A

THESIS

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DISPERSION OF ARSENIC AND MOLYBDENUM IN SURFACE DRAINAGE, SIERRA LEONE.

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ABSTRACT

The secondary dispersion of molybdenum and arsenic in various components of drainage systems, related to known mineralisations has been studied in the Sula Mountains of Sierra Leone. The magnitude of the drainage anomalies is closely related to the nature of the host rocks, the form of the mineralisation and the size of the barren catchment area upstream from the mineralisation.

In the drainage from the Sende mineralisation, where molybdenum occurs in veinlets in amphibolite over a wide area, anomalous concentrations of the metal were detected for a distance of over two miles downstream. By contrast, little molybdenum is entering the drainage from the disseminated mineralisation in the Wankatana granite and the drainage anomaly in the large stream crossing this small deposit is of negligible extent. An arsenopyrite mein mineralisation in talc schist gives rise to a drainage anomaly over 4,000 ft. in length.

The dispersion of both arsenic and molybdenum in the stream sediments of the Sula Mountains is considered to be dominantly mechanical. Both ferric molybdate and ferric arsenate are stable under the conditions encountered.

In duricrusted (indurated latosol) areas, the coarse fractions of the sediment are composed dominantly of duricrust fragments derived from the stream banks. Coarse fractions of sediment in the immediate vicinity of mineralisation underlying duricrust contain strongly anomalous concentrations of metal, but the longest dispersion train, both in duricrusted and unduricrusted areas, are detectable in the fine fractions, and particularly in the iron oxides of these fractions.

The displacement downstream from mineralised sources of the anomaly peaks in the fines is considered to be due to the entry of metal-rich groundwater. Additional increments of such groundwater at greater distances downstream will prolong the anomalous sediment train. However, the chief factor controlling the rate of decay of anomalies in the sediments is the nature of the stream banks. In particular, drainage trains of maximum length will be found where banks are alluvial and of minimum length where there are banks composed of easily eroded barren material.

The high content of molybdenum in the silt fraction of many streams draining late-kinematic granites is held in mineral lattices and is considered to reflect the high molybdenum content of certain rock-forming minerals in granites associated with molybdenum mineralisation.

In comparison with data from other parts of the world the molybdenum content of the stream waters is exceptionally low (not exceeding 0.2 µg/litre), even in the immediate vicinity of extensive mineralisation and special techniques were developed to estimate the molybdenum and arsenic content of the natural waters. The low molybdenum and arsenic content of the surface waters is considered to be due to rapid absorption of the metal dissolved in groundwater by active components of the banks and stream sediments.

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PART ONE. INTRODUCTION

The value of geochemical prospecting as an integral part of a mineral exploration programme is now widely recognised. With the establishment of rapid and effective field analytical methods for most of the elements of economic interest, attention is now being turned to the elucidation of some of the factors controlling the formation of dispersion patterns.

The object of the present work was to examine the dispersion in drainage systems, under humid tropical conditions, of molybdenum and arsenic from known mineralisations, with the aim of devising more effective methods of geochemical reconnaissance prospecting.

A. Previous Work

The few data on the geological distribution of molybdenum and arsenic in the earth's crust have been presented by Clarke (1924), Rankama and Sahama (1950) and Goldschmidt (1954). Kuroda and Sandell (1954) and Onishi and Sandell (1956), have summarised the available information on the geochemistry of molybdenum and arsenic respectively. However, only a very limited amount of the material they quote refers to the dispersion of these elements in the zone of weathering, (i.e. secondary dispersion).

Most of the data on the secondary dispersion of molybdenum and arsenic has been contributed by soil scientists. Much of this work concerns abundances in soils and the "availability" and toxicity of the elements to plants and animals, with but a few more fundamental studies, particularly on exchange phenomena.

The work of Wiklander (1950) and his co-workers (1946, 1950), on the solubility and exchange behaviour of arsenates and the similar studies on molybdates by Jones and Milne (1954, 1956, 1957) deserve special mention. Further reference to these studies will be made in the body of the thesis.

In the U.S.S.R., extensive prospecting for polymetallic mineral deposits, involving the detection of molybdenum in overburden and drainage systems is taking place (Ginsburg 1959). Early work, such as that of Tikhomirov and Miller (1946), in the Lake Balkhash area, indicated the usefulness of molybdenum in prospecting in semi-desert conditions. Russian experience has now extended into the wide variety of climatic and geological conditions occurring in such a vast country, for instance, the studies of Belyakava (1958) in Central Kazakhstan, a highly dissected terrain with an arid continental climate, and those of Krainov (1958) in Northern Armenia, a temperate mountain region, both of which concern the use of molybdenum for drainage reconnaissance prospecting.

Both molybdenum and arsenic determinations are believed to have been an important feature of the geochemical exploration programmes of a number of North American mining companies. However, few data have appeared in print.

In Africa, specific studies of the geochemistry of arsenic and molybdenum and their utilisation in mineral exploration have been carried out by the Geochemical Prospecting Research Centre of the Royal School of Mines, under the general direction of Professor J.S. Webb. The dispersion of arsenic in soils and rocks in Southern Rhodesia has been studied by Webb (1953) and James (1957). Similarly,

Mather (1959) has made a detailed investigation of the secondary dispersion of molybdenum in soils in Sierra Leone. The experience of these workers makes a valuable contribution to the coverage of climatic types encountered in prospecting.

All the practical applications mentioned above required a greater or lesser amount of research into the parameters controlling secondary dispersion. Further improvements in prospecting techniques are dependent on a fuller understanding of these factors in a wide variety of geological and physical environments.

The present study stems directly from the work of Mather and extends his precursory investigation of the drainage dispersion of molybdenum and arsenic.

B. General Description of the Field Areas

The field work was carried out in selected areas in Sierra Leone between February and June 1960 and January and April 1961. Following the initial recommendations of the Sierra Leone Geological Survey and the subsequent work of Mather, three areas in the Sula Mountains were chosen; two for the work on molybdenum, and one location for the arsenic study.

The following description of the geology of the field areas is based on the work of the officers of the Sierra Leone Geological Survey. The general geology of Sierra Leone has been described by Pollett (1952). Wilson and Marmo (1959) have dealt with the geology, geomorphology and mineral resources of the Sula Mountains and Kangari Hills. A simplified map of the geology of Sierra Leone showing the location of the field areas is given in Figure (1). Table (1) is a general stratigraphical column for Sierra Leone.

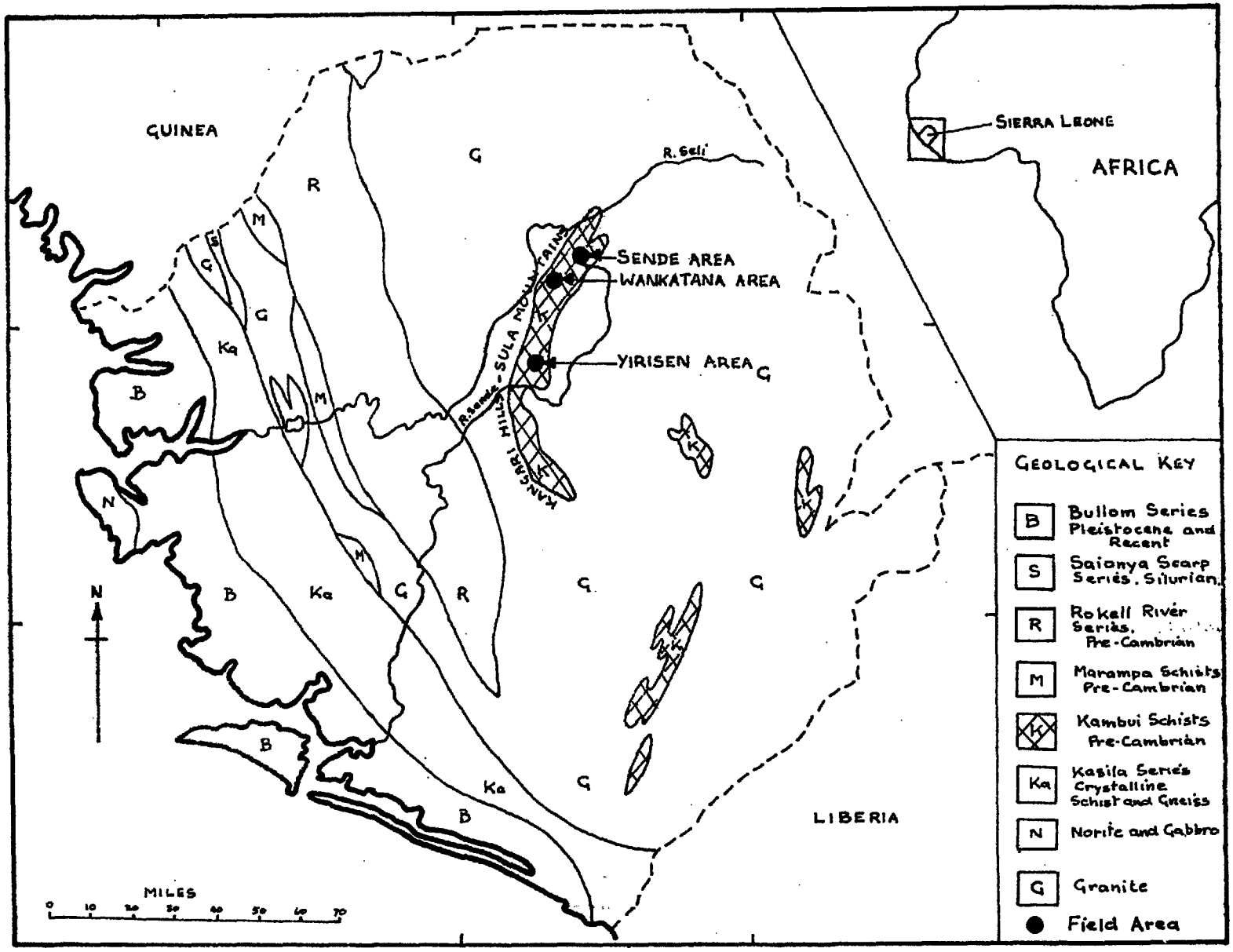


Figure 1. General Geology of Sierra Leone.

Table 1. General Stratigraphic Column for Sierra Leone (after Wilson and Marmo 1959)

Period	Geological Formation	Description
Recent	Coastal sediments	Sands and gravels.
Cenozoic	Bullom Series	Pleistocene sediments of the coastal plain.
Palaeozoic	Saionya Scarp Series	Horizontally bedded arkoses, grits and flagstones, assumed mid-Silurian age.
	Unconformity	
	Rockell River Series	Folded arenaceous and argillaceous sediments with intercalated volcanic lavas and ashes.
Pre-Cambrian	Marampa Schists	Dominantly metamorphosed sediments with subordinate orthoschists.
	Kambui Schists	Very varied metamorphics of igneous and sedimentary origin, often deeply weathered and mineralised.
	Kasila Series	Crystalline basement rocks, gneisses, schists, granulites.
Intrusives	Synkinematic Granites	Foliated migmatite with diffuse contacts. No proven economic mineral associations.
	Late-kinematic Granite	Intrusive into schists possibly late Pre-Cambrian age. Associated with mineralisations.
	Basic Intrusives	Colony gabbro mass and numerous dolerite dykes and sills.

I. The General Geology and Topography of Sierra Leone.

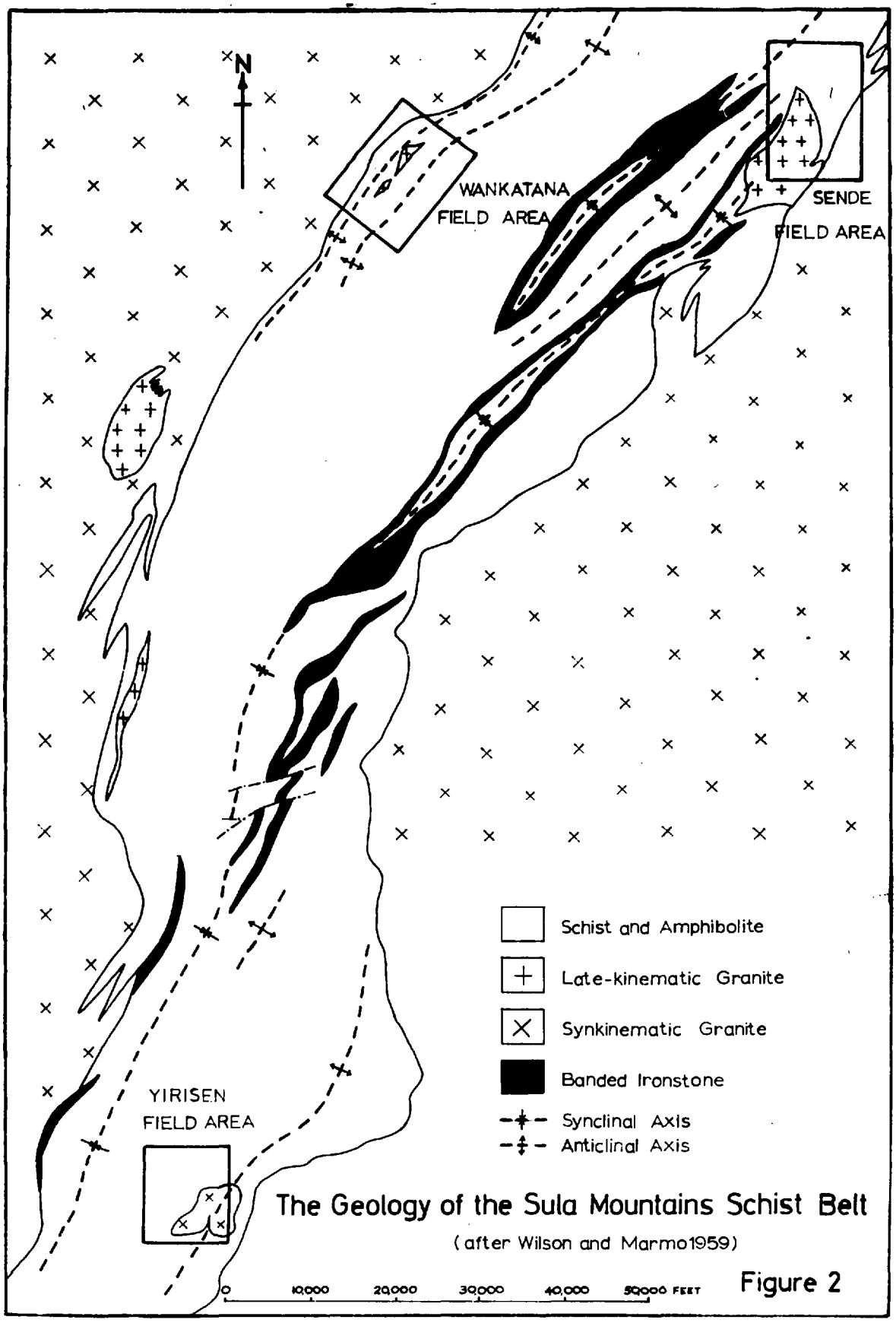
Except for a twenty-five mile wide coastal belt of Recent and Pleistocene sediments, and a small area of Silurian sediments, the rocks of Sierra Leone are all considered to be of Pre-Cambrian age. Crystalline basement rocks occupy the region east of the coastal sediments, forming an undulating plain up to sixty miles wide, with an elevation of 400 - 500 ft. above sea level. On its inland margin the plain is bounded by a granite plateau which occupies practically the whole of the eastern half of Sierra Leone, rising 1000 - 1500 ft. above the plain.

