A

THESIS

entitled

GEOCHEMICAL DISPERSION PATTERNS RELATED TO KIMBERLITE INTRUSIVES IN NORTH AMERICA

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ABSTRACT

Geochemical investigations have been made on the distribution of selected elements, principally Nb, Cr, Ti, Sr, Zr, Ni, P, V, Fe, Co, Ba, Mn and Mg, in the bedrock and soils over a diamondiferous kimberlite and non diamondiferous mica peridotite at Prairie Creek, Arkansas. The dispersion of selected elements in soil and drainage components downslope from kimberlite was studied at the nearby American Mine area. Very limited comparative data was obtained over an apparently non diamondiferous kimberlite at Buell Park, Arizona. In both areas the dominant country rocks are sialic sediments.

The results obtained illustrate trace element content of the Prairie Creek kimberlite to be similar to that of kimberlites from other parts of the world: i.e. containing high concentrations of elements characteristic of ultrabasic and alkalic rocks. So far as has been determined, the composition of the Prairie Creek kimberlite and mica peridotite are very similar. Enrichment of the "alkalic" elements in the Buell Park kimberlite was not found in the limited number of samples studied. This suggests the name is a misnomer.

Investigations in Arkansas have shown that the elements have been redistributed during soil formation, with a marked tendency for many of them to be concentrated in iron-manganese nodules. Comparison of losses and gains in the kimberlite soil profile are made relative to constant Sr, and the mechanisms of redistribution are discussed. In Arizona where chemical weathering is not so marked, the elements are little redistributed.

Dispersion in the drainage and freely drained soils in Arkansas is dominantly by mechanical agencies. However, appreciable saline aureoles may have been developed in the recent past when the water table was higher than at present. Some saline dispersion of certain elements occurs in seasonally waterlogged soils of the present day. Dispersion in Arizona is almost entirely mechanical

Geochemical prospecting methods for kimberlites are shown to be particularly useful in Arkansas. They may find application in many other areas, especially when used to complement existing procedures.

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INTRODUCTION

Diamonds in economic concentrations are obtained from kimberlite rocks or from alluvial or eluvial deposits originally derived from kimberlite. For many years prospecting for primary diamond occurrences has been based on the detection in the drainage system of heavy mineral suites characteristic of kimberlites (containing in particular pyrope garnet, chrome diopside and picro ilmenite), and on investigation of structures observed on air photographs. Once a kimberlite has been located its diamondiferous nature is tested by bulk sampling.

There is no doubt that these established methods, where applicable, are efficient and have proved themselves highly successful. However, by their very nature they are subject to certain limitations. In particular:

(1) In areas where the streams are flanked by flats or the head waters are swampy (e.g. on peneplains), heavy minerals are filtered out by vegetation and may not reach the streams in sufficient quantities to be detectable by samples of practical size.

(2) Some kimberlites contain extremely low concentrations of the common characteristic minerals and therefore will not be readily detected by examination of heavy mineral suites.

The problems then are firstly to assess the applicability of geochemical methods in prospecting for kimberlites, especially in areas where conventional methods are not applicable; and secondly, to differentiate diamondiferous kimberlites from similar non-diamond bearing rocks.

The possibility of using Ni analyses of residual soils to delineate kimberlite in areas of less basic rocks has been mentioned by various writers (Holman, 1956; Jedwab, 1958 and 1959; Alcard, 1959). Litinskiy (1961 and 1963) found anomalous concentrations of Ti, Nb, as well as Ni and Cr in kimberlite and the associated soil debris in Yakutsk, Siberia. Webb (1956) records soils over kimberlite in Sierra Leone to contain an appreciable quantity of montmorillonite and to have a higher base exchange capacity than soils over the adjacent country rocks. This gives rise to anomalous cxZn concentrations in soil over kimberlite. Anomalous concentrations of Zn were also detected in streams draining kimberlite in Yakutsk by Kosolopova and Kosolopov (1963). Zinc was not present in anomalous amounts in the kimberlite itself but was contained in the limestone wall rocks at the kimberlite/limestone contact.

The main objectives of the present study are fourfold:

(1) To supplement previous workers' investigations on the minor element content of kimberlite.

(2) To investigate the distribution of selected elements in the weathering and erosion products of kimberlite, and to gain an understanding of the factors controlling the dispersion of these elements.

(3) To assess the applicability of geochemical prospecting methods for kimberlite, especially in areas where conventional methods are not applicable.

(4) To devise methods of differentiating anomalies due to kimberlite from those due to other igneous rocks and to differentiate diamondiferous kimberlites from similar non-diamondiferous rocks.

The primary area chosen for investigation was in south west Arkansas, U.S.A., where previous exploration by Selection Trust Ltd., had shown diagnostic minerals to be absent from kimberlites. Moreover the largest intrusion, the Prairie Creek pipe, consists of both diamondiferous kimberlite and non-diamondiferous mica peridotite and tuff. The drainage from this intrusion is so heavily contaminated due to past mining activity that dispersion studies had to be conducted at the nearby American Mine area, which is typical of three other small kimberlites in the region.

Very limited comparative studies were made in Arizona at the non-diamondiferous Buell Park and Garnet Ridge East areas. Unlike the kimberlites in Arkansas, the typical "indicator" minerals are present in Arizona.

There is a considerable climatic difference between Arkansas and Arizona. In the former area the rainfall is 30 to 40 inches per year and the mean average temperature range 28°F to 95°F. In Arizona, rainfall is about 10 inches per year and the average temperature range 25°F to 68°F.

PRESENTATION OF DATA

Chapter 1: The geology and physiography of the study areas in Arkansas and Arizona are described.

Chapter 2: The general geological and petrological features of kimberlites are described. The major and minor element content of kimberlites are reviewed and suitable elements selected for investigation.

Chapter 3: The field and laboratory procedures are described and the nature of the attacks discussed. Sampling limitations are briefly mentioned.

Chapter 4: The morphology and mineralogy of soils over the kimberlitic and country rocks are described. The distribution of selected elements in the soil profiles is illustrated. In Arkansas the elements are classified into three groups depending upon their vertical distribution in soils over the Prairie Creek kimberlite. The results are discussed in terms of mobility and mode of occurrence of the elements.

Chapter 5: The distribution of an element(s) selected from each of the groups detailed above in soils at the American Mine are illustrated and discussed. Investigations are made both in vertical section downslope from kimberlite suboutcrop, in areal extent about the American Mine and on the flood plain of American Creek.

Chapter 6: The threshold for selected elements in the Arkansas drainage is evaluated. The optimum size fractions established and the distribution of selected elements in the American Mine drainage presented. The results are discussed in terms of mode of occurrence of the elements and factors influencing the length of anomalous patterns. The variation of selected elements with particle size in stream sediments near kimberlite in Arizona are given.

Chapter 7: The distribution of Ni and exNi and exMg in a limited number of samples taken from the Quaternary alluvium about the Prairie Creek pipe is illustrated and discussed.

Chapter 8: The fundamental reasons for the observed distribution of the elements are discussed; and conclusions drawn on the mechanisms of secondary dispersion operating in the study areas.

Chapter 9: Semiquantitative analyses for the heaviest 47 naturally occurring elements (excluding Ru, Ta, Rh, Xe and Kr) of the periodic system are given for the Buell Park kimberlite tuff, the ultrabasic rocks of Arkansas and the soil and sediment associated with kimberlite in Arkansas. Elements for potential use in exploration are selected and the rare earth distributions discussed.

Chapter 10: The applications of the results to prospecting in Arkansas, Arizona and elsewhere are discussed.

Chapter 11: The main conclusions are summarized and suggestions for future research proposed.

Summaries are given at the end of Chapters 4, 5, 6, 7, and 9.

ACKNOWLEDGEMENTS

The research described in this thesis forms part of the general research in geochemical prospecting undertaken at the Applied Geochemistry Research Group of Imperial College, London, under the auspices of Professor J.S. Webb. The writer is grateful to the analytical and academic staff of this establishment, but most especially to Dr. J.S. Tooms under whose supervision the research was conducted. The assistance of Dr. G.D. Nicholls of Manchester University with the mass spectrograph determinations is acknowledged.

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Particular thanks are due to the owners of (a) the former American Diamond Mine (A.F. Flournoy, M. Hudson and H. Bernstein), (b) the Arkansas Diamond Mine (Arkansas Diamond Trust No. A.), (c) the Crater of Diamonds (H. Miller), and to various other local land owners in the vicinity of these deposits for permission to work on their respective properties. The cooperation of Mr. and Mrs. Johnston, lessees of the Arkansas Diamond Mine is appreciated.

Permission of the Navajo Tribal Council to visit Buell Park is gratefully acknowledged.

CHAPTER 1

DESCRIPTION OF STUDY AREAS

1.1 ARKANSAS

1.11 Location

The Arkansas kimberlites are located several miles south west and south of Murfreesboro and approximately 95 miles south east of Little Rock, Arkansas, U.S.A. (Fig. 1.1).

There are four known areas of kimberlite:

1.	The Prairie Creek Area :	Lat.	34° 02' 01" N
		Long.	93° 40' 24" W
2.	The American Mine :	Lat.	34° 03' 12" N
		Long.	93° 38' 24" W
3.	The Kimberlite Mine :	Lat.	34° 03' 22" N
		Long.	93° 38' 39" W
4.	The Black Lick Prospects :	Lat.	34° 02' 48" N
		Long.	93° 38' 36" W and
			93° 38' 45" W.

1.12 Regional Features

1.121 Geology

The area has been mapped in some detail by Miser and Ross (1923) and Miser and Purdue (1929). Their interpretation is presented as Fig. 1.2. A geological column illustrating the salient rock types comprises Table 1.1.

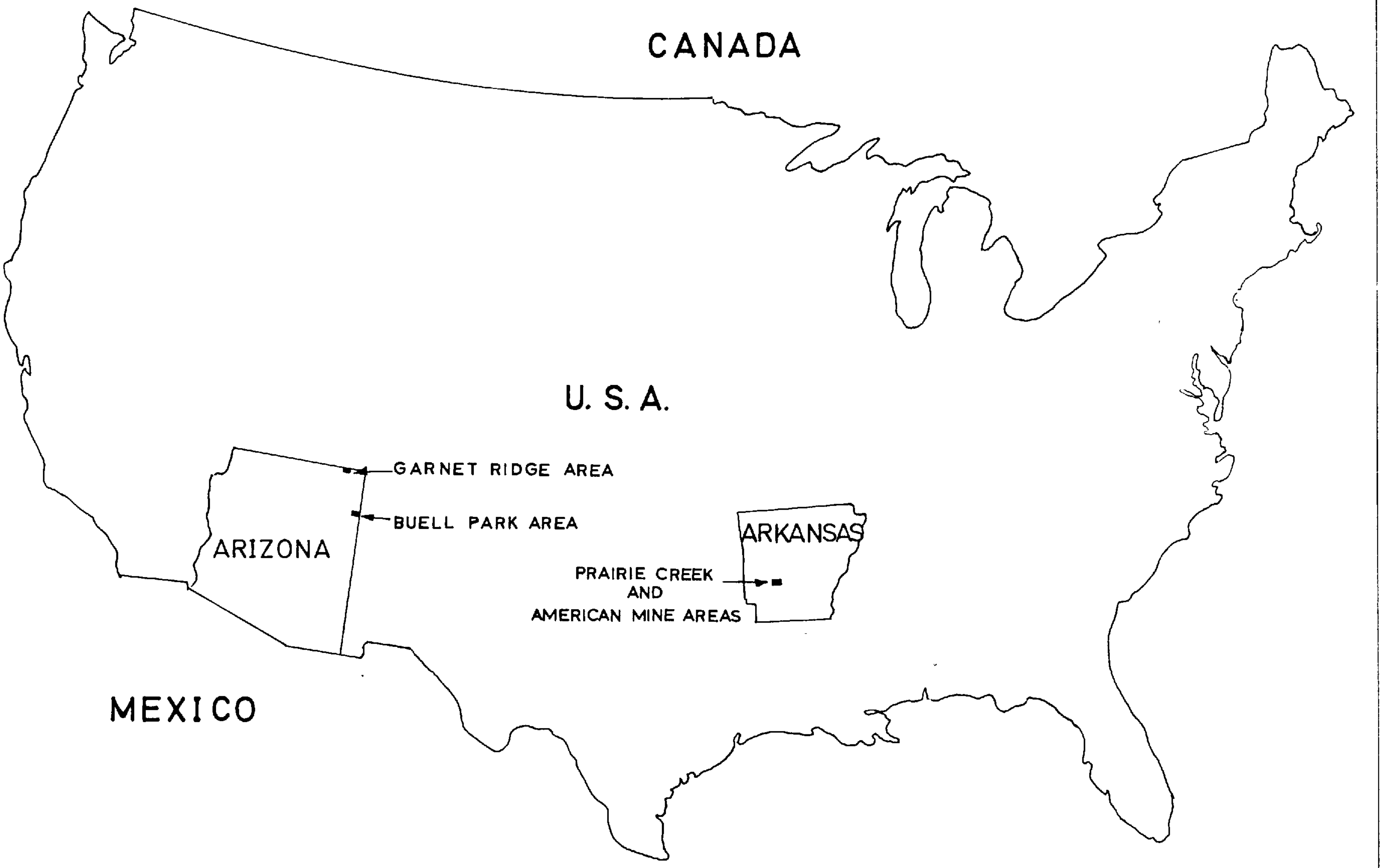


FIG. 1·1 LOCATION OF THE STUDY AREAS

Table 1.1 Geological column in the vicinity of kimberlites, Arkansas

QUATERNARY		Rudaceous to argillaceous alluvial terraces and valley fill
	UNCONFORMITY	
CRETACEOUS	Brownstone Marl Formation	Marls
	Tokio Formation	Interbedded conglomerate and clay. Basal conglomerate contains pebbles of peridotite. (Iron staining and cementation at the American Mine).
	Woodbine Formation	Conglomeratic clays and water laid tuffs. (Absent in the study areas.)
	UNCONFORMITY	
	Intrusives	Peridotite and diamondiferous kimberlite breccias.
	UNCONFORMITY	
	Trinity Formation	Clays and siltstones with interbedded gravels, limestone and marls. Dips gently to the south.
	UNCONFORMITY	
PALEOZOIC		Sediments, highly folded.

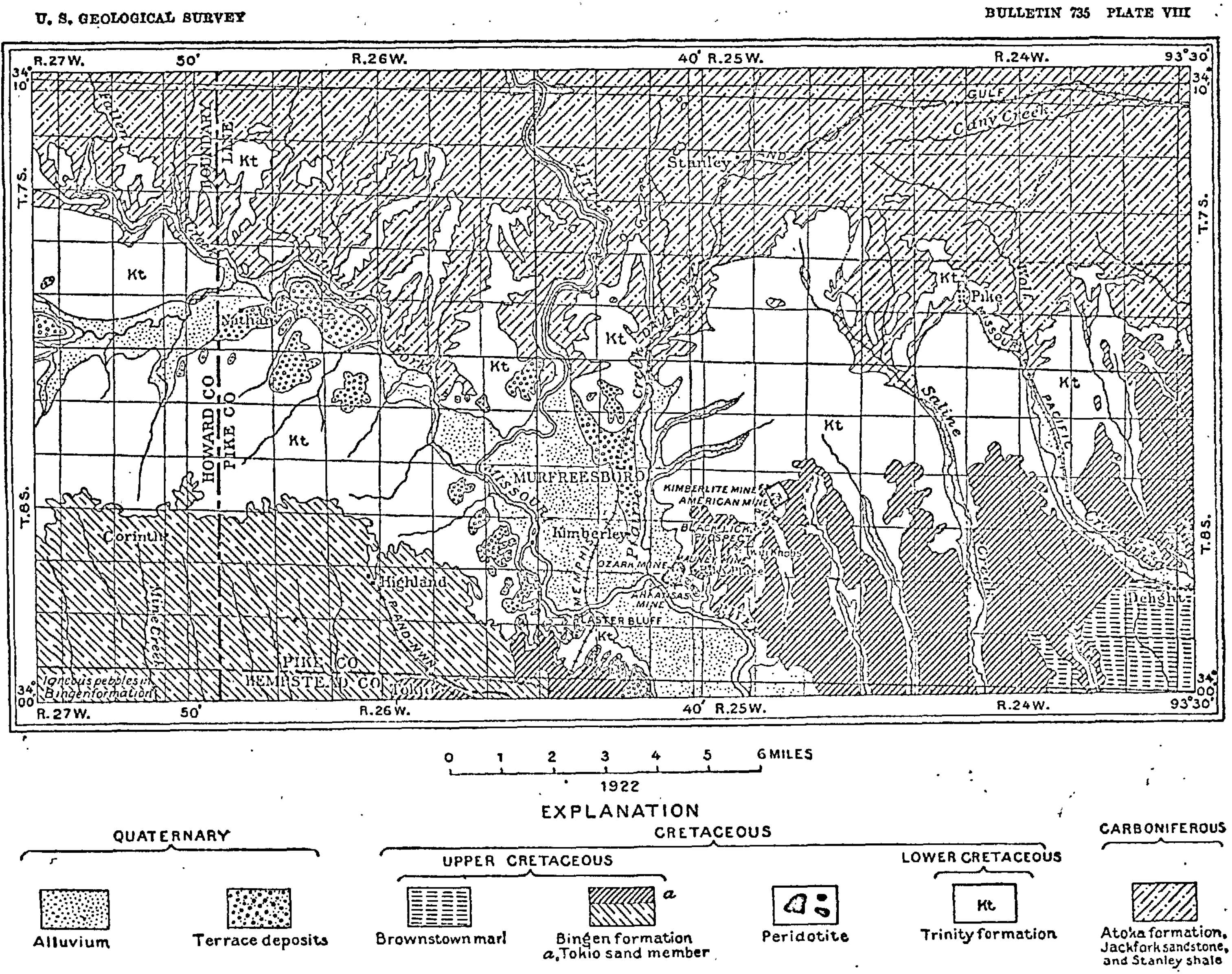


FIGURE 1.2: GEOLOGIC MAP OF PARTS OF PIKE, HOWARD, AND HEMPSTEAD COUNTIES, IN SOUTHWESTERN ARKANSAS after Miser and Ross, (1923).

1.1211 Paleozoic Rocks

These rocks outcrop about 4 miles to the north of the kimberlites and are largely composed of carboniferous argillaceous and arenaceous sediments. Older sediments, particularly novaculite (chert) form the Ouchita Mountains 20 miles further north.

The Paleozoic rocks have been highly folded with their axial plains striking E-W. Prominent mineralised strike faults are also present, often with a length in the order of 40 miles.

1.1212 The Trinity Formation (Lower Cretaceous)

These form the dominant country rocks and consist of loosely consolidated clay, sand, gravel, limestone, gypsum and celesite in order of decreasing abundance.

The limestones occur as two thin bands; the older near the base of the formation and the younger towards the middle. Their nearest outcrop to the kimberlite is $\frac{3}{4}$ mile downstream from the American Mine.

In the upper parts of the formation, near the American Mine, clay and silt are common. Near the base of the formation sand and gravel are prominent.

The Trinity formation unconformably overlies the Paleozoic basements and dips to the south between 60 and 100 feet per mile.

1.1213 Intrusive Rocks

Kimberlite and peridotite intrude the Trinity formation at four known localities and are described in detail later in the chapter. Their age is post Trinity and probably contemperaneous with the Woodbine tuff; although some activity may have persisted until early Tokio times.

1.1214 The Woodbine Formation

Although this rock type does not occur east of the Little Missouri River, extensive deposits, having a strike length of 150 miles, are present to the west. The formation is composed of gravels, clay and basic alkalic tuff.

Pirsson (1915) recognised two main types of pyroclastics: (1) lithic tuff, and (2) vitric tuff. In addition, cobbles of phonolite have been found in Mine Creek (about 11 miles from the Prairie Creek area), and other places (Ross et al, 1929).

The sources of the Woodbine tuff are unknown, although three "volcanoes" were encountered in drill holes near the western extremity of the formation (Ross et al, 1929). Ross suggests that in south west Arkansas the vents are covered by the later Tertiary and/or Quaternary deposits.

A brick red bentonitic or kaolinitic $B_{2.1}$ horizon is generally developed over the tuffaceous parts of the Woodbine formation.

1.1215 The Tokio Formation

This formation unconformably overlies the Woodbine formation to the west of the Little Missouri River and transgresses across the Trinity formation to the east. It is composed largely of sand, gravel and clay.

The gravel beds are interspersed throughout the formation, the lowest being recorded at the base. These are composed of novaculite and quartz pebbles parts of which, especially near the American Mine, are cemented with a ferruginous cement.

In addition, to the east of the Little Missouri River, several small deposits of kaolin are recorded. Investigations by Ross et al (1929) shows them to be derived from volcanic dust, originally of phonolitic composition.

At the base of the Tokio formation, near Riley Place and Twin Knobs (Fig. 1.2), altered serpentine and peridotite are recorded. Miser and Ross (1923) suggest these ultrabasics to be derived from the nearby kimberlite pipes by explosive ejection.

1.1216 Tertiary Deposits

These are absent from the immediate study area. However, extensive deposits are recorded from some 30 miles to the south and extending to the Gulf of Mexico. This age has also been assigned to some small terrace gravels on the Paleozoic rocks.

1.1217 Quaternary Deposits

These occur as terrace gravels, sands and clays on the flanks of the major rivers at heights of 35 to 150 feet above the mean water level.

Recent alluvium occupies the floors of many of the major and not so major rivers. The deposition of this alluvium is thought to be due to vertical movements of the land surface during mid Quaternary times and is discussed later.

1.122 Topography and Drainage

The area may be divided into three main physiographic units:

(1) The Ouchita Mountains which comprise a series of E-W striking ridges whose main drainage is roughly E-W but which are

transected by the head waters of the antecedant trunk streams.

(2) The Athens Plateau which is a greatly disected southerly dipping plateau of Carboniferous rocks. The main drainage is via a series of N-S antecedant trunk streams with subsequent E-W streams dominantly located in the shale members.

(3) The Gulf Coastal Plain which consists of southerly dipping Cretaceous sediments in the north and Tertiary sediments in the south. The harder gravel members of the Cretaceous rocks weather to form prominant cuestas (Davis, 1899) particularly west of the Little Missouri River. East of the Little Missouri River where the Tokio gravels are not so thick, the cuestas are dissected by southerly flowing streams.

Drainage of the Cretaceous rocks is dominantly to the south along the dip slope of the beds. However, near the junction with the Paleozoics, where the edges of the beds are exposed, numerous lateral streams flow along the strike of the beds and short obsequent streams down the faces of the cuestas.

Except near their headwaters the major valleys are wide, flat bottomed and steep sided.

1.123 Climate and Vegetation

The climate is generally mild, free from intense cold in winter but hot (80 to 100°F) and humid in the summer.

Rainfall is often torrential and the 30 to 40 inches falls mainly in the late spring and winter. At such times the streams carry considerable quantities of detrital material.

Originally, most of the area was covered with forest or heavy undergrowth. However, the most fertile areas have now been cleared but the primeval forest still persists in many of the upland areas. Secondary growth preponderates in abandoned cleared areas.

A list of the dominant species of trees and shrubs on the various Cretaceous rocks (excluding the Woodbine formation and Trinity limestone) is presented on Tables 1.2 and 1.3. This data was compiled from information supplied by Dr. J.T. Bean of the Soil Conservation Society when he visited the field area. Generally, the most abundant trees are listed first.

There are differences between the vegetation observed on the upland and valley bottom areas and between the ultrabasic and acidic rocks. For example, on the alluvial areas species of trees prefering poorly drained soils predominate (e.g. water oak, wet land hickory, box elda, cedar and willows). In addition, there is a vigorous growth of secondary vegetation. On the upland soils pine and oak trees predominate.

Over the ultrabasic rocks, species typical of alkaline soils are common, e.g. osage orange, sweet clover, etc. Pine trees are stunted and depleted of needles, possibly due to a high concentration of toxic elements. Hickory trees are generally absent.

Slight differences are recorded between the individual trees over the Prairie Creek igneous rocks, for example, water oaks are more abundant over the peridotite than kimberlite and black jack oaks are common on the poor dry soil of the tuff.

1.124 The Physiographic History of the Area

The physiographic history of the area is summarised in chronological order in Table 1.5.

Table 1.2 Typical trees and shrubs developed over the igneous rocks of the Prairie Creek, American Mine and Black Lick Areas. (After Dr. J.T. Bean, Soil Conservation Society, Arkansas. Pers. Comm.)

Prairie Creek Area			American Mine	Black Lick
Peridotite	Kimberlite	Tuff	Kimberlite	Kimberlite
Chinkupen oak	Post oak	Post oak	Rattan vine	White oak
Water oak	Sweet gum	Black Jack oak	Water oak	Post oak
Post oak	Southern red oak	Winged elm	Osage orange	Winged elm
Southern red oak	Cherry bark red oak	Sweet gum	Black hickory	American elm
Sweet gum	Winged elm	Dwarf sumac	Flowering dogwood	Red mulberry
Loblolly pine	Red Mulberry	Box elda	Sasparus	Sugarberry
Devil's walking stick	Sugar berry			Waxmyrtle
Paw paw	Hawthorn			Sweet gum
Shinnard oak	Eastern red cedar			Hawthorn
Hawthorn	Chinkupen oak			Wild plum
Sweet clover	Ratton vine			Loblolly pine
American holly	Poison ivy			Green briar
Wild black cherry	White oak			
Wild plum	Short leaf pine			
Lagoon	Osage orange			
White ash	Cactus			
Flowering dogwood	Green briar			
Eastern hophornbean	Sweet clover			
	Wild plum			
	French mulberry			

Table 1.3 Typical trees and shrubs developed over the sialic country rocks, Arkansas.
(After Dr. J.T. Bean, Soil Conservation Society, Arkansas. Pers. Comm.)

Trinity Formation	Tokio Formation	Quaternary Terraces	Alluvium
Loblolly pine	White oak	Post oak	Water oak
Short leaf pine	Cherry bark oak	Winged elm	Sweet gum
Waxmyrtle	Southern red oak	Wild plum	Cherry bark oak
Green briar	Sumac	Red cedar	Loblolly pine
Red maple	Post oak	Black hickory	Blackgum
Black hickory	Winged elm	Wild black cherry	Slippery elm
Southern red oak	Huckleberry	Red mulberry	Wild plum
Spanish mulberry	French mulberry	Sweet gum	Dwarf sumac
Winged elm	Black Jack oak	Black Jack oak	American sycamore
Rattan vine		Short leaf pine	American holly
Flowering dogwood		Rattan vines	Devil's walking stick
Sawbriar			Shell bark hickory
White ash			Green briar
Holly			Box elder
			Wild grape
			Willow oak
			Flowering dogwood
			Persimmon
			Sugarberry

Table 1.5 The physiographic history of the Arkansas study area (from Veatch, 1906; Miser and Purdue, 1929; Dane, 1929; and pers. obs.)

Recent		Gradual progress of physiographic cycle to completion, development of oxbow lakes, obsequent streams etc.
Quaternary		Rejuvenation, possibly accompanied by a climatic change. Entrenchment of rivers into their own alluvium. Development of consequent rivers on uplifted terraces.
		Depression, extensive stream aggradation, formation of terrace deposits.
		Long period of quiessence, possibly punctuated by small vertical oscillations. Development of major (and not so major) valleys; much lateral cutting and some aggradation. Valley bottoms deeper than at present.
Early Quaternary Late Tertiary		Uplift, etching of present topography from erosion of a south dipping peneplain. Area somewhat higher than at present. (Veatch mentions 100 feet.)
Tertiary		Uplift and downwarping of Mississippi Embayment with tilting to east south; conformable deposition of Tertiary south of study area. Area much lower than at present, erosion of Cretaceous in study area and development of major drainage system. Some terrace deposits formed on Athens plateaux.
Upper Cretaceous		Deposition of Tokio formation in shallow sea which transgresses to north east. Some regenerated or continued igneous activity in Prairie Creek area.
	unconformity	Uplift, erosion, tilting to south east, downwarping.
		Further downwarping of Mississippi embayment, advance of Gulf waters. Deposition of Woodbine formation, initially on beaches, deltas etc. Extensive volcanic activity. Probably intrusion of peridotite, kimberlite and some tuff at Prairie Creek, American Mine etc. Possibly along deep seated fractures produced by fundamental crustal movements.
	unconformity	Uplift, erosion of some Trinity formation, especially in the east.
Lower Cretaceous		Downwarping of the Mississippi embayment, deposition of the Trinity formation, firstly as beaches, deltas, etc. and then in a clear Cretaceous sea.
	unconformity	Erosion, development of gently dipping southerly plateaux to the sea.
Paleozoic		Deposition of Paleozoic sediments, folding, erosion and possibly mineralisation.

Of particular interest is the history of the area in post Quaternary times during and subsequent to the development of the present topography. This is mentioned briefly with reference to the American Mine in Chapter 5.

1.13 Local Features

1.131 The Prairie Creek Area

1.1311 Geology

The intrusion at Prairie Creek has a pipe like form and penetrates Trinity clays and siltstones. It is bounded to the north, west and south by alluvium of the Little Missouri River. Several areas of Carboniferous sandstone are recorded within the margins of the pipe, no doubt due to stoping by the magma.

The intrusion itself is somewhat complex (Fig. 1.3) and Miser and Ross (1923) recognised three main rock types:

(1) Earliest hypabyssal peridotite.
(2) Volcanic breccia; hitherto called kimberlite.
(3) Tuff or fine grained breccia.

The salient differences between these individual rock types are tabulated in Table 1.4.

1.13111 The Hypabyssal Peridotite

This is a hard blue black, brown black or green black porphyritic rock containing olivine phenocrysts. Over much of its outcrop it has weathered through a yellow granular powder and a dirty yellow clay to a gumbo like black soil. The hardness of the rock is responsible for the formation of Middle and East Hills where relatively fresh rock is exposed.

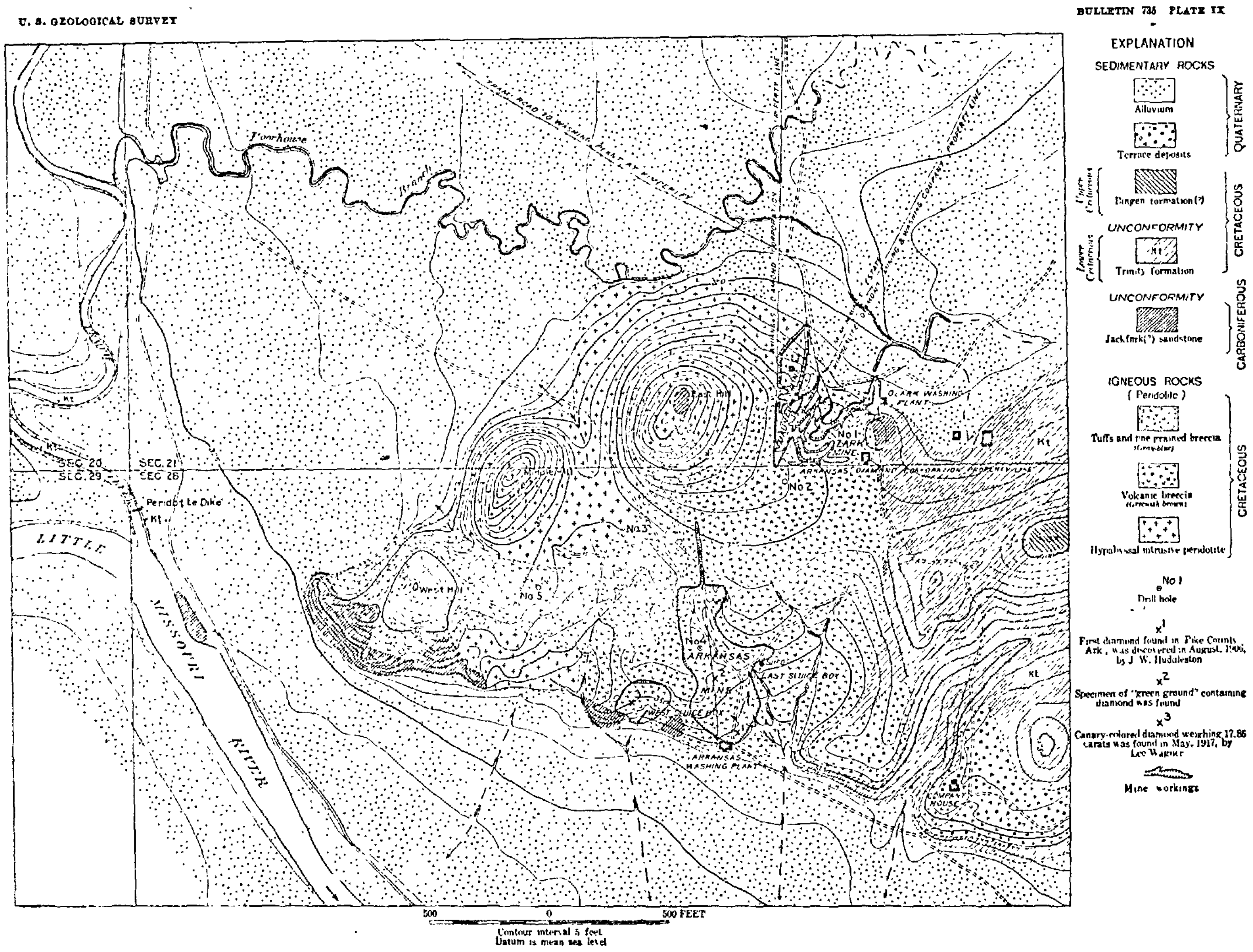


Figure 1.3: Geological Map of the Prairie Creek area of peridotite. (after Miser and Ross, 1923).

Table 1.4 Comparison of the igneous rocks of the Prairie Creek pipe.

	Peridotite	Kimberlite	Tuff
Texture	coarse grained, porphyritic	coarse grained, brecciated, porphyritc.	wide range of grain sizes, brecciated
Colour	black to brown black	yellow, browny, greeny black.	blue
Colour of weathered products	black dirty yellow yellow	black yellow blue	brown blue
Xenoliths*	few	many, mainly shale some sandstone.	many, mainly shale.
Metamorphism of xenoliths*	slight	little if any	little if any
Sedimentary structures	none	none	few locally
Diamonds	few, if any	diamondiferous	none

*accidental

In thin section the rock is seen to consist largely of olivine phenocrysts in a ground mass of pale red-brown mica (phlogopite). Miser and Ross (1923) give the following modal composition:

Augite	6%
Olivine	11%
Serpentine (after Olivine)	24%
Phlogopite	56%
Perovskite	1%
Magnetite/Ilmenite	2%

The olivines, about 10% fayalite, show various stages of alteration and have a reaction rim of amphibole. The phlogopite is usually unaltered and often poikilitic. Veinlets of barite are also present.

Miser and Ross (1923) record the presence of metamorphosed accidental xenoliths in the peridotite; however, none were observed by the author. Also recorded are igneous inclusions (probably cognate) of a very coarse grained igneous rock composed largely of serpentine, secondary amphiboles and pyroxene.

A few small diamonds are reported to have been recovered from the soft decomposed material over this rock type (Miser and Ross,1923).

A vein of "peridotite" is also known to outcrop near the confluence of Prairie Creek and the Little Missouri River. Insufficient data is available to determine whether this vein is peridotite or kimberlite.

1.13112 The Kimberlite

The bedrock is only exposed in several isolated areas and is a brown to greeny brown prophyritic breccia containing abundant yellow olivine phenocrysts and fragments of shale. It weathers through blue and yellow decomposition products to a black waxy soil.

In thin section the rock is seen to consist of largely decomposed olivine phenocrysts in a partially decomposed olivine and phlogopite rich ground mass. Perovskite and opaques are common as are shale fragments. A few small veinlets of barite are present. Other minerals which have been recorded in heavy mineral concentrates include hematite, limonite, barite, quartz, amethyst, magnetite, tourmaline, chromite, almandine, pyrope, pyrite diamond, diopside and epidote in order of decreasing abundance. It is noticeable that unlike many of the African pipes, pyrope, chrome diopside and ilmenite are extremely rare.

1.13113 The Tuff and Fine Grained Breccia

These rocks are of sky blue colour and vary greatly in grain size and texture. Xenoliths of shale are common.

In thin section they are seen to be composed largely of secondary minerals, especially chlorite and calcite. Opaque minerals are scarce and in some specimens detrital quartz is observed.

It is thought that this is a tuffaceous form of the kimberlite and possibly deposited in a caldera.

No diamonds have been recorded from this rock type.

1.1312 Exploratory Activity and Mining

Following the discovery of the first diamond in 1906, the Prairie Creek area has been mined intermittantly from 1908 to 1941; initially by the Arkansas Diamond Corporation and later by the Diamond Corporation of America. In 1944 and 1945 the deposit was sampled by the U.S. Bureau of Mines. Currently (1966) the deposit is exploited as a tourist attraction.

1.1313 Topography and Drainage

Whilst the topography of the kimberlite south of Section 21 has no doubt been modified by mining activity since Dr. Miser first mapped the pipe in 1916 (Fig. 1.3), the essential features are probably much the same. Three prominant hills form the north western extremity of the property; the overall ground slope is south to the flood plain of the Little Missouri River.

The area is drained to the north by a minor tributary of Prairie Creek and a prominant gulley between East and West Hills. The southern part of the pipe is drained by a series of small gulleys and sheet wash.

1.1314 Field Sampling

Mining and other activity has resulted in extensive disturbance of the area south of Section 21 and the removal of the entire solum and much of the yellow ground. Consequently, the drainage is not only contaminated with tailings but with debris eroded by sheet wash. Fortunately, a relatively undisturbed area was located north of Section 28/Section 21 boundary line and west of the Diamond Corporation of America property line. It was in this area that the residual soil profiles were collected. An enlarged geological map illustrating the locations of the profiles analysed is presented as Fig. 1.4.

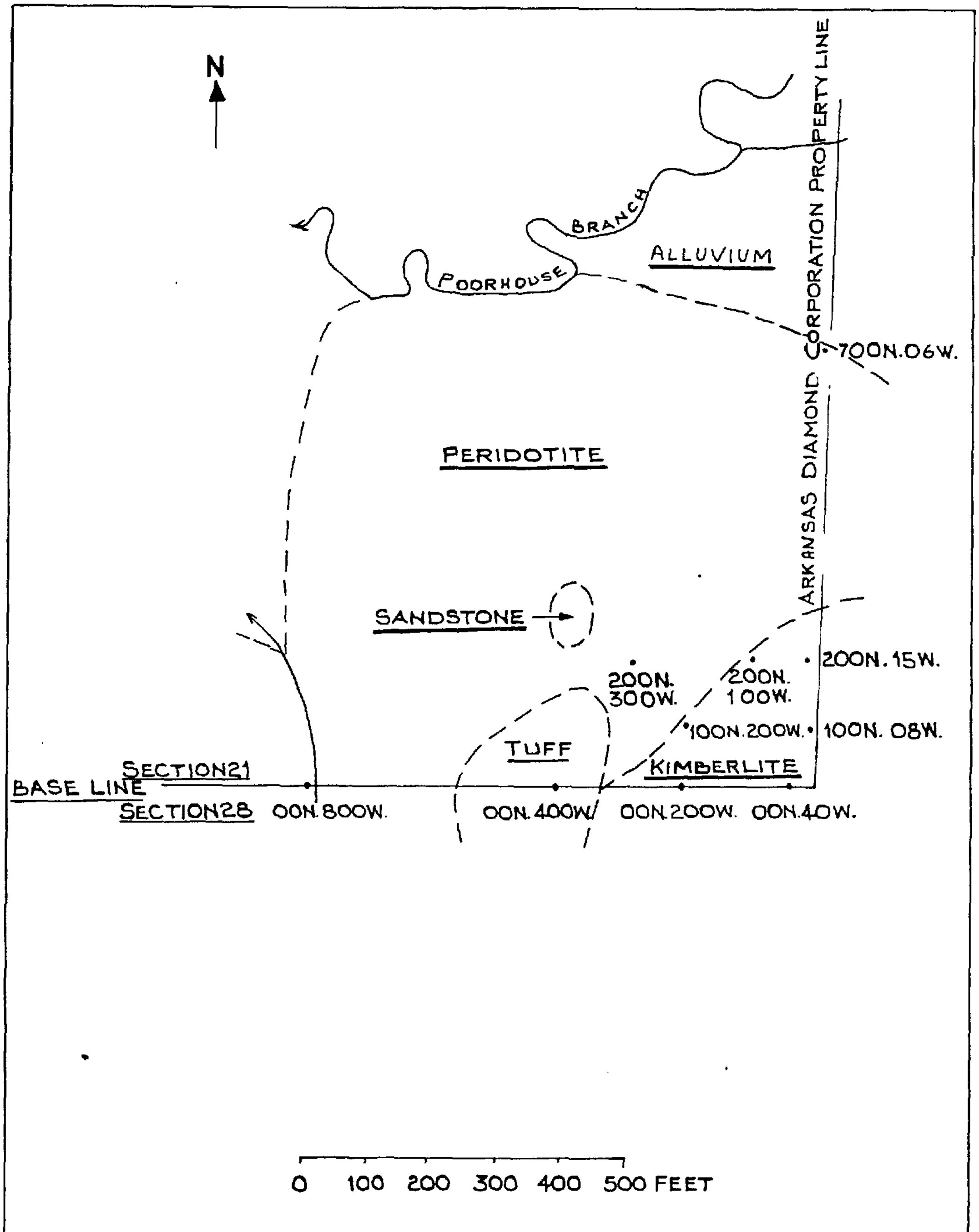


FIG 1·4 LOCATION OF SOIL PROFILES OVER PERIDOTITE, KIMBERLITE AND TUFF. PRAIRIE CREEK AREA.

1.132 The American Mine Area

1.1321 Geology

Kimberlite at the American Mine is exposed in a series of shallow pits, cuts and trenches and an adit and shaft on the steep north slope of a wooded ridge (Fig. 1.5). Its overall areal extent is not known although it has been encountered in several drill holes (Fig. 1.6).

Kimberlite intrudes the Trinity formation which consists of loosely consolidated silt with some clay and sand members. It is directly overlain by the Tokio formation, represented by a basal layer of limonite cemented novaculite cobbles (conglomerate) and interbedded clay, sand and gravel. No trace of kimberlite or kimberlite debris was observed in hand specimen of the Tokio formation.

Miser and Ross (1923) report that in some places the Trinity clay has been metamorphosed to a "hard grey stone" for some 2 feet away from the kimberlite contact. However, no contact metamorphism was observed in the limited number of sections examined by the writer, although some of the abundant accidental shale xenoliths appear to have been baked slightly.

No thin section examinations were made by the author, but Miser and Ross (1923) suggest the American Mine kimberlite to be the same as the breccia at Prairie Creek. They report the olivines have been completely serpentinised and magnetite, phlogopite and probably perovskite and augite were identified. A few small red garnets were also recovered during panning.

At the American Mine the kimberlite has weathered through a green "earth" and yellow granular powder to a chocolate brown soil. The blue ground as observed at Prairie Creek, is absent.

FIG. 1·5

SKETCH MAP OF THE TOPOGRAPHY, DRAINAGE, AND GEOLOGY OF THE AMERICAN MINE AREA.

(GEOLOGY MODIFIED FROM MISER, 1923)

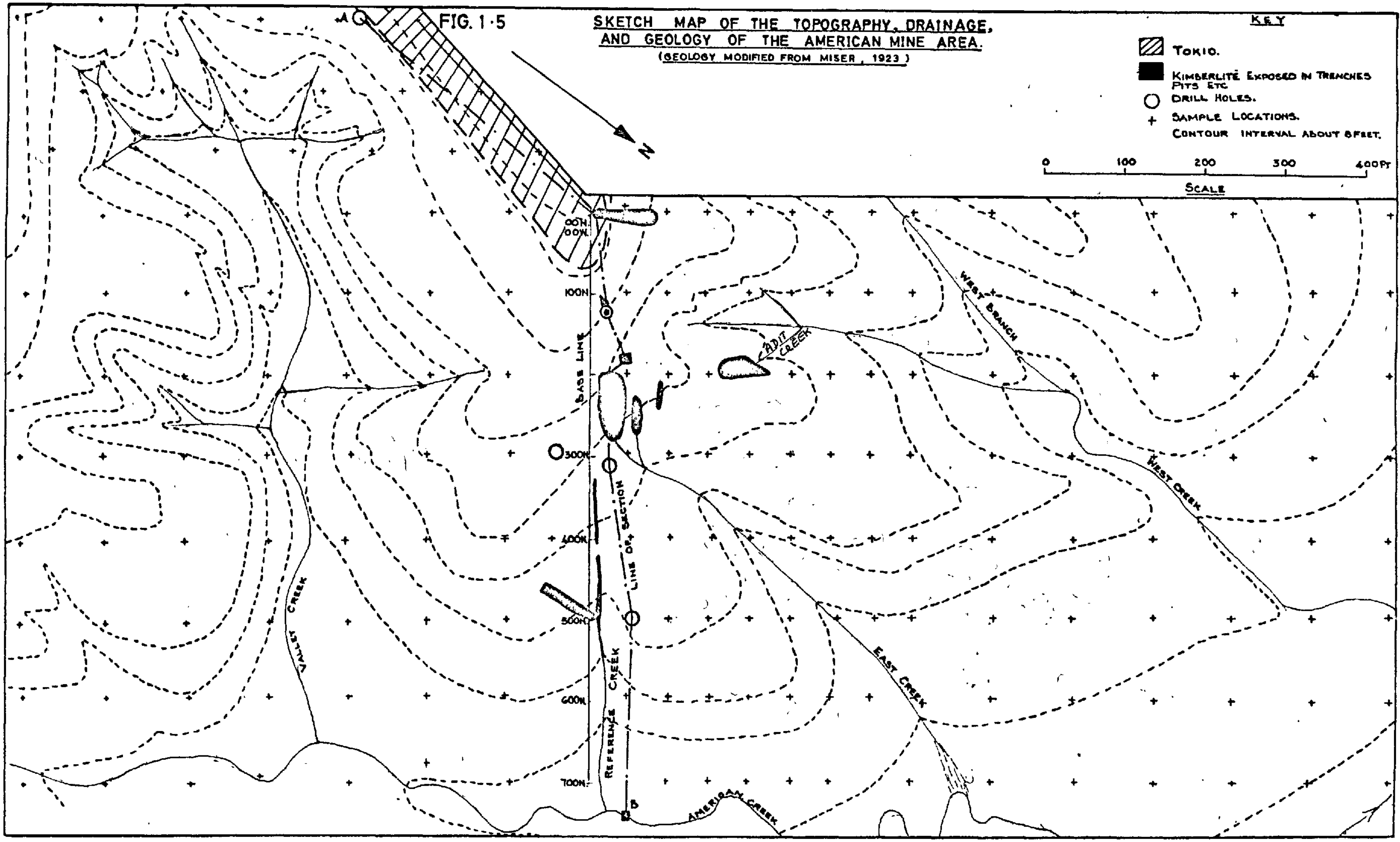
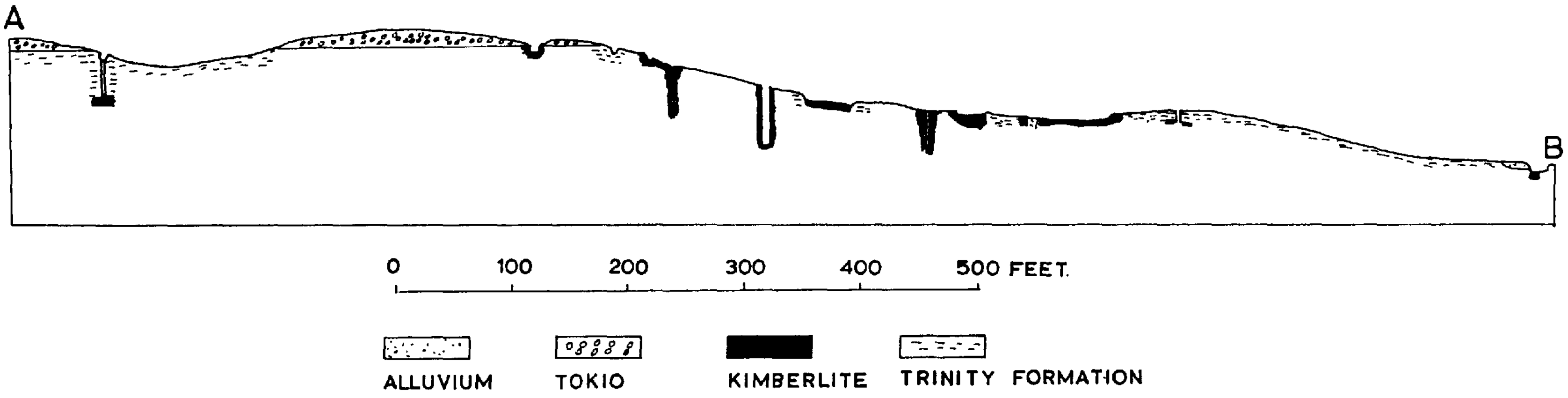


FIG. 1·6

SECTION ACROSS THE AMERICAN MINE AREA.

(MODIFIED FROM MISER & ROSS, 1923).



Soils over the Trinity formation vary considerably in maturity. Adjacent to the kimberlite, the $B_{2.1}$ horizon is brick red and rich in clay. In other areas this horizon may be a pale orange loam. The low lying areas in the valley bottoms are often covered with silt rich colluvium eroded from the A horizons up slope.

Soils over the Tokio formation are skeletal, presumably due to their rapid rate of erosion. Tokio detritus litters the adjacent hill slopes.

1.1322 Topography, Drainage and Vegetation

Broadly speaking the area is located on the south east wall of a mature flat bottomed but steep sided valley which disects a Tokio capped cuesta (Fig. 1.5).

It is drained by a series of small consequent tributaries running in prominant valleys, and by the obsequent American Creek. A small gulley drains the main kimberlite trenches (Reference Creek) and may in fact be partially artificial.

1.1323 Field Sampling

The drainage, topography and known distribution of the kimberlites make the American Mine the most suitable location for secondary dispersion studies. However, the possibility of contamination by previous exploratory investigations must be considered.

No spoil heaps were seen near the trenches and thus the excavated samples were probably removed to a source of water for treatment. With the exception of ground immediately adjacent to the three parallel trenches (and access roads) continuous soil profiles are represented. Thus it appears that contamination of residual soils is negligible and if present, is confined to the zone immediately surrounding the excavations.

Exploratory investigations will have affected the drainage in three ways:

(a) by contamination with tailings,
(b) by causing accelerated erosion of kimberlite exposed on the sides of trenches, and
(c) by localising and removing rain waters which might otherwise have entered the ground water phase.

The banks of the excavations are now largely grass covered and probably stabilised. Thus accelerated erosion at the present time is probably negligible or only very slight.

There is the remains of a small dam, probably part of a sluice box, 200 feet upstream from the confluence of Reference and American Creeks. Sediment from the floor of this dam contains a small, but appreciable, proportion of kimberlite C horizon, presumably tailings. Similar material was not encountered in sediment elsewhere in American Creek, but extensive mineralogical studies of the sediment were not made. It is concluded, therefore, that some contamination of the American Creek drainage has undoubtedly occurred, but the greatest bulk of the tailings have long since been removed.

Soil samples were collected on a grid pattern over the entire American Mine area and a limited number of profiles were taken downslope from kimberlite suboutcrop and along the banks of American Creek. In addition the components of the drainage system were collected.

1.133 The Kimberlite Mine

The Kimberlite Mine is located ^{3}/8ths of a mile north west of the American Mine and ^{1}/8th of a mile up the south west bank of American Creek.

The weathered rock is exposed in a series of trenches and suggests a N.E. trending crescent shaped dyke (Miser and Ross, 1923).

Unlike the American Mine and Black Lick areas, the unweathered rock resembles the hypabyssal peridotite of Prairie Creek. Furthermore, both the Trinity wall rocks and accidental shale xenoliths have been distinctly metamorphosed. The weathered rock is of green to yellow colour.

Two lines of soil profiles were collected over the dyke but were not investigated in the laboratory.

1.134 The Black Lick Prospect

Two exposures of kimberlite, 900 feet apart, known as the Black Lick Prospect are located ½ a mile south south west of the American Mine and on the south side of the watershed.

Kimberlite at the western Black Lick occurs towards the crest of a steep slope and is exposed in a forest road cut and a few small pits. The kimberlite is directly overlain by the basal conglomerate of the Tokio formation, here cemented with ferric oxides.

The eastern Black Lick kimberlite is exposed in a shallow pit on relatively level ground 900 feet east and the other side of the Tokio capped ridge. Miser and Ross (1923) suggest the outcrop may represent a single intrusion of kimberlite.

Although fresh bedrock was not found, the textural characteristics of the decomposed rock are similar to the kimberlite of Prairie Creek (Miser and Ross, 1923). Weathering has developed a yellow green earth and a black soil.

Field sampling was restricted to the drainage components of the west Black Lick Prospect. Whilst contamination of residual soils from the pits is unlikely, a recent road cut through kimberlite has allowed accelerated erosion of the soil.

1.2 ARIZONA

1.21 Introduction

Two main areas of kimberlite type intrusions are known in western north America, all of which are within the Navajo Hopi Province of Utah, New Mexico and Arizona, Fig. 1.1. Of the six known separate intrusions, Garnet Ridge West, Garnet Ridge East, Green Knobs and Buell Park were visited by the writer. The prevailing drainage and other conditions led to the selection of Buell Park as the major study area. However, all the intrusives are located in similar environments and the conclusions at Buell Park are probably applicable to the other areas.

1.22 Location

The broad location of the Navajo Hopi intrusions are illustrated on Fig. 1.1. Buell Park is located 2½ miles due west of the Arizona-New Mexico State Boundary and about 11 miles north of Fort Defiance, Arizona. It is readily accessible by road.

1.23 Geology

The geology of the Buell Park area and its environs is described by Allen and Balk (1954) (Fig. 1.7).

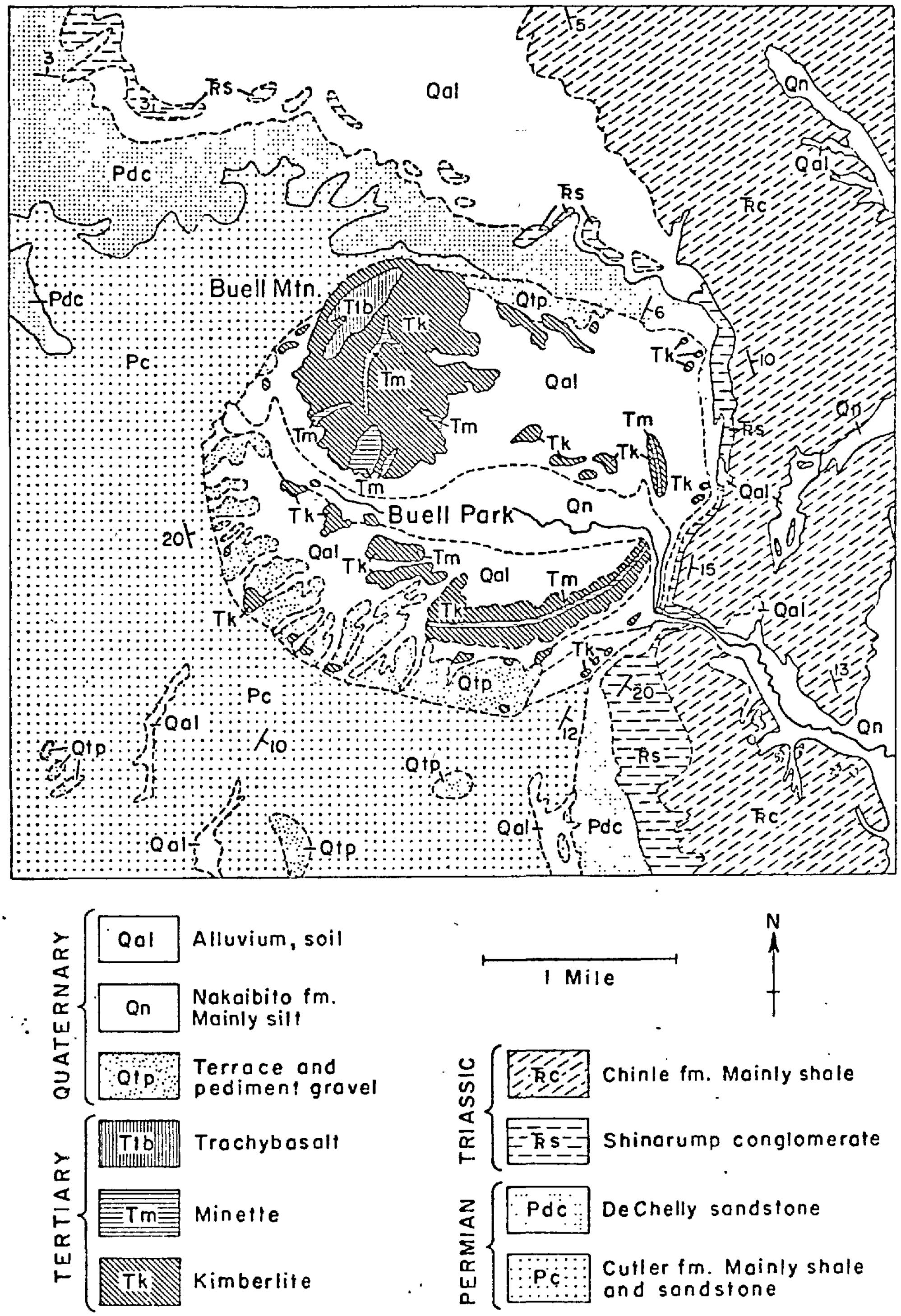


FIGURE 1.7: Geological map of the Buell Park area, Arizona. (After Allen and Balk, 1954; from Wyllie, 1967).

1.231 The Pre-Igneous Rocks

The Buell Park caldera is bounded to the north, south and west by Permian sandstones of the Cutler and De Chelly formations. Triassic sandstones, shales and conglomerates outcrop only a slight distance away to the east and the whole is underlain by a basement of Precambrian quartzite.

Where the contact of the wall rocks with the tuff is exposed there is no identifiable metamorphism.

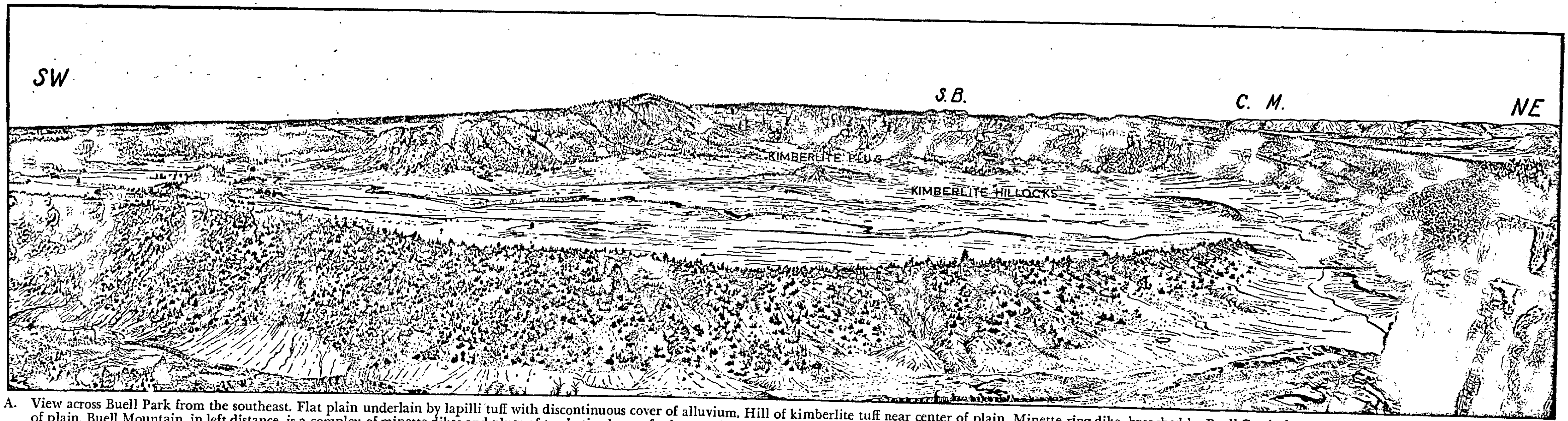
1.232 The Igneous Rocks

Allen and Balk (1954), recognise two main types of igneous rocks outcropping within the Buell Park caldera: (a) kimberlite, (b) minnette. Other rocks include the extrusive and tuffaceous phases of these types.

Kimberlite outcrops as three low rounded hillocks and as a prominant plug, Fig. 1.8. Alteration has transformed the kimberlite of the first mentioned occurrence to a green clay with abundant xenoliths. In contrast, the plug is composed of a compact, purplish brown to locally olive green, highly fractured brecciated rock. Xenoliths are common and macroscopically the rock is little altered.

Mineralogically, the rock is composed of phenocrysts of olivine, enstatite, chrome diopside, pyrope garnet, with accessory magnetite, titan clinohumite, clinopyroxene, ilmenite and apatite in a fine grained largely altered ground mass. Various stages of alteration of the olivines are present, the secondary products being antigorite, possibly sepiolite and talc, chlorite and iron oxides. Some alteration of the pyroxene is also recorded.

In ground over the kimberlite hillocks, residual con-



A. View across Buell Park from the southeast. Flat plain underlain by lapilli tuff with discontinuous cover of alluvium. Hill of kimberlite tuff near center of plain. Minette ring-dike, breached by Buell Creek, forms ridge in foreground and near right edge of plain. Buell Mountain, in left distance, is a complex of minette dikes and plugs of trachytic phases of minette, piercing lapilli tuff. Trachybasalt masses near summit may have approached surface of eruption. Rim rocks are upper Cutler sandstone overlain on right side by De Chelly sandstone, Shinarump conglomerate, and lower Chinle shales. Cliff in right foreground is top of De Chelly sandstone. Sonsela Buttes (S.B.) and Chuska Mountain (C.M.) on skyline.

Figure 1.8 (After Allen and Balk, 1954).

concentration of comparatively fresh olivines, pyropes and other garnets, chrome diopside and ilmenite are noted on ant hills.

Lapilli tuff (kimberlite ejected as tuff) is the most abundant rock and is thought to underlie the alluvium of the caldera. It is a light green earthy, fragile, fine grained rock; containing abundant xenoliths which are more common than in the kimberlite. Unlike the kimberlite, fresh olivines, chrome diopside and garnets are relatively rare. In thin section (Allen and Balk, 1954), the olivines are seen to have been completely altered.

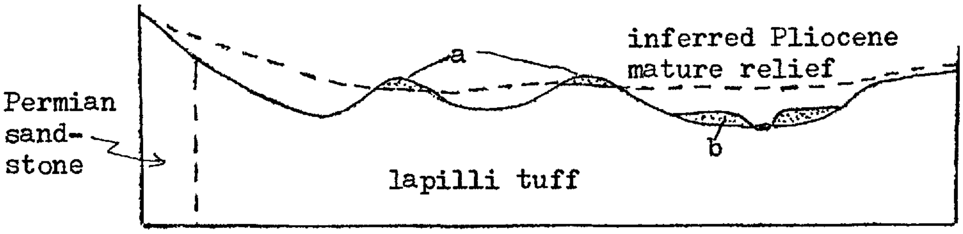
Minnette, and its extrusive form, trachybasalt, occur in the caldera as ring dykes, plugs and possibly lava flows. Unlike the kimberlitic material this rock was intruded at a comparatively high temperature as seen from the metamorphism of the accidental sandstone xenoliths to quartz grains and buchite (glass). It is generally olivine free and composed of biotite, potash felspar and green clinopyroxene. Williams (1932, p. 132) records the presence of leucite. It is a fine grained to aphanitic dark grey to almost black rock.

No diamonds have been recorded in the Buell Park area. However, the deposit has not been sampled in bulk, although Allen and Balk washed 'promising patches of gravel or sand' without success. A trench has been cut across the kimberlite but no details are available. Perhaps the best indication of the non-diamondiferous nature of the kimberlite is provided from the lack of detection of economic size diamonds (or any other), by the Indians who frequently search the area for precious stones. These stones are concentrated at the ground surface by eluvial means. A small diamond (^{1}/5th the carat) was easily recognised by the writer's assistant in a salted sample of one pound of eluvially concentrated kimberlite detritus.

1.233 The Post-Igneous Rocks

These consist of Pleistocene to recent alluvium, terrace gravels, peat, talus, landslide debris, etc.

Alluvium and wind blown sand cover much of the caldera at Buell Park. Allen and Balk (1954) recognise two ages for the alluvium within the caldera, Fig. 1.9 (below):



After Allen and Balk (1954)

(a) Remnants of late Pleistocene piedmont veneer comprising gravelly fragments of the Cutler and De Chelly formations and pebbles of the Shinarump chert. It occurs dominantly on the crest of some of the low rounded hillocks, i.e. kimberlite. It is, however, dispersed some distance down slope no doubt due to sheet wash. Wind blown sand and kimberlite detritus are also common.

(b) Recent alluvium, peat etc., of the Nakaibito formation, which flanks and may form the bed of the main drainage of the region.

Olivines, pyropes, chrome diopside etc., are also recorded over an area 9 miles south and 4 miles west of Buell Park. Allen and Balk attribute this occurrence to residual concentration from a local tuff bed which once covered the region.

1.24 Topography and Drainage

The general area is that of a plateau bisected by a subsequent monoclinal valley (Black Valley). The edges of the plateau are incised by canyons and large gulleys so as to give the appearance of a dissected upland. The more resistant sedimentary rocks often form cliffs or mesas whilst the igneous rocks manifest their superior hardness as plugs.

Buell Park itself is a căldera on the dissected east edge of the Fort Defiance plateau a few miles west of Black Valley. It is a depressed circular area 2 miles in diameter and bounded by steep cliffs. Some of the igenous rocks form distinct plugs, walls etc., e.g. Buell Mountain which rises above the level of the surrounding sandstone plateau.

The dominant drainage is to the south along broad river bottoms or large gulleys whose size bears little relation to the average water flow. Only the largest rivers are perennial. Buell Park itself is bisected by an antecedent river which is seasonal, and was flowing at the time of the author's visit (May). Various springs are also present, notably to the east of the kimberlite plug. However, their flow is quite small.

1.25 Climate and Vegetation

The elevation of Buell Park is about 6,500 feet, thus the mean summer temperatures are not high (mean July about 80°F). Winter temperatures are not abnormally low (mean January about 25°F). The average annual rainfall is about 12 inches, of which 40% falls in the July, August and September.

This relatively mild climate and low rainfall results in very little chemical weathering of the rock; consequently, mechanical dispersion is prevalent. Soils are very sparse except in areas of impeded drainage, where they are invariably cultivated.

Most of the Buell Park area has a thin grass cover with abundant small trees.

1.26 Field Sampling

A suite of soil profiles were collected over the kimberlite and lapili tuffs, together with soil profiles over the sandstone country rocks and a large sandstone xenolith in the floor of the caldera.

Samples of the surrounding igenous rocks were also collected as was a suite of stream sediments draining Buell Park and background rocks.

1.3 COMPARISON OF ARKANSAS AND ARIZONA KIMBERLITE AND ENVIRONS

A comparison of the Arkansas and Buell Park kimberlite and their environs is presented in Table 1.6. The most significant features are the differences in weathering, soils, age of the kimberlites and diamondiferous character.

Table 1.6 A comparison of the Arkansas and Buell Park kimberlites and environs.

	Arkansas	Arizona
Age	Mid to upper Cretaceous.	Probably Pliocene.
Kimberlitic minerals	Olivine, phlogopite, pyroxene, perovskite, opaques, diamond.	Olivine, pyrope garnet, chrome diopside, pyroxene.
Texture	Porphyritic breccia.	Porphyritic breccia.
Xenoliths	Abundant accidental, rare cognate	Abundant accidental, many cognate.
Metamorphism	Near surface accidental xenoliths and wall rocks little metamorphosed.	Near surface accidental xenoliths and wall rocks little metamorphosed.
Undecomposed olivines at surface	No	Yes
Diamonds	Diamondiferous	Non diamondiferous.
Weathered Bedrock	Black (soil Yellow Blue	Brown (if thin veneer of soil present) Green
Soil cover	Usually thick and mature.	Thin and rudimentary.
Dominant country rocks	Siltstone, alluvium, tuff.	Sandstones, alluvium, minnette.
Climate	Mild	Cool mild
Rainfall	30 to 40 inches	About 12 inches
Vegetation	Abundant and luxurious trees, shrubs, underbrush, etc.	Sparse grassland, small pines etc.

CHAPTER 2

GEOLOGY AND GEOCHEMISTRY OF KIMBERLITES

2.1 GEOLOGY

2.11 Structure

According to Wagner (1914), kimberlite intrusives may be readily classified into:

(1) True volcanic pipes
(2) Dykes and sills
(3) Chonoliths, i.e. more or less lenticular shaped enlargements of dykes in which the longer axis of the lens may be either vertical or horizontal.

The pipes may vary in diameter from a few tens of yards to ½ a mile or more. With depth they shrink until they are no more than irregular "blisters" associated with dykes.

2.12 Occurrence

Dawson (1960) reviewed occurrences of the main kimberlite throughout the world and came to the following conclusions:

(1) Most kimberlite intrusions are found in stable shield areas which have not undergone major tectonic deformation since Precambrian times. Some kimberlites, e.g. in the Rockies, Urals and Appalachians, occur in oregenic zones. In these cases oregeny took place long before kimberlite intrusion.

(2) In shield areas, kimberlites are usually intruded into areas which have undergone gentle flexing and uplift prior to intrusion. In some instances kimberlites are associated with doming which has caused rifting as a result of up-

warping and tension. During intrusion the kimberlite often used old lines of weakness to facilitate its penetration into the upper levels of the earth crust.

The kimberlite occurrences in eastern North America are parallel to the Appalachian disturbances.

(3) The majority of kimberlites were intruded during the latter part of the Cretaceous. However, some diamonds are present in Precambrian terrains, e.g. in the Archean phyllites of Ghana.

(4) There is a close association in space and time between kimberlites and other alkaline rocks, e.g. nepheline syenites, carbonatites, melilites, etc.

2.13 Mineralogy

The mineralogy of kimberlite is complicated by the contributions of the xenoliths and the metasomatic processes involved during or after emplacement. Williams (1932) classifies minerals in kimberlite (excluding accidental xenoliths) into the three groups illustrated in Table 2.1.

The most important minerals from the point of view of the minor element content, distribution and fixation are: olivine and its secondary minerals, pyroxene phlogopite, ilmenite and other metallic oxides, perovskite, apatite, pyrope garnet, chrome diopside, celestine, barite, calcite.

Diamond may also be present sometimes in economic amounts.

Texturally the rock varies from a tuff or breccia to a homogenous rock. Phenocrysts of serpentine, after olivine, make up much of the rocks with the ground mass composed mainly of

Table 2.1 A classification of the minerals found in kimberlite; excluding accidental xenoliths. (After Williams, 1932)

Primary	Transported minerals of primary origin	Secondary
Olivine	Olivine	Serpentine
Phlogopite	Enstatite	Talc
Ilmenite	Garnet	Chlorite
Perovskite	Zircon	Calcite
Magnetite	Diopside	Siderite
Apatite	Chrome diopside	Magnetite
	Phlogopite	Limonite
	Spinel	Perovskite
	Chromite	Phlogopite
	Ilmenite	Amphibole
	Rutile	Hematite
	Augite	Pyrite
	Magnetite	Leucoxene
	Hornblende	

serpentine, phlogopite, olivine, calcite, perovskite and iron ores.

During weathering, progressive alteration of the major silicate minerals, particularly in the ground mass, transforms the hard rock, nicknamed 'hardebank', through distinct zones called 'blue ground' and 'yellow ground'.

The blue ground is composed largely of serpentine with phenocrystic structures still recognisable. The yellow ground consists of decomposed olivines and phlogopite in a zeolitic, calcitic and limonitic secondary mineral aggregate (Nixon, 1960).

2.14 Classification of Kimberlites

Wagner (1914, pp 78 and 79) recognised two types of kimberlite, (a) basaltic, phlogopite less than 4%, and (b) lamprophyric, phlogopite greater than 4%. He defines basaltic kimberlite as "porphyritic peridotite of basaltic habit" and lamprophric kimberlite as "porphyritic peridotite of lamprophric habit".

2.15 Xenoliths

Two contrasting suites of xenoliths generally occur within kimberlite, (a) deep seated, and (b) near surface varieties.

2.151 Deep Seated Xenoliths

Nixon (1960) classifies deep seated xenoliths into three types:

2.1511 Ultrabasic Xenoliths

These present a great variety of rocks and are usually fresh and coarsely crystalline. They may consist of varying proportions of forsteritic olivine, enstatite, chrome diopside, pyrope garnet, ilmenite and phlogopite.

Chemically the xenoliths are ultrabasic in composition with higher SiO_2, MgO, Fe, Ni and Cr than kimberlite (Williams, 1932, pp. 343 and 347); volatiles are lower but $Na_2O > K_2O$.

2.1512 Eclogites and Related Xenoliths

These include eclogites and granulites and are similar in texture to rocks found in high grade metamorphic alpine terrains and basement complexes.

They consist of pyrope - almandine garnet, omphacite pyroxene with varying amounts of kyanite, plagioclase, scapolite and hornblende. Apatite and rutile are abundant accessories. Olivine is rare or absent.

2.1513 Pyrope and Diopside Xenoliths

These may occur as discrete nodules of pyrope rich garnet and diopside or both.

2.1514 Discussion

Whilst the ultrabasic xenoliths have been generally accepted as being of cognate origin, i.e. having a genetic relationship with the kimberlite, the origin of the eclogites is somewhat controversial. Wagner (1928) distinguishes igneous and metamorphic types whereas Williams (1932) places all eclogites in the cognate category although he admits the possibility of accidental metamorphic types. Nixon (1960) suggests that accidental eclogite may exist; he concludes the eclogite to represent "deep seated portions of the earth's crust and possibly the outer parts of the mantle", he further suggests that the pyrope diopside xenoliths to be related to the kimberlite magma. Dawson (1960) includes the few eclogites found by him in his "accidental" category along with granulites etc. Davidson (1964) from a review of the kimberlite pipes of Yukatia, postulates the eclogites and garnet peridotites to be of crustal origin and therefore accidental.

2.152 Near Surface Xenoliths

These may comprise any rock through which the kimberlite has penetrated, both above and below the present stratigraphic level, e.g. Dawson (1960) records Karroo sediments in Basutoland kimberlites, the surface expression of which has long since been eroded. Williams (1932, pp. 259) records inclusions of the Waterburg formation in kimberlite of the Premier Diamond Mine, the formation having been eroded from the immediate mine area.

The size of these xenoliths may vary from a few microns to several hundred feet in length. Frequently, in the larger blocks, orientation may be noted although this may bear no relationship to their original attitude, Dawson (1960) and personal observation at Garnet Ridge, Arizona.

2.16 Temperature of Intrusion

Williams (1932, pp. 161) mentions that accidental xenoliths, particularly carbonaceous shale, show little or no thermal metamorphism. Davidson (1964) discussing the kimberlite pipes of Yukatia postulates that the temperature of intrusion was less than 200°C based on the lack of argon diffusion in phlogopite. Lack of magnetic orientation shows the magma came to rest below the Curie point, which is approximately 500°C for magnesian magnetite.

Sosman (1938), derived an intrusion temperature of 440-520°C after comparative heating of coal with a metamorphosed accidental coal xenolith included in a mica peridotite (Kemp and Ross, 1907).

2.17 Genesis

Perhaps there is no subject which has aroused more speculation and controversy than the origin of diamonds and kimberlites. The genesis of kimberlite can be divided into two problems; the origin of the magma and the mode of emplacement.

2.171 Generation of a Suitable Magma

Wagner (1914), Williams (1932) and Holmes (1936) postulated that kimberlite magma originated in the peridotite layer. However, whereas Wagner suggested liquefaction of potentially fluid portions of the holcrystaline peridotite consequent upon relief of pressure, Williams and Holmes proposed kimberlite to result from 'emanations' mixed with inclusions from the peridotite layer and melilite basalt magma. Whereas Williams favoured settling of peridotite and eclogitic rocks in a reservoir of basic magma then intrusion, Holmes postulated intrusion as olivine melilite basalt plus emanations consisting mainly of water, CO_2, P_2O_5 with the addition of ultrabasic mantle material.

Von Eckerman (1948) and Leontiev and Kedensky (1957) suggested the kimberlites of Alno Island and Siberia respectively were due to differentiation of an alkaline magma. Dawson (1960) proposes kimberlite magma to have been derived from the mixing of carbonatite and granite, i.e. carbonatite + granite = ultrabasic silicates + 'fluid' with sufficient pressure being generated by the evolved CO_2 to form diamond. He suggests kimberlite formed from the fragmentation of ultrabasic rocks and reaction with the 'fluid'.

Dawson's theory was strongly contested by Nixon (1960) who suggested the kimberlite magma was a liquid approaching the composition of olivine or nepheline melilite basalt and is derived from partial fusion and migration to cooler parts of the mantle. He concluded the phenocrysts and comparable rocks to separate followed by the intrusion of the residual fluid which is enriched in some trace elements and volatiles.

Davidson (1964) discussing the kimberlites of Yukatia postulated the kimberlite breccia to have been derived from pre-existing solid kimberlite which was first emplaced in the crust in Sinian times; at the same time as the Aldan carbonatites and alkali - ultrabasic complexes which were formed at a somewhat higher level.

2.172 Modes of Emplacement

Theories on the mode of emplacement may be divided into three categories; (a) explosive, (b) fluidization, and (c) a pulsating magma column.

The explosive origin was favoured by the earlier writers, mainly in an attempt to explain the brecciated nature of the pipes, Wagner (1914) states "the pipes appear to have been formed by violent explosive liberation of highly compressed gases and vapours emanating from a deep seated ultrabasic magma". Daly (1933), states "an outstanding feature is the evidence of tremendous explosions when the pipes were filled with kimberlite and its many xenoliths".

Fluidization was favoured by Shoemaker and Moor (1956), Renolds (1954) and Dawson (1960), though the latter qualifies by stating "the initial contact with the land surface was most probably of an explosive nature". Davidson (1964) postulates "kimberlite as being emplaced as a cold mush or slurry of rock highly charged with gases". He goes on to say "the temperature of the kimberlite mush... was very low, probably no more than 200°C".

Support for the fluidization theories is based on cold 'intrusion'; a control of the intrusion by jointing of the country rocks; rounding and striation of inclusions; the metasomatic alteration, particularly serpentinisation which cannot take place above 500°C (Bowen and Tuttle, 1949); corrosion of ilmenite grains (Dawson, 1960); and the presence of very large sub-orientated xenoliths.

Advocates of the pulsation magma column are Williams (1932, p. 235-242), who suggests that kimberlite magma was injected slowly up pre-existing fractures and Du Toit (1967), who suggests emplacement as a "pulsating fluid column... and that gas streaming plays no more than a subordinate role".

2.2 GEOCHEMISTRY

The mean trace and major element content of basaltic and lamprophyric kimberlite along with other common rock units is presented on Table 2.2. Data for the composition of the Prairie Creek igneous phases and the kimberlite tuff at Buell Park are also presented.

Inspection of the table allows the following salient features to be noted:

2.21 The Major Elements

(1) Kimberlite is by definition an ultrabasic rock. (SiO_2 less than 45%, Holmes, 1920, p. 231). However, for an ultrabasic

		Peridotite (3) Prairie Creek	Kimberlite (3) Prairie Creek	Tuff Prairie Creek	Kimb. Tuff (5) Buell Park	Mean Kimberlite		Ultrabasics		Basalts		Intermediate	Granites (6a)		Syenites	Clays and Shales	Shales	Sandstones	Carbonate Rocks
						(1) basaltic	(2) lampro.	(6a)	(6b)	(6a)	(6b)	(6b)	high Ca	low Ca	(6a)	(6b)	(6a)	(6a)	(6a)
per cent	Si	18.1	22.35		22.18	16.33	16.96	20.5	19	23	24	26	31.40	34.70	29.10	23.8	7.30	36.8	2.40
	Al	3.62	3.05		0.73	2.06	2.69	2	0.45	7.80	8.76	8.85	8.20	7.20	8.80	10.45	8	2.50	0.42
	Fe	7.73	4.84	1.12	4.86	6.82	7.83	9.43	9.85	8.65	8.56	5.85	2.96	1.42	3.67	3.33	3.72	0.98	0.38
	Mg	15.8	13.11		18.78	19.02	16.09	20.4	25.9	4.60	4.5	2.18	0.94	0.16	0.58	1.34	1.50	0.70	4.70
	Ca	2.78	2.26		0.46	4.85	4.84	2.5	0.7	7.6	6.72	4.65	2.53	0.51	1.80	2.53	2.21	3.91	30.23
	Na	0.58	0.22		0.08	0.25	0.27	0.42	0.57	1.80	1.94	3	2.84	2.58	4.04	0.66	0.96	0.33	0.04
	K	2.12	1.19		0.31	0.87	2.02	0.004	0.03	0.83	0.83	2.3	2.52	4.20	4.80	2.28	2.66	1.07	0.27
	Ti	0.53	1.63	0.70	0.05	0.73	0.13	0.03	0.03	1.38	0.9	0.8	0.34	0.12	0.35	0.45	0.46	0.15	0.04
	Mn	0.06*	0.05*	0.05	0.09	0.05	0.08	0.162	0.15	0.15	0.2	0.12	0.054	0.039	0.085	0.067	0.085	0.00X	0.11
	P		0.38*		0.01	0.38	0.29	0.022	0.017	0.11	0.14	0.16	0.092	0.06	0.08	0.077	0.07	0.017	0.04
	C	0.04	0.13		0.00	0.91	0.55		0.01		0.01	0.02				1.0			
parts per million	Ni	1450	1290	210	1250	1116(7)		2000	2000	130	160	55	15	4.5	4	95	68	2	20
	Co	82	57	43	105	69(8)		150	200	48	45	10	7	1	1	20	19	0.3	0.1
	Cr	1660	920	120	1075	1500(9)		1600	2000	170	200	50	22	4.1	2	100	90	35	11
	V	40	115	60	60	170(10)		40	40	250	200	100	88	44	30	130	130	20	20
	Cu	51	45	39	4	100(10)		10	20	87	100	35	30	10	5	57	45	X	4
	Li					16(10)		0.X	0.5	17	15	20	24	40	28	60	66	15	5
	Hg	0.05	0.11	0.01				0.X	0.1	0.21	0.2	0.5	0.72	2.3	1.4	1	1.4	0.82	0.0X
	Ba	6600	530	>7000	200	740(10)		0.4	1	330	300	650	420	840	1600	800	580	10X	10
	Sr	930	400	1200	30	445(10)		1	10	465	440	800	440	100	200	450	300	20	610
	Rb	1100(15)				21(10)		0.2	2	30	45	100	110	170	110	200	140	60	3
	Nb	126(16)	111(16)	82	<7	240(10)		16	1	19	20	20	20	21	35	20	11	0.0X	0.3
	La		264(17)			84(11)		0.X		15	27		45	55	70	40	92	30	X
	Ce		358(17)			291(11)		0.X		48	45		81	92	161	50	59	92	11.5
	Pr		60(17)			17.2(11)		0.X		4.6	4		7.7	8.8	15	5	5.6	8.8	1.1
	Nd		166(17)			66(11)		0.X		20	20		33	37	65	23	24	37	4.7
	Yt		42.4(17)			8.4(11)		0.X		21	20		35	40	20	36	26	40	30
	Sc	8(14)				8.1(13)		15	5	30	24	2.5	14	7	3	10	13	1	1
	Zr	634(16)	527(16)			500(10)		45	30	140	100	260	140	175	500	200	160	220	19
	Hf	19.8(16)	16.2(16)					0.6	0.1	2	1	1	2.3	3.9	11	6	2.8	3.9	0.3
	Ta	6.8(16)	8.6(16)					1	0.018	1.1	0.48	0.7	3.6	4.2	2.1	3.5	0.8	0.0X	0.0X
	Th					8.1-39(12)		0.004	0.005	4	3	7	8.5	17	13	11	12	1.7	1.7
	U					0.9-5.0(12)		0.001	0.003	1	0.5	1.8	3	3	3	3.2	3.7	0.45	2.2

TABLE 2.2.- *A comparison of the chemistry of kimberlitic and other rocks. (Source in parenthesis, detailed in the appendix) (X = 1-9)*

rock, Si, Fe, Mg and Mn contents are below average and K, P and Ti are contained in highly abnormal amounts.

(2) Along with other ultrabasic rocks, the Mg content is in excess of that of other common rock types (excluding dolomite). Phosphorus and Ti are contained in amounts generally in excess of other rock types although high Ti concentrations are recorded in some basalts.

(3) Iron is present in amounts in excess of that in sialic igneous rocks and sediments.

(4) The lack of mica in basaltic kimberlite is reflected by the lower K content than in lamprophyric kimberlite. On the other hand, the Mg content of basaltic kimberlite is higher.

(5) On mineralogical grounds the kimberlite at Prairie Creek may be classed as a lamprophyric kimberlite. However, the Ti content is in excess of the average lamprophyric kimberlite and nearer to basaltic in composition. Silica and alumina are also contained in higher concentrations and Fe, Mg and Ca below the average.

(6) The composition of the Prairie Creek peridotite is similar to that of a lamprophyric kimberlite although the Ca content is much lower and the Ti and Al contents much higher. The content of Na is closer to that of ultrabasic rocks than to kimberlite.

