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THE FEASIBILITY OF BIOGEOCHEMICAL
AND GEOBOTANICAL PROSPECTING AT
SPARGOVILLE, WESTERN AUSTRALIA

A thesis presented in partial fulfilment
of the requirements for the degree
of Master of Science
in Chemistry
at
Massey University

Jeppe Søndergaard Nielsen
1972
ABSTRACT

Several plant species together with their associated soils from Spargoville, Western Australia, were analysed for chromium, copper, cobalt, manganese, nickel and zinc by atomic absorption spectrophotometry. Particular reference was given to nickel and copper to evaluate the usefulness of plant analysis for biogeochemical prospecting.

The nickel content in the soils gave plateaus of high values over ultrabasic rock types whereas the copper levels in the soils gave peaks over areas of mineralization at ultrabasic contacts. Consideration of the plant data showed that each species accumulated different amounts of the above elements, and that they distributed these trace elements in different ways between their leaves and twigs, or between their bark and wood.

Relationships between nickel and copper concentrations in the plants and in the soils were evaluated by computing correlation coefficients; promising statistical results were checked graphically. The nickel and copper concentrations in the bark of Eucalyptus lessuefii most accurately depicted the concentrations of these metals in the soils. It was also found that the barks of Eucalyptus lessuefii, Eucalyptus longicornis and Eucalyptus torquata could be used together for prospecting purposes. In the cases where the soil-plant relationship was either very good or very poor, it seemed to make no difference whether parametric or non-parametric correlation coefficients were used. When the relationship was intermediate between these extremes, however, the non-parametric statistic was superior.

A geobotanical study was also carried out to determine whether the distributions of the plant species was related to the geology. Dodonaea lobulata, Pittosporum phillyraeoides and Trymalium ledifolium were found to grow only on ultrabasic rock types, and the outer, black bark of E. lessuefii growing in mineralized ground was observed to grow to a greater height on the trunk than occurred when this species grew in non-mineralized soils.

When discriminant analysis was applied to plant mapping data, the different rock types could be effectively discriminated using
the relative abundances of as few as one-third of the species present. These results were markedly superior to those obtained when discriminant analysis was applied to some biogeochemical data.
ACKNOWLEDGEMENTS

I would like to express my sincere thanks to the following:

My supervisor, Dr. K.R. Brooks, for his enthusiastic guidance during the course of this project.

Dr. C.R. Boswell, Computer Unit, Massey University, for his valuable assistance with the computer programmes and the statistical aspects of this work.

Australian Selection (Pty.) Ltd. for extensive financial and logistic support; in particular Mr. A.D. Gibbs, Mr. N.J. Marshall and Mr. J.E. Martin are thanked for their useful criticisms.

Mr R.D. Royce, Dept. of Agriculture, Perth, for identification of the plants collected during the field work.
TABLE OF CONTENTS

ABSTRACT ............................................................................................................... ii
ACKNOWLEDGEMENTS ....................................................................................... iv
TABLE OF CONTENTS .......................................................................................... v
LIST OF FIGURES ................................................................................................ viii
LIST OF TABLES .................................................................................................... ix
GENERAL INTRODUCTION .................................................................................... 1
SECTION I - THE AREA OF STUDY ........................................................................ 6
   A. Introduction ..................................................................................................... 7
   B. Climate ........................................................................................................... 8
   C. Lithology ....................................................................................................... 9
   D. Vegetation ................................................................................................... 11
SECTION II - METHODS .......................................................................................... 12
   A. Biogeochemical sampling techniques. .............................................................. 13
       (1) Introduction ............................................................................................ 13
       (2) Soils ....................................................................................................... 13
       (3) Plants .................................................................................................... 13
   B. Geobotanical techniques. .............................................................................. 14
   C. Chemical analysis. ....................................................................................... 15
       (1) Chemicals and instruments ................................................................... 16
       (2) Treatment of soil samples ..................................................................... 16
           (a) Preliminary treatment ....................................................................... 16
           (b) Extraction of the total content of the elements determined .......... 16
           (c) Extraction of the readily-available nickel and copper ................. 16
       (3) Treatment of plant samples ................................................................... 16
           (a) Preliminary treatment ....................................................................... 16
           (b) Leaching procedure ......................................................................... 16
           (c) Dissolution procedure ...................................................................... 17
   D. Statistical treatment of data. ........................................................................ 18
       (1) Biogeochemical data .............................................................................. 18
       (2) Geobotanical data ................................................................................ 21
SECTION III - BIOGEOCHEMICAL STUDY .............................................................. 24
   A. Introduction. ................................................................................................. 25
   B. Orientation survey on Grid 5B. ................................................................... 29
       (1) Soils ....................................................................................................... 29
           (a) Choice of soil fraction ...................................................................... 30
           (b) Total concentrations of the elements determined in the soils ....... 31
           (c) The readily-available concentrations of the elements determined in
                the soils .............................................................................................. 33
           (d) Statistical analysis ............................................................................ 34
(2) Plants
   (a) The distributions of the elements determined  
   (b) Statistical analysis
(3) Soil-plant relationships for nickel and copper
   (c) Correlation coefficients
   (b) The usefulness of correlation coefficients
   (c) The use of several plant species collectively
   (d) Discussion
C. Some factors affecting biogeochemical prospecting
   (1) The choice of a useful plant species
   (2) Variation between plant parts
   (3) The availability to plants of nickel and copper in the substrate
   (4) Inter-element relationships in the various plant tissues
   (5) Conclusions
D. The usefulness of biogeochemistry on Grid 5D
   (1) Introduction
   (2) Soil-plant relationships for nickel and copper
E. Conclusions

SECTION IV - GEOBOTANICAL STUDY
A. Introduction
B. Orientation survey on Grid 5B
   (1) Morphological changes
   (2) Plants indicative of mineralization
   (3) Plants indicative of a particular geological structure
   (4) Statistical treatment of the data
C. Geobotanical data from Grid 5D
   (1) Introduction
   (2) Plants indicative of a particular geological structure
   (3) Statistical treatment of data
D. Conclusions

SECTION V - GENERAL CONCLUSIONS

BIBLIOGRAPHY

APPENDICES
   I Plant species recorded
   II Illustrations of some plant species
      A. E. lesuefii growing on non-mineralized ground
B. E. Lucusfii growing on mineralized ground 103
C. Podocarpus lobulatus 104
D. Piformis phillyraeoides 105
E. Trigileium ledifolium 106

III Discriminant analysis of some biogeochemical data from Grid SE. 107
A. Introduction 107
B. Results and discussion 108
C. Conclusions 112

IV Computer programmes. 113
A. Introduction 113
B. Pearson product moment correlation coefficient programme 114
C. Spearman rank correlation coefficient programme 115
D. Discriminant analysis programme 116

V Publications arising from this thesis 117
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>After Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 1</td>
<td>The &quot;prospecting prism&quot;.</td>
<td>2</td>
</tr>
<tr>
<td>I - 1</td>
<td>Locality map</td>
<td>7</td>
</tr>
<tr>
<td>I - 2</td>
<td>The two grids.</td>
<td>10</td>
</tr>
<tr>
<td>III - 1</td>
<td>Total nickel and copper contents in the -30 mesh and the -10+26 mesh soil fractions (Grid 5B).</td>
<td>31</td>
</tr>
<tr>
<td>III - 2</td>
<td>The total and readily available concentrations of the elements determined in the -10+26 mesh soil fractions compared with the lithology (Grid 5B).</td>
<td>31</td>
</tr>
<tr>
<td>III - 3</td>
<td>Cumulative frequency diagrams for the total content of the elements determined in the -10+26 mesh soil fractions (Grid 5B).</td>
<td>34</td>
</tr>
<tr>
<td>III - 4</td>
<td>Typical cumulative frequency diagrams for the elements determined in plants (Grid 5B).</td>
<td>41</td>
</tr>
<tr>
<td>III - 5</td>
<td>Nickel concentrations in the barks of the three Eucalyptus species compared with the total nickel concentrations in the soils and with the lithology (Grid 5B).</td>
<td>48</td>
</tr>
<tr>
<td>III - 6</td>
<td>Copper concentrations in the barks of the three Eucalyptus species compared with the total copper concentrations in the soils and with the lithology (Grid 5B).</td>
<td>48</td>
</tr>
<tr>
<td>III - 7</td>
<td>The relationship of the nickel and copper contents between the various ashed plant organs (Grid 5B).</td>
<td>53</td>
</tr>
<tr>
<td>III - 8</td>
<td>Nickel concentrations in the barks of the three Eucalyptus species compared with the total nickel concentrations in the soils and with the lithology (Grid 5B).</td>
<td>64</td>
</tr>
<tr>
<td>III - 9</td>
<td>Copper concentrations in the barks of the three Eucalyptus species compared with the total copper concentrations in the soils and with the lithology (Grid 5D).</td>
<td>64</td>
</tr>
<tr>
<td>IV - 1</td>
<td>Histograms showing the distribution of the most significantly distributed plant species (Grid 5B).</td>
<td>74</td>
</tr>
<tr>
<td>IV - 2</td>
<td>Histograms showing the distributions of the most significantly distributed plant species (Grid 5D).</td>
<td>82</td>
</tr>
<tr>
<td>Plate I - 1</td>
<td>The vegetation cover in the vicinity of the two grids.</td>
<td>11</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>II - 1</td>
<td>Levels of significance for the correlation coefficients.</td>
<td>20</td>
</tr>
<tr>
<td>III - 1</td>
<td>Mean concentrations for the elements determined in the various soil fractions (Grid 5B).</td>
<td>32</td>
</tr>
<tr>
<td>III - 2</td>
<td>Median values, arithmetic means and geometric means for the trace elements determined in the soils (Grid 5B).</td>
<td>36</td>
</tr>
<tr>
<td>III - 3</td>
<td>Mean concentrations for the elements determined in the ash of the three most common species (Grid 5B).</td>
<td>37</td>
</tr>
<tr>
<td>III - 4</td>
<td>Mean relative accumulations of the elements determined in the ash of the most common species (Grid 5B).</td>
<td>39</td>
</tr>
<tr>
<td>III - 5</td>
<td>Median values, arithmetic means and geometric means for the trace elements determined in the ash of the various plant systems (Grid 5B).</td>
<td>42</td>
</tr>
<tr>
<td>III - 6</td>
<td>Correlation coefficients between concentrations of nickel and copper in the soils and in the plant ash (Grid 5B).</td>
<td>44</td>
</tr>
<tr>
<td>III - 7</td>
<td>The comparison of correlation coefficients with the degree of overlap between anomalous nickel and copper concentrations in the soil and in the different ashed plant tissues (Grid 5B).</td>
<td>46</td>
</tr>
<tr>
<td>III - 8</td>
<td>Values of Students &quot;t&quot; for the significance of difference between the mean relative accumulations of nickel and copper by the barks of the three Eucalyptus species (Grid 5B).</td>
<td>49</td>
</tr>
<tr>
<td>III - 9</td>
<td>Means and ranges of values for nickel and copper concentrations in the ash of the different plant systems (Grid 5B).</td>
<td>52</td>
</tr>
<tr>
<td>III - 10</td>
<td>Correlation coefficients between the nickel and copper concentrations in the ash of the various plant tissues and the element concentrations in the soil (Grid 5B).</td>
<td>55</td>
</tr>
<tr>
<td>III - 11</td>
<td>Correlation coefficients between the element concentrations in the ash of the various plant tissues (Grid 5B).</td>
<td>57</td>
</tr>
<tr>
<td>III - 12</td>
<td>Mean values for nickel and copper concentrations in the soils and in the ash of the three most common species (Grid 5D).</td>
<td>60</td>
</tr>
<tr>
<td>III - 13</td>
<td>Mean relative accumulations of nickel and copper in the ash of the three most common species (Grid 5D).</td>
<td>62</td>
</tr>
<tr>
<td>III - 14</td>
<td>The comparison of correlation coefficients with the degree of overlap between anomalous nickel and copper concentrations in the soil and in the different ashed plant tissues (Grid 5D).</td>
<td>63</td>
</tr>
<tr>
<td>Table No.</td>
<td>Description</td>
<td>Page No.</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>IV - 1</td>
<td>The arithmetic mean nickel and copper concentrations in the ash of vegetation growing in mineralized ground</td>
<td>72</td>
</tr>
<tr>
<td>IV - 2</td>
<td>Values for the $D^2$ statistic and the associated degrees of discrimination of the quadrats (Grid 5B).</td>
<td>78</td>
</tr>
<tr>
<td>IV - 3</td>
<td>Values for the $D^2$ statistic and the associated degrees of discrimination of the quadrats (Grid 5D).</td>
<td>83</td>
</tr>
<tr>
<td>A - 1</td>
<td>Mean (arithmetic) elemental concentrations in the ashed bark of <em>Eucalyptus lesuefii</em> (Grid 5E).</td>
<td>109</td>
</tr>
<tr>
<td>A - 2</td>
<td>Values for the $D^2$ and $F$ statistics and the associated degree of discrimination of the sampling sites (Grid 5B).</td>
<td>110</td>
</tr>
</tbody>
</table>
GENERAL INTRODUCTION
The present level of civilization, allied as it is to ever-expanding populations, necessitates the demand for a continuous and adequate supply of raw materials. This demand not only includes fossil and nuclear fuels to fulfill energy requirements, but also metallic and non-metallic elements for use in the manufacture of consumer goods.

The result has been a world-wide "boom" in exploration for mineral resources since World-War II.

Prior to World-War II, metalliferous deposits were discovered by relatively untrained prospectors, guided only by what could be seen with the unaided eye. These surface deposits have long since been exploited, and more recently the search has been under way for the big deposits to be found under the various types of blanketing soil cover or barren bedrock.

The "great leap-forward" in technology during the last three decades has led to the use of increasingly sophisticated techniques for the mapping of geological structures and for detecting ore deposits at depth. These include geophysical techniques such as magnetics, electromagnetics, induced polarization and self-polarization, as well as photogeological methods such as aerial remote sensing.

Consideration of the rock-soil-plant system has led to the use of geochemical prospecting as yet another tool in mineral exploration. The principles involved in this method are as old as man's first use of metals and can be considered using the concept of the prospecting prism (Fortescue and Hornbrook, 1967). This is a three dimensional representation of the different components of a landscape system which may be involved in geochemical mineral exploration (Fig 0-1). Hence mineralization at depth can theoretically be discovered by consideration of all the components of the prism, i.e. rocks, soils, and vegetation.

As defined by common usage, geochemical prospecting is the measurement of one or more chemical properties of a naturally-occurring material (Hawkes and Webb, 1962). The chemical property measured is most commonly the trace content of some element or group of elements, while the naturally-occurring material is a component of the prospecting prism. The purpose of the
**Geophysical Methods of Exploration**

**Airborne Methods**
1. Remote Sensing
2. Photography
3. Magnetics
4. Electromagnetics
5. Radioactivity

**Ground Methods**
1. Magnetics
2. Electromagnetics
3. Induced Polarization
4. Self Potential
5. Gravity
6. Resistivity
7. Seismic
8. Radioactivity

**Geochemical Methods of Exploration**
1. Plant Geochemistry
2. Soil Geochemistry
3. Bog Geochemistry
4. Water Geochemistry
5. Stream Sediment Geochemistry
6. Overburden Geochemistry
7. Rock Geochemistry

**Specialized Geological Methods of Exploration**
1. Heavy Mineral Analysis
2. Boulder Tracing
3. Diamond-Drilling
4. Trenching
5. Exploratory Mining

---

**Figure 0-1**

The "prospecting prism"
measurements is the discovery of abnormal chemical patterns, or geochemical anomalies, related to mineralization.

The most widely used geochemical prospecting technique has been the analysis of soil samples. This method relies on the principle that under suitable weathering and topographical conditions, the ore metal will be dispersed chemically or mechanically from the mineralization at depth into the overlying soil. In areas of good drainage where soil samples may not be readily available, sampling of stream sediments has been used successfully; in this method the assumption is made that the sediment represents a composite sample of the soil and unweathered rock in the area drained by the stream.

Plant exploration geochemistry involves two fields of study. These are geobotanical prospecting and biogeochemical prospecting. Although these two methods are different in scope and application, the principles underlying both are the same. The root systems of plants act as powerful sampling mechanisms, collecting aqueous solutions from a large volume of moist ground below the surface. These solutions then serve as a source of inorganic salts that may be deposited in the upper parts of the plant, or that may stimulate, inhibit or otherwise modify the growth habits of the plant.

Geobotanical prospecting involves a visual survey of the vegetation cover in order to determine whether the presence or absence of distinctive plant communities, individual species, or whether morphological changes in the vegetation can be attributed to mineralization.

The associated technique, biogeochemical prospecting, relies on the analysis of plants to obtain evidence of mineralization at depth. This method may have the following advantages over the analysis of soil samples:

(i) The amount of ground sample- both vertically and horizontally by a given plant represents a much larger area than that of a given soil sample.

(ii) The depth of penetration of roots may permit the sampling of a deep horizon not accessible by surface soil sampling.

This is particularly true where "geochemical barriers", such as
siliceous hardpans, are found beneath the surface soil.

(iii) Plant sampling eliminates the possibility of interference from transported surface soils and permits prospecting in areas where residual soil is either nonexistent or varied.

(iv) Some plants have the ability to concentrate higher levels of certain elements in their ash than exists in the underlying soil.

Where a significant relationship exists between plant distributions and mineralization, geobotanical prospecting would be expected to be superior to all other methods because no analytical work is required, and maps of mineralized ground may be drawn directly from observation of occurrences of plants.

The use of biogeochemistry as a guide to mineralization has not been as readily accepted as the more conventional geochemical techniques such as soil or stream sediment sampling. This may seem surprising when it is remembered that two-thirds of the world's land surface is covered with vegetation (Draeger and Lauer, 1967). However, biogeochemistry is considerably more complex than soil geochemistry because it involves a study of such factors as the particular plant species sampled, the particular part of the plant sampled, the availability of elements in the soil, and plant nutrition. These factors have been discussed by Webb and Millman, 1951; Carlisle and Cleveland, 1958; Shacklette, 1962; Fortescue and Hornbrook, 1967. Finally a major disadvantage of plant geochemistry in general is the need for skilled personnel, both in the execution of the work and in the interpretation of the data.

It is to be hoped however, that in the field of mineral exploration, the presence of vegetation will come to be regarded as an asset rather than as a hinderance. The distribution and the elemental content of plant species should be regarded as extra "tools" to be utilized in building up the complex picture necessary for the discovery of mineral deposits.

The work described in this thesis was initiated to evaluate the usefulness of biogeochemistry and geobotany in the search for nickel mineralization in Western Australia. It was carried out with the permission and assistance of Australian
Selection (Pty.) Limited on part of their concession area at Spargoville, Western Australia. The particular region of study was chosen because it was known to contain nickel mineralization, and the geological structure was known.

The aims of this thesis can be summarized as follows:

(i) To carry out an orientation survey to discover which, if any, of the plant species present were suitable for biogeochemical prospecting for nickel.

(ii) To evaluate the usefulness of correlation coefficients in the handling of biogeochemical data.

(iii) To investigate some factors affecting the usefulness of biogeochemical prospecting in this area.

(iv) To carry out an orientation survey to evaluate the usefulness of geobotany in mineral exploration in the area of study.

(v) The application of discriminant function analysis to geobotanical data.

(vi) To test the biogeochemical and geobotanical conclusions obtained during the orientation survey on another area of similar lithology and ecology.
SECTION 1

THE AREA OF STUDY
A. INTRODUCTION

The area chosen for this work was at Spargoville, Western Australia, located about 330 miles east of Perth and 60 miles south of Kalgocrlie (Fig. I-1).

Two grids of different sizes were used. Systemmatic soil and plant sampling for the biogeochemical orientation survey and plant mapping for the geobotanical orientation survey were carried out on Grid 5B. Grid 5D was used to test the findings from the orientation work. These two grids were separated by a distance of approximately three-quarters of a mile.

Grid coordinates used in this thesis contain the south coordinate followed by the east coordinate.

The topography is gently undulating. On Grid 5B, the elevation is from 1115 ft. at the outer extremities rising to 1140 ft. at the centre of the grid, whereas for Grid 5D, the elevation ranges from 1150 ft. to 1170 ft.

There are no definite drainage patterns. However, there does exist a number of shallow watercourses which very rarely carry running water through more than a limited portion of their channels. The directions of these channels closely follow topographical trends.
B. CLIMATE

At Spargoville, the annual average rainfall is approximately 10 inches, falling mainly during the winter months of June, July and August. However, summer rain is also experienced in March.

The average temperature per annum ranges from 60°F to 70°F. The summer months of December, January and February are the hottest with an average temperature of approximately 75°F, and the winter months of June and July are the coolest with an average of 50°F.

The region also experiences strong, dry winds from the southern and south-western quarters.
C. LITHOLOGY

Spargoville lies on a pronounced magnetic trend which correlates with a greenstone belt comprising basic and ultrabasic rocks, as well as minor sediments.

The basic rocks are amphibolitic and readily recognized in the field by their reddish-brown texture, while the sediments are usually fine-ground shales and cherts. The composition of the ultrabasic rocks vary from tremolite to tremolite-chlorite to talc carbonate; a few small pockets of serpentineite are also present. In contrast to other rock types, the ultrabasics occur as relatively narrow banks which have a N.N.W. trend.

The bedrock is weathered and highly altered in places by processes of lateritisation and by carbonate replacement. It seems that the laterite, which occurs as a norted zone over the whole area, is much deeper than the soils; in fact the whole of the weathered profile probably bears the imprint of lateritisation. The weathering profile extends from the surface to fresh bedrock, which is encountered at depths down to 200 ft. vertically.

Magmatic nickel-copper sulphide mineralization occurs at the ultrabasic-basic rock contacts. The grade of the ore can be as high as 2%, while the concentration of copper is approximately 1/10th this value (Pers. comm. J.E. Martin). Arsenic also occurs in areas of mineralization; up to 1.5% arsenic has been detected in some of the ore concentrates now being mined at Spargoville (Pers. comm. N.J. Marshall).

A total of three gossans occur at ultrabasic rock contacts on the two grids used for the present study. Gossans consist of residual hydrous iron oxides derived from the weathering of sulphides (or carbonates). Other minerals, as well as metallic constituents of the ore, may be associated with the ubiquitous iron oxides. Thus, depending on the parent material and on the degree of weathering that has occurred in the gossan, it is not surprising that elemental concentrations in these outcrops often reflect bedrock geochemistry.

Soils are seldom more than 2 ft. deep and are not differentiated into horizons. This implies that they are relatively
young, and if not residual, are locally derived. Hence the chemical composition of the soils in the study area could be expected to reflect the underlying geological structure.