Enclosed in the granite are remnants of older, metamorphosed sediments and volcanics comprising the Kambui Schists. These rocks form the main mass of the Sula Mountains - Kangari Hills range in the north and the Gori, Nimi and Kambui Hills in the south-east.

II. Description of the Sula Mountains Schist Belt

1. Geology

The originally geosynclinal sediments forming the Kambui Schists have been folded into an arcuate system of complementary anticlines and synclines; the trend of the fold axis varying from about N40°E in the north to N10°E in the south of the schist belt, (Figure 2). Dips are very steep in the north but flatten southwards and become more variable in direction. This roughly north-south trending arcuate system has been intruded by the late-kinematic granites and



The Geology of the Sula Mountains Schist Belt

(after Wilson and Marmo1959)

Figure 2

their associated metaliferous late-stage pegmatites. During intrusion there was considerable assimilation of country rock by the granite, resulting in hybridisation.

A brief description of the principal rock types is given below:-

Amphibolites are the predominant metamorphic rocks in the area and are believed to be derived from basic lavas. Consisting chiefly of green hornblende, plagioclase and variable amounts of biotite and quartz, the amphibolites frequently carry disseminated sulphides as accessory minerals. These rocks form the end member of a continuous series. Other members of the series are quartz hornblende schist, mica horr blend schist and mica schist.

Chlorite and Talc Schists, considered by geologists of the Geological Survey to represent sheared metamorphosed volcanic rocks, occur chiefly on the margins of the Schist Belt. Mineralogically they consist of chlorite, talc, tremolite, serpentine and magnetite in varying proportions. Carbonate rich varieties are also common. Typically there is a gradational variation in the composition of the rock over short distances and mineralogical banding is often observed.

Quartzites occurring in the Sula Mountains are often sericitised and frequently interband with hornblende rich sediments and banded ironstones. The iron tenor of the latter is sufficiently high to support a mining industry, e.g. at Simbili and Numbara.

The granitic rocks of Sierra Leone have been divided by Marmo on mineralogical and physical features into synkinematic and late-kinematic types. The synkinematic granites are believed to be the result of granitisation of the country rock, while the late-kinematic granites have the characteristic features of an intrusive pluton, Table 2.

Pegmatites are associated with both types of granite. Synkinematic granite pegmatites are of the simple type, being composed of quartz with subordinate amounts of felspar. They occur as small veinlets or augen.

Pegmatites associated with the late-kinematic granite are of two types, simple and complex. The former resemble the synkinematic type in their mineralogy. The complex pegmatites consist of quartz and felspar with numerous accessory minerals including cassiterite, columbite, ilmenorutile and monazite. Base metal mineralisation is often found in the complex pegmatites.

Table 2. Comparison of synkinematic and late-kinematic granites (after Wilson and Marmo 1959)

Item	Synkinematic Granite and Granodiorite	Late-kinematic Granite
Grain size	Usually coarse.	Fine to medium.
Gneissosity	General: mostly marked by parallel oriented biotites.	Uncommon: usually the result of movement.
Porphyroblastic variety	Common.	Scarce.
Basic Intrusions	Intact inclusions are characteristic	Occasional inclusions partly assimilated.
Contacts	Gradational.	Sharp.
Area	Greater than 300 square miles.	About 30 square miles.
Microcline	Usually less than 20%. Is youngest constituent and is interstitial.	Greater than 20%. Crystals of same size and age as other minerals.
Plagioclase	Generally An(20 - 28)	Generally An(less than 12)
Sphene and apatite	Common.	Uncommon.
Fluorite	Exceptional, veinlets and clusters.	Veinlets and clusters with base metals & MoS_2.
Associated base Metals.	None observed.	Occur.

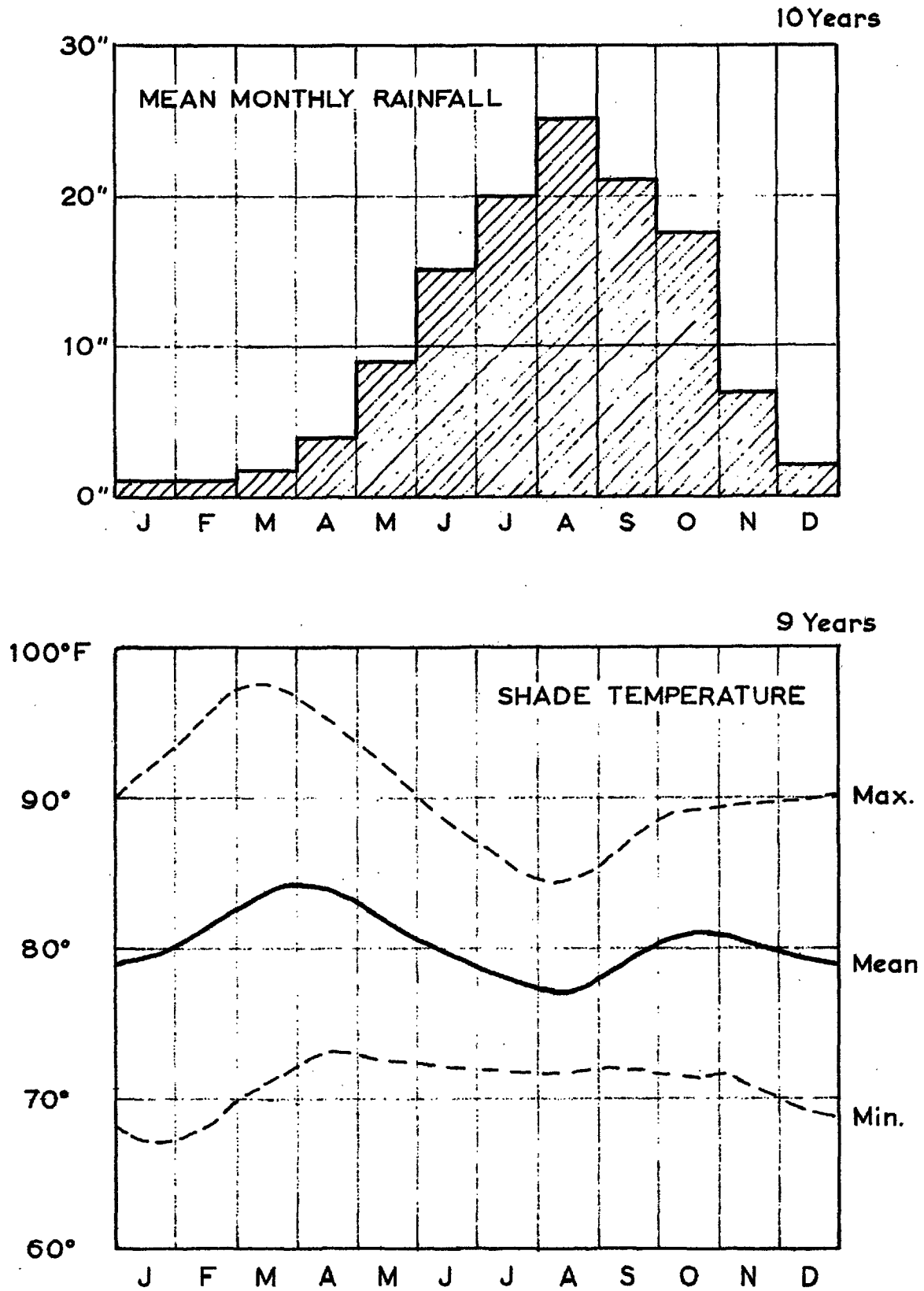


Fig. 3 CLIMATE STATISTICS FOR MAKENI

2. Climate

The nearest meteorological station to the field areas is Makeni, a town on the plain below the western scarp of the Schist Belt plateau. The statistics for Makeni (Figure 3) are therefore only a general indication of the climatic conditions of the field areas, which are situated on the plateau. The climate at Makeni is tropical with an average shade temperature of $80^{\circ} \pm 4^{\circ}F$ and a humidity of from 60 to 90%. The rainfall averages 130 inches annually, most of which falls between July and September. In addition, sporadic heavy thunderstorms occur both before and after this period. Only between December and March is there normally no precipitation.

3. Pedology

Under the conditions of relatively high rainfall and temperature met with in the Sula Mountains, decomposition of both mineral and organic matter is rapid. In the zone of weathering the content of silica and alkalies is low whilst sesquioxides tend to be present in high concentrations. These conditions give rise to soils which can be defined as having

a) low silica/sesquioxide ratio in the clays,

b) low to medium cation exchange capacity of the mineral fraction,

c) low activity of clays,

d) low content of primary minerals except highly resistant ones,

e) low content of soluble minerals,

f) reddish colouration.

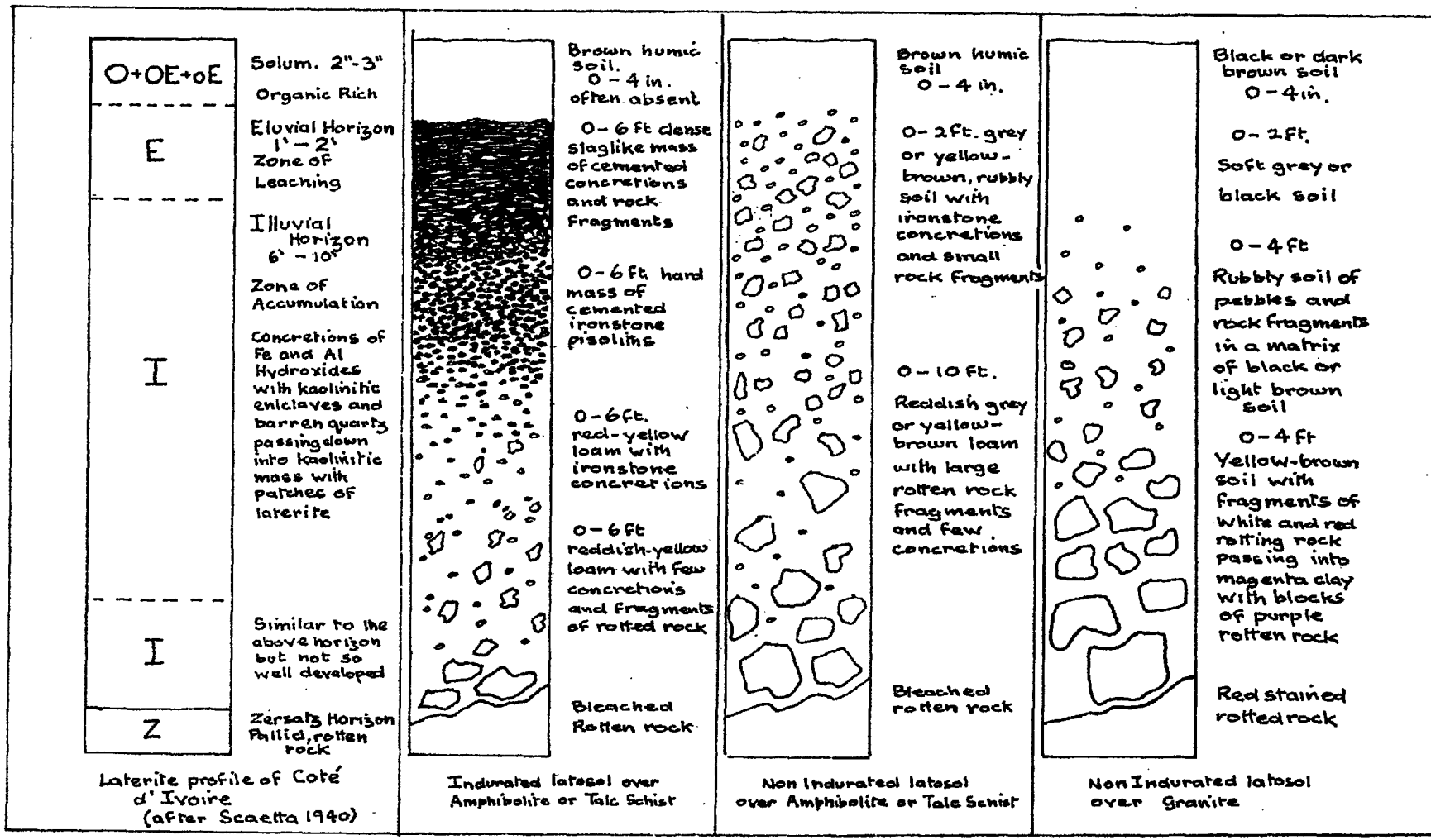


Figure 4 Variation in Soil Profiles developed in the Sula Mountains

These characteristics are typical of latosols as defined by Kellog (1949). Woolnough (1927), suggested the term "duricrust" for an indurated, mature latosol and this graphically describes the slaglike surface latosol, covering much of the 2000 ft. erosion surface in the Sula Mountains. Following the practice of the Sierra Leone Geological Survey and that of Mather (1959), the use of the term "duricrust" will be restricted in this report to indurated surface latosols and "latosol" will include both indurated and non-indurated profiles.

