A

T H E S I S

entitled

INVESTIGATION OF THE SECONDARY DISPERSION OF NICKEL IN RHODESIA AND ZAMBIA

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ABSTRACT.

Geochemical investigations aimed at obtaining a better understanding of the secondary dispersion of nickel under conditions encountered in Rhodesia and Zambia were carried out in the vicinity of nickel - copper sulphide deposits, a nickel arsenide deposit and non mineralized ultrabasic rocks.

Significant nickel anomalies related to mineralization in rocks other than ultrabasics occur in freely drained soils. Nickel anomalies in soil over mineralization in ultrabasic rocks are very weak in the singularly high local background. There is no difference in the character of the nickel dispersion train from mineralized and barren serpentinite.

Investigations have been biased towards differentiating geochemically between sulphide and silicate nickel. The secondary dispersion of nickel is predominantly controlled by chemical factors, which affect both sulphide and silicate nickel in a similar manner, though not necessarily at the same rate.

Dispersion in high rainfall areas in Zambia is almost entirely saline whilst in semi-arid parts of Rhodesia dispersion is dominantly mechanical. The amounts of nickel moved vary with climate, pattern of distribution of ground water, topography and geomorphological history.

The distribution of nickel in soil profiles is related to soil pH, iron, percentage clay size material and organic matter. Profile distribution in weathered bedrock is different over barren and mineralized rocks.

Nickel readily enters the biochemical cycle and the presence of biogeochemical anomalies has been established in some areas.

Study of the form of nickel in some geologic materials has been carried out. Greater amounts of exchangeable nickel have been found in weathered bedrock over deposits of nickel sulphide minerals than in corresponding material over barren rocks.

Preliminary investigations into the distribution of elements associated with the nickel ore deposits have indicated that copper, selenium and/or arsenic, can be employed as pathfinders in geochemical prospecting for sulphide and/or arsenide nickel.

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The writer wishes to convey his thanks to Mr. J.A. Gee and Miss M. Doe of the Royal School of Mines for advice and assistance in the reproduction of the diagrams in this thesis.

ERRATA. For "Fairey's claims (near the Noel nickel mine) read "Fair's claims".

INTRODUCTION.

Nickel is known to occur in the lattices of some rock-forming minerals, notably olivines and serpentines, where it is thought to replace magnesium or iron. Bodies of ultrabasic rock such as peridotite or serpentinite, rich in the above mentioned minerals, frequently contain up to 0.4% nickel. Under favourable conditions the weathering products of ultrabasic rocks can be enriched in nickel. Material containing more than 1% nickel may result. Such deposits are not considered to be likely to occur in Central Africa in economic tonnages. The main alternative sources of nickel are the deposits of nickel sulphide minerals, e.g. nickeliferous pyrrhotite and pentlandite. Several such deposits have been discovered in Rhodesia and Zambia, most of them in or adjacent to ultrabasic rocks to which they are believed to be genetically related. Additional sulphide deposits may well exist and are being actively sought.

The object of the present investigation has been to study the distribution of nickel in rocks, products of weathering and erosion, natural waters and vegetation in order to obtain a better understanding of the secondary dispersion of nickel under the conditions encountered in

Rhodesia and Zambia. This fundamental knowledge is required with a view to improving:-

(i) The interpretation of nickel soil and drainage anomalies and

(ii) Geochemical prospecting techniques.

Field studies were carried out during 1963 and 1964 in both Rhodesia and Zambia. These territories were Southern Rhodesia and Northern Rhodesia respectively until October 1964 when Northern Rhodesia became the independent country, Zambia. Southern Rhodesia is now known as Rhodesia. The bulk of the work has been carried out in Rhodesia, that undertaken in Zambia being confined to one area in the North Western Province. A wide range of climatic and topographic conditions were encountered in the eight study areas chosen for investigation which were :-

(i) The Darwendale section of the Great Dyke of Rhodesia. This part of the Dyke, which has been drilled, contains no known deposits of sulphides. The area is gently undulating and experiences temperate conditions with a mean annual rainfall of between 30 and 40 in. per annum and a temperature range of 40° to 90° F.

(ii) Dalmainy Farm near Umvuma in the Rhodesian Midlands where a serpentinite mass devoid, as far as can be ascertained, of sulphide minerals forms a well pronounced topographic feature under climatic conditions comparable to those prevailing at Darwendale and in the other study areas in the Midlands of Rhodesia.

(iii) The Perseverance prospect ; the first of four mineralized study areas in the Rhodesian Midlands. Nickel-copper sulphides occur in serpentinite which outcrops as a strong topographic feature. The area is

10 miles from the village of Chakari.

(iv) The Maritzani area ; on a farm of the same name a few miles south of Perseverance. Nickel-copper sulphides occur in and adjacent to serpentinite which outcrops on a gentle slope to a vlei.

(v) The Empress prospect, which is the third deposit of sulphide minerals studied, and where nickel-copper sulphides occur in an amphibolite body.

(vi) Bare Bottom Hill, which is situated only one mile from the Empress prospect, comprises greenstones in which occur disseminated nickel-copper sulphides.

(vii) The Noel Nickel Mine ; in the extreme south of Rhodesia where the conditions are semi-arid. Nickel arsenide minerals occur in fault zones in and around serpentinite in the mine and it's environs. The rainfall in the area in the last three wet seasons has not exceeded 8 in. per annum. The temperature range is from 35° to 100° F. This is greater than the average range in the Midlands.

(viii) The Kalumbila area in Zambia which experiences temperatures comparable to those in most of the Rhodesian study areas (40° to 90°F) but with higher rainfall (approximately 55 in. per annum). The secondary dispersion of nickel from a deposit of nickel-copper sulphides in carbonaceous shale has been examined.

Company data.

Prior to the 1963 and 1964 field seasons geological and geochemical investigations were carried out at Darwendale, Perseverance and Maritzani by Rhodesian (now Roan) Selection Trust Exploration Limited, at Kalumbila by Rhodesian Selection Trust Mine Services Limited (now Roan Selection Trust Technical Services Limited),

at Dalmainy Farm, Empress and Bare Bottom Hill by Mineral Search of Africa Limited (now Rio Tinto (Rhodesia) Limited) and in the environs of the Noel Nickel mine by the Southern Rhodesian Geological Survey. The above mentioned companies and the Geological Survey generously made their results available to the project. These results provided very useful information. In addition to data : RST Exploration Ltd., RST Mine Services Ltd. and the Southern Rhodesian Geological Survey provided some sample material which supplemented the rock, soil, stream sediment, water and vegetation samples collected by the writer.

Analytical work.

Some analytical work was carried out in the laboratories of the Geology Department at the University College of Rhodesia and Nyasaland in Salisbury, where the writer was based when in Africa. The bulk of the analyses were made, however, at the Applied Geochemistry Research Group laboratories, Imperial College, London.

Acknowledgements.

The studies formed a part of the general

research programme of the Applied Geochemistry Research Group, Royal School of Mines, London, under the direction of Professor J.S. Webb. They have been carried out in conjunction with the Department of Geology at the University College of Rhodesia and Nyasaland in Salisbury, Rhodesia, where the work was supervised by Professor G. Bond.

The project has been financed by RST Exploration Ltd., RST Technical Services Ltd., Anglo American Corporation Ltd. and the British South Africa Company Ltd. The writer wishes particularly to express his thanks to these companies for the scholarship granted for the period of study.

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The writer is indebted to the above mentioned companies, Rio Tinto (Rhodesia) Ltd. and the Southern Rhodesian Geological Survey for samples and data. In the respective study areas the work has been carried out in co-operation with the companies concerned. In many cases the companies arranged for the provision of labour and necessary facilities while the writer was in the field. This help is gratefully acknowledged. The writer would like, furthermore, to convey his appreciation to

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In particular the assistance received from Mr. G. Woodward, Mr. W. G. Garlick and Dr. J. W. N. Sharpe has been most valuable.

Mr. R. D. Moxon, on behalf of the Noel Nickel Mine (Pvt.) Ltd., gave permission to work and collect samples in the environs of the mine. His co-operation is very much appreciated.

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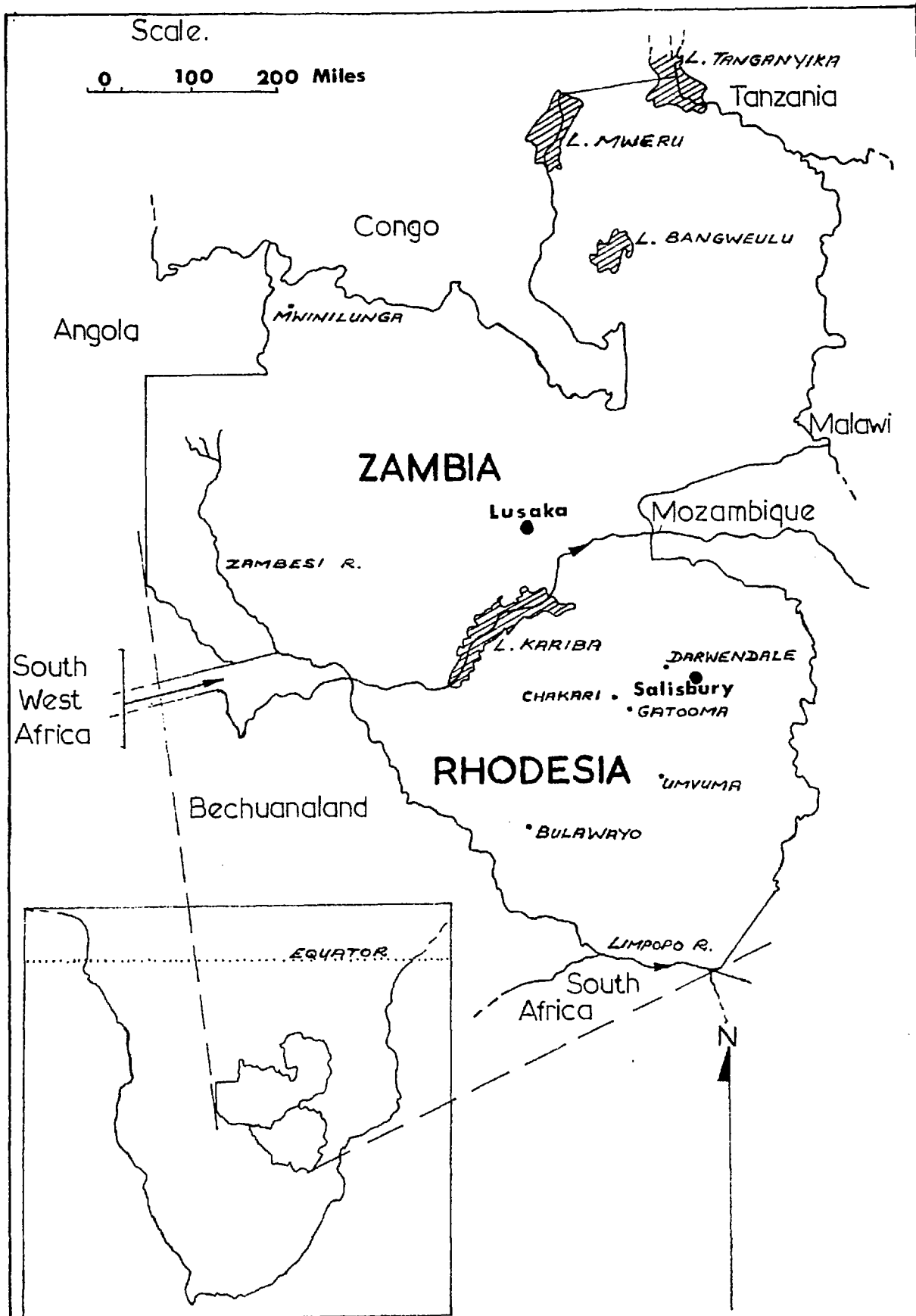
The writer is sincerely grateful to Dr. J. S. Tooms, for helpful guidance and criticism during supervision of the course of investigation both in Central Africa and in London.

Chapter 1. DESCRIPTION OF THE STUDY AREAS.

Lack of time has prevented the writer from carrying out geological mapping and detailed petrological and mineralogical examinations. The information about the geology and mineralizations has been taken, in the main, from published literature and company data (Appendix I).

A. Locations of the study areas.

Studies were carried out in seven areas in Rhodesia and at one locality in Zambia (Figure 1). The most northerly of the Rhodesian study areas is a few miles south of the village of Darwendale. This village is situated on the Great Dyke approximately 40 miles west of Salisbury, at 17° 43' south latitude, 30° 33' east longitude. Dalmainy Farm is 17 miles west of Umvuma at 19° 22' south latitude, 30° 18' east longitude. Both the Perseverance and Maritzani study areas are in the same Exclusive Prospecting Area (No. 85). The Perseverance prospect is approximately 10 miles north west of Chakari. The locality is latitude 18° south, longitude 29° 48' east, about one mile north of Madakwe beacon (Figure 6). The Maritzani area is centered eight miles



Rhodesia and Zambia; location.

1

south of Perseverance, seven miles west of Chakari. The Empress prospect and Bare Bottom Hill are in the Ngondomo region 30 miles west of the town of Gatooma. The Empress prospect is at 18° 28' south latitude, 29° 25' east longitude. Bare Bottom Hill is one mile north west of the Empress prospect. The Noel Nickel mine and it's environs constitute the southernmost study area, approximately 100 miles south of Bulawayo at 21° 19' south latitude, 28° 34' east longitude. Kalumbila is the northernmost study area being located at latitude 12° 20' south, longitude 25° 30' east, approximately 80 miles south east of the settlement of Mwinilunga in the North Western Province of Zambia.

B. General geology of Rhodesia and Zambia.

The broad geological structures of Rhodesia and Zambia are similar. In both countries younger sediments rest on a basement of very old rocks which form the stable Central African Shield. These younger sediments have been subjected to varying degrees of metamorphism. The two countries are, however, separated by the Zambesi rift valley and stratigraphical correlation between the two is difficult. Accordingly the general geology of

the two countries can be conveniently described separately.

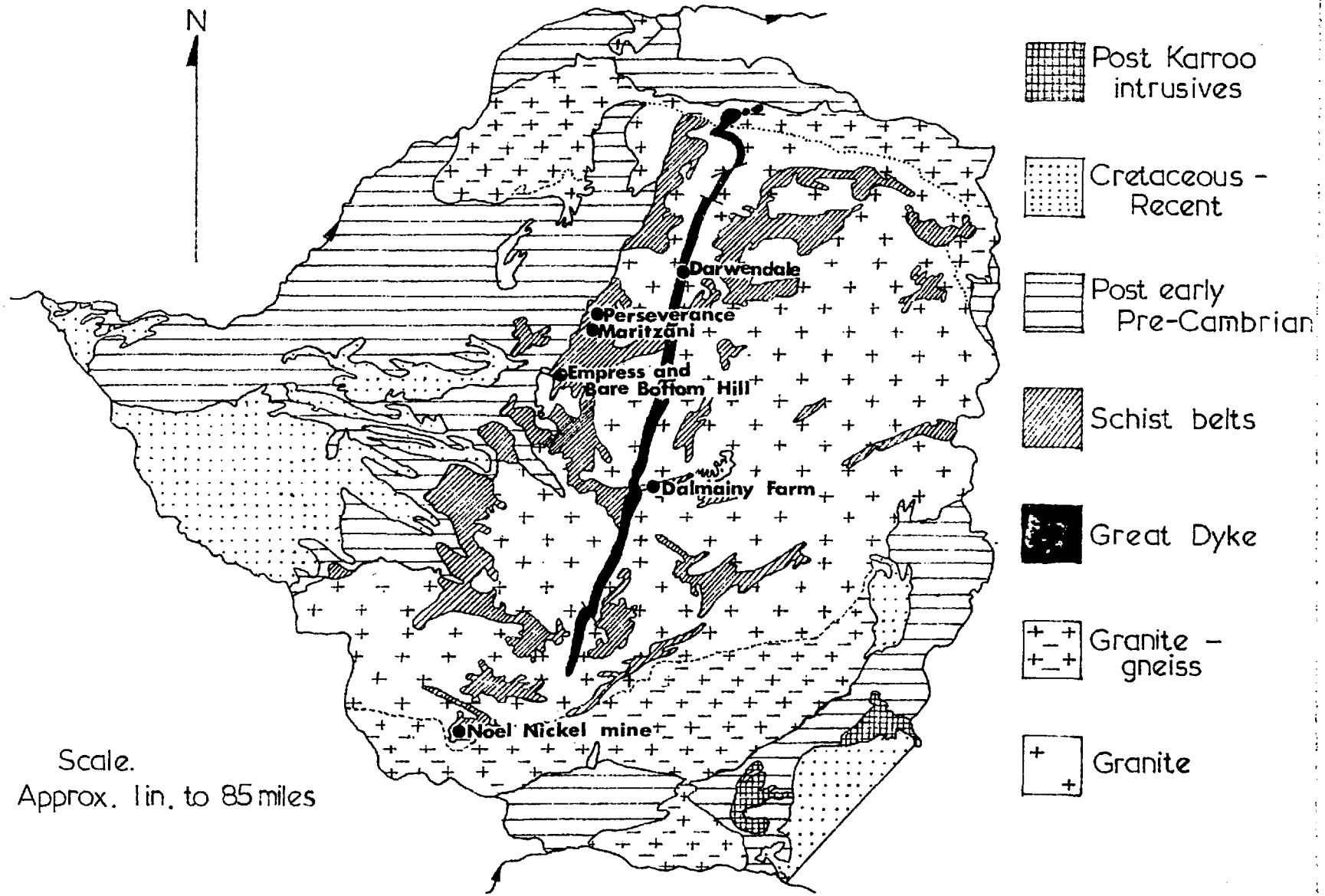
1. Rhodesia.

The greater part of Rhodesia's 150,000 square miles of surface area is underlain by batholiths and stocks of granite and granite gneiss. These batholiths and stocks, although shown on Figure 2 as a single mass, are of widely differing ages and were intruded into extrusives and sediments at stages during a long period of time. The intruded Archean volcanics and sediments, the oldest rocks in Rhodesia (Table 1), have been intensely metamorphosed. Erosion has been severe and today only relics of these metavolcanics and metasediments remain. They are of great interest in that they contain most of the country's gold mines, a fact which has led them to be called the 'Gold Belts'[1]. Many of the

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[1]Many of the rocks of the 'Gold Belts are schistose and some geologists prefer the term 'schist belts' to describe collectively the rocks of the Basement Complex. The term 'schist belt' is used in this context in this thesis.

General geology of Rhodesia. (after Cooper and Pullan, 19



2

metavolcanics have a greenish hue about them when seen

Table 1. Table of geological formations in Rhodesia. (after Tyndale-Biscoe (1960) with a recent modification proposed by Bliss and Tennick (1964).

Age	System	Series/Lithology
Recent	Recent	surface soil and alluvium
.	Pleistocene	(Kalahari sand and upper
.	.	(gravels
.	Pliocene	Lower Kalahari beds
Cretaceous	(Cretaceous)	(conglomerates, grits
	(system)	(and marls
POST KARROO GRANITE AND RING COMPLEXES		
Jurassic	( )	(basalt and rhyolitic lavas
	(Karroo)	(sandstone
.	(system)	(coal measures
Carboniferous	( )	(glacial conglomerate (tillite?)
GREAT DYKE AND DOLERITE INTRUSIONS		
	(Umkondo system	sediments
	(	(Piriwiri series
Later	(Lomagundi)	(Argillaceous series
pre-	(system)	(Arenaceous series
Cambrian	(Deweras 'formation'	(Deweras series
	((Bliss and Tennick)	
	(Frontier system	sediments
MAIN GRANITES		
	(Shamvaian)	(Phyllite series
Basement	(system)	(Conglomerate series
Complex	(Bulawayan)	(Upper series
(early	(system)	(Lower series
pre-Cambrian)	(Sebakwian)	(Magnesian series
	(system)	(sediments

in hand specimen and have come to be called collectively 'greenstones'.

Intercalated serpentinites, together with talc and actinolite schists are also considered to be of early pre-Cambrian age.

A series of younger sediments have been laid down on the eroded Basement Complex and older granites, and subsequently metamorphosed to a greater or lesser degree. In the western half of Rhodesia they are disposed in open folds and they crop out successively westwards, culminating in a blanket of Cretaceous to Recent strata.

In addition to the early pre-Cambrian ultramafic intrusions into the Basement Complex from which serpentinite has been derived, intrusive rocks are represented by the Great Dyke, abundant dolerite dykes and sills of varying ages and other minor intrusions, notably a number of ring complexes with which are associated serpentine rocks. The distribution of nickel in and around ring complex serpentinite has not been studied during the course of the present investigation but examination of the distribution of the metal in areas of Archean and Great Dyke serpentinites has formed an important part of the project.

2. <u>Zambia</u>.

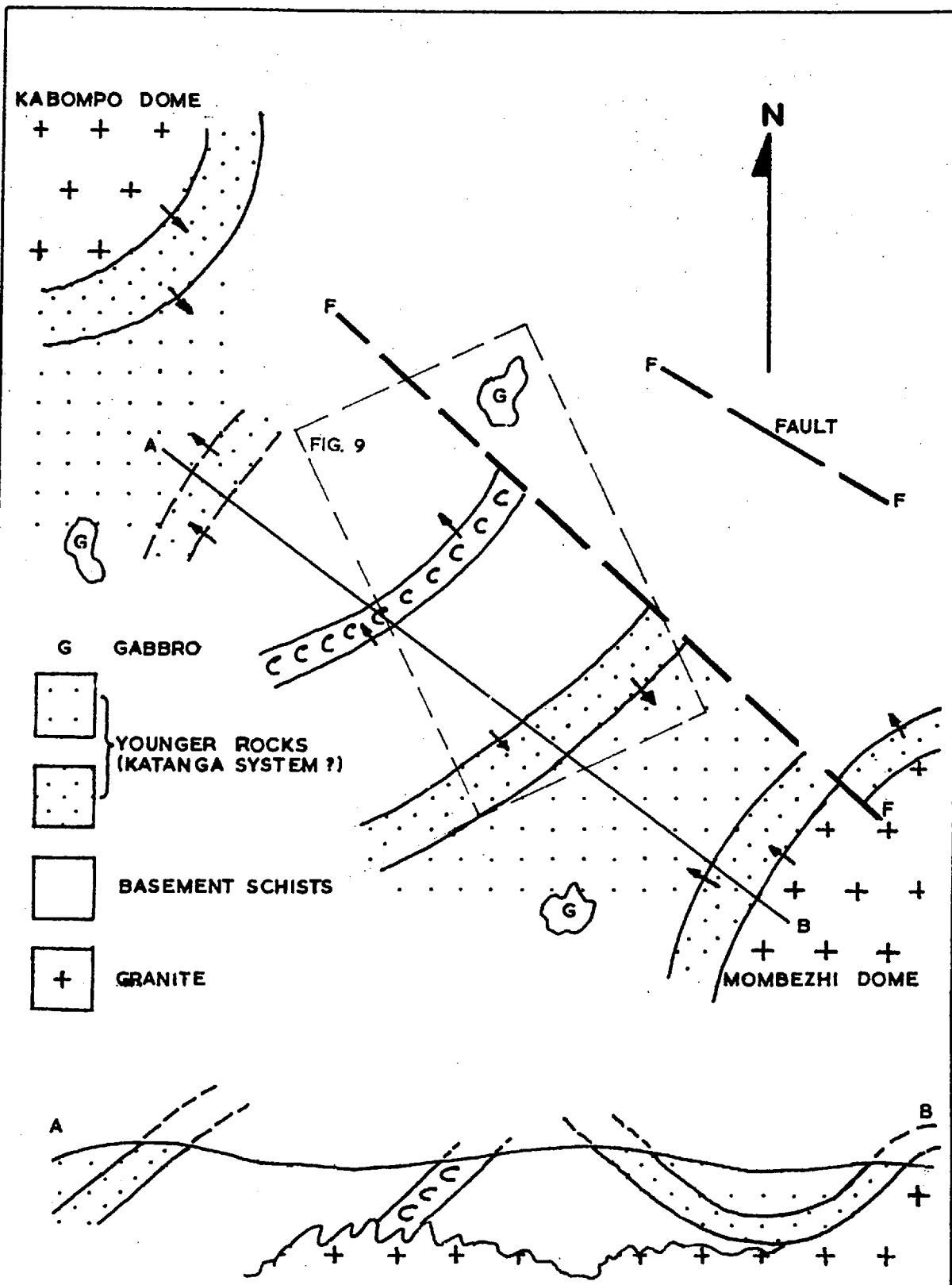
The oldest rocks known in this country are the schists and gneisses of the Basement Complex (Table 2). The Basement Complex is exposed mainly in the east of Zambia.

In the south west, west and north west younger sediments overlie the early pre-Cambrian basement and older granite (Figure 3 and Table 2).

Intrusive gabbros occur in the north west of Zambia. Their age is not known with certainty but they are probably post Upper Roan.

C. Geology and mineralization of the study areas.

In five of the eight study areas the most important rock type is serpentinite (ultramafic) and in two of the other three areas mafic rocks (amphibolite and mafic greenstones) are important. The geology and mineralization of each study area is described below; those wherein ultramafic rocks are dominant being presented first. The rocks of the Darwendale and Dalmainy Farm areas contain no known sulphide or arsenide mineral deposits. All the other areas include deposits of sulphide and/or arsenide minerals.



Not to scale: A–B several tens of miles

Diagrammatic geological sketch map to illustrate the setting of the Kalumbila area.

3

1. The Darwendale section of the Great Dyke.

The location and broad configuration of the

Table 2. Table of geological formations in Zambia. (after Reeve (1960)).

Age	System	Series/lithology
Recent		alluvium and eluvium
Pliocene	Kalahari system	Kalahari beds
	DOLERITE	
	Karroo system)	(Stormberg series (Lower Beaufort series (Ecca series (Dwyka series
	YOUNGER GRANITE	
Later pre-Cambrian	GABBRO	
	Katanga system)	(Kundelungu series (Mwashia series (Upper Roan series (Lower Roan series
	BASIC INTRUSIVES AND OLDER GRANITE	
Basement Complex (early pre-Cambrian)	Muva system)	(quartzite, schist (Kafue and Rufunsa (volcanics
	Lufubu system	Lufubu schists

Great Dyke is indicated on Figure 2.

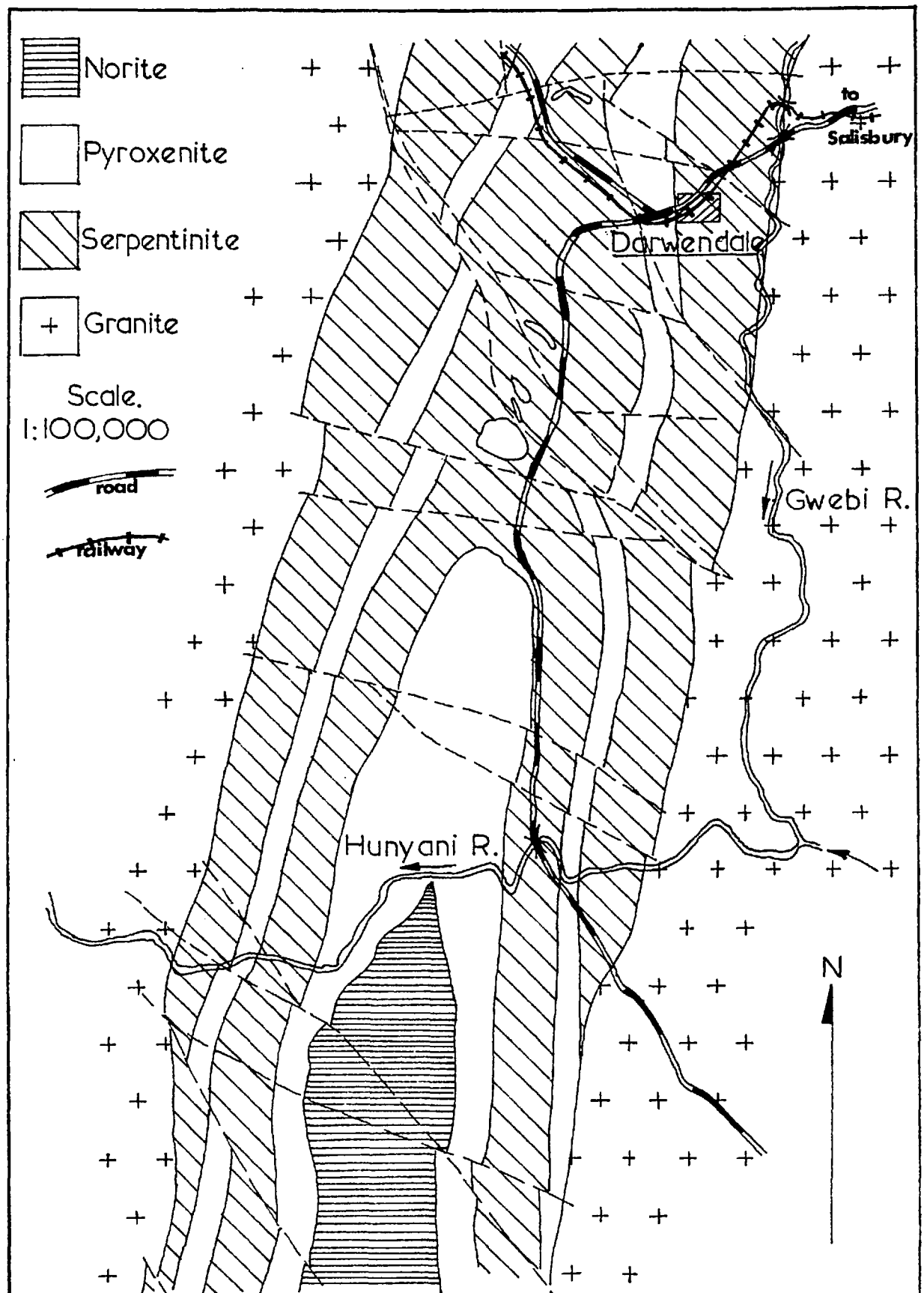
It is a layered intrusion made up essentially of serpentinite, pyroxenite and gabbroic rocks. Gravity

differentiation has played a part in the layering of the dyke rocks. Lithologically it has similarities with the Bushveld Igneous Complex of the Republic of South Africa. The cross sectional shape of the Dyke is not known with certainty and discussion of a number of hypothetical shapes appears in the literature (Weiss, 1940 ; Worst, 1960).

Near Darwendale serpentinite, thought to be derived from dunite, underlies by far the largest part of the Dyke surface (Figure 4). According to Worst the most common serpentine rock of the Dyke here is a fine grained granular rock containing two to three per cent chromite by volume. Relict olivine textures are clearly evident. Worst has suggested that these olivine outlines indicate that the original minerals underwent very little (if any) increase of volume during the process of serpentinization.

The pyroxenite in the area is generally unaltered. It is a coarse grained anchi-monomineralic rock made up of orthopyroxene with very subordinate olivine and very occasional plagioclase and chromite.

Worst terms the rocks made up of varying proportions of plagioclase and pyroxene, gabbroic rocks.



General geology of the Darwendale area. (After Worst (1960))

4

He refers to those in which orthopyroxene is dominant as norites and those wherein clinopyroxenes predominate as gabbros; the term gabbroic rocks thus includes both types. The only outcrop of gabbroic rocks in the area under discussion is the norite south of the Hunyani river (Figure 4).

2. Dalmainy Farm.

The Dalmainy Farm serpentinite mass is a typical example of the serpentinite bodies occurring within a number of schist belts ranging in age from Sebakwian to Shamvaian. In general they are more or less conformable but they do have intrusive features. The country rocks are commonly greenstones, tremolite-chlorite schists, banded ironstones (magnetite - quartz - goethite schists) and other interbedded metasediments.

The body is thought to be intrusive into the rocks of the Umvuma schist belt (Figure 5). It is poorly exposed but clearly more resistant to weathering and erosion than the enveloping tremolite - chlorite schists in that it forms a low ridge.

Large scale faulting has affected the body (Figure 5) but there is no obvious cleavage or fracture.

General geology of a part of the Umvuma schist belt around Dalmainy Farm. (After Bliss, 1962)

5

Present knowledge is based on a study of the rather poor exposures and drill hole data. Serpentinite appears to be encasing a dunite core. The writer has had no chance to examine the rocks in thin section but Bliss (1962) found textures which he thought were relics of olivine pseudomorphs and has suggested that the entire body was once dunite.

In hand specimen the serpentinite is a grey-green colour, fine to medium grained, possibly dominantly serpentine and talc. There is, however, some quartz and limonite. The siliceous, ferruginous boxwork observed in many outcrops is probably a secondary feature and has little significance in terms of the chemistry of the serpentinite itself. Bliss has found evidence to suggest that Karroo rocks once covered the area and he thinks that silicification at the base of the Karroo succession might have extended into the underlying serpentinite now exposed after erosion.

3. <u>The Perseverance prospect</u>.

The Perseverance prospect is within the Exclusive Prospecting area (E.P.A.) No. 85. The E.P.A.

covers part of the Lower Umfuli schist belt in which occur lenticular pods of serpentinite similar to those of the Umvuma schist belt. The study area includes one of these serpentinite bodies.

(a) Geology.

The rocks enveloping the serpentinite are metavolcanics, locally altered lavas and sheared and metamorphosed agglomerates and tuffs. These rocks strike approximately north east and are generally very steeply dipping. They are possibly of Shamvaian age. Epidiorites, probably belonging to the Bulawayan system crop out to the east of Perseverance (Figure 6). Deweras lavas lie unconformably on the Basement rocks to the west of the prospect.

No prominent cleavage has been observed in the serpentinite but it exhibits a blocky fracture. It is thought to be a metamorphosed sill of ultrabasic rock, probably granular peridotite (Dobell, 1938). Like the Dalmainy Farm serpentinite it is grey - green and reported by Dobell to be, in common with other serpentinite bodies of the Lower Umfuli schist belt, "a fine grained felt of microscopic laths and fibres

General geology of the area around the Perseverance prospect. (After Dobell, 1938)

of crysotile and antigorite".

(b) Mineralization.

Massive and disseminated sulphides occur in a shear zone which is vertically disposed and slightly oblique to the serpentinite - metavolcanics contact down to 100 ft. Below this depth the mineralized shear zone flattens and follows the serpentinite - metavolcanics contact. The paragenic problem of sulphide mineralization in relation to shearing has not been satisfactorily solved.

The principal ore minerals, which occur as disseminations, fracture fillings and along shear planes, are pyrrhotite, pyrite, and chalcopyrite. Other minerals are pentlandite (flame-like exsolution bodies in pyrrhotite) and sphalerite together with magnetite and ilmenite, the latter in parts altered to leucoxene. Gersdorffite, maucherite, ullmanite and chloanthite have been noted locally in one drill hole.

The depth of the oxidized zone is not known with certainty but it is reported that oxidation is incomplete at 65 ft. below surface (Woodward, 1962). The secondary nickel mineral garnierite[1] has been

[1]The term is used here to denote nickel - magnesium hydrosilicates, probably of variable composition.

observed in the area. It occurs, together with fibrous crysotile and antigorite, in fracture planes in the serpentinite away from the mineralization. There is a well developed gossan over the ore horizon and a blue encrustation in this gossan may be an hydrated nickel-iron mineral.

4. The Maritzani area.

This study area is centered on a second lenticular serpentinite body of the Lower Umfuli schist belt.

(a) Geology.

The serpentinite mass outcrops on Maritzani Farm, some eight to ten miles south of Perseverance. The geological setting is analagous to that at Perseverance and the rock types are the same. The Maritzani serpentinite is, however, elongate in an east-west direction (the direction of the trend of the Lower Umfuli schist belt and the strike of the schistosity locally). The serpentinite is flanked to the south by metavolcanics and to the north by metasediments and

other rocks. Whereas the Perseverance serpentinite mass outcrops as a strong topographic feature the Maritzani body crops out on a gentle slope to a vlei. The blocky fracture observed in the serpentinite at Perseverance is less prominent at Maritzani.

(b) Mineralization.

Nickel-copper sulphides occur in a shear zone at and slightly oblique to the southern margin of the serpentinite. The mineral assemblage and fabric is also essentially the same as that at Perseverance. There is however, no gossan at Maritzani.

5. The Region of the Empress Prospect and the adjacent Bare Bottom Hill.

(a) Geology.

The following description is based on data published by Sharpe (1961), and on company data (M.S.A. (Pvt.) Ltd.).

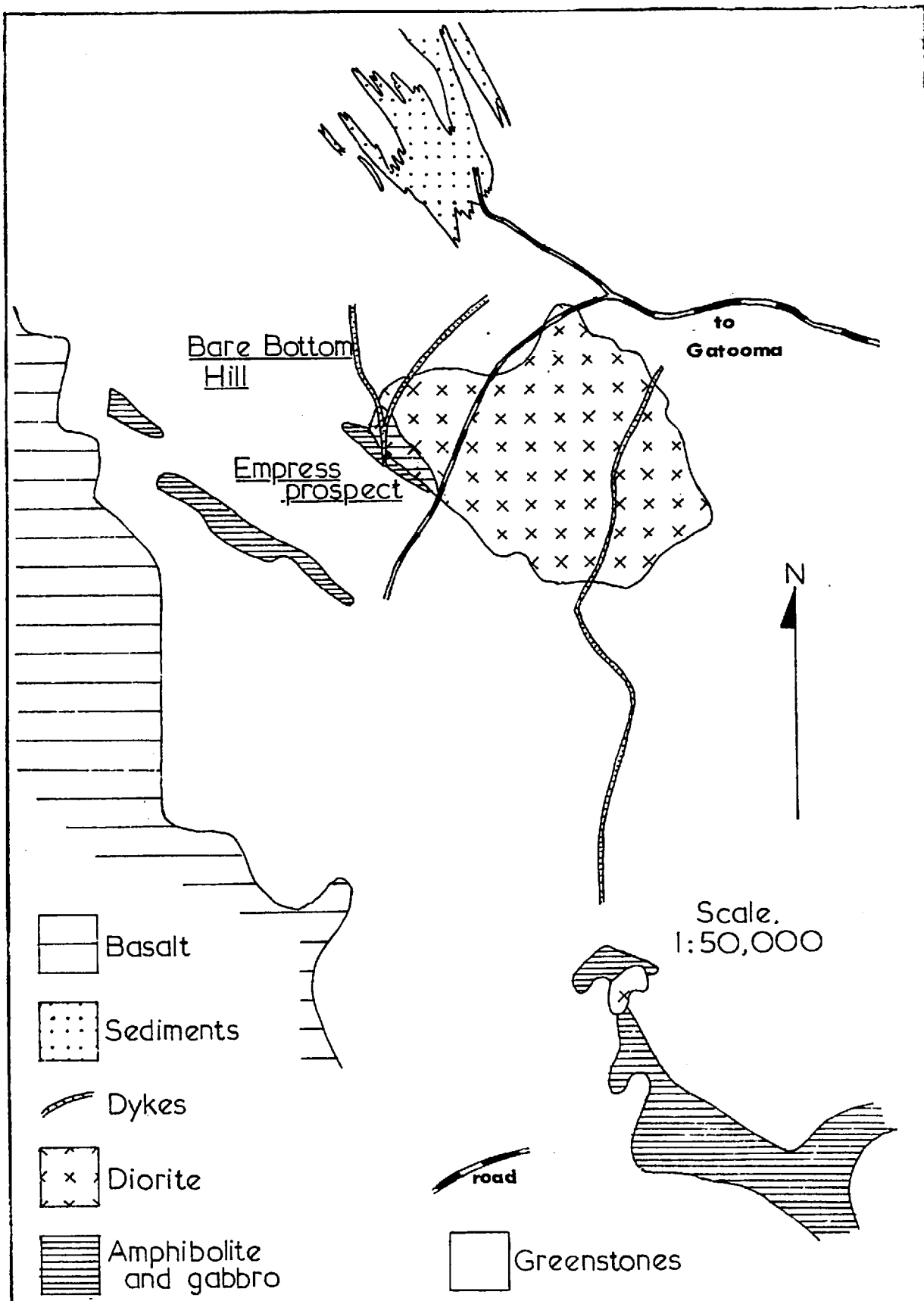
The region is for the most part underlain by rocks of the Basement Complex but attention has been

focussed around a dioritic stock, ovoid in shape and surrounded by pre-Cambrian greenstones of the Bulawayan system. At the south west margin of the stock there is an amphibolite body between the diorite and the Basement rocks (Figure 7).

The stock terminates abruptly against the greenstones but the contact between diorite and amphibolite is a transitional one (the 'mixed zone') consisting of alternating leucocratic (dioritic) and melanocratic (amphibolitic) bands. The gradation from the stock to the amphibolite takes place over a maximum of 450 ft., the number and width of the amphibolite bands increasing with distance from the diorite. In the mixed zone the individual rock types range from one inch to several feet in thickness. The general direction of banding is parallel to the periphery of the stock as is the strike of the amphibolite-greenstone contact.

Crossing the area are two andesitic dykes. They strike north to north north east.

The amphibolite at the Empress prospect suboutcrops on fairly level ground but the greenstones comprising Bare Bottom Hill form a pronounced topographic feature.



General geology of the region including the Empress and Bare Bottom Hill study areas.

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M.S.A. (Pvt.) Ltd.

(b) Mineralization.

The Empress prospect mineralization is a zone of disseminated nickel-copper sulphides within the amphibolite body sandwiched between the dioritic stock and the greenstones. On average, the ore zone has a true thickness of 50 ft. and a surface strike of the order of 2000 ft. which is reduced to 500 ft., 2000 ft. below surface.

The principal ore minerals are, in order of abundance, pyrrhotite and pentlandite, chalcopyrite, pyrite, violarite and some chalcocite. Pentlandite, intimately associated with pyrrhotite, is the most important nickel bearing mineral.

Widespread pyrrhotite and chalcopyrite minerals also occur erratically in the mixed zone.

At Bare Bottom Hill nickel - copper sulphide minerals occur as disseminations in the greenstones.

The oxidized zone extends to 50 ft. below surface.

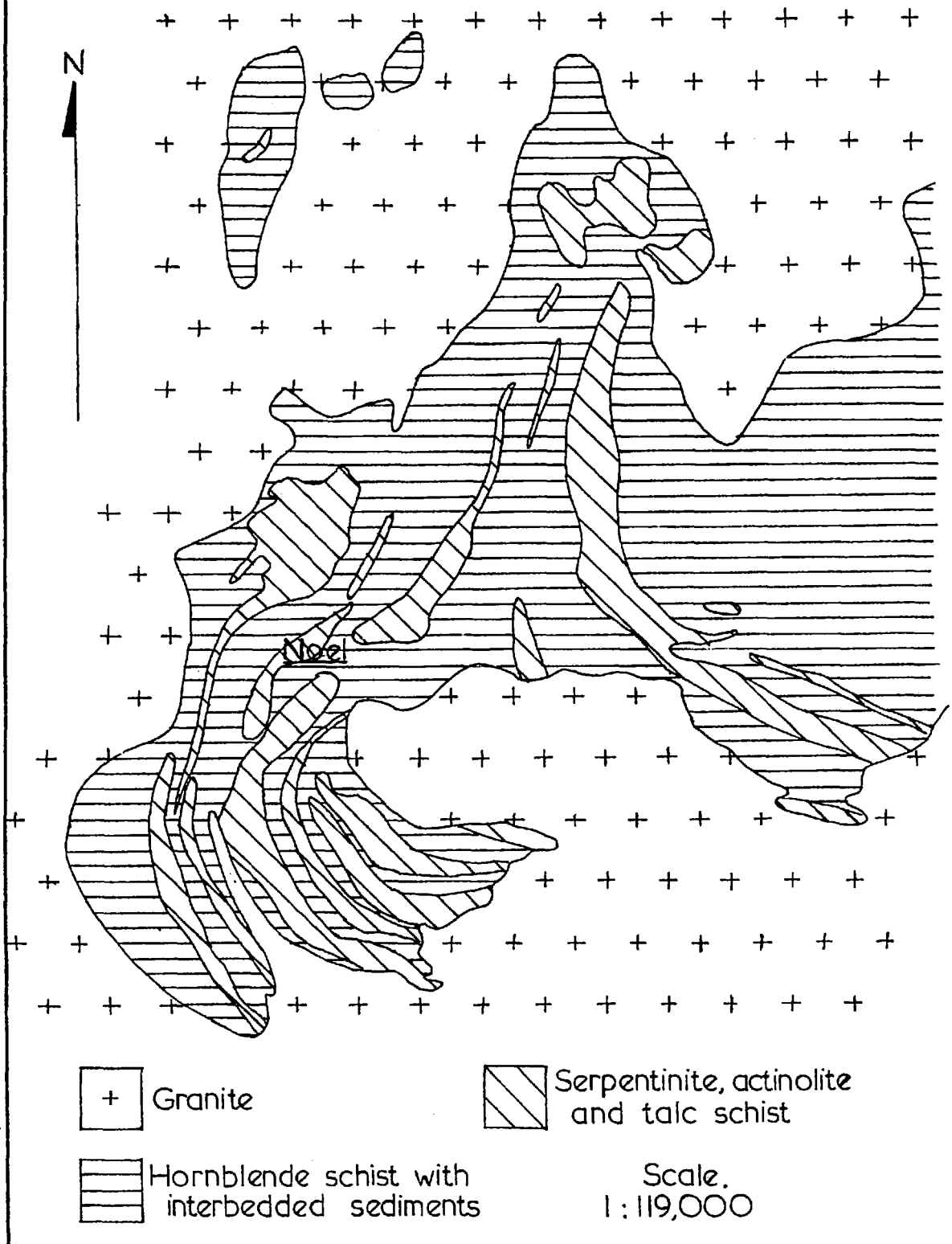
6. <u>The Noel Nickel mine and environs.</u>

(a) Geology.

The Noel Nickel mine is in serpentinite and schists which form part of the Lower Gwanda schist belt. Serpentinites, actinolite rocks and talc schists forming a 'serpentinous group' have been intruded into hornblende schists (Phaup, 1933). The rocks of the serpentinous group are thought by Phaup to be derived from peridotite and the hornblende schists are considered to be derived from basaltic lavas. Metamorphism, folding and faulting have been severe. There has been intensive carbonate replacement.

The Basement Complex in this area includes pure crystalline magnesite, banded ironstones, mica schists and quartzites as well as the serpentinous group and the hornblende schists (Figure 8).

There is an early set of faults trending between north north east and north north west and dipping westwards at 35-60°. A second fault system trends east north east roughly paralleling the strike of the rocks. This latter fault system is almost vertical but dips of faults, where obvious, are to the north north west. Most of the faults in the area have, as far as can be ascertained, a small throw and both sets affect all the rocks of the Basement Complex.



General geology of part of the lower Gwanda schist belt.(After Phaup, 1933).

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(b) Mineralization.

The mineralization is the only known arsenide nickel deposit in Rhodesia or Zambia. It is closely related to and controlled by the structure, the main features of which have been described in the previous paragraph.

The principal ore minerals are chloanthite and niccolite. The best mineralization occurs as massive and disseminated arsenides in the fault zones. It occurs in the main in the faults of the younger system (striking east north east) and ore shoots pitch westwards paralleling the dip of the early fault system into which the mineralization has extended where faults of the two systems intersect. The fissures containing the mineralization are slickensided and along the fault lines are zones of dark green, fine grained chlorite schists in which conspicuous octahedral crystals of black magnetite have been developed.

The oxidized zone is thought to be shallow but no quantitative data about this zone is available. The zone is characterised by green blooms - probably garnierite. In addition there are black powdery materials, thought to be mixtures of limonite, pyrolusite and

other oxides. Calcite and silicates occur as veinlets and interstitial gangue minerals.

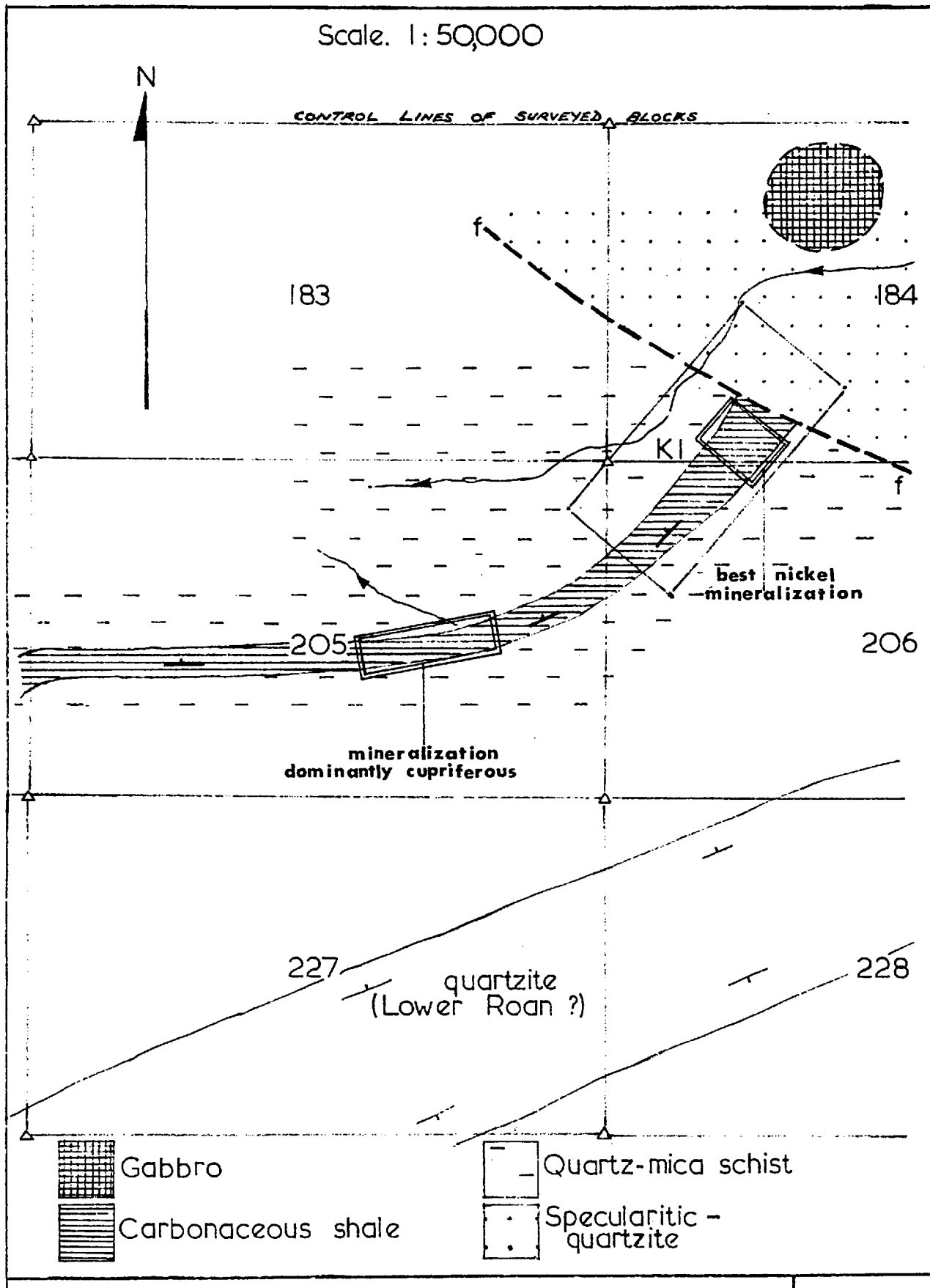
7. The Kalumbila area, North Western Province, Zambia.

(a) Geology.

The area lies between the Mombhezi and Kabompo domes, the granites and gneisses of which are representatives of the Basement Complex in the North Western Province (Table 2). Younger rocks in the Kalumbila area are quartz-mica schists, sericitic-specularitic quartzites and a carbonaceous shale (Figure 9).

The data available to the writer is insufficient to permit any attempt at correlation between rocks of the North Western Province and those of the Copperbelt. Westwards from the Copperbelt there are marked facies changes as the degree of metamorphism increases, thus complicating correlation, especially in a country so poorly endowed with outcrops.

The carbonaceous shale is the mineralized horizon at Kalumbila. It is a highly contorted shale or phyllite having a maximum true thickness of 1500 ft. It dips north-westwards at angles of 30-60°. It is



General geology of the Kalumbila area, North Western Province, Zambia.

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schistose and foliated throughout, compositionally banded, variegated in texture and colour and intensely folded and fractured.

Samples of the shale have been examined by Zurbrigg and Podolsky (1963) and in their descriptions they have used the terms "banded graphitic schist", "kyanite/muscovite schist" and "corundum-kyanite gneiss".

The shale is composed of quartz, mica (sericite, muscovite, chlorite) and kyanite with minor quantities of tourmaline, graphite, phlogopite and traces of green spinel and corundum. Secondary quartzose material is common in stringers either discordant or parallel to the bedding. Carbonate (principally calcite) occurs in small amount, particularly near the base of the sequence. The shale does outcrop in parts and the outcrops at the north eastern end of the strike are silty in character. Gibson, (pers. comm., 1962), has suggested the possibility of surface silicification to explain the silty nature. However, a more likely explanation is that there is a gradation from a graphitic shale in the south west to a silty shale in the north east.

The hanging wall, footwall and interlensed schists are all rather similar and composed essentially of quartz, sericite, muscovite and talc. These rocks

are less resistant than the shale. They are similar in attitude and extremely schistose but not fractured to the same extent as the shale.

(b) Mineralization.

Nickel-copper sulphides occur within the carbonaceous shale. There are lenses, pockets and bands of mineralized shale. The principal ore minerals are pyrite, chalcopyrite, pyrrhotite and nickeliferous pyrrhotite and minor pentlandite and siegenite. These minerals are present as anhedral, massive grains and as fracture fillings in some of the silicate minerals. There is some limonite staining in the hanging wall margin of the shale.

Sparse disseminations of sulphide minerals do occur in the interbedded and adjacent schists but it is not known whether they are nickeliferous.

D. Geomorphological and drainage features.

A number of erosion surfaces have been identified in Southern Africa. They have been recognised and described by several authors, notably Dixey (1944) and King (1951).

The oldest erosional surface is the 'Gondwana' surface, (King). It is evidenced in Rhodesia by the flat topped hills and peaks and in Zambia by monadnocks of resistant strata which rise, to an approximately common altitude, out of the main 'African' surface. A third cycle of erosion is represented today by the broad valleys carved into the African surface. Dixey has described this third surface, the Late Tertiary, as"a valley form peneplain".

The extensive African surface is the dominant geomorphological feature. In Rhodesia this surface forms the main watershed which runs in a broad arc from Bulawayo through Que Que and Enkeldoorn to Umtali (Figure 10), and which divides the Makarikari depression/ Zambezi basin on the west and north from the Sabi/Limpopo basin in the south east.

The average altitude of the African pediplain

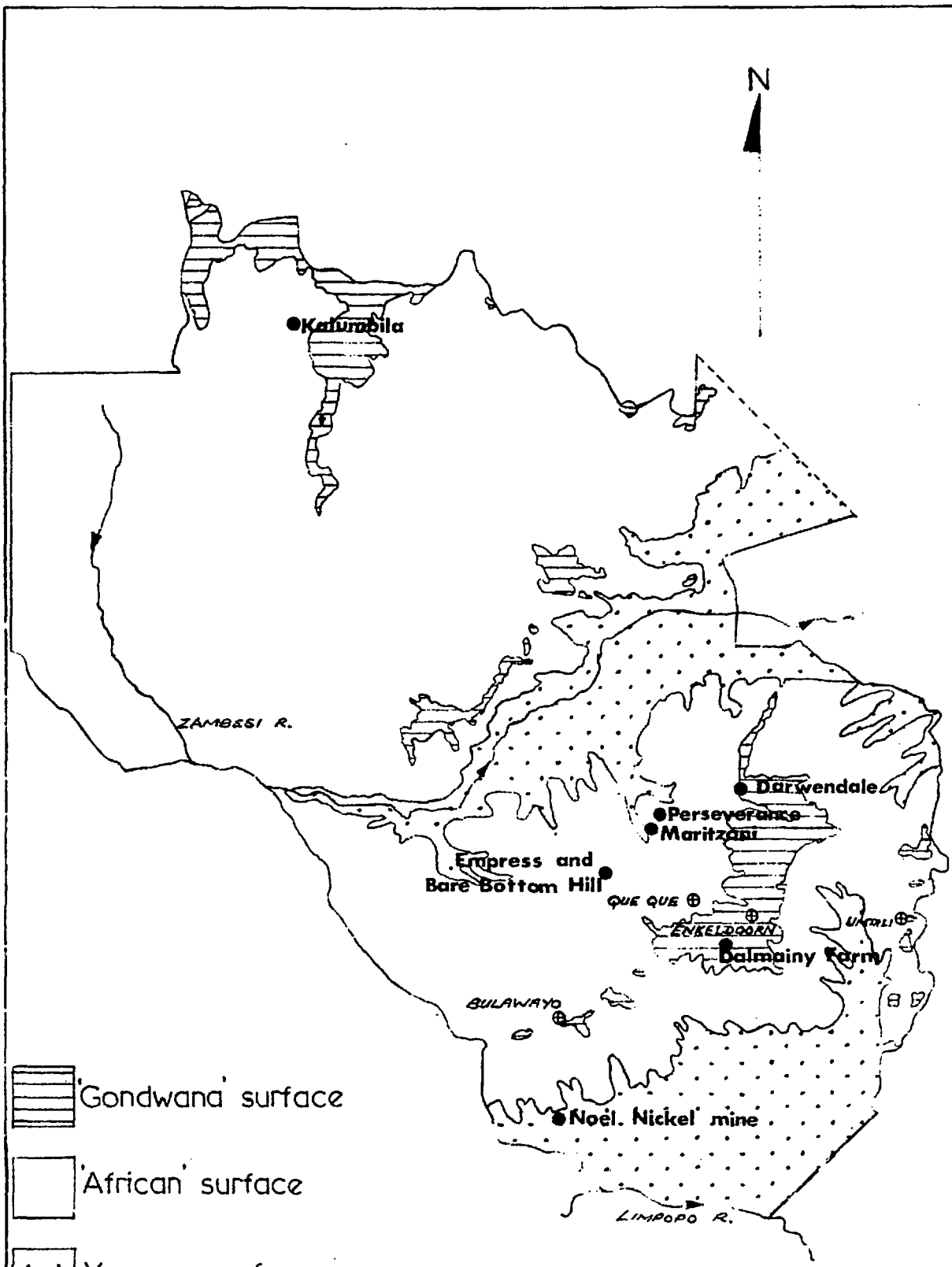
(King) in Rhodesia is a little greater than it is in Zambia. It is possible that there has been flexing along a line parallel and close to the Zambezi river in Recent times and that as a result Rhodesia has been fractionally uplifted relative to Zambia. Along the watersheds in Rhodesia the average altitude of the African surface is close to 4500 ft., in Zambia, it is nearer 4200 ft. There is some evidence to suggest that this surface in Zambia has been warped in parts.

Practically the whole of the western half of Zambia is drained by rivers flowing, ultimately, into the Zambezi. The main watershed extends from Broken Hill, through Kapiri Mposhi and the Copperbelt, to form the Zambia - Congo border (Figure 10).

1. Relationship between topography and geology.

The terrain in both countries can be described as undulating, more gently so in Zambia than in Rhodesia. In the latter territory the undulating land surface is punctuated by local features of sharp relief.

In Rhodesia, the topography largely reflects the geology. The higher ground, the hills and ridges, is



Erosion surfaces in south-central Africa. (After King, 1951).

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commonly rocky and indicates the presence of the more resistant rocks. Larger river valleys may follow contacts and fault and fracture zones. Shallow depressions devoid of trees but frequently supporting a good grass cover are also often found to be developed over contacts between different rock types.

In the North Western Province of Zambia, as in Rhodesia, the more resistant formations form the topographic high features and short steep valley slopes occur where streams flow close to the higher ground. Low lying, well grassed treeless areas are also prominent features of the Zambian landscape (see below).

The sharper topographic features result from recent ~~the~~ incisions into the African and Late Tertiary surfaces.

2. Vleis and dambos.

In Rhodesia the low lying, open, well grassed areas referred to above are termed 'vleis', in Zambia they are known as 'dambos'. The typical vlei is not common in large river valleys but is best developed in tributary valleys. They may or may not have a definite watercourse.

In the Copperbelt area and North Western Province of Zambia there are two distinct types of dambo, viz:-

(i) The headwater dambos.

(ii) The riverine dambos.

The headwater dambos are level or very shallow basin shaped dambos wherein many streams have their origins. The riverine dambos, occurring at slightly lower altitudes, have a ribbon like configuration and flank the watercourses for many miles. Open watercourses are present in most riverine dambos. Between headwater and riverine dambos the drainage way is commonly incised.

Both types of dambo are commonly swampy, seasonally at least, and there is a flow of water from the higher to the lower parts. In some areas of Zambia dambos may dry out during the dry season but in the Kalumbila area most dambos remain moist, if not saturated, all year. Most vleis are swampy during the rainy season. They dry out on the surface during winter but the deeper horizons may be still damp at the end of the dry season.

The various shapes and sizes of dambos and the pattern of their distribution are related to geology

and weathering. Garlick (1961), writing about the Copperbelt area of Zambia, has summarized the characteristics of dambos. He says; "The sizes and shapes of the dambos reflect the type and depth of weathering of bedrock. Dambos over granite are long, wide and gently curving, following major fractures. Over Basement schists they are commonly small, spatulate, and arranged on a reticulate pattern. Over well drained arenaceous beds they are rare, whereas over carbonate formations they may be wide and discontinuous, with heavy bracken and shrub growth, poorly defined margins and occasional sink holes and standing ponds." Garlick's summary is also applicable to the dambos in the Kalumbila area.

E. Soils

The soils of the Rhodesian study areas contrast markedly with those at Kalumbila. Of all the factors affecting soil formation and deciding the soil characteristics that playing the dominant role in Rhodesia is the nature of the parent material. The factor exerting the most influence in the North West of Zambia is the climate (see below).

Many types of Rhodesian soils have shallow profiles and, inasmuch as the degree of chemical weathering and profile development are not well advanced, can be regarded as being immature. The

possibility of uplift of Rhodesia in Recent geological times has been suggested. With such uplift considerable erosion must have taken place and the present cycle of soil formation is thought to be developing on the recently exposed bedrock or the C horizon of an earlier cycle of soil formation.

The soils in both countries are forming under a markedy seasonal climate (Section F). In the general case two types, (1) the freely drained soils and (2) soils developed under conditions of impeded drainage, can be distinguished.

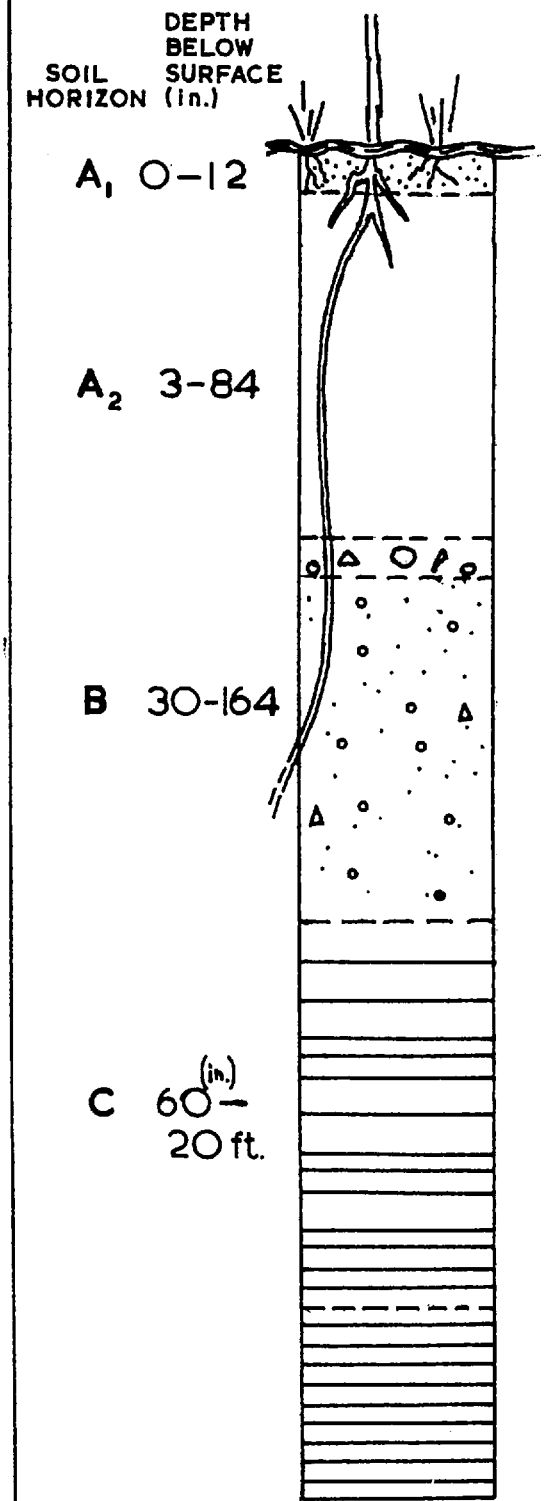
1. The freely drained soils.

There is a gradation in the character of the soils from well developed latosols in the Kalumbila area, southwards through the chernozemic soils of the Rhodesian Midlands to a lithosolic soil in the environs of the Noel Nickel mine.

Latosols cover much of the North Western Province of Zambia and they are, due to the high rainfall, severly leached and low in alkali and alkaline earth elements. They are, consequently, more often than

not of acid reaction. Accumulations of iron and aluminium hydroxides are usually present in a reasonably well defined horizon a few feet below surface. This horizon, commonly called the laterite layer, is usually composed of unconsolidated, predominantly ferruginous nodules and other angular rubble. Where the profile has been truncated by erosion the laterite layer is indurated and often forms small scarps overlooking the streams. The near-surface horizons are characteristically sandy and the profile as a whole often of considerable depth (Figure 11).

Many of the freely drained soils of the Rhodesian study areas are characterized by a darker coloured A horizon overlying paler coloured parent material. The A_1 horizon often includes detrital raw organic matter (leaf and twig fragments and plant roots) and probably some humic substances but there is no true surface humus layer. The upper layers of the profile are often varying shades of red-brown thought to be due to ferruginous and possibly, in some instances, calcareous compounds. The reaction is frequently weakly acid or alkaline. There is not always a B horizon. In many profiles the A horizon soil grades with depth into fractured and weathered bedrock (the C horizon).



Leaf mould
Sandy topsoil, penetrated by grass roots, loose texture

Sandy-silty soil, more compact than A_1, fewer roots

Stone line

Rubble zone, clay size particles to small boulders, fragments of rotten rock, quartz and nodular ferruginous concretions

Silty-clay, after rotten bedrock in situ, bedding and/or schistosity often visible, iron staining decreasing in intensity with depth, grades with depth into ...

Weathered bedrock

Generalized profile through typical freely drained soil in the Kalumbila area.

The soil profiles in Rhodesia (Figures 12 and 13) are generally very much shallower than in Zambia.

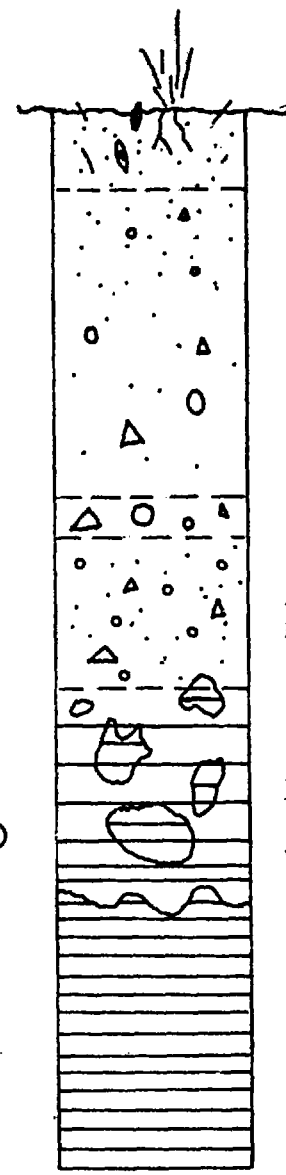
There is considerable diversity in Rhodesian soils which is believed to reflect the different mineralogical compositions of the parent materials. For example, over the extensive areas of granite and granite gneiss the soils are sandy. Over the greenstones of the schist belts red loams prevail. Over Archean serpentinite the soil cover is extremely thin. It is made up of a high proportion of physically comminuted mineral particles and profiles are very shallow indeed, rarely exceeding five feet from surface down to the C horizon.

The soils in the environs of the Noel Nickel mine, however, have the characteristics of low rainfall area (desert) soils. The skeletal profile is extremely shallow. Chemical weathering is retarded and the soils are poor in clay minerals. As a result of the limited leaching the soils are relatively well supplied with bases and are of alkaline reaction.

2. Soils developed under conditions of impeded drainage.

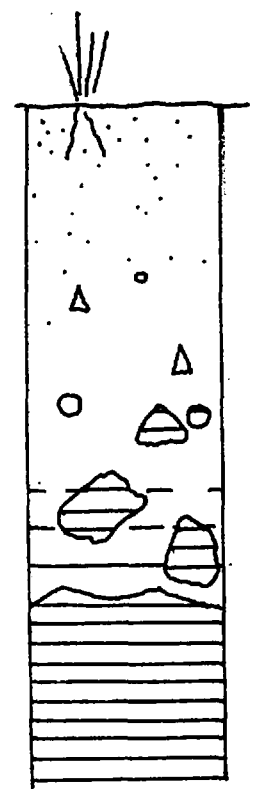
Whereas the freely drained soils are

SOIL HORIZON	DEPTH BELOW SURFACE (in).	
A_1	0 – 9	Sandy clay (loam), loosely friable, containing raw organic matter (leaves, twigs and grass roots)
A_2	3 – 36	Clay-grit, often with rubble up to coarse gravel size, in some instances grading into fractured bedrock, elsewhere culminating in a stone line
B	12 – 48	Accumulation of ferruginous material, with the formation of nodules in some areas, not always present
C	24 – >60	Rotten and weathered bedrock



Generalized profile through typical freely drained soil of the Rhodesian Midlands.

SOIL HORIZON	DEPTH BELOW SURFACE (in.)	
A	0-24	Sandy soil with much weathered rock and quartzitic rubble, grading with depth into ...
C	3 →36	Weathered bedrock and fresh bedrock



Generalized profile through typical freely drained soil of the Noel area.

classified as zonal the soils developed under conditions of impeded drainage are intrazonal. The soils of this type are those that form in the low lying areas, the vleis and dambos. They are commonly grey or black, the colouring probably being due to dark humus substances. The vlei and dambo soils are not well aerated. Parts of some dambos may be saturated all year and others, and most vleis, are usually saturated for a period each year. The pH is variable, commonly alkaline in areas of low rainfall where calcrete nodules may be present at a depth of a few inches, but acid in wet climates.

Vleis formed over Great Dyke serpentinite in the Darwendale area are characterised by clay rich soil which forms wide cracks when it starts to dry out.

In the lowest parts of the dambos in the Kalumbila area abundant organic matter in all stages of decomposition has accumulated at the surface. Because of the high organic carbon content the uppermost few inches are black but pale in depth to a grey and sometimes rusty mottled zone. The iron is kept in the ferrous state in the essentially reducing conditions although the mottling is taken to indicate periodic changes to oxidizing conditions, possibly

for a short time each year. The reaction in the grey dambo soil (glei soil) is acidic, frequently very strongly so but the pH may increase with depth.

Examples of soil profiles are presented in Chapter 4 where the distribution of nickel in the profiles is discussed.

F. Vegetation.

The character of the vegetation over the freely drained soils of the study areas varies from open woodland and savannah in the Rhodesian areas to denser woodland in the North Western Province of Zambia. The trees of the deciduous woodland are well spaced and in the north west of Zambia of fairly even density. At Kalumbila the leafy canopy is almost continuous, being interrupted only by the open, grassy dambos. In Rhodesia the woodland is more open and less regular, broken by the vleis and tracts of rolling, grassy savannah. Even at Kalumbila the leafy canopy does not seriously exclude light and there is an undergrowth of perennial grasses, shrubs and herbs.

The woodland of Zambia is a Brachystegia-

Isoberlinea (Jubelnardia) assemblage, so named after the two most common genera. Brachystegia is also the commonest genus over much of Rhodesia except in the lowveld (low rainfall, low altitude regions) where Colophospermum and Acacia abound and where the ground cover is sparse compared to that of the Rhodesian Brachystegia woodland. The trees of Zambia may attain heights of 90 ft. in the North Western Province although 40-50 ft. is nearer the average and they are finer and larger specimens than their Rhodesian counterparts, clearly thriving on the greater precipitation and deeper soils. Some common trees of the deciduous woodland of the North Western Province of Zambia are listed in Table 3 and common species of the Rhodesian savannah and lowveld in Table 4.

The unusual drainage conditions prevailing in dambos are responsible for the special flora. The absence of trees in the dambos has been reported as being ascribed to lack of oxygen in the ground waters of the dambos, (Tooms, 1955). This explanation may also be applicable to vleis. Riverine dambos are, however, frequently characterised by an extremely dense growth of trees, shrubs and creepers along, and

limited to, the stream banks. This dense foliage is called 'mushito'.

Table 3. Some common trees of the deciduous woodland, North Western Province, Zambia.

Vernacular name.	Botanical name.
Muputu	Brachystegia spiciformis
Musamba	Brachystegia boehmii
Muwombo	Brachystegia longifolia
Mutobo	Isoberlinea tormentosa
Mutondo	Jubelnardia paniculata
Museshe	Marquesia macroura
Mwenge	Dipplorrynchus mossambicensis

Table 4. Some common trees of Rhodesia.