Fig. 1-2 shows the topography, the sampling stations, the geological contacts between the various rock types and the positions of the gossans on the two grids.
The two sampling grids

- Contact
- Gossan
- Sampling site

-130- Topographic isocontour

A Amphibolite
M Metasediment
U Ultrabasic
D. VEGETATION

The following description is taken from Elkington, 1969, as well as from the author's own observations.

The vegetation consists of sclerophyllous woodland in which several *Eucalyptus* species occur. The dominant species is *Eucalyptus lesuefii*, together with lesser numbers of *E. calycocoma*, *E. longicornis*, *E. salmonophloia*, *E. salubris*, and *E. torquata*. These trees may grow up to sixty feet in height.

Several types of low, woody, perennial shrubs are also present. In particular, *Acacia colletioides*, *A. aff. -colletioides*, *Dodonaea stenozyga*, *Eremophila dempsteri*, *E. ionantha*, *E. oppositifolia* and *E. pachyphylla* are common.

Other species of shrubs occur in lesser numbers as well as some ephemeral herbaceous species and a few perennial grasses.

Plate I-1 shows the topography and vegetation cover in the vicinity of the sampling areas.
PLATE I-1. The vegetation cover in the vicinity of the two grids
SECTION II

METHODS
A. BIOGEOCHEMICAL SAMPLING TECHNIQUES

(1) Introduction

In a biogeochemical orientation survey, it is imperative to collect both soil and vegetation at each sampling station. There are, however, five sources associated with the sampling programme which can lead to large errors:
(i) The depth from which the soil is taken.
(ii) The position of the soil sample in relation to the plant.
(iii) The height on the plant from which it is sampled.
(iv) The side of the plant sampled.
(v) The age of the plant organs sampled.

The effects of these factors have been extensively investigated by Warren and Delavault, 1948; Warren, Delavault and Irish, 1952; Warren, Delavault and Fortescue, 1955; Carlisle and Cleveland, 1958; Barakso, 1969; Timperley, Brooks and Peterson, 1972.

In order to eliminate these sources of error as much as possible, the following methods of sampling were employed at each sampling station.

(2) Soils

Each soil sample was collected from a depth of not more than 3 inches at various points within a radius of 10 feet around each sampling station. Soils were sieved in situ using nylon mesh to give a final weight of approximately 20 grams.

(3) Plants

Each plant sample was collected from various points around the circumference of the tree or shrub at a constant height of approximately 3-4 ft. above the ground. Twigs approximately \( \frac{1}{4} \) inch in diameter and a composite sample of old and young leaves were sampled from shrubs. The leaves and twigs on trees were too far from the ground to be easily sampled, so only the outer sap wood and bark were collected. Ten to fifteen gram samples of vegetation were collected; leaves were stripped from their associated twiglets, and twigs, bark and wood were cut into suitable small sizes whilst sampling was in progress.
B. GEOROBOTANICAL TECHNIQUES

The numbers of each type of vegetation present were counted in a number of sample plots called quadrats. There is no general rule concerning the most suitable size or shape for quadrats; this depends primarily on the density and distribution of the vegetation. The smaller the quadrat, the greater the length of quadrat boundary per unit area, and consequently the greater the chance of significant edge effects due to the observer consistently including individuals that ought to be excluded and excluding individuals that ought to be included. Hence quadrats should not be too small. Past work has also shown that rectangular-shaped quadrats are the most suitable (Greig-Smith, 1964).

In this work, the size of quadrats used was 100 ft. (east-west) X 50 ft. (north-south), and each quadrat was centred at the sampling stations used for the biogeochemical work (Fig. 1-2). Hence each type of vegetation present was counted in belt transects consisting of adjacent quadrats running across the profiles of the grids. On Grid 5B, the vegetation was counted along four belt transects, each consisting of fifteen quadrats, whereas for Grid 5D, four belt transects, each of eleven quadrats, were used.
C. CHEMICAL ANALYSIS

(1) Chemicals and instruments

Aqueous solutions and standards were prepared using Analytical Grade reagents. Standards were made up in 2M hydrochloric acid and stored at a concentration of 1000 ppm; these were diluted immediately prior to use.

All quantitative analyses for elements were carried out by atomic absorption spectrophotometry using a Varian-Technicon Model A.A.5.

(2) Treatment of soil samples

(a) Preliminary treatment:
The sieved samples collected in the field were stored in Kraft paper containers for transportation. Prior to extraction of the trace elemental content, all soils were ground to pass through a 200 mesh sieve.

(b) Extraction of the total content of the elements determined:

There are a wide range of methods for dissolving silicate materials.

Techniques involving concentrated sulphuric acid - nitric acid and hydrochloric acid - nitric acid mixtures have been used (Strasheim, Strelow and Butler, 1960).

More efficient extraction methods utilize acid mixtures containing hydrofluoric acid. It is common practice for commercial analytical laboratories to use a concentrated hydrofluoric acid - perchloric acid mixture (Langmyhr and Paus, 1968). This method, however, does not give complete dissolution either.

The most efficient method of attack is probably by concentrated hydrofluoric acid in a teflon-lined bomb (Langmyhr and Paus, 1968). Even though this method does give complete dissolution of soil samples, it is too slow and tedious for the routine analysis of large numbers of samples.

In this work, a modification of the procedure described by Brooks, 1960, was used.

Ten cm$^3$ of a concentrated hydrofluoric acid - nitric acid mixture (1:1) was added to 200 mg samples of soils in 50 cm$^3$
polypropylene beakers, and each was evaporated to dryness on a water bath. To each beaker, 10 cm$^3$ of 2M hydrochloric acid was then added and the mixture heated on a water bath until the residue had dissolved. The solutions were then cooled, made up to a volume of 10 cm$^3$ with 2M hydrochloric acid, and analysed for nickel, copper, cobalt, chromium, manganese and zinc.

(c) Extraction of the readily available nickel and copper:

Several weak buffer and acid systems have been used in the past to extract the exchangeable, or perhaps more accurately, the readily-available trace elemental content of soils. In particular, 2.5% acetic acid solution has been extensively used (Mitchell, 1964; Lyon, 1969).

The technique used in this work is as follows:

Ten cm$^3$ of 1M hydrochloric acid was added to 2 g samples of soil in 20 cm$^3$ glass vials and the vials rotated about their longest axes for 18 hours at approximately 15 r.p.m. The solutions were then filtered and analysed without further dilution for nickel and copper.

(3) Treatment of plant samples

(a) Preliminary treatment:

Contamination of vegetation by wind-blown soil or dust may be a possible source of error in plant analyses (Mitchell, 1960). Hence all plant samples were washed under running water, and dried for 24 hours at 100°C in brown paper bags.

This type of contamination was a distinct possibility at Spargoville as strong winds were often experienced, the annual rainfall was very low, the vegetation canopy was relatively thin, and soils were exposed.

(b) Ashing procedure:

Dry ashing at 450°C for 24 hours was used in preference to wet ashing using mixtures of concentrated perchloric, nitric and sulphuric acids at approximately 100°C (Scharrer and Munk, 1956).

Wet ashing techniques must be employed if volatile elements such as arsenic, mercury and selenium are to be determined. Other
less volatile metals such as lead, zinc and cadmium can also be lost during dry ashing (Mitchell, 1964). However, wet ashing has the disadvantage that plant samples can easily be contaminated by impurities in the acids used; if the plant contains low levels of the element, then the use of acid blanks cannot always overcome this problem. Also dry ashing does not require constant supervision as does wet ashing.

Of the elements that were analysed in plants, zinc was the most volatile (B.P. = 907°C). However, in view of the fact that the boiling point of zinc is twice the temperature used for the dry ashing, losses would not be expected to be significant. Hence the following ashing procedure was used:

Plant samples in pyrex beakers were heated at 100°C on hotplates until all the volatile carbonaceous material had been evolved. The ashing was then completed at 450 - 500°C for 24 hours in a muffle-furnace.

(c) Dissolution procedure:

Ten cm³ of 2M hydrochloric acid was added to 200 mg of plant ash in test tubes, and heated on a water-bath until any carbonaceous matter present had coagulated (approximately 15 minutes). The solutions were then cooled and made up to a volume of 10 cm³ with 2M hydrochloric acid. After the extraneous solid matter had been removed by decanting or filtering, the samples were analysed for nickel, copper, cobalt, chromium, manganese and zinc. The elements calcium and magnesium were also determined in some of the ashed plants after a further dilution of 1000x with 0.8% Sr(NO₃)₂ in 2M hydrochloric acid.

Unless adequate precautions are taken, problems may be encountered in the analysis of calcium and magnesium (Ramakrishna, Robinson and West, 1966). These elements form stable molecular species with any aluminium or phosphate present which are not readily broken down at the temperature of the air-acetylene flame (David, 1958). The addition of excess strontium to the solution, however, overcomes this interference (David, 1960; Elwell and Gidley, 1967).
D. STATISTICAL TREATMENT OF DATA

As geological data become more numerous and more quantitative due to the increasing sophistication in techniques and instrumentation, and the search for orebodies becomes more difficult as the emphasis shifts to less obvious targets, there has become an increasing need for the application of statistical methodology to evaluate the data. Fortunately, the large masses of data accumulated by modern techniques are amenable to rapid statistical evaluation with high speed electronic computers.

During this project, two statistical devices were used as preliminary devices for scanning the data:

(i) Correlation coefficients were calculated to determine the degree of association between variables in the biogeochemical data.

(ii) Discriminant function analysis was applied to the geobotanical data.

A description of the programmes used is included in the appendix.

(1) Biogeochemical data

An IBM 1620 II computer was used to calculate both parametric (Pearson Product Moment) and non-parametric (Spearman Rank) correlation coefficients in order to evaluate whether any relationships existed between elemental concentrations in the soils and in the plants. The levels of significance of both types of correlation coefficients were determined by reference to the tables of Fisher and Yates, 1957.

The Pearson Product Moment correlation coefficient, r, is termed parametric because for its use the following requirements must be met (Siegel, 1956):

(i) The variable under study is assumed to have underlying continuity, i.e. it is not restricted to having isolated values.

(ii) The observations must be independent.

(iii) The observations must be drawn from normally-distributed populations.

(iv) These populations must have the same variance, i.e. they
must be unimodal.

The first two conditions listed are common to all statistical tests, whether parametric or non-parametric. The meaningfulness of the Pearson statistic thus depends on the validity of the last two conditions. If Pearson correlation coefficients are calculated for data for which these two conditions do not apply, then it is difficult to say what is really the power of the test. Norris and Hjelm, 1962, found however, that if the data distributions did not depart too far from normality, then the parametric correlation coefficient was valid.

The use of the Spearman correlation coefficient, \( r_s \), has no conditions concerning the distribution of the data; hence it is termed non-parametric. In fact, the form of the distribution need not be known at all. Also sample sizes as small as \( N=6 \) can be treated and correlations can be determined on observations from several different populations.

It is obvious that the fewer or weaker the assumptions, the more general the conclusions. However, the most powerful tests are those which have the strongest or most extensive conditions associated with their use; it has been shown that the Spearman \( r_s \) is only 91% as efficient as the parametric \( r \), provided that the more rigid requirements of the latter are satisfied (Hotelling and Pabst, 1936).

Even when these conditions are satisfied, the Spearman correlation coefficient can be used with the same power as the Pearson correlation coefficient merely by increasing the number of samples by 10%. This avoids having to meet the conditions concerning the distribution of the data. However, this is in fact a limitation of the non-parametric test because it means that it is wasteful of data. For this project, this method for equalizing the power of the two types of correlation coefficients was impossible. Instead, lower levels of significance were used for the Spearman correlation coefficients than for the corresponding Pearson coefficients. Table II-1 lists the symbols and the levels of significance used.
TABLE II-1

Levels of significance for the correlation coefficients.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Symbol</th>
<th>level of probability</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pearson r</td>
<td>Spearsman r&lt;sub&gt;s&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>very highly significant</td>
<td>S**</td>
<td>&lt; 0.1%</td>
<td>&lt; 1%</td>
<td></td>
</tr>
<tr>
<td>highly significant</td>
<td>S*</td>
<td>0.1-1%</td>
<td>1-5%</td>
<td></td>
</tr>
<tr>
<td>significant</td>
<td>S</td>
<td>1-5%</td>
<td>5-10%</td>
<td></td>
</tr>
<tr>
<td>not significant</td>
<td>NS</td>
<td>&gt; 5%</td>
<td>&gt;10%</td>
<td></td>
</tr>
</tbody>
</table>
As will be subsequently shown, the elemental concentrations in soils and in plant ash often spanned more than one order of magnitude, and most often appeared to be log-normally distributed. (Ahrens, 1954; Tennant and White, 1959). All data sets were thus transformed to base ten logarithms prior to computation of Pearson Product Moment correlation coefficients. As a further consequence of the apparent distributions of the various data sets, mean values have been expressed as geometric means rather than as arithmetic means.

A comparison of the relative merits of the parametric and non-parametric methods for calculating correlation coefficients necessitates an evaluation of the requirements inherent in both models. In particular, the distribution requirement for the parametric model to be valid is most important.

The cumulative frequency of the concentrations of elements, calculated as a percentage of the total number of samples, has been shown to be a good method for determining the type of distribution of geochemical data (Tennant and White, 1959; Williams, 1967; Lepeltier, 1969). Log-normal distributions will show a straight line when plotted on log-probability paper, whereas normal and other types of distributions will give curved lines. If there is more than one population within the data such as could occur in mineralized and un-mineralized soil samples, a distinct change of slope or a point of inflection in the graph will be observed. This break can be considered to occur at the minimum concentration of the mineralized samples, although some overlap of distributions will occur (Williams, 1967).

This procedure, though more explicit than the use of histograms, is still qualitative. A line obtained by this procedure is seldom completely straight, and it may be difficult to decide whether a minor deviation should be taken as significant or not.

(2) Geobotanical data

An IBM 1130 computer was used to carry out
discriminant function analysis of this data to determine whether particular plant communities could be associated with particular geological structures.

If there are two or more groups of individuals and it is known a priori that the individuals represent two or more different populations (e.g., ultrabasic rocks from a mineralized environment versus barren rocks of different types), then a discriminant analysis will compute scores such that the differences between the populations are maximized.

In this work, the numbers of different types of vegetation occurring across ultrabasic and basic rocks from mineralized and unmineralized localities were counted. A discriminant function was calculated for each rock type, and each function took the form:

$$D = ax_1 + bx_2 + cx_3 + \ldots$$

where $x_1, x_2, x_3, \ldots$ etc. are the variables, i.e., the numbers of each species occurring over a particular rock type.

$a, b, c, \ldots$ etc. are the weights assigned to each rock type.

The discriminant function effectively combines the weighted variables in such a manner that the $D$ scores forming each population will have a minimum spread and a maximum of means.

![Diagram showing relative frequency and discriminant scores for group 1 and group 2](image)

Hence if the occurrences of the same species are determined over an unknown rock type, the value of its score can be computed from the solution of the equation, and one can determine whether this places it in group 1 or group 2.

Scores falling in the region of overlap will be associated with more uncertainty. Where a large region of overlap occurs, this indicates that the variables selected for separating the environments do not have much discriminating efficiency, and
perhaps other variables should be studied.

The validity of the discrimination was tested by calculating the Mahalanobis $D^2$ statistic. This can be used to determine whether the mean values of the variables are the same over all the rock types. A high value for the $D^2$ statistic infers that the means of the variables are different for the various rock types and hence that discrimination is good; conversely, low $D^2$ values mean that discrimination is poor.

The discriminant function is a linear function of the weighted variables, and its calculation does not make any assumptions concerning the distribution of the data. However, it is parametric in the sense that the variables are assumed to be grouped differently according to which population they represent (Kendall and Stuart, 1968).

In contrast, the $D^2$ statistic does assume that the data are normally distributed. When discriminant analysis is used, however, as an initial scanning device in order to determine whether all the individuals present are necessary to categorise the different populations, then this distributional-dependence becomes unimportant.

Rao, 1952, gives a comprehensive discussion on discrimination in general and on the use of the $D^2$ statistic.
SECTION III

BIOGEOCHEMICAL STUDY
A. INTRODUCTION

The suggestion that analysis of plant material might be an effective method of prospecting was first made by V.M. Goldschmidt in the early 1930's when he observed that the humus of forest soils was enriched in many of the trace elements. From this he deduced that the same elements must be correspondingly enriched in the plants from which the humus was derived.

This method is now known as biogeochemical exploration. It was first used in the Soviet Union when Tkalich, 1938, showed that orebodies at the Unvashinsk arsenopyrite deposits of Eastern Siberia could be delineated by the iron content of the local vegetation. Almost simultaneously, Brundin, 1939, found that ash from plants growing over soils in Sweden containing large proportions of vanadium contained correspondingly high levels of this element.

Biogeochemical methods were actively developed during World War II by various Scandinavian workers (Vogt, 1939, 1942b; Vogt and Braadlie, 1942; Vogt and Bugge, 1943). Rankama, 1940, however, was the first to discover that the deep root systems of some plants could be used to indicate anomalous metal concentrations under a considerable depth of overburden when he used plants to obtain positive indication of nickel mineralization through ten feet of glacial drift.

Since the pioneering work of Tkalich, by far the most extensive use of biogeochemistry has been in the Soviet Union. The Russians claim many successes in mineral exploration using this method (Malyuga, 1964); in fact, a biogeochemist is included on all major mineral exploration expeditions in the U.S.S.R.

In 1945, Warren and his co-workers in Canada undertook a research programme on the metal content of vegetation, and since then have carried out very extensive biogeochemical studies (Warren and Howatson, 1947; Warren and Delavault, 1948, 1950, 1952, 1955; Warren, Delavault and Irish, 1951; Warren, Delavault and Cross, 1959; Warren, 1962).

More recently, the use of pathfinders as a guide to
mineralization has also been investigated by the Canadian school. These are elements occurring in trace amounts together with major deposits of other elements, and they may have greater mobility than the ore-metals themselves; hence prospecting for pathfinders may be more lucrative than prospecting for the ore-metal itself. Warren, Delavault and Barakso, 1964, 1968, have reported that the Douglas Fir in Canada contains arsenic at a higher concentration than is found in associated soils or in other plant species. Warren and Delavault, 1965, also reported the usefulness of molybdenum concentrations in trees for delineating copper anomalies.

The biogeochemical method of exploration has been used with success in other parts of the world.

Carlisle and Cleveland, 1958, working on molybdenum deposits in California, reported that plants contained higher concentrations of this element than the soils in which they were growing; they concluded that plants were more sensitive prospecting tools than soils in this instance. Keith, 1968, successfully used the metal content in vegetation to detect lead and zinc mineralization under an overburden of loess in the Upper Mississippi Valley area where no soil anomalies were present. More recently, Chaffee and Hessin, 1970, working in Southern Arizona, have again demonstrated the usefulness of plants for detecting mineralization in areas overlain by thick postmineralization alluvium; their work showed that copper and molybdenum levels in plant ash were more useful in delineating a "porphyry" copper-molybdenum deposit at depth than soil analyses.

Webb and Millman, 1951, in their studies on the Nigerian lead-zinc belt, found that the heavy metal content in the twigs of savannah trees could assist in the location of buried ore-deposits.

Very recent survey work by Cole, 1970, showed that in the humid tropical rain-forest environment on Bougainville Island, the copper levels in plants could be useful for detecting copper mineralization, particularly where bedrock was masked by transported cover.
In New Zealand, the first biogeochemical study was carried out by Brooks and Lyon, 1966. This, together with subsequent work by these authors (Lyon and Brooks, 1969), showed that molybdenum concentrations in the leaf ash of Olearia ranii could be satisfactorily used for prospecting for this element in the soil. Timperley, Brooks and Peterson, 1970, have also shown that in the Nelson area of New Zealand, nickel concentrations in the leaf ash of the Nothofagus species can be used to predict anomalous nickel levels in the substrate.

Australia has seen only a limited use of biogeochemical exploration techniques. Nicholls et al., 1965, showed that in the Dugald River area, biogeochemical prospecting was an effective tool for the detection of zinc mineralization. Cole, Provan and Tooms, 1968, used this method in the Bulman-Wamuma Springs area, Northern Territory, with varying results. To the author's knowledge, however, the systematic application of biogeochemistry to determine the presence of nickel mineralization in an area consisting predominantly of Eucalyptus woodland has not been reported.

Success has been achieved using plant analytical methods in mineral exploration for such elements as cobalt, lead, lithium, molybdenum, nickel and zinc. Unfortunately, some results have not been encouraging. Beryllium and boron, for instance, have not been found to be particularly suited to this technique (Shazley et al., 1970). Difficulty has also been experienced with copper, particularly in arid regions (Lovering, Huff and Almond, 1959; Huff, 1969).

In the area of study, nickel sulphide orebodies occur at the contact of ultrabasic and basic rocks. The main difficulty confronting the use of any geochemical technique in the search for nickel mineralization is that of distinguishing false anomalies over ultrabasic rocks from true anomalies over sulphide orebodies. However it has been established in this area that anomalous concentrations of copper are associated with such ore-deposits, whereas the copper content in non-mineralized rocks is substantially lower. Hence the possibility of having found a nickel orebody using geochemical techniques...
can only be assumed when anomalous copper values are obtained in positions corresponding to anomalous nickel values.

If biogeochemistry is to prove its worth in this area, it will thus have to be a good technique for determining anomalous concentrations of both nickel and copper in the substrate. This seemed worth investigating, especially in view of the possibility of extending its use to areas of alluvium in the general vicinity of the study area, where soil sampling techniques have not proved to be successful.
B. ORIENTATION SURVEY ON GRID SB

The concurrent sampling of soils and vegetation was carried out during January, 1971. Sampling sites were located at 100 ft. intervals, from 70E to 85E, along lines 342S, 344S, 346S, 348S and 350S (Fig. 1-2); adjacent lines were 200 ft. apart.

An initial ground survey of this area showed that *Eremophila dempsteri*, *E. oppositifolia* and *Eucalyptus lesueurii* were the most widely distributed species. Hence, as well as a soil sample, leaves and twigs of the above *Eremophila* species, and bark and wood samples of *E. lesueurii* were collected whenever they occurred at the sampling stations; sampling techniques have been described in Section II-A.

None of these species occurred at all of the sampling stations. In fact, *E. dempsteri*, *E. oppositifolia* and *E. lesueurii* occurred at 33%, 48% and 83% of the sampling sites respectively. It was thus important to determine whether more than one species could be used collectively in order to achieve greater sample coverage. With this in mind, the appropriate organs of *Eremophila iowantha*, *E. pachyphyllo*, *Eucalyptus longicornis* and *E. torquata* were also sampled if they occurred at the sampling stations. With the exception of *E. torquata*, these species occurred in reasonable quantities.

All samples were prepared using the methods described in Section II-C, and analysed by atomic absorption spectrophotometry. Although cobalt concentrations were determined, this element occurred at such low concentrations (130 p.p.m. in soil samples and 30 p.p.m. in plant ash) that errors due to scattering were considered to be highly significant (Gidley, 1964; Billings, 1965; Koirtyoham and Pickett, 1966); hence no cobalt results are presented.