The latosol profile developed in the Sula Mountains resembles that described by Scaetta (1940) from the Ivory Coast. The variations from this type profile which were observed in the field areas are illustrated in Figure 4.

4. Geomorphology

The metamorphic rocks of the Kambui Schist group are more resistant to weathering than the surrounding granites. Furthermore, the nigh iron content of the metamorphic rocks has contributed to the formation of a resistant capping of duricrust. The Sula Mountains - Kangari Hills Schist Belt, therefore, tends to form an elongated plateau with a relief of 1000 - 1500 ft. above the western granite plain. The plateau, 4 - 7 miles wide and about 80 miles long from north to south, is bounded on the east and west by scarp slopes. This area of high ground is cut on the north by the River Seli and is divided by the River Sende (or Pampana) into the Sula Mountains in the north and the Kangari Hills in the south. Both the major rivers in their upper courses flow swiftly in rejuvenated valleys with many rapids and waterfalls.

The almost continuous expense of duricrust which covers the Sula Mountains is increasingly dissected further south in the Kangari Hills until only a few outliers, capping the higher hills, remain. The duricrusted northern part of the Schist Belt and the tops of the hills further south, with an average altitude of 2000 ft. are believed to be the remains of a pre-Tertiary erosion surface.

The presence or absence of indurated latosol influences the form and extent of the drainage developed. Rivers flowing on duricrust have few tributaries and a characteristic drainage pattern. Baker (1955) has compared stream mileages per square mile over various rock types in the Sula Mountains and has demonstrated that the surface drainage density in the duricrusted areas is only about half that in unduricrusted areas, (Table 3).

Table 3. Comparison of Rock Types and Drainage Density (after Wilson and Marmo 1959)

Country Rock	Kind of drainage	Miles of river per square mile	Remarks
Granite	Trellis	4.8	Duricrust poorly developed or absent.
Granite	Rectangular	3.9	
Schist	Dendritic	7.9	Duricrust absent.
Schist	Sub-parallel	3.6	Partially duricrusted.
Schist	Parallel	2.1	Duricrusted.
Alluvium	Parallel and dendritic	3.6	Partially duricrusted. 450 ft. erosion surface.

The meagre surface drainage in duricrusted areas is attributed to widespread subterranean drainage, which is also considered to be responsible for the extensive landslips.

Landslides and slumps are common and important topographic features along the major river valley slopes and the scarps of the plateau. In duricrusted areas slumps are almost essential to the foundation of villages as it is only here that agriculture can be practised. Further south where the duricrust has been removed by erosion, landslides are less common and result only in a wilderness of bedrock boulders.

A notable geomorphological feature of the Sula Mountains is Lake Sonfon, a triangular stretch of reed-choked water, 2 miles long and $1\frac{1}{2}$ miles wide, forming the head of the swampy upper reaches of the River Sende. The formation of the lake is attributed to the back-tilting of the Sende drainage system about a NW-SE axis, traceable at the present day by nick points and windgaps in the catchments affected. These earth movements are directly responsible for the rejuvenation of part of the Sende River and for the misfit streams in the Sula Mountains as well as, in some instances, river capture and reversal of drainage.

5. Biology

Geological and pedological conditions closely control the vegetation of the Sula Mountains. In the northern duricrusted areas sparse "orchard" bush, with scattered stunted trees and tussock grass, covers the exposed hill surfaces. In sheltered depressions elephant grass predominates. By contrast, the deeply incised valleys and slump areas are choked with dense secondary bush.

Farming is very intensive, on a 7 - 10 year fallow cycle, the main crop being hill rice. This results in a further impoverishment in the soluble salt content of the soil. The practice of deforestation and intensive farming may be important factors, according to Aubert (1950), in the formation of indurated latosols in the recent past.

Where the duricrust is less widespread further south and over granitic areas, more extensive cultivation is possible. Swampy alluvial flats are more common, giving a much better farming soil. The fallow areas are covered with thick secondary thorn bush, penetrable only with great difficulty.

The activity of micro-organisms in tropical climates is an important factor in the translocation of elements in soil and drainage systems. Their effects are considerably greater than in temperate climates.

C. Acknowledgments

As already mentioned, this work forms part of the general research programme carried out under the direction of Professor J.S. Webb at the Geochemical Prospecting Research Centre of the Royal School of Mines. The Research Centre is supported by a grant from the Department of Scientific and Industrial Research. The personal financial assistance of a research studentship award to the author by D.S.I.R. is gratefully acknowledged.

The writer is greatly indebted to Professor Webb for suggesting the problem and for his guidance and encouragement during the progress of the work. Dr. A.L. Mather, during the early part of this study, and Dr. J.S. Tooms, gave much constructive advice and criticism to the writer both in the field and during laboratory studies in London. In addition, Dr. Tooms kindly undertook to read the manuscript of the thesis.

The analytical staff of G.P.R.C. are thanked for the analytical assistance, especially Mr. R.E. Stanton and Miss A.J. MacDonald, whose extensive advice on analytical problems made the writer's task much easier.

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Finally the author expresses his gratitude to all those people who have given so freely of their time and specialised knowledge during the course of the work, in particular, Dr. J. Zussman, who undertook the X-ray diffraction analyses referred to in the text, Mr. T. Deans of Overseas Geological Survey for the use of the ultrasonic apparatus and Mr. J.A. Gee who kindly undertook the duplication of the diagrams.

D. Presentation

This thesis is divided into six principal parts. Following the general introduction in Part One, the established sampling and analytical techniques employed in the study are briefly summarised and analytical methods developed during the course of the work are described in more detail, (Part Two).

Parts Three and Four concern the secondary dispersion of molybdenum in the soils, stream sediments and natural waters of the Sula Mountains. Data are presented in Part Three and discussed in Part Four in the light of various factors which appear to control the dispersion behaviour of the element.

The secondary dispersion of arsenic is similarly treated in Parts Five and Six.

A general commentary on the dispersion behaviour of molybdenum and arsenic under the conditions obtaining in the field areas comprises Part Seven. The application of this study to prospecting for molybdenum and arsenic deposits and recommendations for future research are made in Parts Eight and Nine respectively.

The bibliography (Part Ten) and an Appendix, containing detailed procedures for the analytical methods used in the work, complete the thesis.

PART TWO. SAMPLING AND ANALYTICAL TECHNIQUES

A. Sampling Techniques

I. Sample Collection

1. Soils

Two types of routine soil sample were collected:

a) Freely drained soil from valley slopes and the upper part of stream banks, at a depth of 6 - 12 inches below the surface of the organic rich layer and

b) waterlogged soils of stream margins, collected by digging pits adjacent to the channel or, where well defined banks existed, by digging into the bank below the water level to a depth of 6 - 12 inches.

The samples were collected in previously numbered kraft paper envelopes and allowed to dry in the sun in their containers.

2. Stream sediments

Samples of stream sediment were collected from the middle of the watercourse, to avoid contamination by collapsed bank material and like the soils, were dried in their packets.

3. Heavy mineral concentrates

Stream sediments were panned to obtain a heavy mineral concentrate which was then passed through an 82-mesh (B.S.S) sieve and the oversize material discarded. The samples were stored and dried in a manner similar to the soils.

4. Fine grained bottom sediments

This material was obtained by gentle agitation of the water just above the stream bed so as to bring into suspension the very fine grained sediment which was then collected in a beaker and

filtered. Two types of material were sampled;

a) coarse material, obtained by fairly vigorous agitation to dislodge the coarser sediment particles which were filtered onto Whatmann No. 542 cellulose filter papers and subsequently dried on the papers in kraft envelopes. This type of material is referred to in the text as 542 suspension, and

b) fine grained material, obtained by gentle agitation which dislodged only the very fine flocculant material found "suspended" just above the surface of the stream as sediment proper. This floc appeared to be rich in organic matter, a supposition which was borne out by subsequent analysis. Glass fibre filters were used to collect this material so that the carbon content determinations would be referable to the sediment material only.

5. Water

Water samples were filtered at the site through Whatman No. 542 papers having a pore size of 1.4 - 2.9 microns by which means it was hoped to exclude clay particles from the sample. Hand pumps were used to apply suction through the Buchner apparatus and in this way, water could be collected at the rate of approximately 60 litres per hour using 6 pumps manned by 12 Africans.

Whilst some of this water was treated immediately by the solvent extraction or coprecipitation procedures, for molybdenum and arsenic respectively, samples of ten litres volume were passed through ion exchange columns at the base camp the same day. In addition, samples of 20 litres volume from selected sites, required for experimental studies in London, were stored in screw-topped polythene bottles, with a capacity of one litre, or in five litre capacity

plastic cubitainers. The cubitainers possess certain advantages over bottles in that, a) practically all the air can be expelled from the cubitainer before it is heat sealed, thus minimising oxidation during storage, b) four cubitainers occupy a smaller volume than twenty bottles and c) they make a lighter and more convenient headload, as they can be folded flat when empty.

Before sealing the cubitainers, the water was treated with 10 ml concentrated hydrochloric acid per litre to bring the pH to approximately 1.0. The object of this procedure was to inhibit coprecipitation of the trace elements by hydrated iron oxides during transit. Previous experience had shown that, in the absence of such preventive methods, a considerable amount of hydrated iron oxides came out of solution and coprecipitated molybdenum in the process. The acid treatment greatly diminished iron oxide precipitation but was not completely effective. Iron material which was precipitated from the acidified samples was found to be associated with a fungus which had grown in the water. The growth of practically all other forms of micro-organism is inhibited by the acid treatment (Small 1954) and the writer has been advised (Commonwealth Mycological Institute) that the addition of a small concentration of thymol might prove an effective and geochemically innocuous fungicide.

II. Sample Preparation

1. Dry sieving.

The sun-dried soils and sediments were dry sieved into fractions approximating to B.S. sand sizes (Table 4) through nylon or silk bolting cloth. Soil crumbs were destroyed by lightly pounding the

sample in its packet before sieving. Material larger than $\frac{1}{4}$ inch diameter was discarded.

Table 4. Relationship of mesh size of sieves to aperture size.

Sieve Material	Brass	Nylon			Silk		Obtained by sedimentation	
Mesh size	$\frac{1}{4}$"	20	38	82	125	197	silt	clay
Aperture mm	6.5	1.0	0.5	0.2	0.1	0.05	0.02	<0.002
B.S. Sand Size	Coarse Sand			Fine Sand			Silt	Clay

All size fractions greater than 82-mesh were ground to pass through an 82 mesh sieve and well mixed before taking a sample for analysis. For many routine purposes it was found adequate to divide the sample into plus and minus 82-mesh fractions by agitation of the dry material for 20 minutes in a sieve mounted on a test sieve vibrator.

2. Wet Dispersion

For the more detailed analyses in which quantities of clay and silt fractions were extracted and separated, the method followed was similar to that of Piper (1944). However, sodium hexametaphosphate was used as the dispersant (Tooms 1955).

Method

1. Weigh 100 g of minus $\frac{1}{4}$ in. sample into a tall 600ml beaker.
2. Add 150 ml of 1 percent sodium hexametaphosphate solution and stir with a mechanical stirrer for 15 minutes.
3. Transfer the mixture to a 1 litre stoppered cylinder and dilute until there is at least 30 cm depth of water above the sediment at the bottom of the cylinder.

4. Turn the cylinder end over end several times to obtain a uniform suspension.

5. Stand the cylinder upright and note the time.

6. A Bouyoucos hydrometer is placed in the suspension and read 5 minutes after the cylinder was set down. This reading gives the number of grammes of silt plus clay in the sample. After 5 hours standing the hydrometer is read again to obtain the number of grammes of clay in the sample. The silt content is obtained by difference.

7. If the temperature of the suspension differs markedly from 19° - 20°C a correction must be made to the reading, 0.3 units being added to the reading for every degree above 19.4°C and the same amount subtracted for every degree below this temperature.

8. To separate the silt plus clay material, i.e. less than 20 microns diameter, from the coarser material, the sample is resuspended and allowed to stand for a specific time depending upon the height of the suspension to be decanted from the cylinder and on the temperature of the suspension, (Table 5).

Table 5. Settling Time for 10 cm of (Silt + clay) and clay only (after Piper 1944)

Temperature °C	Silt + Clay		Clay only	
	Minutes	Seconds	Hours	Minutes
18	5	0	8	25
19	5	0	8	10
20	4	48	8	0
21	4	40	7	50
22	4	30	7	40
23	4	30	7	25
24	4	20	7	15
25	4	15	7	5

9. The silt and clay are removed by taking off the calculated depth of suspension by means of a pipette into a 2 litre Buchner flask. The suspension is then transferred to a 1 litre beaker and the procedure repeated until no solid matter is present in the calculated depth of water.

10. The coarse fractions are removed from the cylinder, dried, and passed through a nest of sieves of selected mesh size.

11. The clay is separated from the silt by repeated decantation in accordance with the data of Table (5).

12. The two fractions are then dried. These materials generally need crushing in a pestle and mortar to minus 82-mesh size before analysis as some aggregation takes place on drying.

13. Where the weight of the clay sample is low an allowance must be made for the weight of hexametaphosphate used in the dispersion.