(7) Mineralogically the kimberlite plug at Buell Park is a basaltic kimberlite, however, for a kimberlite P, Ti, K, Na, Ca, Al and Fe are contained in abnormally low concentrations.

2.22 The Minor Elements

Abnormal concentrations of many trace elements are recorded in kimberlite; these may be divided into three contrasting suites:

(1) Those concentrated in ultrabasic rocks, i.e. Ni, Co and Cr.

(2) Those concentrated in basic rocks, i.e. V, Cu and Sc.

(3) Those concentrated in alkalic rocks, especially in residual liquors, i.e. Nb, Ta, La, Ce, Pr, Nd, Yt, Zr, Hf, U, Th, Li, Ba, Sr and Rb.

2.221 Minor Elements Concentrated in Ultrabasic Rocks, i.e. Ni, Co and Cr

These elements are incorporated in the lattice of minerals crystallising at an early stage in the magmatic process. In kimberlites Ni and Co occur dominantly in olivines and other ferro magnesian minerals where they replace Mg^{2+} or less likely Fe^{2+}. Chromium replaces Fe^{3+} and occurs preferentially in clino pyroxenes to olivine or magnetite (Rankama, 1950, p. 622). Other possible sources of these metals include ilmenite, magnetite, chromite, garnet, etc.

Concentration of these elements in kimberlite are considerably in excess of concentration on basic, intermediate or acid igneous and sedimentary rocks.

It is noticeable that the content of metal is greater (Table 2.2) in the ultrabasics and the Prairie Creek peridotite than in kimberlites. Abnormal concentrations of Co are observed in the Buell Park kimberlite tuff.

A basic nature of the tuff at Prairie Creek is indicated by the relatively low Ni and Cr contents and the similarity of Co concentrations with that of basalts.

2.222 Minor Elements Concentrated in Basic Rocks i.e. V, Cu and Sc

This group of elements are concentrated in basic rocks. Copper and Sc are usually removed from the magma during the earliest stages of crystallisation; Cu^{2+} as sulfides or replacing Fe^{2+} and Sc with ferromagnesians replacing Fe^{3+}. However, metals not removed may well remain until the very last stages of crystallisation when they are precipitated from hydrothermal fluids. Vanadium is usually removed from the magma during the initial stage of crystallisation when it may replace Ti^{4+}, Fe^{3+} or Al^{3+}.

In kimberlite Cu may occur with sulfides or in the lattice of ferromagnesian minerals, possibly olivine. Scandium probably occurs in the pyroxene lattice and V in ilmenite, magnetite or apatite. It is unlikely that Ti will be present in magnetite derived from serpentine phenocrysts since this magnetite is the result of oxidation of Fe^{2+} (Dawson, 1960).

With the exception of the basic rocks, Cu and V are contained in the kimberlite in amounts in excess of the other common rock units.

It is noticeable that the V content of the kimberlite at Prairie Creek is not markedly dissimilar from the average kimberlite, but the content of V in the peridotite is similar to that of ultrabasic rocks.

2.223 Minor Elements Concentrated in Alkalic Rocks Especially in Residual Liquors

As indicated by the heading, this group of elements is concentrated in intermediate alkalic rocks, especially nepheline seyenites. However, with the exception of Ba, Sr and Rb, they are also concentrated in residual liquors and thus abnormal concentrations are recorded in nepheline seyenite pegmatites and to a lesser extent granitic and diabase pegmatites. This late stage concentration is due primarily to the reluctance of these metals to enter the lattice of rock forming minerals because of their ionic size. Thus whilst they tend to occur as distinct minerals, some substitution of elements may occur, for example, the light rare earths may replace Ca^{2+}; Nb and Ta may replace Ti^{4+} or Zr^{4+}, U and Th may replace Zr^{4+} and Hf replaces Zr^{4+}. In kimberlite these elements may occur in the lattice of perovskite ($CaTiO_3$), e.g. (CaRE) $(TiNbTa)O_3$; apatite, zircon, monazite, etc.

Rubidium, Ba and Sr are generally concentrated in the latest stages of crystallisation and only exceptionally form independent minerals due to the ready substitution of K by Ba and Rb, and Ca by Sr. In kimberlite these elements may occur in phlogopite (Ba and Rb), perovskite (Sr) or apatite (Sr), or zircon. Veinlets of barite are recorded in the igneous rocks of Prairie Creek.

It can be seen from Table 2.2 that Nb, Ta, Ce and Hf are present in the kimberlite in concentrations in excess of other common rock types, and La, Pr, Nd and Zr are present in highly abnormal concentrations. In addition to the above elements, the Li, Ba, Sr, Rb, Yt, Th and U content will differentiate kimberlite from most other ultrabasic rocks.

With the exception that the rare earths occur in excess, and Nb less than the mean, the trace elements content of the Prairie Creek kimberlite is not dissimilar from the mean African kimberlite.

Higher concentrations of many of the determined trace elements occur in the Prairie Creek peridotite than in the kimberlite. Highly anomalous concentrations of Ba, Sr and Nb are recorded in the Prairie Creek tuff.

Concentrations of Nb, Ba and Sr in the kimberlite tuff at Buell Park are not characteristic of kimberlite. The possibility must be considered therefore that this intrusion is not a true kimberlite.

2.23 Selection of Suitable Elements for Prospecting

No single element is sufficiently concentrated in kimberlite to differentiate this rock from all others. Thus ones choice of elements for prospecting must be primarily controlled by the nature of the country rocks. In areas where ultrabasic rocks are absent or scarce, the ultrabasic elements, i.e. Ni, Mg, Co, Cr, etc., may well give optimum contrast. In areas where ultrabasic rocks are common but alkalic rocks are absent, then alkalic element(s), i.e. Nb, La, Ce, Sr, Hf, etc., may well find application. In areas where both alkalic and ultrabasic rocks are common, i.e. carbonatite dykes in ultramafics, then geochemical reconnaissance methods will not be applicable.

The choice of element(s) will also be influenced by their behaviour during secondary dispersion. This is the subject of the body of the thesis. In dissimilar areas an orientation survey must be conducted.

The following elements were selected for determination in soils overlying kimberlite in Arkansas:

'ultrabasic elements'	Mg, Ni, Co, Cr, Mn and Fe.
'basic elements'	V and Ti.
'alkalic elements'	Nb, Sr, Ba, Zr and P.

Although the rare earths and several other elements also give a high contrast, rapid analytical methods are not readily available for their routine determination. Whilst suitable methods can no doubt be developed, there was insufficient time for this during the present study. A great many elements were, however, analysed semi quantitatively on the mass spectrograph at Manchester University. The results of this investigation are given in Chapter 9, and the possible use of Te, Hf and the rare earths in prospecting for kimberlite is discussed.

CHAPTER 3

FIELD AND LABORATORY STUDIES

3.1 FIELD SAMPLING

3.11 Rocks

Most of the rock samples were composite and made up of small chips to hand size specimens depending upon the texture.

Only two outcrops of kimberlite rock were found at Prairie Creek. These samples may not be representative of the whole.

3.12 Soils

The majority of the soil samples were collected using a 2 inch diameter screw auger with a shaft 3 feet long. Graduated extensions enabled samples to be collected to a depth of 15 feet. In the clay rich soils over the ultrabasic rocks, it was often necessary to lift the auger from the ground with jacks. In deeper profiles over the peridotite yellow ground, it was necessary to first pulverise the sample by hitting the auger with a sledge hammer. The powdered material was subsequently removed with a 2 inch post hole auger. Using these methods a 10 foot depth hole over the ultrabasics usually took 1 to 3 hours to complete.

Some soil profiles were collected with Mr. J. Hoelscher of the Soil Conservation Society, Arkansas, U.S.A., using a Bull Soil Sampler. (Available from A.D. Bull Enterprises, 520 So 16th, Chichasha, Oklahoma, U.S.A.) Essentially this machine consists of a steel tube, cut away down much of its length and with a cylindrical tungsten carbide bit. The tube is pushed into the ground by means of a hydraulic mechanism mounted on a four wheeled vehicle. Various extension rods are available allowing a sampling depth up to 12 feet.

The advantages of this machine are:

(1) The considerable speed with which a profile can be taken. For example, an 8 foot profile can be recovered in about one minute.

(2) The profile is generally undisturbed.

There are however several disadvantages:

(1) The sample site must be accessible to a four wheeled vehicle. On steep slopes the vehicle must be anchored to avoid distortion of the tube.

(2) It is unsuitable for sandy and pebbly soils.

(3) It is relatively expensive. The hydraulic mechanism cost $800, the probes $34 to $67 and the bits $$7^{50}$ to $$12^{50}$. (1967 prices.)

In soils where pebbles were so numerous as to prevent deep augering, i.e. in the flood plain of the Little Missouri River, Arkansas, a series of pits were sunk. Channel samples were taken on these occasions.

Soil samples less than 9 inches from the surface were collected as channel samples from shallow pits dug with a shovel.

Samples were separated on the basis of soil horizons or every 6 to 9 inches, whichever was the shallower.

3.13 Drainage Components

3.131 Stream Sediment

Both poorly and well sorted material were collected from each sample site. In both cases samples were composite from two or three locations not more than 10 feet apart. The top 4 inches of sediment was collected and the plus $\frac{1}{4}$ inch material discarded. When the sediment was less than 4 inches thick, the entire profile was taken.

3.132 Slime

Scrapings, $^1/8$ inch deep, were taken of the slime which is present at most sediment locations in the American Mine drainage.

3.133 Wad

At selected locations at the American Mine Creek, pits were dug through the sediment to the creek bed. Channel samples were collected of black sesquioxides both coating pebbles and infilling interstices. The sesquioxides were subsequently removed from the pebbles by scraping with a polythene spatula.

3.134 Stream Banks

Channel samples 2 inches wide and $\frac{1}{4}$ inch deep were taken from the creek banks. The length of the channel was controlled by soil horizon or morphology and in any case was not more than 6 inches. At selected locations, grab samples were taken from 6 inches inside the bank just above the wet season water level.

3.135 Vegetation

Moss was collected from the banks of American Creek and grass from soils over the ultrabasic and background rocks. No attempt was made to identify individual species.

3.14 Storage

All samples were stored in Kraft paper envelopes and dried in an oven maintained at less than 60°C.

3.2 SAMPLE PREPARATION

3.21 Rocks

Two hundred to 600 gms of rock were crushed to minus 10-mesh (B.S.S.) in a manganese-steel jaw crusher. A representative sample of 100 gms was taken by coning and quartering then further reduced to minus 20-mesh with a tungsten carbide pulveriser. After further coning and quartering, about 30 gms of material was ground in a mechanised agate pestle and mortar to pass 80-mesh.

3.22 Mechanical Analysis

Selected soil samples were separated into their component size fractions using a wet dispersion and sedimentation method modified from that given by Piper (1950).

Briefly, 100 gms of minus ¼ inch material were placed in 150 ml of 1% calgon solution and vibrated ultrasonically for 60 minutes to disperse the soil particles. The slurry was diluted to 1000 ml with deionised water in a stoppered cylinder and homogenised by shaking. After settling for 7½ to 8½ hours, depending upon the ambient temperature (Piper, p. 76), the top 10 cm of liquid was siphoned off and the clay content separated by centrifuging at 4000 rpm for 15 minutes. After a further 7½ to 8½ hours a second 10 cm of liquid was siphoned off and the clay separated. After this cycle the supernatant liquid was poured back into the cylinder. This process of sedimentation was repeated until no more clay was removed.

The plus clay size material was separated by wet sieving through a nest of stainless steel screens. No Ni or Zn contamination from the screens was found by comparison with several duplicate samples sieved through nylon bolting cloth.

All the size fractions were washed twice with deionised water to remove any remaining calgon solution. The clay and silt fractions were dried in a vacuum dessicator at 21°C and the sand in an oven at 60°C. A loss in weight of about 5-8% was observed. This was irrespective of the clay content of the sample. The proportion of minus 10-mesh material was weighted to give 100%.

Using the method as outlined, the coarse fraction of the ultrabasic C horizon tended to disintegrate during even the most gentle drying. This is thought to be due to dehydration of the clay mineral phenocrysts. A certain number of samples were dispersed by wet autogenous grinding prior to sedimentation, i.e. 100 gms of sample in 75 ml of 1% calgon solution were stirred for 12 hours with a mechanical stirrer. This resulted in breaking down the weaker clay structures but allowing the individual, though decomposed, primary minerals to remain.

Stream sediments were separated into their component size fractions by first lightly grinding in a porcelain pestle and mortar to break up the soil textures and then sieving through a nest of perspex and nylon sieves. The silt and clay fractions were not differentiated.

The size terminology used in this thesis is illustrated on the table overleaf:

Table 3.1 The Mechanical Classification Used in this Thesis

Maximum diameter (microns)	Mesh (B.S.S.)	Grade Term
>1000	>16	Gravels
1000	16	Coarse Sand
500	30	Medium Sand
250	60	Fine Sand
100	150	Very Fine Sand
50	300	Silt
2		Clay

3.23 Routine Sieving

3.231 Soils

Many analyses were made on the 'complete' sample. This was first lightly ground in a porcelain pestle and mortar and sieved through a 10-mesh steel sieve. The oversize was discarded. About 10 gms of the undersize was taken by coning and quartering and ground in an agate pestle and mortar to pass 80-mesh.

Considerable difficulty was experienced with the clay rich samples of the Arkansas ultrabasic solum. When dry these are very hard but are still sufficiently plastic to hinder comminution. These were crushed by alternate pulverization on a tungsten carbide block and grinding in a porcelain pestle and mortar. It is possible that some plus 10-mesh material was inadvertantly crushed but this would be of very small amount and mainly sandstone xenoliths.

Preparation of the normal minus 80-mesh fractions was accomplished by lightly breaking the soil structures of about

20 gms of sample in a porcelain mortar and sieving through 80-mesh bolting silk. The ultrabasic soil had to be ground in order to provide some minus 80-mesh material.

3.232 Stream Sediments

Preparation of the normal minus 80-mesh fraction was identical to the method used for the soils.

The plus 80-mesh fractions, mainly minus 10 plus 20, were prepared by grinding a representative 10 gms of material to minus 80-mesh in a ceramic ball mill. Smaller samples were ground by hand in an agate pestle and mortar.

3.24 Organic Matter

Slight quantities of soil adhere to the roots of the moss. This was removed by agitation in deionised water until three successive washes were absolutely clear. The moss was then dried to constant weight at 60°C. Analyses were made by digesting the moss directly in nitric acid.

The A_{00} horizons were prepared in a similar manner but were ashed at 450°C in an electric muffle furnace. After cooling a known weight of ash was used in analysis.

3.25 Separation of Nodules

Sesquioxide nodules were separated by specific gravity methods from the minus 10 plus 80-mesh fractions of selected samples. These nodules were subdivided into:

(a) Those less dense than quartz (Mn rich)
(b) Those denser than 2.95 (Fe rich).

The washed, dried and sieved sample was placed in tetrabromoethane (S.G. 2.95) contained in a $2\frac{1}{2}$ litre separating funnel. The funnel was gently agitated to allow all the heavy particles to sink. When equilibrium had been established the heavy particles were drawn through the tap. More tetrabromoethane was then added and diluted with carbon tetrachloride so that a piece of introduced quartz only just sank. The sink was drawn off through the tap. It was often necessary to repeat this latter procedure in order to remove particles adhering to the funnel and to ensure a clean separation. The various fractions were filtered, washed with acetone and air dried. The acetone was previously tested for Ni.

3.3 SAMPLING ERRORS

A geochemical result is subject to a number of errors including:

(a) The lack of areal representivity: It is unlikely that the content of specific elements in any given sample is representative of a large area about the sample location. This is especially true in areas of rapidly changing lithology or adjacent to decaying anomalies. Error is minimized to some extent, however, by the collection of a large number of samples.

(b) Sampling error: It is improbable that two samples taken at the same location will give identical analytical results. This error may be reduced to some extent by the collection of a composite sample.

(c) Preparation error: Errors may also be incurred during the preparation of a sample for analysis by grinding, sieving and weighing.

(d) Analytical error: These are errors inherent in the analytical process and are discussed in Section 3.42.

Tooms (1955), working on the Copperbelt, investigated the effect of the above errors in some detail. He concluded that sampling and preparative errors were insignificant compared with analytical errors and did not effect the interpretation of the analytical result. Govett (1958), found sampling and analytical errors were of the same magnitude for Cu in Zambian stream sediments. Jay (1959), working on Co in Zambian soils found sampling error to be insignificant in the A horizon but appreciable in the B horizon.

The writers mentioned above worked on the minus 80-mesh fraction. Since the weight of sample required for a given correctness varies directly with the cube of the average grain size according to the formulae below, their conclusions may not be applicable to coarser grain sizes.

$$W = \frac{0.45\ X\ d\ (ma)^3}{2\ Y^2} \ * \qquad = \frac{2250\ (ma)^3\ A^2\ D\ M}{C}$$

where W = the required weight of sample for a given correctness
X = the approximate volumetric content of the host grain
Y = the permissable volumetric error
d = the specific gravity of the sample
a = the limiting grain size in cm
m = the ratio of the average to the limiting size
A = the reciprocal of the required correctness expressed as a fraction
M = the average per cent of metal in the host grain
C = the metal content of the sample (ppm)
D = the specific gravity of the host grain

This is well illustrated on Table 3.2 where the weight of sample required for a ±10% correctness is calculated for various simple forms of metal, at various grain sizes and metal concentrations.

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*Modified from a Camborne School of Mines Mineral Dressing Worksheet and based on the theory of errors.

Table 3.2 The sample weights required for a ±10% correctness for various forms of Ni at various grain sizes and concentrations.

Form of Metal	Assumptions	Size fraction taken Mesh B.S.S.	Assumed mean grain size microns	Sample weights (gms) required for various Ni contents				
				Ni content ppm				
				13	25	100	300	1000
Within discrete Ni silicates, e.g. garnerite	33% Ni SG. 2.67	-10+20	1225[1]	2800	1450	364	121	36.4
		-80	104[2]	1.72	0.9	0.2	0.07	0.02
		-80	52[3]	1.0	0.5	0.12	0.04	0.01
Within heavy mineral grains e.g. magnetite	2% Ni SG. 5.18	-10+20	1225[1]	330	172	43	14.3	4.3
		-80	104[2]	0.15	0.08	0.02	<0.01	<0.01
		-80	52[3]	0.1	0.05	0.02	0.01	<0.01
Within sesqui-oxide nodules	0.4% Ni SG. 3.1	-10+20	1225[1]	39.4	20.6	5.1	1,73	0.51
		-80	104[2]	0.02	0.01	<0.01	<0.01	<0.01
		-80	52[3]	0.01	<0.01	<0.01	<0.01	<0.01
Within olivine	0.2% Ni SG. 3.3	-10+20	1225[1]	21	11	2.7	0.9	0.11
		-80	104[2]	0.01	<0.01	<0.01	<0.01	<0.01
		-80	52[3]	<0.01	<0.01	<0.01	<0.01	<0.01
Evenly distributed	SG. 2.67	-10+20	1225[1]	0.11	independent of concentration			
		-80	104[2]	<0.01	independent of concentration			
		-80	52[3]	<0.01	independent of concentration			

1. Arithmetic mean size
2. Probable mean size of stream sediment over the Trinity siltstone. Calculated from table 6.21.
3. Probable mean size of soil over the Trinity siltstone. Calculated from fig. 4.5.

Table 3.3 Replicate analyses of the minus 10 plus 20-mesh and minus 80-mesh fractions of sediment from the American Mine drainage

		Trinity siltstone			limestone	anomalous	normal analytical precision
		550121	550122	530125	550128	556501	
-10+20 mesh	Ni ppm	14 18	12.5 10	12.5 16	64 46	374 340	±15%
	Variation %	±13	±10	±14	±16	±5	
-80 mesh	Ni ppm	5 10	5 5	5 7.5	12.5 15	80 60	±15%
	Variation %	±30	0	±20	±10	±14	

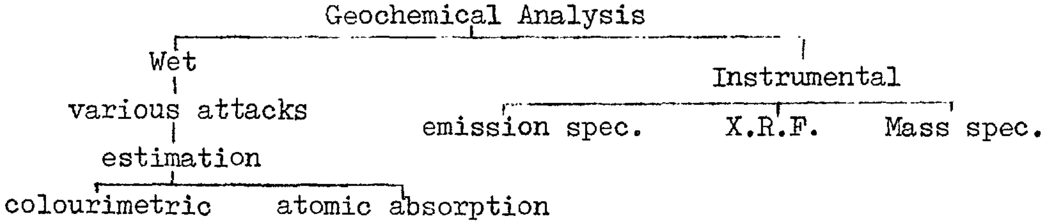
It can be seen that whereas 1 gm of sample, and commonly less than 0.2 gms, are adequate for a ±10% correctness in the minus 80-mesh fraction; several grams to several hundred grams of material may be necessary for the same correctness in the minus 10 plus 20-mesh fraction.

Five samples from the minus 10 plus 20-mesh and minus 80-mesh fractions of sediment from the Arkansas drainage were prepared and analysed in duplicate (Table 3.3.). **It can** be seen that in both the minus 10 plus 20-mesh and minus 80-mesh fractions the results are generally within the analytical precision. It is concluded therefore that for Ni in the Arkansas drainage, sampling errors in both the coarse and fine fractions are less than the analytical error and will not affect the interpretation. These conclusions may be reasonably extended to include other elements present in similar forms to Ni. They may not be applicable to elements which are very highly concentrated in particular minerals, especially when the overall metal content is low and small sample weights are taken.

3.4 DETERMINATION OF THE ELEMENTS

3.41 Introduction

The analytical methods used in this thesis may be classified into (a) Wet, and (b) Instrumental methods. Wet methods may be further subdivided into two usually independent stages (i) the attack, and (ii) the estimation (Fig. 3.1 below). These categories form the headings of this sub-chapter.



With a few exceptions, the methods have been described in previous publications. Accordingly, a brief description only is presented. For detailed procedures the reader is referred to the original paper. Any modification to the standard technique, however, is described in greater detail.

The instrumental methods usually determine the total concentration of metal in the sample whereas the wet attacks are often only partial. Accordingly, a brief discussion of the likely forms of metal extracted with the wet attacks is presented.

3.42 Control of Analyses

Analytical precision was controlled by the method of Craven (1953) and described by Stanton (1966). The statistical series was **prepared** from homogenised samples from the soil solums over the Prairie Creek kimberlite and background Trinity siltstone. The control samples were included every 10 or 15 routine determinations and a blank was included in every batch of analyses.

A summary of the precision at the 95% confidence level for the various analytical methods is given on Table 3.4. For the wet methods the best precision of ±15% or better were obtained for Mg, Ni and Fe and worst of ±50% for Nb. The strong acid and bisulfate attacks gave the best precision for Ni and the 0.025% v/v HNO_3 and NH_4 acetate the worst.

Precision for the emission spectrograph was much worse than for the wet methods, especially over the complete range of results. This is attributed partly to matrix effects and is discussed in Section 3.441.

Table 3.4: The mean precision, at the 95% confidence level, for the elements as determined by spectrographic and wet methods; and for Ni determined by various attacks

(a) Elements determined with the emission spectrograph

	Mean precision ±%				
	Ni	Co	Fe	Cr	Sr
$\sigma = 1.0$	103	79	49	76	35
$\sigma = 0.4$	49	59	45	63	25

(b) Elements determined by wet methods

	Co	Fe	Mn	Nb	P	Cr	Mg	exMg
mean precision ±%	25	15	30	50	20	25	10	12

(c) Nickel determined using various attacks

Attack	$HF/HClO_4$	$HClO_4$		$KHSO_4$	Na citrate dithionite	0.5M HCl	0.025% v/v HNO_3	NH_4 Ac	
		1	2					1	2
Mean precision ±%	12	15	15	15	33	15	70	40	70

1. colourimetric estimation
2. atomic absorption estimation

3.43 Wet Methods

3.431 The Attacks

A summary of the attacks used for the various elements is given on Table 3.5.

3.4311 Hydrofluoric-perchloric Acid

Experimental details of this attack are given in Technical Communication No. 38 of the Applied Geochemistry Research Group (A.G.R.G.) and is based on a method developed by Stanton, MacDonald and Carmichael (1962).

The sample is digested with hydrofluoric, perchloric and nitric acids. These are evaporated to dryness and the residue leached with M hydrochloric acid. The insoluble products are fused with sodium carbonate. After cooling the melt is digested with 1M hydrochloric acid; hydrofluoric and nitric acids are added and evaporated to dryness. The resulting residue is leached with 1M hydrochloric acid, filtered and mixed with the previous filtrate after adjustment of the volumes of both to 10 mls by evaporation. Heavy metals are extracted from a 10 ml aliquot of the mixed filtrates by shaking with dithizone in carbon tetrachloride in the presence of a citrate buffer at pH 10.8. The organic phase is evaporated to dryness and oxidised with sulfuric and perchloric acids. The residue, after heating to dryness, is dissolved in a known volume of 0.5M hydrochloric acid. The required metals are determined by taking suitable aliquots and using the appropriate estimation stage.

This attack is usually regarded as total. Harden and Tooms (1964) report close agreement between this attack and the emission spectrograph for Ni, Co, Cu and Zn in pyroxene, amphi-

Table 3.5: Summary of the attacks used for the various elements

Element	Attacks
Ni	Hydrofluoric-perchloric acid; nitric-perchloric acid; potassium bisulfate; 0.5M hydrochloric acid; sodium citrate-dithionite; ammonium oxalate-oxalic acid; 0.25% v/v nitric acid; M ammonium acetate.
Co	Hydrofluoric-perchloric acid; nitric-perchloric acid; potassium bisulfate.
Fe	Nitric-perchloric acid; potassium bisulfate; 0.025% v/v nitric acid.
Mn	Perchloric-nitric acid; potassium bisulfate.
Cr	Sodium peroxide-hydroxide fusion.
Nb	Hydrofluoric acid.
P	Potassium bisulfate.
Mg	Hydrofluoric-perchloric acid; M ammonium acetate.

boles and feldspars. A similar agreement between the two attacks is recorded for Ni in the Trinity solum (Table 3.6) but not in the kimberlite solum where only 70% of the Ni is extracted by $HF/HClO_4$. The reason for this is unknown. It could be due to spectrographic inaccuracy or to an extremely resistant form of metal in the kimberlite.

3.4312 Nitric and Perchloric Acids

This attack is described by Stanton (1966) for Fe but with slight modification can also be used for Co, Cu, Pb, Mn, Ni and Zn.

A known weight of sample is digested with nitric and perchloric acids in a glass beaker. The acids are completely evaporated and the residue dissolved in a known volume of M hydrochloric acid. Suitable aliquots are taken and the acid molarity adjusted as the estimation stage demands.

This attack is not as strong as the $HF - HClO_4 - HNO_3$ attacks described above and is similar in strength to the potassium bisulfate fusion (Table 3.5 and Tooms, pers. comm.). It is a useful attack when organic matter is contained in the sample or when a large quantity of dissolved matter is objectionable, e.g. in atomic absorption spectroscopy.

3.4313 Potassium Bisulfate Fusion

This attack is described for Ni by Stanton (1966). However, by using the appropriate leach it may also be used for As, Co, Cu, Bi, Fe, Ni, Mn, P, Pb, V and Zn.

A known weight of sample is fused with excess of potassium bisulfate in a pyrex test tube. The melt is dissolved in

Table 3.6: The amounts of Ni extracted from the soil **solum** of kimberlite and Trinity formation by various attacks. Data on minus 80-mesh fraction

	Ni extracted (ppm)								
	Emission Spec.	HF/$HClO_4$ HNO_4	$HClO_4$	$KHSO_4$	Ammonium oxalate	Na nitrate dithionite	0.5M HCl	0.025% HNO_3	NH_4Ac
Kimberlite solum	2000	1390	1300	1300	380 1200	407	1230	20-50	12.5
Trinity solum	50	50	15	12.5	9	3	20	3	1
Contrast	40	27	87	105	41-133	133	62	7-17	12

0.5N HCl, H_2SO_4 or HNO_3 according to the element to be determined.

The efficiency of this attack has been discussed by Harden and Tooms (1964). They found that only a limited amount of Ni, Co and Zn but almost all the Cu was extracted from pyroxenes and amphiboles. Biotite is strongly attacked and most of the metal is extracted from feldspars. They concluded that the efficiency of the attack is a reflection of the mineralogy and the degree of alteration or weathering. This is consistant with data obtained by the writer where 94%* of the Ni is extracted from weathered and highly decomposed kimberlite, but only 25% of the metal is extracted from the quartz and detrital mineral rich Trinity formation (Table 3.6).

3.4314 Hydrofluoric Acid

This attack was used for Nb and is described by Stanton (1966).

Essentially a known weight of sample, usually 0.5 to 1 gm, **is** placed in a polythene recepticle, i.e. a beaker or ice cube tray etc. Hydrofluoric acid is added and allowed to evaporate overnight on a water bath. The residue is leached with 10% hydrofluoric acid for the determination of Nb.

This attack will decompose all but the most refractory silicates (Stanton). Perovskite and other common Nb bearing minerals are decomposed but ilmenite and zircon may be only partially attacked (Deer et al, 1962). Thompson (1964) observed only 66% of some Nigerian zircons to be decomposed by HF but other zircons were completely dissolved.

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*compared with the HF/$HClO_4$ attack.

3.4315 Alkaline Fusion

This attack was used for Cr and is described by Stanton (1966).

A known weight of sample is fused with sodium hydroxide and peroxide in a nickel crucible. After cooling the melt is leached with 10% ethyl alcohol, boiled and filtered. The filtrate can then be compared with standard potassium dichromate solutions or suitable aliquots taken and determined colourimetrically.

This attack will decompose chromite and all but the most refractory substances.

3.4316 Ammonium Oxalate - Oxalic Acid

This attack is described by Le Riche and Weir (1963) and was used by Horsnail (1968).

One gram of sample is dried to constant weight at 60°C and placed in a conical flask containing 50* ml of ammonium oxalate in oxalic acid at pH 3.3. (Prepared by mixing 0.275M solutions of ammonium oxalate and oxalic acid in the proportions of 100 to 65 respectively.) The samples are allowed to soak for 120 to 125 hours and then stirred with a magnetic stirrer under a Hanovia ultra violet lamp (Model 16). The slurry is filtered through previously weighed (constant weight at 60°C) and numbered No. 502 filter paper. The metal content of the filtrate may be estimated either colourimetrically or using an atomic absorption spectrophotometer. The residue and filter paper are washed 4 times with deionised water to remove oxalic acid and then dried to constant weight at 60°C.

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*Le Riche and Weir used 3 gms sample in 150 ml of leach solution.

Using the method as described gave erratic results for the Arkansas statistical series. Accordingly, limited studies were made on the amounts of Ni extracted at various sample to leach solution ratios and at various leaching times.

The results of the leach volume to sample weight investigations are presented on table 3.7 below.

Table 3.7 The amounts of Ni extracted by NH$_4$ oxalate/oxalic acid solution at various sample weight to leach volume ratios

Leach Volume	5ml		10ml	20ml		50ml	
Sample weight	0.2	0.5	0.1	0.2	0.5	1.0	1.0
Ni ppm	200	96	625	850	240	260	385
Final pH			4.5	4.2	6.7	8.2	7.0

It can be seen that highest amounts of Ni are extracted when the ratio of sample to leach volume is least and the smallest amounts when the sample to leach solution is greatest. The final pH of the leach solution rises considerably at high sample to leach volume ratios. It is suggested therefore that the kimberlitic material progressively neutralises the oxalate solution and that the extraction is retarded (cf Table 1 of Le Riche and Weir).

To investigate the variation in Ni extracted with stirring time, the leach solution was increased to 150 ml and the sample weight to 3 gms. Ten 2 ml aliquots were removed from the leach solution at progressively increasing time intervals up to 75 minutes. A further 9 aliquots were taken from an identical sample after 60 minutes to 2700 minutes (4½ hours). Care was taken not to include any soil material in the aliquot and a correction was applied for the loss in leach volume. Nickel was determined using the atomic absorption spectrophotometer (described later).

The results of this extraction are plotted logarithmetically on Figure 3.2. It can be seen that extraction increases with time and ultimately 86% of the Ni is extracted from the kimberlite solum. There are distinct "kinks" in the curve at 220 and 430 ppm, respectively. These may correspond to different forms of metal being released (Kagule-Mgambo, 1965; Ellis et al, 1967).

According to Le Riche and Wier the attack dissolves secondary Fe oxides. Organic matter is attacked and the solution dissolves Fe from certain silicate minerals containing a large amount of lattice ferric Fe, e.g. nontronite. Metal sorbed on clay minerals is also removed. During the attack the trace elements associated with the above phases are released and may go into solution.

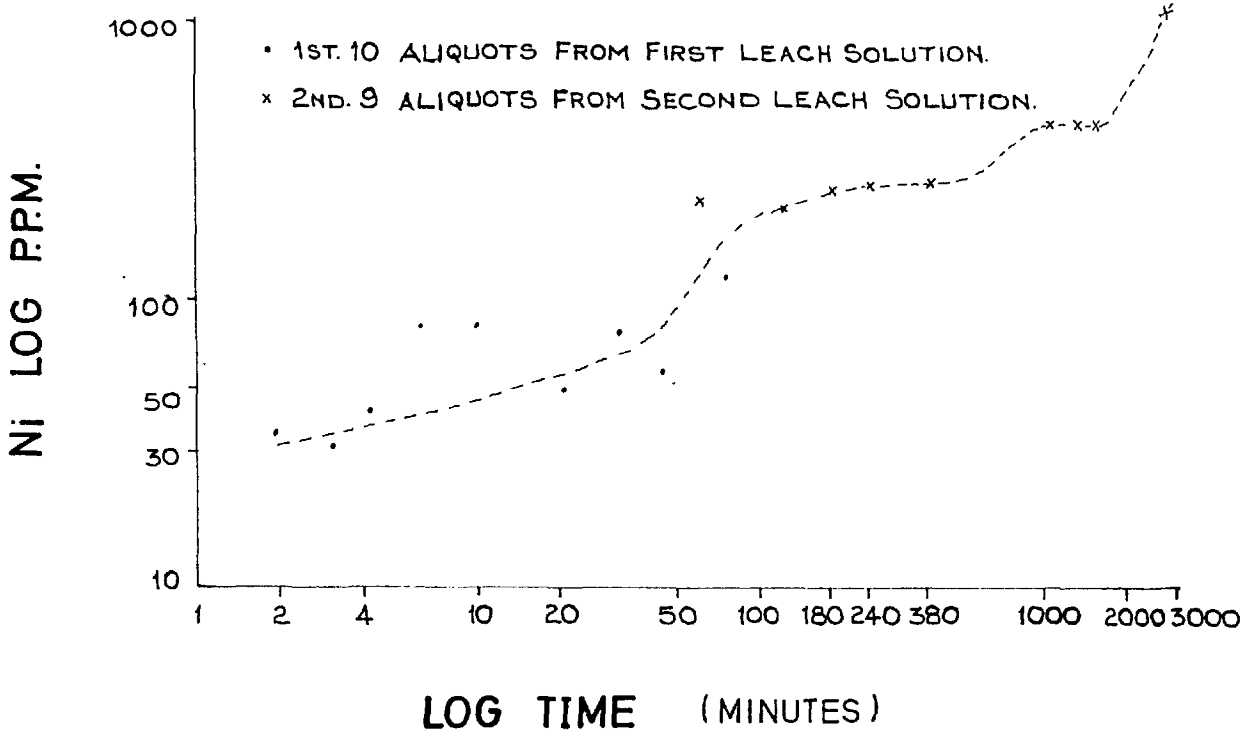
The variable results obtained from the kimberlitic solum in no way detract from the conclusions of Le Riche and Wier. It does appear, however, that this attack is more suitable for some soils than others. Because of the variation of the efficiency of this attack between the kimberlitic and sialic soils, very limited work was undertaken using this method.

3.4317 <u>Sodium Citrate - Sodium Dithionite</u>

This attack is described by Aquilera and Jackson (1953) and was used in the extraction of Ni by Wilding (1965).

The sample (0.1-0.2 gm), dried to constant weight at 60°C, is placed in a conical flask and 10 ml of sodium citrate

FIG. 3·2 THE AMOUNTS OF Ni EXTRACTED FROM THE KIMBERLITE SOLUM WITH AMMONIUM OXALATE/OXALIC ACID SOLUTION AT VARIOUS LEACHING TIMES.



reagent added. (75 gm dissolved in 900 ml of water and the pH adjusted to 7.3 with 5M citric acid.) The flask is placed on a water bath maintained at 85°C and mechanically agitated for 15 minutes. Five mls of sodium dithionite solution (1 gm in 5 ml adjusted to pH 7.3 with M NaOH) is added and the sample agitated for a further 15 minutes. The slurry is filtered through a filter paper (No. 542) previously dried to constant weight at 60°C, and the filtrate is retained for analysis. The residue is washed 4 times with deionised water and dried to constant weight at 60°C.

According to Aquiliera and Jackson (1953) secondary Fe oxides are dissolved by this attack. Presumably elements associated with these oxides are released and available for solution. It is likely also that sulfides, sulfo salts and clay minerals may also be partially attacked (Wilding, 1965).

This attack gave a reasonable precision (±33% at the 95% confidence level) and reproducibility. 407 ppm Ni is extracted from the kimberlite solum. This compares favourably with a point of inflexion on the ammonium oxalate - oxalic acid extraction at 430 ppm Ni. The amount of Ni extracted from the Trinity siltstone solum is also less than with the oxalate attack. Increasing the agitation time to 60 minutes does not remove any more Ni.

It appears, therefore, that for the kimberlite and Trinity solums at least, this attack is weaker than the oxalate extraction.

3.4318 <u>0.5M Hydrochloric Acid</u>

A known weight of sample (0.1-0.2 gms) is placed in an 18 x 180 mm test tube calibrated at 10 ml. 10 mls of 0.5M

HCl are added and heated for 1 hour just below boiling on a sand tray. At the end of the attack deionised water is added to replace evaporation losses. The solution is centrifuged and a suitable aliquot taken for estimation. During the attack the tube is agitated at 15 minute intervals.

The amount of Ni extracted from the kimberlite solum at various extraction times is presented on Figure 3.3. It can be seen that there are points of inflexion at 135, 440 and 1200 (maximum) ppm Ni. These may reflect different forms of metal taken into solution.

Just what is attacked by 0.5M HCl is uncertain. Sulfo salts and sulfides, clay minerals and secondary iron oxides are almost certainly leached and olivine, ilmenite and magnetite may be partially attacked (Deer et al, 1962).

The coincident inflexions of 410-440 ppm Ni observed for 0.5M HCl, ammonium oxalate and sodium citrate - dithionite attacks, may reflect a similar occurrence of metal taken into solution, possibly that associated with sesquioxides.

A greater proportion of metal is extracted from the Trinity solum with hydrochloric acid than with $KHSO_4$ (Table 3.6).

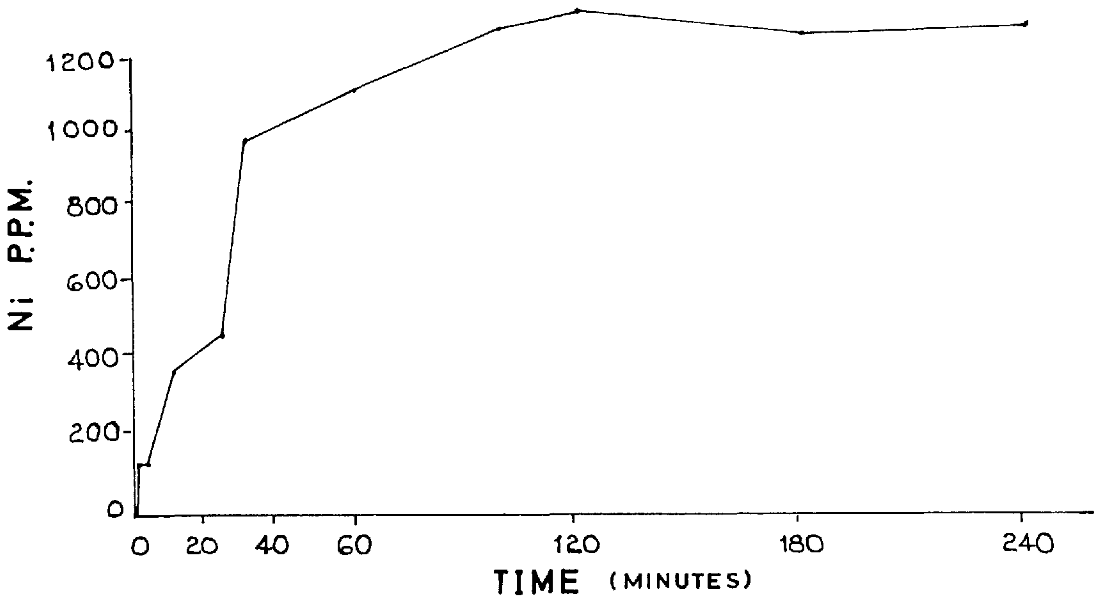
Lower contrasts between the kimberlite and country rocks were obtained using this attack than with a bisulfate fusion, accordingly the 0.5M HCl attack was not further developed.

3.4319 0.025% v/v HNO_3

This attack is described by Taylor (1968).

A known weight of sample (0.1-0.2 gms) is placed in an 18 x 180 mm test tube calibrated at 10 ml. 10 mls of 0.025% HNO_3

FIG. 3·3 THE AMOUNTS OF Ni EXTRACTED FROM THE KIMBERLITE SOLUM WITH 0·5 M HCl AT VARIOUS LEACHING TIMES. DATA ON -80 MESH FRACTION.



are added and heated for 30 minutes just below boiling on a sand tray. At the end of the attack deionised water is added to replace evaporation losses. The solution is centrifuged and a suitable aliquot taken for estimation. During the attack the tube is agitated at 15 minute intervals.

On soils from Arkansas the precision was ±70% at the 95% confidence level. Sensitivity is poor and cannot be increased by increasing the sample weight since the major components tend to neutralise the acid.

Taylor reports oxidised Pb and Zn minerals in Northern England and some secondary Zn silicates to be attacked. Metal is not removed from Fe oxides even when co-precipitated.

It is unknown what forms of metal are attacked in Arkansas. It is likely, however, that weakly held forms of metal, i.e. adsorbed on clay minerals, sulfo salts etc., will be leached.

3.4320 M Ammonium Acetate

A known weight of sample is placed in a test tube and 10 mls of M Ammonium Acetate at pH 7.0 added. The tube is tightly corked and shaken for 30 minutes on a mechanical shaker. At the end of the extraction the tube is centrifuged for 3 minutes at 2000 rpm and a suitable aliquot taken from the supernatant liquid.

Varying the sample weight from 0.1 to 1 gm has no effect on the concentration of Mg extracted by the attack (Table 3.8). Reproducibility is very good for Mg but less good for Ni (Table 3.9). Over 2 minutes, the time of agitation has little effect on the amount of Ni or Mg extracted (Table 3.10). However to be in accord with other workers the shaking time was standardised to 30 minutes. No experiments were made to study the amount

Table 3.8 The amounts of Mg extracted with neutral molar NH_4 acetate at various sample to leach volume ratios

	exMg (ppm)				
Sample weight (gm)	0.1	0.2	0.3	0.5	1.0
Kimberlite solum	4480	4168		4390	4510
Trinity solum	98	90	90	100	98

data on minus 80-mesh fraction. Leach volume 10 mls

Table 3.9 The reproducibility of the molar NH_4 acetate attack for Mg and Ni. Sample weight 1 gm. Temperature 21°C. Shaking time ½ hour.

Sample	Element	Number of determinations	Metal content (ppm)	
			range	mean
Kimberlite solum	Mg	4	4160 - 4750	4510
20% Kimberlite solum) 80% Trinity solum)		7	940 - 1080	1010
Trinity solum		8	90 - 120	98
Kimberlite solum	Ni colorimetric	3	8 - 12.5	10
20% Kimberlite solum) 80% Trinity solum)		2	<1 - 1.25	
Trinity solum		2	<1	
Kimberlite solum	Ni atomic absorption	3	9 - 17	13
20% Kimberlite solum) 80% Trinity solum)		3	<0.5 - 4.5	<2
Trinity solum		3	<0.5	

Table 3.10 The effect of shaking time on the extraction of Ni and exMg by molar NH_4 acetate from the kimberlite and Trinity solums.

Time (mins)	Kimberlite solum		Trinity solum	
	Mg ppm	Ni ppm	Mg ppm	Ni ppm
1	3640	9.4	108	0.5
2	4300	9.4	100	0.5
4	4155	7.3	90	0.5
8	4020	11.0	97	0.5
16	3900	10.5	96	0.5
32	4395	11.0	98	0.5
64	5265	10.5	110	0.5
128	5130	14.0	147	0.5
720	4200	12.0	110	0.5

of metal extracted at varying temperatures.

This attack has been used by soil scientists to determine the exchangeable cations (ex metal); the NH_4^+ ions (ionic radius 1.43A) replacing other cations sorbed in exchange positions. The metal ions so displaced pass into solution and can be determined in the leachate. In addition to exchangeable cations, the following forms of metal are also taken into solution (Jackson, 1958):

1. Soluble salts
2. Cations released from minerals during weathering
3. Ca and Mg from the dissolution of Ca and Mg carbonates.

Indeed Kelley (1948) concludes the "exchangeable data" for Ca and Mg on calcareous soils to be meaningless.

The use of this attack to determine loosely held metal is not in question but it must be remembered that several forms of metal may be taken into solution.

3.432 Estimation of the Elements

3.4321 Colourimetric Methods

As previously mentioned, the elements were estimated using well tried and documented procedures. A summary of the reagents and buffers used for the various elements are presented on Table 3.11. The methods are not further described here but have been fully documented by Stanton (1966). There are however several practical details concerning Ni, Cr and Nb which should be mentioned.

Nickel

When Fe^{2+} is present in large amounts in the leach solution, an insoluble purple precipitate is formed with α-furidioxime.

Table 3.11 Summary of colourimetric methods used for the determination of the elements

Metal	Composition of leach solution	Buffer	pH of Buffer	Reagent colourimetric	Production man day	Colour of highest standard
Ni	0.5 M HCl	Ammoniacal NH_4 citrate	10.3	alpha furidioxime in benzine	100	yellow
Co	0.5 M HCl	Na acetate and pyrophosphate hydroxylamine hydrochloride, HCl, K thiocyanate	4.5-5.2	tri "n" butylamine in amyl alcohol	100	blue
Nb	10% HF	Paper chromatography. Separation in ethyl methyl ketone		tannic acid in the presence of ammonia	60	yellow
Cr	10% ethanol in dilute NaOH	E.D.T.A. in acid solution.	<7.0	diphenylcarbazide in acetone and acetic acid	60	pink
Fe	0.5 M HCl	Tartaric acid		ammoniacal solution of thioglycollic acid	150	pink
Mn	0.25M sulfuric acid	Sulfuric, nitric and orthophosphoric acids		potassium periodate	100	pink
P	4M HNO_3	nitric acid		NH_4 meta vanadate and NH_4 molybdate in nitric acid.	100	yellow

Although this tends to settle at the benzine/aqueous interface, the yellow colour of the Ni furidioxime complex is often masked. Thus in non-oxidising attacks, especially those involving reducing reagents, e.g. sodium dithionite, Fe^{2+} may cause interference. This can generally be overcome by the addition of a small amount of potassium dichromate to the leach solution. A similar interference by Fe^{2+} may occur when the sample is shaken in bright sunlight.

In the colourimetric determination of exNi, 0.2 mls of 5M hydrochloric acid should be added to the buffer prior to the sample aliquot.

Chromium

Samples containing high concentrations of Fe tend to give high results when read on the "high range" method. Indeed, a sample of ferric chloride analysed for Cr gave 3000 ppm Cr on the high range method but only 140 ppm using diphenylcarbazide as the colourimetric agent. This is due to the masking of the pale yellow dichromate solution (at low Cr concentrations) with a yellow brown colouration. Thompson (pers. comm.) observed a similar yellow brown solution from samples rich in Fe during the preparation of hafnium peroxidates and thought this may be due to the formation of Fe peroxidate complexes. It is possible that these (Fe) complexes are formed during the peroxide fusion and subsequent hydrolysis utilized in the Cr method; however, this was not further investigated. All chromium determinations were done using the diphenylcarbazide method.

Niobium

In an attempt to improve the precision of the Nb determinations, duplicate chromatograms were prepared. If the readings differed by more than ±20% then a further duplicate set of chromatograms were prepared. The Nb content was calculated from the mean of the readings. Using these methods the precision was often better than ±50% at the 95% confidence level.

3.4322 Atomic Absorption

Magnesium and some Ni determinations were made using a Perkin Elmer Spectrophotometer Model 303. The experimental conditions are set out on Table 3.12 below.

Table 3.12

Wave length counter	285 (2852Å)
Slit width	5 (3mm 20Å)
Source	6 ma hollow cathode
Burner	Perkin Elmer premix
Air pressure	30 psi
Acetylene	8 psi
Air flow	4
Fuel flow	4
Flame	reducing

In the determination of Mg, phosphorus and Al were suppressed with 1% lanthanum oxide in HCl as recommended by Perkin and Elmer (1966).

3.44 Instrumental Methods

3.441 Emission Spectrograph

The method is described by Nichol and Henderson-Hamilton (1965).

The minus 80-mesh sample is heated to 400 to 500°C in a silica crucible to oxidise organic matter and expel combined water. A suitable quantity of cooled sample is mixed with an equal weight of buffer (1:1 mixture of lithium carbonate and carbon) to which Ge has been added as an internal standard. The homogenised mixture is burnt and the concentration of the various elements estimated by comparing the spectra of the sample with spectra on a standard plate.

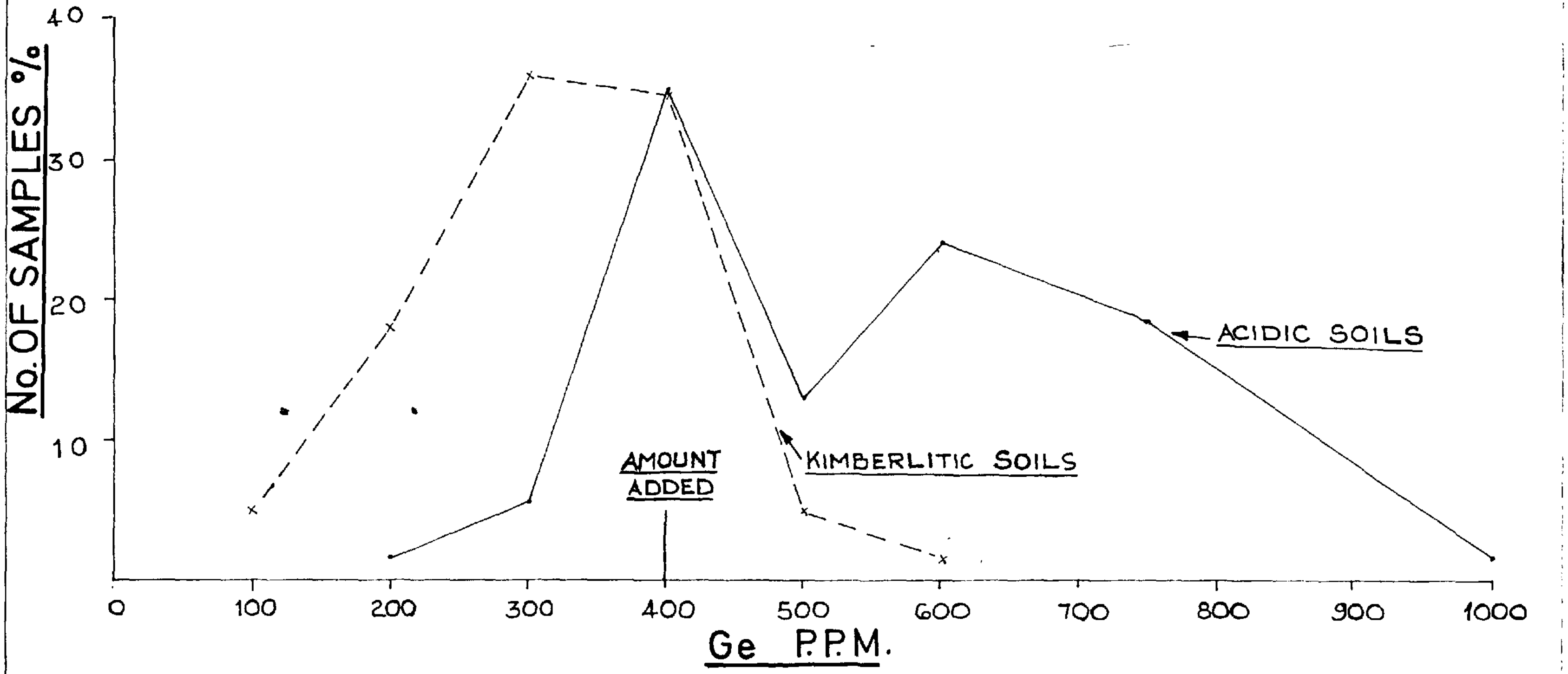
The specifications of the instrument used and the operating conditions are summarised on Table 3.13.

The mean precision at the 95% confidence level for various elements is illustrated on Table 3.4. Insufficient samples were inserted during the initial run of routine determinations and the statistical series was determined independently at a later date.

It can be seen that precision is considerably better for low values of Q than over the complete gradation of kimberlite to country rocks. This is thought to be due to matrix effects which for the ultrabasic samples tend to give low values for the Ge internal standard (Fig. 3.4). It is likely that other elements are also suppressed but the degree of suppression is unknown.

3.442 X-ray Fluorescent Analysis

Rubidium, Sr, Yt, Zr and Nb in the statistical series were determined using an A.R.L. production X-ray Quantometer. (40KV, 30MA, W target tube OEG - 60, integration time 300 secs with an argon filled proportional counter.) G.1, W.1, SY-1 and a standard albite riebeckite granite were taken as the standards. The metal content was estimated by plotting the ratio from the relative $K\alpha$ lines. Allowance was made for the coincidence of $RbK\beta$ with $YtK\alpha$; $SrK\beta$ with $ZrK\alpha$ and $YtK\beta$ with $NbK\alpha$.



THE FREQUENCY DISTRIBUTION OF THE Ge INTERNAL STANDARD FOR ACIDIC AND KIMBERLITIC SOILS
(SPECTROGRAPHIC ANALYSES)

FIG. 3·4

Table 3.13 Spectrographic equipment and operating conditions

Source Unit	Hilger FS 131
Spectrograph	Hilger Large Quartz FS 55
Arc Stand	Hilger FS 56
Comparator	Hilger JS CO.L. 90
Wavelength Range Å	2800-4950
Emulsion	Ilford N.30
Anode	Morganite SG. 305H - 5 mm carbon, 2.91 mm diam. 5 mm deep crater
Cathode	Morganite SG. 305H - flat
Exposure	20 seconds
Gap	3 mm
Arc Current	12.5 Amps
Slit	15μ
Collimator	Internal
Stop Sector	Two steps giving three intensities in proportion $1:\frac{1}{4}:\frac{1}{16}$

The results are presented on Table 3.14. Rb, Nb and Yt are close to the sensitivity of the method in the kimberlite and well below in the Trinity solum. Strontium is readily determined in the kimberlite but is below instrumental sensitivity in the Trinity siltstone solum; this is the reason for the relatively poor precision for this element. Zirconium is readily determined in both types of soil and precision is good.

Table 3.14 Rb, Nb, Yt, Zr and Sr in the Kimberlite and Trinity Solums as Determined by X-ray Fluorescence

	Metal Content ppm Rb	Nb	Yt	(1) Zr	(2) Zr	(1) Sr	(2) Sr
Kimberlite Solum	100	70	50	1050	994	600	615
Trinity Solum	<25	<25	<20	630	629	<25	62
Mean % precision at 95% confidence level					±12		27

(1) determined value

(2) calculated value from statistical series

3.443 Mass Spectrograph Determinations

A limited number of samples were analysed semi quantatively on the mass spectrograph (Type M.S.7. Maker A.E.I.) at Manchester University. The instrument and operating procedure is fully described by Taylor (1965) and Nicholls (1967). However, considerable modifications of their techniques are used both in sample preparation and determination.

The sample is ground until no gritty bits could be felt when a small fraction is rubbed between the palm and middle fingers. About 400 mg of the ground sample is mixed with an equal weight of Ringsdorffwerke RWA grade graphite, initially by grinding and finally mechanically. Approximately 200 mg of the homogenised mixture is compressed into a rod 20 mm x 2 mm x 2 mm in a small die under 7500 psi. The rod is then broken and mounted in previously cleaned tantalum electrodes.

The normal operating and exposure conditions used by the writer are presented on Table 3.15.

Photographic plates used were Ilford Q - 22. 2 x 10 inch and were processed according to the manufacturers instructions.

The lines due to various mass numbers are readily identified against a marked master plate. Interpretation is based upon the faintest visible line being 0.01 ppm atomic at 100 millimicrocoulombs (Nicholls, pers. comm.). Metal content in ppm (by weight) is calculated from the formulae:

$$C = \frac{1}{E} \times \frac{100}{I} \times \frac{AW}{AW'} \times \frac{R'}{R}$$

where C = the metal content in weight ppm
E = the exposure of the faintest visible line in millimicrocoulombs
AW = the atomic weight of the element considered
AW' = the mean atomic weight of the matrix, taken as 21
I = the relative abundance of the isotope considered
R' = an arbitary assigned relative sensitivity factor of 21
R = the relative sensitivity factor

An internal standard was not used and thus the plate sensitivity is unknown. According to Taylor, this may vary by a

Table 3.15 Operating Conditions of the M.S.7. Mass Spectrograph

Exposure (millimicro -coulombs)	Range Factors		Meter	Pulse Repetition rate (c/s)	Pulse Length (micro sec.)
	Int.	Mon.			
0.1	10	10	1	30	50
0.5			5		
1.0	100	10	1	100	100
2.0			2		
3.0			3		
5.0			5		
7.0			7		
10.0	1000	100	1	300	200
20.0			2		
30.0			3		
40.0			4		
50.0			5		
70.0			7		
80.0			8		
100.0			10		

Spark voltage	30%
Magnet Current	309mA
Accelerating voltage	19.4KV

factor of 3.

It must be emphasised that using the method as outlined above, the results are, at the best, only semi quantitative.

3.5 MISCELLANEOUS

3.51 Tellurium

Attempts were made to determine Te using:-

(a) the method described by Hikime et al (1961) which employs comparison of standard solutions of the Te diethyldithiocarbamate complex. However, even when kept in the dark, the standards faded very rapidly (15 to 30 minutes);

(b) employing the catalytic precipitation of gold in a solution of 6N HCl, auric chloride, cupric chloride and hypophosphorus acid (Lakin and Thompson, 1963). A blank could not be obtained, even when nitrogen was bubbled through the hypophosphorus acid before use. Lakin and Thompson have, however, used the method with some success.

3.52 Measurement of pH

The pH of waters and some soils were measured in the field using a BDH Universal Indicator.

Most of the soil and sediment pH measurements were made in the laboratory using a battery powered pH meter. Measurements were made on a slurry containing 1 gm of sample in 5 ml of distilled water which had been shaken mechanically for 1 hour. Several duplicate samples determined both in the field and laboratory gave results within 0.5 pH units.

3.53 X-ray Diffraction Examination

The mineralogy of the crystalline components in a limited number of samples was investigated using an X-ray diffraction technique. The samples were finely ground and mounted in Al holders as flat surfaced powdered cakes measuring 1 x 2 x 0.16 cm. Analysis was conducted using a Phillips Proportional Counter X-ray diffractometer with a wide angle goniometer using CuKα radiation at the following instrument settings (Table 3.16).

Table 3.16

Tube	Run at 40 KV and 20 mA
Scanning Speed	2° 20 per minute
Counter Receiving Slit	0.1 mm
Recorder Time Constant	1 second
Chart Speed	1600mm/hour
Range of Scanning	4° to 40° 20

CHAPTER 4

THE SOIL PROFILE

4.1 INTRODUCTION

During weathering there is a progressive mechanical and often chemical breakdown of the near surface rocks, the products of which may be differentiated into horizons comprising the soil profile.

The results of this differentiation on the physical and selected chemical components of the Prairie Creek kimberlite are presented and discussed in terms of mobility and mode of occurrence of the elements. Various degrees of comparative studies are given for the associated peridotite and nearby country rocks. Limited data is given for the Buell Park kimberlite and country rocks.

It is convenient to divide the chapter into 2 parts. Part 1 deals with the physical changes accompanying soil formation, and part 2 with the geochemical changes.

4.2 PHYSICAL FEATURES

4.21 Morphology

Slightly differing definitions of soil morphology are frequently used by various authors; to avoid confusion the classification shown on Table 4.1 applies throughout this thesis.

A general description of the morphological characteristics of the soil profiles developed over the Arkansas and Arizona kimberlitic and dominant country rocks are presented on Figures 4.1 and 4.2. The salient differences between the individual rock

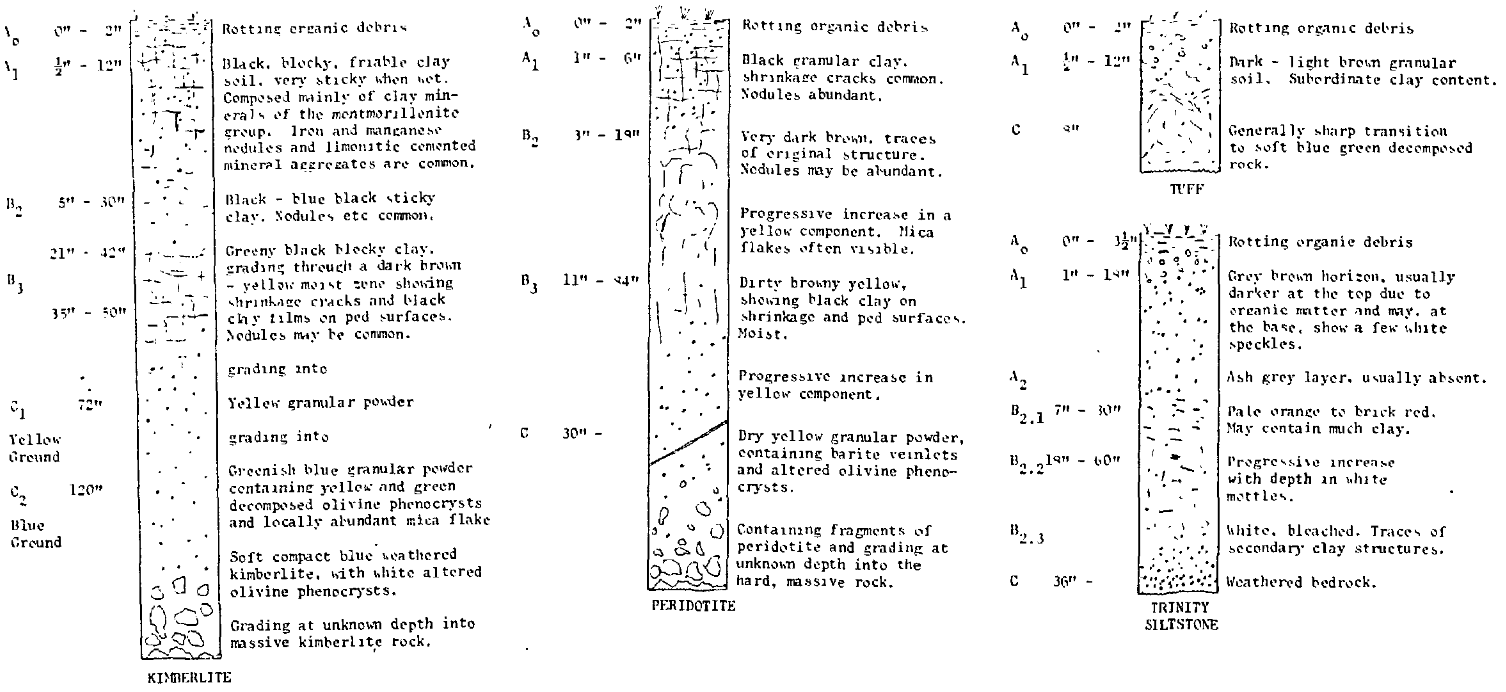


FIGURE 4.1: The morphology of typical soil profiles developed over the Prairie Creek igneous rocks and nearby Trinity Siltstone, Arkansas.

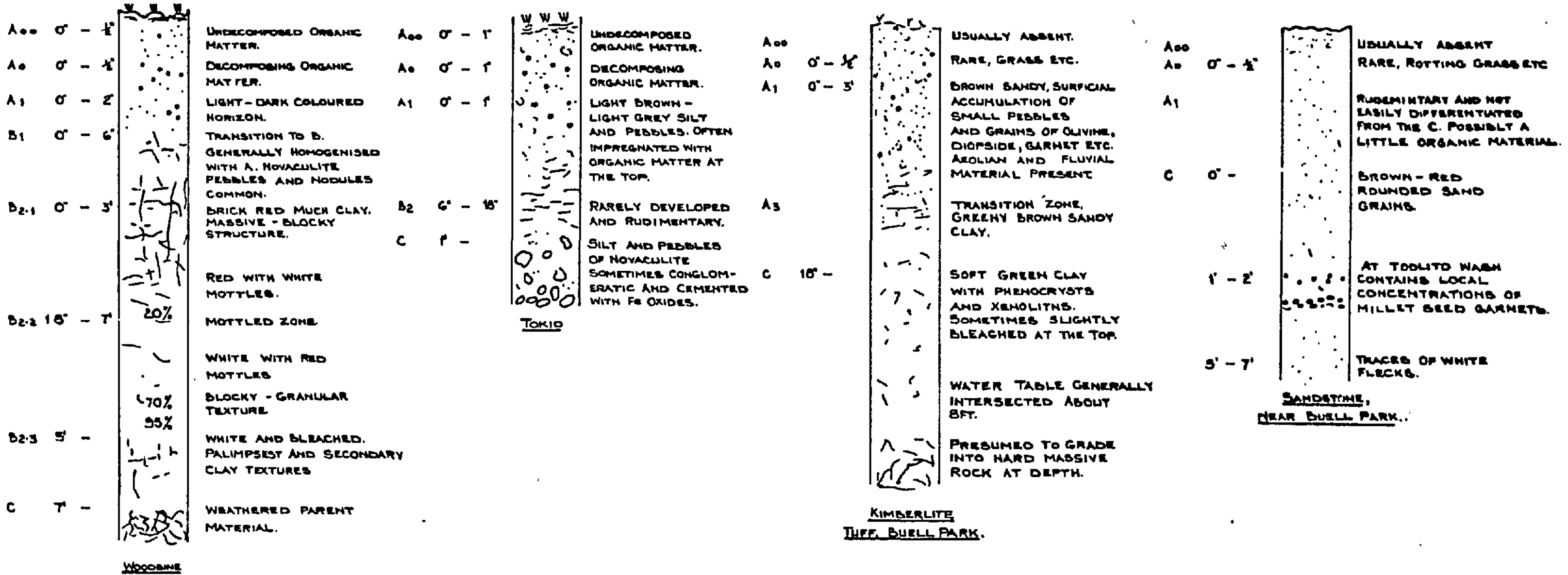


FIG. 4·2

THE MORPHOLOGY OF SOIL PROFILES DEVELOPED OVER THE WOODBINE AND TOKIO FORMATION, ARKANSAS; AND THE KIMBERLITE AND SANDSTONE COUNTRY ROCK, BUELL PARK, ARIZONA.

Table 4.1

The classification of soil morphology used in this thesis.

Kimberlitic soils (Ark.).				Country rock soils (Ark.).
Undecomposed organic matter.	A_{00}	A horizon zone of eluviation	A_{00}	Undecomposed organic matter.
Decomposing organic matter.	A_0		A_0	Decomposing organic matter.
Black, organic rich	A_1		A_1	Dark to light coloured organic rich.
			A_2	Ash grey. Zone of maximum eluviation.
Transition zone. A predominates.	A_3		A_3	Transition zone. A predominates.
Transition zone. B predominates.	B_1	B horizon zone of illuviation	B_1	Transition zone. B predominates.
Zone of clay accumulation	B_2		$B_{2.1}$	Zone of secondary ferric oxides and/or clay accumulation
			$B_{2.2}$	Mottled zone.
Transition to C Secondary clay structures present.	B_3		$B_{2.3}$	Bleached zone. Secondary clay structures present.
Yellow ground	C_1	C horizon parent material	C	Weathered bedrock.
Blue ground. (kimberlite only)	C_2			

types are tabulated on Table 4.2.

In Arkansas, soils over the ultrabasic rocks have a black coloured solum and a yellow (or blue) C horizon. In contrast, soils over the sialic rocks have a light coloured A horizon and an orange to red $B_{2.1}$ horizon which grades through a mottled zone to a light coloured C horizon.

Different types of soil profiles are observed over the Prairie Creek peridotite and kimberlite. The peridotite soil profile is vertosolic with a gradational change from a black, clay rich A horizon to a yellow C horizon. The kimberlite soil profile is more mature with a similar black A horizon, but also a black, clay rich B_2 and a greeny B_3 horizon. Further, the yellow C_1 is underlain by a blue C_2 horizon.

A rudimentary soil profile is observed over the Prairie Creek tuff. The reasons for this lack of soil development are not understood. Possibly many of the elements were leached during deposition and only the relatively immobile forms are left. This suggestion is supported by the highly oxidised nature of the bedrock as seen in thin section. In addition, the steep topography would favour rapid erosion and surface "run off".

The well developed soils found over the Trinity siltstones and Woodbine tuff differ in the colour and nature of the $B_{2.1}$ and C horizons. Except in areas of high "available" Fe content, e.g. adjacent to ultrabasic rocks, the $B_{2.1}$ horizon of the Trinity is an orange to pale red colour. In contrast, the $B_{2.1}$ of the Woodbine formation is a brick red clay rich horizon. A mottled zone, due to ground water fluctuation, is seen in both profiles. Whereas the Trinity C horizon is of a silty or loamy character, that of the Woodbine formation is of a tuffaceous nature. These differences between the soils over

Table 4.2: The salient physical differences between soil profiles developed over the kimberlitic and dominant country rocks, Arkansas and Arizona.

	Praire Creek, Arkansas.			Country Rocks, Arkansas.			Buell Park, Arizona.	
	Kimberlite	Peridotite	Tuff	Woodbine	Trinity	Tokio	Kimberlite	Sandstone
Maturity	mature	vertosolic	rudimentary	mature	usually mature	rudimentary	skeletal	skeletal
Colour	black	black	brown	brown	lt. to dk. brown	brown	red brown	red brown
Clay content	much	much	little		little	little	little	little
Peculiarities	many shrinkage cracks			cultivated			surface conc kimb minrls	
Colour	black green yellow	yellow blk dirty yell yellow	absent	brick red mottled cream	usually orange mottled cream	absent	absent	absent
Clay content	much	some		much	little			
Colour	yellow blue	yellow	blue grey	blue grey	cream	red to cream	green	red
Texture	massive	granular	tuffaceous	tuffaceous	gravel/silt/clay	conglom	clay	sand grains
Concretions in solum	many	many	none	some	few	rare	none	none
Dominant clay mineral	montmorillonite			kaolinite and illite .				

the two formations are due to the much greater amount of "available"* metal, and a greater number of primary minerals, in the Woodbine formation.

In some deep road cuts through soils developed over the Trinity formation, two $B_{2.1}$ horizons were seen. These may be the result of local lowering of the water table or due to a deeper water table in the past.

In the study area the Tokio formation occurs on ridge crests, and the rudimentary soils found over this rock type are attributed to erosion proceeding faster than soil formation.

In Arizona the soils are extremely rudimentary, and except in areas of impeded drainage near Buell Park, only a very thin organic layer is present. Even this is absent or scattered at the Garnet Ridge areas.

The top 12 to 20 inches of the kimberlite at Buell Park are covered with alluvium (Fig. 4.2). Typically eluvial concentrations of fresh looking olivine, pyrope and chrome diopside and other kimberlitic minerals are present at the ground surface, especially on "ant hills". Since olivine is one of the first minerals to be decomposed during chemical weathering (Goldich, 1938), this would indicate very little chemical weathering to have occurred in Arizona. However, the ground mass of the kimberlite has altered to a green xenolithic clay and has a whitish bleached appearance at the junction with the alluvium, thus some chemical weathering has occurred.

The C horizon of the sandstone country rocks consists of loosely consolidated reddish sand grains.

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*metal able to be "released" by soil forming processes in the study area.

4.22 Particle Size Distribution

Histograms of the particle size distributions for selected soil horizons over the ultrabasic and country rocks are presented on Figs. 4.3 and 4.4.

During weathering of the ultrabasic rocks in Arkansas, the coarse fraction is broken down into silt and clay. However, in the solum, particularly in the B_2 horizon, the coarse fractions are regenerated. This is due to the formation of nodules and aggregates. The content of clay size material in the A horizon is considerably less than in the B_2 horizon. This is presumably due to eluviation of clay from the A to the B horizon by soil forming processes. Some eluvial concentration of silt size material may also have occurred.

The kimberlitic soils contain a much higher proportion of clay than do those over the peridotite. This no doubt reflects the greater weathering of the kimberlite.

The samples prepared by wet autogenous grinding are taken from slightly different depths to those dispersed ultrasonically (Fig. 4.3). The particle size distributions obtained by the two methods are therefore not directly comparable. However, the only apparent difference between the two dispersal processes appears to be a greater proportion of clay size material produced, mainly at the expense of the silt fraction, in the kimberlite C horizon by wet autogenous grinding. The apparently greater breakdown of the coarse fraction of the yellow ground (sample number 550197, figure 4.3) by ultrasonic dispersion is attributed to the more weathered nature of this sample, since it is taken from slightly higher in the profile than the sample of yellow ground (550237) dispersed by wet autogenous grinding.

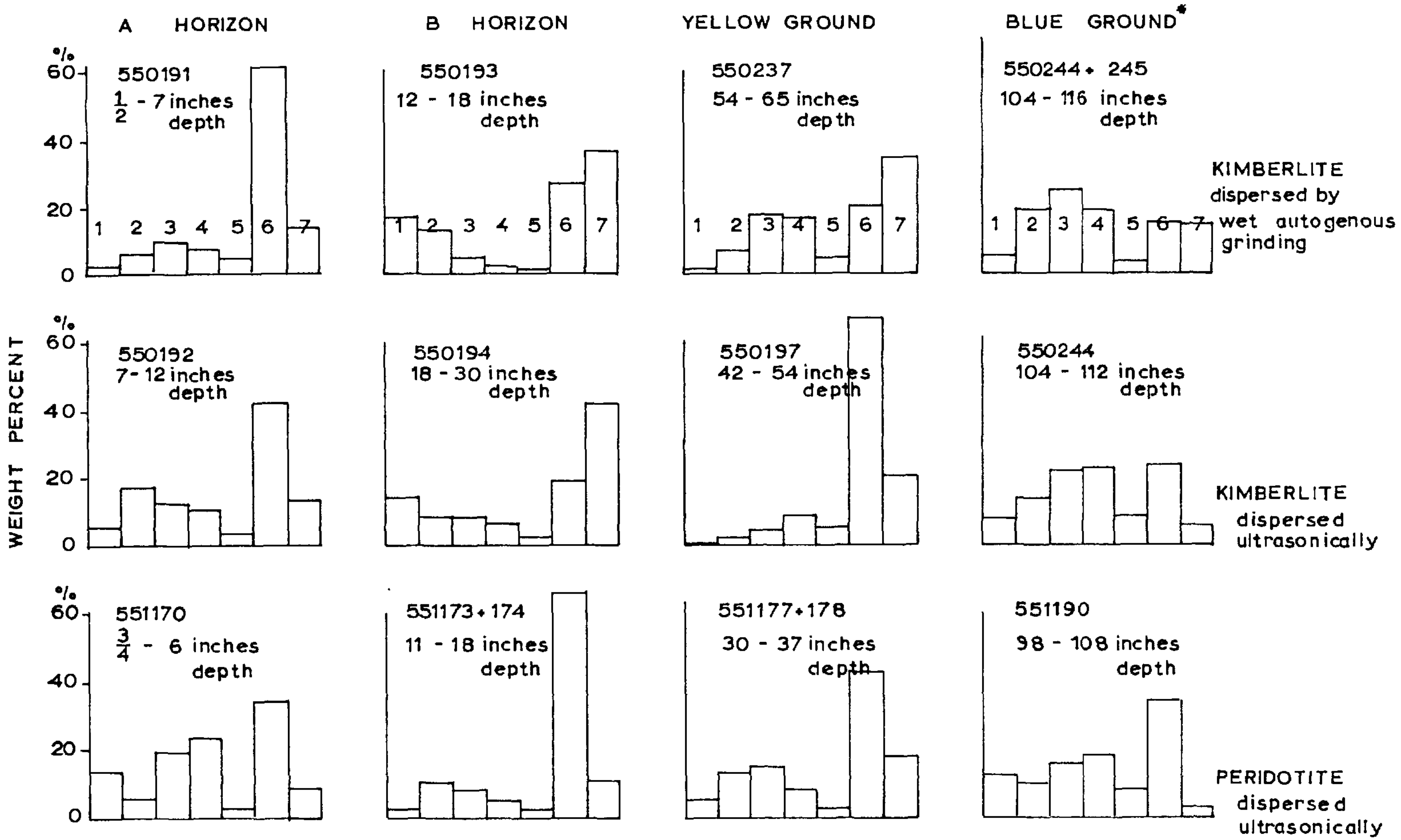

FIGURE 4.3: THE PARTICLE SIZE DISTRIBUTION OF SELECTED SOIL HORIZONS OVER THE PRAIRIE CREEK ULTRABASIC ROCKS, ARKANSAS.

1 minus 10 plus 20 mesh**
2 " 20 " 36 "
3 " 36 " 80 "

4 minus 80 plus 200 mesh**
5 " 200 " 300 "
6 silt
7 clay

* kimberlite only
** B.S.S.

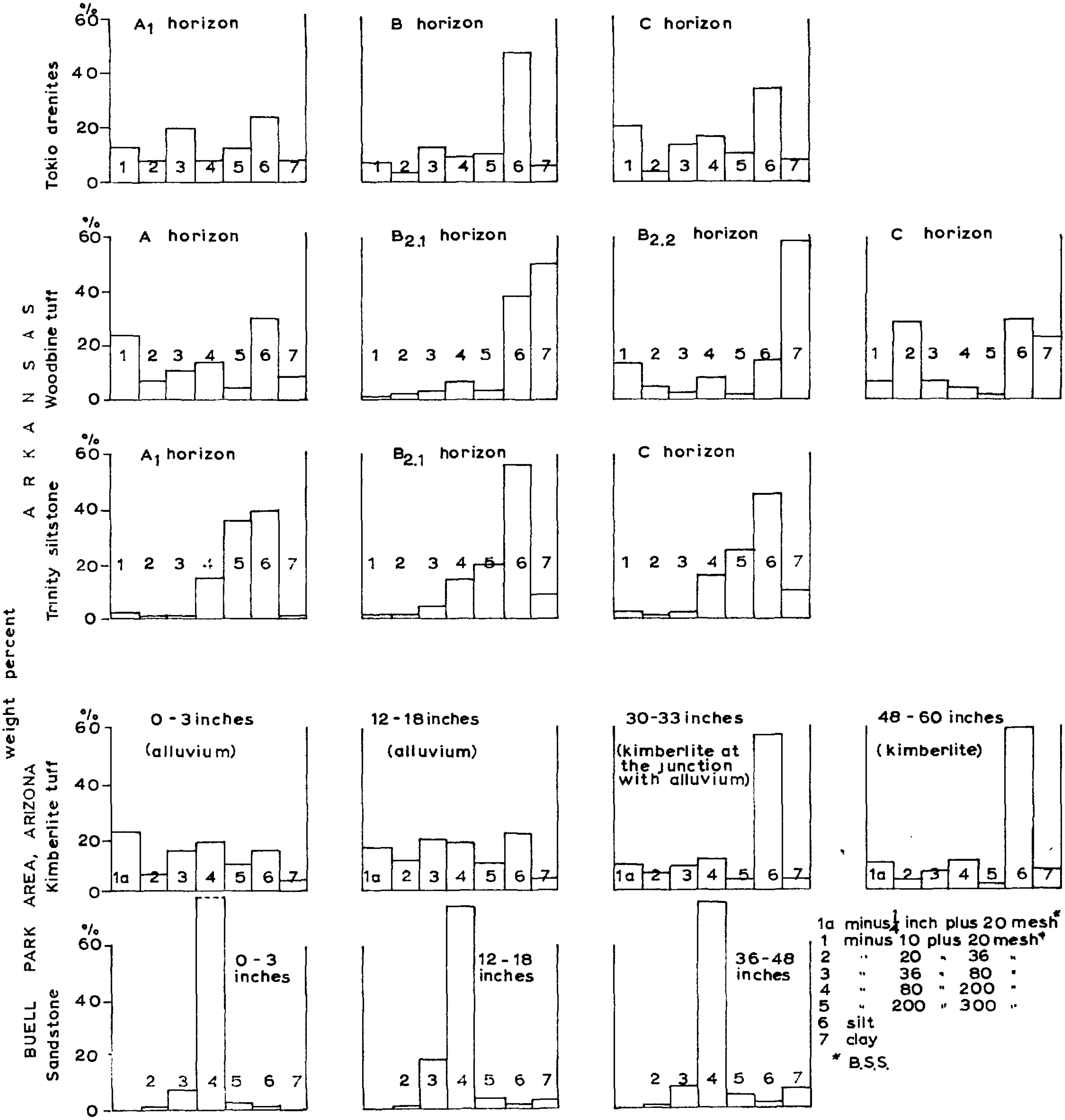

FIGURE 4.4 THE PARTICLE SIZE DISTRIBUTION OF SELECTED SOIL HORIZONS OVER THE ARKANSAS COUNTRY ROCKS; AND AT SELECTED DEPTHS IN PROFILES OVER THE KIMBERLITE TUFF AND SANDSTONE COUNTRY ROCK AT BUELL PARK, ARIZONA.

As with the ultrabasic rocks, the Woodbine formation is broken down to silt and clay during weathering. However, unlike the ultrabasic rocks, the coarse fraction of the $B_{2.1}$ horizon is not regenerated. This reflects limited concretion development. Accumulation of detrital material is responsible for the large amount of coarse material in the A horizon. The clay content of the A horizon is less than the B, no doubt due to eluviation.

With the exception of depletion of the clay of the A horizon, very little variation in particle size is seen in profiles over the Trinity and Tokio formations. This well illustrates the resistant nature of these re-worked sediments.

Considerably less clay size material is developed in the Buell Park kimberlite than in the Prairie Creek kimberlite. This is due to the less weathered nature of the Arizona rocks. No eluviation of clay is apparent in the Buell Park kimberlite profile. The particle size distribution of the two near surface samples reflects the grain size of the overlying alluvium, which is composed of sand grains and phenocrystic kimberlitic minerals.

The only profile variations seen in the Buell Park sandstone are an increase in the proportion of the minus 36 plus 80-mesh (B.S.S.) fraction of the middle sample, and a progressive increase in clay size with depth. The former is due to the occurrence of garnet grains and the latter possibly to eluviation of clay during the infrequent but torrential rains.

4.23 Mineralogy

Mineralogical weathering of ultrabasic rocks is a complex process and, in the limited time available, is beyond the scope of this thesis. Nevertheless, a limited amount of work has been undertaken to assist in the interpretation of the metal distribution patterns.

Because a wide variation in trace element content is observed with particle size; mineralogical investigations, which were made on each individual size fraction throughout a Prairie Creek kimberlite soil profile, are presented with regard to particle size as well as soil horizon. Limited studies (no size fractions) were made on the Arkansas country rocks. No investigations were made on the Buell Park soils.

Data was obtained using binocular and polarising microscopes supplemented with limited X-ray diffraction studies.

Prior to the presentation of the data a few words with regard to the treatment of clay mineralogy are necessary. It is convenient to classify the clay minerals as shown below:

Those with a basal spacing of approximately 14Å (12Å - 15Å)	Others
Montmorillonite group	Illite group
Vermiculite group	Kaolinite group
Chlorite group	

The 14Å group has not been differentiated. However, there is some evidence* that in the kimberlite profile at least, these 14Å minerals are members of the montmorillonite group. One cannot, however, on this data, exclude the vermiculite group entirely.

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*The basal spacing is generally in excess of 14Å. After heating a sample of 14.3Å clay from the kimberlite B_2 horizon at 550°C the basal spacing collapsed to approximately 10Å. Development of montmorillonite is favoured by the high Mg content.

4.231 Kimberlite (Fig. 4.5)

4.2311 The C Horizon

The blue ground and more weathered parts of the kimberlite are seen to be composed of yellow and/or white alteration products of olivine phenocrysts in a bluish white ground mass. In thin section the olivines are seen to have completely altered to a colourless to dark green almost isotropic mineral similar to the phyllosilicates described by Baker and Haggerty (1967) in weathered basaltic lava. Also present in the coarse fraction are rounded, fine grained blue aggregates of a clay mineral of 14.2Å basal spacing.