(1) **Soils**

Soils are formed by the disintegration and subsequent decomposition of rock material in situ due to the various chemical, physical and biological processes collectively known as **weathering**. The product of the decay is a mixture of resistant primary materials as well as several new secondary minerals of very fine particle size (< 0.02m.m.) such as clay minerals, hydrous oxides
of iron and aluminium, oxy salts and carbonates. Hence the elemental content of soils could be expected to reflect the underlying geology.

On a world-wide basis, however, this is not usually the case, because environmental factors such as climate, relief and the time scale interval involved, exercise a very strong influence on metal dispersion.

As soils mature, upward and downward movement of materials in solution and suspension results in the various soil components being differentiated into layers, or horizons. This process imposes new chemical patterns unrelated to the parent material. Further complications are created by factors such as leaching by rain water, erosion, and uptake of mineral matter by plants, which tend to remove elements from the soil. New material may also be brought in from the outside due to deposition from groundwater solutions, and additions of metal from decaying organic matter.

In an area such as that studied at Spargoville where the soils are skeletal and locally derived, the annual rainfall is low, the topography does not vary significantly, and where the vegetation cover is not very dense, it would be expected that soils would be representative of the underlying geology.

Because the usefulness of biogeochemistry was to be gauged by comparison with the soil sampling technique, the aim of this subsection is to determine whether the trace elemental values in soils from the orientation area can accurately reflect the underlying geological structure. This involved determining which soil fraction would most accurately depict changes in geology, as well as a comparison of the distribution of the metals determined with the geology.

(a) Choice of soil fraction:

Two soil fractions were considered: these were the -80 mesh and the -10+26 mesh fractions.

At each sampling site along lines 344S and 348S soils were sieved to give the two required aggregates. The total
nickel and copper content was determined in both fractions.

The results are included in Table III-1 and shown as profiles in Fig. III-1.

Visual inspection of the profiles shows that the nickel and copper contents in both fractions accurately depicts the geology. However, elemental values in the -10+26 mesh soil fraction give much better anomaly contrast.

These findings indicate that as a result of the low annual rainfall, chemical weathering and leaching have been restricted. The soils have not been differentiated into horizons, and consequently there has been little breakdown of the coarser-grained primary materials into the various secondary mineral types.

Relative to the -10+26 mesh soil fraction, the -80 mesh fraction contains a higher percentage of copper than nickel. This implies that nickel occurs mainly in the high proportion of the relatively fresh undifferentiated parent material in the soil, whereas copper occurs to a larger extent in the proportion of secondary minerals present.

On the basis of these results, it was decided to do the remaining soil analyses on the -10+26 mesh fraction.

(b) Total concentrations of the elements determined in the soils:

The results are shown in Table III-1, and can be visually compared to the lithology in Fig. III-2.

Chromium values are possible indicative of ultrabasic rocks. On line 346S, the major peak is downslope from the gossan; this probably reflects the mobility of the chromate ion under mildly alkaline conditions.

The term total chromium used in this instance is not strictly correct because only the free chromium (Cr³⁺) and the chromate (CrO₄²⁻) ions are extractable into hot concentrated hydrofluoric-nitric acids; extraction of the chromite (CrO₂⁷⁻) ions requires more drastic measures. However, for all practical purposes, the free chromium and chromate ion content is considered to be the total content.
**TABLE III-1**

Mean concentrations for the elements determined in the various soil fractions (Grid 5E).

<table>
<thead>
<tr>
<th>Data Sets</th>
<th>No. of Samples</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80 mesh fraction</td>
<td>32</td>
<td>492.4</td>
<td>82.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10+26 mesh fraction</td>
<td>77</td>
<td>1290.0</td>
<td>165.9</td>
<td>4311.3</td>
<td>1057.0</td>
<td>325.2</td>
</tr>
<tr>
<td>cold HCl extraction</td>
<td>77</td>
<td>105.7</td>
<td>29.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% in -80 mesh fraction c.f. -10+26 mesh fraction</td>
<td>38.2</td>
<td>49.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% extractable from the -10+26 mesh fraction</td>
<td>8.2</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure III-1

Total nickel and copper contents in the -80 mesh and the -10 + 26 mesh soil fractions (Grid 5B).

A Total copper content
B Total nickel content
C Lithology

-80 mesh soil fractions
-10 + 26 mesh soil fractions

Amphibolite
Ultrabasic
Gossan
Surface laterite
Distances along traverses
Figure III-2

The total and readily-available concentrations of the elements

determined in the \(-10 + 26\) mesh soil fractions

compared to the lithology (Grid 5B)

A  Total chromium content
B  Total copper content
C  Readily-available copper content
D  Total manganese content
E  Total nickel content
F  Readily-available nickel content
G  Total zinc content
H  Lithology

Amphibolite
Ultrabasic
Gossan
Surface laterite
Copper values show very distinct peaks over areas of mineralization at ultrabasic rock contacts, with peak positions corresponding to positions of gossans. Copper values, though, cannot be used to delineate the various rock types.

In general, manganese values are higher over basic amphibolites than over ultrabasics.

The nickel content in the soils give plateaus of high, erratic values over ultrabasic rocks, but do not specify mineralization.

Although peaks for the zinc concentrations generally occur over ultrabasics, zinc values cannot be related to geology.

The presence of surface laterite does not seem to have any effect on the metal concentrations in the soil.

In conclusion, it can be said that the nickel, and possibly also the chromium content of soils in the study area, can be used to delineate ultrabasic rocks, whereas mineralization can only be assumed to be present if high copper values in the soil occur at the same places as anomalous nickel values. The zinc peaks in all probability denote the presence of sedimentary shales; as anomalous zinc and nickel values usually occur together, this is evidence of igneous ultrabasic rocks having intruded into sediments in this area.

(c) The readily-available concentrations of the elements determined in the soils:

Soil solutions were prepared as described in Section II-C, and analysed for nickel and copper.

The mean concentrations are shown in Table III-1, and Fig. III-2 depicts the results graphically.

As with the total nickel content in the soils, the values for the readily-available nickel show broad peaks over the ultrabasics. However, the range of values is much less than for the total nickel soil concentrations.

The values for the readily-available copper show peaks in exactly the same positions as the peaks obtained on analysing soils for the total copper content. Even though the range of readily-available copper values is much less, these peaks are
more pronounced than peaks obtained using total copper values.

The most significant finding to emerge from these results is that there is a source of readily-available copper in the vicinity of the gossans. This, of course, means that the gossans are not very weathered.

The mean content of the readily-available nickel as a function of the total nickel content in the soils was only 8.2%. This agrees with the premise made earlier that this element is present mainly in the silicate material present in the soil.

In contrast, the percentage of the readily-available copper was considerably higher (17.5%). This is further evidence that copper is associated with the secondary metalliferous minerals, most probably the hydrated iron oxides, to a greater degree than nickel. As the extent of weathering does not seem to be very advanced in this area, and as the soil fraction collected did not contain a significant proportion of fine particles, it seems probable that the iron oxides may occur associated with the coarser-grained silicate material.

(a) Statistical analysis:

Cumulative frequency diagrams were plotted on logarithmic probability paper for the total content of each element determined in the -10+26 mesh soil fractions (Fig. III-3).

These graphs indicate that there are at least two overlapping populations for each of the elements. Each population seems to have a distribution approximating more closely to log-normality than to normality, because straight lines can be drawn through most of the points in each population.

The copper data shows two distinct populations, with the point of intersection occurring at about 250 p.p.m. This change of slope indicates that values greater than 250 p.p.m. could be caused by mineralization, whereas lower values are due to non-mineralized areas.

Similarly, the manganese data shows a point of inflection at 1080 p.p.m.; values greater than this occur only on basic rock types whilst lower values occur randomly.
Figure III-3

Cumulative frequency diagrams for the total content of the elements determined in the -10 + 26 mesh soil fractions (Grid 5B).

A  Nickel
B  Copper
C  Chromium
D  Manganese
E  Zinc
The other elements have more than two populations, and conclusions are difficult to make. For the nickel data, however, values greater than 2,500 p.p.m. may denote mineralization.

For the use of the Pearson correlation coefficient, it is necessary to know the overall distribution of each data set rather than the distributions of the various populations within them. The overall distribution can be ascertained by comparing arithmetic and geometric means with the corresponding median values. Data which are normally distributed have the median and arithmetic means closest together, while for log-normally distributed data the median is closest to the geometric mean.

Table III-2 lists the median values, arithmetic means and geometric means for the total concentrations of the trace elements determined in the -10+26 mesh soil fractions.

Only for nickel and chromium do the overall distributions appear to be normal; those for the other elements are log-normal.

Deviations from log-normality probably occur when the element exists in several minerals all more or less equally distributed in the soil particles. In such a case, even though the element is log-normally distributed in each of the mineral constituents, the overall distribution function may be normal (Rodionov, 1965).

(2) Plants

(a) The distributions of the elements determined:

The means of the metal concentrations in the organs of the three most widely occurring species are shown in Table III-3. These results are presented on an ash-weight basis because earlier workers have found that analyses expressed on this basis rather than as the content in dry matter are generally more suitable for indicating biogeochemical anomalies (Warren, Delavault and Fortescue, 1955; Malyuga, 1964).

The salient feature of these results is the difference in trace element content that exists not only between the different species, but also between different organs of the same
### TABLE III-2

Median values, arithmetic means and geometric means for the trace elements determined in the soils (Grid 5B).

<table>
<thead>
<tr>
<th>Element</th>
<th>Arithmetic mean</th>
<th>Geometric mean</th>
<th>Median</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1540.3</td>
<td>1290.0</td>
<td>1500.0</td>
<td>normal</td>
</tr>
<tr>
<td>Cu</td>
<td>179.1</td>
<td>165.9</td>
<td>160.0</td>
<td>log-normal</td>
</tr>
<tr>
<td>Cr</td>
<td>4311.3</td>
<td>3940.0</td>
<td>4300.0</td>
<td>normal</td>
</tr>
<tr>
<td>Mn</td>
<td>1158.4</td>
<td>1057.0</td>
<td>1000.0</td>
<td>log-normal</td>
</tr>
<tr>
<td>Zn</td>
<td>389.4</td>
<td>325.2</td>
<td>350.0</td>
<td>log-normal</td>
</tr>
</tbody>
</table>
Mean concentrations for the elements determined in the ash of the three most common species (Grid 55).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LEAVES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>86.3</td>
<td>242.9</td>
<td>35.9</td>
<td>540.2</td>
<td>540.7</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1450.0</td>
<td>170.9</td>
<td>3406.6</td>
<td>1375.3</td>
<td>346.0</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>37</td>
<td>117.2</td>
<td>172.6</td>
<td>59.6</td>
<td>476.4</td>
<td>511.7</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1418.6</td>
<td>173.8</td>
<td>4872.7</td>
<td>877.4</td>
<td>357.4</td>
</tr>
<tr>
<td><strong>TWIGS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>60.7</td>
<td>189.2</td>
<td>35.3</td>
<td>639.8</td>
<td>500.1</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1450.0</td>
<td>170.9</td>
<td>3406.6</td>
<td>1375.3</td>
<td>346.0</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>36</td>
<td>78.9</td>
<td>212.2</td>
<td>81.7</td>
<td>369.3</td>
<td>476.4</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1413.8</td>
<td>173.1</td>
<td>4835.9</td>
<td>879.0</td>
<td>352.5</td>
</tr>
<tr>
<td><strong>BARK</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. leseuefii</td>
<td>64</td>
<td>146.9</td>
<td>64.2</td>
<td>175.7</td>
<td>302.6</td>
<td>59.3</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1287.4</td>
<td>167.5</td>
<td>4046.9</td>
<td>1017.6</td>
<td>325.9</td>
</tr>
<tr>
<td><strong>WOOD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. leseuefii</td>
<td>64</td>
<td>72.1</td>
<td>36.4</td>
<td>12.7</td>
<td>610.8</td>
<td>42.5</td>
</tr>
<tr>
<td>soil</td>
<td></td>
<td>1287.4</td>
<td>167.5</td>
<td>4046.9</td>
<td>1017.6</td>
<td>325.9</td>
</tr>
</tbody>
</table>
The mean metal concentrations in the soils corresponding to the plants are also presented in Table III-3, and show that the observed differences are not due to varying soil concentrations. This can be appreciated more clearly by considering the relative accumulation values (concentration in the plant tissue divided by the concentration in the soil) as tabulated in Table III-4.

(i) Leaves of the Eremophila species: When the mean trace element contents in the leaves are compared, it can be seen that the two Eremophila species are similar. Despite this general uniformity, however, the metals nickel and manganese are accumulated to a larger extent in the leaves by *E. oppositifolia*, while for copper and zinc, *E. dempsteri* shows the highest uptake. The behaviour by the leaves of both these species for chromium is virtually identical.

(ii) Twigs of the Eremophila species: Similarly, the relative accumulations of the metals do not vary markedly between the twigs of the two Eremophila species. The elements nickel, chromium and zinc show the same distributional trends between the twigs as they showed in the leaves of the *Eremophila* species. Copper, though, occurs at a higher concentration in the twig ash of *E. oppositifolia* than in *E. dempsteri*; this is in contrast to the uptake of this metal by the leaves. An analogous though opposite trend is evident for manganese where in the twigs, *E. dempsteri* contains slightly higher levels of this metal than *E. oppositifolia*, though not as high as in the leaves of the latter species.

(iii) Bark and wood of *E. lesouefii*: By comparison to the Eremophila species, the mean trace element content in *E. lesouefii* is distinctly different. The concentration of both nickel and chromium is higher in the *Eucalyptus* than in either of the *Eremophila* species, whereas the reverse is true for copper and zinc. Manganese, however, shows similar distributions between the three species.

Of importance also is the fact that with the possible exception of copper, the variations in the elemental content is more marked between the bark and wood of *E. lesouefii* than
Mean relative accumulations of the elements determined in the ash of the three most common species (Grid 5B).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEAVES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>0.060</td>
<td>1.42</td>
<td>0.011</td>
<td>0.393</td>
<td>1.56</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>37</td>
<td>0.083</td>
<td>0.993</td>
<td>0.012</td>
<td>0.543</td>
<td>1.43</td>
</tr>
<tr>
<td>TWIGS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>0.042</td>
<td>1.11</td>
<td>0.010</td>
<td>0.465</td>
<td>1.45</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>36</td>
<td>0.056</td>
<td>1.23</td>
<td>0.017</td>
<td>0.421</td>
<td>1.35</td>
</tr>
<tr>
<td>BARK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesuefii</td>
<td>64</td>
<td>0.114</td>
<td>0.383</td>
<td>0.043</td>
<td>0.297</td>
<td>0.182</td>
</tr>
<tr>
<td>WOOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesuefii</td>
<td>64</td>
<td>0.056</td>
<td>0.217</td>
<td>0.003</td>
<td>0.600</td>
<td>0.130</td>
</tr>
</tbody>
</table>
between the leaves and twigs of either of the shrubby *Eremophila* species.

The distributional trends observed are undoubtedly related to the role that these metals have in the metabolism of the above plants.

Neither nickel nor chromium are essential to plant growth (Bowen, 1966). It has however been established that high concentrations of these elements in soils can nevertheless prove toxic to plant growth (Nemec, 1954, 1957; Paribok and Alexeyeva-Popova, 1966). As all of the species sampled contain very low levels of these elements in relation to the content in the soils, this could be indicative of an exclusion mechanism operating in the plants sampled. Furthermore, the highest concentrations of nickel and chromium occur in the bark, whereas substantially lower concentrations occur in leaves and wood. This possibly implies that although the plants may assimilate these metals in proportion to their occurrence in the soil, toxic amounts are either deposited in the bark or translocated from the aerial tissues of the plant through the bark back into the soil.

The elements copper, manganese and zinc have been shown to be essential to plant growth, probably for all species (Bowen, 1966). These elements are accumulated to a much greater degree by all the species sampled than nickel or chromium. It can also be seen that the *Eremophila* species have a greater tendency to accumulate copper and zinc than *E. lesouefii* and that concentrations of these metals within the different tissues of the species do not vary substantially. This trend is not evident with manganese; in this case the greatest variation in uptake is between the bark and wood of *E. lesouefii*.

Unequivocal conclusions concerning the behavior of the essential metals are difficult to make. However, it does seem that the plants in the study area do not actively exclude these elements to the same degree as nickel or chromium.

Finally, because the plants sampled in the study area seem to be tolerant towards all the elements considered, it
can be asserted that the accumulations of both the non-essential and essential elements is regulated not only by the soil concentrations, but also by the plants themselves. The relative degree of regulation by these two factors undoubtedly depends on the metal considered. For biogeochemistry to be successful, regulation by the soil must be the prime factor.

(b) Statistical analysis:

The distribution functions of the trace element content in the plants were considered by plotting cumulative frequency graphs on logarithmic probability paper. In all, thirty of these diagrams were drawn. Although no two plots were the same, there were certain features common to all of them, and these can be readily seen in the typical cumulative frequency diagrams shown in Fig. III-4.

The distributions of the metals show that in all cases there are at least two overlapping populations. Furthermore, the number of populations for each element in the plants bears a relationship to the number of populations observed for the same element in the soil. For example, copper exhibits two overlapping populations in both soils and in plants.

It is difficult to make a decision concerning the type of distribution of the individual populations in each data set, because the points comprising each population do not follow straight lines very closely. This may be because relatively few samples were used. However, there are no distinct trends towards curvature, so in all probability the distributions of the various populations in plants approach log-normality more closely than they approach normality.

Table III-5 lists the median values, arithmetic means and geometric means for the five elements determined in the ashed organs of *Eremophila dempsteri*, *E. oppositifolia* and *Eucalyptus leucoxefii*.

Examination of these data indicate that for most elements in each species, the geometric means approximate most closely to the medians, and hence distributions appear to be log-normal. Four exceptions can be noted. These are for copper in the leaves.
Figure III-4

Typical cumulative frequency diagrams for the elements determined in plants (Grid 5B).

A. Nickel in the leaves of *E. oppositifolia*
B. Nickel in the bark of *E. lesouefii*
C. Nickel in the wood of *E. lesouefii*
D. Copper in the leaves of *E. oppositifolia*
E. Copper in the bark of *E. lesouefii*
F. Copper in the wood of *E. lesouefii*
<table>
<thead>
<tr>
<th>Species</th>
<th>Samples</th>
<th>Element</th>
<th>Arithmetic mean</th>
<th>Geometric mean</th>
<th>Median</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. dempsteri</td>
<td>leaves</td>
<td>Ni</td>
<td>92.5</td>
<td>86.3</td>
<td>82.5</td>
<td>log-normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>254.7</td>
<td>242.9</td>
<td>250.0</td>
<td>log-normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>598.3</td>
<td>540.7</td>
<td>480.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>44.8</td>
<td>35.9</td>
<td>35.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>601.0</td>
<td>540.2</td>
<td>510.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>twigs</td>
<td>Ni</td>
<td>74.8</td>
<td>60.7</td>
<td>52.5</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>200.7</td>
<td>189.2</td>
<td>185.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>533.0</td>
<td>500.1</td>
<td>480.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>62.8</td>
<td>35.3</td>
<td>32.5</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>676.7</td>
<td>639.8</td>
<td>700.0</td>
<td>normal</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>leaves</td>
<td>Ni</td>
<td>125.9</td>
<td>117.2</td>
<td>115.0</td>
<td>log-normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>182.6</td>
<td>172.6</td>
<td>182.5</td>
<td>log-normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>562.0</td>
<td>511.7</td>
<td>520.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>71.2</td>
<td>59.6</td>
<td>50.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>524.6</td>
<td>476.4</td>
<td>440.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>twigs</td>
<td>Ni</td>
<td>102.4</td>
<td>78.9</td>
<td>70.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>227.8</td>
<td>212.2</td>
<td>218.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>537.6</td>
<td>476.4</td>
<td>500.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>100.1</td>
<td>81.7</td>
<td>90.0</td>
<td>normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>392.2</td>
<td>369.8</td>
<td>400.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>bark</td>
<td>Ni</td>
<td>182.1</td>
<td>146.9</td>
<td>130.0</td>
<td>log-normal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>69.3</td>
<td>64.2</td>
<td>65.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>67.0</td>
<td>59.3</td>
<td>55.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>301.8</td>
<td>175.7</td>
<td>222.5</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>340.8</td>
<td>302.6</td>
<td>300.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>wood</td>
<td>Ni</td>
<td>80.2</td>
<td>72.1</td>
<td>70.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>44.0</td>
<td>36.4</td>
<td>35.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>56.5</td>
<td>42.5</td>
<td>35.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>15.0</td>
<td>12.7</td>
<td>10.0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>1034.9</td>
<td>610.8</td>
<td>620.0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
and for manganese in the twigs of the *Eremophila* species; the differences between the arithmetic and geometric means are however small.

(3) **Soil-plant relationships for nickel and copper**

The aim of the present sub-section is to determine whether concentrations of nickel and copper in the plant tissues can be readily used to determine anomalous concentrations of these metals in the substrate. As the nickel and copper contents in the soils have been shown to reflect the presence of mineralization, the usefulness of biogeochemistry in this area must depend on a close relationship between the concentrations of these metals in the soils and in the plants. Whether in fact any significant relationships between these two systems did exist was ascertained both statistically (by the computation of correlation coefficients) and graphically.

(a) **Correlation coefficients:** Table III-8 shows the parametric Pearson Product Moment and the non-parametric Spearman Rank correlation coefficients calculated between the total concentrations of nickel and copper in the soils and in the various plant systems on an ash-weight basis. Only correlation coefficients with at least a significant level of probability are presented in this and in subsequent tables.

The leaves of the two *Eremophila* species as well as the bark and wood of *E. lesueurii* all show good correlations between the concentration of nickel in the plant and the concentration of this metal in the soil, irrespective of which statistic is used. In particular, the bark of *E. lesueurii* seems very promising.

For copper, only the *Eucalyptus* bark shows a highly significant relationship between the levels of this metal in the soil and in the plant. The correlation between the soil and the wood of this species is less, whereas for the *Eremophila* species, the correlations are not significant.

Of interest is the finding that neither nickel nor copper values in the twigs of the *Eremophila* species apparently bear
Correlation coefficients between concentrations of nickel and copper in the soils and the plant ash.

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>$\text{Ni}<em>{\text{soil}} \times \text{Ni}</em>{\text{plant}}$</th>
<th>$\text{Cu}<em>{\text{soil}} \times \text{Cu}</em>{\text{plant}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Pearson } r$</td>
<td>$\text{Spearman } r_s$</td>
</tr>
<tr>
<td>LEAVES</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>.541 S*</td>
<td>.350 S</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>37</td>
<td>.415 S</td>
<td>.283 S</td>
</tr>
<tr>
<td>TWIGS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BARK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>64</td>
<td>.621 S**</td>
<td>.605 S**</td>
</tr>
<tr>
<td>WOOD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td></td>
<td>.419 S**</td>
<td>.404 S**</td>
</tr>
</tbody>
</table>
any relationships to the concentrations of these elements in the soil.