All the samples used in the molybdenum work were dispersed using a mechanical stirrer. The possibility that abrasion of the sample particles takes place to a serious degree during dispersion in the confined space of a 600 ml beaker was tested by using ultrasonic apparatus for the sample dispersion. As when using a mechanical stirrer it was necessary with the ultrasonic apparatus to use a dispersing agent; hexametaphosphate was therefore added to the solution prior to dispersion. Without a chemical dispersant a similar degree of dispersion could be obtained but the suspension was not stable for longer than about one hour. Thus, despite the possible disadvantages of chemical interference, a dispersion agent is necessary if the sedimentation method of separating clay and silt

is used. Such a separation could possibly be made on a solution dispersed without the addition of a dispersant by passing the suspension through a suitably sized cyclone apparatus immediately after dispersion.

Ultrasonic dispersion procedure

1. 1. Weight 200 g of the sieved sample (minus $\frac{1}{2}$ inch) into a 1 litre beaker.

2. Add 300 ml of 1 percent sodium hexametaphosphate solution and stir to mix.

3. Place the beaker in the tank of the ultrasonic apparatus, which contains warm water. This water is the medium through which the ultrasonic waves are transmitted to the sample.

4. Switch on the machine and allow to run for 15 minutes. It is necessary to stir the sample with a glass rod to prevent the material from packing down.

5. Decant the liquor into another beaker and add 300 ml water to the sample.

6. Allow the sample to disperse for a further 15 minutes.

7. Pour the decanted liquor back into the sample beaker and continue the dispersion for 10 more minutes.

8. Remove the sample and liquor into a 1 litre stoppered cylinder and add sufficient water to give at least 30 cm height of liquor above the sediment surface.

9. Proceed as in the previous instructions for stirred dispersion from stage 4.

Comparison of stirred and ultrasonic dispersions of 100 g samples reveals certain differences (Table 6). The stirred dispersion produces a lower percentage of the very coarse fraction, whilst the intermediate and very fine fractions are notably increased. These effects could be due to a) abrasion of the coarse particles during stirring, or b) less efficient dispersion by the ultrasonic apparatus. Further trials are required to assess the relative importance of these factors. However, when a larger sample weight is dispersed by mechanical stirrer the weight of the coarse fraction is, in general, still further reduced and that of the fines increased whilst the intermediate fractions show relatively little change. Thus, there is a strong suggestion that stirred dispersion modifies, to a greater or lesser degree, the natural mechanical composition of the sample by abrasion of the coarser particles.

Table 6. Comparison of Mechanical Analyses obtained by stirred and ultrasonic dispersions

Sample	BEI Granitic Sediment			DAL Duricrust Sediment			29 Duricrust Sediment		
Apparatus	Stirrer		Ultra-sonic	Stirrer		Ultra-sonic	Stirrer		Ultra-sonic
Sample wt g	100	200	100	100	200	100	100	200	100
Fraction	Weight percent			Weight percent			Weight percent		
-¼ in.+20	31.1	26.3	50.7	74.9	60.0	79.5	75.3	75.0	96.7
+ 20 - 38	50.0	55.5	42.5	8.4	10.5	12.2	4.6	7.4	1.4
- 38 + 82	9.4	10.2	4.4	2.1	5.6	3.5	1.7	1.9	0.07
- 82 + 125	2.1	1.8	0.4	0.8	1.5	0.5	0.9	0.6	0.02
- 125+197	1.4	1.1	0.25	0.6	1.1	0.2	0.9	0.6	0.15
- 197 + silt	2.0	1.5	0.25	2.5	1.9	0.5	3.6	2.5	0.10
silt	1.3	(	0.27	5.5	(	0.9	5.9	(	0.20
clay	2.7	(18	1.5	5.3	(20	2.2	6.7	(12	1.5

B. Analytical Techniques

I. Physical Analysis

At each of the sample sites measurements of redox potential and hydrogen ion concentration were made using a portable meter supplied by Analytical Measurements Ltd. The meter was calibrated before use with standard Eh and pH solutions. Eh readings were made by reference to a calomel electrode and these data converted to the equivalent hydrogen electrode values by the use of the equation

$$Eh_{(H)} = (0.43 - Eh_{(Cal)}\text{standard sol.}) + Eh_{(Cal)}\text{sample.}$$

Where $Eh_{(H)}$ is the redox potential with reference to the hydrogen electrode $Eh_{(Cal)}$ is the redox potential with reference to the calomel electrode, i.e. observed potential.

The temperature of the stream waters was measured at the same time as the above data were recorded.

II. Chemical Analyses

1. General summary of the performance of the analytical methods

It is intended here to give only a brief summary of the published analytical methods used in this work and their precision at the 95 percent confidence level, (Table 7), calculated by the method of Craven (1954). Many of the procedures have minor operating modifications which are referred to in the full description of the methods given in the Appendix to this report. New analytical developments are described more fully in the following pages.

Table 7. Source and Precision (95 percent confidence level) of Standard Analytical Methods

Element or Ion	Material	Reagent	Precision percent	Source
Molybdenum	Soil, sediment	Zinc dithiol	± 40	North (1955)
Arsenic	Soil, sediment	Mercuric chloride	± 25	Almond (1953)
Manganese	Soil, sediment	Potassium periodate	± 25	Almond (1953)
Iron	Soil, sediment	Thioglycollic acid	± 25	Sandell (1950)
Organic carbon	Soil, sediment	Potassium dichromate	± 15	Schollenburger (1927)
Sulphate	Water	Barium chloride	± 15	Boltz (1958)
Bicarbonate	Water	Hydrochloric acid	± 10	Scott (1950)

III. Analytical Development Work

1. Methods for the determination of molybdenum and arsenic in natural waters.

The work of Mather (1959) in Sierra Leone indicated that the metal concentrations in the Sula Mountains stream waters were very low. However, using ion exchange resins he achieved some success in detecting arsenic in waters draining mine workings. On the basis of these results Mather suggested that further work should be undertaken on the application of ion exchange and coprecipitation techniques to geochemical prospecting in the Sula Mountains.

The writer's experience in 1960, confirmed the inadequacy of the ion exchange and evaporation methods, in use at that time, for the detection of quantities of molybdenum and arsenic less than 1 ppb (1 part per billion, i.e. 1 part in 1,000,000,000). As a result of this work, a search was made for alternative methods of concentration amenable to use under field conditions. Several techniques were available, of which coprecipitation and solvent

extraction seemed to be most promising. Further work was also carried out on ion exchange and evaporation procedures in the hope of improving their efficiency.

(i) Evaporation Techniques

The chief difficulties arising out of the use of this procedure in the present work were low productivity, lack of sensitivity and the hazards of contamination.

The natural waters of the Sula Mountains, in common with those of other tropical regions of high rainfall, often contain less than 50 ppm (parts per million) dissolved solids. This necessitates the evaporation of between five and ten litres of water to obtain sufficient residue for analysis and the evaporation of this volume of water takes a considerable time.

When evaporations are carried out in glass vessels the weight of the residue from even ten litres of water is extremely small compared with that of the vessel and this raises difficulties in accurately weighing the residue. In addition, complete removal of the residue from the vessel for analysis presents further difficulties. Furthermore, the amount of residue is sufficient for only one spectrographic analysis.

The use of glass or porcelain vessels also raises the problem of adsorption of trace constituents by the walls of the vessel; an effect noted by Gorsuch (1959).

The evaporation of water samples in open containers, in order to speed up the procedure, exposes the sample to possible contamination by airborne dust, especially in the field. This risk can be minimised in a permanent laboratory by working in a room or enclosure used only for this purpose.

(a) Experiments

Initial evaporation experiments were carried out in long-necked, round-bottomed, one litre pyrex flasks. The flask was clamped with its neck inclined and a small beaker placed over the end of the neck to minimise contamination from dust. The water was kept boiling vigorously to flush the walls of the flask free of precipitated salts. As the first precipitation of solids took place, the liquor, with a volume of about 100 ml, was transferred to an evaporating dish and reduced to dryness on a hotplate surrounded by a shield. The residue was taken up in a small volume of hydrochloric acid and analysed for molybdenum.

Using this procedure molybdenum concentrations of about 0.3ppb were detected in water samples from the Sula Mountains, (Table 8). The low recovery of the control is probably due to adsorption on the flask walls and the lack of precision of the analytical method.

Table 8. Molybdenum and Arsenic content of evaporated water residues.

Sample Site	Sample volume, litres	Dissolved solids, ppm	Molybdenum ppb	Arsenic ppb
Sende 29	1.0	20	0.3	
Sende 29	1.0	22	0.3	
Sende 29	1.0	Not determined	0.3	
Sende 32	3.0	"	0.2	
Fundiburu F2	3.0	"	0.3	
Fundiburu F2	2.8	"	0.3	
Control (100 µg/l Mo)	1.0	"	60.0	
Yirisen G26	5.1	"		0.2
Yirisen N23	5.0	"		0.1
Yirisen K37	5.0	"		0.4

Water samples containing arsenic similarly treated gave arsenic values of 0.1 - 0.4 ppb (Table 8). These figures are also possibly low, perhaps due to loss of arsenic in the last stages of the evaporation, in addition to the other losses referred to above. This problem will be further considered at a later stage.

Marranzino has used a most effective method, to which the writer's attention was drawn by Professor Hawkes, in which the difficulties of weighing and recovering the residue are minimised. The evaporation vessel, a beaker or dish, is lined with Saranwrap, a thin plastic foil. The foil is light in weight so that the residue forms an appreciable proportion of the final weight, and on completion of the evaporation the residue flakes off easily from the ultrasmooth surface.

Experiments, made by the writer, revealed certain disadvantages in the use of this technique in the present work. In particular, Saranwrap has a low melting point which prevents the use of an oven to dry the residue and if kept at 100°C, e.g. on a water bath, for the prolonged period required to evaporate ten litres of water, it becomes brittle. A further difficulty arises with waters acidified with hydrochloric acid due to the formation of an azeotropic mixture having a boiling point (110°C) above that of the waterbath and near that of the melting point of the Saranwrap, which softens between 100-120°C.

Residues obtained by this method were analysed spectrographically for molybdenum. Iron was determined colorimetrically, (Table 9). The poor reproducibility of the method is obvious from the iron data but the cause of these disappointing results is not known and further emphasises the difficulties of determining such small amounts of material.

Table 9. Iron and Molybdenum content of waters evaporated in Saranwrap.

Sample	Volume litres			Dissolved solids ppm			Iron ppb			Molybdenum ppb		
Dalakaru	4.0	3.9	9.2	n.d.	n.d.	30	90	224	50	n.d.	n.d.	n.d.
Wusungba	4.1	5.0	9.9	n.d.	n.d.	10	180	160	n.d.	n.d.	n.d.	n.d.
Sende 29	4.3	5.0	7.1	n.d.	n.d.	21	600	275	800	n.d.	n.d.	0.1
Fundiburu	4.2	4.6	9.5	n.d.	n.d.	n.d.	326	315	n.d.	n.d.	n.d.	n.d.

n.d. - signifies not determined

The evaporation of samples containing arsenic posed additional problems. Owing to the addition of hydrochloric acid to the water to prevent iron precipitation during transportation, there was a danger that, during evaporation, the relatively high temperature required to evaporate the azeotropic mixture would result in the loss of arsenic as a volatile chloride. Accordingly, water samples of five litres volume were only evaporated to about a fifth of their volume, i.e above the azeotropic concentration, and the arsenic removed by the coprecipitation technique developed for waters. Poor agreement was found between the laboratory results and those obtained using the coprecipitation method by the writer in the field, the reasons for which are not known.

(b) Conclusions

As a result of the experiments described above it was considered that the evaporation technique is unsuitable for the determination of molybdenum and arsenic in the waters of the field areas because of the lack of precision of the method and the long operational time involved.

(ii) Ion Exchange Techniques

The process of ion exchange has been defined as a "reversible interchange of ions furnished from the solution phase with ions present in a solid matrix of an ion exchange material without any significant concommitant changes" (Clarke 1957).

Synthetic resin materials have been developed for both cation and anion exchange which have no direct effect on non-ionised substances. Since most of the economic metals occur in nature as cations, the cation type of exchanger has been widely used in geochemical prospecting. Both molybdenum and arsenic occur naturally as anions hence the anion type of exchanger was of most interest in the present work.

(a) Experiments

The anion exchangers used in this study were of the resin bead form. Two varieties were investigated, Deacidite FF, a strongly basic resin used by Mather, and Dowex 21K, a more recently developed strongly basic resin of the chelate type.

Deacidite FF

To investigate the efficiency of this material in concentrating arsenic and molybdenum, water samples containing known amounts of the elements were treated with 10 ml of resin. Two techniques were used:

Column operation

The water sample was passed slowly through the resin contained in an 8 cm x 2 cm plastic column at a rate of 1 litre per hour. As metal concentrations in the Sula Mountains waters were expected to be in the region of 1 ppb, this was chosen as a reference concentration.

It will be seen from Table (10) that neither molybdenum nor arsenic is extracted to any great extent at the 1 ppb level, whilst at higher concentrations greater proportions of the elements are extracted, arsenic giving better results than molybdenum. However, even with these higher concentrations, the effluent of a 100 ppb molybdenum sample, passed through the resin, contained 30 micrograms of molybdenum. Molybdenum was recovered by ashing the resin and analysing the residue whilst arsenic was determined by treating the resin directly with the analytical reagents.

Table 10. Performance of Deacidite FF in Column Operation

10ml Deacidite FF, OH^- Form, 14 - 52 mesh (BSS) beads in 8 x 2 cm column. Flow rate 1 litre per hour.			
Element conc. ppb	Sample volume litres	Element recovered from resin micrograms	Recovery percent
Molybdenum			
1.0	1.0	less than 0.2	less than 20
1.0	1.0	less than 0.2	less than 20
1.0	2.0	0.5	25
100.0	1.5	60.0	40
Arsenic			
1.0	2.0	1.0	50
1.0	1.2	0.4	30
5.0	2.0	2.0	20
10.0	2.0	17.0	85

Shaking method

Mather treated water samples from the Sula Mountains by shaking a small volume of the resin with several litres of water contained in a Winchester quart bottle. A similar technique has also been described by Aleskovskii et al (1957). In the present experiments 10ml of the resin were shaken for five minutes with the water sample.