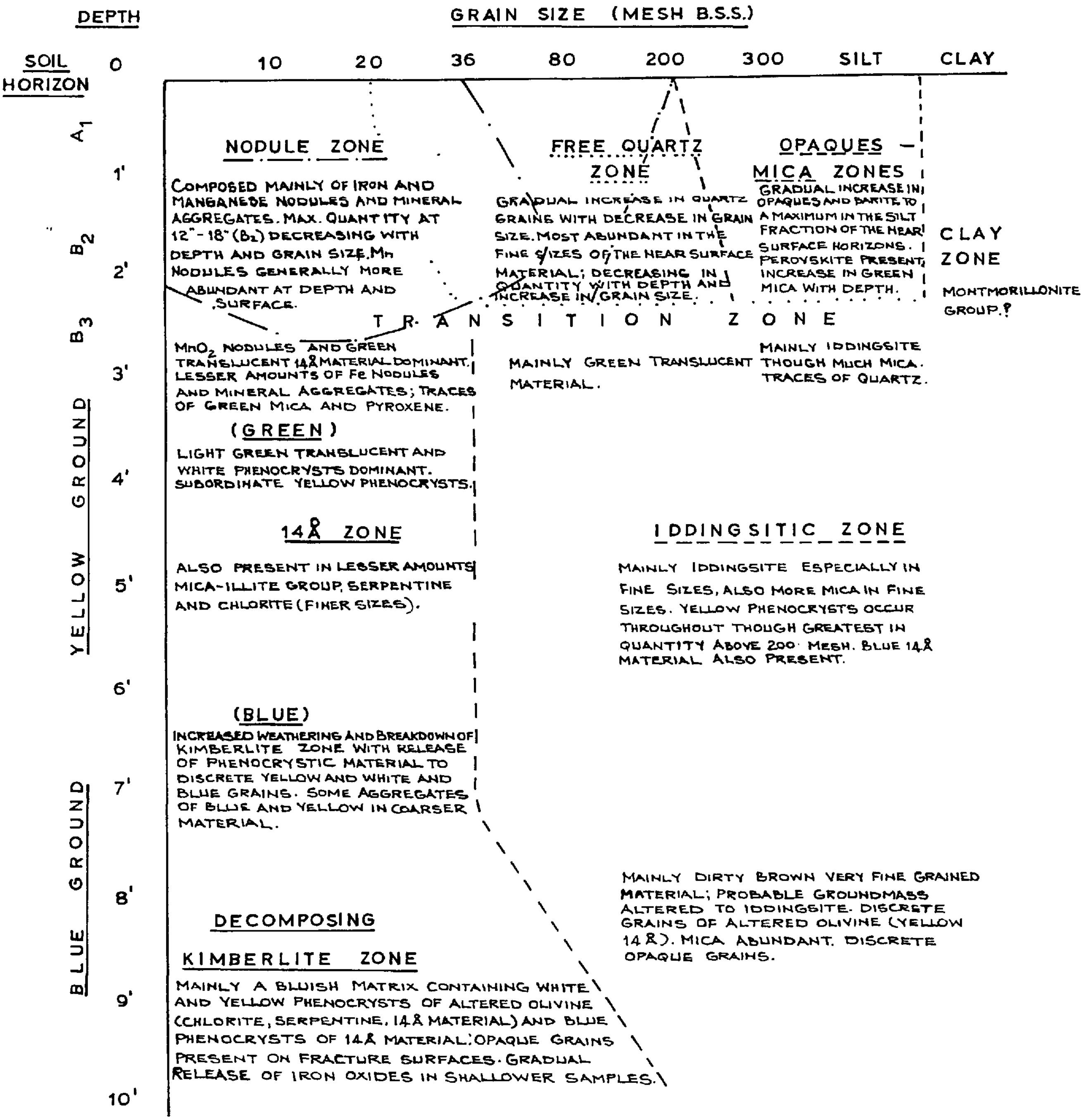
The bulk of the fine sand size of the blue ground is composed of an intimate mixture of mica-illite, goethite and a mineral of 14.2Å basal spacing. Wilshire (1958) assigned the name "iddingsite" to a mixture of smectite, chlorite and goethite; which is not dissimilar from that mentioned above.

Greeny brown mica is also present and it is particularly abundant in the fine sizes. Opaques are of small grain size but also occur on fracture surfaces on some of the phenocrysts. Serpentine was only rarely observed.

The coarse fraction of the yellow ground consists of yellow altered olivine phenocrysts of 14.7Å basal spacing. Rounded blue phenocyrsts similar to those seen in the blue ground are also present. Fragments of green mica (10Å basal spacing) are common.

At the top of the yellow ground, just below the transition zone, the coarse yellow phenocrystic material has disappeared leaving a blue green mineral of 14.7Å basal spacing. Iddingsite is still dominant in the finer sizes although the yellow grains are more common.

FIG. 4·5: DIAGRAMMATIC PRESENTATION OF THE MINERALOGY OF A KIMBERLITE SOIL PROFILE PRAIRIE CREEK ARKANSAS



NODULE ZONE

COMPOSED MAINLY OF IRON AND MANGANESE NODULES AND MINERAL AGGREGATES. MAX. QUANTITY AT 12"-18" (B_2) DECREASING WITH DEPTH AND GRAIN SIZE. Mn NODULES GENERALLY MORE ABUNDANT AT DEPTH AND SURFACE.

FREE QUARTZ ZONE

GRADUAL INCREASE IN QUARTZ GRAINS WITH DECREASE IN GRAIN SIZE. MOST ABUNDANT IN THE FINE SIZES OF THE NEAR SURFACE MATERIAL; DECREASING IN QUANTITY WITH DEPTH AND INCREASE IN GRAIN SIZE.

OPAQUES – MICA ZONES

GRADUAL INCREASE IN OPAQUES AND BARITE TO A MAXIMUM IN THE SILT FRACTION OF THE NEAR SURFACE HORIZONS. PEROVSKITE PRESENT; INCREASE IN GREEN MICA WITH DEPTH.

MONTMORILLONITE GROUP.?

MnO_2 NODULES AND GREEN TRANSLUCENT 14Å MATERIAL DOMINANT. LESSER AMOUNTS OF Fe NODULES AND MINERAL AGGREGATES; TRACES OF GREEN MICA AND PYROXENE.

MAINLY GREEN TRANSLUCENT MATERIAL.

MAINLY IDDINGSITE THOUGH MUCH MICA. TRACES OF QUARTZ.

(GREEN)

LIGHT GREEN TRANSLUCENT AND WHITE PHENOCRYSTS DOMINANT. SUBORDINATE YELLOW PHENOCRYSTS.

14Å ZONE

ALSO PRESENT IN LESSER AMOUNTS MICA-ILLITE GROUP, SERPENTINE AND CHLORITE (FINER SIZES).

IDDINGSITIC ZONE

MAINLY IDDINGSITE ESPECIALLY IN FINE SIZES, ALSO MORE MICA IN FINE SIZES. YELLOW PHENOCRYSTS OCCUR THROUGHOUT THOUGH GREATEST IN QUANTITY ABOVE 200 MESH. BLUE 14Å MATERIAL ALSO PRESENT.

(BLUE)

INCREASED WEATHERING AND BREAKDOWN OF KIMBERLITE ZONE WITH RELEASE OF PHENOCRYSTIC MATERIAL TO DISCRETE YELLOW AND WHITE AND BLUE GRAINS. SOME AGGREGATES OF BLUE AND YELLOW IN COARSER MATERIAL.

MAINLY DIRTY BROWN VERY FINE GRAINED MATERIAL; PROBABLE GROUNDMASS ALTERED TO IDDINGSITE. DISCRETE GRAINS OF ALTERED OLIVINE (YELLOW 14Å). MICA ABUNDANT. DISCRETE OPAQUE GRAINS.

DECOMPOSING KIMBERLITE ZONE

MAINLY A BLUISH MATRIX CONTAINING WHITE AND YELLOW PHENOCRYSTS OF ALTERED OLIVINE (CHLORITE, SERPENTINE, 14Å MATERIAL) AND BLUE PHENOCRYSTS OF 14Å MATERIAL. OPAQUE GRAINS PRESENT ON FRACTURE SURFACES. GRADUAL RELEASE OF IRON OXIDES IN SHALLOWER SAMPLES.

The transition to the B horizon is marked by the co-existence of the green translucent 14.7Å mineral with iron and manganese concretions; the manganese rich nodules appearing to predominate. The middle fraction is composed of the previously mentioned green mineral and the presence of up to 10% quartz is recorded. Green mica and opaques are more common in the fine sizes at the expense of iddingsite.

4.2312 The Solum

It is convenient to describe the mineralogy of the solum under three main headings based upon grain size:

A. The minus 10 plus 36 mesh (B.S.S.) fraction
B. The minus 36 mesh plus 2 microns fraction
C. The clay fraction (less than 2 microns)

The minus 10 plus 36 mesh (B.S.S.) fraction

This fraction consists of the following mineralogical groups:

(a) Manganese rich nodules (black)
(b) Iddingsite grains (brown)
(c) 1. Rounded nodules of iron cemented quartz grains (brown)
    2. Irregular iron cemented mineral aggregates (brown)
(d) Detrital accumulations.

(a) Manganese Nodules: These consist of soft porous spheres often showing a poorly developed concentric structure. In thin section they are seen in the main to consist of fine grained aggregates of quartz cemented with dark sesquioxides. Although some grains do not contain quartz they are accompanied by large holes in the slide, presumably where the quartz has been plucked out during polishing. Frequently a zonal structure is seen, notably in nodules from the surface of the poorly drained peridotite, where the interior may be more ferruginous than the exterior. Other nodules, particularly in the B_2 horizon of the kimberlite currently described, may be coated with secondary iron oxides.

Black sesquioxides also occur on grain boundaries and coating limonitic nodules, particularly in the near surface material.

The quartz grains mentioned above are more or less of equal grain size and have a sharp outline. They usually show strained extinction and, rarely, recrystallisation.

(b) Iddingsite Grains: Are reddish brown ovoid grains which in thin section show optical orientation and relict fragments of olivine (now probably a clay mineral). Quartz grains are usually absent although one particle was seen to contain a large, subhedral, strained quartz grain. This was of detrital origin.

(c) 1. Rounded Iron Nodules: These consist of aggregates of usually disorientated quartz grains in a light coloured limonitic cement; some nodules however show orientation of the quartz grains in a bedded form, other nodules exhibit a concentric structure.

2. Mineral Aggregates: Are irregularly shaped grains consisting mainly of quartz with a few opaques in a limonitic cement.

(d) Detrital Accumulations: Consist of xenolithic material, quartz fragments, novaculite pebbles, etc. They are not abundant.

The minus 36 mesh (B.S.S.) plus 2 microns fraction

Nodules and aggregates decrease in amount with decrease in grain size, and in general, aggregates are more abundant in the deeper samples. Manganese rich nodules are more abundant towards the surface. Quartz increases in amount both towards the surface and with decrease in grain size. Opaque minerals occur in maximum amounts in the silt fraction of the A horizon. In this horizon the four strongest lines of perovskite were identified using X-ray diffraction techniques. Green mica is present throughout though more abundant in the fine sizes of the deeper samples. The green translucent mineral recognised in the transition zone only rarely occurs at the surface and then only in the plus 200 mesh size. A slight increase in the amount of this mineral is observed with depth. Also recorded in the silt fraction of the A_1 horizon is a mineral with a basal spacing of 14.3Å.

The Clay Fraction

The clay of the A_1 and B_2 horizons is composed mainly of a mineral with a 14.3Å basal spacing. As previously suggested, this mineral is probably montmorillonite. Mica-illite is also present though subordinate in concentration.

4.2313 Discussion

Whilst the change from the blue to the yellow ground is most likely a reflection of an increase in weathering; the mineralogical cause is somewhat obscure. The difference may be related either directly or indirectly to the alteration of the phyllosilicates of the blue ground to the clay minerals of the yellow ground. Further, the amount of brown iddingsite is greater in the yellow ground, especially in the fine sizes. This latter point is probably due to the release of Fe during the saponization of the olivines. A further contributary factor is the progressive decomposition of the phlogopite from the greeny brown in the blue ground to the green colour of the yellow ground.

The green ground is probably due to predominance of the green mica and green clay developed during a further increase in weathering.

Miser and Purdue (1929) attribute the colour zoning to a variation in the grain size of the olivines. Whilst this may cause local colour variation it is unlikely to be responsible for the thick yellow zone which consistently overlies the blue horizon in all the profiles studied. Further, nowhere was a blue band observed in the yellow ground.

Size fraction studies indicate the dark colour of the solum to be associated with the silt and clay sizes. There is no reason, therefore, to dispute Miser and Purdue's suggestion that the black colour of the solum is due to the presence of organic matter. However, no determinations of organic content were made.

The detrital appearance and crystalline nature of the quartz, at least in the coarse fraction, strongly suggests this mineral to be of detrital origin. However, Fairbairn and Robertson (1966) record the release of free silica and brucite during the partial decomposition of serpentine over a Sierra Leone kimberlite. It is possible, therefore, that a certain amount of amorphous silica may be present in the fine material.

4.232 The Country Rocks

4.2321 X-ray Diffraction Studies

The B_2 horizon of the Trinity formation is composed dominantly of quartz grains; members of the illite (100), kaolinite (50) and the 14Å (50) groups. The figure in parenthesis indicates the relative intensities of the clay peaks. Not detected but apparent from visual observation is limonitic material.

In the $B_{2.3}$ horizon of soils over the Woodbine formation, kaolinite (I = 100) is the predominant mineral although the 14Å group (I = 75) and the illite group (I = 50) are present. Feldspar is also abundant. Quartz was detected and ilmenite and magnetite may be present. In addition, four small peaks corresponding with the strongest lines of perovskite were observed, but were inadequate for positive identification.

The $B_{2.1}$ horizon of the Woodbine formation differs in that the 14Å peak is almost absent. Kaolinite predominates (I = 100) and illite is present (I = 40). Quartz is abundant but feldspar is not detected. Goethite was found and magnetite and ilmenite may be present. No perovskite lines could be differentiated from the background.

4.2322 The Coarse Fraction of the Solum

Only in the Woodbine formation were manganese nodules observed and these were not common. Iron nodules, which are usually absent in the Tokio, not excessive in the Trinity, and more common in the Woodbine formations, consist of rounded aggregates of limonite cemented quartz grains. In some specimens a concentric structure is seen.

The balance of the coarse fraction over these rocks is mainly quartz and novaculite grains.

4.2323 Discussion

Whilst the high MgO, high pH and self induced impeded drainage conditions of the kimberlite favour the development of montmorillonite; the low MgO, low pH and well drained nature of the Trinity and Woodbine formations favour the development of kaolinite. Thus the presence of a 14Å mineral is difficult to explain. Ross et al (1929) attributed the presence of beidellite (montmorillonite group) in the Woodbine formation to unusual conditions prevailing during deposition and similar argument might be advanced in the case of the Trinity formation. An alternative explanation is that the 14Å material may be the fossil product of weathering under different conditions in the past. In either case it appears to be reverting to the more stable kaolinite at the present time.

4.3 GEOCHEMISTRY

4.31 Scope and Presentation of Data

Variations in the content of Nb, Cr, Ti, Sr, Zr, Fe, Mn, Ni, Co, V, Ba and exMg were investigated with both depth and particle size in soil profiles over the Prairie Creek kimberlite. Varying degrees of comparative data was obtained for soils over the Prairie Creek peridotite, tuffaceous and sialic country rocks. Very limited comparative studies were made on profiles over the Buell Park kimberlite and sandstone country rocks.

Data is presented as a series of diagrams and tables from which the salient features are tabulated. These features are interpreted and discussed in terms of (a) mobility of the

the elements in the soil profile and (b) the mode of occurrence of the elements. Only for Ni in Arkansas were partial extractions used; this data is presented when appropriate.

It is convenient to consider the Arkansas and Arizona areas under separate headings.

In Arkansas the elements are conveniently classified into the three groups detailed in Section 4.32. There are however several features common to some elements from the three groups: viz. concentration in sesquioxide nodules and mineral aggregates, and depletion in the kimberlite and/or peridotite C horizon. These are discussed under separate headings.

A certain amount of data was obtained by spectrographic analysis. It was mentioned in Chapter 3 that the overall spectrographic precision was poor (between ±35% and 103% at the 95% confidence level), when computed for a sialic λ and an ultrabasic ϑ*. This is attributed to matrix effects (page 71). For low values of ϑ the precision is considerably improved. Many of the spectrographic results presented in this section are systematic, particularly for sialic matrices. In addition, there is a reasonable similarity of distribution with several duplicate samples determined by wet analyses. It is suggested, therefore, that whilst individual spectrographic results may be suspect, the overall patterns are probably valid.

4.32 Arkansas

It is convenient to classify, describe and discuss the elements under three main headings based upon their general

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*Using the method of Craven (1953) as described by Stanton (1966).

overall vertical distribution (Table 4.4).

(1) Those elements which decrease in content with increasing depth, i.e. Nb, Cr, Ti, Sr and Zr.

(2) Those elements which are enriched in the B_2 horizon, i.e. Fe, V, Ni, Co, Ba and Mn.

(3) Those elements in which concentration increases with increasing depth.

4.321 Nb, Cr, Sr, Ti and Zr

4.3211 Distribution in soil profiles over the Prairie Creek kimberlite

4.32111 Variation with depth

The variation of Nb and Cr contents in selected soil profiles over the Prairie Creek kimberlite is illustrated on Fig. 4.6. The mean content of the elements in selected horizons are given on Table 4.4. Attention is drawn to the following points:

(1) Metal content decreases with increasing depth.

(2) Nb and Cr are slightly concentrated in the B_2 horizon.

(3) The mean Nb and Ti contents of the blue ground are less than the mean bedrock.

4.32112 Variation with particle size

The variation in Cr and Nb contents with particle size for selected horizons in soil profiles over the Prairie Creek kimberlite are presented as histograms on Fig. 4.9. Analyses were made using wet methods and the samples were dispersed by wet autogenous grinding. Comparable data obtained for Cr, Sr,

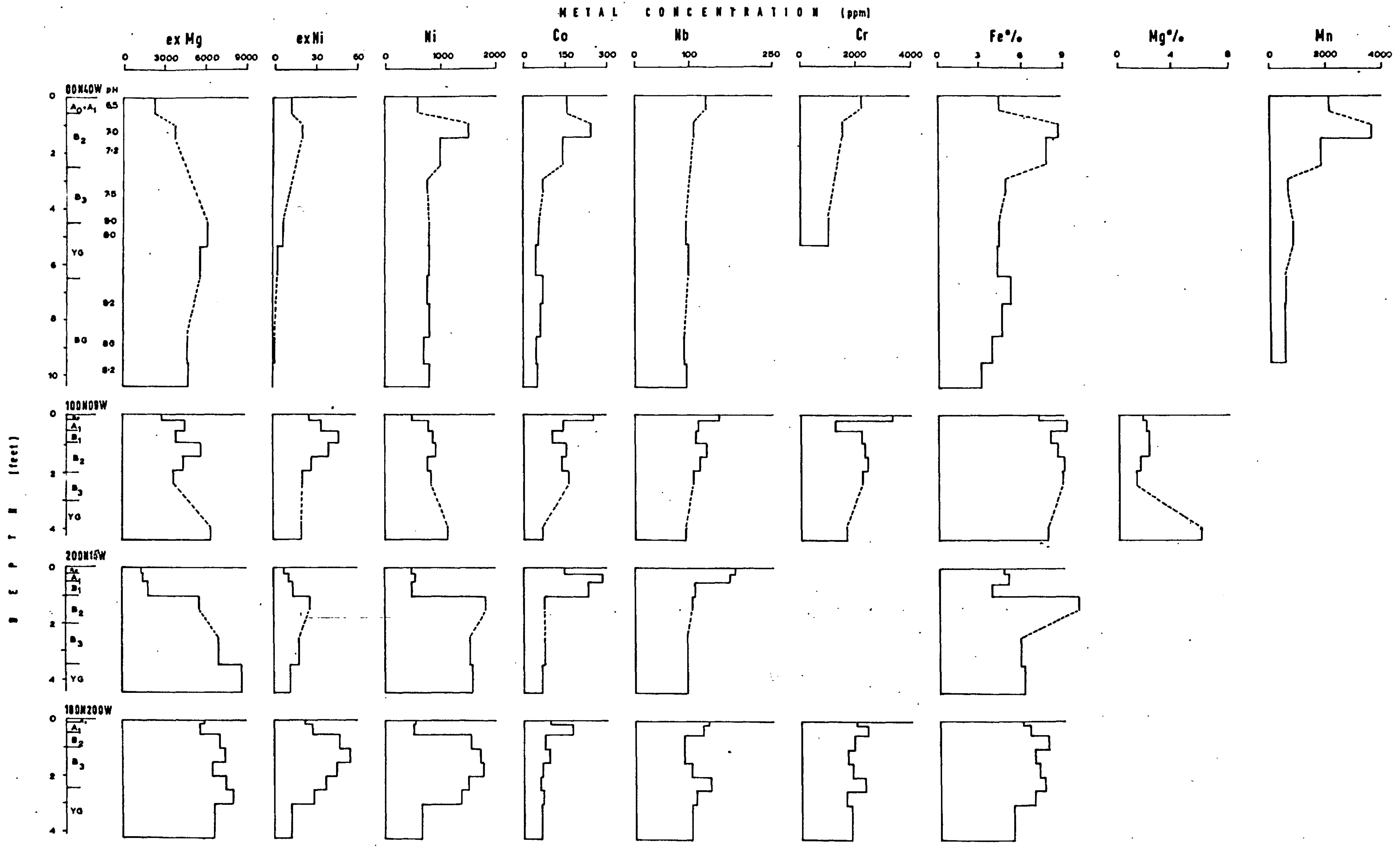


FIGURE 4.6: THE VERTICAL DISTRIBUTION OF SELECTED ELEMENTS IN FOUR RESIDUAL SOIL PROFILES DEVELOPED OVER KIMBERLITE PRAIRIE CREEK, ARK.

Complete Sample, Wet Attacks.

ELEMENT ATTACK READING			NICKEL KHSO$_4$ & HClO$_4$ / Furidioxime	%IRON Fe$_2$O$_3$ KHSO$_4$ & HClO$_4$ / Thioglycollic Acid	MANGANESE KHSO$_4$ A.A.	COBALT KHSO$_4$ & HClO$_4$ / Tri-N-Butylamine	VANADIUM Emission Spec.	CHROMIUM Alkali Fusion / Diphenyl Carbozide	ZIRCONIUM Emission Spec.	TITANIUM Emission Spec.	NIOBIUM HF / Tannic Acid	BARIUM Emission Spec.	STRONTIUM Emission Spec.	PHOSPHORUS KHSO$_4$ / NH$_4$ Molybdate	MAGNESIUM HF A.A. %	Ex. Mg Molar NH$_4$ Acet. / A.A.	Ex. Ni. Molar NH$_4$ Acet. / A.A.
ARKANSAS PRAIRIE CREEK	KIMBERLITE	Ao	450 - 1050 650 3/3	4·7 - 6·0 5·3 2/2	—	95 - 180 128 2/3	—	2000 - 3300 2650 2/2	—	>1% 1/1	132 - 180 155 3/3	3000 1/1	2000 1/1	—	1·8 1/1	1400 - 5920 3400 3/3	6 - 25 17 3/3
		A$_1$	450 - 1010 690 3/17	4·36 - 6·5 5·4 2/8	2096 1/1	100 - 310 196 3/17	86 3/20	1220 - 2400 1720 4/12	300 - 5500 2/18	2000 - >1% >1% 4/21	108 - 171 139 4/14	780 - 2000 1800 4/21	980 - 1110 1030 4/21	1882 1/2	1·42 - 2·15 1·94 3/3	1045 - 5640 2960 5/10	3·5 - 46 16 5/10
		B$_2$	1110 - 1860 1570 4/13	6·8 - 10·0 8·3 3/11	3632 1/7	75 - 295 132 4/13	74 - 144 109 2/18	1340 - 2400 1880 4/15	<200 - 1700 2/19	5800 - 6500 6170 2/18	71 - 140 101 5/16	>885 - 5000 2750 2/18	630 - 1060 845 2/18	4772 1/2	1·3 - 5·3 3·5 2/5	3700 - 7040 5427 5/10	19 - 60 36 5/10
		YELLOW GROUND	800 - 1755 1250 5/26	4·4 - 7·8 6·1 5/21	816 1/7	44 - 75 66 4/26	40 - 105 72 4/20	1490 - 2300 1560 5/14	<200 - 660 2/18	5000 - >1% >7500 4/20	83 - 136 103 5/21	660 - 7500 3370 4/20	500 - 1000 650 4/20	3090 1/2	5·9 - 10·7 8·3 2/3	3350 - 8840 6160 5/15	5 - 44 15 5/15
		BLUE GROUND	630 - 790 730 1/16	3·86 - 4·36 4·16 1/14	462 2/14	42 - 54 48 1/16	43 - 60 53 3/19	1036 1/7	<200 - 636 3/19	4200 3/19	61 - 140 94 2/12	1500 - 6000 4300 3/19	300 - 600 400 3/19	3790 1/2	13·8 1/2	3840 - 4750 4100 2/3	1·4 - 3·0 2·2 2/3
		ROCK	1000 - 1440 1290 3/3	2·7 - 7·0* 4·7 4/5	300 - 850* 490 4/5	50 - 60 57 3/3	60 - 160 115	850 - 1000 920 3/3	<200 2/2	3000 - 6000 4800 4/5	80 - 123 111 3/6	400 - 600 530 3/3	200 - 600 400 3/3		14·5 1/1	1310 1/1	N.D. 1/1
	PERIDOTITE	Ao	665 - 1100 860 3/4	4·8 1/1	—	110 - 175 125 3/4	—	2450 - 3000 2725 2/2	—	—	168 - 280 214 4/5	—	—	—	4·3 1/1	3520 - 3740 3645 3/6	6 - 17 11 3/6
		A$_1$	980 - 1225 1060 3/4	5·0 - 5·5 5·25 1/2	—	115 - 250 166 3/4	—	1320 - 3700 2485 2/3	—	—	104 - 232 178 5/6	—	—	—	5·5 1/1	3480 - 5220 3070 3/5	13 - 37 25 3/5
		B$_2$	1020 - 1800 1580 3/11	6·0 - 6·8 6·3 1/4	—	60 - 250 150 3/11	—	2800 - 3200 3000 1/4	—	—	74 - 182 135 4/13	—	—	—	2·3 - 5·2 4·2 1/3	3660 - 8000 5380 3/15	8 - 70 33 3/15
		YELLOW GROUND	940 - 1600 1350 3/9	7·8 - 8·0 7·9 1/2	—	70 - 125 87 3/9	—	925 - 2700 1760 2/3	—	—	96 - 132 111 4/10	—	—	—	8·3 - 8·7 8·5 1/2	3320 - 8200 5880 3/4	4 - 37 19 3/4
		DEPTH: TO BLUE GROUND	1320 - 1470 1395 2/2			62 - 75 68 2/2		1150 106 1/1			64 - 144 5/5				10·5 1/1	5680 - 8000 6895 2/3	6 - 13 10 2/3
		ROCK	1280 - 1680 6/6	2·7 - 7·0* 5/5	200 - 1300* 5/5	76 - 92 6/6	30 - 50 5/5	1250 - 1750 6/6	<200 2/2	4000 - 6000 5/5	110 - 126 2/6	6000 - 8000 3/3	800 - 1000 3/3			406 - 1780 2/2	1·4 - 1·8 2/2
	TUFF	A	170 - 200 190 1/4			20 - 25 22 1/4			—		89 - 96 92 1/4			—	—	860 - 1770 1220 1/8	0·6 - 3 4·2 1/8
		C	210 1/1	1·2 - 2·1* 1·6 3/3	300 - 1000* 530 3/3	40 - 50 43 3/3	40 - 85 60 3/3	100 - 130 120 3/3		4000 - 8500 7000 3/3	82 1/1	400 - >1% >7000 3/3	600 - 2000 1200 3/3			1520 - 1580 1550 1/2	6·0 2
BUELL PARK ARIZONA	KIMB TUFF	ROCK		2·0 - 2·3* 2·15 1/2	400 - 1000* 700 1/2	85 - 130* 105 1/2	10 - 20 15 1/2	850 - 1300 1075 1/2		100 - 130 115 1/2	< 7 SOIL PROFILE	200	30				
MURFREESBORO ARKANSAS	TRINITY	Ao	5 - 12·5 8·5 2/4	0·9 - 1·2 1·05 2/4	275 1/1	2·5 - 5·0 3 2/3	—	70 - 110 90 1/2	—	—	0·8 - 8·8 5·2 3/2	—	—	124 - 160 150 2/5	0·046 - 0·054 0·048 2/5	35 - 115 75 2[illegible]	1·6 1/1
		A$_1$	6 - 14 11 2/4	0·7 - 1·7 1·57 2/4	50 1/1	1·25 - 3 2 2/4	21 1/9	37 1/1	^{56} 420 1/9	2900 1/9	6·4 - 9 7 2/3	105 1/9	—	80 1/1	0·043 1/1	62 1/1	1[illegible] 1/1
		B$_2$	5 - 25 11 2/10	0·8 - 3·9 2·1 2/10	25 - 100 50 1/4	1·25 - 5 3 1/6	47 1/9	10 - 220 70 1/4	3440 1/9	4000 1/9	1·6 - 11·2 6 2/6	146 1/9	<30 1/9	125 - 160 142 1/4	0·14 - 0·18 0·16 1/3	66 - 13[illegible] 93 1/[illegible]	<1 - 2 <1 [illegible]
		C	5 - 15 8 2/6	0·95 - 2·6 1·35 2/6	<25 1/2	<1·25 - 2 1/3	17 1/9	40 - 75 55 1/3	1370 1/9	2760 1/9	3·2 - 7·6 4·4 2/5	108 1/9	<30 1/9		0·124 1/1	35 1/1	N[illegible] 1/1
TYPICAL HOST MINERALS IN KIMBERLITE.			OLIVINE, PYROXENE, PHLOGOPITE AND THEIR SECONDARY PRODUCTS MAGNETITE, ILMENITE, CHROMITE.				PYROXENE PHLOGOPITE OLIVINE OPAQUES	OPAQUES PYROXENE OLIVINE	ZIRCON	ILMENITE MAGNETITE CHROMITE PEROVSKITE	PEROVSKITE ILMENITE ZIRCON	BARITE PHLOGOPITE	BARITE PHLOGOPITE PEROVSKITE APATITE ZIRCON	APATITE	FERRO-MAGNESIAN PYROPE PICRO-ILMENITE		

TABLE 44 METAL CONTENT (IN p.p.m. UNLESS OTHERWISE STATED) OF IGNEOUS ROCKS, TRINITY SILTSTONES ARKANSAS; AND THE BUELL PARK KIMBERLITE TUFF ARIZONA; AND ASSOCIATED SOILS.

KEY

RANGE OF VALUES
MEAN No OF LOCATIONS / No OF DETERMINATIONS

* SPECTROGRAPHIC ANALYSES DATA ON COMPLETE SAMPLE

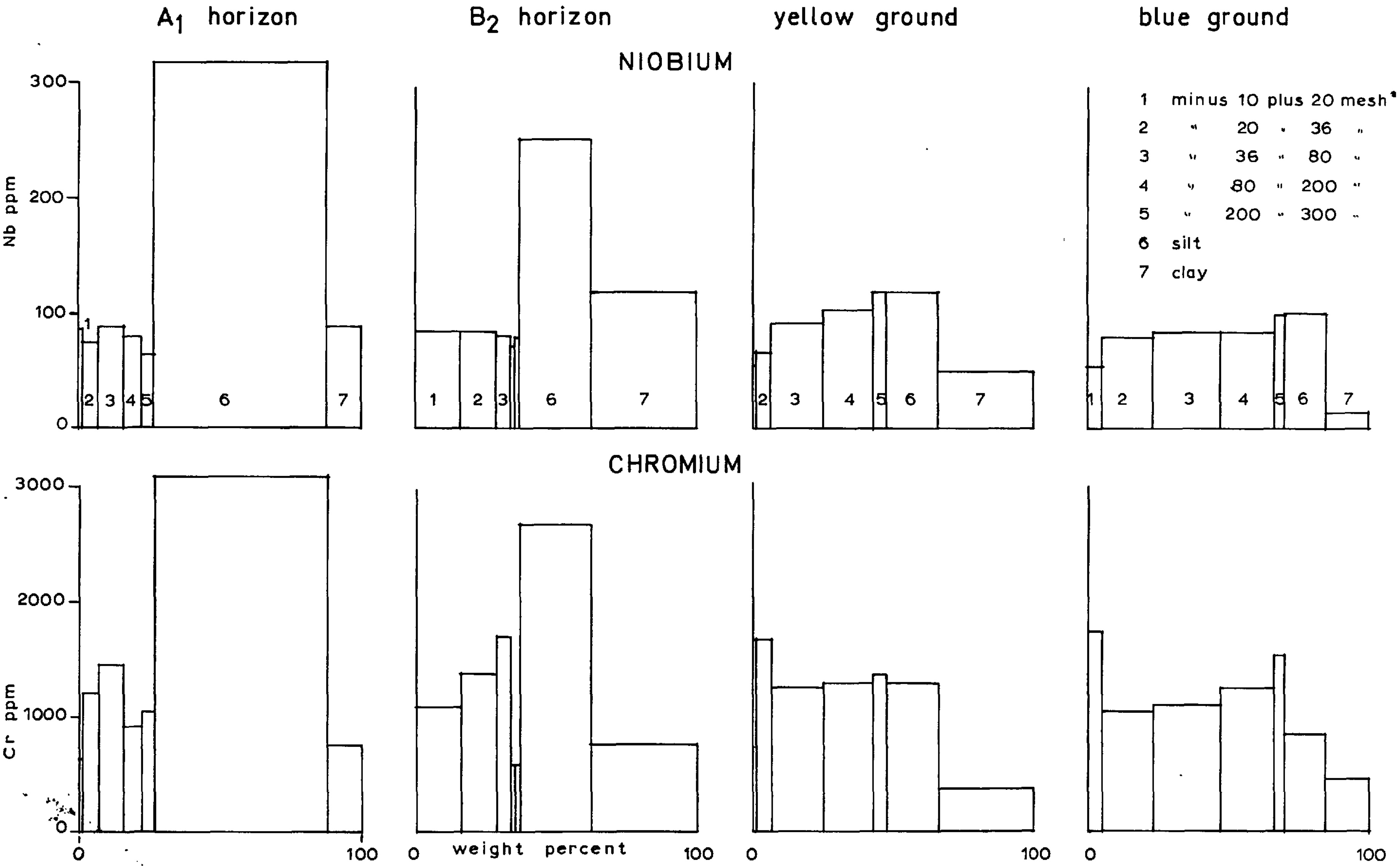
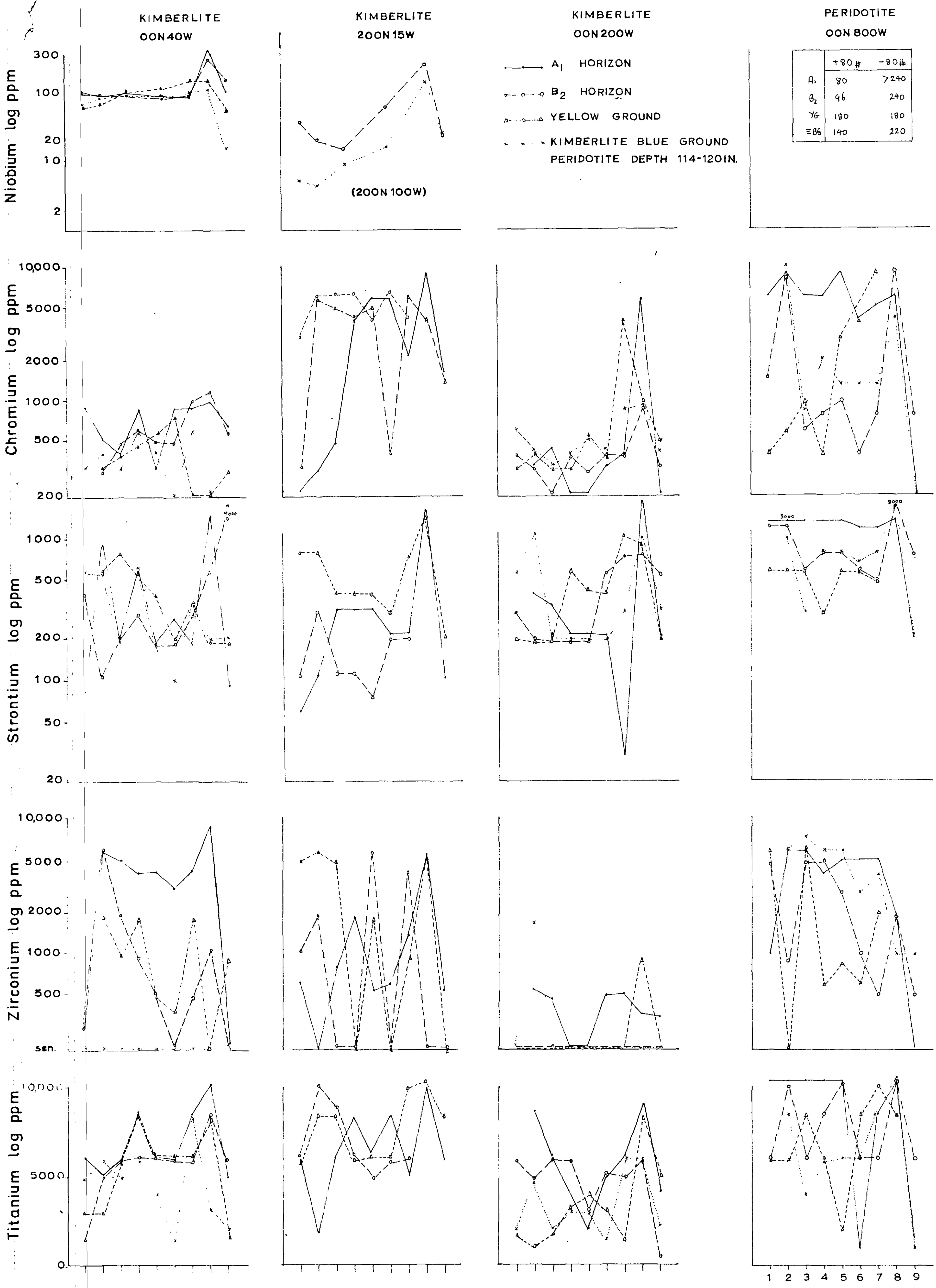


FIGURE 4.9 HISTOGRAMS OF NIOBIUM AND CHROMIUM CONTENT PLOTTED AGAINST WEIGHT PERCENT FOR VARIOUS SIZE FRACTIONS IN A RESIDUAL SOIL PROFILE OVER KIMBERLITE AT 00N40W, PRAIRIE CREEK AREA, ARKANSAS.

* (B.S.S.)



	+80 #	-80 #
A1	80	>240
B2	96	240
YG	180	180
≡BG	140	220

FIG. 4·10 THE VARIATION IN CONTENT OF Nb, Cr, Sr, Ti AND Zr WITH PARTICLE SIZE IN SELECTED SOIL HORIZONS OVER THE PRAIRIE CREEK KIMBERLITE AND PERIDOTITE. SPECTROGRAPHIC ANALYSES ULTRASONICALLY DISPERSED.

1. MINUS 10 PLUS 20 MESH
2. MINUS 20 PLUS 36 MESH
3. MINUS 36 PLUS 60 MESH
4. MINUS 60 PLUS 80 MESH
5. MINUS 80 PLUS 100 MESH
6. MINUS 100 PLUS 200 MESH
7. MINUS 200 PLUS 300 MESH
8. SILT
9. CLAY

Ti and Zr using spectrographic methods, for selected horizons in three profiles over kimberlite, are given on Fig. 4.10. These samples were dispersed ultrasonically. The following features are noted:

Fig. 4.9

1. Nb and Cr increase in amount and concentration in the silt fraction towards surface. The silt fraction of the A_1 horizon contains $2\frac{1}{2}$ times as much metal as the silt size of the B_2 horizon.

2. The amount of Nb and Cr in the clay size increased towards the B_2 horizon.

3. Large amounts of metal are contained in the coarse fraction of the B_2 horizon.

4. Higher concentrations of Nb are recorded in the coarse fraction of the A horizon than at depth.

5. In the plus 80-mesh material, Cr is concentrated in the minus 10 plus 20-mesh fraction of the blue ground, but in the minus 36 plus 80-mesh fraction of the solum.

Fig. 4.10

6. There is a reasonable correlation between the distribution of Cr as determined by wet and spectrographic methods in the solum, but not in the C horizon.

7. Highest concentrations of metal are generally recorded in the silt size, especially in the A horizon.

8. High concentrations of metal are recorded in the coarse fraction.

9. In the A horizon Zr is concentrated on the minus 100 plus 200-mesh fraction.

10. There is a tendency for Sr and possibly Ti to be concentrated in the clay size of the B_2 horizon.
11. There appears to be a broad sympathetic variation between Ti and Cr in the blue ground.

4.3212 Discussion

4.32121 Mobility in the soil profile

The enrichments* of Nb, Ti, Cr and Sr in the component soil horizons over kimberlite are given on Table 4.5. Calculations were made from the mean metal contents detailed on Table 4.4. Insufficient data are available to establish a reliable mean Zr content for the soil horizons and the enrichments given for this element are computed from a single profile. The corresponding enrichments for Sr in the same profile are given for comparison.

According to Miser and Ross (1923) and Vitt (1943) diamonds are concentrated in the black ground over kimberlite. The range of diamond enrichment in the "black ground" (assumed to be the kimberlite solum) as calculated by Vitt (1943) is included on Table 4.5.

It can be seen from Table 4.5 that the enrichment of this group of elements increases towards surface. This would suggest them to be relatively immobile. Niobium is enriched the least and Sr and Zr the most. On this basis the following relative mobilities are suggested:

least immobile $\quad Nb < Cr \leqslant Ti < Sr \leqslant Zr \leqslant$ diamond $\quad$ most immobile

---

*$\frac{\text{concentration in appropriate soil horizon}}{\text{concentration in bedrock}}$

Table 4.5 The enrichment of Nb, Cr, Ti, Sr, Zr, and diamond; and Nb and Cr; in selected horizons in soil profiles developed over the Prairie Creek kimberlite and peridotite, respectively.

Soil horizon	KIMBERLITE									PERIDOTITE			
	Nb		Cr	Ti		Sr		Zr	Diamond	Nb		Cr	
	1	2	1	1	2	1	3	3	4	1	2	1	2
A_0	1.41	1.65	2.88	>2.1	>2.4	5.0				1.78	2.02	1.65	2.38
A_1	1.26	1.48	1.87	>2.1	2.4	2.58	2.58	10.4		1.48	1.68	1.50	2.16
B_2	0.92	1.07	2.04	1.27	1.47	2.11	2.64	3.24		1.13	1.27	1.82	2.61
Y.G.	0.94	1.09	1.70	1.56	>1.8	1.63	1.75	1.25		0.94	1.05	1.06	1.57
B.G.*	0.85		1.13	0.87		1.0	0.77	1.21		0.88		0.79	
mean solum	1.21		1.77	>1.76		2.34	2.62	4.35	range 1.35-5.0 mean 2.9				

1. $\frac{\text{concentration in horizon considered}}{\text{concentration in bedrock}}$

2. $\frac{\text{concentration in horizon considered}}{\text{concentration in blue ground}}$

3. data for profile 00N40W

4. **Vitt** (1943)

*absent from peridotite. Samples from an equivalent depth.

Diamond has been found in a variety of sedimentary deposits and is considered to be chemically highly immobile. Since the average enrichment of Sr in the solum is just below that of diamond, it is suggested that Sr is highly immobile and may be used as a norm to measure:

(1) The approximate deflation of the soil profile.
(2) The approximate loss/gain of the other elements.
(3) The part of the profile where diamond is most enriched.

It must be emphasised, however, that (1) and (2) are subject to the following limitations:

(a) There is no such thing as absolute chemical immobility, Polynov (1944).
(b) Zirconium was seen to be enriched to a greater degree than Sr in the same profile, thus Sr has been leached to some extent. Calculations, therefore, based on Sr as the norm, give the minimum amount to which the elements have been leached.
(c) The data for Sr (and Ti and Zr) are based on a limited number of spectrographically analysed samples, the precision of which leaves much to be desired.

As mentioned above, Zr is apparently more immobile than Sr and is therefore a more suitable element on which to base deflation calculations. However, the Zr content of the same soil horizon in different profiles varies considerably (e.g. 300 to 5500 ppm Zr in the A_1 horizon), and some samples are below the spectrographic sensitivity (200 ppm Zr). It is not possible therefore to calculate a meaningful average Zr content and enrichment for the soil horizons from the limited number of determinations. Moreover, there is a discrepancy for the Zr content of the bedrock as determined by spectrographic and neutron activation methods. The former method gives less than 200 ppm Zr whilst the mean of triplicate analyses of a duplicate sample determined by neutron activation (Date, pers. comm.) is 527 ppm Zr.

The loss of Nb, Cr and Ti, relative to Sr, in the component horizons over the kimberlite profile are given on Table 4.6. Calculations are made according to the formulae:

$$\text{Amount of metal lost (or gained) from horizon } X_y = 100 - \frac{C \times 100}{R \times E_{Sr}}$$

where C = the concentration of the element considered in the horizon (X_y) considered

R = the concentration of the element considered in the bedrock

E_{Sr} = the enrichment of Sr in X_y

It can be seen from Table 4.6 that Nb and Ti are depleted in the solum but Cr is depleted in the A horizon only. Maximum depletion occurs in the A_0 horizon. Unlike Ti and Cr, Nb is strongly depleted in the yellow ground.

Both Nb and Ti are depleted in the blue ground compared with the bedrock. This is briefly discussed in Section 4.326.

4.32122 Mode of occurrence of the elements

Niobium

In igneous minerals Nb^{5+} ($r^* = 0.69$) may isomorphously substitute for Ti^{4+} ($r = 0.68$), W^{4+} ($r = 0.70$), Sn^{4+} ($r = 0.71$)

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* ionic radius (Å) from Ahrens (1952)

Table 4.6 The per cent loss (or gain) of Nb, Cr and Ti; relative to constant Sr, in selected horizons in soil profiles over kimberlite at Prairie Creek

	Per cent loss or gain				
Soil horizon	Nb 1	Nb 2	Cr 1	Ti 1	Ti 2
A_o	-72	-66	-47	<-59	<-52
A_1	-51	-42	-28	<-20	<-7
B_2	-55	-49	-3	-40	-31
Y.G.	-43	-37	+4	>+2	>+10
B.G.	-15		+3	-12	
mean solum	-54		-21		

1. relative to mean bedrock
2. relative to blue ground

- = loss of metal
+ = gain of metal

and under certain circumstances, Al^{3+} (r* = 0.51), Fe^{3+} (r = 0.64), Th^{4+} (r = 1.02) and P^{5+} (r = 0.35), Parker and Fleischer (1968). The main possible host minerals in the Prairie Creek kimberlite are therefore perovskite, ilmenite, zircon, magnetite, pyroxene, amphibole and phlogopite.

During weathering Nb accumulates largely in the silt fraction (Fig. 4.9). This fraction is composed of fine grained primary minerals and coarse secondary minerals. Since secondary minerals are concentrated in the clay fraction but Nb is not, relative to the silt fraction, it is concluded that Nb occurs largely in silt size primary minerals, e.g. perovskite, ilmenite, magnetite or zircon.

According to Smith (1953) both perovskite and zircon are soluble in sulfuric acid but ilmenite and magnetite are not. A sample from the silt fraction of the kimberlite A_1 horizon, in which perovskite had been detected by X-ray diffraction studies, contained 320 ppm Nb when determined using a hydrofluoric acid attack. A duplicate sample attacked with sulfuric acid gave a content of 240 ppm Nb. Whilst the chemistry of the sulfuric acid attack, and its effect on the separation stage is unknown in detail, it is suggested that the Nb extracted with sulfuric acid is not associated with ilmenite or magnetite.

There is little parallelism between the Zr and Nb distributions (Fig. 4.10) and thus a major source of Nb in zircon is considered unlikely. It is concluded therefore that most of the Nb in the Prairie Creek kimberlite is contained in perovskite. This is in accord with other writers, e.g. Kukharenko (1961 and 1965), Erikson and Blade (1963) and Grantham and Allen (1960),

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*ionic radius (Å) from Ahrens (1952)

who found Nb to be concentrated in perovskite in some alkalic and ultrabasic alkalic rocks.

The slight concentration of Nb in the B_2 horizon is partly due to the increase in Nb content of the clay fraction. This may be due to either precipitation of metal from leach solutions or to the presence and eluviation of fine grained alteration products of the Nb host minerals, i.e. leuxoxene.

Appreciable concentrations of Nb are recorded in the coarse fractions throughout the profile. In the C horizon this is due largely to multimineral grains although the possibility of some Nb contained in ferromagnesian phenocrysts cannot be ignored. In the coarse fraction of the solum Nb is contained in sesquioxide nodules and/or mineral aggregates. This is discussed in Section 4.325.

Chromium

Chromium^{3+} (r* = 0.63) may diadochially replace Fe^{3+} (r = 0.64); Fe^{2+} (r = 0.74); Mg^{2+} (r = 0.66) and, under certain conditions, Al^{3+} (r = 0.51) in igneous minerals. In the Prairie Creek kimberlite Cr^{3+} may be expected to occur in ferromagnesian minerals, ilmenite, chromite and magnetite.

Like Nb, Cr accumulates largely in the silt fraction during weathering. This is attributed to a dominant occurrence in silt size opaque minerals i.e. chromite, magnetite and ilmenite. The increasing concentration towards surface is due to both the release of silt size host minerals from the matrix during weathering and eluvial concentration.

Chromium is enriched in the clay size of the solum where the concentrations of metal in the clay size of the B_2

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* ionic radius (Å) from Ahrens (1952)

is the same as that in the clay of the A_1 horizon. This is most easily explained as metal associated with clay minerals derived from ferromagnesian silicates.

In the coarser fractions of the solum, maximum Cr concentrations occur in the minus 36 plus 80-mesh fraction, and decrease in content with increasing grain size. This is attributed to occurrence with ferric sesquioxide nodules. Whilst this is further discussed in Section 4.325 and 8.61, it seems that there has either been some co-precipitation of Cr with ferric sesquioxides or the Fe nodules may partly reflect altered femic phenocrysts. This latter suggestion is supported by the presence of iddingsite particles of this grain size in the solum (page 88).

Strontium

Strontium^{2+} ($r^* = 1.12$) may replace Ca^{2+} ($r = 0.99$) and sometimes K^+ ($r = 1.33$), Ba^{2+} ($r = 1.34$), Pb^{2+} ($r = 1.20$) and Zr^{4+} ($r = 0.79$) in igneous minerals. In the Prairie Creek kimberlite Sr may therefore occur in zircon, perovskite, barite, apatite, pyroxenes, amphibole and phlogopite.

Strontium is usually an extremely mobile element (Rankama, 1950). Its immobility in the kimberlite soil is attributed to occurrence within resistant minerals. This suggestion is supported by the considerable concentration of Sr in the silt fraction, especially in the A horizon. Of the "resistant" minerals in the Prairie Creek kimberlite which may contain Sr, Rankama (1950) records up to 0.5% Sr in zircon, 10% in apatite and 0.6% in perovskite. In addition, celestine ($SrSO_4$) forms

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*ionic radius (Å) from Ahrens (1952)

a solid solution series with barite (Grahmann, 1920).

A sympathetic variation between Sr and Ba is not observed. Furthermore, celestine is soluble in water to the extent of 132 ppm (Deer et al, 1962). Thus a major occurrence of Sr in barite is considered unlikely.

A sympathetic distribution between Sr and Zr is not observed, although in the A_1 horizon of profile 200N15W some similarity in their distribution does occur. If all the Sr were to be contained in zircon, this would imply a Sr content in zircon of 1% to 12%. Such a high concentration is most unlikely due to the considerable difference in ionic radius between Zr and Sr (0.79 and 1.12, respectively). In addition, the difference in their respective charges does not favour substitution. It is suggested therefore that whilst some Sr may occur in zircon, this is not the major source of metal.

Although size distribution studies of P were not made, and thus it is unknown whether there is any degree of sympathetic variation between Sr and P, there is little relationship between their respective vertical distributions. It is thought therefore that apatite is unlikely to be a major host mineral of Sr.

This leaves perovskite. A sympathetic variation between Sr and Nb and Ti does not occur. This may be due to the fact that Sr replaces Ca whereas Nb replaces Ti. Moreover, perovskite is not the only Ti host mineral. It is suggested therefore that, in the absence of a more likely alternative, perovskite is the major Sr host mineral in the kimberlite.

The reason for the concentration of Sr in the clay size of the B_2 horizon is uncertain. It could be that metal released during the weathering of perovskite is immediately sorbed by clays. Alternatively, some clay size perovskite grains may exist and are eluviated to the B_2 horizon.

As with Nb and Cr, Sr is present in the coarse fractions throughout the profile. This is attributed to occurrence in sesquioxide nodules and aggregates and is discussed in Section 4.325.

Zirconium

Although several rare Zr bearing minerals exist, most Zr in igneous rocks occurs in zircon. Subordinate amounts of metal may also occur in femic minerals, Rankama (1950).

Zircon was identified in the silt fraction of the A_1 horizon and in the minus 80 plus 100 mesh fraction of the B_2 horizon at 200N15W. Zirconium is concentrated in these samples. There is no reason therefore to dispute zircon as the major source of Zr in kimberlite.

Since zircon is generally highly immobile, the distribution of Zr in the minus 80-mesh plus 2 micron size is thought to largely reflect the grain size of the kimberlitic zircons. No coarse sized zircons were detected and the presence of Zr in the coarse fractions is attributed to multimineral grains.

Appreciable concentrations of Zr are present in the clay size of the A_1 horizon at 200N15W and 00N200W. This may reflect metal released from femic minerals and subsequently hydrolysed, or it may reflect some slight dissolution of zircon which according to Poldervaart (1955) may occur at high pH's.

Titanium

Titanium may occur in a variety of igneous minerals of which the most important in the Pairie Creek kimberlite are ilmenite, magnetite, perovskite and femic minerals.

During weathering Ti tends to concentrate in the silt fraction, especially of the A_1 horizon. However, this is not so marked as with the other elements of this group, presumably reflecting the diverse occurrence of Ti.

Only at 200N15W and 00N200W does Ti concentrate in the coarse fraction during weathering. This is thought to be due to occurrence in nodules and aggregates and is discussed in Section 4.325.

The content of Ti in the clay fraction is variable; at 00N40W metal accumulates in the clays of the B_2 horizon (cf. Nb) whilst at 00N200W the clay fraction is depleted in Ti.

4.3213 Comparison with the Prairie Creek Peridotite

4.32131 Variation with Depth

Only Nb and Cr were investigated in the peridotite soil profile. The vertical distribution of Nb in two poorly drained and a well drained profile, and Cr in a poorly drained profile are illustrated on Fig. 4.7 and summarised on Table 4.4. It can be seen that:

(1) The vertical distribution of Nb and Cr in soils over the peridotite and kimberlite are similar. However, unlike the kimberlite profile, Nb is not slightly concentrated in the B_2 horizon.

(2) Both Nb and Cr are depleted in the peridotite profile at a depth equivalent to the kimberlite blue ground.

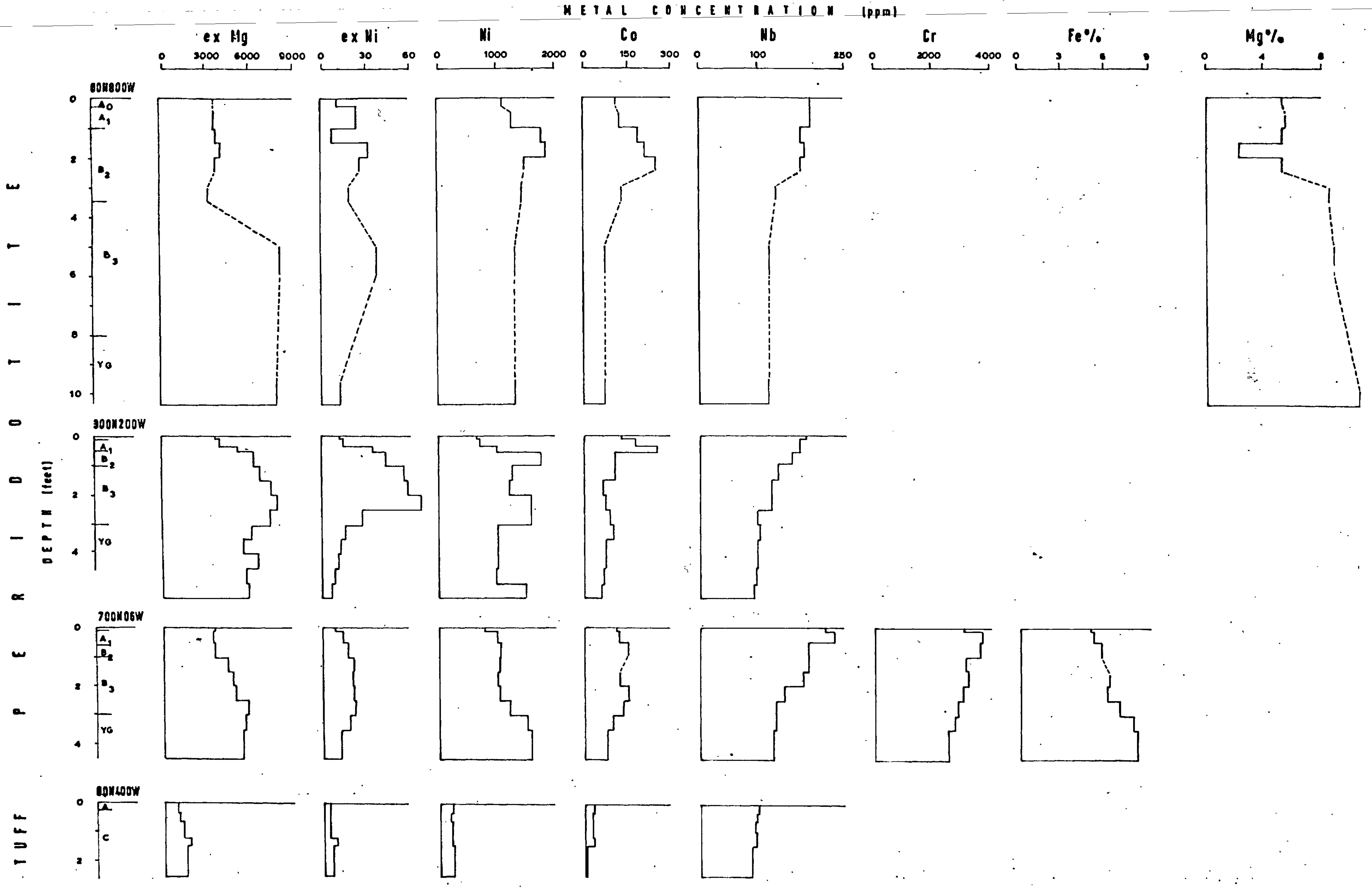


FIGURE 47 THE VERTICAL DISTRIBUTION OF SELECTED ELEMENTS IN RESIDUAL SOIL PROFILES DEVELOPED OVER PERIDOTITE AND TUFF, PRAIRIE CREEK, ARK.

Complete Sample. Wet Attacks.

4.32132 Variation with Particle Size

The variation of Nb, Cr, Sr, Zr and Ti with particle size in selected horizons in a poorly drained profile over the Prairie Creek peridotite are illustrated on **Figure** 4.10. It can be seen that the distribution of the elements in the kimberlite and peridotite profiles are very similar. However, the following minor differences are noted:

(1) Higher concentrations of metal are present in the coarse fraction of soils over the peridotite, particularly in the A horizon, than in the corresponding fraction over the kimberlite.

(2) Absolute concentrations of metal are higher in the peridotite, particularly in the silt sizes (excluding Zr as below).

(3) Zr is not particularly concentrated in the silt size of the A horizon.

4.3214 Discussion

4.32141 Mobility in the Soil Profile

It was shown in the previous section that this group of elements are relatively immobile in the kimberlite soil profile. The similar overall distribution of the elements in the peridotite and kimberlite soils indicate a similar immobility during weathering of the peridotite. It is noticeable, however, that both Nb and Cr are enriched to a greater extent in the A horizon of the peridotite than kimberlite (Table 4.5). This suggests that either they have been less strongly leached from the peridotite A horizon, or that deflation is greater in the peridotite profile than kimberlite.

The enrichment of Zr and Sr in the peridotite profile is unknown. The probable degree of deflation cannot therefore be calculated. It is noticeable however (Table 4.4) that the Mg content of soil over the peridotite is higher than in soils over the kimberlite. Since Mg is highly mobile (Chapter 8) and probably present in the same form in both rocks, it would appear that the peridotite is less strongly leached. This in turn would suggest a lesser degree of deflation over this rock type. This implies Nb and Cr to be less mobile in the peridotite than in the kimberlite profile.

4.32142 The form of metal in soils over the peridotite

The peridotite and kimberlite are composed of more or less the same mineralogical assemblage. It is likely, therefore, that metal is present originally in similar forms in both rock types.

The tendency for metal to remain the coarse fraction of the kimberlite during soil formation is probably due to a lesser degree of weathering of the peridotite than kimberlite. This is reflected by their differences in particle size distribution (Fig. 4.3).

The higher absolute concentrations of elements in the peridotite than kimberlite is thought to be due to both dilution of the latter with accidental xenoliths, and loss of metal by leaching.

4.3215 The Sialic Country Rocks

4.32151 Variation with depth

The variation of Nb and Cr contents with depth in poorly and well developed soil profiles over the Trinity siltstone are illustrated on Figure 4.8. Both profiles are well drained. The contents of Nb, Cr, Ti and Zr in selected horizons of the well drained profile are summarised on Table 4.4. It can be seen that:

(1) Metal is particularly concentrated in the B_2 horizon.

(2) Zirconium is depleted in the A horizon but Nb, Ti and Cr are slightly concentrated.

(3) Strontium is below the spectral sensitivity (30 ppm).

4.32152 Variation with particle size

The variation of Cr, Ti and Zr content with particle size in selected horizons of a poorly developed soil profile over the Trinity siltstone and Tokio arenites is illustrated on Figure 4.11. Determinations were made using the emission spectrograph. The following salient features are noted:

(1) With the exception of Cr as in (3) below, the elements are overwhelmingly concentrated in the silt size fraction.

(2) In soils over the Trinity formation, the content of Ti and Cr in the silt fraction increases towards surface. However, greatest amounts of the Zr occur in the silt size of the B_2 horizon.

(3) Chromium, and to a much smaller extent, Ti and Zr, are considerably concentrated in the coarse fraction of the Trinity solum. Slight concentrations of Cr are also recorded in the coarse fraction of the Tokio formation.

FIGURE 4.8 THE DISTRIBUTION OF SELECTED ELEMENTS IN SOIL PROFILES OVER THE DOMINANT COUNTRY ROCKS NEAR PRAIRIE CREEK, ARKANSAS.

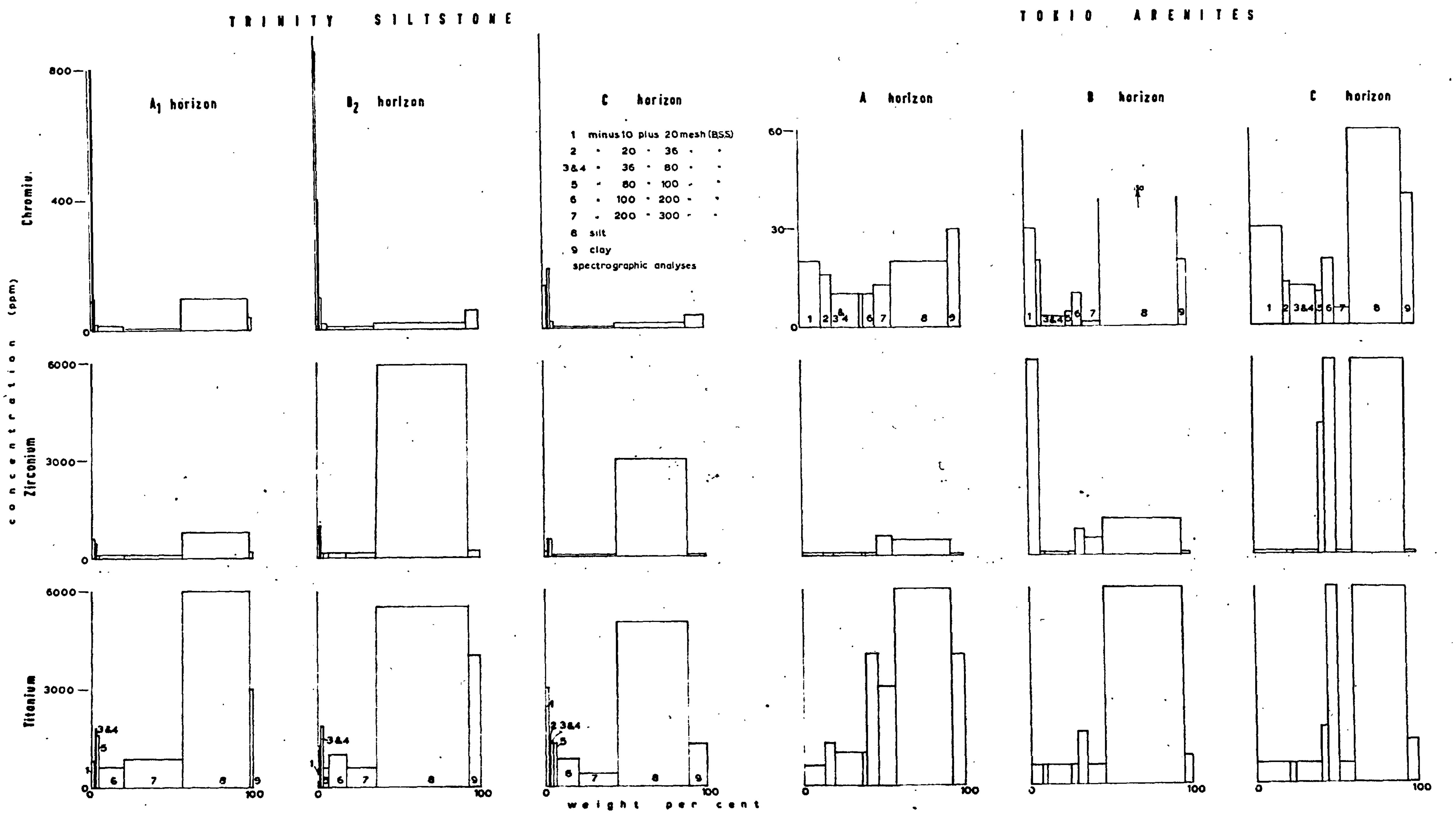


FIGURE 4.11 HISTOGRAMS OF Cr, Zr AND Ti CONTENT PLOTTED AGAINST WEIGHT PER CENT FOR VARIOUS SIZE FRACTIONS IN RESIDUAL SOILS OVER THE TRINITY AND TOKIO FORMATIONS.

(4) In soils over the Tokio formation the elements are slightly concentrated in the minus 100 plus 200-mesh fraction; this increases in prominence with depth.

Limited studies were made of the variation of Nb with particle size in soils over the Trinity siltstone (Table 4.7 below).

Table 4.7

Horizon	Niobium ppm 10 to 80 mesh	80 to 300 mesh	minus 300 mesh
A_1	2.4	0.8	4.0
B_2	1.6	2.4	8.0
C	3.2	0.8	3.2

It can be seen that Nb is concentrated in the minus 300-mesh and minus 10 plus 20-mesh fractions, particularly the former.

4.3216 Discussion

The sialic bedrocks of the Trinity and Tokio formations are composed of loosely consolidated reworked sediments. Metal in the C horizon is therefore present as resistant primary or stable secondary minerals. Distribution of metal in the C horizon is believed to reflect the grain size of these minerals.

Over 95% of the Zr occurs in the silt fraction, no doubt as zircon. Since eluviation of silt size minerals is unlikely, the concentration of metal observed in the B_2 horizon is most probably due to a variation in the composition of sediment. This is also possibly the reason for the enrichment of Ti and possibly Nb (page 111) in the B_2 horizon of the Trinity formation. The slight concentration of Ti, Nb and Cr in the A horizon may be due to eluvial concentration of silt size host minerals or a slight difference in the nature of the sediment.

Although Ti, Nb and Zr are concentrated in the coarser fractions, only Cr is enriched in the coarse fraction of the B_2 horizon where there is a similar distribution with Fe (Fig. 4.14). This is attributed to occurrence with sesquioxide nodules and is discussed in Section 4.325. If this is the case then it appears that some mobilisation of Cr has occurred.

Only Ti is enriched in the clay size of the Trinity solum. It is uncertain whether this is due to soil forming processes or to metal associated with clay minerals deposited with the Trinity formation.

Insufficient data are available to establish the behaviour of Nb during weathering of the Trinity formation. However, as previously mentioned Nb usually accompanies Ti or Zr. Since Nb is not depleted in the A horizon (cf. Zr) it is probable that Nb accompanies Ti.

Soils over the Tokio formation are rudimentary and there is no apparent redistribution of this group of elements. It is suggested therefore that they remain largely in the form in which they were deposited. Concentration of Ti and Cr in the clay fraction of the C horizon is thought to be due to their occurrence in a sesquioxide cement. This cement occurs in a conglomerate a few inches deeper in that particular profile.

4.3217 The Tuffaceous Country Rocks

4.32171 Variation with depth

The vertical distribution of Nb in the Prairie Creek tuff and Cr and Nb in the Woodbine tuff is illustrated on Figures 4.7

and 4.8, respectively. It can be seen that:

(1) The Nb content of the Prairie Creek tuff decreases slightly with depth.

(2) Distribution of the highly anomalous Nb content of the Woodbine tuff is markedly dissimilar from the ultrabasic and sialic rocks. Concentration increases from the surface to a maximum at a depth of 2 feet. Little variation in Nb content is seen in the deeper samples.

(3) Maximum Cr content is recorded at a depth of 2 feet. However, unlike Nb, concentration decreases in the $B_{2.2}$ horizon.

4.3218 Discussion

Two possible reasons for the near surface depletion of Nb in the soils over the Woodbine formation are considered:

(a) Leaching of metal during soil forming processes.

(b) A change in character of the tuff.

Insufficient data is available to disprove either of the above suggestions. However, the circumstantial evidence discussed below does not support the leaching suggestion.

During secondary dispersion Nb tends to concentrate in the hydrolizate fraction, Rankama (1950). Thus if leaching of Nb were to have occurred, some concentration of metal in the clay and sesquioxide rich $B_{2.1}$ horizon would be expected. This does not occur.

Perovskite was tentatively identified in the Woodbine $B_{2.3}$ horizon (page 91). This is thought to be the dominant Nb host mineral at Prairie Creek. Since the igneous rocks at Prairie Creek probably belong to the same genetic assemblage as the alkalic Woodbine tuff, it is possible that perovskite is the dominant Nb host mineral in the tuff. At Prairie Creek perovskite is seen to be relatively stable during soil formation. Since the Woodbine soils are formed under the same conditions of weathering, it might be expected, but is by no means certain, that perovskite would be relatively stable in the Woodbine soils also.

Thus the most simple explanation for the observed Nb distribution is that it reflects a variation in the character of the tuff. This would imply Nb to be relatively immobile, and is in accord with previous data.

It is unknown whether the variation of Cr content with depth is due to soil forming processes or to a variation in the character of the tuff. Probably both mechanisms are responsible to some extent.

4.322 Iron, Ni, Co, Mn, P, V and Ba

4.3221 The Kimberlite

4.32211 Variation with depth

The vertical distribution of Fe, Ni, Co, Mn and exNi in selected soil profiles over the Prairie Creek kimberlite are illustrated on Fig. 4.6. The mean metal contents in the component horizons are given on Table 4.4. Attention is drawn to the following features.

(1) This group of elements are concentrated in the B_2 horizon.

(2) Cobalt, Mn, and to a much lesser extent, V and Fe, are enriched in the A horizon, but Ni and P are depleted.

(3) In profile 200N15W Co is concentrated in the A and B_1 horizons where black (Mn) nodules are prolific; it is not concentrated in the B_2 horizon where they are scarce.

(4) Maximum exNi contents occur in the B_2 horizon.

(5) A relatively low Ni content is recorded in the B_2 horizon of profile 100N08W.

(6) Cobalt, V and Ni are depleted in the blue ground compared with the bedrock.

(7) Barium increases in concentration from the A_0 horizon to the blue ground. Minimum concentrations are recorded in the bedrock.

4.32212 Variation with particle size

The soil profile at 00N40W was separated into its component size fractions which were analysed for Ni, Co, Mn, Fe and exNi using wet methods. The results are plotted as histograms on Fig. 4.12. The following salient features are noted:

(1) During soil formation the elements have been considerably redistributed in the solum but to only a slight extent in the blue and yellow ground.

(2) In the solum, the elements are considerably concentrated in the coarse (plus 80-mesh) fractions. Greatest concentration of Mn, Co and Ni are found in the coarsest fraction, particularly in the A horizon. Maximum concentration of Fe occurs in the minus 20 plus 36-mesh fraction, especially in the B_2 horizon. With the exception of Ni, the greatest amounts of metal are present in the two coarsest fractions of the upper B_2 horizon.

(3) Both Ni and Fe are concentrated in the clay fraction of the solum. Only a very slight concentration of Mn and Co occur in the clay fraction of the A horizon and not at all in the B_2 horizon.

(4) The distribution of exNi is similar to that of total Ni. The lowest proportion of exNi in the solum occurs in the clay fraction.

(5) A slight concentration of Ni and Mn occurs in the clay sizes of the upper yellow ground.

(6) In contrast to Nb and Cr, this group of elements do not concentrate in the silt fraction towards surface.

The distribution of Mn, Co, Ni, V, Ba and Fe, as determined by spectrographic analyses, in selected horizons of three soil profiles over kimberlite are illustrated on Fig. 4.13. Samples were dispersed ultrasonically. Attention is drawn to the following features:

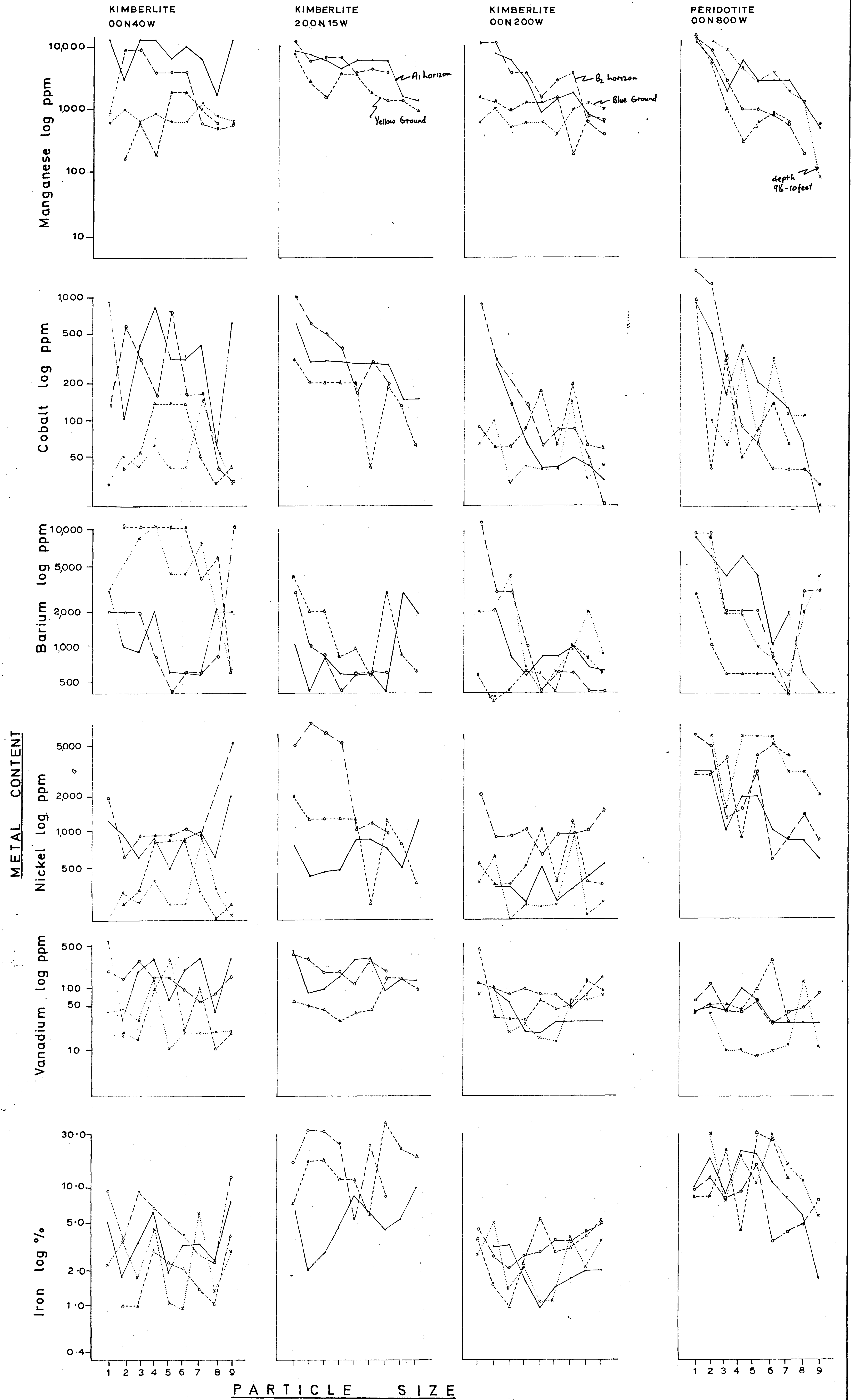
(7) Although there are slight differences between individual profiles, little overall variation is apparent from the distributions determined by wet methods.

(8) Spectrographic levels of Mn are slightly higher than determined by wet methods. In addition there is a tendency for the Mn content of the coarsest fraction of the B_2 horizon to exceed that of the A.

(9) Barium, which was not determined by wet methods, tends to have a bimodal distribution, though generally deficient in the clay size of the C horizon. There appears to be a sympathetic variation between Mn and Ba in the coarse fraction of the solum.

FIG. 4·13

THE VARIATION IN CONTENT OF Mn, Co, Ba, Ni, V AND Fe WITH PARTICLE SIZE IN SELECTED SOIL HORIZONS OVER THE PRAIRIE CREEK KIMBERLITE AND PERIDOTITE.



PARTICLE SIZE

1 MINUS 10 PLUS 20 MESH 4 MINUS 60 PLUS 80 MESH 7 MINUS 200 PLUS 300 MESH
1 MINUS 20 PLUS 35 MESH 5 MINUS 80 PLUS 100 MESH 8 MINUS 300 MESH PLUS 2 μ
3 MINUS 35 PLUS 60 MESH 6 MINUS 100 PLUS 200 MESH 9 MINUS 2 (CLAY)

SPECTROGRAPHIC ANALYSES.

(10) Similar distributions occur between Fe and V, particularly in the solum.

4.3222 Discussion

4.32221 Mobility in the soil profile

Since this group of elements are enriched in the B_2 horizon, presumably by accumulation of metal translocated from the A horizon (Chapter 8), they are considered semi mobile.

The enrichment of metals (calculated from the mean values given on Table 4.4) in selected horizons are given on Table 4.8. On the assumption that Sr has remained largely immobile during soil formation (page 99), the amounts by which the elements are depleted or enhanced in the soil horizons are detailed on Table 4.9.

Calculations for V are based on its content in the blue ground, since the figure given for the mean bedrock is thought not representative of rock underlying the profiles (Section 4.327). From these tables the following conclusions are drawn:

(1) Maximum leaching of metal occurs in the A horizon, especially the A_0. Phosphorus and Ni have been leached the most but Co and Mn have accumulated (relative to Sr) in the A_1 horizon, i.e.

most depleted $P=Ni>V=Fe>Sr<Ba=Co<Mn$ most enhanced

(2) Manganese, Ba, Co and Fe have accumulated in the B_2 horizon. Although P, V and Ni are also concentrated in this horizon, they are depleted with respect to Sr, i.e.

least enhanced $Ni=P<V<Sr<Co<Fe<Ba<Mn$ most enhanced

Table 4.8 The enrichment of Ni, V, Fe, Co, Mn, P, Ba and Sr in selected horizons in soil profiles developed over the Prairie Creek kimerlite.

Soil horizon	Ni		V		Fe	Co		Mn	P	Ba		Sr
	1	2	1	2	1	1	2	1	2	1	2	1
A_0	0.50	0.89			1.60	2.24	2.67			5.7	0.7	5.0
A_1	0.54	0.95	0.75	1.62	1.63	3.44	4.08	4.3	0.5	3.4	0.42	2.58
B_2	1.22	2.16	0.95	2.06	2.50	2.32	2.76	7.35	1.25	5.2	0.64	2.11
Y.G.	0.98	1.72	0.62	1.36	1.85	1.16	1.37	1.63	0.82	6.35	0.78	1.63
B.G.	0.56		0.46		1.27	0.84		0.94		8.1		1.0
mean solum	0.98	1.76	0.88	1.91	2.21	2.68	3.20	6.33	1.0	4.6	0.57	2.34

1. $\frac{\text{concentration in horizon considered}}{\text{concentration in bedrock}}$

2. $\frac{\text{concentration in horizon considered}}{\text{concentration in blue ground}}$

Table 4.9 The per cent losses (or gains) of Fe, Mn, Ni, Co, V and P; relative to constant Sr, in selected horizons in soil profiles over kimberlite, Prairie Creek, Arkansas

Soil horizon	Sr enrichment	Fe	Mn	Co		Ni		V		P
		1	1	1	2	1	2	1	2	2
A_0	5.0	-68		-55	-47	-90	-82			
A_1	2.58	-36	+66	+33	+58	-79	-64	-71	-37	-80
B_2	2.11	+20	+250	+10	+30	-42	+2	-55	-3	-41
Y.G.	1.63	+10	+4	-29	-16	-40	+5	-62	-16	-50
B.G.	1.0	+25	-6	-15		-42		-54		
Mean solum		-1	+188	+15	+38	-55	-22	-60	-14	-54

1. Compared with mean bedrock
2. Compared with blue ground

(3) Phosphorus, Ni, Co and V are depleted in the yellow ground but Fe may have accumulated.

(4) Nickel, Co and V are depleted in the blue ground.

It is suggested that the general overall mobility of this group of elements in the kimberlite soil profile is:

most semi mobile Ni = P>V>Fe>Co>Ba>Mn least semi mobile

The depletion of metals in the blue ground are discussed in Section 4.327 and Chapter 8.

4.32222 <u>Mode of occurrence of metal in the kimberlite soil profile</u>

<u>Manganese, Co, Ni and Fe</u>

Divalent Mn (r* = 0.80) usually replaces Fe^{2+} (r = 0.74) in igneous rocks, although it may, with difficulty, replace Mg^{2+} (r = 0.66) (Rankama, 1950). Divalent Co (r = 0.72) may replace Mg^{2+} (Sandell and Goldich, 1943; Nockolds and Mitchell, 1948) or Fe^{2+} (Nickel, 1954, Ringwood, 1955). Divalent Ni (r = 0.69) may replace Mg^{2+} (Vogt, 1923; Goldsmidt, 1954) or Fe^{2+} (Nickel, 1954; Ringwood, 1955). The main possible host minerals of these metals in kimberlite are therefore olivine and its alteration products, pyroxene, amphibole, phlogopite, magnetite, ilmenite, sulfides, etc.

Opaque minerals in the Prairie Creek kimberlite are largely silt size. Since these minerals are generally resistant to weathering, the lack of concentration of metal in the silt size of the A horizon, (cf. Cr and Ti), indicates only a small proportion of the Mn, Co, Fe and Ni to be contained in these minerals,

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*ionic radius (Å) Ahrens (1952)

i.e. ilmenite, magnetite, etc.