(b) The usefulness of correlation coefficients:

This was determined by comparing the calculated correlation coefficients with the degree of overlap between the sampling sites corresponding to anomalous plant values and anomalous soil values. The procedure for calculating the degree of overlap involved the following steps:

(i) The highest 30% of the nickel and copper concentrations in the soil samples were considered to be anomalous, and the sampling stations corresponding to these anomalous values were recorded.

(ii) The highest 30% of the values for nickel and copper in the plant were considered to be anomalous, and the sampling stations corresponding to these values were recorded.

(iii) The degree of overlap between the anomalous sampling stations recorded for the soils and those recorded for the plants was determined and expressed as a percentage of the number of anomalous plant sites for the various plant systems. Perfect biogeochemical results would require 100% overlap.

The results are shown in Table III-7.

It should be noted that correlation coefficients are a measure of the relationship between the entire range of values in both the soils and the plants while the percent overlap only considers the highest values within each data set. Hence it is not surprising that the numerical values of either the Pearson or the Spearman correlation coefficients do not vary in the same manner as the values for the percent overlap.

When, however, the probability levels associated with the correlation coefficients are considered, it is obvious that this type of statistic is useful as an initial scanning device. The obviously poor-soil-plant relationships have non-significant correlation coefficients, while the potentially useful relationships, with the exception of copper in the leaves of *E. oppositifolia* - copper in the soils, have correlation coefficients
The comparison of correlation coefficients with the degree of overlap between anomalous nickel and copper concentrations in the soil and in the different ashed plant tissues (Grid 5B).

<table>
<thead>
<tr>
<th>Soil Variable</th>
<th>Plant Variable</th>
<th>Overlap</th>
<th>Correlation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pearson r</td>
</tr>
<tr>
<td>E. dempsteri leaves (30)</td>
<td>Ni</td>
<td>Ni</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>33.3</td>
</tr>
<tr>
<td>E. oppositifolia leaves (37)</td>
<td>Ni</td>
<td>Ni</td>
<td>42.7</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>50.0</td>
</tr>
<tr>
<td>E. dempsteri twigs (30)</td>
<td>Ni</td>
<td>Ni</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>33.3</td>
</tr>
<tr>
<td>E. oppositifolia twigs (36)</td>
<td>Ni</td>
<td>Ni</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>36.4</td>
</tr>
<tr>
<td>E. lesouefii bark (64)</td>
<td>Ni</td>
<td>Ni</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>76.5</td>
</tr>
<tr>
<td>E. lesouefii wood (64)</td>
<td>Ni</td>
<td>Ni</td>
<td>40.9</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Cu</td>
<td>49.1</td>
</tr>
</tbody>
</table>

Figures in parenthesis denote the number of samples.
associated with at least significant levels of probability.

There seems to be little to choose between the use of the Pearson or Spearman correlation coefficients. In the cases where there are obviously poor soil-plant relationships, as exemplified by the twigs of both the *Bremophila* species, both types of correlation coefficients give similar results. Where the relationship between soils and plants is extremely high, the same conclusions can similarly be arrived at. This can be seen when the nickel and copper concentrations in the bark of *E. lesouefii* are compared with the contents of these metals in the soil. When it is remembered that nickel in the soil is normally and not log-normally distributed, it furthermore appears that when a very good soil-plant relationship does occur, the use of the Pearson statistic is not very dependent on the distribution functions of the data sets.

In the cases where the existences of soil-plant relationships are less obvious, distribution functions become more important for the use of the Pearson *r*. Thus in the relationship of nickel in the soil with nickel in the leaves of *E. demeteri* where the percent overlap between anomalous values of the two variables is 44.4%, the Spearman correlation coefficient is probably more reliable than the Pearson statistic.

The reason why copper in the wood of *E. lesouefii* only shows a good relationship with this element in the soil on the non-parametric basis is not known. However, in view of the value obtained for the percent overlap, it seems that the Spearman *r* is a truer indication than the Pearson *r*.

In summary, the following points can be emphasized:

(i) In the cases where there is a very distinct relationship, or a very distinct lack of relationship between the variable in the soil and in the plant, either parametric or non-parametric correlation coefficients can be used.

(ii) Where the presence of a relationship is less obvious the non-parametric statistic is probably the most reliable.

(iii) Correlation coefficients are useful as an initial screening device for relatively small data sets.
It is likely that a few individual samples which deviate from the overall trend, as for example copper soil values occurring over gossans, may be swamped out by the mass of data if large numbers of samples are used.

(c) The use of several plant species collectively:

It can be seen from Table III-7 that the bark of *E. lesueufii* shows the greatest potential for the prediction of nickel and copper concentrations in the soil. In order to increase the sample coverage, and also to enhance the use of plant analysis, it was worth investigating whether the barks of other *Eucalyptus* species could be used to the same effect. This was achieved by calculating values of Student's "t" on the geometric means and standard deviations for the relative accumulations of nickel and copper by the barks of *Eucalyptus lesueufii*, *E. longicornis* and *E. terquata*.

These values are given in Table III-8 together with the theoretical "t" - value at the 95% confidence level for the appropriate degrees of freedom (Fisher and Yates, 1957).

Examination of this table shows that at the 95% confidence level, there is in fact no significant difference in the behaviour of the barks of the three *Eucalyptus* species towards nickel and copper in the soil. Hence if for instance *E. lesueufii* does not occur at a particular sampling station, the bark of one of the other *Eucalyptus* trees can equally well be used.

(d) Discussion:

Graphs comparing the nickel and copper concentrations in the ash of the barks of the three *Eucalyptus* species to the total content of these elements in the soil and also to the lithology, are shown in Fig. III-5 and Fig. III-6.

(i) Nickel: Very distinct plant peaks are obtained directly over the ultrabasic contacts. Whereas the soil peaks are in effect broad plateaus occurring over ultrabasics, the plant peaks for the *Eucalyptus* barks are sharp and very distinct. Furthermore, the contrast of nickel values in the barks is high (60-600 p.p.m.), although not quite as high as in the soils.
**TABLE III-3**

Values of Student’s "t" for the significance of difference between the mean relative accumulations of nickel and copper by the barks of the three *Eucalyptus* species (Grid 5B).

<table>
<thead>
<tr>
<th></th>
<th>E. lesouefii : E. longicornis</th>
<th>E. lesouefii : E. torquata</th>
<th>E. longicornis : E. torquata</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NICKEL</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>log means</td>
<td>1.057</td>
<td>2.946</td>
<td>1.057</td>
</tr>
<tr>
<td>log stand. devs.</td>
<td>0.246</td>
<td>0.227</td>
<td>0.246</td>
</tr>
<tr>
<td>no. of samples</td>
<td>64</td>
<td>14</td>
<td>64</td>
</tr>
<tr>
<td>&quot;t&quot; calc</td>
<td>1.551</td>
<td></td>
<td>1.442</td>
</tr>
<tr>
<td>&quot;t&quot; 0.95</td>
<td>2.000</td>
<td></td>
<td>2.000</td>
</tr>
<tr>
<td><strong>COPPER</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>log means</td>
<td>1.584</td>
<td>1.551</td>
<td>1.584</td>
</tr>
<tr>
<td>log stand. devs.</td>
<td>0.160</td>
<td>0.244</td>
<td>0.160</td>
</tr>
<tr>
<td>no. of samples</td>
<td>64</td>
<td>14</td>
<td>64</td>
</tr>
<tr>
<td>&quot;t&quot; calc</td>
<td>0.621</td>
<td></td>
<td>0.479</td>
</tr>
<tr>
<td>&quot;t&quot; 0.95</td>
<td>2.000</td>
<td></td>
<td>2.000</td>
</tr>
</tbody>
</table>
Nickel concentrations in the barks of the three Eucalyptus species compared with the total nickel concentrations in the soils and with the lithology (Grid 5B).

A Nickel concentrations in the barks
- E. lesouefii
- E. longicornis
- E. torquata

B Nickel concentrations in the soils

C Lithology
- Amphibolite
- Ultrabasic
- Gossan
- Surface laterite
Copper concentrations in the barks of the three *Eucalyptus* species compared with the total copper concentrations in the soils and with the lithology (Grid 5B).

A Copper concentrations in the barks
- E. lesouefii
- E. longicornis
- E. torquata

B Copper concentrations in the soils

C Lithology
- Amphibolite
- Ultrabasic
- Gossan
- Surface laterite
(300-3700 p.p.m.)

(ii) Copper: The relationship between the barks and lithology for this metal is not as convincing as for nickel; peaks occur randomly on all types of rocks. It is interesting to note, though, that peaks for copper concentrations in the barks do occur in the vicinity of gossan outcrops; these peaks, however, are only slightly more distinct than other peaks.

Hence to conclude, the barks of the three *Eucalyptus* species sampled are the most useful of all the plant tissues for predicting anomalous levels of nickel and copper in the substrate. Whereas the nickel concentrations in the barks can be used with confidence for delineating ultrabasic contacts, the relationship between anomalous copper values in the bark of this tree with anomalous copper soil values is less clear-cut.

These results are not altogether unexpected. It has previously been asserted that the accumulation of nickel and copper must be regulated to some degree by the plants themselves.

In the cases where significant soil plant relationships are observed, the accumulation of the element by plants must be predominantly regulated by levels of the element in the soil. This seems to be especially the case for nickel, which, as previously noted, is non-essential to plant growth, and hence its accumulation by vegetation is expected to be mainly controlled by the plants themselves. This would result in poorer soil-plant relationships, which in fact is observed.
C. SOME FACTORS AFFECTING BIOGEOCHEMICAL PROSPECTING

If the element content of a sample of plant material is to be useful in prospecting, it should bear a fairly simple relationship to the metal content of the supporting medium. That this is not always the case in the study area has already been demonstrated.

Some comments on the effect of essentiality and non-essentiality of elements have previously been made, and the aim of the present sub-section is to briefly discuss other factors which may affect the usefulness of plants for prospecting.

(1) The choice of a useful plant species:

The major initial requirement in a biogeochemical orientation survey is the sampling of species which are well distributed and which can be easily sampled. Furthermore, the species chosen must have a reasonably deep root system; this is of particular importance in areas overlain by transported material.

Even though a higher average trace content in plant organs usually increases the reliability of those figures indicating mineralization (Warren, Delavault and Fortescue, 1955), this does not necessarily mean that the closest soil-plant relationship is found in the plant that is most highly enriched in a given element. Similarly, the plant that shows the greatest range of values for a given element is not always the most suitable for biogeochemical prospecting.

These facts can be readily appreciated from an examination of Table III-9, which shows the means and the ranges of values for nickel and copper concentrations in the ash of the various plant systems.

The closest correlation between nickel and copper in plants and in the substrate has been shown to be given by the bark of *E. lesouefii*. The nickel concentrations in the bark of this species show both a higher mean value and a greater variation than in the other plant systems. In contrast, however, the copper values are lower and have far less variation than concen-
TABLE III-9

Means and ranges of values for nickel and copper concentrations in the ash of the different plant systems (Grid 5B).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean range</td>
<td>Mean range</td>
</tr>
<tr>
<td>LEAVES</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>86.3  40.0-180.0</td>
<td>242.9  120.0-415.0</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>37</td>
<td>117.2 70.0-300.0</td>
<td>172.6  80.0-300.0</td>
</tr>
<tr>
<td>TWIGS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>60.7  30.0-380.0</td>
<td>189.2  110.0-490.0</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>36</td>
<td>78.9  20.0-220.0</td>
<td>212.2  95.0-400.0</td>
</tr>
<tr>
<td>BARK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>64</td>
<td>146.9 60.0-600.0</td>
<td>64.2  25.0-125.0</td>
</tr>
<tr>
<td>WOOD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>64</td>
<td>72.1  35.0-260.0</td>
<td>36.4  15.0-230.0</td>
</tr>
</tbody>
</table>
trations of this element in the other plant systems.

(2) Variation between plant parts

As a result of metabolic processes, the element content of different organs of the same plant may be widely divergent.

Differences in the absorption of nickel and copper by the organs sampled from the two Eremophila species and from *E. leucosiphon* are revealed in Fig. III-7. Lines drawn on these graphs are the visual lines of best fit. The author considers that in the absence of a mathematical approach, such as a least squares fit, the human eye is generally the best judge of two-dimensional trends.

The increase in the nickel content in the leaves of the *Eremophila* species is accompanied by an increase in the twigs, but only to a certain limit, characteristic of each species. Similarly in *E. leucosiphon*, the wood does not accumulate this metal to the same extent as the bark.

For copper, the same trends are noticeable, except that there is a sharp decline in the concentrations of this metal in the woody tissues of all the species above a certain value.

The existence of a limit of absorption for nickel and copper by the woody tissues of the plants sampled suggests that these older organs are not as metabolically active as the leaves or bark of the *Eremophila* species or *Eucalyptus* trees respectively. An alternative, or perhaps an additional reason, is that excess amounts of both nickel and copper absorbed through the root system are deposited in the leaves and in the bark. Whatever the reason for the observed limits of absorption, it seems clear that twigs from the *Eremophila* shrubs or wood from *Eucalyptus* trees should not be sampled.

(3) The availability to plants of nickel and copper in the substrate.

The mere presence of nutrients in the soil does not mean that they are necessarily available to the plant. The clay content of the soil, drainage, climate and a host of other factors alter the availability of ions to the plants. Added to
The relationship of the nickel and copper contents between the various ashed plant organs (Grid 5B).

A Nickel in the leaves and twigs of *E. dempsteri*
B Nickel in the leaves and twigs of *E. oppositifolia*
C Nickel in the bark and wood of *E. lesouefii*
D Copper in the leaves and twigs of *E. dempsteri*
E Copper in the leaves and twigs of *E. oppositifolia*
F Copper in the bark and wood of *E. lesouefii*
different species of plants absorb different amounts of elements, and Ernst, 1966, has shown that the method of absorption is characteristic for a given species.

An important factor in this scheme arises because all the mineral nutrients interact and influence each other (Schutte, 1964). Certain ions may antagonise each other in the substrate and prevent the ready absorption of each other by the plant. For example, copper and manganese have been shown to exhibit a relationship where high concentrations of one element in the supporting medium reduced the concentration of the other in the plant (Muldur, 1953). Mizuno, 1968, working on serpentine soils in Japan, observed that as the copper or iron contents of the soils increased, the uptake of nickel by a number of different plants decreased.

In view of these findings it was of interest to investigate whether the total concentrations of nickel, copper, chromium, manganese and zinc had an effect on the accumulation of nickel and copper by E. dematieri, E. oppositifolia, and E. lascufii. The relationships were evaluated by computing Pearson correlation coefficients, shown in Table III-10.

With the exception of the twigs of the Bremophila species, the nickel and zinc concentrations in the soils are directly correlated to the nickel contents in the plant systems. This is not surprising as nickel and zinc are very significantly correlated in the soils (r=0.858). Furthermore, the accumulation of nickel by plants is expected to bear some relationship to its occurrence in the substrate, as this metal is nonessential to plant growth. Neither nickel nor zinc in the soils, however, seem to be particularly related to copper in any of the plant tissues. The reason for this observation is probably related to the physiological function which copper has in the metabolism of plants.

Copper in the soil and nickel in the plants are only highly correlated for the bark of E. lascufii. The reason for this is not known.

The chromium content in the soil is directly related to
TABLE III-10

Correlation coefficients between the nickel and copper concentrations in the ash of the various plant tissues and the element concentrations in the soil (Grid 5B).

<table>
<thead>
<tr>
<th>PLANT</th>
<th>SOIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Variable</td>
</tr>
<tr>
<td>LEAVES</td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>TWIGS</td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>BARK</td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>WOOD</td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
</tbody>
</table>

Note: S*, S**, S*** denote significance levels.
both the nickel and copper concentrations in all the plant systems to varying degrees, with the exceptions of the twigs of *E. dempsteri* and *E. oppositifolia*. These results are not unexpected because as previously noted, both the nickel and chromium levels in the soils can be used to delineate ultrabasics, and also, chromium peaks in the soils occur in the vicinity of the gossans corresponding to positions of the copper soil peaks. Statistically, in fact, nickel x chromium, copper x chromium, and nickel x copper in the soil all have highly significant correlation values (r=0.649, 0.548 and 0.731 respectively).

Manganese in the soil is inversely related to nickel in the leaves of *E. dempsteri*, copper in the bark of *E. lesouefii*, and to both nickel and copper in the wood of *E. lesouefii*. Neither the nickel nor the copper contents in the soils correlate significantly with manganese in the soils, so it may be possible that high concentrations of manganese in the soil prevent the absorption and/or the translocation of both nickel and copper in the plants. The correlation coefficients obtained with manganese are not very significant, so the effect is undoubtedly small.

In summary, it can be said that there seem to be no strong antagonistic effects between the nickel and copper contents in the plants and the various variables measured in the soils.

(4) **Inter-element relationships in the various plant tissues**

The relationships between the elements determined in the tissues from *E. dempsteri*, *E. oppositifolia* and *E. lesouefii* were determined by computing Pearson correlation coefficients. The correlations associated with significant or better levels of probability are presented in Table III-11.

For most of the plant systems considered, nickel, copper, chromium and zinc are all well correlated with each other. This is to be expected as these elements correlate well with each other in the soil. The reason why these elements are not well correlated in all of the plant tissues is difficult to interpret; however, it will be noted that all the cases where no significant relationships apparently exist involve copper and zinc. These
### TABLE III-11

Correlation coefficients between the element concentrations in the ash of the various plant tissues (Grid 5B).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Variable</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LEAVES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>.537 S*</td>
<td>.585 S**</td>
<td>.620 S**</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>.537 S**</td>
<td>1.00 S**</td>
<td>.465 S*</td>
<td>.518 S*</td>
<td></td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>37</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>.440 S*</td>
<td>1.00 S**</td>
<td>.348 S</td>
<td>.375 S</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>.440 S*</td>
<td>1.00 S**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TWIGS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>30</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>.406 S</td>
<td>.789 S**</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>.406 S</td>
<td>1.00 S**</td>
<td>.475 S*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>36</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>1.00 S**</td>
<td>.690 S**</td>
<td>.583 S**</td>
<td>.604 S**</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>1.00 S**</td>
<td>.375 S</td>
<td>.583 S**</td>
<td>.604 S**</td>
<td></td>
</tr>
<tr>
<td><strong>BARK</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>64</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>.602 S**</td>
<td>.635 S**</td>
<td>.379 S*</td>
<td>.721 S**</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>.602 S**</td>
<td>1.00 S**</td>
<td>.662 S**</td>
<td>.563 S**</td>
<td>.625 S**</td>
</tr>
<tr>
<td><strong>WOOD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>64</td>
<td>Ni</td>
<td>1.00 S**</td>
<td>.422 S**</td>
<td>.406 S*</td>
<td>.214 S</td>
<td>.385 S*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>.422 S**</td>
<td>1.00 S**</td>
<td>.554 S**</td>
<td>.396 S*</td>
<td>.662 S**</td>
</tr>
</tbody>
</table>
elements are believed to be universally essential to plant nutrition, so the lack of significant relationships may well have some physiological basis.

Manganese is well correlated with copper in the leaves and twigs of *E. oppositifolia*, and with both nickel and copper in the bark and wood of *E. losquerii*. This is surprising as in the soils manganese does not correlate significantly with either nickel or copper, and as an inverse relationship has previously been observed between manganese in the soils with nickel and copper in plant tissues.

(5) Conclusions
The antagonistic effects observed have only a minor influence on the uptake of nickel and copper by the plants studied. If in fact strong antagonistic factors do occur, then they must be caused by variables not measured in this work.

Some of the results observed are in contrast to those reported by other workers; for instance, an inverse relationship between copper in the soil and nickel in any of the plant tissues studied has not been observed. Most of the previous work, however, was carried out in nutrient solutions in which many diverse effects of the soil were absent. This may well be a plausible reason for any differences between the reported effects and those observed in the present study.

The importance of choosing the appropriate plant system for biogeochemical prospecting has also been demonstrated. It is apparent that the nickel and copper contents in woody tissues do not reflect anomalous values of these elements in the substrate.

Finally, the magnitude or the range of values for nickel and copper in plant tissues does not necessarily determine the usefulness of a particular plant for biogeochemical prospecting. The most useful plant species is assumed, a priori, to be the most widespread. This was in fact found to be the case for the work described in this thesis.
D. THE USEFULNESS OF BIOGEOCHEMISTRY ON GRID 5D

(1) Introduction

The sampling of soils and vegetation on this grid was carried out during the latter half of February, 1971. Sampling sites were located at 100 ft. intervals, from 57E to 66E along lines 308S, 310S, 312S, 314S and 316S (Fig. I-2); adjacent lines were approximately 200 ft. apart.

In common with Grid 5B, the three most commonly occurring species at the sampling stations on Grid 5D were *Bromophila dempsteri*, *E. oppositifolia* and *Eucalyptus lesueurii*. As well as a soil sample, the leaves and twigs of the two *Bromophila* species and the bark of *E. lesueurii* were collected whenever they occurred at the sampling stations. In addition, the bark of *Eucalyptus longicornis* and *E. torquata* were also sampled if these species occurred at the sampling stations. Sampling techniques have been described previously. All soil and vegetation samples were prepared using the methods described in Section II-C, and analysed by atomic absorption spectrophotometry for nickel and copper.

Table III-12 presents the mean values of nickel and copper in the soils and in the ash of the various plant tissues sampled.

The first feature to notice is that the nickel and copper contents in the soils of Grid 5D are less than in the soils of Grid 5B; this is particularly the case for nickel. Secondly, the differences in the mean concentrations of these two elements between the different species and between the different organs of the same species have the same trends as observed for Grid 5B. One exception can be noted. The mean nickel content in the leaves of *E. dempsteri* is higher than in the leaves of *E. oppositifolia*; the reverse was observed on Grid 5B.