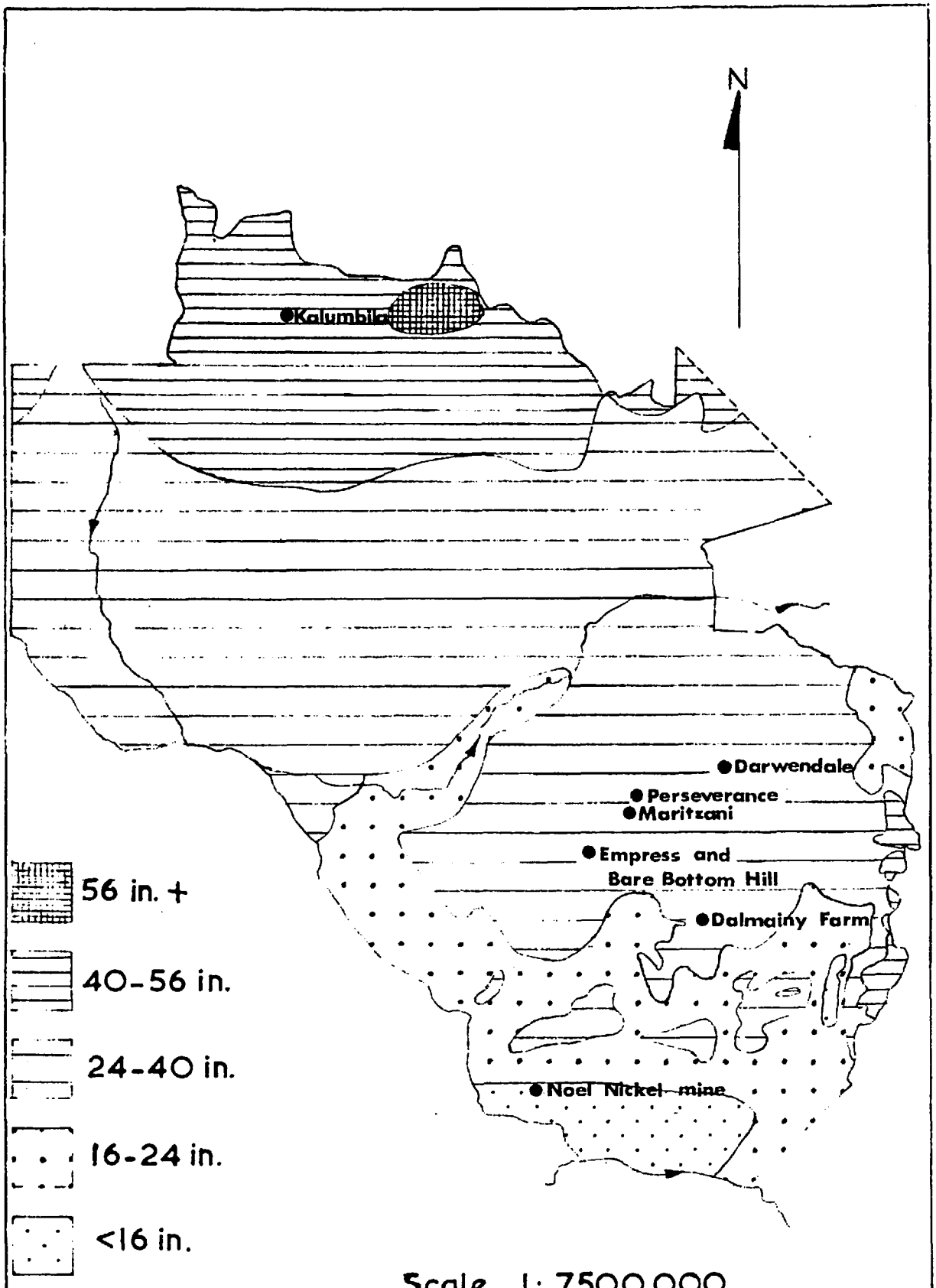
Vernacular name.	Botanical name.
(a) Trees of open savannah woodland.	
Msasa	Brachystegia spiciformis
Mfandaludzi (Mfuti)	Brachystegia boehmii
(b) Trees of areas transitional between open savannah woodland and lowveld.	
Mklama	Combretum apiculatum
Mplingo	?
-	Acacia (many species)
(c) Trees of the lowveld.	
Mopani	Colophospermum mopane
-	Acacia (many species)

G. Climate.

Rhodesia and Zambia, despite being well within the tropics, have a temperate, strikingly seasonal climate with warm wet summers and temperate dry winters.

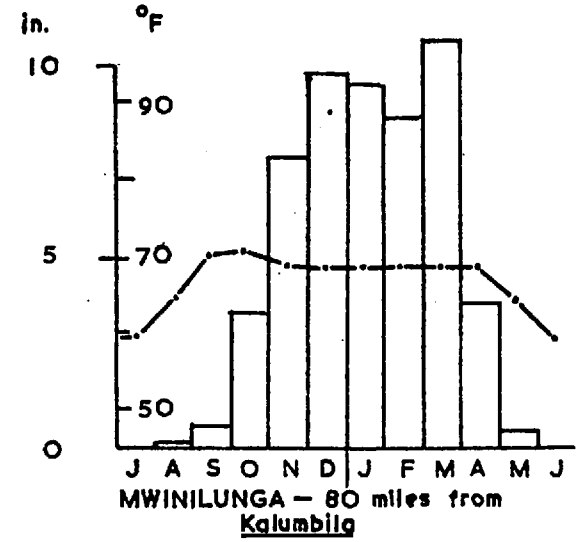
The rainfall varies from less than 10 in. per annum in the southernmost parts of Rhodesia to over 50 in. per annum in the North Western Province of Zambia (Figure 14). There is a distinct rainy season lasting from about the beginning of November until the latter half of April. In the Kalumbila area there are some indications of a break in January-February (Figure 15). In the extreme south of Rhodesia where conditions are very dry one cannot really speak of a rainy season. During the last four years the annual rainfall at the Noel Nickel mine has not exceeded 8in.

The study areas are plotted on Figure 14 and the climatic data presented in Figure 15. This data is important, as reference to climatic differences between areas will be made in later chapters. Climate is, furthermore, fundamental insofar that it influences the flow of water in rivers and streams and ground water level. Few Rhodesian rivers have a perennial flow whereas

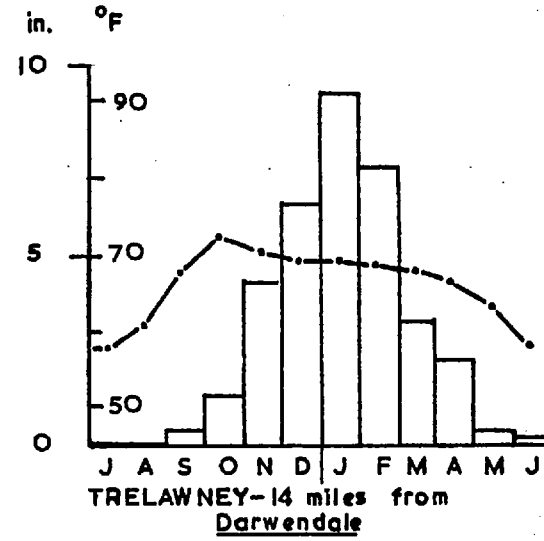


Mean annual rainfall; Rhodesia and Zambia.
(After Peake, 1961)

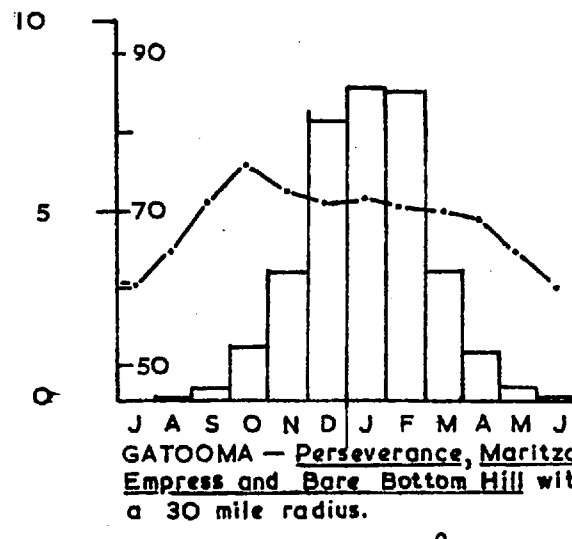
14



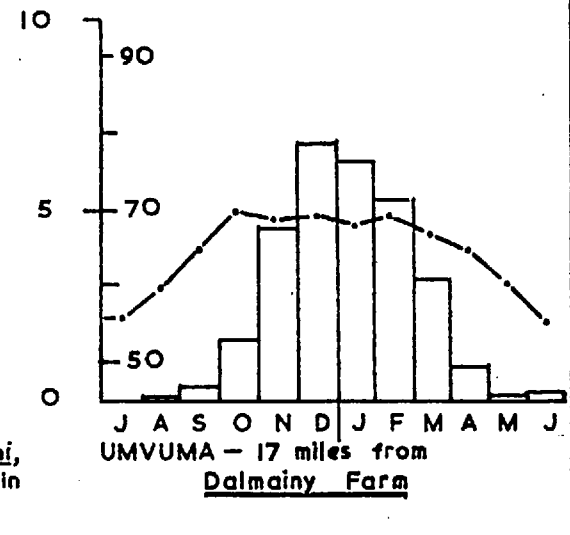
MWINILUNGA — 80 miles from Kalumbila



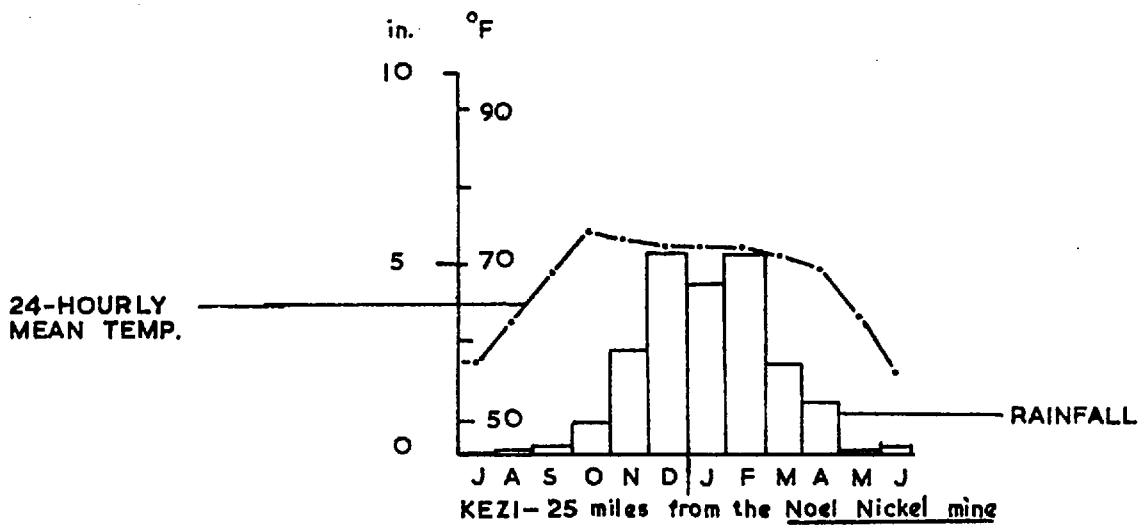
TRELAWNEY — 14 miles from Darwendale



GATOOMA — Perseverance, Maritzani, Empress and Bare Bottom Hill within a 30 mile radius.



UMVUMA — 17 miles from Dalmainy Farm



KEZI — 25 miles from the Noel Nickel mine

Climatic data for meteorological stations closest to the respective study areas.

many rivers and streams in the Kalumbila area contain water all year round.

Temperatures are high in the low lying parts of the countries but are moderated over wide areas by altitude (large areas of both countries stand above 3500 ft.).

Chapter 2. FIELD AND LABORATORY TECHNIQUES.

Field techniques are described first followed by a discussion of the analytical methods used and other laboratory procedures followed. Analytical methods employed during the course of the investigation are reported in outline only, with a reference to relevant literature, except in cases where the procedures are unique or very important when they are more fully described. Discussion of company analytical data is included at the end of the analytical section.

Part I. METHODS OF SAMPLING.

The procedures followed in sampling are described below. The discussion is divided into sections according to the different materials sampled.

A. Near-surface soils. (soil sampling)

Company samples were collected between surface and 18 in. Commonly they were grab samples from between 6 and 12 in. below surface.

Samples collected by the writer were vertical

channel samples with a maximum length of channel of 1 ft. Soil sampling was not related to soil horizons and in most cases the writer adopted the procedure of taking two samples at each site, one above the other, usually 0-3in. and 3-12in. respectively. In certain instances maximum depth of sampling was extended to 18 in. in three samples of varying channel length.

Generally speaking all samples were from the A soil horizon.

All samples were collected in pre-numbered kraft paper envelopes.

B. Sampling of the soil profile. (Pitting)

In all pits vertical channel samples were collected. The sample channel length was varied and related to soil horizons, channels being cut up to but not across the boundaries between the horizons. Except in the Kalumbila area the channels were confined to a maximum length of 1 ft.

C. Sampling in the drainage ways.

1. Stream sediment sampling.

Samples of the stream sediment were collected from the uppermost 3 in. of the sediment profile at each sample site. At selected points where the sediment profile exceeded 3 in. in thickness samples were collected from the different layers constituting the profile. At a great many sites the sediment profile did not exceed 3 in. in thickness and the entire profile was included in the sample.

2. Bank soils.

Materials of stream banks were sampled; in some instances up to 9 in. in from the bank surface. Where the channel contained water the banks were sampled above and below water level.

3. Water samples.

In addition to water from the open drainage, ground water exposed by pitting, artesian water and water in underground workings was sampled. In all cases the procedure followed was the same. Two

samples were collected at each site. For the first sample the natural water was filtered through a Whatman 542 filter paper using a Buchner filter funnel and flask that was evacuated using a hand operated pump, and the filtrate stored in a cleaned polythene bottle. Unfiltered natural water was collected in a second cleaned polythene bottle to which was added 5 ml. concentrated hydrochloric acid in order to inhibit precipitation of nickel.

D. Sample representivity and error.

The content of specific elements in any given sample is unlikely to be truly representative of all the soil within a very large radius around the sample point. This is especially true in areas of rapidly changing lithology or adjacent to mineralization. It is, however, to some extent compensated for by the collection of a large number of samples.

In addition to the lack of areal representivity there is a sampling error. That is to say that it is improbable that two samples taken at the same site will give identical analytical results.

There are errors involved in actually taking

the sample. (i.e., variation in the relative proportions of different parts of the sample channel), errors involved in sample preparation (in the processes of grinding and sieving) and errors in the analytical procedure (see later). Tooms (1955), working on the Copperbelt of Northern Rhodesia (Zambia), concluded that sampling and preparative errors were insignificant compared with analytical errors and that they had no effect on interpretation of the geochemical results. In studies of the distribution of cobalt in Northern Rhodesia, Jay (1959) found sample error insignificant in the A horizon but appreciable in the B horizon. Govett (1958), also working in Northern Rhodesia, found, in a study of copper in stream sediment, that the sampling error was similar in magnitude to the analytical error. The writer has not made any quantitative study of sample error but has kept a constant check on analytical error (see below) as previous studies have shown the latter factor to be the more important of the two.

E. Vegetation.

Leaves, twigs and bark were collected and

stored in the same type of kraft paper envelopes as those used for soil and sediment samples. The sampling was standardised in that for any given species, the part of the plant sampled at any one site was of comparable age, size and position within the plant, to that part sampled at other sites. The sites were circles of radius 25 ft. with centres 100 ft. apart.

Samples (Leaves, twigs or bark) from 3 to 5 specimens of any given species growing within each site circle were placed in one envelope to form the site sample.

Details of the sizes and physical characteristics of the plants sampled have been recorded and variations in population densities noted.

Part II. SAMPLE PREPARATION.

All samples (soil, sediment and vegetation) were air dried in their containers. In the case of soil and sediment a representative portion of the dried sample was lightly broken up using a porcelain pestle and mortar in order to disaggragate the soil or sediment particles without crushing individual mineral grains. The soil was then sieved through 80 mesh bolting silk

in a perspex frame and the minus 80 mesh fraction was retained in a new envelope.

The minus 80 mesh fraction is used in many geochemical prospecting programmes and company data is from the analysis of the minus 80 mesh fraction. In order to be able to compare and contrast results obtained during the investigation with the company data this fraction was analyzed in the great majority of cases. In addition, certain analyses were made on other size fractions separated by sedimentation. The sedimentation procedure followed was that described by Piper (1950). Briefly; a known weight of dried sample (conveniently 100 gm.) was placed in 150 ml. of 1% Calgon (Sodium hexametaphosphate) in deionized water and vibrated ultrasonically for 30-60 minutes to disperse the soil particles. Following this dispersion the slurry was diluted to approximately 1000 ml. with deionized water. It was then homogenized by shaking in a one litre stoppered cylinder and allowed to settle. Using a Bouyoucous hydrometer the specific gravity in the uppermost 10 cm. was determined after standing for five minutes as a means of estimating the content of silt plus clay size material. The hydrometer reading was repeated after five hours to

enable the content of clay size material alone to be determined. Subsequent to those measurements sand, silt and clay size materials were separated by successive decantations following settling for varying lengths of time as set out in the tables by Piper.

In preparation for analysis vegetation samples were ashed in an electric muffle furnace at 450 - 500°C for four hours. After cooling a known weight of ash was used for the analysis.

Part III. SAMPLE ATTACKS.

Rock, soil and stream sediment samples were subjected to chemical attacks of varying strength. The forms of the metals being extracted is briefly discussed. The attacks are dealt with in order of decreasing severity.

A. Hydrofluoric-Perchloric acid attack.

1. Procedure. 10 ml. of hydrofluoric acid, 2 ml. of perchloric acid and 1 ml. of nitric acid were added to the sample (0.5 - 1.0 gm.) in a platinum dish and allowed to evaporate overnight on a water-bath or sand-tray. After heating on a hot plate to expel perchloric acid the residue was warmed with 15 ml. of 1N - hydrochloric acid and transferred to a 50 ml.

beaker which was left on a water-bath until all the salts had dissolved. The solution was then transferred to a 150 ml. separating funnel containing 25 ml. of a sodium citrate buffer of pH 10.8 - 11.0. The reacting metals were extracted with successive 5 ml. portions of 0.015% dithizone in carbon tetrachloride. The carbon tetrachloride extracts and washings were combined and evaporated to dryness in a 100 ml. beaker on a water-bath before 2 ml. of concentrated sulphuric acid and 1 ml. 60% perchloric acid were added to destroy the dithizonates. To do this the beaker was covered with a watch glass and heated until colourless, when the watch glass was removed and the solution evaporated to dryness. The residue was taken up in 0.5 N - hydrochloric acid. Aliquots of this solution were used in the colorimetric determinations.

The attack, that set out in the Geochemical Prospecting Research Centre (G.P.R.C.)(now the Applied Geochemistry Research Group (A.G.R.G.)) Technical Communication No. 38, is based on a method proposed by Stanton, Mcdonald and Carmichael (1962).

2. Discussion.

The attack is usually total and all the metal in the sample is extracted and determined. Harden and Tooms (1964) have reported that spectrographic and hydrofluoric-perchloric acid results show an extremely close agreement when determining the nickel, cobalt copper and zinc contents of pyroxenes, amphiboles and feldspars. The burn in spectrographic analysis can,

therefore, also be regarded as a total attack.

B. Fusion with potassium bisulphate ($KHSO_4$).

1. Procedure. The weighed sample (0.1 - 1.0 gm.) was fused with an excess of $KHSO_4$ in a pyrex glass test tube. Six samples were fused at a time, held in a specially designed coronet attached to a primus stove. The average fusion was complete in 4 minutes. The melt was dissolved, with gentle heating, in 0.5N - hydrochloric acid (5 or 10 ml.).

2. Discussion.

Fusion of rock, soil and sediment samples with $KHSO_4$ does not necessarily or generally extract the total amount of metal. Plant ash was fused with $KHSO_4$ in the same way but in this case the attack is believed to be complete as no visible residue remains after fusion and dissolution of the melt. In the attacks on rocks, soils and sediments an insoluble residue is usually left in the fusion tube after the melt has been dissolved. In the attacks on pyroxenes and amphiboles described by Harden and Tooms a potassium bisulphate fusion extracted only a limited portion of the nickel, cobalt and zinc but almost all the copper and the authors made the suggestion that the copper occurs in

a different form to the other elements studied. It is generally believed that the $KHSO_4$ attack extracts only certain forms of specific elements from rock, soil or sediment samples.

Just what is being attacked is not known with certainty but sulphides, sulpho - salts, the majority of the clay minerals and some weathered silicates are thought to be almost certainly attacked. In contrast, it is thought that some oxides (notably magnetite) and fresh silicates are resistant to a potassium bisulphate attack. Harden and Tooms believe that the efficiency of the attack on rocks, soils and stream sediments is a reflection of the mineralogy and degree of weathering and alteration.

As Harden and Tooms point out the applicability of the $KHSO_4$ attack in geochemical prospecting is not in question but it must be remembered that the attack is not total.

C. Sodium citrate - dithionate attack.

1. Procedure.

Sodium citrate (75 gm. in 900 ml. water and 4 ml. Fe - 3 specific versene) is adjusted to pH 7.3 with 5 M citric acid (approx. 10 ml.) and diluted to 1 litre. The sample is attacked with a small quantity of this reagent in a conical flask in a water bath (85°C). Sodium dithionate (1 gm./5 ml. distilled water adjusted to pH 7.3 by 10% NaOH) is then added. On completion of the attack the filtered leachate is retained.

2. Discussion.

According to Aquilera and Jackson (1953) secondary iron oxides are dissolved by this attack. In the study described in this report the amount of nickel in the citrate - dithionate extract was determined and this nickel is reported as being associated with secondary iron oxides. Strictly speaking this may or may not be the case. It is not known whether all the nickel determined in the citrate - dithionate leach is in fact associated with secondary iron oxides. Sulphides, sulpho - salts and even some clay minerals may be, at least partially, attacked. The attack is, however, weaker than the $KHSO_4$ fusion.

D. Leaching with ammonium acetate.

1. Procedure. 0.2 - 1.0 gm. of the dried sample was weighed into a test tube to which was added 10 ml.

N- ammonium acetate of pH 7.0. The tube was tightly corked and shaken mechanically for 30 minutes. The tube was then put aside and allowed to settle until the supernatant liquid was clear. Alternatively, to speed up the procedure, especially with samples rich in clay size material, the soil- ammonium acetate mixture was centrifuged for 5 minutes at 2000 r.p.m. A 2 ml. aliquot of the clear supernatant leachate was acidified with 0.2 ml. 5 N HCl for the estimation stage.

2. Discussion.

Agricultural scientists leach soils with neutral, normal (molar), aqueous ammonium acetate of pH 7.0 in order to determine the exchangeable cations. The large, strongly charged NH_4^+ ions (ionic radius 1.43 A^o) exchange places with other cations adsorbed in the soil exchange positions. The metal cations so displaced pass into solution and can thus be determined in the leachate.

The writer used the ammonium acetate leach as a means of determining the amount of exchangeable nickel in rocks and soils. The procedure was based on the technique of Bray and Willhite (1929) which is used by soil scientists. Experiment showed that a 30 minute shake is double the minimum time required for complete extraction. When seven separate portions of

a sample were shaken for periods of time varying from one minute to one hour it was shown that no additional extraction resulted with shakes longer than 15 minutes (Figure 16). The exchangeable nickel content was determined directly on the acetate leachate.

Part IV. ESTIMATION OF THE ELEMENTS.

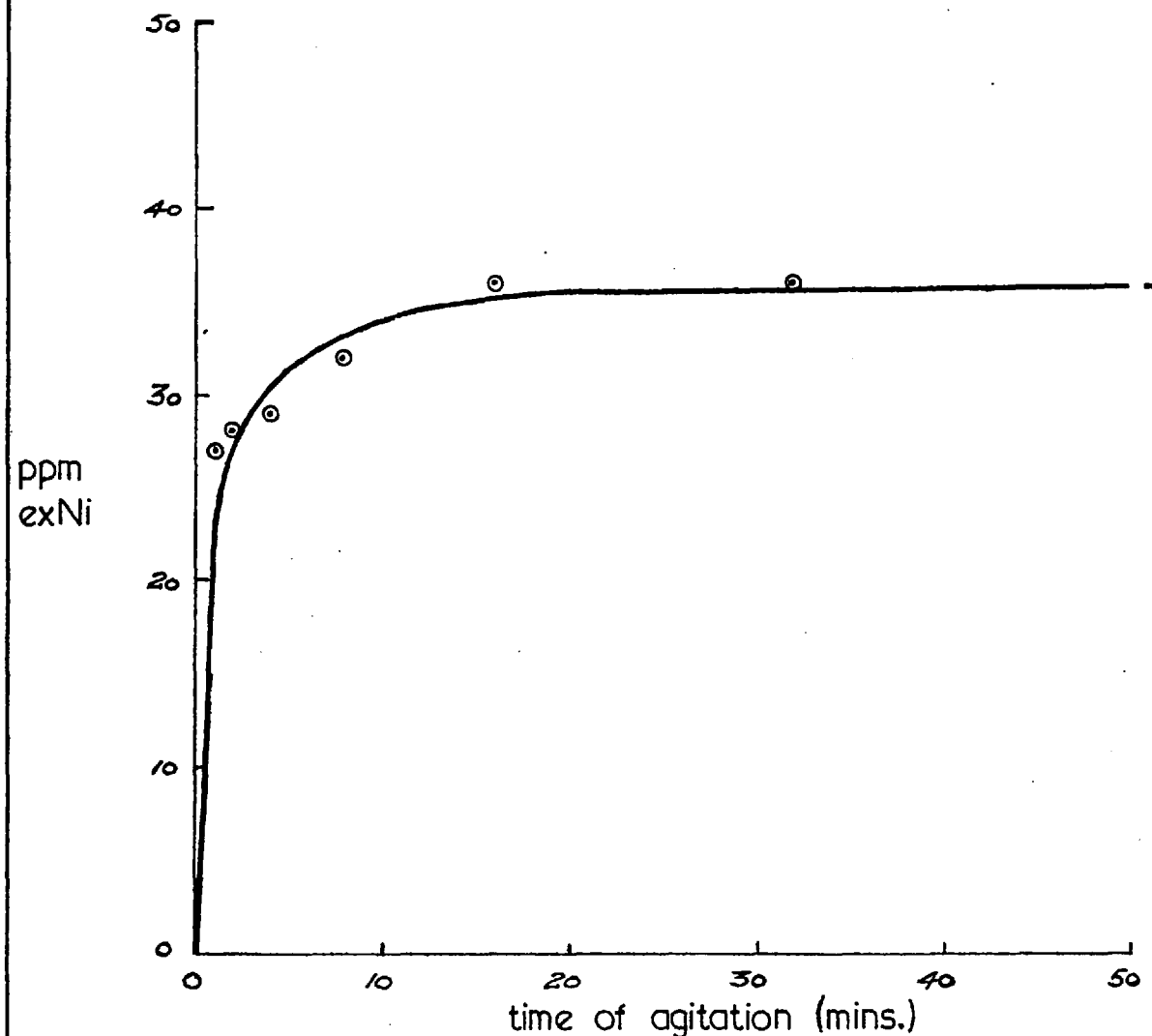
For any given element the estimation stage has been independent of the sample attack and has been based on a previously published method. The analytical methods are only summarized here. The reader is referred to the original papers for detailed analytical procedures.

Control of accuracy has been maintained by using the method formulated by Craven (1953). Twelve mixtures of a sample of high metal content and a sample of low metal content were included at random amongst batches of samples being analyzed and the results were interpreted statistically.

A. Colorimetric methods.

1. Nickel.

Sample No. 1033
Temperature 20-25°C



Effect of time of agitation on extraction of nickel from soils by neutral, normal ammonium acetate.

16

Nickel in 0.5N- hydrochloric acid buffered with ammoniacal tri-ammonium citrate of pH 10.3 was reacted with a 0.3% solution of ∝- furildioxime in a benzene - ethyl alcohol (9-1) mixture. The colour of the resultant yellow nickel - ∝ - furildioxime complex was matched with standards, the intensity of the yellow colouration of the solvent phase being proportionate to the amount of nickel in the original sample (Appendix II)

The method (G.F.R.C. , Technical Communication No. 28) is that developed by Stanton and Coope (1958). It may be conveniently operated in the range 1- 18,000 ppm. This is adequate for geochemical prospecting purposes. During the course of the investigations described in this thesis constant control of the accuracy of batch analyses using the method suggested by Craven has been undertaken and an average mean accuracy of ±25% at the 95% confidence level was attained. 80 samples can be analyzed per man-day of 8 hours but with a suitable production line this could be increased.

2. Copper.

Copper, like nickel was determined in 0.5.N-

hydrochloric acid buffered with a solution of sodium acetate, potassium sodium tartrate and hydroxylamine hydrochloride of pH 5.9 - 6.2 by reaction with 0.2% 2 - 2' diquinolyl in amyl alcohol. The complex formed between the cuprous ion and diquinolyl imparts a magenta colour to the solvent phase. This colour was compared with standards and the copper content of the original sample calculated.

This procedure (G.P.R.C. Technical Communication No. 23) has been adapted from the method proposed by Almond (1955). The range covered is 5 to 20,000 ppm and results may be obtained within $\pm$ 25% at the 95% confidence level and this range. As for nickel, 80 samples can be analyzed per man-day of 8 hours but it is believed that productivity can be increased with a suitable production line.

3. Cobalt.

Cobalt in 0.5N - hydrochloric acid was buffered with a mixed sodium acetate - tetra sodium pyrophosphate - hydroxylamine hydrochloride buffer including potassium thiocyanate at a pH of 4.5 - 5.2 and shaken with 10% tri - n - butylamine in amyl alcohol. The blue tri - n - butylammonium tetrathiocyanatocobaltiate

was formed, the colour intensity of which was compared with standards.

The procedure is that described by Stanton and Mcdonald (1961 - 62) and outlined in the G.P.R.C. Technical Communication No. 14. Results within the ±20% limit at the 95% confidence level are commonly obtained in the range 1 - 5000 ppm.

It is important to note that in the presence of 5% or more calcium results may be low due to coprecipitation of cobalt with calcium pyrophosphate. Productivity per 8 hour man-day is 60 - 80 samples.

4. Arsenic

Arsenic was determined only following a potassium bisulphate fusion. The melt was dissolved in 0.5 N - hydrochloric acid. An aliquot of the acid solution was pipetted into a small quantity of 2.5% potassium iodide solution which was subsequently diluted with 0.75% stannous chloride. Zinc pellets were added to this solution and the gases generated (amongst them arsine) were passed up a Gutzeit tube and through a mercuric chloride paper at the head of the tube. The interaction of arsenic and mercury

produces a spot on the mercuric chloride paper which is yellow at low concentrations of arsenic, brown at high concentrations. The yellow - brown spot was compared with artificial standards.

The range covered is conveniently 5 - 5000 ppm with results within ±25% at the 95% confidence level. 80 samples can be analyzed per man-day of eight hours.

The method is a modification of the classical Gutzeit test for arsenic and the procedure has been that suggested by Stanton (1964) and outlined in the G.P.R.C. Technical Communication No. 49.

5. Antimony.

The method chosen for the determination of antimony necessitated a special sample attack. The sample was mixed with ammonium chloride and heated until sublimation was complete. After cooling the sublimate was dissolved in 6N - hydrochloric acid. An aliquot of this acid solution was further diluted with 6N hydrochloric acid. A little sodium nitrite was introduced before mixed sodium hexametaphosphate - brilliant green aqueous reagent solution and toluene were added. After shaking the entire mixture the intensity of the blue

colouration of the solvent phase was compared with standards. The colour is due to a complex between chloro - antimonate anions and brilliant green.

Abbreviated operating instructions are given in the G.P.R.C. Technical Communication No. 17 which is based on the method of Stanton and Mcdonald (1961-62). The range covered is 0.2 - 2200 ppm with results within $\pm$25% at the 95% confidence level. 100 samples can be analyzed per man-day of 8 hours.

6. Selenium.

The selenium analyses were made using a procedure recently developed by Stanton and Mcdonald in the laboratories of the Applied Geochemistry Research Group, Royal School of Mines, London. Their description of the method (Appendix III) is in press (The Analyst, 1965).

The sample is decomposed with a mixture of nitric and perchloric acids. The selenium is co-precipitated with arsenic and taken up again in the same acid mixture. It is then reacted with 3 - 3^1 diaminobenzidene to form a yellow complex extractable in benzene. The yellow colouration of the solvent is

compared with standards and the selenium content of the original sample is calculated.

No data on the range or productivity is available at present but the accuracy within batches of analyses has been better than ±20% at the 95% confidence level in the range 1 - 100 ppm.

7. Iron.

The iron content of selected samples was determined after a potassium bisulphate fusion. An aliquot of the leachate was added to a known volume of an aqueous ammoniacal reagent solution containing tartaric and thioglycollic acids which was then diluted with deionized water. The reddish purple colouration was compared with standards.

The method is a modification of that outlined in the G.P.R.C. Tech. Comm. No. 40 which has been adapted from the procedure described by Sandell (1959).

The range is conveniently 100 ppm to 2% but can be extended by varying the dilutions and aliquot

size. Results can be obtained within ±25% at the 95% confidence level. Productivity is at the rate of about 80 samples per man-day of 8 hours.

B. Instrumental analysis.

1. Spectrochemical.

A limited number of rock and soil samples were analyzed spectrochemically by the staff of the spectrographic laboratory of the A.G.R.G. The elements determined were Ag, Bi Co, Cr, Cu, Ga, Ge, Mg, Mn, Mo, Ni, I b, Sn, Ti, V, and Zn.

The soil samples were ignited in a silica crucible at 400 - 500°C for 3 hours to oxidize organic matter and eliminate combined water. Rock samples were not subjected to this preliminary ignition. The samples were mixed with a 1:1 mixture of lithium carbonate and carbon with germanium added as an internal standard. The homogenized mixture was burnt and the concentrations of the given elements in the sample was estimated by comparing the spectra of the sample with spectra on a standard plate.

The specifications of the instrument used

and conditions of the burn are summarized in Table 5.

Table 5. Spectrochemical analysis; Instrument specifications and conditions of burn.

Data supplied by Dr. I. Nichol,
Applied Geochemistry Research Group, Royal School of Mines.

Source unit	Hilger FS 131
Spectrograph	Hilger Large Quartz FS 55
Arc stand	Hilger FS 56
Comparator	Hilger JA Co L.90
Wavelength Range A	2800 - 4950
Emulsion	Ilford N.30
Anode	Morganite SG.305H - 5 mm. carbon, 2.91 mm. diam. crater, 5 mm. deep crater
Cathode	Morganite SG.305H - flat ended
Exposure	20 secs.
Gap	3 mm.
Arc current	12.5 amps
Slit	15 u
Collimator	Internal
Step sector	Two steps giving three intensities in proportion 1:1/4:1/16

2. Mercury.

Selected samples were analyzed for mercury. The analyses were made using the Mercury Vapour Meter (James and Webb, 1964). Although this instrument is still being developed the preliminary data using RF (Radio Frequency) induction heating has indicated that previous results without this refinement are reasonably reliable. Accordingly it has been decided to include the results of some preliminary mercury analyses in this thesis.

Part. V. MEASUREMENTS OF MISCELLANEOUS PARAMETERS.

A. Base exchange capacity.

Base exchange capacity was determined on selected samples by displacing the adsorbed bases with the ammonium ion from an aqueous ammonium acetate solution according to the method of Bray and Willhite (1929). Briefly; the technique involves the treatment of a sample of soil with excess ammonium acetate and the subsequent distillation of the adsorbed ammonia into

standard acid which is back titrated with standard alkali.

B. Total exchangeable bases.

The total amount of exchangeable bases was determined from the ammonium acetate by taking up the residue from an evaporated aliquot of the leachate in standard acid and back titrating with standard alkali (Bray and Willhite).

C. Soil pH.

The procedure followed in determining soil pH is described below.

1 gm. of the sample was weighed into a clean, dry polythene bottle. 5 ml. of boiled, deionized water was added and the bottle was immediately tightly stoppered. The soil - water slurry was vigorously agitated for 1 hour in a mechanical shaker after which time a portion of the slurry was poured into the electrode cup of a battery operated pH meter (supplied by Analytical Measurements Ltd.) and the pH was read from the dial.

D. pH of natural waters.

The pH of natural waters was recorded in the field using a pH meter (detailed above). On each day that readings were taken the pH meter was standardised with buffer solution. At each site the electrode was rinsed in the water being sampled before the cup was put onto the electrode, filled with water and the reading taken.

E. Eh of natural waters.

Eh of natural waters was also recorded in situ using the pH meter but to which was attached a platinum electrode in the place of the glass electrode used for the pH reading. The practical procedure adopted was the same as that followed in taking pH readings.

F. Carbonate and bicarbonate in natural waters.

Carbonate and bicarbonate radicals in the natural water samples were determined as soon after the time of sampling as practicable (usually back in the field camp a few hours after the time of

sampling). To determine the carbonate content an aliquot of the water sample was titrated against standard hydrochloric acid to the neutral point using phenolpthalein as indicator. Bicarbonate was determined by continuing the titration to the end point indicated by screened methyl red.

The detailed procedure followed was that described in the G.P.R.C. Technical Communication No. 26 which is based on the method put forward by Scott (1955).

Water with a pH of less than 8.35 does not contain carbonate and will give a pink cclouration with phenolphalein.

With a suitable adjustment of aliquot size and acid strength the range in which bicarbonate can be determined is very flexible.

G. Sulphate in natural waters.

Sulphate was determined by a turbidometric technique. A solution of sodium chloride in hydrochloric acid was first added to the sample of filtered water followed by barium chloride crystals. After a short shake the turbidity (caused by the

formation of Barium sulphate) was compared with standards. The comparison was carried out against a dark background. 1 to 200 mg. per litre can conveniently be detected by this method.

Part VI. COMPANY DATA.

Widely different analytical techniques have been used by the different companies and the levels of precision differ considerably.

A. RST Exploration Ltd.

The analytical techniques employed by this company are basically the same as those used during the course of the present investigation. The company determined nickel, copper and cobalt by colorimetric procedures similar to those described earlier in this chapter. RSTE Ltd., have controlled the accuracy of their analyses using the statistical series principal of Craven. Much analytical data made available by the company has been included and interpreted in this thesis.

B. RST Technical Services Ltd.

Nickel and copper analyses have been made using paper chromatography. In addition, data from copper analyses carried out colorimetrically using dithizone was made available to the writer. Unfortunately the accuracy of the analyses is unknown.

The data was, however, of considerable value in guiding the field work but it was decided that it was necessary to re-analyse some of the company samples with a higher precision than that required for the company's purposes.

C. Rio Tinto (Rhodesia) Ltd. (M.S.A. (Pvt.) Ltd.).

Analyses carried out by this company on samples from Dalmainy Farm, Empress and the Bare Bottom Hill areas were spectrochemical or by wet chemical assay. No details of the techniques or degree of analytical control are known. The reader's attention is drawn to this unknown factor at the relevant points in the text where data made available by this company is presented.

Chapter 3. PRIMARY DISPERSION FEATURES.

The secondary dispersion of nickel is controlled to a considerable extent by the mineral form of the element in the unweathered rocks. A limited consideration is presented below of the primary dispersion, at high pressure and temperature, of nickel during the formation and metamorphism of rocks.

A. Geochemical characteristics of nickel.

Geochemically nickel follows magnesium and iron. Goldschmidt (1954), in explaining the geochemical behaviour of nickel, gives the ionic radii of the three elements mentioned above and cobalt, in order of increasing size, as :-

Ni^{++}	Mg^{++}	Co^{++}	Fe^{++}	
0.78	0.78	0.82	0.83	(A^{o})

and states that it is this order that controls .... , "the sequence of crystallization of isomorphous mixtures in such cases in which the electrostatic energy constitutes the main force in the lattice". He goes on to say that nickel and magnesium are, in consequence, concentrated in early differentiates of ultrabasic magma.

Vogt (1923) has shown that nickel occurs in the ferromagnesian rock-forming silicates, especially in olivines. He has also observed a correlation between the nickel content of the ferromagnesian minerals in basic igneous rocks and the tenor of nickel in associated pyrrhotite ores.

Olivine is one of the common rock-forming silicates in which nickel is known to occur (mentioned above and Table 6). Nickel is believed to replace

Table 6. Some common rock forming silicates that can contain nickel in the crystal lattice.

Group	Mineral or series	Chemical composition
Olivine	forsterite - fayalite	Mg_2SiO_4 - Fe_2SiO_4
Pyroxene	enstatite - orthoferrosilite	$(Mg,Fe^2)Si_2O_6$
	diopside - hedenbergite	$Ca(Mg,Fe^2)Si_2O_6$
	augite	$(Ca,Mg,Fe^2,Al)_2(Si,Al)_2O_6$
Mica	talc	$Mg_3Si_4O_{10}(OH)_2$
	chlorite	$(Mg,Al,Fe)_{12}((Si,Al)_8O_{20})(OH)_{16}$
Serpentine	antigorite - crysotile	$H_4Mg_3Si_2O_9$

magnesium in the crystal lattices of the silicates (Nickel, 1959). Egorova (1938) has found up to 0.41% nickel in naturally occurring olivine minerals and in 1937 Grigoriev synthesized a nickel olivine. Ringwood (1956) has shown that Mg_2SiO_4 forms a complete solid solution series with Ni_2SiO_4. During the crystallization of basic magma most of the nickel is incorporated in the magnesium rich olivines and according to Wager and Mitchell (1951) nickel shows a greater tendency to enter the olivine structure than does magnesium. This is, however, not in accord with the lower melting point of Ni_2SiO_4 relative to Mg_2SiO_4 and Ringwood has suggested that the entry of nickel into the olivine structure in excess of the magmatic magnesium: nickel ratio is due to the presence of iron in natural olivines which lowers their thermal stability. Ringwood considers that the nickel goes into the structure at the expense of ferrous iron rather than magnesium.

Nickel (1959) has reported a single phase Ni - Fe alloy formed during the serpentinization of primary olivine and orthopyroxene which contained approximately 0.2% nickel. Further evidence of the association of nickel and iron is found in the occurrence of the mineral trevorite ($NiFe_2O_4$) which is also known as nickeliferous magnetite. It is a nickel - ferric iron

spinel and contains about 30% NiO. It has been observed at one locality in the Transvaal (South Africa) and at Mwahanza hill in Tanganyika. The naturally occurring mineral is closely similar to the synthetic nickel ferrite prepared by Longuet (1941) in that it is strongly magnetic and has a black streak. It will be shown later in this thesis that nickel and iron can also be associated in secondary dispersion patterns.

According to Nickel (1959) there is a redistribution of nickel during the alteration of olivine (to serpentine, chlorite, talc, amphibole, carbonates and iron oxides) but he has concluded that there has been no appreciable overall gain or loss of nickel during serpentinization. Data obtained during the present study (presented in detail in Chapter 4) has shown progressively less nickel in the sequence dunite, serpentinite to talc schist. One of the possible interpretations of this distribution is that there has been redistribution with an overall decrease in nickel content during serpentinization. If, however, Nickel's conclusion is correct the distribution observed in the Rhodesian study areas is probably reflecting variations in the initial primary distribution in the unserpentinized rock.

Talc, chlorite and serpentine containing nickel have all been reported. Avias (1962) has found antigorite from New Caledonia containing 7.78% Ni. In the literature there is very little mention of nickel in amphiboles but the pyroxenes can contain nickel. The metal is more abundant in orthorhombic pyroxenes than in clinopyroxenes. Natural diopside containing a substantial quantity of nickel is unknown. The NiO content of the magnesium rich augite is generally about 0.1% but the amount decreases as the iron content increases.

In addition to the lithophile and siderophile tendencies described above nickel also has a strong affinity for sulphur. In a study of iron and nickel sulphides from sulphide ores associated with basic igneous masses in the U.S.S.R. Betekhin and Genkin (1951) suggested that during syngenetic magmatic ore forming processes nickel has a greater affinity for sulphur than for oxygen. Both iron and nickel form a series of sulphides. Iron oxides form abundantly but nickel oxides rarely.

Despite it's strong affinity for sulphur nickel rarely forms it's own sulphides, millerite and maucherite (Table 7). It is frequently found as nickel-iron sulphides (such as pentlandite, bravoite

and nickeliferous pyrrhotite) and forms the complete isomorphous series siegenite-linnaeite with cobalt. Nickel also forms the natural sulpho salts gersdorffite, niccolite and chloanthite and, together with cobalt, skutterudite. These latter mentioned minerals frequently occur in hydrothermal vein deposits of which the Noel mineralization may be an example.

Table 7. Chemical composition of some nickeliferous sulphides, sulph-arsenides and arsenides.

Sulphides		Sulph-arsenides and arsenides	
Mineral	Composition	Mineral	Composition
Millerite	NiS	gersdorffife	NiAsS
maucherite	$Ni_{11}S_8$	niccolite	NiAs
pentlandite	$(Fe,Ni)_9S_8$	skutterudite	$(Co, Ni)As_3$
bravoite	$(Ni,Fe)S_2$		
siegenite - linnaeite	Ni_3S_4-$(Ni,Co)_3S_4$		
	$(Co,Ni)_3S_4$-Co_3S_4		

The two dominant geochemical characteristics of nickel are, then, it's ability to occupy sites in ferromagnesian silicate lattices and it's affinity for sulphur. The weight of evidence suggests that it should be included with the siderophile group of elements (Goldschmidts' classification).

Another siderophile element closely associated with nickel both in sulphide and arsenide ore

minerals and in rock-forming silicates is cobalt. The factor of enrichment for nickel in ultrabasic rocks relative to the average for igneous rocks is similar to that for cobalt but greater than that for copper. All three of these above mentioned elements are preferentially associated with ferromagnesian minerals in silicate rocks but whereas nickel and cobalt are at their maximum in ultrabasic rocks copper is concentrated in basic rocks. Copper has a very strong affinity for sulphur. Its geochemical association is chalcophile in contrast to the siderophile associations of nickel and cobalt.

B. Nickel in ultrabasic rocks.

Since nickel is included preferentially in ultramafic minerals the nickel content of igneous rocks generally might be expected to vary according to the percentage ultramafic minerals and as far as can be ascertained from the data of Table 8 this expectation is broadly confirmed.

The first nickel and cobalt analyses were made on ultrabasic and basic rocks rich in nickel (dunite, peridotite, pyroxenite and norite in the main) which were shown to have a cobalt: nickel

Table 8. The metal content of some selected rock types.

Rock type	Range and/or mean metal content (ppm) (mean values in parenthesis)			Location. (Source of data in parenthesis)
	Ni	Co	Cu	
Average igneous	(100)	(18)	(70)	(Green, 1959)
Ultrabasic igneous	650-3600			Germany (Goldschmidt) Scotland (Nockolds and Mitchell) Greenland (Wager and Mitchell)
	(1200)	(200)	(80	(Vinogradov, 1956)
Serpentinite	900-3200			Basement Complex, Rhodesia (SRGS and present study)
	1200--2600			Great Dyke, Rhodesia (SRGS), (present study)
Basic igneous	50-230			Germany(Goldschmidt) Scotland (Nockolds and Mitchell) Finland (Sahama) Greenland (Wager and Mitchell) USA (Sandell and Goldich)
	(160)	(45)	(140)	(Vinogradov, 1956)
Intermediate igneous	15-80			do
Acid igneous	2.5-20 (8)	(5)	(30)	do (Vinogradov, 1956)
Sedimentary rocks	(2-300)	(0.2-50)	(5-300)	(Krauskopf, 1955)

ratio of about 1:12. For example in 1931 Vogt published the figures 0.001% cobalt, 0.010% nickel, a ratio of 1:10. Sandell and Goldich (1943) reported 0.0023% cobalt : 0.008% nickel for the upper lithosphere. Goldschmidt's figures of 0.004% cobalt : 0.01% nickel are closely comparable to those of Sandell and Goldich but these ratios (4:10 and 3:10 respectively) are substantially different to the early figures based on analyses of ultrabasic and basic rocks, given by Vogt (1931) and Washington and Clarke (1924). The reason for the difference in the cobalt:nickel ratio is that relative to the average for the upper lithosphere nickel is enriched in the ultrabasic rocks to a greater extent than cobalt.

Cobalt : nickel ratios in the Maritzani and Great Dyke serpentinites are 1 : 20 (150 : 3000 ppm) and 1 : 13 (200 : 2600 ppm) respectively. These analyses are in agreement with the published data discussed above. Relative to nickel and cobalt, the copper content of the serpentinite (70ppm at Maritzani, 10ppm at Darwendale) is low.

C. Nickel in other rocks.

As indicated earlier the data of Table 8 suggests

that the nickel content of igneous rocks decreases with decreasing percentage mafic minerals. In metavolcanics at Maritzani for example, the ratio cobalt : nickel is 1 : 3 (50 : 150 ppm). The level of the cobalt content is not substantially higher than the copper content (40 ppm). The nickel content is four times that of the copper but the ratio copper: nickel in metavolcanics (1 : 4) contrasts markedly with that in serpentinite (1 : several 100).

D. Sulphide mineralization.

There is a worldwide intimate association between nickel sulphide ore deposits and basic and ultrabasic rocks (Table 9). Many students have recognised that in a crystallizing basic or ultrabasic magma rich in nickel and sulphur the nickel is distributed in both the sulphides and early formed ferromagnesian silicates. It is possible that the Empress, Perseverance and Maritzani mineralizations may have originated in this way. It is believed however, that there has been some redistribution during subsequent metamorphism, especially in the two last mentioned areas. The Perseverance and Maritzani mineralizations could, alternatively, be

hydrothermal deposits.

Table 9. List of some of the sulphide nickel deposits of the world.

Deposit	Host rocks		Genetically associated rocks		Source of information
	Ultra-basic	Basic	Ultra-basic	Basic	
Sudbury, Ontario		x			Hawley(1962)
Jumbo Mt., Washinton	x				Mills(1960)
Mackinaw mine, Washington	x				Milton and Milton(1958)
Hardy mine, Ontario				x	Mitchell and Mutch(1957)
Banat, Rumania	x				Petrulian and Steclaci(1954)
Sebes Mts., Rumania	x				do
Eastern metals, Quebec	x				Pollock(1959)
Taimyr region, USSR				x	Rogover(1959)
Caraiba district, Brazil		x			Schneider(1957)
Saline county, Arkansas	x				Sterling and Stone(1961)
Western Tasmania			x	x	Williams(1958)
Pacific Nickel Property, B.C.	x				Aho(1957)
Quill Creek and White River, Yukon			x	x	Campbell(1960)
Werner Lake - Rex Lake, Ontario			x	x	Carlson(1958)
Sao Pedro da Cova, Portugal		x			Costa Fonseca and Thadeu(1948)
Thomson - Moak Lake, Manitoba	x				Davies(1960)
Sannae mine, Korea	x				Kim and Ruie (1958)

The origin of the sulphides at Kalumbila is not known. There are two alternatives:-

(i) The sulphides are of a syngenetic sedimentary origin redistributed during folding and metamorphism or

(ii) They are of epigenetic origin, possibly the result of the introduction of hydrothermal emanations derived from the basic intrusives in the area.

The zones of highest grade nickel and copper mineralization are not coincident, the highest grade copper mineralization being two to three miles south west of the area of highest grade nickel mineralization in the north east - south west striking carbonaceous shale horizon. The cobalt : nickel ratio is approximately 1 : 1.25 in the vicinity of the best copper mineralization but along strike to the north east and nearer the gabbroic and other intrusive bodies it increases to 1 : 2.75. This can be explained by postulating migration of the elements from the north east to the south west along the carbonaceous shale with copper and cobalt being more mobile than nickel. Alternatively the observed distribution of the metals could be due to varying physico - chemical or biological conditions prevalent at the time of sedimentary deposition, leading

to a separation into dominantly cupriferous and nickeliferous facies.

During ore forming processes the rocks immediately around the ore deposits may be enriched in ore metals. Vogt's correlation between the nickel content of ferromagnesian silicates in basic rocks and the tenor of nickel in related pyrrhotite ores being an example of a syngenetic primary dispersion aureole. Epigenetic primary dispersion aureoles can result from redistribution of the ore metals subsequent to their initial deposition and may be effected by solutions passing through the mineralized zone. The size of the primary dispersion aureole will be dependent on the temperature, pressure and concentration gradients in the environment, composition and physical state of the solutions, composition of the wall rock and the attitude, size and extent of available openings (Webb, 1954).

At Kalumbila there is no recognisable primary dispersion aureole. However, at Perseverance and Maritzani the main mineralization (highest grade) occurs within a very much broader zone of sparsely disseminated sulphides. The ore minerals are concentrated in the fracture zone (the highest grade mineralization) and only relatively sparsely disseminated

in the adjacent more massive rock. On average this aureole contains up to twice as much nickel as the barren host rock but still substantially less than the highest grade mineralization. Widely disseminated sulphides in the mixed zone rocks at the Empress prospect, like the broad zones of disseminated sulphides at Perseverance and Maritzani are regarded as constituting a primary dispersion aureole.

E. Arsenide mineralization.

The Noel deposit is believed to be a hydrothermal vein deposit and as such is epigenetic. No information on primary dispersion in the wall rock is available.

F. Primary dispersion of associated elements.

The similarity in geochemical behaviour between nickel and cobalt has been mentioned and contrasted with copper. It is thus, important to relate the distribution of nickel to that of copper and cobalt in the lower temperature and pressure environment in which secondary dispersion takes place place as this relationship will have a bearing on the differentiation of nickel anomalies related to sulphide and silicate

minerals.

As mentioned earlier nickel not only forms sulphides but also sulph-arsenides and arsenides. The normal arsenic content of igneous rocks ranges from 1.5 (in average felsic types) to 3.0 ppm (in average ultramafic types). In sedimentary rocks it can frequently be present up to 225 ppm (in black shales). Comparison of the distribution of arsenic and nickel in the environment of secondary dispersion could be an aid to interpretation of secondary nickel anomalies.

Selenium is commonly associated with epigenetic sulphides. The average selenium content of igneous rocks is 0.9 ppm (Rankama and Sahama, 1950). In sedimentary rocks this element can occur in amounts up to 1 ppm. It occurs in almost all sulphides. Mineralized serpentinite at Maritzani has been found to contain several ppm selenium. This element is yet another with a chalcophile association and it's distribution may be a further help in differentiating sulphide from silicate nickel.

Chapter 4. OBSERVED DISTRIBUTION

A considerable amount of company data has been made available to the project. This data, together with that obtained during the course of the investigation, has helped to show how nickel and associated elements are distributed.

The distribution of nickel is described first, followed, for comparison, by a description of the distribution of associated elements. Dispersion mechanisms will be discussed, on the basis of the observed distributions, in the next chapter.

For convenience in the remainder of this thesis potassium bisulphate extractable nickel will be referred to as Ni. Similarly with other elements, that is to say potassium bisulphate extractable copper as Cu, etc. Nickel extracted in normal (molar) aqueous ammonium acetate at pH 7.0 will be referred to as exchangeable nickel or exNi. Hydrofluoric-perchloric acid extractable nickel and spectrographically determined nickel will be designated total Ni or $Ni_{(HF/HClO4)}$ or $Ni_{(spec.)}$. When the sample attack has been other than those mentioned above it will be referred to in full. Unless otherwise stated the determinations have been

made on the minus 80 mesh fraction of the sample.

Part I. THE DISTRIBUTION OF NICKEL IN SOIL AND SEDIMENT.

As indicated earlier the research has tended to be concentrated on the ultrabasic rocks which normally have a higher nickel content than other rocks and with which nickel sulphide mineralization is most commonly associated. This is reflected in the division of the following part of the chapter into:-

A. The distribution of nickel in areas of non mineralized[1] serpentinite,

B. The distribution of nickel in areas of mineralized serpentinite and

C. The distribution of nickel in areas of nickel mineralization in rocks other than serpentinite.

A. The distribution of nickel in areas of non mineralized serpentinite.

Two unmineralized serpentinite masses have been

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[1]The term mineralization is used throughout this thesis to describe deposits of nickeliferous sulphide and/or arsenide minerals of either economic or subeconomic grade. It does not include deposits of nickel silicate or nickel oxide minerals.

studied; a serpentinite body at Dalmainy Farm and the Great Dyke at Darwendale. The Dalmainy Farm body has been drilled by Mineral Search of Africa (Pvt.) Ltd. (M.S.A.(Pvt.) Ltd). Unfortunately the core was not available to the writer. According to the company geologists there is no evidence of any sulphide minerals. The Great Dyke serpentinite is very much younger than those of the schist belts, of which the Dalmainy Farm body is an example. The serpentinite masses of the schist belts are Archean, the Great Dyke early Palaeozoic. The Great Dyke serpentinite which has been drilled by Rhodesian Selection Trust Exploration Ltd. (R.S.T.E. Ltd.), is similarly devoid of sulphides although a few grains have been seen associated with vein minerals in fracture fillings (R.S.T.E. Ltd., pers. comm.).

The older serpentinite will be considered first.

1. Dalmainy Farm area.

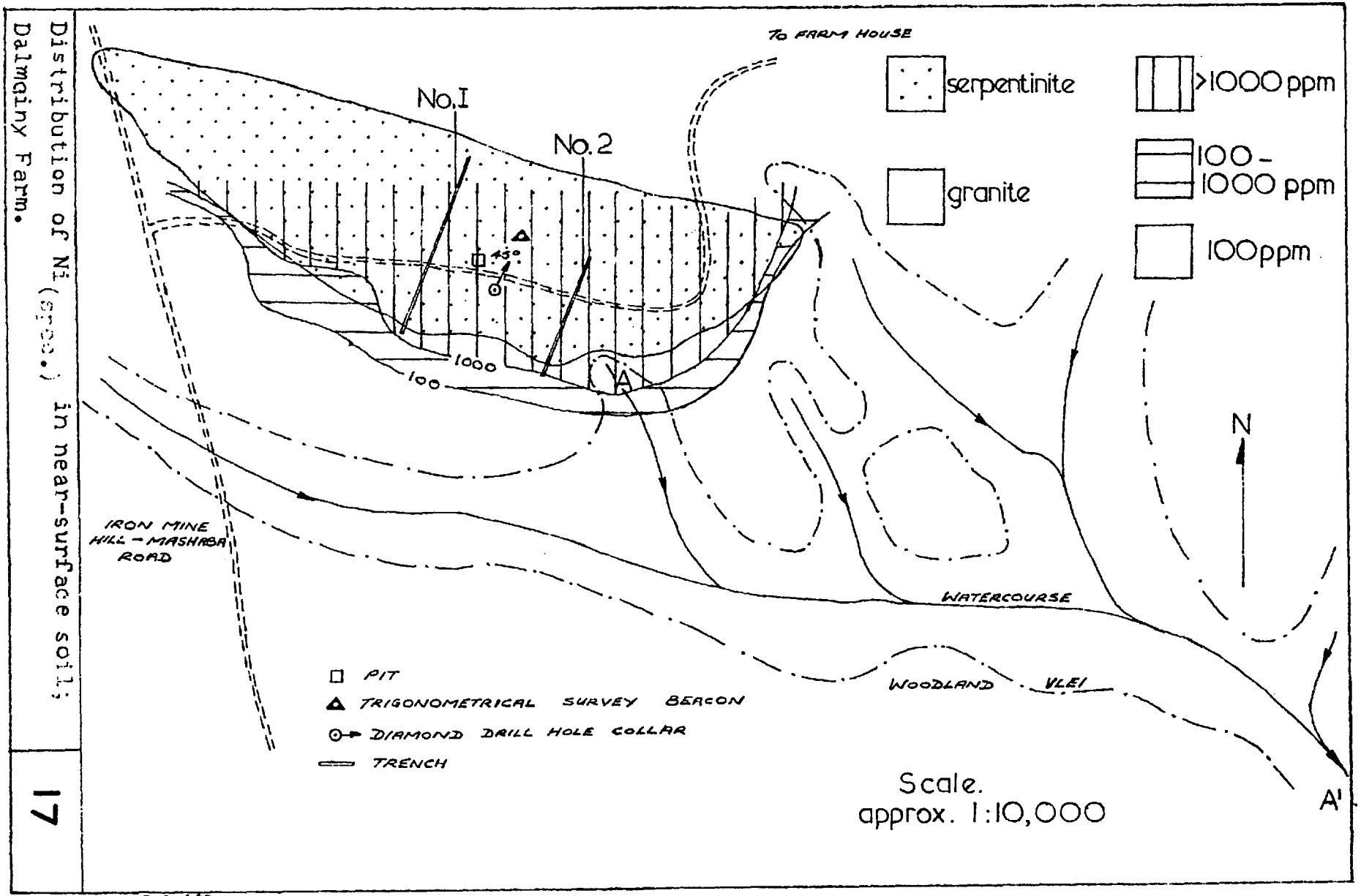
A body of serpentinite crops out on Dalmainy Farm as a strong topographic feature and is flanked on the south by granite and on the other sides by early Pre-Cambrian schistose metavolcanics.

(a) Nickel in fresh serpentinite.

One diamond drill hole has been drilled into the serpentinite. The location of the collar is indicated on Figure 17. The hole, inclined at 45°, was stopped in serpentinized dunite after 1000 ft. of drilling. Chemical assay of the core carried out by M.S.A. (Pvt.) Ltd. showed the nickel content of the ultrabasic mass to vary between 0.16 and 0.36% and generally to increase with depth. The increase with depth corresponds broadly with a petrological transition from serpentinite to dunite. It is not known whether the variation in nickel content observed reflects an original variation in the primary distribution in unserpentinized dunite or is the result of decreasing nickel content with serpentinization. The values are within the usual range for ultrabasic rocks but on the whole a little above average (Chapter 3).

(b) Nickel in the weathered bedrock.

Above 48ft. (35ft. vertically) the nickel content of the serpentinite increases slightly. Since at least some of the serpentinite of the uppermost



Distribution of Ni (ppm.) in near-surface soil; Dalmainy Farm.

17

GEOLOGY : M.S.A. LTD.

35 ft. will be weathered the increase would appear to be a secondary dispersion feature.

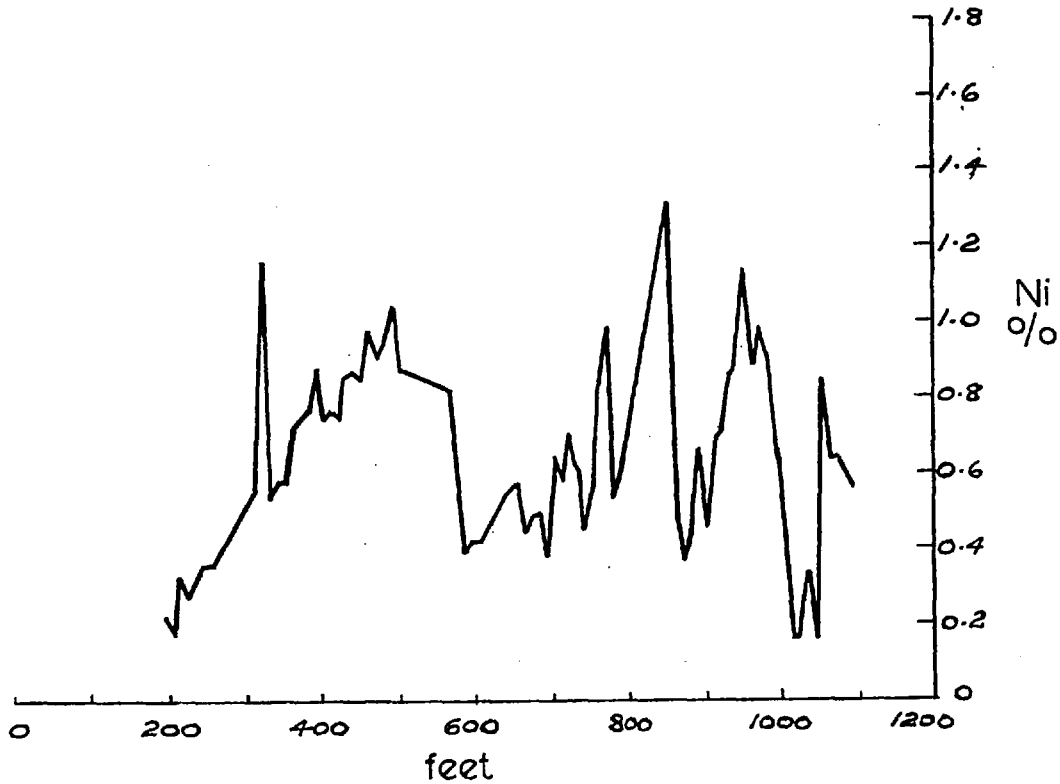
Rotten serpentinite (reached in pits and trenches) contains nickel in amounts ranging from 0.34 to 1.31% with an overall mean, calculated from 67 analyses, of 0.68%. The distribution is, however, patchy, with bands of weathered serpentinite of high nickel content intercalated with lenses of similar rock of relatively low nickel content (Figure 18). This distribution can to some extent be correlated with the variations in the fresh rock. However, the nickel content of the weathered serpentinite and dunite is

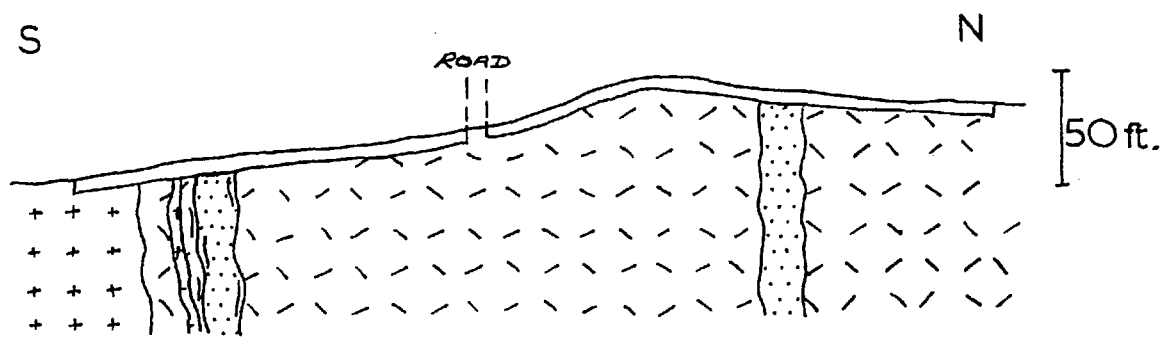
Table 10. Variation in nickel content of ultrabasic rocks in the Dalmainy Farm mass. (1)

Diamond drill hole inclined at 45°

Depth on incline below collar (ft)	Rock type	Nickel content(%)		No. of samples
		Range	Mean	
0 to 48	Serpentinite	-	0.32	1
48 to 340	do	0.16-0.29	0.23	49
340 to 449	Dyke	-	-	-
449 to 578	Serpentinite	0.20-0.36	0.30	26
578 to 581	Aplite	-	0.04	1
581 to 592	Chlorite schist	-	0.15	1
592 to 598	Amphibolite	-	-	-
598 to 745	Serpentinite	0.23-0.34	0.30	30
745 to 911	Dunite	0.26-0.36	0.31	32
911 to 1001	Serpentinized dunite	0.30-0.35	0.33	9

- no data available. (1) Data from M.S.A. (Pvt.) Ltd.





Granite

Basic intrusives

Serpentinite

Variation in nickel content of weathered bedrock; Dalmainy Farm.

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GEOLOGY AND GEOCHEMISTRY : M.S.A. (Pvt.) Ltd.

two to three-fold greater than that of the fresh rock.

(c) Ni in soil and sediment.

The soil profile in the area is juvenile, especially over the serpentinite. The $Ni_{(spec.)}$ content of near-surface soil over the serpentinite varies from 2000 to 5000 ppm, 19 analyses being distributed lognormally about a mean of 3500 ppm. There is insufficient data to know whether the variations in the nickel content of the soil reflect those observed in fresh and weathered bedrock.

The soil over granite contains conspicuously less $Ni_{(spec.)}$ than that over serpentinite. The contrast is more than one hundred-fold (Figure 17).

The distribution of Ni in a profile over serpentinite midway between the two trenches (Figure 17) is indicated in Table 11. There is no B horizon and the Ni content is not significantly greater at the base of the A horizon than right at surface. There is an appreciable increase in Ni content on passing from the A soil horizon to the weathered bedrock. The profile is sited on a gentle slope and it is possible that the soil of the A horizon is transported material from upslope. The profile is, however, close

to the hill crest and there is no change in the soil characteristics between the profile studied and the hilltop other than a thinning of the A horizon. What is perhaps more important is that there has probably been leaching of the nickel from the A horizon.

Table 11. Example of a freely drained soil profile over the Dalmainy Farm serpentinite showing the distribution of Ni.

Sample No.	Depth (in)	Soil horizon	Description	Ni (ppm)
712	0- 3	A	Red-brown sandy clay, dry, loosely friable, with gravel size fragments of weathered serpentinite.	4000
713	3- 9	A	Red-brown sandy clay, dry, loosely friable, with rubble up to large pebble size of silicified, ferruginous rotten serpentinite.	4200
714	9-24	C	Yellow-ochre, weathered, poorly schistose and jointed serpentinite.	6700

The nickel is dispersed far beyond the boundaries of the serpentinite. In the vlei paralleling the serpentinite-granite contact south of the body (Figure 17) there is an intermittent stream channel. The near-surface soil in the vlei north of the channel (or low point of the vlei where there is no channel)

contains more Ni than the corresponding soil south of the watercourse (Table 12.). Since the serpentinite

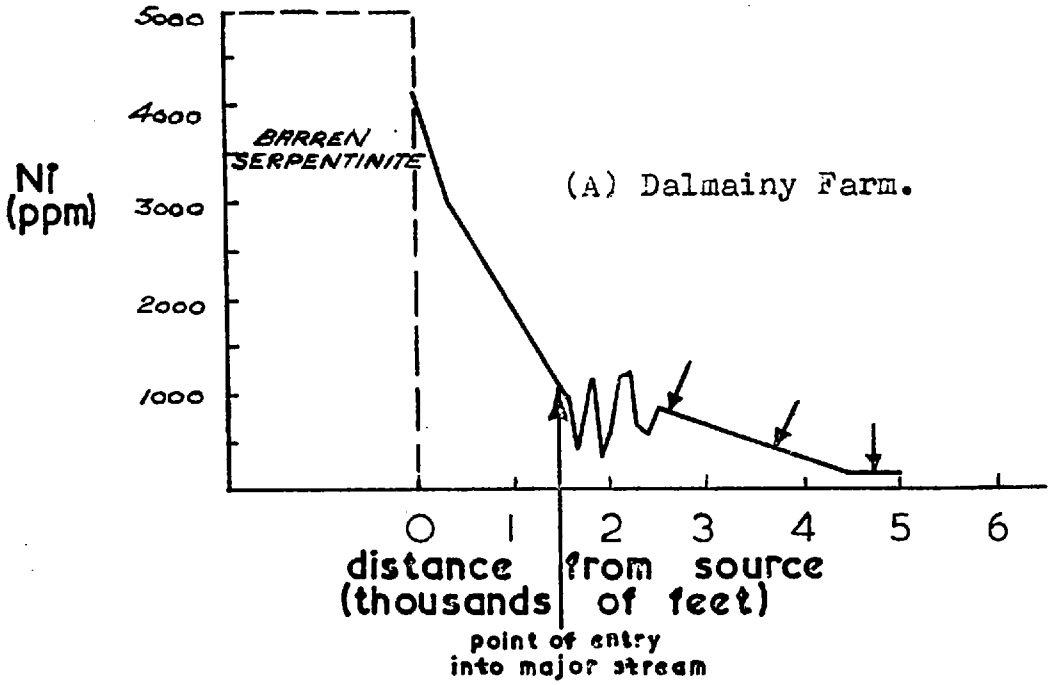
Table 12. Comparison of Ni content of near-surface vlei soil north and south of a watercourse over granite and downslope from serpentinite on Dalmainy Farm (Figure 17).