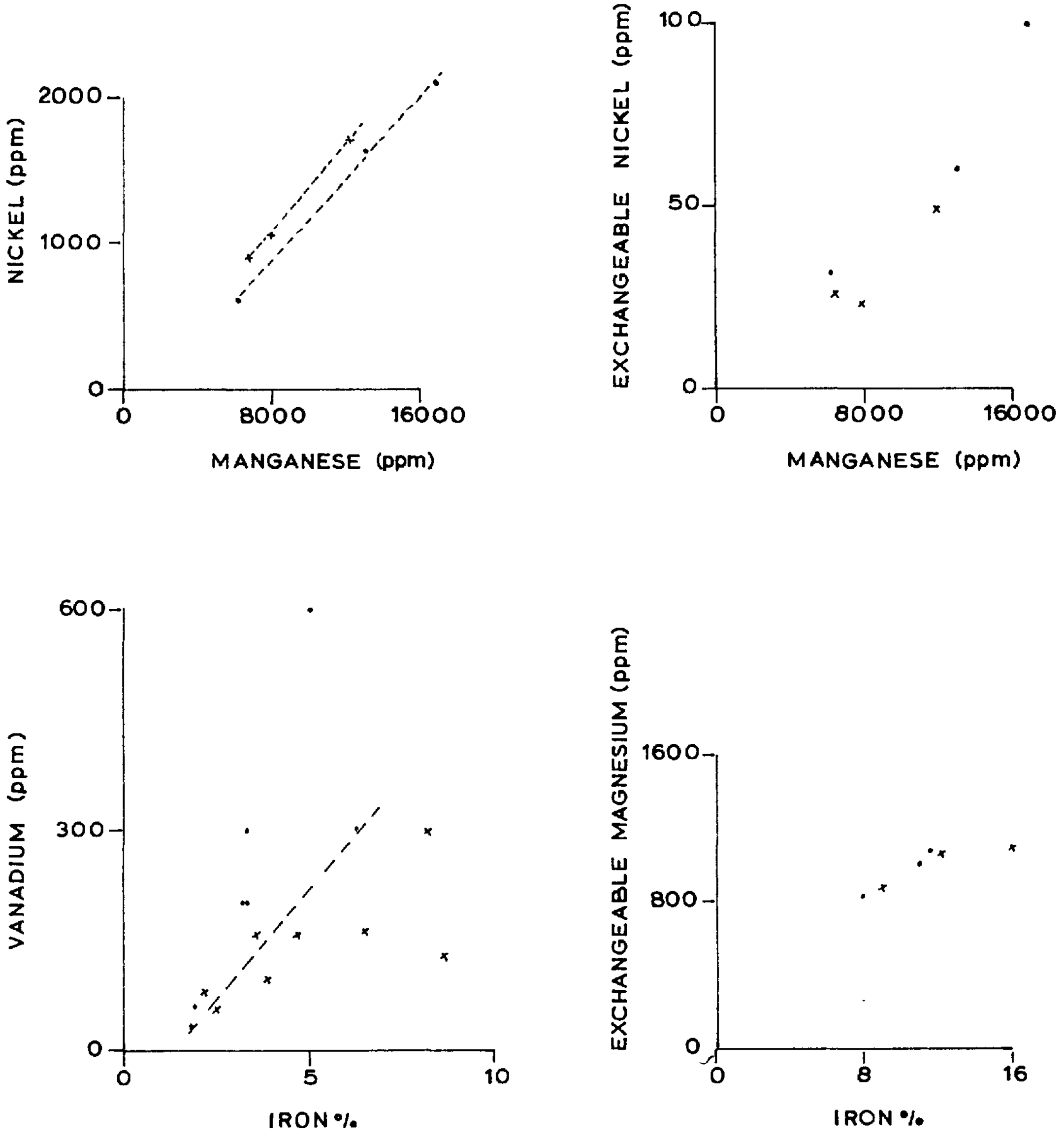
With the exception that Mn and Co are not concentrated in the clay size fraction, the elements vary sympathetically in the kimberlite C horizon (Figs. 4.12 and 4.13). This would suggest a similar occurrence of these metals and is in accord with the ionic radii data.

In the coarse fractions of the C horizon, the distribution of metal probably reflects the dominant grain size of the femic phenocrysts and their alteration products.

There is a tendency, especially in the blue ground (Figs. 4.12 and 4.13), for slight concentrations of metal to occur in the minus 200 plus 300-mesh fraction. This is the dominant grain size of the femic silicates of the kimberlite ground mass and of the iddingsite grains. About 5% opaque minerals are also present as discrete and multimineral grains. The mode of occurrence of the elements in this fraction was not further investigated. It is noticeable, however, that the proportion of exNi in this fraction is relatively low (Fig. 4.12). This would suggest Ni to be present as a more resistant form than in other size fractions.

The considerable concentration of the elements in the coarse fraction of the solum is due to occurrence within sesquioxide nodules and mineral aggregates. This is discussed in Section 4.325 where it is shown that Ni, Co and Mn are enriched in the black nodules, which are most abundant in the minus 10 plus 20-mesh fraction. Iron is concentrated in the brown nodules which are most common in the minus 20 plus 36-mesh fraction. It is noticeable that an appreciable proportion of Ni is contained in exchange positions on nodules, particularly those rich in Mn (Fig. 4.15).

FIG. 4·15 THE VARIATION BETWEEN Ni AND Mn; EX.Ni AND Mn; EX.Mg AND Fe IN THE THREE COARSEST FRACTIONS OF THE KIMBERLITE SOLUM; AND V AND Fe IN THE PLUS 2 MICRON SIZE OF THE KIMBERLITE SOLUM.



• A horizon

× B horizon

data for Ni-Mn, EX Ni-Mn and EX Mg-Fe is obtained from -10+20, -20+36 and -36+80 mesh (BSS) fractions. wet analyses

data for V-Fe is obtained on the silt and coarser sizes and spectrographic analyses.

Before discussing the form of Ni in the minus 80-mesh fraction, it is convenient to interpret the partial attack data presented in Chapter 3 (Table 3.6 and Figs. 3.2 and 3.3). The interpretation of this data is given on Table 4.10 where it is suggested that, in the minus 80-mesh fraction of the kimberlite solum, the greater part of the Ni is relatively strongly bonded. A small part is very strongly held and about a third of the metal is associated with sesquioxides. Small amounts of metal are held in exchange positions.

Nickel is enriched in the clay size of the A_1 horizon, where it occurs in a relatively resistant form as seen from the low exNi/Ni ratio of 1.6%. Although the exact form is unknown, the following possible modes of occurrence are suggested:

(a) within the lattice of clay minerals,
(b) as hydrous Mg-Ni silicates (e.g. garnierite),
(c) irreversably sorbed on the fibrous constituents of plants (Ng Siew Kee and Bloomfield, 1962),
(d) as insoluble metallorganic compounds.

Both Ni and Fe are enriched in the clay size of the B_2 horizon. This is attributed to normal soil forming processes. Iron translocated by such processes usually accumulates as sesquioxides. Some Ni similarly translocated may be co-precipitated with these sesquioxides.

Vanadium

In igneous rocks V^{4+} ($r^* = 0.61$) readily replaces Ti^{4+} ($r = 0.68$); Fe^{3+} ($r = 0.64$) and probably Al^{3+} ($r = 0.51$). V^{5+} ($r = 0.59$) may replace P^{5+} ($r = 0.35$) (Rankama, 1950). Thus in kimberlite V may occur within femic silicates, magnetite, ilmenite and apatite.

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*ionic radius (Å) Ahrens (1952)

Table 4.10 Interpretation of the partial attack data for Ni presented in Chapter 3 and detailed on Table 3.6 and figures 3.2 and 3.3 (Data on minus 80-mesh fraction.)

Form of Ni		% Exchangeable	% Loosely held	%Associated with sesquioxides	% Extracted with $KHSO_4$
Attack		M. NH_4 Ac	0.025% HNO_3	Na citrate/ dithionite	
Kimberlite solum	1.	0.6	1 - 2.5	20	65
	2.	0.9	1.5 - 3.5	29	93
Trinity solum	1.	2	6	6	25

1. Relative to "total" determined by emission spectrograph.

2. Relative to "total" extracted with $HF/HClO_4$ attack.

In profiles over the Prairie Creek kimberlite, V tends to vary sympathetically with Fe (Figs. 4.13 and 4.15), although the Fe:V ratio is much higher in the coarse fraction of the B_2 horizon than the corresponding fractions in the A or C (Fig. 4.15). It seems likely therefore that in the C horizon, V is present largely within femic phenocrysts (or their alteration products). In the solum, metal is probably partly associated with ferric sesquioxides.

Barium

Barium^{2+} (r* = 1.34) may replace K^+ (r = 1.33) in igneous rocks. In addition it forms independent minerals such as barite, witherite, etc. In the Prairie Creek kimberlite Ba may occur, therefore, both in barite veinlets and in phlogopite.

Heavy mineral fractions were taken from five samples of the kimberlite C horizon and studied microscopically. The Ba content of the original samples ranged from 500 to 10,000 ppm. Barite was found in all five heavy mineral samples. It is concluded, therefore, that barite is the major source of Ba in the Prairie Creek kimberlite.

Barium is concentrated in the coarse fraction of the solum. There is a slight sympathetic variation between Mn and Ba and it is suggested that Ba is concentrated in Mn nodules (discussed in Section 4.325). Barium is also present as coarse grains of barite.

The slight concentration of Ba in the silt size of the A horizon probably reflects some eluvial concentrations of barite grains. In the clay size, Ba may occur within the lattice of secondary minerals derived from phlogopite, sorbed on clay minerals or organic matter, or as finely ground barite.

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*ionic radius (Å) Ahrens (1952)

Phosphorus

The form of P in the kimberlite was not investigated. However, according to Rankama (1950), 95% of P in igneous rocks is contained within apatite, although some replacement of Si^{4+} (r* = 0.42) by P^{5+} (r = 0.35) may occur. Although apatite was not found in the kimberlite, either by the writer or Miser and Purdue (1929), this may be due to the limited number of sections examined.

4.3223 Comparison with the Peridotite

4.32231 Variation with depth

The vertical distribution of Ni, exNi, Co and Fe in a well drained and two poorly drained profiles are illustrated on Fig. 4.7. The mean contents in selected horizons are given on Table 4.4. It can be seen that:

(1) Although there is a similar vertical distribution of the elements in profiles over the kimberlite and peridotite, the B_2 horizon is less chemically prominent in soils over the latter.

(2) Exchangeable Ni is concentrated in the B_3 horizon.

(3) In the poorly drained profile at 700N06W, Fe and Ni contents increase from the surface to the yellow ground.

4.32232 Variation with particle size

The variation of Fe, V, Ni, Ba and Co and Mn with particle size in selected horizons of a poorly drained soil profiles over the peridotite are illustrated on Fig. 4.13. It can be seen that the distributions of the elements are very similar to the corresponding horizons in the kimberlite; there are, however, the several slight

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*ionic radius (Å) Ahrens (1952)

differences noted below:

(1) In the C horizon, Mn increases in content with increasing grain size.

(2) The levels of Mn, Co, Ni and Fe in the coarsest fraction of the C horizon are in excess of the same fraction in the kimberlite.

(3) Barium is concentrated in the clay size of the deepest sample.

(4) Nickel is not concentrated in the clay size of the solum, and Fe is not concentrated in the clay size of the A horizon.

4.3224 Discussion

4.32241 Mobility in the soil profile

Nickel is not depleted in the A horizon of soils over the peridotite to the same extent as the corresponding material over the kimberlite, nor have Ni and Co accumulated to the same extent in the B_2 horizon (Tables 4.11 and 4.8). Since the composition of the bedrocks are very similar (Table 2.2) this would indicate a lesser degree of leaching of metal from the peridotite A horizon. This is in accord with its vertosolic morphology.

Table 4.11 The enrichment of Ni, Co and Fe in selected horizons of soil profiles developed over the Prairie Creek peridotite

	A_0	A_1	B_2	YG	Depth ≡ BG
Ni	0.59	0.73	1.09	0.93	0.97
Co	1.53	2.03	1.83	1.06	0.83
Fe	1.33	1.46	1.75	2.19	

The peridotite soil profile at 700N06W is located on the flank of an alluvium filled valley and is periodically water-logged. It is thought that the depleted Ni and Fe contents in the solum of this profile are due to leaching of metal during periods of water-logging.

Maximum exNi concentrations and exNi/Ni ratio (Table 4.12 below) tends to occur slightly deeper in the peridotite profile than in the kimberlite. Since at similar depths, weathering is more advanced in the kimberlite than peridotite, the reason for this is uncertain. Perhaps the B_3 horizon is the zone of maximum "release of Ni" from the phenocrystic minerals, i.e. olivine and pyroxene, of the peridotite, whereas dissolution of metal from the kimberlite is more progressive. Alternatively, it could be that a substantial proportion of the Ni released in the B_3 horizon of the kimberlite is leached from the profile.

Table 4.12

		A_0	A_1	B_2	B_3	Y.G.	B.G.	Bedrock
$\frac{exNi}{Ni}\%$	kimberlite	2.6	2.3	2.3	1.65	1.2	0.3	0.007
	peridotite	1.3	2.4	2.1	3.2	1.4	0.7	0.011

4.32242 Mode of occurrence of metal in the peridotite soil profile

The kimberlite and peridotite are composed of similar mineralogical assemblages and it is more than likely that the elements occur initially in the same minerals in each rock type.

The general tendency for higher concentrations of metal to occur in the coarser fractions of the C horizon of the peridotite, than in the corresponding samples of the kimberlite, may reflect either a difference in the composition of the host minerals, or depletion of kimberlite hosts. Such depletion may be due either to leaching of metal or dilution with accidental xenoliths.

The reason why Ni is not concentrated in the clay size of the solum nor Fe in the clay size of the A horizon is uncertain. It may be that metal is leached from this fraction during periods when the profile is water-logged.

4.3225 The Sialic Country Rocks

4.32251 Variation with depth

The variation of Fe, Mn, Ni, exNi and Co with depth in a well drained, well developed profile of the Trinity siltstone, and Fe, Co and Ni in a poorly developed profile over the Trinity silstone and Tokio arenites, are illustrated on Fig. 4.8. The mean contents in selected horizons of the well developed profile are given on Table 4.4. Vanadium, P and Ba contents are included. The following features are notable:

(1) Manganese is overwhelmingly concentrated in the A horizon.

(2) The elements are enriched in the B_2 horizon. Generally, highest Fe concentrations are recorded where the colour is reddest; lowest concentrations occur at the base of the mottled zone.

(3) In the Fe rich samples, the $HClO_4$ attack extracts more Fe and Ni than does the $KHSO_4$ attack. In samples low in Fe the reverse occurs.

(4) In the poorly developed profiles metal content tends to

increase with depth. In addition, Ni is concentrated at the Tokio ground surface and Ni and Fe at a depth of 5 to 12 inches in soils over the Trinity formation.

4.32252 Variation with particle size

Histograms of the variation of metal content with particle size for a poorly developed soil profile over the Trinity siltstone and Tokio arenites are presented on Fig. 4.14. Metal was determined spectroscopically. The following features are noted:

The Trinity Formation

(1) Metals are concentrated in the coarse fraction of the solum, particularly in the B_2 horizon. Maximum concentration of Fe, Co and Mn occurs in the minus 10 plus 20-mesh fraction whereas Ni and V are concentrated in the minus 20 plus 36-mesh fraction.

(2) Vanadium, Co, Ni, Fe and to a lesser extent Ba, are particularly enriched in the clay size of the B_2 horizon. Nickel and Ba and, unlike the ultrabasic rocks, Mn and Co are enriched in the clay fraction of the A_1 horizon.

(3) A large proportion of the Ni, Ba and Co is contained in the silt fraction of the A_1 horizon where both concentration and amount of metal decreases with increasing depth.

(4) Vanadium is enriched in the silt fraction of the B_2 horizon and is depleted in the silt size of the A horizon (cf. Zr).

The Tokio Formation

(5) Metal is not concentrated in the coarse fraction of the rudimentary soils developed over the Tokio arenites.

(6) The content of Mn, Co, Ba and Fe in the silt fraction

decreases with depth whilst the V content increases. Greatest amounts of Ni occur in the silt fraction of the middle sample.

(7) Higher concentrations of the elements are presented in the clay fraction of the Tokio C horizon than in the same fraction of the Trinity formation.

4.3226 Discussion

With the exception of Mn, there is a similar vertical distribution of this group of elements in soil profiles over both the kimberlite and Trinity limestones. Unlike profiles over the kimberlite, however, Fe is depleted to a greater extent than Ni in the A horizon of the well developed Trinity siltstone soil profile (Table 4.13 below).

Table 4.13

		Ni	Co	Fe	Mn
well developed profile	enrichment in A horizon	1.5	2	1.4	8
	enrichment in B_2 horizon	2.25	2.5	3.1	> 1.2

This would imply Fe to be more readily translocated from the A to the B horizon than is Ni. The Mn content of the C horizon is unknown and thus the degree of translocation of Mn cannot be calculated.

In the poorly developed soil profile, the clay size of the B_2 horizon is enriched in this group of elements compared to the same fraction in the A and C horizons. Thus in even the rudimentary profiles, some translocation of metal occurs. It is noticeable, however, that the bulk of the metal is contained within the silt fraction, presumably as resistant minerals.

The concentrations of metal in the coarse fraction is attributed to occurrence in sesquioxide nodules. This is discussed in Section 4.325.

No profile development or redistribution of metal is evident in the profile over the Tokio formation. It is suggested that the elements remain largely in the form in which they were deposited. The concentration of elements in the clay fraction of the C horizon is thought to be due to association with ferric sesquioxide cement. This occurs as a conglomerate a few inches deeper in the profile.

4.3227 The Tuffaceous Rocks

4.32271 Variation with depth

The vertical distribution of Ni, Co, Mn, exNi and Fe in soils over the Woodbine formation and Ni, exNi and Co over the Prairie Creek tuff are illustrated on Figs. 4.8 and 4.7, respectively. The following features are noted:

(1) Other than a slight decrease in Co content and increase in exNi concentrations with depth, little variation in metal content is recorded in the profile over the Prairie Creek tuff.

(2) Distribution of the elements in the A and $B_{2.1}$ horizons of soils over the Trinity siltstone and Woodbine formations are very similar. However, unlike soils over the Trinity siltstone, maximum Ni and Co contents and elevated concentrations of Mn, occur in the $B_{2.3}$ and lower $B_{2.2}$ horizon.

4.3228 Discussion

The lack of marked redistribution of the elements in the profile over the Prairie Creek tuff indicates the elements to be relatively immobile over this rock type. This is due to the lack of weathering of their host minerals and is reflected by the skeletal soil profile. However, whilst Nb does increase slightly in content towards the surface, Ni does not. This would suggest some Ni to have been leached from the profile. Similarly, Co appears to have accumulated slightly near the ground surface.

The similar distribution of the elements in well developed soil profiles over the Trinity siltstone and upper parts of the Woodbine formation indicates the elements to behave similarly during weathering over both rock types.

Concentration of Ni, Co and Mn at depth in the Woodbine soil profile may be due to either (a) precipitation of metal, or (b) a variation in the character of the tuff. Coincident red ferric oxide staining is not observed. This would suggest Fe to be in the divalent state. Since Mn^{2+}, Ni^{2+} and Co^{2+} are generally more mobile than Fe^{2+} (Chapter 8) this would not support the precipitation suggestion. The most likely answer, therefore, and one consistant with the Nb distribution, is that the concentrations are due to a difference in the character of the tuff.

4.323 Magnesium

4.3231 Distribution in Soil Profiles over the Prairie Creek Kimberlite

4.32311 Variation with depth

The variation of Mg and exMg contents with depth in selected profiles over the Prairie Creek kimberlite are illustrated on Fig. 4.6 and summarised on Table 4.4. Attention is drawn to the following features:

(1) Total Mg increases in content with increasing depth.

(2) The content of exMg first increases with depth and then decreases. Maximum concentration occurs in the yellow ground.

(3) Both Mg and exMg are slightly concentrated in the B_2 horizon.

4.32312 Variation with particle size

The variation of Mg content with particle size in soil horizons over the Prairie Creek kimberlite is tabulated on Table 4.14 below.

Table 4.14

		A1	B2	Y.G.	B.G.
Mg %	plus 80-mesh	1.60	3.38	11.24	13.30
	minus 80-mesh	1.34	5.52	10.54	13.90

The variation of exMg with particle size in component horizons of a kimberlite profile are illustrated on Figure 4.12. The following salient features are noted:

(1) With the exception that metal is concentrated in the minus 80-mesh fraction of the B_2 horizon, total Mg is more or less evenly apportioned between the plus and minus 80-mesh fractions throughout the profile.

(2) Exchangeable Mg has a bimodal distribution in the C horizon with maximum concentrations occurring in the clay size. During the increase in weathering from the blue to the yellow ground, the content of exMg in the clay size tends to decrease and that in the coarse size tends to increase.

(3) A similar bimodal distribution of exMg occurs in the solum where metal is concentrated in the clay size. In the coarse size, maximum values occur in the minus 20 plus 36-mesh size and are considerably lower than in the same fraction of the C horizon.

4.3232 Discussion

4.32321 Mobility in the profile

The decrease in metal content towards surface indicates Mg to be considerably leached during weathering. On the assumption that Sr has remained immobile (page 99) the following depletions of Mg are observed:

Table 4.15

Soil horizon	A_0	A_1	B_2	Y.G.	B.G.
Mg % depleted	97	96	89	65	5

4.32322 Mode of occurrence in the kimberlite profile

Magnesium is a major element in kimberlite and is generally contained in olivine, pyroxene, phlogopite and other ferromagnesian silicates. Some accessory minerals, e.g. picro-ilmenite and pyrope garnet, when present, also contain appreciable concentrations of Mg.

During chemical weathering at Prairie Creek, olivine, phlogopite and pyroxene are altered more or less according to the sequence:

$$\left.\begin{array}{l}\text{olivine}\\\text{pyroxene}\\\text{phlogopite}\end{array}\right)\longrightarrow\left.\begin{array}{l}\text{serpentine}\\\text{phyllosilicates}\end{array}\right)\longrightarrow\text{clay minerals}\dashrightarrow\begin{array}{l}\text{quartz}\\\text{iron oxides}\end{array}$$

Basically, each stage involves the addition of water ± silica and the loss of Mg. Whilst the bulk of released Mg is probably leached from the profile (Table 4.15), some may be precipitated either as the hydroxide (brucite) or by sorbtion on suitable materials.

Molar ammonium acetate will extract Mg held in exchange positions and will dissolve soluble Mg compounds. Magnesium carbonate and hydroxide are also probably dissolved to some degree. Indeed, Kelley (1934), concludes that the accurate determination of exMg in alkali soils is impossible. Thus metal extracted from the ultrabasic rocks by NH_4Ac comprises at the least the following forms:

(a) Metal "released" from decomposing host minerals.

(b) Metal held in exchange positions on clays, organic matter, etc.

(c) Metal present as soluble Mg compounds.

Whilst it is not possible to discriminate between these forms of metal from the data available, one may speculate as to the dominant form in particular parts of the profile.

It is possible that in the clay size fraction throughout the profile, where clay minerals are concentrated, that exMg is largely present in exchange positions. This suggestion is supported by the similar concentrations of exMg in the clay fraction of the B and C horizons, which may reflect saturation of exchange positions. This was not investigated. The depleted Mg content of the clay size of the A horizon is explained as due to both dilution of clay minerals with quartz and other minerals, and to leaching of metal. This would be facilitated by the lower pH of the A horizon (Fig. 4.6).

In the coarse fraction of the C horizon, Mg is presumably derived from decomposing phenocrystic minerals, since its content tends to increase with increasing alteration of the femic phenocrysts. In the coarse sizes of the solum, the distribution of exMg is similar to that of Fe. Moreover, there is a more or less linear distribution between exMg and Fe in the coarse fractions

(Fig. 4.15). This may reflect metal associated with iddingsite grains, which comprise some 3% of the minus 20 plus 36-mesh fraction of the solum. If exMg were to be contained simply in exchange positions on nodules, then one would have expected Mg to accompany Mn rather than Fe. The theory for this being that the Mn sol has a negative charge, whilst that of Fe usually has a positive charge (Rankama, 1950), thus Mg^{2+} cations would tend to be attracted to the Mn sol.

4.3233 Comparison with the Prairie Creek Peridotite

The distribution of Mg and exMg in selected profiles over the Prairie Creek peridotite are illustrated on Fig. 4.7 and summarised on Table 4.4. The following features are noted:

(1) As with profiles over the kimberlite, Mg increases in content with increasing depth in profiles over the peridotite. However, the Mg content of the solum is higher in the peridotite than in the kimberlite, whilst at depth, lower concentrations of Mg occur in the peridotite.

(2) Magnesium is strongly depleted in the water bearing clay of the B_2 horizon at 00N800W.

(3) Concentration of exMg in the B_2 horizon is not so marked in soils over the peridotite.

The variation of exMg and Mg with particle size was not investigated in soils over the peridotite.

4.3234 Discussion

The depletion of Mg towards surface indicates metal to be strongly leached during weathering of this rock type. However, Mg is not as strongly leached from the peridotite solum as from the kimberlitic solum. This is due to the less advanced weathering of the component minerals of the peridotite.

Profile 00N800W is located in a shallow but prominent valley. A near surface water table is encountered in an adjacent profile through colluvium (00N760W), and parts of the peridotite profile are damp. This is particularly marked at a depth of 21 to 24 inches where water bearing clay is encountered. The considerable depletion of Mg observed at this depth is thought to be due to active removal of metal by percolating waters.

The value of 10.5% Mg found at a depth of $9\frac{1}{2}$ to 10 feet in the same profile is substantially less than that present at the same depth in a freely drained kimberlite profile (13.8% Mg at 00N40W). Since the blue ground of the kimberlite is normally more decomposed than material at the same depth over the peridotite, it is suggested that the low Mg content at depth in profile 00N800W is anomalously low. This is probably due to leaching by ground waters which, as just mentioned, are more active in this profile.

4.3235 The Sialic Country Rocks

4.32351 Variation with depth

The variation of Mg and exMg content in a well developed profile over the Trinity siltstone is given on Table 4.4 and illustrated for exMg on Fig. 4.8. The following features are noted:

(1) Magnesium is depleted in the A horizon, but unlike soils over the ultrabasic rocks, is considerably enriched in the B_2 horizon.

(2) The distribution of exMg is similar to total Mg but metal is also enriched in the A horizon.

4.32352 Variation with particle size

The variation of exMg and Mg content with particle size in various horizons of a well developed profile over the Trinity siltstone are given on Table 4.16 below.

Table 4.16

	Mg %		exMg ppm		
	+80 mesh	-80 mesh	+80 mesh	-80+300 mesh	-300 mesh
A_1	0.054	0.046	46	18	24
B_2	0.166	0.134	139	84	120
C		0.13		18	30

It can be seen that both Mg and exMg are concentrated in the plus 80-mesh fraction of the solum. Exchangeable Mg is also concentrated in the minus 300-mesh fraction.

4.3236 Discussion

Femic silicates were not found in the C horizon of the Trinity formation. Presumably therefore Mg occurs largely within secondary minerals probably clays. However, evidently some metal is released and leached from the A horizon during weathering.

The enrichment of metal, especially exMg in the B_2 horizon is probably due to sorbtion or reaction with sesquioxides. This is indicated from the similar vertical distributions of Fe and exMg (Fig. 4.8) and the concentration of metal in the coarse fraction. It is difficult to explain this latter occurrence other than by concentration in nodules.

The slight enrichment of exMg in the A horizon is probably due to sorbtion by organic matter, which may have a very high sorbtive capacity.

4.3237 The Tuffaceous Country Rocks

The variation in exMg content with depth in soil profiles over the Prairie Creek and Woodbine tuffs are presented on Figs. 4.7 and 4.8, respectively. Attention is drawn to the following points:

(1) Exchangeable Mg content increases slightly with depth over the Prairie Creek tuff.

(2) Exchangeable Mg is concentrated at the surface, and in the $B_{2.1}$ horizon of the Woodbine tuff.

4.3238 Discussion

The distribution of exMg over the Prairie Creek tuff is not dissimilar from that over the ultrabasic rocks, and probably reflects some slight leaching of metal to have taken place.

The distribution of exMg in the A and $B_{2.1}$ horizons of the Woodbine formation is similar to that over the Trinity siltstone and is probably due to similar processes.

It was suggested earlier in the thesis that there is a variation in the composition of the tuff with depth. This would conveniently explain the considerable concentration of exMg in the $B_{2.3}$ horizon. Metal presumably being derived from the weathering of Mg rich host minerals. This might also explain the presence of beidellite in the Woodbine formation, Ross et al, (1929).

4.324 Trace Elements in Nodules, Aggregates, etc.

It has been shown that certain elements are considerably concentrated in the coarse fraction of the solum. In soils over the ultrabasic rocks, mineralogical evidence indicates this fraction to be composed largely of Fe or Mn nodules and sesquioxide cemented mineral aggregates. In order to further investigate the form of the metal the following procedure was carried out:

The coarse fraction of the ultrabasics was split into three parts depending upon specific gravity:

a. S.G.<2.67 : mainly black (Mn) sesquioxide cemented quartz grains and nodules.

b. $2.67<$S.G.<2.95 : quartz grains, black and brown nodules and mineral aggregates.

c. S.G.>2.95 : Mainly brown (Fe) nodules and mineral aggregates cemented with a brown sesquioxide cement. A few barite fragments are present.

Items (a) and (c) were analysed spectrographically.

Selected samples were also leached with a sodium citrate-sodium dithionite solution and the residue analysed spectrographically. As mentioned in Chapter 3, secondary iron oxides and associated elements are considered to be dissolved by this attack; although weakly held forms of metal are also taken into solution.

Spectrographic analyses were also made of ferriferous nodules separated from the Trinity formation by both hand picking and specific gravity methods. Nodules in the Trinity formation may comprise between 25 to 50% of the coarse fraction of the $B_{2.1}$ horizon. Also analysed was mottled material taken from anomalous Trinity and alluvial profiles. Comparison is made between light and dark mottles.

Selected samples were analysed for various elements using 'wet' methods.

No attempt was made to study the variation of metal content within nodules taken from different parts of the soil profile.

The results of the investigation are given on Table 4.17. Attention is drawn to the following points:

4.3241 The Ultrabasic Nodules

(1) The previous suggestion that the black nodules are dominantly manganiferous and the brown nodules ferriferous is confirmed.

(2) Highest concentrations of Ba, Co and Ni occur in the Mn nodules and V and Cr in the Fe nodules/aggregates.

(3) Over 90% of the Mn, Co and Ba (Ba from the peridotite only) is extracted from the Mn nodules with dithionite solution. Much smaller amounts are extracted from the Fe nodules. Similarly, about 90% of the V and Fe, together with appreciable quantities of Cr and Ti, are extracted from the Fe nodules.

(4) More metal is extracted with dithionite from nodules developed over the peridotite than from over the kimberlite.

(5) No Sr is extracted with dithionite from nodules over the kimberlite, but 60% Sr is extracted from Mn nodules over the peridotite.

(6) No Nb was extracted with dithionite solution. This might mean no Nb is associated with secondary Fe oxides or, more likely, any Nb released is immediately hydrolysed. Since Nb ions are stable in oxalate solution a more suitable attack may be the oxalate extraction of Le Riche and Wier (1963).

(7) With the notable exception of Nb, Cr and Sr, nodules are enriched in all the determined elements when compared with the B_2 horizon.

(8) Spectrographically determined samples containing high concentrations of Fe give low values for the Ge internal standard. This was more fully discussed in Chapter 3.

4.3242 Trinity Formation

(9) Chromium and Sr are evenly distributed between light and dark mottles.

(10) Manganese, Fe, Ba and to a lesser extent Ni, Co and Ti are concentrated in the dark mottled zone.

(11) With the exception of V and possibly Ni, all the determined elements are concentrated in the sesquioxide nodules when compared with the minus 10 plus 20-mesh fraction.

(12) Titanium, Sr and Fe are concentrated in the heavy fraction but Cr, Ni and V are depleted.

4.325 Discussion

4.3251 Nodules over the Ultrabasic Rocks

The preceding data confirm that much of the metal within nodules is associated with sesquioxides. This may have been co-precipitated, or floculated from leach solutions (the term solution is taken to include colloidal form), and/or derived from iddingsite grains. The presence of dithionite extractable Ti and Cr is in accord with a previous suggestion that these elements have been mobilized to some extent. The affinity of Co and Ba for Mn sesquioxides and Cr and V for Fe sesquioxides is substantiated.

The lack of dithionite extractable Sr in the kimberlitic nodules supports the contention that this element has not been leached to any significant degree. The reasons why some Sr is extracted from a Mn nodule in the peridotite is unknown, possibly some Sr occurs in a different form in this rock type.

The higher amounts of extractable metal in the peridotitic than the kimberlitic nodules is probably due to dilution of the latter with quartz grains and/or fragmentary xenolithic material.

4.3252 Nodules over the Trinity Formation

Concentration of Mn, Fe, Ba, Ni and Co in the mottled zone of the sialic sediments is attributed to mobilization and precipitation of these metals during fluctuating thermodynamic conditions. This is in accord with observations made by Brooks (1965) on a New Zealand grey earth.

The previous suggestion that Sr occurs as a resistant mineral in the Trinity siltstones is supported by the lack of concentration in the mottled zone combined with concentration in the heavy fraction. Chromium is concentrated in Fe nodules but not in the limonitic mottles. This would suggest that either Cr is mobilized only under conditions in which Fe nodules are developed, or it is not precipitated in Fe mottles.

The lack of concentration of Ni and V in nodules compared with the minus 10 plus 20-mesh fraction would suggest metal to occur largely in a resistant form.

4.326 Depletion of the Elements in the Ultrabasic C Horizon

Certain elements are depleted in the C horizon of the kimberlite and/or peridotite at Prairie Creek. This depletion may be either:

(1) "Real" i.e. due to removal of metal; or
(2) "Apparent" i.e. the value given for the mean bedrock or blue ground is not representative.

A summary of the amounts by which the elements are depleted in the blue ground of the kimberlite and at an equivalent depth in the peridotite are given on Table 4.18 below.

Table 4.18

		Mg	Ni	V	Nb	Ti	Co	Cr	Mn
Amount by which the elements are depleted %	kimberlite blue ground	5	43	54	15	13	16		5
	peridotite 9½ to 10 feet	33			12		17	31	

Magnesium is considered highly mobile and is readily leached from the soil profile (Chapter 8). Thus, unless peculiar conditions prevailed at some time, then the maximum amounts by which the elements may be leached from the kimberlite blue ground is in the order of 5%. If this is the case then the depletions of Nb, Ti, Co, and particularly V and Ni in the kimberlite blue ground, are largely "apparent".

The V content of the component horizons of the soil profile overlying kimberlite increases progressively towards the B_2 horizon. This tends to suggest that the values given for the mean blue ground are not erroneous. Since it is difficult to explain the depletion of V by any other way, it is suggested that the values given for the mean bedrock are not representative of those underlying the soil profiles. In this context it should be mentioned that the kimberlite rock was float collected some 100 feet to the north east of OONOOW.

Niobium is depleted in the C horizon of both the kimberlite and peridotite. This would tend to suggest erroneous values for the C horizon to be minimal, although a wide variation in Nb content is present. It is suggested, therefore, that as with V, the major cause of the apparent depletion is due to a different Nb content of the bedrock sample analysed to that in the bedrock underlying the soil profiles.

The Ni content of the kimberlite blue ground is from a single profile at 00N40W. The Ni and Co contents of the yellow ground of this profile are substantially lower than the mean (Fig. 4.6 and Table 4.4). Assuming the vertical distribution of the elements in this profile to be typical, then it is suggested that the Ni and Co contents are substandard in this profile, i.e. that the figures given for the blue ground are not representative.

The slightly depleted Mn content of the kimberlite blue ground is probably "apparent" in that the bedrock was analysed spectrographically, whilst the profile was determined by an $HClO_4$ attack. This wet method is unlikely to extract all the metal from the sample.

It is unknown whether the depleted Co and Cr contents of the deepest sample of the peridotite are "real" or "apparent".

4.33 ARIZONA

4.331 Introduction

Comparative analytical investigations in Arizona were confined to the spectrographic analyses of various size fractions, at selected depths, of a profile over the Buell Park kimberlite and background sandstone. In addition, the sandstone and a second kimberlite profile were analysed for exNi, exMg, Ni and Fe using wet methods.

As previously mentioned, the kimberlite is located in an old caldera which is bisected by a river. Parts of the ground surface are covered with alluvium. A certain amount of residual concentration of coarse kimberlitic minerals has occurred, particularly on ant hills.

The spectrographic results are presented in Table 4.19; the variation with depth for the elements analysed using wet methods on Fig. 4.16, and the variation of trace element content with particle size (spec. data) as histograms on Figs. 4.17 and 4.18.

With regard to the reliability of the spectrographic results, the Ge internal standard fluctuated from 400 to 1200 ppm in the kimberlite and 300 to 2000 ppm in the sandstone. 400 ppm was added. Thus, either a strong matrix effect is present or the Arizona rocks contain appreciable Ge.

4.332 Buell Park Kimberlite

4.3321 Variation of metal content with depth

(1) It can be seen from the spectrographic results on Table 4.19 that the elements may be divided into three main groups:

- (a) Those which are concentrated in the alluvium:
  - (i) At the surface. Ti, V and possibly Nb.
  - (ii) Near the base. Cr and Zr.
- (b) Those which are depleted in the alluvium and in which concentration increases with depth. Ni, Mn, Co, Ba and Fe.
- (c) Others. Sr.

(2) Nickel, Cr, Co and Fe are present in highly anomalous concentrations in the kimberlite. Manganese, Ba and

Table 4.19 The content of selected elements in profiles over the Buell Park kimberlite and sandstone country rock, Arizona.

	depth inches	metal content in ppm (unless stated otherwise)										
		Cr	Sr	Ti	Zr	Nb	Ni	Fe%	V	Mn	Co	Ba
Kimberlite profile	0- 6†	4180	125	2270	200	3.2	1200	4.43	125	900	130	850
	12-24†	5290	180	1000	260		2230	4.76	80	820		980
	30-33*	4400	280	730	200		4670	5.82	58	1110		1200
	48-60*	2806	77	460	200	1.6	4700	7.31	54	1360	300	1450
	Rock[1]	1075	30	115			1250	2.15	15	700	105	200
Sand-stone	0- 3	25	160	3720	4375	1	52	2.11	72	760	9	880
	12-18	13	120	850	760	1	35	1.61	45	207	15	1000
	36-48	20	90	926	300	1	28	1.55	43	215	8	975

1. This sample was collected from an outcropping plug about 300 yards ENE of the profile. It may not be representative of the rock underlying the profile.

With the exception of Nb, analyses are by emission spectrograph.
*altered kimberlite †overlying alluvium

possibly Nb* are slightly anomalous whilst V, Zr and Ti are not anomalous.

Comparison with Fig. 4.16 illustrates:

(3) Very much lower concentrations of Ni and Fe are obtained using wet than spectrographic methods.

(4) The overall distribution of Ni is similar by both analytical methods.

(5) The exNi/Ni ratio increases with depth to a maximum just above the water table.

(6) Iron is locally enriched in the alluvium and just below the water table.

(7) Maximum concentrations of exMg are recorded at the junction with alluvium.

4.3322 Variation of metal content with particle size

Examination of Figs. 4.17 and 4.18 reveals the following features:

(1) Marked differences are obtained between the particle size distributions of the kimberlite and alluvium. In the former the silt size is the dominant host size whilst in the latter material is more or less evenly apportioned between all grain sizes coarser than the clay.

(2) In the kimberlite maximum amounts and concentrations of Fe, Mn, Co, Ba and Ni occur in the silt fraction. In the alluvium the distribution of these elements is somewhat erratic.

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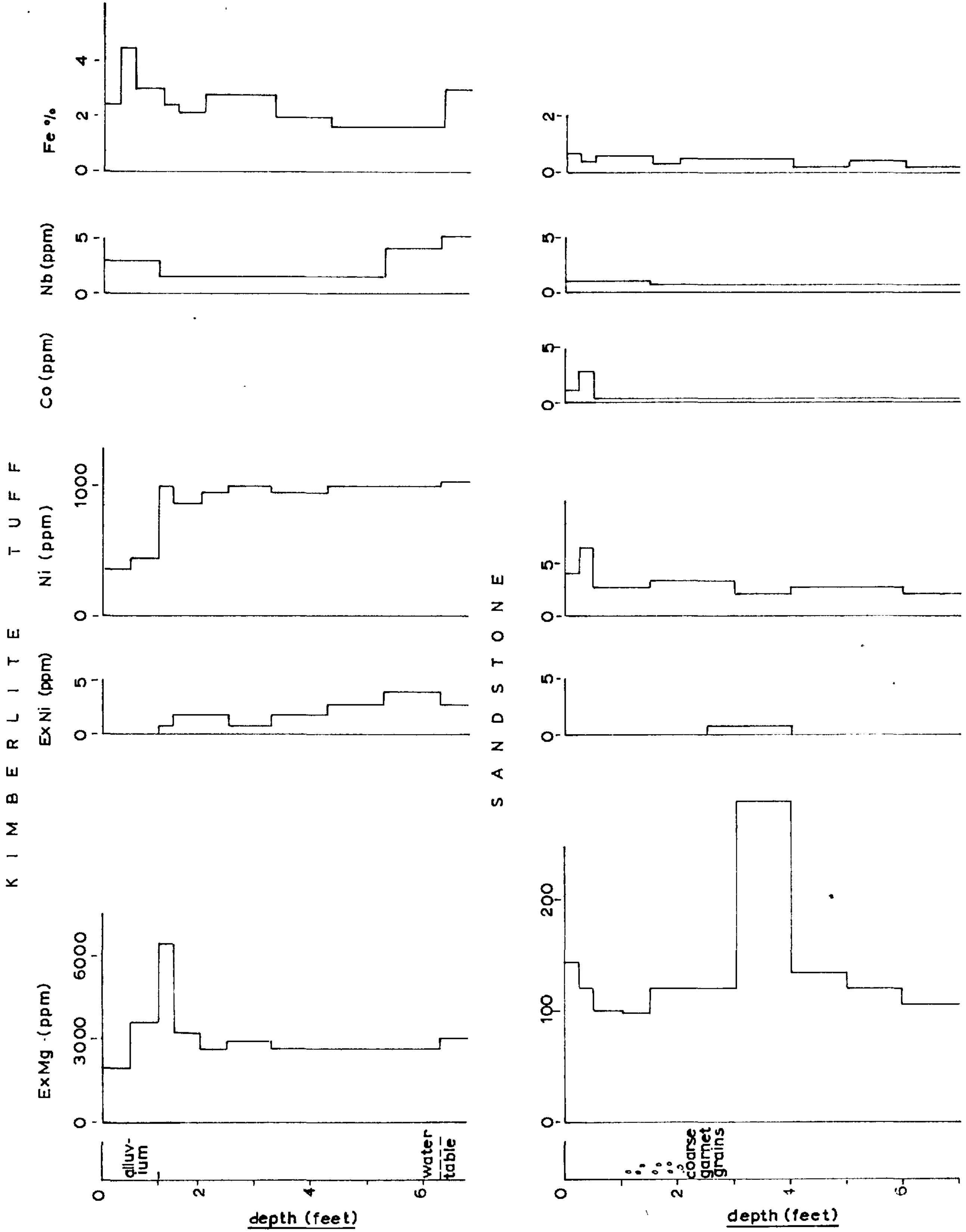
*relative to sandstone only. Nb itself is not present in anomalous concentrations in the kimberlite compared with other igneous rocks.



THE DISTRIBUTION OF EXMg, EXNi, Ni, Co, Nb, AND Fe, IN PROFILES OVER THE BUELL PARK KIMBERLITE TUFF AND SANDSTONE COUNTRY ROCK, ARIZONA (DATA ON COMPLETE SAMPLE, WET ATTACKS)

FIG. 4·16

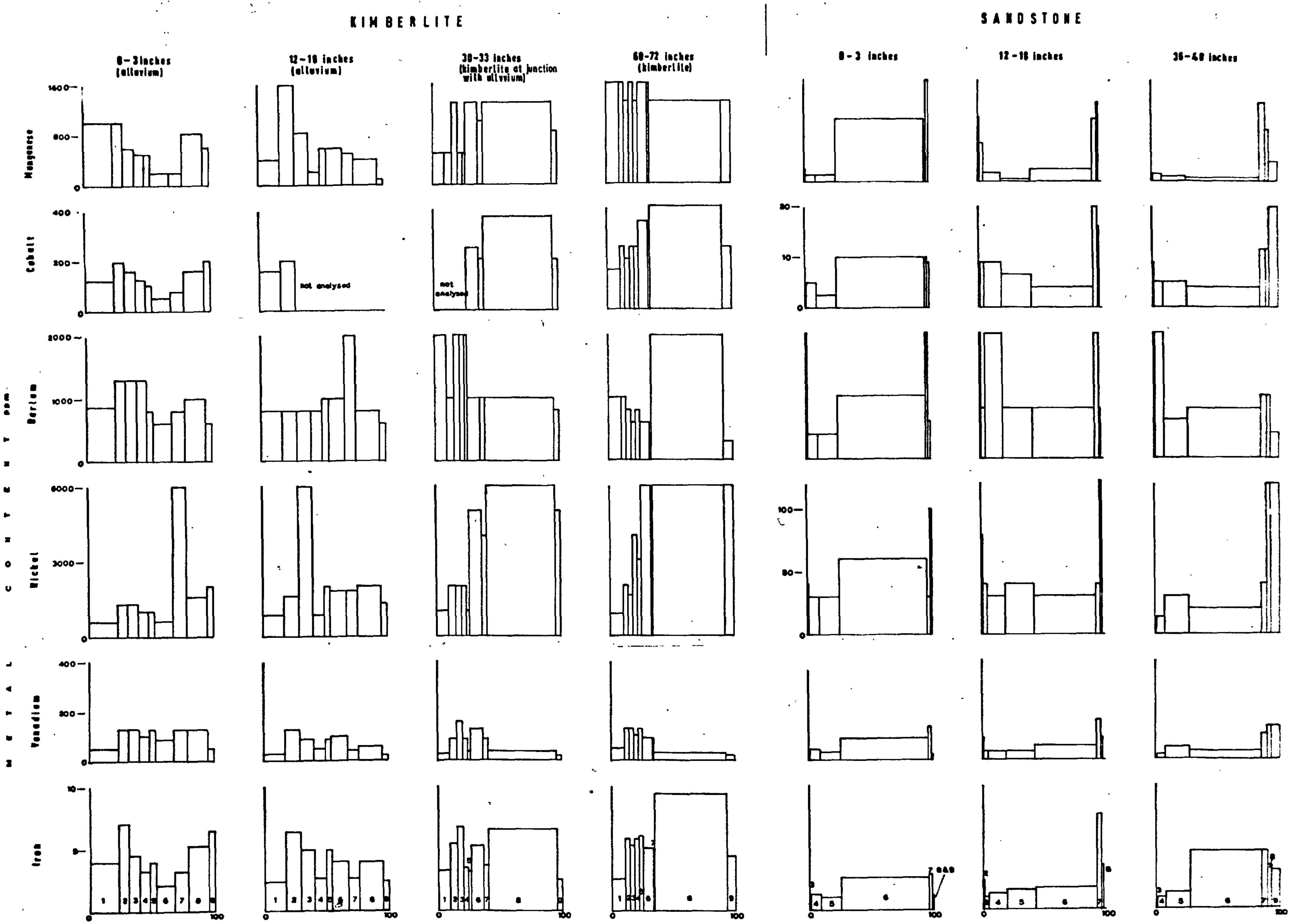


FIGURE 4.17

HISTOGRAMS OF Fe, V, Ni, Ba, Co AND Mn CONTENT PLOTTED AGAINST WEIGHT PER CENT FOR VARIOUS SIZE FRACTIONS AT SELECTED DEPTHS IN PROFILES OVER THE BUELL PARK KIMBERLITE AND SANDSTONE COUNTRY ROCK, ARIZONA.

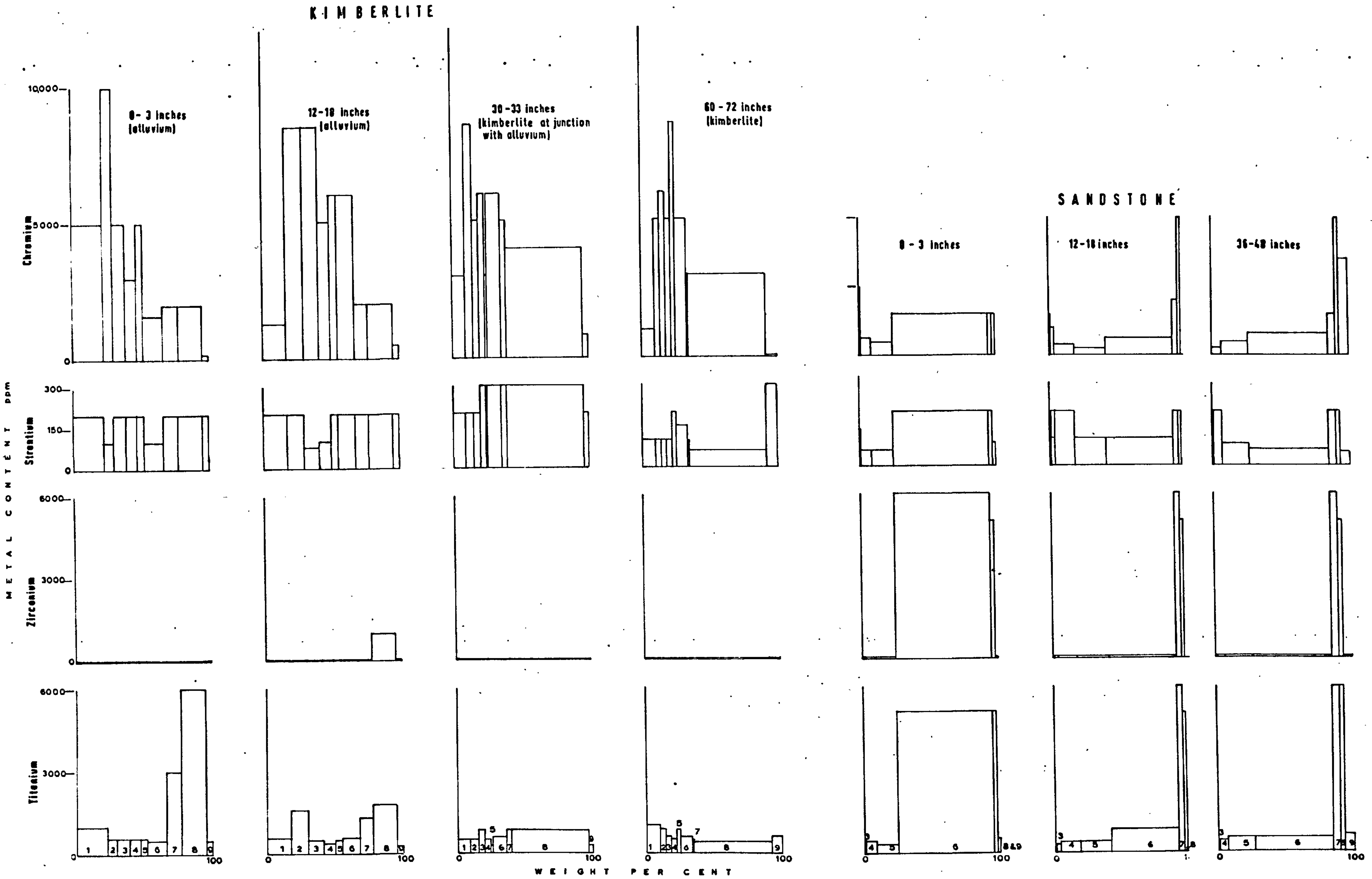


FIGURE 4.18

HISTOGRAMS OF Cr, Sr, Zr AND Ti CONTENT PLOTTED AGAINST WEIGHT PER CENT FOR VARIOUS SIZE FRACTIONS AT SELECTED DEPTHS IN PROFILES OVER THE BUELL PARK KIMBERLITE AND SANDSTONE COUNTRY ROCK, ARIZONA.

1 minus 10 plus 20 mesh (B.S.S.)
2 minus 20 plus 36 mesh (B.S.S.)
3 minus 36 plus 60 mesh (B.S.S.)
4 minus 60 plus 80 mesh (B.S.S.)
5 minus 80 plus 100 mesh (B.S.S.)
6 minus 100 plus 200 mesh (B.S.S.)
7 minus 200 plus 300 mesh (B.S.S.)
8 silt
9 clay
spectrographic analyses

(3) In the clay size, Mn, Ni, Fe and Ti and possibly Co are concentrated at the ground surface. Minimum concentrations are observed in the lower sample of alluvium and thereafter concentration increases with depth.

(4) Vanadium, Cr and possibly Ba are prominent in the coarse size range of the kimberlite. In the alluvium, Cr is concentrated in the coarse size range but Ba and V are erratic.

4.333 Discussion

The considerably higher concentrations of the Ni and Fe extracted with the spectrographic attack compared with a $KHSO_4$ attack is thought to reflect the lack of chemical weathering in Arizona. However, the possibility of analytical error must be considered.

Harden (1962) records only 16% of Ni to be extracted from fresh amphiboles and pyroxenes with the $KHSO_4$ attack. A slightly higher amount (22%) of the Ni was extracted from the Buell Park kimberlite, no doubt due to its occurrence in less stable olivine.

The distribution of the elements in the kimberlite at depth probably largely reflects the distribution of the primary host minerals. Nickel, Ba, Co and Fe are concentrated in the fine sizes presumably in the matrix whilst Mn, Cr, Ti and some Ba and Fe are concentrated in the coarse sizes presumably in phenocrysts of olivine, garnet, chrome diopside, etc.

The anomalous concentrations of Ni, Cr, Co, Fe, Mn and V in the alluvium overlying kimberlite, especially in the coarse fractions, is attributed to the presence of phenocrystic kimberlitic minerals, i.e. olivine, chrome diopside, pyrope garnet, etc.

This is presumably a placer deposit.

The lower concentrations of Fe, Mn and Ba in the kimberlite at the junction with alluvium than in the kimberlite at depth, are thought to be due to dilution with alluvium rather than leaching. The high content of Ti, which is not concentrated in the kimberlite, in the near surface sample supports this suggestion.

The concentration of exMg in the kimberlite at the junction with alluvium may reflect either decomposition of the Mg host minerals or sorbtion of metal from infrequent percolating leach solutions.

In the kimberlite the exNi/Ni ratio increases with depth possibly reflecting an increase in weathering of the Ni host minerals perhaps promoted by ground water fluctuations. The high pH (8.9) would favour sorbtion of any metal released since there would be little competition for exchange positions by hydrogen ions.

4.334 The Sandstone Country Rocks

4.3341 Variation of metal content with depth

(1) With the exception of Co and Ba, all the spectrographically determined elements are concentrated at the ground surface. Cobalt and Ba are enriched in the middle sample and Cr is depleted.

(2) As in the kimberlite, much lower concentrations of the elements were obtained using wet methods.

(3) Exchangeable Mg is concentrated at the ground surface and at 42 and 48 inches depth.

(4) Cobalt and Ni, as determined using wet methods, are concentrated at 3 to 6 inches depth.

4.3342 Variation of metal content with particle size

(1) Iron, Sr, Zr, Ti and Ba are prominant in the minus 200 plus 300-mesh fractions and Ni and Cr in the silt fraction throughout the profile. Manganese, V and Co are prominant in the finer sizes.

(2) The amounts of Ni, V, Zr, Mn, Ti and Sr in the minus 100 plus 200-mesh fraction are particularly concentrated at the ground surface and decrease in content with depth.

(3) In the middle sample, Mn, V, Fe, Cr and Sr are concentrated in the minus 20 plus 36-mesh fraction.

(4) Barium and Sr are concentrated in the coarse fraction throughout the profile. Chromium and Ni are concentrated in the coarse fraction of the two uppermost samples.

(5) Nickel, Cr, Mn, Co, V and Fe are prominant in the clay size of the deepest sample. This was the only clay sample investigated.

4.335 Discussion

The concentration of the elements at the ground surface is due to a progressive increase in the minus 100 plus 200-mesh fraction towards surface. This is most easily explained as due to a variation in the parental composition of the sediment.

The concentration of Mn, V, Fe, Cr and Sr in the minus 20 plus 36-mesh fraction coincides with an occurrence of garnet grains. However, Ba and Sr are also concentrated in samples devoid of garnets, as are Cr and Ni. Thus Mn, Fe and V, with some Cr and Ni are thought to be incorporated in the garnet lattice.

Exchangeable Mg is concentrated at the ground surface and may be due to concentration of soluble salts brought to the surface by capilliary action, etc. during the dry season. The reason for the concentration of exMg at 42 to 48 inches is unknown.

4.4 SUMMARY

4.41 Arkansas

(1) Soil profiles have developed over the Arkansas rocks in varying degrees of maturity. Generally, profiles over the Trinity siltstone, Woodbine tuff and Prairie Creek kimberlite are mature with a reasonably well developed B_2 horizon. Profiles over the Prairie Creek peridotite and some profiles over the Trinity siltstone are vertosolic with an ill-defined B horizon. Soils over the Prairie Creek tuff and rapidly eroded parts of the Tokio formation are rudimentary.

(2) Soils over the ultrabasic rocks are readily differentiated from those over the sialic country rocks by the colour of their B and C horizons. The C horizon of the Prairie Creek kimberlite differs from the peridotite in that over the former a blue zone underlies a yellow zone whereas the C horizon of the peridotite is yellow.

(3) The ferromagnesian silicates of the kimberlite are decomposed during soil formation through serpentine and phyllosilicates, to clay minerals and Fe oxides.

(4) In mature soil profiles the elements are extensively redistributed during soil formation. They may be classified into three groups based upon their general vertical distribution.

a. Nb, Cr, Ti, Sr and Zr
b. Fe, V, Ni, Co, Mn, P and Ba
c. Mg

(5) Niobium, Cr, Ti, Sr and Zr increase in content towards surface in the kimberlite soil profile and are considered relatively immobile. A comparison of their relative enrichments, together with that of diamond, indicates Nb to have accumulated least and Zr and Sr the most. The following relative mobilities are suggested:

least immobile $\mathrm{Nb} < \mathrm{Cr} \leqslant \mathrm{Ti} < \mathrm{Sr} \leqslant \mathrm{Zr}$ most immobile

There is a similar enrichment of Sr and diamond in the solum and it is suggested that Sr has remained almost immobile during weathering. This being the case then Sr may be used to calculate the approximate losses and gains of the other elements. Zirconium, although enriched to a greater degree than Sr, was not used because of inadequate analytical data.

During weathering the elements are concentrated in the silt fraction towards surface where they occur dominantly as resistant minerals. However, appreciable concentrations of metal occur in the coarse fraction within sesquioxide nodules. A substantial proportion of Ti and Cr is extracted from these nodules, especially iron nodules, with sodium citrate/dithionite solution.

Niobium, Ti and Cr are also enriched in the clay fraction of the solum.

(6) Niobium, Cr, Ti, Sr and Zr have a generally similar distribution in soils over the peridotite to those over kimberlite. However, they are concentrated to a greater

extent in the coarse fractions of the peridotite soil and Nb has accumulated to a greater extent than Cr (cf. kimberlite). Enrichment of Cr and Nb in the B_2 horizon is not so marked as in the kimberlite.

(7) In soils over the sialic country rocks, Ti, Cr and Zr are concentrated in the silt fraction, no doubt as heavy minerals. Some slight redistribution of metal occurs in soil over the Trinity formation where Cr is concentrated in Fe nodules and Ti and Cr in the clay fraction of the B_2 horizon. Very limited size distribution studies show Nb to be concentrated in the plus 80 and minus 300-mesh fractions of the Trinity soils.

In mature soils over the Woodbine tuff, Nb initially increases in content with increasing depth. This is considered to be due to a variation in the character of the tuff rather than to leaching of metal. Chromium is concentrated in the $B_{2.1}$ and $B_{2.2}$ horizons of these soils.

(8) Iron, Mn, Ni, Co, V, P and Ba are enriched in the B_2 horizon of the kimberlite and are considered semi-mobile. Comparison of their relative enrichments, together with that of Sr, illustrates Ni and P to be the most semi mobile and Mn the least, i.e.

most semi mobile $\quad Ni = P > V > Fe > Co > Ba > Mn \quad$ least semi mobile

Moreover, Mn, Co and Ba have accumulated in the A horizon with respect to Sr.

During soil formation Mn, Co, Ba and Ni concentrate in the coarse fraction within Mn nodules of dominantly minus 10 plus 20-mesh size. Iron and V are concentrated in iron nodules which are generally of minus 20 plus 36-mesh size. Substantial proportions of metal are extracted with sodium citrate/dithionite solution from both types of nodule. A number of the so called Fe nodules are grains of iddingsite. Manganese and Co are not concentrated in the clay size of the solum. Iron is enriched in the clay size of the B_2 horizon and Ni is enriched in the clay size of both the A and B horizons.

(9) A similar distribution of the elements occurs in soils over the peridotite but enrichment of the elements in the B_2 horizon is not so marked. Nickel is not leached to the same extent from the A horizon.

(10) In soils over the Trinity siltstone Fe, Ni, Co and V have been leached from the A horizon and accumulated in the coarse and clay fractions of the B_2 horizon. However, most metal occurs in the silt fraction which increases in amount towards surface. Manganese is considerably enriched in the A horizon where, unlike soils over the ultrabasic rocks, it is highly concentrated in the clay size. There is a broad sympathetic variation between Mn and Ba and probably Mn and Co.

(11) In soils over the Woodbine tuff Mn is concentrated in the A horizon. Iron and to a lesser extent Ni, Co and Mn are concentrated in the $B_{2.1}$ horizon. Nickel, Co and Mn are also considerably concentrated in the lower $B_{2.2}$ and $B_{2.3}$ horizons, probably due to a variation in the nature of the tuff.

(12) No marked redistribution of metal has occurred in the rudimentary soils over the Tokio formation.

(13) The Mg content decreases considerably towards surface in soil profiles over the kimberlite. Comparison with

Sr indicates over 90% of the metal to have been leached from the solum. Exchangeable Mg is concentrated in both the coarse and clay fractions, especially the latter. In the coarse fraction of the C horizon distribution of exMg is thought to reflect metal released from its host minerals during weathering. In the coarse fraction of the solum exMg may be associated with iddingsite grains and/or sorbed on Fe nodules. In the clay sizes exMg is believed to be largely held in exchange positions on clay minerals.

(14) Magnesium has been considerably leached from soils over the peridotite but not to the same extent as from the kimberlite. This is believed to reflect the lesser degree of weathering in this rock type.

(15) Magnesium has been leached from the A horizon and enriched in the B_2 horizon of soils over Trinity siltstone. Exchangeable Mg is concentrated slightly at the ground surface and in the $B_{2.1}$ horizon of the country rocks. This is attributed to sorbtion by organic matter and sesquioxides, respectively. In the Woodbine formation exMg is concentrated in the $B_{2.2}$ and C horizons supporting the suggestion for a change in the nature or proportion of the tuff.

4.42 Arizona

(16) In Arizona there is very little chemical weathering and soils are extremely rudimentary. Typically over the kimberlite, eluvial concentrations of olivine, pyrope and chrome diopside occur at the ground surface especially on "ant hills".

(17) No marked redistribution of the elements has occurred in profiles over the kimberlite or sandstone country rocks. Exchangeable Mg is concentrated slightly at the junction of kimberlite and the overlying alluvium and at depth in the sandstone profile.

(18) Very much higher amounts of metal are extracted from these profiles with a spectrographic than with a bisulfate attack.

CHAPTER 5

DISPERSION OF ELEMENTS IN SOILS AT THE AMERICAN MINE

5.1 INTRODUCTION

The dispersion of selected elements in soils was studied at the American Mine where surface disturbance is minimal and suitable drainage conditions prevail.

Soil samples were collected in a profile section downslope from a kimberlite suboutcrop, from the $B_{2.1}$ horizon about the entire American Mine area, and in profiles from the banks and flood plain of American Creek.

5.2 DISPERSION DOWNSLOPE FROM A KIMBERLITE SUBOUTCROP

5.21 Location of Section

Secondary dispersion studies were made, for selected elements, in a limited number of samples taken in a vertical section downslope from a kimberlite suboutcrop. This section is located in a forested area some 15 feet east of an adit exposing kimberlite, (C–D on Fig. 5.6). With the exception of sites 178, 179 and 1024, the traverse line is situated in residual soils on a minor ridge and follows the general topographic slope of 1°-3°. Sites 178, 179 and 1024 are located in colluvium on the east side and near the base of a small valley.

Although in the upper margins of the section there is a small adit and a drainage trench some 15 feet to the west, there appears to be little, if any, surface disturbance since a continuous soil profile is represented. However, at site 173 the top few inches were disturbed, and site 177 was offset 5 feet to the east to avoid the possibility of contamination from a small pit some 15 feet upslope.

5.22 Morphology

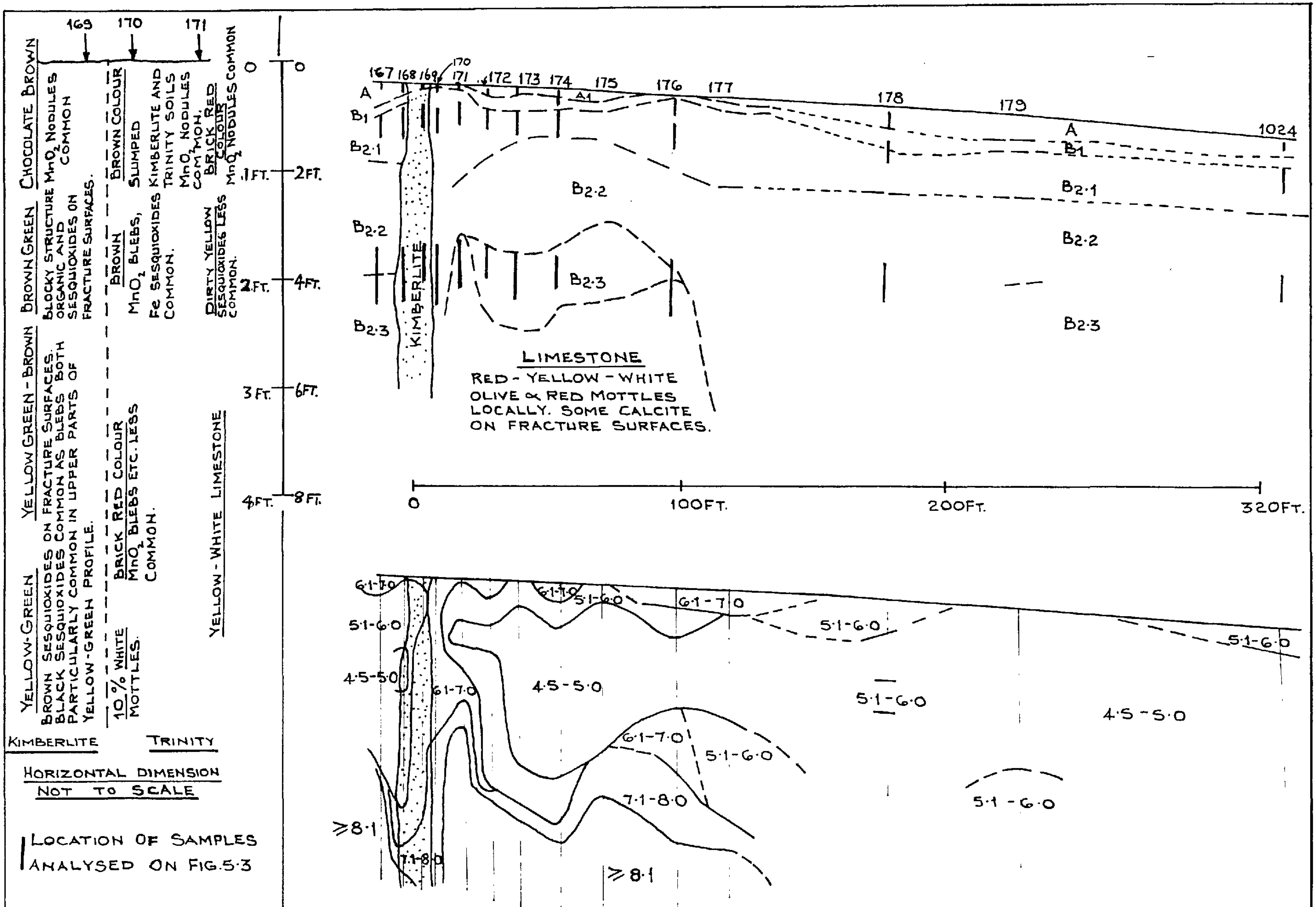
The salient morphological features of the section (Fig. 5.1) are tabulated below:

(1) Immediately adjacent to the kimberlite, the $B_{2.1}$ horizon is of high clay content (visual obs.) and a brick red colour. Further downslope the horizon is an orange colour similar to that of the background soils. In the colluvium only a cambic B_2 development is evident.

(2) Except immediately downslope from the kimberlite where the red soils persist to a depth of 64 inches, the $B_{2.1}$ horizon is underlain by a mottled zone ($B_{2.2}$) at depths in excess of 15 inches to 21 inches. In only a few of the profiles was the bleached zone reached.

(3) The kimberlite intrudes an impure limestone (CO_3^{--} 49%) which has an apparent dip in the direction of the section. The weathered limestone varies from dirty white, through various shades of yellow to brick red; the red colour generally occurring close to the limestone/siltstone contact. Olive and red mottles are common locally as are black sesquioxide coated fracture surfaces. Sometimes calcite veinlets are prominent.

(4) Unlike the black solum over the ultrabasics at Prairie Creek, the A and B horizons over the kimberlite at the American Mine are of a brown colour. Concretions are plentiful though less abundant than at Prairie Creek.



HORIZONTAL DIMENSION NOT TO SCALE

| LOCATION OF SAMPLES ANALYSED ON FIG. 5·3

FIG. 5·1

THE MORPHOLOGY AND pH OF RESIDUAL SOILS OVERLYING THE TRINITY FORMATION DOWNSLOPE FROM KIMBERLITE SUBOUTCROP. AMERICAN MINE, ARKANSAS.

5.221 Discussion

Whilst soils over the Trinity formation immediately adjacent to ultrabasic rocks may be recognised from the brick red colour of the $B_{2.1}$ horizon, a similar horizon is also observed over the Woodbine tuff. This characteristic colour is attributed to both a high iron and clay content of the horizon.

The difference between the soils developed over the American Mine and Prairie Creek kimberlites reflects the lesser maturity of the former. This is probably due to its more recent exposure and less luxuriant overlying vegetation; the latter being responsible for the black colour of the Prairie Creek soils (Miser and Purdue, 1929). In addition, the slopes at the American Mine would favour faster erosion.

5.23 Hydrogen Ion Concentration

The wide variation in pH values encountered in the section (Fig. 5.1) may have an important influence on the secondary dispersion of some of the elements. Attention is therefore drawn to the following points:

(1) pH decreases from the A_0 through the A_1 and B_1 horizons.

(2) Lowest pH values occur in the $B_{2.1}$ and $B_{2.2}$ horizons and are generally less than 5.5 and commonly less than 5.0. Values in the mottled zone are not dissimilar from those in the $B_{2.1}$.

(3) Very high pH values are observed in the limestone band. A change from pH 8.0 to 4.5 can take place over a matter of inches.

(4) Excluding the high pH of the limestone; in the same soil horizon, higher pH values occur over the kimberlite than over the Trinity siltstone.

5.24 Geochemistry

Detailed studies of secondary dispersion, using the minus 80-mesh fraction (B.S.S.), have been made for Ni and exMg (Fig. 5.2). Critical samples were analysed for Nb. In addition, a limited number of total samples from selected profiles (locations illustrated on Fig. 5.1) have been analysed for Mn, Fe, P, Co, Cr and Ni (Fig. 5.3). Exchangeable Ni was determined on the minus 80-mesh (B.S.S.) fraction.

From a comparison of the minus 10 and minus 80-mesh fractions taken from selected positions in the kimberlite and Trinity soil profiles (Table 5.1) the following conclusions may be drawn:

(1) In the kimberlite B and C horizons, highest concentrations of "total" metal occur in the minus 80-mesh fraction. Maximum exchangeable metal values occur in the complete sample. In the kimberlite A horizon most metal is contained in the coarse fraction.

(2) In the residual and colluvial soils over the Trinity siltstones, highest metal concentrations (excluding exNi) are generally recorded in the coarse fraction

The dispersion of selected elements downslope from kimberlite suboutcrop is illustrated on Figs. 5.2 and 5.3. Attention is drawn to the following points:

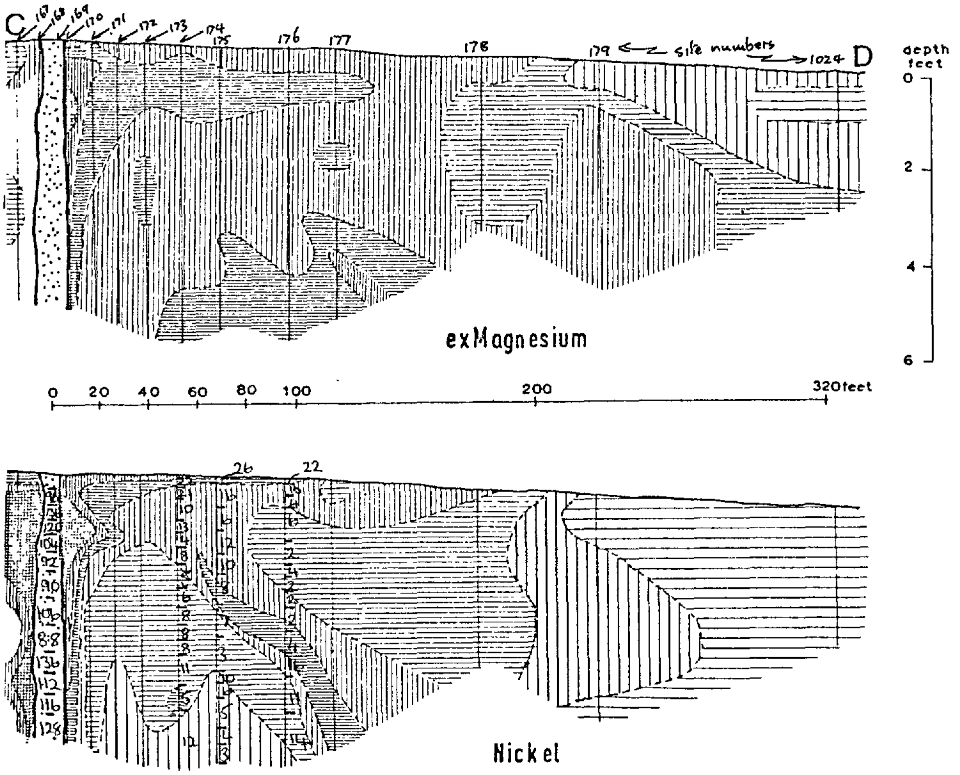
(1) In the kimberlite soil profile the Mn content decreases and Mg content increases with depth. Niobium, Cr, Fe, Ni, P, exNi, and possibly Co, are depleted in the A and enriched in the B_2 horizons. A second Nb maximum is also recorded in the C horizon at a depth of 42 to 46 inches.

Table 5.1 A comparison of the Ni, Co, exNi and exMg contents of the complete sample and minus 80-mesh (B.S.S.) fraction for kimberlite and associated anomalous soils. American Mine, Arkansas.

Sample number	Location*	Depth (inches)	Soil horizon	Ni ppm comp	Ni ppm -80	Co ppm comp	Co ppm -80	exNi ppm comp	exNi ppm -80	exMg ppm comp	exMg ppm -80
556111	168	36-48	C	1240	1225	44	42	85	55	1800	1040
556122	169	¼-2	A_1	820	225	44	12				
556124		5-11	B_2	1220	1375	52	69	77	44	4200	3800
556132		36-46	C	1040	1125	40	41	29	23	5200	4800
556141	171	1-3	A_1	260	252	27	19	<1	5	830	700
556143		6-12	$B_{2.1}$	480	610	50	54	4	17	4000	3000
556148		36-51	C	480	270	44	7				
556267	178	1-3	A_1	75	52	9	7				
556271		8-12	$B_{2.1}$	32	25	6	3				
556276		36-45	$B_{2.2}$	34	19	6	3				
556972	1024	1-2	A_1	11	6	10	1	<1	5	66	72
556974		6-12	$B_{2.1}$	10	6	1	1	<1	1½	64	62
556978		30-36	$B_{2.2}$	18	12	6	1	<1	1½	200	146

*see figure 5.1 comp = complete sample -80 = minus 80-mesh fraction (B.S.S.)

THE PROFILE DISTRIBUTION OF EXCHANGEABLE (ex) MAGNESIUM AND NICKEL DOWNSLOPE FROM A KIMBERLITE OUTCROP, AMERICAN MINE.



	exMg ppm	Ni* ppm
▩	2401 -	401 -
▥	1201 - 2400	201 - 400
▤	601 - 1200	101 - 200
▥	301 - 600	51 - 100
▤	151 - 300	26 - 50
▯	76 - 150	14 - 25
▭	0 - 75	0 - 13

▒ Kimberlite

—— Auger holes

Data on minus 80 mesh (B.S.S.) fraction

|10 Nb content (ppm) of selected samples.

* KHSO$_4$ attack

FIGURE 5.2

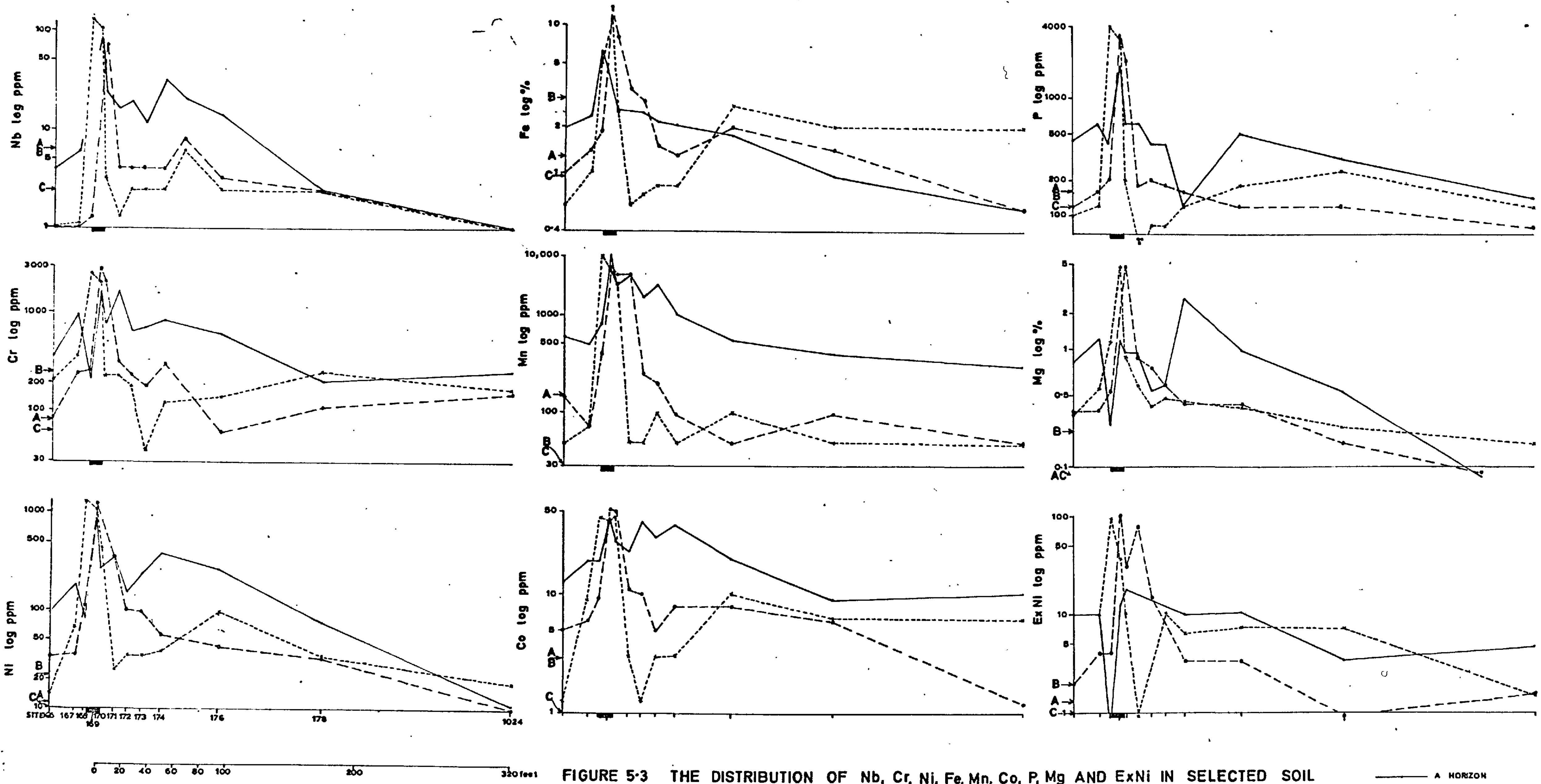


FIGURE 5·3 THE DISTRIBUTION OF Nb, Cr, Ni, Fe, Mn, Co, P, Mg AND ExNi IN SELECTED SOIL HORIZONS DOWNSLOPE FROM A KIMBERLITE SUB-OUTCROP, AMERICAN MINE.

DATA (EXCEPT ExNi) ON COMPLETE SAMPLE. ExNi MINUS 80 MESH (B.S.S.) FRACTION. WET ATTACKS.

←A METAL CONTENT IN THE A_1 HORIZON OF A MATURE BACKGROUND SOIL PROFILE OVER TRINITY SILTSTONE
←B " " " " B_{21} " " " " " " " " " "
←C " " " " C " " " " " " " " " "

——— A HORIZON
— — B HORIZON
- - - - - DEPTH APPROX 39 TO 48 INCHES

LOCATION ILLUSTRATED ON FIG. 5·1

(2) In the residual soils downslope from kimberlite, maximum and anomalous concentrations of the determined elements (excluding Fe and exMg) generally occur in the A horizon. In contrast maximum Fe and exMg values are recorded in the $B_{2.1}$ horizon.

(3) In the $B_{2.1}$ horizon of the residual soils, anomalous concentrations of Nb, P and Fe are confined to within 15 feet from the kimberlite. The remaining determined elements generally occur in varying degrees of anomalous concentrations throughout the section.

(4) Maximum Ni concentration (minus 80-mesh fraction) immediately adjacent to the kimberlite occurs in the $B_{2.1}$ and $B_{2.2}$ horizons and coincident with the lowest observed pH values.

(5) Anomalous concentrations (relative to the Trinity siltstone) of exMg, exNi, Ni, Mg, Cr, Mn and Co are generally observed in the limestone and $B_{2.2}$ and $B_{2.3}$ horizons throughout the section. Except as detailed in (6), anomalous concentrations of Nb, Fe and P are confined to within a few feet from the kimberlite.

(6) In the profile through colluvium (site 1024), some 320 feet downslope from the kimberlite, anomalous concentrations of Mn, Co, Cr, exNi and P are observed in the A horizon, and of Mn, Co, Cr, Ni, Fe and Mg in the $B_{2.2}$ horizon.

(7) A gently dipping tongue of high Ni values is observed in profiles 175, 176 and 177. Accompanying anomalous Nb concentrations are also detected but are not exactly coincident with the Ni maxima. This tongue is not reflected at the surface (site 174) by P, Mn or Fe nor in the $B_{2.2}$ horizon (site 176) by P, Cr or Mg.

5.25 Discussion

The distribution of elements in the kimberlite soil profile at the American Mine is generally similar to that observed at Prairie Creek (Chapter 4). There are, however, two main differences:

a. Maximum concentration of Nb, Cr and Co occurs in the B horizon, cf. A at Prairie Creek.

b. Maximum Mn content occurs in the A horizon, cf. B at Prairie Creek.

Niobium and Cr were seen to be relatively immobile at Prairie Creek, thus it is difficult to explain their depletion in the A_1 horizon of the less mature soils at the American Mine by leaching. The steep slopes of the American Mine would favour rapid erosion and it is suggested, therefore, that the depletion is due to dilution with background material during soil creep.

Although the size distribution of Mn in the American Mine soils is unknown, Co is considerably concentrated in the coarse fraction of the A horizon (Table 5.1). It has been shown that Co follows Mn in the kimberlite soil profile (Chapter 4), thus in all probability Mn is similarly concentrated in the coarse fraction. If this is the case, then concentration of Mn in the American Mine kimberlite A horizon may be partly due to residual concentration of metal by preferential elutriation of fine sized material.

The second Nb maxima, observed at depth in the kimberlite soil profile, is thought to be due to a heterogenous distribution of this element in the kimberlite. The possibility that it is the result of concentration of metal in a previous $B_{2.1}$ horizon is thought unlikely since morphological evidence is lacking. Furthermore, there is some dispersion of Nb into the present day $B_{2.1}$

horizon and only background values are detected adjacent to the kimberlite at depth.

In the residual soils downslope from the kimberlite, the prolonged anomalous trains in the A horizon indicate mechanical dispersion to be prevalent. Concentration of certain metals in the $B_{2.1}$ horizon is attributed to soil forming processes. However, adjacent to the kimberlite, maximum Ni values occur in the lower $B_{2.1}$ and upper $B_{2.2}$ horizons and correspond with the lowest observed pH values. This is unlikely to be due to soil forming processes since it would suggest Ni to be least mobile at low pH values, which is not the case (Chapter 8). The possibility must be considered therefore that some dispersion of Ni (and other semi mobile metals) has occurred in ground waters when the water table was much higher than at the present.

It is not known whether the anomalous concentrations of Ni, Mg, Cr, Mn and Co observed in the limestone*, reflect a locally higher threshold in this rock type or are the product of saline dispersion from the kimberlite. The high pH developed in this rock would severely restrict saline dispersion of many cations, indeed the brick red colour observed near the limestone/siltstone contact is attributed to the precipitation of ferric sesquioxides because of this high pH. However, some redistribution of Mn and Ni has taken place as seen from their concentration on limestone fracture surfaces (below).

Ni content in limestone	24 ppm
Ni content in Mn sesquioxides coating limestone fracture surfaces	165 ppm

---

*the morphological locations of the samples analysed on Fig. 5.3 are illustrated on Fig. 5.1.

Whilst it is likely that the limestone would contain an appreciable quantity of Mg, Ni and Cr occur in greater amounts than in the average limestone (Hawkes and Webb, 1962), and Mn and Fe are depleted.

The anomalous concentrations of Mn, Co, Cr and P in the A and $B_{2.2}$ horizons in the colluvium at site 1024 are attributed largely to mechanically dispersed material. The lack of associated anomalous Fe, Mg and Ni contents in the A horizon would suggest these elements to have been leached during dispersion.

The reason for the anomalous tongue of high Ni content is not at all clear. It may be related to a minor kimberlitic stringer or to secondary dispersion processes. This is discussed in tabular form below.