With the exception of the leaves of *E. oppositifolia*, the nickel content in the vegetation from Grid 5D is higher than the content of this element in the same plant tissues from Grid 5B. This is surprising as the soil nickel content is lower on Grid 5D, but it may indicate the operation of an exclusion mechanism for nickel to a greater extent in the plants growing on Grid 5B than on Grid 5D. In contrast, however, the mean copper values in the ash
Mean values for nickel and copper concentrations in the soils and in the ash of the three most common species (Grid 5D).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Ni (P.P.M.)</th>
<th>Cu (P.P.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soils</td>
<td>52</td>
<td>614.5</td>
<td>129.0</td>
</tr>
<tr>
<td>LEAVES</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>26</td>
<td>109.8</td>
<td>267.9</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>24</td>
<td>98.6</td>
<td>139.1</td>
</tr>
<tr>
<td>TWIGS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>26</td>
<td>72.5</td>
<td>153.2</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>23</td>
<td>84.4</td>
<td>194.2</td>
</tr>
<tr>
<td>BARK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>39</td>
<td>153.2</td>
<td>62.7</td>
</tr>
</tbody>
</table>
of the plants from Grid 5 D are lower than the copper values from similar plants growing on Grid 5B, with the exception of the leaves of E. dempsteri. The differences in mean metal contents in the ashed plant tissues between the two grids are however least in the case of the bark of E. leaquredii. Hence this particular tissue may be the most suitable for biogeochemical prospecting on Grid 5D also.

It thus appears that the behaviour of the plants sampled towards nickel and copper in the substrate is different between the two grids. This can be appreciated more readily by considering Table III-13, which shows the mean relative accumulations of nickel and copper by the three species.

Exactly similar trends in the relative accumulations are found in all cases on Grid 5D as on Grid 5B. However, the relative accumulations of nickel and copper by the plants on Grid 5D are in all cases higher than for the same plants growing on Grid 5B.

In view of these findings it was of interest to ascertain whether similar biogeochemical conclusions would be obtained on Grid 5D as on Grid 5B. Both statistical (by the computation of correlation coefficients) and graphical techniques were used.

(2) Soil-plant relationships for nickel and copper

Table III-14 shows both the Pearson and Spearman correlation coefficients for the relationships of nickel and copper between plants and the associated soils as well as the degree of overlap between the sampling sites corresponding to anomalous plant values and anomalous soil values.

Similar results are obtained for Grid 5D as for Grid 5B when the degrees of overlap are compared to the correlation coefficients, i.e. Non-significant correlation coefficients on either a non-parametric or a parametric basis are obtained when the soil x plant relationships are obviously poor. Correlation coefficients associated with more significant levels of probability are obtained when the relationships between the two variables are better, although the magnitude of the correlation coefficient cannot always be related to the degree of association between plants and soils.
Mean relative accumulations of nickel and copper in the ash of the three most common species (Grid 5D).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LEAVES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>26</td>
<td>0.156</td>
<td>1.99</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>24</td>
<td>0.173</td>
<td>1.10</td>
</tr>
<tr>
<td><strong>TWIGS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. dempsteri</td>
<td>26</td>
<td>0.106</td>
<td>1.17</td>
</tr>
<tr>
<td>E. oppositifolia</td>
<td>23</td>
<td>0.145</td>
<td>1.50</td>
</tr>
<tr>
<td><strong>BARK</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. lesouefii</td>
<td>39</td>
<td>0.191</td>
<td>0.456</td>
</tr>
</tbody>
</table>
The comparison of correlation coefficients with the degree of overlap between anomalous nickel and copper concentrations in the soil and in the different ashed plant tissues (Grid 5D).

<table>
<thead>
<tr>
<th>Soil Variable</th>
<th>Plant Variable</th>
<th>% Overlap</th>
<th>Correlation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pearson r</td>
</tr>
<tr>
<td>E. dempsteri leaves (26)</td>
<td>Ni Ni</td>
<td>87.5</td>
<td>.828 S**</td>
</tr>
<tr>
<td></td>
<td>Cu Cu</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>E. oppositifolia leaves (24)</td>
<td>Ni Ni</td>
<td>42.9</td>
<td>.655 S**</td>
</tr>
<tr>
<td></td>
<td>Cu Cu</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>E. dempsteri twigs (26)</td>
<td>Ni Ni</td>
<td>36.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu Cu</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>E. oppositifolia twigs (23)</td>
<td>Ni Ni</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu Cu</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>E. lesouefii bark (39)</td>
<td>Ni Ni</td>
<td>66.7</td>
<td>.599 S**</td>
</tr>
<tr>
<td></td>
<td>Cu Cu</td>
<td>40.0</td>
<td>.402 S**</td>
</tr>
</tbody>
</table>

Figures in parenthesis denote the number of samples.
With the exceptions of the twigs of the *Eremophila* species, the nickel concentrations in all the plant organs sampled seen to bear a significant relationship to the levels of this element in the soil. Although the use of the leaves of *E. dempsteri* seem to be the most useful for predicting the occurrence of anomalous levels of nickel in the substrate, the bark of *E. lesouefii* is also very promising.

For copper, the best relationship between vegetation and soils is shown by the bark of *E. lesouefii*.

Thus it can be appreciated that the *Eucalyptus* bark is the most useful plant tissue for predicting anomalous values of both nickel and copper in the substrate. Furthermore, this species also has a wider distribution than either *E. dempsteri* or *E. oppositifolia*.

Graphs comparing the nickel and copper concentrations in the ashed barks of *E. lesouefii* to the total contents of these elements in the -10+26 soil fraction and also to the lithology are shown in Fig. III-8 and Fig. III-9. These diagrams also include nickel and copper values in the barks of *E. longicorona* and *E. torquata*, as it has previously been shown that the barks of these three *Eucalyptus* species can be used collectively to predict anomalous concentrations of the above elements in the supporting medium.

(i) **Nickel**: The magnitudes of the nickel values in the ashed barks of the *Eucalyptus* species are much lower than in the soils and the contrast for this element in these barks is also lower than in the soils (150-2500 p.p.m. in the soils; 55-500 p.p.m. in the ashed barks). Despite this, however, very distinct plant peaks are obtained in the same positions as the soil peaks along lines 308S, 312S, 314S and 316S. Very few bark samples were able to be collected on line 310S, and this is a possible reason why no meaningful conclusions can be drawn in this case.

(ii) **Copper**: The values for this element in the ashed barks of the *Eucalyptus* species give rise to peaks in the vicinity of the gossans; this is particularly evident on lines 312S and 314S. On line 314S, the copper plant peak occurs 100 ft. downslope from the position of the soil peak. In view of the fact that no displacement of plant peaks in relation to the soil peaks was
Figure III-8

Nickel concentrations in the barks of the three *Eucalyptus* species compared with the total nickel concentrations in the soils and with the lithology (Grid 5D).

A Nickel concentrations in the barks
- E. lesouefii
- E. longicornis
- E. torquata

B Copper concentrations in the soils

C Lithology

- Amphibolite
- Metasediment
- Ultrabasic
- Gossan
- Surface laterite
Copper concentrations in the barks of the three *Eucalyptus* species compared with the total copper concentrations in the soil and with the lithology (Grid 5D).

A Copper concentrations in the barks
- E. lesouefii
- E. longicornis
- E. torquata

B Copper concentrations in the soils

C Lithology

- Amphibolite
- Metasediment
- Ultrabasic
- Gossan
- Surface laterite
Distances along traverses
observed on line 308S or 312S, it seems probable that the root system of the Eucalyptus sampled at 31463 has a pronounced lateral trend as well as vertical penetration.

Inspection of Fig. III-9 also shows that only on line 308S are copper values in the plants growing on unmineralized soils larger than in the plants sampled from mineralized areas. On lines 312S and 314S, the copper values in the barks of the Eucalyptus trees occurring over areas of mineralization show quite distinct peaks.
E. Conclusions:

Similar observations concerning the usefulness of the barks of the three Eucalyptus species considered for biogeochemical prospecting can be drawn for the grids.

There seems little doubt that the Eucalyptus trees are more useful than any of the shrubby species for predicting the locations of anomalous concentrations of nickel and copper in the substrate. This conclusion is related not only to the metabolic processes of the various plants, but also to the fact that the Eucalyptus species are much more widely distributed than any other plant types in the area of study.

Using the barks of these three trees, the results for nickel are very convincing. For copper, however, the plant values show peaks over background areas as well as over gossans. If the two sets of data are used in conjunction, however, the areas of mineralization can be delineated quite accurately.

Appendix II includes photos of Eucalyptus leucophylla growing on both mineralized and unmineralized ground.
SECTION IV

GEOBOTANICAL STUDY
A. INTRODUCTION

"In mountains in which ores or other minerals are present, growing trees usually are not healthy......".

This observation by M.V. Lomonosov in 1733 probably represents the earliest written record of the effect that mineralization can have on plants (Malyuga, 1964). The visual observation of vegetation has, however, been employed since the Roman times, not only in the search for minerals, but also for underground water in arid regions. The history, present status and the use of the various geobotanical methods have been extensively reviewed by Viktorov, 1955; Cannon, 1960; Thaler, 1962; Chikishev, 1965.

As implied by the above quotation, a plant may respond to its geological environment by showing characteristic morphological variations. Chlorosis of the leaves is possibly the most widely documented effect that mineralization can have on plants. This effect has been attributed to manganese deficiency in plants (Stiles, 1958), or to high levels of chromium, cobalt, copper, manganese, nickel or zinc in the substrate which are antagonistic to iron uptake (Löhris, 1950, 1951; Hewitt, 1953; Dvigneaud, 1959). In New York State, for example, the extent of zinc-bearing dolomites covered by glacial till was delineated by chlorosis in crops growing in peats nearby. Abnormality of growth has also been used in prospecting. In Katanga, the magnitude of the copper concentration in soils can be estimated by the extent of stunting of Protea goetzeana; a creeping, sterile form of this plant develops over soils containing particularly high concentrations of copper (Dvigneaud, 1959). In New Zealand, the flowers of Lentospermum scoparium growing in soil containing 6% chromium have been observed to be a blue-red colour rather than the normal white or pale pink. (Pers. comm. R.R. Brooks).

The realization that different plant associations may exist on different geological substrates was made as early as 1841, by Karpinsky. Perhaps the most extreme effects on the vegetation by the substrate are those found on ultrabasic serpentine floras. Typical examples of this type of flora show a general shortage of species as well as of individuals, retardation of growth, and the absence of broadleaf plants (Robinson, Edgington and Byers, 1935; Rune, 1953; Sarosiek, 1964; Igoshina, 1966; Lyon et al.,
1968, 1970). There are usually a few species endemic to a particular serpentine area, such as *Mycotis morrei* and *Pinalea suteri* in the Dun Mountain area of New Zealand. The difference between vegetation growing on serpentine areas and surrounding rock types is often so great that boundaries between them are readily observed. Calcareous rocks often carry a characteristic flora also (Ellenberg, 1958; Chikishev, 1965), although this type of vegetation is not morphologically different from other plant communities. However, certain species such as the genera *Dianthus*, *Fagus*, *Bromus*, *Festuca* and *Linaria* are known to thrive on these soils.

Some soils may be so toxic that they are unable to support normal assemblages of vegetation; the existence of these open areas has been used to advantage in the past for prospecting. In some generally forested districts of Central Africa, soils containing anomalous concentrations of copper are unable to support any tree growth (Rickard, 1936). A similar phenomenon occurs over areas of high iron content near pyrite deposits in Northern Italy (Braun-Blanquet, 1932).

For several centuries it has been known that certain plants grow only over ore deposits, or even if they also grow in background areas, seem to have a preference for certain types of mineralization. These indicator plants have always been found to have very high contents of certain elements in their ash. However, plants which cannot be classified as indicators of mineralization may also accumulate some elements to a surprising degree. Brooks, 1972 gives a comprehensive table of known indicator plants.

One of the earliest indicator plants to be used in prospecting was the "Calamine violet", which grows only in the zinc-rich soils of parts of Belgium and Germany. Since then, *Gomphrena canescens*, *Polycarpacea symmodra* var. *gracilis* and *Tephrosia polyzyga* have been suggested as possible indicators of lead-zinc mineralization in the Bulman-Waimuna Springs area of Northern Australia (Cole, Provan and Toons, 1968). Perhaps the most successful of all the ore indicators has been the "copper plant", *Becium homblei*, discovered in Zambia in 1949. It is said that this plant will not grow in soils containing less than 100 p.p.m. copper, and will thrive on concentrations of over 5000 p.p.m. (Anon., 1959). Other
copper indicators include Elsholtzia haichowensis from China (Tsung-Shan, 1957), Acrocephalus robbertii and A. katangaensis from Katanga (Duvalleaud, 1958, 1959), Gypsophila patrinii which is found in the U.S.S.R. (Nesvetaylova, 1961), and Eschscholtzia mexicana from Arizona (Lovering, Huff and Almond, 1950). Nickel indicators have also been found. These include Aspleniun adulterum in Norway (Vogt, 1942a), Allysium bertolonii in Italy (Minguzzi and Vergnano, 1948), and Pulsatilla patens in the U.S.S.R. (Storozheva, 1954).

The author considers that a study of the usefulness of plants in mineral exploration is not complete without a geobotanical study. Hence this work was undertaken in conjunction with the biogeochmistry to ascertain whether:

(i) the presence of mineralization caused morphological changes in any of the species present.

(ii) any of the species present could be used as indicators of ore or as indicators of particular geological structures.

(iii) distinctive plant communities were associated with particular geological substrates.

As with the biogeochmistry, the geobotanical orientation study was carried out on Grid 5B. This work was extended to Grid 5D in order to ascertain whether there were any ecological similarities between the two grids. Plant mapping and associated geobotanical field work was carried out on both grids during late January and early February.

Samples of each of the plant species recorded were collected and categorized by the author and subsequently identified by the staff of the Department of Agriculture, Perth.
B. ORIENTATION SURVEY ON GRID 5B

(1) Morphological changes

Certain characteristics which could possibly be related to mineralization, such as dwarfism, gigantism, and potting or chlorosis of the leaves, were not noticed with any of the plants. However, the dark outer bark of specimens of Eucalyptus leucoeiii growing on mineralized ground very often covered considerably more of the trunk than for trees of this species growing on non-mineralized ground. Although this effect was not observed for all specimens of E. leucoeiii growing on gossans, it was never observed for examples of this species growing in non-mineralized soil.

(2) Plants indicative of mineralization

As stated in the introduction to the present section, a universal characteristic of indicator plants is their ability to accumulate particular elements. This accumulation is usually at least one order of magnitude greater than occurs in other plants in the same community.

In order to determine whether any plants indicative of sulphide mineralization were present, the aerial tissues of all species growing on gossans as well as the corresponding soils (-10+26 mesh fraction) were collected from these areas of outcropping mineralization using the methods described in Section II-A. All samples were analysed for nickel and copper by atomic absorption spectrophotometry.

Table IV-1 shows the arithmetic mean nickel and copper contents in soils and the ashed plant tissues from mineralized ground compared to the concentrations of these elements in the same plants sampled from background areas. For this particular subsection, the results from Grids 5B and 5D have been combined, and the average values used.

Inspection of these results shows that there were no species which accumulated nickel or copper to any marked extent. Hence it was concluded that in the two areas of study, no indicators of nickel or copper sulphide mineralization were likely to occur.
The arithmetic mean nickel and copper concentrations in the ash of vegetation growing in mineralized ground. (Background values in parenthesis).

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Samples from gossans</th>
<th>Ni (p.p.m.)</th>
<th>Cu (p.p.m.)</th>
<th>Ni (p.p.m.)</th>
<th>Cu (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SOILS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Acacia eff. colletioides</em></td>
<td>3</td>
<td>151.7(128.2)</td>
<td>73.3(71.6)</td>
<td>282.5(253.1)</td>
<td>30.0(76.4)</td>
</tr>
<tr>
<td><em>Acacia graffiana</em></td>
<td>3</td>
<td>52.5(44.0)</td>
<td>52.5(51.5)</td>
<td>47.5(41.5)</td>
<td>57.5(55.5)</td>
</tr>
<tr>
<td><em>Alyxia buxifolia</em></td>
<td>2</td>
<td>117.5(120.5)</td>
<td>113.5(109.5)</td>
<td>100.0(107.0)</td>
<td>153.5(143.0)</td>
</tr>
<tr>
<td><em>Dodonaea lobulata</em></td>
<td>4</td>
<td>151.3</td>
<td>116.3</td>
<td>102.0</td>
<td>103.0</td>
</tr>
<tr>
<td><em>Dodonaea stenozygae</em></td>
<td>2</td>
<td>95.0(105.0)</td>
<td>82.5(95.0)</td>
<td>100.0(105.0)</td>
<td>72.5(100.0)</td>
</tr>
<tr>
<td><em>Eremophila dempsteri</em></td>
<td>3</td>
<td>80.0(83.7)</td>
<td>245.0(236.0)</td>
<td>70.0(54.5)</td>
<td>170.0(133.3)</td>
</tr>
<tr>
<td><em>Eremophila ionantha</em></td>
<td>3</td>
<td>76.7(65.0)</td>
<td>63.3(61.4)</td>
<td>73.3(63.5)</td>
<td>41.7(42.0)</td>
</tr>
<tr>
<td><em>Eremophila oppositifolia</em></td>
<td>4</td>
<td>120.0(112.0)</td>
<td>222.5(171.5)</td>
<td>97.5(72.5)</td>
<td>227.5(211.8)</td>
</tr>
<tr>
<td><em>Eremophila pachyphylla</em></td>
<td>4</td>
<td>125.0(110.0)</td>
<td>270.0(200.0)</td>
<td>70.0(50.0)</td>
<td>120.0(147.2)</td>
</tr>
<tr>
<td><em>Eucalyptus lesueurii</em></td>
<td>1</td>
<td>N.A.</td>
<td>N.A.</td>
<td>200.0(150.0)</td>
<td>80.0(57.5)</td>
</tr>
<tr>
<td><em>Eucalyptus torquata</em></td>
<td>3</td>
<td>394.0(268.7)</td>
<td>102.0(128.2)</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td><em>Exocarpos aphyllus</em></td>
<td>3</td>
<td>330.3(243.5)</td>
<td>231.7(150.8)</td>
<td>153.6(104.4)</td>
<td>105.0(95.6)</td>
</tr>
<tr>
<td><em>Melaleuca sheathiana</em></td>
<td>2</td>
<td>252.5(153.5)</td>
<td>50.0(52.8)</td>
<td>52.5(72.7)</td>
<td>72.5(53.1)</td>
</tr>
<tr>
<td><em>Olearia muelleri</em></td>
<td>2</td>
<td>155.0(168.0)</td>
<td>217.5(203.0)</td>
<td>240.0(184.0)</td>
<td>175.0(131.0)</td>
</tr>
<tr>
<td><em>Santalum spicatum</em></td>
<td>1</td>
<td>70.0(73.3)</td>
<td>70.0(73.3)</td>
<td>140.0(120.0)</td>
<td>80.0(50.0)</td>
</tr>
</tbody>
</table>

| **LEAVES**               |                             |             |             |             |             |
|--------------------------|                             |             |             |             |             |
| *Eucalyptus lesueurii*   | 4                          | 203.3(143.1)| 53.3(50.8) | 112.5(68.4) | 50.0(33.5)  |
| *Eucalyptus torquata*    | 1                          | 88.0(110.6)| 52.0(55.9) | N.A.        | N.A.        |

continued ...
<table>
<thead>
<tr>
<th>Species</th>
<th>Count</th>
<th>COMPOSITE SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia colleticoides</td>
<td>1</td>
<td>166.0(132.5)</td>
</tr>
<tr>
<td>Acacia resinosulfa</td>
<td>1</td>
<td>122.0</td>
</tr>
<tr>
<td>Scaevola spinoscens</td>
<td>1</td>
<td>120.0(113.5)</td>
</tr>
</tbody>
</table>

A composite sample is one where the leaves and twigs have been ashed together.
(3) Plants indicative of a particular geological structure

The numbers of each type of vegetation present, with the exceptions of ephemerals and grasses, were counted in belt transects starting at 70E and terminating at 05E along lines 342S, 344S, 346S and 348S. This technique has been more fully described in Section II-B.

All plant species recorded have been tabulated in Appendix I. Histograms of the frequency of distribution against the distance along the belt transects were plotted for each of the species. A visual comparison of these histograms with the lithology showed that most of the species appeared to be randomly distributed, and that there were apparently no characteristic plant communities associated with either amphibolitic or ultrabasic rock types. However, a few plant types were found to grow only on particular rock types, and these are listed below:

(i) The only species found to grow only on amphibolites was Cratystylis microphylla.
(ii) Two species were found which grew only on ultrabasics. These were Cratystylis subspinoseps and Pittosporum phillyracoides.
(iii) Dodonaea lobulata occurred only in the vicinity of amphibolite-ultrabasic contacts.
(iv) Eremochila caerulea and Trymalium lodifolium grew either on ultrabasics or near amphibolite-ultrabasic contacts.

Each of these six "significant" plants is a small species. This agrees with the findings of previous workers (Brooks, 1972) who have postulated that the typical indicator is more likely to be a shrub or a herb than a tree.

Fig. IV-1 presents the histograms for the distributions of the above six plant species along the belt transects.

It is immediately apparent from an inspection of this figure that these species are very sparsely distributed. As trenching, drilling and other exploration activities had caused only minor destruction of the vegetation of Grid 5B, it seems unlikely that human interference has had any marked effect on the distributional frequencies of these species. Of these plants, only D. lobulata
Figure IV-1

Histograms showing the distributions of the most significantly distributed plant species (Grid 5B).

A  Cratystylis microphylla
B  Cratystylis subspinescens
C  Dodonaea lobulata
D  Eremophila caerulea
E  Pittosporum phillyraeoides
F  Trymalium ledifolium
G  Lithology

- - -  Amphibolite
-----  Ultrabasic
  Gossan
  Surface laterite
was found to grow on gossans (Table IV-1). Hence the elemental content in the soil may influence the occurrences of these indicator plants. However, other edaphic and ecological factors such as soil pH, the clay and water contents in the soil, the nutrient status of the soil and competition from other plants should not be discounted.

The random distribution of the Eucalyptus species is surprising as Cole, 1970, claimed that these species seldom grew in skeletal soils over near-surface bedrock. As soils were seldom more than 2 ft. thick, the wide occurrence of these trees could be attributed to less toxic levels of metals in the soils, or to a greater tolerance by these plants in the present study area to high metal concentrations in the soil.

(4) **Statistical treatment of the data**

Observations made of the vegetation cover during the field work and the subsequent visual evaluation of the plant mapping data failed to show whether particular plant communities were associated with particular geological substrates. Discriminant analysis was then applied to the data to determine whether the substrates could be identified by considering the relative abundances of the various species growing on different rock types. The harsh climate in this region has created a general sparseness of the flora, and any differences in the density of the vegetation over ultrabasics may have been very subtle. Although the graphed results did show certain trends of this nature, it was considered that a statistical, rather than a visual, approach would also serve to make interpretation of the data more objective.

Greig-Smith, 1964, has described statistical methods used in plant ecology, and has referred to the work of Rao, 1952, and Hughes and Lindley, 1955. These authors used discriminant analysis in biometric work, though not in the field of mineral exploration. Discriminant analysis is essentially a multivariate technique applied in order to characterize units into one of several groups on the basis of many measurable variables. The problem is reduced to the case of a single variable by using a linear combination of the several variables such that the differences between the various groups are maximized. The principles underlying this technique
have been more fully described in Section II-D. It involves computation of the Mahalanobis $D^2$ statistic (Mahalanobis, 1936) as well as the determination of the probability that each unit can be assigned to a particular group.