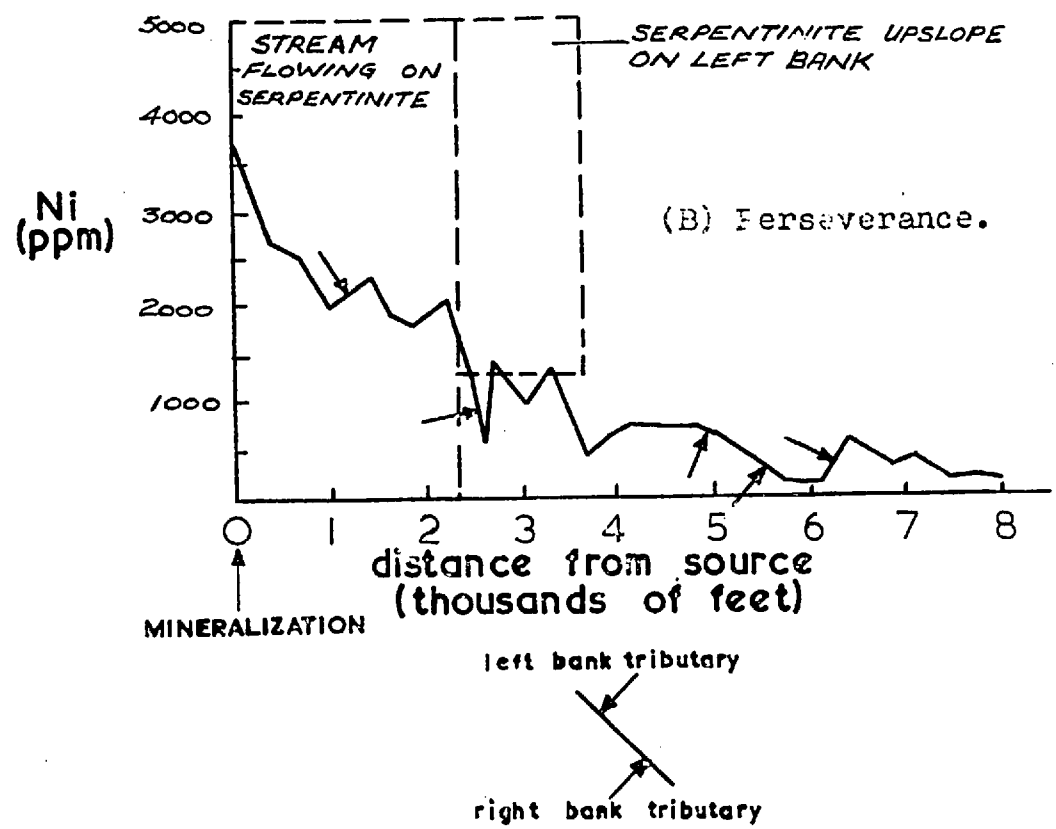
Distance downstream of road (ft.)	Ni content of near-surface soil (ppm)	
	North of channel	South of channel
200	225	45
800	1075	35
1100	360	70
1400	145	155
2100		80
2400	390	60
2700	210	70

crops out upslope to the north it is concluded that much of the Ni in the vlei soil north of the watercourse has originated from the ultrabasic rocks. Outcropping granite in the area was found to contain 60 ppm Ni and freely drained near-surface soil over granite 10 to 30 ppm $Ni_{(spec.)}$ (M.S.A. (Pvt.) Ltd.) with a mean of 13 ppm in 14 samples. The vlei soil is enriched in nickel which is thought to have migrated from the serpentinite. Since the $Ni_{(spec.)}$ content of the near-surface soil between the vlei and the serpentinite is very much less than the Ni content in parts of the vlei, it is concluded that much of the nickel has moved

in the ground water and been deposited in the vlei where the water table comes to surface in the wet season. The Ni content of the near-surface vlei soil south of the watercourse is greater in the lower reaches than near the source (Table 12). This may be due to flooding of the vlei in the wet season and the deposition of nickel in the southern part at this time.

Much of the sediment in the drainage is essentially eroded soil and collapsed bank material. The Ni content of the sediment in a stream rising on the serpentinite decreases from 4000 ppm to 170 ppm in 5000 ft. (A-A', Figure 17). This is still greater however, than the Ni content of sediment in streams draining granite away from any serpentinite (40 to 60 ppm). The decay in Ni content of stream sediment downstream is probably the result of dilution with collapsed bank material and material brought in by tributary streams (Figure 19(A)). In the upper reaches the drainage way is an intermittent channel cut into the vlei soil. The vlei soil is residual except for a thin veneer of alluvium only a few inches thick right at surface in the lowest point of the vlei cross-section. Where there is no well defined channel it is this alluvium (essentially eroded soil) that has





Ni in stream sediment from streams draining barren (A) and mineralized (B) serpentinite.

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(A) DATA: M.S.A. (Pvt.) Ltd. (B) DATA : R.S.T.E. Ltd.

been sampled as sediment. In the channels cut into the vlei there are thicker accumulations of alluvium and vlei soil collapsed from the banks.

Transportation of nickel in solution in ground waters has already been mentioned as a possible mode of dispersion. In addition, it is believed that running water plays an important role in mechanically transporting nickel bearing soil particles into the drainage ways. Mechanical dispersion is believed to be a major factor contributing to the observed distribution of Ni in this study area.

(d) Summary of the main features of the distribution of nickel at Dalmainy Farm.

Analyses have shown that nickel is not distributed uniformly throughout the ultrabasic mass. There is very tentative evidence of zoning around the dunite core.

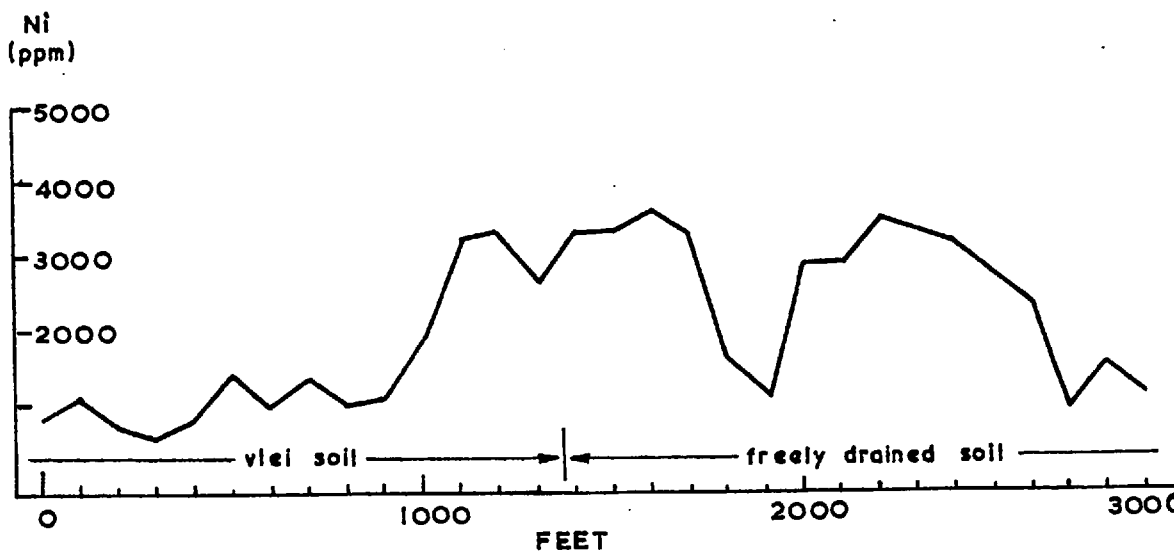
The nickel content of surface soil is higher than the nickel content of the rock but the nickel is even more concentrated at the base of the true soil and in the weathered bedrock. The contrast between nickel in rock (serpentinite) and soil is less than two-fold,

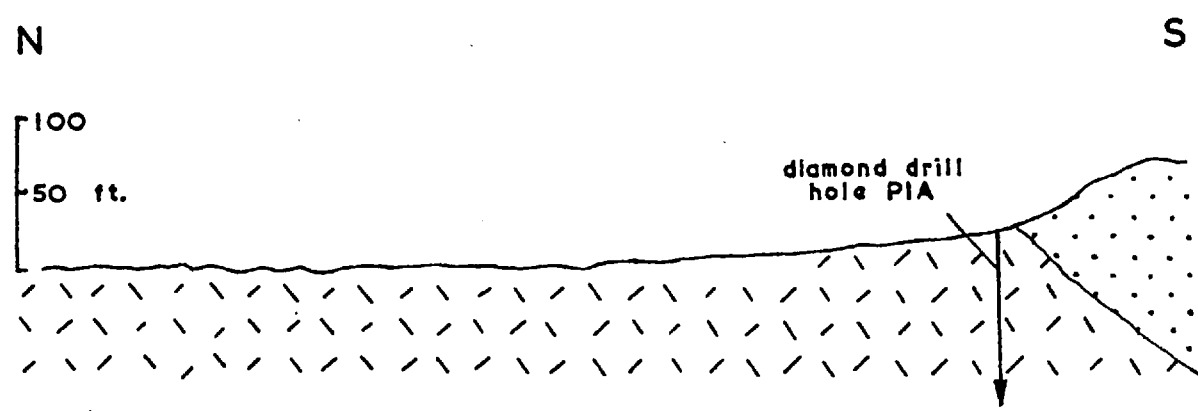
between rock and weathered rock it is approximately three-fold. The variations in primary distribution persist in the weathered bedrock but it is not known whether they are reflected in the nickel content of near-surface soil. The metal is dispersed into the vleis and stream channels considerable distances beyond the boundaries of the serpentinite.

2. Darwendale area.

The Great Dyke serpentinite has been drilled by RSTE Ltd. near Darwendale. No systematic analysis of the core samples has been undertaken but analysis of samples of serpentinite from 208 and 274 ft. below surface in drill hole PIA (Figure 20) gave values of 2650 and 1700 ppm respectively. These results are comparable to published analyses from other parts of the Dyke which range from 1200 to 2100 ppm nickel (Chapter 3). In nickel content Dyke serpentinite and Archean serpentinite of Dalmainy Farm (1600 - 3600 ppm) are also comparable.

The distribution of the metal in near-surface soil has been studied in detail. A soil survey carried out along a line of traverse 3000 ft. in





Serpentinite

Pyroxenite

Distribution of Ni in near-surface soil; Darwendale area.

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length and crossing the serpentinite/pyroxenite contact showed the serpentinite soil to contain, in general, the greater amount of Ni. The range of Ni content in the freely drained soils is 1250 to 3700 ppm (Figure 20). The low Ni content of soil over serpentinite 1800 - 1900 ft. from the northern end of the traverse may reflect a variation in the primary dispersion pattern in the bedrock similar to that at Dalmainy Farm. The difference between the Ni content of near-surface soil over serpentinite and pyroxenite is thought to reflect a difference in primary nickel content. There is less nickel in fresh pyroxenite than in fresh serpentinite (Chapter 3).

The soil survey extended over the low lying parts of the serpentinite where the soil in depth is damp nearly all year round. This poorly drained soil is generally black and rich in clay size material in contrast to the loosely friable, freely drained, red sandy soil on the gentle slopes underlain by serpentinite. The near-surface vlei soil contains less Ni than it's more freely drained counterpart but whether this is a reflection of an initial low nickel content in the fresh rock or of drainage conditions is not known.

In order to get data for comparison with that

from Dalmainy Farm, pits were sunk in freely drained serpentinite soil. The soil profile, (Table 13) is more mature than that at Dalmainy Farm. The true soil

Table 13. Example of a freely drained soil profile over non mineralized serpentinite of the Great Dyke showing the distribution of Ni.

Sample No.	Depth (in.)	Soil horizon	Description	Ni content (ppm)
1045	0-3	A_1	Dark red-brown clay to medium sand, dry and friable and penetrated by fine grass roots.	3000
1046	3-12	A_2	Dark red-brown clay to medium sand, dry and friable.	3600
1047	12-24	A_2	Dark red-brown clay to medium sand, dry and friable but lumpy.	4200
1048	24-36	B	Dark brown clay to fine gravel, slightly damp but still loosely friable. Nodules (probably essentially iron oxide) of fine gravel size abundant 30-36 in.	7200
1049	36-42	C	Variegated grey-yellow weathered serpentinite. Relict olivine texture clearly evident at base of pit.	7800

is very much thicker than it is at Dalmainy Farm and

there is evidence of the formation of a B horizon in that there has been precipitation of iron oxides in a definite horizon within the soil. In all of nine pits the Ni content increases with depth through the solum (true soil of the A and B horizons) and in six of the nine the increase continues into the weathered serpentinite in which relict olivine textures are clearly evident. In two pits there is indication of a decrease further into weathered bedrock. In two pits the B horizon contains more Ni than the underlying weathered serpentinite (Figure 21). Nodules, probably ferruginous and possibly manganiferous, were found near the base of the solum. The nodules are coarser than 80 mesh and were not included in the material analysed. However, nodules separated from the soil from pit No. 4 (Sample 1048) were found to contain more than 4.5% Ni compared to 0.7% in the minus 80 mesh matrix.

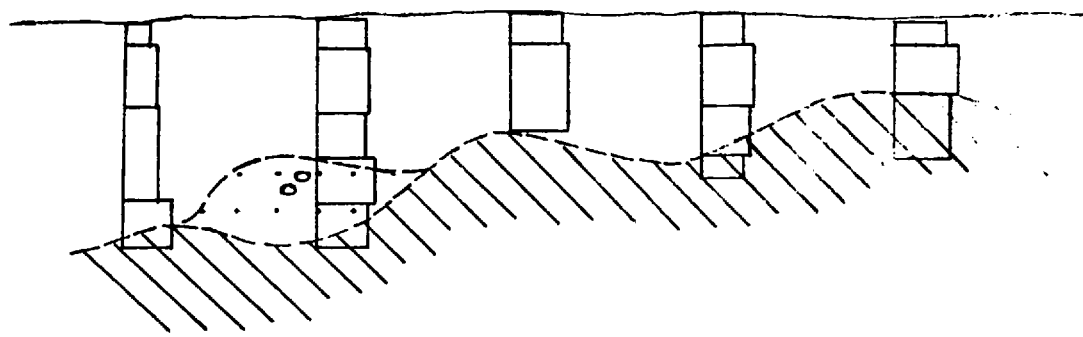
In preparation of the weathered bedrock samples for analysis there has probably been some crushing of individual mineral grains since more force was required to break down the texture of the rotten and weathered rock than that needed to disaggragate soil particles. This may have contributed

Distribution of Ni in the freely drained soil profile over Great Dyke serpentinite.

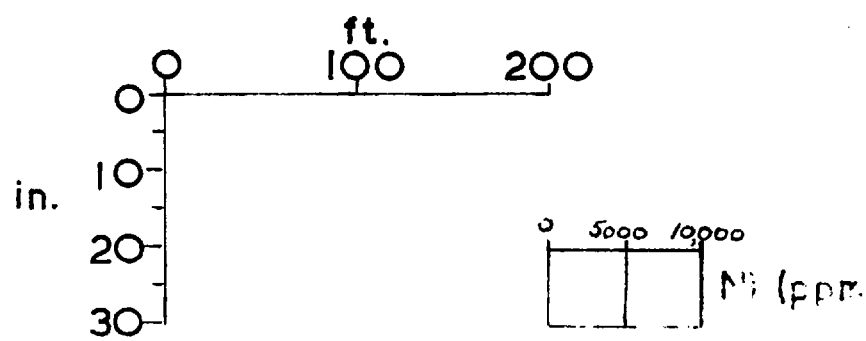
to the higher Ni content in the weathered bedrock. It has, however, been noticed that in all four profiles where there is no B horizon the horizon of maximum Ni content is the top of the weathered bedrock and in two of five profiles where there is a B horizon the B horizon is the layer of maximum Ni content. It is possible then, that the B horizon for nickel is developed lower in the profile than the B horizon for iron.

In only two of five pits put down into vlei soil overlying serpentinite was there a progressive increase in Ni content with depth into rotten serpentinite. In the remaining three pits the horizon of maximum Ni content was higher in the profile but at varying depths below surface. The soil is not true glei soil. There is some evidence of profile differentiation and in one pit nodules were observed in the base of the solum just above the rotten serpentinite. This layer containing the nodules is regarded as a poorly developed B horizon. It contains slightly more Ni than any other horizon in the profile (Figure 22).

The drainage ways in the area are not well defined and many streams lose their identity in the low lying swampy ground. Sediment is essentially



A horizon B horizon C horizon



Distribution of Ni in vlei soil profiles over Great Dyke serpentinite.

collapsed bank soil and in terms of Ni content is closely correlated with the bank soil. For example, sediment in an intermittent channel in a serpentinite vlei contains 760 ppm Ni and the adjacent bank soil 820 ppm. In a more continuous channel over pyroxenite the Ni content (720 ppm) of the sediment is also of the same order of magnitude as that of the bank soil (570 to 750 ppm). At this site however, half the bank was above the level of the water in the stream. The Ni content of the bank soil above the water line is greater than that below the water line by 180 ppm. This is probably due to leaching of nickel from the stream bank below the water level.

Summary of the main features of Ni distribution over the Great Dyke near Darwendale.

Little is known about the distribution of nickel in fresh rock in this area but it is very probable that the amount of nickel varies with mineralogy as is the case in general (Chapter 3) and at Dalmainy Farm in particular (previous sub-section). A soil survey has shown that the serpentinite soil is richer in Ni than pyroxenite soil and that the range in the freely drained serpentinite soil is comparable to that in

corresponding soil at Dalmainy Farm. Another secondary dispersion feature observed here as well as in the older serpentinite is the increase in Ni content from surface down through the soil and in many profiles on into the weathered bedrock. Soil profile development is more advanced at Darwendale than it is at Dalmainy Farm. In the Darwendale area the serpentinite forms the low ground whereas at Dalmainy Farm it forms the high ground.

There is less Ni in the vlei developed over serpentinite than in the freely drained soil but there is little difference in Ni content between bank soil and stream sediment.

3. The non mineralized parts of the Perseverance and Noel serpentinites.

The serpentinite in both these areas is intercalated amongst metavolcanics and metasediments of the Archean schist belts. Although sulphide mineralization at Perseverance and arsenide mineralization at Noel occurs within the serpentinite there are portions of the ultrabasic bodies in which there is no evidence of mineralization and it is these

portions that are considered briefly here. Unfortunately the Maritzani area cannot be included as the barren serpentinite there is downslope of the mineralization.

Both the Perseverance and Noel serpentinites crop out as rocky hills. The soil is nearly everywhere only a thin covering, a few inches thick, over weathered bedrock. There is no soil profile differentiation. The areas compare more closely with Dalmainy Farm than they do with Darwendale.

(a) Ni content of fresh serpentinite.

Company data shows that in 24 samples of fresh, massive, non mineralized serpentinite from Perseverance the Ni content varies from 1100 to 2800 ppm (mean 1900 ppm). Schistose serpentinite contains only 900 - 1600 ppm Ni with a mean of 1100 ppm and talc schist, believed to be after serpentinite, even less (850 ppm ; average of 10 determinations in the range 650 to 1050 ppm). As a possible explanation of the observation that serpentinite contains less nickel than serpentinized dunite or dunite of the Dalmainy Farm mass it was suggested

that there may have been a decrease in nickel content with serpentinization. The Perseverance data lends weight to the suggestion that there is a decrease in nickel content with alteration of dunite to serpentinite in that there appears to be a further decrease in nickel content during the subsequent alteration of serpentinite to talc. Although, in the opinion of many scholars, alteration has taken place at temperatures and pressures considerably lower than those prevailing at the time of the initial crystallization of the rock the resultant redistribution of nickel is not a secondary dispersion feature in the context of this thesis. The temperature and pressure at which alteration took place was probably still quite appreciably higher than that encountered in weathering and secondary dispersion at or near surface.

No data on the distribution of nickel in fresh serpentinite is available for the Noel area.

(b) Soil Surveys.

At the Perseverance prospect RSTE Ltd. have sampled an area, approximately 12,000 ft. by

6,000 ft., at 50 or 100 ft. intervals along lines 500 ft. or less apart. The discussion here pertains only to the background areas. The main features of the distribution of Ni in near-surface soils in the area of the prospect are described in the following section which deals with anomalous distributions.

The Ni content of near-surface soil over non mineralized serpentinite at Perseverance ranges from 1200 to 4350 ppm. The values (50 analyses) appear to be lognormally distributed about a mean of 2250 ppm.

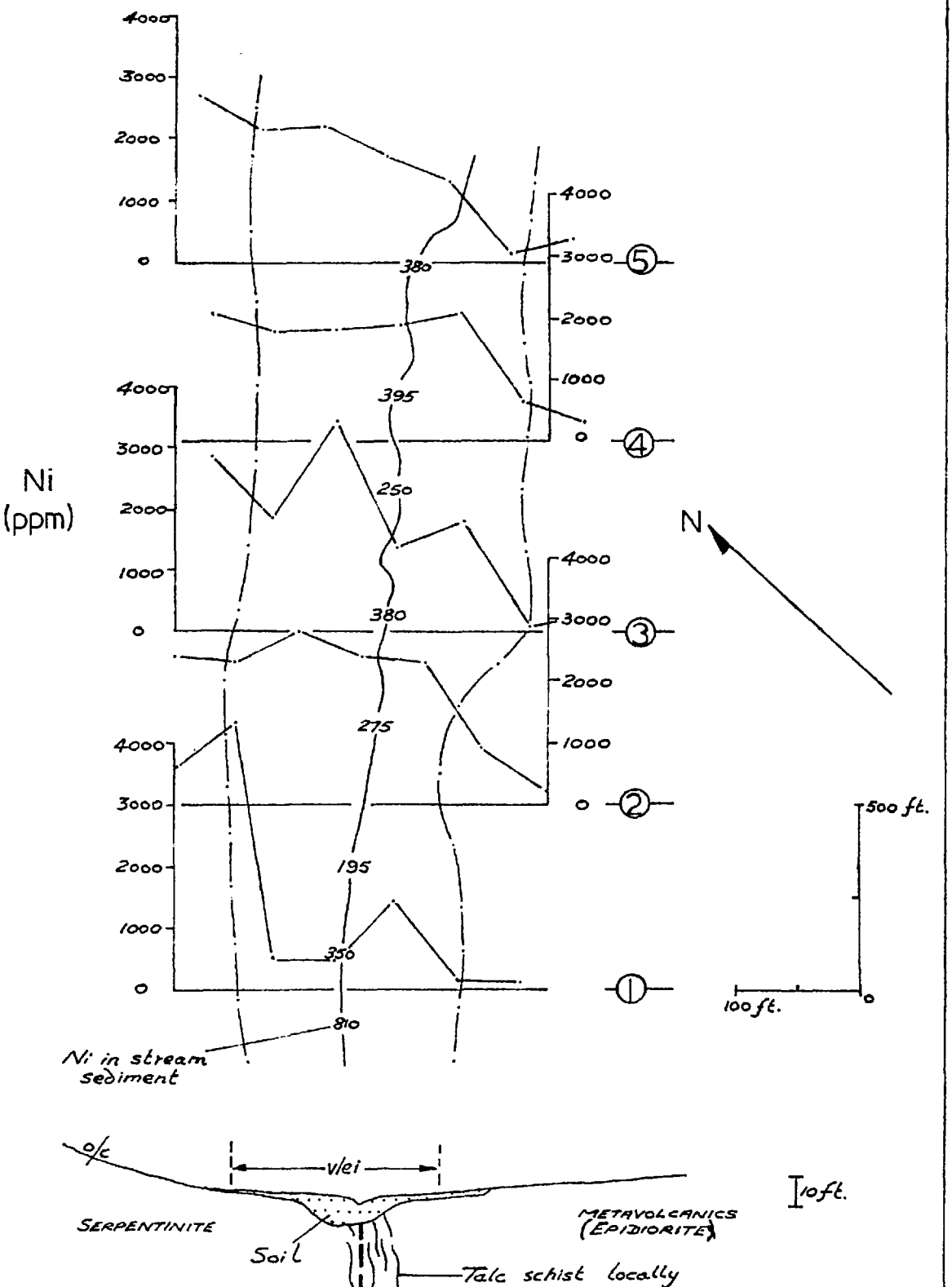
In the environs of the Noel Nickel mine near-surface soil samples were collected by the Southern Rhodesia Geological Survey at 100 ft. intervals along lines 200 ft. apart. Analysis of these samples in the Applied Geochemistry Research Group laboratories showed that the range of Ni content of near-surface soil over serpentinite (1200 - 3800 ppm) is similar to that at Perseverance. The mean Ni content of 30 samples collected over the serpentinite is 2000 ppm.

(c) Distribution of Ni in the drainage.

At Perseverance a poorly developed vlei with an intermittent channel drains barren serpentin-

ite. This vlei is developed over the contact between serpentinite and metavolcanics and the Ni content of the near-surface soil decreases across the vlei from serpentinite to metavolcanics (Figure 23). The amount of Ni in the vlei appears to be greater than that in the immediately adjacent more freely drained soil and is markedly greater than that in stream sediment. This distribution is similar to that observed at Dalmainy Farm but different to the Darwendale area where there is less Ni in the vlei than in the freely drained soil. The drainage at Perseverance is similar to the Dalmainy Farm drainage and the dispersion mechanisms are believed to be similar. In these two areas the vleis do not hold water like the vlei soil developed over Dyke serpentinite does. This difference in water relationships is probably related to the different Ni distributions and will be referred to again later.

No drainage way suitable for studying the dispersion of nickel from barren serpentinite in the environs of the Noel Nickel mine could be located.



Geological section : Traverse ②

Distribution of Ni in a vlei draining non mineralized serpentinite at Perseverance.

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GEOCHEMISTRY : R.S.T.E. Ltd.

(d) Summary of the features of Ni distribution in non mineralized sections of the Perseverance and Noel serpentinites and comparison with the Dalmainy Farm and Darwendale areas.

Fresh, non mineralized serpentinite at Dalmainy Farm, Darwendale and Perseverance contains large amounts of Ni (Table 14). In the series dunite-serpentinite-talc schist there is a decrease in Ni content. The Ni content of near-surface soil is

Table 14. Ni content of fresh non mineralized serpentinite of the Rhodesian study areas.

Area	Ni content (ppm) Range	Mean	No. of analyses
Dalmainy Farm	1600-3600	2900	105
Perseverance	1200-2800	1900	24
Great Dyke (Darwendale)	1700-2650	2200	2

similar at Perseverance and Noel but less in these areas than that at Dalmainy Farm and Darwendale (Table 15). Despite the lack of development of a soil profile, the rugged topography and lower rainfall of the Perseverance and Noel areas, especially the latter, the distribution of Ni over barren serpentinite in these areas is essentially similar to the distribution in the two non mineralized study areas (Dalmainy Farm

and Darwendale). There are, however, differences in level of local background (summarized in Table 15) which may result not only from variations in primary dispersion but also from the influence of diverse topographic and climatic factors on secondary dispersion.

Table 15. Ni content of freely drained near-surface soil over barren serpentinite of the Rhodesian study areas.

Area	Ni content (ppm) Range	Mean	No. of analyses
Dalmainy Farm	2000-5000	3500	19
Darwendale	1250-3700	3000	10
Perseverance	1200-4350	2300	50
Nocl	1200-3800	2000	30

The distribution of Ni in the unmineralized Perseverance drainage is, to some extent, similar to the distribution in the vlei at Dalmainy Farm although the level in the latter area is very much lower than it is at Perseverance due to the vlei there being about 1000 ft. from the serpentinite. Drainage conditions in these two areas are different to those at Darwendale and the dissimilarity is thought to be a cause of the different distribution of Ni at Darwendale where vlei soil contains less Ni than freely drained soil.

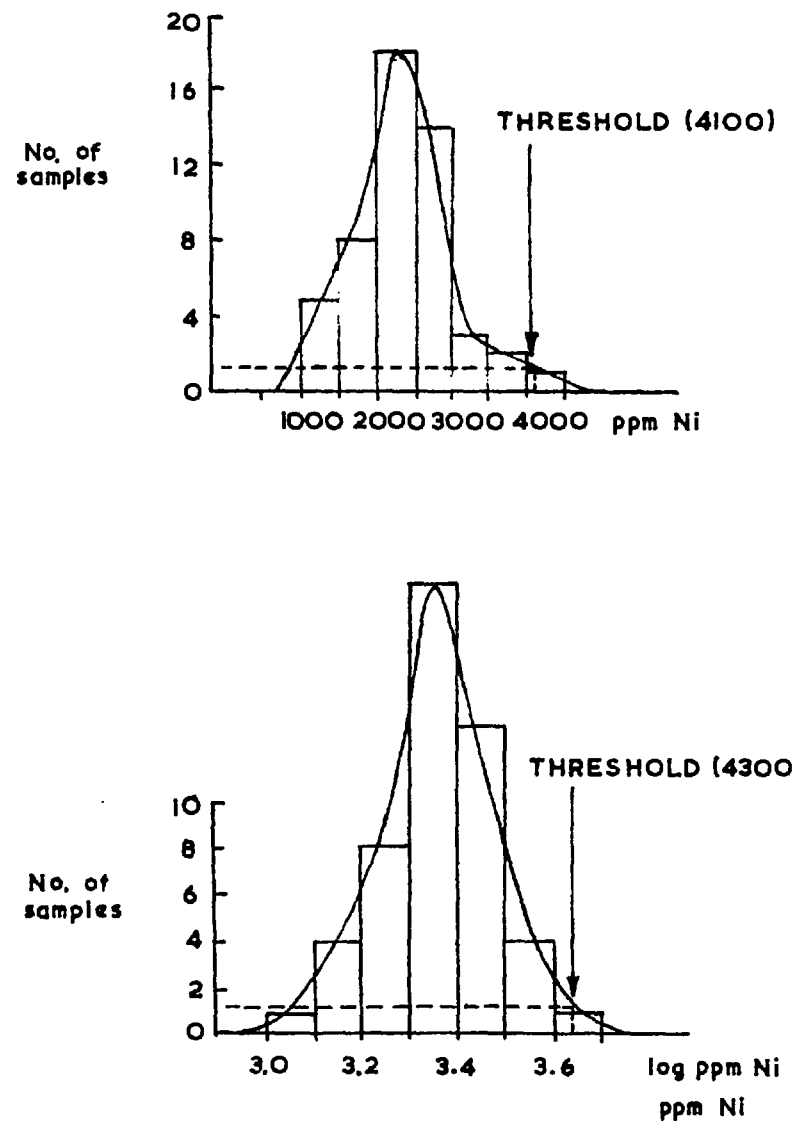
4. Interpretation of background data.

In the foregoing description of the distribution of nickel in areas of barren serpentinite reference has been made to the fact that the distribution is lognormal. Logarithmic plots have been used, therefore, in determining the upper limit of normal background variation (threshold) in these cases, e.g. Figure 24. The upper limit of background was read from the curve. For confirmation the threshold value was also calculated, where the distribution approximated to normality or log normality, as the mean plus two standard deviations. The agreement between the two procedures was good.

However, statistical treatment of the data has been employed only as an aid to presentation. It has not been used as a strict mathematical approach to interpretation.

Local anomaly threshold for near-surface soil over serpentinite rocks of the study areas.

Attention has been drawn to the variations in level of local background over serpentinite in the



Frequency distribution diagrams: Ni in near-surface soil over barren serpentinite; Perseverance.

different study areas. The anomaly threshold varies accordingly (Table 16). The variations may be due to a number of reasons, particularly :-

Table 16. Anomaly threshold for Ni in near-surface soil over serpentinite of the study areas.

Area	Ni content (ppm)			No. of samples
	Mean	Standard deviation	Anomaly threshold[1]	
Dalmainy Farm	3500	700	4900	19 [2]
Darwendale	3000	300	3600	10
Perseverance	2300	800	3900	50
Noel	2000	575	3100	30

[1] by calculation. [2] Exception - $Ni_{(spec.)}$

(i) Variations in mineralogy, that is variations in the original primary distribution and

(ii) Differences in soil type brought about by the diverse climatic and topographic conditions in the study areas.

B. The distribution of Ni in areas of mineralized serpentinite.

Deposits of nickel sulphide and/or arsenide minerals themselves constitute a geochemical and geo-

logical anomaly. Likewise, above average amounts of nickel in the soils overlying such deposits comprise an anomaly. In this section the distribution patterns that have resulted from the secondary dispersion of nickel from sulphide minerals in serpentinite are described. The study areas involved are Perseverance and Maritzani.

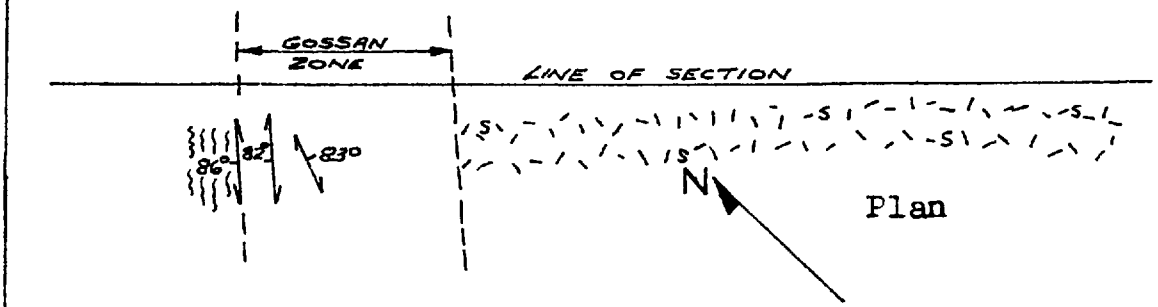
1. The Perseverance prospect.

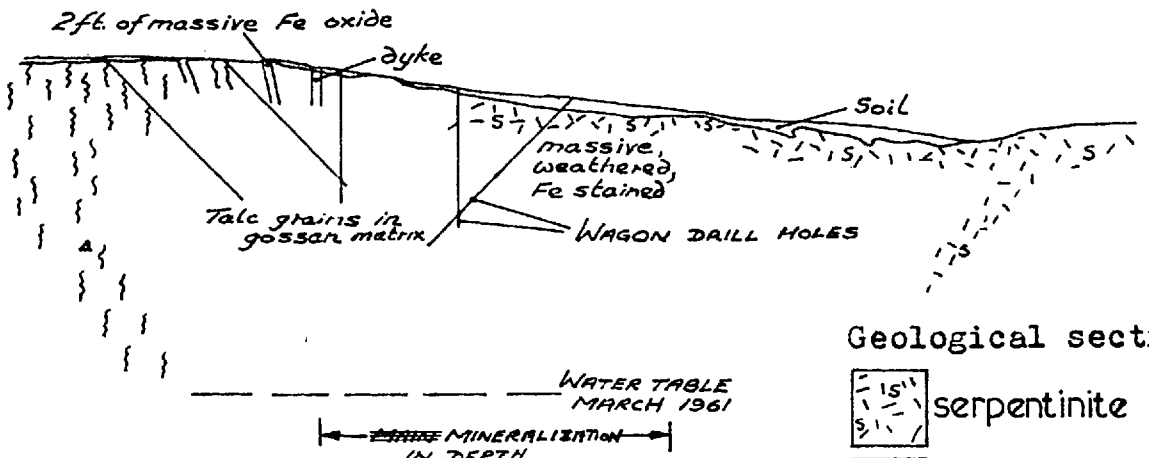
Fresh non mineralized serpentinite at Perseverance contains, on average, 1900 ppm Ni (Table 14). Mineralized serpentinite has been found to contain more than 0.5% nickel in the section along line 12R (Figure 26). The contrast between the ore horizon and barren serpentinite is then, in this section, more than two and a half - fold at maximum. Sparse disseminations of the sulphides occur in the serpentinite. As far as can be determined the sparsely mineralized serpentinite away from the shear zone contrasts with the barren serpentinite by no more than two - fold at the most.

The Ni content of non mineralized metavolcanics varies between 15 and 35 ppm.

(b) Ni in weathered bedrock.

Anomalous amounts of Ni indicate the outcrop of the weathered orebody (Figure 25). Unlike Dalmainy Farm and Darwendale it is not clear whether weathered serpentinite contains, on average, more nickel than the fresh rock. At three of five randomly selected sites the weathered rock contains, in general, more nickel than does the immediately subjacent and fresher material (Table 17). The degree of enrichment is, however, fractional and very much less than that observed at Dalmainy Farm. It must be pointed out furthermore, that the data is from wagon drill holes inclined at 45^{o} and the variations in Ni content observed may be lateral rather than vertical especially at the anomalous sites where the Ni content can vary quite appreciably over a very



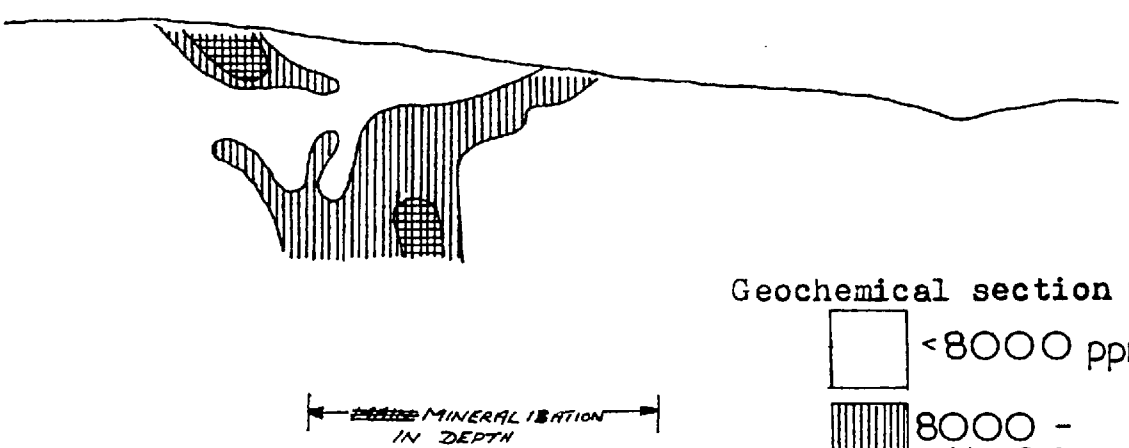


Geological section

serpentinite

metavolcanics

Scale 1:500



Geochemical section

<8000 ppm

8000 - 16000 ppm

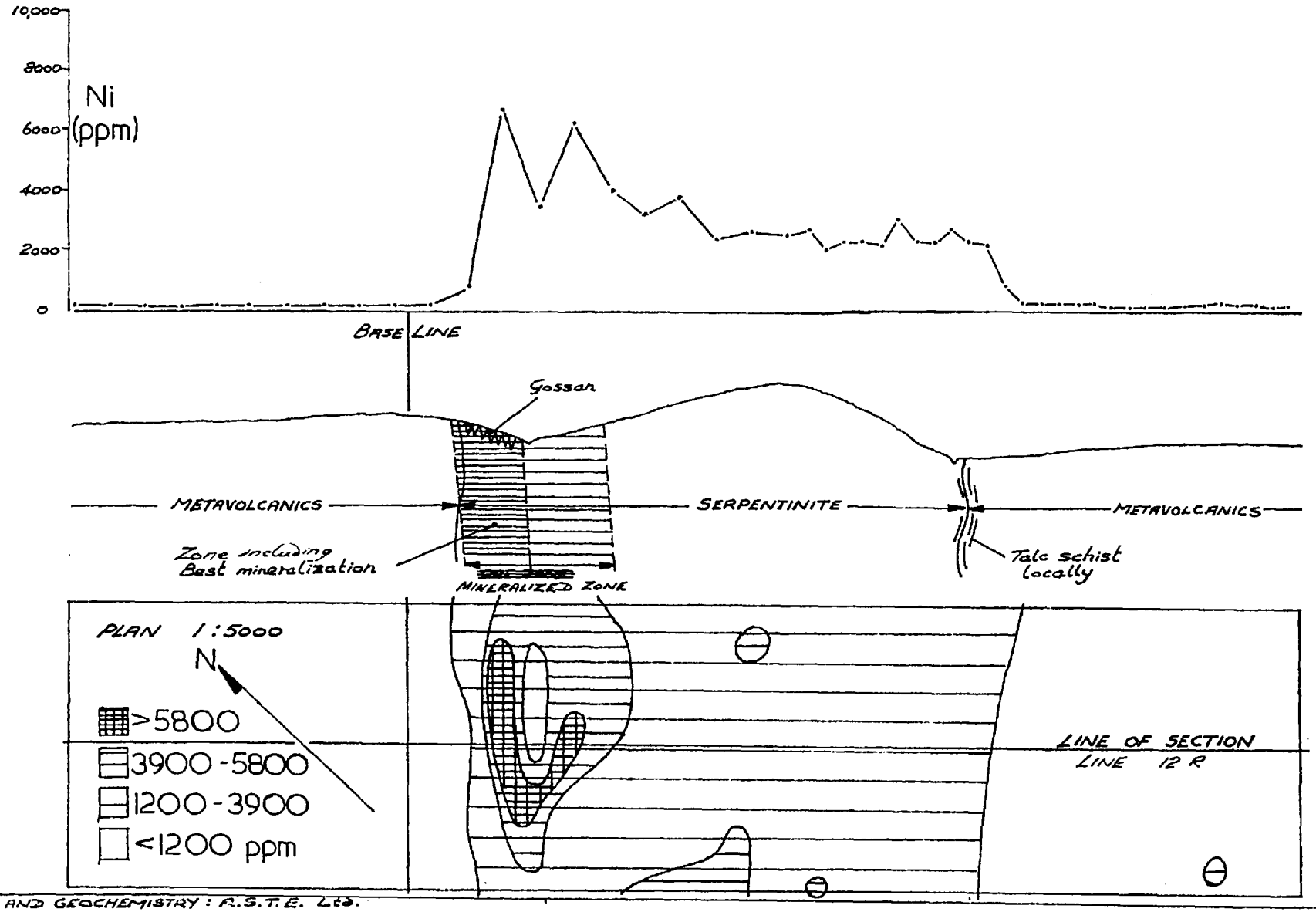
>16000 ppm

Typical section across the Perseverance mineralization showing the distribution of Ni.

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GEOLOGY AND GEOCHEMISTRY: R.S.T.E. Ltd.

Ni in near-surface soil over a characteristic portion of the Perseverance area.



26

GEOLOGY AND GEOCHEMISTRY : F.S.T.E. Ltd.

limited distance.

(c) Soil Survey.

The intensive soil sampling programme carried

Table 17. Ni in fresh and weathered serpentinite, Perseverance area. (Data : RSTE Ltd.)

Physical condition	Samples from randomly selected wagon drill holes									
	No. 78		76		50		75		83	
	Depth (ft.)	Ni ppm	Depth (ft.)	Ni ppm	Depth (ft.)	Ni ppm	Depth (ft.)	Ni ppm	Depth (ft.)	Ni ppm
Weathered	1	3700	3	3600	5	6500	5	3900	17	9500
do	3	2700	5	2900	7	9000	7	3100	19	8000
do			7	3900	9	7800	9	3200	21	12000
Fresh	5	2600	9	3600	11	6800	11	2700	23	9500
do	7	2000	11	3700	13	5200	13	2900	25	15000
do	9	2800	13	3100	15	4600	15	2700	27	10500

out in this area has been mentioned already (Section A). The serpentinite forms a well pronounced ridge with abundant outcrop and a skeletal soil profile. Although the ground rises either side of the mineralization there is no vlei in the vicinity (Figure 26).

The predominant feature of the areal distribution of Ni in soils is the manner in which it reflects the geology (Figure 26). Figure 26 represents a portion of the area covered by the soil survey and

includes the mineralized shear zone. The area covered by the plan is typical of the study area as a whole and illustrates the features described. The general tenor of Ni in the soil over serpentinite is more than ten times that in the soil over metavolcanics. The Ni content of the soil over the mineralization has nowhere been found to exceed 8000 ppm, the maximum nickel content observed in the survey being 7400 ppm. Values for Ni in near-surface soil in excess of 3900 ppm (the local anomaly threshold, Table 16) by definition, are anomalous but the maximum anomaly over the mineralization is less than two-fold. This contrast is less than that in the fresh rock. It is probably limited in extent as a result of the topographic configuration. In the low point of the gulley the amount of Ni in the soil is not anomalous. There has probably been some transportation of barren soil from upslope which has accumulated in the gulley and dilution with barren soil from upslope may also account to some extent for the poor contrast between anomalous and background near-

surface soil. Several hundred feet south of the gossan anomalous amounts of Ni in the soil may reflect another patch of mineralization.

Elsewhere over the serpentinite patches of soil containing anomalous amounts of Ni have been detected but they are of small extent and unrelated to any known mineralization. The Ni content of the soil in these small anomalous areas, which may be reflecting slight mineralogical variations in the fresh rock, does not exceed the mean plus three standard deviations (4700 ppm, Table 16). Isolated values of less than the mean plus three standard deviations do not, thus, appear to have any significance in terms of mineralization.

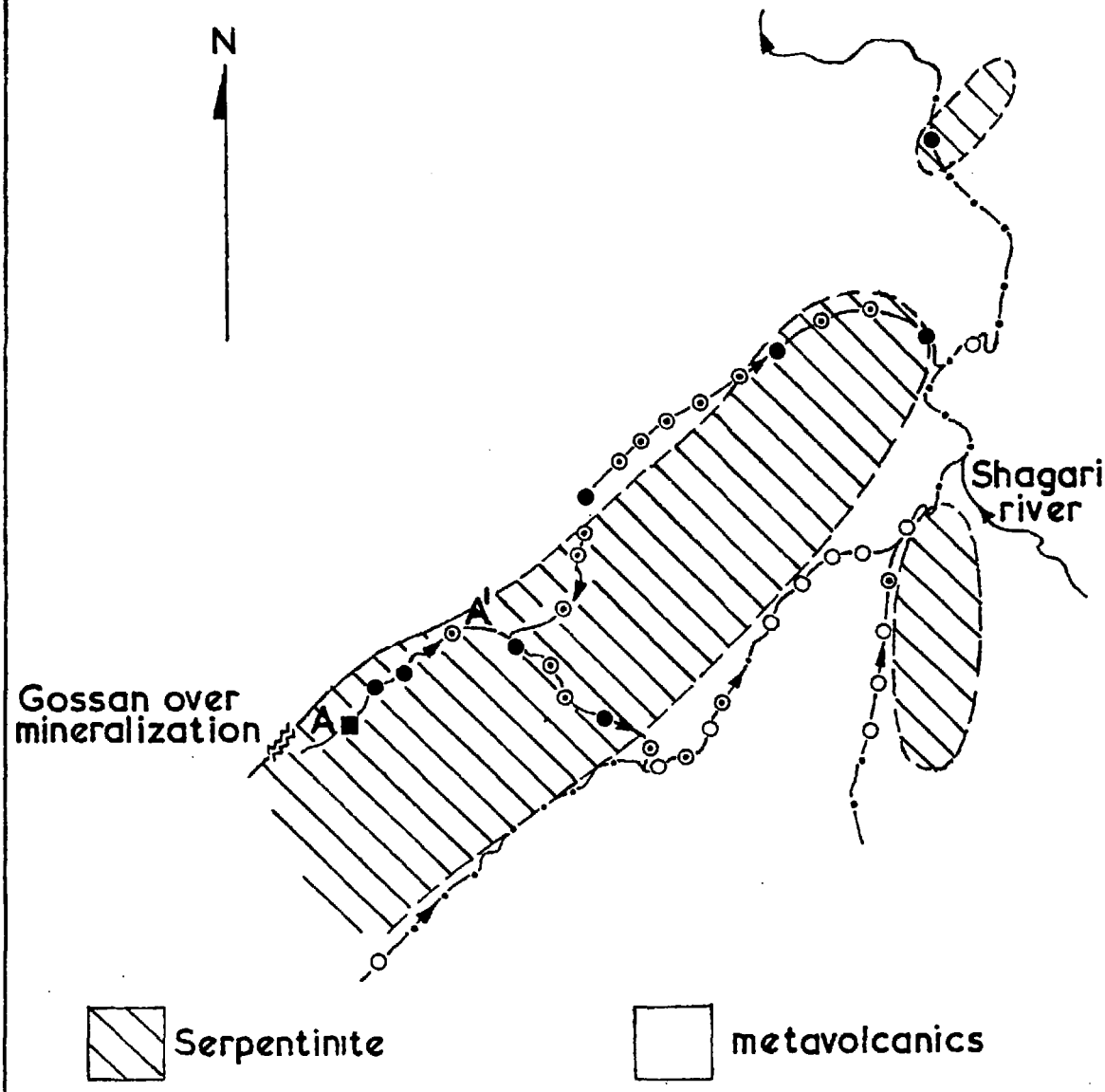
(d) Ni in stream sediment.

Since the initial drainage reconnaissance carried out by RSTE Ltd., water from exploratory underground workings has been pumped into the drainage. This will undoubtedly have contaminated the drainage to some extent. In view of this the writer did not under-

take any sampling in the drainage in this area. The results of stream drainage reconnaissance carried out by the company are presented in Figures 27 and 19. In the stream draining the mineralized area (A - A^1, Figure 27) the Ni content of the stream sediment 400 ft. downslope from the gossan outcrop is 3100 ppm. This decreases to 180 ppm in the Shagari river just over a mile downstream.

Immediately below the points of entry of right bank tributaries at 2600 and 5000 ft. from the source and directly below the confluence with the Shagari river there is a decrease in Ni content. Slight increases in Ni content of stream sediment occur just downstream from the junction with the left bank tributary at 1400 ft. from the source and just downstream of the point of entry of the left bank tributary into the Shagari river (Figure 27). These two last mentioned tributaries drain barren or only very sparsely mineralized serpentinite and metavolcanics. The decay downstream is probably by dilution with material of relatively low Ni content entering via tributary streams and with collapsed bank soil.

The distribution is very similar to that in the stream draining non mineralized serpentinite at



Scale. 1:15,250
(1cm. : 500 ft.)

Drainage reconnaissance, Perseverance area: Ni in stream sediment.

27

GEOCHEMISTRY: R.S.T.E. Ltd.

Dalmainy Farm (compare (A) and (B) of Figure 19).

The 2600 ppm Ni in the sediment in the Shagari river in the extreme north of the area has been checked and found correct. It is directly over a small serpentinite outlier which straddles the river at this point. Diamond drilling has revealed some sulphide minerals within the metavolcanics near the serpentinite contact.

(c) Summary and discussion of Ni distribution at Perseverance.

The main mineralization at Perseverance is at the metavolcanics/serpentinite contact but widely scattered sulphide minerals have been observed in the serpentinite.

The contrast in Ni content between the main mineralization and fresh non mineralized serpentinite is 2.5 - fold plus at maximum.

In the weathered bedrock the mineralization gives rise to an anomalous Ni content. In general the weathered rock contains fractionally more Ni than does fresher rock except directly over mineralization where the Ni content increases with depth through uppermost 30 ft.

The soil survey showed that the soil over mineralized serpentinite contains anomalous amounts of Ni but that the contrast between anomalous values and threshold (less than two-fold) is lower than it is in fresh or weathered rock. The soil anomaly does not extend far beyond the limits of the primary dispersion aureole. This limitation is thought to be due to the topographical setting of the mineralized suboutcrop.

The distribution of Ni in stream sediment is comparable with that at Dalmainy Farm. There is no obvious difference in the distribution of Ni in the stream sediment at Perseverance that can be correlated with the presence of sulphide mineralization.

2. The Maritzani area.

In contrast to Perseverance, the serpentinite at Maritzani forms no pronounced topographic feature but suboutcrops on a gentle slope to a vlei. There is no gossan in this area. Soil profile development is immature and consists usually of a layer of A horizon soil grading with depth through a rubble zone to the rotten and weathered bedrock. There are traces of B horizon development in parts where apparently ferruginous nodules have been observed just above the top

of the weathered bedrock. The serpentinite in this area is downslope from metavolcanics.

(a) Nickel in fresh rock.

The main mineralized zone, as at Perseverance, is at the contact between serpentinite and metavolcanics and enclosed within a primary dispersion aureole of sparsely disseminated sulphides. The content of sulphide nickel in the primary dispersion aureole decreases, in general, with distance from the main mineralized zone. A geological section compiled mainly from diamond drill hole data is included in Figure 28 which shows the distribution of Ni in the uppermost 30 ft. of the section.

(b) Ni in Weathered bedrock.

Within the uppermost 30 ft. of section just referred to the Ni content decreases with depth, there being more Ni in weathered bedrock near surface than

Typical section across the Maritzani mineralization showing the distribution of Ni.

28

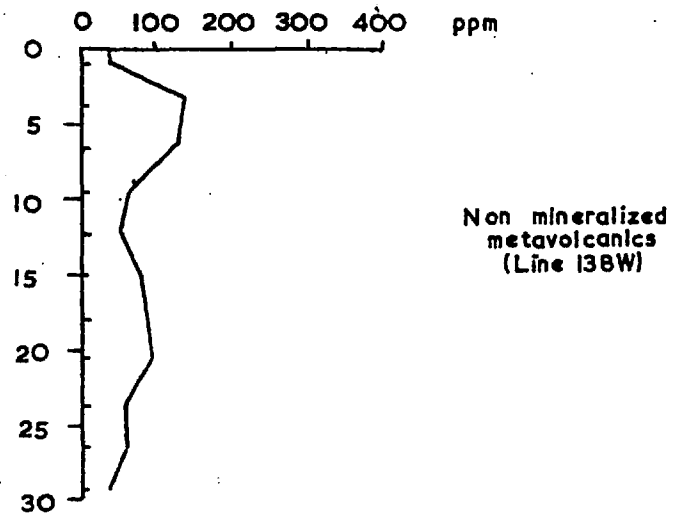
GEOLOGY AND GEOCHEMISTRY: R.S.T.E. Ltd.

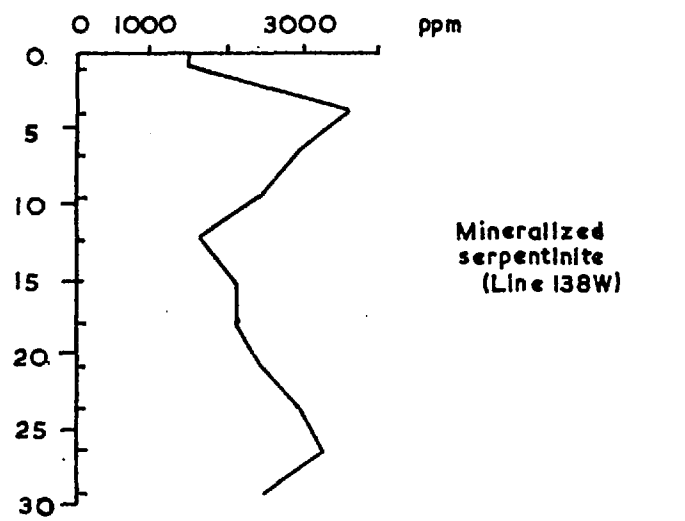
in the fresher rock deeper down (Figure 29). The enrichment occurs in both barren serpentinite and barren metavolcanics. By contrast there is an increase in Ni content with depth over the main mineralization. The mineralized zone is poorly delimited by the Ni content of weathered bedrock (Figure 30). The maximum contrast between mineralized and non mineralized weathered serpentinite appears to be about three-fold.

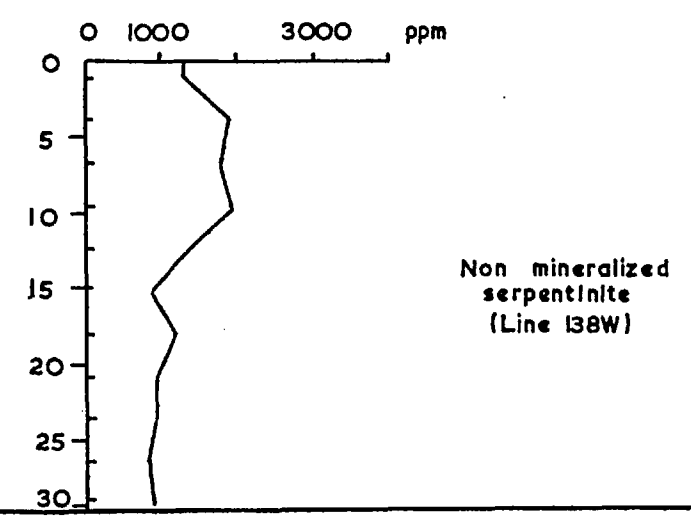
(c) Soil Survey.

Intensive soil sampling carried out by RSTE Ltd. within the Exclusive Prospecting area No. 85 included the Maritzani study area. Samples were collected at 50 ft. intervals along lines 200 ft. apart within an area approximately 8000 ft. by 3200 ft. The grid was not regular and in parts the density of sample sites is greater than that described above, in other parts of the area it is less.

As in the case of Perseverance the most striking feature is the relationship of Ni distribution to geology (Figure 31). Serpentinite soil is markedly



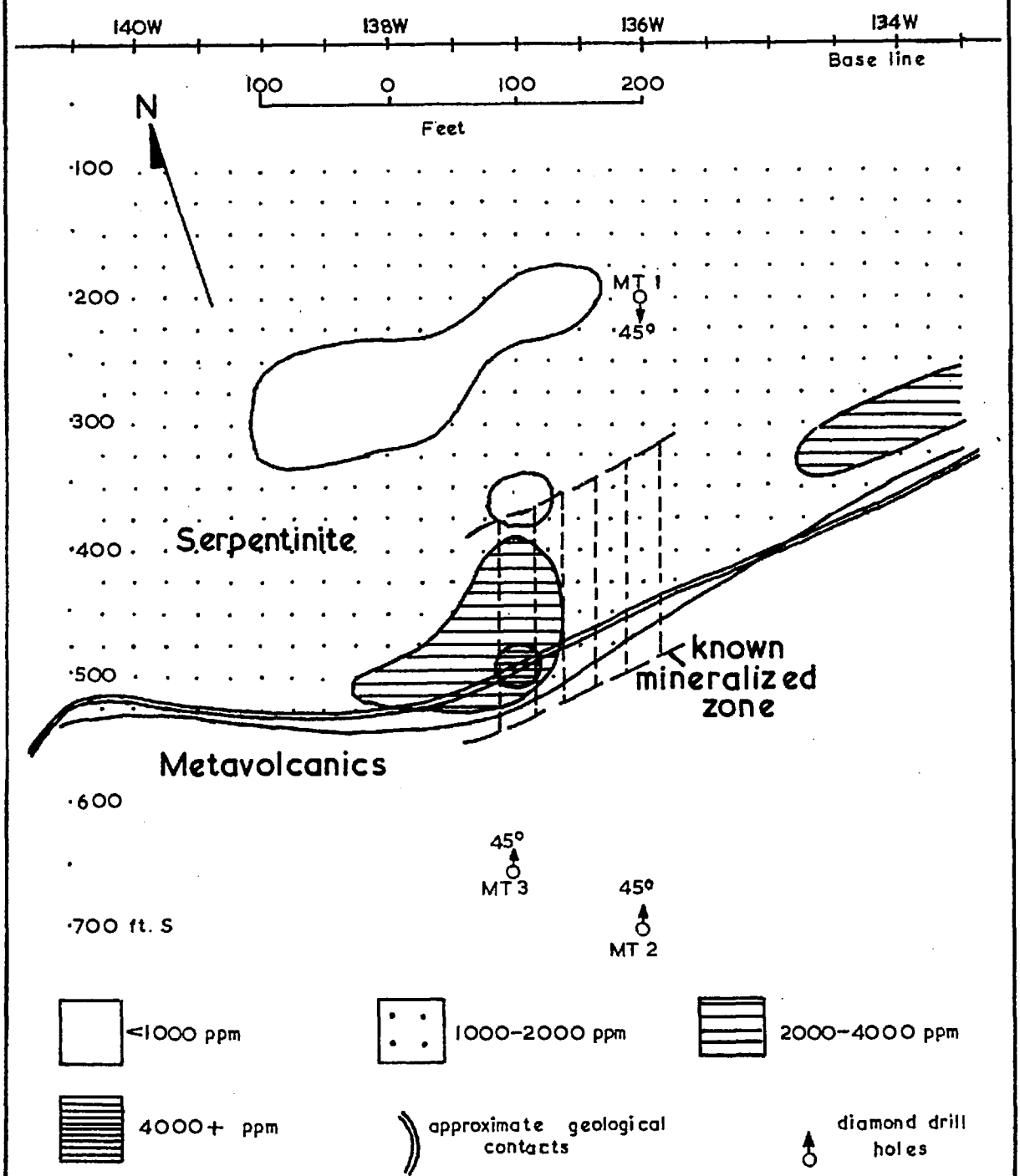




Profile distribution of Ni in the weathered mantle; Maritzani.

29

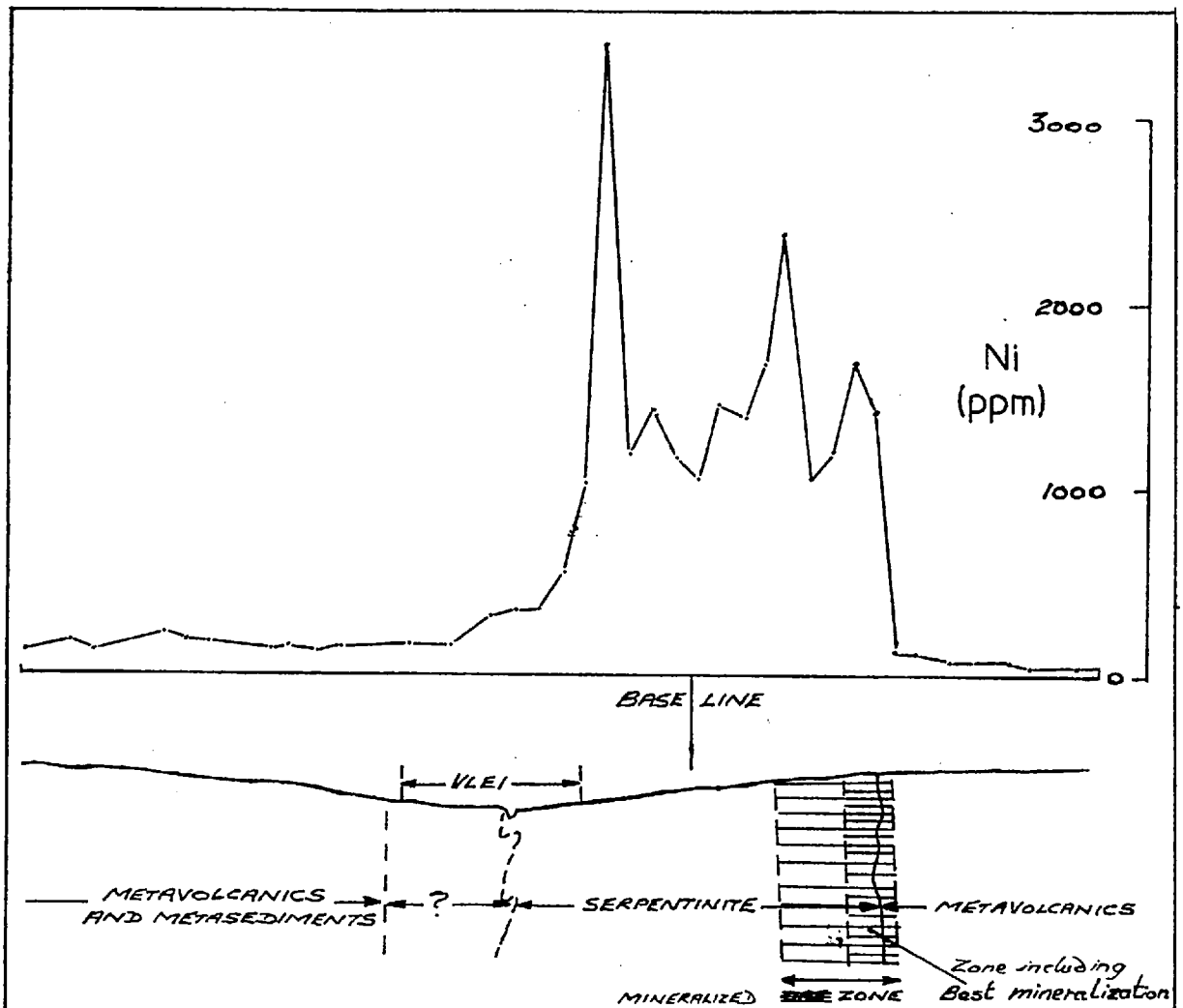
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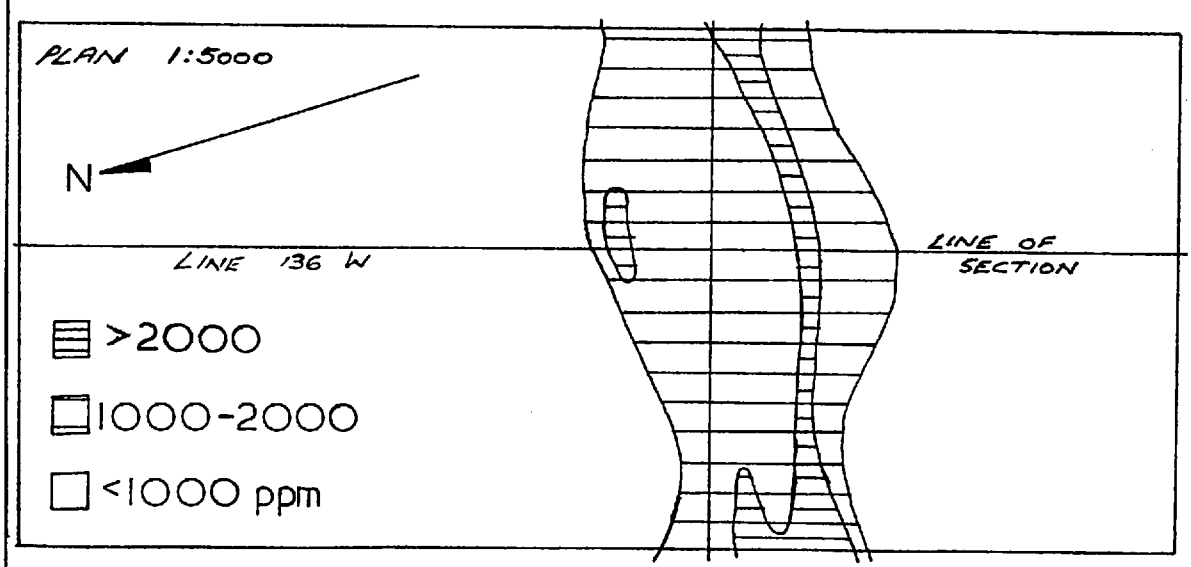


Distribution of Ni in weathered bedrock 15 ft. below surface; Maritzani.

30

DATA: R.S.T.E. Ltd.





Ni in near-surface soil over a characteristic portion of the Maritzani area.

31

GEOLOGY AND GEOCHEMISTRY : R.S.T.E. Ltd.

richer in Ni than are soils derived from metavolcanics or metasediments. Near-surface soil containing more than 3000 ppm is rare, the maximum Ni content recorded in the survey here being 3900 ppm. Values in excess of 2000 ppm may be anomalous but are by no means obviously so although there is a continuous strip of soil of more than 2000 ppm along strike parallel to the mineralized belt. Although the continuous strip of soil of high Ni content is displaced 100 - 200 ft. downslope from the projected suboutcrop of the mineralized zone the writer believes it to be related to the mineralization. The displacement is thought to be due to lateral dispersion of the soil downslope. Soil of low Ni content derived from barren metavolcanics is believed to be diluting the soil directly over the projected ore suboutcrop from which some nickel is being dispersed downslope. The reason for the broadening of the zone of soils of Ni content of more than 2000 ppm is not known.

At the edge of the vlei 600 ft. downslope from the main patch of Ni rich soil discussed above one analysis revealed 3400 ppm Ni in the soil. This value

is not considered to be related to any sulphide minerals. As mentioned, the site is close to the vlei margin and serpentinite crops out not more than a few feet away. The difference in soil type is thought to be responsible for this erratic high value.

The near-surface vlei soil over serpentinite is impoverished in Ni relative to the freely drained soil over serpentinite. This is the reverse to the observed distribution at Perseverance and is thought to be due to dilution with material of low nickel content washed along and across the gently sloping vlei. In addition, some nickel may be leached by water passing along the vlei.

It is perhaps, useful to recall here, that at Dalmainy Farm and Perseverance where the serpentinite forms a topographic high feature and the vlei is developed off the serpentinite the vlei is enriched in Ni. Conversely, at Darwendale and Maritzani where the serpentinite underlies low lying ground and the vlei is developed over the serpentinite the vlei is impoverished in Ni relative to the freely drained soil. In the two former areas nickel is accumulating in the vleis, in the two latter mentioned areas it is being diluted and leached.

(d) Ni in the soil profile.

It is regretable that there is no barren serpentinite upslope of the mineralization. Nevertheless, the distribution of Ni in profile over metavolcanics has been studied at three points (Figure 32). The differentiation of the soil into horizons is very limited (Table 18). The level of Ni content is generally very low. Nowhere in the profile over barren metavolcanics does the Ni content exceed 225 ppm. There is slightly more Ni in the top 3 in. than in the material directly below 3 in. in two pits but the general trend is an increase in Ni content with depth through the true soil. At two of the three points studied this increase continues into the weathered bedrock.

Over the main mineralization in both metavolcanics and serpentinite (Table 19) there is a steady increase in Ni content with depth but overlying the zone of sparse sulphide disseminations and in the non mineralized serpentinite downslope the Ni is at maximum at or near the top of the C horizon (Table 20). In the freely-drained profile over non-mineralized serpentinite downslope of mineralization the upper horizons are richer in Ni than the corresponding horizons in the profile directly over mineralization. In the deeper

soil (A Horizon)

rubble

rotten and weathered bedrock

in. 0 6 12 18 24 30

0 1000 2000 3000 ppm

Scale of ft.

1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 0

BASE LINE

vlei soil

serpentinite

MINERALISED Zone

metavolcanics

vlei soil

NORTH

SOUTH

Distribution of Ni and Cu in soil profiles, Maritzani.

32

layers of the two profiles the reverse is true. The reason for this is believed to be that already given to

Table 18. Example of a freely drained soil profile over non mineralized metavolcanics at Maritzani showing the distribution of Ni.

Sample No.	Depth (in.)	Horizon	Description	Ni content (ppm)
822	0- 3	A	Pale brown clay to fine sand, dry and friable.	115
823	3-12	A	Pale brown clay to fine sand, dry and friable, as matrix to fragments of weathered, poorly schistose metavolcanics. Stained red-ochre with iron oxides.	85
824	12-24	A	do - but with a greater proportion of red-ochre stained rock fragments.	145
825	24-33	C	Variegated red, purple and ochre, weathered, fine grained, fractured and schistose metavolcanics heavily impregnated with iron oxides.	90
826	33-45	C	do - but more massive with traces of talc and less ferruginous material.	85
827	45-48	C	Pale buff-pink talcose schist.	not determined

explain the downslope displacement of the near-surface soil of high Ni content. That is that there is effective lateral dispersion downslope. Study of the distribution of Ni in the two profiles confirms another feature already discussed, namely the decrease in Ni content

with depth into weathered barren serpentinite in contrast to an increase with depth into weathered mineralized serpentinite.

Table 19. Example of a freely drained profile over well mineralized serpentinite at Maritzani showing the distribution of Ni.

Sample No.	Depth (in.)	Horizon	Description	Ni content (ppm)
841	0- 3	A	Brown clay to grit, dry and friable.	700
842	3-12	A	Brown clay to grit, dry and loose, extending into rubble zone which includes some irregularly rounded ferruginous nodules of up to medium gravel size.	900
843	12-24	B	Zone of nodular lateritic rubble.	980
844	24-36	B	Variegated pale buff/red brown rubble, dry and loose. Angular fragments of talcose, weathered basement schists, nodular lateritic fragments and rounded and angular fragments of weathered serpentinite.	1800
845	36-48	C	Variegated yellow-brown-black-ochre, dry, rotten serpentinite intensely impregnated with iron oxides. Traces of blue-green encrustations with the iron.	2500
846	48-60	C	do - but somewhat fresher with fragments of weathered serpentinite covered with a green nickel bloom.	3200

In the vlei soil the distribution of Ni is

more erratic and the 3-12 in. horizon contains the largest amount of the metal (Figure 32). Only 100 ft. beyond into the vlei across the stream channel where the

Table 20. Example of a freely drained soil profile over non mineralized serpentinite of the Maritzani mass showing the distribution of Ni.

Sample No.	Depth (in.)	Horizon	Description	Ni content (ppm)
848	0- 3	A	Dark brown silt to sand, dry and friable.	975
849	3-12	A	Dark brown silt to sand, dry and loose.	1015
850	12-24	A	Dark brown silt to sand, dry and loose between pale buff fragments of weathered, fractured and sheared serpentinite impregnated with iron oxides.	1435
851	24-36	C	Variegated yellow-brown, fine grained, weathered, sheared and fractured serpentinite impregnated with iron oxides.	1665
852	36-48	C	do	1710
853	48-60	C	Yellow-brown, weathered fine grained, sheared and fractured serpentinite with considerably less oxide staining and with traces of talc.	925

typical black clay is several feet thick the tenor of Ni in the profile is markedly lower. Further to the north, both in the vlei and in the freely drained profile over epidiorite the variation in Ni content in the profile is barely perceptible but does, if anything, increase with

depth. The increase is more regular in the freely drained soil than in the vlei. The Ni content at the base of the profile No. 11 is 270 ppm, a value closely comparable to those at the bases of the profiles over metavolcanics south of the serpentinite.

(c) Ni in bank soil and stream sediment.