In order to increase the efficiency of the technique, beads of a small diameter were used (100 - 200-mesh B.S.S), thus giving a greatly increased active surface. This grade of resin was available only in the Cl^- form. In general, the salt, (e.g. Cl^-) form of an anion resin is more stable and has a higher reaction rate than the free base (i.e. OH^-) form, (Samuelson 1953). Hence this factor was expected to enhance the performance of the small diameter beads.

However, in spite of increasing the active surface and using a more active resin the experiments indicated a poorer performance by the shaking technique than by column operation (cf Tables 10 and 11). Again arsenic gave better results than molybdenum.

Table 11. Performance of Deacidite FF in Shaking Technique

10 ml Deacidite FF, Cl^- form, 100 - 200 mesh (BSS) beads. 5 minutes shake.			
Element conc. ppb	Sample volume litres	Metal content of resin micrograms	Recovery percent
Molybdenum			
1.0	2.0	less than 0.2	less than 10
0.1	5.0	less than 0.2	less than 40
Arsenic			
1.0	1.5	less than 0.2	less than 15
1.0	1.5	0.3	20
5.0	1.5	0.17	10

From the above experiments it was considered that Deacidite FF would not be satisfactory for extraction molybdenum and arsenic from the waters of the field area.

In view of the disappointing results obtained with Deacidite FF, attention was turned to resins which had been used successfully in America. The two resins used were Dowex A1, a cation resin, and Dowex 21K, an anion type. Both are so-called chelating resins and are produced in the form of porous beads having a very large active surface.

Dowex A1/21K

For the present experiments a mixed bed system was used with a 1:3 volume ratio of cation to anion form. In American usage a very high flow rate of 1 litre in four minutes (15 litres per hour) was employed. However, because of the low metal content expected in the field area waters the flow rate was reduced to 1 litre per hour. Samuelson (1953) comments that, in general, a low flow rate gives a higher operating exchange capacity and Arden (1961) has further mentioned that chelating resins suffer from the disadvantage of a low reaction rate, necessitating very low flow rates in operation.

Table 12. Performance of Dowex A1/21K in extracting Molybdenum

10 ml Dowex A1 H^+ form/Dowex 21K Cl^- form. Ratio 1 : 3. 20 - 50 mesh beads. 16 x 1.5 cm column. Flow rate 1 litre per hour. 1 litre sample volume.

Molybdenum concentration ppb	Molybdenum in effluent micrograms	Molybdenum in eluate micrograms	Resin blank micrograms	Recovery percent
		1st 2nd		
1.0	0.05	1.5 0.25	0.6	115
1.0	0.25	1.0 0.25	0.6	65

Dowex resins are superior in performance to Deacidite resins at the 1 ppb level (cf Tables 10 and 12). Although a large proportion of the extracted molybdenum is removed by a single elutriation, a more complete recovery is obtained by making two elutriations.

An attempt was made, in subsequent trials with arsenic, to achieve the flow rate of 15 litres per hour used in American operation, but this was not successful, even with a 10 ft. hydrostatic head. With flow rates of 3 - 6 litres per hour better

results were obtained than with Deacidite resins (cf Tables 10 and 13).

Table 13. Performance of Dowex A1/21K in extracting Arsenic

Dowex A1 H^+ form/Dowex 21K Cl^- form. Ratio 1 : 3. 20 - 50-mesh beads. 16 x 1.5 cm column. 1 litre sample volume.

Arsenic concentration ppb	Resin volume ml	Rate of flow litres per hour	Arsenic in eluate micrograms	Recovery percent
10.0	10	3	4.4	44
10.0	8	4	5.0	50
10.0	8	4	5.2	52
10.0	10	5	4.0	40
10.0	10	5	4.0	40
10.0	12	6	3.6	36
10.0	12	6	5.0	50
1.0	10	6	1.0	100

On the basis of these experiments it was decided to use Dowex resins in the fieldwork in 1961.

(b) Field Performance

Water samples of 10 litres volume were used in the field trial. The water was passed through 10 ml resin contained in a 16 x 1.5 cm column at the rate of 1 litre per hour. Analysis of the resin eluate revealed no detectable molybdenum. Hence it was concluded that the molybdenum content of these waters was less than 0.02 ppb.

The resins analysed for arsenic gave values of 0.02 to 0.35 ppb but these results are unreliable owing to suspected contamination in the analytical procedure.

The cation resin was elutriated and the eluate analysed for iron. This revealed a notable feature of this resin; its low affinity for iron under the operating conditions used. This

character may be of some practical advantage in analytical operations where iron needs to be excluded. Laboratory trials (Table 14) substantiated these observations.

Table 14. Performance of Dowex A1/21K in extracting Iron

10 ml Dowex A1 H^+ form/Dowex 21K Cl^- form. Ratio 1 : 3. 20 - 50 mesh beads. 16 x 1.5 cm column. Flow rate 1 litre per hour. 1 litre sample volume.

Iron concentration ppb	Iron in effluent micrograms	Iron in eluate micrograms		Iron recovered by resin percent
		1st	2nd	
360	260	125	5	37
440	400	50	5	11

It is of some interest that copper was successfully detected in the cation eluates of the field resins at a level of 1 ppb.

Thus, although the Dowex resins functioned satisfactorily in the laboratory their field performance was disappointing, lower results being obtained than by other methods. This may be due to the fact that the synthetic solutions used for the laboratory trials did not contain the same complement of active ions as the natural waters.

(iii) Coprecipitation Technique

Coprecipitation is a well-established laboratory technique for scavenging solutions of impurities or valuable constituents. The mechanism of the reaction is attributed to two main effects; adsorption of trace material by the highly active surface of the precipitate and the isomorphous crystallisation of the trace constituent and the precipitate. The first effect is considered

to be of most importance and, therefore, the quality of the precipitate, which depends on a number of uncontrollable, often unknown factors, is of prime importance.

(a) Experiments

The hydrated oxides of iron and manganese are well known for their sorption activity.

Molybdenum

Tanaka (1950) has shown that the manganese compound is more efficient in scavenging molybdenum from solutions than hydrated iron oxides. However, manganese oxide requires heat for its formation and this was considered to be a disadvantage for field operation. The use of ferric hydroxide as a coprecipitant for molybdenum was investigated but was abandoned due to the gross interference by iron in the colorimetric stage of the molybdenum determination.

Further work on a coprecipitation method for molybdenum was suspended as better results were obtained from a solvent extraction procedure.

Arsenic

Kolthoff and Carr (1943) have achieved quantitative precipitation of arsenic from solutions using magnesium ammonium phosphate, $MgNH_4PO_4$, which forms crystals isomorphous with $MgNH_4ASO_4$. A sensitivity of 0.15 ppm, with an accuracy of $\pm$ 2 percent was claimed.

This method is specific for arsenates (As^{V}) and will not coprecipitate arsenite (As^{III}). It was assumed that the arsenic in the surface waters of the field areas would be in the higher valency state and this was confirmed by Eh and pH measurements in the field.

The application of a coprecipitation technique for arsenates, using magnesium ammonium phosphate, devised by the analytical staff of G.P.R.C., was examined by the writer. Experiments using water samples containing arsenic in each of the oxidation states confirmed the low reactivity of As^{III} (Table 15).

Table 15. Influence of Valency on the Coprecipitation of Arsenic by Magnesium Ammonium Phosphate

Sample volume 2 litres					
As added ppb	1.0	2.0	5.0	1.0	2.0
As valency	III	III	III	V	V
Percentage recovery	20	12	5	95	100

Full details of the procedure are given in the Appendix, but briefly, the sample is made strongly alkaline with ammonia solution, (addition of ammonium chloride promotes the conditions for the minimum solubility of the magnesium ammonium arsenate salt), trisodium phosphate and magnesium sulphate then being added to produce the precipitate. The concentrations of the last two reagents were altered to see if an increase in the weight of the precipitate increased recoveries, but no appreciable improvement was achieved, (Table 16).

Table 16. Effect of increase in precipitate weight on Arsenic recovery by $MgNH_4PO_4$

Sample volume ml	100	100	100	100	100	100
As^V added µg	1.5	2.0	1.5	2.0	0.5	2.0
Vol. of Na_3PO_4 ml	0.5	0.5	5.0	5.0	10.0	10.0
Vol. of $MgSO_4$ ml	0.5	0.5	5.0	5.0	10.0	10.0
Recovery percent	50	85	80	65	60	80

Prior to analysis it is necessary to dissolve the precipitate in concentrated hydrochloric acid and, in order to minimise the volume of acid used, the smallest effective weight (that produced by 5 ml of the two precipitating reactants) was used in the subsequent trials.

Recoveries achieved were erratic and therefore the effect of a repeat precipitation was examined. This was found to improve the recovery in some cases, especially at concentrations above 1ppb, but the efficacy of the second precipitation was unpredicable, (Table 17).

Table 17. Effect of repeated precipitation on Arsenic recovery by Magnesium Ammonium Phosphate

Arsenic added ppb	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	2.0	2.0	2.0
Recovery % 1st ppt.	60	60	60	100	35	20	80	60	45	65	80
Recovery % 2nd ppt.	20	0	0	0	0	0	10	10	20	20	10
Total recovery %	80	60	60	100	35	20	90	70	75	85	90

A series of trials was made, under the conditions to be used in the field, at various levels of arsenic concentration (Table 18) and on the basis of these experiments the method was considered to warrant field trial. The variable recovery is ascribed to the variation in the nature of the precipitates.

Table 18. Summary of Arsenic recoveries by Coprecipitation with Magnesium Ammonium Phosphate

Arsenic concentration ppb	0.0	0.15	0.5	1.0	2.0
Recovery percent	0.0 0.0 0.0 0.0	100 80 80 60 33	64 44 50 50 50 60 80 80 100 100	80 75 70 80 80 50 70 60 70 60 60 70 60 75 70	70 65 70 75
Av. recovery percent	0.0	72	68	70	69

(b) Field Performance

The coprecipitation method for arsenic was used in the field and found to be easy to operate under field conditions. Precipitations were made in triplicate at each site. Very low concentrations of soluble arsenic were detected in the stream waters examined but it was not possible, with certainty, to distinguish waters draining mineralised areas from those draining barren ground.

Whilst the recoveries achieved in the laboratory were satisfactory, under field conditions the reproducibility of the technique was disappointing ($\pm$ 200 percent at the 95 percent level).

As an illustration of the empirical nature of the coprecipitation mechanism it is interesting to note that when the trials were carried out in the field the formation of the precipitate was always immediate and spontaneous whilst in laboratory trials, where particular care could be taken over the cleanliness of the apparatus, it was sometimes necessary to initiate precipitation by scratching the outside of the vessel with a file.

(iv) Solvent Extraction Techniques

Many metals combine readily with organic or organic-inorganic radicals to form relatively stable complexes which are often characteristically coloured and soluble in organic solvents. When the metal concentration is sufficiently high the coloured complex may be visible in aqueous solution, e.g. the red complex formed between iron and thiocyanate ions. If, however, very low metal concentrations are involved the complex can be extracted into a small volume of a suitable solvent, the coloured compound is thus concentrated and can be colorimetrically assessed. The technique is very versatile since by careful choice of operating conditions, complexing agent and solvent, great selectivity for a particular element or group of elements can be achieved. The present approach was to apply this concentration procedure to a water sample of several litres volume.

Molybdenum

The thiocyanate complex of molybdenum is well known as the basis of an analytical method for this element (Sandell 1950). Popova (1957) also notes the use of KCNS with butyl alcohol in a solvent extraction method for determining molybdenum in natural waters.

The application of the complex formed by molybdenum with diethyldithiocarbamate (DDC) in hydrogeochemical prospecting in the U.S.S.R. has been described by Aleskovskii et al (1957).

Oxine, (8-hydroxyquinoline), is another well known complexing reagent, reacting with many metals over a wide pH range (Morrison and Freiser 1959). By selection of an optimum operational pH of 4.6 - 4.8 and chloroform as a solvent, a scheme of extraction was evolved, with the assistance of the analytical staff of the department, which is suitable for molybdenum.

Arsenic

A number of solvent extraction techniques for arsenic were examined by the analytical staff of the department on the writer's behalf (Wadelin and Mellor 1952, Morrison and Freiser 1959 and Sandell 1959), but they were found to be unsuitable for the present study and the use of a solvent extraction procedure for arsenic was not further pursued.

(a) Experiments

In the initial work with molybdenum, the water sample was adjusted to a particular pH within the range of reaction given by Sandell (1950), i.e. pH 3.6 - 7.3, and the oxine added as a solution in acetic acid. However, oxine is amphoteric in aqueous solution and its addition to the sample caused a change in the hydrogen ion concentration to pH 3.8, (Table 19), which is outside the optimum extraction range.

To keep the pH within the optimum range of 4.6 - 4.8 (Morrison and Freiser 1959) a sodium acetate - acetic acid buffer was added to the sample prior to treatment with an alcoholic solution of oxine. The improvement in results can be seen by comparison of Tables 19 and 20.