Prior to the statistical analysis, each of the units (quadrats) was sorted according to which type of substrate it was derived from. Each of the variables (plant species) for each quadrat was used separately, and only if the $D^2$ statistic and/or discrimination increased, was a particular variable used in the discriminator.

In the case where more than two multivariate populations are considered, the $D^2$ statistic is given by:

$$D^2_{pk} = \sum_{p=1}^{k} \sum_{i,j}^{\alpha_{ij}} \frac{N_p}{(x_{ir} - \bar{x}_i)(x_{jr} - \bar{x}_j)}$$

where $p$ is the number of variables
$k$ is the number of populations
$(\bar{x}_{ir}, \bar{x}_{jr})$ are the mean values of the $i$th and $j$th characters in the $r$th population.

$$\bar{x}_i = \frac{(EN_p/\bar{x}_{ir})/\bar{x}_i}{EN_p}$$

$\alpha_{ij}$ is the inverse of the common covariance matrix,

$(\alpha_{ij})_p$, (where $i,j = 1,2,\ldots,p$).

$x_r$ is the sample size from the $r$th population.

This statistic (assuming normality) can be used as chi$^2$ with $(k-1)$ degrees of freedom to test the hypothesis that the mean values are the same in all the $k$ populations for these $p$ variables. The levels of significance of the $D^2$ statistic were determined by reference to the chi$^2$ tables of Fisher and Yates, 1957.

Two types of geological structures were present in the study area. These were basic amphibolite and ultrabasic rock types. Plant mapping was carried out on 44 quadrats along lines 342S, 344S, 346S and 348S. (Section II-B). The quadrats were divided according to which substrate they were derived from as follows:

- **Group I** = Amphibolite (A) - 26 quadrats
- **Group II** = Ultrabasic (UB) - 11 quadrats
- **Group III** = Contact areas (A/UB) - 7 quadrats
Although all the variables were considered, the most commonly occurring species were considered first for practical reasons. The total number of each species recorded on Grid 5B is listed in Appendix I.

Table IV-2 summarizes the discriminatory results using various combinations of the species. The numbers used to denote the variables are identical to the numbering of the species in Appendix I.

Inspection of this table shows that the best discrimination was obtained using a linear combination of the following species:

- Acacia acuminata
- A. colleticidae
- A. erinacea
- A. graffiana
- Cratytus subspinosus
- Dendroba stenozyza
- Eremophila damasiori
- E. ijonanta
- E. pachyphylla
- Eucalyptus lesuefii
- E. salubris
- Helaleuca sheathiana
- Rhabodia sp.
- Santalum spicatum
- Scacrola spinescens
- Trumalium ledifolium

It is evident that not all the species are needed for efficient discrimination, and indeed, not many of the quadrats are misassigned when only about one-third of the 54 species are used. There is also a general, though not invariable tendency for $D^2$ values to be related to the number of correct predictions for the nature of the substrate in the three classes of quadrat.

It is interesting to note that the species used in the above discriminator with the exceptions of Eucalyptus lesuefii, E. salubris and Helaleuca sheathiana are shrubs. This, however, probably reflects the greater abundance of shrubby species than of species of trees present.
**TABLE IV-2**

Values for the $D^2$ statistic and the associated degrees of discrimination of the quadrats (Grid 5E).
(The numbers in the first column refer to the species in Appendix 1)

<table>
<thead>
<tr>
<th>Variables used</th>
<th>$D^2$</th>
<th>Discrimination (no. of correct predictions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A/UB (26 quadrats) (11 quadrats) (7 quadrats)</td>
</tr>
<tr>
<td>22</td>
<td>0.520</td>
<td>11</td>
</tr>
<tr>
<td>25</td>
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<td>35</td>
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<td>19</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>9.50</td>
<td>31</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>9.38</td>
<td>13</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>12.14</td>
<td>17</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>21.15*</td>
<td>19</td>
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<td>22, 22, 25</td>
<td>29.10**</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>29.12*</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>32.39**</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>43.37**</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>44, 35**</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>44.16**</td>
<td>22</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>43.44**</td>
<td>25</td>
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<tr>
<td>22, 22, 25</td>
<td>50.37**</td>
<td>22</td>
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<tr>
<td>22, 22, 25</td>
<td>51.77**</td>
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</tr>
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<td>22, 22, 25</td>
<td>55.00**</td>
<td>24</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>56.71**</td>
<td>24</td>
</tr>
<tr>
<td>22, 22, 25</td>
<td>67.82**</td>
<td>24</td>
</tr>
</tbody>
</table>

Continued ...
| 1,2,4,5,9,13,15,16,18,22,33,34,35,36 | 150.2*** | 24 | 9 | 5 |
| 1,4,5,9,13,15,16,18,22,25,30,33,34,35,36 | 125.0*** | 34 | 9 | 5 |
| 1,2,4,5,9,13,15,18,22,23,30,33,34,35,36 | 133.2*** | 35 | 9 | 5 |
| 1,2,4,5,9,13,15,16,18,22,30,33,34,35,36 | 39.43*** | 33 | 9 | 6 |

*P < 0.05;  **P < 0.01  ***P < 0.001

A - amphibolite; UB - ultrabasic; A/UB - amphibolite ultrabasic contact.
C. GEOBOTANICAL DATA FROM GRID 5D

(1) Introduction

Plant mapping was carried out along lines 303S, 312S, 314S and 316S starting at 57E and finishing at 68E; the total number of quadrats along these four belt transects was thus 44. Many of these quadrats were so damaged from the various exploration activities which had been carried out in the vicinity that the vegetation in them was unable to be accurately counted. In fact, accurate geobotanical data was able to be obtained from only 50% of the 44 quadrats. Appendix I lists the total number of each species recorded on Grid 5D during the plant mapping survey.

It has previously been shown that no indicator plants for nickel or copper mineralization were likely to occur on Grid 5D (Section IV-B). Furthermore, the only morphological variation found on this grid was similar to that found on Grid 5B, i.e. the outer black bark on specimens of *Eucalyptus lesueurii* growing on gossans very often grow to a greater height on the trunk than occurred for trees of this species growing in non-mineralized soil.

(2) Plants indicative of a particular geological structure

Histograms of the frequency of distribution for each of the recorded species in the quadrats were plotted and compared with the lithology. Inspection of these graphs revealed that as on Grid 5B, most of the species appeared to be randomly distributed and that apparently no characteristic plant assemblages grow on amphibolites, metasediments or ultrabasics. However, seven species were found to only occur on particular rock types, and these are listed below:

(i) *Acacia resinosipinulae* was found to grow only on amphibolites

(ii) *Melaleuca sheathiana* was only observed on metasediments.

(iii) *Acacia aff. collisticodes* apparently grew only on ultrabasics.

(iv) *Alyxia buxifolia*, *Dodonaea lobulata*, *Pittosporum*
phillyraecoides, and Trymalium ledifolium were found to grow only on ultrabasics or in the vicinity of amphibolite-ultrabasic contacts.

Fig. IV-2 presents the histograms for the distributions of these species. In order to obviate the damaged quadrats, all such areas have been omitted, and the quadrats grouped together according to lithology as one belt transect.

On inspection of these histograms, the same general conclusions can be drawn as for Grid 5B. Although some different "indicator" species occurred on Grid 5D, the plants listed above, with the exception of Melaleuca sheathiana, are shrubby species, and they all occur in small numbers.

(3) Statistical treatment of data

Although a few species growing on Grid 5D were found to apparently grow only on particular substrates, each of these species did not occur in sufficiently large numbers to be practically useful for predicting the nature of the substrate of each of the quadrats. Furthermore, no distinctive plant communities were visually evident. Discriminant analysis was then applied to the data in an attempt to identify the substrate of each individual quadrat. The use of this statistical device in the case where more than two multivariate populations are to be considered has been described in Section IV-B.

Three broad types of geological structures were present on Grid 5D. These were amphibolites, metasediments and ultrabasics. The quadrats used for the plant mapping were divided as follows:

- Group I = Amphibolite (A) - 8 quadrats
- Group II = Ultrabasic (UB) - 7 quadrats
- Group III = contact areas (A/UB) - 3 quadrats
- Group IV = Metasediment (MS) - 4 quadrats

Table IV-3 summarizes the discriminatory results using various combinations of the species. The numbers used to denote the variables are identical to the numbering of the species in Appendix I.

Inspection of this table shows that the best discrimination
Figure IV-2

Histograms showing the distributions of the most significantly distributed species (Grid 5D).

A  Acacia aff. colleticioides
B  Acacia resinostipulea
C  Alyxia buxifolia
D  Dodonaea lobulata
E  Melaleuca sheathiana
F  Pittosporum phillyraeoides
G  Trymalium ledifolium
H  Lithology

Amphibolite
Metasediment
Ultrabasic
Gossan
Surface laterite

Quadrat
1  MS(NL)  316S: 57E-58E
2  MS(NL)/MS(L)  316S: 58E-59E
3  MS(L)  308S: 57E-58E
4  MS(L)  308S: 58E-59E
5  A(L)  316S: 58E-59E
6  A(L)/A(NL)  316S: 59E-60E
7  A(NL)/UB(NL)  308S: 61E-62E
8  UB(NL)  308S: 62E-63E
9  UB(NL)  308S: 63E-64E
10  UB(NL)  314S: 62E-63E
11  UB(NL)  314S: 63E-64E
12  UB(L)  312S: 60E-61E
13  UB(L)  312S: 61E-62E
14  UB(L)  312S: 62E-63E
15  UB(L)/A(NL)  312S: 63E-64E
16  A(NL)  308S: 66E-67E
17  A(NL)  312S: 67E-68E
18  A(NL)  314S: 65E-66E
19  A(NL)  314S: 67E-68E
20  A(NL)  316S: 67E-68E

Where  A  =  Amphibolite
        MS  =  Metasediment
        UB  =  Ultrabasic
        NL  =  No Surface Laterite
        L  =  Surface Laterite
### TABLE IV-3

Values for the $D^2$ statistic and the associated degrees of discrimination of the quadrats (Grid 5D). (The numbers in the first column refer to the species in Appendix I).

<table>
<thead>
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<th>Variables used</th>
<th>$D^2$</th>
<th>Discrimination (no. of correct predictions)</th>
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<tbody>
<tr>
<td></td>
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<td>A</td>
</tr>
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<td>(6 quadrats)</td>
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<td>6</td>
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<td>208.0***</td>
<td>6</td>
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<td>7</td>
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<td>161.2***</td>
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<td>116.4***</td>
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<td>4</td>
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<td>2,4,5,11,13,15,15,22,24,25,28,30,32,36</td>
<td>519.6***</td>
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<td>2,4,5,13,15,16,22,25,27,30,32,36</td>
<td>251.7***</td>
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*P < 0.05;  **P < 0.01;  ***P < 0.001

A - amphibolite; UB - ultrabasic; A/UB - amphibolite-ultrabasic contact; HS - host sediment.
is achieved using a linear combination of the following twelve species:

*Acacia collettoides*, *A. erinacea*, *A. maffiana*, *Dodonaea stenozygma*, *Eremophila demysteri*, *E. ionantha*, *Eucalyptus leucoxenii*, *E. salmonophloia*, *E. salubris*, *Melaleuca sheathiana*, *Pittosporum phillyracoides* and *Artemisia ledifolia*.

In common with the findings from Grid 5B, it can be seen that although the degree of discrimination is generally related to the number of species used in the discriminator, by no means all the species are necessary for efficient discrimination. Furthermore, most of the species listed above are shrubs.
D. CONCLUSIONS

Only one morphological variation which could possibly be attributed to a high metal content in the substrate was observed on the study areas. Although it may have been profitable to study the morphology of flowers, the flowering season had ended when the geobotanical field work for this project was executed.

Although no indicator plants for mineralization were found, it was apparent that certain of the species grew only on particular substrates. Some of these "indicator" plants were different for the two grids. The distributions of Dodonaea lobulata, Pittosporum philyraecides and Trymalium lepidolium however, were similar for both areas; these species apparently only grew on or very near to ultrabasics. None of the above three species though, were found to be sufficiently widely distributed to be useful for predicting the geology over the whole of the study areas. In an area of similar ecology where the geology is unknown, it is possible that the presence of these indicator plants could find application if instead of trying to assign the lithology in each of the quadrats individually, the occurrences of these species are mapped. From this, a contour map showing the location of ultrabasic rock types could possibly be formulated.

Photographs of the above three species are included in Appendix II.

The application of discriminant analysis to the plant mapping data gave very good results; on Grids 5B and 5D respectively, the geology was able to be correctly predicted in 93.2% and 95.5% of the quadrats on the basis of the relative abundances of the species present. By no means all of the species were required in order to obtain definite discrimination. On Grid 5B, only 16 of the 34 variables (47.1%) were found to be necessary for the maximum discrimination achieved, whereas only 12 of the 26 variables (46.2%) were used on Grid 5D.

When the best discriminator derived for Grid 5B was tested by using the geobotanical data from Grid 5D, the $D^2$ statistic was calculated to be 209.6 (significant at the 99.9% confidence level for the number of variables used), and 86.4%
of the quadrats were correctly assigned. Similarly, when the data from Grid 5B was used to test the best discriminator computed for Grid 5D, 84.1% of the quadrats were correctly assigned, although the value of the $D^2$ statistic was only significant at the 99.0% level of confidence ($D^2 = 44.16$).

Although the best discriminators obtained were different for the two grids, the following ten species were common to both discriminators:

Acacia colleticidae, A. erinacea, A. graffiana, Dodonaea stenogyra, Eremophila dempsteri, E. ionantha, Eucalyptus lescuerii, E. salubris, Melaleuca sheathiana and Trymalium ledifolium.

When only these species were used, 86.2% of the quadrats from both Grid 5B and Grid 5D were correctly assigned and the value for the $D^2$ statistic in both cases was significant at the 99.9% confidence level ($D^2 = 45.72$ and 149.3 respectively).

It was thus concluded that effective discrimination of geology in both the areas studied was possible on the basis of the above ten variables.
SECTION V

GENERAL CONCLUSIONS
The general aim of this project was to investigate the use of vegetation for prospecting for nickel and copper in an area of sclerophyllous woodland in Western Australia. It was concerned with determining whether established biogeochemical and geobotanical techniques could be fruitfully employed under the conditions encountered at Spargoville. The author considers that this has been largely achieved. Specific problems such as sampling error and analytical error have been discussed by other workers, and thus were not dealt with in detail.

Although the generally harsh environmental conditions at Spargoville may not be duplicated in other areas of the world, the general lessons may be of use elsewhere. One is that computer techniques may enable the rapid discovery of relationships to be made, even though such relationships may not be visually evident. Another is that future work should take all chemical, physical and environmental factors into account, as all of these are intimately related.

The specific findings of this project were:

(i) Elemental values in the -10+26 mesh soil fraction gave much better anomaly contrast than values in the -80 mesh soil fraction. Furthermore, the cold hydrochloric acid-soluble nickel and copper content of the soils gave superior contrast of values compared to the total (hot HF/BrO₃ extraction) values.

(ii) Consideration of the analytical data for the plants sampled showed that different species distributed some metals in different ways between their leaves and twigs or between their bark and wood.

(iii) The barks of the three species, Eucalyptus leueuefii, E. longicoryns and E. torquata were useful for biogeochemical prospecting, particularly for nickel.

(iv) Three species were found which apparently only grew on or very near to ultrabasic rock types. These were Dodonaea lobulata, Pittosporum phillyreoides and Trymalium ledifolium.

(v) The application of discriminant analysis to plant mapping data could be used in this area to determine the nature of the substrate. The use of this statistical technique with
some biogeochemical data (Appendix III) showed that the geobotanical data gave markedly superior results.

Versatile computer programmes were developed in the course of this work for non-parametric correlation calculations and for discriminant analysis.

The results reported have indicated promising avenues for future research. In particular, the usefulness of the various Eucalyptus species should be tested on an area where the bedrock is covered by a thick layer of transported material. Aspects related to the general use of vegetation in mineral exploration, such as the application of improved multivariate statistical techniques, the use of aerial remote sensing methods, and the search for "pathfinder" elements, should also provide stimulating and profitable results.


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### APPENDIX I

#### Plant Species recorded

The following is a list of the total number of each species recorded on Grids 5B and 5D during the plant mapping survey (SECTION IV). Although ephemerals and grasses were not considered, all trees and shrubs growing on these areas have been included.

<table>
<thead>
<tr>
<th>Plant species</th>
<th>No of specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grid 5B</td>
</tr>
<tr>
<td>1. Acacia acuminata Benth.</td>
<td>38</td>
</tr>
<tr>
<td>2. A. colletioides A. Cunn.</td>
<td>35</td>
</tr>
<tr>
<td>3. A. aff. colletioides A. Cunn.</td>
<td>168</td>
</tr>
<tr>
<td>4. A. erinaceae Benth.</td>
<td>39</td>
</tr>
<tr>
<td>5. A. graffiana F. Muell.</td>
<td>9</td>
</tr>
<tr>
<td>6. A. resinosistipula W.V. Fitzg.</td>
<td>0</td>
</tr>
<tr>
<td>7. Alyxia buxifolia R. Br.</td>
<td>10</td>
</tr>
<tr>
<td>8. Cratylis microphylla (F.Muell. et Tate) S. Moore.</td>
<td>3</td>
</tr>
<tr>
<td>9. C. subspinosaece (F.Muell. et Tate) S. Moore</td>
<td>1</td>
</tr>
<tr>
<td>10. Dodonaea filifolia Hook.</td>
<td>17</td>
</tr>
<tr>
<td>11. D. lepidota F. Muell.</td>
<td>1</td>
</tr>
<tr>
<td>12. D. micronyza F. Muell.</td>
<td>4</td>
</tr>
<tr>
<td>13. D. stenosyza F. Muell.</td>
<td>112</td>
</tr>
<tr>
<td>14. Eremophila caerulea (S. Moore) Diels.</td>
<td>7</td>
</tr>
<tr>
<td>15. E. demateri F. Muell.</td>
<td>467</td>
</tr>
<tr>
<td>16. E. ioniantha Diels.</td>
<td>161</td>
</tr>
<tr>
<td>17. E. oppositifolia R.Br.</td>
<td>236</td>
</tr>
<tr>
<td>18. E. rachyphylla Diels.</td>
<td>219</td>
</tr>
<tr>
<td>19. Eremophila sp. 1 (unidentified)</td>
<td>8</td>
</tr>
<tr>
<td>20. Eremophila sp. 2 (unidentified)</td>
<td>45</td>
</tr>
<tr>
<td>21. Eucalyptus calycoquina Turcz.</td>
<td>60</td>
</tr>
<tr>
<td>22. E. lesueurii Maiden</td>
<td>2498</td>
</tr>
<tr>
<td>23. E. longicornis F. Muell.</td>
<td>68</td>
</tr>
<tr>
<td>24. E. salmonophloia F. Muell.</td>
<td>0</td>
</tr>
<tr>
<td>25. E. salubris F. Muell.</td>
<td>52</td>
</tr>
<tr>
<td>26. E. torquata Luehn.</td>
<td>3</td>
</tr>
<tr>
<td>27. Exocarpus asphyllus R.Br.</td>
<td>34</td>
</tr>
<tr>
<td>28. Grevillea sp. (unidentified)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>29.</td>
<td>Kochia pyramidata Benth.</td>
</tr>
<tr>
<td>30.</td>
<td>Melaleuca sheathiana W.V. Fitzg.</td>
</tr>
<tr>
<td>31.</td>
<td>Closaria muelleri (Sond.) Benth.</td>
</tr>
<tr>
<td>32.</td>
<td>Pittosporum phillyraoides. DC.</td>
</tr>
<tr>
<td>33.</td>
<td>Rharodia sp. (unidentified)</td>
</tr>
<tr>
<td>34.</td>
<td>Santalum spicatum (R.Dr.)DC.</td>
</tr>
<tr>
<td>35.</td>
<td>Scaevola spinoceans R.Dr.</td>
</tr>
<tr>
<td>36.</td>
<td>Trymalium ledifolium Fenzl.</td>
</tr>
<tr>
<td>37.</td>
<td>Westringia cephalantha F. Muell.</td>
</tr>
</tbody>
</table>
APPENDIX II
Illustrations of some plant species

The following plates show the general form and size of the more "interesting" and useful plant species found at Spargoville during the course of this project.

Plate A. Eucalyptus lesuefii growing on non-mineralized ground.
Plate B. Eucalyptus lesuefii growing on mineralized ground.
Plate C. Dodonaea lebulate.
Plate D. Pittosporum phillyreaecides.
Plate E. Trymalium ledifolium.
A. *Eucalyptus* lesouefii growing on non-mineralized ground
B. *Eucalyptus lesueurii* growing on mineralized ground
C. *Dodonaea lobulata*
D. Pittosporum phillyraeoides
E. Trymalium ledifolium
APPENDIX III

Discriminant analysis of some biogeochemical data from Grid 5B

1. Introduction:

The application of discriminant analysis to geobotanical data has been demonstrated previously in this thesis to be useful for establishing the nature of the bedrock upon which the plant community is growing (Section IV). This statistical technique was also applied to some biogeochemical data in order to compare the usefulness of biogeochemistry and geobotany for the same purpose.

The bark of *Eucalyptus lesueurii* was chosen for this work because it has been shown to be the most useful plant system for prospecting for nickel and copper in the study area (Section III). Samples were collected at 100 ft. intervals along lines 342S, 344S, 346S, 348S and 350S, and analysed by atomic absorption spectrophotometry for calcium, chromium, cobalt, copper, lead, magnesium, manganese, nickel and zinc.

The 63 samples were categorized according to substrate as follows:

- Group I: Amphibolite (A) - 34 sampling sites
- Group II: Ultrabasic (UB) - 29 sampling sites

In the case where only two populations are considered, the Mahalanobis $D^2$ statistic is given by:

$$D^2 = \frac{pp}{\Sigma w_{ij} (\bar{x}_{i1} - \bar{x}_{i2}) (\bar{x}_{j1} - \bar{x}_{j2})}$$

where $\bar{x}_{i1}$ and $\bar{x}_{i2}$ are the sample means for the $i$th character for the first and second samples respectively.

$(w_{ij})$ is the reciprocal of the covariance matrix, $(w_{ij})$.

$p$ is the number of variables used.

To test the hypothesis specifying no difference in mean values of the $p$ characters for the two populations, the following statistic can be used as a variance ratio with $p$ and $(n_1 + n_2 - 1 - p)$ degrees of freedom:
\[ F = \frac{n_1 + n_2 - p - 1}{(n_1 + n_2 - 2)p} \cdot \frac{n_1 \cdot n_2}{n_1 + n_2} D^2 \]

where \( n_1 \) and \( n_2 \) are the number of samples in each population.