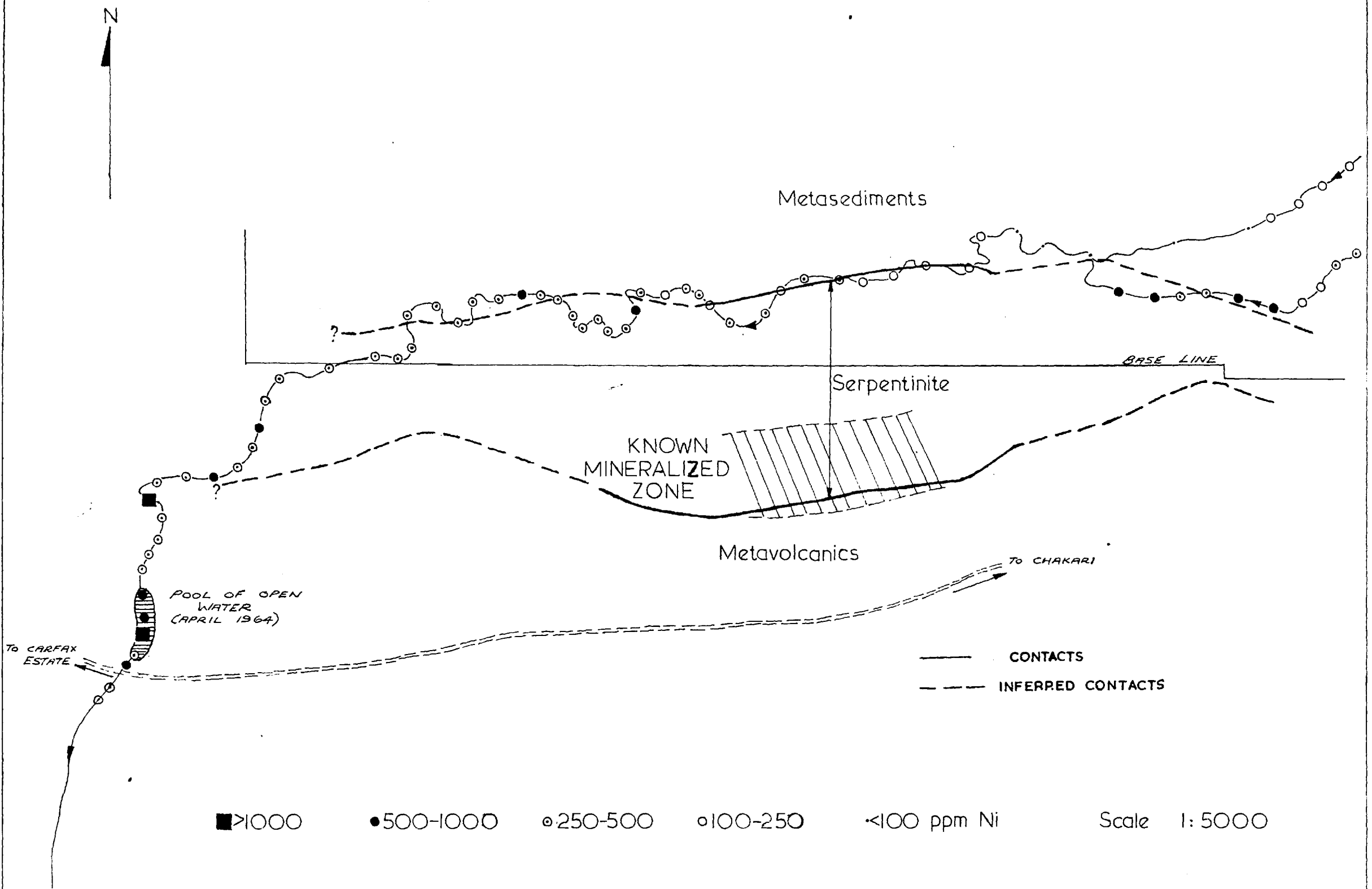
Stream sediment has been sampled along a limited stretch of a stream channel in a vlei developed over the contact between serpentinite and other rocks. In addition, the banks of the open watercourse were sampled at several points. The Ni content of the stream sediment was found to vary between 145 and 1350 ppm. This Ni content is higher than that in a stream draining metasediments and epidiorite from which values of 60-130 ppm Ni in the sediment were obtained.

In the study area as a whole the drainage channels are continuous except near the sources of streams where they are intermittent. The channels are cut into vlei soil or, where there is no vlei, are rocky. The Ni content of the banks differs little from that of the adjacent near-surface soil but is usually less than that of the deeper horizons of adjacent profiles.

Pits were sunk in the stream channel at

regular intervals from a point immediately downslope from the ore suboutcrop (line 136 W) as far as the Carfax - Maritzani road (Figure 33), a distance of about four-fifths of a mile. From the point downslope of the ore suboutcrop the stream follows a westerly course for approximately 2000 ft. No water was reached in pits (put down five feet into the stream bed) in this section. In the lower half of the pitted section the stream alters course from westerly to southerly and in the lowermost reaches, immediately upstream of the Carfax - Maritzani road, water, if not present in standing open pools was met in the excavations only a few feet below the surface of the stream. Where the road crosses the stream there is no vlei. The stream here flows through a gap cut into an east-west striking belt of relatively resistant rocks as evidenced by the locally rugged topography. It is possible that these resistant rocks (metavolcanics) may be to some extent impermeable and acting as a dam to the ground waters. Directly upstream of the resistant rocks where the water table is relatively near the surface the Ni content of the sediment, which in the main is aggraded soil, is higher than it is further upstream ~~or downstream~~ (Figure 33).

The increase in Ni content of the stream sediment in the area where the ground water table ap-



Drainage reconnaissance ; Maritzani area : Ni in stream sediment.

33

proaches surface is regarded as more than coincidental and it is tentatively suggested that the nickel has been introduced into the stream sediment from the ground water. There is, however, no evidence to link the observed pattern of distribution with the mineralization as the direction of ground water movement has not been precisely established.

As mentioned above there is a close correlation in Ni content between bank soil and stream sediment and it is believed that much of the sediment has been derived from bank collapse. There is evidence of dilution with material of low Ni content entering from a tributary stream draining metasediments and other rocks to the north of the serpentinite (Figure 33).

(f) Summary.

The pattern of distribution of Ni in the area has a number of features in common with other areas of serpentinite, barren or mineralized. The enrichment of Ni in unmineralized weathered rock relative to the fresh rock is in contrast to the distribution in the mineralized profile where there is more Ni in the fresh rock than in the weathered. The increase in Ni content

with depth through the solum in many profiles is a noteworthy feature of the secondary dispersion pattern.

The contrast between the mineralized and non mineralized parts of the serpentinite is small, especially in the near-surface environment.

No features of the distribution of Ni in the drainage can be related to the mineralization.

C. Distribution of nickel in the vicinity of nickel mineralization in rocks other than serpentinite.

The rock types dealt with in this section are amphibolite (adjacent to a dioritic stock), greenstones, carbonaceous shale (and adjacent quartz - mica schist and specularitic quartzite) and metasediments. Local backgrounds will be considered for each area in turn. Areas where the ore deposits are nickeliferous sulphides will be discussed first. There are two such areas in Rhodesia and one in Zambia In Rhodesia deposits of nickeliferous sulphides occur in amphibolite and greenstones at the Empress prospect and at Bare Bottom Hill respectively. In Zambia, studies have been confined to the Kalumbila area where nickel bearing sulphides occur in carbonaceous shale. A description of the distribution of nickel in the environs of the Noel Nickel mine, a

deposit of nickel arsenides in metasediments, serpentinite and metavolcanics, concludes the section.

1. The Empress prospect and Bare Bottom Hill.

The Empress deposit is in amphibolite at the south west margin of a dioritic stock intruded into greenstones (Figure 7). The same assemblage of sulphide minerals as those observed in the ore horizon at this prospect also occur in greenstones at Bare Bottom Hill about one mile to the north west.

Sharpe (1961) has described the Empress prospect and stated that the orebody is up to 90 ft. wide with an average width of 48 ft. He reports an average of 0.83% nickel for an economic tonnage. The grade of the nickel mineralization at Bare Bottom Hill is similar to that of the main Empress ore.

(a) Soil survey.

The data of the geochemical soil survey described in Sharpe's paper were made available to the writer. In the survey carried out by M.S.A. (Pvt.) Ltd., soil samples were collected at 50 ft. intervals along lines 200 ft. apart and subsequently analysed

spectrochemically.

The $Ni_{(spec.)}$ content in near-surface soil over non mineralized diorite ranges from 50 to 1000 ppm with a mean of 200 ppm and an anomaly threshold of 350 ppm. Local background over greenstones is slightly higher than it is over diorite. The corresponding figures for greenstones are a range of 100 to 1000 ppm, mean 245 ppm and anomaly threshold 600 ppm. No data from barren amphibolite is available. These ranges of $Ni_{(spec.)}$ content in near-surface soil over diorite and greenstones are quite considerable. They may result from one or both of the following factors:-

(i) The rocks underlying the sample sites may not be entirely barren of sulphides and/or

(ii) There may be some analytical error.

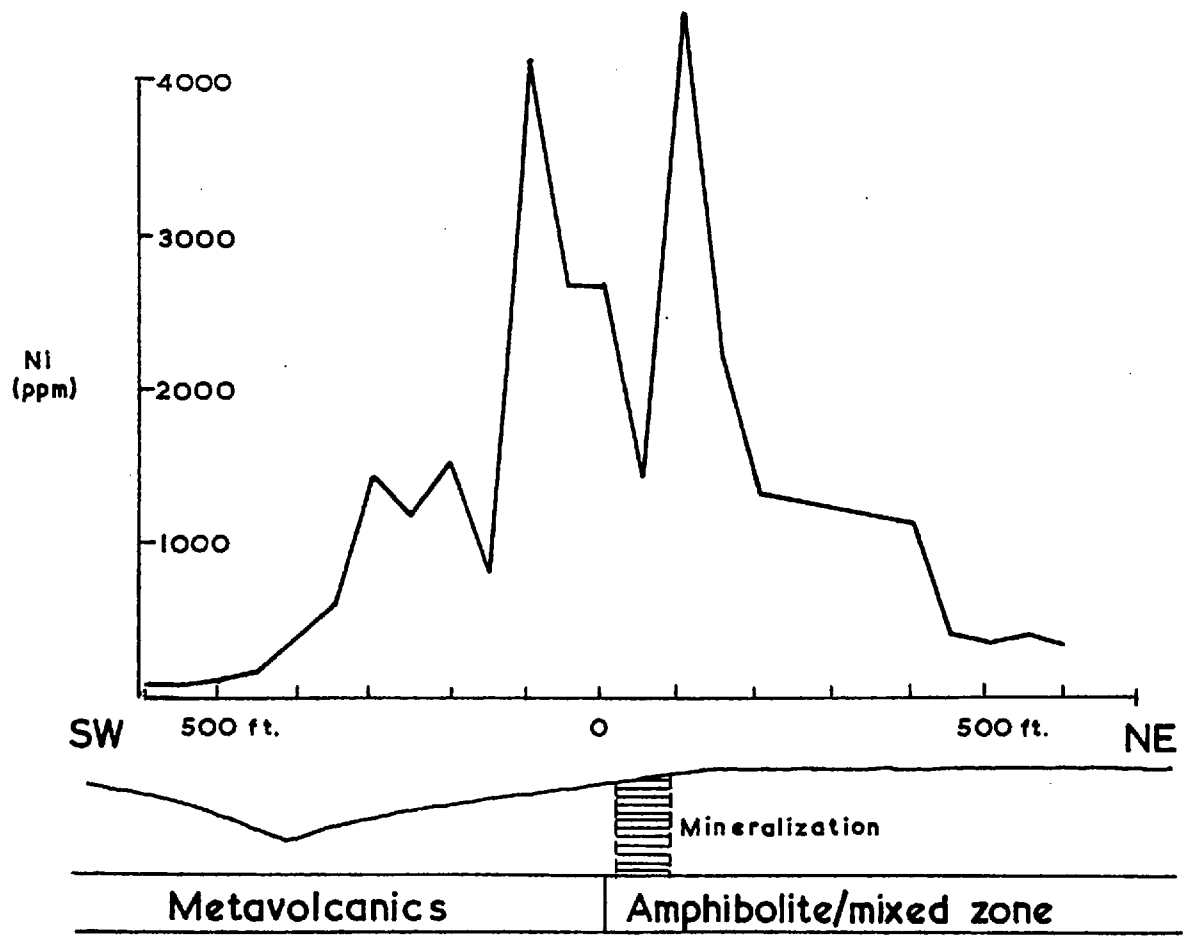
When sampling background one can never be entirely certain about the absence of ore minerals as areas chosen as background have, understandably, been subjected to the least detailed geological examination. It must be pointed out, in addition, that the statistics for soils over diorite are based on the analyses of 40 samples and only one of the 40 is above the 350 ppm threshold (i.e. the sample containing 1000 ppm $Ni_{(spec.)}$). Furthermore, the results are those of spectrochemical analysis of unknown precision and there could be some

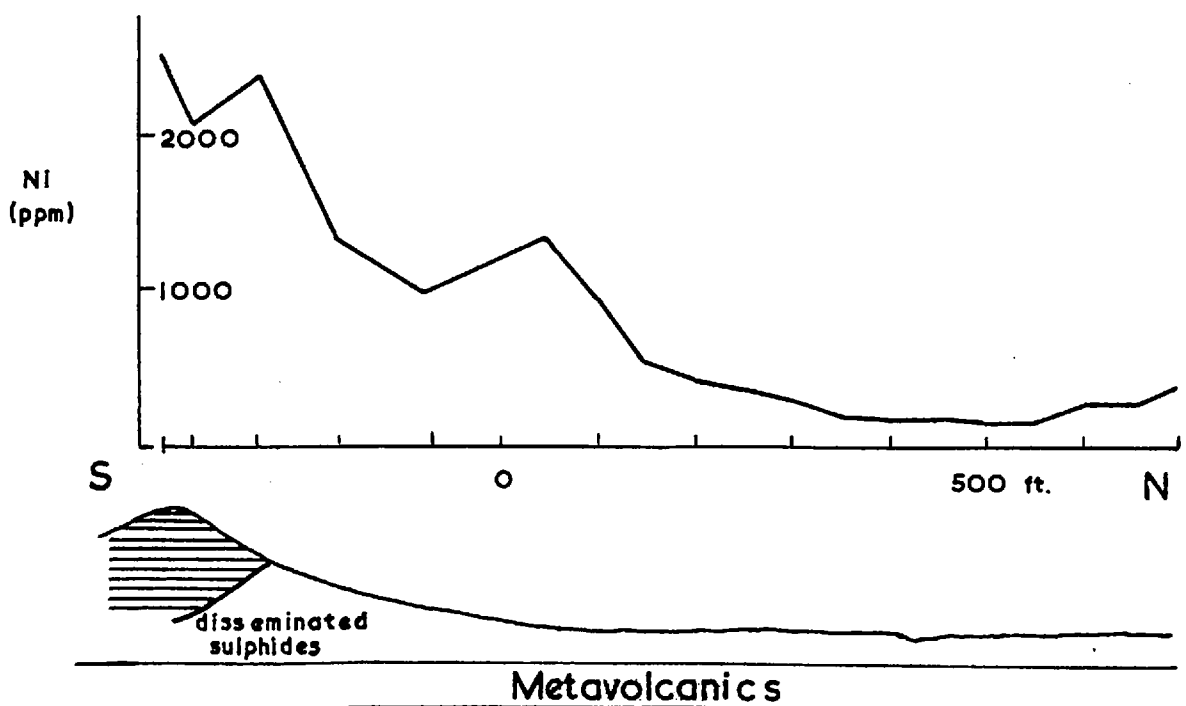
analytical bias or error. It is possible, therefore that the ranges of values given are abnormally wide. This possibility is not thought likely to debase interpretation.

Colorimetric analyses, following a potassium bisulphate fusion, gave results closely analagous to those shown by the spectrographic analysis but over a slightly narrower range (Figure 34). For example, the range of Ni content in near-surface soil over non mineralized metavolcanics, determined colorimetrically, is 100 to 435 ppm with a mean of 250 and an anomaly threshold of 425 ppm. The difference in level of Ni content determined spectrochemically and colorimetrically may be the result of the different sample attacks (Chapter 2).

A grab sample collected over a very small outlier of apparently barren amphibolite about a mile south of the Empress shaft showed the near-surface soil to contain 90 ppm Ni. This value is less than the mean over greenstones.

The $Ni_{(spec.)}$ content of near-surface soil over the mineralization was found to be as high as 1%. Sharpe has said that the surface area of the ore body is closely defined by soils containing 3000 ppm or more $Ni_{(spec.)}$ (Figure 35). The maximum Ni ($KHSO_4$) content

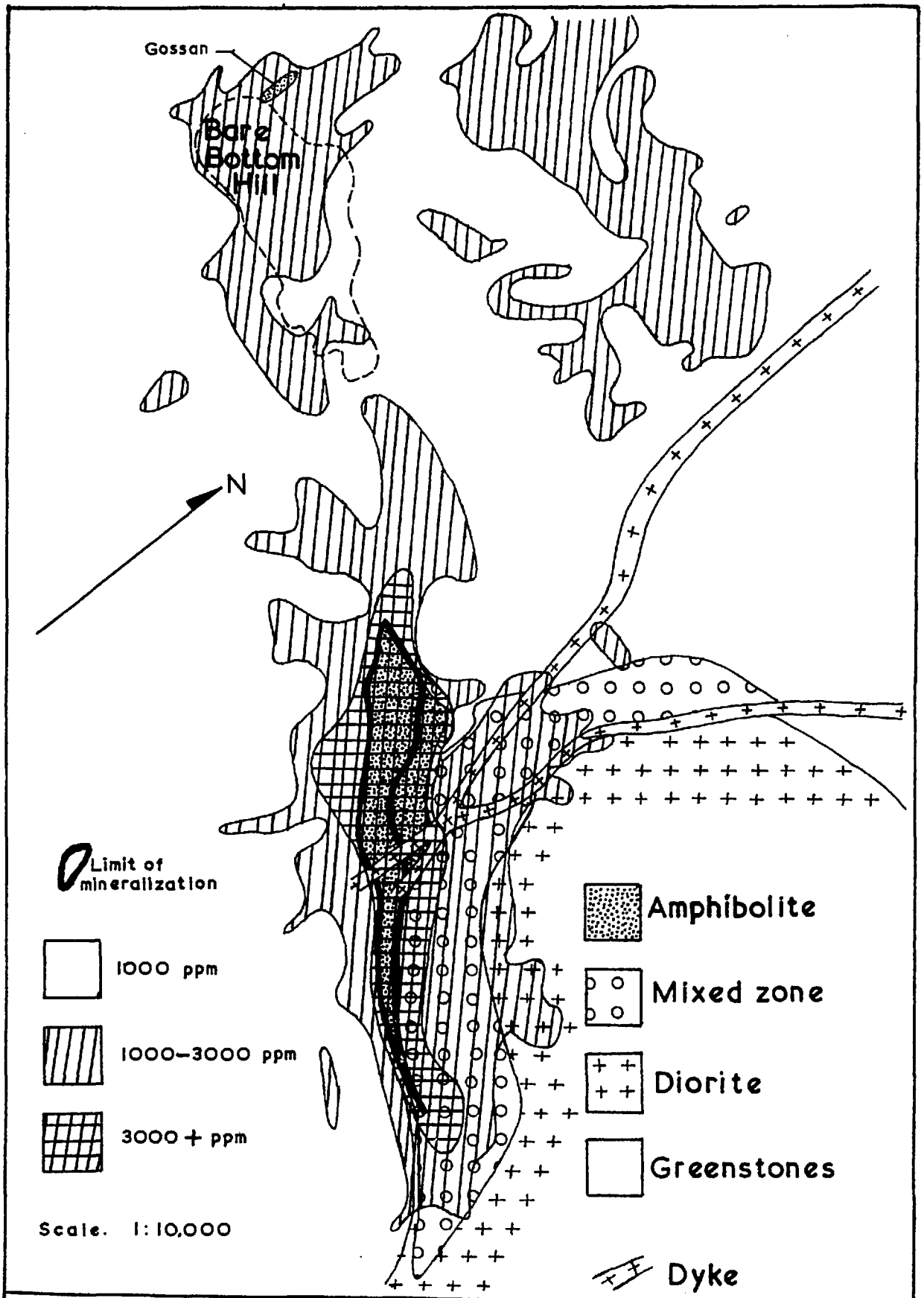




Ni in near-surface soil along traverses crossing the Empress orebody (A) and Bare Bottom Hill (B).

34

GEOLOGY : M.S.A. (Pvt.) Ltd.



$Ni_{(spec.)}$ in near-surface soil at the Empress prospect.

35

DATA: M.S.A (Pvt.) Ltd.

in near-surface soils is 8000 ppm. Viewed against a local background of 90 ppm[1] for near surface soil over non mineralized amphibolite the contrast is eighty to ninety - fold. Contrasted against 425 ppm (anomaly threshold for near-surface soil over greenstones) the anomaly at Bare Bottom Hill is six - fold.

Whether contrasted against amphibolite or greenstone background the anomalies in the Empress - Bare Bottom Hill area are more conspicuous than those over mineralization in serpentinite (less than two - fold).

(b) Ni in the soil profile.

The profile over non mineralized greenstones near the Empress prospect contains 100 to 190 ppm Ni. The barren greenstones at Bare Bottom Hill, however, contain more Ni than their counterparts nearer to the Empress prospect. The Ni content of weathered bedrock and soil sampled in the pits on the flanks of Bare Bottom Hill ranges between 140 and 660 ppm. These pits were on the lesser slopes and level ground north of the Hill and it is possible that the higher Ni content in the

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[1] A single analytical result - not, strictly speaking, background.

greenstones here, compared to that in similar rocks near the Empress prospect, is the result of the secondary dispersion of nickel from the sulphides disseminated in the rocks comprising the hill. On the other hand, there are belts of soil and weathered greenstones of relatively high Ni content intercalated with zones of lower Ni content (Figure 36). It is difficult to explain this alternation in terms of dispersion from upslope especially since the strike and schistosity are roughly parallel to the topographic contours. The alternative explanation is that the distribution of Ni is related to variations in the mineralogy of the greenstones. As pointed out earlier the term greenstones (metavolcanics) is used to describe a collection of rock types, amongst others altered lavas and metamorphosed agglomerates and tuffs. Both felsic and mafic types are included. The more mafic rocks are usually the richer in nickel (Chapter 3) It is thought that alternate bands of mafic and felsic greenstones might be responsible for the variations in Ni content of the soil profiles on the lower slopes of Bare Bottom Hill.

In the soil profile in the study area generally there is virtually no horizon differentiation visible. However, in 14 of 19 pits over barren greenstones there is an increase in Ni content with depth to an horizon of

BARE
BOTTOM
HILL

NICKEL

1330 1330 1365 1505 1260 975
950 950 1060 675 975
610 600 576 430 420 405 390 210 330
485 555 510 345 570 525
345 345 180 165 210 225 256
286 270 450 315 265 195 210 180
210 225 285 270 360 315 210 195
210 225 270 195 180 170
210 225 165 155 210 140 185
205 206 210 225 195
255 170 345 270 420 285 270 285
255 270 360 345 315 240 210 210
360 345 330 316 310 318
345 255 330 480 660 570
405 390 480 510 285
270 300 510 495 480
160 216 300 345 465 525 480
0 1 2 ft. 3 4

COPPER

790 785 685 710 890 545 660 430 315 235 125
600 380 440 335 170 260 265 230 215 240
365 425 285 160 360
305 285 190 170 95 110 70 120
280 150 160 175 130 115 360
120 125 160 170 140 125 120
135 150 160 80 80 110 60
115 145 80 70 125 48 65
95 90 126 115 115 125 70 60
60 135 125 115 160 45 205 80
125 235 220 195 160 230 140 110 80
115 180 140 130 115 60 70
195 130 95 70 60 80
180 135 126 75 70 110
135 126 95 85 70
180 128 85 70
95 50 56 60 70
65 80 90 85 80 75
0 1 2 ft. 3 4

ORE ◄ greenstones

S 0 500 1000 ft. N

Ni & Cu: <200 | 200-400 | 400-800 | >800 ppm

Distribution of Ni and Cu in soil profiles, Bare Bottom Hill.

36

weathered and fractured greenstone fragments in a matrix of finer particles which grades upwards into the near-surface soil. Below the rubble zone the Ni content decreases with increasing depth into the fresher and less severly fractured greenstones. In the five pits not exhibiting the characteristics described the distribution of Ni is too erratic to determine any trend.

The weight of evidence suggests that there has been some differentiation of the nickel into layers in the profile over the barren greenstones.

The distribution of Ni in profile varies quite considerably in the vicinity of mineralization.

Over mixed zone rocks and diorite adjacent to but upslope of the mineralized amphibolite there is an increase in Ni content from surface into the top of the weathered bedrock. Deeper in the weathered bedrock the Ni content generally, though irregularly, decreases with depth. This pattern is similar to that observed over barren greenstones.

Directly over mineralization the amount of Ni is very high relative to the country rocks (a ten-twenty fold contrast) but of the same order of magnitude as that in the profile over mineralized serpentinite at Maritzani. The profile distribution, like

that in some background profiles, is erratic and it is difficult to establish a trend.

Over greenstones just downslope of the mineralized suboutcrop the upper horizons contain unusually large amounts of Ni while the deeper parts of the profiles contain Ni in amounts well within the normal range in profiles over greenstones in barren areas (100 to 660 ppm). This distribution in greenstones downslope from mineralization is almost certainly a secondary dispersion feature. It is thought to be the result of the dispersion of nickel, mechanically and hydromorphically, from mineralization upslope (Figure 37).

At eight of the twenty sites in the study area where the profile distribution was determined the 0-3in. sample contained more Ni than the 3-12in. sample and in four of the eight was the horizon of maximum Ni content in the entire profile. The eight profiles are randomly distributed along the transect (Figure 37). Some of the Ni in the 0-3in. horizon may have been involved in the biochemical cycle. That is to say it may have been taken up by plants only to be redeposited at surface when the plants shed their leaves or were destroyed in some way, e.g. by bushfires. Nickel moving in this way may have been important in forming the distribution observed in the area downslope from

LINE OF TRENCH CE3

PROJECTED FROM LINE OF TRENCH CE2

NICKEL

COPPER

FT.

greenstones — ORE — amphibolite ---- mixed zone ----- diorite

SW 500 FT. 100 0 100 500 FT. NE

Ni & Cu		< 200		200-400		400-800		800-1600		1600-3200		> 3200 ppm

Distribution of Ni and Cu in soil profiles, Empress prospect.

37

the mineralized suboutcrop where there is markedly more Ni in the upper part of the profile as a whole than there is in the lower part. This is discussed in more detail in chapter 5. Three of the eight profiles in question are from a trench dug several years prior to the writer's sampling and at these three sites there may have been some leaching of nickel from the excavated material dumped at surface. Some of this nickel may have been redeposited in the topsoil.

On the slopes of Bare Bottom Hill the lateral dispersion feature is again evident but less pronounced (Figure 36).

(c) Bank soil and stream sediment.

Stream sediment in the region is mainly comminuted mineral fragments and eroded soil. Channels are more or less continuous. There was no sign of water anywhere in the drainage system during the second half of the dry season. The water-table level in the flooded shaft in July was 150 ft. below surface and this is probably representative of the level of the ground water table a short distance upslope from the stream channels or vleis in the study area generally.

Unfortunately water from the mine workings

has been pumped down the stream draining the prospect. In addition ore and treatment plant residues have been dumped at surface in the catchment area. It was felt that no useful results could be gained by investigating the distribution of nickel in bank soil and sediment of this stream draining the mineralized zone since the materials will have almost certainly been contaminated.

(d) Summary.

There are conspicuously anomalous amounts of Ni in all soil horizons over mineralization in amphibolite at the Empress prospect and in greenstones at Bare Bottom Hill.

In weathered greenstones and overlying soil there is a variation in Ni content believed to be reflecting the primary distribution.

There is some evidence of differentiation of Ni in the youthful soil profiles over barren greenstones. Over mineralization the profile distribution is erratic.

There is good evidence of lateral dispersion both at Empress and Bare Bottom Hill.

2. The Kalumbila area.

At Kalumbila there is, compared to the Rhodesian study areas, very little outcrop and the geology is not well known. Stratigraphical correlation, even from one diamond drill hole to the next, is very difficult. The diamond drill holes are widely spaced and the strata highly contorted. Consequently any correlation can be no more than tentative. Despite this there is no doubt that nickeliferous sulphide minerals occur in the carbonaceous shale horizon.

(a) Tenor of nickel in mineralization.

The tenor of nickel in the mineralized horizons is highly variable. Analyses of diamond drill hole core samples from the ore horizon range from more than 3.0 to 0.1% nickel. Broadly speaking the decrease is along strike from north east to south west.

(b) Soil Survey.

Only relatively slight variations in the background Ni content of freely drained near-surface soil over different rock types has been observed. The Ni

content of near-surface soil is lowest in soil over carbonaceous shale and highest over gabbro (Table 21). The local background not only varies over the different rock types but also over the same rock type in different parts of the study area. There is a decrease in the Ni content of soils over non mineralized carbonaceous shale and quartz-mica schist from the north east to the south west. For example, anomaly threshold for Ni in the 3-12 in. horizon over carbonaceous shale is 60 ppm in block K1 but only 25 ppm in block 205 (Table 21 and Figure 9). This is the same direction as the decrease

Table 21. The Ni content of near-surface freely drained soil over various rock types encountered in the Kalumbila area.

Rock type	Ni content (ppm)			No. of samples
	Range	Mean	Threshold[1]	
	In block 205 (the south west)			
Carbonaceous shale	5-15 (0- 3in.)	9	13	9
	13-25 (3-12in.)	19	25	9
Quartz-mica schist	13-30 (0- 3in.)	16	25	12
	15-45 (3-12in.)	25	45	12
Gabbro	40-155 (0-6in.)	75	150	16
	In block K1 (the north east)			
Carbonaceous shale	18-70 (3-12in.)	40	60	62
Quartz-mica schist	33-68 (3-12in.)	45	65	22

[1] by calculation

in percentage nickel in the mineralized horizon. The variation in local background is thought to be reflecting differences in the nickel content of the fresh non mineralized bedrock.

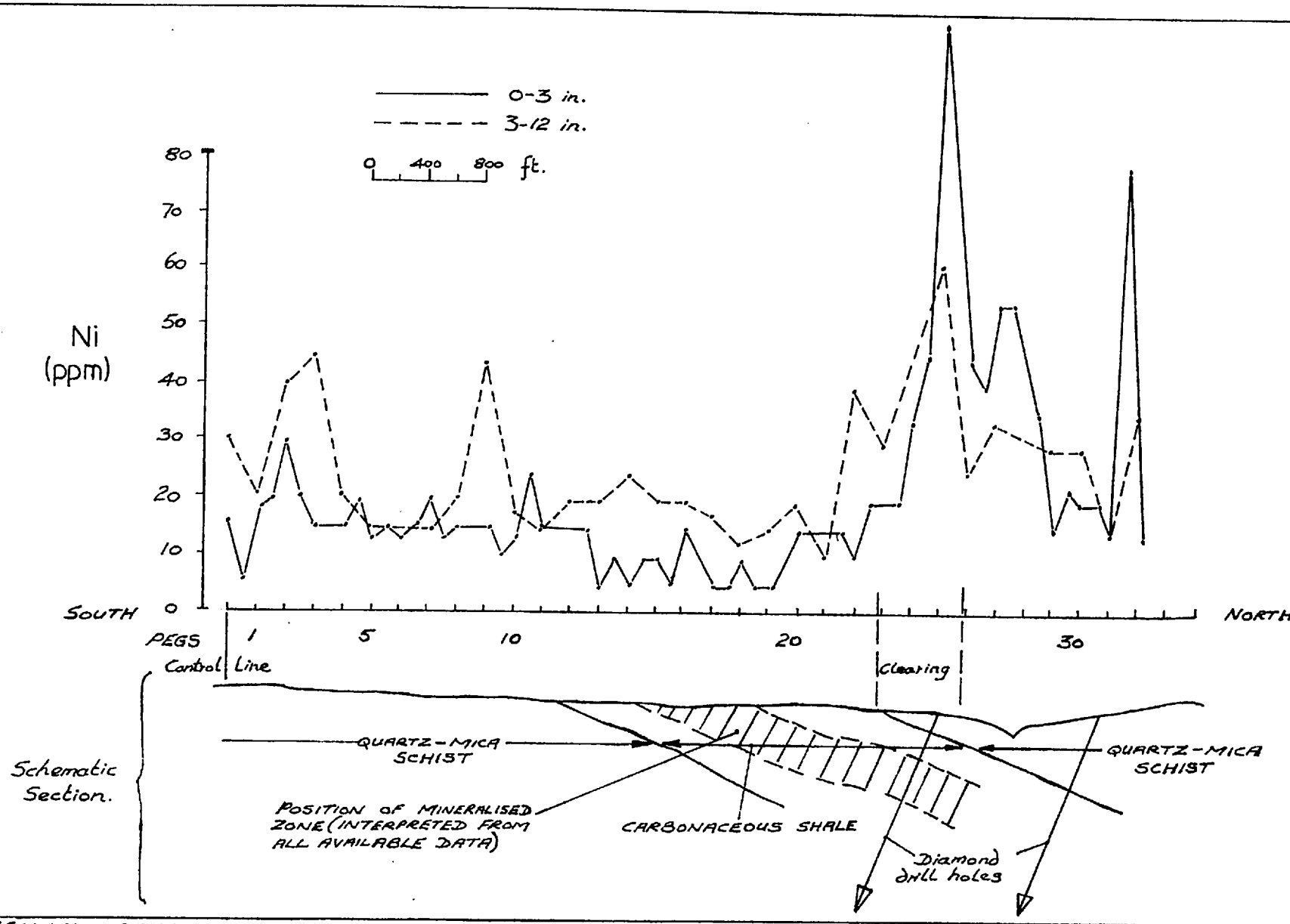
At Kalumbila, near-surface soil over or downslope from the projected outcrop of the nickel sulphide deposits intersected in the diamond drill holes contains no anomalous nickel or copper (see later). By contrast, along strike to the south west there is a strong Ni (and Cu) anomaly downslope from the projected outcrop of the dominantly cupriferous sulphide deposit detected in the diamond drill holes. There are two possible explanations for this inconsistency. It is conceivable that nickel from suboutcropping mineralization in the north east has been entirely leached away. The alternative explanation is that there never was any suboutcropping nickel at this site (in the north east), the mineralization known to be present in depth pinching out somewhere down dip from the present land surface. This latter explanation is considered the most likely since the absence of emplacements of ore minerals at points within the shale is not out of character and it is furthermore, difficult to understand severe leaching at one point and not at another closely similar site only a few miles away.

The anomalous amount of Ni in the soil in and just downslope of the clearing on line 12 of block 205 is displaced several hundreds of feet downslope from the projected outcrop of the mineralization (Figure 38). That the geology is only poorly known has already been mentioned. The possibility of the abnormal features under discussion being due to another band of mineralization cannot, therefore, be entirely ruled out. Diamond drilling operations have been carried out in the clearing but the anomalous concentration of Ni is considered unlikely to be due to contamination. Nickel moving in solution may be being precipitated where the ground water table comes to or approaches surface where the laterite has been truncated by erosion. The anomaly may be a seepage anomaly.

(c) Ni in the freely drained soil profile.

Examples of freely drained soil profiles over barren carbonaceous shale and quartz-mica schist are presented as Tables 22 and 23. In contrast to the Rhodesian study areas the soils at and around Kalumbila are very deep. Over barren carbonaceous shale and quartz-mica schist in the Kalumbila area the variation in the profile is not great. Ni is at a minimum in

Variation in Ni content of A horizon soil over the highest grade copper mineralization at Kalumbila.



GEOLOGY : R.S.T.M.S. Ltd.

the 0-3in. horizon and in 14 of 16 profiles studied the maximum Ni content was found to be in the zone of unconsolidated nodular lateritic rubble. The nodules are coarser than 80 mesh and were not incorporated in the material analysed. Separated ferruginous nodules contained 160 ppm Ni.

Analysis of samples from pits dug at 100 ft. intervals across the carbonaceous shale suboutcrop in the north east revealed no significantly anomalous Ni contents, thus confirming the observations in the near-surface soil for which an explanation has already been put forward. In the anomaly downslope of the projected outcrop of the mineralization in the south west (block 205) not only is the amount of Ni in the soil anomalous but also the partition of the metal between the 0-3 in. and 3-12 in. horizons. In background soil the top 3 in. of the profile is the horizon of minimum Ni content. In the soil containing above average amounts of Ni there is more Ni in the 0-3 in. horizon than in the 3-12 in. layer. No data appertaining to the distribution of the metal in the deeper parts of the profile over the carbonaceous shale and enveloping quartz-mica schist in the south west is available. Pits were not dug in this sector since the significance of the areal distribution was not recognised until after the field

work had been completed.

Table 22. Example of a freely drained soil profile over carbonaceous shale in the Kalumbila area showing the distribution of Ni.

Sample No.	Depth (in.)	Horizon	Description	Ni content (ppm)
253	0- 3	A_1	Pale grey-brown clay to fine sand, loose and dry and penetrated by roots. Leaf mould 0-½ in. (A_0).	35
252	3-36	A_2	Orange-brown silt to fine sand, friable though slightly damp.	50
251	36-84	B	Mainly uncolsolidated nodular laterite, some quartzose rubble. Coarse pebble bed (stone line) at 36-42 in.	80
250	84-108	B	Lateritized carbonaceous shale.	60
249	108-132	C	Carbonaceous shale with lateritized bands.	35
248	132-144	C	Pale grey carbonaceous shale.	50

(d) Ni in the drainage ways.

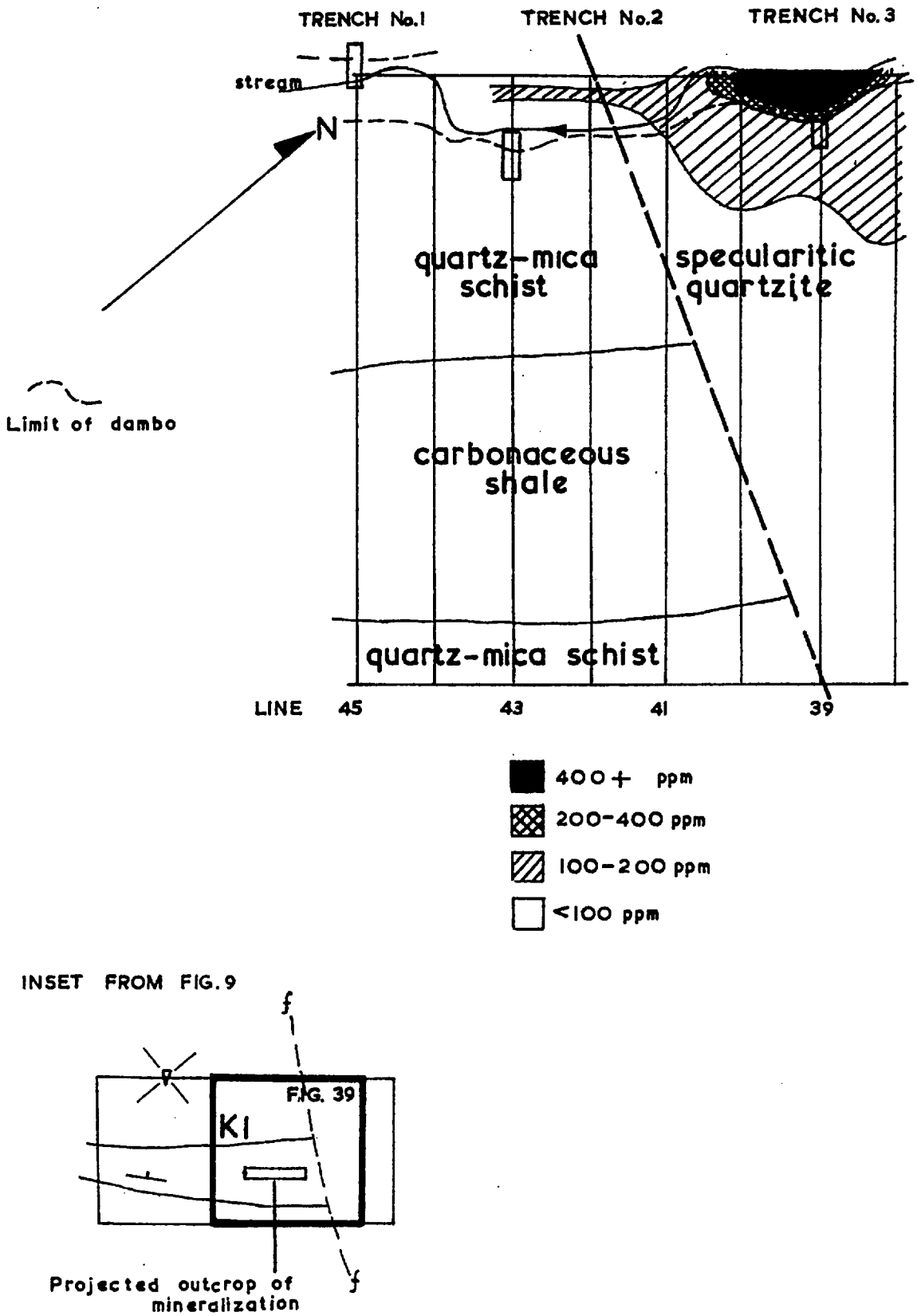
The distribution of Ni in dambos, bank soil and stream sediment is described here. The contrast between the Ni content of dambo soil and that of adjacent freely drained soil over the same lithological unit is far more pronounced that the vlei/freely drained soil contrast in Rhodesia. In near-surface soils there is a

very marked if variable enrichment of Ni in the dambos even well away from mineralization(Table 24). This enrichment is found over all rock types.

Table 23. Example of a freely drained soil profile over quartz-mica schist in the Kalumbila area showing the distribution of Ni.

Sample No.	Depth (in.)	Horizon	Description	Ni content (ppm)
275	0- 6	A_1	Pale brown silt to sand, loose and dry, penetrated by grass roots. Leaf mould 0-½ in. (A_0).	35
274	6-18	A_2	Orange-brown silt to sand, friable, slightly damp.	45
273	18-72	B	Zone of unconsolidated nodular laterite and quartz rubble. Also pebbles and boulders of weathered quartz-mica schist.	128
272	72-132	B	do	88
276	132-144	C	Partially decomposed quartz-mica schist.	70

Specularitic quartzite occurs north east of the Kalumbila fault (Figure 39). The distribution of Ni over this sector of the study area is illustrated on the above mentioned diagram. The data has been obtained from analysis of the minus 80 mesh fractions of soil samples collected by RST Mine Services Ltd. The Ni content of near-surface soil over the specularitic quartzites ranges between 35 and 135 ppm with a mean of 70 ppm and a local anomaly threshold of 105 ppm. That



Distribution of Ni in near-surface soil over part of the Kalumbila area.

39

GEOLOGY : R.S.T. M.S. Ltd.

is to say that the background locally over specularitic quartzite is higher than it is over carbonaceous shale. There is more Ni in the dambo over sericitic-specularitic

Table 24. Comparison of the Ni content of near-surface soil from dambos and freely drained ground over non mineralized gabbro and over barren quartz-mica schist: Kalumbila area.

Underlying rock type	Dambo soils Ni content (ppm) Range	Mean	Freely drained soils Ni content (ppm) Range	Mean
Gabbro	45-175	120	40-155	75
Quartz-mica schist	50- 95	75	20-45	35

quartzite (Maximum 475 ppm) than there is in the dambo over quartz-mica schist away from any known mineralization (50-95 ppm) and in the dambo underlain by gabbro (45-175 ppm) (Table 24). The large amount of Ni in the dambo over specularitic quartzite may reflect either:-

(i) Accumulation of nickel dispersed from the specularitic quartzites,

(ii) Nickel deposited following hydromorphic dispersion from the known mineralization within the adjacent carbonaceous shale, possibly via a fault or fissure,

(iii) The presence of additional ore, or

(iv) The presence of gabbroic rocks in an environment favouring a greater degree of concentration in

the dambo than in the area of gabbro already referred to.

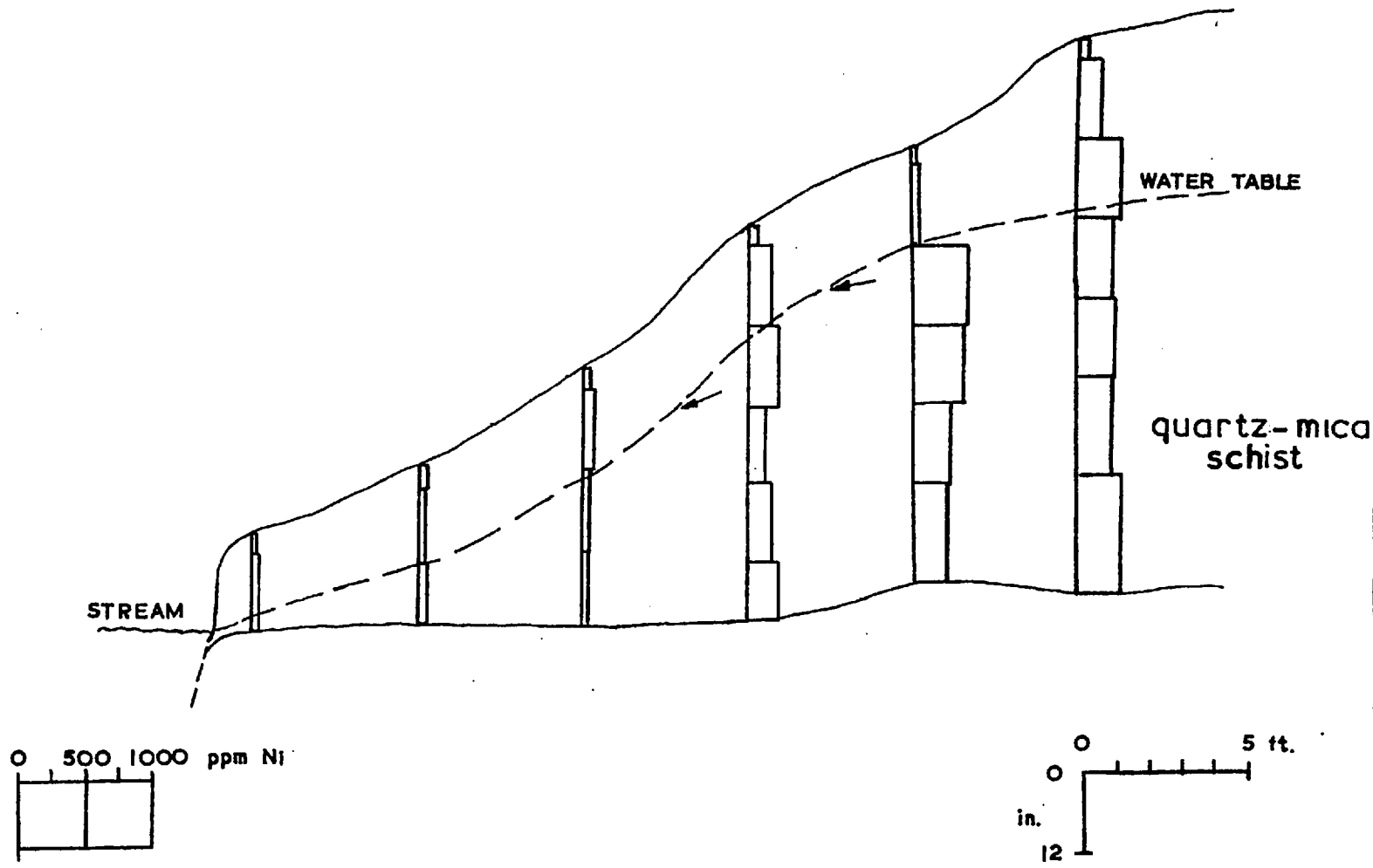
In order to investigate these possibilities further, three trenches were dug across the dambo/freely drained soil contact;

No. 1., over quartz-mica schist away from any known mineralization or soils of high Ni content was on the northwest (right) bank of the stream at line 45, block K1,

No. 2., also over quartz-mica schist was downslope from outcropping carbonaceous shale, on the south east bank of the stream where it crosses line 43, block K1 and

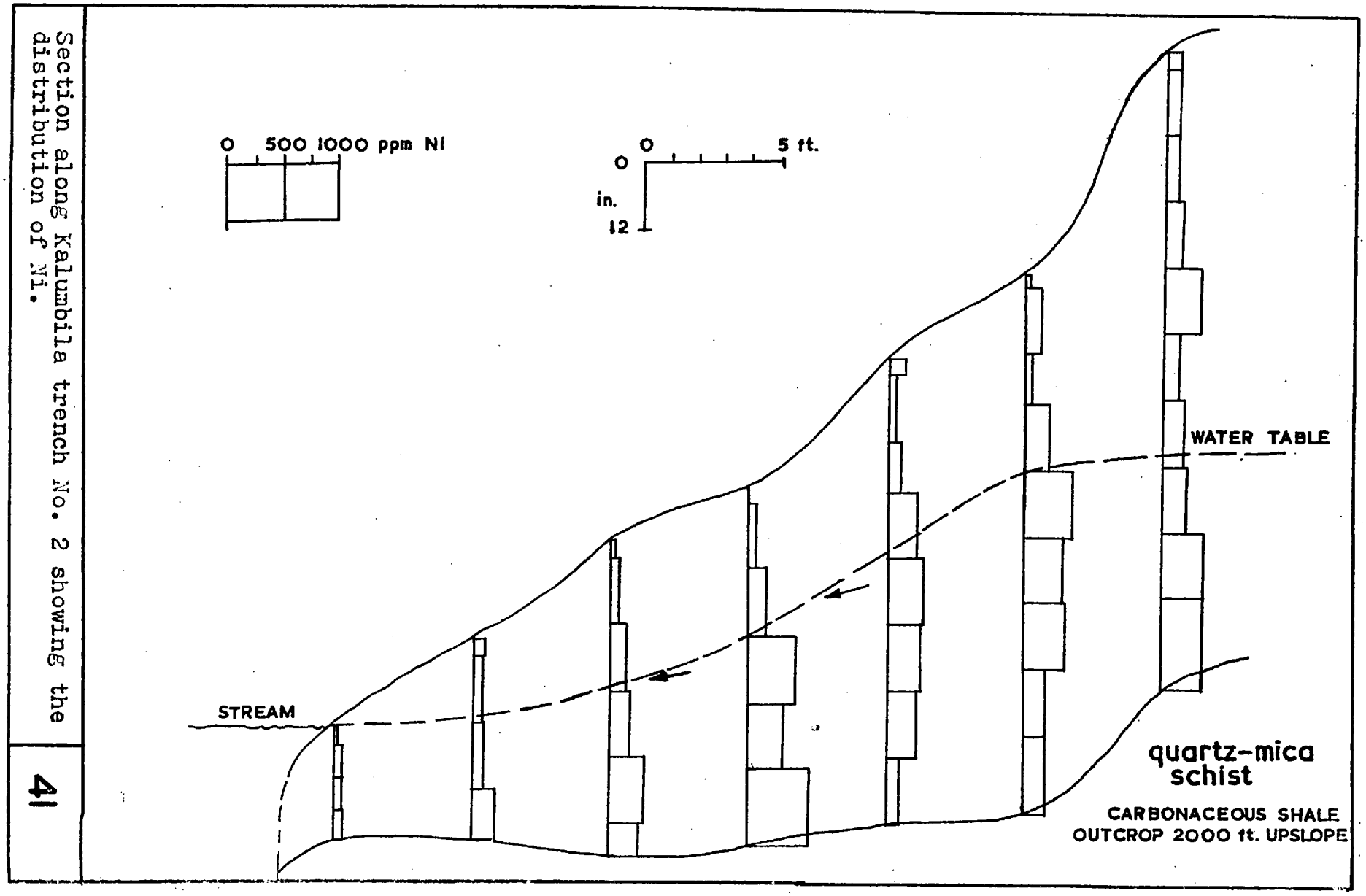
No. 3., at the south east margin of the dambo underlain by specularitic quartzites was in the high Ni zone on line 39, block K1 (Figure 39).

The distribution of Ni in these trenches is illustrated in Figures 40, 41, and 42. It is seen that the materials close to and below the water table in all three trenches contain the greatest amounts of Ni. Above the water table the Ni content decreases towards surface. It is thought that nickel is being deposited from the ground waters as they approach surface. At times the water table will almost certainly have been higher than that observed at the time of sampling.

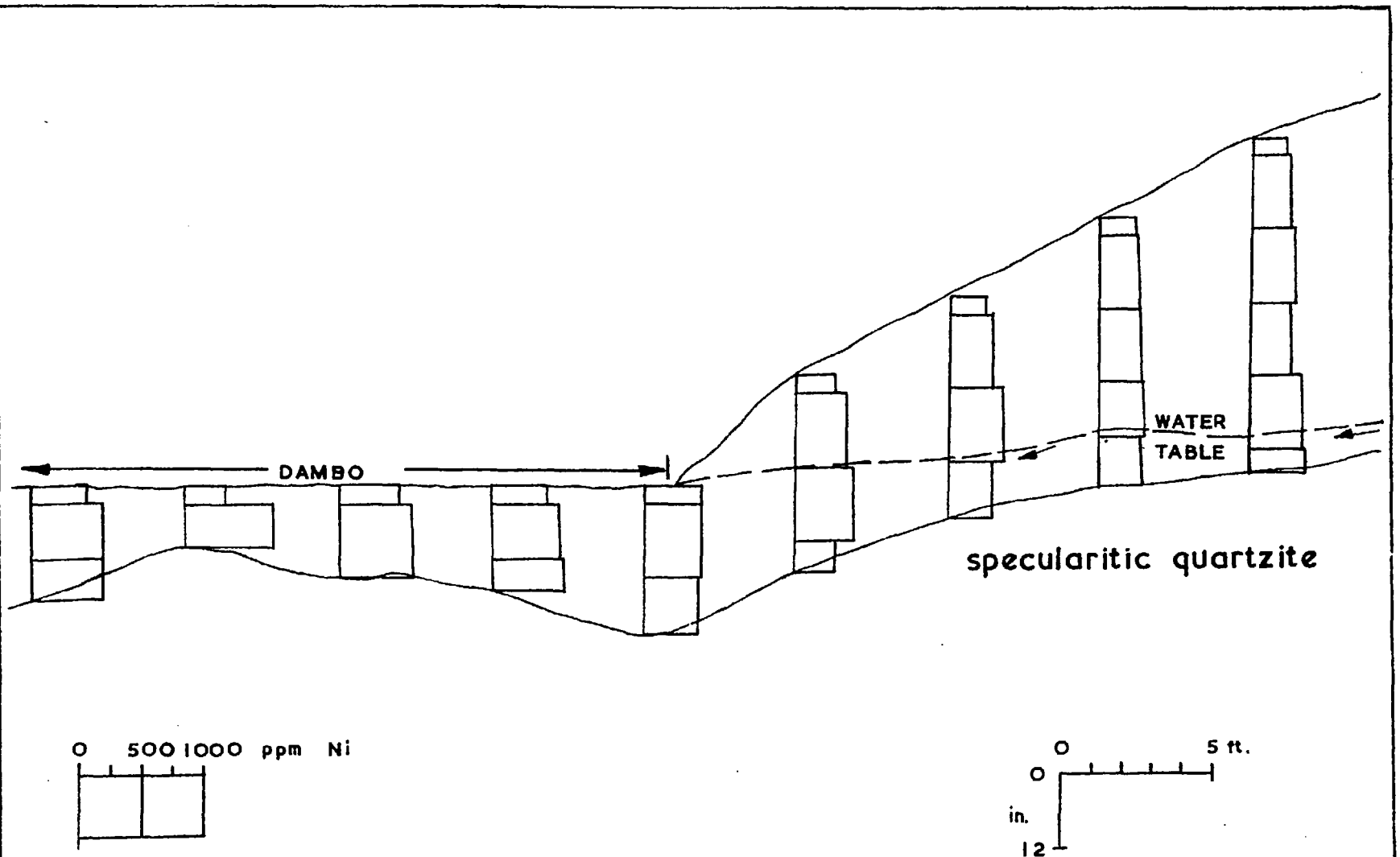


Section along Kalumbila trench No. 1 showing the distribution of Ni.

40



Section along Kalumbila trench No. 2 showing the distribution of Ni.



Section along Kalumbila trench No.3 showing the distribution of Ni.

The Ni in the soil above the water table may have been deposited at the water table at a time when it was nearer surface. In the more freely drained profile further upslope leaching has been most severe in the uppermost 3 in. Leaching by downward percolating water may have played a part in the formation of the observed distribution of Ni in these trenches. The trench (No. 2) cut into the slope at the dambo margin downslope of the carbonaceous shale outcrop has, on the whole, a Ni content higher than that in the trench No. 1 which is downslope from unmineralized quartz-mica schist but the samples from trench No. 3 have the highest Ni content of all three trenches. It is concluded that in all three trenches the nickel is entering in the ground water and being deposited at or close to the ground water table as the ground water approaches surface.

This being the case, the accumulation of Ni in the dambo over the specularitic quartzites could reflect dispersion from the rocks. It has been shown that the freely drained soil over specularitic quartzites normally contains more Ni than that over quartz-mica schist and carbonaceous shale and this is taken to be reflecting a larger proportion of nickel in the fresh quartzite. Since the quartz and mica of the schist

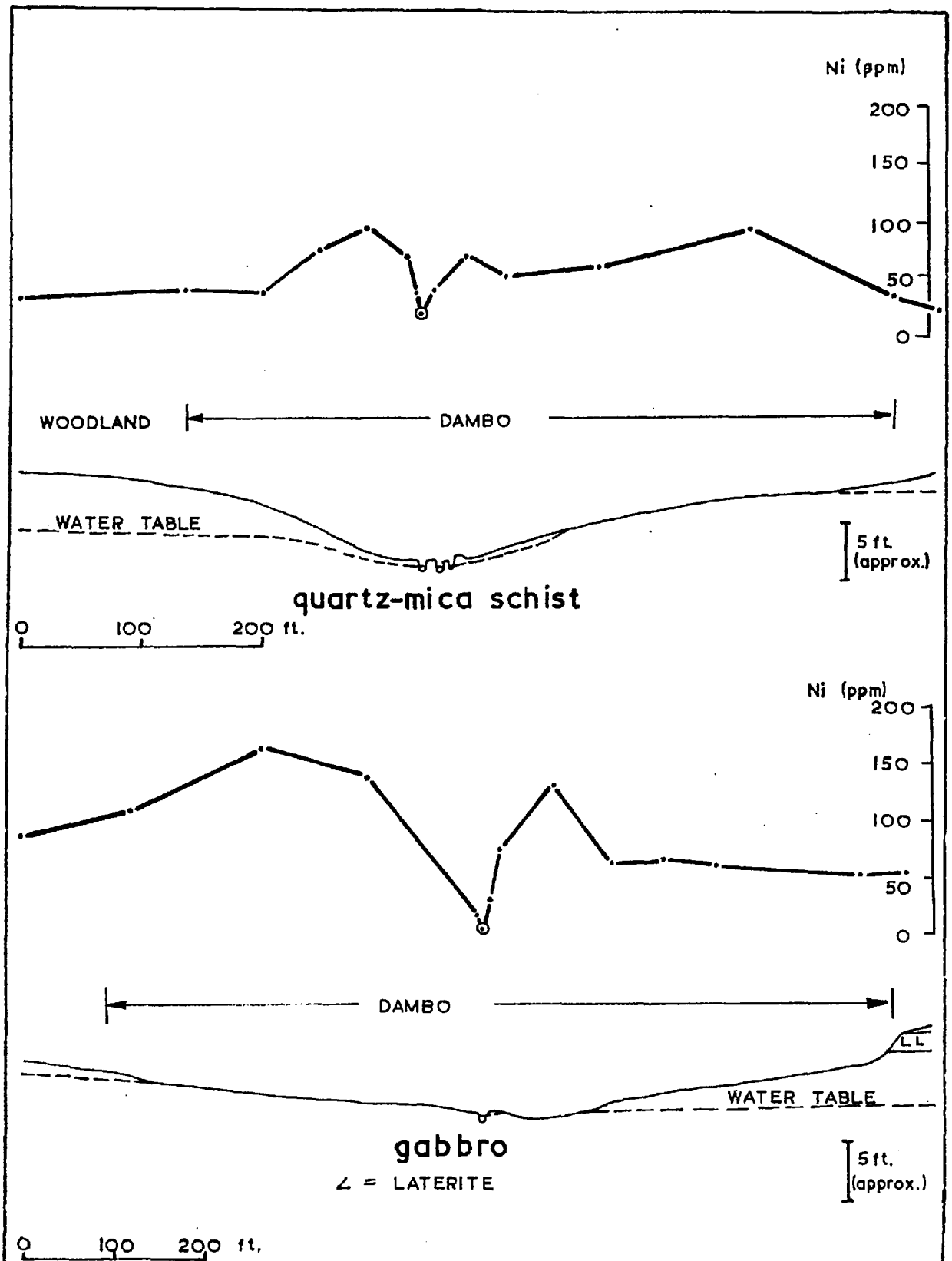
appear to be carrying only very small amounts of nickel the extra nickel in the quartzite is probably in the specularite and it is possibly this nickel that is accumulating in the dambo.

Trench No. 2 has been found to contain, on average, more Ni than trench No. 1. Since both trenches are over quartz-mica schist the higher values detected in No. 2 are probably the result of hydromorphic dispersion of the metal from the nickeliferous sulphides, known to be present in depth in the carbonaceous shale, towards the dambo via the ground water. In the light of this the possibility of the large amount of Ni in the dambo over specularitic quartzite being due to deposition following hydromorphic dispersion along faults or fissures cannot be entirely ruled out but it is thought to be the least likely of the possible explanations.

Additional ore or gabbroic rocks in the area upslope of the high Ni section of the dambo could be the source of the metal. Gabbroic rocks are known to be present only a short distance up drainage of the section under discussion.

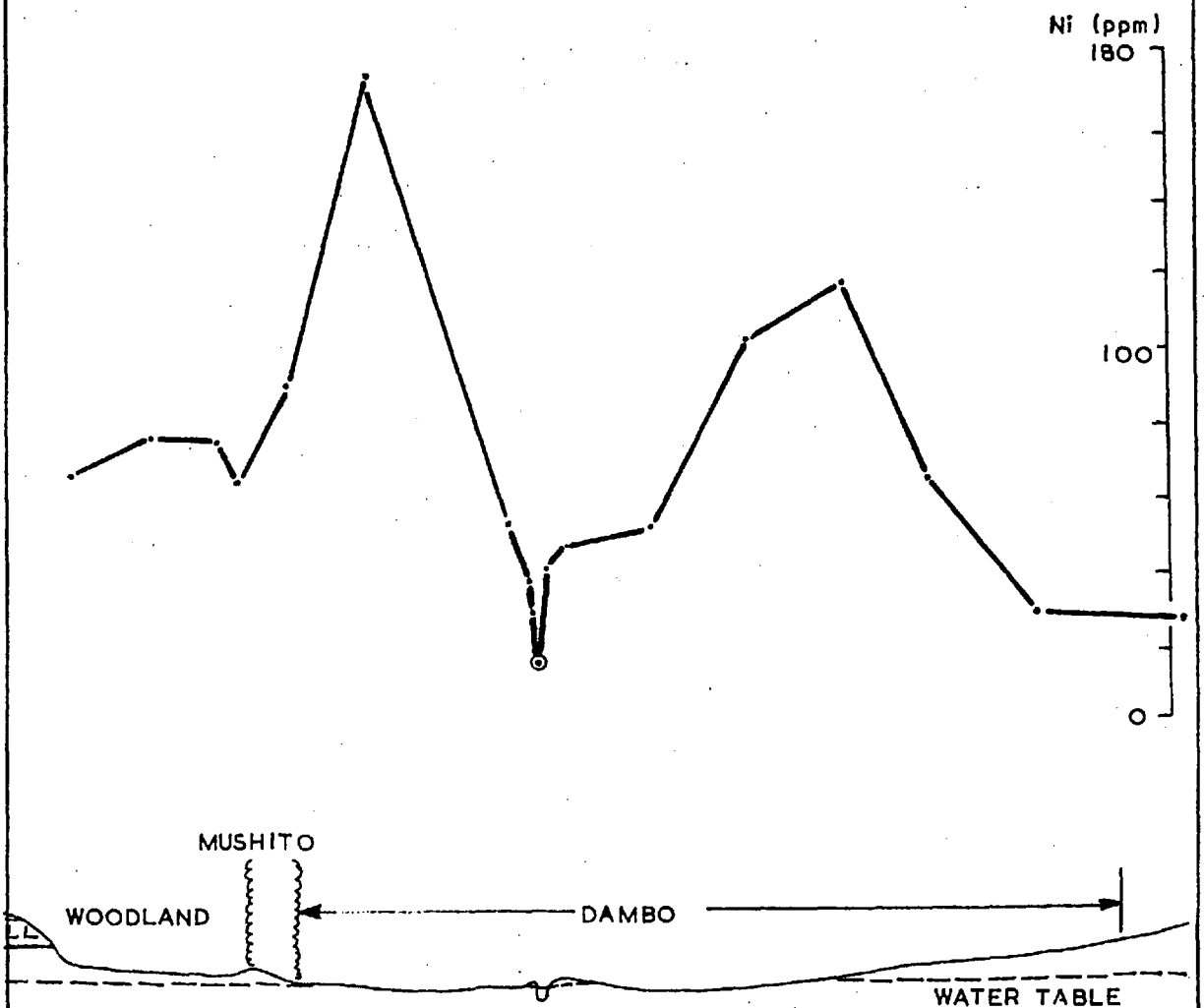
The enrichment of Ni in near-surface dambo soil compared to freely drained soil has already been referred to as a widespread and not unusual geochemical

feature. More detailed study of the distribution within the dambos reveals that the stream sediment and stream bank materials of open watercourses in dambos in the Kalumbila area contain the least amounts of Ni, the swampy low lying parts the largest amounts of the metal (Figures 43 and 44). The higher level dambo **soils** contain Ni in amounts which differ little from those in adjacent near-surface freely drained soil. The Ni content increases sharply where the water table outcrops or approaches very close to surface. This appears to confirm the conclusion reached from a study of the distribution of Ni in the trenches, viz., that the metal is moving and entering the dambo in the ground water. Nowhere in the Kalumbila study area has the stream sediment been found to contain more than 20 ppm Ni. The maximum Ni content of stream bank soils is 65 ppm. In the low lying swampy parts of the dambos the Ni content can be as high as 475 ppm. The dambo low points appear to be acting as a trap for nickel. Nickel being moved mechanically may be held in the dambo when the progress of the materials being moved is checked in what is effectively a sediment trap. In the case of movement in solution the special physico-chemical conditions prevailing in the swampy dambo would seem to have an important influence on deposition of nickel.



Distribution of Ni in near-surface dambo soils and stream sediment(ringed) at Malumbila. (I)

43



Distribution of Ni in near-surface dambo soils and stream sediment (ringed) at Kalumbila. (II)

44

In conclusion, then, it appears as though much of the nickel, whether from sulphide or silicate minerals is prevented from reaching the stream banks and sediment. The distribution described here is discussed in further detail in chapter 5.

(e) Summary.

Local background in near-surface soils varies not only from one lithological unit to the next but also over the same rock type in different sections of the study area.

In the freely drained soils the horizon of maximum Ni content is the B horizon comprising unconsolidated nodular lateritic rubble.

The contrast between Ni in dambos and freely drained soils at Kalumbila is more pronounced than it is between the vlei and freely drained soils of Rhodesia. The swampy parts of the dambos appear to be effective traps for nickel which is moving in the ground water but not reaching the bank soils and stream sediment in which materials the Ni content is singularly low.

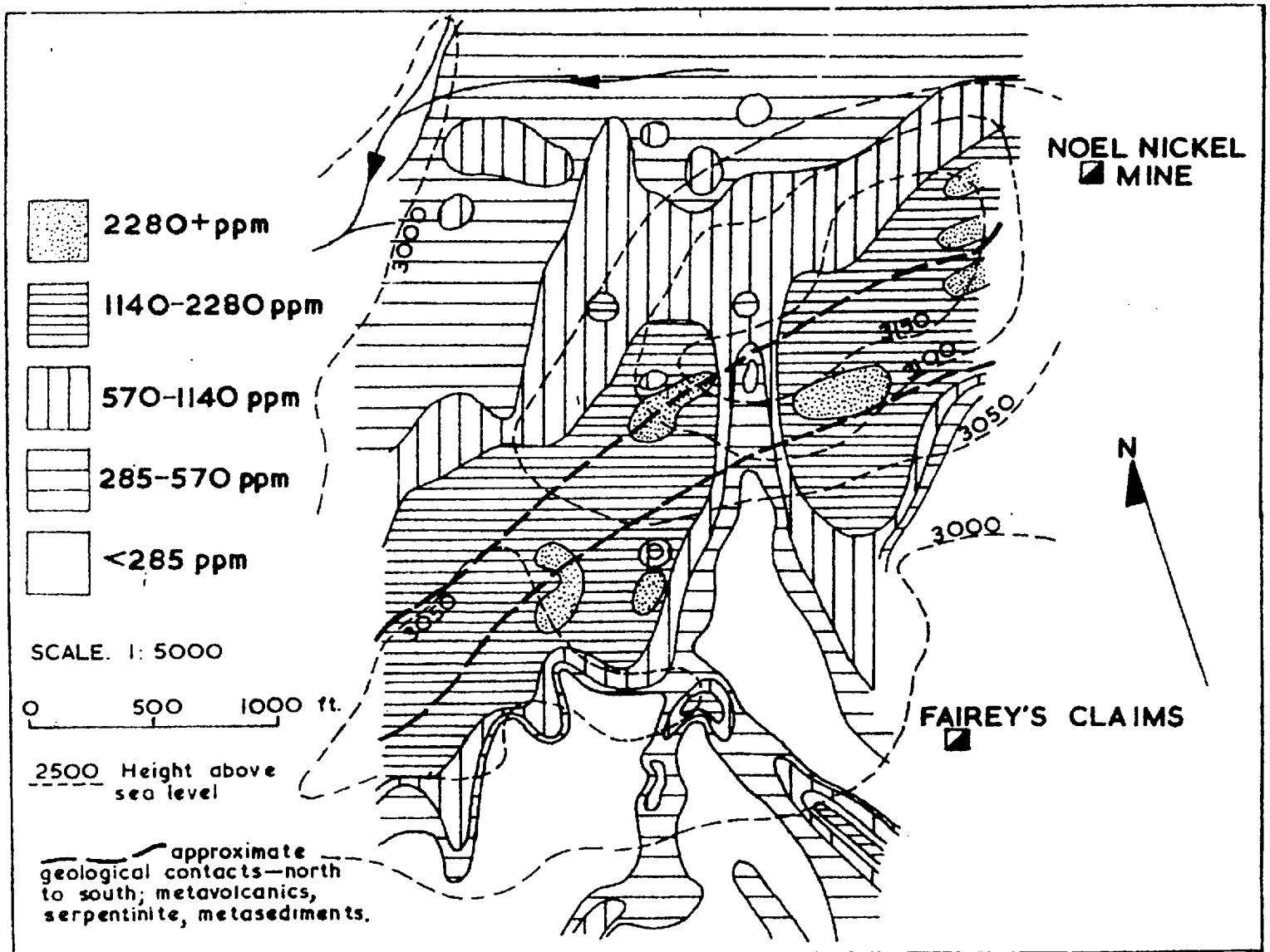
3.The environs of the Noel Nickel Mine.

The Noel Nickel mine itself is in serpentinite but nickel arsenide mineralization also occurs in fault zones in metasediments south west of the mine. Underground exploration of the nickel mineralization in fractures through metasediments has been carried out at Fairey's Claims half a mile south west of the Noel Nickel Mine (Figure 45). The ore in the Noel Nickel Mine is very rich in nickel (as much as 8% in patches) and highly arsenical.

The soil cover is extremely thin and over more than half the area is absent, especially on the ridges. In the valleys where there is soil cover much of it is alluvium, in the main physically comminuted mineral particles affected only by a minimum of chemical weathering. There is no soil profile differentiation.

(a) Soil survey.

The immediate vicinity of the Noel Nickel mine is heavily contaminated with dust from the crushing plant and no geochemical soil survey has been carried out there. However, an extensive area to the west of the mine workings has been sampled. Soil samples collect-



Distribution of Ni in near surface soil in the environs of the NOEL Nickel mine.

ed by the Southern Rhodesian Geological Survey at 100 ft. intervals along lines 200 ft. apart have formed the basis for the soil survey. The samples have been made available to the project. Analysis of these samples at the Applied Geochemistry Research Group has revealed that the Ni content of the soil reflects the geology (Figure 45). Over serpentinite the Ni content is higher than it is over the metavolcanics (hornblende schist derived from basalt) to the north and metasediments to the south although the area of soil of high Ni content extends beyond the boundaries of the serpentinite. The serpentinite forms a rocky ridge and the spread of the near-surface soil of high Ni content may be due to dispersion of soil down the hillsides by sheet wash and soil creep. Serpentinite soil containing more than 3100 ppm Ni (anomaly threshold, Table 16) is technically considered to be anomalous, 3100 ppm being equivalent to the mean plus two standard deviations. However, samples exceeding this figure are erratically distributed and no sample contains more than 3800 ppm (i.e. the mean plus three times the standard deviation). Accordingly, these samples are also considered to be within the normal background population.

The local background for the metavolcanics (north of the serpentinite) is higher than that for the

metasediments (south of the serpentinite,) (Figure 45 and Table 25).

Table 25. Local background Ni content for soils over metavolcanics and metasediments in the environs of the Noel Nickel mine.

Rock type	Ni content (ppm) Range	Mean	Threshold	No. of samples
Metavolcanics	435-700	545	665	20
Metasediments	90-330	170	285	30

Within the metasediments to the north and west of the shaft on Fairey's claims, anomalous amounts of Ni occur in the soil. The trends of the anomalous areas (shown by a Ni content of more than 285 ppm, Figure 45) line up very well with the directions of the two known fault systems (north north east/north north west and west south west) which have been mapped in the area and with which the ore at Fairey's Claims and at the Noel is closely associated.

The nickel arsenide mineralization in the fault systems in the area is reflected by the anomalous Ni content of the overlying soil where the mineralized fissures are in metasediments. It is not known whether such mineralization can be detected in serpentinite or metavolcanics. There are no known mineralized faults in the serpentinite away from the Noel Nickel mine

itself.

Dispersion is believed to be predominantly mechanical and the amount of nickel moved in solution in the semi-arid climate is thought to be small. Distribution of nickel in the drainage in the area has not been investigated. Most of the drainage from mineralized areas is to the east through the sector of the study area which has been contaminated as the result of mining operations. The sediment in the gulleys and watercourses (which are dry nearly all year) is essentially soil washed in from the high ground. The nickel content of the sediment can probably be correlated with that of adjacent soils.

(b) Summary.

The Ni content of the immature soil of this study area reflects both the geology and the mineralization (where it occurs in metasediments).

Because of the dry climate dispersion is believed to be limited and the anomalies are clearly defined.