Feature	Kimberlite stringer	Secondary dispersion processes
Tongue occurs along the limestone siltstone contact in lower parts of profile.	Coincidence. Possibly structurally favourable.	Precipitation of cations at low/high pH interface. In which case the limestone must have been leached from the upper parts of the profile on the upslope side of the tongue.
Shallow dip.	No simple explanation. Possibly as above.	Along dip of limestone
Associated anomalous Nb concentrations. Not coincident with Ni maxima and generally confined to the limestone.	Supported. Displacement of Ni and Nb maximums due to zoning during intrusion. Possible reaction of Nb vapours with limestone.	No simple explanation. Might be due to an exceptionally high background. Average limestone 0.3 ppm Nb.
No anomalous P content.	No simple explanation. Possible that P differentiated prior to intrusion of stringer.	Within normal limestone range.

In the light of the present data the explanation favoured by the writer is that the tongue is due to a minor kimberlitic stringer. If the silica rich soils on the upslope of the tongue in the B_2 horizon were derived from limestone, then very considerable leaching and consequent surface deflation would have to have taken place. There is no field evidence to support such deflation.

5.3 AREAL DISTRIBUTION ABOUT THE AMERICAN MINE

Soil samples were collected at 100 feet intervals along traverse lines 100 feet apart, and additional samples at 50 feet intervals near to the kimberlite. Samples were taken from the $B_{2.1}$ horizon or an equivalent depth when the horizon is absent. The minus 80-mesh fraction was analysed for Nb, Ni, Co and exMg which are considered representative elements of each of the groups detailed in Chapter 4.

5.31 Geology

Whilst the geology of the American Mine is described in Section 1.1321 and Fig. 1.5, and sections through the deposit and flood plain are illustrated on Figs. 1.6 and 5.4, respectively, there are certain aspects of the physiography which need to be elaborated in order to explain the observed dispersion patterns.

Since the etching of the present topography in early Quaternary time, the area has been subjected to several vertical oscillations, Table 5.2.

The most important influences effecting secondary dispersion are:-

(1) A long period of quiessance during which American Valley was widened rather than deepened.

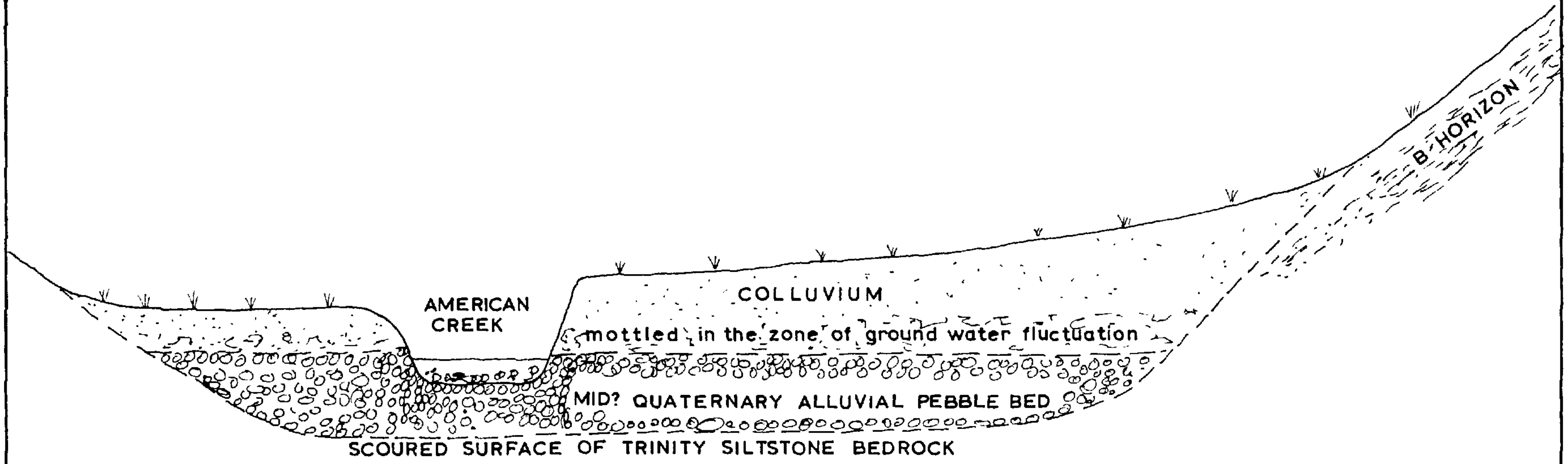


FIGURE 5.4 DIAGRAMMATIC SECTION THROUGH THE FLOOD PLAIN OF AMERICAN CREEK ABOUT 200 FEET DOWNSTREAM FROM REFERENCE CREEK.

Table 5.2 The physiographic history of the American Mine area

Recent	Gradual progress of physiographic cycle to completion, development of oxbow lakes etc. Further headward erosion of Valley, East and West Creeks.
Rejuvination Possibly also climatic change	Entrenchment of American Creek into its own alluvium. Further headward advance of Valley Creek. Formation of consequent streams, i.e. East and West Creeks.
Subsidence	Aggradation of American valley with material eroded dominantly from the headwaters of American Creek and its tributaries. Headward advance of Valley Creek.
Long period of structural quiessence	Widening and deepening of American valley. Erosion of the Tokio formation and exposure of part or most of the kimberlite. Lateral development of American valley to give an anomalously wide, flat bottomed valley with steep sides. Formation of Valley valley.
	Etching of obsequent American Creek into the scarp slope of the Tokio cuesta to form American valley.
	Development of obsequent streams on the scarp slope.
Late Tertiary to Early Quaternary	Development of a southerly dipping Tokio capped cuesta with steep northerly scarp slopes reflecting different hardnesses of Trinity the sedimentary rocks. American Creek formed initially as a lateral stream draining westwards to the Little Missouri River which cuts through the escarpment.

(2) A later period of subsidence allowing infilling of the Valley with alluvium.

(3) Rejuvination and entrenchment of American Creek into the alluvium. The consequent East and West Creeks were probably developed at this time.

5.32 Variation in the $B_{2.1}$ Horizon

A wide variation in the character of the $B_{2.1}$ horizon is experienced over the American Mine area, Fig. 5.5.

Near to the kimberlite the horizon is a brick red clay, which grades into an orange clay to clay loam at greater distances from the ultrabasic rock. Several other areas of brick red to orange clays are also recorded which are not near known kimberlites.

The remaining soils are dominantly silt or silt loams of varying colour. Soils on the flood plain in the northwest part of the area are varigated white/cream to pale orange silt or silt loams; in the Valley Creek catchment area the horizon is a brown to mottled orange brown colour.

Close to the Tokio formation the soils are silt rich and vary from a cream to white brown colour.

5.33 Metal Distribution Patterns

The distribution of Ni, cxMg, Co and Nb about the American Mine is illustrated on Figs. 5.6, 5.7, 5.8 and 5.9.

Examination of the appropriate figures reveals the following salient features:

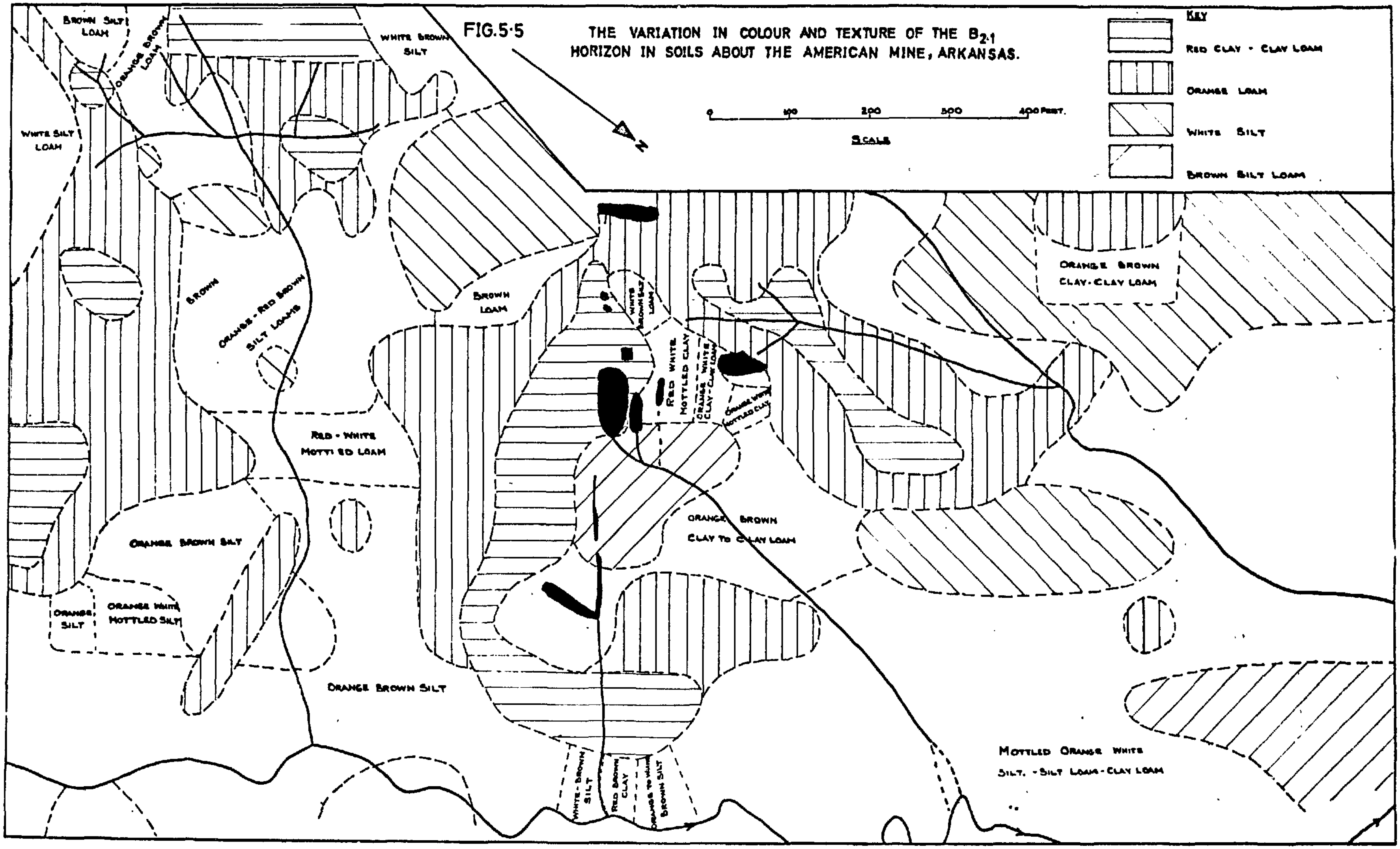


FIG.5·5

THE VARIATION IN COLOUR AND TEXTURE OF THE $B_{2\cdot 1}$ HORIZON IN SOILS ABOUT THE AMERICAN MINE, ARKANSAS.

FIG. 5·6

THE DISTRIBUTION OF NICKEL IN SOILS AT THE AMERICAN MINE.

-80mesh fraction of the B_2 horizon

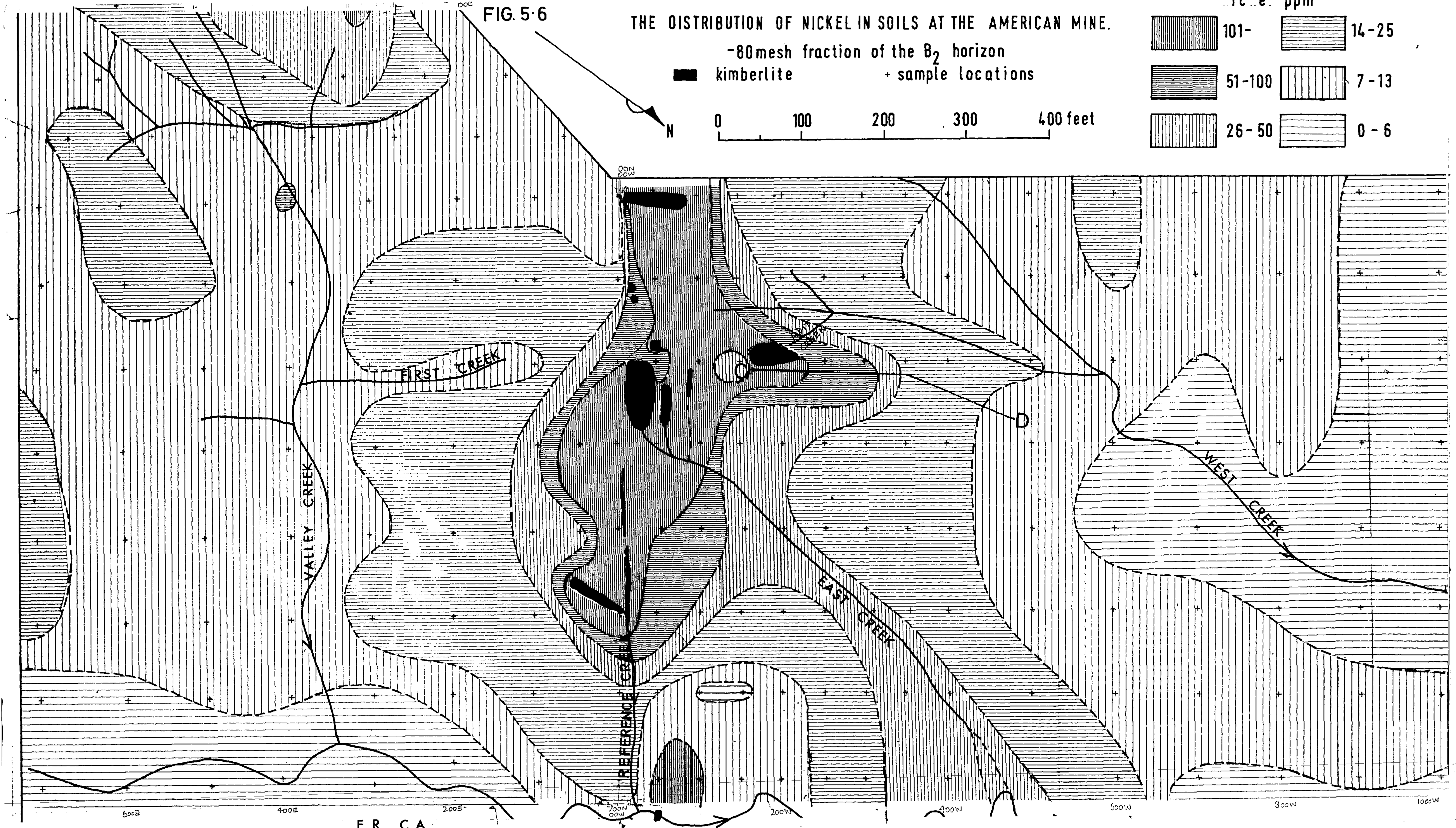


FIG. 5·7 THE DISTRIBUTION OF EXCHANGEABLE MAGNESIUM IN SOILS AT THE AMERICAN MINE, ARKANSAS.

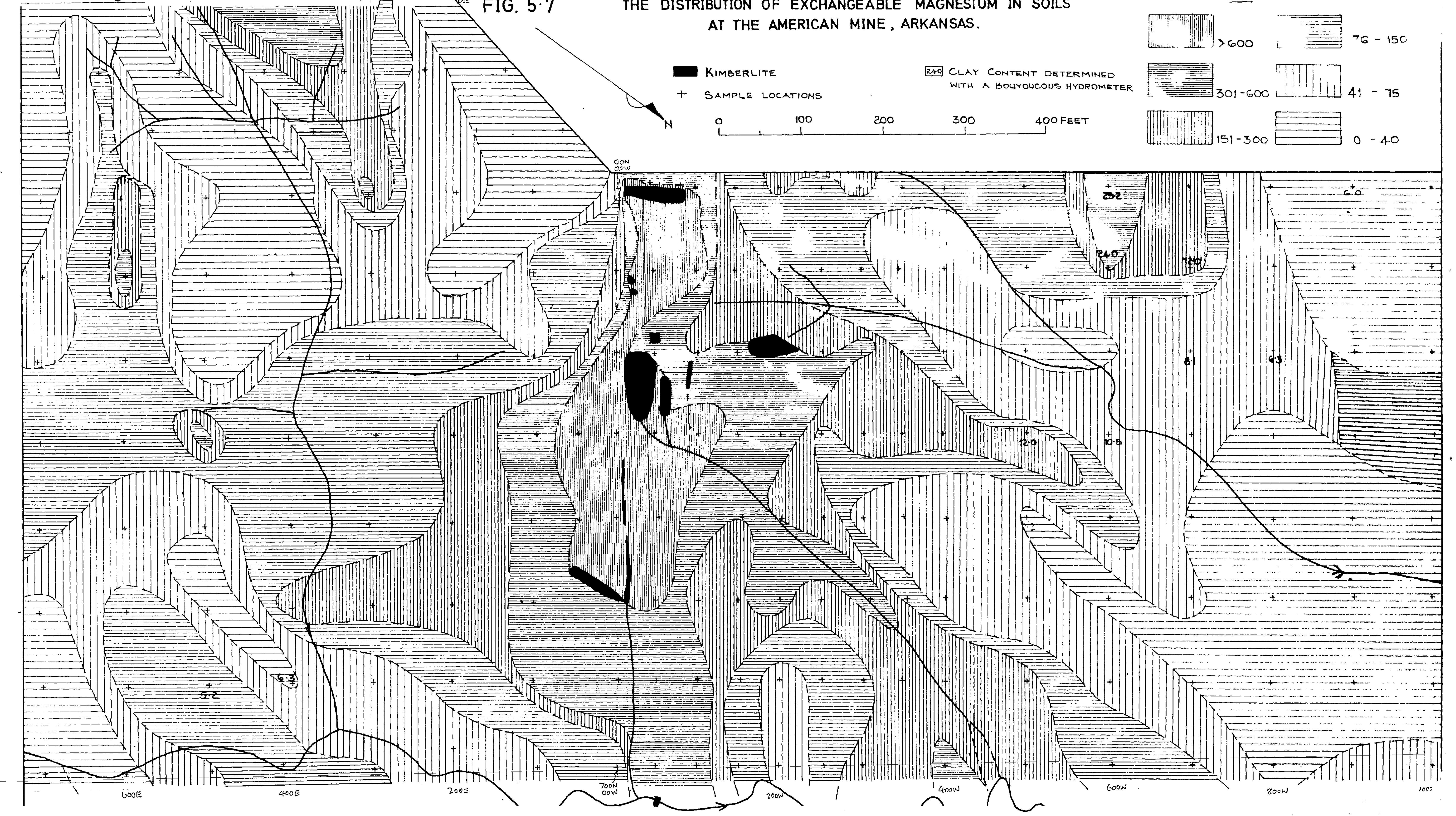
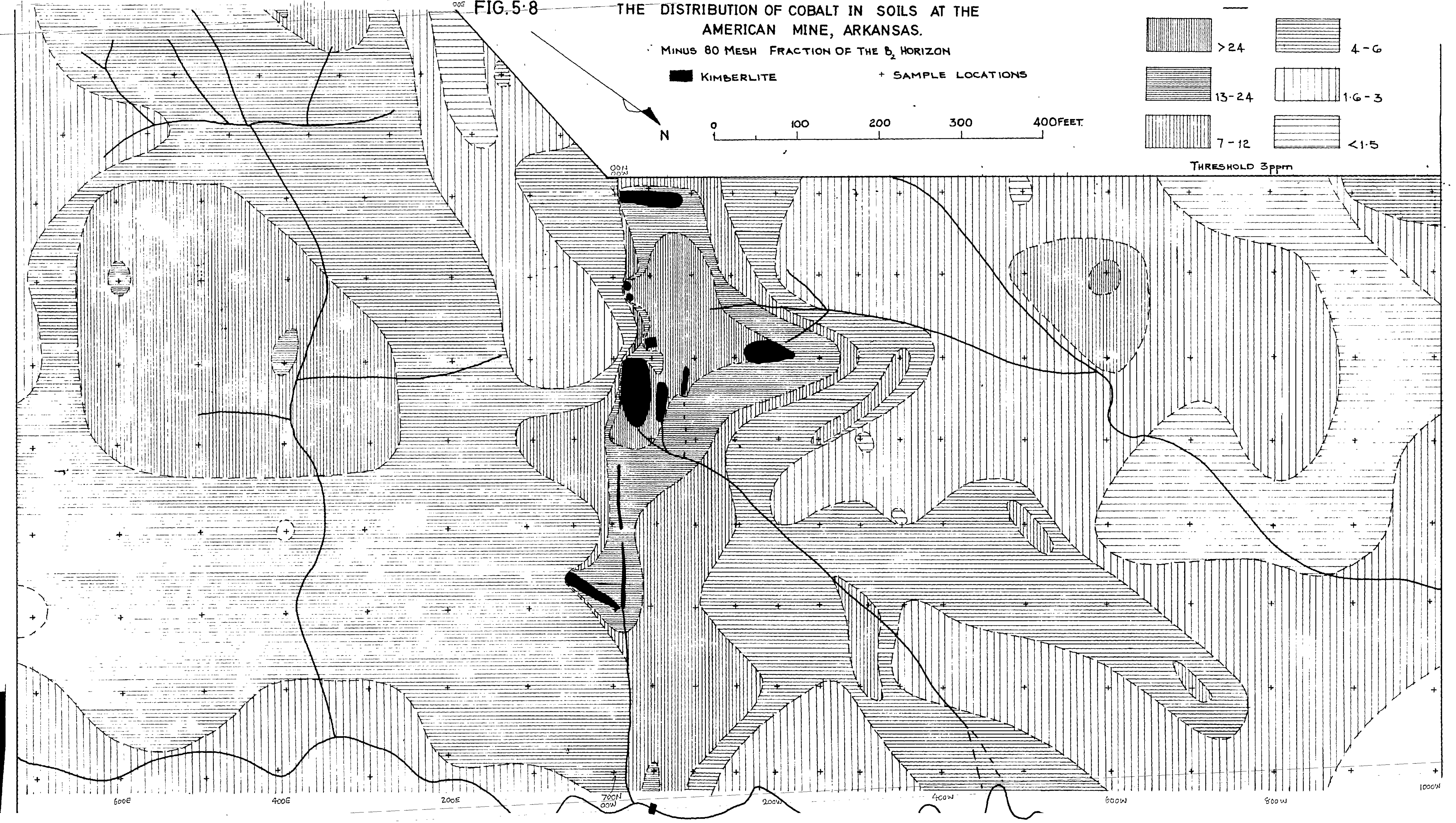
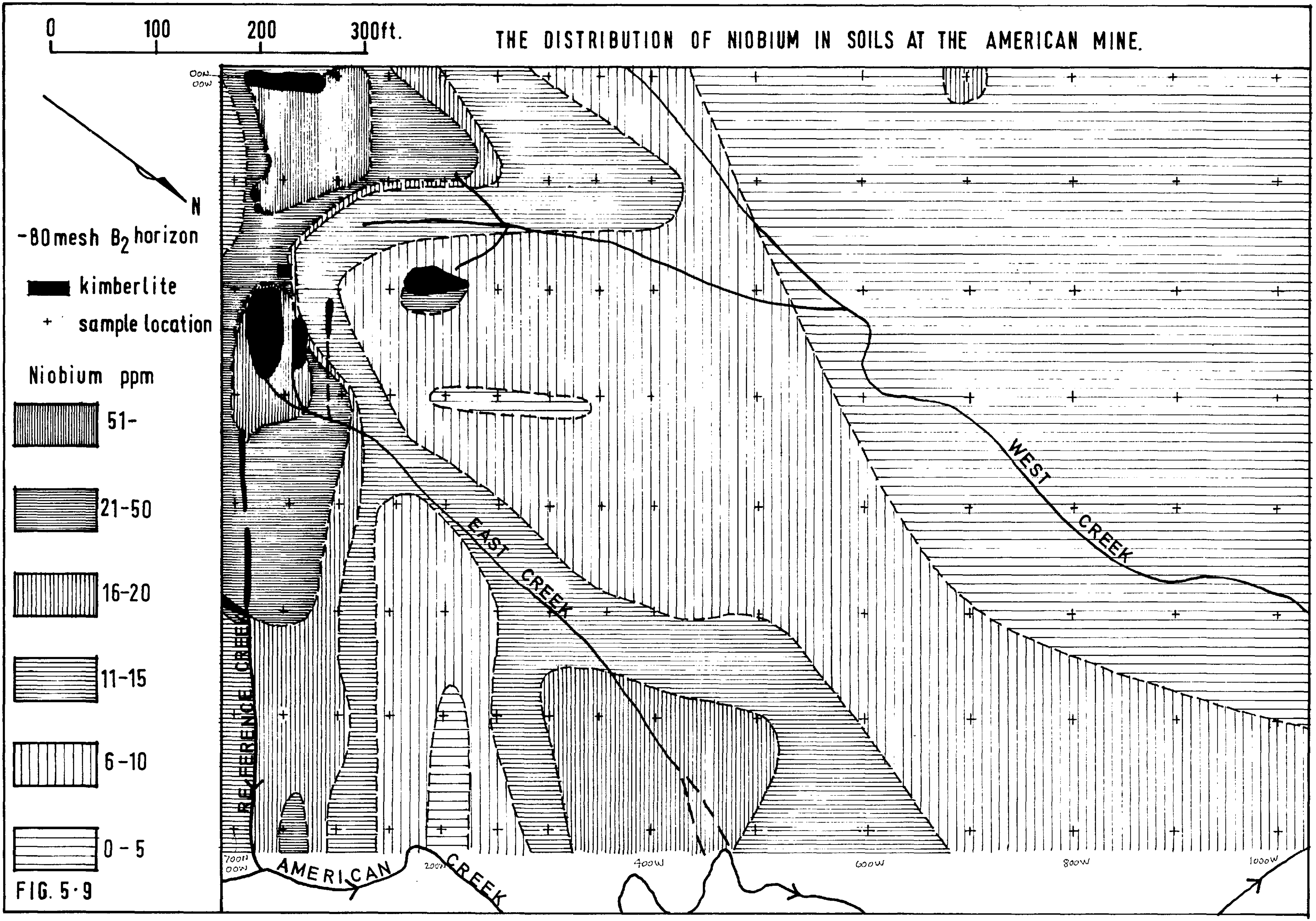


FIG. 5·8 THE DISTRIBUTION OF COBALT IN SOILS AT THE AMERICAN MINE, ARKANSAS.

Minus 80 Mesh Fraction of the B_2 Horizon





THE DISTRIBUTION OF NIOBIUM IN SOILS AT THE AMERICAN MINE.

FIG. 5·9

(1) Anomalous concentrations of all four metals are detected downslope from the known kimberlite. Dispersion is greatest in the case of exMg and Ni (more than 300 feet) and least in the case of Nb (70 to 100 feet).

(2) Whilst the distribution of exMg has a broad relationship with the present day topography, drainage and soils, the relationship is much less marked in the case of Ni and obscure for Co and Nb.

(3) All four elements have low background values in the northern and western part of the area. In addition, Ni, Co and exMg are also contained in very low concentrations on parts of the flood plain of American Creek.

(4) Anomalous concentrations of metal are detected in the banks and on the flood plain of East Creek.

(5) Several areas of highly anomalous metal concentration are apparent which are not related to known kimberlite outcrops.

(6) In the area to the southeast of the baseline, anomalous concentrations of Co are much more widespread than either exMg or Ni.

5.34 Discussion

Prior to discussing the observed dispersion patterns, one must consider the possibility of anomalous aureoles developed by:

(a) Primary dispersion,

(b) Secondary dispersion during Cretaceous time.

It was seen in Section C-D that Nb was not dispersed to any great extent beyond the kimberlite/Trinity contact in the C horizon; thus a significant primary aureole is considered unlikely. However, some thin stringers may be present.

The products of secondary dispersion during Cretaceous time would occur along or close to the Tokio/Trinity contact. Highly anomalous Nb concentrations (21-31 ppm) are recorded in the Tokio formation at 410S10W about 4 feet topographically above the highest level reached by the kimberlite. Only slightly anomalous Co, but background Ni and exMg, contents are observed at the same location. It appears likely, therefore, that some tuff or fine grained kimberlite detritus is present in the Lower Tokio formation at the American Mine.

Only background (8 ppm) Nb concentrations are recorded in the B_2 horizon at 100S50E immediately downslope from the Tokio formation, thus Tokio colluvium does not significantly affect the content of Nb in the Trinity B_2 horizon. However, it is possible that local anomalous metal concentrations in the A horizon adjacent to the Tokio formation, and possibly in the associated drainage, may occur.

It was shown by profile sampling that anomalous Nb concentrations are largely confined to the A horizon and that this element is mainly dispersed mechanically. Thus the following features are difficult to explain in terms of present day topography and drainage:

(a) Anomalous Nb (and Ni, Co and exMg) values extend for some tens of feet laterally and several feet vertically above the present course of East Creek.

(b) Anomalous Nb values at the head of West Creek occur along the height of land.

(c) An area of low background Nb values occurs in the northern part of the American Mine area.

The possibility must be considered therefore that the observed anomalies were developed, at least in part, under different conditions in the past.

In considering the anomalies flanking East Creek in detail the following points must be explained:

(1) Extensive anomalous concentrations of metal occur on the flood plain of East and American Creeks at the mouth of East Valley.

(2) Anomalous Nb concentrations, though confined to East Valley, extend for several feet vertically above the present floor. Anomalous Ni concentrations extend over the Valley shoulder but anomalous exMg values are confined to the Valley itself.

(3) Anomalous Co concentrations are erratic and restricted in area.

Profile sampling across the mouth of East Creek (Figs. 5.10 and 5.12) indicates the presence of a buried drainage channel. It is noticeable that the anomalous Nb concentrations extend in depth at least to the Quaternary alluvium, thus East Creek was in existence during, or before, the rejuvination of the area.

It is suggested that the Ni and exMg anomalies were formed initially on the scarp slope of the Trinity formation either prior, or during the early development of East Creek. The more mobile exMg has since been partially leached leaving behind a relic aureole of the less mobile Ni. As rejuvination proceeded so the headward advance of East Creek continued ultimately eroding the kimberlites. At that time the floor of East Creek was somewhat higher than at present.

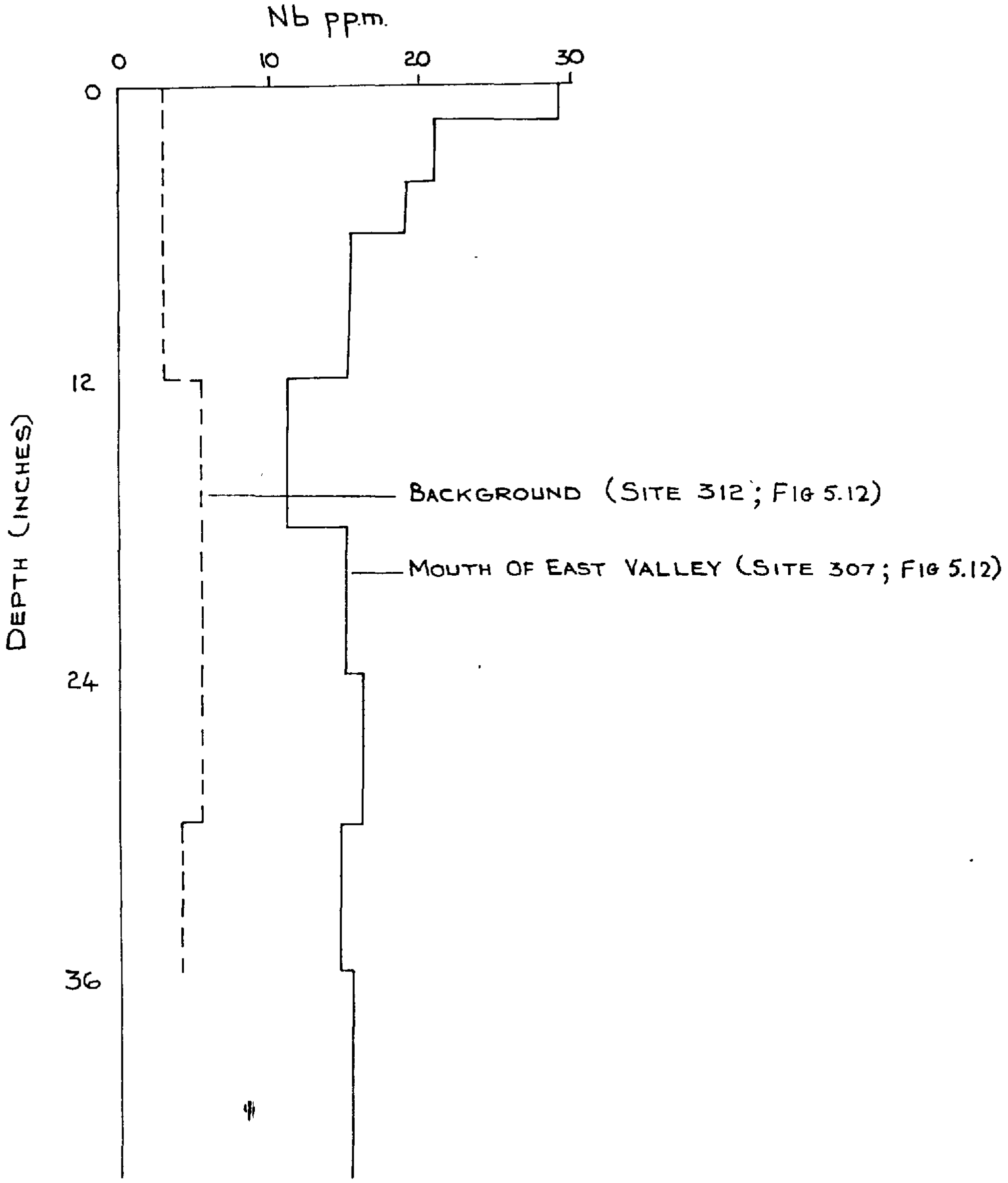


FIG. 5·10 The Profile Distribution Of Niobium In Soils At The Mouth Of East Valley, American Mine Arkansas Data On Minus 80 Mesh Fraction.

Additional evidence for the relic nature of parts of the Ni anomaly is provided by the incisement of First Creek into the anomaly which is now preserved on the flanking higher ground.

The latest stage in the development of the placer deposit at the mouth of East Creek is illustrated by the considerable increase in metal content in the top few inches of the profile (Figs. 5.10 and 5.12). This is due to a higher metal content of the silt size fraction (Fig. 5.11) and is thought to reflect accelerated erosion of the kimberlite during exploratory activity early in the century.

It is noticeable that whereas Nb and Ni are concentrated in the coarse and fine fractions of the placer deposit (Fig. 5.11), Co occurs dominantly in the coarsest fraction. This is no doubt partly responsible for the erratic distribution of this element about East Creek since analyses were made on the minus 80-mesh fraction. The reason for the much higher content of Nb in the clay size of the near surface sample than at depth is uncertain. It could be due to some redistribution by saline processes, breakdown of the Nb host mineral, or less likely to comminution of the Nb host during mining activity.

The large area of "low" Nb content to the northwest of the area is difficult to explain. It is noticeable that the associated soils are sand and silt rich and are of white to pale orange colour. Thus it is possible that the "low" values represent a lower threshold due to a lithological change. However, if this is the case, then since the beds dip only very slightly to the south, anomalous concentrations of Nb are more widespread than hitherto envisaged. In this case the 5 to 6 ppm boundary may reflect the northernmost limit of mechanical dispersion from the known kimberlites and possibly an old course of West Creek.

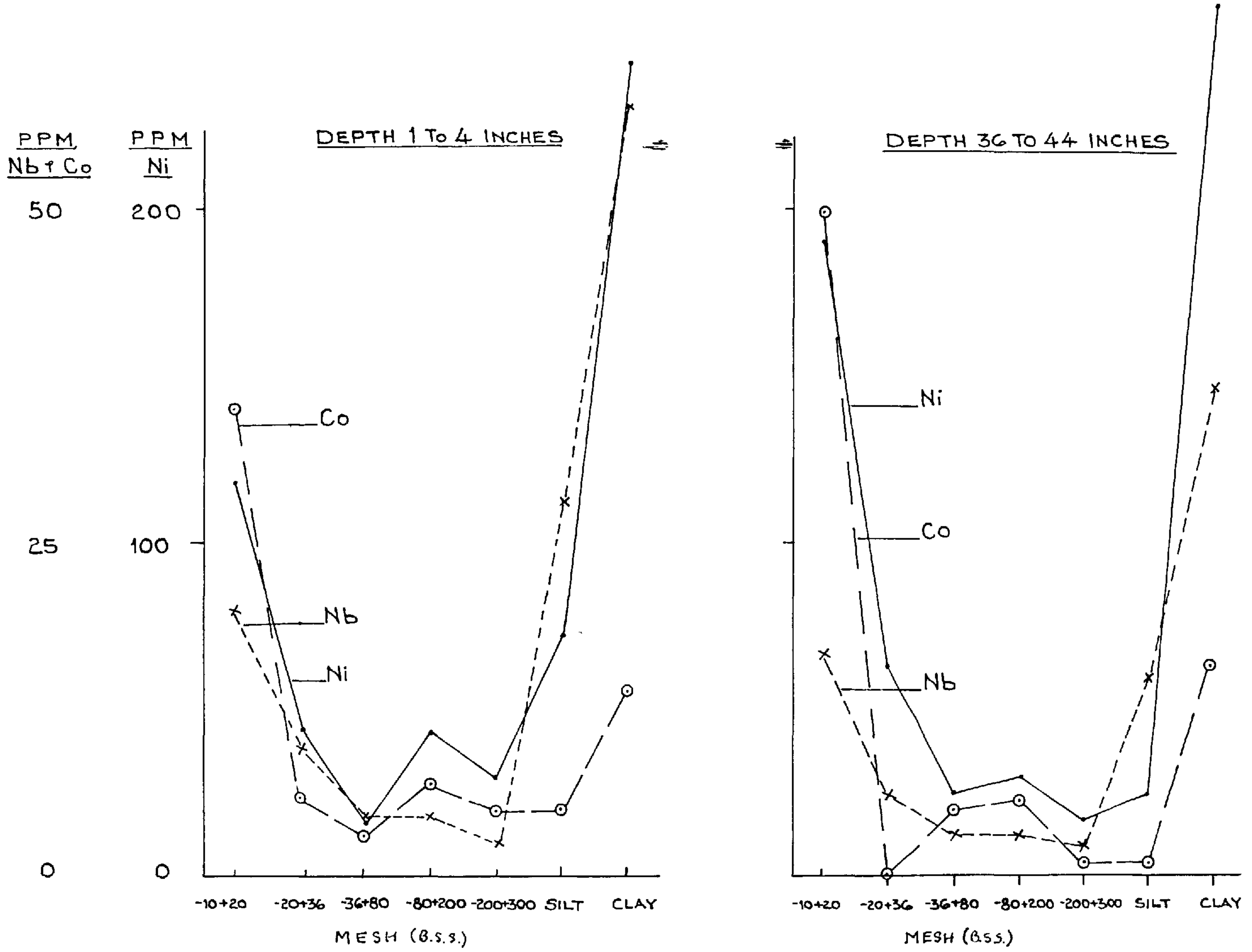


FIG. 5·11

THE VARIATION WITH PARTICLE SIZE OF Nb, Ni, AND Co BOTH NEAR TO THE SURFACE AND AT DEPTH AT THE MOUTH OF EAST VALLEY AMERICAN MINE, ARKANSAS.

"High" background Ni, Co and exMg contents are present over a considerable part of the area mentioned above. This might be due to the greater mobility of these elements, possibly from the anomaly at 00N600W which may reflect a yet undiscovered kimberlite.

"Low" background Ni, Co and exMg concentrations flank parts of West and American Creeks. These are attributed to samples being collected from A horizon colluvium eroded from the valley walls and deposited at the break of slope (Fig. 5.4). This is further discussed in section 5.4.

Anomalous metal concentrations extending up the northwest slope of Reference Valley are related to kimberlite as suggested by profile sampling (Fig. 5.12) and confirmed by the discovery of kimberlite, underlying alluvium, in American Creek at 740N50W. Relatively low metal concentrations at the surface, especially at 700N100W are attributed to dilution of surface material with background colluvium.

Anomalous Nb concentrations along the height of land between Adit and West Creeks are attributed to residual concentrations of metal dispersed from the kimberlite immediately upslope.

Kimberlite was intersected in a drill hole at a depth of 30 feet (Miser and Ross, 1923) near the head of Valley Creek. Since this kimberlite is not known to outcrop, the associated exMg, Ni and Co anomalies are almost certainly of saline origin.

Whilst the reason for the two Ni anomalies east of Valley Creek is unknown, two possibilities are considered:

a. Secondary dispersion from yet undiscovered areas of kimberlite

b. Remnants of an anomalous aureole from the known kimberlite at 320S100E and later bisected by Valley Creek.

Whilst the remnant suggestion cannot be disproved, there are several features which are difficult to explain by this theory:

(1) Strongly anomalous coincident Co, Ni and exMg concentrations are obtained at 100N600E.

(2) Exchangeable Mg has a larger aureole to the East of Valley Creek than has Ni. It was suggested earlier that exMg is partially leached from relic Ni anomalies.

(3) The lack of anomalous Ni concentrations about 200N700E.

The most plausable explanation therefore is that the anomalies are derived from a local undiscovered kimberlitic source. In this connection, it would be interesting to investigate the possibility of a linear feature through 320S100E, 100N600E and 400N800E.

It is noticeable that anomalous Co concentrations are more widespread to the south of the base line than those of Ni and exMg; whilst to the northwest, the reverse occurs. The reason for this differing distribution is unknown but three suggestions are considered:

a. A change in threshold due to a change in lithology.

b. Co being more mobile than Ni.

c. Co being less mobile than Ni.

Assuming the regional dip of about 1:60 south to apply at the American Mine, then there are stratigraphically similar levels to the northwest of the base line where only background Co concentrations are observed, but which are anomalous southeast of the base line. This does not support the suggestion of a change in threshold due to a change in lithology. Furthermore, it is extremely difficult to explain the almost square shaped area of strongly anomalous Co content by lithological changes.

It was found in Chapter 4 that Co is less mobile in the soil profile than Ni. The smaller anomalous Co aureole, than the Ni and exMg aureoles, to the north of base line is consistent with these findings. Thus, unless dispersion occurs(ed) under different conditions in the areas to the southeast and northwest of the base line, it is difficult to explain the larger Co aureole to the southeast of the base line by a greater mobility of Co than Ni.

If Co is less mobile than Ni, as seems likely therefore, then the anomalies must be explained by residual concentration of metal. In this case the source of the Co presents a problem.

Clearly further work is required before a satisfactory explanation for the difference in distribution can be given.

The reasons for the north trending lobe of anomalous Co content between East and West Creeks is unknown. It is noticeable that this lobe transgresses the flood plain of American Creek and that the associated exMg content is very low but that of Ni is of "high" background.

There are several areas of anomalous exMg content which are not associated with anomalous Ni contents, e.g.

a. On the nose of the ridge between East and West Creeks.
b. About 300N900W.
c. About 600N500E.

The clay content of selected samples from these anomalies and adjacent background samples was determined using a Boyoucous hydrometer. The results are plotted on Fig. 4.7.

Although a higher clay content is observed in the sample taken from the anomaly on the ridge between East and West Creeks, than in normal background samples, it is only 20% higher than a background sample taken from 100 feet to the northwest. Moreover, these two samples have the same morphological appearance. This would tend to suggest that the anomalous exMg concentrations on the ridge are not due entirely to an elevated clay content. It must be pointed out, however, that the total exchange capacity of the two samples mentioned above were not compared. A further possible explanation for this anomaly is that it is the eastern remnant of an anomaly which once extended to 00N600W but which has been subsequently bisected and partly eroded by West Creek.

The clay contents of the anomalous samples at 300N900W and 600N500E are not dissimilar from the adjacent background samples. Profile sampling at site 219 (620N550E; Fig. 5.12) indicates exMg content to increase with depth. It is noted in section 5.4 that anomalous concentrations of exMg occur near the water table in the flood plain of American Creek. It is suggested therefore that the anomalies about 600N500E and 300N900W are due to metal deposited from a near surface water table. Presumably the source of exMg giving rise to the anomaly about 600N500E is located upslope or upstream from this area. This is in accord with a previous suggestion that an undiscovered kimberlite is present in this area.

5.4 DISTRIBUTION OF ELEMENTS IN THE FLOOD PLAIN AND BANKS OF AMERICAN CREEK

As previously mentioned, the flood plain of American Creek consists of colluvium overlying Quaternary alluvium or Trinity clays and siltstones (Fig. 5.4). The colluvium is mainly silt or silt loam, light coloured at the surface and mottled at depth.

The Quaternary alluvium is composed mainly of novaculite gravel and is exposed in the banks and bed of American Creek downstream from Reference Creek.

Profiles were collected from the flood plain of American Creek especially on the south bank, i.e. the bank nearest the intrusion. In addition, channel samples were taken from the stream banks of American and Valley Creeks at selected locations.

The minus 80-mesh fraction was analysed for Ni and exMg, and for a very limited number of samples, Co and Nb. The results for the section through American Creek flood plain are illustrated on Fig. 5.12; those for the bank samples are given on Table 5.3.

5.41 Section through the Banks of American Creek (Fig. 5.12)

(1) Exchangeable Mg, Ni and Co increase in concentration towards the water table. At some locations a slight concentration of metal occurs near the ground surface.

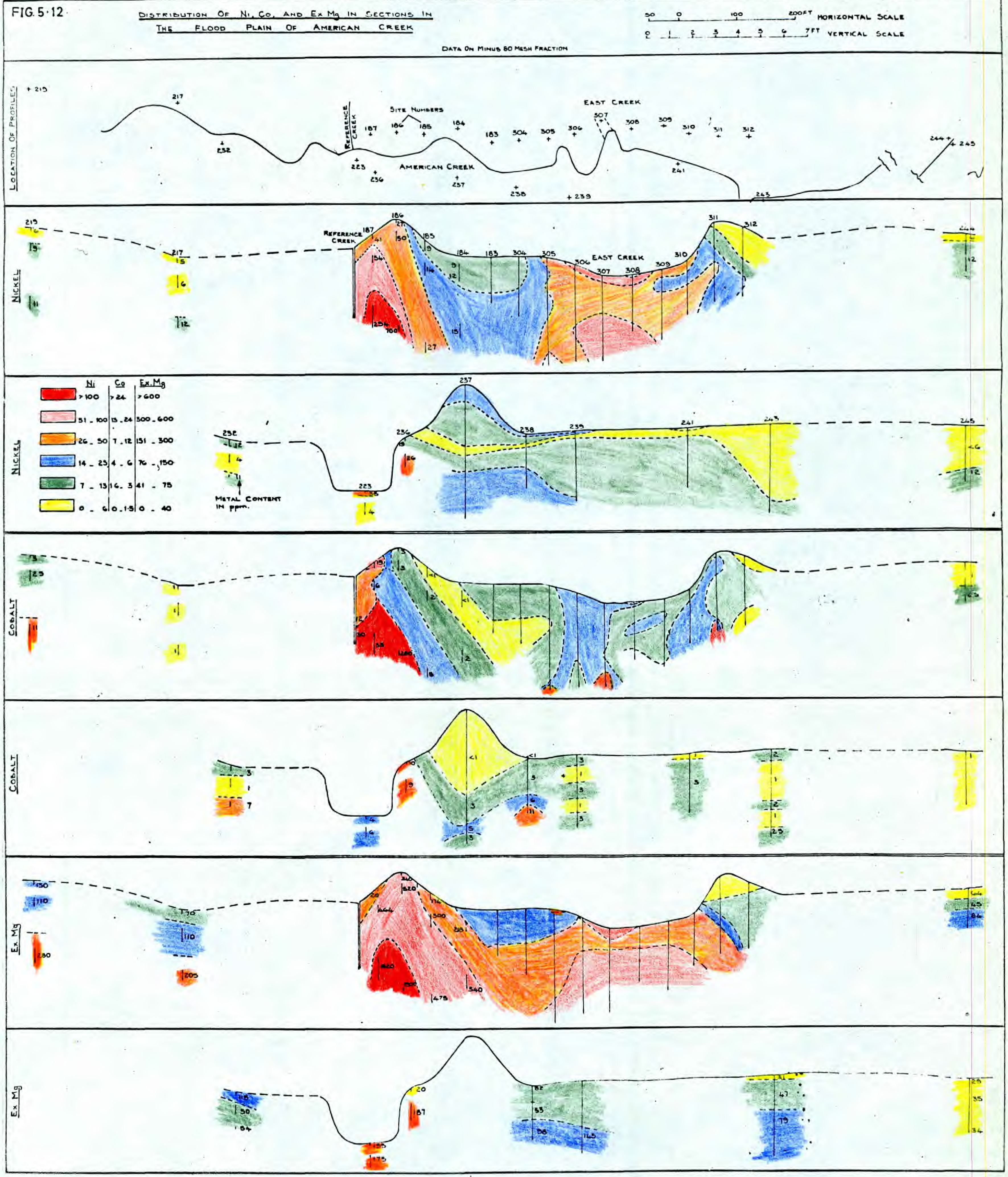
(2) Highly anomalous concentrations of metal are present at depth in profiles 186 and 187. Metal content, especially Co, appears to decrease rapidly towards the surface.

(3) Anomalous concentrations of metal extend for some distance downstream from (2). Exchangeable Mg

FIG. 5·12

DISTRIBUTION OF Ni, Co, AND Ex Mg IN SECTIONS IN THE FLOOD PLAIN OF AMERICAN CREEK

DATA ON MINUS 80 MESH FRACTION



has the largest aureole and Co the smallest.

(4) The existence of a buried drainage channel about East Creek is confirmed. Metal is concentrated both near to the surface and at depth. Distribution of Co is erratic.

(5) Anomalous contents of exMg are present at depth in profiles 219 and 244.

5.42 On the Stream Banks of American and Valley Creeks (Table 5.3)

(6) Highest metal contents are generally found below the wet season water level. Exchangeable Mg is usually concentrated in the mottled zone, whilst higher contents of Ni and Co occur in the pebble bed (cf. sites E, M and O). At some locations, i.e. site K, metal, including Nb, is also concentrated at the top of the bank.

(7) Anomalous concentrations of exMg occur below the wet season water level at all locations examined on the north bank, including site S, 3200 feet downstream from Reference Creek. With the exception of site B, coincident anomalous Ni contents are also recorded. Insufficient data is available to determine the extent of anomalous Co and Nb concentrations, but they are more restricted than those of Ni.

(8) There appears to be a broad tendency for higher exMg and Ni concentrations to occur on the bank surface than in adjacent profiles. However, insufficient analyses have been made to determine whether this is truly the case. Sites K and 187, and Q and 307 are special exceptions to this tendency.

(10) Anomalous concentrations of exMg and Ni are present at several locations on the bank remote from kimberlite; metal content is generally lower on this bank than on the south bank. Especially noticeable is the anomalous content of exMg at depth on the north bank at site R, 3200 feet downstream from the intrusion.

5.43 **Discussion**

The colluvium overlying the pebble bed has probably been derived from the A horizon more or less immediately upslope. Since this colluvium is a relatively recent deposit and has probably been stripped of its easily weathered forms of metal by soil forming processes prior to deposition; the increase in metal content towards the water table is thought to be due to deposition of metal from ground waters draining the intrusion. Presumably the orange mottling of the lower colluvium indicates fluctuating Eh conditions due to a seasonally fluctuating water table.

That the elements are dispersed by saline processes in the colluvium is illustrated by the substantial anomalous aureoles in the colluvium downstream from sites 186 and 187. These sites are located on a projection from the known kimberlite exposures and the associated highly anomalous metal contents at depth are no doubt due to kimberlite suboutcrop. The largest aureole downstream is given by exMg and least by Co. This indicates exMg to be more mobile than Ni which is more mobile than Co.

It is thought that concentration of metal in the colluvium at depth on the north bank is due to saline dispersion from the northward projection of the kimberlite.

The concentration of metal near to the ground surface in some profiles is attributed in most instances to mechanical dispersion from kimberlite suboutcrop upslope. The reasons for the anomalous exMg concentrations near the surface at site 232 is unknown.

In the alluvium below the wet season water level, exMg is concentrated in fine grained sediment, especially in orange mottles (Table 6.25). However Ni and Co appear to be concentrated in the pebble bed. This would tend to suggest Ni and Co to have been dispersed partly mechanically during deposition of the alluvium. This is strongly supported by the presence of anomalous concentrations of Ni, Co and Nb in samples of the pebble bed taken from 6 inches inside the bank (Table 5.4). Ferriferous and manganiferous nodules are also observed in these samples and were probably deposited contemporaneously with the alluvium. However, the possibility that they have been formed in situ cannot be ignored.

<u>Table 5.4</u> <u>The variation of exMg, Ni, Co and Nb contents between the surface and "inside" the Quaternary alluvium on the banks of American Creek</u> (minus 80 mesh).

Site		ppm exMg	Ni	Co	Nb
K	Sample from bank surface	500	75	6	17
	Sample from 6 inches inside the bank	460	59	11	25
P	Sample from bank surface	112	13	<1	
	Sample from 6 inches inside the bank	242	35	6	

It is uncertain whether the anomalous exMg and Ni contents at site R, some 3200 feet downstream from the American Mine are due to sorbtion of metal from ground or surface waters draining the American Mine, or whether they are derived from the Kimberlite Mine about $\frac{1}{4}$ of a mile upslope.

5.5 SUMMARY AND CONCLUSIONS

(1) The $B_{2.1}$ horizon in residual soils over the Trinity formation varies from a brick red clay rich horizon adjacent to the kimberlite to a pale orange silt in background areas. Soils over the kimberlite are less mature than at Prairie Creek but concretions are plentiful. Tokio soils are skeletal. Colluvium on the American Creek flood plain is a light coloured silt and mottled in the zone of ground water fluctuation.

(2) High pH values are observed over the kimberlite and limestone, and low values over the sialic country rocks.

(3) As at Prairie Creek, considerable concentration of the elements occur in the plus 80-mesh fractions, presumably within nodules.

(4) In residual soils downslope from kimberlite, maximum dispersion of most elements occurs in the A horizon but exMg and Ni are also considerably dispersed in the B horizon. In areal distribution exMg has the largest aureole and Nb the smallest.

(5) Considerable saline dispersion of exMg is observed, especially near the water table in the flood plain of American Creek. Significant saline dispersion of Ni, and to a lesser extent Co, has also occurred.

(6) In order to explain various features of the metal distributions it is suggested that the anomalies were developed partly under slightly different physiographic conditions in the past. Additional evidence is obtained from the presence of a placer deposit at the mouth of East Creek.

(7) Anomalous concentrations of metals are recorded in the Mid-Quaternary alluvium flanking American Creek.

(8) Several anomalies are recorded which are not related to known kimberlites.

(9) There are various features of the Co distribution which are unexplained.

(10) A significant primary dispersion aureole was not observed but some thin anomalous stringers may be present. The lower parts of the Tokio formation may contain tuffaceous material.

CHAPTER 6

DISPERSION OF ELEMENTS IN THE DRAINAGE SYSTEM

6.1 ARKANSAS

6.11 Introduction

Drainage investigations were conducted mainly at the American Mine with limited comparative studies at the Black Lick Prospect.

Samples were collected from poorly and well sorted sediment, slime, black wad from the stream bed, moss and colluvial and alluvial banks. Limited studies were also made on concretions and heavy mineral samples separated from the active sediment.

During the wet season the rainfall may be torrential, and at these times the streams carry considerable quantities of detrital material. During the dry season, flow is minimal and there is deposition of the fines; indeed some of the smaller streams may dry completely. A variation in the nature of the sediment is therefore expected; however, this was not investigated.

6.12 Distribution of metal in stream sediments from background rocks

The variation in the Ni and Co contents in a limited number of local* and regional background sediments is presented on Fig. 6.1. Data is for the minus 80-mesh fraction. Insufficient analyses are available to allow a statistical interpretation

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*within 5 miles from the kimberlite.

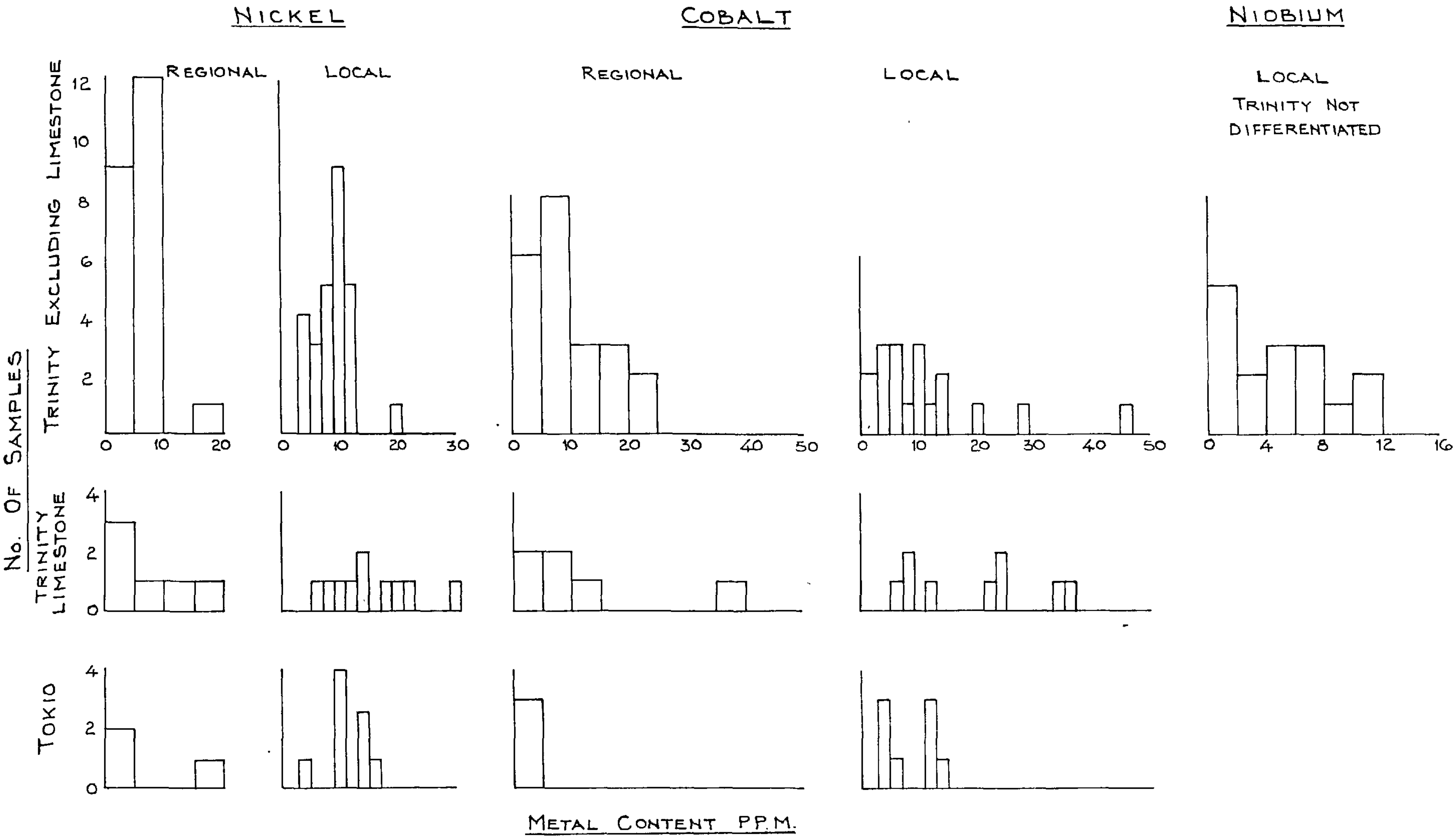

FIG. 6·1 THE VARIATION OF Ni, Co, AND Nb, CONTENTS IN THE MINUS 80-MESH FRACTION OF BACKGROUND STREAM SEDIMENTS ARKANSAS.

and the allocated thresholds (Table 6.1) have been derived by inspection.

Attention is drawn to the following points:

(1) Very different thresholds are obtained for Ni, Co and exMg over the different rock types. The difference is most marked between the limestone and sialic rocks.

(2) There appears to be an elevated local threshold for Ni in the minus 80-mesh fraction.

(3) The minus 10 plus 20-mesh threshold is higher than that of the minus 80-mesh for Ni and Co but lower for Nb.

(4) Cobalt tends to exhibit erratic high values.

6.13 Discussion

Greater concentrations of Ni, Co and exMg are recorded in all size fractions of the limestone than the sialic rocks but the greatest difference is observed in the coarser fractions, and to a lesser extent the minus 300-mesh material (Table 6.2).

The minus 10 plus 20-mesh fraction of sediments over the limestone is composed mainly of sesquioxide cemented quartz aggregates and concretions. Sesquioxide nodules are not common in sediment over the Trinity siltstone and rare in sediments over the Tokio formation (Table 6.3).

These concretions are considerably enriched in trace elements compared with the minus 10 plus 20-mesh fraction of stream sediments (Table 6.2). Thus the variation in threshold in the coarse fraction between the sialic rocks and the limestone is attributed to the relative abundance and composition of the nodules and aggregates.

Table 6.1 The threshold value (ppm) for Ni, Co, Nb, exMg and Cr in various size fractions of stream sediments collected over background rocks, Arkansas

	NICKEL				COBALT		
	-10+20	local -80	regional -80	-300	-10+20	local -80	regional -80
Tokio	20(11)	18(9)		16(3)	15(11)	15*(8)	5(3)
Trinity Limest.	60(9)	30(10)	20(6)	45(8)	70(9)	40*(9)	15*(5)
Trinity Siltst.	20(6)	13(27)	10(21)	30(8)	15(8)	30 (15)	25*(22)

	NIOBIUM			exMg		CHROMIUM
	-10+20	-80	-300	-10+20	-300	-10+20
Tokio	7 (11)			75(2)	260(4)	25(4)
Trinity Limest.	3.5(8)	12.5(18)	11(7)	150(9)	275(9)	25(5)
Trinity Siltst.	3.5(8)			40(5)	260(5)	25(5)

Number of samples in parenthesis

*erratic

Table 6.2 The variation of Ni and Co content with particle size in active sediment in streams draining local Trinity limestone and siltstones

Bedrock and Sample No.	Element	Metal Content ppm							
		Nodules		Size fraction (Mesh B.S.S.)					
		NH*	NL†	-10+20	-20+36	-36+80	-80+300	-300	-80
Limestone 550131	Ni	94	105	50	70		20	45	30
	Co	75	100	45	42				25
	exMg	480	280	136			70	120	90
Siltstone Upper Trinity 550122	Ni	60		13	11	9	14	18	15
	Co	18		15	19	13	88		45
	exMg			33	32	28	119	120	120
Siltstone 554385	Ni			19	14	9	8	8	8
	Co			11	1	<1	2	2	2

*NH S.G. >2.95
†NL S.G. <2.67

Table 6.3 Proportion of sesquioxide nodules in the minus 10 plus 20 mesh (B.S.S.) fraction of poorly sorted background stream sediments, Arkansas

Sample No.	Rock	Sesquioxide Nodules	Quartz, Sandstone and Shale Grains
550161	Tokio	1%	99%
550131	Trinity Limestone	91%	9%
550122	Trinity Siltstone	12%	88%

Table 6.6 The amounts of Ni extracted from the fine fractions of the stream sediment over the Trinity siltstone by various attacks

	Ni ppm			
	$KHSO_4$	Dith/cit.*	0.025% HNO_3	M/NH_4Ac
-80+200	5	2	2	0
-200+300	5	2	4	0
-300	16	5.5	6.5	1

*sodium citrate/sodium dithionite solution

It is seen on Table 6.4 that Mn, Co and Ba are concentrated in the light (S.G.<2.67) nodules (dominantly aggregates); and Fe, Cr, V, Ni and exMg in the heavy (S.G.>2.95) concretions (often possessing a concentric structure).

Most of the Co, Mn, Fe, V and Ba is extracted from the 'light' nodules with sodium citrate/dithionite solution. This attack is thought to be specific for metal associated with secondary sesquioxides* (Chapter 3). Thus it is suggested that the bulk of these metals, together with lesser amounts of Ni, Cr and Ti are contained in the sesquioxide cement. Smaller amounts of metal are extracted from the 'heavy' nodules, possibly due to some encapsulation of heavy detrital minerals.

Whilst nodules in the Trinity drainage probably originate in the soils, nodules in the limestone drainage may have accumulated either by:

(1) precipitation of metal from stream waters due to the high pH (6.9 to 7.8), or

(2) erosion of bank material containing residual accumulations of nodules.

Unfortunately, soil profiles over the limestone were not available to the writer and the source of the nodules could not be differentiated.

Considerably higher amounts of Ni, Co, Mn and Cr† are extracted using the emission spectrograph than with a $KHSO_4$ attack (Table 6.5). Since the $KHSO_4$ attack is very effective on weathered minerals (Harden and Tooms, 1964) it is suggested that a high proportion of metal in the coarse fraction of the Trinity siltstone is present in resistant primary minerals, probably as multi-

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*Loosely held forms of metal, i.e. sorbed on clay minerals etc. will also be attacked.

†alkaline fusion.

Table 6.4 The content of selected elements in light* and heavy** sesquioxide nodules separated from sediment over the Trinity limestone; and the proportion of metal extracted with sodium citrate-dithionite solution.

	Metal content ppm (unless stated otherwise)									
	Ni	Co	Cr	Fe%	Mn	Ba	V	Ti	Sr	Nb
Nodules S.G.<2.67	130	300	60	10.0	>1%	4000	160	1600	<30	4.0
Residue	85	30	60	0.82	160	2000	30	1000	100	6.6
% extracted with dithionite†	55	93	31	95	>99.9	66	87	14	0	0
Nodules S.G.>2.95 <3.27	200	130	200	>30	4000	800	400	1300	<30	4.0
Residue	130	60	300	25	1300	1000	400	2000	40	16.0
% extracted with dithionite†	40	76	22	<53	83	35	48	20	0	0

Data on -10+80 mesh fraction, spectrographic analyses (except Nb)

* S.G. <2.67
**S.G. >2.95 <3.27
†sodium citrate-sodium dithionite solution.

Table 6.5 The amounts of Ni, Co, Fe, Mn and Cr extracted from the -10+20 mesh (B.S.S.) fraction of stream sediments over the Trinity country rock by various attacks.

Rock type and Sample No.	Attack	Metal content ppm (unless stated otherwise)				
		Ni	Co	Fe%	Mn	Cr
550122 and 550123 Trinity Siltstone	Spec.	40	50	2.48	1000	60
	$KHSO_4$	15	15	3.12	250	25*
	Dith/cit.	9				
	$M.NH_4$ Ac	1				
550128 Trinity Limestone	Spec.	85	160			100
	$KHSO_4$	64	66			25*

*alkaline fusion

mineral grains. However, appreciable proportions of Ni are relatively loosely held as seen from the amounts extracted by the relatively weak attacks.

It is noticeable that only a small proportion of the Cr is extracted with an alkaline fusion. The reason for this is not understood since this attack is thought to be total.

The amounts of Ni extracted from the fine fraction of the Trinity formation by various attacks are illustrated on Table 6.6. It is seen that about 40% of the metal is extracted with very weak nitric acid. Since this attack is not thought to attack secondary sesquioxides (Taylor*, pers. comm.), it is suggested that a high proportion of the background Ni occurs in a loosely held form, possibly associated with clay minerals or semi-stable secondary silicates. It is interesting to note that no additional metal was extracted with dithionite† solution, thus occurrence with sesquioxides in the fine fractions is considered negligible.

Comparable data is not available for the Trinity limestone.

Markedly higher concentrations of Co occur in the poorly sorted compared with the well sorted sediment (Table 6.7). Most of this Co is present in the minus 80 plus 300-mesh fraction (Table 6.2). This is thought to be due to occurrence in black (Mn) sesquioxide nodules which are common in this fraction. Presumably these nodules are 'too light' to concentrate in the well sorted sediment. Evidence in support of this suggestion is given by the substantial proportion of Co extracted from the minus 80 plus 300-mesh size with sodium citrate/dithionite, overleaf:

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*Imperial College.

†sodium citrate-sodium dithionite solution.

Table 6.7 Comparison of Co and Ni contents of poorly and well sorted sediments over the background Trinity formation, Arkansas.

Sample No.	Rock Type	Cobalt ppm poorly sorted	Cobalt ppm well sorted	Nickel ppm poorly sorted	Nickel ppm well sorted
550122/123	Siltstone	45	10	5	5
550125/124	Siltstone	28	5	5	5
550127/128	Limestone	25	8	15	13

Table 6.8 The variation of Nb content with particle size in sediment over the Trinity formation, Arkansas.

Sample No.	Rock Type	Niobium ppm -10+20	-20+36	-36+80	-80+200	-200+300	-300
550125	Siltstone	1.6	<0.8	0.8	14.4	18.4	16.0
550122	Siltstone	3.6	5.6	5.6	9.6†		8.0
550159	Limestone	2.4	2.4	4.0			
550128	Limestone		0.8*		0.8†		0.8

*-10+80 mesh
†-80+300 mesh

Sample Number	Cobalt ppm KHSO$_4$	citrate/dithionite	0.025% HNO$_3$
550122 (-80+300 mesh B.S.S.)	88	45	12

It was suggested in the previous chapter that some tuffaceous material may be present in the lower Tokio formation near the American Mine. This is thought to be the reason for the slightly higher Ni and Nb thresholds of the Tokio sediment compared with the Trinity siltstone. Similarly, the slightly higher local threshold for Ni may be due to residual concentration of metal in the northward flowing obsequent streams which drain(ed) the Tokio formation.

6.14 Distribution of Metal Downstream from Kimberlite

6.141 In stream sediments

In addition to the rare earths, Hf, Te, I and In which are contained in abnormal contents in sediment downstream from kimberlite (Chapter 9), anomalous concentrations of Ni, Co, Sr, Ba, Mn, Cr, Fe, Ti and V are also recorded. However, only Ni, Sr and Cr are present in anomalous amounts compared with sediments over the Trinity limestone (Table 6.9).

From the elements mentioned above, Ni, Co, Cr, Nb and exMg were selected for investigation since they represent a wide range of mobilities and have good contrasts. Additional limited data was also obtained for Mn, Fe and P. Exchangeable Mg was selected in preference to total Mg since this is the dominant form deposited from ground waters draining kimberlite. Strontium was not further investigated owing to analytical limitations.

Table 6.9 Contrast between anomalous and background sediment for selected elements at the American Mine, Arkansas. (Data on minus 10 plus 20 mesh (B.S.S.) fraction.)

	Sample No.	Rock Type	Pb	Ga	V	Cu	Ti	Ni	Co	Mn	Cr	Fe%	Ba	Sr
metal content ppm (unless otherwise stated)	556501/542	Anomalous sediment	40	4	100	40	2000	300	160	3000	130	2.66	1000	200
	550122	Background siltstone	40	4	60	30	850	40	50	1000	60	2.28	300	30
	550128	Background limestone	200	5	130	40	2000	85	160	8000	100	14.7	2000	30
contrast		with siltstone	1	1	1.7	1.3	2.4	7.5	3.2	3	2.2	1.2	3.3	6.7
		with limestone	<1	<1	<1	1	1	3.5	1	<1	1.3	<1	<1	6.7

Sn, Bi, <5 ppm; Mo <2 ppm; Ag <0.2 ppm; Zn, sialic seds. <50 ppm; limestone 200 ppm.

Spectrographic determinations.

With the exception of Cr, higher metal contents are recorded in the poorly sorted compared with the well sorted anomalous sediment at the American Mine (Table 6.10). This occurs in both the plus and minus 80-mesh fractions and is irrespective whether the sample is collected near or some distance downstream from the kimberlite. Similarly, maximum contrast, including Cr, is observed in the poorly sorted sediment. Accordingly, unless otherwise specified all the following data on stream sediments concerns the poorly sorted material.

Size distribution studies (Fig. 6.2) of anomalous sediment from the American Mine and Black Lick Prospects indicate Ni, Co, Fe, Mn, Cr and exMg and possibly Nb to be concentrated in the coarsest fractions. It is noticeable that not only are Cr and exMg concentrated in a slightly less coarse fraction but they are also concentrated in the minus 300-mesh fraction. Similarly maximum contrast is observed in the minus 10 plus 20-mesh fraction both near the kimberlite and for some distance downstream (Table 6.12).

Maximum contrast for Ni is given by the $KHSO_4$ attack (Table 6.11), both near to and 3200 feet downstream from the kimberlite.

The distribution of Ni, Co, exMg, Nb and Cr in various size fractions of the poorly sorted sediment in the American Mine drainage is presented as "worm" diagrams on Figs. 6.3 to 6.12. Comparative data for Ni and Co in the Black Lick drainage is given on Fig. 6.13. A summary of the dispersion features of the elements, and the distance downstream to which anomalous concentrations of the elements may be detected are presented on Table 6.13 and 6.14, respectively.

Inspection allows the following conclusions:

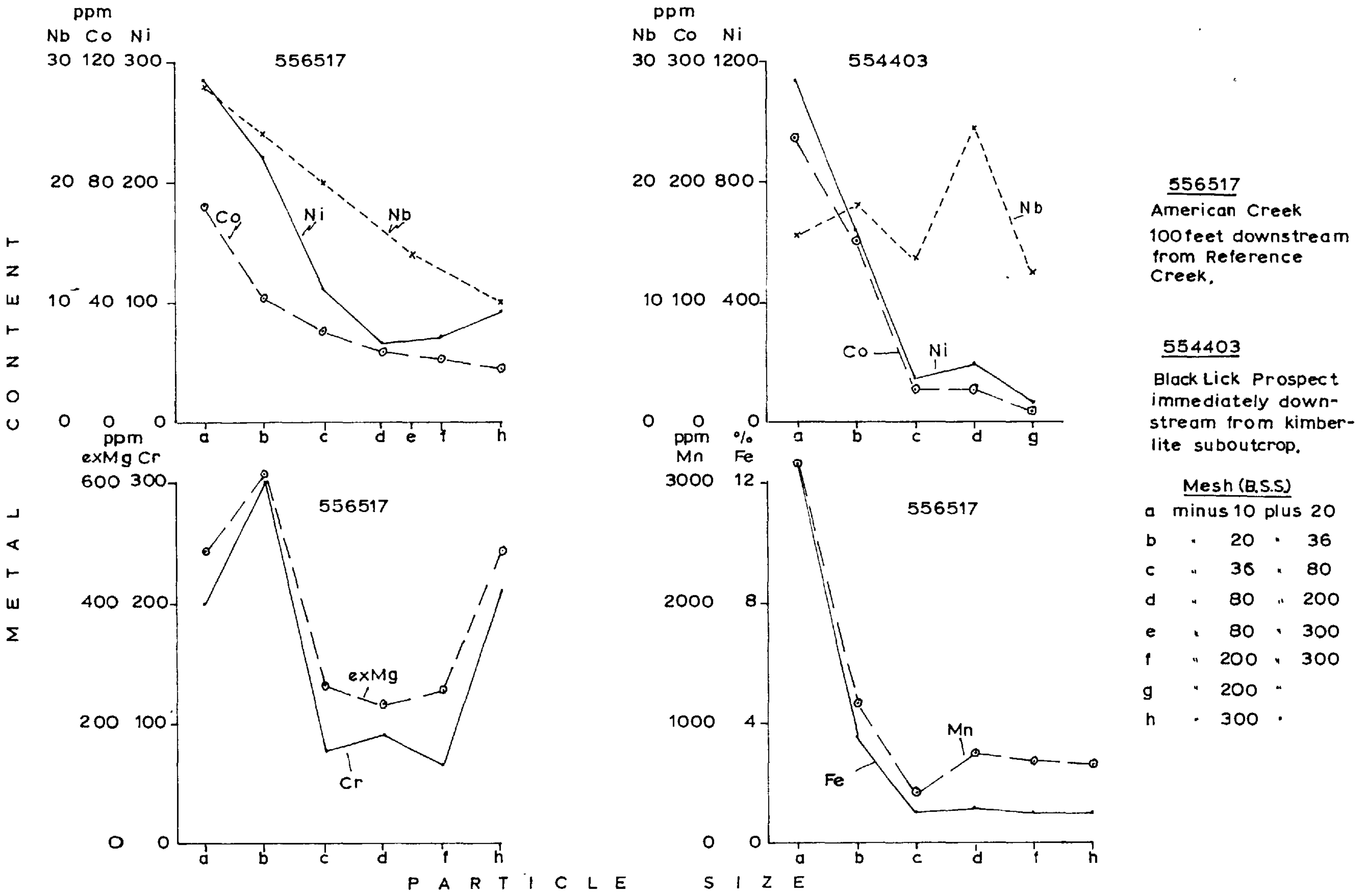


FIGURE 6·2 : The variation of Nb, Co, Ni, $Fe_n^{Cr, ex Mg}$ and Mn content with particle size in anomalous sediment, Arkansas.

Table 6.10 Comparison of the Ni, Co, Cr and Nb contents of poorly and well sorted sediment at selected locations in American Creek, American Mine.

	700 feet upstream from Reference Creek				20 feet downstream from from Reference Creek				3200 feet downstream from Reference Creek			
Element and contrast	-10+80		-80		-10+80		-80		-10+80		-80	
	poor*	well†	poor	well	poor	well	poor	well	poor	well	poor	well
Ni ppm	20	22	15	10	250	170	80	45	25	26	17	12
contrast					12½	8	5.3	4.5	1.3	1.2	1.1	1.2
Co ppm	12	9	10	12	60	18	10	10	16	18	4	4
contrast					5	2	1	0.8	1.3	1.3	0.4	0.3
Cr ppm	35	100	100	70	300	680	130	90	<10	<10	125	25
contrast					8.5	6.8	1.3	1.3	<1	<1	1.3	0.4
Nb ppm	4	3.2	6	4	24	12	12	4	2.4	0.8	2.4	0.8
contrast					6	4	2	1.3	0.6	0.03	0.6	0.03
Mg ppm	540	850	800	1170	14800	2600	7200	2180	540	800	740	720
contrast					27	3	9	2	1	1	1	0.6

contrast is in the ratio between the metal content in samples downstream from Reference Creek to that in the background sample 700 feet upstream from Reference Creek.

*poor = poorly sorted sediment
†well = well sorted sediment

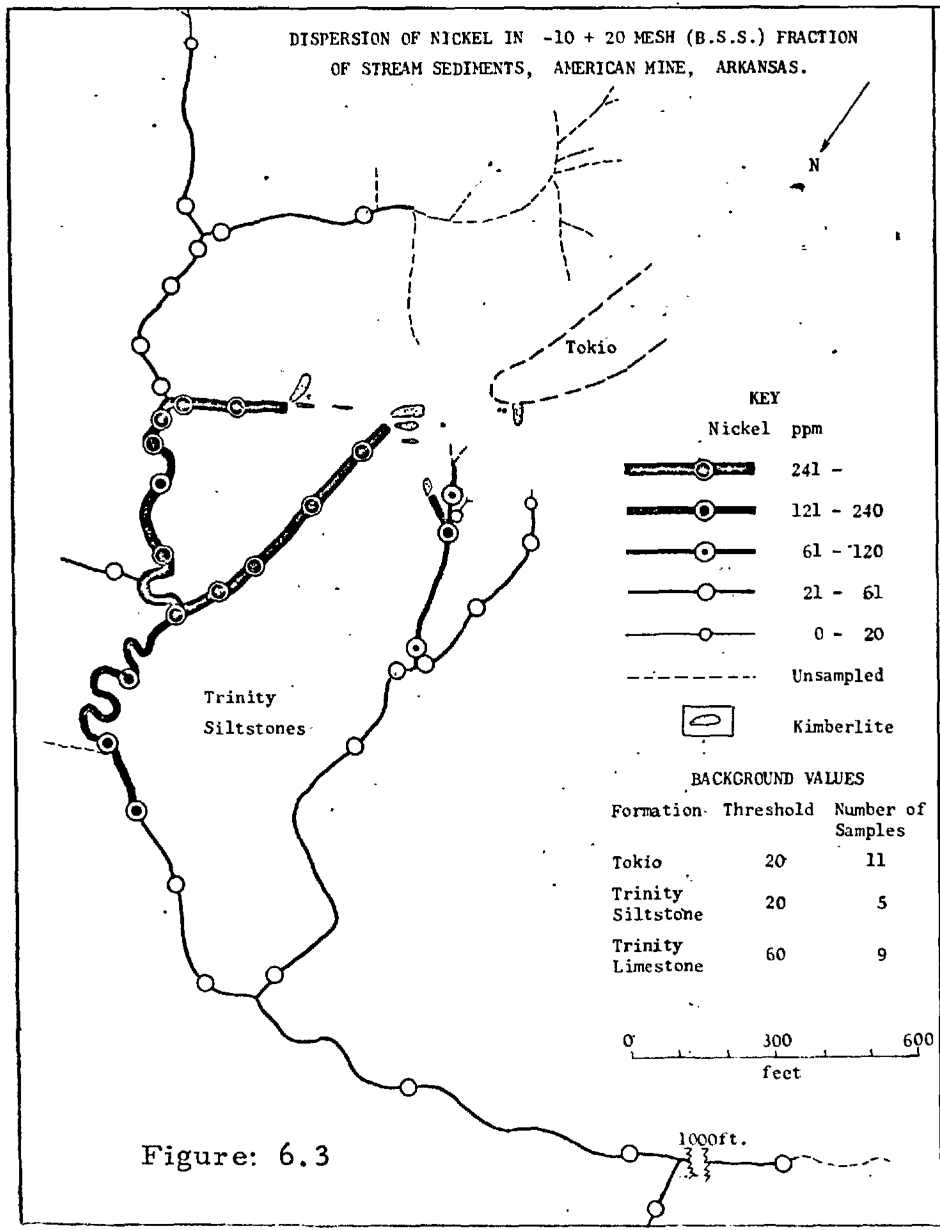
Table 6.11 The amounts and contrast of Ni extracted from anomalous sediment by various attacks, American Creek, Arkansas.

Distance from source		Spec.	$KHSO_4$	dith/cit.	0.025M HNO_3	M/NH_4Ac
220 feet (556517)	Ni ppm	300	268	140	25	2.5
	contrast with siltstone	7.5	17	15.5	5	<1
	contrast with limestone	3.5	4	2.8		
3200 feet (556751)	Ni ppm		55	28	6	0
	contrast with siltstone		3.7	3	1.2	<1
	contrast with limestone		<1	<1		
Ni content of background sediment	siltstone (550122)	40	15	9	5	6.2
	limestone (550128)	85	64	50		

data on -10+20 mesh fraction

Table 6.12 Contrast between anomalous and background sediment for selected ranges in particle size, American Creek

	Distance downstream from Reference Creek	Contrast						
		-10+20	-20+36	-36+80	-80+300	-300	+80	-80
Nb	100 ft	5	5	2	2	2½	4	2
Ni		11	9	10	7	3	10	8
exMg		14	18	9	3	4	14	3
Co		5	2	1½	2½	1½		2½
Cr		10	15		2½	5		
Nb	3200	1	<1	<1	<1	<1		<1
Ni		3	<1	1	1	<1	1	1½
exMg		2				<1		
Co		2½				<1		1
Cr		2	2½			1		

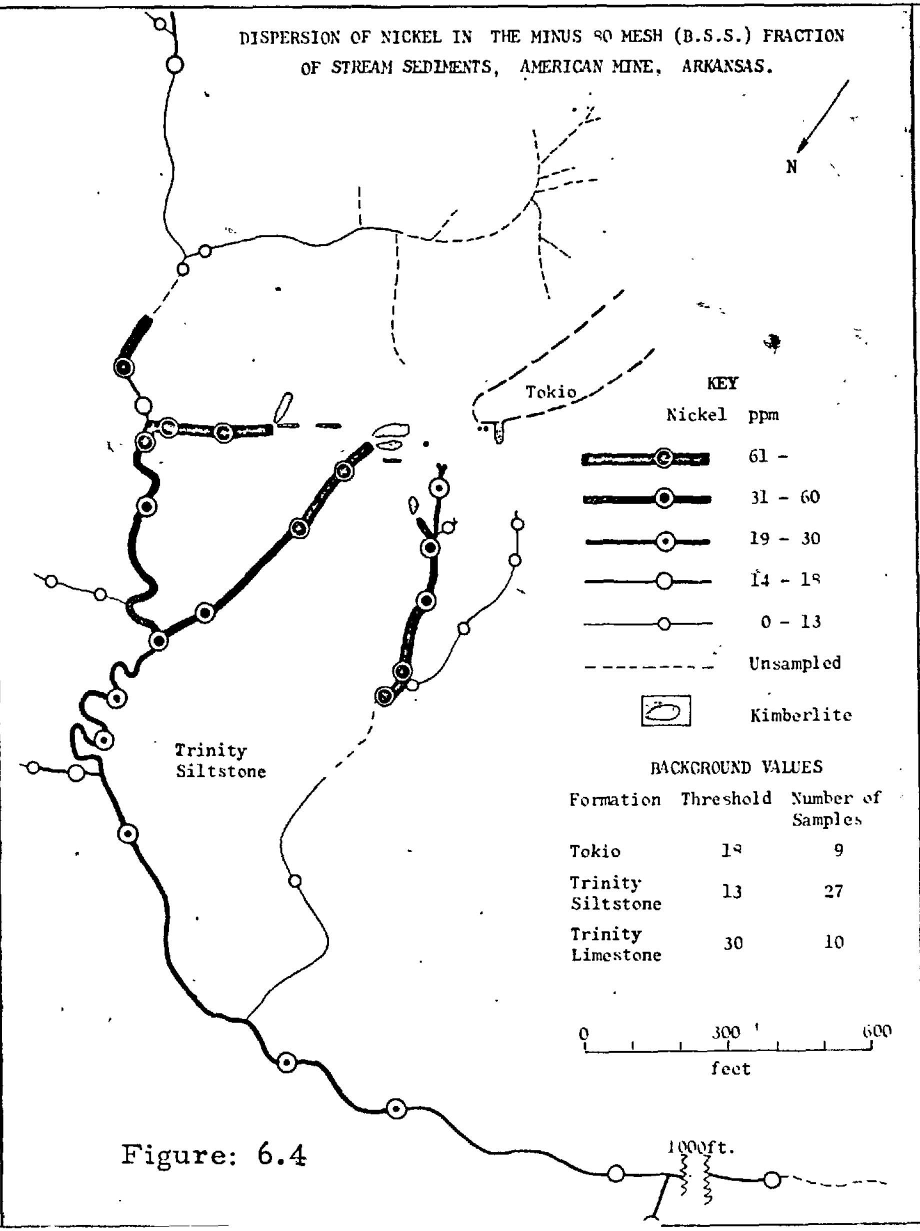


DISPERSION OF NICKEL IN -10 + 20 MESH (B.S.S.) FRACTION OF STREAM SEDIMENTS, AMERICAN MINE, ARKANSAS.

BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	20	11
Trinity Siltstone	20	5
Trinity Limestone	60	9

Figure: 6.3

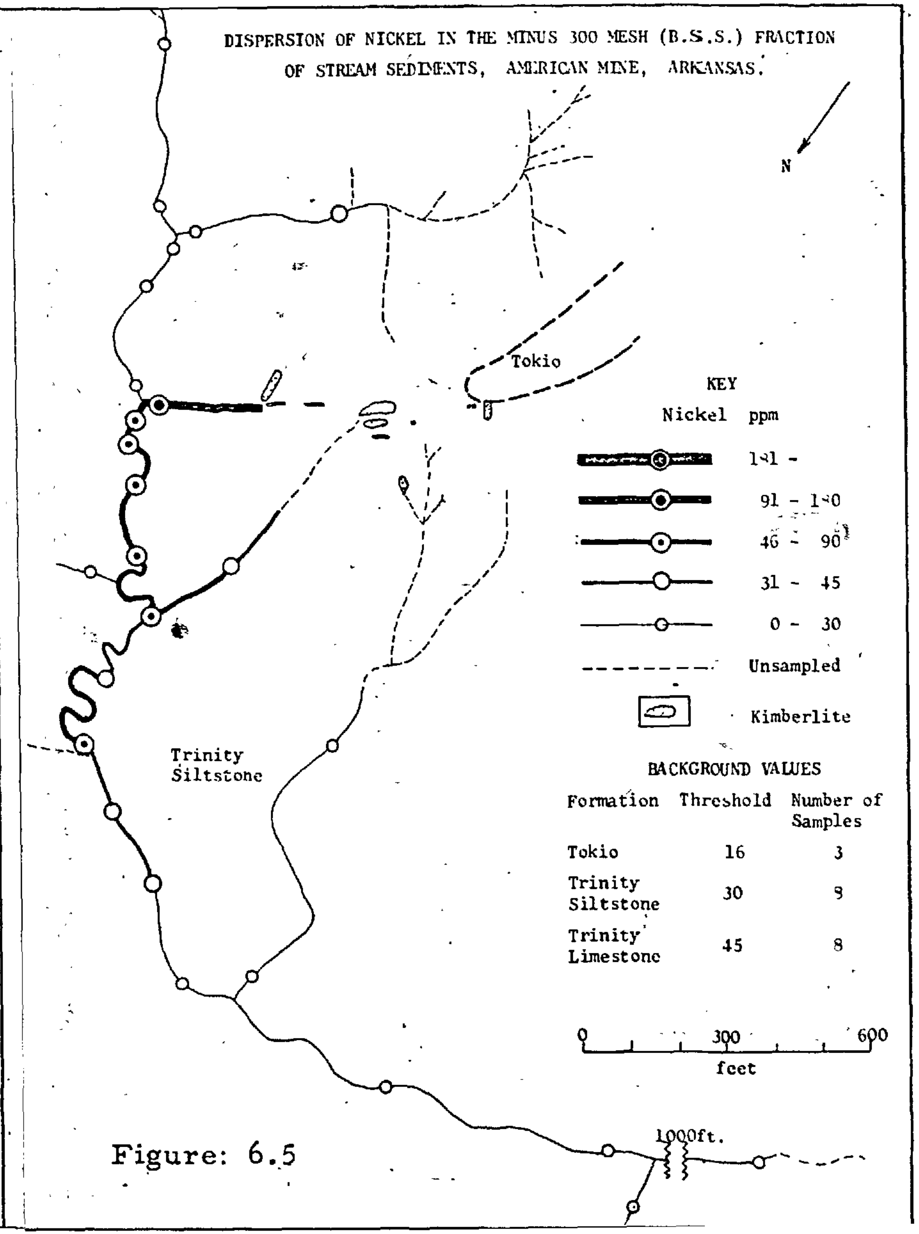


DISPERSION OF NICKEL IN THE MINUS 80 MESH (B.S.S.) FRACTION OF STREAM SEDIMENTS, AMERICAN MINE, ARKANSAS.

BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	18	9
Trinity Siltstone	13	27
Trinity Limestone	30	10

Figure: 6.4

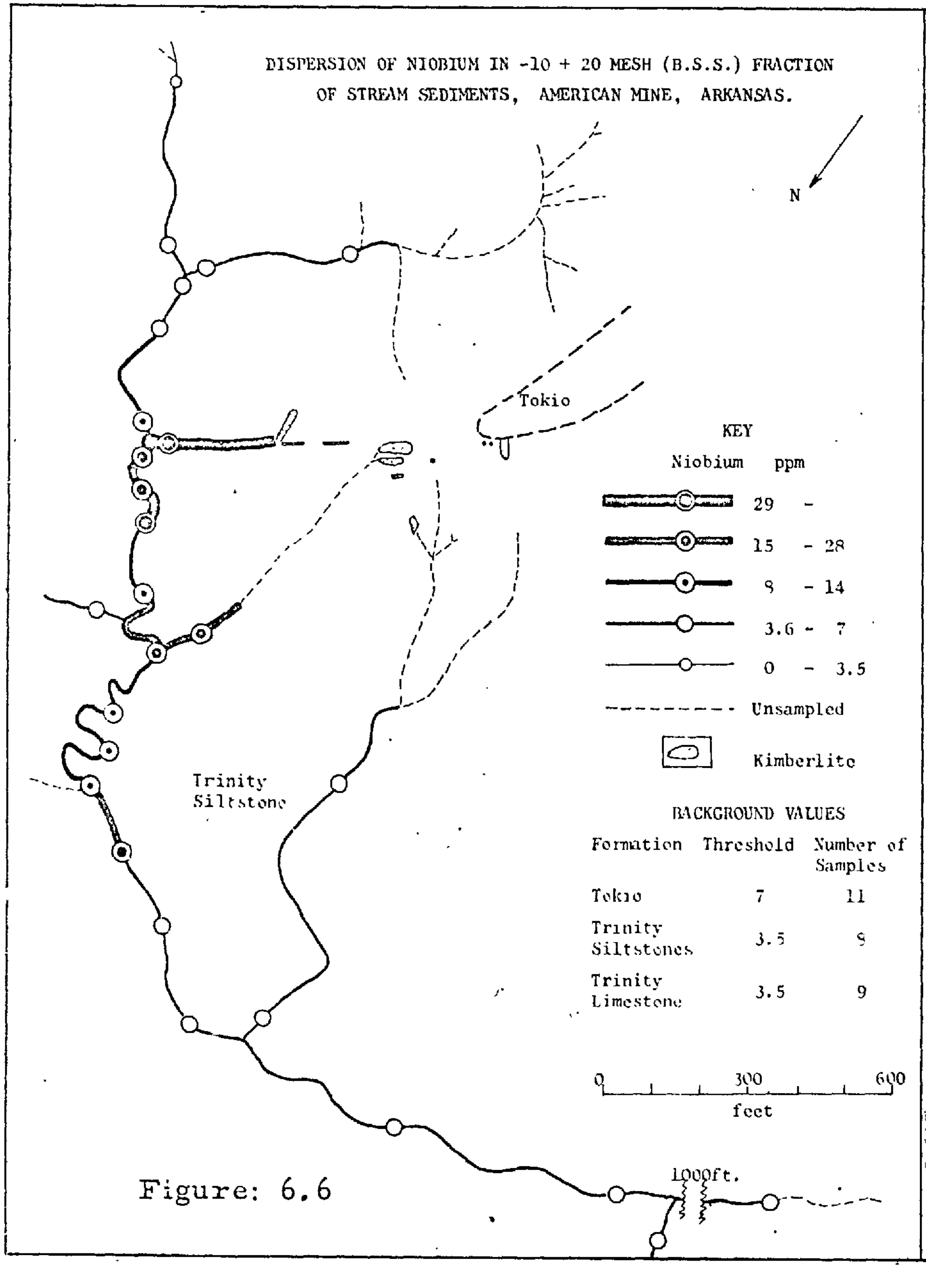


DISPERSION OF NICKEL IN THE MINUS 300 MESH (B.S.S.) FRACTION OF STREAM SEDIMENTS, AMERICAN MINE, ARKANSAS.

BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	16	3
Trinity Siltstone	30	8
Trinity Limestone	45	8

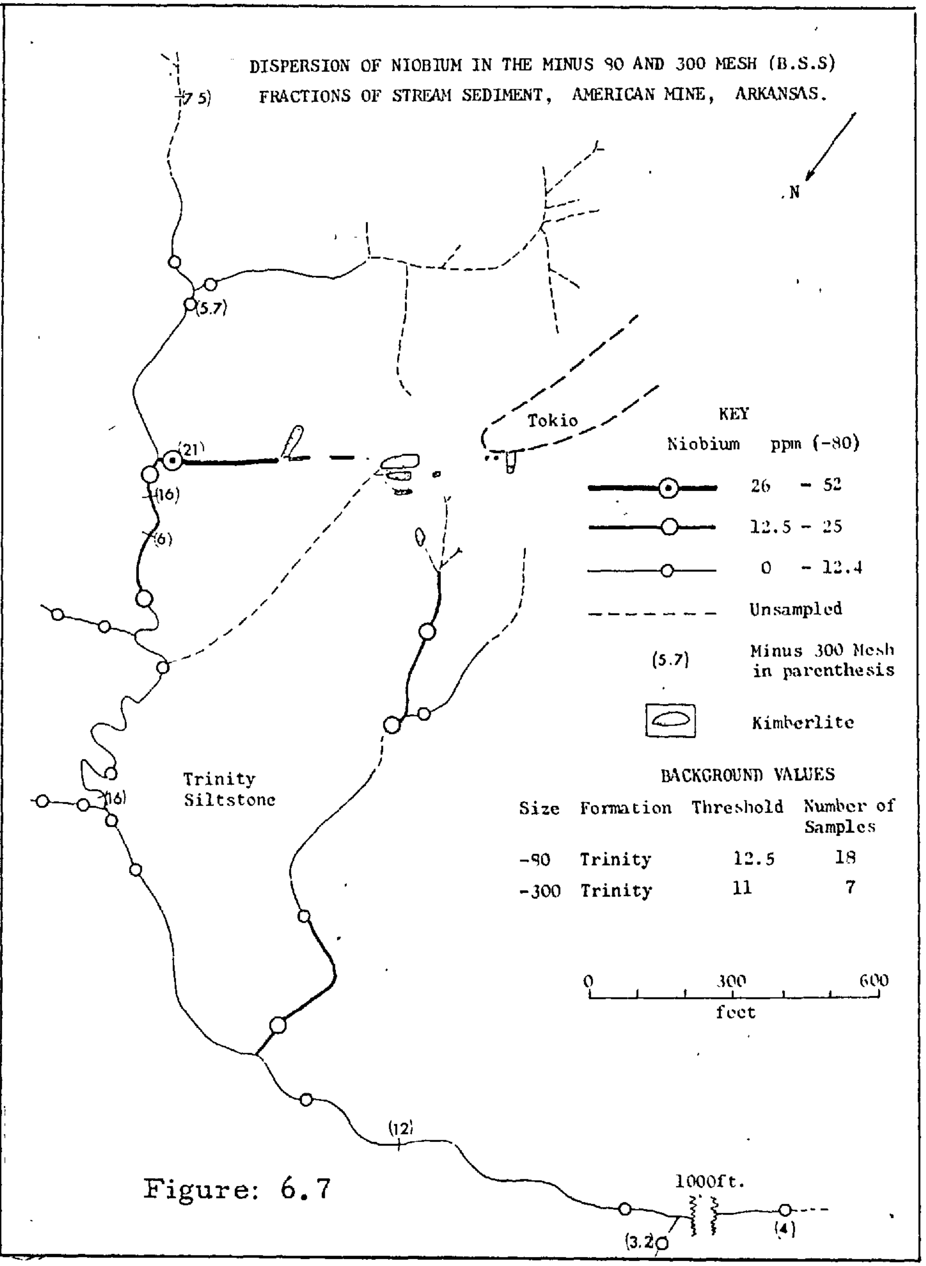
Figure: 6.5


DISPERSION OF NIOBIUM IN -10 + 20 MESH (B.S.S.) FRACTION OF STREAM SEDIMENTS, AMERICAN MINE, ARKANSAS.

BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	7	11
Trinity Siltstones	3.5	9
Trinity Limestone	3.5	9

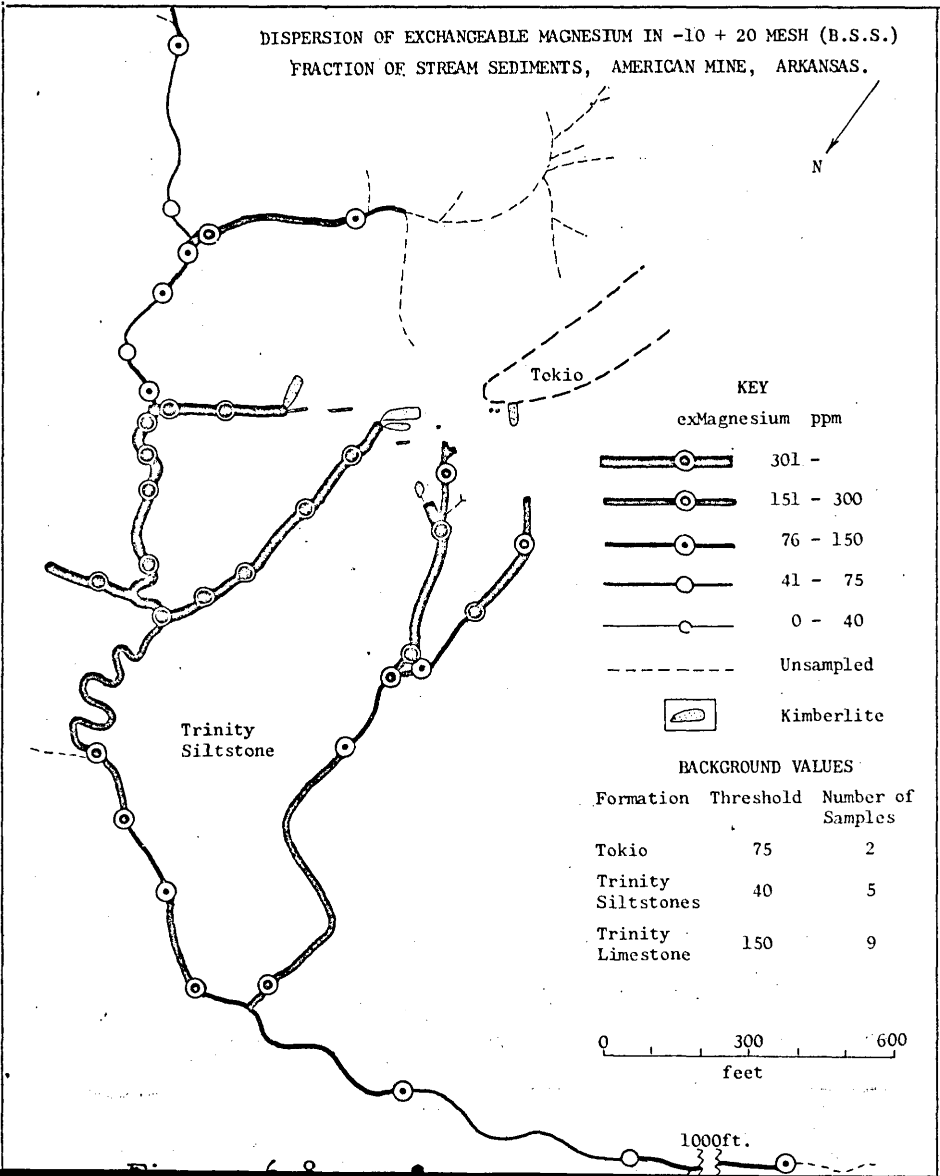
Figure: 6.6


DISPERSION OF NIOBIUM IN THE MINUS 80 AND 300 MESH (B.S.S) FRACTIONS OF STREAM SEDIMENT, AMERICAN MINE, ARKANSAS.

BACKGROUND VALUES

Size	Formation	Threshold	Number of Samples
-80	Trinity	12.5	18
-300	Trinity	11	7

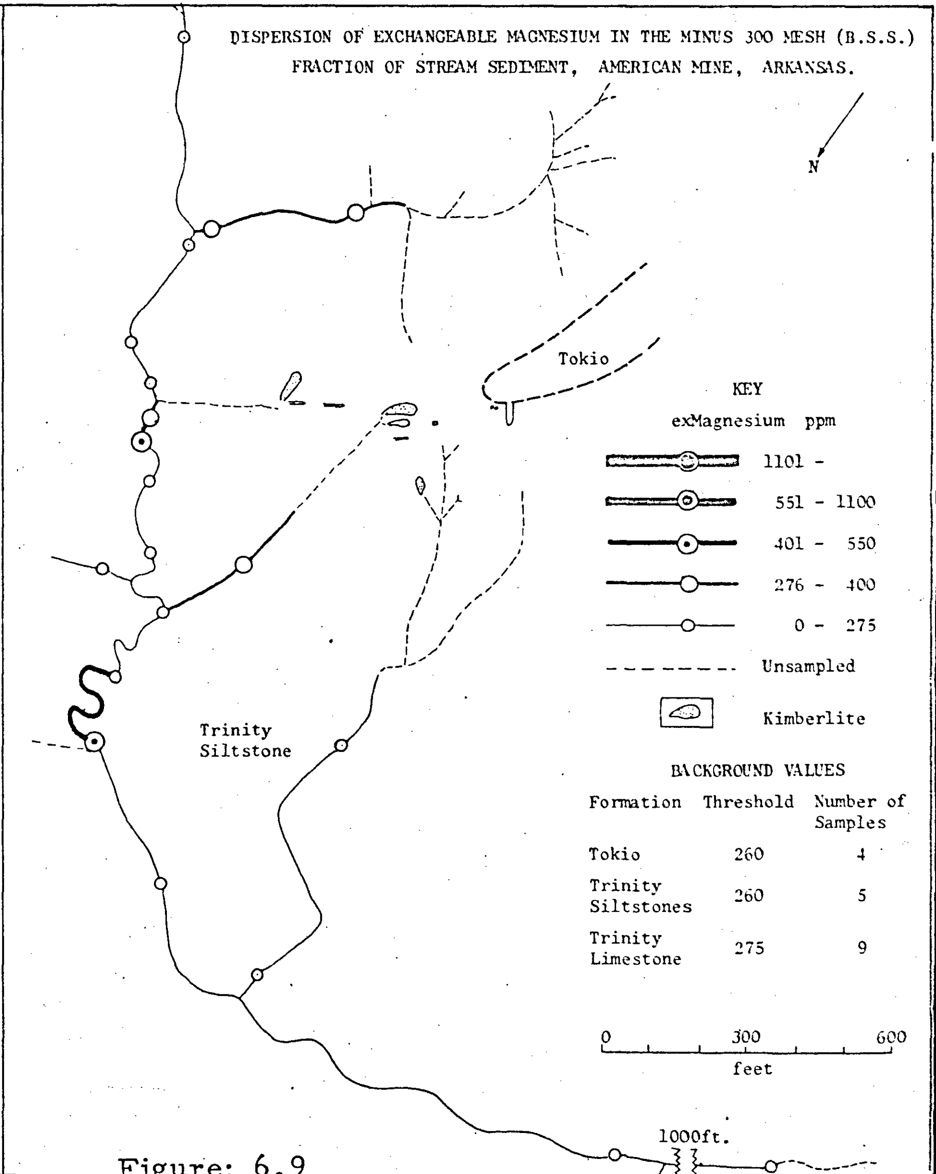
Figure: 6.7



BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	75	2
Trinity Siltstones	40	5
Trinity Limestone	150	9

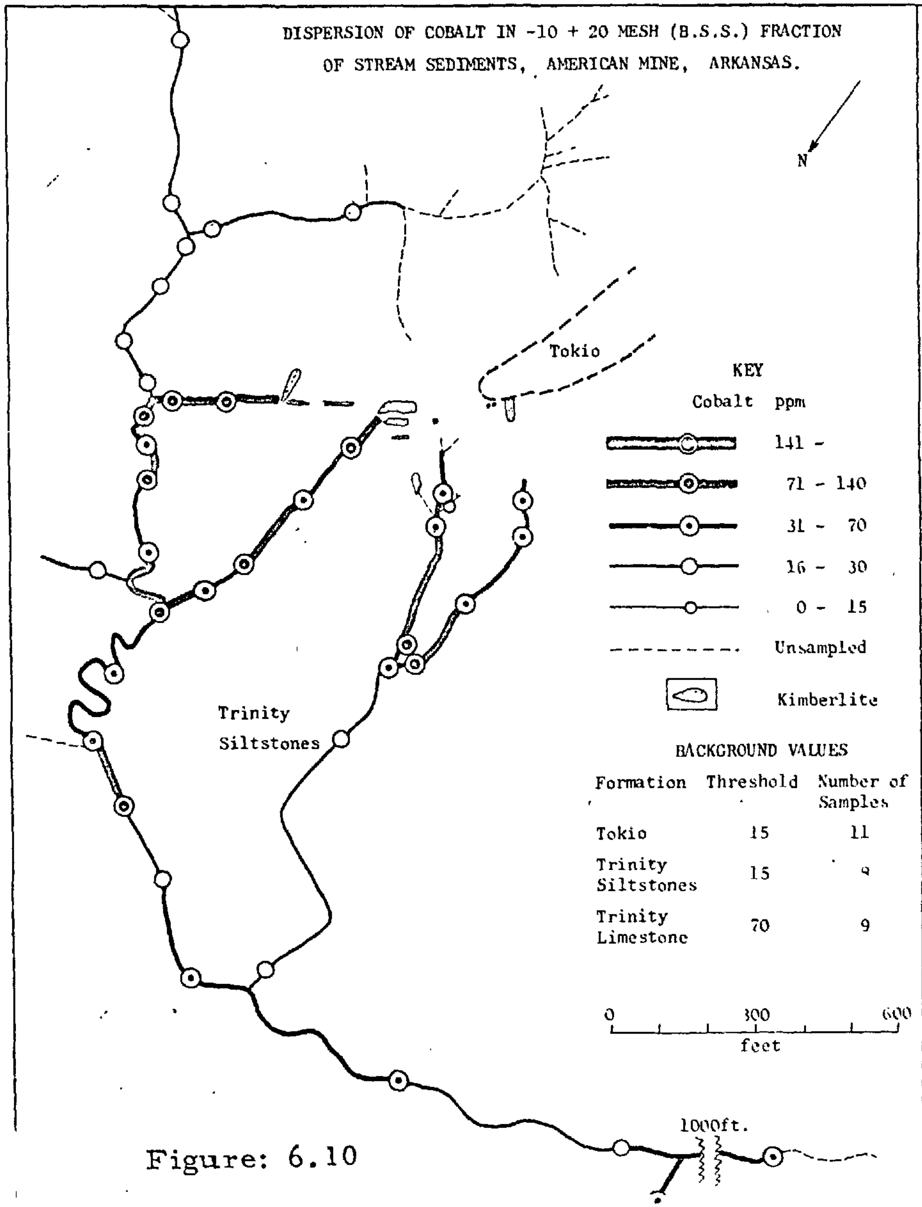
Figure 6.8



BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	260	4
Trinity Siltstones	260	5
Trinity Limestone	275	9

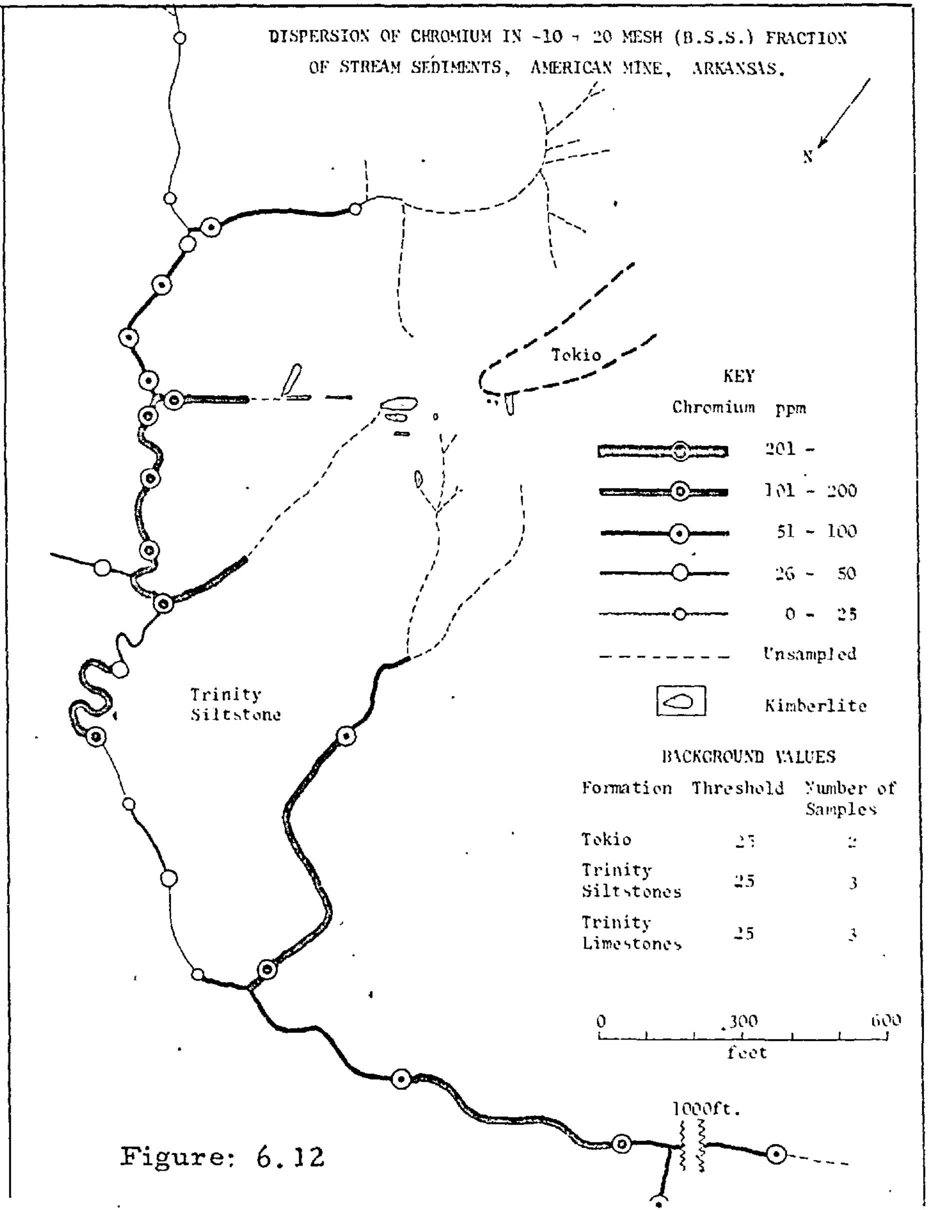
Figure: 6.9



BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	15	11
Trinity Siltstones	15	9
Trinity Limestone	70	9

Figure: 6.10

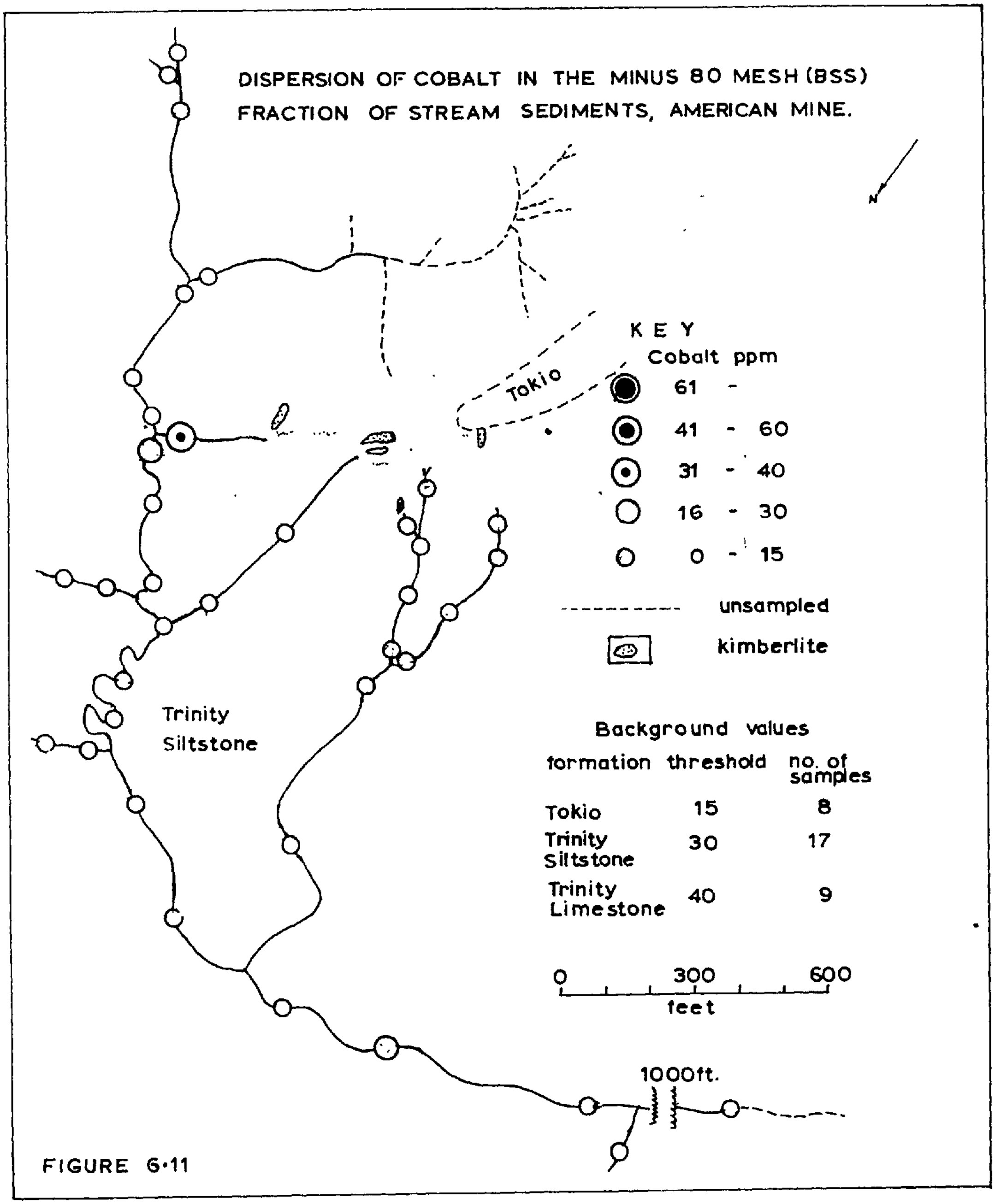


BACKGROUND VALUES

Formation	Threshold	Number of Samples
Tokio	25	2
Trinity Siltstones	25	3
Trinity Limestones	25	3

Figure: 6.12

DISPERSION OF COBALT IN THE MINUS 80 MESH (BSS) FRACTION OF STREAM SEDIMENTS, AMERICAN MINE.



Background values

formation	threshold	no. of samples
Tokio	15	8
Trinity Siltstone	30	17
Trinity Limestone	40	9

FIGURE 6·11

FIGURE 6·13 DISTRIBUTION OF Ni AND Co IN THE MINUS 80 MESH, AND Ni, Co AND Nb IN SELECTED MINUS 10 PLUS 20 MESH (BSS) FRACTIONS OF STREAM SEDIMENT FROM THE BLACK LICK DRAINAGE.

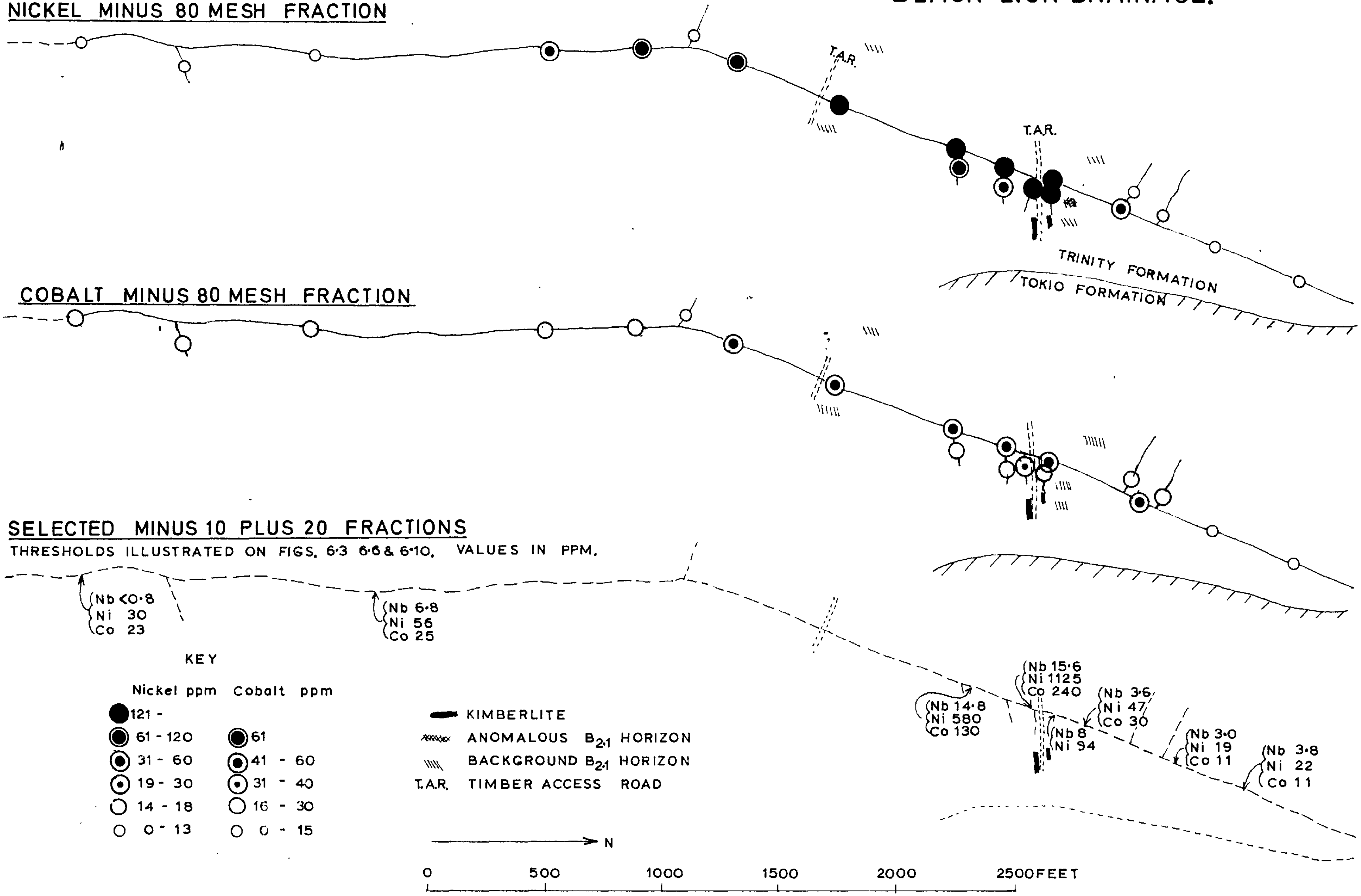


Table 6.13 Summary of the main features of the dispersion patterns for various elements in stream sediments at the American Mine, Arkansas

	minus 10 plus 20-mesh	minus 80-mesh	minus 300-mesh
Cr	Sharp cut off upstream from Valley Creek. Erratic rapid initial fall off of anomalous values builds up to highly anomalous values 2200 feet downstream. Anomalous concentrations of metal in flood plain tributaries.		
Nb	Relatively sharp cut off. Rapid initial fall off to barely anomalous values extending from 1000 to 3200 feet downstream. Barely anomalous concentrates in West Creek. Anomalous concentrations of metal in flood plain tributaries.	Anomalous concentrations confined to a few hundred feet from kimberlite.	Erratic and generally restricted to streams very close to kimberlite.
Co	Sharp decrease in anomaly upstream from Reference Creek but no cut off. Erratic and slow overall fall off downstream. Anomalous concentrations in flood plain tributaries.	Extremely restricted anomalous concentrations confined to Reference Creek.	
Ni	Sharp decrease in anomaly upstream from Reference Creek and relatively sharp cut off. Rapid initial fall off, then little difference from 1000 to 3200 feet downstream. Anomalous concentrations in flood plain tributaries.	Anomaly restricted to those streams draining kimberlite, although some flood plain tributaries anomalous Barely anomalous values over 2200-3200 feet.	Anomaly restricted to streams draining kimberlite.
exMg	Highly anomalous concentrations spread over a considerable area. Rapid fall off upstream from Reference Creek. Strongly anomalous concentrations in Valley Creek. Relatively slow fall off downstream. Anomalous concentrations in flood plain tributaries.		Anomalous values generally restricted in distribution to those parts of the stream directly draining kimberlite.

Table 6.14 Maximum distance downstream in which anomalous concentrations of elements have been detected in various size fractions of poorly sorted sediment from the American Mine and Black Lick drainage systems.

		distance (feet)										
		Ni ppm			Nb ppm			exMg ppm		Co ppm		Cr ppm
	Threshold taken	-10+20	-80	-300	-10+20	-80	-300	-10+20	-300	-10+20	-80	-10+20
American Creek	Trinity limestone	800	500	700	>3200	350	1700?	1200	120	500	<20	>3200
	Tokio arenites	>3200	1700		800			1700	120	>3200	<20	>3200
	Trinity siltstones	>3200	>3200	1000	>3200	350	1700?	>3200	120	>3200	<20	>3200
Black Lick Prospect	Trinity limestone		2200?								1400	
	Tokio arenites	>4000	2200?							>4000	>4000	
	Trinity siltstones	>4000	2200?							>4000	1400	

Distances at the American Mine are measured from the confluence of Reference and American Creeks.

(1) Longest anomalous dispersion trains are recorded in the minus 10 plus 20-mesh fraction and shortest in the minus 300-mesh material.

(2) In areas of limestone, where anomalous Ni, Co and exMg trains are somewhat curtailed, anomalous Nb and Cr trains are unaffected. However, close to the Tokio formation shorter anomalous Nb patterns would occur.

(3) Anomalous concentrations of the determined elements are detected in the minus 10 plus 20-mesh fraction of sediment from tributaries in the American Creek flood plain. Generally, these anomalies are not recorded for Ni in the minus 300-mesh fraction.

(4) Barely anomalous concentrations of metal occur in the minus 80 and minus 300-mesh fractions of sediment from Valley Creek.

(5) Chromium and Nb give the sharpest "cut-offs" and exMg the broadest.

(6) Anomalous concentrations of Co are not observed in the minus 80-mesh fraction of sediment from American Creek. However, an appreciable anomalous train occurs downstream from the Black Lick Prospect.

6.142 Dispersion in nodules

The two types of nodule recognised in residual soils over the ultrabasic rocks are also recorded in the kimberlite drainage (Table 6.15). The black nodules are soft porous spheres, consisting of dark, Mn rich, sesquioxide cemented quartz aggregates, with a specific gravity similar or slightly less than quartz. In contrast, the Fe nodules are relatively hard, compact, dense

Table 6.15 Composition of highly anomalous sediment from the Black Lick Prospect, Arkansas.

Fraction	-10+80 mesh	% of total	-80+300 mesh	% of total
S.G. <2.67	Black spongy nodules and aggregates	21	Quartz, sandstone, shale etc.	4.1
	Quartz, sandstone, shale etc.	14	Black spongy nodules	0.25
			Brown Fe rich nodules	0.25
			Unidentified	0.5
S.G. 2.67 -2.95	Black spongy MnO_2 nodules	18	Black MnO_2 nodules	0.52
	Brown Fe nodules	14	Fe nodules	0.26
	Quartz, sandstone etc.	8	Unidentified	0.52
S.G. >2.95	Compact Fe concretions	16.8	Fe concretions	0.75
	Magnetite octahedra	0.2	Magnetite	0.45
			Rutile	0.15
			Unidentified	0.15

(S.G.2.95 to 3.27), and often possess a concentric structure. Hybrid types are common.

Nickel and Co are considerably concentrated in the Mn nodules and Cr in the Fe concretions. Niobium is not concentrated in either type (Table 6.16).

Since coarse Mn nodules are rare in the background sediment, including that over limestone, it is possible that enhanced anomalous trains of Ni and Co may be obtained by analysis of the S.G.<2.67 part of the minus 10 plus 20-mesh fraction. This was not investigated.

The metal content of 'heavy' nodules downstream from the American Mine Kimberlite is presented on Table 6.17. It can be seen that only for Cr are outstanding anomalous concentrations observed for more than 3200 feet downstream. It is possible, therefore, that analysis of the S.G.>2.95 fraction of the minus 10 plus 20-mesh fraction may provide extended anomalous Cr trains. This was not further investigated.

6.143 Dispersion in heavy mineral concentrates

Heavy mineral concentrates (S.G.>3.27) were separated from the minus 80-mesh fractions of sediment from the Trinity Siltstone (background), and from the Black Lick drainage both near to the kimberlite and 3000 feet downstream. Analyses were made using the emission and mass spectrographs.

The mass spectrograph results are tabulated and discussed in Chapter 9. From the emission spectrograph results (Table 6.18) it can be seen that only Cr, Ni, Pb and Zn provide anomalous trains in excess of 3000 feet. It is possible, therefore, that prolonged anomalous drainage trains may occur in the

Table 6.16 Distribution of Ni, Co, Nb and Cr in manganese and iron nodules at the Black Lick Prospect, Arkansas.

	Metal content ppm Ni	Co	Nb	Cr
Sediment (-10+20 mesh)	900	194	16.0	
Mn rich S.G. <2.67	1400	850	9.6	400
Fe rich S.G. >2.95	219	80	9.6	4200

Table 6.17 Distribution of metal in "heavy"** nodules downstream from kimberlite at the American Mine, Arkansas.

Sample No.	Distance from†	Metal content ppm (unless stated otherwise) Ni	Co	Cr	Mg	P	Mn	Fe%	Ba*	Sr*	Ti*	Nb
556906	700 ft upstream	60	9	275	1040	600	2600	35	200	30	5000	16.0
556815	100 ft upstream	60	11	1760			6000*	>30*	>1%	30	2000	
556775	In Reference Creek	300*	10*	8600			5000*	17*	200	<30	880	
556501	20 ft downstream	180	16	2750								
556542	200 ft downstream	160	19	1400	11400	1400	2600	20	2000	300	3000	8.0
556705	2200ft downstream	60	10	600			8500*	>30*	200	30	3000	
556751	3200ft downstream	90	13	1300	1000	480	3200	30	100	<30	1300	8.0

*spectrographic data on minus 10 plus 80-mesh fraction

**S.G. >2.95

†the confluence of Reference and American Creeks.

Table 6.18 The content of selected elements in sediments, and the associated heavy mineral fractions from streams draining the background Trinity siltstone and the Black Lick Prospect.

Location		Metal content ppm (unless stated otherwise)										
		Pb	Ga	V	Cu	Zn	Ti	Ni	Co	Mn	Cr	Fe%
Background Trinity siltstone	Sediment	16	6	8	13	<50	600	13	8	600	30	0.67
	S.G. >3.27	6	4	50	30	<50	>1%	16	<5	6000	200	3.02
Black Lick Prospect	Sediment	30	6	40	30	100	3000	400	40	3000	300	1.68
	S.G. >3.27	40	2	60	30	160	8500	400	4	6000	1%	1.54
3000 feet downstream from above	Sediment	30	10	60	40	100	1300	20	16	4000	60	1.96
	S.G. >3.27	40	6	300	40	850	>1%	85	4	8500	600	1.09

Sn and Bi <5 ppm; Mo <2 ppm and Ag <0.2 ppm

Data on minus 80 fraction
Spectrographic analyses.

heavy mineral fraction of stream sediments. However, in view of the paucity of heavy minerals in the Arkansas streams this was not further investigated.

6.144 Dispersion in other drainage components

The concentration of the elements in wad, slime and banks at selected locations in American Creek are presented on Table 6.19. Additional data for the wad is given on Table 6.20, and the content of Ni in bank moss illustrated on Fig. 6.14. Prior to examining these figures, some explanation of the sample medium is warranted.

Slime is a veneer of surface mud deposited during the 'drying up' of the streams. It is therefore rich in clay size components.

The so called wad consists of quartz grains coated with dark sesquioxides. It occurs in the stream bed, especially at the junction with the underlying Trinity siltstone bedrock.

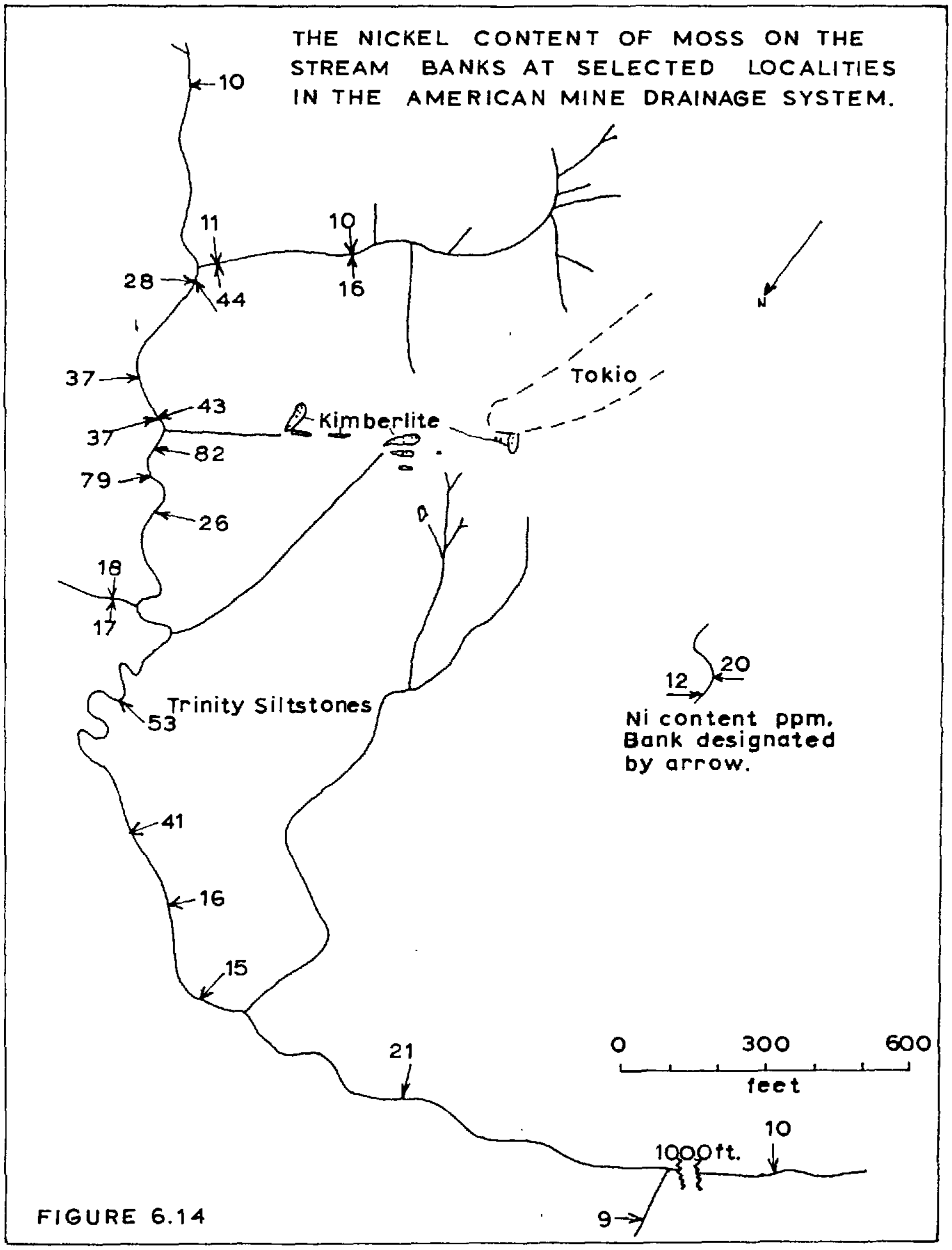
The bank material was discussed in the previous chapter. Two inch long, quarter inch deep, channel samples were taken from above and below the wet season water level. Moss was collected from the upper parts of the banks.

From inspection of Tables 6.19, 6.20 and Fig. 6.14 the following points are significant:

Wad

(1) Distribution of metal in the wad is erratic. Highest Ni and Co contents correspond with maximum Fe and Mn concentrations but absolute values are surprisingly low.

(2) Cobalt and to a lesser extent Ni are concentrated in the minus 10 plus 80-mesh fraction.



THE NICKEL CONTENT OF MOSS ON THE STREAM BANKS AT SELECTED LOCALITIES IN THE AMERICAN MINE DRAINAGE SYSTEM.

FIGURE 6.14

Table 6.19 The Distribution of Ni, Co, Mg, Cr, Nb, Fe, Mn and P in Slime, Wad, the Left Bank, and Sediment in the American Mine Drainage, Arkansas.

Sample Material	Distance from R.T.	Metal content ppm (unless stated otherwise)							
		Ni	Co	Mg%	Cr	Nb	Fe%	Mn	P
Slime	700 ft upstream	15	60	2940	65	4.0	5.5	7500	80
Wad		35	10		60	4.0	2.2	2150	80
Left Bank A		10	10	880	35	11.0	0.56	25	60
" " B		10	4	740	40	11.0	0.36	100	40
Sed. -80		15	10	800	110	4.0	1.0	500	65
" -300		25	4	1140	95	7.5	1.0	550	80
Slime	Reference Creek	155	12		225		1.6	900	60
Left Bank A		130	30		350		0.54	900	120
" " B		160	24		280		0.54	800	100
Sed. -80		200	30	8000	300	34	2.4	1100	330
" -300		140	20	6320	450	21	1.7	900	300
Slime	220 ft downstream	55	10	3000	40	6.4	0.6	200	80
Wad		95	60		<5	6.4	4.5	4000	160
Left Bank A*		66	12			20.0			
" " A		37	4	1400	45	14.0	0.7	200	130
" " B		75	16	1660	50	17.0	1.5	1500	140
Sed. -80		60	10	2600	20	15.0	1.1	420	85
" -300		60	10	2460	5	6	1.6	450	100
Slime	800 ft downstream	25	8	1760	40	4.0	0.7	250	160
Wad		20	4		40	5.0	1.1	300	40
Left Bank A		15	4		85	5.0	0.4	100	100
" " B		12	4		40	6.0	0.55		80
Sed. -80		28	6	2000	70	11.0	0.5	300	130
" -300		35	6	2540	350	8.0	0.6	100	160
Slime	3200 ft downstream	20	4	860	30	0.8	0.54	500	160
Left Bank A		10	4		40	0.8		450	40
" " B		20	4		30	0.8		300	80
Sed. -80		14	4	1000	115	4.0	0.5	200	80
" -300		20	4	1060	100	2.4	0.6	200	80

The Left Bank is that on the observer's left when facing downstream.
A* At the top of the bank.
A Just above wet season water table.
B Just below wet season water table.
Data on the minus 80-mesh fraction.
R.T. is the confluence of Reference and American Creeks.

Table 6.20 The concentration of Ni and Co in wad from the bed of American Creek, American Mine.

Distance from the confluence of American and Reference Creeks.	Ni ppm				Co ppm			
	Wad		Sediment		Wad		Sediment	
	-10+80	-80	-10+80	-80	-10+80	-80	-10+80	-80
700 ft upstream		35		15		10		10
100 ft "		35		70		20		10
100 ft downstream	83	34			91	25		
220 ft "		95	300	60	12	3		60
350 ft "	48	73			36	16		
490 ft "	144	112			72	29		
600 ft "	28	29			44	25		
700 ft "	28	15			41	5		
800 ft "	27	15	105	28	52	6	24	6
1000 ft "	31	19			50	9		
1200 ft "	109	8			25	6		
2200 ft "	166	44	80	20	37	17	32	12
3200 ft "	56		25	14	62		6	4

(3) Relatively high Ni and Co contents are recorded opposite the mouth of East Creek.

Slime

(1) With the exception of the furthest sample upstream, little difference is observed between the content of metal in the slime and the sediment. At the furthest site upstream, Mn, Co and Fe are enriched.

Banks

The distribution of Ni, Co and exMg in the stream banks has been discussed in the previous chapter; however, the following additional points are noted:

(1) With the exception of P and Cr close to the kimberlite, higher concentrations of metal are recorded in sediment than bank material.

(2) In the bank close to kimberlite, most metal, especially Mn and Co, is concentrated below the wet season water table.

Moss

(1) Anomalous concentrations of Ni are recorded in the bank moss for more than 1700 feet downstream from Reference Tributary.

6.15 Discussion

6.151 The Form of Metal in Anomalous Sediment

It has been shown that Ni and Co are considerably concentrated in the coarse fractions (Fig. 6.2, Table 6.10), especially in the light concretions (Table 6.16). This is consistant with soil profile studies where these elements are overwhelmingly concentrated in Mn nodules in the A_1 horizon, Table 4.17. However, unlike the soil profile, Ni is not particularly concentrated in the fine fractions; the reason for this is discussed later.

In the minus 10 plus 20-mesh fraction, about 30% of the Ni is associated with the sesquioxide phase (Table 6.11) but 89% is extracted with $KHSO_4$. This would suggest only about 50% of the $KHSO_4$ extractable Ni to occur with sesquioxides, the remaining metal being present in a more resistant form, possibly as stable secondary or weathered primary silicates. The 10% of the metal not extracted with $KHSO_4$ (cf. background siltstone 60% and limestone 25%; Table 6.11), is probably associated with resistant primary minerals. A small proportion of metal is extracted with 0.025% HNO_3 and probably held loosely on clay minerals or as secondary silicates. The amount of metal extracted by this attack increases with decreasing grain size (Table 6.21).

The proportion of Co associated with sesquioxides is unknown. However, whereas Ni is only enriched 1½ times in the Mn nodules, Co is enriched 4½ times (Table 6.16). Furthermore, Co is depleted in heavy nodules in the American Mine drainage, cf. Table 6.10 and 6.17. It is suggested, therefore, that a considerable proportion of the Co in the coarse fraction is associated with the Mn sesquioxide cement.

An appreciable quantity of Co is extracted with 0.025% HNO_3 from the fine sediment (Table 6.21) thus some Co occurs in a loosely held form.

Unlike Mn, Co, Ni and Fe, exMg and Cr are considerably concentrated in the minus 20 plus 36-mesh and minus 300-mesh fractions (Fig. 6.2). It was seen in soil profile studies that

Table 6.21 The amounts of Ni and Co extracted from the fine fractions of "anomalous" sediment with various attacks, American Creek, Arkansas.

Size fraction mesh (B.S.S.)	Element	Metal content ppm $HClO_4$	0.025% HNO_3	ratio %
-80+200	Ni	65	8	12
-200+300		70	19	27
-300		90	42	47
-80+200	Co	23	6	26
-200+300		21	4	19
-300		18	6	33

Table 6.22 The distribution of Cr and Nb in sesquioxide nodules at the Black Lick Prospect, Arkansas.

Nodule type	Metal content ppm		Metal content in residue after leaching with dithionite* ppm	metal content of leachate ppm	%residue	%loss of metal	
						observed	calculated
Manganiferous S.G. <2.67	Cr	400	450	44		11	15.5
Ferriferous S.G. >2.95	Cr	4200	5500	123		3	7.5
Manganiferous S.G. <2.67	Nb	9.6	30		75		gain 232
Ferriferous S.G. >2.95	Nb	9.6	10		70		27

*sodium citrate/sodium dithionite solution in the coarse fraction of the A horizon, exMg occurs largely associated with sesquioxides and possibly altered silicate minerals (iddingsite, etc.). Thus the lack of coincident exMg and Fe peaks in the minus 20 plus 36-mesh fraction of the sediments, suggests exMg to be associated largely with weathered Mg rich silicates rather than nodules.

Although Cr is considerably enriched in the heavy nodules (Table 6.22), only a very small amount of metal occurs in the sesquioxide cement. Thus whilst some mobilisation has occurred, the bulk of the metal is present in a relatively resistant form. Possible modes of occurrence in the nodules are therefore:

(a) As residual remnants of 'lattice' metal within concretions derived from olivine, i.e.

olivine -- secondary minerals -- Fe concretion
e.g. iddingsite

This conveniently explains the coincidence of maximum Cr and exMg concentrations in the minus 20 plus 36-mesh fraction, OR

(b) within primary heavy mineral grains encapsulated by secondary iron oxides.

The high concentrations of Cr and exMg in the minus 300-mesh fraction are coincidental. Exchangeable Mg is no doubt associated with clay minerals whilst the Cr probably occurs as fine grained primary minerals as seen from the considerable concentration in the heavy mineral fraction compared with normal sediment (Table 6.18).

Lower concentrations of Nb occur in the 'light' and 'heavy' nodules than in the normal minus 10 plus 20-mesh fraction. This would suggest highest metal content of this size fraction to occur in the S.G.>2.67 but <2.95 material. Since the most likely kimberlite host mineral is perovskite (or its secondary products, anatase and brookite), which have a specific gravity of about 4; it seems likely that the metal occurs largely in multimineral grains.

The progressive decrease in Nb content with particle size observed at the American Mine (Fig. 6.2) may be due to incorporation of Nb host minerals within altered primary phenocrysts and/or encapsulated within sesquioxide nodules. The peak population in the minus 80 plus 200-mesh size at the Black Lick Prospect indicates some 'free' host mineral grains.

6.152 Some Factors Influencing the Effective Length of the Anomaly

6.1521 The minus 80 and minus 300 mesh fractions

It was seen in soil profile studies (Chapter 4) that a substantial proportion of metal occurs in the coarse fraction as sesquioxide nodules. This is reflected by size distribution studies of highly anomalous sediment. Thus the content of some metals in the fine sizes at source is not excessive and contrast may be very low. This factor is perhaps most important for Co where minimal amounts of metal are present in the minus 80-mesh size range. This is no doubt one of the reasons for the very short anomalous Co trains in the fine fractions at the American Mine. It is of lesser importance for those metals which occur as heavy minerals and which concentrate in the silt fraction during weathering, e.g. Nb, Cr.

About 96% of the Trinity A horizon is less than 80-mesh of which about 40% is silt size (Table 6.23). The corresponding figures for the kimberlite are 84% and 60%, respectively. Since many metals are concentrated in the silt fraction of the Trinity A horizon and the areal extent of this formation is considerably

Table 6.23 Comparison of the mechanical distribution of anomalous and background sediment with parent soils, Arkansas.

Sample Type	Location	Weight per cent -10+20	-20+36	-36+80	-80+200	-200+300	-300	silt	clay	-80
Sediment	Upper Trinity	46	31	21	1.4	0.4	0.2			2.0
Sediment	Upper Trinity near Black Lick	17	47.5	22	8.5	3.0	2.1			13.6
Sediment	Anomalous Upper Trinity	22	44.5	23.5	5.2	2.2	2.5			9.9
Sediment	Limestone	23.0	18.0	31.0	17.0	8.0	3.0			28.0
Soil A_1 horizon	Trinity Siltstone	1.7	0.4	1.5	17.6	36.7	42.0	40.3	1.7	96.3
Soil A_1 horizon	Kimberlite	1.4	5.7	9.0	6.7	4.3	72.9	60	12.9	83.9

Table 6.24 The pH of surface waters and sediment of American Creek, Arkansas.

Distance from the confluence of Reference and American Creeks	pH of Surface Waters	pH of Sediment
700 ft upstream	5.9	5.9
100 ft "	5.8	6.3
Reference Creek	7.0	7.1
220 ft downstream	6.9	7.0
500 ft "	6.5	6.5
800 ft "	6.1	6.3
1200 ft "	5.9	6.0
1700 ft "	5.9	5.9
2200 ft "	6.0	6.4
3200 ft "	6.0	6.8

in excess of that of the kimberlite, there is an extremely rapid dilution of anomalous fine sized sediment.

Particle size studies of sediment over the Trinity formation (Table 6.23) indicates the proportion of material to decrease with decreasing grain size. Excluding the clay fraction, this is virtually inversely proportional to the supply and demonstrates the considerable 'flushing out' of fine sediment. Indeed, the clay content of Trinity sediment is only about 0.1%. It is possible that this very small proportion of clay may be partly responsible for the short exMg dispersion trains in the minus 300-mesh fraction. However, it is not known whether all the exchange positions are satisfied.

Longer anomalous trains are observed in the fine fractions for Ni than in the corresponding fractions for the less mobile Nb and more mobile exMg. Whilst this is undoubtedly partly due to an initially greater contrast, it is believed that additional factors also contribute to this longer dispersion train. For example, it was seen in Chapter 5 that anomalous concentrations of Ni are present in Quaternary alluvium downstream from kimberlite. Anomalous metal contents are also present in some tributaries on the American Creek flood plain. Although the possibility of an undiscovered kimberlite source cannot be excluded, it is thought that these anomalies, and presumably some of the metal in American Creek, is derived from erosion of the Quaternary alluvium.

It was also concluded in Chapter 5 that appreciable quantities of Ni and other metals are transported in ground waters. This metal is partly precipitated in the banks at or near the wet season water level where it tends to concentrate in orange mottles (Table 4.17). However, this is not always the case for Ni (Table 6.25 overleaf).

Table 6.25

	Metal Content ppm					
	Ni	Co	Mn	Fe%	exMg	Nb
White Mottle	80	4	200	0.6	300	15
Orange Mottle	80	15	1900	3.0	800	15

Metal is also concentrated in the wad no doubt due to coprecipitation or sorbtion. Erosion of these 'bank precipitates' will enhance the effective length of the anomalies.

6.1522 <u>The coarse fraction</u>

That maximum contrast and dispersion occurs in the minus 10 plus 20-mesh fraction is due to four fundamental features:

(1) The concentration of the elements, especially the considerable enrichment in nodules, in the coarse fraction of the kimberlite soils.

(2) A minimum of dilution with background sediment due to the very small amounts of minus 10 plus 20-mesh material present in soils over the sialic country rocks (Table 6.23).

(3) The small proportion of nodules in the A horizon of the above.

(4) The presence of alluvial banks containing anomalous concentrations of metal.

Since the Ni and Co are considerably concentrated in Mn nodules, the effective length of the anomaly will depend upon the original contrast and ratio between anomalous and background nodules. Since Mn nodules are absent over the country rocks (excluding the Woodbine tuff), it is probable that enhanced drainage trains would occur by analysis of the light fraction of minus 10 plus 20-mesh stream sediments.

The ratio of Mn to Fe nodules decreases downstream from the kimberlite (Table 6.26). This could be due to:

(a) Comminution.
(b) Leaching of Mn.
(c) Preferential mechanical dispersion of 'light' material.
(d) Dilution with Fe nodules provided from background rocks.

Whilst (a), (c) and (d) undoubtedly occur, the extent to which leaching of Mn takes place is unknown. However, Mn nodules are recorded in the flood plain tributaries and this would not be expected if major leaching of Mn had occurred.

Anomalous proportions of Fe nodules are observed in the minus 10 plus 20-mesh fraction for more than 3200 feet downstream from the kimberlite (Table 6.26). This is in accord with (2) on the previous page. However, the possibility should be considered that some nodules may be developed in situ either by precipitation from surface waters due to a rise in pH (e.g. over limestone), or by precipitation of Fe round nuclei in the stream banks. Nodules developed by this means should contain an extremely high proportion of dithionite* extractable metal and very low concentrations of the immobile elements.

As previously mentioned, the precipitation of metal at a high pH may be responsible for the accumulation of nodules over the limestone. However, anomalous concentrations of Ni, Co and exMg related to limestone are readily differentiated by their associated background content of relatively immobile elements, e.g. Nb and Cr.

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*sodium citrate-sodium dithionite solution.

Table 6.26 Estimated composition of minus 10 plus 20-mesh (B.S.S.) fraction of stream sediments from American Creek, American Mine.

Sample No.	Distance from the confluence of Reference and American Creeks	Nodules %		Quartz, Sandstone and Shale Fragments %
		Brown (Fe)	Black (Fe)	
556906	700 ft upstream	10	1	89
556833	200 ft "	30	8	62
556517	220 ft downstream	37	4	59
556558	350 ft "	30	1	69
556607	600 ft "	30	2	68
556627	700 ft "	25	1	74
556661	1200 ft "	9	1	90
556705	1700 ft "	25	3	72
556723	2200 ft "	15	1	84
556742	tributary in flood plain at 2300 ft.	24	3	73
556752	3200 ft downstream	20	1	79

6.16 Summary and Conclusions

(1) Maximum metal content and contrast occurs in the poorly sorted rather than well sorted sediment.

(2) The $KHSO_4$ attack gives maximum contrast.

(3) Differing Ni, Co and exMg thresholds occur over the limestone and sialic rocks, especially in the coarse fraction. This is due to a variation in the amount and composition of sesquioxide nodules.

(4) Maximum anomalous trains occur in the minus 10 plus 20-mesh fraction. This is due to the considerable concentration of elements in this size of kimberlitic soils and to the minimum of dilution with background sediment.

(5) Minimum anomalous trains occur in the minus 300-mesh fraction due to the rapid dilution with background sediment and removal of fine sediment during heavy rains.

(6) Restricted Ni, Co and exMg anomalies occur in limestone environments. Niobium and Cr are unaffected.

(7) Enhanced anomalous trains for Cr may occur in the heavy mineral fraction and for Ni and Co in the S.G.<2.67 fraction of the minus 10 plus 20-mesh size.

(8) Stream sediment gives longer anomalous dispersion trains than banks, wad or slime.

(9) Anomalous Ni concentrations are recorded for some 1700 feet downstream in moss on the banks of American Creek.

6.2 ARIZONA

6.21 Introduction

Drainage investigations in Arizona were confined to size distribution studies of sediment from the Buell Park and Garnet Ridge East areas.

Samples at Buell Park were taken from 3000 feet upstream and 1000 and 7000 feet downstream from the caldera. As previously mentioned, the country rocks are dominantly sandstones whilst kimberlite and minnette, and their extrusive equivalents occur in the caldera. Analyses were made for Ni, exNi, Co, exMg and Nb.

At Garnet Ridge East, samples were collected 1000 feet upstream and 100 and 7500 feet downstream from the intrusion. The country rocks are dominantly sandstones and the intrusion is a serpentine breccia. Analyses were made for Ni and Co.

The width of the rivers bear little relation to their annual flow which is intermittent in all but the largest. In times of heavy rains the waters may extend across the entire width of the creek bed but more usually flow is confined to a shallow channel in the alluvium. There is, therefore, a lateral variation in the nature of the sediment.

6.22 Composition of the Sediment

There is little chemical weathering in Arizona and the primary minerals occurring as eluvial concentrations over the igneous rocks are common in the drainage downstream from such rocks. For example, fresh olivines, pyrope garnets, etc., are readily visible in sediment 7000 feet downstream from the Buell Park caldera. At Garnet Ridge the readily visible train of these minerals is much shorter, due no doubt to the smaller area of the intrusion.

These heavy minerals are generally coarser than the sand grains of the sandstone country rocks and this is reflected by the mechanical composition of sediment downstream from kimberlite (Table 6.27).

Whilst 90% of the sandstone soil at Buell Park is less than 80-mesh, less than 20% of the sediment is of this grain size

Table 6.27 The particle size distribution of sediment from the Buell Park and Garnet Ridge East drainage systems.

Location	Weight per cent in mesh size -10+20	-20+36	-36+80	-80+200	-200+300	-300	-80	Sample No.
Background	2.2	7.6	33	51.5	5.1	0.6	57.2	558025
100 ft*	27.9	27.2	25.6	17	2.0	0.3	19.3	558026
7500 ft*	8.4	13.4	38.2	36.7	3.1	0.2	40.0	558037
Background	13.3	31.2	38.7	12.9	3.8	0.1	16.8	558060
1000 ft*	23.6	26.8	31.5	14.2	3.1	0.8	18.1	558041
7000 ft*	9.5	28.7	44.4	15.1	1.9	0.2	17.2	558051
Near surface 'soil' over kimberlite at Buell Park	23.5	7.7	17.4	19.3	11.4	20.7	51.4	
Near surface 'soil' over sandstone near Buell Park	0	0.1	8.9	87.3	2.3	1.4	91.0	

*distance downstream from kimberlite

(Table 6.27). This may be due either to a wide variation in grain size of sand grains of the country rocks or it may be due to 'flushing out' of fine sediment during the infrequent rains. At Garnet Ridge where the river is much smaller and presumably flows over a shorter period, a greater proportion of the sediment is present in the minus 80-mesh fraction.

No clay size particles were detected in one gram of minus 300-mesh sediment from either area.

6.23 Variation of Ni, exNi, Nb, Co and exMg with Particle Size

The variation of Ni, exNi, Nb, Co and exMg content with particle size in sediment from the Buell Park drainage is presented on Fig. 6.15 and for Ni and Co in the Garnet Ridge East drainage on Fig. 6.16. Contrasts for various size fractions both near to the kimberlite and 7000 feet downstream are tabulated on Table 6.28. Attention is drawn to the following points:

(1) Cobalt is very considerably concentrated in the plus 80-mesh fractions both at the Buell Park and Garnet Ridge areas. Only slightly anomalous metal contents are observed and these occur in the minus 80-mesh fractions.

(2) Nickel, Nb and exMg are concentrated in both the coarse and fine fractions in the anomalous and background rocks alike. Maximum Ni and exMg contrasts occur in the minus 20 plus 36-mesh fraction but maximum Nb contrasts occur in the minus 80 plus 200-mesh size.

(3) Exchangeable Ni is concentrated in the finest size although significant amounts are observed in the coarse size of the anomalous samples.

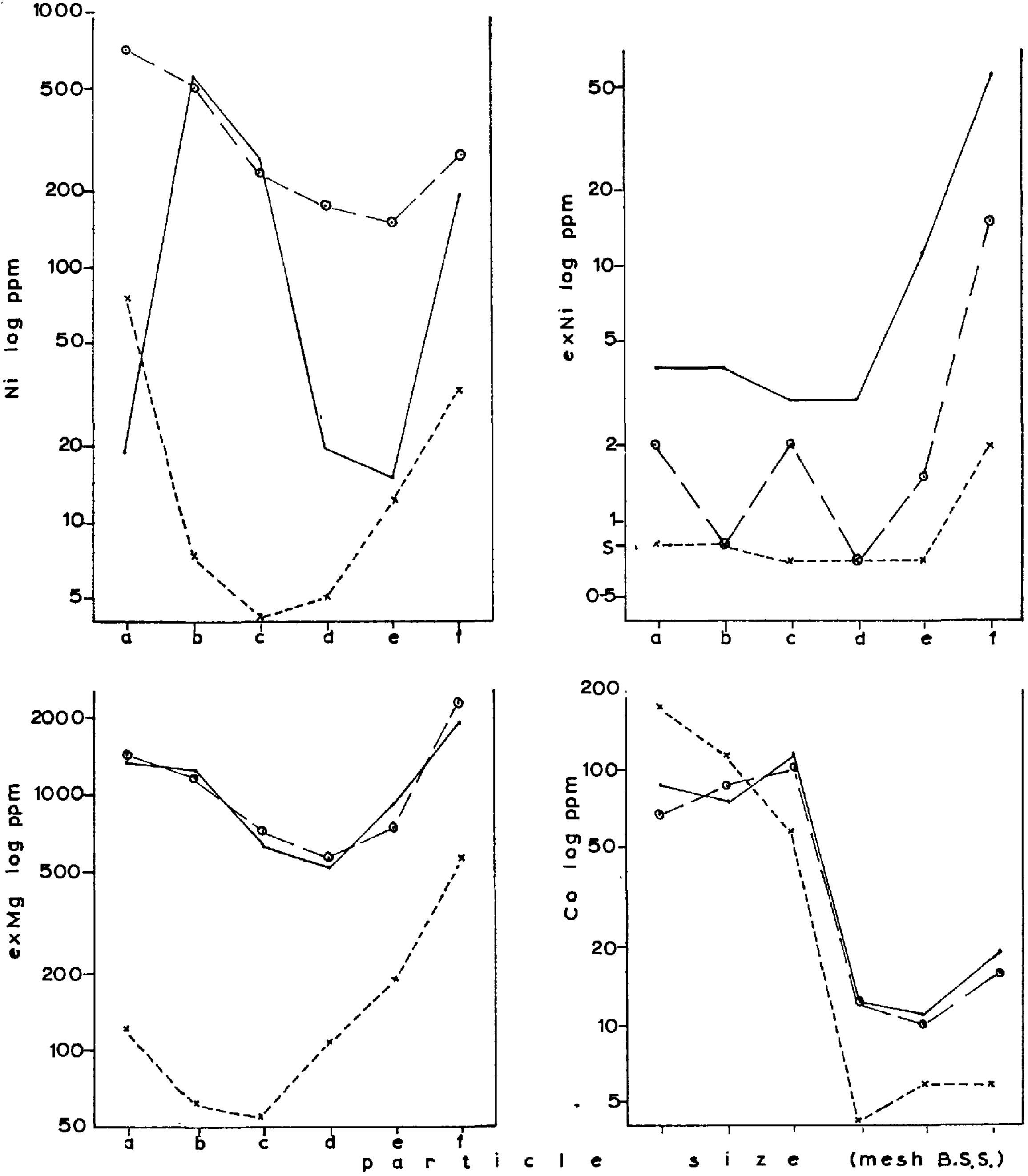


FIGURE 6.15: The variation of Ni, exNi, Nb, exMg and Co contents with particle size in sediments from the Buell Park drainage.

a minus 10 plus 20 mesh
b do. 20 do. 36 do.
c do. 36 do. 80 do.
d do. 80 do. 200 do.
e do. 200 do. 300 do.
f do. 300

--x-- background
—•— 1000 feet downstream from caldera
—⊙— 7000 do. do. do. do.
S sensitivity

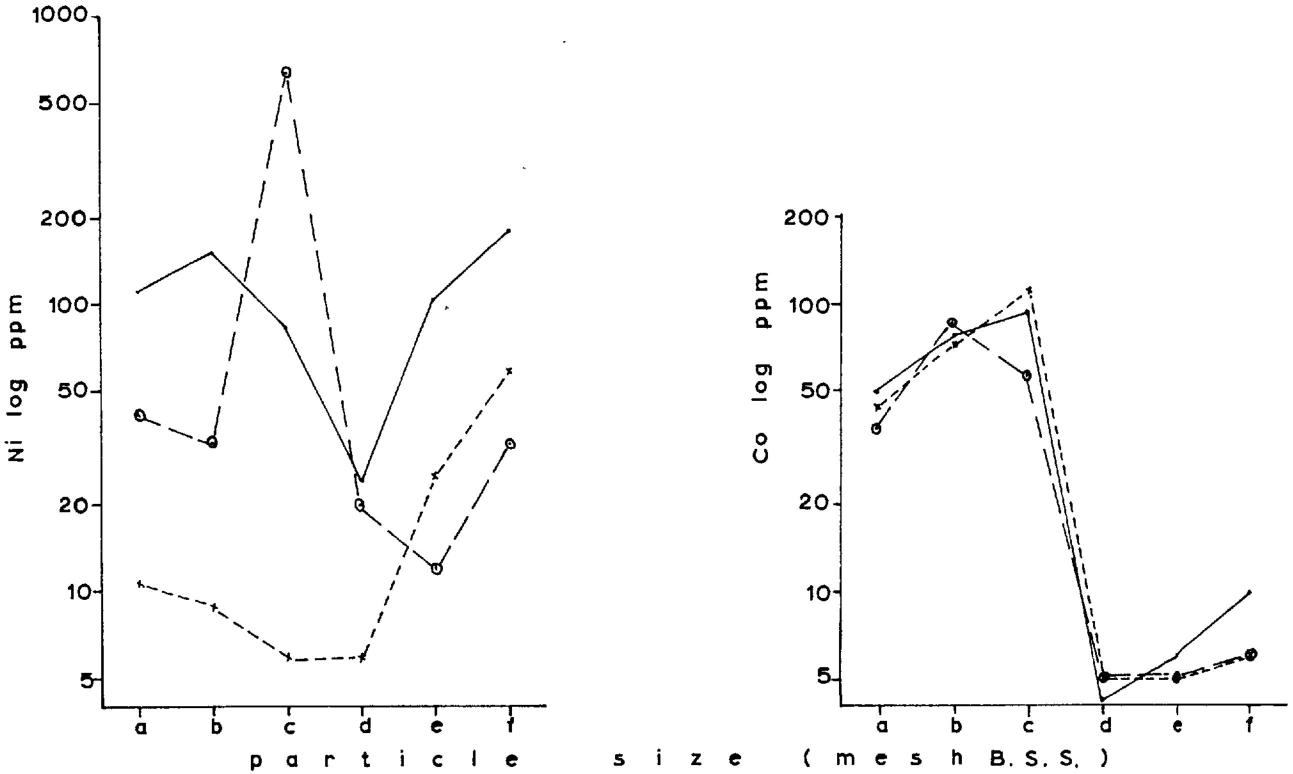


FIGURE 6.16: The variation of Ni and Co contents with particle size in sediments from the Garnet Ridge East drainage.

a	minus 10 plus 20 mesh	d	minus 80 plus 200 mesh
b	do, 20 do. 36 do.	e	do, 200 do, 300 do.
c	do 36 do 80 do	f	do 300 mesh

---x--- Background ——•—— 100 feet downstream ——⊙—— 7500 feet downstream

Table 6.28 Contrast between anomalous and background sediment at the Garnet Ridge East and Buell Park areas.

		Distance downstream from kimberlite	Contrast -10+20	 +20-36	 -36+80	 -80+200	 -200+300	 -300	 -80
Garnet Ridge East	Ni	100 ft.	10	17	14	4	5	3	4
		7500 ft.	4	4	110	3	3	3	1
Buell Park	Ni	1000 ft.	1	75	62	4	1	6	4
		7000 ft.	9	69	60	39	12	8	24
	exMg	1000 ft.	11	21	11	5	5	3½	5
		7000 ft.	11	20	12	5	4	4	5

(4) Very little decrease in contrast is observed between the samples close to kimberlite and those 7000 feet downstream.

6.24 Discussion

Unlike Ni, exMg and Nb which occur in similar concentrations in both background soil and sediment, cobalt is enriched in the plus 80-mesh sediment compared with the same fraction of the background soils. The possibility must be considered, therefore, that either:

(1) There is a very high Co threshold in the coarse fraction, or

(2) Some ultrabasic material is present at the background sediment locations.

The considerable concentration of Co in the plus 80-mesh fraction of sediment strongly suggests this metal to occur within coarse grained detrital minerals. Allen and Balk (1954) report the presence of tourmaline, zircon, hematite, leucoxene and pyrite in the De Chelly Sandstone and a similar assemblage, including ilmenite and magnetite, in the Summerville formation. These horizons comprise the country rocks at the background sediment locations at Buell Park and Garnet Ridge East, respectively. It is possible that Co, and lesser amounts of Ni and Mg are concealed within the lattice of one or more of these minerals.

Since mechanical dispersion is prevalent, the lack of associated anomalous Ni and Mg contents with the Co as mentioned above, would preclude a nearby ultrabasic source. It is possible however, that Co could occur in a Ni and Mg deficient primary mineral subsequently concentrated by eluvial means from a local tuff sheet. Clearly further work is needed in order to explain this problem.

Unlike Co, Ni, exMg and Nb are also concentrated in the finer fractions of background sediment, the reason for this was not investigated.

Concentration of anomalous metal in the coarse fraction of anomalous sediments is attributed to occurrence of metal within coarse grained primary minerals i.e. Ni and Mg within olivine (Table 6.29), and Nb probably with ilmenite. A high metal content in the fine fraction is thought to reflect metal derived from the kimberlite ground mass.

Table 6.29

	green olivine	pink garnet	chrome diopside
Ni ppm (spec)*	3600	23	18
Ni ppm ($KHSO_4$)	907	50	37

*from Allen and Balk (1954)

Maximum contrast in the minus 20 plus 36-mesh fraction is due primarily to the mechanical dispersion of coarse primary minerals and to the low metal content of this size fraction in background sediments.

Neither exMg or Ni 'fall off' in content downstream from the Buell Park caldera although Ni does decrease in content downstream from the Garnet Ridge intrusion. Since the proportion of olivine tends to decrease downstream, due to dilution with background sediment, this is difficult to explain. The possibility must be considered that the olivine decomposes progressively downstream thus the $KHSO_4$ attack for Ni becomes increasingly more efficient than at source; where only 25% of the Ni is extracted from olivine with a $KHSO_4$ attack (Table 6.29). The lack of decrease in exMg content downstream may reflect the exchange positions to be fully satisfied at all sites. This was not investigated.

It is seen that the Nb content of the Buell Park kimberlite is far from anomalous (Table 2.2). Thus the presence of anomalous concentrations of Nb in the drainage must have been provided by some of the other igneous rocks which inhabit the caldera. In addition, there may have been some concentration of the Nb host mineral in placer deposits.

Although analyses of stream sediment for Ni and exMg may provide anomalous trains for some considerable distance downstream for the Arizona kimberlites, the lack of chemical weathering may permit even longer pannable trains. For example, olivine would have to comprise at least 0.15% of the minus 20 plus 36-mesh fraction to be detectable by analytical methods. Panning should readily reveal these concentrations. It is possible that in country rocks, of coarse grain size, where dilution of the coarse fraction is considerable, analysis of the minus 80-mesh fraction may be of use. Clearly, if prospecting in this area is envisaged then further work will have to be done, and in particular, the relative lengths of the chemical and pannable anomalous trains must be investigated.

CHAPTER 7

DISPERSION IN ALLUVIUM

7.1 ARKANSAS

7.11 Introduction

Very limited studies were made of the dispersion of Ni, exNi and exMg into the Quaternary alluvium bounding three sides of the Prairie Creek pipe (Fig. 7.3). Determinations were made on the minus 80-mesh fraction of selected samples from profiles collected about the pipe and for some distance above and below.

7.12 Character of the Alluvium

Alluvium in the flood plain of the Little Missouri River consists of three main types (Fig. 7.1):

(1) A widespread pebble bed
(2) An overlying zone of fine grained sediment
(3) Channels of sand.

The pebble bed occurs at various depths in all the profiles sampled and probably extends over the entire area of the flood plain. Where pits were dug in the bed, e.g. A.1 and A.8, it is seen to consist of loosely consolidated bands of very well sorted sediment whose size varies from very coarse gravel 8 inches in diameter to finer gravel only ½ an inch across. In occasional bands some pebbles are coated with clay.

Over most of the area the pebble bed is overlain by fine grained alluvium 2 to 9 feet thick. This varies from silt, or rarely coarse sand, to a compact clay. In some clay rich zones, e.g. A.8, a prominent B_2 horizon is present. Often the junction

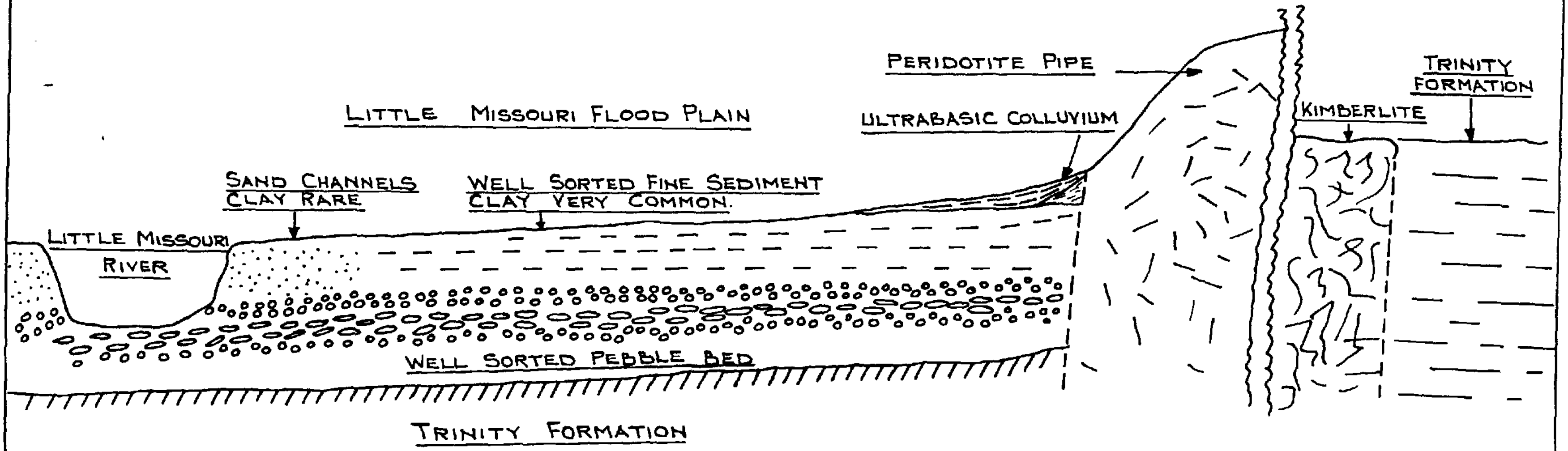


FIG. 7·1 A DIAGRAMMATIC SECTION ACROSS THE LITTLE MISSOURI RIVER FLOOD PLAIN with the underlying pebble bed is mottled but is always sharp.