The levels of significance of the \( F \)-statistic were determined by reference to the variance ratio tables of Fisher and Yates, 1957.

In the simplest case when \( p = 1 \), the \( D^2 \)-statistic reduces to a simple t-test.

B. Results and discussion:

Table A-1 shows the arithmetic mean values of the elements determined in the ashed bark of \( E. lesqueri \) on both substrates. With the exceptions of calcium and lead, the elemental content in the ash of plants growing on ultrabasic rock types is higher than that collected from amphibolite areas.

Table A-2 summarizes the discriminatory results using different combinations of the variables measured. The best discrimination of ultrabasic rock types was obtained by using the variables chromium, lead, magnesium and nickel; the result using only these four elements was slightly better than when all the elements were used. This demonstrates the superfluity of using too many variables. For amphibolites, equal discrimination was obtained either when all the variables were used or when only chromium, cobalt, lead, magnesium and nickel were employed.

Overall, the best discrimination was achieved using all the variables. In this case, 29 of the 34 amphibolite and 17 of the 29 ultrabasic sites were correctly assigned (73.0% discrimination). However, only a very slight degree of discrimination was lost when only chromium, cobalt, lead, magnesium and nickel were used (71.4% discrimination).

The inclusion of chromium, cobalt, magnesium and nickel in the discriminator is understandable as ultrabasic rocks are enriched in these elements compared to amphibolites. Plants should therefore reflect this difference as they would be expected to accumulate elements proportional to their concentration in the soil.
TABLE A-1

Mean (arithmetic) elemental concentrations in the ashes of *Eucalyptus leucoxene* (Grid 5B)
(The elements Cr, Co, Cu, Pb, Mn, Ni Zn are expressed as p.p.m. while Ca and Mg are expressed as percentages).

<table>
<thead>
<tr>
<th>Element</th>
<th>Nature of substrate</th>
<th>A</th>
<th>UB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3%</td>
<td>20</td>
</tr>
<tr>
<td>Calcium</td>
<td></td>
<td>12.63</td>
<td>12.53</td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>205.1</td>
<td>222.9</td>
</tr>
<tr>
<td>Cobalt</td>
<td></td>
<td>35.15</td>
<td>30.79</td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td>85.00</td>
<td>79.00</td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td>44.56</td>
<td>40.69</td>
</tr>
<tr>
<td>Magnesium</td>
<td></td>
<td>3.49</td>
<td>3.96</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td>333.5</td>
<td>352.5</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>153.5</td>
<td>208.9</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td>68.33</td>
<td>77.07</td>
</tr>
</tbody>
</table>

A = amphibolite; UB = ultrabasic
### Table A-2

Values for the $D^2$ and $F$ statistics and the associated degree of discrimination of the sampling sites (Grid 5B).

<table>
<thead>
<tr>
<th>Variables used</th>
<th>$D^2$</th>
<th>$F$</th>
<th>Discrimination (number of correct predictions)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ (34 sites)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.122</td>
<td>25.32***</td>
<td>29</td>
</tr>
<tr>
<td>Co</td>
<td>1.63</td>
<td>78.05***</td>
<td>27</td>
</tr>
<tr>
<td>Cr</td>
<td>9.36***</td>
<td>55.63***</td>
<td>23</td>
</tr>
<tr>
<td>Cu</td>
<td>2.18*</td>
<td>27.40***</td>
<td>23</td>
</tr>
<tr>
<td>Mg</td>
<td>0.769</td>
<td>51.26***</td>
<td>27</td>
</tr>
<tr>
<td>Mn</td>
<td>0.465</td>
<td>60.25***</td>
<td>27</td>
</tr>
<tr>
<td>Ni</td>
<td>3.15**</td>
<td>70.30***</td>
<td>25</td>
</tr>
<tr>
<td>Pb</td>
<td>1.22</td>
<td>61.53***</td>
<td>29</td>
</tr>
<tr>
<td>Zn</td>
<td>3.76***</td>
<td>53.08***</td>
<td>27</td>
</tr>
<tr>
<td>Ca,Co,Cr,Cu,Mg,Mn,Ni,Pb,Zn</td>
<td>16.76</td>
<td>50.18***</td>
<td>26</td>
</tr>
<tr>
<td>Cr,Ni</td>
<td>10.14</td>
<td>52.71***</td>
<td>25</td>
</tr>
<tr>
<td>Cr,Ni,Zn</td>
<td>10.62</td>
<td>61.53***</td>
<td>29</td>
</tr>
<tr>
<td>Co,Cr,Mn</td>
<td>13.29</td>
<td>39.51***</td>
<td>25</td>
</tr>
<tr>
<td>Cr,Cu,Ni</td>
<td>15.92</td>
<td>37.83***</td>
<td>27</td>
</tr>
<tr>
<td>Cr,Mg,Ni,Pb</td>
<td>16.54</td>
<td>44.58***</td>
<td>27</td>
</tr>
<tr>
<td>Co,Cr,Mg,Ni,Pb</td>
<td>15.65</td>
<td>50.89***</td>
<td>27</td>
</tr>
<tr>
<td>Cr,Mg,Mn,Ni</td>
<td>14.03</td>
<td>52.19***</td>
<td>25</td>
</tr>
<tr>
<td>Cr,Cu,Mg,Mn,Ni</td>
<td>11.15</td>
<td>41.32***</td>
<td>26</td>
</tr>
</tbody>
</table>

Continued...
<table>
<thead>
<tr>
<th>Elements</th>
<th>Quantity1</th>
<th>Quantity2</th>
<th>T-test</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca, Cr, Cu, Mg, Mn, Ni</td>
<td>14.20</td>
<td>32.94***</td>
<td>26</td>
<td>17</td>
</tr>
<tr>
<td>Cr, Cu, Mg, Mn, Ni, Zn</td>
<td>14.32</td>
<td>34.22***</td>
<td>26</td>
<td>18</td>
</tr>
</tbody>
</table>

*P < 0.05; **P < 0.01; ***P < 0.001

A - amphibolite; UB - ultrabasic
C. Conclusions:

Certain basic conclusions can be made when the above results are compared with the results from the discriminant analysis of the plant mapping data from Grid 53 (Section IV-B).

The results using the geobotanical data are markedly superior to those using the biogeochemical data (93.2% and 75.0% discrimination respectively). This implies that ecological factors are more closely related to the underlying substrate than are the nutritional requirements of the plant species in the area.

By no means all the variables are required in order to achieve definite discrimination. With either set of data, in fact, discrimination did not markedly improve when more than about one-third of the variables were used.

It is possible that the use of different biogeochemical variables would improve the resulting discrimination. However, if biogeochemical data are used in conjunction with the geobotanical data, the results would be expected to be even better than when these data sets are used individually.
APPENDIX IV

Computer Programmes

4. Introduction:

The programmes listed in Appendices III-B, III-C and III-D, although written or modified specifically for the application described in this thesis, are adaptable to other sets of data.

All the data for a particular sample, e.g. 10 metal concentrations, the percentage ash, and the site number for a plant sample, are punched onto one card with each variable occupying the same columns on each data card. With the exception of the percentage ash, the variables are punched using format F6.0. The format for the percentage ash is F6.2.

Instructions pertaining to the computer programmes are given prior to each listing.
B. Pearson product moment correlation coefficient programme:

In preparation for the computation of the correlation coefficients, a data matrix is read into disc storage. Although this matrix may contain up to 15 variables, only the first 12 are correlated. The number of samples read in is limited by the amount of disc storage available. The variables placed in the matrix may be read from one or two data decks as follows:

(1) Up to 15 variables may be read from either the plant data deck or the soil data deck.

(2) Up to 6 variables from the plant data deck and up to 5 variables from the soil data deck may be read. If less variables are used, the number of soil variables must be one less than the number of plant variables.

All the variables are transformed to base 10 logarithms and correlation coefficients and the slopes of the reduced major axes are computed and printed out for all possible combinations of two variables.

Further options allow the plant variables in the matrix from (2) above to be replaced by the plant variable divided by the corresponding soil variable (i.e. relative accumulation). In addition, all the metal concentrations in the plants may be converted from an ash weight basis to a dry weight basis. A printout of the data may also be made. Instructions for the implementation of these options, as well as for the requirements of the control cards to precede the data are given at the head of the programme listing.
PEARSON PRODUCT MOMENT CORRELATION COEFFICIENT PROGRAMME
FORTRAN IID

C CORRELATION COEFFICIENTS, GEOMETRIC MEANS, STANDARD DEVIATIONS,
C REDUCED MAJOR AXES
C
C PROGRAMME ALLOWS DATA TO BE READ FROM ONE OR TWO DATA DECKS
C PLANT DATA IS FED IN AS ASH CONCENTRATION
C ALL INPUT DATA TRANSFORMED TO BASE 10 LOGARITHMS
C SENSE SWITCH 1 ON CONVERTS DATA TO DRY WEIGHT CONCENTRATION
C SENSE SWITCH 2 ON REPLACES ODD VARIABLES WITH ODD VARIABLES
C DIVIDED BY NEXT EVEN VARIABLES
C SENSE SWITCH 3 ON PRINTS OUT INPUT DATA
C SENSE SWITCH 4 OFF, READS NEW FORMAT CARDS BUT USES PREVIOUSLY
C READ IN DATA DECK
C SENSE SWITCH 4 ON REPEATS COMPUTATIONS WITH SAME DATA DECK
C SENSE SWITCH 4 OFF READS NEXT DATA DECK
C CARDS TO PRECEDE DATA DECK ARE AS FOLLOWS
C TITLE CARD. TITLE MAY OCCUPY UP TO 79 COLUMNS
C READ FORMAT FOR FIRST DATA DECK
C READ FORMAT FOR SECOND DATA DECK, A FORMAT CARD MUST BE INSERTED
C IN THIS POSITION EVEN IF NO SECOND DATA DECK IS USED
C CARD CONTAINING VARIABLES KL, IJ, JK, IJK, K, N, IN FORMAT 615 WHERE
C KL=TOTAL NUMBER OF VARIABLES TO BE READ, KL MAX=13
C IJ=NUMBER OF VARIABLES TO BE CORRELATED, IJ MAX=12
C JK=NO. OF CORRELATION COEFFICIENTS TO BE COMPUTED, JK MAX=66
C IJK=COLUMN CONTAINING FRACTION ASH, IF NO ASH THEN IJK=1
C K=1, ALL VARIABLES ARE CHANGED TO DRY WEIGHT CONCENTRATION
C K=2, ODD VARIABLES ARE CHANGED TO DRY WEIGHT CONCENTRATION
C N=1, ONE DATA DECK TO BE READ
C N=2, TWO DATA DECKS TO BE READ
C A CARD CONTAINING A NUMERAL 9 IN COLUMN 1 MUST FOLLOW EACH
C DATA DECK
C MEANS ARE GEOMETRIC
C STANDARD DEVIATIONS IN UNITS OF LOGARITHM TO BASE TEN
C
C DIMENSION A(13), S(12), SQ(12), AV(12), GM(12), SD(12), B(12)
DIMENSION SP(66), X(66), Y(66), Z(66), R(66), RMA(66), MD(12)
DIMENSION IFOR(80), JFOR(80)
DEFINE DISK(13,1000)
10 READ 20
20 FORMAT (80H 1)
21 READ 22, IFOR
22 FORMAT (80A1)
READ 22, JFOR
23 FORMAT (615)
DO 11 I=1, 12
11 A(I)=0
IDEX=1
30 READ IFOR, M, (A(I), I=1, KL, N)
50 RECORD,IDEX)A
GO TO 30
31 IDEX=1
32 FETCH(IDEX)A
IDEX=IDEX-2
READ JFOR, M, (A(I), I=2, KL, N)
51 RECORD(IDEX)A
GO TO 32
60 GO TO (61, 31), N
61 ISAVE=IDEX
70 DO 80 I=1, IJ
80 AV(I)=0
SQ(I)=0
80 AV(I)=0
DO 90 J=1, JK
90 SP(J)=0
AN=0.0
IF(SENSE SWITCH 1)100, 120
100 PRINT 110
110 FORMAT (25H DRY WEIGHT CONCENTRATION)
GO TO 140
120 PRINT 130
130 FORMAT (21H CONCENTRATION IN ASH)
140 IF(SENSE SWITCH 2) 150, 161
150 PRINT 160
160 FORMAT (7H RATIOS)
161 PRINT 162
162 FORMAT (//)
PRINT 20

C
C START OF MAIN LOOP
C
IDEX=1
170 FETCH(IDEX)A
180 IF(IDEX-ISAVE)180, 180, 350
181 JM=IJ-1
190 DO 200 I=1, JM, K

C
C FIRST OPTION MANIPULATION FOLLOWS
C
200 A(I)=A(I)*A(IJK)
210 IF(SENSE SWITCH 2) 211, 240
211 KJ=IJ-1
220 DO 230 I=1, KJ, 2

C
C SECOND OPTION MANIPULATION FOLLOWS
C
KK=I+1
230 A(I)=A(I)/A(KK)
240 IF(SENSE SWITCH 3) 250, 280
250 PRINT 270, (A(I), I=I, KL)

C
DATA PRINTOUT FOLLOWS
270 FORMAT(13F10.4)
280 AN=AN+1, O
DO 290 I=1, IJ
290 B(I)=0.43429448*LOGF(A(I))
S(I)=S(I)+B(I)
SQ(I)=SQ(I)+B(I)*B(I)
J=0
I=0
300 I=I+1
JJ=IJ
310 J=J+1
   IF(J-JK)320, 320, 330
320 X(J)=B(I)*B(JJ)
   JJ=JJ-1
   IF(JJ-(I+1))300, 310, 310
330 DO 340 J=1, JK
340 SP(J)=SP(J)+X(J)
   GO TO 170
C END OF MAIN LOOP
C START OF MAIN CALCULATIONS
350 DO 360 I=1, IJ
   AV(I)=S(I)/AN
   GM(I)=EXPF(AV(I)/0.43429448)
360 SD(I)=SQRTRFD(SQ(I)-AN*AV(I)*AV(I))/(AN-1.0))
      J=0
      I=0
   370 I=I+1
    KE=IJ
   380 J=J+1
      IF(J-JK)390, 390, 400
390 Y(J)=AV(I)*AV(KE)
   Z(J)=(SQ(I)-AN*AV(I)**2)*(SQ(KE)-AN*AV(KE)**2)
   RMA(J)=SD(I)/SD(KE)
   KE=KE-1
      IF(KE-(I+1))370, 380, 380
400 DO 410 J=1, JK
410 R(J)=(SP(J)-AN*Y(J))/SQRTRF(Z(J))
C C C END OF CALCULATIONS
C C PRINT OUT OF RESULTS FOLLOWS
C
PRINT 420
420 FORMAT (/16H GEOMETRIC MEANS)
PRINT 430, (GM(I), I=1, IJ)
430 FORMAT (12F10.4)
PRINT 440
440 FORMAT (/12H STD. DEVS. )
PRINT 450, (SDK I), I=1, IJ
450 FORMAT (12F10.4)
PRINT 460, AN
460 FORMAT(/19H NUMBER OF SAMPLES=, F6.0/)
PRINT 470
470 FORMAT(25H CORRELATION COEFFICIENTS/)
   KL=1
   DO 480 I=1, IJ
480 MD(I)=IJ+1-1
490 PRINT 500, (MD(I), I=1, IJ)
   KC=1
   MA=1
500 FORMAT (11H COLUMN NO., 12(2X, F4.0, 4X))
   LA=IJ-2
510 NA=MA+LA
   PRINT 520, KC, (R(J), J=MA, NA)
520 FORMAT (4X, I2, 4X, 12F10.4)
   KC=KC+1
   LA=LA-1
   MA=NA+1
   IF(KC-IJ)510, 530, 530
530 GO TO (540, 580), KL
540 PRINT 550
550 FORMAT(/17H SLOPES OF R M. A./)
   KL=2
560 DO 570 J=1, JK
570 R(J)=RMA(J)
   GO TO 490
580 PAUSE
   IF(SENSE SWITCH 4)70, 10
END
C. Spearman rank correlation coefficient programme:

This programme was designed to read 8 variables, the last being the percent ash. The formats for the data cards and for the parameter card are given at the beginning of the programme. Although INA may have any value between 1 and 7, the value of JVB must be 7.

Correlation coefficients between the variables in the first and second data decks are calculated and printed out on an ash weight basis and on a dry weight basis.
SPEARMAN RANK CORRELATION COEFFICIENT PROGRAMME

FORTRAN IV

MAIN PROGRAM FOR OBTAINING RANK CORRELATIONS

DATA IS SUPPLIED IN TWO BLOCKS
  FIRST HAS CONCENTRATIONS FOR SOILS
  SECOND HAS CONCENTRATIONS FOR PLANTS

FORMAT IS F6 FOR FIRST 7 REGIONS, F6.2 FOR REGION 8 IN PLANT BLOCK
  THE LAST REGION CONTAINS THE ASH WEIGHT OF THE PLANT (PERCENT)

PARAMETERS ARE
  A - MATRIX OF POINTS
  N - NO. OF OBS.

  NVA - NO. OF REGIONS TO USE IN 1ST BLOCK
  NVB - NO. OF REGIONS TO USE IN 2ND BLOCK

OBJECT IS TO OBTAIN RANK COR. COEFF. BETWEEN ALL ITEMS IN 1ST
  BLOCK WITH ALL ITEMS IN 2ND BLOCK

SUBROUTINES REQD.. RANK, TIE, SRANK, SPBRF

DIMENSION LOC(24)
DIMENSION TITLE(10)
DIMENSION IA(100,8), S(101), P(101), R(202), WT(101)
COMMON S, P, R
FLOATF(I)=I
EQUIVALENCE (S, WT)
DEFINE DISK(10, 2400)
NR=1
1 NPASS=0

READ A TITLE
READ 4000, TITLE
PRINT TITLE
PRINT 5000, TITLE
READ PARAMETERS REQD.
READ 1000, N, NVA, NVB
NV=NVA+NVB
NVB1=NVB+1
NN = N + 1
NSEC = NN / 10 + 1
IDS K = NSEC + 1

C READ DATA OFF CARDS IN TWO BLOCKS AND RECORD ON DISK AFTER RANKING

C BLOCK 1

DO 10 J = 1, N
READ 2000, (IA(J, I), I = 1, NVA)
10 CONTINUE

DO 20 I = 1, NVA
DO 25 J = 1, N
S(J) = IA(J, I)
25 CONTINUE

CALL RANK(S, R, N)
LOC(I) = IDSK
RECORD(IDSK)(R(L), L = 1, NN)
IDS K = IDSK + 1
20 CONTINUE

C BLOCK 2

DO 30 J = 1, N
READ 2000, (IA(J, I), I = 1, NVB1)
30 CONTINUE

DO 40 I = 1, NVB1
DO 45 J = 1, N
S(J) = IA(J, I)
45 CONTINUE

IN VB = I + NVA
LOC(IN VB) = IDSK
IF (1 - 8) 47, 46, 48
46 IDSK3 = 1
RECORD(IDSK3)(S(L), L = 1, N)
GO TO 40
47 RECORD(IDSK)(S(L), L = 1, N)
GO TO 49
48 RECORD(IDSK)(S(L), L = 1, N)
INV B1 = INV B - 1
LOC(INVB1) = LOC(IN VB)
49 IDSK = IDSK + 1
40 CONTINUE

DO 50 I = 1, NVB
NVAI=NVA+1
JDSK2=LOC(NVAI)
FETCH(JDSK2)(S(L), L=1, N)
CALL RANK(S, R, N)
INVC=NV+1
LOC(INVC)=IDSK
RECORD(IDSK)(R(L), L=1, NN)
IDSK=IDSK+1
50 CONTINUE

C
C DISK NOw CONTAINS
C 1 SOIL DATA (RANKED) STARTING AT NSEC+1
C 2 PLANT DATA (RAW) STARTING AT LOC(NVA+1)
C 3 PLANT DATA (RANKED) STARTING AT LOC(NV+1)
C 4 WEIGHT PERCENT OF ASH AT IDSK3
C USING (1) AND (3) CAN NOW GET RANK CORRELATIONS BETWEEN
C CONCENTRATION IN THE SOIL AND THE
C CONCENTRATION IN THE PLANT (ON THE ASH WEIGHT)
C
C PRINT HEADINGS
PRINT 3000, NVA, NVB, N
100 PRINT 3100
DO 60 J=1, NVA
JDSK1=LOC(J)
FETCH(JDSK1)(S(L), L=1, NN)
DO 65 K=1, NVB
NVAI=NV+K
JDSK2=LOC(NVAI)
FETCH(JDSK2)(P(L), L=1, NN)
CALL SRANK(S, P, R, N, RS, T, NDF, NR)
P2=SPRBF(1., FLOATF(NDF), T**2)
PRINT 3200, J, K, RS, T, P2, NDF
65 CONTINUE
60 CONTINUE
NPASS=NPASS+1
IF (NPASS-1)80, 90, 80
90 CONTINUE
PRINT 3300

C
C CALCULATE CONCENTRATIONS ON A DRY WEIGHT BASIS AND OBTAIN RS

JDSK2 = 1
FETCH(JDSK2)(WT(L), L = 1, N)
DO 70 J = 1, NVB
NVAI = NVA + J
JDSK2 = LOC(NVAI)
FETCH(JDSK2)(P(L), L = 1, N)
DO 75 I = 1, N
P(I) = P(I) * WT(I)
75 CONTINUE
CALL RANK(P, R, N)
NVAI = NV + J
JDSK4 = LOC(NVAI)
RECORD(JDSK4)(R(I), I = 1, NN)
70 CONTINUE

C C PLANT DATA (CORRECTED FOR ASH WEIGHT), (RANKED) IS NOW STORED ON
C THE DISK STARTING AT POSITION IDS4
C
C NOW GET CORRELATION BETWEEN THE
C CONCENTRATION IN THE SOIL AND THE
C CONCENTRATION IN THE PLANT (ON THE DRY WEIGHT)

GO TO 100
80 CONTINUE
GO TO 1
1000 FORMAT(14, 12, 12)
2000 FORMAT(1216)
3000 FORMAT(32H *** RANK CORRELATION ANALYSIS ***/1X, 31(1H =)/1X, 56H PLANT
1 CONCENTRATIONS EXPRESSED AS FUNCTION OF ASH WEIGHT/36H NUMBER OF V
2ARIABLES IN SOIL BLOCK =, 15/37H NUMBER OF VARIABLES IN PLANT BLOCK
3 =, 14/37H NUMBER OF VALUES FOR EACH VARIABLE =, 14)
3100 FORMAT(40H ELEMENTS RS T P(T) DF/13H ROCK PLAN
1T)
3200 FORMAT(1H , 14, 4X, 14, F6.3, F7.3, F9.4, 17)
3300 FORMAT(54H PLANT CONCENTRATIONS EXPRESSED ON BASIS OF DRY WEIGHT)
4000 FORMAT(10A4)
5000 FORMAT(1H1, 10A4)
END
SUBROUTINE RANK

PURPOSE - TO RANK A VECTOR OF VALUES
PARAMETERS ARE - A - INPUT VECTOR OF N VALUES
R - OUTPUT VECTOR OF SIZE N, SMALLEST VALUE RANKED 1, LARGEST RANKED M, TIES ASSIGNED - AVERAGE OF TIED RANKS AND R(M+1) SET TO 1 WHEN TIES HAVE OCCURRED
N - NO. OF VALUES

SUBROUTINE RANK(A, R, N)
DIMENSION A(1), R(1)
COMMON A, B, R
NN=N+1

C INITIALIZE
DO 10 I=1, NN
10 R(I)=0.