Table 19. Extraction of Molybdenum by Oxine in Acetic Acid from unbuffered solution

Molybdenum concentration ppb	Sample volume litres	Initial pH	Final pH	2.5% Oxine in Acetic Acid ml/1 sample	Chloroform ml/1 sample	Molybdenum detected micrograms	Recovery percent
1.0	1.0	3.4	3.6	10	10	0.7	70
1.0	1.0	4.0	3.8	10	10	0.2	20
1.0	1.0	4.8	3.8	10	10	0.2	20
1.0	1.0	6.1	3.8	10	10	0.5	50
0.1	5.0	-	3.8	4	20	$\leq$0.2	$\leq$20
				4	20	<0.2	<20
0.0	1.0	3.5	-	10	10	<0.2	-

Table 20. Extraction of Molybdenum by Oxine in Ethanol from buffered solution

Molybdenum concentration ppb	Sample volume litres	Buffer pH 4.6 ml	5% Oxine in Ethanol ml	Chloroform ml		Molybdenum detected micrograms	Recovery percent
				1st	2nd		
0.5	1.5	50	10	20	10	0.7	120
0.5	1.5	50	10	20	10	0.6	120
1.0	1.5	50	10	20	10	1.3	130
1.0	1.0	50	10	20	10	0.9	90
2.0	1.5	50	10	20	10	1.1	65
2.0	1.5	50	10	20	10	1.9	95
0.0	1.0	50	10	20	10	<0.2	-

After formation of the metal-oxine complex the water sample was shaken with chloroform to extract this compound, the extraction being repeated until the chloroform remained colourless after shaking. Two extractions were found to be sufficient in the majority of cases.

The chloroform extracts were evaporated to dryness and the black organic residue destroyed by fuming with nitric and perchloric acids. The yellow-white residue obtained after the fuming treatment was dissolved in hydrochloric acid and the solution analysed for molybdenum.

Since it was anticipated that large volumes of water would constitute a single sample in the field, the effect of combining the extracts from several smaller samples was examined. A number of 1.5 litre water samples, each containing an amount of molybdenum below the limit of detection, were extracted according to the procedure proposed for field application, and the chloroform extracts combined for the rest of the analytical steps, (Table 21).

Table 21. Extraction of Molybdenum by Oxine from several combined samples

Molybdenum concentration ppb	No. of sub-samples	Sub-sample volume litres	Total sample volume	Buffer volume ml/sub-sample	Chloroform ml/sub-sample		Molyb-denum detected micro-grams	Recovery percent
					1st Extr.	2nd Extr.		
0.1	5	1.5	7.5	50	20	10	0.5	60
0.1	5	1.5	7.5	50	20	10	1.2	120
0.016	8	1.5	12.0	50	20	10	0.3	150

The results obtained were considered to warrant the use of this multiple sample technique in the field trials.

In addition to reacting with molybdenum under the conditions used, oxine also extracts iron. The green colouration imparted to the sample by the iron-oxine complex is a useful indication both to the concentration of iron present and to the amount of interference to be expected.

Iron was found to cause a yellow discolouration in the amyl acetate solvent phase of the final colorimetric stage of the molybdenum determination. This difficulty was overcome by dissolving the fumed residue in sodium carbonate solution instead of hydrochloric acid, resulting in the formation of an insoluble iron compound whilst the molybdenum passes into solution and can be determined free of interference. That this procedure does not critically affect the recovery is shown in Table (22).

Table 22. Effect of Sodium Carbonate leach on the recovery of Molybdenum by Oxine

Molybdenum concentration ppb	Iron concentration ppm	Sample volume litres	Leach	Molybdenum detected micrograms	Recovery percent
1.0	100	1.0	Conc. HCl	1.2	120
1.0	100	1.0	N. Na_2CO_3	1.0	100
1.0	100	1.0	N. Na_2CO_3	0.7	70

However, there are advantages in being able to determine iron and molybdenum from the same sample. Initially, it was thought that using an acid leach, molybdenum could be extracted into the amyl acetate solvent phase and the iron content determined on the aqueous phase after the molybdenum determination was completed. This was found to be possible when iron concentrations were low. At concentrations less than 100 ppb, the addition of a drop of thioglycollic acid discharged the yellow iron colouration from the aqueous phase and made matching of the supernatant green phase possible.

When higher iron concentrations are involved, the yellow aqueous discolouration invades the solvent phase. Washing the solvent phase with 6N-hydrochloric acid causes the yellow compound to be extracted back into the acid, clearing the green molybdenum solvent phase. Colour matching is then possible, (Table 23).

Table 23. Determination of Molybdenum and Iron from the same sample by Oxine extraction procedure

Molybdenum concentration ppb	Iron concentration ppb	Sample volume litres	Thioglycollic acid ml	Molybdenum detected micrograms	Iron detected micrograms	Recovery percent	
						Molybdenum	Iron
0.0	0.0	1.5	0.1	<0.2	<2.0	-	-
1.0	10.0	1.5	0.1 D	1.3	12	80	80
1.0	20.0	1.5	0.1 D	1.5	28	100	90
1.0	50.0	1.5	0.1 D	1.6	80	105	105
1.0	100.0	1.5	0.1 D	1.5	140	100	90
0.0	0.0	1.5	0.1	<0.2	<2.0	-	-
1.0	66.0	1.5	0.1 D	1.7	80	110	80
1.0	133.0	1.5	0.1 D	1.5	140	100	70
1.0	200.0	1.5	0.1	1.4	180	90	60
1.0	333.0	1.5	0.1	1.5	360	100	72

D = Yellow colour in aqueous phase discharged by thioglycollic acid

The evident success of the solvent extraction technique in extracting molybdenum from synthetic solutions at a level of 1 ppb encouraged the analysis of water samples from the field areas. The samples had been stored for several months and, despite the addition of acid, some material had precipitated. This suspended material was removed by filtration and analysed separately for molybdenum.

The water samples were extracted in units of 1.5 litres volume and an acid leach was used, the leach volume being increased to enable separate aliquots to be taken for the molybdenum and iron determinations. The results of these experiments are given in Table (24) and the laboratory extraction of the stored samples is compared with results obtained from samples extracted in the field, and analysed in London at a later date.

It will be seen that there is fair agreement between the results of the two sets of extractions. No claim is made that these are total values for the molybdenum content of the waters involved. They do, however, allow comparisons of metal content of the samples to be made.

Table 24. Solvent extraction of Sierra Leone waters.

Sample volume litres	Sample Location	Iron in solution ppb	Molybdenum in solution ppb	Molybdenum in suspension ppb	Total Molyb-denum ppb (Lab.)	Total Molyb-denum ppb (Field)
22.5	Sende 29	15	0.01	n.d.	0.01	(0.4, 0.12,
12.0	Sende 29	n.d.	0.016	n.d.	0.016	(0.2
13.0	Sende F2	80	0.07	0.06	0.13	(0.13, 0.10,
15.0	Sende F2	120	0.10	0.08	0.18	(0.05
9.0	Wankatana	400	0.07	0.01	0.07	0.08, 0.10
9.5	Mapoke X	5	0.08	0.26	0.34	n.d.
9.0	Mapoke Y	90	0.13	0.66	0.79	n.d.

n.d. = not determined

(b) Field Performance

The solvent extraction method developed for waters has been used in the field and found to be simple and trouble free in operation. Full details of the procedure are given in the Appendix.

Owing to the low concentration of molybdenum in the water, very large samples were required, with consequent loss in productivity. Three fifteen litre samples could be obtained and extracted in less than three hours. The sensitivity of the method with this sample volume (15 litres) is 0.02 ppb molybdenum. Whilst the reproducibility of the method is fairly satisfactory when only 1 litre samples are being treated, the precision of the method suffers when several

extractions are needed. The precision of the field trials is estimated at ± 100 percent at the 95 percent confidence level. With this poor reproducibility the distinction of waters from mineralised areas and those of barren streams is difficult.

(v) Summary and Conclusions

1. Evaporation, ion exchange, coprecipitation and solvent extraction have been examined as concentration techniques for molybdenum and arsenic in natural waters.

2. All these procedures lack precision and are slow in operation when large sample volumes are required, e.g. at the levels of concentration (2.0 - 0.02 ppb) encountered in the waters examined.

3. Experiments with ion exchange materials have shown the importance of selecting the correct grade and form of resin for the purpose in view.

4. It is considered that both coprecipitation and solvent extraction will have very useful application for waters carrying somewhat higher metal concentrations than those examined in the present work, where a smaller sample volume can be used. Solvent extraction is particularly useful because of the wide reaction range and the ease with which highly selective extractions can be made.

2. Method for the Determination of Molybdenum in Soils and Stream Sediments.

In the present work molybdenum has been determined by the method of North (1955). After fusion with an alkaline flux the melt is leached with water and transferred to a test tube.

When the insoluble residue has settled, an aliquot of the clear supernatant liquor is taken for analysis. Comparison with results obtained by spectrographic analysis indicates that the attack on the sample is satisfactory, (Table 25).

Table 25. Comparison of Spectrographic and Wet Chemical Analyses of Sediment for Molybdenum

Sample No.	220068/3	220008/2	220082/8	220082/9	220082/2	220822/8
Dithiol Mo Method ppm	2	100	60	10	5	20
Spec. Mo Method ppm	7	100	50	10	7	15

The leaching stage is, however, difficult to control since the melts are often extremely difficult to remove completely from the crucible, even after leaching with warm water overnight. Thus, this critical stage of the analysis is time consuming and subject to error, particularly due to inefficient leaching and losses during transference of the leach to the test tube.

In geochemical prospecting it is often unnecessary to extract all the metal present in the sample and the efficiency of the technique is increased if only those forms of the metal associated with mineralisation are attacked during analysis. The present work has indicated that a large proportion of the molybdenum in soils and sediments of mineralised areas is associated with the free iron oxide component of these materials. Furthermore, the iron oxides are possibly the cause of much of the exchange capacity of the soil and sediments, and the molybdenum which is associated with them can be displaced with anions such as phosphate and hydroxide, or can be attacked with dilute acids.

Unfortunately an acid attack also renders iron soluble and is rather indiscriminate. A further disadvantage, in this particular case, is that iron grossly interferes in the determination of molybdenum with zinc dithiol. The use of an alkaline attack entirely eliminates interference by iron. The disadvantage of this attack is that when organic matter is present in the sample, a yellow discolouration of the solvent phase is observed, which interferes with the colorimetric estimation. This discolouration was unaffected by the reagents usually effective in removing iron interference colour, e.g. thioglycollic acid, citric acid and hydrochloric acid, indicating that iron is not responsible for the discolouration. The possibility that the organic matter directly caused the discolouration was considered and experiments were undertaken to overcome this interference.

(i) Experiments

The method proposed was to remove the organic matter by heating the sample prior to the extraction of the molybdenum with sodium hydroxide solution. Initial trials, carried out in test tubes, indicated that the yellow discolouration of the solvent phase could be removed by a preliminary roasting. This was taken to support the idea that organic matter was responsible for the interference.

It was thought that heating might decrease the amount of readily extractable molybdenum, but this proved not to be the case.

Various strengths of sodium hydroxide solution were used for the extraction stage but a 10 percent solution was found to be the most suitable concentration.

The time of roasting was maintained at one minute but the temperature was varied. The judgement of the temperature of roasting was based on the time taken for the dry sample to become agitated by the heat. After about 7 - 10 seconds of heating the dry powder of the sample appears to boil: this intensity of heating is defined as "intense heat", medium heat refers to a lapse of 10 - 15 seconds before the sample "boiled" and low heat to a lapse of 15 - 20 seconds.

Table 26. Effect of temperature of roasting and strength of NaOH on level of extraction of Molybdenum from soil.

Sample No.	201	202	203	204	205	206	207	208	209	210	211	212
	Molybdenum ppm											
Low Heat 10% NaOH	13	15	5	24	13	12	3	8	18	15	6	15
Low Heat 5% NaOH	9	12	7	15	14	11	1	6	14	7	3	13
Medium Heat 10% NaOH	14	15	7	24	18	12	2	9	20	12	5	25

The stronger NaOH solution is the better extractant and an increase in roasting temperature does not greatly affect the level of the results, (Table 26). However, fewer discoloured solvent phases were obtained with the medium heat roasting. The colour of the solvent phase was found to be stable for at least 30 minutes, i.e. it showed no visible change over this period.

Complete elimination of the organic matter could not be achieved by simple heating, due to lack of oxygen in the test tube. An addition of a few grains of ammonium nitrate to the sample before roasting resulted in a great improvement in oxidation, with virtual elimination of the interfering discolouration, (Table 27).

Table 27. Molybdenum content of Sende sediments by Roasting Method using test tubes

Site Number	7	10	13	15	17	20	23	26	29	31	35	37
	Molybdenum ppm (minus 82 mesh sediment)											
Total molybdenum by fusion	32	40	45	25	40	90	35	50	35	40	20	4
Medium Heat 10% NaOH	20	15	10	5	9	25	17	7	8	12	2	1
Medium Heat 10% NaOH NH_4NO_3	15	14	18	9	6	35	14	9	18	15	5	-
Intense Heat 10% NaOH	19	14	11	3	-	25	8	-	7	2	10	1
Intense Heat 10% NaOH NH_4NO_3	22	17	24	7	3	29	19	3	14	15	4	1

Unfortunately, decomposition products of the reaction which condensed on the walls of the test tube caused interference in the colorimetric stage of the analysis. To overcome the handling difficulties arising out of the need to remove the condensate, the roasting stage was carried out in small silica crucibles with no addition of oxidising agent. The sample was well exposed to the atmosphere and the organic matter readily burnt off. With the use of this technique no further interference troubles were encountered, (Table 28).

Table 28. Molybdenum content of Stream Sediments by the Roasting Method using crucibles

Sample Site River Sende	1	5	10	15	20	23	27	29	32	39	41	F9
	Molybdenum ppm											
Roasting Method	14	16	15	12	48	18	45	27	28	3	3	1
Fusion Method	20	32	40	25	90	35	90	35	40	2	2	2

Sample Site R. Wankatana	W8	W9	W10	W12	W13	W14
	Molybdenum ppm					
Roasting Method	1	1	1	1	2	1
Fusion Method	2	4	5	<2	<2	<2

0.25 g minus 82-mesh Stream sediment, 1 minute roast at intense heat. Leached with 5ml 10% NaOH

Using this latter method the mineralised tract of the stream bed in the River Sende below site 32 can be distinguished from the barren drainage above it whilst in the case of the Wankatana sediments little molybdenum is detected by either roasting or fusion analyses. This is considered to be a reflection of the amount of molybdenum held in the sediment by free iron oxides. It will be shown in the following pages that whilst in the Sende drainage an appreciable proportion of the total molybdenum content of the stream sediment in the vicinity of mineralisation is associated with free iron oxides, the molybdenum in the Wankatana sediments is chiefly held in mineral lattices.