D. General comments on the distribution of nickel and its relationship to mineralization.

The most important observation to be made from the data is unfortunately of a negative nature. It is that anomalous features of the secondary dispersion pattern related to deposits of sulphide or arsenide nickel in ultrabasic rocks can not be readily distinguished from high nickel values caused by high concentrations of silicate nickel minerals in bands or areas of ultrabasics.

The best contrast between mineralized and non mineralized serpentinite (apart from the ore/ fresh host rock contrast) is in weathered bedrock. Not only is the amount of Ni in weathered, mineralized rock greater than it is in the weathered barren rocks but also the decrease in Ni content with depth from the top of the weathered bedrock, normally observed in weathered non mineralized rocks, is often imperceptible, or even reversed over mineralization.

Generally the Ni content of sedentary soils varies directly with the nickel content of the fresh parent material. It is not unusual for soil developed over non mineralized serpentinite to contain as much as 5000 ppm Ni in the near-surface horizons. In the

deeper layers of the soil profile a Ni content several thousand ppm more than this is not extraordinary. Increasing Ni content from surface to the base of the solum is a very definite and important characteristic of the normal freely drained soil profile over all the lithological units studied in Rhodesia and Zambia. In the poorly differentiated soil profiles the pattern is less conspicuous and sometimes irregular.

Strongly anomalous concentrations and distributions of Ni have been observed over subout-cropping nickel sulphide mineralization in rocks other than serpentinites. The lack of any anomaly in parts of the Kalumbia area, where interpretation is hindered by lack of precise geological information, is ascribed to the tentatively postulated absence of nickel mineralization in the outcrop or suboutcrop.

Dambo soil is enriched in Ni relative to the surrounding freely drained soil. This enrichment has not been observed to the same degree in the Rhodesian vleis. At Darwendale the vlei contains less Ni than the freely drained ground as is the case at Maritzani.

Stream drainage from ultrabasic masses is abnormally high in Ni, reflecting the high nickel content of the rocks and their overlying residual soil. Stream sediment materials of Rhodesian streams are essentially

eroded soils and their Ni content can be closely correlated with that of adjacent soil. The Ni content of sediment at Kalumbila is markedly lower than the surrounding dambo and freely drained soil.

From the foregoing data it is clear that there is a need for a greater understanding of the dispersion of nickel from silicate and sulphide minerals.

Part II. THE DISTRIBUTION OF NICKEL EXTRACTED BY VARIOUS SAMPLE ATTACKS.

The preceding part of this chapter has been given over to a description of the spatial distribution of nickel without special concern about it's form within the materials tested. Attention ha been drawn to the fact that the Ni content of soil and rotten rock overlying nickel sulphides in ultrabasic rocks is little different from that in the same materials over barren ultrabasic rocks. Indeed this is a major prospecting problem.

In order to learn more of the dispersion of nickel from silicates and sulphides two aspects must be considered. These are :-

(i) The distribution of nickel extracted by various sample attacks from specific size fractions and

(ii) The distribution of elements commonly associated with nickel.

A. Preliminary investigations into the form of nickel in weathered bedrock and near-surface soil over barren and mineralized serpentinite.

To avoid unnecessary analysis initial studies were confined to selected critical samples.

Four samples (Table 26) were each split into three size fractions; minus 80 mesh plus silt (hereafter designated 'sand'), silt and clay sizes. Two samples from Maritzani are from a freely drained profile over mineralized serpentinite. The two from Darwendale are from a comparable profile over barren serpentinite.

The size fractions were analysed for exNi, nickel associated with secondary iron oxides and nickel extracted by fusion with potassium bisulphate (Ni). The exNi was determined by leaching the sample with an aqueous, neutral ammonium acetate solution (Chapter 2). The secondary iron oxides were extracted by sodium citrate - dithionate at pH 7.3 as proposed by Aguilera and

Jackson (1953) (Chapter 2).

The 'sand' fraction of each of the four samples was split into a magnetic fraction, a weakly

Table 26. Location and description of samples selected for studies of the form in which nickel is held in soil materials.

Sample No.	Area	Description	Depth (in.)
841	Maritzani (over cre)	Brown friable clay to grit, dry.	0-3
847	do	Variegated yellow-ochre-brown-green, rotten serpentinite intensely impregnated with iron oxides; dry.	48-60
1070	Darwendale (background)	Dark brown-black, lumpy but friable sandy clay containing some grit and penetrated by fine grass roots; dry.	0-3
1075	do	Variegated ochre-khaki-green fragments of rotten serpentinite of up to small pebble size in matrix of dark brown-black silty clay.	42-48

magnetic fraction and a non magnetic fraction after removal of the secondary iron oxides and Ni was determined in these fractions.

1. Sample preparation.

The size fractionation of samples 841, 847,

Table 27. The distribution of nickel in 'sand', silt and clay size fractions of soil and rotten rock over serpentinite of the Great Dyke (1075) and over mineralized serpentinite at Maritzani (847).

Sample No.	Form of nickel: Exchangeable		Associated with secondary iron oxides		Potassium bisulphate extractable	
	(ppm)	%	(ppm)	%	(ppm)	%
1075 'sand'	8	0.1	1310	23.9	5500	100
847 'sand'	14	0.6	1050	42.0	2500	100
1075 silt	26	0.5	3850	67.0	5750	100
847 silt	50	1.2	2560	63.2	4050	100
1075 clay	120	3.4	1590	45.4	3500	100
847 clay	300	7.5	1940	47.8	4050	100

Table 28. The Ni content of magnetic, weakly magnetic and non magnetic materials of 'sand' size particles from rotten rock over Great Dyke serpentinite (1075) and over mineralized serpentinite at Maritzani (847).

	Magnetic fraction		Weakly magnetic fraction		Non magnetic fraction	
Sample No.	1075	847	1075	847	1075	847
wt. of material (mg.)	104	114	48	150	88	34
wt. of material (% total fraction)	43.4	38.2	20.0	50.3	36.6	11.5
Ni content (ppm)	3370	1270	4580	1230	2720	1180

1070 and 1075 was by sedimentation following dispersion in a 1% solution of calgon in deionised water by ultrasonic vibration (Chapter 2).

In the further separation of the 'sand' size fraction the magnetic fraction comprised grains attracted to a hand magnet. Grains not attracted to a hand magnet were separated into weakly and non magnetic fractions with a Franz Isodynamic Separator with a current amperage of 0.5, a 10^{o} forward slope and a 15^{o} lateral tilt.

2. Results and Discussion.

Between the two deeper samples some small but appreciable differences were observed (Tables 27 and 28). In the Maritzani sample the Ni content of the silt and clay size material has been found to be the same but appreciably greater than that of the 'sand'. By contrast, the silt fraction contained the most Ni in the Darwendale sample, only very slightly more than the 'sand' fraction but substantially more than the clay size material. There is more Ni in the clay size material at Maritzani than at Darwendale but the position is reversed in the silt and 'sand'. The difference is difficult to interpret but could be

reflecting differences in the soil characteristics unrelated to mineralization (see later, chapter 5).

In both samples there is an increase in exNi content in the finer fractions but the Maritzani material contains, in all three fractions, a greater amount of exNi than does the Darwendale material. This difference is accentuated in the coarser fractions when expressed as a percentage of the potassium bisulphate extractable nickel. It should be remembered, however, that nickel extracted as the result of fusion with potassium bisulphate is generally not the total amount of the metal present (Chapter 2).

In both the deeper samples the amount of nickel extracted with secondary iron oxides is at maximum in the silt. Both the 'sand' and clay size fractions contain substantially less nickel associated with the secondary iron oxides but there is more nickel extracted by the citrate-dithionate reagent from the clay size fraction than from the 'sand'. In the 'sand' and silt there is more metal associated with secondary iron oxides at Darwendale than at Maritzani but in clay size material the relationship is reversed. Expressed as a percentage of the Ni content, nickel associated with secondary iron oxides is greater at Maritzani in both 'sand' and clay size material but in

the silt the Darwendale sample still gives the higher value. It is not known whether the differences have any significance in terms of mineralization.

The magnetic and weakly magnetic fractions of the 'sand' from which exNi and nickel extracted with secondary iron oxides had been removed were found to contain more Ni than the non magnetic fraction both at Darwendale and at Maritzani. All three fractions in the former area contain appreciably more nickel than their counterparts at Maritzani. This contrast between the two areas is not one that can be explained in terms of mineralization at Maritzani and not at Darwendale. It is attributed to the different primary distribution and mineralogy of the two areas. For example, chromite abounds in the Darwendale area but is rare at Maritzani. It is possible that magnetite, and perhaps trevorite, is associated with the chromite and that it is nickel in these minerals that is being detected in the magnetic fractions.

In the surface samples the finest fractions are the richest in Ni. At Darwendale there is a progressive increase in Ni content with decreasing particle size from 'sand' to clay size material. At Maritzani, however, there is very slightly less Ni in silt than in 'sand' with a marked increase in the clay

size material. The amount of nickel associated with secondary iron oxides at Darwendale decreases with decreasing particle size (although the values in 'sand' and silt are essentially the same) but at Maritzani it is similar in 'sand' and clay size material which fractions contain very much less of this form of the metal than does the silt fraction.

At Maritzani the ox_{Ni} content increases with decreasing particle size but at Darwendale it is at maximum in the silt and at minimum in the 'sand'.

In the case of all the above mentioned attacks the amount of nickel extracted is, in all fractions, greater at Darwendale than Maritzani (Table 29). This is the opposite to the observed distribution of ox_{Ni} in the deeper samples. It is probably the result of different climatic and drainage conditions and different soil characteristics. For example the Darwendale area has a slightly higher mean annual rainfall than Maritzani and the water table in the former area was at the time of sampling (August - September), approximately 10 ft. below surface compared with a depth of about 60 ft. at Maritzani. Visual observation suggests there is more organic matter in near-surface soil at Darwendale as compared to Maritzani. Soil pH in the

two areas is not the same. The effect of these factors is discussed in detail in chapter 5.

The difference in exNi content in weathered

Table 29. The form of nickel in 'sand', silt and clay size fractions of surface soil over Great Dyke serpentinite (1070) and over mineralized serpentinite at Maritzani (841).

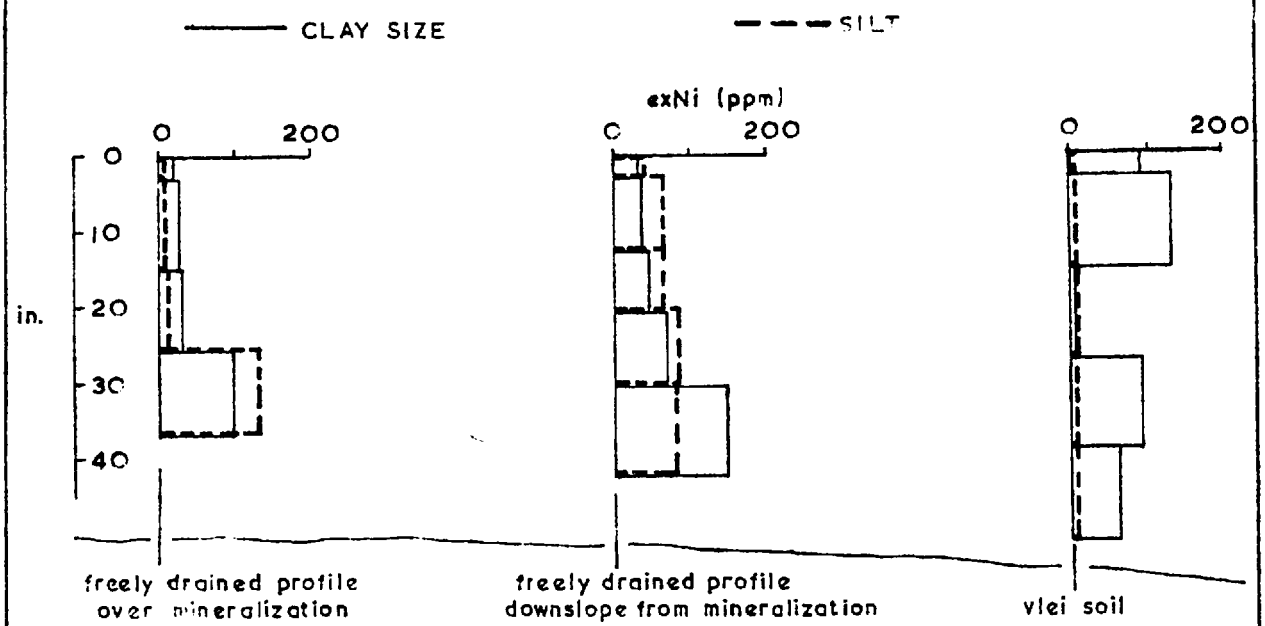
	Form of nickel					
	Exchangeable		Associated with secondary iron oxides		Potassium bisulphate extractable	
	(ppm)	%	(ppm)	%	(ppm)	%
1070 'sand	59	4.2	940	67.0	1400	100
841 'sand'	15	2.2	290	44.1	650	100
1070 silt	240	12.5	935	49.3	1900	100
841 silt	28	4.4	440	70.6	625	100
1070 clay	140	4.2	870	26.2	3320	100
841 clay	34	3.1	260	23.7	1100	100

bedrock as determined in the preliminary study appears to be a factor giving positive contrast between mineralized and non mineralized serpentinite. This contrast is believed to be related to a difference in secondary dispersion of nickel from sulphides and silicates. Investigations have, accordingly, been extended.

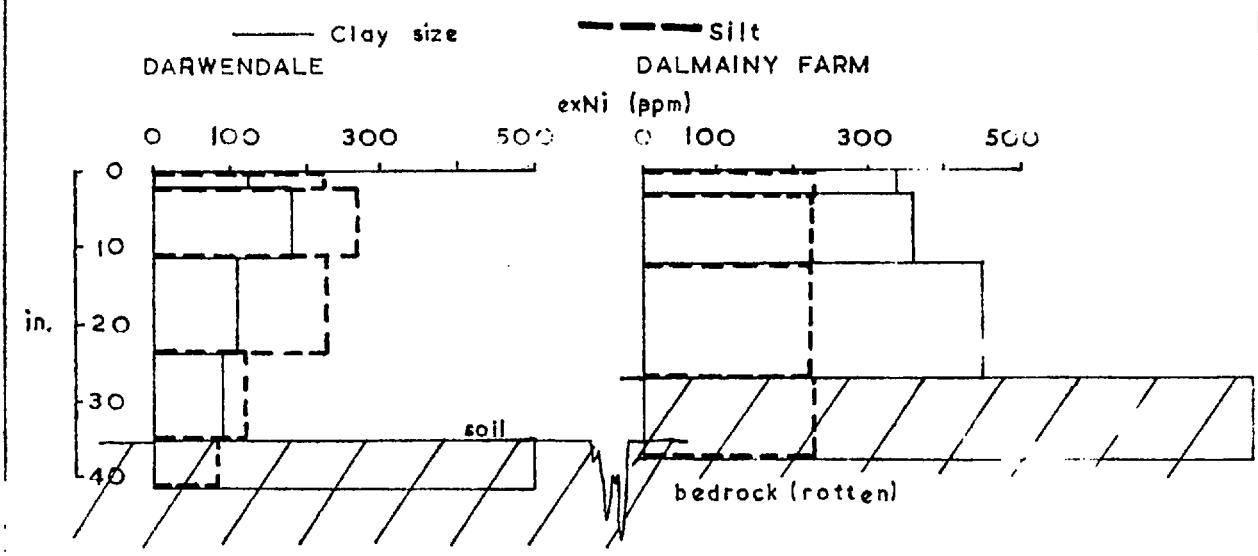
B. Distribution of exchangeable nickel.

The distribution of exNi in the minus 80 mesh fraction as a whole has been examined and the study has been expanded to include rocks other than ultrabasics.

The exNi content, which in most instances increases with decreasing particle size (Tables 27 and 29), has been determined on separated silt and clay size material from samples from two pits over serpentinite downslope of mineralization (Figure 46), from a pit in the vlei at Darwendale, a second pit in freely drained soil at Darwendale and from a pit in freely drained soil over serpentinite on Dalmainy Farm (Figure 47). The results confirmed the observation made earlier regarding the increasing exNi content with decreasing particle size. exNi is generally greater in clay size material than in silt. In the vlei profiles the exNi content is on the whole, greater than it is in the freely drained profiles although more irregularly differentiated in profile. Over freely drained ground at Maritzani and Dalmainy Farm exNi consistently increases with depth. At Darwendale, the relatively high exNi content in the near-surface horizons and decrease with depth was confirmed in the second profile.



Profile distribution of exNi in silt and clay size materials; Maritzani area. **46**



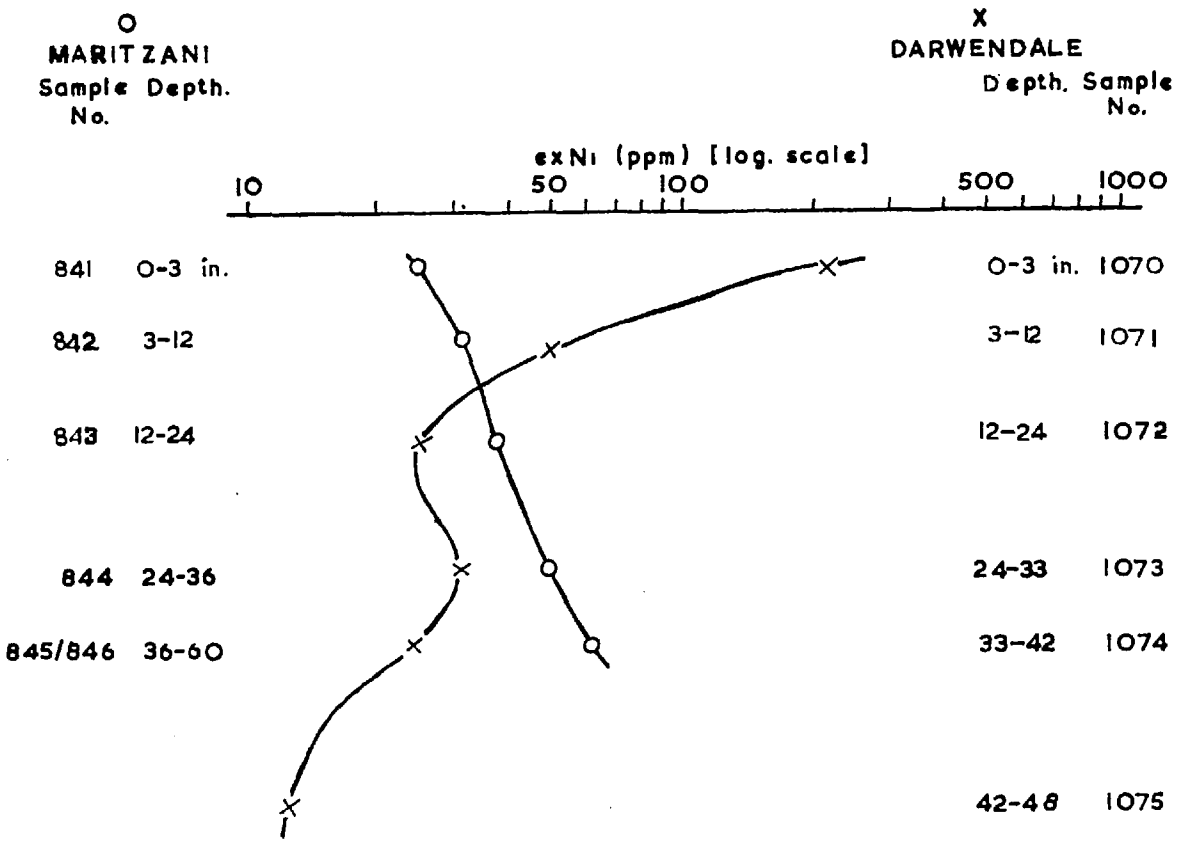
Profile distribution of exNi in silt and clay size materials; Darwendale and Dalmainy Farm areas. **47**

The profile distribution of exNi appears to differ from one profile to another according to the physico - chemical conditions at the site. These physico-chemical conditions and their effect on the distribution of exNi are discussed in the next chapter.

1. exNi in minus 80 mesh material.

The distribution of exNi in the minus 80 mesh fraction of soil samples from profiles at Darwendale and Maritzani was determined. In the upper soil horizons the exNi content of the minus 80 mesh fraction is greater at Darwendale than at Maritzani. In the lower horizons the position is reversed (Figure 48). This pattern of distribution is the same as that observed in the more specific size fractions and confirms that there is a contrast in exNi in weathered bedrock between barren and mineralized serpentinite. It also substantiates the observation that there is a reversal in the upper horizons at Darwendale which is believed to be due to the local conditions.

The exNi content of weathered bedrock appears to be greater where some of the exNi detected has probably been derived from sulphide minerals as opposed to where it has been derived solely from silicates.

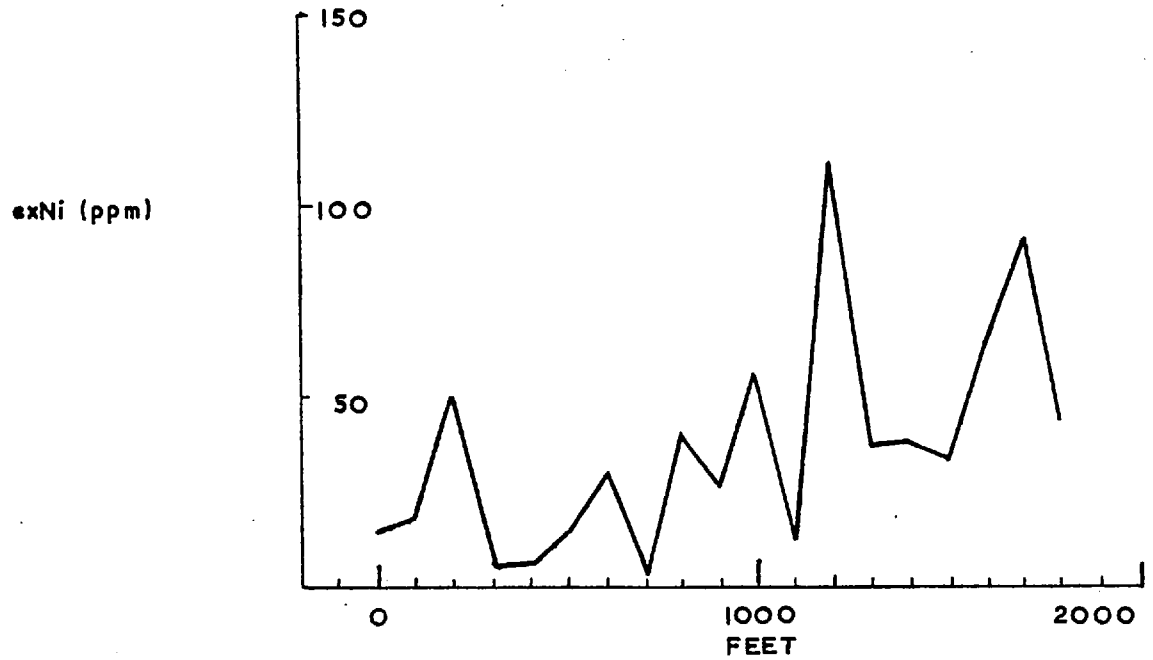


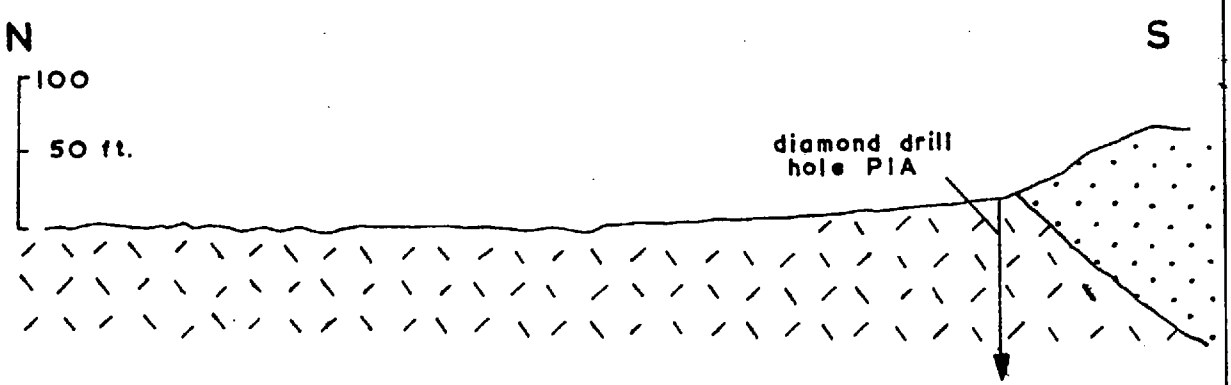
Comparison of profile distribution of exNi over Great Dyke serpentinite and mineralized serpentinite at Maritzani.

48

Further investigation of the distribution of exNi in weathered bedrock collected at the base of pits at Darwendale has shown a very erratic variation in the range 5 to 115 ppm (Figure 49). On average the higher values were obtained in the more freely drained ground. The reason for the large and erratic variation is not known but must be regarded as the normal background range in the area.

At Maritzani a maximum of 16-30 ppm exNi in material from the base of pits (usually in the upper C horizon) can be correlated with the sulphide mineralization. Away from the mineralized belt the exNi content of rotten serpentinite is less than 12 ppm (Figure 50). This observation is corroborated by a similar correlation between exNi content of weathered bedrock 15ft. below surface and the subjacent mineralization. At this depth a maximum of 10.0 ppm compared to an anomaly threshold of 3.5 ppm is indicative of mineralization (Figures 50 and 51). The bedrock at 15 ft. is less weathered than that at the base of the pits. There is an increase in exNi content from the fresh rock in depth into the weathered rock nearer surface (Figure 52). The Ni content increases from depth to the top of the weathered bedrock in a similar manner (Figure 29).

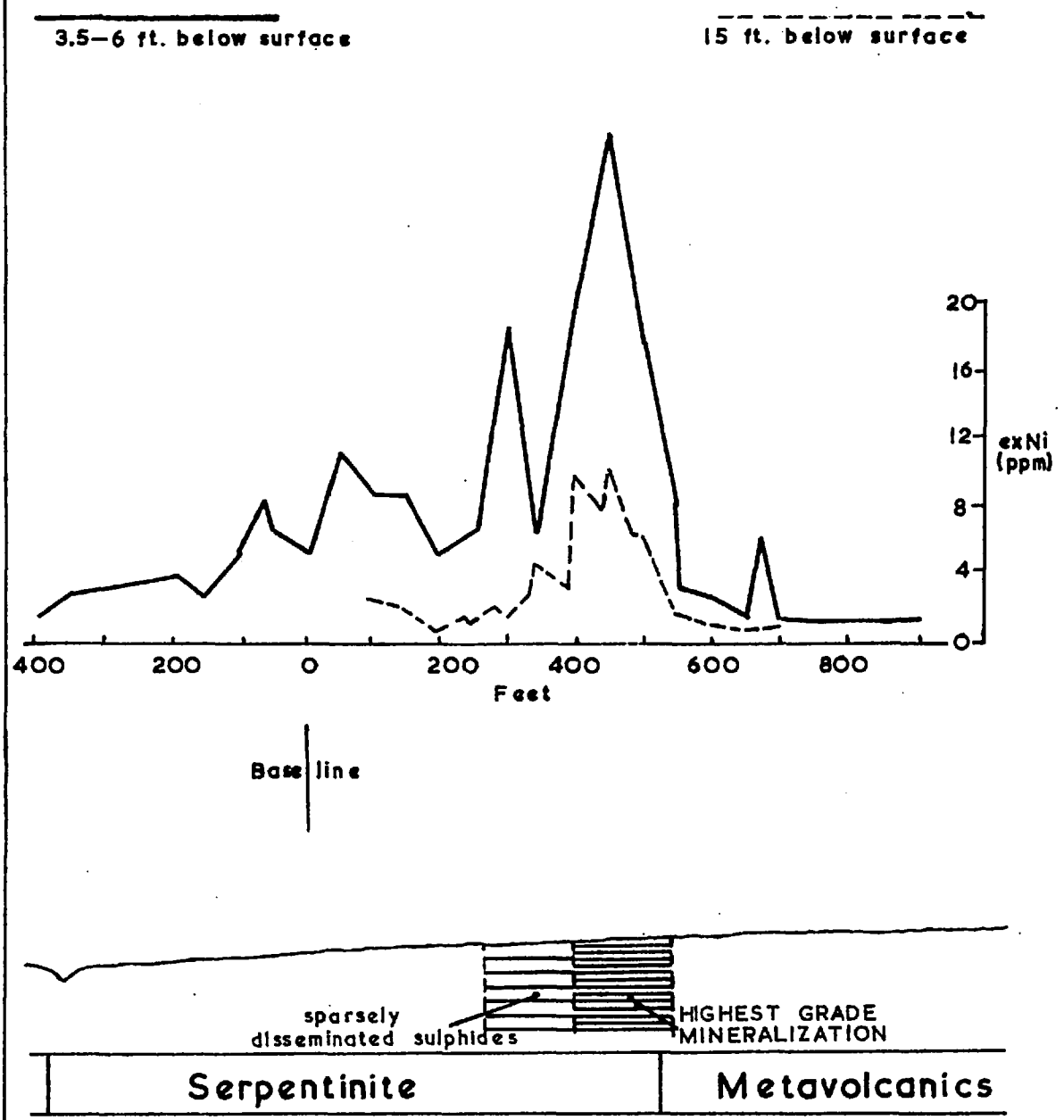




Serpentinite

Pyroxenite

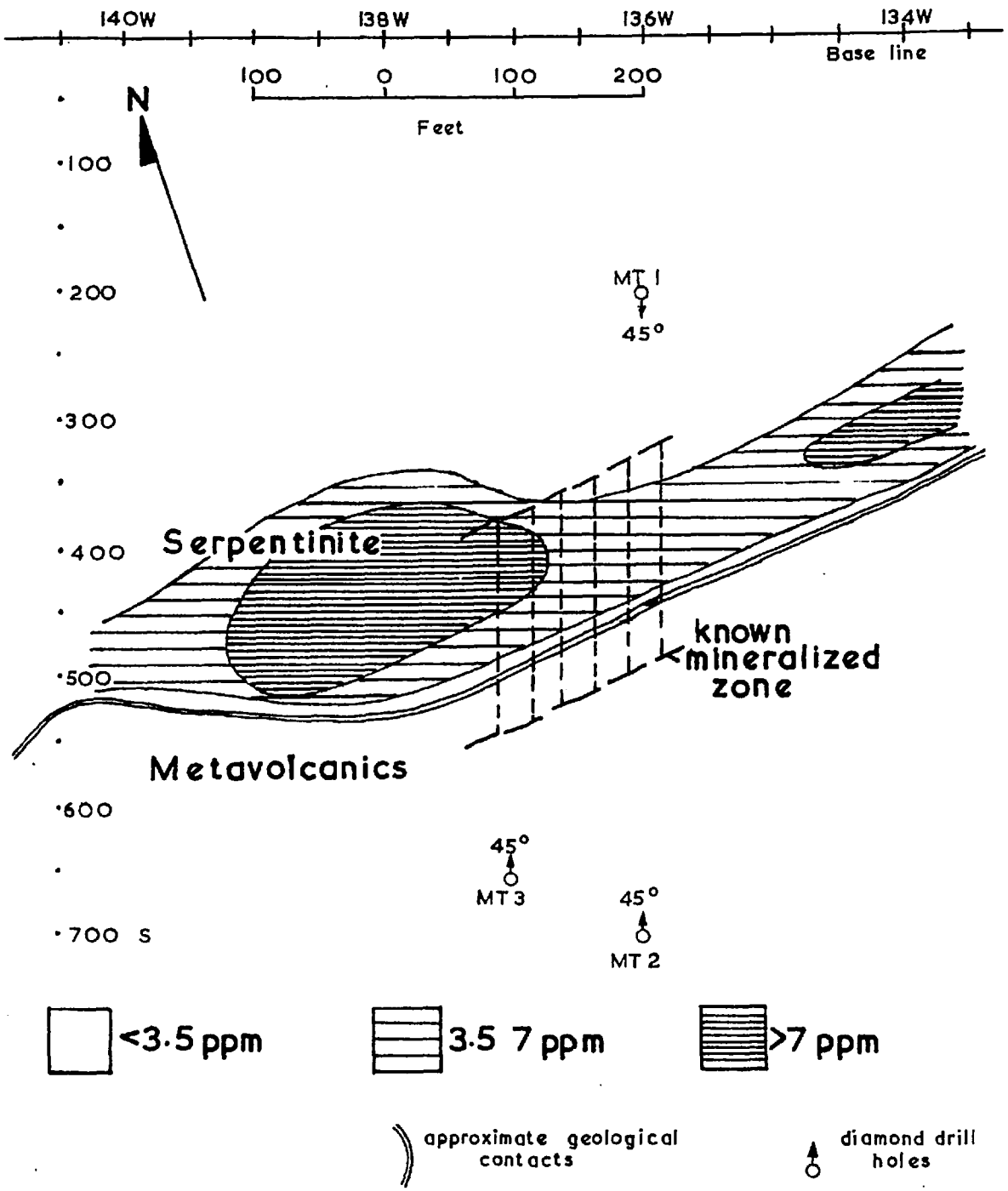
Variation in exNi content in weathered bedrock 3½-6 ft. below surface; Darwendale.



Distribution of exNi in weathered bedrock at Maritzani.

50

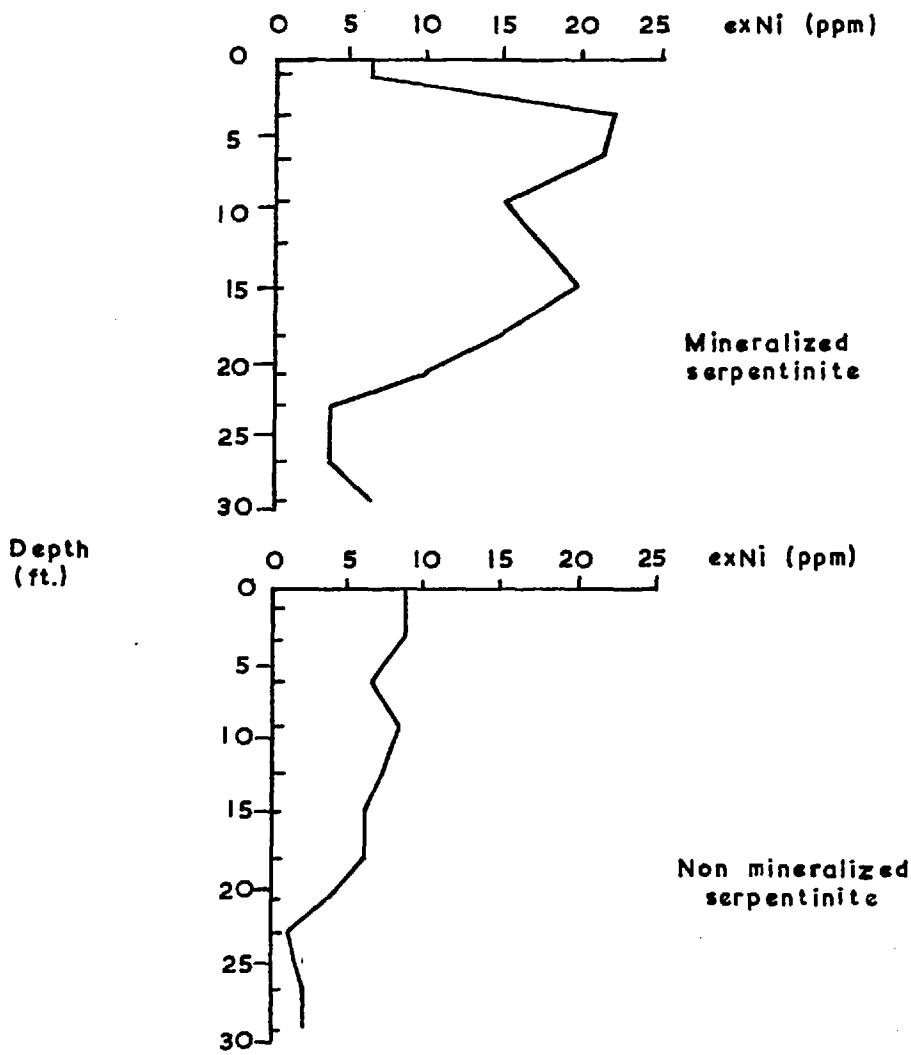
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Plan showing the distribution of exNi in weathered bedrock 15 ft. below surface; Maritzani.

51

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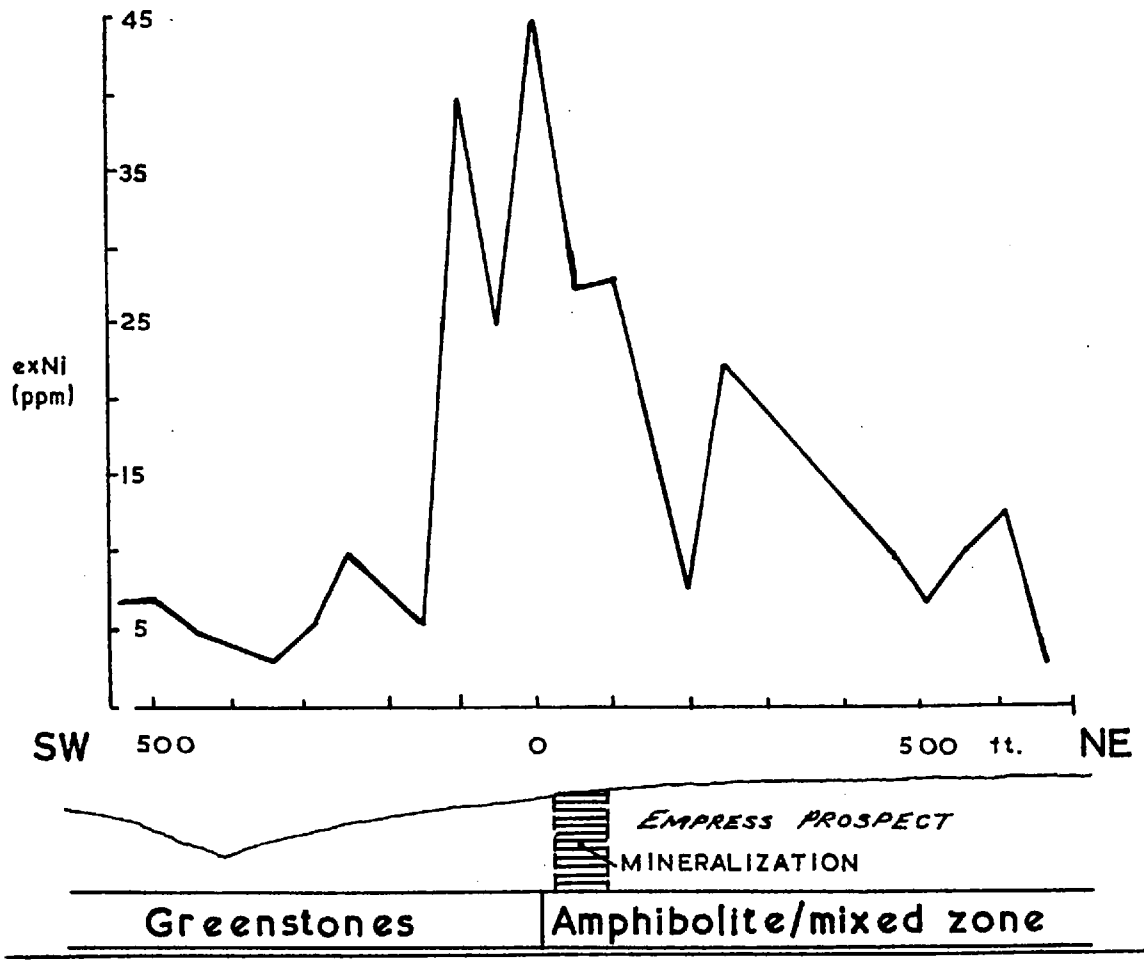
Comparison between the distribution of exNi in mineralized and barren serpentinite; Maritzani.

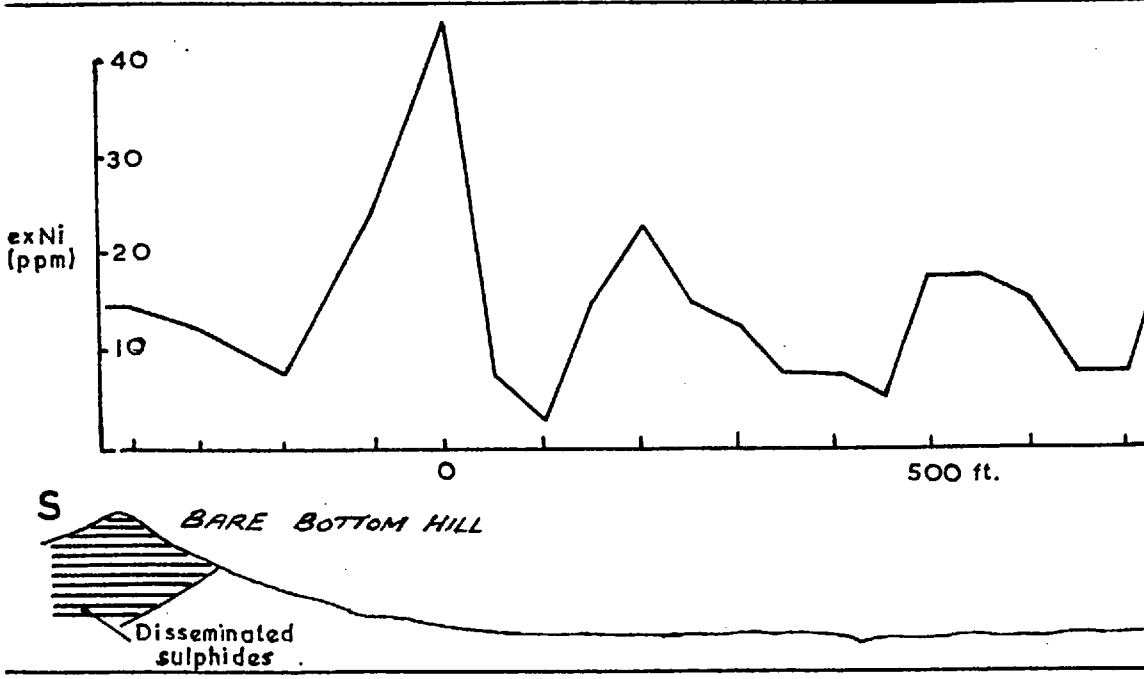
Within the Maritzani area there is a definite contrast in the exNi content of weathered rock between mineralized and unmineralized serpentinite. This contrast, a maximum of three-fold both at 15ft. below surface and at 3½-6ft. below surface, is greater than the contrast in Ni content (two-fold 15 ft. below surface, less than two-fold nearer surface). By comparison the contrast in the Ni content of near-surface soil is also less than two-fold.

These differences in the exNi and Ni contents of weathered rock and soil over mineralized and non mineralized serpentinite, no doubt reflect differences in the dispersion of nickel originally present as a sulphide and as a silicate.

At Empress and at Bare Bottom Hill (Figure 53) also the exNi in weathered and rotten bedrock is greater over and downslope from mineralization than over adjacent non mineralized rocks. However, the proportion of the Ni in the weathered rock which is exchangeable is less over the mineralization than over barren rocks. This is in contrast with observations at Maritzani.

In the environs of the Noel Nickel mine exNi has been determined only on the soils and not on the weathered rocks. The background over serpentinite (anomaly threshold 50 ppm) was found to be higher than the





exNi in weathered bedrock at the Empress prospect and at Bare Bottom Hill.

background over metasediments (anomaly threshold 20 ppm). Anomalous amounts of exNi were found in the soil over mineralization (Figure 54). One sample contained 500 ppm exNi - an amount twenty-five times anomaly threshold. In the study area generally the patterns of exNi and Ni distribution are very similar.

exNi in the weathered bedrock at Kalumbila is below the limit of detection (0.1 ppm). This is evidence of the intense leaching that is believed to have taken place in the freely drained ground in the Kalumbila area.

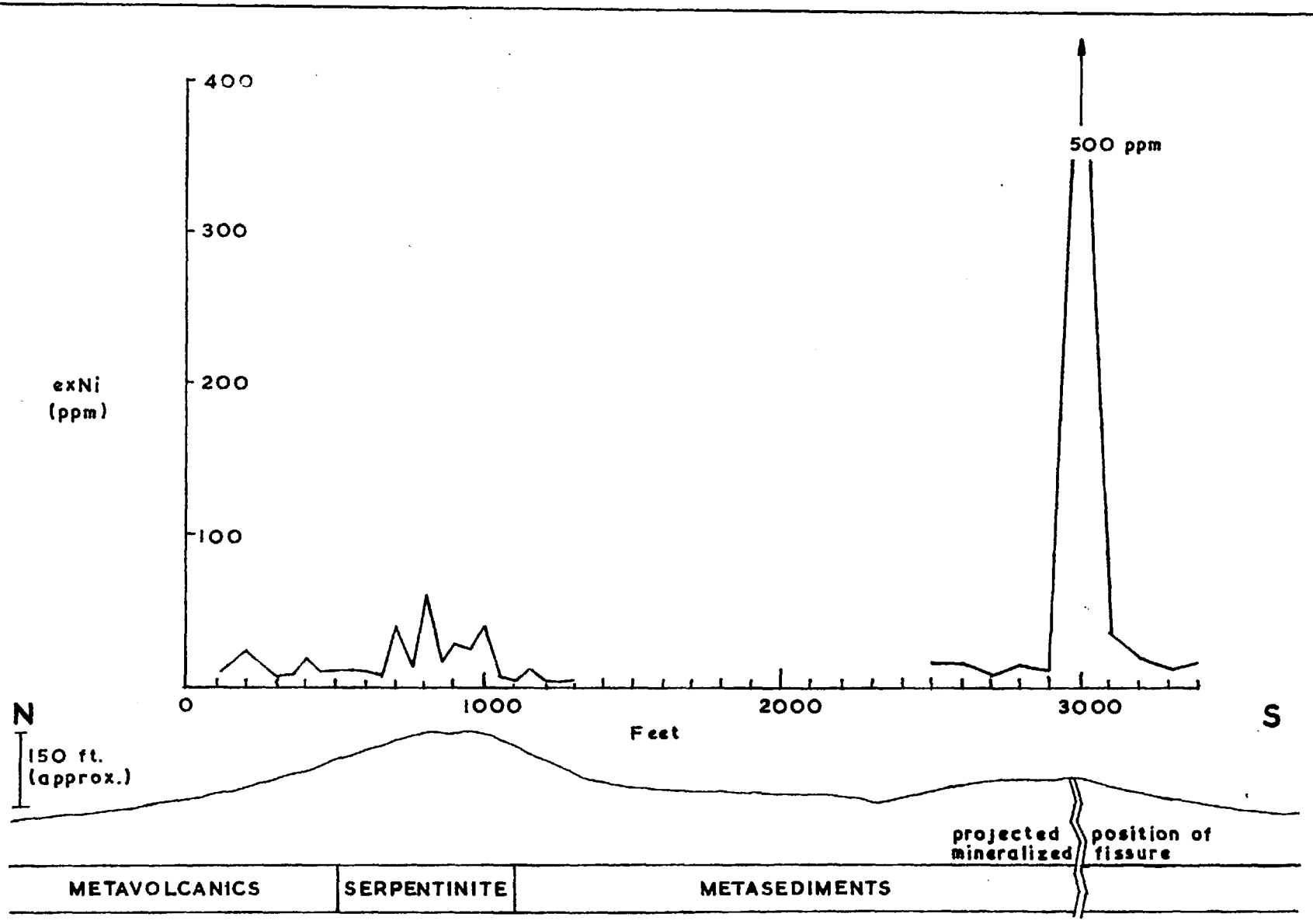
2. Summary.

The distribution of exNi is radically different in different environments. It's distribution in soils is believed to be readily influenced by varying physico-chemical factors which can overshadow any variations related to mineralization.

The distribution of exNi relative to varying physico-chemical conditions is discussed in the next chapter.

There is a positive contrast in the exNi content of weathered serpentinite between mineralized and barren zones at Maritzani which is greater than

exNi in near-surface soil in the environs of the Noel Nickel mine.



the Ni contrast. exNi in weathered bedrock at Empress and Bare Bottom Hill is present in larger amounts over mineralization than over barren rocks but the contrast is not as good as it is in terms of Ni.

At the Noel exNi is distributed similarly to Ni in soils. In the Noel study area exNi provides no better contrast between anomalous and background soils than does Ni.

Part III. THE DISTRIBUTION IN SOIL AND SEDIMENT OF ELEMENTS ASSOCIATED WITH NICKEL

Cobalt is generally associated with nickel in both silicate and sulphide minerals, both elements being siderophile in character. However, copper, with strong chalcophile tendencies, is associated with the sulphide nickel to a very much greater extent than it is with silicate nickel. All the sulphide mineralizations of the study areas are cupriferous. In contrast, there is little copper associated with the arsenide mineralization at the Noel. The distribution of copper and cobalt in the study areas is described first.

Selenium is commonly associated with sulphur in hydrothermal and magmatic mineralizations and its distribution has, accordingly, been investigated.

Arsenides and sulph-arsenides have been identified amongst the ore minerals in the Perseverance and Maritzani mineralizations. Consequently a limited study of the distribution of arsenic has been made in the Exclusive Prospecting Area No. 85 as well as the more comprehensive investigation in the environs of the arsenide deposits of the Noel Study area.

Antimony is known to be associated with many mineralizations of the Rhodesian schist belts and a preliminary look into the distribution of this element has been carried out.

A few selected samples were also analyzed for mercury.

A. Copper.

1. Dalmainy Farm.

No fresh rock samples from Dalmainy Farm have been analysed for copper but a sample of weathered serpentinite was found to contain 20 ppm Cu and granite from an outcrop 25 ppm Cu.

The distribution of copper in the freely drained soils has not been studied in this area but analyses of near-surface vlei soils for Cu have been

made (Table 30). The vlei soil north of the watercourse in the vlei running parallel to the serpentinite - granite contact (Figure 17) contains more Cu than similar soil from the vlei south of the channelway. Nickel is distributed in a similar manner. The origin of the copper is unknown. Some of the copper may have migrated, along with some of the nickel into the northern part of the vlei from the serpentinite upslope to the north. Although the figures reported above show more Cu in the acid rock it may not be the true position for the serpentinite sample was extremely weathered relative to the granite and some copper will have almost certainly been leached away.

2. Darwendale Area.

Fresh serpentinite from a depth of 208 ft. in diamond drill hole PIA contains 7 ppm $Cu_{(spec.)}$. The Cu content of weathered serpentinite varies between 12 and 110 ppm, to some extent with Ni.

The Cu content of the serpentinite soil is low and has nowhere been found to exceed 125 ppm. Cu is distributed more erratically than Ni but in eight of the nine profiles through freely drained soil the

horizon of maximum Cu content occurs at a higher level in the profile than the horizon of maximum Ni content.

Table 30. Comparison of Cu content of near-surface vlei soil north and south of a watercourse over granite and paralleling the serpentinite - granite contact at Dalmainy Farm (Figure 17)

Distance downstream of road. (ft.)	Cu content of near-surface soil (ppm)	
	North of channel	South of channel
200	30	10
800	40	15
1100	25	10
1400	23	20
2100		10
2400	48	15
2700	25	20

In the eight pits the Cu is at maximum in the A horizon, in four of them in the uppermost 3 in. of soil (Figure 55).

The nodules observed in the B horizon were found to be very rich in Ni. The Cu content of the nodules is, in contrast, low. The Cu content of minus 80 mesh material from a sample of B horizon soil was found to be 45 ppm. The nodules, coarser than 80 mesh, contain 90 ppm Cu. Corresponding figures for Ni are 4.5% (in the nodules) and 0.7% (in the matrix). The ratio Cu in nodules / Cu in minus 80 mesh matrix is 2/1 in contrast to the same ratio for Ni of 6.5/1.

Comment on the difference in distribution

Distribution of Cu in the freely drained soil profile over Great Dyke serpentinite.

between Ni and Cu in the soil profile in this study area is included in chapter 5.

On the basis of Cu, unlike Ni, there is little to distinguish between freely drained soil and vleis and there is sensibly no significant difference in Cu content between bank soil and stream sediment.

Throughout the two areas of non mineralized serpentinite (Dalmainy Farm and Darwendale) the tenor of copper in the areas as a whole is several tens to several hundred-fold less than nickel. The whole 'copper landscape' is subdued. In the mineralized areas there is very much more variation as described below.

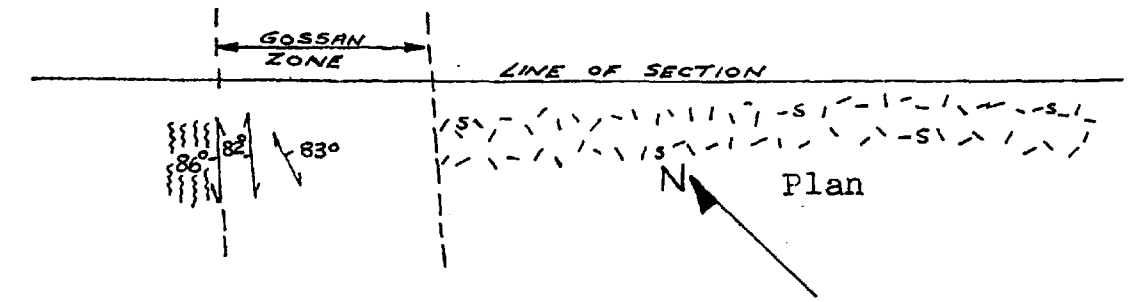
3. E.P.A. 85.

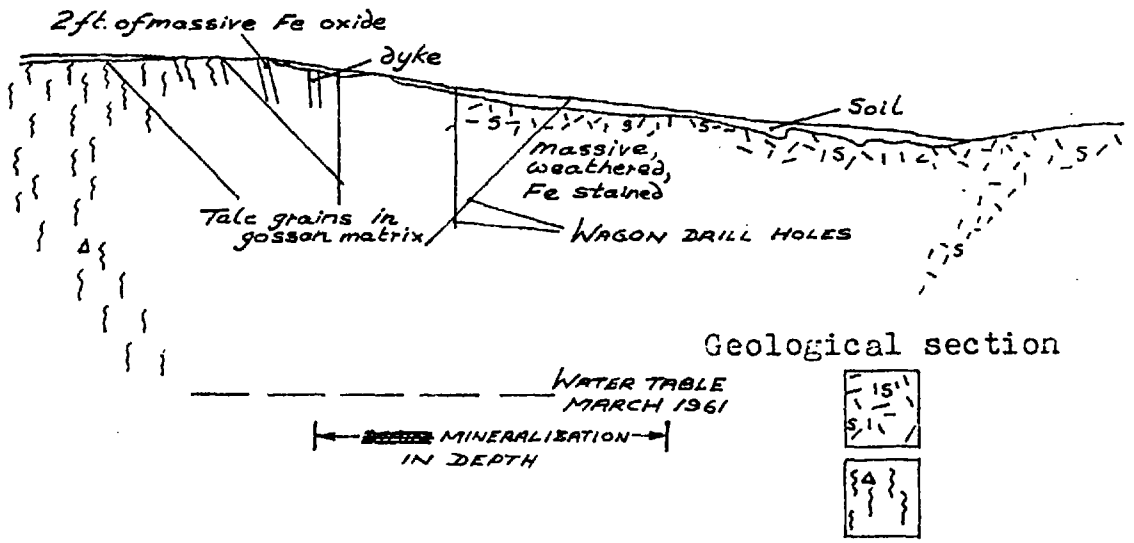
Fresh serpentinite of the E.P.A. 85 bodies, devoid, as far as can be ascertained, of sulphide minerals contains 10 to 420 ppm Cu, 85 ppm on average (82 analyses). The Cu content of metavolcanics is similar, the mean Cu content being 100 ppm (32 analyses). The ore at Perseverance contains copper in amounts greater than 0.2% in the section along line 12R. The maximum contrast between barren and mineralized serpentinite at Perseverance is greater on the basis of Cu than the

contrast between ore and barren serpentinite on the basis of nickel. Similarly at Maritzani.

The distribution of Cu in the weathered bedrock and soil of the uppermost 30 ft. of section at both Perseverance and Maritzani is very similar to the Ni distribution in the respective areas (compare Figures 56 and 57 with 25 and 28). The main mineralization is well defined in both areas by the Cu content of weathered bedrock.

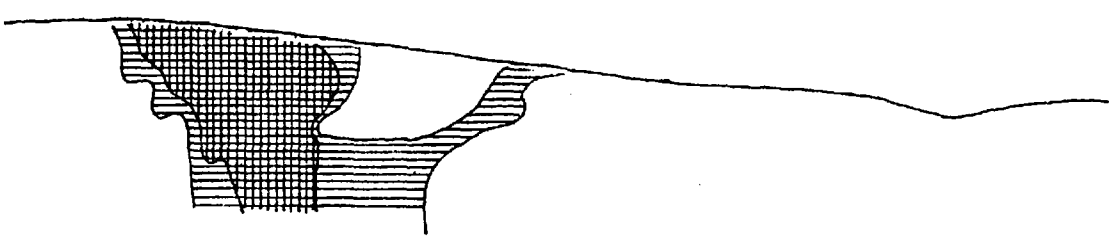
The anomaly threshold for Cu in near-surface soil at Perseverance is 130 ppm over serpentinite and 115 ppm over metavolcanics. These values are a little higher than that for non mineralized serpentinite at Darwendale (75 ppm) but lower than that for barren metavolcanics at Maritzani (175 ppm). These differences may be resulting from variations in the copper content of the fresh parent rocks. The soil survey revealed anomalous amounts of Cu in the near-surface soil over the mineralized zones with a contrast of the order of sixteen-fold at Perseverance but only three-fold at Maritzani. (Figures 58 and 59). The difference is believed to reflect the differences in grade of mineralization and local background. These contrasts are an improvement over the Ni contrast of less than two-fold in both study areas. The widths of the Cu anomalies



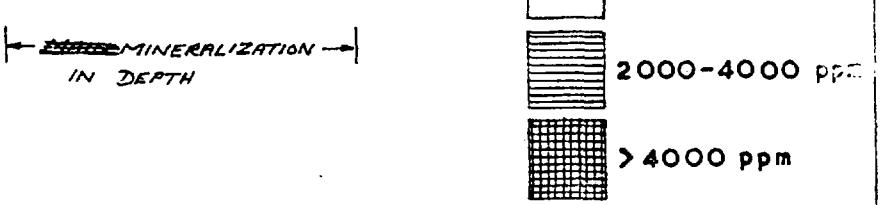


Geological section

Scale 1:500



Geochemical section



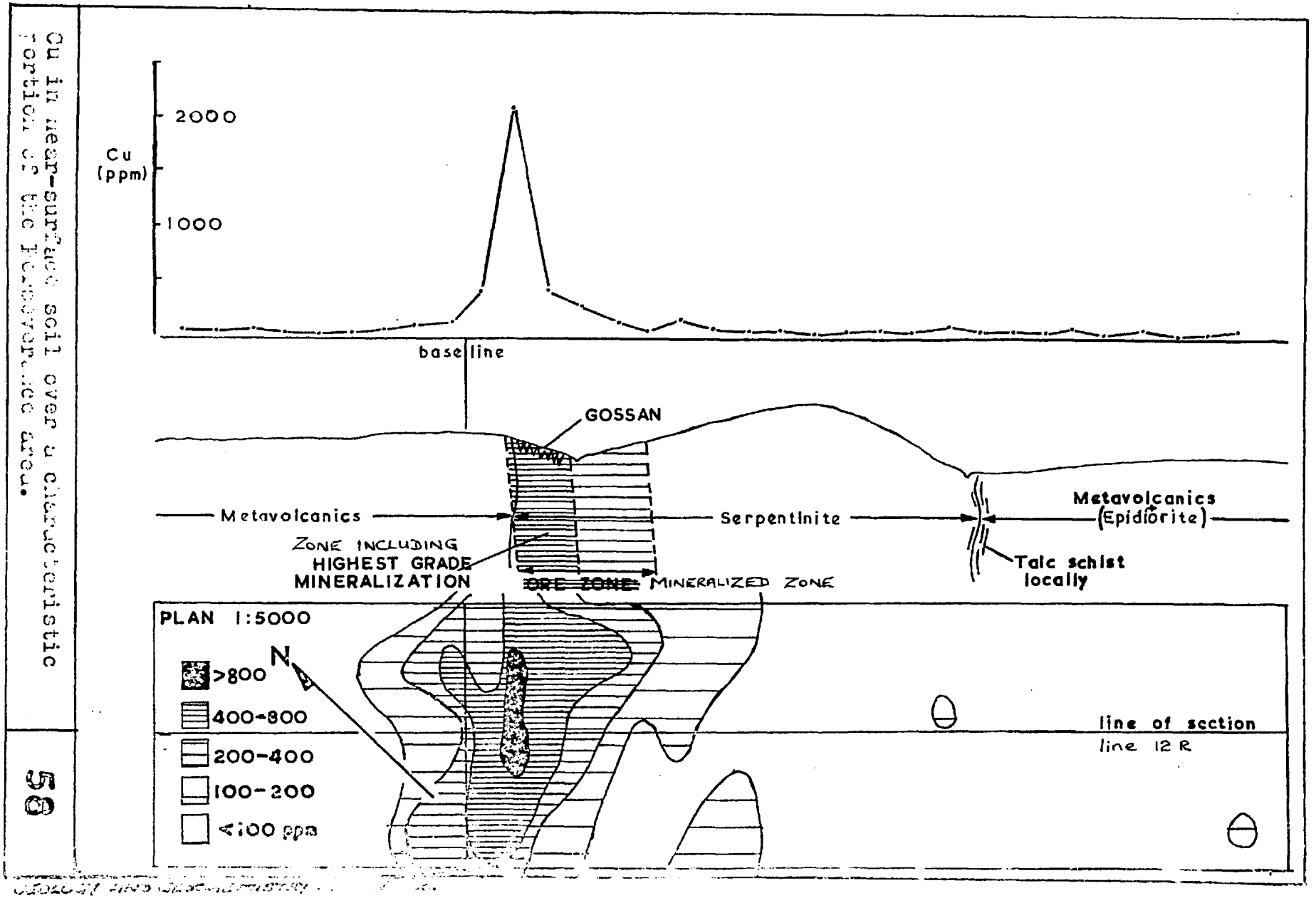
Typical section across the Perseverance mineralization showing the distribution of Cu.

56

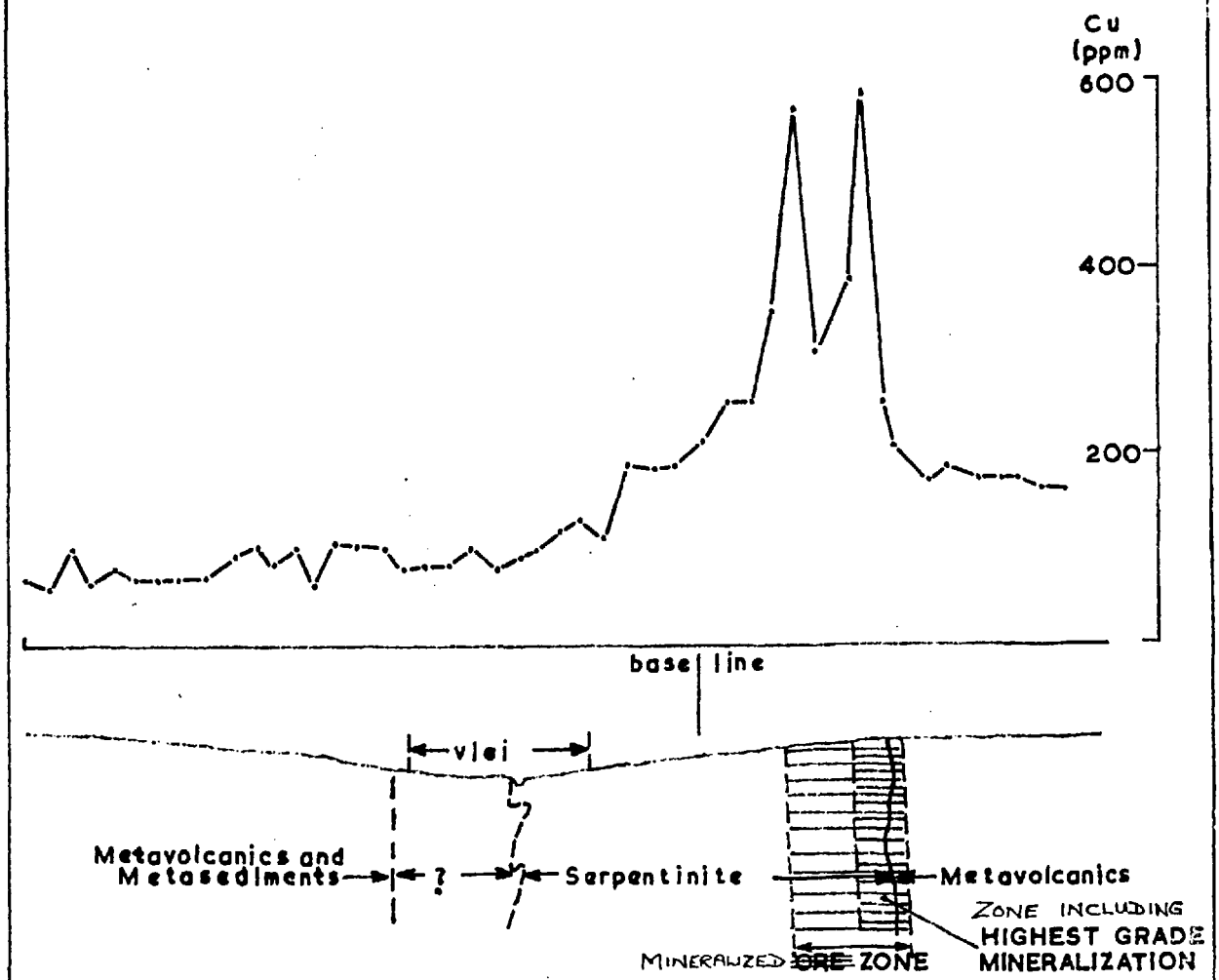
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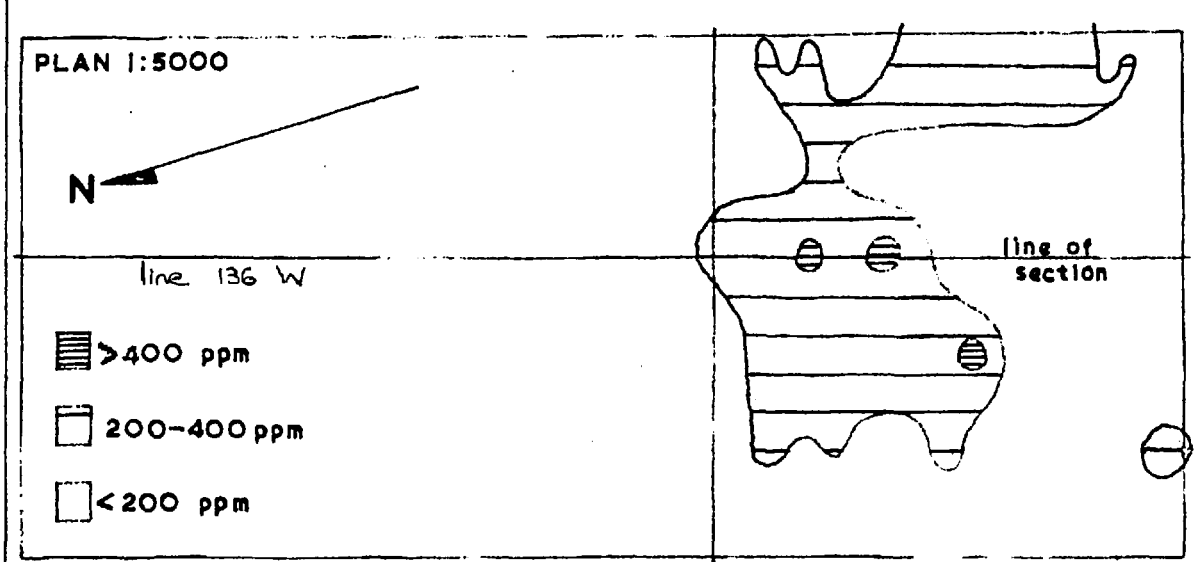
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Typical section across the Maritzani mineralization showing the distribution of Cu.



Cu in near-surface soil over a characteristic portion of the Tennessee area.





Cu in near-surface soil over a portion of the Maritzani area.

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in the near-surface soil are greater than those of the Ni anomalies in the same horizon. This is attributed to the more prominent primary dispersion halo for copper. Sparse disseminations of cupriferous sulphides in serpentinite are almost certainly more readily detected chemically than similarly sparse disseminations of nickeliferous sulphides since the background for Ni in or over serpentinite is thirty-fold more than that for Cu.

The distribution of Cu in the soil profiles of the Maritzani area has been determined and is described briefly, in sequence from barren metavolcanics upslope of the ore zone, across the ore zone to the soil over sparsely disseminated sulphides in serpentinite, soil over barren serpentinite downslope of the mineralization and ultimately to the vlei and the metasediments beyond it to the north (Figure 32).

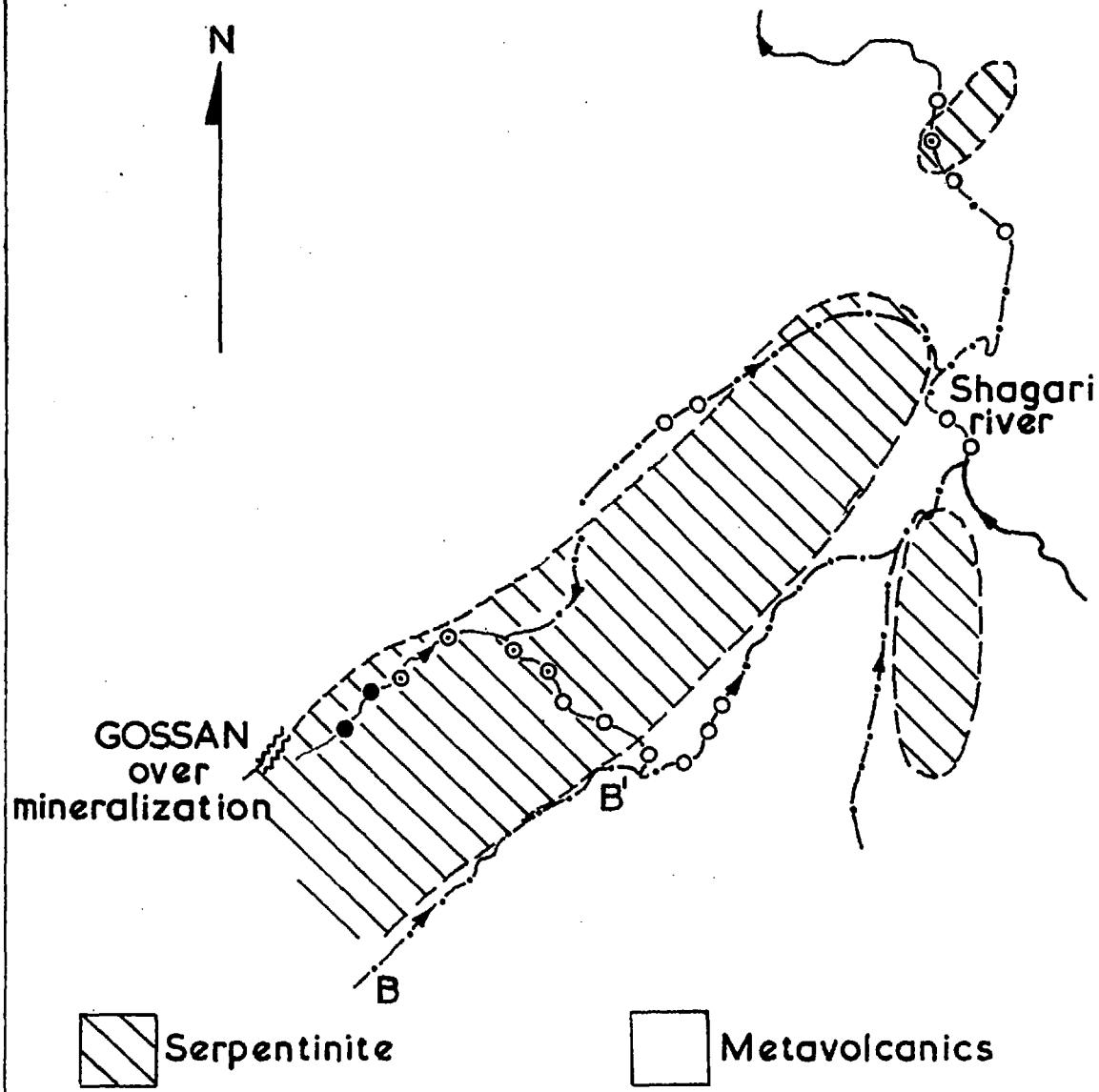
The distribution of Cu in the freely drained profile over background metavolcanics is very similar to the distribution of Ni in the same profiles. There is an increase in Cu content with depth through the true soil. The increase continues, in two of the three profiles, into the underlying bedrock. Over the main mineralization there is a steady increase in Cu content with depth but over the sparsely disseminated sulphides

the horizon of maximum copper content is the top of the weathered bedrock. Still further downslope, over non mineralized serpentinite and in the vlei, Cu is at maximum in the B horizon. North of the stream channel, in the vlei and freely drained soil, the Cu content is uniformly low and there is very little differentiation of Cu in the profile (Figure 32). In all these profiles the pattern closely follows that for Ni.