C FIND RANK OF DATA
DO 100 I=1, N

C TEST IF DATA PT ALREADY RANKED
IF(R(I))20, 20, 100

20 SMALL=0.
EQUAL=0.
X=A(I)
DO 50 J=1, N
IF(A(J)-X)30, 40, 50
30 SMALL=SMALL+1.
GO TO 50

C COUNT NO. OF DATA PTS. THAT ARE EQUAL
40 EQUAL=EQUAL+1.
R(J)=-1.
50 CONTINUE

C TEST FOR TIES
IF(EQUAL-1)60, 60, 70

C STORE RANK OF DATA PT. WHERE NO TIE
60 R(I)=SMALL+1.
GO TO 100
C CALCULATE RANK OF TIED DATA PTS.
70 P=SMALL+EQUAL*(EQUAL+1.)/(EQUAL*EQUAL)
R( NN)=1.
DO 90 J=1, N
  IF( R( J)+1. )90, 80, 90
80 R( J)=P
90 CONTINUE
100 CONTINUE
RETURN
END

C SUBROUTINE TIE
C CALCULATES CORRECTION FACTOR DUE TO TIES
C PARAMETERS ARE:
C R-INPUT VECTOR OF RANKS OF LENGTH N, CONTAINS
C -VALUES 1 TO N
C N-N-Q. OF RANKED VALUES
C KT-INPUT CODE FOR CALCULATION OF CORRECTION FACTOR
C -1 SOLVES T=SUM(CT**3-CT)/12
C -2 SOLVES T=SUM(CT*(CT-1)/2)
C CT-NO. OF OBS. TIED FOR A GIVEN RANK
C T-CORRECTION FACTOR(OUTPUT)
SUBROUTINE TIE(R, N, KT, T)
DIMENSION R(N)
COMMON A, B, R
C INITIALIZE
T=0.
Y=0.
5 X=1.38
IND=0
C FIND NEXT LARGEST RANK
DO 30 I=1, N
  IF( R(I)-Y)30, 30, 10
10 IF( R(I)-X)20, 30, 10
20 X=R(I)
  IND=IND+1
30 CONTINUE
C IF ALL RANKS HAVE BEEN TESTED RETURN
IF(IND) 90, 90, 40
40 Y=X
   CT=0.
C COUNT TIES
   DO 60 I=1, N
      IF( R(I)-X) 60, 50, 60
50   CT=CT+1.
   60 CONTINUE
C CALCULATE CORRECTION FACTOR
   IF(CT) 70, 5, 70
   70 IF(KT-1) 75, 80, 75
   75   T=T+CT*(CT-1.)/2.
      GO TO 5
   80   T=T+(CT*CT*CT-CT)/12.
      GO TO 5
90 RETURN
END

C SUBROUTINE SRANK
C PURPOSE -TO CALCULATE SPEARMANS RANK CORRELATION BETWEEN 2 VARIABLES
C PARAMETERS ARE-A-INPUT VECTOR OF N OBS. FOR 1ST VARIABLE
   B-INPUT VECTOR OF N OBS. FOR 2ND VARIABLE
   R-OUTPUT VECTOR OF RANKED DATA-SIZE 2*N+2
   N-NUMBER OF OBS.
   RS-SPEARMANS RANK CORRELATION (OUTPUT)
   T-TEST OF SIG. OF RS(OUTPUT)
   NDF-NO. DEGREES OF FREEDOM(OUTPUT)
   NR-CODE 0 FOR UNRANKED DATA IN A AND B
   1 FOR RANKED DATA IN A AND B
C NOTE T=0 IF N LESS THAN 10
C RANK AND TIE SUBROUTINES REQUIRED
C
SUBROUTINE SRANK(A, B, R, N, RS, T, NDF, NR)
DIMENSION A(1), B(1), R(1)
COMMON A, B, R
FLOATF(I) = I
NN = N + 1
FNNN = N * N * N * N - N

C DETERMINE IF DATA ALREADY RANKED
IF( NR - 1) 5, 10, 5
C RANK DATA IN A AND B AND TIED OBSVNS. ARE GIVEN AVERAGE OF TIED RANKS
5 CALL RANK( A, R, N)
   CALL RANK( B, R( N+2), N)
   GO TO 40
C MOVE RANKED DATA TO R VECTOR
10 DO 20 I = 1, N
20 R(I) = A(I)
   DO 30 I = 1, N
   J = I + N + 1
30 R(J) = B(I)
C COMPUTE SUMS OF SQS OF RANKED DIFFERENCES
40 D = 0.
   DO 50 I = 1, N
      J = I + N + 1
50 D = D + (R(I) - R(J)) * (R(I) - R(J))
C COMPUTE TIED SCORE INDEX
KT = 1
   IF( R( N N)) 21, 22, 21
21 CALL TIE( R, N, KT, TSA)
   GO TO 25
22 TSA = 0.
25 IR = 2 * N + 2
   IF( R( IR)) 23, 24, 23
23 CALL TIE( R(N+2), N, KT, TSB)
   GO TO 26
24 TSB = 0.
C COMPUTE SPEARMAN RANK CORRELATION
26 IF( TSA) 60, 55, 60
55 IF( TSB) 60, 57, 60
57 RS = 1. - 6. * D / FN N N
   GO TO 70
60 X = FN N N / 12. - TSA
Y = X + TSA - TSB
RS = (X + Y - D) / (2 * SQRTF(X * Y))
T = 0.
70 IF(N-10) 80, 75, 75
75 T = RS * SQRTF FLOATF(N-2) / (1 - RS*RS)
80 NDF = N - 2
RETURN
END
D. **Discriminant analysis programme:**

The data cards are punched using format F6.0; a maximum of 13 fields can be used per card. All the variables used are stored on disc. Although a maximum of only 20 variables can be used to compute any one discriminant function, more variables can be stored. The number and identity of the variables to be used are typed into the computer prior to each calculation. Directions for the execution of this programme are included in the listing.
DISCRIMINANT ANALYSIS PROGRAMME
FORTRAN IV

C MAIN PROGRAM DISCF FOR OBTAINING DISC. FUNCTIONS

DEFINE FILE 1(140, 50, U, NIN)
DEFINE FILE 2(140, 50, U, NOUT)
DIMENSION NV(35)
DIMENSION DATA(35), DAT(20), N(10)
EQUIVALENCE (NVAR, M)
WRITE (1, 3333)
3333 FORMAT(' CURRENTLY THE PROGRAM IS SET UP FOR - '/
1' NO. OF VARIABLES = 20, NO. OF GROUPS = 10, NO. OF SAMPLES = 150
2'/ ' IF ANY OF THESE IS EXCEEDED DIMENSION STATEMENTS MUST BE CHANG
3ED')

C SUBROUTINES REQD.... MDISC, DMATX, MINV, DISCR

NIN=1
READ (2, 1000) MX, MY
1000 FORMAT(212)
READ (MY, 2000) PR, PRI, K, M, (N(I), I=1, K)
2000 FORMAT(A4, A2, 212, 12F15/(1415))
NSMPL=0
DO 5 I=1, K
5 NSMPL=NSMPL+N(I)
1 DO 10 I=1, NSMPL
READ (MY, 2500) (DATA(J), J=1, NVAR)
2500 FORMAT(13F6.0)
WRITE (1*NIN) (DATA(J), J=1, NVAR)
10 CONTINUE

C TAKE FROM TYPEWRITE THE NO. OF VARIABLES FOR THE DISC FUNCTION
C
20 WRITE (1, 3000)
3000 FORMAT(' ENTER THE NO. OF VARIABLES TO BE CONSIDERED IN THE DISC.
1 FUNCTION'/ ' FORMAT 12 WITH 99 FOR END OF JOB')
READ (6, 4000) NVAR
4000 FORMAT(12)
C TEST FOR NVAR1) 21

IF (NVAR1-20) 30, 30, 25
25 IF (NVAR1-99) 20, 26, 20
26 CALL EXIT
30 WRITE (1, 5000) NVAR1

5000 FORMAT(' ENTER THE IDENT. NO. OF ', 13, ' VARIABLES TO BE USED IN THE
1 DISCR. FUNCTION (FORMAT 12)')
DO 40 I=1, NVAR1
READ (6, 4000) NV(I)
40 CONTINUE
WRITE (3, 6000) (NV(L), L=1, NVAR1)
6000 FORMAT('IDENTITY NUMBERS OF THE VARIABLES USED IN DISCRIMINANT AN
ALYSIS'//(1514))

C TAKE ONE SAMPLE OFF THE DISK, PICK OUT DESIRED VARIABLES AND REWRITE
ON DISK
NOUT=1
NIN=1
DO 100 J=1, NSMPL
READ (1`NIN) DATA(L), L=1, NVAR)
DO 110 I=1, NVAR1
NVI=NV(I)
DAT(I)=DATA(NVI)
110 CONTINUE
WRITE (2`NOUT) (DAT(I), I=1, NVAR1)
100 CONTINUE
CALL MDISC(PR, PR1, K, NVAR1, N, MX, MY, NOUT)
GO TO 20
END

C SUBROUTINE MDISC(PR, PR1, K, N, MX, MY, NOUT)

C SAMPLE MAIN PROGRAM FOR DISCRIMINANT ANALYSIS - MDISC
C THE FOLLOWING DIMENSION MUST BE GREATER THAN OR EQUAL TO THE
C NUMBER OF GROUPS, K.
C DIMENSION K 10)
C THE FOLLOWING DIMENSION MUST BE GREATER THAN OR EQUAL TO THE

MDISC 1
MDISC 2
MDISC 3
MDISC 5
NUMBER OF VARIABLES, M.

DIMENSION CMEAN(20)
THE FOLLOWING DIMENSION MUST BE GREATER THAN OR EQUAL TO THE
PRODUCT OF M*K.

DIMENSION XBAR(200)
THE FOLLOWING DIMENSION MUST BE GREATER THAN OR EQUAL TO THE
PRODUCT OF (M+1)*K.

DIMENSION C(210)
THE FOLLOWING DIMENSION MUST BE GREATER THAN OR EQUAL TO THE
PRODUCT OF M*M.

DIMENSION D(400)

DIMENSION P(150), LG(150)

DIMENSION TOTAL OF SAMPLE SIZES OF K GROUPS COMBINED, T (T = N(1)+N(2)+..)
+N(K)).

DIMENSION TOTAL DATA POINTS WHICH IS EQUAL TO THE PRODUCT OF T*M.

DIMENSION X(3000) .

1 FORMAT( A4, A2, 212, 1215/(1415))
2 FORMAT(//27H1DISCRIMINANT ANALYSIS.... A4, A2//19H NUMBER OF GROUPS,
10UPS, 7X, 13/22H NUMBER OF VARIABLES, 17/17H SAMPLE SIZES.../12X, 
25HGROUP)
3 FORMAT(12X, 13, 8X, 14)
4 FORMAT( //2X)
5 FORMAT(13F6. 0)
6 FORMAT(//6H GROUP, 13, 7H MEANS/(8F15. 5))
7 FORMAT(//25H POOLED DISPERSION MATRIX)
8 FORMAT(//4H ROWN, 13/(8F15. 5))
9 FORMAT(///13H COMMON MEANS/(8F15. 5))
10 FORMAT(///33H GENERALIZED MAHALANOBIS D-SQUARE, F15. 5//)
11 FORMAT(///22H DISCRIMINANT FUNCTION, 13//6X, 27HCONSTANT * COEFFI
11ENTS///F14.5, 7H * , 7F14. 5/(22X, 7F14. 5))
12 FORMAT(///60H EVALUATION OF CLASSIFICATION FUNCTIONS FOR EACH OBS)
13 FORMAT(///6H GROUP, 13/19X, 27HPROBABILITY ASSOCIATED WITH, 11X, 7H
13 TEST/13H OBSERVATION, 5X, 29H LARGEST DISCRIMINANT FUNCTION, 8X, 12HFUN MD
14 FORMAT(17, 20X, F8. 5, 20X, 16)
15 FORMAT (212)

C

NOUT = 1

C PR1 Problem number (may be alphabetic)

C PR1 Problem number (continued)

C K Number of groups

C M Number of variables

C N Vector of length K containing sample sizes

WRITE (MX, 2) PR, PR1, K, M

DO 110 I = 1, K

110 WRITE (MX, 3) I, N(I)

WRITE (MX, 4)

C

READ DATA

L = 0

DO 130 I = 1, K

N1 = N(I)

DO 120 J = 1, N1

READ (2'NOUT) (CMEAN(IJ), IJ = 1, M)

L = L + 1

N2 = L - N1

DO 120 IJ = 1, M

N2 = N2 + N1

120 X(N2) = CMEAN(IJ)

130 L = N2

CALL DMATX (K, M, N, XBAR, D, CMEAN)

C

PRINT MEANS AND POOLED DISPERSION MATRIX

L = 0

DO 150 I = 1, K

DO 140 J = 1, M

L = L + 1

140 CMEAN(J) = XBAR(L)

150 WRITE (MX, 6) I, (CMEAN(J), J = 1, M)

WRITE (MX, 7)

DO 170 I = 1, M

L = I - M

DO 160 J = 1, M

L = L + M

160 CMEAN(J) = D(L)

170 WRITE (MX, 8) I, (CMEAN(J), J = 1, M)
CALL MINV (D, M, DET, CMEAN, C)
CALL DISCR (K, M, N, X, XBAR, D, CMEAN, V, C, P, LG)
C
PRINT COMMON MEANS
WRITE(MX, 9) (CMEAN(I), I=1, M)
C
PRINT GENERALIZED MAHALANOBIS D-SQUARE
WRITE (MX, 10) V
C
PRINT CONSTANTS AND COEFFICIENTS OF DISCRIMINANT FUNCTIONS
N1=1
N2=M+1
DO 180 I=1, K
WRITE (MX, 9) (C(J), J=N1, N2)
N1=N1+(M+1)
180 N2=N2+(M+1)
C
PRINT EVALUATION OF CLASSIFICATION FUNCTIONS FOR EACH OBSERVATION
WRITE (MX, 12)
N1=1
N2=N1
DO 210 I=1, K
WRITE (MX, 13) I
L=0
DO 190 J=N1, N2
L=L+1
190 WRITE (MX, 14) L, P(J), LG(J)
IF (I-K) 200, 100, 100
200 N1=N1+N(I)
N2=N2+N(I+1)
210 CONTINUE
100 RETURN
END
C
SUBROUTINE DMATX (K, N, X, XBAR, D, CMEAN)
DIMENSION N(1), X(1), XBAR(1), D(1), CMEAN(1)
MM=M*M
DO 100 I=1, MM
100 D(I)=0.0
C
CALCULATE MEANS
N4=0

MDISC 86
MDISC 87
MDISC 88
MDISC 89
MDISC 90
MDISC 91
MDISC 92
MDISC 93
MDISC 94
MDISC 95
MDISC 96
MDISC 97
MDISC 98
MDISC 99
MDISC 100
MDISC 101
MDISC 102
MDISC 103
MDISC 104
MDISC 105
MDISC 106
MDISC 107
MDISC 108
MDISC 109
MDISC 110
MDISC 111
MDISC 112
MDISC 113
MDISC 114
MDISC 115

DMATX 1
DMATX 2
DMATX 3
DMATX 4
DMATX 5
DMATX 6
DMATX 7
L=0
LM=0
DO 160 NG=1, K
   N1=N(NG)
   FN=N1
   DO 130 J=1, M
      LM=LM+1
      XBAR(LM)=0.0
   DO 120 I=1, N1
      L=L+1
120 XBAR(LM)=XBAR(LM)+X(L)
130 XBAR(LM)=XBAR(LM)/FN
C CALCULATE SUMS OF CROSS-PRODUCTS OF DEVIATIONS
   LMEAN=LM-M
   DO 150 I=1, N1
      LL=N4+1-N1
   DO 140 J=1, M
      LL=LL+N1
      N2=LMEAN+J
140 CMEAN(J)=X(LL)-XBAR(N2)
      LL=0
      DO 150 J=1, M
      DO 150 JJ=1, M
      LL=LL+1
150 D(LL)=D(LL)+CMEAN(J)*CMEAN(JJ)
160 N4=N4+N1*M
C CALCULATE THE POOLED DISPERSION MATRIX
   LL=-K
   DO 170 I=1, K
      LL=LL+N(1)
      FN=LL
   DO 180 I=1, MM
      D(I)=D(I)/FN
180 RETURN
END
C SUBROUTINE MINV(A, N, D, L, M)
DIMENSION A(1), L(1), M(1)
C SEARCH FOR LARGEST ELEMENT

D=1.0
NK=-N
DO 80 K=1,N
NK=NK+N
L(K)=K
MK(K)=K
KK=NK+K
BIGA=A(KK)
DO 20 J=K,N
IZ=N*(J-1)
DO 20 I=K,N
IJ=IZ+I
15 IF(ABS(BIGA)-ABS(A(IJ))) 15,20,20
15 BIGA=A(IJ)
L(K)=I
MK(K)=J
20 CONTINUE

C INTERCHANGE ROWS

J=L(K)
IF(J-K)35,35,25
25 KL=K-N
DO 30 I=1,N
KI=KI+N
HOLD=-A(KI)
JL=KI-K+J
A(KI)=A(JL)
30 A(JL)=HOLD

C INTERCHANGE COLUMNS

35 I=MK
IF(I-K)45,45,38
38 JP=N*(I-1)
DO 40 J=1,N
JK=NK+J
JL=JP+J
HOLD=-A(JK)
A(JK)=A(JL)
A(JL)=HOLD
40 C DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT IS
CONTAINED IN BIGA)

DO 55 I = 1, N
    IF (I - K) 50, 55, 50
    IK = NK + I
    A(IK) = A(IK) / (BIGA)
55 CONTINUE

REDUCE MATRIX

DO 65 I = 1, N
    IK = NK + I
    HOLD = A(IK)
    IJ = I - N
    DO 65 J = 1, N
        IJ = IJ + N
        IF (I - K) 60, 65, 60
        IF (J - K) 62, 65, 62
        KJ = IJ - 1 + K
        A(IJ) = HOLD * A(KJ) + A(IJ)
65 CONTINUE

DIVIDE ROW BY PIVOT

KJ = K - N
DO 75 J = 1, N
    KJ = KJ + N
    IF (J - K) 70, 75, 70
    A(KJ) = A(KJ) / BIGA
75 CONTINUE

PRODUCT OF PIVOTS

D = D * BIGA

REPLACE PIVOT BY RECIPROCAL

A(KK) = 1.0 / BIGA

FINAL ROW AND COLUMN INTERCHANGE

K = N
100 K = (K - 1)
    IF (K) 150, 150, 105
    I = L(K)
    IF (I - K) 120, 120, 108
SUBROUTINE DISCR (K, M, N, X, XBAR, D, CMEAN, V, C, P, LG)

DIMENSION N(1), X(1), XBAR(1), D(1), CMEAN(1), C(1), P(1), LG(1)

CALCULATE COMMON MEANS

N1=N(1)
DO 100 I=2, K
100 N1=N1+N(1)
FNT=N1
DO 110 I=1, K
110 P(I)=N(1)
DO 130 J=1, M
CMEAN(I)=0
N1=I-M
DO 120 J=1, K
N1=N1+M
120 CMEAN(I)=CMEAN(I)+P(J)*XBAR(N1)
130 CMEAN(I)=CMEAN(I)/FNT

CALCULATE GENERALIZED MAHALANOBIS D SQUARE

DISCR
L = 0
DO 140 I = 1, K
DO 140 J = 1, M
L = L + 1
140 C(L) = XBAR(L) - CMEAN(J)
V = 0.0
L = 0
DO 160 J = 1, M
DO 160 I = 1, M
N1 = I - M
N2 = J - M
SUM = 0.0
DO 150 IJ = 1, K
N1 = N1 + M
N2 = N2 + M
150 SUM = SUM + P(IJ) * C(N1) * C(N2)
L = L + 1
160 V = V + D(L) * SUM
C CALCULATE THE COEFFICIENTS OF DISCRIMINANT FUNCTIONS
N2 = 0
DO 190 KA = 1, K
DO 170 I = 1, M
N2 = N2 + 1
170 P(I) = XBAR(N2)
IQ = (M + 1) * (KA - 1) + 1
SUM = 0.0
DO 180 J = 1, M
N1 = J - M
DO 180 L = 1, M
N1 = N1 + M
180 SUM = SUM + D(N1) * P(J) * P(L)
C(IQ) = -(SUM/2.0)
DO 190 I = 1, M
N1 = I - M
IQ = IQ + 1
C(IQ) = 0.0
DO 190 J = 1, M
N1 = N1 + M
190 C(IQ) = C(IQ) + D(N1) * P(J)
FOR EACH CASE IN EACH GROUP, CALCULATE:

DISCRIMINANT FUNCTIONS

LBASE=0
N1=0
DO 270 KG=1, K
NN=N(KG)
DO 260 I=1, NN
L=I-NN+LBASE
DO 200 J=1, M
L=L+NN

200 D(J)=X(L)
N2=0
DO 220 KA=1, K
N2=N2+1
SUM=C(N2)
DO 210 J=1, M
N2=N2+1
210 SUM=SUM+C(N2)*D(J)
220 XBAR(KA)=SUM

THE LARGEST DISCRIMINANT FUNCTION

L=1
SUM=XBAR(1)
DO 240 J=2, K
IF(SUM-XBAR(J)) 230, 240, 240
230 L=J
SUM=XBAR(J)
240 CONTINUE

PROBABILITY ASSOCIATED WITH THE LARGEST DISCRIMINANT FUNCTION

PL=0.0
DO 250 J=1, K
250 PL=PL+EXP(XBAR(J)-SUM)
N1=N1+1
LG(N1)=L
260 P(N1)=1.0/PL
270 LBASE=LBASE+NN*M
RETURN
END
APPENDIX V

Publications arising from this Thesis

Nielsen, J.S., Brooks, R.R., Boswell, C.R., and Marshall, N.J.,
The statistical treatment of geobotanical and biogeochemical data using discriminant analysis: