Biogeochemical Exploration for Chromium

Our report of the inability of manzanita to readily translocate Cr from roots to aerial tissue is apparently a common characteristic of serpentine vegetation in general (Koenigs and others, 1982; Wallace and others, 1982). That plant species physiologically block the transport of, or selectively accumulate, potentially toxic metals is well documented (Gough and others, 1979). Nevertheless, it may be possible to use manzanita, and possibly pine, as an aid in the exploration of concealed chromite deposits.

Our data show complementary Cr trends across the study area for both manzanita and pine. Although highly immobile and resistant, detrital chromite is the most common form of Cr in these soils; if oxidized to the hexavalent state, a large amount of Cr could be made available for uptake. We have semiquantitatively

measured highly variable amounts of mobile Cr(VI) in about half of the excavated soil pits, as well as in water from ephemeral streams that drain the study area (Meadows and others, 1987). The occurrence of Cr(VI) in soils and waters offers an explanation as to the probable Cr form absorbed by plants. Investigations into the mechanism for the oxidation of Cr(III) to Cr(VI) and of Cr speciation in these ultramafic soils are ongoing.

The vegetation shows high levels of Cr in samples collected in the steep ridge and gully region (fig. 4), which was, until the early 1950's, the area of chromite mining. Two inactive chromite mines are on the western edge of this region (fig. 2). This study, however, cannot definitively distinguish between the relative importance of the old chromite mines and prospects and the possible influence of the concomitant highly dissected topography.

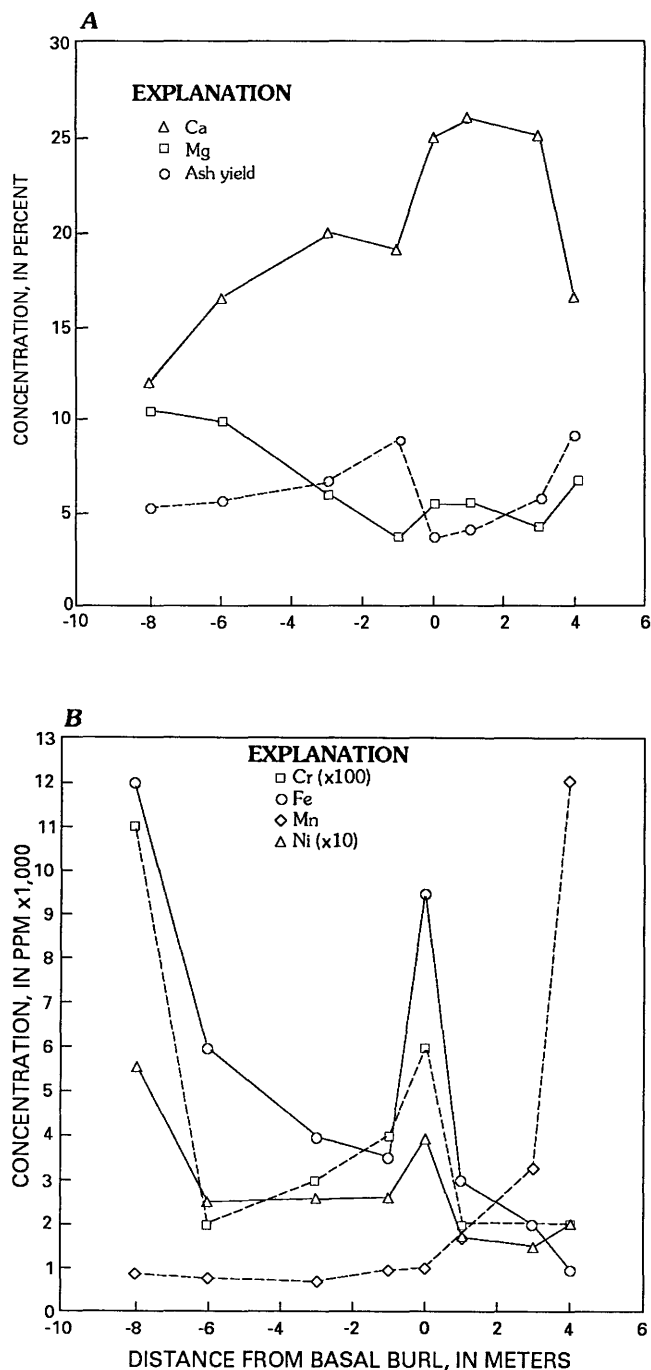


Figure 7. Relation between distance from the basal burl (noted as zero) of an excavated manzanita shrub and (A) the concentrations of Ca and Mg and ash yield and (B) the concentrations of Cr, Fe, Mn, and Ni in samples of roots (negative distance) and stems and leaves (positive distance). All concentrations are on an ash-weight basis.

In general, we found that the uptake of Cr by manzanita and pine in these serpentinized, chromite-rich soils probably involves both the physical dissemination of chromite and the active formation of Cr(VI) by the

oxidation of Cr(III). The north-trending shear zones that form the prominent erosional gullies in the western half of the study area appear to have accentuated the breakup of chromite pods and dissemination of chromite in general. Chromium is geochemically immobile as detrital chromite (mixed oxides and hydroxides of Cr and Fe); however, the dispersed chromite grains offer greater surface area for potential oxidation. Preliminary studies show that soil Cr is being oxidized to Cr(VI) (Gough and others, 1986). Once it is oxidized, it apparently remains in the hexavalent state for some time and concentrations of Cr(VI) as great as 250 ppb have been found (Meadows and others, 1987). These concentrations were observed in both the dry season (August) and when ephemeral streams were flowing through the area (March). This discovery implies either that the residence time of Cr(VI) in these soils can be measured in months or years or that oxidation actively occurs throughout the year. The presence of organic matter can serve to reduce Cr(VI) and thus decrease its residence time in the soil; however, organic carbon is never greater than 4 percent in the soils (fig. 5) and it is concentrated in only a few centimeters near the surface.

A mechanism for the oxidation of Cr(III) is still being sought. We have observed Fe- and Mn-oxide coatings on pebbles in the shear-zone gullies; oxidized Mn has been reported by Bartlett and James (1979) as an electron acceptor that affects the oxidation of Cr(III) to Cr(VI) in many field soils. Oxidation of Cr may also be aided by the occurrence of brush fires (Cary, 1982), which are common in the chaparral ecosystem. These fires may oxidize both surface-soil Cr and Cr in plant material that then becomes part of the soil. Also, soil pH and aeration in the study area are certainly favorable for oxidation.

A mechanism for biogeochemically defining the occurrence of concealed chromite deposits is far from refined. It would appear, however, that in areas where chromite surface area is increased (through weathering and dissemination) and Cr oxidation can occur, it may be possible to use plant chemistry to identify general target areas for further exploration.

Future biogeochemical exploration studies in similar terrain should investigate the use of basal burl tissue. Because the root system translocates absorbed elements to the burl from a volume of surrounding soil, the burl both concentrates and integrates the geochemistry of a large area. Because of this integration process there is probably less seasonal variability in the concentration of elements in burl as compared to stem or leaf tissue. Further, we found that the concentration of Cr and Ni is about 3.0 and 2.5 times greater, respectively, in the burl as compared to stems and leaves, thus enhancing the analytical detection of these elements.

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