The Cu content was found to vary between 38 and 200 ppm in the main Maritzani stream draining the mineralized serpentinite. In a stream draining metasediments and other rocks the Cu content ranges between 35 and 80 ppm and immediately below the point of entry of this latter stream into the main stream the Cu content of the sediment is lower than at most other sites upstream and downstream in the main channel. Anomaly threshold for Cu in the stream draining metasediments is 90 ppm and in the stream draining the serpentinite 160 ppm. In the lower reaches of the Maritzani stream where the water table is close to surface the stream sediment at two sample points contains marginally anomalous amounts of Cu (190 and 200 ppm compared to an anomaly threshold of 160 ppm). This high Cu content is coincident with the highest Ni content but it is not known whether this copper

is related to the mineralization half a mile away. It is conceivable that some of the nickel and copper found at the site in question has travelled from mineralization in the ground water but there is no substantial evidence to prove this hypothesis.

The anomaly threshold for Cu in stream sediment at Perseverance, as adjudged from a stream draining non mineralized serpentinite, is 100 ppm (stream B-B^1, Figure 60). The Cu content of sediment in the stream draining the mineralization is clearly anomalous. 400 ft. from the Perseverance gossan stream sediment contains 580 ppm Cu. The Cu content gradually decreases downstream to less than 100 ppm 3800 ft. from the gossan. The values for Cu in stream sediment in the Shagari river may be unnatural as the river is contaminated from the producing gold mines upstream. A value of 320 ppm Cu in stream sediment over the Shagari serpentinite is higher than most other values obtained in the Shagari river sediment. Despite the known contamination it is believed that this value is indicative of the mineralization in the ~~serpentinites~~ metavolcanics adjacent to the serpentinite.



Drainage reconnaissance: Cu in stream sediment; Perseverance.

60

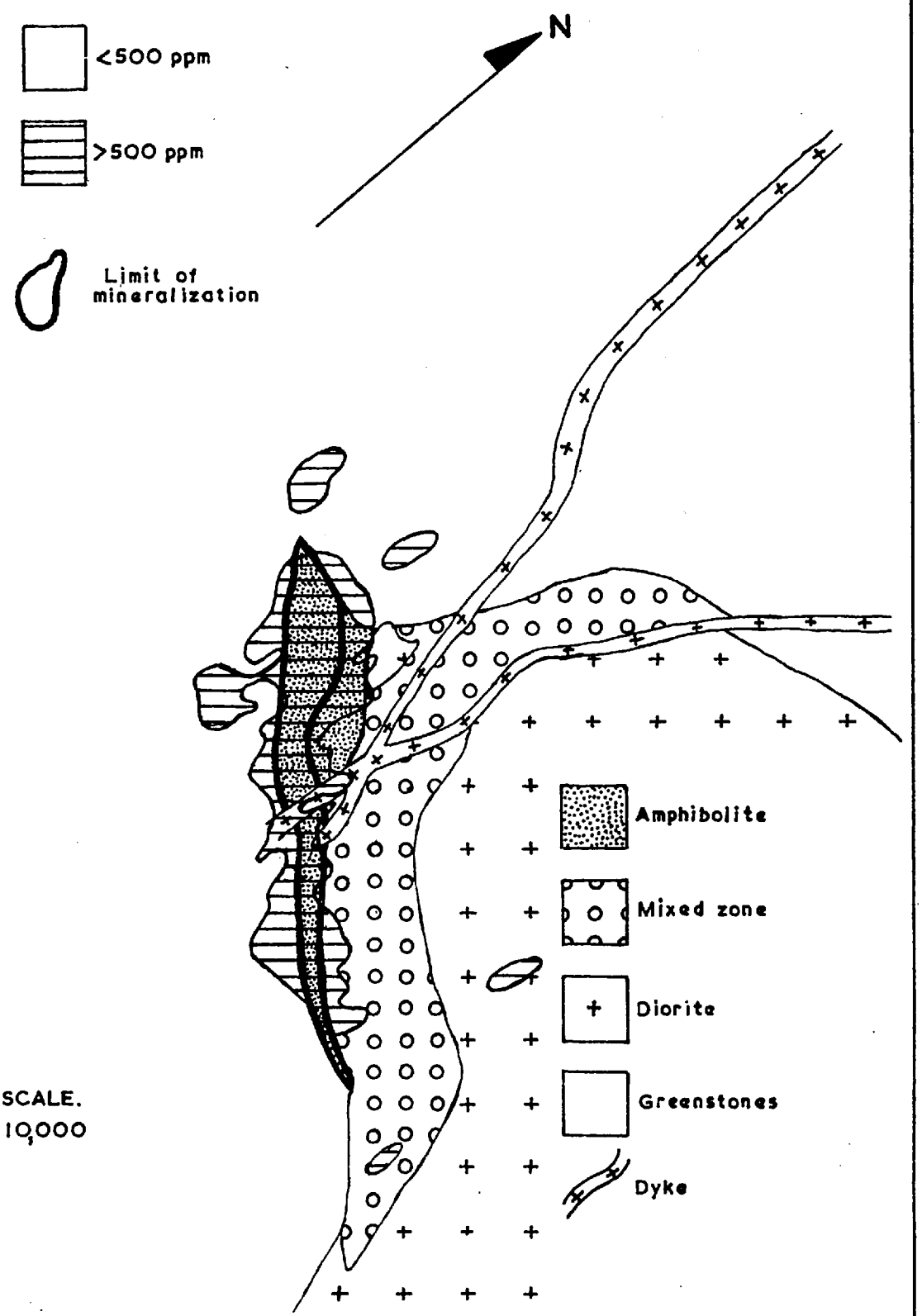
GEOCHEMISTRY R.S.T.E. Ltd.

4. Empress prospect and Bare Bottom Hill.

The average copper content of the ore reserves at the Empress prospect is 0.65%, a little less than the overall average nickel content (0.83%) (Sharpe, 1961).

The geochemical soil survey revealed a pattern of $Cu_{(spec.)}$ distribution (Figure 61) very similar to that of $Ni_{(spec.)}$ (Figure 35). Anomaly threshold for $Cu_{(spec.)}$ in near-surface soil over greenstones and dionite is 45 ppm and the maximum $Cu_{(spec.)}$ content of anomalous soil is 5500 ppm. Sharpe (1961) has made the observation that soils containing more than 500 ppm $Cu_{(spec.)}$ delimit the orebody suboutcrop, being nearly coincident with the area of soils containing 3000 or more ppm $Ni_{(spec.)}$. The contrast between background and peak anomaly at Empress is more than one hundred-fold on the basis of $Cu_{(spec.)}$. Two grab samples of near-surface soil over barren amphibolite of the small body south of the shaft were found to contain 55 ppm Cu in contrast to the maximum of 4200 ppm on a traverse across the mineralized zone; a sixty-fold anomaly. It is emphasized that this is a contrast with a single background result not threshold. The corresponding contrast for Ni is eighty to ninety-fold.

At Bare Bottom Hill the contrast on the basis



$Cu_{(spec.)}$ in near-surface soil at the Empress prospect.

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of $Cu_{(spec.)}$ is more than one hundred-fold and on the basis of Cu sixty-fold.

The profile over barren greenstones near the Empress prospect contains 13 to 18 ppm Cu, appreciably less than in similar profiles at Bare Bottom Hill. The Cu content of weathered bedrock and soil on the lower slopes of Bare Bottom Hill ranges between 45 and 235 ppm. There is a zonal variation in Cu content that is correlated with the Ni distribution although the zones are less readily distinguished by the difference in Cu content (Figure 36). This may be due to the differences in copper content between the rock types comprising the greenstones being smaller than the differences in their nickel content. The distribution of Cu in the soil profile is comparable to, but more irregular than Ni. However, in 10 of 19 profiles the layer of maximum Cu content is higher in the profile than the horizon of maximum Ni content. In six profiles both metals are at maximum in the same horizon leaving only three sites where the Cu is at maximum at a point in the profile below the layer of maximum Ni content. On average, therefore, the Cu is at a maximum higher in the profile than Ni. This distribution is the same as that observed at Darwendale. Comment on this observation is reserved until chapter 5.

Over mixed zone rocks, adjacent to but upslope from mineralized amphibolite, Cu, like Ni is more abundant in the upper horizons than in the lower parts of the profile. Directly over mineralization the Cu content increases to more than 0.5% but is, again like Ni, erratically distributed in the soil profile. Over greenstones downslope from the Empress mineralization lateral dispersion of copper appears to have been closely analagous to the lateral dispersion of nickel as is also the case at Bare Bottom Hill (Figures 36 and 37). That is to say that copper, again like nickel (page 136) has probably been dispersed, mechanically and hydromorphically (and possibly via the biogeochemical cycle) from the mineralization upslope.

The Cu content of bank soil and stream sediment is correlated with the Cu content of adjacent soils. As explained in the section on nickel the drainage below the main mineralization has not been sampled because of the probability of contamination.

5. Kalumbila area.

At Kalumbila there is an increase in the tenor of copper in the ore from north east to south west. This is the reverse of the variation in nickel

content. The best copper mineralization occurs in block 205 (Figure 9).

Local background in near-surface soil is slightly higher over carbonaceous shale than quartz-mica schist and, over the respective rock types, is greater in the south west than in the north east (Table 31). These variations are, in all aspects, the reverse of the variations in nickel distribution. The fundamental reason for the difference in distribution between nickel and copper is thought to be the difference in the primary dispersion pattern, which, as indicated in chapter 3, is thought to have formed at the time of ore deposition.

In the soil in and just downslope of the clearing crossed by line 12, block 205 there are clearly anomalous amounts of Cu (Figure 62). The Cu is present, in the 3-12 in. horizon for example, in amounts exceeding 400 ppm compared with an estimated local anomaly threshold of 75 ppm for carbonaceous shale. The contrast is six-fold in both the 0-3 and 3-12 in. horizons (Figure 62). By comparison the Ni contrast is eight-fold in the 0-3 in. horizon and two-fold in the 3-12 in. horizon (Figure 38). No anomalous amounts of Cu have been observed in the freely drained soils in block K1, i.e. in the area

Variation in Cu content of A horizon soil over highest grade copper mineralization; Kalumbila.

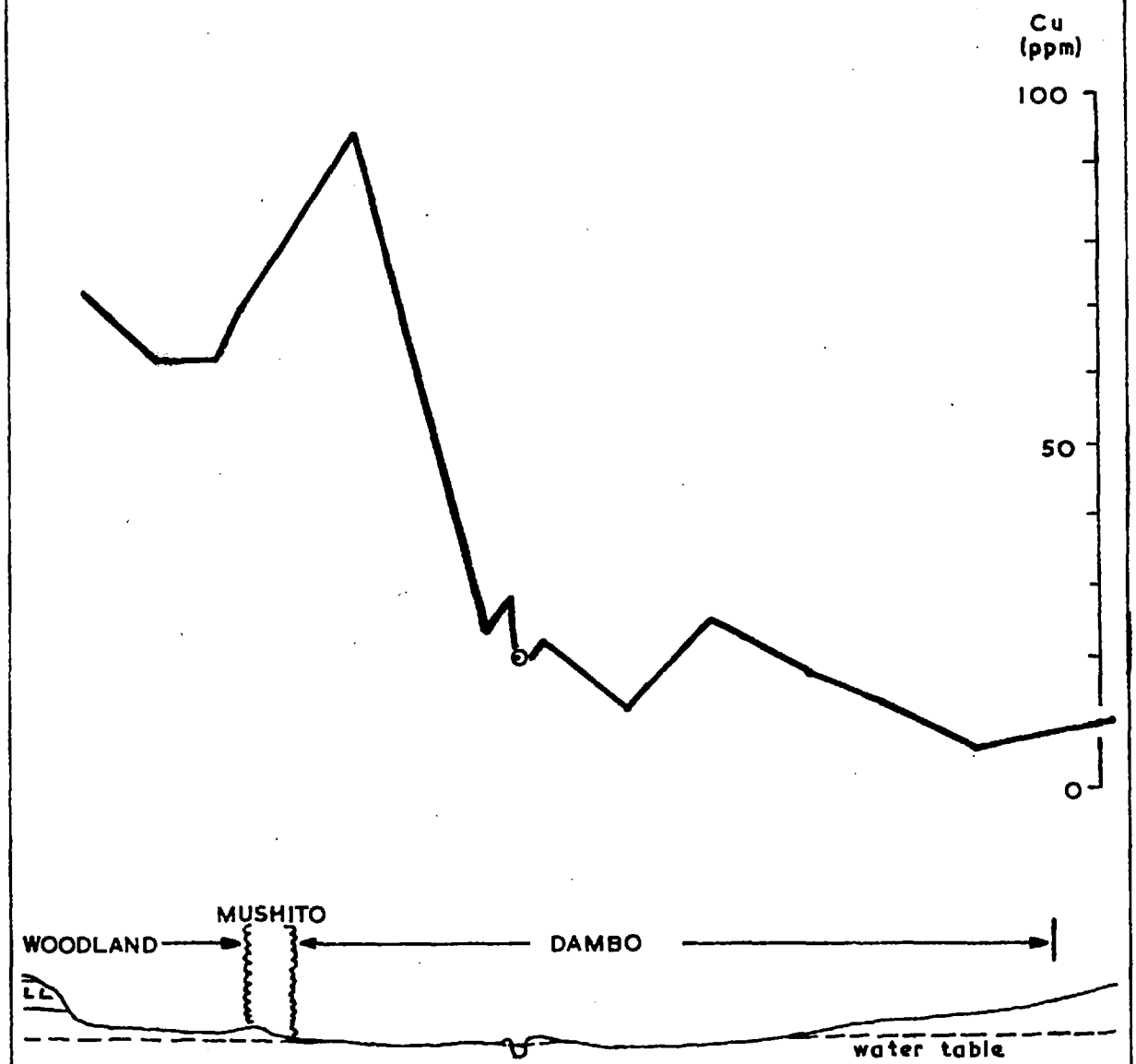
GEOLOGY; RST.MS. Ltd.

where nickel sulphides have been detected in drill holes (Figure 39).

Table 31. Copper content of near-surface soil over non mineralized rocks, Kalumbila area.

Rock type.	Sample Depth (in).	Cu content (ppm) Range	Mean	No. of samples
Carbonaceous Shale (SW)	3-12	35-90	60	7
Carbonaceous Shale (NE)	3-12	15-25	20	5
Quartz-mica Schist (SW)	3-12	10-30	17	12
Quartz-mica Schist (NE)	3-12	5-25	13	12
Gabbro	0-6	10-15	14	10
Sericitic-Specularitic Quartzite	3-12	5-10	6	7

In the dambo downslope from outcropping carbonaceous shale in block K1 there is more Cu on the carbonaceous shale side of the stream channel than there is on the opposite, quartz mica schist, side (Figure 63). This distribution could be explained by the geology. Some of the copper in the south east part may have originated from the carbonaceous shale. It has been shown that the soil over the carbonaceous shale normally contains more Cu than that over quartz-mica schist. The Ni content in this dambo is slightly anomalous but as pointed out earlier it is not clear how much of the nickel has been derived from the sulphide minerals.

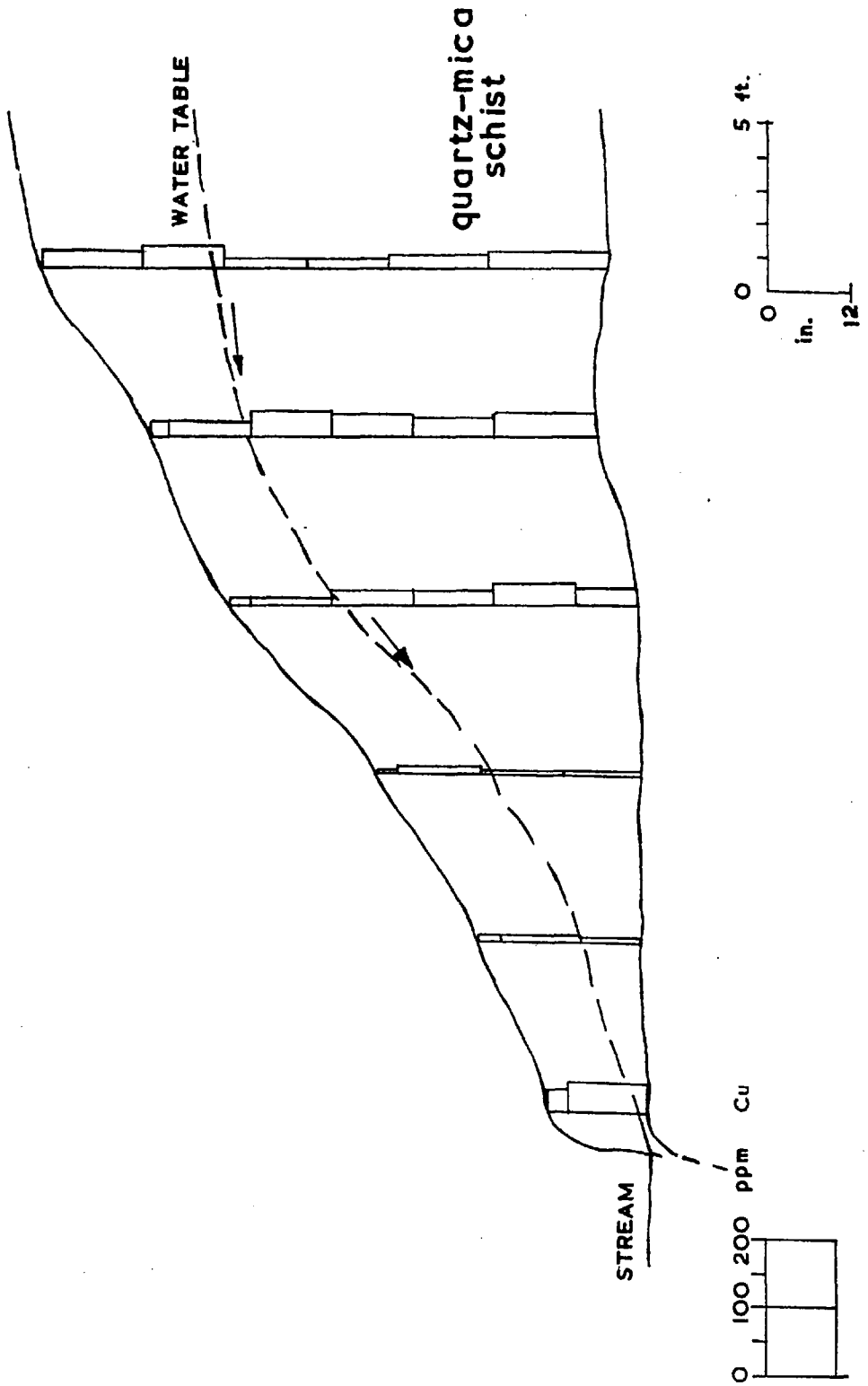


Cu in near-surface Dambo soil and stream sediment (ringed) at Kalumbila.

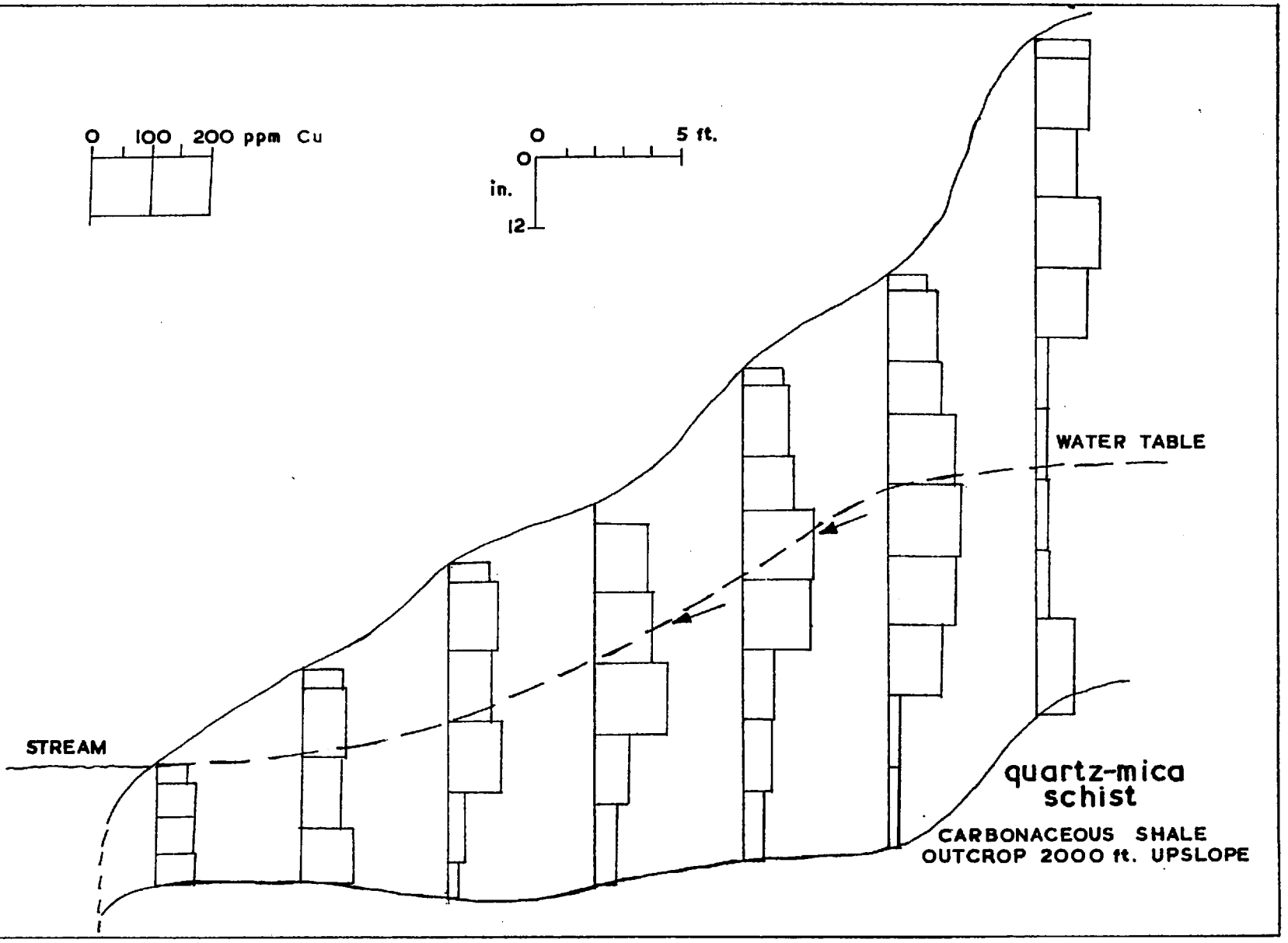
63

In the trenches cut into the dambo/freely drained soil contact Cu, like Ni, is, in most parts, more abundant close to the water table than it is above and below (Figures 64 to 66). The trench downslope of the outcropping carbonaceous shale is richer in Cu than are either of the other two trenches (downslope of quartz-mica schist and sericitic-specularitic quartzite). The copper in the first mentioned trench may have originated from the carbonaceous shale itself or from the nickel-copper sulphide minerals known to be present at depth within the carbonaceous shale horizon, having moved via ground water towards the dambo. Some of the nickel in this trench downslope of the shale outcrop is believed to have moved in the same way. In the case of nickel, however, the soil over the carbonaceous shale contains less of the metal than does the soil over quartz-mica schist (Table 21). The slightly anomalous Ni values (i.e. anomalous for quartz-mica schist) coincident with the highest Cu values in dambos are probably due to dispersion from mineralization but the hypothesis is difficult to substantiate without precise knowledge of ground water movement.

The materials of the trench on line 39 contain very little copper (Figure 66). A marked predominance of Ni over Cu is an observed geochemical



Section along Kalumbila trench No. 1 showing the distribution of Cu.



Section along Kalumbila trench No. 2 showing the distribution of Cu.

Section along Columbia trench No. 3 showing the distribution of Cu.

characteristic of the soil over gabbro in the study area (Table 32). It is, thus, very probable that the

Table 32. Nickel and copper in near-surface soil over gabbro in the Kalumbila area, Zambia.

Sample No.	Ni (ppm)	Cu (ppm).
140	120	15
141	155	15
142	110	15
143	110	10
144	135	15

part of the dambo containing relatively large amounts of Ni just upstream of the downslope projection of the carbonaceous shale outcrop (Figure 39), reflects the presence of a gabbroidal body beneath, adjacent to or up drainage from the section of the dambo in question.

Within the dambos, as for Ni, the bank soil and stream sediment contain less Cu than the swampy flats on either side (Figure 63).

6. Noel.

The mineralization at the Noel is not cupriferous and there is nothing in the distribution of Cu in the soils that can be related to mineralization. There is, furthermore, no clear correlation between the Cu content of soil and the underlying geology. Soil richest in Cu is that over serpentinite on the hill

crest and the material in the valleys over metavolcanics (north of the serpentinite) and over metasediments (south of the serpentinite). This distribution would suggest that there is more copper in serpentinite than in other rocks of the study area, some of which has been moved ~~leached~~ and redeposited in the swales and valleys.

7. Summary of the main features of the distribution of copper.

In background areas of ultrabasic rocks Cu is uniformly distributed and generally in small amounts (less than 100 ppm). Relative to Ni the contrast in Cu content between freely drained **vlei** and dambo environments is small.

In the profile away from mineralization there is a tendency for copper to be fixed nearer surface than is nickel.

The pattern of the relationship of copper to mineralization is similar to that between nickel and mineralization but in the serpentinite environment it is more conspicuous.

There is a greater contrast between the copper content of barren and mineralized serpentinite, overlying soil and related stream sediment than there

is between the nickel contents of the same materials.

In areas of rocks other than ultrabasics there is little difference in the contrast between anomalous and background materials based on nickel or copper except at the Noel (where the mineralization is not cupriferous) and possibly in the drainage at Kalumbila.

B. Cobalt.

Investigation of the distribution of cobalt has been confined to the Exclusive Prospecting Area No. 85 where, in a soil survey, the Co content of near surface soil overlying mineralization was shown to be no greater than that over barren serpentinite. Like Ni, the Co content of near-surface soil reflects the geology in that there is noticeably more Co in the soil over serpentinite than there is over metavolcanics. (Figure 67). As in the case of Ni the degree of differentiation between serpentinite and greenstones is about ten-fold. It is of interest to note the slightly smaller cobalt content of the soil on the ridge compared to that of the soil on the lower slopes. This may be reflecting a primary dispersion feature - the zoning of cobalt content around the core of the serpentinized peridotite intrusion. Alternatively it may be a secondary dispersion

Co in near-surface soil over a characteristic portion of the Perseverance area.

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feature related to weathering and depth of soil.

Weathered bedrock samples from wagon drilling at Perseverance have not been analysed for cobalt but those from Maritzani have. The results, some of which are presented in Figure 68, illustrate the clear contrast in Co content between serpentinite and metavolcanics. The mineralized serpentinite is a little richer in cobalt than the non mineralized rock. Downslope from the mineralization there is more Co in the soil than in the underlying bedrock but it is not clear whether this is normal enrichment in the soil over serpentinite bedrock or dispersion downslope from the mineralized zone (Figure 68).

In stream sediment at Perseverance the samples 400 and 800 ft. from the gossan contain 90 and 85 ppm cobalt respectively. Values of 60-80 ppm Co are attained in all streams in the drainage system and a Co content of 115 ppm has been recorded at one point unrelated to any known mineralization (Figure 69). 90 and 85 ppm can not, thus be regarded as particularly anomalous.

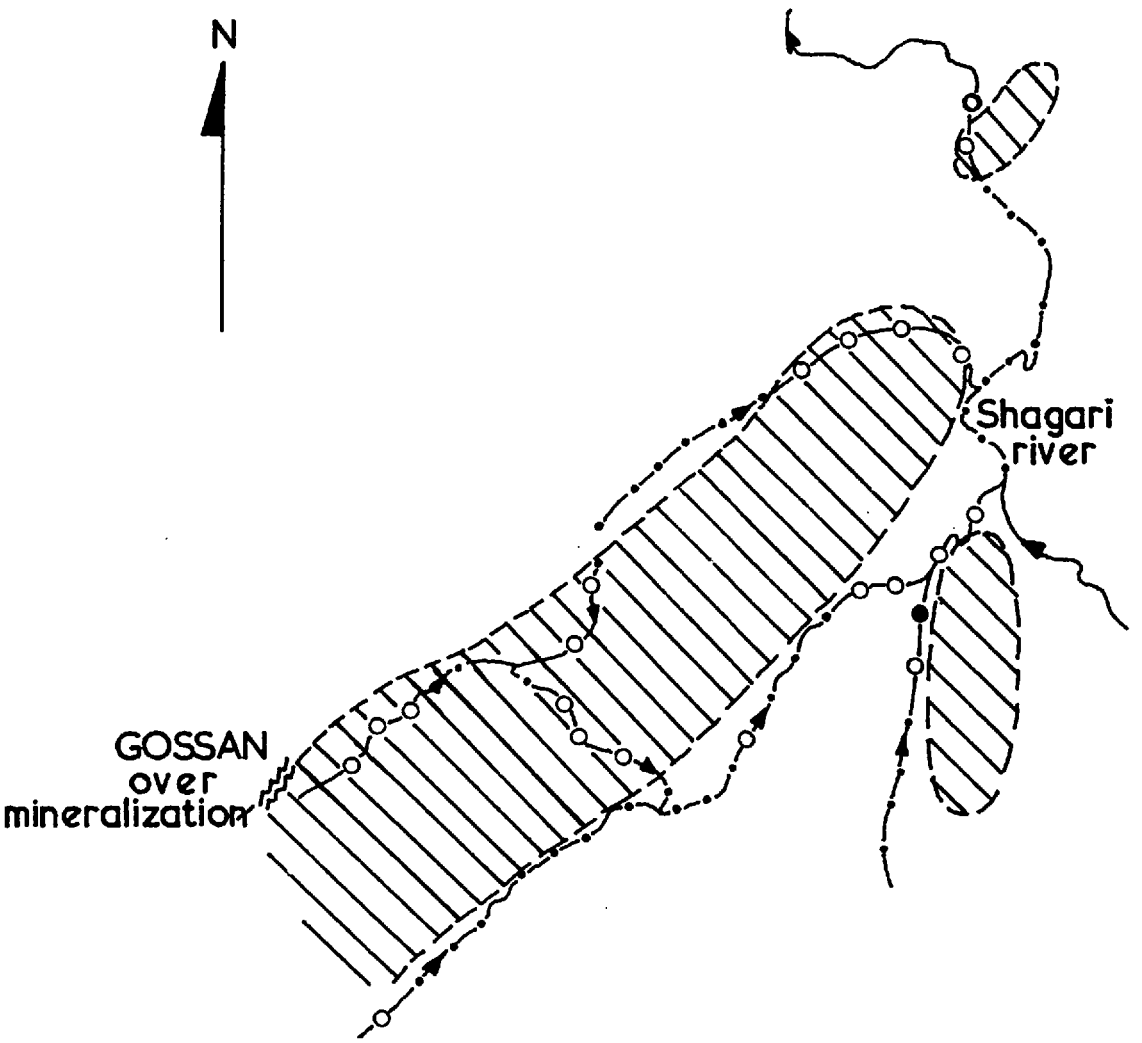
C. Arsenic.

The samples collected by the Southern Rhodesian Geological Survey in the environs of the Noel Nickel

Typical section across the Maritzani mineralization showing the distribution of Co.

68

DATA: R.S.T.E. Ltd.



Drainage reconnaissance: Co in stream sediment; Perseverance.

69

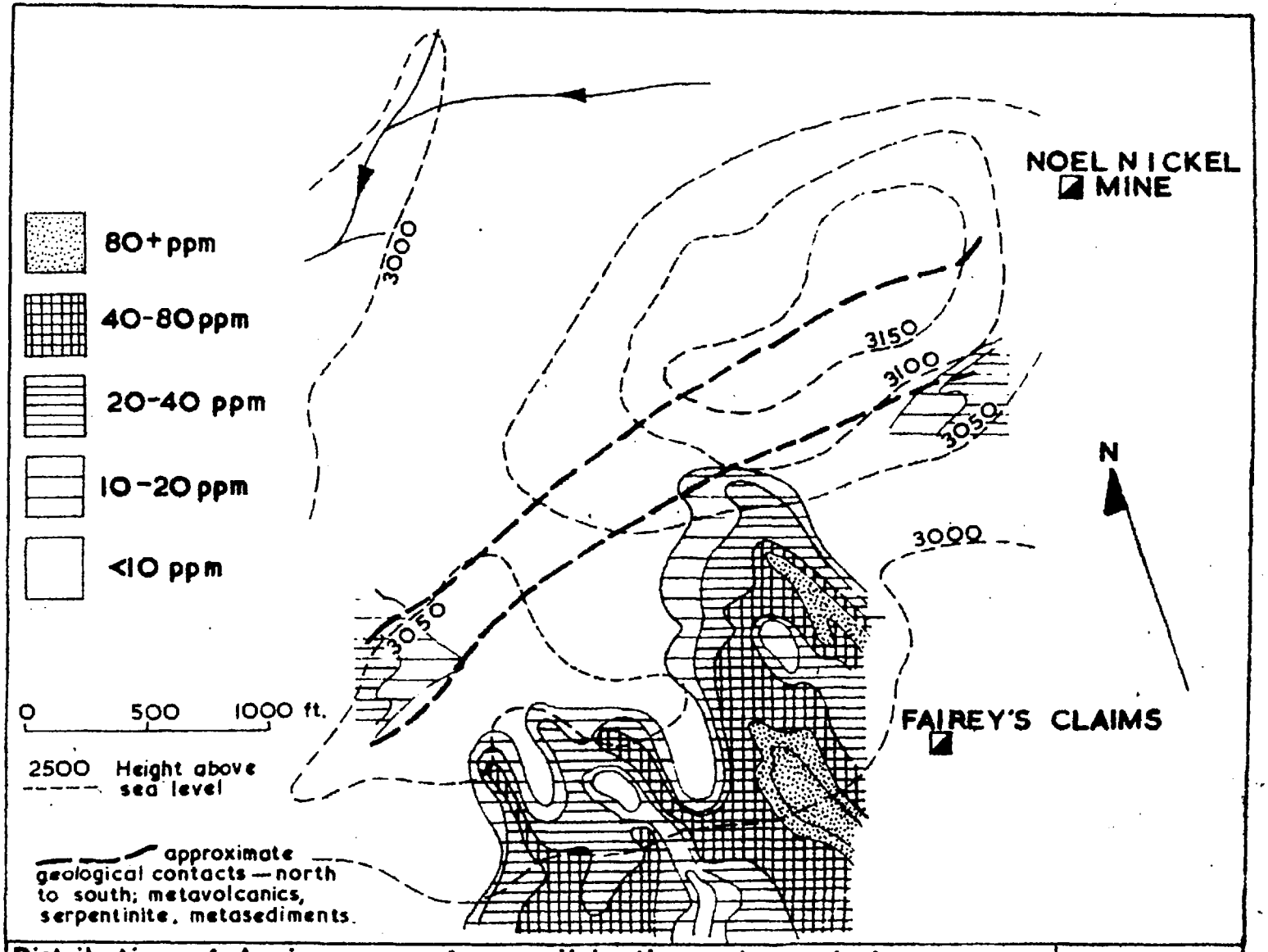
GEOCHEMISTRY : R.S.T.E. Ltd.

mine have been analysed for As. The As content of the soil over barren serpentinite, metavolcanics and metasediments is very low (less than 5 ppm). In contrast several hundred ppm of As is present in soil overlying probable mineralized fissures (Figure 70).

The soil containing anomalous amounts of As is that which also contains anomalous amounts of Ni. Like Ni, anomalous arsenic values form a reticulate pattern, the linear trends of which line up very well with the directions of the two known fault systems (NNE/NNW and WSW) which have been mapped in the area and with which the mineralization is associated. The width of the anomaly is greater than that of the Ni anomaly.

Nickel arsenides and sulph-arsenides also occur in the mineralization in the Exclusive Prospecting Area No. 85. In mineralized serpentinite 30 ft. below surface ~~over~~ the ~~main~~ mineralized zone at Maritzani there is 2600 ppm As while 400 ft. away downslope there is less than 2 ppm As in serpentinite at the same depth below surface. In the gossan outcrop at Perseverance the As content is 25 ppm compared with an As content of 2 ppm in the weathered bedrock 600 ft. uphill to the east.

The distribution of As in rock and weathered rock 15 ft. below surface was determined along one line



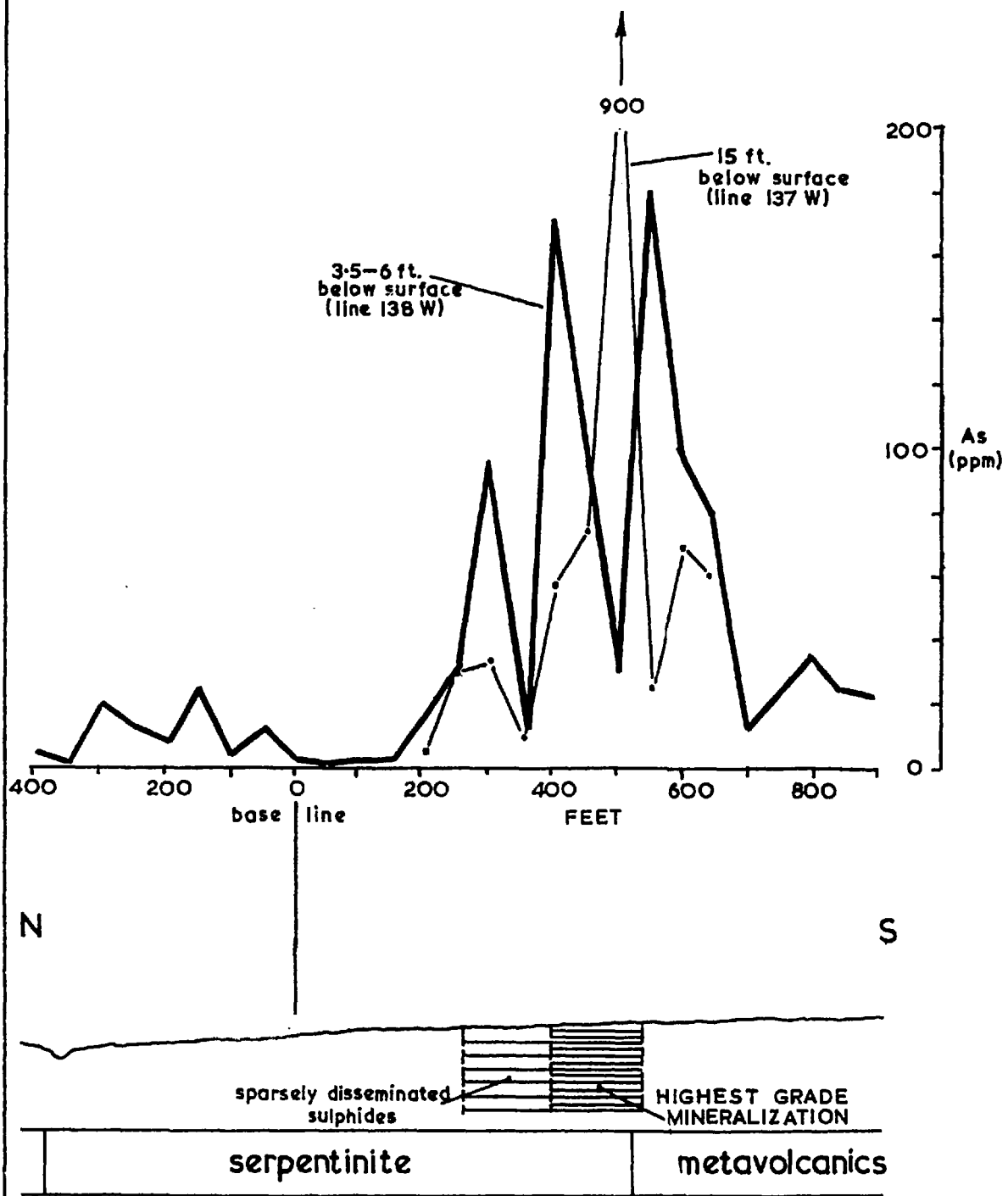
Distribution of As in near-surface soil in the environs of the NOEL Nickel mine.

of wagon drill holes at Maritzani. Over the main mineralization the As content is as high as 900 ppm but only 150 ft. away, still within the zone of sparsely disseminated sulphides, it decreases to 10 ppm (Figure 71). In barren metavolcanics upslope the As content varies between 25 and 70 ppm and if the upper limit of normal background fluctuation is taken as 70 ppm then the maximum contrast is thirteen-fold.

In weathered bedrock 3½-6 ft. below surface at the base of eleven pits over barren serpentinite (but downslope from mineralization) the ~~contrast~~ background varies between 2 and 25 ppm. The amount of As in weathered bedrock over the mineralized zone varies between 10 and 180 ppm. (Figure 71). The contrast appears to be about seven-fold but the distribution is very erratic in an anomalous zone 400 ft. in width.

The erratic distribution of As in weathered bedrock may be the result of a patchy primary dispersion. Alternatively it may reflect irregular weathering and leaching. There is evidence to suggest that As is being removed from the environment since a maximum of 2600 ppm As at 30 ft. reduces to 900 ppm at 15 ft. and to 180 ppm at 3½ ft. below surface although the variation could also be explained by a patchy primary distribution.

This preliminary investigation was not taken



Distribution of As in weathered bedrock at Maritzani.

any further. There is a need for a more detailed investigation of the primary distribution of the arsenical minerals and the secondary dispersion patterns since there is a suggestion in these preliminary results that associated As may help in differentiating sulphide and silicate Ni.

D. Antimony.

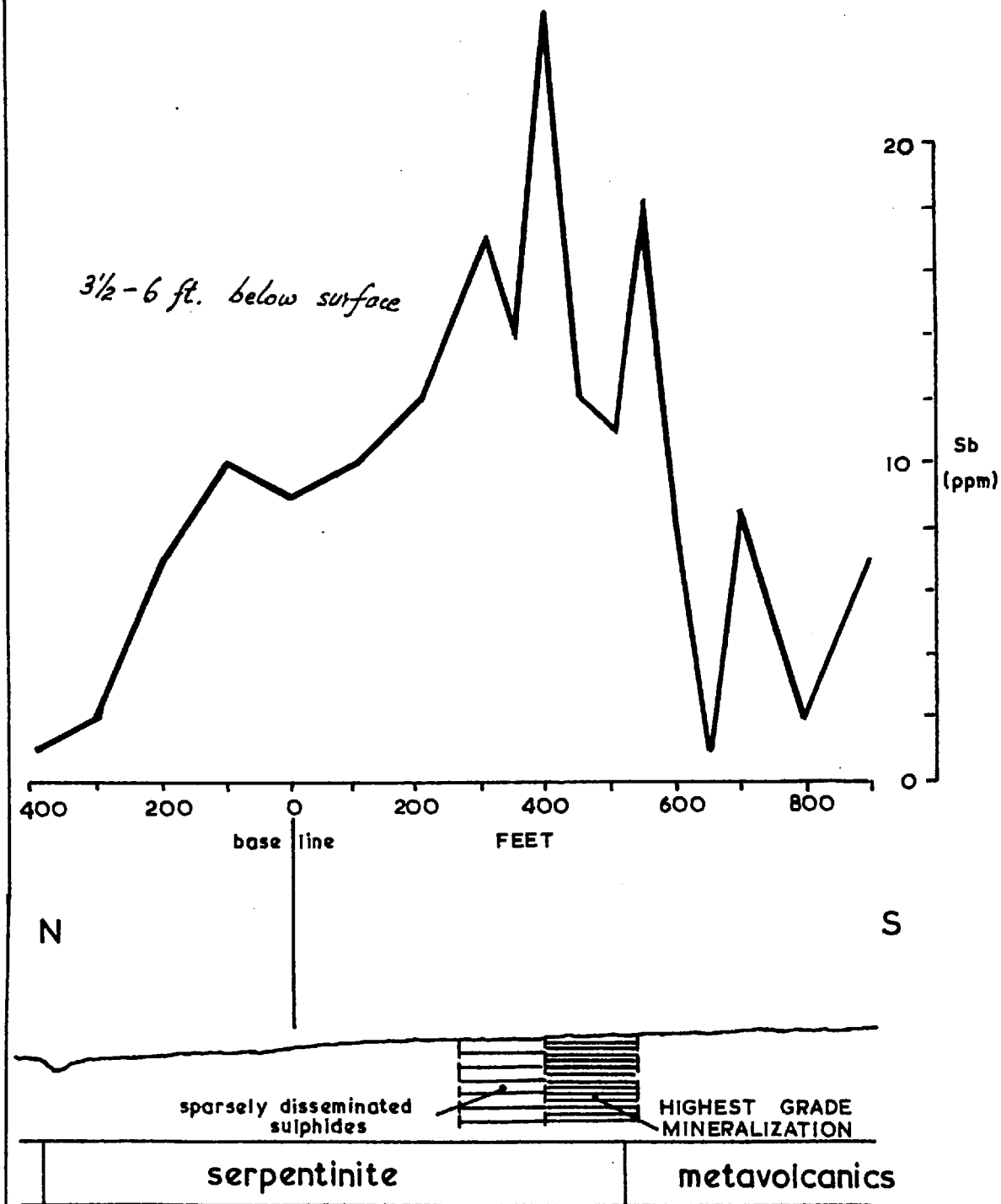
The Rhodesian schist belts contain gold-arsenic-antimony mineralizations. Since arsenic is associated with three known nickel mineralizations within rocks of the early Pre-Cambrian schist belts analyses were made to find out whether antimony was similarly associated. The results of the preliminary survey are given in Table 33.

At Perseverance the antimony content ranges between 1 and 6 ppm. A maximum of 3 ppm antimony was detected in soil over barren metavolcanics compared with a maximum of 6 ppm in soil over the gossan. The contrast between mineralized and non mineralized materials is therefore two-fold. At Maritzani the ~~proportion~~ range of antimony is higher (8 - 35 ppm). Mineralized weathered serpentinite contains 35 ppm, non mineralized

weathered serpentinite 13 ppm, a contrast just less than three-fold. It is interesting to note that the tenor of antimony (as far as can be ascertained from the limited data) is, like As, greater at Maritzani than Perseverance. In serpentinite at Darwendale and in weathered serpentinite and soil over serpentinite at Darwendale and Dalmainy Farm there is less than 1 ppm antimony. At the Empress prospect in soil over mineralized amphibolite and barren metavolcanics and in weathered mineralized amphibolite and non mineralized greenstones there is less than 1 ppm antimony.

The distribution of antimony was investigated a little further at Maritzani where the greatest difference between mineralized and barren serpentinite in terms of the antimony content was attained. The contrast between barren and mineralized serpentinite of two to three-fold was confirmed. There appears to be more antimony in serpentinite than in metavolcanics as adjudged by the antimony content of weathered bedrock $3\frac{1}{2}$ - 6 feet below surface (Figure 72).

Antimony, associated with the nickel - copper mineralization only at Maritzani (where the contrast is barely larger than the Ni contrast) appears to have no special general association with the mineralizations of the study areas.



Antimony in weathered bedrock at Maritzani.

Table 33. The antimony and selenium content of selected samples.

Sample No.	Study area	Material	Sb (ppm)	Se (ppm)
8002	Perseverance	gossan	1	17.0
3875	do	do	3	9.0
957	do	weathered metavolcanics	1	0.2
975	do	weathered serpentinite	6	0.1-
3888	do	soil over metavolcanics	6	3.5
963	do	do	1-	0.1-
956	do	do	3	0.5
974	do	soil over serpentinite	2	0.1-
983	do	do	1-	0.2
8003	Maritzani	massive sulphides		16.0
2214	do	weathered serpentinite over ore	35	0.5
2323	do	weathered serpentinite	13	0.1-
1870	do	weathered metavolcanics	8	0.2
4041	do	rotten serpentinite over ore	23	0.7
4037	do	soil over mineralization	23	0.5
8004	Darwendale	serpentinite	1-	0.1-
1056	do	weathered serpentinite	1-	0.1
1053	do	soil over serpentinite	1-	0.1-
5403	Dalmainy Farm	weathered serpentinite	1-	1.0
5401	do	soil over serpentinite	1-	0.8
4829	Empress	weathered greenstones	1-	
4827	do	soil over greenstones	1-	
4875	do	weathered mineralized amphibolite	1-	
4872	do	soil over mineralized amphibolite	1-	

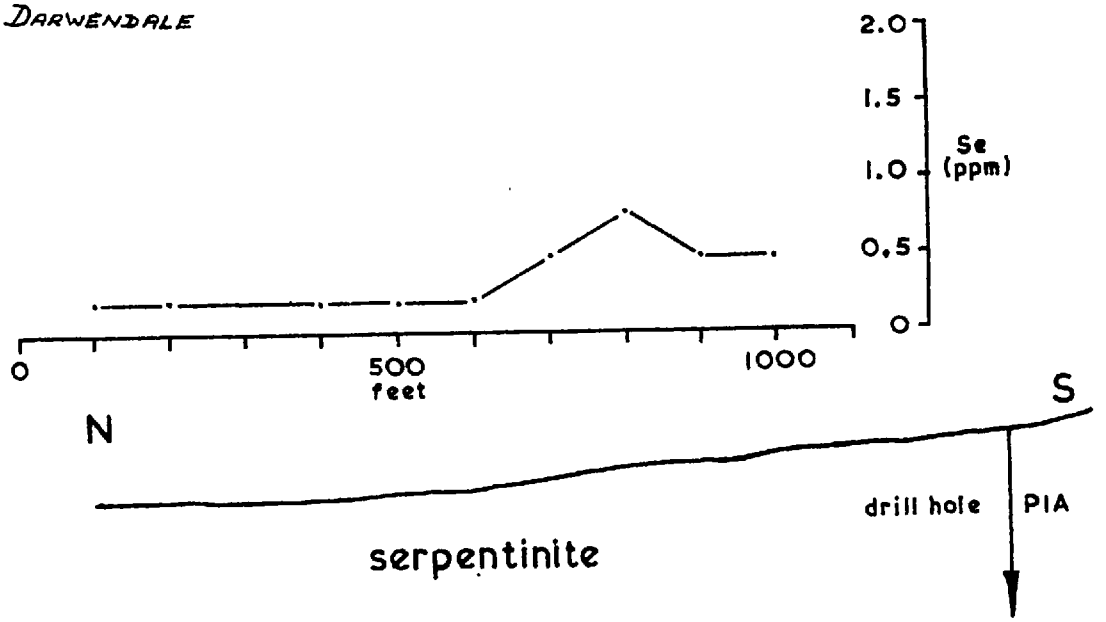
E. Selenium.

The association of sulphur and selenium is well known. The selenium content of gossans and residual soils has been used as a pathfinder for epigenetic sulphide minerals (Hawkes and Webb, 1962).

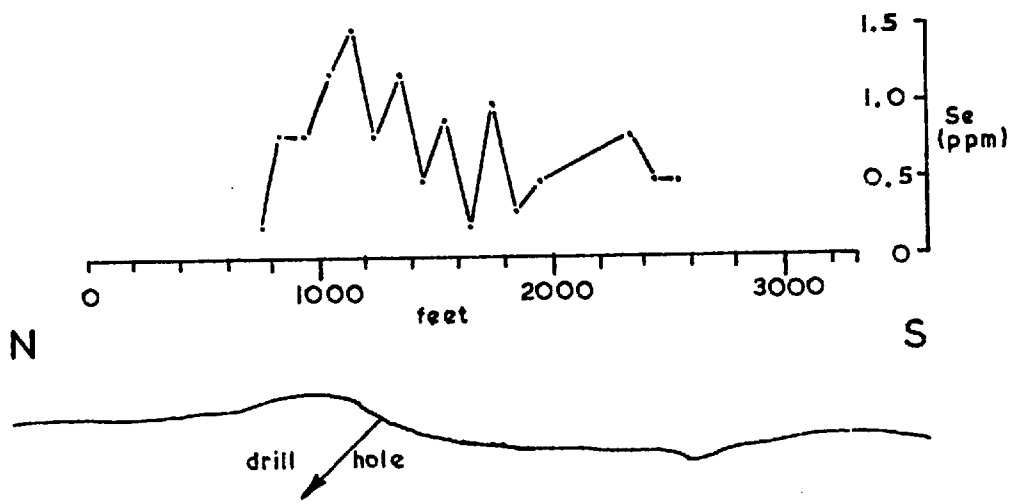
Mineralized serpentinite at Perseverance contains 4 ppm selenium. This is very considerably higher than the normal selenium content of rocks. The average for igneous rocks quoted by Rankama and Sahama (1950) is 0.09 ppm. The association of selenium with the sulphide mineralizations in the Perseverance and Maritzani areas has been confirmed by further analyses (Table 33).

The weathered serpentinite and overlying soil at Dalmainy Farm contain appreciably more selenium than similar barren materials at Perseverance and Maritzani. 10 analyses of soil over serpentinite from the Darwendale area had a mean selenium content of 0.35 ppm and in 8 analyses of soil over non mineralized serpentinite at Perseverance the mean selenium content was 0.30 ppm. The mean selenium content of soil over the Dalmainy Farm serpentinite is 0.90ppm (10 analyses) (Figure 73). This is considerably higher than in the other areas

DARWENDALE



DALMAINY FARM



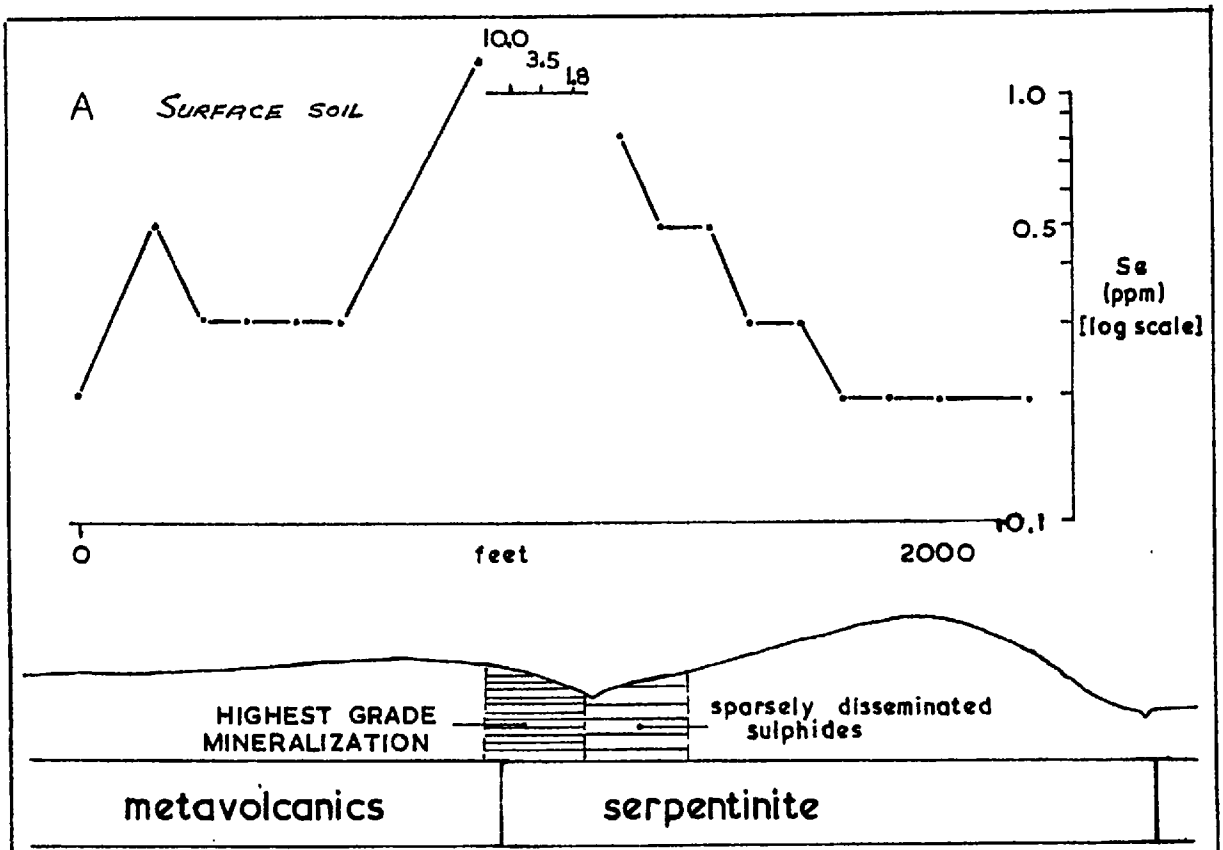
schist	serpentinite	granite

Selenium in soil at Darwendale and Dalmainy Farm. (3-12 in. below surface).

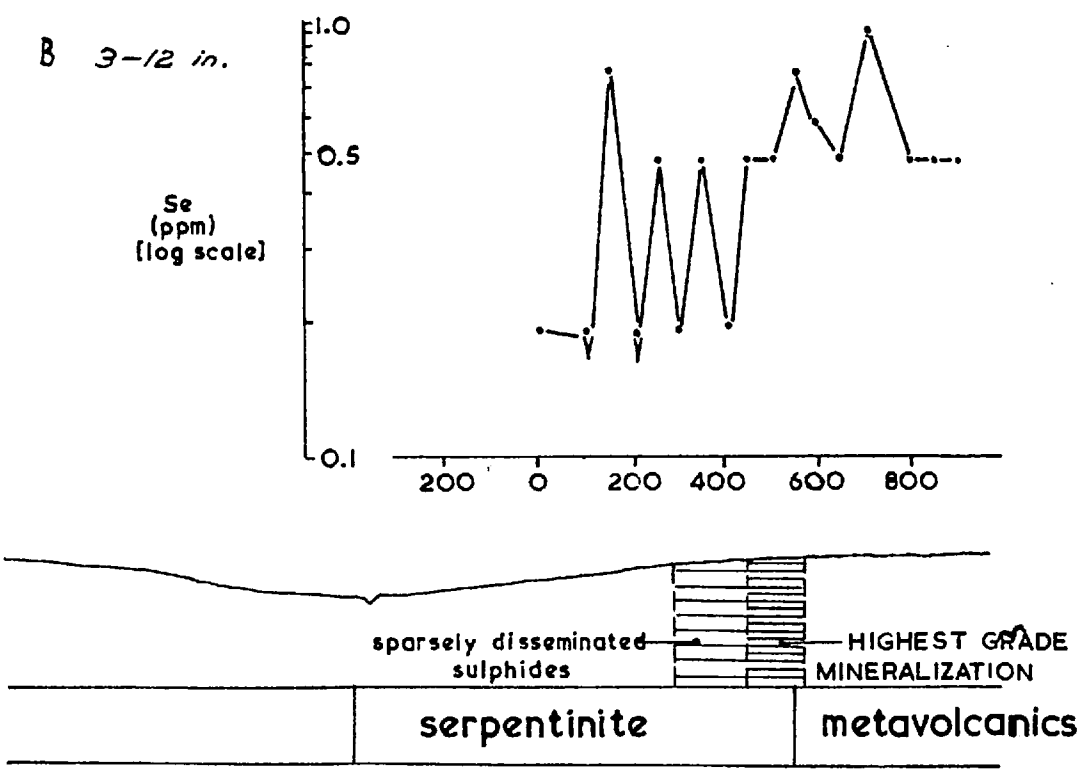
where sulphides are absent and is considered to reflect an abnormally high content in the Dalmainy Farm serpentinite. There is no evidence from other areas that the climate or soil conditions at Dalmainy Farm have resulted in an accumulation of selenium in the soil.

In both the Perseverance and Maritzani areas the background level over metavolcanics is higher than it is over serpentinite. Sparse disseminations of pyrite are known to occur in the metavolcanics and it is possible that selenium associated with the iron sulphide is responsible for the relatively high background over the metavolcanics.

Selenium is associated with the sulphide deposits of the Perseverance and Maritzani areas. Selenium must be moving out of the environment in some way since there is very much less of the element in soil over mineralization than there is in underlying bedrock. Nevertheless there is more selenium in the soil over mineralized serpentinite than over non mineralized serpentinite at Perseverance (Figure 74). Here, against an estimated upper limit of normal background fluctuation of 0.6 ppm the maximum contrast is seventeen-fold and the anomaly is more sharply defined than the Ni anomaly. On the other hand at Maritzani there is no recognisable anomaly. This is



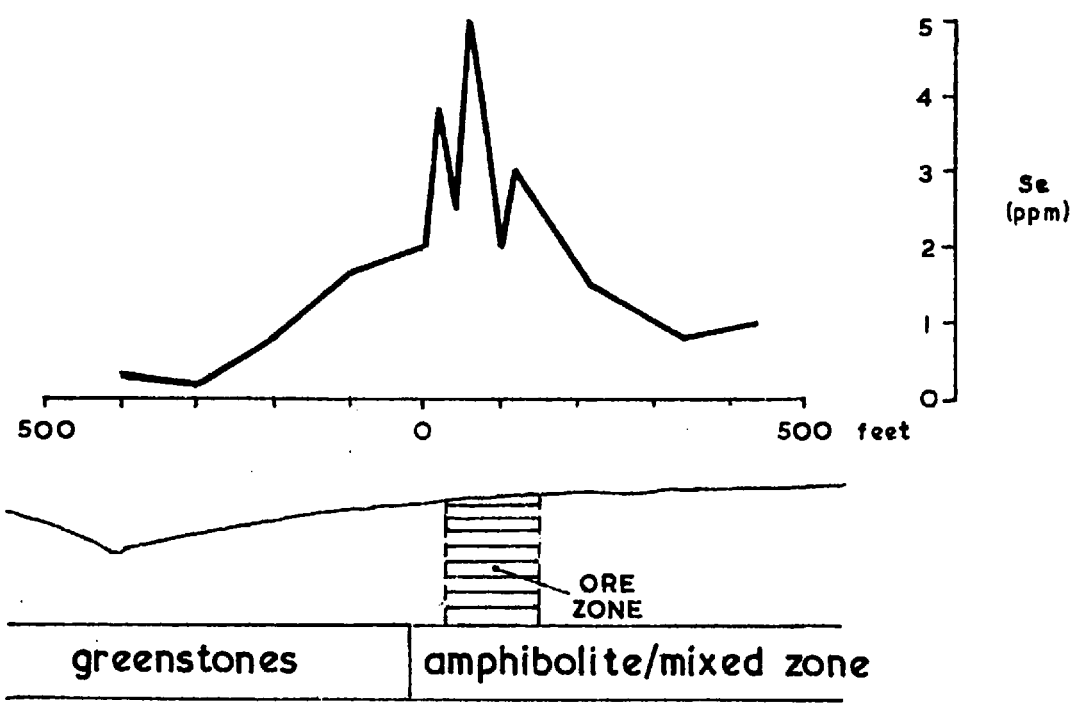
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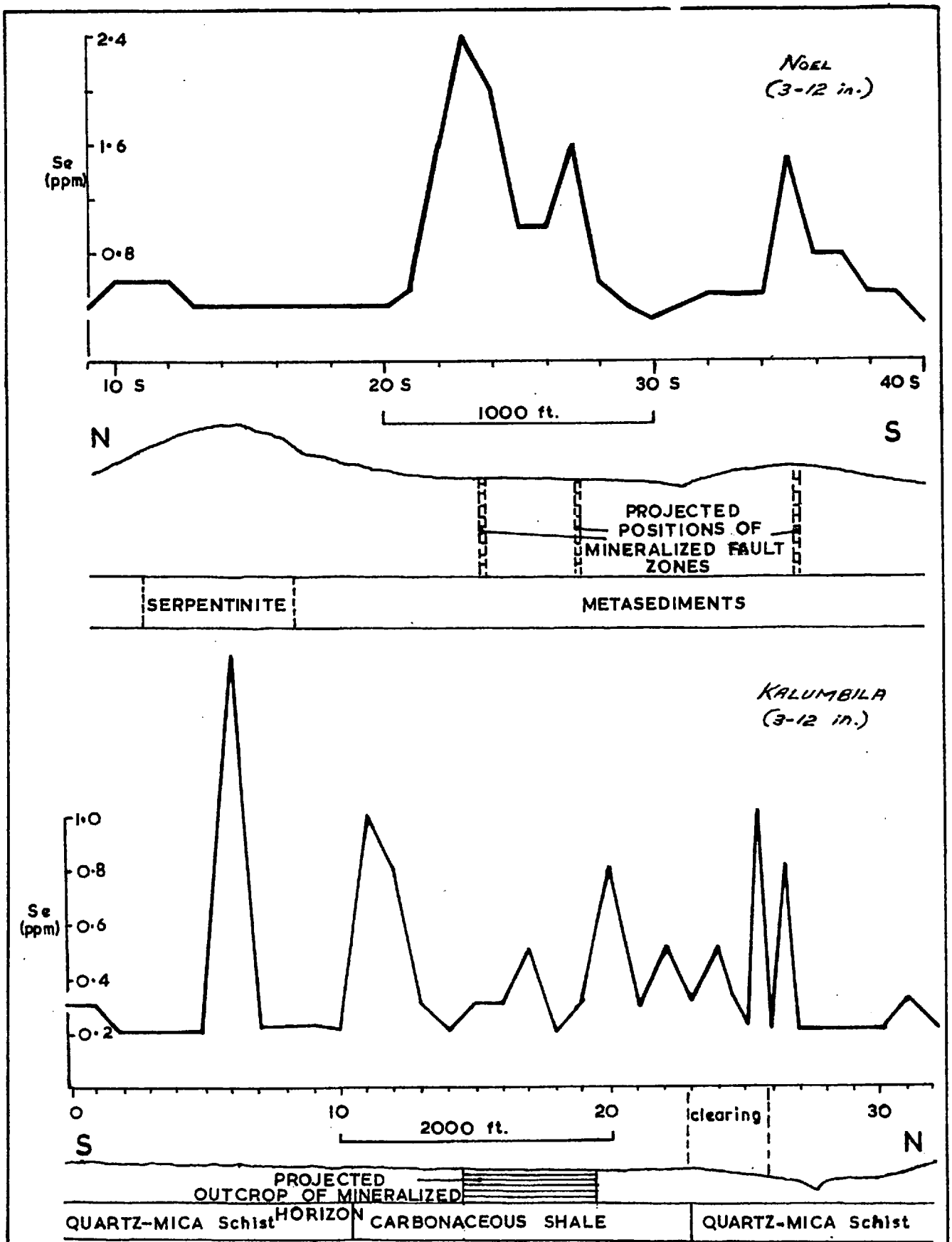
Distribution of selenium in soil at Perseverance (A) and at Maritzani (B).

surprising because a sample of massive sulphides contained 16 ppm selenium. It would seem that selenium is being leached to a greater extent at Maritzani than at Perseverance. This supposition is in accordance with the fact that soil formation and soil profile differentiation at Maritzani is more advanced than at Perseverance.

Weathered, mineralized amphibolite at the Empress prospect contains 5.5 ppm selenium. Fresh Carbonaceous shale containing coarse grains of the sulphide minerals and massive arsenide from the Noel contain 3.0 and 1.0 ppm selenium respectively. There is more selenium in the soil over mineralization at the Empress prospect than there is in soil over adjacent barren rocks (Figure 75). Similarly the soil in the environs of the Noel Nickel mine contains quite variable amounts of selenium. Soil containing anomalous amounts of Ni and As contain, as might be expected, the largest amounts of selenium (Figure 76). At Kalumbila the distribution of selenium is more complex and irregular (Figure 76). There is no apparent correlation between the selenium content of soil 3-12 in. below surface and the Ni and Cu content although two samples collected downslope of the copper clearing, on line 12, block 205, and which contain



Distribution of selenium in soil 8-12 in. below surface at the Empress prospect.



Distribution of selenium in soil in the environs of the Noel Nickel mine and at Kalumbila, (Line 12, 205).

anomalous amounts of Ni and Cu contain 1.0 and 0.8 ppm selenium respectively. These values are slightly above the overall mean of 0.4 ppm. Viewed broadly there is more selenium in the soil over carbonaceous shale than in the soil over quartz-mica schist. However, one sample collected over quartz-mica schist assayed 1.6 ppm selenium. The reason for this is not known.

The amount of selenium in weathered bedrock near-surface is generally greater than in overlying residual soil and in underlying weathered bedrock (Table 34).

The profile distribution of selenium was examined in two pits at the Empress prospect. In a soil profile over mineralization the selenium content increases with depth through the soil down to 12.0 ppm in a layer of rubble and weathered rock fragments 16 - 30 in. below surface. Deeper down, in fractured and weathered amphibolite showing a palimpsest equigranular texture, the selenium content is 6.5 to 7.0 ppm. In a profile over non mineralized greenstones the maximum selenium content is 27-39 in. below surface in fractured weathered metavolcanics in which the schistosity can be still clearly seen. The selenium content increases much more rapidly with depth in the barren profile than in that over mineralization and there is

Table 34. Selenium content of weathered bedrock and overlying residual soil, Perseverance.

Distance from Gossan (ft.)	(1)	(2)	Selenium content (ppm)		
			Bedrock (2-10ft.)	Bedrock (½-2ft.)	Soil (0-6 in.)
1100 W	L	M	–	0·2	0·2
500	L	M	–	1·9	0·3
400	L	M	–	2·0	0·3
100	E	M	1·2	1·2	1·2
50	E	M	9·0	–	10·0
0	E	S	1·5	9·0 – 16·0	1·2
100	E	S	0·4	2·5	1·8
200	W	S	0·4	1·0	0·8
300	W	S	–	1·0	0·5
400	W	S	–	1·2	0·5
500	W	S	–	1·3	0·3
600	W	S	–	0·3	0·3
800 E	E	S	–	0·8	0·2

(1) Slope down to (E = East, W = West, L = Level)

(2) Rock type (S = Serpentinite, M = Metavolcanics)

no evidence of any decrease in the selenium content with depth into the bedrock in the former profile. Accordingly the maximum contrast in the selenium content of the two profiles is in the upper horizons (Tables 35 and 36). This is consistant with the results obtained at Perseverance.

These introductory studies have shown that selenium is associated with all the nickel mineralizations that have been the subject of the investigation described in this thesis in amounts greater than the average in rocks. There is less selenium in the soil than in

Table 35. Typical profile through the soil overlying mineralized amphibolite at the Empress prospect showing the distribution of selenium.

Sample No.	Depth (in.)	Description	Se content (ppm)
4871	0-3	Brown-ochre clay to grit, hard and lumpy.	3.5
4872	3-16	Brown-ochre clay to gravel, some gravel quartz rubble and irregularly rounded ferruginous nodules.	5.5
4873	16-30	do; including fragments of weathered amphibolite.	12.0
4874	30-48	Rotten amphibolite	6.5
4875	48-64	Weathered amphibolite showing palimpest equigranular texture.	7.0

weathered rock but sufficient to enable soil containing

Table 36. Typical profile through the soil overlying non mineralized metavolcanics at the Empress prospect showing the distribution of selenium.

Sample No.	Depth (in.)	Description	Se content (ppm)
4830	0-3	Brown clay to fine sand, dry and friable.	0.2
4831	3-15	Brown sandy clay dry and friable as matrix to greenstone fragments and quartz rubble to small pebble size.	0.2
4832	15-27	do	0.2
4833	27-39	Variegated weathered, fractured greenstones with schistosity clearly evident.	0.5

anomalous quantities of ore metals (Ni and Cu) to be distinguished from background soil in the Perseverance, Empress and Noel study areas. No selenium soil anomaly was detected at Maritzani or Kalumbila. There is need for further research.

F. Mercury.

During the course of investigations selected samples were analysed for mercury to determine whether this element is associated with the nickel sulphide

Table 37. The mercury content of selected samples collected in Rhodesia and Zambia.

Sample No.	Study area	Material	Hg content (ppb) (1)	(2)	(3)	Mean
8002	Perseverance	Gossan	175	220	180	192
957	do	weathered metavolcanic	70	120	70	87
975	do	weathered serpentinite	38	70	60	56
3888	do	soil over gossan	248	340	240	276
963	do	soil over metavolcanics	90	120	60	90
956	do	do	185	120	120	145
974	do	soil over serpentinite	100	90	70	87
983	do	do	170	140	120	144
8003	Maritzani	sulphide ore	(i100)	160	180	170
2214	do	weathered serpentinite over mineralization	235	240	180	218
2323	do	weathered serpentinite	138	120	120	126
1870	do	weathered metavolcanics	95	120	100	105
4041	do	rotten serpentinite over ore	95	120	100	105
4037	do	soil over mineralization	120	140	120	127
3833	do	soil over serpentinite		70	90	80
8004	Darwendale	serpentinite	70	60	60	63
1056	do	weathered serpentinite	200	140	50	130
1053	do	soil over serpentinite	1350	750	1000	1033

(Continued overleaf)

Table 37. (Continued)

Sample No.	Study area	Material	Hg content (ppb) (1)	(2)	(3)	Mean
5403	Dalmainy Farm	weathered serpentinite	30	30	50	37
5401	do	soil over serpentinite	(5-)	90	60	75
5414	do	do		60	90	75
4879	Empress	weathered mineralized amphibolite		60	70	65
4877	do	soil over mineralization		120	120	120
4884	do	soil over mixed zone		60	60	60
4920	do	soil over diorite		30	60	45
4827	do	soil over greenstones		30	90	60
6051	Noel	arsenide ore		50	120	85
1W36S	do	soil over mineralization		3000	3000	3000
4W35S	do	soil over metasediments		70	140	105
2935	Kalumbila	sulphide ore		60	90	75
2972	do	soil in copper clearing		60	100	80
2988	do	soil over projected outcrop of mineralization		30	136	83

(1), (2) and (3) replicate analyses.

deposits. The results of the analyses made using the Mercury Vapour Meter (Chapter 2) are presented in Tables 37 and 38.