(ii) Performance

Analyses of the statistical series samples by the fusion and roasting methods have been compared; at the 95 percent confidence level the roasting method gives more reproducible results (± 15 percent) than the fusion technique (± 40 percent). Productivity is greatly increased by the roasting method since the tedious leaching stage has been eliminated. While an output of about 40 samples per day could be achieved by the fusion method, the productivity of the roasting method is about 70 samples per day.

The sensitivity of both methods is the same at 1 ppm molybdenum with an 0.25 g sample weight but the roasting method possesses the additional advantage that the sample weight could be increased to 1 g, thus giving a fourfold increase in sensitivity, with no further modifications whilst extensive adjustments of reagent strengths would be needed to analyse a 1 g sample by the fusion method.

PART THREE. OBSERVATIONS ON THE SECONDARY DISPERSION OF MOLYBDENUM IN THE SOILS, STREAM SEDIMENTS AND NATURAL WATERS OF THE SULA MOUNTAINS.

A. Introduction

The principal aim of this part of the writer's study was to obtain a better understanding of the secondary dispersion of molybdenum under tropical conditions with a view to improving prospecting techniques.

Mather (1959) has made a detailed study of the dispersion of molybdenum in the soil of the field areas. His limited investigation of the distribution of molybdenum in the drainage system formed the basis of the present work and will be referred to where appropriate in the following pages.

The writer's research has been largely confined to the study of the dispersion of molybdenum in the drainage system and in the adjacent bank and valley slope soils.

I. Description of the Field Areas

1. The River Sende Field Area (Figure 5).

The present study was carried out in the vicinity of the molybdenite mineralisation, occurring in metamorphosed pillow lavas (amphibolites), south of Dalakaru. Some 500 ft. to the south of the mineralisation, a pink, fluorite rich, late-kinematic granite has intruded the amphibolite. At the intrusive contact the granite has assimilated the amphibolite producing a hybrid rock with which is associated sulphide bearing drusy quartz.

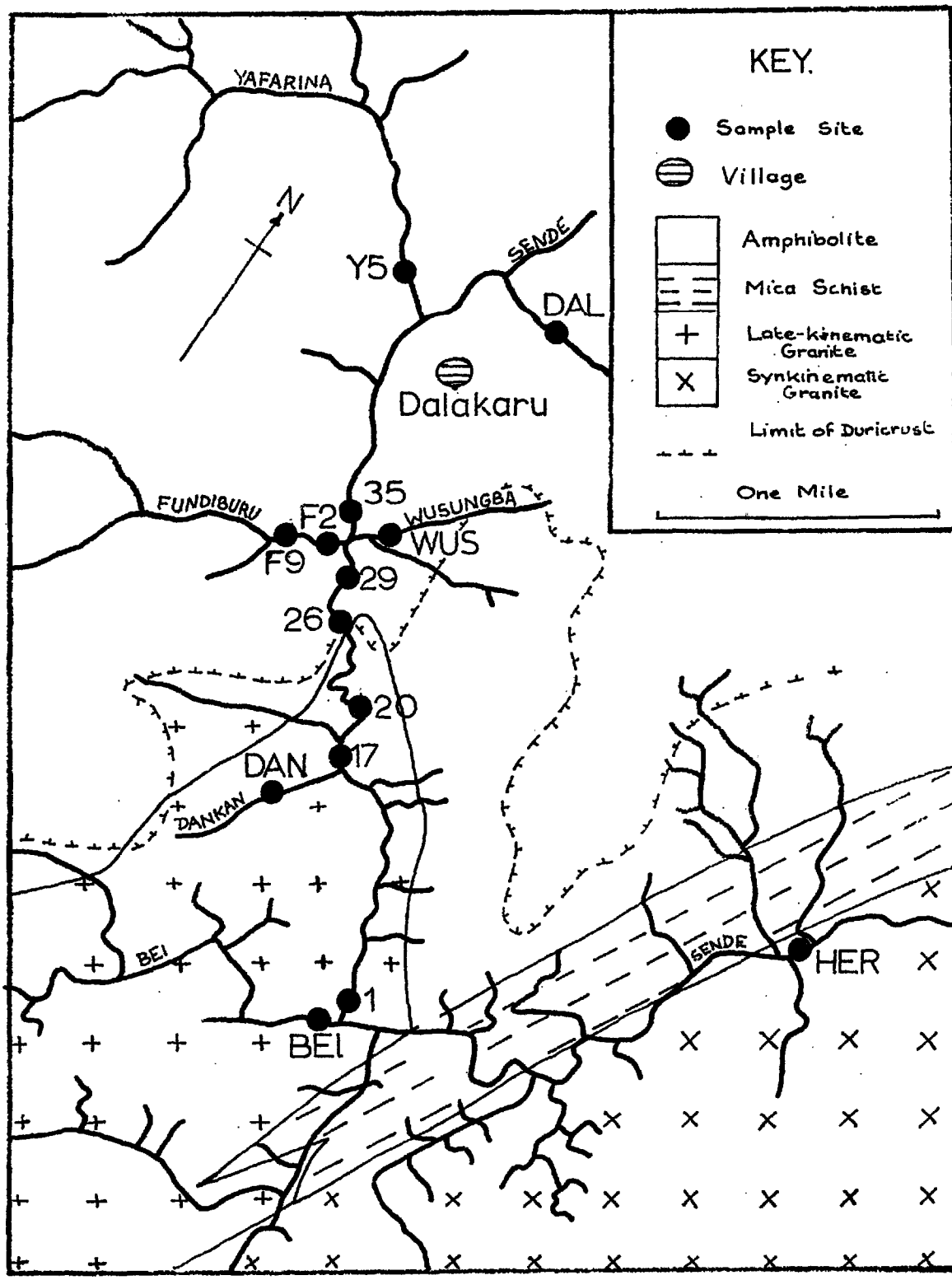


Figure 5 SENDE AREA Geology and Sample Site Location

The molybdenite mineralisation is exposed in the Sende River, to the south of its confluence with the Fundiburu, over a distance of 700 ft. and was originally discovered by officers of the Sierra Leone Geological Survey. Mather, then a research student at the Geochemical Prospecting Research Centre, traced an extension of the mineralisation outcropping in the river bed to an area on the south-west slope of the S nde River on either side of the Fundiburu stream.

Three principal galena and molybdenite bearing hybrid dykes up to 18 inches wide strike 165° and 170° E of N, filling tension cracks nearly normal to the foliation of the amphibolite. None of the mineralised veins is traceable for more than 90 ft.

In order of abundance, the minerals occurring in the veins are pyrite, chalcopyrite, galena, molybdenite, zincblende and aikenite: common gangue minerals are magnetite, quartz, tourmaline, epidote, ankerite, calcite and fluorite. A sample of the drusy quartz from one of the veins assayed 0.2 dwt gold per ton. In addition to the mineralised veins, quartz-tourmaline-pyrite veins, barren of base metals, have also been observed, e.g. near the Sende - Yafarina confluence.

Nearly all the streams in the district have been worked for gold, the workings in the Sende and the Yafarina being particularly extensive.

As a result these streams have banks consisting of large boulders and rubble excavated during mining operations. Thus, some departure from natural conditions may be expected, in spite of the fact that large-scale mining of alluvial gold ceased over thirty years ago.

The River Sende, above Dalakaru village, has cut through the hard duricrust that is so extensively developed in the surrounding areas. The river bed is strewn with rocks, boulders and occasionally larger blocks, chiefly of duricrust and amphibolite. Outcrops of rock occur and in places form waterfalls. Near the mineralisation the stream gradient is about 160 ft. per mile, but further downstream the gradient flattens and islands of alluvium become more frequent.

Away from the river bed exposures of rock are practically absent. On the north-west slope of the Sende valley the soil is largely residual but the steep gradient, in places over 40°, facilitates soil creep and rainwash. Here the weathered zone is up to 80 ft. thick. By contrast, on the south-east slope a thin layer of rubbly soil overlies rotten rock and there is abundant evidence of landsliding. On both the lower valley slopes the soils are immature and apart from a dark humus rich surface layer from 0 - 18 inches thick there is no appreciable soil horizon development. Higher up the slopes and forming the capping of the hilly plateau, a mature, indurated latosol profile is extensively developed.

Along the river margins extends a belt of high forest and thick secondary bush a few hundred feet wide. On the slopes above the deeply incised valleys where duricrust is developed there is a sparse covering of orchard bush and grass.

2. <u>The River Wankatana Field Area</u> (Figure 6).

About $\frac{3}{4}$ mile south-east of Worowaia, a stock of pink, fine grained late-kinematic granite, with porphyritic and gneissose phases, outcrops in the bed of the River Wankatana. The stock is about 3,000 ft. in length, from east to west, and 1,800 ft. wide. Tremolite serpentines

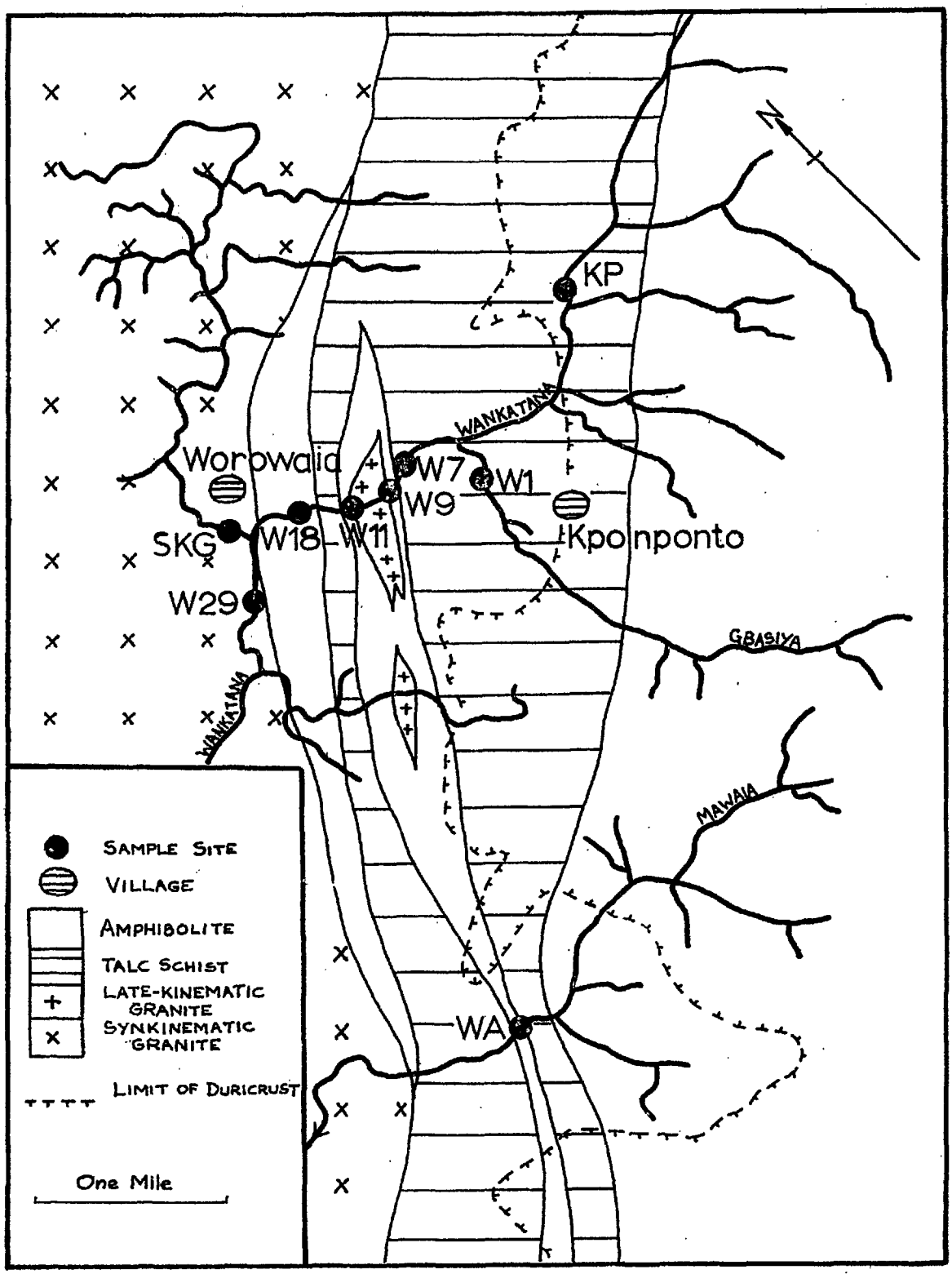


Figure 6. WANKATANA AREA Geology and Sample Site Location

and schists form the country rocks, separated from the granite by marginal strips of amphibolite.

Some of the phases of the granite contain disseminated sulphides. Molybdenite occurs in association with clusters of biotite and rounded fractured garnets in these phases, or as minute scattered flakes throughout the rock. There are two chief molybdenite bearing zones in the granite, one to the north and the other to the south, measuring 1,200 ft. by 300 ft. and 750 ft. by 150 ft. respectively.

A little over a mile upstream from the mineralisation, near the village of Kponponto, the River Wankatana leaves the duricrust plateau and flows swiftly down the scarp into a narrow rejuvenated valley with steep sides and an almost continuously rocky bottom. This watercourse differs from that of the Sende in having gigantic blocks of rock in its bed and banks undisturbed by gold workings.

However, a long prospecting trench has been cut across the granite, parallel and about 100 ft. to the west of the river. The spoil from this trench may be contributing molybdenum rich material to the drainage, otherwise contamination hazards are absent.