A wedge of black ultrabasic derived soil, no doubt due to solifluction, overlies the alluvium adjacent to the pipe, e.g. at sites 00N1300W to 00N1600W. The alluvium to the south of the pipe, e.g. A.11 and A.12 is covered to a depth of several feet with kimberlite debris eroded from the pipe by sheet wash.

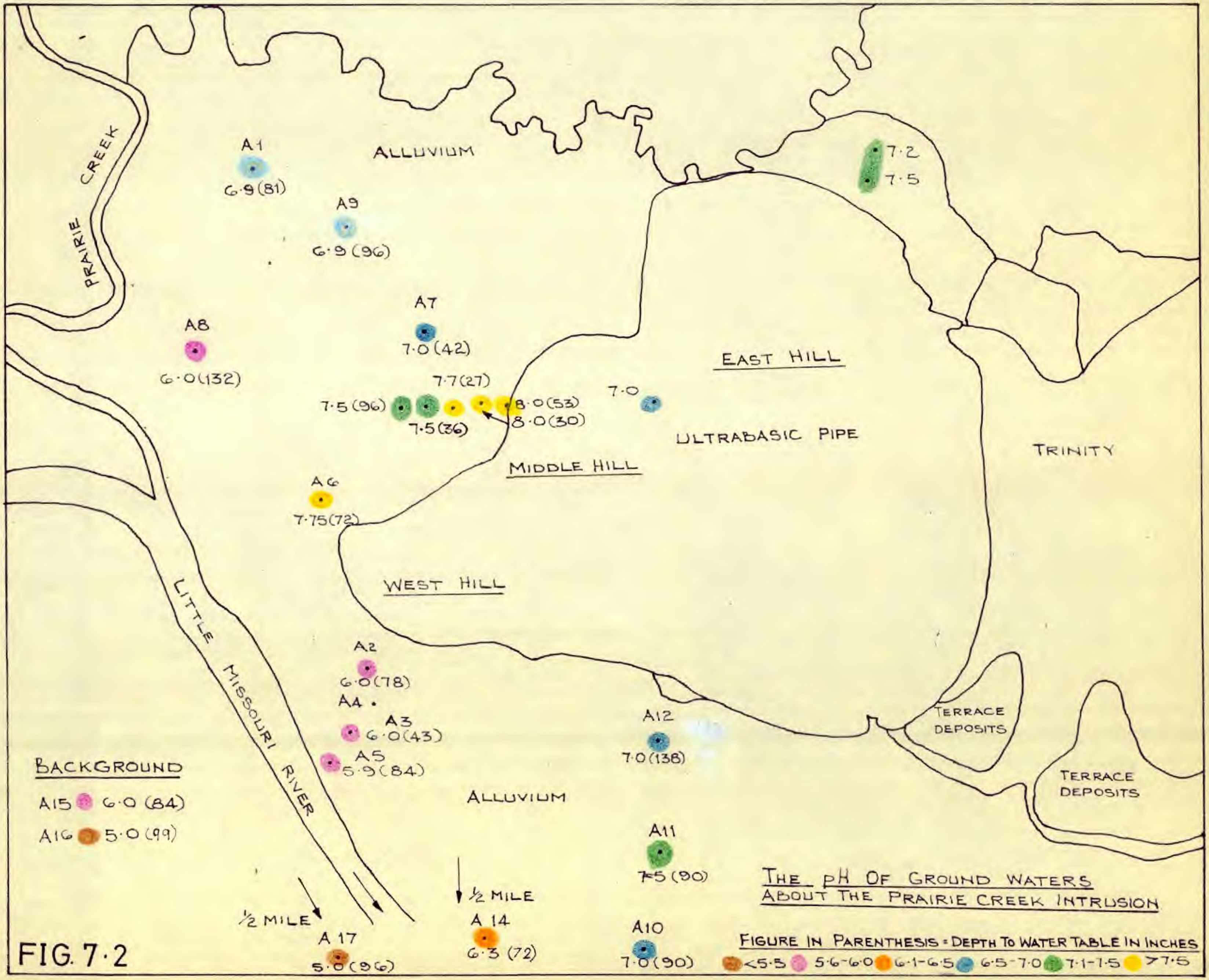
Near to the Little Missouri River, the alluvium e.g. A.5, A.14 and A.16 consists of clean very well sorted alternating layers of fine to coarse sand with occasional pebbles; clay size particles are scarce. This is thought to represent the most recent alluvium. It is underlain by the pebble bed.

7.13 The Hydrogen Ion Concentration

The pH of ground waters near the Little Missouri River some 2 miles upstream from the pipe (A.16) is 5.0. Thus the high pH values to the north and south of the ultrabasics (Fig. 7.2) are probably due to the pipe itself. The pH decreases from the pipe towards the Little Missouri River, no doubt due to dilution with background ground waters. This is particularly noticeable where the waters are funnelled between West Hill and the Little Missouri River.

Elevated pH values due to the intrusion may well extend over ½ a mile downstream, for at site A.14 a pH of 6.3 is recorded compared with 5.0 (A.17) on the opposite and remote bank from the kimberlite.

A considerable difference in pH is recorded in the surface waters upstream and downstream from the intrusion (Table 7.1, overleaf).



THE pH OF GROUND WATERS ABOUT THE PRAIRIE CREEK INTRUSION

FIG. 7·2

Table 7.1

Location	pH of surface waters
Little Missouri River. 2 miles upstream from the pipe.	5.0
Prairie Creek at the confluence with Little Missouri River.	7.5
Little Missouri River. ½ mile downstream from the pipe.	7.5

However, it is not known whether the high pH values are due to the intrusion or whether they reflect a bed of limestone drained by a minor tributary to Prairie Creek, one mile upstream from the confluence with the Little Missouri River. Similar results were obtained at the American Mine where the pH of the surface waters immediately downstream from the kimberlite is 7.0. The pH of surface waters draining the Trinity siltstone varies from 5.0 to 6.0.

It may be possible to utilize the local elevation in pH of waters draining kimberlite in prospecting for this rock type. However, additional work is necessary to establish the background and seasonal variations.

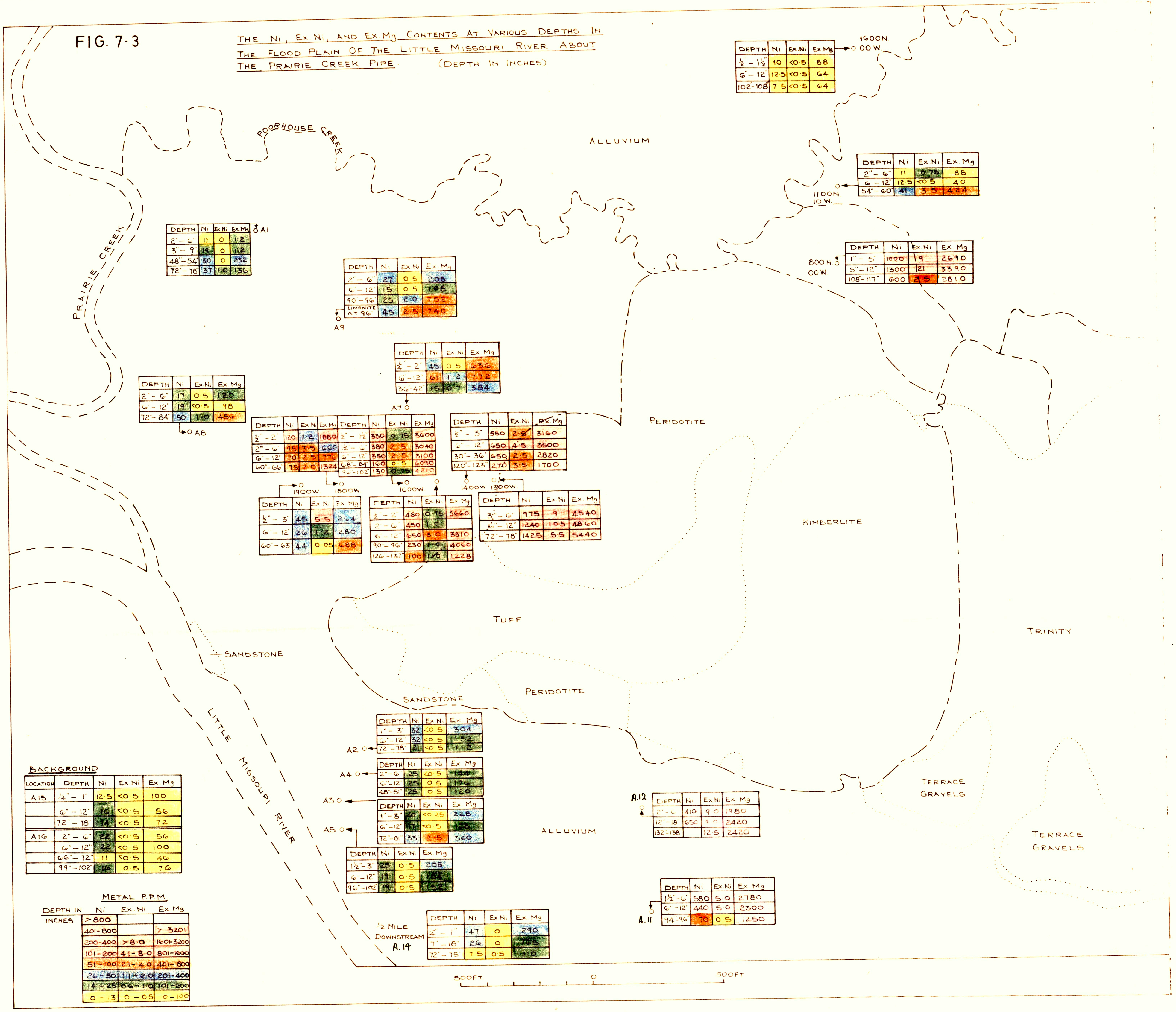
7.14 The Distribution of Ni, exNi and exMg in Alluvium about the Prairie Creek Intrusion

The content of Ni, exNi and exMg at various depths in the flood plain of the Little Missouri River are illustrated on Fig. 7.3. With the exception of A.8, A.14 and A.15, the deepest samples are located immediately above the pebble bed. Attention is drawn to the following points:

FIG. 7·3

THE Ni, Ex Ni, AND Ex Mg CONTENTS AT VARIOUS DEPTHS IN THE FLOOD PLAIN OF THE LITTLE MISSOURI RIVER ABOUT THE PRAIRIE CREEK PIPE

(DEPTH IN INCHES)



A1

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	11	0	112
3"–9"	19	0	112
48"–54"	30	0	232
72"–78"	37	1.0	136

A9

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	27	0 5	208
6"–12"	15	0 5	108
90"–96"	25	2·0	752
LIMONITE AT 96"	45	2 5	740

A7

DEPTH	Ni	Ex Ni	Ex Mg
¼"–2"	45	0 5	636
6"–12"	61	1 2	772
36"–42"	15	0 7	384

A8

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	17	0·5	120
6"–12"	19	<0·5	98
72"–84"	50	1·0	486

1800W.

DEPTH	Ni	Ex Ni	Ex Mg
½"–2"	120	1·2	1880
2"–6"	95	3·5	660
6"–12"	70	2·5	776
60"–66"	75	2·0	1324

1600W.

DEPTH	Ni	Ex Ni	Ex Mg
½"–1½"	330	0 75	3600
1½"–6"	380	2 5	3040
6"–12"	350	2 5	3100
68"–84"	160	0·5	6090
96"–102"	130	0 75	4210

1400W

DEPTH	Ni	Ex Ni	~~Ex Mg~~
½"–3"	550	2·~~5~~	3160
6"–12"	650	4·5	3500
30"–36"	650	2·5	2820
120"–123"	270	3·5	1700

1900W.

DEPTH	Ni	Ex Ni	Ex Mg
½"–3"	45	5·5	264
6"–12"	26	1·2	280
60"–63"	44	0 05	688

DEPTH	Ni	Ex Ni	Ex Mg
½"–2"	480	0·75	3660
2–6"	450	1·0	
6–12"	650	3·0	3810
90"–96"	230	1·0	4060
126"–132"	100	1·0	1228

1300W.

DEPTH	Ni	Ex Ni	Ex Mg
3"–6"	975	9	4540
6"–12"	1240	10·5	4860
72"–78"	1425	5·5	5440

1600N. 00 W.

DEPTH	Ni	Ex Ni	Ex Mg
½"–1½"	10	<0·5	88
6"–12"	12·5	<0·5	64
102"–108"	7·5	<0·5	64

1100N 10 W.

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	11	0·75	88
6–12"	12·5	<0·5	40
54"–60"	41	3·5	424

800 N. 00 W.

DEPTH	Ni	Ex Ni	Ex Mg
1"–5"	1000	9	2690
5"–12"	1300	121	3390
108"–117"	600	2·5	2810

A2

DEPTH	Ni	Ex Ni	Ex Mg
1"–3"	32	<0·5	304
6"–12"	32	<0·5	152
72"–78"	21	<0·5	112

A4

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	25	<0·5	144
6"–12"	25	0·5	176
48"–51"	25	0·5	120

A3

DEPTH	Ni	Ex Ni	Ex Mg
1"–3"	20	<0·25	228
6"–12"	17	<0·5	128
72"–81"	33	2·5	360

A5

DEPTH	Ni	Ex Ni	Ex Mg
1½"–3"	25	0·5	208
6"–12"	19	0·5	[illegible]
96"–102"	19	0·5	152

½ MILE DOWNSTREAM A. 14

DEPTH	Ni	Ex Ni	Ex Mg
¼"–1"	47	0	290
7"–18"	26	0	165
72"–75"	15	0·5	110

A.12

DEPTH	Ni	Ex Ni	Ex Mg
2"–6"	410	9·0	1980
12"–18"	650	9·0	2420
132"–138"		12·5	2420

A.11

DEPTH	Ni	Ex Ni	Ex Mg
1½"–6"	580	5·0	2780
6"–12"	440	5·0	2300
94"–96"	70	0·5	1250

BACKGROUND

LOCATION	DEPTH	Ni	Ex Ni	Ex Mg
A15	¼"–1"	12·5	<0·5	100
	6"–12"	16	<0·5	56
	72"–78"	14	<0·5	72
A16	2"–6"	22	<0·5	56
	6"–12"	22	<0·5	100
	66"–72"	11	<0·5	46
	99"–102"	16	0·5	76

METAL P.P.M.

DEPTH IN INCHES	Ni	Ex Ni	Ex Mg
	>800		
	401–800		>3201
	200–400	>8·0	1601–3200
	101–200	4·1–8·0	801–1600
	51–100	2·1–4·0	401–800
	26–50	1·1–2·0	201–400
	14–25	0·6–1·0	101–200
	0–13	0–0·5	0–100

(1) Anomalous Ni, exNi and exMg concentrations are widespread about the intrusion in the Little Missouri flood plain.

(2) Very close to the kimberlite, highest metal concentrations occur in the near surface samples. In the more distant profiles maximum metal content and contrast generally occurs in the deepest sample analysed.

(3) Exchangeable Mg gives the largest contrast and aureole.

(4) Although the distributions of Ni and exMg are similar, exMg tends to concentrate at the ground surface in certain profiles whereas Ni does not, e.g. A.1, A.8, 1100N10W, 1600N00W.

(5) Relatively low metal concentrations are recorded between West Hill and the River. Only in A.3 is metal concentrated at depth.

(6) At A.14, $\frac{1}{2}$ a mile downstream from the pipe, metal content decreases with depth. Barely anomalous exMg and only background Ni concentrations are detected in the deepest sample analysed.

(7) At 1100N10W, anomalous concentrations of metal are restricted to the zone immediately above the pebble bed.

(8) A higher threshold is observed for Ni and exMg in the alluvium than in the soils derived from the Trinity siltstone.

7.15 Discussion

Insufficient data has been obtained to establish how the observed distributions were formed. One can, however, briefly speculate as to the possible processes.

Emplacement of metal in the alluvium is thought to be affected by three fundamental mechanisms:

(1) Dispersion of metal from the intrusion DURING deposition of the alluvium.

(2) Dispersion of metal from the intrusion AFTER deposition of the alluvium.

(3) Precipitation of certain metals from the Little Missouri ground waters due to the pipe forming a "precipitation barrier".

(1) and (2) are self explanatory but (3) requires further elaboration.

As previously mentioned, the pH of the Little Missouri ground waters rise from 5.0 upstream from the pipe to 8.0 adjacent to the intrusion. This may result in the precipitation of certain semi mobile elements, e.g. Fe, Mn, Cu which are stable in solution at the lower pH but which are hydrolized and/or oxidized as the pH rises. Moreover, some appreciably mobile elements, e.g. Zn, may be coprecipitated with the sesquioxides. Similar precipitation processes to those just proposed were observed by Theobald et al (1963). These authors found heavy precipitation of hydrous Fe and Mn oxides, and other elements, below the mixing of two streams, one of pH 3.5 and the other of pH 8.0.

The high pH about the pipe will also favour sorbtion of cations (Heydeman, 1959; Wilding, 1965; Arnorsson, 1969). Thus even mobile metal may be scavenged from the Little Missouri ground waters.

It is possible, therefore, that anomalous aureoles of certain elements may occur about the Prairie Creek pipe, but which are not contained in anomalous amounts by the intrusion. This was not investigated.

A greater anomalous aureole occurs in the vicinity of the water table than close to the surface. It was seen earlier in the thesis that both exMg and Ni, especially the former, are appreciably mobile. This is also reflected by the appreciable exNi content some distance from the pipe. It is suggested, therefore, that metal at depth has been largely emplaced by saline processes. This is supported by the considerable iron oxide staining present at depth in those profiles near to the intrusion.

The exMg/Ni ratio rises considerably in the anomalous profiles some distance from the intrusion (Table 7.2, below).

Table 7.2

	Increasing Distance Upstream from Intrusion							Background	
Location	00N1300W	00N1400W	00N1600W	A.7	A.9	A.8	A.1	A.16	A.15
exNi at depth %	3.8	6.3	4.3	26	21	10	5	5.2	4.7
pH	8.0	8.0	7.5	7.0	6.9	6.0	6.9	6.[illegible]	5.0

This is thought to reflect the lesser mobility of Ni than Mg.

At A.9 Ni is concentrated in limonite staining at depth, no doubt due to coprecipitation. It is noticeable, however, that exMg is not similarly concentrated in the sesquioxides.

In those profiles between West Hill and the river, only in A.3 are anomalous metal contents recorded at depth. This is also the only profile in which appreciable amounts of clay were found and it is suggested that anomalous metal contents are largely associated with clay particles.

A veneer of phlogopite rich ultrabasic detritus overlies the alluvium adjacent to the pipe, i.e. at 00N1400W to 00N1600W, A.11 and A.12. This is thought to be responsible for the high concentration of metal observed near the surface at these sites. Similarly, it is possible that the much lower, though anomalous, surficial metal contents at A.2, A.7 and A.9 are due to mechanical dispersion of material from the intrusion.

Exchangeable Mg but not Ni is concentrated at the ground surface in some of the more distant profiles. This may be due to association of exMg with organic matter due either to metal released during plant decay or/and to a high sorbtive capacity of the organic material.

Anomalous concentrations of metal are observed at a depth of 6 to 12 inches at A.7 and 00N1900W. Macroscopic ultrabasic material is not evident on the ground surface at these locations and a ferruginous B_2 horizon is not developed. The possibility must be considered, therefore, that the anomalous metal content was deposited during deposition of the alluvium.

A reddish B_2 horizon was observed in profiles A.1, A.8, A.3, A.4 and A.5 but not in the background profiles nor the profiles adjacent to the intrusion. The possibility must be considered that this "B_2" horizon is the result of precipitation of Fe from the Little Missouri ground waters as they approach the higher pH about the pipe. It must be emphasised, however, that this suggestion is highly speculative and is based on very limited morphological data.

A.14, half a mile downstream from the intrusion, is sited in a recently abandoned meander. The anomalous concentrations of metal recorded near the ground surface may be due to deposition of anomalous sediment in times of severe flooding. It is feasible that the increase in metal content towards surface may reflect accelerated erosion of the pipe during mining activity. It is unknown whether the anomalous exMg concentrations at depth, which occur just above the water table, are due to leaching of metal from the surface or to deposition from Little Missouri ground waters.

7.16 Summary and Conclusions

(1) Ground waters about the pipe are of higher pH than in limestone free background areas. This may cause a precipitation barrier about the intrusion.

(2) Anomalous concentrations of Ni and exMg occur for some distance about the pipe. Maximum dispersion occurs in the vicinity of the water table. Close to the pipe, maximum contrast is at the ground surface.

(3) Exchangeable Mg has the greater contrast and larger dispersion aureole.

(4) Insufficient analytical data is available to determine with any confidence the reason for the observed dispersion patterns. However, it is probable that dispersion at depth is largely saline and that near the ground surface dominantly mechanical.

CHAPTER 8

DISCUSSION OF THE BEHAVIOUR OF ELEMENTS DURING WEATHERING

8.1 INTRODUCTION

Having presented the data and discussed the mobility and possible modes of occurrence of the elements in soils and sediment, it is now convenient to discuss the reasons for and controls of their redistribution and dispersion.

Because many of the elements are concentrated in sesquioxide nodules (Table 4.17) the development of these nodules, and the redistribution of Fe and Mn in the soil profile, is discussed in some detail.

In Arkansas some of the elements are depleted in the C horizon compared with the parent kimberlite. This is discussed when appropriate. In Arizona the kimberlite bedrock is taken from a plug 50 feet high and 300 yards away from the profile considered. This is not considered representative of the rock underlying the profile investigated. Consequently, comparisons of the C horizon with parent material are not made for this area.

Before going on to discuss the various elements it is necessary to first outline the mechanisms of secondary dispersion. This may occur by either or both mechanical or saline processes.

Mechanical dispersion involves the physical removal of the elements as solid discrete particles by running water, gravity and/or wind. Dispersion in soils therefore is controlled to a large extent by topography, climate and vegetation. On steep slopes dispersion will occur downhill by means of soil creep, sheet wash and other gravitational influences. Where the slope is minimal, and in areas where a thick vegetal ground cover is present, the elements will tend to remain almost in place.

Mechanically dispersed material enters the drainage system by erosion of the banks, which may be residual, colluvial or alluvial. In areas of steep freely drained bank soils, metal may enter by sheet wash and soil creep. The subsequent dispersal history of an element depends upon the physical and chemical properties of its host mineral and velocity of the stream waters.

Saline dispersion involves the transportation of elements by leach waters, either in solution or as colloids. Precipitation of element(s) may occur either in the underground or surface environment. Elements precipitated in the surface environment may be detected by analyses of stream banks or sediments. Elements not precipitated may be detected by analysis of leach waters.

The dissolution and precipitation of an element is controlled by a multiplicity of factors including the solubility and stability of the host mineral in leach solutions, the composition of the leach solutions, the chemical properties of the element, the physico-chemical conditions of the environment, the reaction of the element with other components of the system including coprecipitation and sorbtion, and by the effect of organic matter and life processes in contact with the leach solution.

8.2 IRON AND MANGANESE

8.21 In the C Horizon

Iron has remained constant or even accumulated slightly in the C horizon of the Prairie Creek kimberlite (Table 4.9). A similar immobility of Fe during the initial stages of weathering of freely drained silicate rocks has been recorded by many writers:

Merill (1897); Goldich (1938); Short (1961); Hotz (1964); and in the laboratory by Keller et al (1963) and Pickering (1962). However, Kelley and Zumberge (1961) found Fe, and very little else, to be leached from weathered quartz diorite in Antarctica.

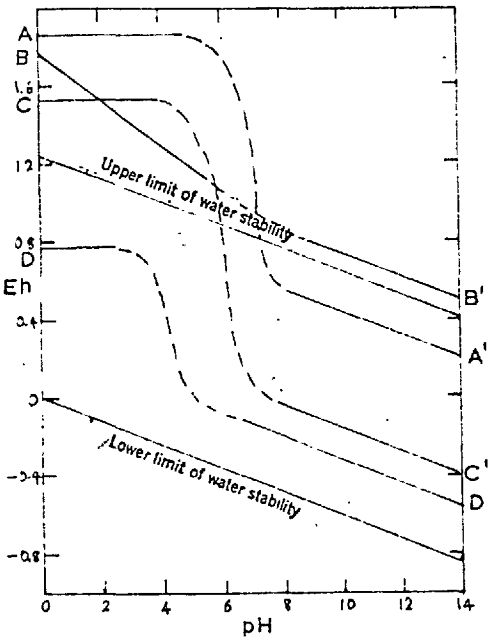
This immobility of Fe is due to oxidation and precipitation of metal released from its host minerals. This is facilitated by the alkaline or only slightly acid pH's developed during silicate rock weathering (Krauskopf, 1967; and Fig. 8.1). However, under poorly drained conditions, Fe may be removed in the divalent state (Melfi and Levi, 1968) if the Eh is low enough.

There is a higher Fe/Mn ratio in the C horizon of the Prairie Creek kimberlite than in the bedrock (below).

	yellow ground	blue ground	bedrock
Fe/Mn	74	91	67

This suggests that Mn has been leached to a slight extent from the C horizon. A similar increase in Fe/Mn ratio during the early stages of weathering of kimberlite rock is recorded by Fairbairn and Robbertson (1966) and for two Oregon peridotites by Hotz (1961 and 1964). This apparent loss of Mn may be explained by the low ionic potential of Mn^{2+} (Table 8.1) and its greater stability in solution than divalent Fe (Figs. 8.1 and 8.3). It is suggested in the following section that some Mn is leached from the B_3 horizon by tree roots. These are absent in the blue and lower yellow grounds and it is probable that Mn lost from the C horizon has been removed by percolating waters.

As mentioned in the introduction, it is considered meaningless to compare the Fe and Mn contents of the plug at Buell Park with those of the profiles investigated.



A. $Co^{2+} = Co^{3+} + e$

B $Ni^{2+} + 2H_2O = NiO_2 + 4H^+ + 2e$

C $Mn^{2+} = Mn^{3+} + e$

D $Fe^{2+} = Fe^{3+} + e$

A' $Co(OH)_2 + OH^- = Co(OH)_3 + e$

B $Ni(OH)_2 + 2OH^- = NiO_2 + 2H_2O + 2e$

C $Mn(OH)_2 + OH^- = Mn(OH)_3 + e$

D $Fe(OH)_2 + OH^- = Fe(OH)_3 + e$

FIGURE 8.1: Variation of oxidation potential with pH for certain reactions. (Modified from Mason, 1965).

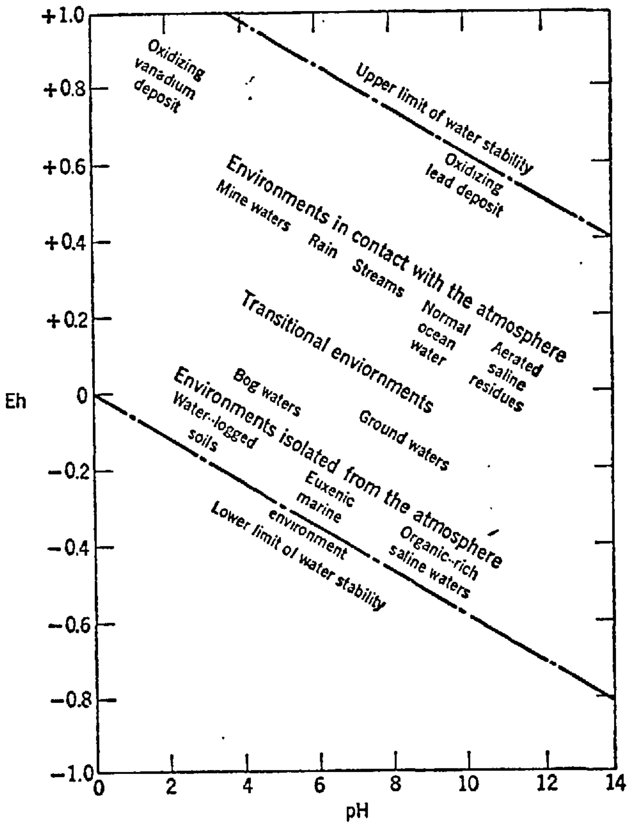


FIGURE 8.2: Approximate position of some natural environments as characterized by Eh and pH. (From Garrels and Christ, 1965).

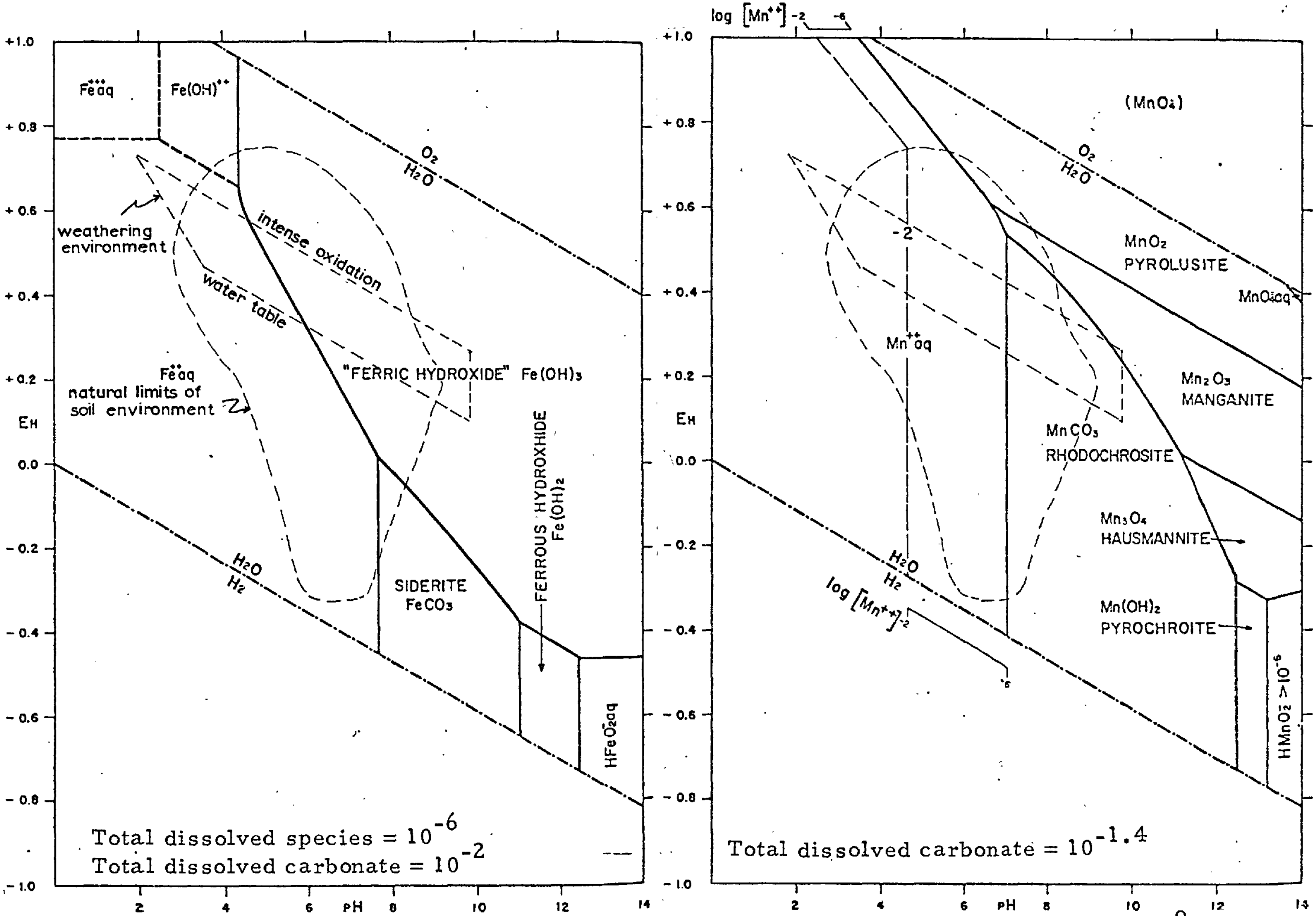


Figure 8.3: Stability relations between some iron and manganese compounds in water at 25°C and 1 atmosphere total pressure. Modified from Garrels and Christ (1965). Weathering environment after Sato (1960). Soil environment after Baas Becking et al (1960).

Table 8.1 The ionic potential of selected elements (modified from Mason, 1966)

Low ionic potential Elements may form soluble cations		Intermediate ionic potential Elements tend to concentrate in the hydrolyzates		High ionic potential Elements may form water soluble complex anions	
Rb^{+}	0.68	Y^{3+}	3.3		
K^{+}	0.75	La^{3+}	3.5	B^{3+}	13
Na^{+}	1.0	Th^{4+}	3.9	P^{5+}	14
Ba^{2+}	1.5	V^{3+}	4.1	may include Nb^{5+}, V^{5+}, Sr^{4+}, Mo^{6+} under certain conditions.	
Sr^{2+}	1.8	Ce^{4+}	4.3		
Ca^{2+}	2.0	Fe^{3+}	4.7		
Mn^{2+}	2.5	Cr^{3+}	4.8		
La^{3+}	2.6	Zr^{4+}	5.1		
Fe^{3+}	2.7	Al^{3+}	5.9		
Co^{2+}	2.8	Ti^{4+}	6.7		
Ni^{2+}		Mn^{4+}	6.7		
Mg^{2+}	3.0	Nb^{5+},	7.5		
		V^{5+}	8.5		
		Sr^{4+}	9.5		
		Mo^{6+}	9.7		

In the semi arid climate of the Buell Park area, where the C horizon extends virtually to the ground surface, little macroscopic alteration of the phenocrystic minerals (olivine, chrome diopside, pyrope garnet, etc.) has occurred. Iron and Mn are probably retained largely within their primary host minerals although small, but appreciable, amounts are found in the clay size fraction. Thus some slight decomposition of the primary minerals does occur. With the exception of a slightly higher concentration of Fe below the water table, which may reflect a greater degree of alteration of the host minerals, no vertical redistribution of Fe or Mn is apparent.

8.22 Iron and Manganese in the Soil Solum

In mature soils over the ultrabasic and country rocks in Arkansas, iron has been appreciably translocated from the A to the B horizon. This is a common process in podzolic and many other soils (Joffe, 1949; Lyon et al, 1952).

Although the fundamental mechanisms of the translocation of iron in the soil profile are still not fully understood, at least three processes may be operative viz.

(a) translocation as inorganic cations,
(b) translocation as colloids,
(c) translocation as organic complexes.

Although these mechanisms are discussed separately, it is likely that they operate together to varying degrees. In any one particular profile, one mechanism may be dominant.

(a) Translocation as inorganic cations

Under normal conditions in well drained soils, the Eh is usually sufficiently high to oxidise Fe^{2+} to Fe^{3+} (Fig. 8.3).

It is generally recognised that the solubility of Fe^{3+} is negligible above a pH of 3.5. In the field areas the pH of soils is in excess of 4.5, thus in freely drained soils Fe^{2+} released from its host minerals during weathering will be oxidised and precipitated in the trivalent form. It must be emphasised, however, that the Eh and pH's just mentioned are the macro values. Their values may be somewhat different on the surface of minerals and near roots etc.

Under reducing conditions iron may be reduced to, or remain, in the divalent form. Organic matter may assist in this reduction process (Gruner, 1922; Jones and Wilcox, 1924; Harrar, 1929; Lossaint, 1959; Stobbe and Wright, 1959). Fe^{2+} begins to hydrolise at pH 5.1 but is incomplete at 7.0 (Rankama, 1950). It is possible therefore that in acidic soils which are saturated with water for appreciable periods of the year, that some iron moves down the profile in the divalent form. This Fe may be precipitated during periodic dessication; where there is an appreciable rise in pH and/or Eh; by sorbtion of negatively charged particles, e.g. clay minerals, and/or by an increase in the content of electrolytes etc.

It is thought that this is one of the mechanisms for translocation of Fe in soils over the ultrabasic rocks, which are appreciably saturated during some periods of the year (discussed later).

(b) Translocation as colloidal sesquioxides

As previously mentioned, under oxidising conditions and at a pH greater than 3.5 iron released from its host minerals is precipitated as ferric sesquioxides. Some of these may be colloidal. These colloids may be "washed down" the profile as either charged or uncharged colloids or as humus protected sols.

Aaernio (1913) was the first to suggest that hydrated free oxides are transported as negatively charged humus protected sols. More recently, Deb (1949) has shown that humus may carry 3 to 10 times its own weight of iron oxide and that different fractions of organic matter vary in their power to "protect" the oxides. The "humus protected sol theory" assumes the oxides are precipitated in the B horizon by the divalent cations (Stobbe and Wright, 1959). Whilst the B horizon of soils over the ultrabasic rocks has an ample supply of divalent cations to make such precipitation possible, the supply of cations in soils over the Trinity formation may be very low and it is uncertain whether they could bring about precipitation of the oxides.

Mattson (1934 and 1942) explained the formation of complexes and the movement and precipitation of sesquioxides by isoelectric weathering. This theory demands a significant pH gradient with depth. Such a gradient is present in soils over the ultrabasic rocks, but not in the well drained soils over the Trinity siltstone.

Uncharged colloids, and the charged and humus protected sols just mentioned, may also accumulate in the profile, along with clay minerals and other fine particulate matter, where the pore space is too small to allow further downwards movement. In addition, charged colloids may be sorbed on certain materials e.g. clay minerals. This process may be operating in the red-yellow podzolic soils of the Trinity formation, where appreciable amounts of clay are eluviated to the B_2 horizon.

(c) Translocation as organic complexes

The possibility of reaction between sesquioxides (and compounds of other elements) with organic matter has been noted by many writers. Iron may react with organic acids to produce anionic complexes (Galagher, 1942; Galagher and Walsh, 1943; Rode, 1937), complex ions (Jones and Wilcox, 1929) and other soluble and insoluble complexes (Sherman, 1953; Alexsandrova, 1954; Kononova, 1956; Yarkov, 1956; Bloomfield, 1957; Bregger, 1954; Kawrichev, 1958; Hem, 1960), including metal chelates (Barshad, 1955; Schnitzer and DeLong, 1952; Wright and Levick, 1965).

The soluble metallo-organic compounds will be carried down the profile by percolating rain waters. They may be precipitated as basic salts (Jones and Wilcox, 1922), by destruction of the organic ligand (Starkey and Halvorson, 1927), due to oxidation probably accelerated by microbiological action (Yarkov, 1956; McKenzie, 1957) and by sorbtion on clay minerals etc., (Bloomfield, 1955; Stevenson, 1960); especially on cracks and fissures in the sub soil (Schatz et al, 1954). Kononova (1956) stated that the mobility of the complexes and their immobilization, depend on the reaction of the medium,the concentration of humic materials, and the oxidation-reducing conditions.

The role played by organic compounds and micro organisms in the redistribution of Fe in the soil profile probably cannot be over emphasised. Processes similar to those just outlined may have played an important role in the translocation of Fe from the A to the B horizon in both the ultrabasic and country rock soils alike.

A substantial proportion of Fe translocated to the B horizon of the ultrabasic rocks is present as sesquioxide nodules and mineral aggregates. Whilst some of these are undoubtedly grains of iddingsite, this mode of occurrence cannot be ascribed to them all. Since many of the trace elements are concentrated in these nodules (Table 4.17) they are discussed in some detail.

Sesquioxide nodules have been recorded by many writers from different types of soil from many parts of the world. Most authors agree that they are typical of soils subjected to seasonally oxidising and reducing conditions, usually brought about by a fluctuating water table. Several writers (Winters, 1938; Bryan, 1952; Fowler, 1928 and Grange, 1934) also record nodules to be present in soils which have suffered considerable degradation.

Several theories have been put forward to explain the origin of these nodules in various areas. The main postulates are summarised below:

Brooks (1965) attributes sesquioxide concretions in a New Zealand yellow grey earth to precipitation of ions leached from the A horizon.

Drosdoff and Nikiforoff (1940) considered two general processes to occur in Dayton soils: (a) it was thought that Fe and Mn after being bacterially oxidised and cemented into solid grains, might become unavailable to micro organisms. The developing colony would therefore be forced to extract its own supply from the surrounding medium. A local precipitation of Fe and Mn at the point of concretion formation might disturb the uniform concentrations of these elements throughout the matrix. To restore equilibrium the elements being depleted would diffuse towards the point of precipitation; (b) alternatively, the large pores are first freed of water, thus leading to the formation of wet and dry areas. As drying proceeds, the water from each saturated area could retreat towards points inside the area with the smallest pore space, with ultimate precipitation of Fe and Mn taking place at the points of final dessication. Once formed the concretions could grow year by year adsorbing and oxidising Fe and Mn ions at their surface.

Similar conclusions were reached by Sherman et al (1949), Joffe (1949) and Vamos (1963). They suggested metal to be reduced during the wet season and to be precipitated during the dry season as pH and Eh values increase. Vamos found a number of amino acids in nodules and concluded that some biological process was instrumental in their formation.

Sherman and Kanehiro (1954) discussing Hawaiian latosols, suggest concretionary aggregates found on an old peneplain to be due to "decomposition" of Fe oxides on the surface of soil aggregates. Ascending capillary waters from just below the surface carried the dissolved Fe towards surface. Hawkes and Webb (1962, pp. 98-99) say "less soluble colloid materials may likewise rise towards the surface and coagulate to form a concretionary horizon near the upper level reached by the water table".

Although soils over the Prairie Creek kimberlite are some distance above the water table and are topographically well drained, it is believed that self induced impeded drainage conditions prevail during the wet season for the following reason. The solum of soils over the ultrabasic rocks contains a considerable proportion of clay minerals, probably montmorillonite (Chapter 4). Montmorillonite has the ability to adsorb interlayer water; for example, at a water vapour pressure of 5 mm, it will adsorb 24% by weight of water (Ross et al, 1945, p. 53). This is equivalent to 7 inches of rainfall per foot depth of montmorillonite. It is probable, therefore, that during the wet season the B horizon contains a substantial proportion of water. During the dry season much of the water is probably removed by plant transpiration, evaporation, capillary action, etc.

It is suggested, therefore, that during the wet season reducing conditions prevail in the B horizon in soils over the ultrabasic rocks. At such times Fe^{3+} is reduced and mobilised most likely assisted by organic matter. During drying up of the B horizon metal ions or colloids migrate towards the points of smallest pore space, as envisaged by Drosdoff and Nikiforoff (1940), and precipitate as drying proceeds and presumably Eh conditions rise. Oxidation may also be accelerated by biological action. The possibility that some nodules are formed by precipitation round centres as postulated by Brooks (1965) is not discounted.

The reason why ferriferous nodules in the soil profiles over the ultrabasic rocks are most abundant in the minus 20 plus 36 mesh fraction is unknown. This is somewhat smaller than the average grain size observed by other writers; although size may range from 0.05 to 10 mm (Winters, 1938).

Unlike soils over the ultrabasic rocks, it is unlikely that low Eh conditions exist in the well drained, clay poor, porous soils over the Trinity siltstone. The possibility must be considered, therefore, that the nodules found in these soils were developed at some time in the past when the water table was higher than at present. This suggested elevated water table is consistent with several other features of these soils (Chapter 5).

The distribution of Mn in the soil profile is broadly similar to that of Fe. There are, however, the following important differences:

(1) In the soil solum over the ultrabasic rocks, Mn occurs as nodules and is not concentrated in the clay fraction. In contrast Mn is concentrated in the clay size of soils over the Trinity siltstone.

(2) In contrast to Fe, Mn is very considerably enriched in the A horizon, especially in soils over the Trinity

siltstone. Assuming Sr to have remained constant in soils over the kimberlite, Mn is considerably enriched in the solum.

(3) Manganese is depleted slightly in the B_3 horizon of the profile over the Prairie Creek kimberlite at 00N40W.

(4) Manganese nodules are of coarser grain size and have a lower specific gravity than those of Fe.

The Mn sol is negatively charged (Rankama, 1950). In the presence of abundant cations, or other positively charged particles, neutralisation and subsequent flocculation of Mn colloids may occur. This is probably the main reason why Mn occurs as nodules in soil over the ultrabasic rocks in which cations such as Mg^{2+} and K^+ are abundant (Pickering, 1963). Cations, excluding H^+, are probably scarce in soils over the country rocks and neutralisation of the Mn sol may not occur. Other factors which may also contribute to the formation of nodules rather than clay size particles include micro-biological action (Rankama, 1950; Drosdoff and Nikiforoff, 1940), and the ready flocculation of certain Mn - humic complexes (Swain, 1963).

Numerous writers have observed Mn to be enriched in the A horizon. Three possible reasons for this are considered:

(1) Manganese dioxide, once precipitated, may be less easily remobilised than Fe (Butler, 1954).

(2) Upward leaching of Mn by capillary action, movement along intergranular moisture films etc.

(3) Ingestion of Mn by plants and restoration in the surface litter (Leeper, 1938).

Suggestion 1 i.e. MnO_2, once precipitated, may be less easily mobilised than Fe

According to Rankama (1950) and Krauskopf (1957 and 1967) and from thermodynamic data (Figs. 8.1 and 8.3), Mn^{2+}

is less readily oxidised to immobile higher valencies and is stable over a wider range of pH-Eh conditions than is Fe^{2+}. It follows, therefore, that the oxides and hydroxides of Mn^{3+} and Mn^{4+} are theoretically easier to reduce and mobilise than are the corresponding compounds of Fe^{3+}. This was confirmed in the laboratory by Takai and Kamura (1961) and Koyama (1964) who found Mn to be leached from a paddy soil at a higher Eh than Fe.

It is difficult therefore to explain why Fe should be leached in preference to Mn, although this does occur in some soils (Butler, 1954). The following reasons may be partly responsible for such a process:

(a) Aging and/or dehydration of Mn oxides to more inert forms (Leeper, 1938), whilst Fe hydroxides may not age so rapidly or completely (Thompson*, pers. comm.).

(b) The preferential reduction of Fe by organic matter. Mandal (1961) found Fe entering solution in a water-logged rice field to be in excess of Mn when green foliage was added. When organic matter was not added the reverse occurred.

(c) The formation of insoluble Mn metallo-organic complexes; or a preferential formation of soluble Fe complexes.

(d) That translocation of Fe and Mn is largely as colloids. The dissociation of Mn nodules would not be favoured by the presence of positively charged particles.

Whilst the process being discussed cannot be disproved in the kimberlite profile at 200N15W where Mn nodules occur higher in the profile than do those of Fe (cf. Pelisek, 1936); it is disproved in the profile at 00N40W where a higher enrichment of Mn than Fe occurs in the B_2 horizon (Table 4.8).

There is insufficient data to comment meaningfully upon the relative mobilities of Fe or Mn in soils over the Trinity formation.

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Suggestion 2 i.e. Upward leaching by capillary action etc.

Experimental studies have established the limits of capillary action to be a few inches in coarse sand to about 30 feet in clays (Hawkes and Webb, 1962). The water table is in excess of 40 feet below the surface in the environs of the kimberlite soils considered (Thoenen, et al, 1949), and probably many tens of feet from the surface of the Trinity siltstone profile investigated. Although some upward movement of metal may occur by movement along intergranular moisture films (Marshall, 1959), upward leaching of Mn from the water table is thought unlikely. However, it is possible that some Mn may be transported towards surface during the "drying up" of the B horizon of the kimberlite soils mentioned on page 246. This would conveniently explain the presence of Mn nodules higher in the profile than those of Fe in profile 200N15W as mentioned on the previous page.

Suggestion 3 i.e. Ingestion by plants and restoration in the surface litter

Low Eh and pH conditions are generally encountered about plant roots and may cause reduction and mobilisation of Fe and Mn compounds (Schroeder and Schwertman, 1955). The mobilised metal may be ingested by the plant and transported to those parts of the plant above the ground surface. On the death and decay of the plant or its appendages, metal will be liberated in the A horizon.

The process just mentioned is the simplest explanation for the enrichment of Mn at the ground surface with respect to Fe, and is therefore thought the most likely. Moreover, Mn is depleted in the B_3 horizon of the kimberlite profile at 00N40W. Roots are abundant in this horizon but seldom penetrate below it.

This observed loss of metal is thought to reflect Mn removed by vegetation.

The reason why Mn is concentrated in the A horizon with respect to Sr, is thought to be due to the preferential removal of the smaller (silt size) Sr host minerals by the natural agencies of soil erosion.

Just why Mn nodules are larger than those of Fe is uncertain but it is a feature noted by several writers, for example, Smolik (1940), Winters (1938), and Drosdoff and Nikiforoff (1940).

8.23 Dispersion from Kimberlites

In freely drained soils downslope from a kimberlite sub-outcrop at the American Mine, anomalous concentrations of Fe extend for over 100 feet in the A horizon but only 15 feet in the $B_{2.1}$ horizon. This indicates dispersion, at the present time, to be dominantly by mechanical processes.

Underlying the orange/red $B_{2.1}$ is a mottled zone. There is no reason to dispute the widely accepted tenet that such mottled zones are due to fluctuating Eh conditions brought about by a fluctuating water table. However, since the present water table is probably several tens of feet below the ground surface, the mottled zone must have been developed at some time in the past when the water table was higher than at present. Thus, some saline dispersion of Fe has occurred in the past. This is reflected by the considerable iron oxide staining at the contact with an impure limestone found at depth immediately downslope from the kimberlite. Precipitation of Fe is due to hydrolysis and oxidation at the high pH (7 to 8.3) developed over the limestone.

Manganese is similarly dispersed, although the initial increase in Fe/Mn ratio of the A horizon downslope from the kimberlite (Table 8.2, below) indicates Mn to be more readily leached from anomalous material than is Fe. In addition, Mn sesquioxides are found on fracture surfaces in the body of the limestone where Fe sesquioxides are not common, this is presumably due to the greater stability of Mn^{2+} than Fe^{2+} ions.

Table 8.2

Distance from kimberlite, ft.	0	4	14	24	34	49	114	174	324	Bkgrd
Fe/Mn in the A_1 horizon	9	12	10	16	11	21	35	24	18	85

American Creek runs in a flood plain of A horizon colluvium overlying Quaternary alluvium. During the wet season the water table rises to within a foot or so of the flood plain surface and water enters the stream through the banks and bed. In the dry season the water table is several feet below the ground surface and the streams may dry up completely. The colluvium is mottled in the zone of ground water fluctuation indicating alternating reduction and oxidation of Fe. Presumably therefore Fe and Mn are dispersed to some extent by saline process during the wet season.

Iron and Mn are concentrated in orange mottles on the bank surface below the wet season water level and as dark sesquioxide coatings in the stream bed, especially in the interstices of the Quaternary alluvium. Encrustations of Fe/Mn oxides coating pebbles and in stream and lake beds have been observed in poorly drained environments by many writers, e.g. Kindle (1936); Boyle et al (1966); Canney (1966); Horsnail (1969); Ljungren (1951).

Precipitation of metal is attributed to oxidation of metal moving in ground waters at the ground surface water interface. Oxidation being due to aeration, an increased oxidation potential of the surface waters and by biological action. A similar mechanism is no doubt responsible for the stream bank deposits in Arkansas.

In stream sediments, which were collected towards the end of the wet season, neither Fe nor Mn are concentrated in the slime or minus 300-mesh fraction compared with the normal minus 80-mesh fraction. This is attributed to the considerable flushing out of clay size components during the wet season (Table 6.23).

Both Fe and Mn are concentrated in the plus 80-mesh fractions of stream sediment where they occur as nodules and mineral aggregates. The proportion of nodules increases towards kimberlite suboutcrop (Table 6.26), and only in streams draining, or downslope from, kimberlite are coarse sized Mn nodules common. There can be little doubt that these nodules are dispersed mechanically. However, the possibility that some nodules may be formed in situ cannot be entirely ignored.

As mentioned in Chapter 6, brown sesquioxide nodules and mineral aggregates are common in sediment over the Trinity limestone. It is unknown whether these are formed in situ by precipitation of metal from surface waters due to the high pH developed over the limestone, or whether they were formed in soils over this rock type.

8.3 NICKEL AND COBALT

8.31 In the C Horizon

Although Mg has been leached from the yellow and blue grounds of the Prairie Creek kimberlite, there is no increase in

Ni content reflecting the subsequent deflation. Cobalt, however, is enriched in the yellow ground, but not to the same extent as Sr, which is thought to have remained constant during weathering. It would appear, therefore, that some Ni and possibly Co have been leached from the weathered bedrock. This may be explained by the mode of occurrence and stabilities of the ions in question.

Divalent Ni usually replaces Mg^{2+} in the silicate minerals of kimberlite due to ionic radii similarities. It is possible, therefore, that the dissolution of Mg is accompanied by the dissolution of Ni. However, the hydrolysis of Ni^{2+} starts at pH 6.5 (Crooke, 1956) to 6.7 (Hawkes, 1957) though incomplete at 8 (Fig. 8.4). The pH of the kimberlite C horizon is 8.0 to 8.3, thus most of the Ni released is immediately hydrolized. This may subsequently react with Mg and silica to form hydrous Ni magnesium silicates, e.g. garnierite (Wilding, 1965). The charged Ni sol may also be sorbed by clay minerals and by the colloids of magnesia and silica (Barth, 1948) and may be removed from the profile along with the latter by percolating waters.

The ionic radius of Co^{2+} is slightly larger than that of Ni^{2+} and Mg^{2+} and in silicate minerals Co may replace either Mg or divalent Fe. Iron released from its host minerals in the kimberlite C horizon is hydrolized and oxidised. Cobalt is readily co-precipitated with sesquioxides (Jenne, 1968). It is probable therefore that Co released during weathering along with Fe is retained largely within the secondary products of the host mineral. However, the hydrolysis pH of Co^{2+} is in the order of 8 to 9 (Fig. 8.4), depending to some extent upon the concentration. It is thought unlikely that the Eh is high enough to oxidise Co^{2+} to Co^{3+} in the kimberlite profile. Thus divalent Co ions which escape from the host minerals may be

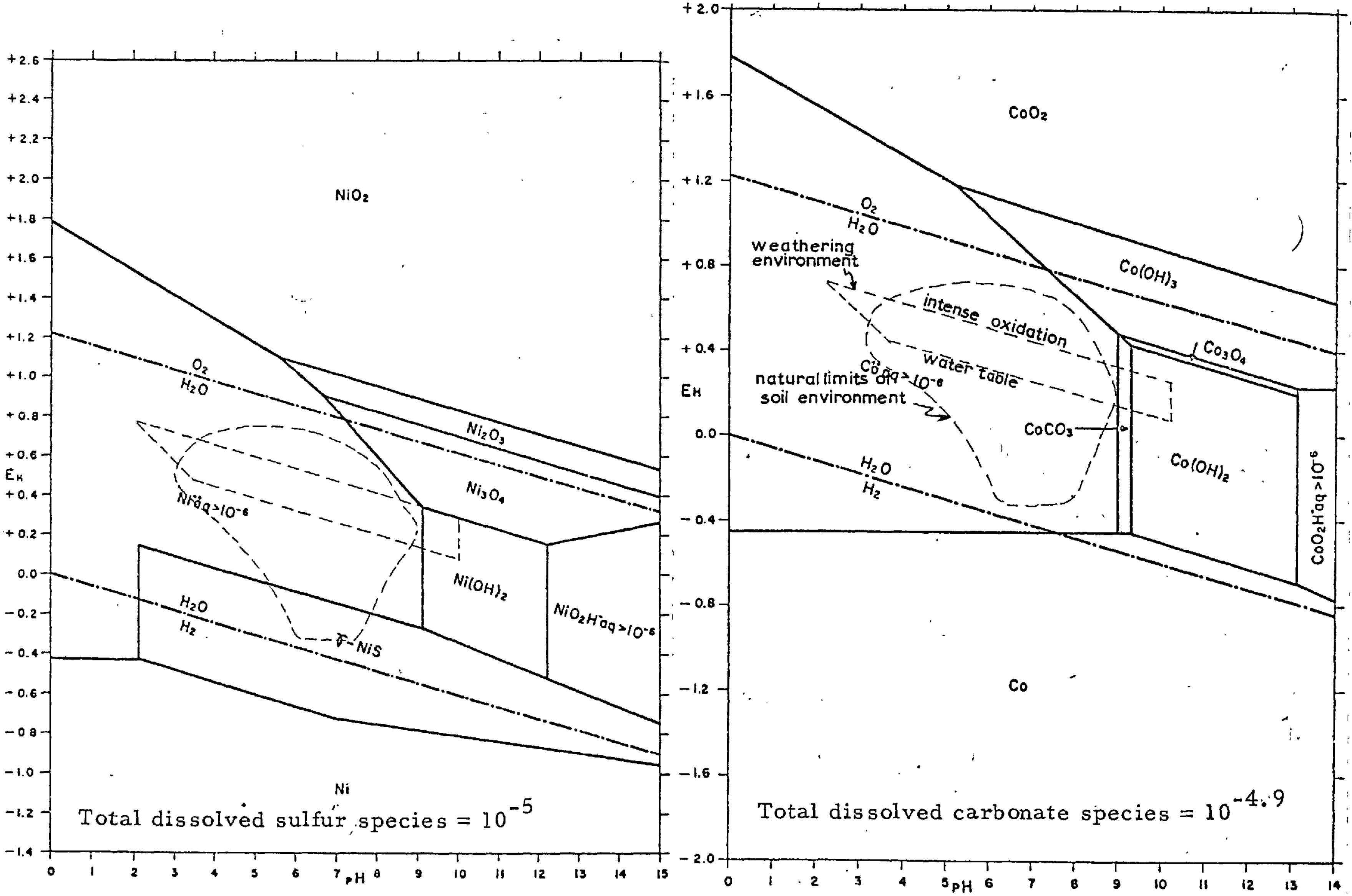

Figure 8.4: Stability relations between some nickel and cobalt compounds in water at 25°C and 1 atmosphere total pressure. Modified from Garrels and Christ (1965). Weathering environment after Sato (1960). Soil environment after Baas Becking et al (1960).

removed from the profile by percolating waters or, like Ni, sorbed on the colloids of magnesia or silica.

In Arizona where the C horizon extends virtually to the ground surface, there is no apparent vertical redistribution of Ni or Co. This is thought to be due to the lack of weathering of the host minerals. There is, however, a slight increase in exNi towards the water table. This may reflect progressive alteration of the host minerals towards the water table.

8.32 In the Soil Solum

Nickel has been leached from the A horizon of the Prairie Creek kimberlite and is concentrated in the B_2 horizon in sesquioxide nodules, principally those of Mn, and in the clay fraction. Since the concentration of Ni is the same in the clay size of the A and B horizons, translocation in this fraction is probably largely by mechanical processes.

An enrichment of Ni and Co in sesquioxide nodules has been recorded by many writers, e.g. Brooks (1965), Kubota (1965), Kennedy*, pers. comm. (1969), and in Mn nodules by Taylor and Mackenzie (1964). The enrichment of Ni in nodules in the Prairie Creek kimberlite is attributed to co-precipitation, adsorbtion of cationic Ni by the negatively charged Mn sol (Fig. 4.15) and to metal present in iddingsite grains.

Assuming Sr to have remained constant, then there is a loss of about 40% of the Ni from the solum. Although Ni^{2+} is appreciably soluble in carbonated waters (Santos Ynigo and Esguerra, 1961) hydrolysis of Ni^{2+} starts at 6.5 (Crooke, 1958).

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The pH of the kimberlite soil profile increases from 6.5 in the A horizon to 8.3 in the C. One might expect, therefore, Ni to become progressively precipitated with increasing depth. This does not occur. The possibilities must be considered therefore that Ni has been removed from the profile either adsorbed on colloids (e.g. those of magnesia or silica as previously mentioned), or as soluble undissociated metallic organic compounds or soluble fulvates (Schnitzer et al, 1966).

An increase in Ni content with depth is recorded in soils over kimberlite by Holman (1966) and Alcard (1959). Numerous writers (Hotz, 1964; Wilding, 1965; Santos Ynigo and Esguerra, 1961; De Vletter, 1955; Anand Alwar and Banerjee, 1963) have noted Ni to be leached from the top few feet of lateritic soils over ultrabasic rocks but to be enriched, with respect to the bedrock, lower in the profile.

The distribution of Co in the solum over the kimberlite is very similar to that of Mn. Association of Mn and Co in the exogenic environment has been observed by a great many writers and is discussed by Jenne (1968). Most authors agree that the association is due to co-precipitation of Co with Mn sesquioxides and there is no reason to dispute this conclusion.

Cobalt, however, is not enriched in the A horizon of the Prairie Creek kimberlite to the same extent as Mn (Table 8.3, overleaf). This is thought to reflect a greater proportion of Mn than Co re-distributed through organic agencies.

In well drained soils over the sialic country rocks both Ni and Co are concentrated in the $B_{2.1}$ horizon. This distribution is similar to that in podzols in other parts of the U.S.A., e.g. Painter et al (1947), Hill et al (1953).

Although enrichment is due partly to occurrence of metal in sesquioxide nodules, Ni and Co, along with Fe, are enriched in the clay size fraction. At the pH of 5.9 found in the $B_{2.1}$ horizon, both Ni and Co are stable in aqueous solution. It is concluded, therefore, that precipitation of Ni and Co in the B_2 horizon is due to coprecipitation with sesquioxides and sorbtion on clay minerals.

Table 8.3

	A_1	B_2(upper)	B_2(lower)	B_3	Y.G.	B.G.
Mn/Co in profile OON4OW	21	13	9	7	9	8.5

In the A horizon, Ni and Co are coprecipitated with Mn in the clay size fraction.

8.33 Dispersion from Kimberlite

Prolonged anomalous trains of Co and Ni are present in the A horizon of freely drained residual soils downslope from a kimberlite suboutcrop at the American Mine. A much shorter anomalous train is present in the $B_{2.1}$ horizon. Moreover, the anomalies are detectable over a greater distance in the complete sample than in the minus 80-mesh fraction (cf. Figs. 5.2, 5.3 and Table 5.1). This indicates dispersion at the present time to be dominantly mechanical.

The longest anomalous train for Ni in a section downslope from kimberlite suboutcrop occurs in the $B_{2.2}$ horizon and is coincident with the lowest pH values. Moreover, adjacent to the intrusion, Ni is concentrated in the profile where the pH is lowest (Figs. 5.1 and 5.2). Since, as a general rule, Ni compounds are more soluble at low pH values than at high ones, this concentration of metal where the pH is minimal is unlikely to be due to precipitation of Ni leached from the overlying A horizon. It is suggested that Ni was emplaced by saline dispersion from the kimberlite at a time in the past when the water table was much higher than at present. Precipitation of Ni is due partly to coprecipitation with limonite since metal is concentrated in the orange compared with white mottles (25 and 12 ppm, respectively re Ni at site 179). However, Ni is also enriched in Mn sesquioxides on fracture surfaces in the body of the limestone no doubt reflecting the high mobility of the Ni^{2+} ion.

From the limited data available for Co it would appear that a generally similar dispersion process is present, although metal is considerably concentrated, along with Mn, in the A horizon.

The suggestion that Ni and Co have been partly dispersed by saline processes in the past is supported by certain features of the areal distribution of these elements in the $B_{2.1}$ horizon at the American Mine. Whilst Ni appears to have been more mobile than Co there are several features of the Co distribution which are not understood. These are mentioned in Chapter 5.

Anomalous concentrations of Ni and Co are detected in the zone of ground water fluctuation down drainage from kimberlite in the banks of American Creek (Fig. 5.12). Anomalous Ni concentrations "fall off" less rapidly than do those of Co. Cobalt is concentrated in the orange compared with the white mottles (Table 6.25) but this is not always the case for Ni. A similar anomalous aureole is detected in the flood plain of the Little Missouri River about the Prairie Creek pipe (Fig. 7.3), where Ni is concentrated in limonitic compared with white mottles (Table 4.17). There can be little doubt, therefore, that under poorly drained conditions Ni, and to a lesser extent Co, are dispersed in ground waters and that precipitation is largely controlled by coprecipitation with limonite.

There is a possible tendency for higher concentrations of Ni to be present on the stream bank below the wet season water level than in mottled material taken from profiles inside the bank. This is probably due to coprecipitation of metal with limonite deposited from emerging ground waters in the wet season.

Both Ni and Co are generally enriched in the wad compared with stream sediments. However, this is not always the case and the enrichment is not particularly marked. This is in contrast to the findings of Boyle et al (1966) and Canney (1966) who found considerable enrichments of Ni and Co in Mn sesquioxide precipitates in Canada. This apparent discrepancy is thought to be due to the very low Fe and Mn content of the "wad" (Table 6.19). This is due to the fact that sesquioxides occur as thin skins coating quartz grains. It is likely that if the sesquioxide cement were separated and determined an appreciable enrichment of Ni and Co would be found.

Although a substantial proportion of Ni in the minus 300-mesh fraction of highly anomalous sediment is extracted with 0.025% HNO_3, and is therefore very loosely held (Table 6.21), metal does not concentrate in the slime compared with the normal minus 300-mesh sediment. Since the slime is richer in clay size components and probably organic matter than is the minus 300-mesh sediment, this would suggest that Ni and Co do not precipitate markedly in the fines downstream from kimberlite. This is consistant with the decreasing pH downstream from the intrusion which would favour dissolution of Ni and Co rather than precipitation. Moreover, metal deposited with the hydrolyzates in the wet season will be swept away by the fast flowing streams. It is concluded, therefore, that the observed dispersion patterns in the minus 80 and minus 300-mesh fractions are largely the result of mechanical dispersion.

There is little doubt that dispersion in the minus 10 plus 20-mesh fraction is by mechanical processes. However, it is possible that some nodules may be formed in situ under certain conditions, for example where there is an appreciable rise in stream pH or Eh, and that Ni and Co may be coprecipitated with the sesquioxides.

The threshold for Co in background stream sediments (30 ppm) is very much higher than the Co content of the minus 80 mesh fraction of background soils (3 ppm). This is attributed to coprecipitation of Co with Mn nodules of minus 80 plus 300-mesh grain size. There is a tendency for a lower Co content in stream sediment from juvenile streams than in streams flanked by an appreciable flood plain. This would suggest these nodules to be formed in the stream by precipitation of metal from emerging ground waters. The Ni threshold in the minus 80-mesh fraction of stream sediments is not disimilar to that for background soils. Thus, if Ni enters the streams in solution in poorly drained background areas, it is either precipitated with the hydrolyzates and flushed out of the system, or remains in solution and is removed by surface waters.

In Arizona, Ni and Co are retained largely within their host minerals during weathering and dispersion is therefore dominantly mechanical. However, appreciable concentrations of exNi are present in the stream sediment, especially in the finer fractions. This is probably due to mechanical dispersion of decomposing Ni bearing minerals, although the possible presence of some Ni dissolved in leach waters cannot be entirely ignored.

8.4 MAGNESIUM

Magnesium has been strongly leached from the soil solum and upper C horizons of profiles over the ultrabasic rocks in Arkansas. A loss of Mg during the earliest stages of the chemical weathering of ultrabasic rock has been recorded by many other writers, e.g. Fairburn and Robbertson (1966), Wright and Salazar (1955), Wilding (1965), Hotz (1961 and 1964) and Pecora (1944).

There can be little doubt therefore that Mg is highly mobile. Indeed, Clark (1904) and Smythe (1913) suggested Mg to be the third most mobile of the common elements, i.e.

most mobile Na > Ca > Mg > K > Si > Al = Fe

Anderson and Hawkes (1958) found Mg to be more mobile than even Na and Ca in stream waters of New England.

This high mobility of Mg may be predicted from its chemical properties. Most Mg compounds are soluble in water the most important exception being the carbonate. Hydrolysis of Mg^{2+} does not occur below a pH of 10 (Atkins, 1930); and even the hydroxide is soluble in water to the extent of 100 ppm (Mial, 1956).

Leaching and redistribution of Mg in soils is believed to be controlled largely by the following factors:

(1) The extent of weathering of the host minerals.

In ultrabasic rocks Mg is present primarily in ferro magnesian silicates. During chemical weathering these decompose through phyllosilicates to clay minerals according to the simplified sequence below:

olivine) serpentine) clay minerals → iron oxides
pyroxene) → phyllosilicates) → silica
phlogopite) iddingsite)
increase in weathering →

This sequence consists basically of addition of water and removal of Mg. Thus the extent to which Mg may be removed from the profile depends how far chemical weathering has progressed.

A difference in the degree of alteration of the Mg host minerals is believed responsible for the higher Mg content of the solum over the Prairie Creek peridotite than kimberlite.

(2) The nature of the leach solutions.

Carbonated waters are more effective leaching agents of Mg than are neutral waters (Keller et al, 1963). This is due to the greater solubility of Mg bicarbonate than hydroxide.

(3) The rapidity of movement of leach solutions.

A rapid circulation of ground waters will allow the quick removal of soluble products. This will be especially important in neutral ground waters because of the low solubility of Mg hydroxide.

A difference in the rate of ground water flow is believed responsible for the greater leaching of Mg at depth in the peridotite profile at 00N800W than at a corresponding depth in the usually more altered kimberlite.

(4) Reaction with other components of the system.

Magnesia may react with alumina and silica to form clay minerals which are relatively stable to weathering solutions. Magnesium ions may also be sorbed by clay minerals, organic matter, sesquioxides, etc. This latter process is believed responsible for the concentration of Mg in the B horizon of soil profiles.

(5) Ingestion by vegetation.

Magnesium is an essential element to plants where it occurs in the protoplasm, chlorophyll and in the sap (Zimmerman, 1947). Metal will be thus extracted by plant roots and deposited at the ground surface on the death and decay of the plant. The liberated metal may be dispersed in ionic solution, sorbed on organic matter or complexed with organic compounds. This process is believed responsible for the concentration of exMg in the A_0 horizon in some profiles.

(6) Upwards movement by capillary action.

This mechanism is important in those areas where precipitation is low and evaporation high, as in Arizona. Upward movement of soluble salts may occur during the dry season with metal being deposited at the capillary fringe and/or at the ground surface.

Because of the high mobility of Mg, and the highly anomalous concentrations present in the ultrabasic rocks, it is an ideal element with which to investigate saline dispersion from the kimberlite. In this study it was decided to determine the exchangeable metal since this will be largely the form deposited from ground waters draining kimberlite.

In soils downslope from a kimberlite suboutcrop at the American Mine (Figs. 5.2 and 5.3), exMg is concentrated in the B_2 horizon near to the intrusion. This is no doubt due to the high clay and sesquioxide content of this horizon, which is able to adsorb metal leached from material dispersed mechanically in the A horizon.

At some distance from the kimberlite where the clay content is not so high and the soil is more porous, Mg is carried down to the water table and dispersed in ground waters. Soil samples taken from the zone of water table fluctuation in the flood plains of American Creek and the Little Missouri River, contain anomalous concentrations of exMg for some considerable distance from the known ultrabasic rocks. Moreover, anomalous concentrations of exMg are detected on the banks of American Creek, below the wet season water level, for some distance downstream from the kimberlite. Generally, contrast decreases with increasing distance from the intrusion. At similar distances from the kimberlite, higher exMg contents are found in clay rich samples and orange mottles than in clay poor samples and white mottles. This is presumably due to the higher sorbtive capacity of the two former materials. There can be little doubt, therefore, that a substantial saline aureole is present for Mg in ground waters draining kimberlite.

The effect of pH on the adsorbtion of Mg by clay minerals was not investigated. But since hydrogen ions will replace Mg^{2+} held in exchange on kaolinite, it is probable that adsorbtion of Mg^{2+} is favoured by a high pH and desorbtion by a low pH.

At some locations on the flood plains of American Creek and the Little Missouri River, notably "S" and A.8 (Table 5.3 and Figure 7.3, respectively), anomalous concentrations of exMg occur at the ground surface but not in the underlying B horizon. This is probably due to ingestion of Mg from ground waters by deep rooted plants, followed by restoration at the ground surface.

In stream sediments a very much higher exMg threshold is present in the minus 300-mesh fraction than in the same size of residual soils. This is thought to be due to leaching of Mg from the country rocks and the ready adsorbtion of Mg^{2+} by clays in the drainage (Noll, 1931).

Only very short anomalous exMg trains are found in the minus 300-mesh fraction of sediment downstream from the American Mine. This is thought to be due to the paucity of clay minerals in the drainage due to the considerable flushing out of fine sediment during the wet season. It is unknown whether all the available exchange positions are satisfied. The content of exMg in the wad and slime was not investigated, but it is possible that longer anomalous trains may occur in these materials.

In contrast to the fine fraction, prolonged anomalous exMg drainage trains are present in the minus 10 plus 20-mesh fraction of sediment. This is undoubtedly due to association of exMg with sesquioxide nodules, metal being presumably both adsorbed on the sesquioxides and liberated by decomposing grains of iddingsite.

From the limited amount of stream sediment data for the Buell Park area, it would seem that considerable anomalous exMg drainage trains are present. Moreover, there is no decrease in contrast between samples collected from 100 and 7000 feet downstream from the intrusion. This would suggest that the exchange positions are satisfied at both sites. However, this was not investigated.

8.5 NIOBIUM

8.51 In Residual Soils

The hydrolysis pH for the hydrates of trivalent and pentavalent niobium oxides is less than 1 (Klimenko and Syrokomski, 1947). Niobium salts which may be liberated during weathering are readily hydrolysed under conditions usually encountered in the exogenic cycle (Rankama, 1950).

In residual soils over the Prairie Creek kimberlite, Nb accumulates mainly in the silt fraction towards surface. This indicates the niobium host mineral, probably perovskite, to be relatively resistant to weathering. However, appreciable concentrations of Nb are present in the clay size and increase in magnitude towards the B_2 horizon. Thus some decomposition and/or dissolution of the Nb host mineral occurs. Translocation of Nb from the A to the B horizon probably involves eluviation of colloidal niobium oxides or fine grained secondary minerals.

On the assumption that Sr has remained constant during weathering, Nb is substantially depleted in the kimberlite solum and, to a lesser extent, the C horizon. In the light of the ready hydrolysis of cationic Nb, this apparent leaching of metal is particularly interesting. Three possibilities by which Nb may be removed from the profile are considered:

(a) As a colloid adsorbed on the colloids of magnesia and/or silica.

(b) In solution as a simple or complex anion. Rankama (1950) reports Nb to be transported as alkali niobates in weathering solutions and Watts (1960) found $5 \times 10^{-8}\%$ w/v anionic Nb in stream waters draining a Zambian carbonatite. According to Parker and Fleischer (1968), there may be some ionic substitution of $Na^{+}Nb^{5+}$ for $Ca^{2+}Ti^{4+}$ in perovskite. On dissolution and oxidation this may yield soluble sodium niobiate. This reaction would be favoured by the relatively high pH of the kimberlite soil profile (Thompson*, pers. comm.).

(c) Leaching as soluble metallo organic compounds. Niobium has been found in many plants (Krauskopf, 1955; Saraswathi and Devi, 1955; Tyutina, 1959), and may be released as metallo organic compounds on the death and decay of the plant. Moreover, Tyutina (1961) has shown that the solubility of Nb in water increases considerably in the presence of fulvates. This suggestion, however, does not explain the loss of Nb from the

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C horizon where plant roots are rare.

Although Nb is present within sesquioxide nodules over the ultrabasic rocks, it does not show any preference for Mn or Fe nodules. Moreover, Nb is not extracted with sodium citrate-dithionite solution, although this may be due to the immediate hydrolysis of any metal released. Lack of concentration of Nb in Mn nodules from the edge of a dambo in Zambia is recorded by Watts (1960). However, Rankama (1944 and 1948), and Pachadzhanov (1963) found appreciable contents of Nb in oceanic Mn nodules.

In soils over the reworked sediments of the Trinity siltstone, Nb is concentrated in the minus 300-mesh fraction. The relative partition of Nb between the silt and clay fractions is unknown. Metal may either be present within the lattice of resistant minerals such as zircon or ilmenite, replacing Zr^{4+} and Ti^{4+}, respectively; or associated with clays, either in sorbed positions or replacing Al^{3+} or Ti^{4+}. There is a slight concentration of Nb in the B_2 horizon of the Trinity formation. This may be due to a variation in the composition of the sediment or to eluviation of Nb colloids from the A to the B horizon during soil forming processes.

8.52 Dispersion from the Kimberlite

Anomalous concentrations of Nb in residual soil downslope from a kimberlite suboutcrop at the American Mine occur almost entirely in the A horizon. This indicates dispersion to be dominantly mechanical. There are, however, several areas of anomalous Nb content which cannot be explained by mechanical dispersion at the present time and it is suggested that they were developed sometime in the past (Chapter 5).

Anomalous concentrations of Nb are present in the colluvium downslope from kimberlite and in the alluvium flanking American Creek.

It was suggested in the previous section that Nb may be appreciably leached from soils over kimberlite. These leach waters will percolate through the sub soil to the water table and will eventually find their way into the surface drainage at points of water table outcrop. Niobium is not concentrated in limonitic compared with white mottles taken from the banks of American Creek below the wet season water level; nor is Nb enriched in the wad or slime compared with the banks and background sediment. This suggests that any Nb transported in solution is not significantly precipitated in the chemical or hydrolyzate deposits in the stream. It must be emphasised, however, that the slime and wad are considerably diluted with sediment and a small enrichment of Nb could go unnoticed.

Since, as previously mentioned, cationic Nb released from its host minerals during weathering is concentrated in the hydrolyzates (Parker and Fleischer, 1968; Pachadzhanov, 1963) the observed distribution of Nb in the drainage is due to mechanical dispersion.

That longest anomalous dispersion trains of Nb occur in the minus 10 plus 20-mesh fraction of stream sediments, is due to two reasons: (a) the paucity of coarse Nb bearing minerals in the country rocks, and (b) the encapsulation of Nb host minerals in sesquioxide nodules in soils over the kimberlite.

Under the semi arid conditions encountered in Arizona, Nb is probably retained within its host minerals and dispersion will be by mechanical processes.

8.6 CHROMIUM

8.61 In Residual Soils

The ionic potential of Cr^{3+} is very similar to that of Fe^{3+} (Table 8.1) and consequently these elements behave similarly during weathering (Rankama, 1950). However, unlike Fe^{3+} which is hydrolized at a pH of about 3, hydrolysis of Cr^{3+} starts at pH 5.5 (Atkins, 1930). Under conditions of high Eh and pH trivalent Cr may be oxidised to the mobile hexavalent form. However, it is thought unlikely that the Eh is sufficiently high for this reaction to occur in the study areas.

Like Nb, in residual soils over the Prairie Creek kimberlite, Cr increases in content in the silt fraction towards surface. This indicates the Cr host minerals, probably dominantly chromite, magnetite, ilmenite, etc., to be relatively resistant to weathering. Nevertheless, assuming Sr to have remained constant, Cr has been leached from the A horizon. A similar depletion of Cr in near surface soils over peridotite is recorded by Hotz (1964). Alcard (1959) notes a higher Cr content at depth than at the surface in soils over kimberlite in the French Sudan.

Some Cr is no doubt contained with ferromagnesian minerals. During weathering of these minerals, any Cr released will be hydrolized and precipitated along with Fe^{3+}. This is reflected by concentration of Cr in samples where iddingsite is common. Chromium is also present in sesquioxide nodules, and the depleted Cr content of the A horizon is no doubt due to translocation of Cr, along with Fe, during soil forming processes. A similar conclusion was reached by Brooks (1965) who found Cr enriched in nodules in a New Zealand yellow grey earth. He attributed these to be developed by leaching of ions from the A horizon under poorly drained conditions.

In soils over the Trinity siltstone, Cr is considerably concentrated in sesquioxide nodules. However, Cr is not particularly enriched in the clay size of the B horizon compared with the clay size of the A horizon in soils developed over the kimberlite or Trinity siltstone. This indicates translocation in the clay size to be largely mechanical, and suggests Cr to be mobilised in the study area only under conditions which give rise to the formation of nodules.

In semi arid conditions of Arizona there is no apparent redistribution of Cr in the soil profile and dispersion will be by mechanical processes.

8.62 Dispersion from the Kimberlites

Maximum dispersion of Cr, like Nb, in residual soils downslope from kimberlite at the American Mine occurs in the A horizon. This indicates Cr to be dispersed mechanically.

Although the areal distribution of Cr about the American Mine was not investigated, the similar dispersion characteristics to those of Nb would probably give rise to a similar anomalous pattern. However, Cr has a greater contrast between the kimberlitic and Trinity siltstone soils than has Nb (27 and 8, respectively), and thus anomalous Cr concentrations would presumably be detectable over a greater distance than those of Nb.

In the drainage, Cr is not concentrated in that part of the bank below the wet season water level nor in the orange compared with the white mottles. Neither is Cr enriched in the wad compared with the banks or sediment. Chromium is, however, concentrated in the heavy mineral fractions of stream sediment. These features indicate the distribution of Cr in the drainage to be due mainly to mechanical dispersion.

As previously mentioned, sesquioxide nodules are recorded in sediment from over the limestone members. However, it is unknown whether these are formed in situ or in the limestone soils. Appreciable amounts of Cr (20%-30%) are extracted from these nodules with sodium citrate/dithionite solution. Thus if these nodules are formed in situ by precipitation of metal from stream waters, then this would suggest appreciable amounts of Cr to be transported in solution or as colloids.

8.7 ZIRCONIUM, STRONTIUM AND TITANIUM

The distribution of these elements in soils downslope from kimberlite and in the associated drainage has not been investigated. However, a limited amount of work has been done on their distribution in the kimberlite soil profile.

Zirconium has remained immobile in the kimberlite soil profile. This is due to the extreme stability of zircon, the dominant host mineral, to weathering solutions. Nevertheless, appreciable concentrations of Zr are present in the clay size of the A horizon and coarse sand sizes throughout the profile.

The ionic potential of Zr^{4+} is intermediate (Table 8.1) thus metal released from its host minerals during weathering concentrates in the hydrolyzates. A certain amount of Zr may occur within the lattice of femic minerals and may be released during their decomposition. In addition, some dissolution of zircon may occur at high pH's (Poldervaart, 1955). The liberated metal will be subsequently hydrolyzed and may form complex Zr ions which may be sorbed on clay minerals and/or sesquioxides. This is probably one of the reasons for the presence of Zr in the clay and coarse sizes in soils over kimberlite. A certain amount of metal in the coarse fraction also undoubtedly occurs as zircon encapsulated by sesquioxides.

Strontium is usually a highly mobile element (Rankama, 1950). However, in the kimberlite soil profile at Prairie Creek it is considered virtually immobile. This is thought to be due to its occurrence within a resistant mineral, probably perovskite. Nevertheless, some Sr is present in the clay fraction, especially in the B_2 horizon. The reason for this is uncertain. It may be that metal released during weathering is immediately sorbed by clay minerals or that some clay size host minerals are present.

The hydrolysis pH of Ti^{4+} is 2. Organic matter may reduce Ti^{4+} to Ti^{3+} which is hydrolised at pH 4 (Rengarten, 1956). Thus only under conditions of high acidity and high organic matter or low Eh will Ti be mobile.

In soils over the Prairie Creek kimberlite Ti accumulates in the silt and fine sand fractions towards surface. This reflects the stability of the host minerals, i.e. ilmenite, magnetite, perovskite, etc., to weathering solutions. Nevertheless, appreciable concentrations of Ti are present in the clay size, especially in the B_2 horizon. Moreover, Ti may be slightly depleted in the B horizon with respect to Sr. It is probable that a certain amount of Ti is present within the femic minerals of kimberlite. On decomposition of these minerals Ti may be either released or retained within the resulting clay minerals. Since the pH is well in excess of 4, any Ti released will be hydrolized. Translocation of metal will therefore be due to mechanical processes.

Haseman and Marshall (1945) report Ti to be immobile in podzolic soils and that it may be used as an "immobility indicator". Similar observations are made by Hotz (1964), but Joffe and Pugh (1934), Robinson (1914) and Salminen (1938), found Ti to be enriched in the clay fraction during soil forming processes.

The immobility of these elements in the soil profile indicate their dispersion from the kimberlite will be by mechanical processes. However, whereas Zr and Ti released from their host minerals will accumulate in the hydrolizates, Sr may be transported as dissolved ions in weathering solutions.

8.8 VANADIUM

The distribution of V in soils downslope from kimberlite and in the associated drainage was not investigated. However, a limited amount of work was done on the redistribution of V in soils overlying kimberlite.

The ionic potentials of V^{3+} and V^{4+} are intermediate and in these valencies vanadium is concentrated in the hydrolizates (Table 8.1). However, under high Eh and pH conditions, metal may be oxidised to V^{5+} which is mobile as a simple or complex anion.

Vanadium may react with organic matter to form insoluble complexes such as V porphyrins. According to Szalug (1967), humic acids may reduce the mobile metavanagate $(VO_3)^-$ anion to the vanadyl $(VO_2)^{2+}$ cation which is subsequently sorbed by humic acid.

In kimberlite V^{3+} may replace Fe^{2+} and V^{4+} and V^{5+} may replace Fe^{3+} and Al^{3+} in femic silicates. This is reflected by the sympathetic distribution of Fe and V in the C horizon.

Assuming Sr to have remained constant in soils over the Prairie Creek kimberlite, then although V is concentrated in the B_2 horizon, metal has been removed from the A and B horizons and from the yellow ground. Since as mentioned above, V^{3+} and V^{4+} are concentrated in the hydrolizates, this depletion is most easily explained by leaching of V^{5+} as a mobile anion. However, since this is formed by oxidation, then leaching of V cannot coincide with leaching of Fe^{2+} unless appreciable amounts of V^{5+} are present in the host minerals.