In the Perseverance, Maritzani, Empress and Noel areas the mercury content of samples known to contain anomalous amounts of ore metals is greater than that of corresponding background materials. The degree of contrast is similar to the Ni contrast.

In all areas except Maritzani the mercury content of the soils is greater than that of the underlying bedrock. The mercury content in the Darwendale area is unusually high. No explanation can be given for this.

Table 38. Summary of the data of Table 37.

Area	Range (ppb)	Contrast between anomalous and background samples (Ratio anomalous: background)	
		In weathered rock	In Soils
Perseverance	38-340	2.7	2.4
Maritzani	70-240	1.9	1.6
Darwendale	50-1350		
Dalmainy Farm	30-90		
Empress	30-120		2.2
Noel	50-3000		29.0
Kalumbila	30-136		

Part IV. NICKEL IN VEGETATION.

Plants obtain their nutrients from the soil and soil water. Ions that are either dissolved in the soil water or held by the soil particles in an exchangeable form are 'available' for uptake by the plants. Nutrients (and toxicants) can be absorbed by the root tips either directly from solution or from the soil particles by complex exchange reactions. The ions subsequently enter the circulatory system of the plants and may stimulate or hinder growth. Elements may be required for a specific function in plant metabolism and are often concentrated in the growing points (buds, shoots). In many species a given element is often present in the leaves in amounts greater than it is in the twigs or bark. However, the content in the leaves is also generally more erratic than that of the bark and twigs. Plants of a given species may react differently to different ions and plants of different species can differ in their behaviour towards a given ion.

Despite the many variables the amount of metal taken up by a plant will be to some extent dependent on the amount of 'available' metal in the soil. This has been demonstrated for nickel by Mitchell (1944-45)

working on the soils of north east Scotland. He has related soil infertility to readily soluble nickel (nickel soluble in 0.5N acetic acid) rather than to the total nickel content of the soil. It is suggested that nickel 'available' for uptake by plants may be identified with the concentration (amount) of nickel in solution and exNi. It has been shown that exNi in the deeper parts of the weathered profile is greater over mineralization that it is over non mineralized rocks in a given area. Plant roots are not limited to the near-surface environment. Many plant root systems do in fact penetrate to some depth. It seems possible, therefore, that the plants may play an important role in the dispersion of nickel from sulphide and silicate minerals. This possibility was investigated by determining the nickel content of plants growing over mineralized and non mineralized serpentinite as well as those over other lithological units, again both barren and mineralized.

While copper, in small amount, is regarded as an essential plant nutrient, nickel is not. However, nickel may well be essential to plant growth in amounts below the limit of detection of present analytical methods. Copper available to plants in large concen-

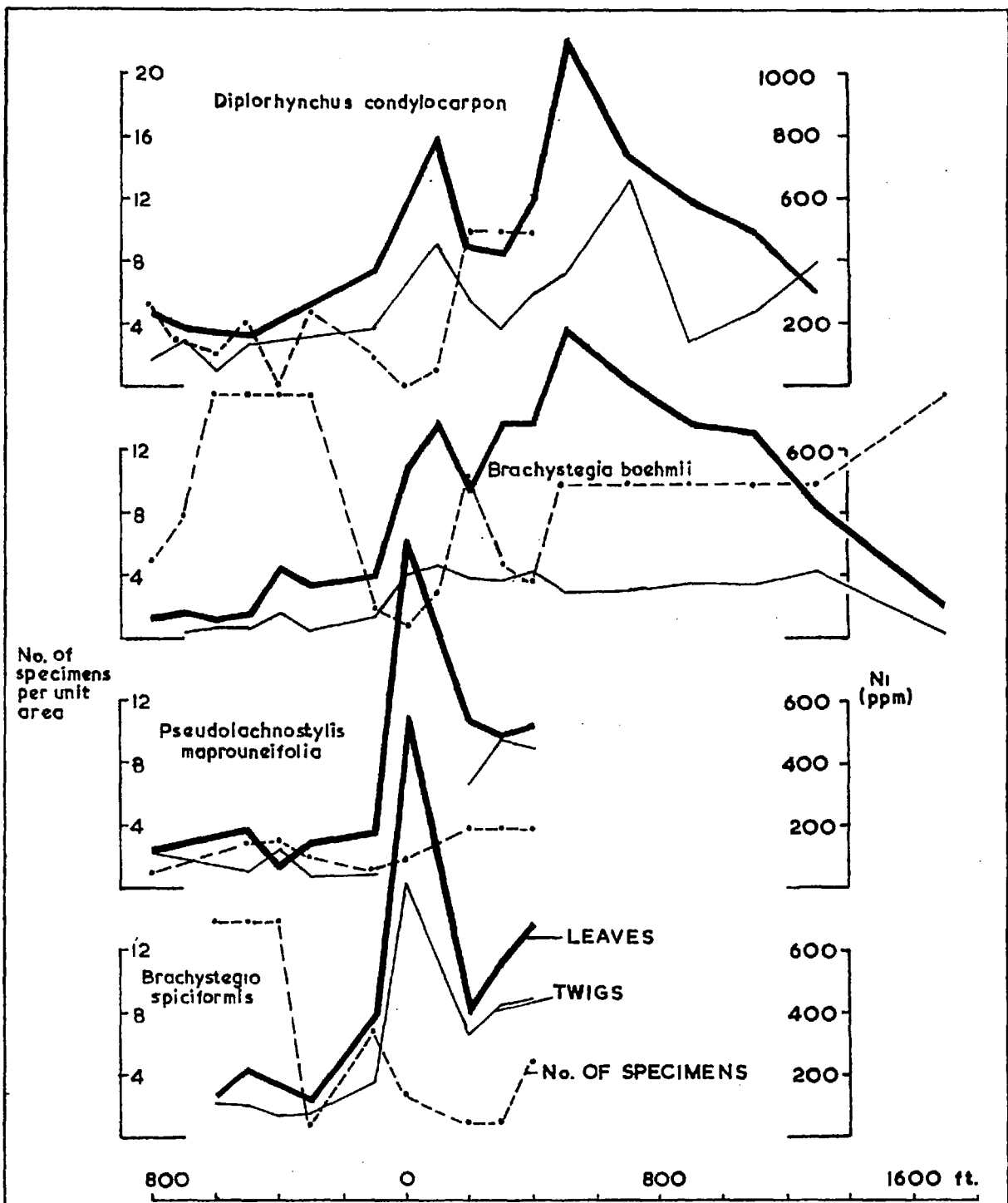
trations is toxic. Clearings, like the one in block 205 at Kalumbila occur over copper mineralization elsewhere in Zambia and are attributed to the poisoning of the young plants in the copper rich soil. Such clearings are called 'copper clearings'.

Nickel has been found present in plants in large amounts. Some plants growing over serpentinite in Rhodesia contain more than 1000 ppm nickel in ash of leaves and twigs. The plants are, however, often visibly diseased. Hunter and Vergnano (1952) have described oat plants with longitudinal stripes of white necrotic tissue on their leaves and have related this deformity to the high concentrations of nickel in the soil. In Rhodesia serpentinite soils are known to be infertile. Poor yeilds from maize crops and stunted and otherwise deformed plants growing on serpentinite soil at Dalmainy Farm have been attributed to nickel toxicity (D.B. Mackay, Pers. Comm.).

The vegetal cover has sometimes been observed to be thinner over serpentinite than it is over adjacent rocks. As a part of the vegetation sampling technique details of the sizes and physical characteristics of the plants sampled were recorded and variations in population density noted. It was found, for example, that the

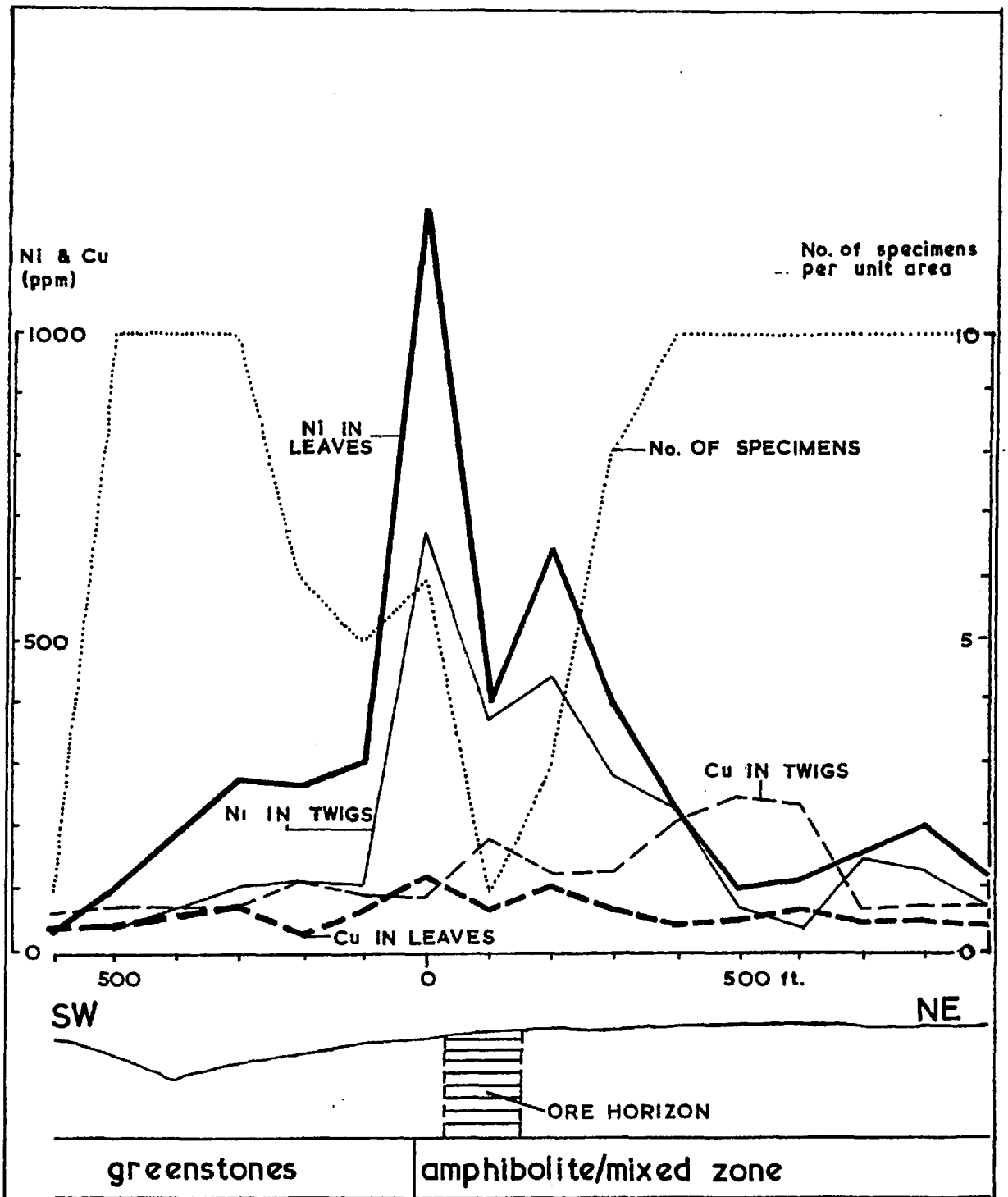
number of specimens of the genus Brachystegia per unit area at the Perseverance prospect was lower over serpentinite than over other rocks (Figure 77). The density of population of specimens of this genus is, furthermore, still less over the sulphide mineralization but it is possible that this has resulted from tree felling during prospecting operations. A similar variation in population density has been observed in the case of several species (notably Combretum apiculatum) at the Empress prospect. The number of plants of a given species per unit area is again lower over mineralization than over the surrounding barren rocks (Figure 78). Density of population appears inversely proportionate to the exchangeable nickel content of the soil. These observations appertaining to the indigenous flora confirm the conclusions obtained from a study of cultivated crop plants (Hunter and Vergnano (1952), Mitchell (1944,1945)), namely that nickel is not an essential plant nutrient and does, in fact, have an overall toxic effect on the plants when present within the limits detected (see below).

Studies have been confined to four areas, Perseverance, Maritzani, Empress and Kalumbila.



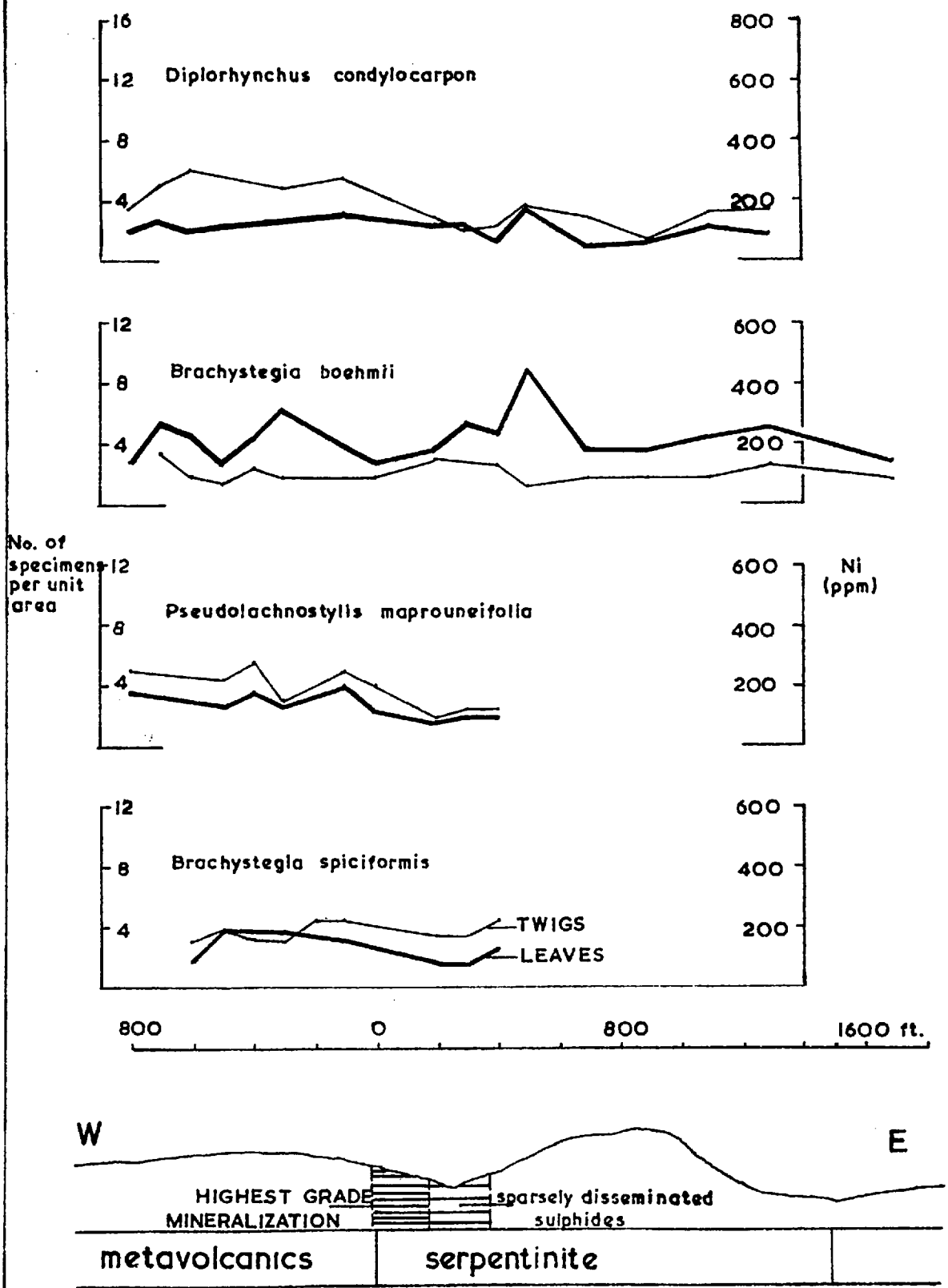
Distribution of Ni in vegetation at Perseverance.

77



Distribution of Ni and Cu in Combretum apiculatum across the Empress mineralization.

78



Cu in vegetation at Perseverance.

79

A. Perseverance Area.

Investigations were carried out in this area so that the effect of sulphide mineralization in serpentinite on the uptake of nickel by plants could be examined. Two species were sampled at 100 ft. intervals along a traverse extending from metavolcanics, across mineralization and serpentinite to more metavolcanics. Two further species were sampled along a more limited length of traverse centered on the suboutcropping mineralization (Table 39 and Figures 77 and 79).

Species of the genus Brachystegia are in greater abundance over metavolcanics than over serpentinite and are particularly rare over the mineralized zone. Diplorhynchus condylocarpon and Pseudolachnostylis maprouneifolia show less of a contrast between serpentinite and metavolcanics and what contrast there is, is in the opposite direction but these species are similarly very sparsely distributed over the ore suboutcrop. Possible interference in the natural distribution following tree felling during prospecting operations has been mentioned above. However, since all species are similarly affected and since the amount of felling has, as far as is known, been limited the distribution is considered to be natural.

All four species appear, as far as can be judged from their nickel content, to behave similarly

Table 39. Details of plants sampled in the Perseverance area.

Vernacular name (Chishona)	Generic and specific name	Parts of species sampled
Mufuti	Brachystegia boehmii	Second leaflet on twig and second year twigs.
Msasa	Brachystegia spiciformis	Second pair of leaves and second year twigs.
Mtowa	Diplorhynchus condylocarpon	Second pair of leaves and second year twigs.
Musonzoa	Pseudolachnostylis maprouneifolia	Second leaf on twig and second year twigs.

towards the metal. The amount of nickel in the ash of leaves and twigs is greater over barren serpentinite than over barren metavolcanics reaching a maximum (in Brachystegia boehmii and Diplorhynchus c.) on the upper slopes of the hill. The reason for this is not clear. One possible explanation is that because of their relatively exposed position the rate of transpiration in the plants on the upper slopes is high. To compensate for this loss of moisture the plants might take up an above average volume of water if it is available and the amount of nickel in the plants might be expected to increase proportionately. Alternatively it may be that the plants on the upper north western facing slopes receive more

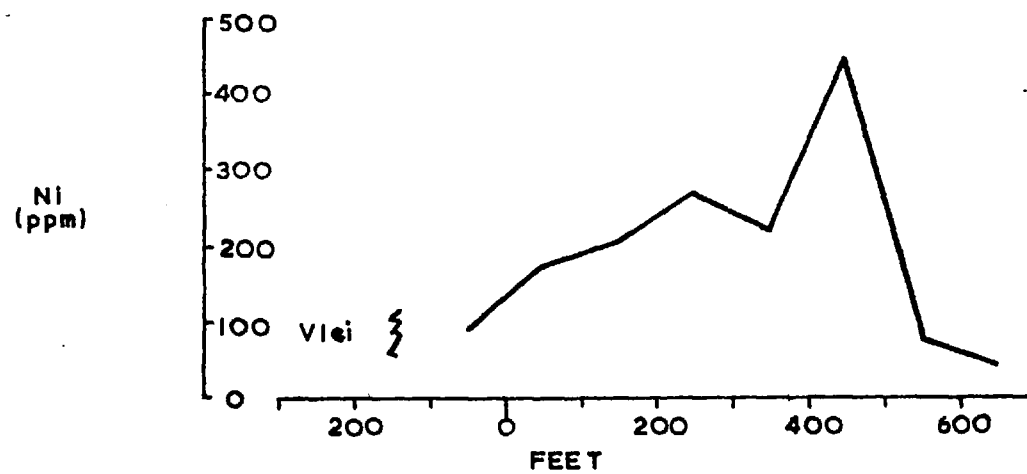
sunlight than those elsewhere and that this factor is influencing the uptake of nickel.

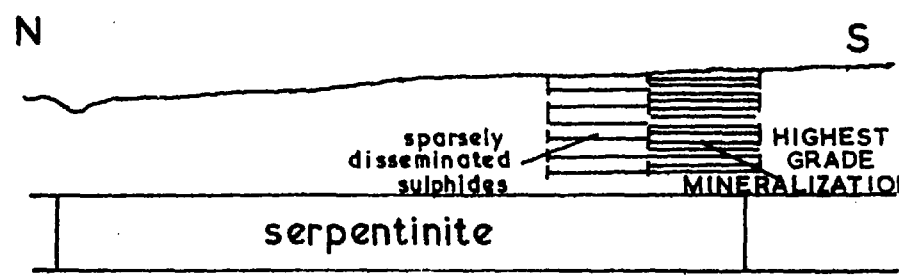
In all species the leaves and twigs of the plants growing directly above the best mineralization contain more nickel than those immediately adjacent. The maximum nickel content in a given plant species growing over the mineralization is, however, less than the maximum nickel content of plants of the same species higher up the hill over non mineralized serpentinite.

Only isolated specimens of the species sampled at Perseverance are to be found at Maritzani where the bush is sparse. Plants of one species (Bauhinia punctata) were sampled along one line of traverse crossing the serpentinite and mineralization suboutcropping on the gentle slope to the vlei. Here the nickel content of the leaves of plants growing over mineralization is greater than that of leaves of plants growing over barren serpentinite albeit the barren rocks are downslope of the mineralization (Figure 80).

The leaves and twigs present the same distribution pattern although the level of nickel content in the leaves is plainly greater than the tenor nickel in twigs.

There is a singular lack of variation in the copper content of the ash of leaves and twigs of plants





Ni content of Bauhinia punctata across the Maritzani mineralization.

growing in the different parts of the Perseverance area. An indication of a difference in behaviour between nickel and copper in the biochemical cycle lies in the observation that there is more copper in twig ash than leaf ash in all but one of the Diplorhynchus condylocarpon and all Pseudolachnostylis maprouneifolia plants sampled. Six out of nine specimens of Brachystegia spiciformis contained more copper than nickel but non of the Brachystegia boehmii specimens did (Figures 77+79).

B. Empress prospect.

Although six species were sampled in the area only Combretum apiculatum was found present at all points along the line of traverse selected. Since all four species examined at Perseverance were found to show similar patterns it was decided to confine analyses at the Empress prospect to a single species. Combretum apiculatum, occuring, as it does, throughout the area, was selected. Leaves and twigs were ashed and the ash analysed for nickel and copper.

Anomalous amounts of nickel were found in the ash of specimens growing in the vicinity of the ore suboutcrop where the density of population of the species

is well below average (Figure 78). As was the case at Perseverance the pattern of distribution of nickel is similar in both leaves and twigs but the level of nickel in the twigs is below that in the leaves.

There is only fractionally more copper in leaf ash over the mineralization contrasted with the copper content away from mineralization. Twigs of maximum copper content are those off plants growing over mixed zone rocks upslope from mineralization. The reason for this is not known. Copper, dissimilarly to nickel, is more abundant in the twigs than the leaves.

C. Kalumbila area.

At Kalumbila, three species growing along a line of traverse crossing the projected suboutcrop of the best copper mineralization, the copper clearing and the area of soils containing anomalous amounts of Ni and Cu were collected. The aim was to learn something of the distribution of nickel in vegetation under climatic and geomorphologic conditions radically different to those prevailing at Perseverance and Empress. Brachystegia boehmii and Jubelnardia paniculata commonly reach heights of several tens of feet and consequently sampling of leaves and twigs is impractical. Dipplorrynchus mossambicensis, however, is a plant of lesser height and the leaves and twigs are more readily accessible and were, accordingly, sampled (Table 40). A preliminary survey revealed little variation in the density of spacing of the trees in the woodland. Variations in population density of the individual species was not determined in this area.

The nickel content of the bark of Brachystegia boehmii and Jubelnardia paniculata showed only little variation along the line of traverse but the maximum values were recorded in the area of the suboutcropping

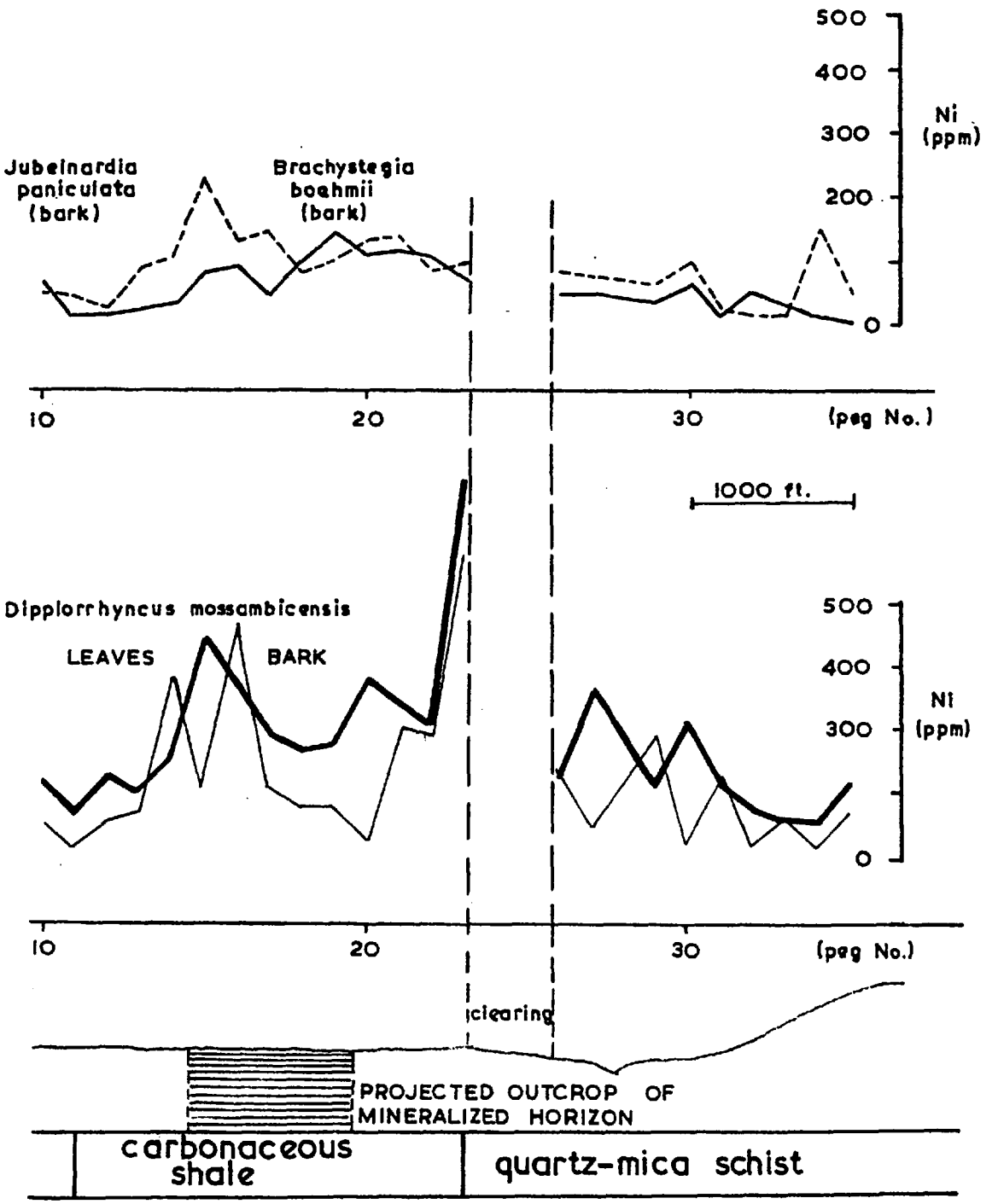
carbonaceous shale at pegs 15 and 19 respectively (Figure 81). The amount of nickel in the bark of Dipplorrynchus mossambicensis is markedly greater than that of the taller species. Apart from a value of just over 500 ppm in plants growing at the edge of the copper clearing near peg 23 the values further upslope

Table 40. Details of plants sampled in the Kalumbila area.

Vernacular name (Bemba)	Generic and specific name	Parts of species sampled
Mwenge	Dipplorrynchus mossambicensis	Third pair ofleaves on twig and bark.
Musamba	Brachystegia boehmii	Bark.
Mutondo	Jubelnardia paniculata	Bark.

over the carbonaceous shale near pegs 14 and 16 are the highest recorded. Leaves, generally with a higher proportion of nickel than is the case with bark, of plants growing around the upslope edge of the copper clearing near peg 23 and over the projected subouterop of the mineralized horizon within the carbonaceous shale at site 15 contain greater amounts of nickel than do specimens at other sample sites.

KALUMBILA.



three

Variation in Ni content of ~~four~~ species of plants across the highest grade copper mineralization.

The uncertainty surrounding the geology in this study area has been discussed earlier. Doubt has been expressed about the precise nature of the anomalous concentrations of nickel and copper in the copper clearing and in the soils directly downslope. Whether they are due to a lens of suboutcropping mineralization or are the result of a lateral seepage where the laterite has been truncated by erosion must, for the present, remain unanswered. There is, however, good geological evidence to suggest that at least one band of mineralization might subouterop upslope of the clearing between pegs 14 and 19. Between these two last mentioned sites there is a partially indurated laterite sheet a few feet below surface. It is believed that some plant roots pentrate the laterite layer and take up moisture from the rotten bedrock below the laterite. The relatively large amounts of nickel in the ash of some plants growing in the area between pegs 14 and 19 suggests an abnormal concentration of available nickel below the laterite, possibly originating from suboutcropping mineralization. As mentioned earlier the soil above the laterite is very sandy, severely leached, and of acid reaction. It is conceivable that any nickel derived from the underlying suboutcropping mineralization by upward moving solutions, or any nickel that was

originally present, has been leached from the upper layers, thus accounting for the lack of Ni in anomalous amount in near-surface soil between pegs 14 and 19 (Figure 38).

Further downslope the nickel content of both vegetation and soil around the copper clearing reflects the presence of either a second band of subouteropping copper-nickel mineralization or a seepage anomaly from the subouteropping mineralization upslope. The Copper Flower (Becium homblei de Wild), known to grow in mineralized areas elsewhere in Zambia, has been observed in the clearing.

The copper content of the bark of Brachystegia boehmii and Jubelnardia paniculata showed even less variation in plants along the line of traverse than did the nickel content. In both species the plants growing on the borders of the clearing are the richest in copper. Copper in the ash of leaves of Dipplorrynchus mossambicensis, which is, on average, higher than the proportion of copper in the bark of plants of the same species, shows a similar pattern of variation to the copper content in the bark of the two taller species already mentioned. Copper content of bark of Dipplorrynchus mossambicensis does, however, vary to a much greater extent and follows

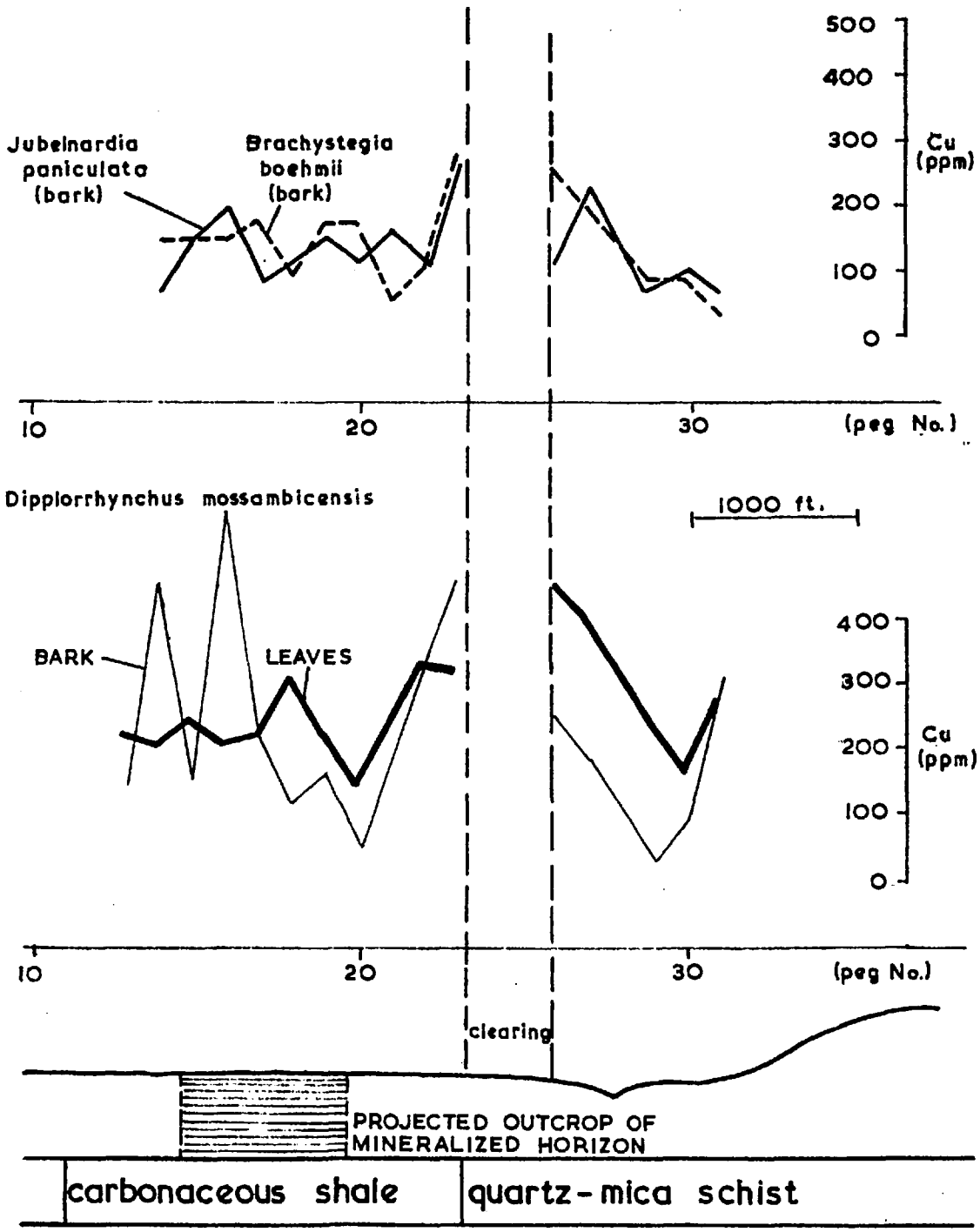
closely the pattern of distribution of nickel in the same material (Figure 82).

D. Summary of conclusions on the distribution of nickel in vegetation.

All species sampled appear to behave similarly towards nickel. Different species do not all react the same way towards copper. For example, Brachystegia boehmii at Perseverance contains more copper in the leaves than in the Bark while in other species growing in the area this difference is reversed.

In any given species leaf ash generally contains more nickel than does the ash of twigs or bark. All three parts of the plants, when analysed, reveal a similar nickel distribution pattern which is, however, a little better defined on the basis of nickel in leaves than in twigs or bark.

The amount of nickel taken up by plants is believed to be dependent on the amount of the metal available in the soil and soil moisture. In view of the high concentration of exchangeable nickelous ions in certain horizons overlying zones of oxidizing sulphides it had been postulated that the nickel content of the



Distribution of Cu in ~~four~~ three plant species across the highest grade copper mineralization; Kalumbila.

plants would be expected to vary accordingly. The data presented has substantiated this premise. The amount of nickel in plants growing over mineralization under a variety of climatic and geomorphologic conditions is anomalous compared to that of plants over adjacent non mineralized rocks.

The nickel content of plants growing over non mineralized serpentinite is greater than that over similarly barren but less basic rocks. The amount of copper in plant matter, at similar concentrations over the various rock types within a given study area, is (if at all) only fractionally higher over mineralization than over non mineralized rocks. It is possible that plants can regulate the entry of copper more readily than they can nickel. Over mineralization in Rhodesia copper has been successfully prevented from entering the plants and there is no anomaly. In part of the Kalumbila area the copper has gained access but proved lethal - hence the copper clearing. It appears as though plants generally have a greater tolerance towards nickel than towards copper when the metals are available in amounts very much in excess of the optimum nutritive requirements.

Chapter 5. DISCUSSION OF SECONDARY DISPERSION OF NICKEL.

Having presented the data it is important to consider the mechanisms whereby the distributions were formed. A discussion on the secondary dispersion of nickel based on published literature and viewed from a theoretical aspect is presented first. The main features of the secondary distribution of nickel in Rhodesia and Zambia will be explained in terms of the secondary dispersion mechanisms outlined. Where relevant, the discussion will, for comparison or contrast, include comments appertaining to copper or other associated elements.

PART I. THEORY OF SECONDARY DISPERSION

Secondary dispersion can conveniently be considered in three stages:-

(i) Mobilization during weathering,

(ii) Transportation and

(iii) Fixation.

Fixation is temporary and results in the distribution

patterns. The distribution of an element as determined by the analysis of natural materials portrays the dispersion process (a dynamic system unlikely to be at equilibrium, except perhaps very locally) as if it were 'frozen' at a given time (the time of sampling).

A. Weathering and mobilization.

Commonly sulphides have a greater susceptibility to weathering than silicates. Olivine, the most important silicate host to nickel (Chapter 3), is, according to Goldich (1938), one of the least stable of the rock forming silicates and, other things being equal, might be expected to be one of the first silicate minerals to decompose as weathering sets in. However, as a generalisation, the order of decreasing susceptibility of minerals to weathering is sulphides > carbonates> silicates> oxides. Olivine is, thus, usually relatively stable compared to nickel bearing sulphide minerals such as nickeliferous pyrrhotite, pentlandite or millerite. In the weathered bedrock at Maritzani and Perseverance palimpest olivine crystals have been observed but there is no fresh sulphide. The nature of the bonding in sulphides is generally different to

that in silicates as is the crystal structure. It is partially because of these differences that there is a difference in susceptibility to chemical attack between the two categories of minerals.

This difference in susceptibility to weathering could lead to a difference in the rate of dispersion of nickel from sulphides and silicates. Furthermore, it is possible that there are differences in the form of nickel in solution and in the form of nickel temporarily fixed, dependent on whether the metal has been derived from sulphide or silicate minerals.

1. Weathering of ore minerals.

In decomposition of sulphides and arsenides oxidation is the most important process. In general oxidation tends to transform metal sulphides and arsenides to oxygen salts and native metals. Simple sulphides are very slightly soluble in water at 18°C. Lindgren (1933) gives the following order of decreasing solubility:-

Mn, Fe, Ni, Cd, Zn, Cu, Pb, As, Ag, Bi, Hg.

He goes on to say that in 0.1N sulphuric acid pyrrhotite and chalcopyrite (among other sulphides) are

readily dissolved while pyrite is attacked to a lesser degree. He adds that decomposition or solution is often hastened in the presence of ferric sulphate. This is because the sulphide minerals decompose during the reduction of the ferric sulphate to ferrous sulphate. According to Stokes (1907) the action of ferric sulphate on pyrite proceeds as follows:-

$$Fe_2(SO_4)_3 + FeS_2 \longrightarrow 3FeSO_4 + 2S$$

$$6Fe_2(SO_4)_3 + 2S \longrightarrow 8H_2O + 12FeSO_4 + 8H_2SO_4$$

Similarly the action of ferric sulphate on pyrrhotite can be represented as:-

$$Fe_7S_8 + 6Fe_2(SO_4)_3 + H_2SO_4 \longrightarrow H_2S + 19FeSO_4 + 7S$$

(Grout, 1913).

Pyrite readily loses one atom of sulphur which is available to combine with oxygen and hydrogen (from the water) in the zone of oxidation to form sulphuric acid ($4S + 4H_2O \longrightarrow H_2SO_4 + 3H_2S$). This acid will accelerate the dissolution of the sulphide minerals especially after formation of ferric sulphate (above).

Nickel and copper released from the sulphides form oxygen salts (oxides and sulphates) but some of the metal is removed in solution. Selenium associated with the sulphides goes to form selenates and arsenic

of sulph-arsenides and arsenides alters to arsenates. The amounts of any particular element that will be removed in solution will be dependent on a complex set of factors such as the concentration of the element (and others) in solution, stability of the secondary minerals (oxygen salts), Eh and pH (see later).

2. Dissolution of nickeliferous silicates.

There is no reason to dispute the widely accepted tenet that natural water, principally that charged with carbon dioxide, is the most important agent of weathering of minerals and largely responsible for the solution and transportation of constituent elements. It is important to know something of the manner in which rock-forming silicates, olivines and serpentines in particular, can be attacked by the natural water and of the factors that influence the rate of their weathering.

(a) Theoretical course of weathering of rock-forming silicates.

Much has been written about weathering and

most authors agree that weathering and decomposition of silicate minerals is accelerated in environments of high acidity such as those expected in zones of oxidizing sulphides.

Keller (1958) has made the interesting suggestion that in some instances in the natural environment minerals may develop high pH values at their interfaces and that aluminium and silica are taken into solution at this time. This high pH was first observed when common rock-forming silicates were ground under water and it has been termed 'abrasion pH' by Stevens and Carron (1948). The importance of this process under natural conditions has been questioned by Gravenor and Govett (1958). They say that pH values of greater than 8.5 are uncommon in most open geologic systems and that rock-forming silicates weather much more rapidly under the acid conditions of the A and B horizons than in the more alkaline C horizon. While these observations regarding the soil horizons are undoubtedly true it must be borne in mind that the conditions within soils are complex and it is conceivable that other factors, such as the chelating action of organic acids, may be partly responsible for the increased weathering in the upper horizons of the soil

profile.

There is, however, no doubt that the concentration of hydrogen ions in solution influences the rate of dissolution of silicate minerals. Gravenor and Govett believe that the rate of dissolution of silicate minerals in nature varies directly with "the availability of hydrogen ions in the weathering system". The two authors, concurring with the widely held opinion regarding the acceleration of weathering in environments of above average acidity, have suggested the following theoretical course of weathering.

They envisage initially, oxygen ions, exposed at the surface of a freshly broken silicate mineral in water, immediately attracting hydrogen ions from the water thereby causing the water at the crystal surface to be slightly alkaline due to the presence of the (OH) groups. Cations, (amongst others Ni^{++}), close to the surface of the mineral in question are said to migrate into the surrounding water creating an electrical imbalance subsequently adjusted by hydrogen (or hydronium) ions entering the mineral lattice. Loss of hydrogen from the water creates a surplus of hydroxyl ions further

increasing the pH. This is the abrasion pH of Stevens and Carron. The high concentration of hydroxyl ions would facilitate removal of aluminium as a complex ion in solution. After removal of most other ions silica in the outer layers of the mineral is probably unstable and is thought to go into solution as $Si(OH)_4$ or small polymers. With the breakdown of an outer layer of the silicate mineral in this way the cations now brought near to the near-surface of the mineral can migrate into the water thus initiating further breakdown of the mineral. Gravenor and Govett emphasize that hydrogen ions in excess of those available through simple displacement of cations are necessary to the dissolution process.

These postulates made by Gravenor and Govett have been summarized here as it is believed that they are theoretical foundations pertinent to the ensueing discussion. Keller, in reply to the comments of Gravenor and Govett points out that he does recognise the importance of hydrogen ions at low pH values and that his theme merely broadens the range of pH in which hydrogen ions are effective in weathering.

Other things being equal, then, it would

appear from the foregoing hypothesis that the more acid the ground waters the more effective is the breakdown of rock-forming silicate minerals and the solution of constituent elements.

(b) Rock weathering.

In the early stages of weathering of any given rock mass ground water enters along fractures and fault planes. The chemical reactions described above commence. Wright and Salazar (1955) think that in ultrabasic rock magnesium begins to dissolve, (that is to say that it begins to migrate from the minerals into the ground waters as Mg^{2+} ions) early. The writer has found evidence of loss of Magnesia in Rhodesia. In serpentinite of the Maritzani mass the MgO content (determined spectrochemically) 30 ft. below surface is 25%. At 7 ft. below surface the MgO content has decreased to 20% and in the soil the MgO content is only 8%. As chemical decay continues porosity develops thus increasing the surface area of the rock forming minerals exposed to the leaching solutions.

The content of nickel (diadochically substituting for magnesium or iron in the virgin

lattice of ultramafic minerals (Chapter 3)), iron and silica in the decaying rock increases slightly at first due to the early loss of alkalies and magnesia.

Metals in solution (e.g. Ni^{2+}, Cu^{2+}) will, in part at least, be removed from the environment. The amount removed will to some extent be dependent on the velocity at which the circulating water is moving as well as on the pH of the water (see below). Some nickel (and other elements) can be sorbed by colloids (those of silicic acid for example (Barth, 1948)) and, depending on prevailing conditions, may be removed from the environment along with these colloids.

3. Summary of factors affecting the rate of solution of nickel(and associated elements)from rocks and minerals.

It is concluded from the foregoing theoretical considerations that four major factors can affect the rate of removal of nickel from rocks and minerals.

(i) pH of the leach solution. Large concentrations of hydrogen ions accelerate weathering and dissolution.

(ii) The exposed surface area of the minerals. The larger the surface area exposed the greater the rate of solution.

(iii) The atomic (crystal) structure of the minerals. Under a given set of conditions minerals of different structural configuration will break down at different rates.

(iv) The rate of movement of the leaching solutions. Rapid circulation of ground water favours quick removal of soluble products.

Nickel can be removed from the zone of weathering in three ways:-

(i) Mechanical movement of nickel-bearing mineral fragments,

(ii) In true solution (including entry into the biochemical cycle), and

(iii) As, or sorbed by colloids.

B. Transportation of nickel.

1. Mechanical dispersion.

Nickeliferous materials can be moved mechanically. Agencies of mechanical dispersion are running water, gravity and wind.

In Rhodesia and Zambia running water is the most active agent of erosion. The bulk of the rainfall in the study areas falls as heavy, sudden showers and there is a lot of surface runoff. Many of the soils (near-surface) are loosely aggragated and such material is more readily dispersed than soil with a more coherent texture. What is more, the vegetal cover at Kalumbila is denser than it is in the Rhodesian study areas. Vegetation

helps bind the soil and reduce erosion. Erosion is, thus, more svere in Rhodesia than in the Kalumbila area of Zambia.

In the southern territory slopes,are, generally speaking, steeper and the rate of runoff consequently faster. Steep slopes encourage gravitational collapse of soil downhill (soil creep) and (where the soil is affected by water) solifluction. The pattern of ground water distribution, that is the position of the water table and the amount of soil moisture, can affect solifluction by the varying degree of the lubricating effect.

Nickel associated with small particles of low specific gravity could become separated from nickel carried by larger particles or particles of higher specific gravity.

The amount of material moved by the wind in Rhodesia and Zambia is very small and unimportant in most parts but in very arid areas such as the Noel Nickel mine some of the finer particles of the topsoil may be moved in the wind. Aeolian dispersion is not however, of any quantative importance.

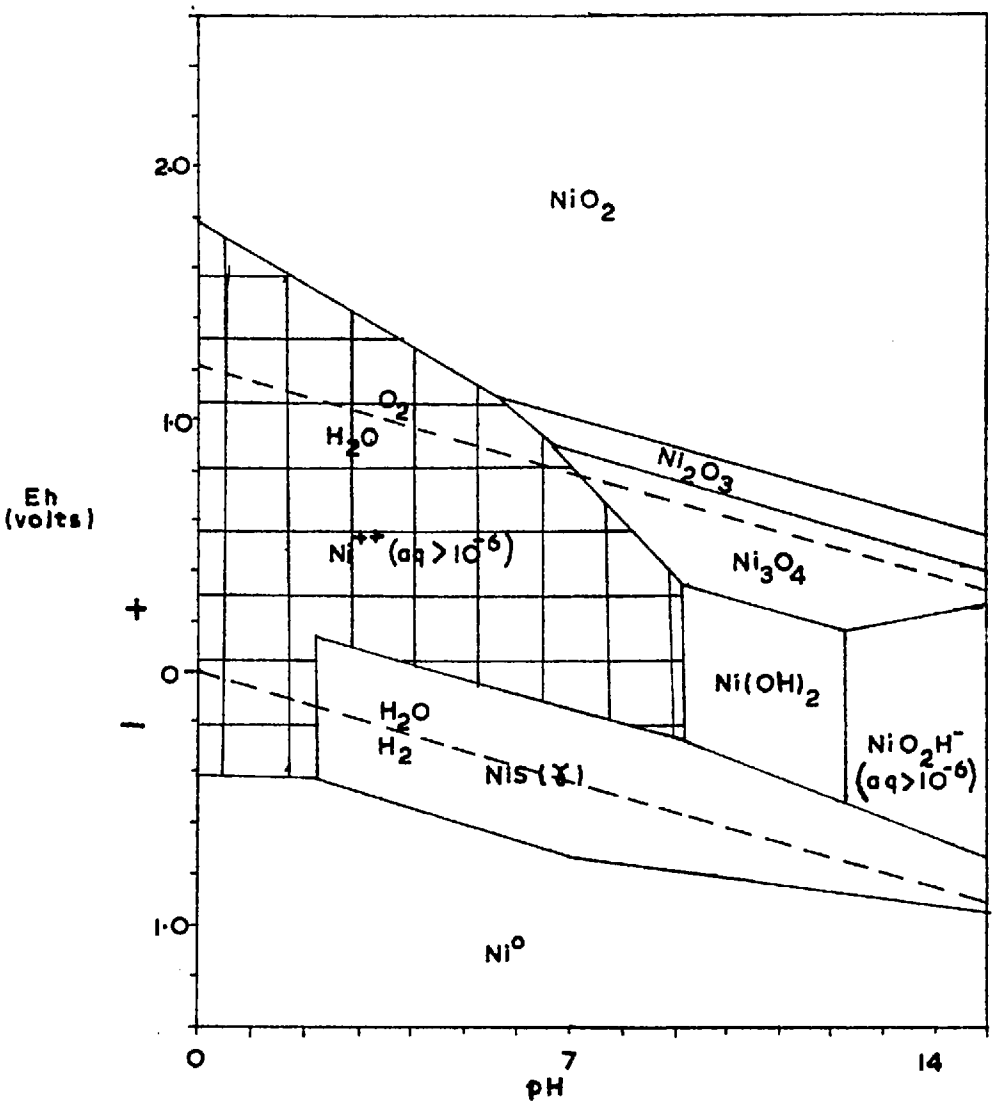
In mechanical dispersion there is no reason for any separation of nickel (or any given element)

from other elements except where one metal is predominantly in the finest fraction and another in the coarser material. A separation could also be effected when one metal is associated with particles of a different specific gravity to the particles bearing another metal.

2. Dispersion in solution.

Santos-Ynigo and Esguerra (1961) showed that divalent nickel is highly soluble in dilute carbonate solutions relative to Ca^{2+}, Fe^{2+} and Co^{2+}, and suggested that it is removed fairly early in the weathering of ultrabasic rocks. Eh - pH stability diagrams presented by Garrels (1960) show that nickel with a valency greater than two cannot exist in nature and that nickel ions (Ni^{2+}) are stable over a wide range in acidic to neutral solutions (Figure 83). The range of stability of the cupric ion (Cu^{2+}) is rather narrower.

Commenting on Eh and pH measurements in natural media Garrels expresses the opinion that the measurement of Eh is difficult and he says that there are very few useful Eh readings available from systems not in equilibrium with the atmosphere. Even in environments in equilibrium with the atmosphere the measurements can



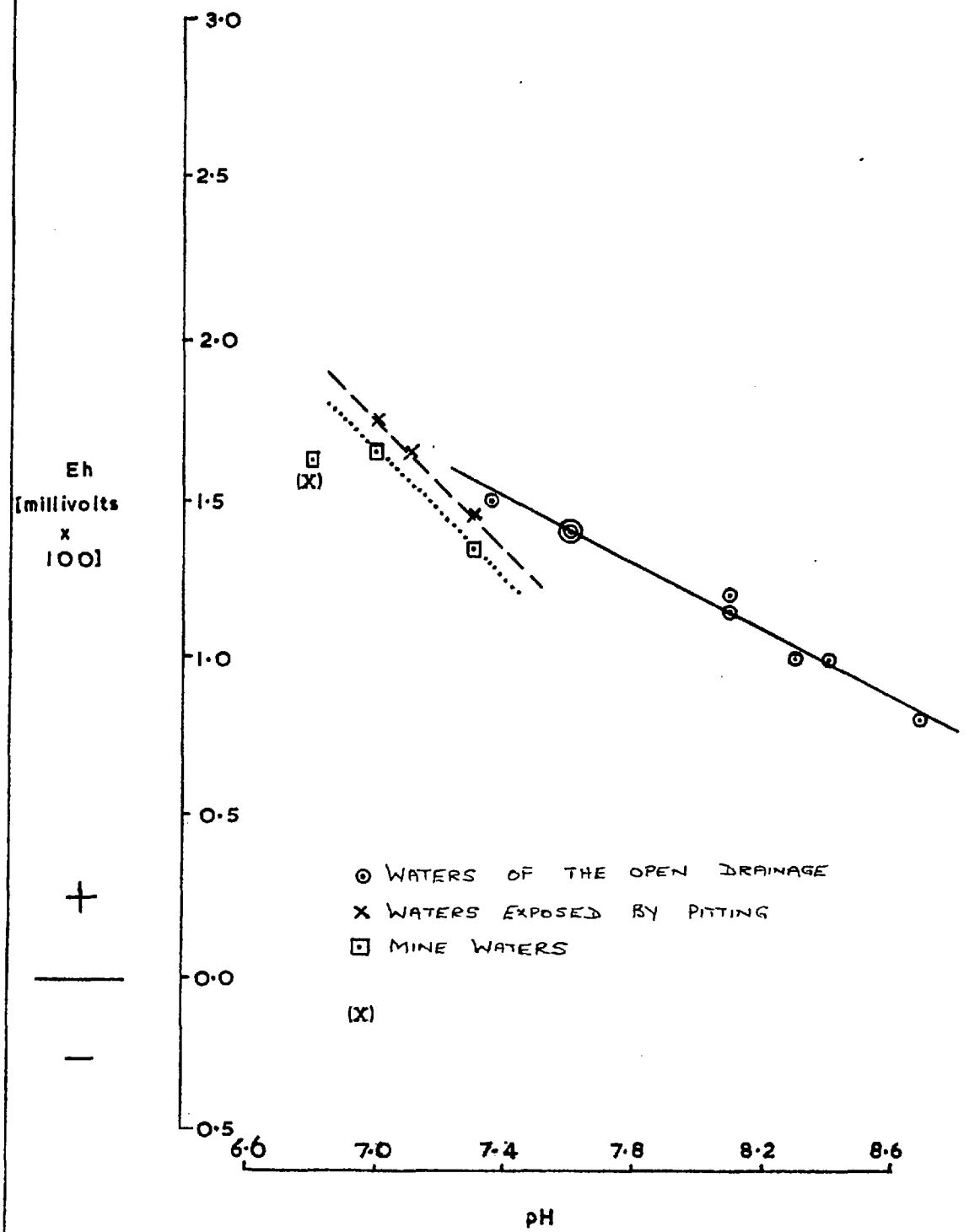
Field of stability of divalent nickel ions. (After Garrels, 1960).

easily be erroneous as a result of contamination of the platinum electrode used for the determinations. He considers pH readings more reliable, particularly those from open water in contact with the atmosphere and especially if made in situ. He goes on to say that in systems in equilibrium with the atmosphere pH and Eh are to some extent interrelated according to the equation

Eh approximates to 0.70 minus 0. 06 pH .

Measurements made on natural waters in the Rhodesian study areas (Table 41) illustrate this relationship between pH and Eh (Figure 84). The plot of observed pH against observed Eh of waters in open drainage ways is, within the limits of experimental error, linear. As far as can be interpreted from the limited data the pH appears lower in ground waters exposed by pitting. The values for these waters do not plot on the lineation referred to above. The waters from pits seem not to have attained equilibrium with the atmosphere. Lack of equilibrium is even more pronounced in the waters from underground workings.

The measurements fall within the field of stability for ionic nickel as determined by Garrels for the system nickel - water at 25°C and one atmosphere total pressure, with the total dissolved sulphur species at 10^{-5} (Figure 83).



Relationship between pH and Eh in some natural waters from Rhodesia.

Table 41. Summary of some parameters of natural waters from Rhodesia.

Description	Study area	Sample No.	pH	Eh (mv x100)	CO_3^{2-} (mg./lit.)	HCO_3^- (mg./lit.)	SO_4^{2-} (mg./lit.)	Ni (ppb)
Open water of surface drainage	MARITZANI	25	7·55	+1·50	0	138	3·75	7·3
"	PERSEVERANCE	27	8·60	+1·00	0	634	125·0	5·2
"	"	37	7·80	+1·40	0	436	30·0	<2·5
"	"	43	8·50	+1·00	0	427	170·0	1·7
"	DALMAINY FARM	29	8·30	+1·20	n.d.	n.d.	<1·25	7·7
"	"	49	7·15	+1·40	0	404	1·25	6·7
"	"	51	8·90	+0·80	40·5	561	7·60	8·3
"	DARWENDALE	58	8·30	+1·15	0	398	<1·25	1·7
"	"	60	7·80	+1·40	0	280	<1·25	3·3
Ground water from pits	MARITZANI	35	7·30	+1·65	0	477	2·50	<2·3
"	"	41	7·20	+1·75	0	259	12·50	1·7
"	PERSEVERANCE	32	7·50	+1·45	0	745	2·50	5·0
Ground water from underground workings	"	45	7·50	+1·35	0	770	17·5	>167·0
	EMPRESS	56	7·20	+1·65	0	628	180·0	12·8
"	NOEL	47	7·00	+1·63	0	770	675	134·0

Clear waters from the flooded underground workings at the Perseverance and Empress prospects and water from the 4th. level of the Noel Nickel mine were found to contain appreciably more nickel than any other waters sampled. Unexpectedly these waters were found to be neutral to weakly alkaline (pH 7.0 - 7.5) within the Eh range +0.135 to +0.165 volts. The reason for this is unknown.

The waters all contained bicarbonate (HCO_3^-) at a concentration in the range 600 to 800 mg./litre. The sulphate (SO_4^{--}) content showed a massive variation, the Noel Nickel mine water being surprisingly rich in this radical (675 mg./litre) compared to the 180 mg./litre at Empress and only 17.5 mg./litre at Perseverance. The high sulphate content of the water from the Noel mine is possibly due to water flowing into the workings through actively oxidizing ore. In contrast both the Empress and Perseverance prospects are flooded and there is no flow of water through areas of sulphide ore exposed to the atmosphere. This difference may account for the high sulphate content of the Noel water relative to that of the Empress and Perseverance waters. It does not however, explain the low level of sulphate in water at Perseverance relative to Empress. This latter difference can only be attributed to the fact that there is a greater volume

of water in the smaller and younger exploratory mine workings at Perseverance. The large volume of water is thought to have diluted the dissolved sulphate species which may not be present in the same amount in the Perseverance area as the Empress as there may have been less solution in the shorter time that the sulphides have been exposed.

At Kalumbila, in Zambia, artesian water flowing from diamond drill holes is of acid reaction (pH 6.2) and carries very much more nickel than any of the surface waters tested although some of the latter are also acid (Table 42). The amount of nickel carried in water is not solely dependent on pH although in a given environment the amount of nickel in solution may vary with pH. For example, in a stream draining barren quartz-mica schist water of pH 6.85 contains 1.5 - 2.5 ppb nickel compared to 1.3 ppb nickel in clear water of pH 7.9 - 8.0 in a second stream draining unmineralized rock (gabbro, Table 42).

Nickel can be deposited from solution in a number of ways, e.g. adsorption, precipitation, (see below) and the amount of nickel travelling in solution at any given time is dependent on the environment through which the water has passed prior to sampling.

To recapitulate, it has been shown by direct analysis

of natural waters from Rhodesia and Zambia that nickel is moving in true solution. Garrels has shown that nickel in solution as Ni^{2+} is stable over a wide pH

Table 42. pH and nickel content of some natural waters, Kalumbila area, Zambia.

Sample No.	Location	Date of sampling	Physical condition	pH	Ni (ppb)
W2	Stream water over quartz-mica schist	30/10/63	clear	6.85	2.5
12	do	29/10/63	clear	6.85	1.5
W1	Dambo ground water over quartz-mica schist	30/10/63	cloudy	5.85	3.5
W3	Stream water over gabbro	30/10/63	clear	7.90	1.3
23	Ground water in dambo draining gabbro	2/6/63	cloudy	5.80	23.5
18	Ground water in dambo over quartz-mica schist down-slope from mineralization	2/6/63	cloudy	5.40	16.0
W4	Stream water downslope mineralization (over quartz-mica schist)	1/11/63	clear	8.00	1.3
13	Artesian water (Drill hole MEA 134)	30/5/63	clear	6.20	155.0
14	Artesian water (Drill hole MM 172)	30/5/63	clear	6.20	55.0

and Eh range. The data presented suggests that pH is

controlling the amount of nickel in solution but only within a given environment, the amount of nickel travelling at any one time being dependent on the environment through which the water has previously passed. This is referred to in more detail later. The positive charge of the Ni cations in solution is balanced by HCO_3^- and/or SO_4^{--} anions.

Nickel in the biochemical cycle.

Metal entering the biochemical cycle is moving in the sense that it is leaving one environment for another. Nickel in solution in water can be absorbed by the root tips of plants. Nickel can also, along with other cations, take part in complex exchange reactions as a method of gaining entry to plants. pH at the surface of the root tips is reported by agricultural scientists as being below 7.0. The low pH, thought to be caused by the hydrolysis of escaping CO_2, is very local but the high hydrogen ion concentration is believed to set up exchange reactions. Ni^{2+} and other cations in exchange positions, and possibly in certain positions within crystal lattices, are displaced by the hydrogen ions from the root tips. The freed cations migrate to the root tips where, as they enter the plant,

they can release more hydrogen to continue the process of cation exchange. It must be emphasized that while exchangeable nickel is certainly available to plants it is not the sole form of the metal available. Once in the plant the nickel enters the circulatory system and is carried upwards to the parts of the plant above ground.

3. Dispersion as a colloid.

In the weathering of minerals nickel (Ni^{2+}) can be adsorbed by colloids, notably those of silica and magnesium as well as organic colloids, and these colloids may be carried away in suspension in natural waters. Most waters sampled in the near-surface environment in Rhodesia and Zambia were cloudy and discoloured and some were still cloudy after filtration. The cloudiness and turbidity is thought to be caused by suspended colloids. No clear surface water analysed contained more than 10 ppb but some unfiltered waters contained nickel in excess of 200 ppb. This is taken as direct evidence that nickel is also moving as a colloid in the study areas. The quantitative importance of this mode of transportation is not known.

Movement of colloids will be affected by factors influencing both mechanical and saline dispersion as

outlined above. For example, colloids will be more readily removed from a given environment the faster the rate of flow of the transporting solution. At the same time pH of the ground water can influence the stability of the colloidal suspension and flocculation is often induced by the presence of an electrolyte (see below).

C. Fixation.

1. Deposition from solution.

Nickel travelling in solution in natural waters can be deposited in a number of ways, principally by sorption (adsorption and absorption) and chemical precipitation (including coprecipitation). Deposition in a given environment is unlikely to take place through the mechanism of only one of the above mentioned processes although one may predominate. However, below, each mode of dispersion is considered separately. Pertinent theoretical considerations and experimental data are presented first followed by a discussion of the factors influencing deposition in the natural environment.

(a) Adsorption.

Adsorption can be reversible. Nickel cations (Ni^{2+}) can take part in cation exchange reactions and can be detected as being in exchange positions when replaced (desorbed) by other ions (e.g.ammonia, NH_4^+). Reversibly adsorbed nickel, (hereafter also designated exchangeable nickel or exNi) is held on the surface of particles as a result of a positive charge balancing a negative one and not as a result of any intrinsic property of the element. Adsorption thus depends to some extent on the surface area exposed. Material with a high surface area / unit weight ratio, that is the finest particles, will have the greatest exchange (adsorption) capacity.

In all environments the finest fraction of a given sample has been found to be the richest in exNi (Tables 27 and 29 and Figures 46 and 47).

Factors influencing the adsorption of nickel by hydrous nickel - magnesium silicates have been reported by Mueller (1954). Applying his conclusions to the general case the major factors are:-

(i) The concentration of nickel in solution,

(ii) The pH of the solution and

(iii) The physical state of the adsorbant.

For example, the amount of nickel adsorbed is,

other things being equal, proportionate to the concentration of nickel (relative to other elements) in solution. Adsorption is favoured at high pH values but it is reported by Mueller that adsorption can take place at pH's as low as 4.5. Intensely weathered minerals with many broken bonds and consequently many unsatisfied charges will have a higher exchange capacity than less severly weathered minerals.

Ginzberg and Ponomarev (1939), investigating the adsorption of nickel and other metals by the hydrosilicates of iron, came to realize the exchange character of the sorption process. They concluded that the quantity of adsorbed nickel is proportionate to the amount of exchangeable bases in geologic materials. The amount of exchangeable bases is said to increase proportionately to the weathering of the rock.

Organic materials, particularly decaying plant fibre, have a high exchange capacity and in the natural environments are effective adsorbants.

(b) Absorption.

Absorption differs from adsorption only in degree and the fact that absorption is irreversible. Absorbed nickel is not exchangeable in that it can not

be replaced by such ions as NH_4^+ or Ba^{2+} from aqueous solutions of ammonium acetate or barium chloride. It is held by the absorbant in a complex manner, probably in voids within the lattice, dependent on the chemical configuration of the element. It is for example, believed that nickel can enter some of the lattice positions of mafic silicates normally occupied by magnesium (and iron) but vacated during weathering. This is made possible by the close similarity in ionic radius between magnesium (0.78 A^o) and nickel (0.78 A^o). Other ions (such as NH_4^+(1.43 A^o) or Ba^{2+}(1.43 A^o)) are too large to occupy these positions. The positive charge on the NH_4^+ or Ba^{2+} ions is also considerably different to that required for the lattice positions. Hence the inability of aqueous ammonium acetate or barium chloride solutions to desorb the absorbed nickel.

Ng Siew Kee and Bloomfield (1962) have made a rigorous study of nickel - plant relations and have concluded that the metal is irreversibly sorbed by the fibrous constituents of plants. According to them the sorption of nickel by plant fibre decreases the mobilization of the metal under anaerobic conditions but the nickel thus fixed is said to be liberated once oxidizing conditions supervene.

The factors influencing deposition of nickel

by adsorption apply equally to the absorption process but the ionic radii and charges on ions concerned are important in deciding the amount taken up by a given absorbant. For instance, nickel would be more readily absorbed by weathered magnesium silicates than would copper since the ionic radius of Ni^{2+} is more closely similar to Mg^{2+} than is Cu^{2+}(0.80 A^{o}). The increase in nickel content of weathered bedrock from depth to surface can be related to the increased weathering of the rock as adjudged by the decreasing magnesia (MgO) content (Table 43).

(c) Chemical precipitation.

Apparently amorphous materials varying in colour from grass green to yellow ochre have been observed in small amounts at many sites in Rhodesia in the base of the solum and top of the weathered bedrock (in many profiles the horizons of highest Ni content). Mueller has prepared precipitates from the system nickel - magnesium - silica - water. His precipitates were gelatinous, amorphous, translucent and differing shades of green according to the magnesium content. They are believed to be the laboratory equivalent of the natural materials described above which are also

regarded as the equivalent of similar materials, identified as hydrous nickel - magnesium silicates, from Brazil (Pecora, 1947), the South Urals (Ginzberg and Ponomarev) and New Caledonia (de Chetelat, 1947).

Table 43. The distribution of exNi, Ni and magnesia in the weathered mantle over serpentinite at Maritzani.[1]

Sample No.	Depth (ft.)	exNi content (ppm)	Ni content (ppm)	MgO content %
2062	1[1]	8.5	1300	8
2066	7	6.5	1750	20
2070	13	7.0	1400	21
2074	19	6.5	1125	24
2078	24	1.3	950	21
2082	29	2.5	900	25

[1]Freely drained soil

Mueller has studied the physico - chemical factors controlling the formation of the hydrous nickel - magnesium silicate precipitates which, he reports, comprise mixtures of two or more of the following substances;

$NiSiO_3 . xH_2O$, $MgSiO_3 . xH_2O$, $H_2NiSi_2O_6$, $H_2MgSi_2O_6$, $Ni(OH)_2$ and $Mg(OH)_2$.

His precipitates were prepared from mixed nickel and magnesium sulphate solutions interacting with a soluble

sodium silicate having an Na_2O/SiO_2 ratio of 1.0. Molecular ratios Ni plus Mg/SiO_3 and Mg/Ni and pH were varied over a wide range and experiments were carried out at the lowest practical concentrations under a range of pressure and temperature conditions normal for the surface and near-surface environment. The precipitation of the substances listed above was found to be dependent on;

(i) The concentration and ratios of nickel, magnesium and silica in solution and

(ii) The pH.

Mueller has concluded that natural ground waters in which the Mg and SiO_2 components (particularly silica) are at a relatively low concentration will precipitate products richer in nickel than those with high concentrations - other factors being equal. He believes, furthermore, that ground waters with pH close to 7.0 on the basic side will precipitate products richer in nickel than will those of higher (and, by implication, lower) pH value.

The natural hydrous nickel - magnesium silicate material, although of variable composition, is often referred to as the mineral 'garnierite'.

Metals are generally more soluble in the lower or acid pH range. Moving in solution they can form insoluble hydroxides and be precipitated as pH rises.

Hawkes (1957) records that Ni hydrolyzes above pH 6.7. The reaction in the general case is reversible, thus:-

$$Ni(OH)_2 + 2H^+ \xleftrightarrow[6.7]{pH} Ni^{2+} + 2H_2O$$

Cupric ions hydrolyse at a lower pH, 5.3 (Hawkes). The experiments from which these figures were derived were carried out using metal salts in solution in concentrations ranging from 0.025 M to 0.0025 M. Although these laboratory conditions are different from those of the natural environment they provide a basis for the explanation of the varying behaviour of different elements. For example nickel and copper in solution as Ni^{2+} and Cu^{2+} ions in acid ground water leaving a zone of oxidizing sulphides could be to some extent separated in the precipitation of the respective insoluble hydroxides. In an environment becoming increasingly alkaline copper would precititate earlier than Ni.

Chemical precipitation from natural waters seldom, if ever, results in pure precipitates and elements of different hydrolysis pH's can occur together although there is usually one present in amounts very much greater than any of the others. Elements whose ions have similar properties (other than hydrolysis pH) are often precipated together.

According to Hawkes and Webb (1962) the mobility of copper is limited dominantly by pH and generally is less mobile than nickel. On the other hand nickel like cobalt, is of moderately high mobility but limited by coprecipitation with limonite (and in the case of cobalt with wad (MnO_2)). Nickel and cobalt have been found to be enriched in nodules relative to weathered bedrock and minus 80 mesh matrix in samples from the Darwendale area to a very much greater extent than is copper (Table 44). All these metals are likely to precipitate along with iron from ground waters entering an oxygenated environment. The general mobility of arsenic is low, being limited by the coprecipitation of AsO_3^{3-} with limonite but in environments of low iron content it is more mobile (Hawkes and Webb).

Unlike the ore metals selenium is reported to be immobile under acid, oxydizing conditions. It probably moves in solution as the SeO_4^{--} ion. Following field studies in Wyoming, Lakin and Trites (1958) have made the observation that the selenium released during the oxidation of seleniferous sulphide minerals tends to be concentrated in the oxidized zone. The form of the selenium in this zone is reported to be elemental selenium and basic ferric selenite (m Fe_2O_3. n SeO_2),

the latter mixed with hydrous iron oxides. In Wyoming, a violet-pink colour characterises the haloes surrounding the seleniferous pyritic lenses. However, the purplish-pink colours observed, for example, in the gossan

Table 44. Comparison between metal content of nodules and weathered bedrock from a freely drained profile over Great Dyke serpentinite at Darwendale.

	Nodules	Bedrock
nickel	4.5%	1.35%
copper	90 ppm	35 ppm
cobalt	5000 ppm	900 ppm
iron	26.0%	12.0%

at Perseverance are unlikely to be caused by high quanties of selenium.

Selenium, in agreement with the published data, has been found to accumulate in the oxidized zone at the Perseverance and Empress prospects and in the environs of the Noel Nickel mine.

Selenium has an outstanding and important relationship with certain plants. Some plants can take up and concentrate large amounts of selenium and some (converter plants) can return the selenium to the soil in a more soluble form than that in which it was originally absorbed so that it becomes available for uptake by other species.

References to nickel-organic matter associations are common in the literature. As well as being sorbed by plant fibre, organo-nickel compounds can form from organic substances and nickel in solution and be deposited but the quantitative importance of such reactions is unknown.

2. Physico-chemical factors inducing flocculation and deposition of suspended colloids.

Flocculation of colloids suspended in water is induced by the presence of dissolved salts (electrolytes). Colloidal particles are rendered crystalloidal; that is to say they are aggragated into an ordered structure and may be deposited. Chemists do not understand the exact mechanism but electrical charge is thought to be important.

Where the rate of flow of circulating ground waters is slowed down suspended colloids may settle and with time, dehydration, diffusion and recrystallization, these settled colloids, as well as the crystalloidal flocculates mentioned above, can solidify to amorphous or crystalline substances. Settling and reconstitution in this manner may also be initiated where water is evaporating, e.g. in standing ponds in the open drainage.

In nature it is thought that nickel-silica colloids resulting from the scrption of nickel by the colloids of silicic acid can attach themselves to other gelatinous, amorphous materials which may subsequently flocculate as impure hydrous nickel silicate materials. Reconstitution of these flocculates may result in the formation of material allied to the hydrous nickel-magnesium silicates precipitated from solution.

3. Deposition of mechanically transported material.

Material being moved mechanically is dominantly under the influence of gravity and deposition takes place when freedom of movement is hindered. To take a case in point, clay size particles may be washed down through an essentially sandy soil profile to a layer where the intergranular spaces are too small to permit the passage of the fine particles and where movement is effectively arrested and the particles deposited. In other profiles large and dense particles can gravitate downwards through a finer and less dense matrix.