Vanadium is concentrated in ferric sesquioxide nodules and a very substantial proportion of metal is extracted with sodium citrate/dithionite solution. This is attributed to sorbtion of the anionic V by the positively charged Fe sol.

The distribution of V in the A_0 horizon was not investigated. Thus it is unknown whether V is concentrated with organic matter in Arkansas. It is noticeable, however, (Figs. 4.13 and 4.14) that with the exception of site 00N40W over the Prairie Creek kimberlite, V is not concentrated in the clay size of the A horizon. This would suggest that association with organic matter in these soils is not particularly marked.

Dispersion of V from the kimberlite in Arkansas will be by dominantly mechanical processes. Some metal may, however, be dispersed in leach waters presumably as anionic metal. Precipitation will be controlled largely by sorbtion on ferric sesquioxides and organic matter.

In Arizona there has been no apparent redistribution of V in the kimberlite profile. Metal will therefore be dispersed mechanically.

8.9 PHOSPHORUS

Investigations for P were confined to a study of its vertical distribution in a single kimberlite profile at Prairie Creek; and, in a limited number of samples, in soils downslope from kimberlite and the associated drainage at the American Mine.

According to Rankama (1950), P is readily leached from its host minerals during weathering. Dissolution of calcium phosphate (apatite) is favoured by CO_2 bearing waters (low pH) and probably by waters rich in organic material. Calcium phosphate is precipitated in the hydrolizates under conditions of high pH. Apatite is often an abundant constituent of detrital deposits.

Phosphorus has a strongly biophile character and is an essential element in cytoplasm.

Assuming Sr to have remained constant during weathering of the Prairie Creek kimberlite, then P is depleted in the solum and yellow ground. It must be pointed out, however, that the P content of the bedrock is unknown and these calculations are based on the P content of the blue ground. This apparent depletion of P is probably due to leaching of soluble phosphates by percolating rain waters.

Phosphorus is concentrated in the B_2 horizon of the kimberlite soil profile. This may be due to either precipitation of Ca and/or Mg phosphates due to the higher pH of the B_2 than A horizon, or to sorbtion of anionic P by the positively charged ferric hydroxide sol (Bauwin and Tyner, 1957). Some P may be present as ferric phosphates, although according to Runge (1963), frequent reducing conditions in poorly drained soils inhibit the formation of these compounds.

In the freely drained soils downslope from kimberlite at the American Mine, anomalous concentrations of P are present for over 200 feet in the A horizon; a much shorter anomalous aureole occurs in the $B_{2.1}$ horizon. This indicates dispersion to be dominantly mechanical. With the exception of samples from the limestone, anomalous concentrations of P are present in the $B_{2.2}$ horizon for several hundred feet downslope from the kimberlite. This is attributed to saline dispersion of metal from the kimberlite at a time in the past when the water table was much higher (cf. Fe, Section 8.23). The low concentrations of P in the limestone probably reflect both a low parent content in this rock type and the immobility of P at high pH's (cf. Ni and Mn).

Insufficient data is available on the distribution of P in the drainage system to make any concrete proposals on the dispersion of this element. There are, however, several apparent trends, viz. Lower concentrations of P are present on that part of the bank below the wet season water level compared with that part of the bank above the wet season water level. This would suggest P to be leached from the bank by surface waters. The ratio of the P content of the slime to that in the minus 80-mesh fraction of stream sediment increases with increasing distance from the kimberlite. This suggests a progressive dissolution of the P host mineral; some of the released metal being precipitated in the clay size presumably as fine grained phosphates or sorbed on positively charged materials.

8.10 BARIUM

The distribution of Ba in soils downslope from kimberlite and in the associated drainage was not investigated. However, a limited amount of work was done on the behaviour of Ba in soils overlying kimberlite.

The ionic potential of Ba^{2+} is relatively low (Table 8.1) thus barium released from its host minerals is appreciably mobile. However, barite, the most common Ba host mineral in the ultrabasic rocks, is highly stable although it is slightly soluble in water (1.3 ppm at 25°C; Seidell, 1940). In spite of the low ionic potential of Ba^{2+} the transfer percentage is relatively low (Rankama, 1950, p. 483). This is due to the ready adsorbtion of Ba^{2+} by hydrolyzates.

Barium is concentrated in the coarse fractions of soils over the ultrabasic rocks and Trinity siltstone. This is due to occurrence both as discrete grains of barite and association with sesquioxide nodules, particularly those of Mn. Indeed, there is a sympathetic distribution between Ba and Mn in the A horizon of several profiles. This is most likely due to sorbtion of Ba^{2+} cations by the negatively charged Mn sol. The Ba^{2+} ions having presumably been derived largely from the dissolution of barite.

Barium is also concentrated in the clay size of some profiles, no doubt due to the ready sorbtion of Ba^{2+} by clay minerals. However, some clay size barite grains may also be present.

One might expect that dispersion of Ba will be dominantly mechanical. However, it is possible that an appreciable saline dispersion may occur by dissolution of barite and the subsequent scavenging of Ba^{2+} ions by the hydrolyzates and precipitates of the drainage.

8.11 CONCLUSIONS ON THE MODE OF DISPERSION OF THE ELEMENTS

In Arizona chemical weathering is only slight and the elements are retained mainly within their host minerals. Dispersion is therefore dominantly by mechanical processes. There may, however, be some slight saline dispersion of Mg, one of the first elements to be removed during weathering.

In Arkansas many of the host minerals are decomposed during weathering and dispersion of the elements depends upon numerous factors including the physico chemical conditions of the environment and the chemical properties of the element in question.

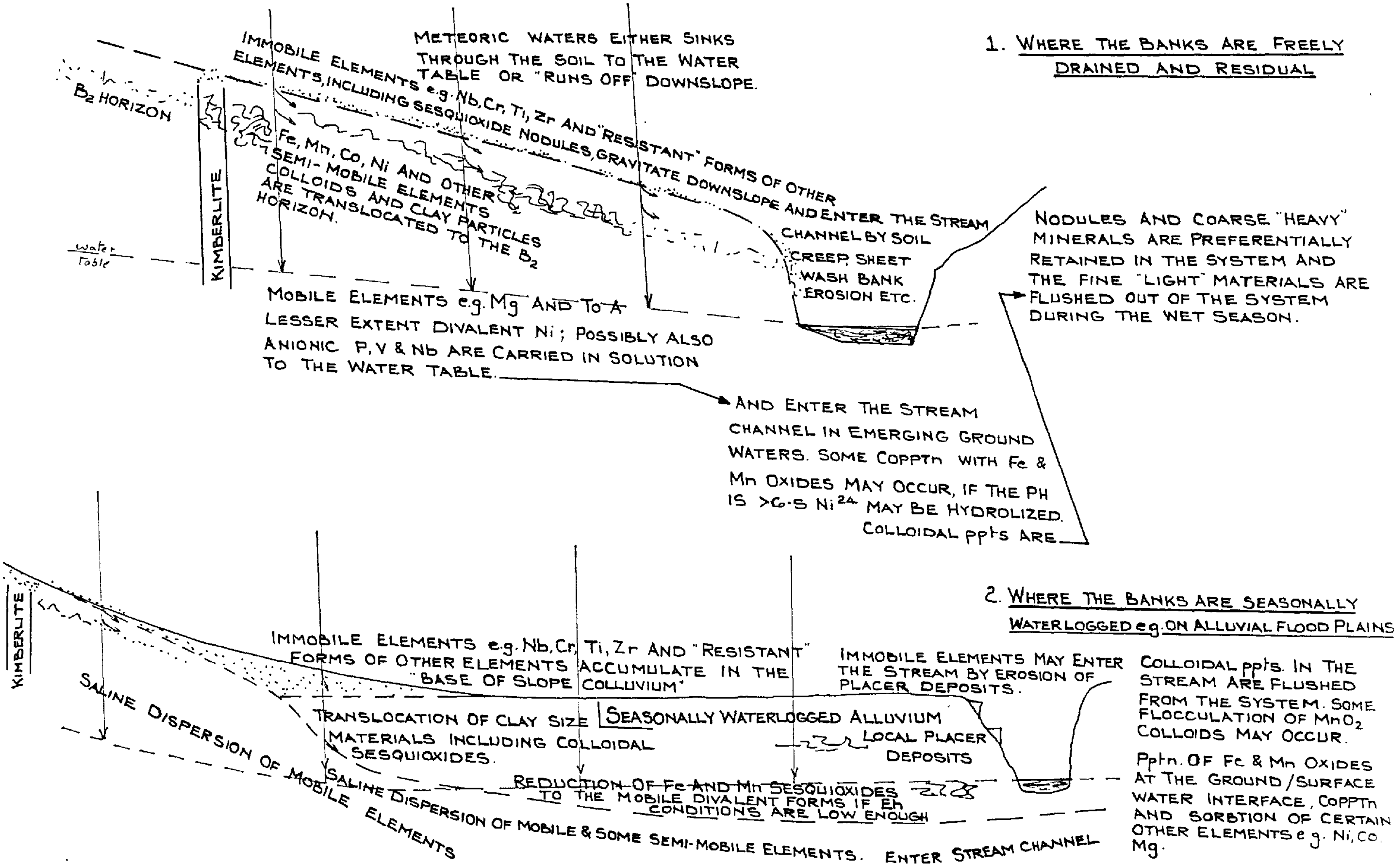
In soils over kimberlite many of the elements are concentrated within sesquioxide nodules; either with the cement or as detrital minerals encapsulated by sesquioxides. Titanium, Zr, Sr, Nb and Cr are present as silt size resistant minerals and Mg, Fe, Ni, V and possibly Ba are concentrated in the clay size. Magnesium, and to a lesser extent Ni, Nb, V and P, are leached from the profile by percolating rain waters and are presumably carried down to the water table.

It is believed that slightly different dispersion mechanisms occur in areas of freely drained soils and those soils which are seasonally water-logged (Figure 8.5).

In freely drained soils Nb, Zr, Sr, Ti, Cr, Fe, Mn, Ni, Co, V, P and Mg are dispersed mechanically as nodules and silt and clay size host minerals etc. Easily weathered forms of metal, e.g. decomposing silt size femic silicates, and clay size host minerals are translocated to the B_2 horizon by soil forming processes. Some of the more mobile elements, e.g. Mg^{2+}, Ni^{2+}, P^{5+} may be carried down to the water table by percolating waters. Less easily weathered forms of metal, including nodules, enter the drainage by the mechanical agencies of soil creep, sheet wash, bank collapse, etc.

In soils which are seasonally water-logged, elements of intermediate ionic potential, e.g. Cr^{3+}, Zr^{4+}, Ti^{4+}, V^{3+}, Nb^{5+} remain either in their host minerals or within sesquioxide nodules or hydrolyzates and are dispersed mechanically. Elements of low ionic potential e.g. Mg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+} may be taken into solution and dispersed in ground waters. Precipitation of Mn and Fe will occur where there is an abrupt rise in Eh and/or pH. For example, at the confluence of the ground with surface

FIG. 8·5 DIAGRAMMATIC ILLUSTRATION OF THE MECHANISMS OF SECONDARY DISPERSION OF THE ELEMENTS IN ARKANSAS



waters. In such instances sesquioxides are deposited on the stream banks and bed and presumably as colloids in the surface waters. A certain amount of flocculation of Mn ensues as seen from the presence of fine (minus 80 plus 300-mesh) Mn nodules in streams flanked by an appreciable flood plain, where the water table is near to surface in the wet season. Cobalt is coprecipitated with the Mn sesquioxides. Nickel is also mainly precipitated with sesquioxides but some metal may be precipitated in the drainage as fine grained hydrosilicates and/or remain in solution. Precipitation of exMg is controlled by the presence of suitable sorbtive materials, e.g. sesquioxides, clay minerals and/or organic matter. Precipitation of P is probably controlled by pH and association with sesquioxides. It is possible that Nb is leached from kimberlite as ionic or organic complexes; it is unknown whether this metal is subsequently precipitated in the drainage.

At the American Mine, elements of low ionic potential have also been dispersed by saline processes at some time in the past, when the water table was much higher that at present. These "fossil anomalies" are currently being eroded by the streams and will provide a much larger target area for prospecting. Similarly, anomalous sesquioxide concretions and detrital minerals are present as placer deposits in the Quaternary alluvium at the American Mine. It is possible that similar placer deposits occur in the drainage which may not be related to a nearby kimberlite.

No matter by which mechanism metal enters the streams, the rapid rate of stream flow in the wet season flushes the fine light material, including colloidal precipitates, from the system. Consequently, the distribution of metal in the drainage is developed mainly by mechanical dispersion. Only in the bank walls and floor are chemical deposits found.

CHAPTER 9

MASS SPECTROGRAPH DETERMINATIONS

9.1 RESULTS

A number of samples were analysed semi quantitatively on the mass spectrograph at Manchester University. These included stream sediments from the Black Lick drainage and background areas, selected heavy (S.G.>3.27) sediment fractions; rock from the Buell Park kimberlite tuff, Prairie Creek kimberlite and peridotite, Trinity sandstone and Tokio arenites. Soils over the Prairie Creek kimberlite and Trinity siltstone were also analysed. The results are given on Tables 9.1 and 9.2. The contrasts for selected elements between kimberlite rock and associated soils and sediment are presented on Table 9.4.

It must be emphasised that the precision and accuracy of the analyses are unknown. An internal standard was not used, nor were the samples fused in glass prior to grinding. Calculations are based on the detection limit of the elements (Chapter 3). Accordingly the results are, at the very best, only semi quantitative. Nevertheless, the known "anomalous" elements, e.g. Nb, Nd, Hf, Sr, etc., are revealed by these results. It is thought, therefore, that the general trends and "anomalous" elements disclosed are probably valid although absolute concentration is highly suspect.

In addition to the above, soils from the B_2 horizon of the Trinity siltstone and from the A_1 horizon over the kimberlite were analysed quantitatively for the writer by Dr. G.D. Nicholls (Manchester University). His results are tabulated on Table 9.3 overleaf.

Table 9.1 Semiquantitative analyses of the Buell Park kimberlite, Prairie Creek peridotite and kimberlite, Trinity sandstone, Tokio arenites and soils over the Prairie Creek kimberlite and Trinity siltstone. Data on complete sample. Mass Spectrograph analyses.

		ARIZONA	ARKANSAS						
			BEDROCK		SOIL OVER KIMBERLITE		BEDROCK	SOIL OVER TRINITY SILTSTONE	BEDROCK
		Kimb. Tuff Buell Park	Peridotite Prairie Creek	Kimberlite Prairie Creek	B_2 horizon Prairie Creek	A_1 horizon Prairie Creek	Trinity Sandstone	A_1 horizon	Tokio Arenites
Parts per million	U	0.22	0.27	1.44	2.16	11	2.1	4.3	2.2
	Th	0.33	0.83	12	12	25	3.6	8.3	12
	Pb	5.4	12	12	18	37	45	12	12
	Tl	0.17	0.17	0.17	0.34	0.22	0.24	0.17	0.57
	W	1	1	1.3	1.3	1.4	20	1.4	2.5
	Hf	0.79	16	11	16	26	11	16	11
	Lu	0.11	0.11	0.11	0.11	0.11	0.54	0.36	0.54
	Yb	0.23	0.29	0.33	1.1	2.3	1.1	1.1	2.3
	Tm	0.35	0.1	0.15	0.42	0.7	2.1	0.52	0.52
	Er	0.71	0.89	1.2	5.1	12	5.5	3.5	5.1
	Ho	0.54	0.27	1	1	1.5	2.2	1	1.5
	Dy	0.76	1.9	9.5	13	38	13	6.3	5.4
	Tb	0.25	1	3.33	1.4	5	2	1.4	1
	Gd	0.8	12	12	12	24	8	4.8	4.8
	Eu	1	1	3.5	5.2	10	2.6	1	1
	Sm	0.93	3.7	18	37	37	19	5.3	12
	Nd	7	33	98	123	490	61	16	24
	Pr	1.8	9	18	91	91	23	9	18
	Ce	12	>60	>60	>>60	>>60	>60	30	>60
	La	7.7	>77	>77	>77	>>77	77	19	77
	Ba		>>22	>>22	>>22	>>22	>>22	>>22	>>22
	Cs	0.51	1.3	0.51	0.76	0.76	1.5	1.5	2.2
	Te	2.6	2.6	6.4	13	13	0.64	1.7	1.3
	I	26	6.5	17	104	260	520	104	174
	Sb	0.28	0.2	0.25	0.4	0.4	0.5	1	1
	Sn	0.25	0.66	2	3.7	2.8	2.8	1	2.8
	In	0.33	0.37	0.48	1.7	0.7	0.8	1.1	1.1
	Cd	0.9	1	1.5	5	5	7.3	5	3.7
	Ag	0.21	2.9	14.4	4.8	4.8	0.72	2.9	3.1
	Pd	68	24	68	53	68	48	32	24
	Ru	8.1	6.5	8.1	8.1	40	46	16	16
	Mo	0.38	0.6	0.75	3	3	3	1	16
	Nb	1.7	>51	>51	>51	>51	12	17	5.1
	Zr	11	>59	>>59	>>59	>>59	>>59	>>59	>>59
	Y	6.3	6.3	21	63	>63	63	63	63
	Sr	3.6	>18	>18	>18	>18	3.6	1.8	6
	Rb	6	>>12	>>12	>>12	>12	>>12	>>12	12
	Br	21	6.3	12	63	63	63	63	9
	Se	16	3.2	8	32	16	160	23	8
	As	4	1.1	2.6	10	8	16	16	40
	Ge	4.6	1.8	3.1	4.6	9.3	4.6	4.6	2.3
	Ga	2.6	4	13	40	10	10	20	40

Bi <0.22; Hg <6.7; Au <2; Pt <5.8; Ir <3.4; Os <7.2; Re <5; Xe <0.6

Table 9.2 Semiquantitative analyses of background and anomalous sediment and selected heavy mineral fractions. (Data on minus 80-mesh fraction.) Mass Spectrographic analyses.

	STREAM SEDIMENT							HEAVY MINERAL FRACTIONS		
	Background			Anomalous				Background	Anomalous	
Parts per million				Source*	1600ft†	2000ft†	3000ft†	Composit	Source*	3000ft†
U	0.4	0.5	0.11	0.3	2.2	2.2	1.1	2.2	43	3.6
Th	0.8	1.2	0.12	1.2	3.6	3.6	2.5	25	8	50
Pb	1.8	7	1.8	4.5	74	18	18	180	120	180
Tl	0.09	0.17	0.8	0.09	0.24	0.42	<0.17	2.4	2.4	3.4
W	0.4	1.3	0.3	0.7	1.4	1.4	<1	14	3.3	5
Hf	0.8		1.1	2.6	3.9	3.9		158	11	113
Lu	0.16	0.16	0.04	0.11	0.27	0.24	0.16	2.3	0.36	3.6
Yb	0.12	0.58	0.33	0.33	0.76	2.3	0.33	7.6	4.6	11
Tm	0.1	0.26	0.1	0.12	0.52	1	0.26	2	1	2.6
Er	0.51	0.9	0.35	0.51	2.38	5.1	0.9	35	5.1	1.8
Ho	0.22	0.27	0.15	0.15	1	1.5	0.4	5.4	1.5	5.4
Dy	0.76	1.3	0.38	0.63	3.8	7.6	3.8	19	13	38
Tb	0.2	0.25	0.1	0.2	0.5	1	1	10	5	10
Gd	0.8	0.6	0.34	0.48	3	3.4	3	48	34	60
Eu	0.21	0.3	0.15	0.21	1	2.1	1	21	21	15
Sm	0.9	1.2	0.37	0.9	7.5	5.3	12	187	12	93
Nd	1.6	12	16	4.9	22	22	49	490	98	130
Pr	>9	4.5	1.8	2.3	23	18	9	180	91	130
Ce	>0.6	7.5	2	>60	60	60	>60	>120	120	>120
La	>0.8	7.7	2.6	77	26	26	39	154	77	154
Ba	>>0.2	5.5	>22	>22	>22	>22	>22	22	>>44	>44
Cs	0.15	0.3	0.08	0.22	1.5	1	0.7	0.51	0.7	1.5
Te	0.13	0.5	0.37	0.86	1.3	3.7	0.9	2.6	52	4.3
I	10	35	7.4	13	74	173	17.3	740	2600	5200
Sb	0.1	0.4	0.1	0.25	1	0.5	0.4	10	2.8	20
Sn	0.3	0.5	0.1	0.4	1	4	0.4	20	2	10
In	0.17	<0.3	0.03	0.33	0.5		0.33	17	4.8	
Cd	0.7	2.5	0.37	1	3.7	3.7	1	73	10	37
Ag	0.14	0.36	0.21	0.29	0.48	2.9	0.72	14	7.2	2.1
Pd	6	10	2.4	3.2	16	96	6.8	160	48	240
Ru	6	9.6	2.4	3.2	16	16	6.8	160	48	240
Mo	0.15	0.43	0.2	0.3	1	1.3	0.7	30	4.3	30
Nb	>0.5	10	1.7	51	26	51	10	>100	100	>100
Zr	>6	>59	3	>59	>59	>59	>59	>>110	>>110	>>110
Y	>0.6	12.5	2.1	63	63	32	12	91	63	91
Sr	>0.2	0.9	0.45	0.6	4.5	6	3.6	2.6	18	18
Rb	>>0.1	3	1.2	>12	>12	>12	>12	6	12	24
Br	3	21	2.1	2.1	32	21	21	63	210	630
Se	>1.6	23	0.8	3.2	40	53	16	23	80	80
As	>>0.8	16	8	8	26	16	16	160	160	137
Ge	0.3	2.3	0.46	0.5	3.1	4.6	3.1	46	31	13

Hg <6; Au <2; Pt <6; Ir <3.4; Os <7.2; Re <5.

*Immediately downstream from West Black Lick Prospect.
†Distance downstream from source.

Table 9.4 Contrasts for selected elements between kimberlite and country rocks; the A_1 horizon of associated soil; stream sediments from the Black Lick drainage, and selected heavy mineral fractions.

	Bedrock		Soil	Sediment				Heavy mineral fractions	
	Kimberlite / To Arenites	Kimberlite / Trin. sstn.	A_1 kimberlite / A_1 Trin. sltstn	Source	1600**	2000**	3000**	Source	3000**
U	<1	<1	$2\frac{1}{2}$		4	4	2	20	$1\frac{1}{2}$
Th	<1	$3\frac{1}{2}$	3	1	2	3	2	<1	2
Pb	<1	<1	3	<1	10	$2\frac{1}{2}$	$2\frac{1}{2}$	<1	1
Hf	<1	1	$1\frac{1}{2}$	2	3	3		<1	<1
Lu	<1	<1	<1	<1	$1\frac{1}{2}$	$1\frac{1}{2}$	<1	<1	<1
Yb	<1	<1	2	<1	$1\frac{1}{2}$	4	<1	<1	<1
Dy	2	<1	6	<1	3	6	3	<1	2
Gd	3	$1\frac{1}{2}$	5	<1	4	4	4	<1	<1
Sm	$1\frac{1}{2}$	1	5	1	8	$4\frac{1}{2}$	5	<1	<1
Nd	4	$1\frac{1}{2}$	30	<1	2	2	4	<1	1
Pr	<1	<1	10	<1	5	4	2	<1	<1
Ce			27*	>8	8	8	>8	<1	<1
La			27*	10	$3\frac{1}{2}$	$3\frac{1}{2}$	4		
Cs					5	2	$2\frac{1}{2}$	$1\frac{1}{2}$	3
Te	5	10	$7\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$	7	$1\frac{1}{2}$	20	2
I	<1	<1	<1	<1	2	5	<1	$3\frac{1}{2}$	7
Pd	3	$1\frac{1}{2}$	2	<1	$1\frac{1}{2}$	<1	<1	<1	$1\frac{1}{2}$
Ag	7	20	2		$1\frac{1}{2}$	8	2	<1	<1
Nb	>10	>4	>4	5	$2\frac{1}{2}$	5	1		
Y	<1	<1	<1	5	5	$2\frac{1}{2}$	1	<1	<1
Sr	>3				5	$6\frac{1}{2}$	$3\frac{1}{2}$	7	7

*from table 9.3 kimberlite A_1 horizon / Trinity B_2 horizon

**distance (feet) downstream from source

Table 9.3

		concentration (ppm)						
		La	Ce	Pr	Nd	Yb	Lu	Y
Soils	A_1 Kimberlite	264	358	60	166	<1.0	<1.0	42.4
	B_2 Trinity Siltstone	9.5	13.1	>1.0	ND	<1.0	<1.0	34.4

The main points from the mass spectrograph results are tabulated below:

(1) The Buell Park kimberlite tuff does not contain anomalous concentrations of the "alkalic" elements. On the basis that the chemical definition of kimberlite is "an alkalic ultrabasic rock", then the Buell Park kimberlite is a misnomer.

(2) Higher concentrations of U, Th, the rare earths, especially the light members, Te, I, Ag, Rh and Y are present in the Prairie Creek kimberlite than peridotite.

(3) Anomalous concentrations of Th, Tb, Gd, Eu, Nd, Ce, La, Te, Ag, Pd, Nb and Sr are present in the kimberlite bedrock compared with the Trinity siltstone bedrock. Maximum contrasts between bedrock and/or soils over the Prairie Creek kimberlite and Trinity formation are given by Nd, La, Ce, Ag, Te, Sm, Gd, Nb.

(4) The following trends are evident in soils over the kimberlite:

U, Th, Pb, Hf, the rare earths, Cs, I, Y, and Ge increase in concentration towards surface.

Tl, Sn, In, Se, As and Ga are concentrated in the B_2 horizon.

Cs, Te, Sb, Gd, Mo and Br occur in both A and B horizons in equal amounts where they are enriched relative to the bedrock.

Ag is concentrated in the bedrock and Ru in the A horizon. No distinct trend is evident for W or Pd.

(5) In stream sediments, strongly anomalous concentrations of Ce, La, Te, Nb and, to a minor degree Hf, are contained in the sample taken at "source". In the samples taken at 1600 feet, 2000 feet and 3000 feet below the Black Lick Prospect, anomalous concentrations of U, Th, Pb, Ho, Dy, Gd, Eu, Sm, Nd, Ce, La, Cs, Te, In, Sr are present.

(6) Maximum overall contrast between anomalous and background sediments is given by Ce, La, Sr, Nb and Sm.

(7) All the elements are concentrated in the "heavy minerals" (S.G. >3.27) fractions. However, only for Te, I, U and possibly Sr is contrast improved in these fractions.

9.2 DISCUSSION

It is evident from the preceeding data that in Arkansas, La, Ce, Te, Sr, Nb and probably Hf are present in highly anomalous concentrations in the kimberlite and its associated soils and stream sediment.

9.21 Tellurium

During primary dispersion Te is highly sulfophile and accompanies sulfur in sulfide minerals (Rankama, 1950). It also forms tellurides with certain metals (e.g. Au), and may occur in the native state.

There is very little data available for the behaviour of Te in silicate rocks and even less for its behaviour during secondary dispersion. According to Vinogradov (1962), the Te content of ultrabasic, intermediate and felsic granitic rocks is 0.001 ppm. Shales contain 0.01 ppm. If, therefore, the figures given for the Te content of the Prairie Creek igneous rocks are to be believed, then Te is present in highly abnormal concentrations. Clearly further work is required in order to establish if this is the case.

The chemistry of Te and Se are very similar, although Te is generally more metallic in its properties and less reactive (Mial, 1956). Consequently, one might expect that Te, like Se, is mobile under high pH-Eh conditions and immobile under acidic reducing conditions. It is unknown whether Te, like Se, is present in some plants.

9.22 Hafnium

Hafnium resembles Zr very closely in its chemical properties and accompanies Zr in nature (Rankama, 1950; Date, 1968). One might therefore expect Hf to be dispersed mechanically along with Zr. If any dissolution does occur, i.e. at high pH's (Poldvaat, 1955), Hf would concentrate with Zr in the hydrolizates.

Rankama (1950) reports the Zr/Hf abundance ratio to be 48.9 and Schutte (1966) gives the average for granitic rocks to be 44.2. However, Butler and Thompson (1965), using a radiochemical method, found a range in Zr/Hf ratio of 11 to 29 in alkalic granites and 36 to 37 in rhyolites from Nigeria. Later work by Gorden et al (1968) showed the Zr/Hf ratio of some igneous rocks to be lower than had hitherto been envisaged and hinted that a revision of the Zr/Hf ratios in rocks is called for.

The Zr/Hf ratio of the Prairie Creek igneous rocks is 32.5 and 32 for the kimberlite and peridotite, respectively

(Date*, pers. comm.; determined using the radio chemical method developed by Butler and Thompson). This ratio is somewhat higher than that found by the previous authors and would suggest that the Prairie Creek ultrabasic rocks are not enriched in Hf with respect to Zr. This being the case, then for prospecting purposes, there is probably no advantage in determining Hf in preference to Zr.

9.23 The Rare Earths

Much has been written on the distribution of the rare earth elements. The salient papers (pre 1966) have been summarised and discussed by Haskin et al (1966). Unless otherwise specified, the general data for the rare earths is taken from this paper.

The rare earth elements have very similar chemical properties and ionic radii and consequently form a very coherent group of elements. They may be considered to move as a single entity and to replace Ca^{2+} in igneous rocks because of ionic radii similarities. In the Prairie Creek kimberlite the rare earths may occur in perovskite and/or apatite. Their increase in content towards the ground surface would strongly suggest the former mineral to be the dominant host (cf. Nb and P, Chapter 4).

Because of their strong geochemical coherence, the relative rare earth pattern in the whole earth is presumed to be the same as that found in chondrites. Sedimentary rocks have very similar relative rare earth distributions and are enriched in the light (La — Sm) rare earths relative to the chondrite average. This is attributed to zoning of the earth's crust and if true would imply the mantle to be deficient in light rare earths. This is partially supported by the rare earth

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*Imperial College.

distributions in high temperature peridotites which are highly deficient in light rare earths (Fig. 9.1).

In complete contrast kimberlite, including that at Prairie Creek, and to a lesser extent alpine peridotites, are considerably enriched in light rare earths (Figs. 9.1 and 9.2). This indicates that either kimberlites and alpine peridotites are derived from a completely different source than high temperature peridotites or some considerable fractionation has occurred.

It would be interesting to compare the relative rare earth distributions and absolute contents in the Prairie Creek peridotite with those in the kimberlite. If similar distributions and absolute contents are obtained in both rock types, this may indicate a common or genetically similar source of the parent magmas. If this is the case then the diamondiferous character of the kimberlite must be due to

(a) a difference in volatiles* and/or
(b) physical parameters.

*The reason for rare earth fractionation is still largely unknown although volatiles are thought to play an important role (Haskin et al, 1966, p. 255). However, these are unlikely to be the only influencing factors. Thus until the fundamental reasons for rare earth fractionation are more fully understood it will not be possible to assess the relative amounts of volatiles in the peridotite and kimberlite magmas.

Clearly further work is needed on the rare earth distributions in the Prairie Creek igneous rocks and on the fundamental controls of rare earth fractionation.

As a general rule rocks rich in silica favour concentration of the heavy rare earths, including Y, whilst those low in

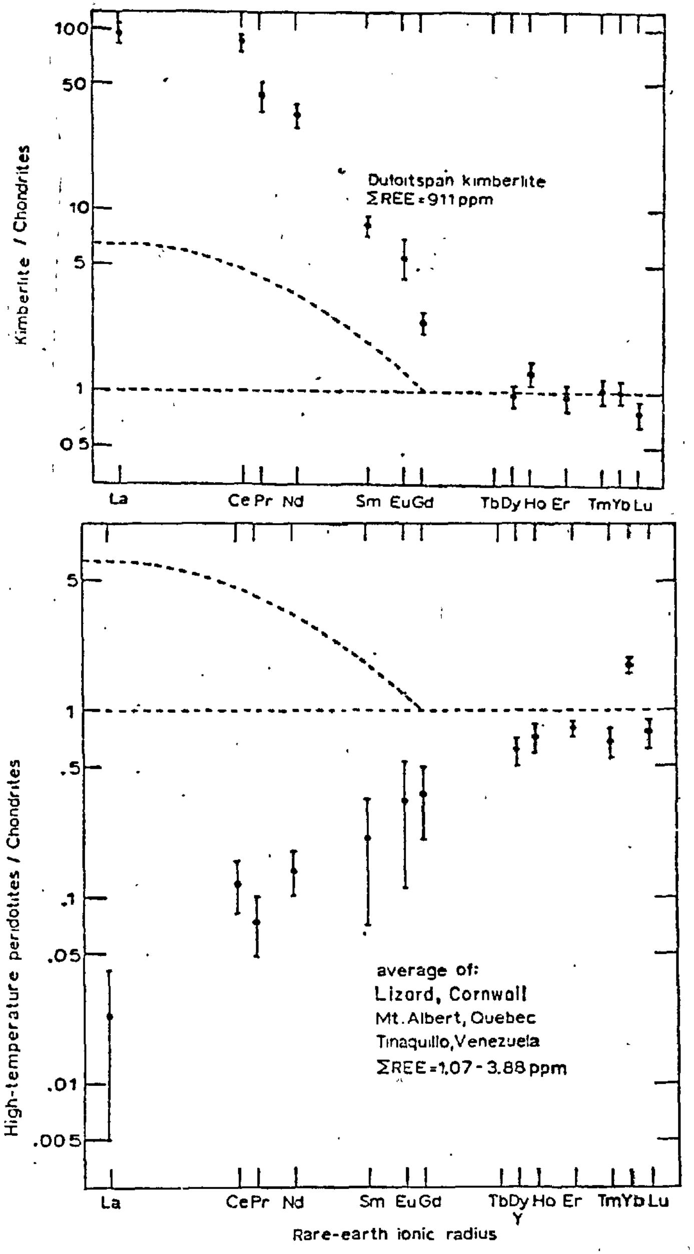

Figure 9.1: Comparison plot for high temperature peridotites and Dutoitspan kimberlite. Upper dashed line represents the North American composite shale. (After Haskin et al 1966).

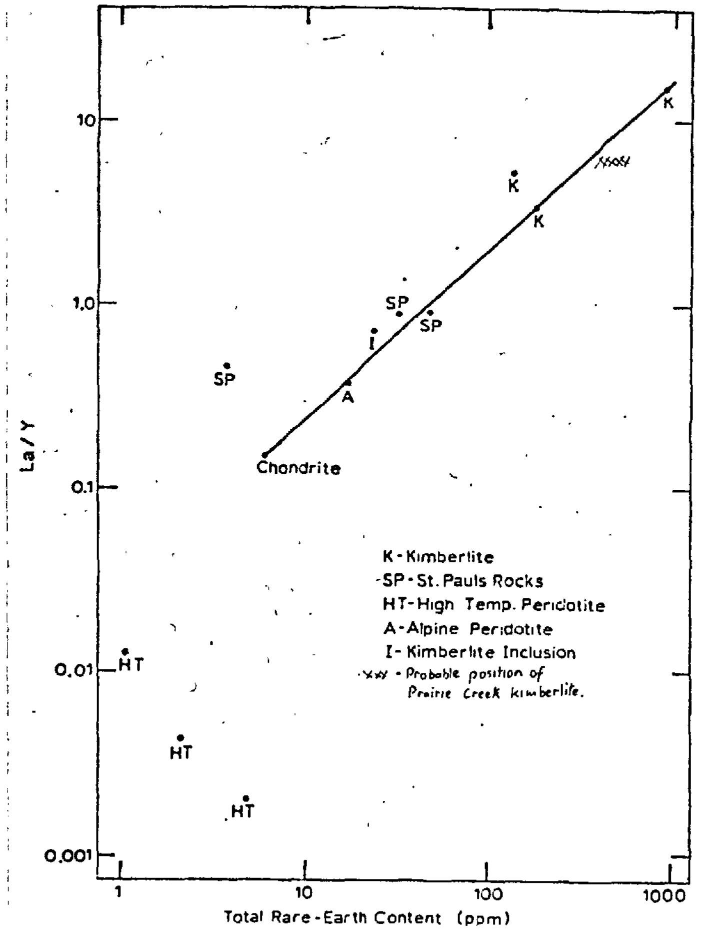

Figure 9.2: La/Y ratio for peridotitic materials plotted against total rare earth content. (Modified from Haskin et al, 1966).

Table 9.5 Comparison of the La/Y ratios between kimberlite and selected alkalic rocks.

	Kimberlite				Carbon-atites		Alkalic seyenites									
	PCK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
La (ppm)	264	26	26	200	180	76	11.4	29	20	230	380	290	360	40	83	49
Y (ppm)	42.6	4.9	7.3	12.9	95	38	10.6	13.4	14.2	76	150	480	210	30	33	31
La/Y	6.35	5.3	3.6	15.5	1.9	2.0	1.1	2.2	1.4	3.3	2.5	1.7	1.7	1.3	2.5	1.6

PCK Prairie Creek Kimberlite (Table 9.3)
1. Premier kimberlite (Haskin et al, 1966)
2. Mwadui kimberlite (Haskin et al, 1966)
3. Dutoitspan kimberlite (Haskin et al, 1966)
4. Panda Hill, Tanganyika (Schofield and Haskin, 1964)
5.. Sangu, Tanganyika (Schofield and Haskin, 1964)
6. Metasomatic nepheline seyenite, Wausan, Wisconsin (Haskin et al, 1966)
7. " " " , Bancroft, Ontario (Haskin et al, 1966)
8. " " " , Red Hill, N.H. (Haskin et al, 1966)
9. Lovozersk phase 1 (Balashov, 1963)
10. " phase 2 (Balashov, 1963)
11. " phase 3 (Balashov, 1963)
12. " Massif average (Balashov, 1963)
13. Sandyk phase 1 (Balashov, 1963)
14. " phase 2 (Balashov, 1963)
15. " Massif average (Balashov, 1963)

silica favour concentration of the light lanthanides (Fleischer and Anschuler, 1969). Thus in areas of granitic and sedimentary rocks one would expect to find anomalous relative rare earth distributions about kimberlite. However, it is not thought that determination of such trends would offer any advantage over analysis for the normal prospecting elements, i.e. Ni, Cr, Mg, Nb, La and Ce. The La/Y ratio may, however, find application in areas of alkalic rocks, e.g. differentiated nepheline seyenites, carbonatites etc., since a higher La/Y ratio is observed in kimberlite than in these other rocks (Table 9.5).

The ionic potentials of the trivalent rare earths varies from 2.5 for La to 3.3 for Lu (Table 8.1). Consequently, the rare earths tend to become enriched in the hydrolizates during weathering. However, in acid media they are appreciably soluble and may move as simple ions. At a pH of nearly neutral they are hydrolized and sorbed on clays, sesquioxides and/or organic matter; however, some metal, especially the heavier members, may move as complex ions (Balashov et al, 1964). Cerium is especially concentrated in marine manganese nodules.

As previously mentioned, in Arkansas the rare earths are thought to be contained dominantly in perovskite which is relatively resistant to weathering in the kimberlite soil profile. Consequently, the initial dispersion of the rare earths will probably be largely mechanical. However, any rare earths released during weathering may be either leached from the profile as soluble complex ions or sorbed by sesquioxide nodules and/or clay minerals and/or organic compounds.

In the slightly acidic waters of the drainage some of the rare earths may be taken into solution either as simple or complex ions. Some hydrolysis and subsequent precipitation may occur over limestone country rocks. Like Nb, rare earths present in fine particlate matter will probably be flushed out of the system during the wet season. There is no reason to suspect therefore that the minus 10 plus 20-mesh fraction would not be the optimum for analysis for the rare earths. However, until analyses are actually undertaken this is by no means certain.

9.3 SUMMARY

Semi quantitative analyses on the mass spectrograph have shown that a wide range of elements are present in anomalous concentrations in the Prairie Creek kimberlite and associated soils and drainage.

Maximum contrast is given by La, Ce, Te, Nb and Sr. Hafnium may also be a useful element but possibly no more so than Zr.

Tellurium may be present in highly anomalous amounts in the kimberlite but additional analyses are required to confirm this.

A study of rare earth distributions may throw some light on the genetic differences between the Prairie Creek peridotite and kimberlite.

During secondary dispersion the rare earths may be appreciably mobile in acid environments and precipitated in alkaline ones.

The Buell Park kimberlite is not especially concentrated in alkalic elements.

CHAPTER 10

APPLICATION TO PROSPECTING

10.1 PROSPECTING IN SOUTH WEST ARKANSAS

10.11 Reconnaissance

The present study has shown that anomalous concentrations of certain elements can be detected in the drainage downstream from kimberlite. Various drainage components have been examined including wad, slime, organic matter, stream bank colluvium and alluvium and many size fractions of poorly and well sorted sediment. Anomalous drainage trains were found in all these materials.

Slightly differing prospecting methods are suggested according to whether the stream banks are residual/colluvial or alluvial, and in prospecting for kimberlites covered by Quaternary alluvium.

10.111 Prospecting where the stream banks are residual or dominantly colluvial

This applies over the greater part of the area including the American Mine and Black Lick Prospects where the orientation studies were conducted.

The best contrasts and dispersion is given by the minus 10 plus 20-mesh fraction of poorly sorted stream sediment. Using this size fraction, kimberlite dykes can be detected confidently by analysis of sediment samples taken at $\frac{1}{4}$ mile intervals. Samples taken at $\frac{1}{2}$ mile intervals would detect most kimberlite occurrences of any magnitude and would almost certainly enable kimberlite pipes to be located.

Samples should be analysed initially for Ni. However, since anomalous concentrations of Ni, Co and exMg are also found in sediment over the limestone members, anomalous samples containing less than 120 ppm Ni should be re-analysed for Nb to differentiate anomalies due to limestone. Marginal Nb anomalies should also be analysed for Cr.

10.112 Prospecting where one or both stream banks are alluvial

Dispersion in the minus 10 plus 20-mesh fraction is by mechanical processes. Consequently, it is possible that where streams are flanked by an appreciable flood plain that anomalous materials are filtered out by vegetation, and not reach the stream in quantities detectable by sediment analysis. Under these circumstances one must look for anomalous concentrations of elements appreciably dispersed by saline processes, e.g. Ni and/or exMg. The problem here is that metal precipitated in the fine fraction of stream sediment is largely swept away by the fast flowing streams of the wet season. However, some metal may be precipitated in the coarse fraction, together with sesquioxides, within nodules. Nickel anomalies derived from this process will not have an accompanying Nb anomaly. It is possible, however, that a coincident Ce and La anomaly may be present but this was not investigated.

Nickel and exMg are precipitated from emerging ground waters in the stream banks below the wet season water level. It is recommended therefore that in streams where the banks are dominantly alluvial, in addition to stream sediment samples, material should also be taken from the alluvial bank(s) below the wet season water table. The relative sizes of the exMg and Ni aureoles are unknown; and in the first instance, the minus 80-mesh fraction of bank samples should be analysed for both these elements.

Where the flood plain is very wide and the inflowing tributary density is very low, as on parts of the flood plains of the Little Missouri, Saline and Cossatot Rivers, it is possible that anomalous ground waters are no longer anomalous when they reach the stream channel. In such cases it is suggested that samples of the A_0 horizon and/or material from the zone of ground water fluctuation (see Section 10.113) be taken from the edge of the flood plain. The minus 80-mesh fraction of such samples should be analysed for Ni and exMg. At the present juncture it is unknown just how wide the flood plain may be before sampling at its edge becomes necessary.

Difficulty may be experienced in differentiating saline anomalies due to kimberlite from those due to precipitation of elements over limestone. Analyses of the limestone soil are not available and a suitable method of differentiation cannot be suggested at the present time.

10.113 Prospecting for kimberlite covered by Quaternary alluvium

A substantial anomalous aureole for exMg, and to a lesser extent Ni, is present in the zone of ground water fluctuation about the Prairie Creek pipe. Anomalous exMg concentrations, which cannot be explained by soil creep, are also recorded in the A_0 horizon in some profiles. Before it is possible to suggest a detailed method of prospecting for ultrabasic intrusions covered by Quaternary alluvium, it is necessary to complete a fuller orientation survey about the Prairie Creek pipe. Attention should be paid to the relative size of the aureoles at surface and at depth, and as to the relative merits of Ni and exMg. There is little doubt, however, that a suitable prospecting method can be established to locate kimberlite pipes buried under the alluvium.

10.12 Follow Up

10.121 Drainage anomalies

In following up stream sediment anomalies when the stream banks are colluvial or residual, samples should be collected at 100 feet intervals of poorly sorted stream sediment and from the A_1 horizon at the top of both banks. In areas of siltstone lithology the minus 80-mesh fraction of stream sediments should be analysed for Ni. In areas of limestone lithology the minus 10 plus 20-mesh fraction should be analysed for Nb. The minus 80-mesh fraction of highly anomalous sediment, together with the associated and near-by bank samples, should be analysed for Nb to determine the 'cut off' of the anomaly and the anomalous bank.

In following up stream sediment anomalies where the banks are alluvial, then a procedure similar to that outlined above should be adopted except that the bank samples should be collected from beneath the wet season water level.

In following up bank anomalies in alluvium where anomalous concentrations of metal are not observed in stream sediment, the bank samples should be collected at 100 feet intervals. At the point of 'cut off' samples should be collected from the zone of ground water fluctuation, or if satisfactory, the A_0 horizon (see Section 10.113) on a grid pattern at right angles to the overall strike of the stream. Samples should also be collected of the colluvium at the base of the valley wall.

10.122 Soil Surveys

Although maximum Ni contrast in residual soils occurs in the C horizon (Table 10.1) the $B_{2.1}$ horizon is very much easier to sample and high contrasts are present.

Table 10.1 Contrast between soils over kimberlite and soils over the Trinity siltstone.

Soil horizon	Contrast														
	Ni	Mn	Co	V	Cr	Ti	Nb	Ba	Sr	P	Mg	exMg	exNi	La	Ce
A_1	57	13	98	4	26	4	24	18	>35	12	36	60	10	28*	27*
B_2	87	120	44	2	25	$1\frac{1}{2}$	18	19	>28	30	19	72	18		
C	125	>24	>40	4	20	2	30	35	>17	28	92	230	>16		

*A_1 Kimberlite/B_2 Trinity

In following up anomalies by soil sampling, it is recommended that samples be collected from the B_2 horizon on a 100 foot grid whose lines make an angle of 45° with the overall ground slope. Samples should be analysed in the first instance for Ni. The existence of an anomaly may be confirmed by analysis of the most anomalous samples for Nb. The source may be delineated by analysis for Nb of material taken from a few feet depth. In some instances, however, a change in soil type may enable rapid delineation of the kimberlite.

In areas where the threshold for Ni is high then the B_2 horizon may be analysed for exMg. If this too is unsuitable, then Nb should be determined in samples collected from the A horizon.

In interpreting soil anomalies, past and present topography must be considered.

10.13 Differentiation of peridotite from kimberlite

From the prospecting point of view, on the present data there appears to be very little chemical difference between the Prairie Creek peridotite and kimberlite. Consequently, chemical methods of differentiating these rock types in stream sediments are not thought applicable.

Substantial magnetic anomalies are recorded over the peridotite but not over the kimberlite (report by Sherwin F. Kelley Geophysical Services Ltd., in John St. Clair, 1953). It may therefore be possible to use kappametric methods (Litinskiy, 1963) to differentiate anomalies due to peridotite.

Magnetometry will differentiate peridotite from kimberlite at Prairie Creek. However, before this can be regionally applied, it must be first established whether the Prairie Creek kimberlite is anomalously non-magnetic. There are also a greater proportion of accidental xenoliths in soils over the kimberlite, and deeper parts of the weathered bedrocks are of different colour.

10.14 Limitations of Geochemical Prospecting in South West Arkansas

Away from the study area and particularly to the west, there are extensive outcrops of intermediate to basic alkalic tuffs of the Woodbine formation. These tuffs, and their associated weathering products, contain more Ni, Nb, Cr, etc., than do other country rocks. Although the content of these elements is considerably lower in the Woodbine than in the kimberlite, it is possible that the trace element content of streams draining these rocks will exceed the threshold values established in the study area. Little work has been undertaken on this problem and it is not possible at the present time to suggest a method of differentiating anomalies related to the tuffs from those due to kimberlite. However, in practice the problem is not serious because only near the contact of the Woodbine with the older rocks will spurious anomalies occur.

Soil anomalies related to the Woodbine tuff can readily be differentiated by their lower metal content as shown on Table 10.2 below.

Table 10.2

	metal content (ppm unless otherwise stated)							
	Ni	Co	Cr	Mg	exMg	Fe	Mn	Nb
Woodbine	25	10	230	1.4%*	180	8.0%	100	150
Kimberlite	1570	132	1880	3.5%	5427	8.3%	3600	101
Contrast	63	13	8	2½	30	1	36	<1

Data on complete sample. *Ross et al, 1928. Bentonite derived from trachytic pumice, S.W. Arkansas

It should be emphasised that recommendations for the stream sediment sampling is based on samples collected at one period of the year, that is towards the end of the wet season. Longer drainage trains might be detected in the fine fractions during the dry season. Whilst seasonal variation in the compositions of the coarse fractions is not expected it cannot be entirely ignored.

10.2 PROSPECTING IN ARIZONA

Anomalous concentrations of Ni and exMg are detected in stream sediment over 7000 feet downstream from the ultrabasic intrusions at Garnet Ridge and Buell Park. Maximum contrast occurs in the minus 20 plus 36-mesh fraction.

Because of the lack of chemical weathering in Arizona, fresh olivine, pyrope garnet and chrome diopside are readily visible in stream sediment 7000 feet downstream from the Buell Park caldera. Olivine is readily recovered from sediment the same distance downstream from the Garnet Ridge East intrusion by panning.

Before a suitable prospecting method and sample interval can be proposed in Arizona, it would be necessary to compare the lengths of heavy mineral and anomalous geochemical trains, their respective efficiencies and costs of eliminating ground.

If geochemical methods are used then the minus 20 plus 36-mesh fraction should be taken and analysed for Ni.

10.3 PROSPECTING ELSEWHERE

Geochemical techniques of prospecting for kimberlites can be employed in areas where there are ultrabasic or alkalic rocks. "Alkalic" rocks, including kimberlite, alkalic peridotites, carbonatites, melilite basalts, etc., may be identified in the ultrabasic environment by analysis for Nb, Ce, La, Ba, Sr, Zr, Hf etc. Kimberlites, alkalic peridotites, etc., can be distinguished from other alkaline rocks by their high content of ultrabasic elements, e.g. Ni, Cr, Mg, Co, etc. No simple geochemical method of differentiating anomalies due to kimberlite from those due to other alkalic ultrabasic rocks are evident; although the La/Y ratios may find some application. An appreciable Te anomaly may be present in kimberlite but this has to be confirmed.

Where alkalic and ultrabasic rocks are intimately mixed, e.g. carbonatites in ultramafics, geochemical methods will not be applicable.

In south west Arkansas, the coarse fraction of stream sediment gives the best results. It is improbable that this fraction will be the most suitable in many other environments. In each area an orientation study should be conducted.

It must be emphasised that geochemical methods are only one of a number of techniques employed in prospecting for kimberlites, e.g. heavy mineral sampling, kappametry, air photography and various geophysical methods. Some of these techniques are highly efficient and geochemical methods may best be used to complement these procedures. The phase of prospecting (i.e. reconnaissance, follow up or detailed), where geochemical methods will prove most useful will vary from area to area.

10.4 DIAMONDIFEROUS FROM NON DIAMONDIFEROUS-KIMBERLITES

The present study has not found a solution to this problem. There are, however, several features which may be common to diamondiferous kimberlites.

So far as has been determined, the major and minor element contents of the Prairie Creek peridotite and kimberlite are much the same. Consequently, the reason why one contains diamonds and the other not is due to either or both:

(1) Physical differences during intrusion.
(2) A difference in the proportion of volatiles.

A physical difference in the nature of the peridotite during intrusion is reflected by the slight metamorphism of the accidental shale xenoliths. Those in the kimberlite are not metamorphosed and are more abundant. However, Miser and Purdue (1929) record the Trinity formation to be baked slightly at the contact with kimberlite at the American Mine; which is reputed to have produced 20 small diamonds. The lack of metamorphism of near surface xenoliths appears to be a common feature of diamondiferous kimberlites from many parts of the world, although there are exceptions. For example, shale fragments at the Premier Mine have been metamorphosed to augite and garnet (Wagner, 1914).

Whilst there has been no appreciable metamorphism of near surface accidental xenoliths in the kimberlite type intrusions in Arizona, these rocks lack the highly differentiated nature of kimberlite. Thus it may be that a highly differentiated magma is a feature of diamond bearing igneous rocks; however, insufficient kimberlite analyses are available to state this without reservation.

According to Milashev (1965), quoted by Dawson (1968), a magma with a high Fe/Ti ratio is most likely to produce diamonds whereas Al, Na and K are diluting factors.

The diamond bearing character of a kimberlite is generally assessed on the plus 60-mesh (approximately) fraction. The possibility must be considered that in some kimberlites the bulk of the diamonds are of finer grain size than this. If this is true, then some of the so called non-diamondiferous pipes may in fact be diamond bearing. However, at the present time such intrusions are unlikely to be ore bodies.

CHAPTER 11

GENERAL SUMMARY OF CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

11.1 SUMMARY OF CONCLUSIONS

11.11 Analytical

(1) A wide range of attacks have been tried for Ni in the soil solum over the kimberlite and Trinity siltstone. Optimum contrast is obtained with the $KHSO_4$ and sodium citrate/dithionite attacks. Precision and productivity is best for the first two attacks.

(2) Emission spectrograph determinations suffered from a severe matrix effect. Precision ranged from ±35 to ±103% at the 95% confidence level.

(3) Precision and reproducibility are within ±15% for Mg extracted with molar ammonium acetate solution and determined by atomic absorption methods. Exchangeable forms of Mg may not be the only form of metal extracted.

(4) Iron rich samples give "high" results for Cr when determined by comparison of dichromate solutions. Such samples should be determined using the diphenylcarbazide method.

(5) In soils over the Prairie Creek kimberlite, the molar ammonium oxalate/oxalic acid attack is not specific for Ni associated with secondary Fe oxides.

(6) Sampling errors are within the analytical precision, even for the minus 10 plus 20-mesh fraction when prepared as described. Errors in this fraction may occur for samples near the threshold value when metal is highly concentrated in discrete particles.

(7) Soil profile sampling is very considerably speeded up when using a Bull Soil Sampler.

11.12 Geochemical Features of Kimberlite

(8) Kimberlites are ultrabasic rocks and contain high concentrations of elements such as Mg, Fe, Mn, Ni, Co and Cr. However, they differ from most other ultrabasics in that there is an enrichment of Ba, Sr, Rb, P, Nb, Zr, Hf and certain rare earths.

(9) The light members of the rare earths are considerably enriched in kimberlite relative to the chondrite average. This gives rise to a high La/Y ratio.

(10) With the exception that the Fe content of the lamprophyric kimberlite at Prairie Creek is lower than the average, the major and minor element content of the Prairie Creek deposits are similar to those of African kimberlites.

(11) So far as has been determined, the composition of the Prairie Creek mica peridotite and kimberlite is very similar. Slightly higher concentrations of many elements are found in the peridotite but this probably reflects a higher degree of weathering and a greater abundance of accidental xenoliths in the more porous kimberlite.

(12) The tuff at Prairie Creek is depleted in many elements compared with the kimberlite.

(13) The alkalic tuff of the Woodbine formation contains high concentrations of alkalic elements and higher concentrations of the ultrabasic elements than the sialic country rocks.

(14) The apparently non-diamondiferous kimberlite tuff at Buell Park is not enriched in "alkalic" elements. This is not considered a true kimberlite.

11.13 Soil Profile Development

11.131 Arkansas

(15) Over most rocks there is a marked differentiation of the soil profile into horizons. Marked differences in colour, morphology, clay content and nature of the clay minerals occur in profiles over the igneous and sedimentary rocks.

(16) The lower C horizon of the kimberlite is blue; that of the peridotite is yellow.

(17) There is an increase in silt-clay fraction towards surface over most rock types reflecting the increasing degree of weathering. Some eluviation of clays from the A to the B horizon has occurred.

(18) The broad sequence of alteration of the ferromagnesian minerals of kimberlite is as follows:

$$\left.\begin{array}{l}\text{olivine}\\ \text{pyroxene}\\ \text{phlogopite}\end{array}\right\}\rightarrow\left.\begin{array}{l}\text{phyllosilicates}\\ \text{serpentine}\end{array}\right\}\rightarrow\begin{array}{l}\text{clay minerals}\\ \text{(montmorillonite}\\ \text{group?)}\end{array}\rightarrow\left\{\begin{array}{l}\text{quartz}\\ \text{sesquioxides}\end{array}\right.$$

increase in weathering ⟶

(19) The elements present in abnormally high concentrations in kimberlite can be grouped on the basis of mobility in the secondary environment in southwest Arkansas into:

(a) Highly mobile: Mg

(b) Moderately mobile: Ni, P, V, Fe, Co, Ba and Mn

(c) Relatively immobile: Nb, Cr, Ti, Sr and Zr.

(20) Magnesium has been strongly leached from soils over the ultrabasic rocks, especially from those over kimberlite. This is probably related largely to the degree of breakdown of the host minerals.

(21) The distribution of exchangeable magnesium (exMg) in the C horizon is related largely to the decomposition of Mg

host minerals. It has been strongly leached from the coarse sizes of the solum and sorbed in the clay size. Subordinate concentrations of exMg are associated with sesquioxide nodules, presumably with the iddingsite grains.

(22) In soils over the Trinity siltstone Mg has been leached from the A horizon and accumulated in the $B_{2.1}$ horizon, where it is presumably sorbed on clay minerals and sesquioxides.

(23) Manganese has accumulated in the A and B horizons of soils over the Prairie Creek kimberlite where it occurs mainly as sesquioxide nodules. These are thought to be largely due to flocculation of the negatively charged Mn sol due to the presence of abundant cations. Whilst Mn is considerably enriched in the A horizon of soils over the Trinity siltstone, metal is present in both the clay and coarse sizes. There are certain features of distribution of Mn which are not clearly understood, but redistribution through organic processes is thought to be important.

(24) Cobalt follows Mn very closely in the soil profile, although there are some minor differences in distribution. This is attributed to coprecipitation of Co^{2+} with Mn hydroxides.

(25) The mobilisation of Ba is limited primarily by the low solubility of barite. However, Ba appears considerably concentrated in Mn nodules presumably due to sorbtion of Ba^{2+} ions. Barium cations may also be readily sorbed by clay minerals.

(26) Iron, Ni, V and P have been leached from the A horizon of soils over the ultrabasic and country rocks. They have accumulated to varying degrees in the B_2 horizon.

(27) Iron is present largely as sesquioxide concretions and mineral aggregates in the B_2 horizon of soils over the ultrabasic rocks, these are scarce in soils over the sialic country rocks. Whilst some nodules over the kimberlite are grains of iddingsite, the remaining nodules are thought to have been derived by alternating wetting and drying of the clay rich B_2 horizon.

(28) Vanadium is concentrated in Fe nodules, probably due to sorbtion of anionic metal by the positively charged Fe sol. Nickel is concentrated in Mn sesquioxide nodules presumably for the opposite reason.

(29) Both Fe and Ni are appreciably concentrated in the clay fraction of soils over the ultrabasic rocks where they occur associated with clay minerals and sesquioxides.

(30) Insufficient data is available to establish the controls of redistribution of P. However, pH and association with ferric sesquioxides are probably important.

(31) The relative mobilities of the elements detailed in groups (23)-(30) are given on the table below. Elements to the left of Sr are thought to have been leached from the solum whilst elements to the right have accumulated (33).

most depleted in solum $Ni = P > V > Fe = Sr < Co < Ba? < Mn$ most enhanced in solum

(32) Niobium, Sr, Ti, Cr and Zr are present largely as resistant minerals and accumulate in the silt fraction during weathering. Zirconium, Ti and Nb cations are readily hydrolyzed at the pH prevailing in the field areas, and are precipitated in the hydrolyzate fraction on dissolution from their host minerals. Translocation in the profile is therefore probably largely by mechanical processes; although some leaching as anionic or metallo organic complexes; especially for Nb (35) may occur. Trivalent

Cr is hydrolized at pH 5.5 and has similar chemical properties to Fe^{3+}; it therefore accumulates with ferric sesquioxides upon its dissolution. Some Cr may also be present within iddingsite grains.

(33) There is, so far as has been determined, a similar enrichment of diamond and Sr in the solum. Strontium is therefore considered to have remained virtually constant during weathering of the kimberlite.

(34) The relative mobilities in the kimberlite solum of the elements detailed in (32) are:

least immobile $Nb < Cr \ll Ti < Sr \ll Zr \ll$ diamond most immobile

(35) Assuming (33) to be true, then Nb has been substantially leached from the kimberlite soil profile. The reasons for this are not fully understood but some leaching as soluble metallo organic compounds or anionic metal should be considered.

11.132 Arizona

(36) Chemical weathering in Arizona is very slight and the soils are extremely rudimentary. The C horizon of the kimberlite is a green xenolithic clay. That of the dominant country rocks is composed of reddish quartz grains.

(37) Eluvial concentrations of relatively undecomposed olivine, pyrope garnet and chrome diopside occur on ant hills over kimberlitic rocks.

(38) With the exception of Mg which may have been leached slightly from the kimberlite, there has been very little redistribution of the other determined elements.

11.14 Dispersion in Soils About Kimberlite

11.141 Arkansas

(39) A primary dispersion aureole about kimberlite at the American Mine was not found. However, some thin kimberlitic stringers may be present.

(40) In freely drained soils downslope from kimberlite, maximum dispersion, in the absence of (43), occurs in the A horizon indicating mechanical dispersion to be prevalent. However, whereas anomalous concentrations of the immobile elements are restricted mainly to the A horizon, anomalous concentrations of the semi mobile elements are present for a limited distance in the $B_{2.1}$ horizon. In the case of the highly mobile exMg, a prolonged anomalous train is present in this horizon.

(41) In soils where the water table is relatively close to the surface, such as in the colluvium flanking American Creek, the semi mobile and mobile elements are appreciably dispersed in ground waters. The resulting aureoles reflect the initial contrast and mobility of the elements. The immobile elements are dispersed by mechanical mechanisms.

(42) Precipitation of the semi mobile Mn and Fe, dispersed as in (41), is probably controlled largely by the Eh and/or pH of the environment. These elements are precipitated in the banks and bed of American Creek, presumably by deposition from emerging ground waters. Cobalt, and to a lesser degree Ni, are coprecipitated with the sesquioxides. Exchangeable Mg is also concentrated in the orange mottles on the stream bank.

(43) There are various features of the areal and vertical distribution of elements in soils at the American Mine, which are remnants of dispersion under different topo-

graphic conditions in the past. In particular, there is an appreciable aureole for the semi mobile elements in the $B_{2.2}$ horizon. This is thought to have been developed by saline dispersion in the past when the water table was much closer to the surface.

(44) Anomalous concentrations of Ni, Nb and Co are present in the Quaternary alluvium flanking American Creek. This indicates the possibility of placer deposits.

11.15 Dispersion in the Drainage

11.151 Arkansas

(45) Most of the fine sized sediment, especially clay size particles, are flushed out of the system during the wet season.

(46) The anomalous distributions of elements in the sedimentary components of the drainage are developed largely as the result of mechanical dispersion.

(47) Maximum contrast and dispersion for Ni, Co, exMg, Cr and Nb occur in the minus 10 plus 20-mesh fraction of poorly sorted stream sediment. In this fraction anomalous concentrations of these elements are detected for over 3200 feet downstream from the kimberlite at the American Mine.

(48) Anomalous Ni contents occur in bank moss for over 1700 feet downstream from the kimberlite at the American Mine.

(49) Anomalous concentrations of Ni, Co, exMg and other semi mobile and mobile elements are found in the coarse fraction of stream sediment over the limestone.

(50 The threshold for Co and exMg in stream sediment is very much higher than in the background soils. In the case of Co this is thought to be due to coprecipitation with fine

sized Mn nodules. In the case of Mg it is due to the extreme mobility of Mg^{2+} and the subsequent sorbtion on suitable materials in the drainage.

11.152 Arizona

(51) With the exception of mobile elements such as Mg, which may be transported in solution; dispersion of metal in Arizona is largely by mechanical processes.

11.16 Application to Prospecting

(52) Geochemical prospecting methods for kimberlite may be used to advantage in Arkansas where the characteristic indicator minerals are absent. Suggested prospecting procedures for this area are given.

(53) Geochemical methods will not differentiate kimberlite from the chemically similar mica peridotite.

(54) Geochemical methods may be applied in prospecting for kimberlite elsewhere, providing alkalic and ultrabasic rocks are not intimately mixed. They can best be used to complement other methods of prospecting, and in each area an orientation survey must be carried out.

11.2 SUGGESTIONS FOR FUTURE RESEARCH

11.21 Primary Features

(1) Semi quantitative analyses indicate the possibility of highly abnormal Te concentrations in kimberlite. This should be checked.

(2) The Buell Park "kimberlite tuff" is not particularly enriched in "alkalic" elements. The possibility that this is a feature of non diamond bearing kimberlites should be investigated.

(3) Those kimberlites for which analyses are available are highly differentiated rocks. The rare earths are not only usually present in highly abnormal amounts but the light members are considerably enriched. Further studies should be made towards an understanding of the controls of rare earth fractionation, particularly with reference to volatiles. Such studies may lead to a greater understanding about the nature of kimberlite.

(4) Now that satellite photographs are becoming available, supplementary investigations on the structural control of kimberlites may well prove profitable. Attention should also be paid to the possibility that kimberlites are concentrated in "areas" analogous to "metallogenetic provinces".

11.22 Suggestions Arising from the Present Study

(5) Additional information is required on the genesis of sesquioxide nodules, particularly the factors controlling their dissolution.

(6) The available data for Nb in the exogenic cycle is scanty. More knowledge is required about its behaviour in soils and the solubility of its complexes.

(7) Several elements, e.g. Mg, Ni, P and Nb, have been appreciably leached from the kimberlite soil profile. No water samples were analysed and the possibility of appreciable anomalous aureoles in leach waters should be investigated. Particular attention should be paid to organically bound metal and, in the case of Nb and P, to anionic metal.

(8) Anomalous concentrations of some elements are found in sesquioxide nodules in stream sediment over the limestone members. It is uncertain whether these have been deposited in situ or have been derived from the limestone soil. If the former is the case then a precipitation barrier occurs over the limestone. If this is the case the investigations should be made as to whether anomalous concentrations of metal are present over limestone when kimberlites are not present in the catchment.

(9) The pH of the Little Missouri ground waters some distance upstream from the pipe is 5.0. The pH of ground water adjacent to the pipe is higher than 7. The probability that a precipitation barrier for some elements occurs about kimberlite is worth investigating. In this connection, studies should be made to see if the red (iron oxides) nature of the clay overlying alluvium upstream from the Prairie Creek kimberlite is due to just such a barrier. The distance to which "high" pH values due to kimberlite may be traced in drainage waters may be worth investigating.

(10) According to Dr. P.H. Nicholls* (pers. comm.) there is a gravimetric anomaly at the Prairie Creek pipe. There are similar gravimetric anomalies in the flood plains of the Cossatot and Saline Rivers, on an easterly projection from Prairie Creek and parallel to the major strike faults of the area. The writer was not shown the results and thus remains sceptical; however, if prospecting in Arkansas were envisaged in the future, then this would be worth checking since the cost would be relatively low.

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*Tyler, Texas

11.23 Suggestions for Other Areas

(11) In kimberlites, perovskite is usually of very fine grain size and consequently receives little attention in heavy mineral prospecting. Chemically, however, it is a very important mineral since it acts as host to Nb and the rare earths. The S.G. of perovskite is 3.98 to 4.26 and it probably has a low magnetic susceptibility. Since abrasion of fine particles in flowing water is very slight (Kuenen, 1959), and perovskite has a poor cleavage, the mechanical dispersion of this mineral will be controlled largely by its resistance to chemical weathering. At the moment this is an unknown quantity although it appears to be a relatively resistant mineral in soils at Prairie Creek. It is possible, therefore, that analysis of the non magnetic fraction of sediment denser than 3.9 may provide reasonable dispersion trains in some areas. Analyses may be made for Nb, although in some areas attention to the Ce/Y or La/Y ratios may prove profitable, especially when trying to differentiate the source of perovskite. In certain areas it may prove advantageous to remove zircon, since this is often a host to Nb and the rare earths, and is common in many rocks.

(12) Certain kimberlitic minerals tend to have a slightly different composition to the same mineral derived from other sources. For example, kimberlitic ilmenite and pyrope is generally enriched in Mg. Schutte (1966) found higher Mg contents in two kimberlitic zircons from South Africa than in zircons derived from granitic and adamellitic rocks. Whilst in many instances, visual identification of a particular form of a

particular mineral, which is known to be associated with kimberlites in a particular area, is often the most expedient method of prospecting; analysis of certain minerals may assist interpretation in doubtful cases.

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APPENDIX 1

Sources quoted in Table 2.2 (See also reference list)

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* Authors data

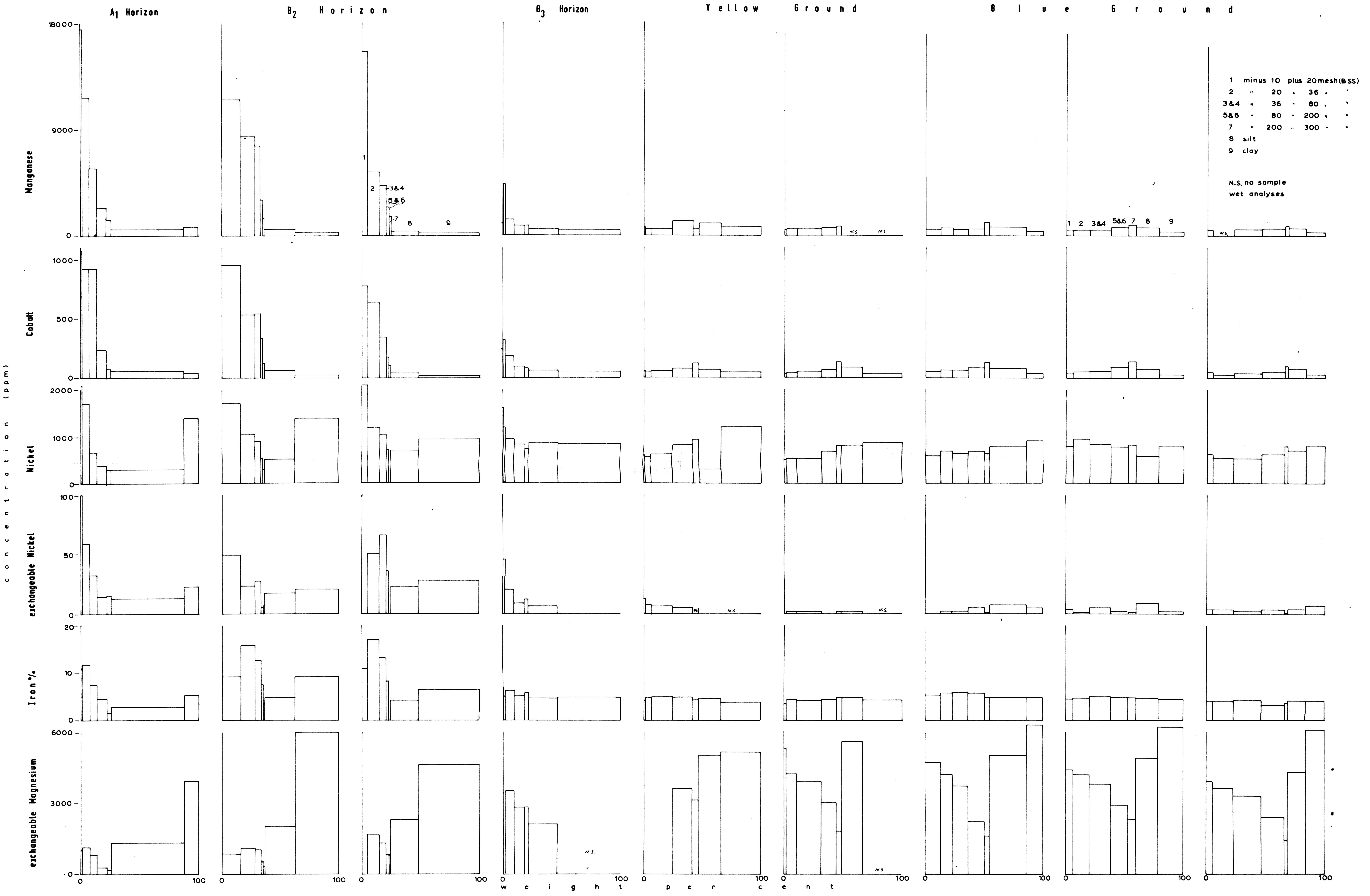

FIGURE 4.12: HISTOGRAMS OF Mn, Co, Ni, exNi, Fe AND exMg CONTENTS PLOTTED AGAINST WEIGHT PER CENT FOR VARIOUS SIZE FRACTIONS IN A RESIDUAL SOIL PROFILE OVER KIMBERLITE, PRAIRIE CREEK, ARKANSAS.

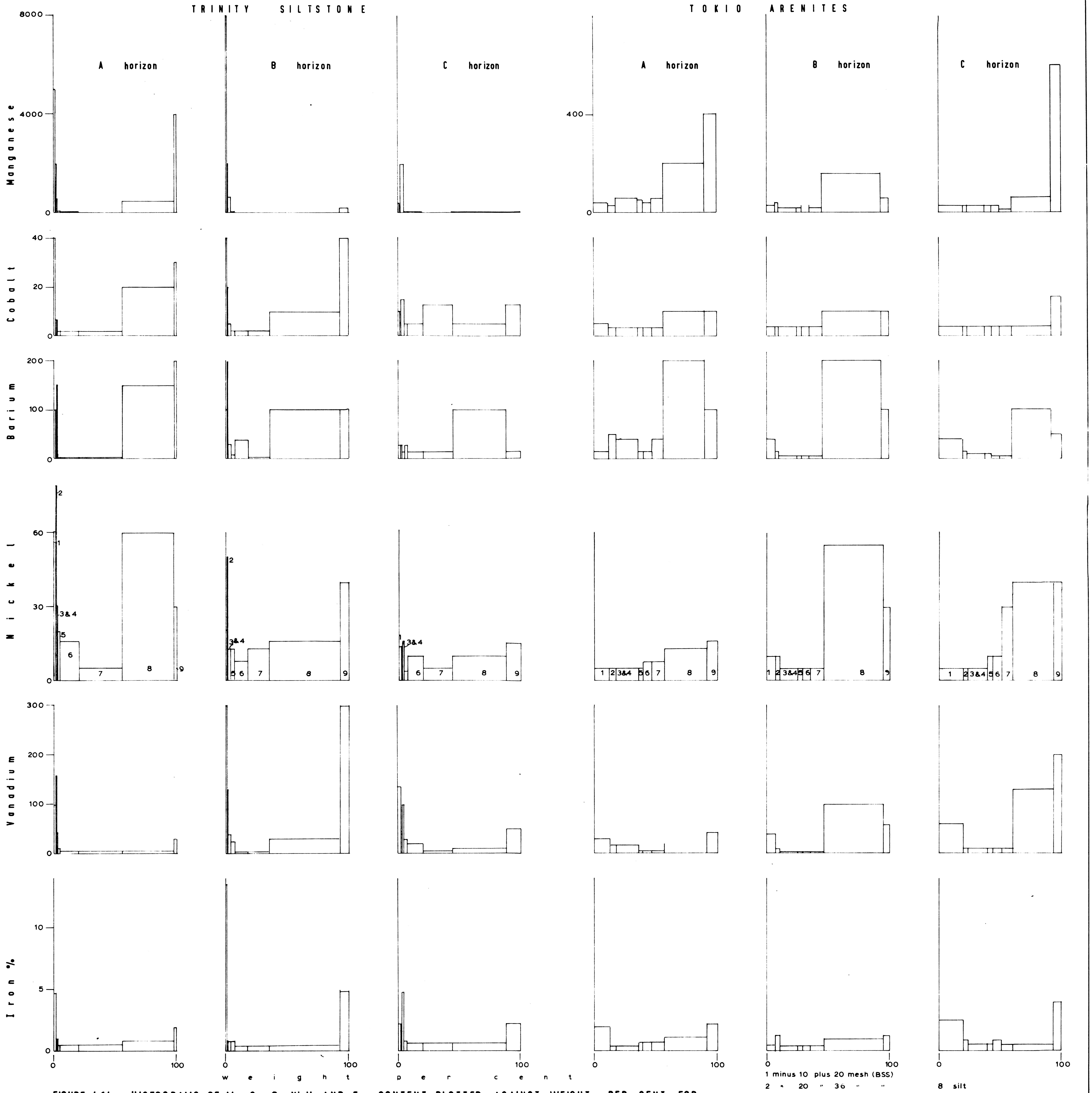

FIGURE 4.14 HISTOGRAMS OF Mn, Co, Ba, Ni, V AND Fe CONTENT PLOTTED AGAINST WEIGHT PER CENT FOR VARIOUS SIZE FRACTIONS IN RESIDUAL SOILS OVER THE TRINITY AND TOKIO FORMATIONS, ARKANSAS.

1 minus 10 plus 20 mesh (BSS)
2 " 20 " 36 " "
3&4 " 36 " 80 " "
5 " 80 " 100 " "
6 " 100 " 200 " "
7 " 200 " 300 " "

8 silt
9 clay
spectrographic analyses.

	Sample Type	Nb	Cr	Sr	Ti	Mn	Co	Ba	Ni	V	Fe%	Mg%	exMg	Analytical Method	Ge ppm	Weight percent	Sample Number
		Metal Content (in ppm unless stated otherwise).															
Kimberlite	Nodules* S.G.<2.67		400	30	8500	1%	1600	1%	2000	300	11.5			Spec.	160	100	5510NL
	L.R.		1000	400	1%	500	200	1%	1300	300	8.4			Spec.	300	55	5510NLRD
	% Extracted		0	0	35	99	93	45	64	45	60						
	Nodules* S.G.>2.95		400	100	1%	6000	600	8000	1600	400	25.0			Spec.	130	100	5510NH
	L.R.		500	300	1%	2000	1600	1%	2000	100	4.4			Spec.	400	43	5510NHRD
	% Extracted		46	0	57	86	0	46	45	89	92						
	Nodules* S.G.<2.67		850	300	1%	1%	1600	1%	2000	400	9.0			Spec.	300		5512NL
	S.G.>2.95		1000	300	8000	1%	850	1%	2000	500	21			Spec.	300		5512NH
	Mean B_2 Horizon	101	1850			3600	132		1570		8.3			Colour.			
				845	6170			2750		109				Spec.			
Peridotite	Nodules* S.G.<2.67	60											1520	Colour.			
			2000	400	1%	1%	2000	1%	2000	300	12.5			Spec.	300	100	551303NL
	L.R.		1000	300	8000	500	100	400	1000	160	9.6			Spec.	500	52	551303NLRD
	% Extracted		74	61	60	97	97	98	74	72	60						
	Nodules* S.G.>2.95	48												Colour.			
			3000	400	8500	8500	400	8000	1300	400	27			Spec.	130	100	551303NH
	L.R.		850	2000	1%	1600	600	1%	1000	85	3.35			Spec.	400	56	551303NHRD
	% Extracted		85	0	35	90	18	35	58	93	93						
	Nodules* S.G.<2.67	64	1550			10%	3280		3150		16.5	2.35	2600	Colour.			
			800	400	1%	1%	2000	1%	2000	200	10.0			Spec.	200	100	551281NL
	L.R.	240	1860											Colour.		67	551281NLRD
	% Extracted	0	20														
	Nodules* S.G.>2.95	68	3500			5500	410		1280		18.1	4.0		Colour.			
			800	1000	1%	5000	1000	8000	1600	100	7.8			Spec.	200	100	551281NH
	L.R.	216	4000											Colour.		54	551281NHRD
	% Extracted	0	38														
	Mean B_2 Horizon	135	3000				150		1580		6.3	4.2	5380	Colour.			
Anomalous Trinity siltst. Alluvium	Light col. mottle	12					8		33		0.07			Colour.			
			85	100	3000	85	13	200	50	50	1.20			Spec.	600		551725
	Lim. colo. mottle.	8					35		46		4.25			Colour.			
			85	100	4000	5000	85	600	85	85	3.35			Spec.	600		551732
	light col. mottle	66					50		250		3.3			Colour.			554433L
	dark col. mottle	66					425		380		4.25			Colour.			554433D
Trinity siltstone	Hand pic. Fe nodule.						18		58		28.5			Colour			
			400	40	2000	6000	85	800	40	100	18			Spec.	200		550135NHP
	Nodules* S.G.>2.95		60	60	3000	3000	20	200	30	40	30			Spec.	300		550135N
	-10 +20 mesh fraction								60					Colour			
			100	30	850	5000	20	200	5	400	4.75			Spec.	300		550135A

TABLE 4.17 The content of selected elements in: (a) sesquioxide nodules* developed in soils over the Prairie Creek ultrabasic rocks and Trinity siltstone country rock; and (b) "light" and "dark" mottles in mottled anomalous soils over the Trinity siltstone and Alluvium of the Little Missouri River; and the proportion of elements extracted from sesquioxide nodules with sodium citrate - sodium dithionite solution.

L.R. = the metal content of the residue obtained after leaching the nodules with citrate/dithionite solution.

* see text, page

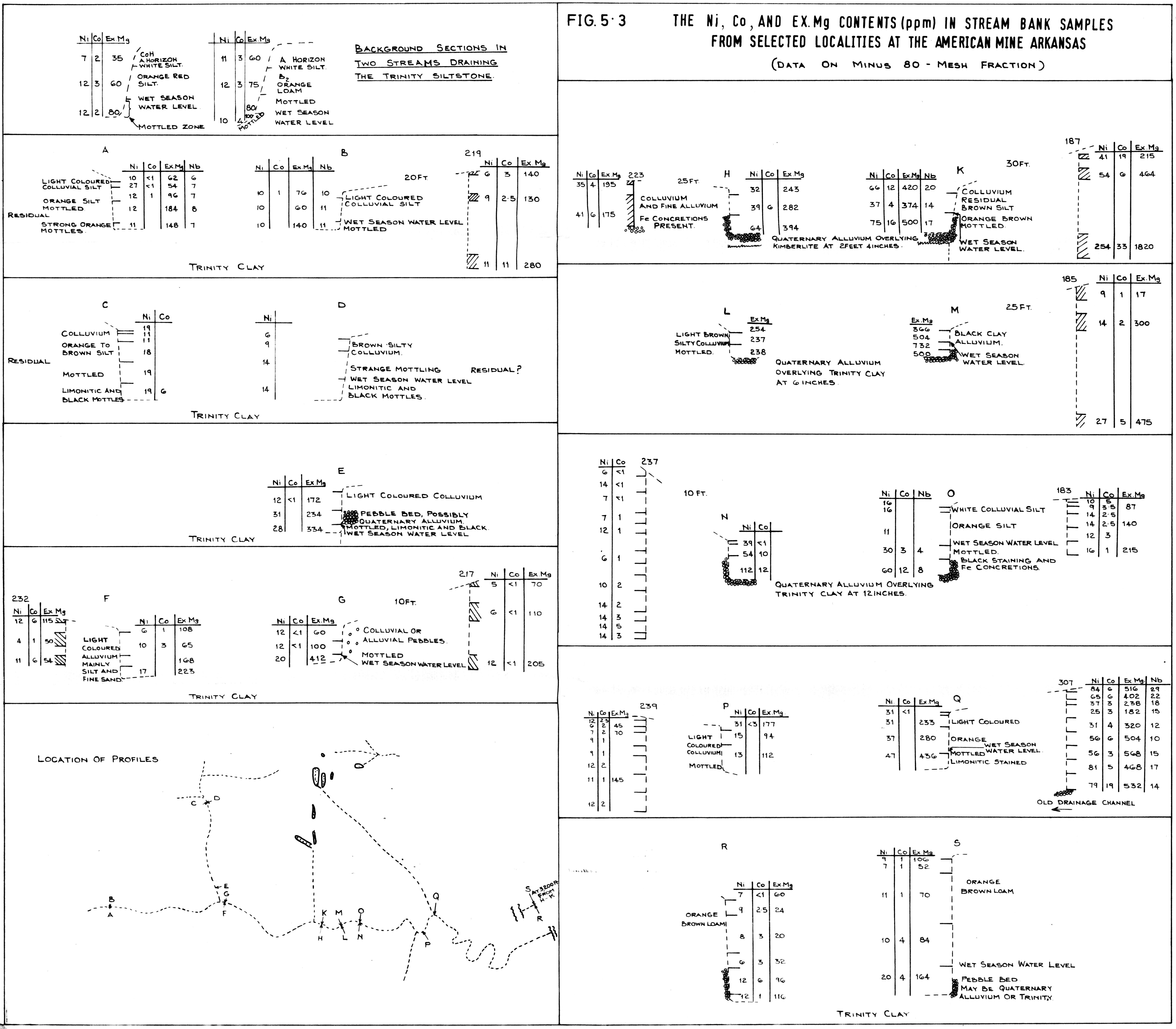

FIG. 5·3 THE Ni, Co, AND EX.Mg CONTENTS (ppm) IN STREAM BANK SAMPLES FROM SELECTED LOCALITIES AT THE AMERICAN MINE ARKANSAS

(DATA ON MINUS 80 - MESH FRACTION)