In the surface environment mechanically moved particles tend to accumulate in topographic low points where gradients and the velocity of running water are reduced.

Part II. FORMATION OF THE OBSERVED DISTRIBUTIONS.

In discussing the formation of the observed distribution patterns it is convenient to first consider the Ni distribution then the exNi (adsorbed nickel)

A. Distribution of Ni.

The most marked feature is the enrichment in weathered bedrock and at the base of the true soil. Most of the investigations have been carried out over serpentinite bedrock where the high Ni content has facilitated study. Because there are fewer complications in the weathered bedrock than in the soil this media is considered first.

1. Distribution of Ni in weathered bedrock.

It has been observed that away from mineralization weathered bedrock contains more Ni than underlying fresh rock. In the case of copper, enrichment, where apparent, is very much less. In mineralized rocks the Ni and Cu content increases with depth down to the zone unaffected by weathering.

The concentration of Ni in weathered bedrock is possibly only relative, resulting from the early removal of some constituents such as the alkalies and magnesia. Copper initially present in silicate minerals could be similarly concentrated. The enrichment of nickel in unmineralized weathered bedrock may result, however, also from deposition by adsorption (discussed later, Section B), absorption, chemical precipitation and/or flocculation and deposition of colloids. Absorption (together with adsorption) of nickel by weathering rock-forming silicate minerals, particularly those of ultrabasic rocks, is the first instance of deposition in the cycle of secondary dispersion. The loss of constituent elements from the serpentinite in the early stages of weathering can lead to a higher proportion of nickel. The quantitative significance of this is unknown. Whatever the source of the nickel (sulphides or silicates) the increase in nickel content of serpentinite in particular may have been by absorption in the margins of the mineral grains where nickel (with an ionic radius of closely similar magnitude to that of magnesium) occupies lattice positions vacated by magnesium. Copper, with larger ionic radius than magnesium can not occupy the vacant sites. It may, however, replace ferrous iron (ionic radius 0.83).

As mentioned previously apparently amorphous materials varying in colour from grass green to yellow ochre and believed to be hydrous nickel-magnesium silicates have been observed in the top of the weathered serpentinite. These substances are thought to have resulted either from direct precipitation from solution or from flocculation, deposition and reconstitution of colloids. In addition weathered serpentinite is often characterised by secondary iron oxides. It has been shown that ferruginous nodules are very much richer in nickel than is the matrix in which the nodules occur and, by analogy, it is probable that secondary iron oxide could coprecipitate or sorb nickel at the time of it's deposition in weathered bedrock.

Nickel in the hydrous nickel-magnesium silicate and iron oxide is believed to contribute to the relatively high Ni content of weathered bedrock.

Over oxidizing sulphides where the pH is often lower than normal weathering may be more advanced and nickel more mobile. With nickel and copper being leached from the sulphides more readily than from the silicates and having greater mobility at the below average pH any relative enrichment of the expense of other components is less likely than it is away from mineralization. Although it is thought that some

deposition takes place over ore it is thought that under the conditions, it is insufficient to raise the nickel content much, if at all, above the nickel content of the primary ore horizon. This is believed to be the reason for the difference in distribution pattern between that in weathered bedrock over mineralization and that in weathered bedrock away from mineralization.

2. Nickel in the freely drained soil profile.

In freely drained soil in Rhodesia the Ni content increases with depth through the true soil to a maximum at the base of the B horizon or in the top of the weathered bedrock. In some instances Cu has been found to be similarly distributed but in other cases the horizon of maximum Cu content is higher in the profile (e.g. Darwendale, Bare Bottom Hill).

The base of the solum is an environment favouring the fixation of nickel in a number of ways. Although no quantitative estimation of the relative importance of the various modes of deposition thought to be operative can be made they are, for convenience, discussed separately. Adsorbed nickel contributes to the Ni content but as the discussion of the distribution of nickel in this form is being deferred until

later it is omitted here except to note that under optimum conditions adsorption of nickel can play an important and part in formation of Ni distribution patterns. Santos-Ynigo and Esguerra, working the Phillipines, are without doubt that percolating meteoric waters containing carbonic acid (waters of weakly acid reaction) carry nickel as Ni^{2+} and believe that an increasingly alkaline condition is a particularly important factor influencing the deposition of nickel by adsorption onto the surface of colloids of MgO and SiO_2, which, they report are abundant in the slightly alkaline conditions at the base of the nickeliferous laterite.

In the typical freely drained profile through the solum over serpentinite in Rhodesia the pH increases with depth (Table 45). The least acid conditions are at the base of the solum.

Absorption of nickel can take place in the soil in the same way that it can in weathered rock. That is to say the most favourable conditions are a weakly alkaline environment and the presence of material of small particle size (high surface area : unit weight ratio). The process will be more efficient, therefore, in the layer with the highest proportion of clay size material and the highest pH. These conditions are best satisfied at the base of the solum. This control also

applies to copper.

The apparently amorphous hydrous - nickel - magnesium silicates observed in the base of the solum are

Table 45. pH variations in freely drained soil over serpentinite in Rhodesia.

Sample Nos. 1045-1049 Darwendale (barren)		Sample Nos. 5239-5243 Dalmainy Farm (barren)		Sample Nos. 4313-4316 Maritzani (mineralized)	
Depth (in.)	pH	Depth (in.)	pH	Depth (in.)	pH
0 - 3	5.95	0- 3	6.20	0- 3	6.05
3-12	6.00	3-12	6.25	3-15	5.65
12-24	6.35	12-27	6.45	15-25	5.82
24-36	6.90	27-39	7.00	25-36	6.95
36-42	7.40				

The lowermost sample is in each case in the top of the weathered bedrock.

thought to be the result of either chemical precipitation from solution or deposition of colloids. Precipitation of nickel compounds takes place most readily at high pH's. Fixation of the metal by this mechanism is, thus, going to be favoured also in the deeper horizons.

On the other hand, copper is sometimes fixed higher in the profile than nickel. This has been especially noticeable in the soil over serpentinite at Darwendale and over greenstones at Empress and Bare Bottom

Hill. It is believed that the explanation lies in the different hydrolysis pH's of the two elements. In the freely drained soil profiles the direction of water movement is essentially downwards; that is in the direction of increasing pH. Of elements moving in solution that with the lower hydrolysis pH will, other things being equal, tend to precipitate first. Accordingly copper, which hydrolyses at pH 5.3, tends to precipitate before, and higher in the profile, than nickel (pH of hydrolysis 6.5).

At Darwendale there is a greater proportion of Ni and Cu in the ferruginous nodules than there is in other material of the same horizon. The nodules are however, enriched in Ni to a greater extent than they are in Cu. The enrichment is thought to be due to coprecipitation and/or sorption of nickel and copper with or onto the iron oxides and hydroxides. From a solution where the ratio of nickel : copper is approximately the same as Ni : Cu in rock and soil, the amount of nickel precipitated would be very much in excess of copper. This is, then, the reason for the observed distributions.

In the Kalumbila area the horizon of maximum nickel content is the B horizon. The illuvial B horizon is one of unconsolidated nodular laterite between an

eluvial A horizon and a strongly leached C horizon. Although the variation of nickel content up and down the profile is of limited range it is believed that coprecipitation with iron is the cause of the slight accumulation in the B horizon in the Zambian study area.

The freely drained soils in Rhodesia are frequently loosely textured. In many parts water percolates easily and fine materials tend to be washed down the profile to accumulate on top of the weathered bedrock in the base of the solum (Table 46). The fines washed down the profile carry with them residual, adsorbed and absorbed nickel and in addition their presence in the more alkaline horizon where they settle increases the sorption capacity of that horizon as a whole. The singularly sharp decrease in percentage clay size material between the base of the solum and the top of the weathered bedrock (due to weathering) is paralleled by a decrease in Ni content (Table 46). This suggests that the horizon of high percentage clay size material at the base of the true soil effectively traps both nickel moving down the profile from the more acidic upper horizons where it has been mobilized and nickel travelling in ascending or otherwise circulating groundwaters. In the main the nickel is trapped by sorption and as a result of the fines physically impeding the movement of

suspended colloids.

Table 46. Variation in Ni content of clay size material in freely drained profiles over serpentinite in Rhodesia.

Sample Nos. 1045-1049 Darwendale (barren)			Sample Nos. 5239-5243 Dalmainy Farm (barren)			Sample Nos. 4313-4316 Maritzani (mineralized)		
Depth (in.)	% of total sample	Ni (ppm)	Depth (in.)	% of total sample	Ni (ppm)	Depth (in.)	% of total sample	Ni (ppm)
0- 3	17.6	3750	0- 3	8.9	8400	0- 3	25.7	800
3-12	24.2	4500	3-12	14.0	9750	3-15	35.6	1100
12-24	37.6	5300	12-27	15.1	11250	15-25	36.6	1550
24-36	45.8	5600	27-39	12.0	14250	25-36	13.2	2000
36-42	12.6	1600						

The lowermost sample in each case is in the top of the weathered bedrock.

In the true soil profile the base is the most alkaline and contains the highest proportion of clay size materials. The fine materials are thought to impede the movement of the water and allow the accumulation of many chemical compounds and colloidal particles as well as readily sorbing metallic cations from solution. Nickel does not appear to be effectively arrested unless the pH is above 6.5 (hydrolysis pH for nickel). For example, at Maritzani in a freely drained profile over barren serpentinite (downslope from mineralization) an unusually

large proportion of clay size material between 3 and 12 in. below surface where the pH is only 6.05 does not contain correspondingly large amounts of Ni. This leads the writer to suggest that the chemical mechanisms are more important than the mechanical factors in controlling the deposition of nickel in the soil profile.

3. Modification of the normal distribution in freely drained profiles by lateral dispersion.

The normal profile over all rock types investigated is characterised by increasing Ni content with depth through the soil. In some instances this can be modified by lateral dispersion. For example, at the Empress prospect there is more Ni in the upper horizons over greenstones downslope from the mineralized suboutcropping amphibolite than there is in the deeper parts of the profile. Moreover, not only is the distribution anomalous but also the amount of metal in the upper soil horizons over greenstones downslope from mineralization is greater than the normal background range. Similarly in the Kalumbila study area where, downslope of the copper clearing over the best copper mineralization, there is more Ni in the 0-3 in. horizon than there is in the 3-12 in. layer. This distribution is the reverse of

the distribution found over non mineralized strata.

These distributions are thought to arise from the lateral dispersion of nickel from rocks of high nickel content. Although they are anomalous, patterns of this type are not necessarily related to mineralization and can equally well arise where serpentinite crops out upslope of rocks of lower Ni content (e.g. in the Noel Nickel mine area). Dispersion may be either saline (dissolution and redeposition of nickel), biochemical or mechanical.

At the Empress prospect part of the lateral dispersion is believed to have been via a saline mechanism. Water from suboutcropping mineralized amphibolite is possibly (because of the oxidizing sulphides) of slightly below average pH and nickel will be going into solution only to be deposited no more than a few hundred feet away where the pH increases. Deposition would be either by precipitation or sorption. The water table at the Empress prospect is however, at some considerable depth and it is also possible that nickel and copper moving out from the ore zone in the ground water is being taken up by plants and returned to the soil when the leaves fall off or when the plants die or are destroyed. It is, furthermore, thought that the distribution pattern is being modified by leaching right at

surface by percolating rain water, thus accounting for the increase in Ni content between the 0-3 in. and 3-12 in. horizons in some of the profiles downslope of mineralization (Figure 37). A contribution to this lateral dispersion pattern at the Empress prospect could have been made by the mechanical movement of nickel-bearing soil downslope from the ore suboutcrop.

At Kalumbila chemical mechanisms are believed to play a role in the lateral dispersion of nickel. Without more precise geological knowledge and information on the distribution of Ni in the complete profile interpretation is difficult. The possibility of the anomaly at Kalumbila being a seepage anomaly has already been mentioned. The unusual partition of Ni between the 0-3 in. and 3-12 in. horizons can also be put down to the possibility that in the section in question the topsoil is largely transported. It is possibly soil of relatively high Ni content moved from a point further upslope by sheet wash.

In the environs of the Noel Nickel mine the spread of the soil of high Ni content beyond the boundaries of the serpentinite is attributed to sheet wash and gravitational collapse down the steep hillside.

4. Ni in vleis and dambos.

Vleis and dambos are environments favouring deposition of nickel in a number of ways. Fixation of nickel in vleis and dambos takes place in a manner analagous to the deposition at the base of the freely drained profile with the additional mechanism involving interaction with organic matter.

As mentioned previously vlei soil generally contains a higher proportion of clay size material than the adjacent freely drained soil and, broadly speaking, has a higher pH. Dambos are similarly rich in clay size materials but the difference in pH between dambo and adjacent freely drained soil is less pronounced than the difference in pH between vlei and freely drained soils. The grey - black colour of vlei soil is believed to be due to the high humus content. Dambo soil is equally black in colour for the same reason, especially near-surface. Dambos are, furthermore, very rich in plant matter in all stages of decomposition.

The amount of nickel in some vlei soils is high compared with that of the freely drained soils. This is considered to be related to the vlei soils being of alkaline reaction and rich in clay size material and because they contain more organic matter

(with a high exchange and absorption capacity) than do the freely drained soils.

The enrichment of Ni in near-surface dambo soils, particularly in the low lying swampy parts, has already been referred to as a widespread and not unusual geochemical feature. The low lying swampy parts are particularly rich in decomposing plant matter and it is thought that much of the nickel in this environment is being held in the decaying organic structures. Plant matter is known to be a good absorbant of nickel and especially so in the reducing environment of the water-logged dambo. References to nickel - organic matter associations are common in the literature. Aleskovskii, Mokhov and Spirov (1959) report that they found 1½ times as much nickel in humus as in the subsoil and they say that ground water of pH 6 does not remove nickel from humus. Crooke has noticed indications of a nickel - soil organic matter complex in a peaty serpentine soil.

Sorption by organic materials is thought to be an important mechanism in fixing nickel in the vlei and dambo environment, especially in the latter.

The distribution of Cu in vleis and dambos is closely similar to the distribution of Ni and it is thought that both elements are subject to similar controls, differing only in degree.

5. Deposition of nickel in the drainage system.

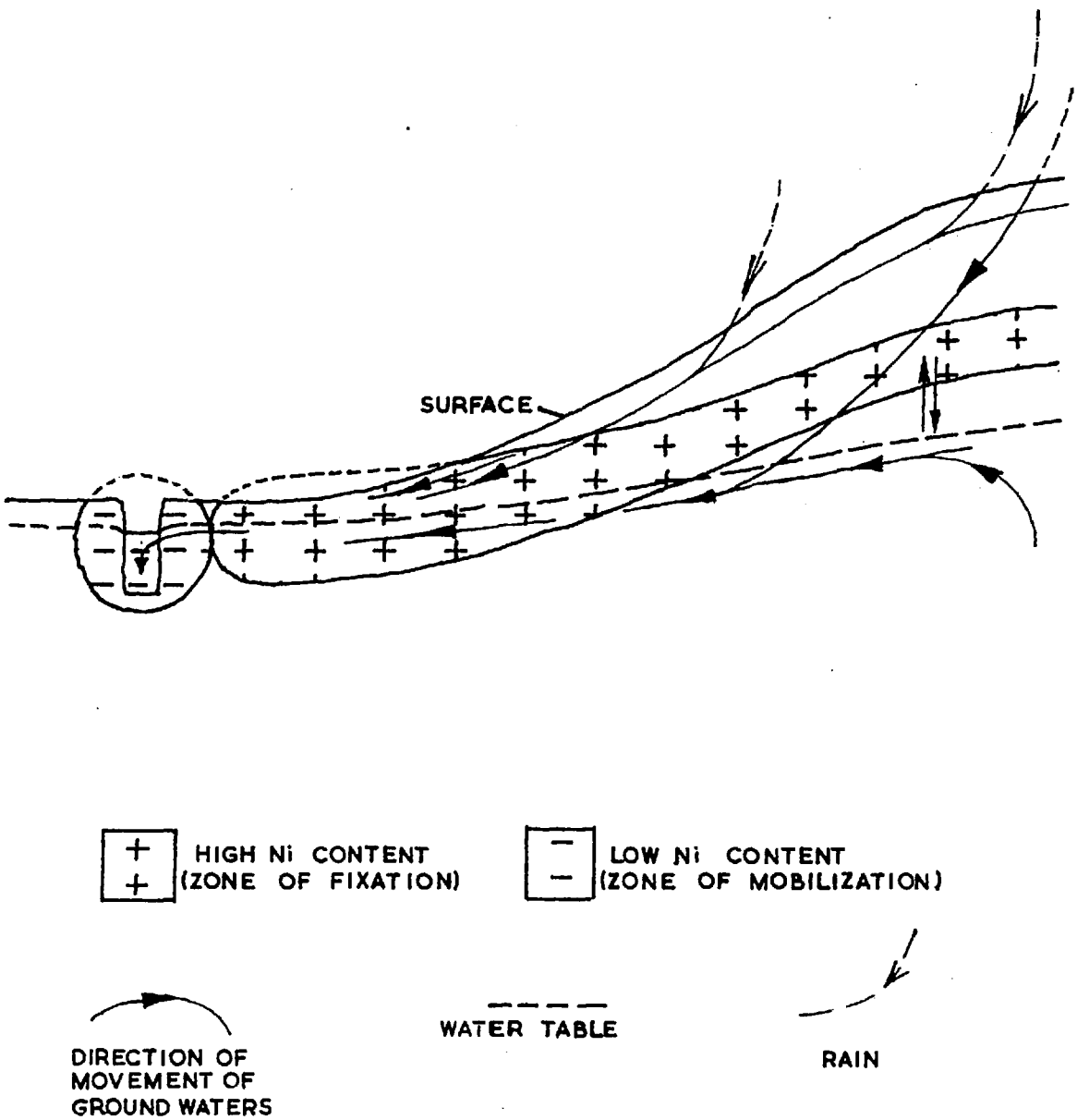
Detailed study has revealed that the stream sediment and stream bank materials of open watercourses in dambos in the Kalumbila area contain the least amounts of Ni, the swampy low lying parts the largest amounts of the metal. The pH of the open stream water is 7.9 to 8.0 compared to a pH as low as 5.2 in the waterlogged depressions. This inverse relationship between pH and Ni content is unusual and incompatible with other data unless some other factor is more influential.

This unusual relationship between Ni content and pH can be explained as follows. Nickel entering the dambo in solution in ground waters (of pH 5.0 to 6.5) is readily sorbed by the organic matter, decaying plant fibre in particular, even at relatively low pH's. It is believed that water infiltrating through the dambo has, by the time it reaches the open stream channel, been stripped of much of its nickel, thus accounting for the comparatively low nickel content of stream water (Table 42) and stream sediment and bank material.

There is no doubt that at points in the open drainage chemical precipitation and sorption of ionic nickel and flocculation of colloids with which nickel is associated occur. Be that as it may, the course followed

by nickel in it's secondary dispersion has, in most instances, been through environments conducive to nickel deposition in one way or another, at some point before it reaches the drainage ways (Figure 86). Nickel moving towards the vleis and dambos at surface or through the upper soil horizons meets an environment favouring deposition when it enters the vleis or dambos. Downward movement through the freely drained profile is checked at the base of the solum and in the top of the weathered bedrock, which horizons also trap nickel moving in ascending or otherwise circulating groundwater. Where ground water is flowing below the base of the soil profile there is little tendency towards deposition of nickel until the water approaches surface - commonly in the vleis or dambos. Much nickel is believed to have been lost from the ground water by the time it reaches theopen drainage. It is thought that copper behaves in a comparable manner although this element is generally less mobile than nickel.

Sediment in Rhodesia is essentially eroded soil and collapsed bank material. It's Ni content is closely correlated with that of adjacent soil. The dispersion is believed to be dominantly mechanical since the ground water in many parts of the Rhodesian study areas does not outcrop. Nickel can enter the open drainage incorp-



Diagrammatic representation of the course followed by nickel moving in solution.

orated in some way (e.g. adsorbed onto clay minerals, in the lattice of weathered silicate mineral fragments) in material washed into the stream channels or collapsed from the banks. In Rhodesia this mode of dispersion is believed to be important. In the study areas of the southern territory there is, compared to Kalumbila, less vegetation to help hold the soil together and, in many areas where the topography is locally rugged, the amount of topsoil washed into the streams during the characteristically heavy thunderstorms is appreciable. The amount of nickel entering the stream channels in this way is thought to be small at Kalumbila as the terrain there is not well suited to much mechanical dispersion.

B. Distribution of exchangeable nickel.

In this section the formation of the observed distributions of exNi are discussed in the light of the theoretical knowledge.

Although exNi content is roughly inversely proportionate to particle size there is no correlation between exNi content of a given size fraction and the percentage of the total soil sample that the fraction constitutes. The surface area/unit weight ratio is not the sole control. For example, in freely drained

soil profiles over serpentinite (mineralized and non mineralized) the distribution of exchangeable nickel in the profile does not vary with the percentage silt and clay size material (Table 47). Since it is known

Table 47. Ni and exNi in silt and clay size material from a freely drained profile over mineralized serpentinite at Maritzani and from a similar profile over barren serpentinite at Dalmainy Farm.

Maritzani					Dalmainy Farm				
Depth (in.)	Silt Ni (ppm)	exNi (ppm)	Clay Ni (ppm)	exNi (ppm)	Depth (in.)	Silt Ni (ppm)	exNi (ppm)	Clay Ni (ppm)	exNi (ppm)
0- 3	150 (36.3)	5	800 (25.7)	20	0- 3	8900 (15.5)	225	8400 (8.9)	335
3-15	250 (31.8)	10	1100 (35.6)	25	3-12	7200 (15.0)	225	9750 (14.0)	360
15-25	650 (22.6)	15	1550 (36.6)	28	12-27	8100 (14.4)	220	11250 (15.1)	450
25-36	2750 (12.2)	135	2000 (13.2)	103	27-38	9450 (10.7)	225	14250 (12.0)	810

(Weight percentages of total sample)

that pH can influence adsorption soil pH was determined in selected soil profiles (Table 45). At Maritzani the exNi content was found to increase with pH; similarly at Dalmainy Farm. In the freely drained soil in the Darwendale area the variation in exNi content can not be correlated with percentage clay size material or pH. However, in this latter area the water table is very

much closer to surface than it is at Maritzani or Dalmainy Farm. The capillary fringe above the water table is thought to extend throughout the Darwendale profile and it is possible that evaporation in the near-surface horizons brings about a relative concentration of Ni^{2+} in solution. Adsorption is known to take place more readily the higher the concentration of the dissolved species and in this way it is possible to account for the distribution of exNi in the freely drained profile at Darwendale. The near-surface horizons are visibly richer in decaying plant matter than are the deeper levels and adsorption from ground water onto decaying plant fibre and organic colloids in the near-surface horizons is believed to be a contributing factor in bringing about the observed distribution.

At Maritzani, deeper into the weathered mantle from the top of the weathered bedrock (C horizon) the exNi content decreases into the fresher rock, the relative degree of weathering being judged by the variation in MgO content (Table 43). Even at 30 ft. below surface at Maritzani the water table is not reached (it is at 60-80 ft. in this area). The increase in exNi content of bedrock from depth towards surface has been observed in both mineralized and non mineralized sections and is attributed to an increase in the exchange

capacity of the rock forming minerals and availability of nickel in solution as weathering proceeds. It must be remembered, however, that the profile on which Table 43 is based is in weathered barren serpentinite downslope from mineralization and it is possible that some of the exNi in the weathered serpentinite may have originated from the mineralization. pH increases slightly with depth both over mineralized and non mineralized serpentinite (Table 50). In the mineralized profile exNi is greater and pH lower than in the non mineralized profile. This is thought to be most significant and representative of a difference in the dispersion of nickel from sulphides and silicates.

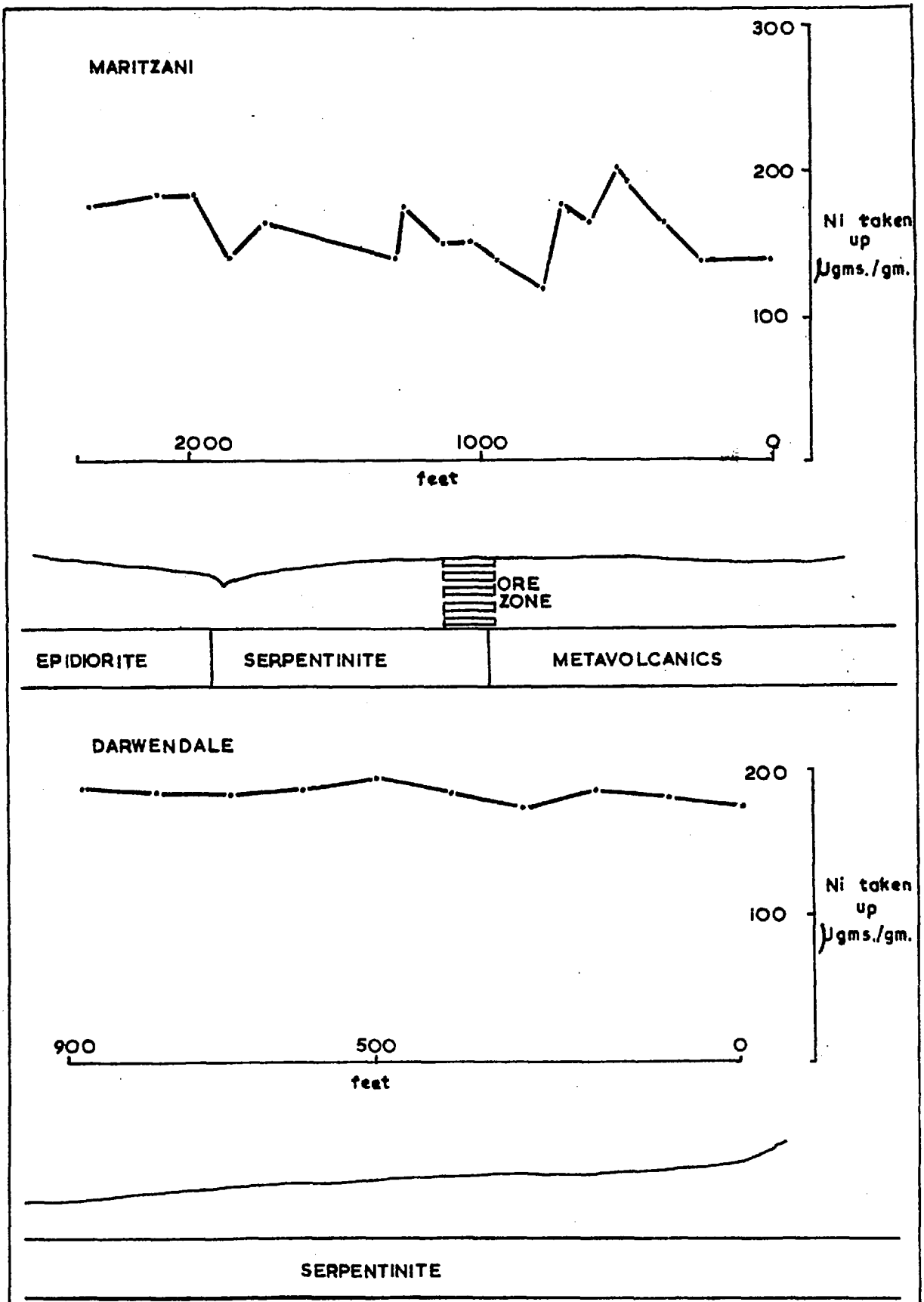
1. Significance of the relationship between exNi content of weathered bedrock and mineralization.

There is no doubt regarding the existence of an exchangeable nickel anomaly in the weathered bedrock at Maritzani. Further detailed study has suggested that the exNi data assumes even greater significance when evaluated in conjunction with other parameters.

(a) The sorption capacity of weathered bedrock.

At the time that the exNi determinations were carried out on the minus 80 mesh fraction of samples collected from the bases of the Maritzani pits a separate portion of the sample (0.1 gm.) was soaked in a known volume (25 ml.) of an aqueous solution containing 0.5 micrograms Ni^{2+}/ml. This solution was prepared by dissolving $NiSO_4.7H_2O$ in water. The sample was in contact with the solution for 30 minutes before the slurry was centrifuged and the supernatant liquor analysed for nickel. The nickel lost from the solution was regarded as having been sorbed by the sample and the method thus provided a means of obtaining information on the relative sorption capacity of different samples. It is important however, to recognise that it is not necessarily, as such, a measure of exchange capacity as the amounts of nickel reversibly and irreversibly sorbed were not determined.

The results are, nevertheless, useful. They suggest that the weathered rock over mineralization has no abnormally high sorption capacity compared to that of the non mineralized weathered rock (Figure 87). If anything, the nickel sorption capacity over Maritzani mineralization is lower than it is over barren serpentinite elswhere in the area. It is possible that the reason for this is that some nickel leached from the



Uptake of nickel from a 0.5 Ugm./ml solution of nickel sulphate by weathered bedrock, 3½-6 ft.

mineralization has already been sorbed by the weathered materials. The difference between the exNi content of weathered bedrock in the mineralized zone and that away from mineralization is 25 ppm. This is the same order of magnitude as the difference in sorption capacity. Since weathered materials are not saturated with sorbed nickel (that is to say that the materials have not sorbed all the Ni^{2+} that they can) it is difficult to relate the distribution of exNi to sorption capacity. exNi is probably reflecting the Ni content of the ground waters from which it is being sorbed.

The study of the capacity for sorption of nickel was extended to other study areas and considerable variation was observed (Table 48).

Table 48. Amounts of nickel taken up from a 0.5 micrograms Ni/ml. solution by the minus 80 mesh fraction of weathered bedrock.

Area	Range (micrograms/gm.)	Mean (micrograms/gm.)
Maritzani	125-175	160
Darwendale	135-200	180
Noel	25-190	100
Kalumbila	25-100	60

From the evidence of the sorption capacity tests it is concluded that the weathered bedrock

containing anomalous amounts of exNi does not have a higher sorption capacity (at least towards nickel) than the weathered barren bedrock within the same area. Regional differences in exNi level can be explained by the varying pH and sorption capacity in rocks weathered to a greater or lesser degree under diverse climatic conditions.

(b) Exchange capacity.

The cation exchange capacity, total exchangeable bases and, by difference, exchangeable hydrogen was determined on clay size materials from the upper C horizon over mineralization in serpentinite at Maritzani and over barren serpentinite at Dalmainy Farm. It was decided to compare the Dalmainy Farm and Maritzani serpentinites because;

(i) They are of similar geologic age,

(ii) The Dalmainy Farm serpentinite contains, as far as can be ascertained, no sulphide minerals and

(iii) Preliminary analyses had revealed very much more nickel and exNi at Dalmainy Farm than at Maritzani (Table 47) which is a good example of how regional variation prohibits any possibility of establishing a countrywide background level

for exNi in weathered bedrock.

Separated clay size material was selected for exchange capacity determinations since this fraction was observed to contain the highest proportion of exNi (Table 47).

The exchange capacity and total exchangeable bases were determined by replacing the adsorbed cations with NH_4^+ ions from an aqueous, neutral, normal (molar) ammonium acetate solution following the widely used technique first described by Bray and Willhite (1929).

Contrary to expectations the Dalmainy Farm material has a cation exchange capacity considerably lower than that of the sample from Maritzani (21.5 and 63.0 m. equiv./100 gm. respectively). Cation exchange capacity is regarded as being the sum of the total exchangeable bases and the exchangeable hydrogen (Piper, 1950). Although the total amount of exchangeable bases in the Maritzani sample is nearly twice that at Dalmainy Farm it represents only just over half the cation exchange capacity (Table 49). Subtraction of 36.0 m. equiv./100 gm. (the total exchangeable bases) from 63.0 m. equiv/100 gm. (the cation exchange capacity) reveals 27.0 M. equiv/100 gm. exchangeable hydrogen in the Maritzani clay size material. A similar calculation for the Dalmainy Farm sample indicates

Table 49. exNi, exchange capacity and associated parameters of clay size material from the top of the weathered serpentinite at Maritzani (mineralized) and Dalmainy Farm (barren).

Property	Maritzani (ppm) (1)	(ppm) (2)	Mean	Dalmainy Farm (ppm) (1)	(ppm) (2)	Mean
Ni content	2000	-	2000	14250	-	14250
exNi content	113	93	103	810	-	810
Theoretical maximum exNi capacity	-	-	18500	-	-	6500
	m.eq./100 gm.	m.eq./100 gm.	Mean	m.eq./100 gm.	m.eq./100 gm.	Mean
Cation exchange capacity(A)	66.0	60.0	63.0	21.0	22.0	21.5
Total exchangeable bases(B)	34.0	38.0	36.0	30.0	8.0	19.0
Exchangeable hydrogen(A-B)	-	-	27.0	-	-	2.5

(1) and (2) : Duplicate analyses.

the presence of only 2.5 M. equiv./100 gm. exchangeable hydrogen (Table 49).

(c) pH.

Tests have shown that the conditions in the weathered bedrock overlying mineralized serpentinite at Maritzani are more acid than in the weathered bedrock above barren serpentinite although the absolute value at both sites is on the alkaline side of 7.0 in the deeper horizons (Table 50), i.e. consistent with the serpentinite environment. The fact that the exNi

Table 50. pH in weathered serpentinite bedrock at Maritzani.

Depth below surface (feet)	Mineralized profile	Non-mineralized profile
3.5	6.75	6.95
12.0	7.85	8.35
25.0	8.10	8.50

content of the weathered bedrock overlying the mineralization in the Maritzani serpentinite body is greater than that of the non mineralized parts is of even greater significance when this pH difference is taken into account (see below).

2. Formation of exNi anomalies.

The data pertaining to the exchange properties of the selected materials helps in explaining the formation of exNi anomalies in the weathered bedrock.

As weathering sets in and nickel-bearing minerals begin to decompose the metal is taken into solution in the ground water. Sulphide minerals, breaking down more rapidly than silicates, release their nickel to the leaching solution proportionately quicker with the result that the nickel content of ground water in zones of weathering (oxidizing) sulphides increases at a faster rate than that in water percolating through barren rock. This being the case, the concentration of nickel in solution at a given time after initiation of weathering will be greater in a zone of oxidizing sulphides than in rock barren of sulphides. The zone of oxidizing sulphides is, moreover, of a lower pH and this will aid the solution of nickel from both sulphide and silicate minerals and the further build up of Ni ions in solution.

Entry of the nickel ions into exchange positions depends on their concentration in solution relative to other critical components of which the hydrogen ion (H^+) is one. There is, therefore, a direct

relationship between the exNi content of the soil and

$$[Ni^{2+}] / [H^{+}]$$

where $[Ni^{2+}]$ is the concentration of nickel ions and $[H^{+}]$ the concentration of hydrogen ions.

In oxidizing mineralization $[Ni^{2+}]$ is above average as is $[H^{+}]$. The country rocks will, however, tend to neutralize rapidly the acid solution so the net result is an increase in the ratio $[Ni^{2+}] / [H^{+}]$. Furthermore, as the rock forming silicates break down (a process accelerated in the relatively acid environment) their exchange capacity increases insofar as they become progressively more porous and a greater surface area per unit volume is exposed. The increase in the ratio $[Ni^{2+}] / [H^{+}]$ and in exchange capacity both act to favour increased adsorption (exchange) of Ni^{2+} ions. Hence the greater Maritzani exNi than Ni anomaly.

The data of Table 49 in no way suggests any dependency of exNi content in exchange capacity since the relationship in the two particular samples is inverse. The only conclusion that can be drawn from the data is that exNi is not simply proportionate to exchange capacity. Consequently the $[Ni^{2+}] / [H^{+}]$ ratio must be a controlling factor in the exchangeable adsorption of nickel. At Dalmainy Farm nickel from the weathering serpentinite (which contains 0.3 to 0.4% of the

metal) has not had to compete with hydrogen ions in the same concentration as at Maritzani and the end result is a noticeably greater exchangeable nickel content and smaller exchangeable hydrogen content in the former area.

In any given mineralized area the relatively high concentration of nickel in the environment and, more especially perhaps, in solution, coupled with the physical state of the weathered materials is thought to be the factor controlling the exchange sorption of nickel in the amounts detected in the face of the lower pH conditions. Since, in a given area, exchange capacity (as adjudged by analogy with sorption capacity) is not significantly different over mineralization compared with that away from mineralization, the amount of nickel in solution and in the exchange positions is significantly anomalous and related to the presence of the sulphide minerals. Mueller has found in experiments that sorption of nickel will still occur at pHs as low as 4.9. To what extent sorption can take place at such a low pH is not clear. There is need for further work before an understanding of the effects of extreme pH variations can be gained and possible allowance for them made.

3. Distribution of exNi in vleis.

In vlei soil generally exNi is present in amounts appreciably larger than in freely drained soil. Broadly speaking vlei soils have a higher pH, contain a greater percentage of clay size material and hold water more readily than freely drained soils. It is difficult to correlate the differentiation of exNi in the profile with any one factor.

exNi is available for uptake by plants. The distribution of nickel in plants is thus, to some extent, reflecting the distribution of exNi in the soil.

It is concluded, then, that the distribution of adsorbed nickel (exNi) is controlled more by environment than by any single factor. It is influenced by the concentration of nickel in solution (both absolute and relative to other cations), adsorption (exchange) capacity of the adsorbant and pH acting together in a complex manner.

C. Comparison of mobility of nickel from sulphide and silicate minerals.

The physical chemistry of the secondary dispersion of nickel as envisaged in the preceding

sections is independent of the source of the nickel. There is no evidence to suggest that nickel originally present in sulphide or arsenide minerals behaves in any way differently to that from silicates. There are, however, differences in the rate at which secondary dispersion proceeds which, when other things are equal, can be related to the differential in susceptibility to weathering between sulphide and silicate minerals. Of particular importance is the distribution of exNi in the weathered bedrock which is considered to reflect differences in the rate of weathering and leaching between sulphide and silicate minerals. The determination of the exNi content of certain materials may well assist, therefore, in the differentiation of nickel anomalies related to sulphides and silicates. The significance of the exNi distribution in terms of mineralization has been discussed.

In secondary dispersion nickel is believed to differ a little in overall mobility from copper especially in areas of ultramafic rock. The higher pH of hydrolysis of the nickel ion (Ni^{2+}) compared to Cu^{2+} is the most important governing factor.

D. Influence of varying climatic and topographic factors on secondary dispersion.

In the text thus far there have been references to regional variations in climate, topography, pattern of distribution of ground water and soil moisture and geomorphological history. These vagaries and vicissitudes of climate and geomorphology influence the secondary dispersion of nickel.

It has, for example, been shown that at Kalumbila the Ni content of near-surface dambo soil is at maximum where the water table reaches or most closely approaches surface. In an area where much of the nickel is moving in solution the position of the water table is important.

In drier climes in Rhodesia there is a marked contrast in climate and geomorphology between study areas. A good example is the contrast between Darwendale and Maritzani. At Darwendale, where the mean annual rainfall is slightly higher than in any other Rhodesian study area (Chapter 1) the water table in excavations 1000 ft. down a 5^{o} slope from the freely drained profiles studied was only 5 ft. below surface at the end of July. It has been suggested that the soils studied lie within the zone of fluctuating water table. At Maritzani

observations made by company personnel during drilling operations showed the water table to be at depths of 60 - 80 ft. in the vicinity of the mineralization. Differences in the distribution of exNi have been attributed to the different ground water relationships. It is important that in interpreting the secondary distribution of nickel ground water movement be taken into account.

The extent of rock weathering and soil profile development at Kalumbila is far in advance of that at the Noel Nickel mine for example and the two areas are quite incomparable in this respect. Variations in distribution and dispersion mechanism are correlated with climatic and geomorphological dissimilarities. For example, the dispersion under the high rainfall conditions at Kalumbila is dominantly via a saline mechanism whereas in the semi-arid climate in the environs of the Noel Nickel Mine mechanical dispersion mechanisms predominate. In general terms relatively high temperature and rainfall favour chemical weathering. Rainfall and topography together control the position of the water table relative to the surface and the data suggests that the position of the water table is a major factor in the secondary dispersion of nickel. The degree of soil profile differentiation is important in controlling

the profile distribution of nickel and this too is influenced by physiography.

The influence of physiographic variations is not confined to saline dispersion but can also affect mechanical dispersion. For example the amount of material moved by sheet wash is influenced by rainfall and surface gradient. Climate influences vegetation; vegetation in turn usually inhibits mechanical dispersion. The pattern of ground water distribution is thought to affect solifluction by the varying degree of it's lubricating effect. Gravitational collapse downhill may be expected to be important on steep hill slopes.

The physiographic conditions have not always remained constant. A given set of conditions prevailing for varying lengths of time will produce different results. This time factor is, however, exceedingly difficult to evaluate.

E. Comparison of the distribution of nickel over serpentinite in Rhodesia with that over similar rocks in other parts of the world.

The writer believes that the physico-chemical, climatic and geomorphologic control of nickel dispers-

ion in Rhodesia and Zambia differs from that of other parts of the world only in degree. This can be illustrated by considering the distribution of nickel in the weathered mantle over serpentinite. Comparison of published data with that of this investigation has been made (e.g. Figure 86). It is known that high grade nickeliferous laterites develop over serpentinite under certain climatic and topographic conditions. Such deposits are best developed in New Caledonia (described in detail by de Chetelat, 1947) and the Phillipines (Santos-Ynigo and Esguerra).

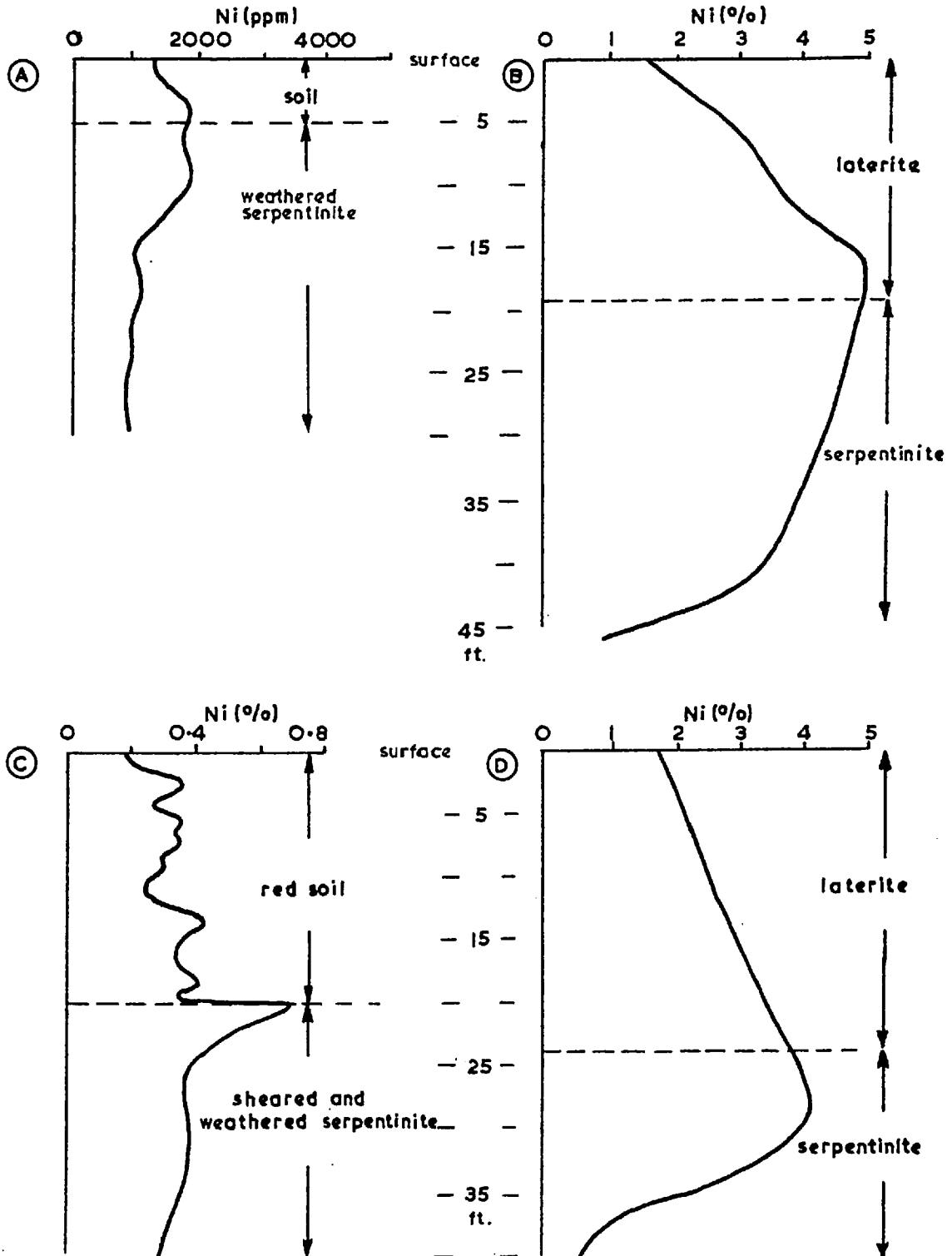
In their report on the nickeliferous laterites of Surigao, Santos-Ynigo and Esguerra record that three conditions are generally thought to be essential for the development of laterites. These are;

(i) A semi-humid or perhumid tropical climate,

(ii) A level land surface sufficiently elevated above sea level to ensure adequate drainage and

(iii) A long period of time during which the two previous conditions must hold.

These conditions are not well met in the Rhodesian study areas. The climate in Rhodesia, although tropical, is tempered by altitude and distance from the sea. The mean annual rainfall in the study areas nowhere exceeds 40 in. per annum (Chapter 1).



A. Maritzani, Rhodesia.

B. Surigao, Phillipines. (Santos-Ynigo and Esguerra)

C. India. (Anand Alwar and Banerjee)

D. Cuba. (de Vletter)

Distribution of nickel in the weathered mantle over ultrabasic rocks.

The mean annual rainfall for Surigao is 144.5 in. It has, furthermore, been pointed out already that the Rhodesian soils are juvenile. On the above evidence the rainfall alone appears inadequate but even allowing that climate and drainage conditions (as observed today) favour the formation of nickeliferous laterite following weathering of ultrabasic rocks they cannot have prevailed for a length of time sufficient to allow laterite formation on the scale of the Phillipines or New Caledonian deposits.

No serpentinites were studied in Zambia and so it is not possible to compare any nickeliferous laterite formation which might occur there with that in Rhodesia and elsewhere. It can only be postulated that the distribution which one might expect in an area such as the North Western Province of Zambia will be intermediate between that of Rhodesia and the Phillipines since the rainfall there (55 in. per annum at Kalumbila) is higher than in Rhodesia and the soils, on a fairly level landsurface, are well drained.

The geochemical forces which bring about the enrichment of nickel in weathered bedrock and at the base of the solum in Rhodesia are regarded as analagous to those concentrating nickel into the high grade secondary silicate deposits of the world, the difference, as discussed above, being only one of degree. The control

is believed to be dominantly climato - topographic.

In Puerto-Rico nickel-cobalt-iron bearing deposits occur in the lower part of the laterite capping and the upper part of the underlying soft, serpentinized peridotite (Heidenreich and Reynolds, 1959). 90 million tons of 0.85% Ni are reported. This deposit appears to have many characteristics in common with the nickel distribution pattern over serpentinized peridotite in Rhodesia. Similar deposits have been located in Tasmania (Hughes, 1957), Germany (Jubelt, 1953), Greece (Petrascheck, 1953), Cuba (de Vletter, 1953), Phillipines (Santos-Ynigo and Esguerra) and New Caledonia (de Chetelat).

At Mwahanza Hill in Tanzania (formerly Tanganyika) a serpentinized basic intrusive containing 0.2 - 0.3 per cent nickel near-surface has been described by Fawley (1957). Nickeliferous serpentine, nickeliferous pyrrhotite and garnierite are believed to be the nickel bearing minerals. The possibility of finding an economic garnierite deposit is thought to be slight but the possibility of producing a magnetite concentrate has been mentioned.

Generally speaking the grade of the deposits has to be at least several per cent nickel to be economic (e.g. New Caledonia) and even in this case treat-

ment of the ore to extract the nickel is difficult and costs are high. Hence the reason for the statement made in the introduction to this thesis regarding the unliklihood of finding economic deposits of this type in Africa.

F. Summary of conclusions on the secondary dispersion of nickel.

Following the discussion of the observed distributions in the light of the theoretical physico - chemical factors it has been possible to arrive at certain general conclusions. They are:-

1. Natural waters, particularly those of weakly acid reaction (brought about by atmospheric CO_2 or sulphuric acid from weathering sulphides), are largely responsible for the decomposition of both rock forming and ore minerals and the leaching and transportation of nickel.
2. It is believed that, other things being equal, nickel is more readily leached and has greater mobility the lower the pH.
3. Nickel moves in true solution, as Ni^{2+} ions in the natural waters containing HCO_3^- and for SO_4^{--} ions.

4. Deposition by any mechanism (adsorption, absorption, precipitation and colloidal flocculation) takes place most readily in environments of weakly alkaline reaction.
5. The amount of nickel sorbed is proportionate to its concentration in solution relative to other critical components.
6. Organic matter has an exceptional ability to sorb nickel even at a pH as low as 5.2.
7. Sorption in weathering bedrock is dependent to some extent on the physical state of the sorbant and, in the case of absorption, on the amount of magnesium (and iron) that can be replaced by nickel.
8. The tenor of nickel in chemical precipitates is proportionate to the concentration of the metal in solution relative to other critical components.
9. Impure hydrous nickel-magnesium silicates (garnierite) can result from the flocculation of nickel bearing colloids after their subsequent dehydration, diffusion and recrystallization as well as from precipitation from solution.
10. In the drainage channels much of the nickel has been deposited along with the stream sediment (which is essentially eroded soil) following mechanical trans-

portation.

11. The amounts of nickel moved varies with climate, topography, pattern of distribution of ground waters and geomorphological history. Climatic and geomorphologic features of Rhodesia are not conducive to the formation of high grade nickeliferous laterites following weathering of ultrabasic rocks. Climate and geomorphology are, nevertheless, variable enough within the country to account to the diversity in distribution pattern between the study areas.

12. Nickel derived from sulphide minerals behaves in the same way as that from silicates although differences in the rate of weathering between the two categories of minerals results in differences in the distribution that can be related to mineralization.

Chapter 6. APPLICATION OF CONCLUSIONS ON SECONDARY DISPERSION OF NICKEL AND ASSOCIATED ELEMENTS TO MINERAL EXPLORATION.

Using current procedures employed in geochemical prospecting for nickel anomalies are readily detectable. There is however, a problem of interpretation. The differentiation between anomalies derived from sulphide and silicate nickel is very difficult. One of the aims of the present project has been to improve interpretation of nickel anomalies, in particular with a view to being able to distinguish between nickel anomalies derived from ultrabasic rocks and sulphide ore deposits.

Much of the previous research work pertaining to geochemical prospecting for nickel has been concerned with differentiating one rock type from another. In 1952 Lakin, Almond and Ward suggested the application of geochemical soil analysis for nickel as a means of distinguishing between serpentinite and more acid rock types. Webb (1957) and Holman (1956) studied the distribution of nickel over kimberlite, basic schists and granite in Sierra Leone. More recently Jedwab (1959) correlated the nickel content of soil at two localities in the Congo with underlying kimberlite breccias.

In India, Anand Alwar and Banerjee (1963)

have described geochemical prospecting for nickel over the serpentinite in the Moreh area, Manipur State. Their work was however, confined to a study of the distribution of nickel in the weathered mantle over the serpentinite. In the Blue Mountain area of Jamaica geochemical prospecting investigations described by Hill (1961) have indicated a zone where the concentration of nickel in the soil over serpentinite is between 0.2 and 0.3%. This was considered by him to be anomalous. The nickel is associated with magnetite, which contains 0.2 to 0.5% nickel, and in some parts also occurs as nickelian serpentine.

Jacobson (1956) has distinguished between copper anomalies over copper sulphide ore deposits and over dolerite intrusions on the basis of the nickel content of the soil. Coope (1958) has described the secondary dispersion of nickel and copper from copper - nickel sulphide deposits and basic and ultrabasic rocks in Bechuanaland and Tanganyika. Nickel may be present in large amounts in ferromagnesian minerals of basic and ultrabasic rocks which do not contain sulphides. Similarly, copper may concentrate in basic rocks (Chapter 3). However, when sulphides are present nickel and copper tend to be concentrated in the sulphides and Coope concluded that in order to differentiate between

anomalies derived from sulphides, basic and ultrabasic rock it was necessary to consider the secondary distribution of nickel and copper together.

Coope detected dispersion trains of copper and nickel in stream sediments in Tanganyika approximately 3000 ft. long at maximum and he concluded that stream sediment sampling at half mile intervals with subsequent analysis of the minus 80 mesh fraction for Ni and Cu could be employed as a prospecting technique. In the relatively poorly developed drainage system in Bechuanaland Coope considered drainage reconnaissance to be generally inapplicable as the drainage trains he observed were of very limited length.

A. Application of drainage reconnaissance in geochemical prospecting for nickel in Rhodesia and Zambia.

In Rhodesia, sampling of the sediment in watercourses at half mile intervals and subsequent analysis for Ni can indicate the position of ultrabasic rock masses. Analysis of the samples for Cu helps to show right at the start whether there are any sulphides present in the ultrabasic rocks. However, the lack of a Cu anomaly does not necessarily mean there are no nickel sulphides associated with the ultrabasic rocks.

There has been no opportunity to appraise the distribution of nickel and copper in the drainage around the nickel - copper sulphide deposit of the Empress prospect nor around the nickel arsenide deposits in the environs of the Noel Nickel mine because of contamination. It is however, probable that a similar technique to that outlined in the preceding paragraph could give an indication of the positions of the deposits but in view of the relatively short drainage trains detected by Coope in Bechuanaland (not more than 1000 ft.), a closer sample interval may be required in areas like the Noel than the minimum needed in the higher rainfall areas in the Rhodesian Midlands. It has been shown that nickel is dispersed over greater distances in wet climates than in relatively dry areas.

For areas physiographically similar to Kalumbila the data of this investigation suggests that sampling of the swampy waterlogged parts of the dambos may be more valuable than the sampling of stream sediment insofar that information about the amounts of metals entering the dambo in the ground water is thus obtained. It is however, still necessary to analyse for Ni and Cu to differentiate between nickel derived from sulphides and silicates. A suitable procedure could be to collect, at each site along the drainage way, samples of dambo soil

from the lowest point of the open dambo either side of the stream channel in addition to a sample of the sediment in the channel. In order to detect the features of the type observed at Kalumbila a sample interval of one quarter of a mile could be used. Such a procedure could lead to the detection of not only outcropping deposits but also blind (non outcropping) deposits.

B. Geochemical soil surveys.

Having delineated areas of interest by means of drainage reconnaissance, geochemical soil surveys should be carried out in order to delimit the anomalies. Large amounts of Ni present in residual soils overlying serpentinite and subcutcropping nickel sulphide and/or arsenide mineralization are detectable by analyzing samples collected from a depth of 12 in. or less depending on the terrain. In areas of skeletal soil and where there has been little chemical weathering samples can be collected nearer surface. In order to locate anomalies of the type described in this thesis a sample interval of 100 ft. along lines 500 ft. apart at right angles to the general strike of the country rocks is convenient and will provide a minimum of two to three anomalous samples along more than one traverse

line.

Ni in amounts up to 0.5% in soils over serpentinite is not unusual but such amounts in soils over rocks other than serpentinite are strongly anomalous. Dispersion of nickel from nickel sulphide and/or arsenide ore minerals usually results in strongly anomalous amounts of Ni in the soil overlying the ore deposit in rocks other than ultrabasics. The dispersion of the element is being effected under the influence of the prevailing physico-chemical conditions as discussed in the preceding chapter. The significance of an anomaly of a given magnitude depends on the position of the fresh ore relative to surface, the size and tenor of the mineralization and the climate.

Interpretation and definition of the anomaly source can be aided by the analysis of the same samples for Cu. There are no known deposits of sulphide nickel without associated copper. The association of copper and nickel in the Perseverance and Maritzani mineralizations (in ultrabasic rocks) and in the Empress, Bare Bottom Hill and Kalumbila areas (in more acid rocks) has been described. The use of copper in geochemical prospecting for sulphide deposits over ultrabasic and basic rocks has been described by Coope and successfully employed by the companies actively engaged in mineral exploration in Central Africa. Coincident high Ni and

Cu values in residual soil are indicative of underlying sulphide mineralization in both serpentinite and other more acid rock types.

Anomalous amounts of As coincident with anomalous amounts of Ni have been shown to indicate underlying nickel arsenide mineralization in the semi-arid conditions in the environs of the Noel Nickel mine and in the higher rainfall Maritzani area.

No previously published accounts of the use of selenium as a pathfinder in the search for sulphide deposits in Africa are known. Differentiation between gossans derived from sulphides and other primary ferruginous minerals has been made on the basis of the selenium content (Sindeyeva, 1955). In 1957 Leutwein and Starke suggested that the element could be used as a pathfinder to selenium rich sulphide ores. Near-surface soil over suboutcropping mineralization, not only in serpentinite at Perseverance but also in more acid rocks at Empress and in the environs of the Noel Nickel mine has been found to contain anomalous amounts of selenium. At Maritzani and Kalumbila the selenium content of the soil is low and the element is erratically distributed. Ore samples from these two latter mentioned areas have been found to contain 4 and 3 ppm selenium respectively. This is substantially higher than the

normal for the host rock types (0.1 ppm and 1.0 ppm for ultrabasic igneous rocks and shales respectively). The lack of any well defined anomaly at Maritzani or Kalumbila is thought to be due to either the non outcrop of the mineralization or the weathering conditions locally. Although some further research is required the data presented shows clearly that the selenium content of near-surface soil can be used in geochemical prospecting for sulphide nickel. Anomalous amounts of selenium in residual soils in conjunction with large amounts of Ni are indicative of nickel sulphide mineral deposits. Selenium analyses can be extremely valuable in distinguishing between mineralized and barren serpentinite.

Where the geology is unknown these additional analyses are vital to the full interpretation of the anomaly as they are over ultrabasic rocks. Over more acid rocks they are desirable though not essential. It is recommended that in addition to analysis of samples , collected 3-12 in. below surface, for Ni, at least one of the three pathfinders (Cu, As or selenium) is determined as a standard procedure in geochemical soil surveys in the search for nickel.

C. Detailed prospecting and prospect appraisal.

As already emphasized, unlike the anomalous features of secondary dispersion from mineralization in rocks other than ultrabasic, secondary dispersion features indicative of deposits of nickel sulphides and/or arsenides in or adjacent to serpentinite are, on the basis of Ni content alone, very weak. There is need to improve the contrast between mineralized and non mineralized serpentinite. It has been found possible to achieve this aim on the basis of the exNi content of weathered rock and by using associated elements as pathfinders (as already mentioned).

The exNi content of weathered serpentinite over mineralization is anomalous compared to the exNi content of non mineralized serpentinite in the same study area (e.g. Maritzani) yet there is no similar distribution in the overlying soil. Consequently the distribution of exNi in soil cannot be used for geochemical prospecting for nickel in many instances. It can however, be used in some areas (for example, the environs of the Noel Nickel mine). The exNi content of soil over nickel arsenide mineralization has been shown to be anomalous and it is believed that analysis

of soil for exNi can be applied in geochemical prospecting in a semi-arid climate but is not recommended for use generally in a detailed appraisal of an anomaly.

However, it has been shown that exNi in weathered bedrock can be used as a guide in the interpretation of nickel anomalies. Within a given area the exNi content of weathered rock (collected, for example, either at the base of pits or at greater depths in wagon drill holes) is greater over deposits of sulphide minerals in serpentinite than over barren serpentinite. The contrast, although only two to three - fold, has been shown to be very significant, particularly when related to pH. exNi in weathered bedrock in amounts two to three times the normal exNi content of weathered non mineralized bedrock (as the writer observed at Maritzani) is indicative of subjacent mineralization, especially if the pH in the weathered bedrock of anomalous exNi content is less than the normal pH in comparable background materials.

The exNi test can be applied in mineral exploration. Its use is not confined to weathered serpentinite; it has also been found applicable in more acid rock types at Empress and Bare Bottom Hill. Although the sampling of weathered bedrock clearly involves more practical problems than, say, soil sampling, the

analytical procedure for the determination of exNi is relatively simple and analyses can be easily carried out in the field. exNi analyses of weathered bedrock samples are recommended in detailed prospecting operations.

As far as the writer is aware there are no previously published accounts of differentiation between nickel anomalies derived from sulphide and silicate minerals on the basis of the form of the metal. While the writer has shown the application of the exNi test on weathered bedrock to be of value in differentiating sulphide and silicate nickel anomalies in Rhodesia it is clear that more research is required before the determination of nickel in this form can be extended to other areas. There is no apparent reason why the test cannot be used to advantage elsewhere.

More research on the distribution of exNi in soils under varying climatic conditions is also needed.

Other elements may have application as pathfinders. For example, antimony has been found associated with the Maritzani mineralization and mercury has been found present in slightly anomalous amounts in rock and soil samples containing anomalous amounts of ore metals, in the Perseverance, Maritzani, Empress and Noel areas. The writer has insufficient data to make any proposals for use of these elements as pathfinders

in the search for nickel sulphide ore deposits. Further research is required.

D. Biogeochemical prospecting.

Reports of researches into biogeochemical prospecting for nickel are common in the literature. As early as 1940 Rankama determined the nickel content of the leaves of birch trees growing on glacial drift covering nickel ore bodies in the Petsamo and Nivala areas of Finland. In Canada, Warren and Delavault (1954) studied the variations in the nickel content of some trees and found evidence in support of biogeochemical prospecting for nickel. In the following year (1955) Walenczak published the results of analyses of the ash of Betula vericosa collected over gabbro, serpentinite, gneiss and brown - red altered serpentinite in Poland. The plants over the last mentioned rock type contained the greatest amount of nickel (0.20%). Nickel determinations are given for the ash of 10 other plant species; the highest results were 0.35% nickel in the ash of Alnus glutinosa and 0.31% nickel in the ash of Alnus incana. It is interesting to note that the level of nickel in the ash of these plants is of the same order as the results obtained (on plants growing over serpentinite)

in the present study. Aleskovskii, Mokhov and Spirov (1959) in the USSR and Miller (1961) in the USA have also conducted investigations into the biogeochemical method of prospecting for nickel and concluded that the method can be a useful tool in mineral exploration.

A detailed study of the distribution of nickel in four species in the Perseverance area has led to an indecisive conclusion. While the nickel content of the leaves and bark of plants growing over the mineralization at the margin of the serpentinite mass is higher than that of plants growing over immediately adjacent serpentinite it is less than that of plants growing further away from mineralization over serpentinite. The high nickel content in the plants growing over barren serpentinite can be attributed to the environment (the plants are on the crest and upper slopes of a hill) but there is still insufficient data to allow any recommendation that plant analyses for nickel can be used to differentiate sulphide from silicate nickel within an ultrabasic body although there is some theoretical evidence that this could be possible.

The biogeochemical method has, however, been used successfully to delimit the ultrabasic mass at Perseverance and the mineralization in amphibolite at the Empress prospect.

At Kalumbila, the nickel content of some plants growing over the projected suboutcrop of the mineralization in block 205 has been found to be greater than that of plants of the same species growing away from any known mineralization. The anomalous amounts of metal (nickel and copper) are in the ash of specific parts (leaves and bark) of plants growing in an area where there is a partially indurated laterite sheet a few feet below surface and where the soil above the laterite contains no anomalous amounts of the ore metals. The high metal content of the plants is thought to be derived from anomalous amounts of available nickel below the laterite and originating from suboutcropping mineralization. To be able to locate such areas without pitting (and pitting through laterite is manifestly more difficult than through a non lateritized profile) is clearly of practical importance. It is proposed that in areas physiographically similar to Kalumbila and with a comparable soil cover the vegetation could be sampled at the same time as the soils and analyzed for nickel. It is believed that the results so obtained would be more valuable than the geochemical data alone.

E. Other factors of practical significance.

In the weathered rock profile over mineralized serpentinite the Ni content increases with depth into the weathered bedrock. This is in contrast to the normal distribution over barren serpentinite where the Ni content is a maximum in the top of the weathered bedrock. Use may be made of such observations in interpreting nickel secondary dispersion patterns.

In discussing and interpreting many of the observed distributions the movement of ground water has been considered. Important distributions are believed to have resulted from hydromorphic dispersion and without knowledge of ground water movement they are difficult to interpret. It is recommended that whenever possible during geochemical sampling a careful note of the movement of the groundwater should be made.

Attention has been drawn to differences in local background and it remains here only to re-emphasize the necessity of taking this into account in any geochemical prospecting programme.

SUGGESTIONS FOR FUTURE RESEARCH.

This investigation of the secondary dispersion of nickel has given rise to several problems of interest. They are:-

(i) The form of nickel in stream sediment in streams draining both barren and mineralized serpentinite.

(ii) The nature of the associations of nickel and iron and nickel and organic matter.

(iii) The effect of extreme pH variations on the distribution of exNi and interpretation of exNi anomalies.

(iv) The distribution of exNi in areas of non nickeliferous sulphides in ultrabasic rocks (if such deposits can be found).

The determination of the variation in nickel content in mafic and ultramafic rock-forming silicate minerals in relationship to sulphide mineralization, especially in ultramafic rocks, is of interest and possibly applicable in mineral exploration. The findings of Vogt (cited on page 71) have prompted this suggestion.

Several suggestions for future research have resulted from the writer's rather limited investigation

of the distribution of associated elements, selenium in particular. Attention is drawn to a number of problems.

(i) A greater understanding of the distribution of selenium in soils.

(ii) The distribution of selenium in stream sediment with particular emphasis on its possible use as a pathfinder in drainage reconnaissance in the search for magmatic or hydrothermal sulphide deposits in tropical and sub-tropical terrain.

(iii) The movement of selenium in the biochemical cycle and the value of this element as a biogeochemical pathfinder.

(iv) The distribution of arsenic and antimony in both barren and mineralized areas of the type described in this thesis.

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APPENDIX I. Sources of information on the geology of the study areas.

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Figure 2.

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APPENDIX II The following is a reprint of Technical Communication No. 28.

Determination of Nickel in Soil and Sediment Samples

Abbreviated Operating Instructions

Procedure:

1. Weigh 0.2 g. of sieved sample into a 16 x 150 mm. test tube.
2. Mix with 1 g. of potassium bisulphate and fuse.
3. Leach with 5 ml. of 0.5M-hydrochloric acid.
4. Pipette a 2 ml. aliquot into 5 ml. of buffer solution contained in a test tube (18 x 180 mm.) previously calibrated at 5, 7, 8, 10, 12, etc. to 20, 22 ml.
5. Add 1 ml. of α- furildioxime solution, cork the tube and shake vigorously for 2 min.
6. Compare with standards.
7. If above the top standard dilute with a known volume of benzene until within the range.

   p.p.m. = 12.5 x (ug. of nickel in matching standard) x (ml. of solvent phase).

Standards:

To each of eleven test tubes, calibrated at 5, 7 and 8 ml., and containing 5 ml. of buffer solution, add respectively 0, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 ug. of nickel and dilute to 7 ml. with 0.5M-hydrochloric acid. Add 1 ml. of α - furildioxime solution and shake vigorously for 2 min.

Reagents:

1. Buffer solution: dissolve 20 g. of tri-ammonium citrate in water, add 130 ml. of ammonia (s.g. 0.880) and dilute to 1 litre with water.

2. Potassium bisulphate: fused, powder.

3. 0.5M-hydrochloric acid: 20 ml. of acid + 420 ml. of water.

4. α- furildioxime: 0.3 g. dissolved in 90 ml. of benzene and 10 ml. of ethyl alcohol (absolute).

5. Standard nickel solution: 100 ug. of nickel per ml. - dissolve 50 mg. of nickel (metal, powder) in 10 ml. of 25% nitric acid and dilute to 500 ml. with water. 5 ug. of nickel per ml.- dilute 5 ml. of the 100 ug. per ml. solution to 100 ml. with 0.5M-hydrochloric acid.

Remarks:

1. The method as described will cover the range 1-900 p.p.m. By using a sample aliquot of 0.1 ml. at Stage 4 of the Procedure, the range can be extended to 18,000 p.p.m. If this size of aliquot is used dilute to 7 ml. with 0.5M-hydrochloric acid before proceeding to Stage 5.

2. Results can be obtained within $\pm$ 20% at the 95% confidence level over the range 5 - 18,000 p.p.m.

3. 80 - 100 samples can be analysed per man-day.

4. Copper will interfere by giving a brown colour when the copper to nickel ratio exceeds 30:1. When maximum tolerance towards this metal is desirable, a solution containing 400 g. of the citrate per litre should be treated with a carbon tetrachloride solution of dithizone until free from copper; use 50 ml. of this solution instead of weighing 20 g. of the solid reagent.

5. If the zero standard is yellow the buffer solution must be purified with respect to nickel. This may be accomplished by using dithizone as in 4, above, but with the pH $>$ 8.9, or by extraction with α-furildioxime, using a solution as in Reagents 4 but containing carbon tetrachloride in place of benzene.

6. Ferrous ions form a purple complex with α-furildioxime and may occur from inadequate fusion of the sample with potassium bisulphate.

7. The buffer solution should have a pH value of 10.3± 0.1.

8. For further information see R.E. Stanton and J. Coope, Trans. Instn. Min. Metall., Lond.,.1958-59, 68, 9-14.

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August, 1962.

APPENDIX III The following information has been supplied by R.E. Stanton and A.J. McDonald.

Provisional method for the determination of selenium in soils and sediments.

Procedure:

1. Weigh 1g. of sieved sample into a beaker (50 ml.)
2. Add 10 ml of acid mixture.
3. When any effervescence has subsided, add further 10 ml. of acid mixture.
4. Evaporate to fumes of perchloric acid and remove when the volume of the solution is between 1 and 2 ml.
5. When cold, add 10 ml. of 6M hydrochloric acid and heat to boiling.
6. Filter the hot solution through a Whatman No. 540 paper, and wash the beaker and residue with 6M hydrochloric acid.
7. Add 2 ml. of arsenic solution and mix.
8. Add 5 ml. of hypophosporous acid and boil the solution gently until the precipitate has flocculated.
9. Filter through a Whatman No. 540 paper, and wash the paper and precipitate with 6M hydrochloric acid.
10. Place the filter paper in the precipitation beaker and add 20 ml. of acid mixture so that the paper is completely immersed.
11. Heat to destroy the paper, and when oxidation is complete evaporate to fumes of perchloric acid until the volume of the solution is between 1 and 2 ml.
12. When cold, transfer the solution to a test-tube (18 x 180 mm., calibrated at 4, 5, 10, 12, and 14. 5ml.).
13. Add 1 ml. of EDTA solution and 0.05 ml. of indicator solution.

14. Add 10M ammonia solution until the colour of the indicator is orange.

15. Dilute to 10 ml. with water.

16. Add 2 ml. of buffer solution.

17. Add 0.5 ml. of 3,3'-diaminobenzidine solution.

18. Mix, and leave to stand for 30 min.

19. Add 2 ml. of 10M ammonia solution.

20. Add 2 ml. of benzene.

21. Cork the tube and shake it vigorously for 30 sec.

22. Compare with standards.

23. If the intensity of colour from the sample is greater than that of the highest standard, dilute the solvent phase with benzene and again compare with the standard series.

Standards:

1. Pipette 0, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, 30, 40, 60, 80 and 100 ug of selenium, respectively, into test-tubes (18 x 180 mm. calibrated at 10, 12 and 14.5 ml.).

2. Treat as described in stages 13-21 of the Procedure, omitting stage 14.

N.B. Store in the dark when not in use.

Reagents:

1. Perchloric acid: 60%, $^{W}/_{W}$, A.R.

2. Nitric acid: Sp.gr. 1.42, A.R.

3. Acid mixture: Mix 800 ml. of nitric acid with 200 ml. of perchloric acid.

4. Concentrated hydrochloric acid: Sp.gr. 1.18, A.R.

5. 6M hydrochloric acid: Mix 240 ml. of the concentrated acid with 200 ml. of water.

6. Arsenic trioxide.

7. Sodium hydroxide: Pellets, A.R.

8. Arsenic solution: Dissolve 250 mg. of arsenic trioxide and 2g. of sodium hydroxide in 200 ml. of water.

9. Hypophosphorous acid: 50% $^{w}/_{w}$.

10. EDTA solution: dissolve 25g. of ethylenediaminetetraacetic acid (di-sodium salt) in 500 ml. of water.

11. Indicator solution: Dissolve 100 mg. of the sodium salt of m-cresol purple in 100 ml. of water.

12. Ammonia solution: Sp.gr. 0.880, A.R.

13. 10M ammonia solution: Mix 550 ml. of ammonia with 450 ml. of water.

14. Ammonium formate: A.R.

15. Formic acid: Sp.gr. 1.22, A.R.

16. Buffer solution: Dissolve 60g. of ammonium formate in about 600 ml. of water, add 200 ml. of formic acid followed by 6M hydrochloric acid until the pH is 1.6. Dilute to 1 litre with water.

17. 3,3'-diaminobenzidine solution: Dissolve 0.125 mgs. of the tetrahydrochloride in 25 ml. of water. Prepare freshly each day and keep in a refrigerator when not in use.

18. Benzene: Crystallisable grade.

19. Standard selenium solutions: 100 ug. of selenium per ml. Dissolve 50 mg. of selenium in 10 ml. of concentrated nitric acid, boil gently to expel brown fumes, cool and dilute to 500 ml.

    5ug. of selenium per ml. - dilute 5 ml. of the 100ug. per ml. solution to 100 ml. with water.

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