The soils overlying the granite consist of up to 12 inches of brown or grey surface soil overlying a soft red loam. The depth of soil above the rotted bedrock is variable but generally exceeds 6 ft.

Strips of primary forest fringe the river but rapidly thin into orchard bush where the duricrust cover remains intact. Except along the river banks the absence of duricrust has resulted in intensive native farming followed by the development of thick secondary bush.

B. The Secondary Dispersion of Molybdenum in the Soil

I. Background Areas

To provide control data against which to compare the conditions obtaining in mineralised areas, Mather made a study of the molybdenum distribution in latosols from barren areas adjacent to the Sende and Wankatana mineralisations.

Two background ranges of molybdenum values were recognised by Mather. Regional background values, averaging 2 ppm molybdenum (1 - 5 ppm), were found in soils overlying a representative selection of rock types about 2 miles from the mineralisation. Higher, local background values were found to occur for a distance of about $\frac{1}{2}$ mile around the mineralisation. In the late-kinematic granite soils the local background molybdenum content ranges from 2 - 7 ppm molybdenum (averaging 4 ppm) and from 2 - 4 ppm molybdenum (averaging 3 ppm) in amphibolite soils. The synkinematic granite contained an average of 1 ppm molybdenum away from the amphibolite contact, as compared to 2.5 ppm molybdenum near the contact.

On the basis of these data Mather selected threshold values, i.e. "that value below which the variations (in metal content) represent only normal background effects" (Hawkes 1957), of 15 ppm molybdenum on a local scale and 5 ppm molybdenum on a regional scale.

No variation in molybdenum content was observed between the various horizons of the residual soil profiles examined over barren rock. Similarly, the metal content of the various size fractions separated by dry sieving showed little variation, except in the illuvial horizon of red loam formed over late-kinematic granite in the Wankatana area, where the molybdenum tenor of the minus 82-mesh fractions was found to be approximately twice that of the plus 82-mesh fractions.

Stream bank soils, the principal source of the stream sediment, from barren parts of the Sende and Wankatana catchment areas were examined by the writer. In both areas the stream banks, consisting of mixed colluvial and alluvial material, are poorly defined and the development of a well-defined bank soil profile is rare. Consequently sample collection from the same soil horizon in different areas is virtually impossible, rendering the comparison of bank soils liable to error arising from differences in their derivation.

The fine fractions (minus 82-mesh) of the bank soil at some distance from the mineralisation contain 1 - 2 ppm molybdenum, rising to 2 - 5 ppm nearer to mineralisation. The number of bank soil samples examined was inadequate to provide a basis for the determination of a reliable molybdenum threshold value. However, the metal levels are similar to those obtained by Mather for residual soils, hence his threshold values may be applicable to stream bank soils.

Freely drained regional bank soils from schist and amphibolite catchments show little variation in molybdenum tenor between the particle size fractions, (Figure 7). Regional background soil from a predominantly late-kinematic granite catchment, however, exhibits a notable concentration of molybdenum in the silt size fraction, (Figure 8). Whether this is due to the influence of the rock type or to the presence of molybdenum rich alluvial material in the sample is uncertain but the latter possibility is favoured since other soil samples from late-kinematic granite sites do not show this concentration, (Figure 8). Furthermore, the stream sediment from the same site contains over 300 ppm molybdenum in the silt size fraction and it would require little of this material to boost the tenor of the soil silt fraction.

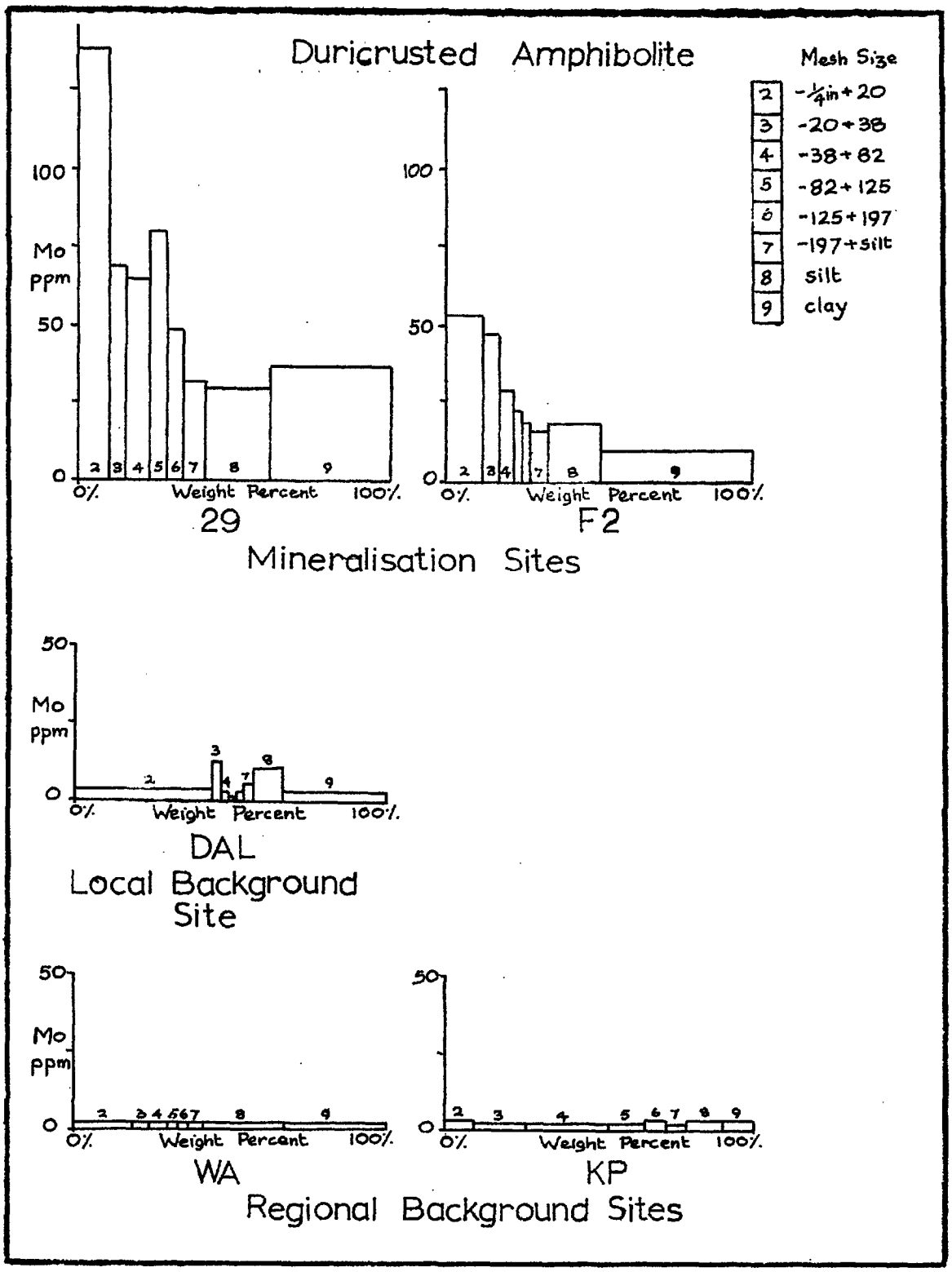


Figure 7. SENDE AREA Freely Drained Bank Soil Mechanical Composition and Molybdenum Distribution

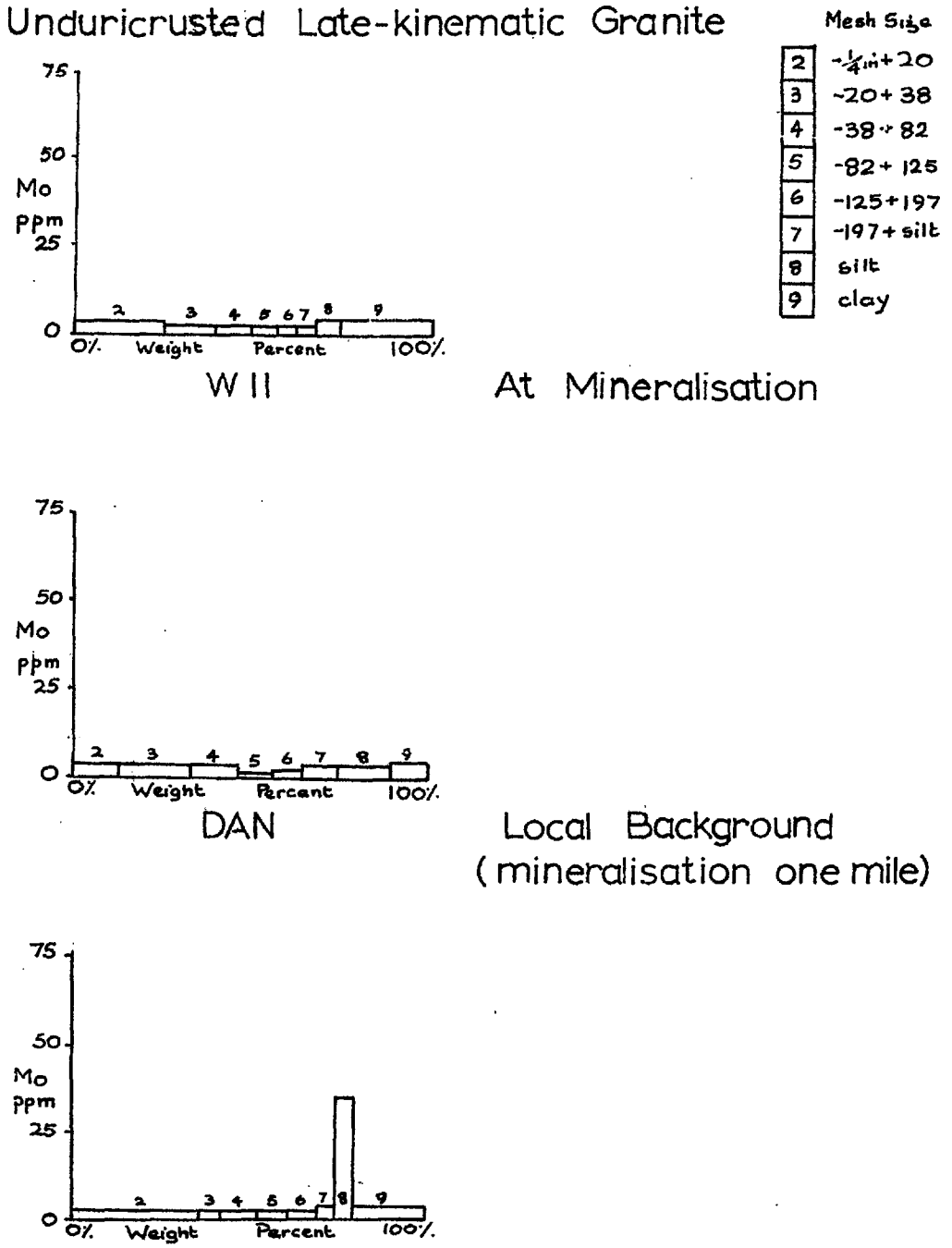


Figure 8. WANKATANA AREA. Freely Drained Bank Soil Mechanical Composition and Molybdenum Distribution

Nearer mineralisation the local background bank soils have a higher molybdenum tenor than the regional background soils and exhibit a slight tendency for the metal to be concentrated in the coarse and fine fractions rather than the intermediate grades. Preferential concentration of the molybdenum in the coarse size fractions becomes most marked in soil from the vicinity of mineralised amphibolite.

II. Mineralised Areas

The two mineralised areas studied differ principally in the nature of the mineralisation and the type of latosol developed over the different host rocks. Contrasts in the molybdenum distribution in the latosols of each area are therefore, to be expected.

1. Sende Area

Amphibolite, containing molybdenite bearing calcite veins occurs in the Sende valley near Dalakaru. The mineralisation is covered by 20 - 80 feet of indurated concretionary latosol and gives rise to anomalous concentrations of molybdenum (50 - 1,000 ppm over an area of 0.2 square miles) in the surface soil. A considerable amount of work was done by Mather to delineate the form and extent of the anomalous area. The axis of the anomaly coincides with the surface projection of known veins and the dispersion aureole is asymmetrically prolonged downslope, with a concommittant fall off in metal values.

Within anomalous residual soil profiles, Mather has demonstrated that, in contrast to the barren areas, the molybdenum tenor of the zone of sesquioxide concretions may be up to four times greater than in the underlying loam. Only in the immediate vicinity of mineralisation

does the pallid zone of bleached rock underlying the sesquioxide zone carry anomalous amounts of molybdenum.

In the illuvial horizons of the anomalous profiles studied, Mather reports a uniform distribution of molybdenum between the size fractions whilst the stream bank soils examined by the writer exhibit an appreciably higher molybdenum content in the coarse fractions, (plus 82-mesh), particularly the very coarse sand size, than in the fine fractions (Figure 7). The difference between these two observations may be attributed to modification of the molybdenum distribution in the eluvial horizon during transport by soil creep downslope to the stream banks. Alternatively, the metal distribution in the eluvial horizon may be markedly different from that in the illuvial horizon but this has not been investigated. A third explanation is that the differences arise, at least in part, from the method used to separate the size fractions. In the dry sieving technique used by Mather, the finer fractions adhere to the larger grains and in this case since they carry lower metal tenors, reduce the overall metal content of the coarse fractions. In the present study a more complete classification of the particles was achieved by wet dispersion of the samples before sieving.

High molybdenum tenors in the coarse fractions of the soil compared to fines are, in many cases, considered to be due to the presence of ironstone concretions and duricrust fragments in the coarse material.

2. Wankatana Area

The late-kinematic granite, containing disseminated molybdenite is overlain by up to 80 ft. of red loam latosol carrying anomalous amounts of molybdenum. Mather obtained values ranging from 10 - 120 ppm molybdenum, and exceeding 50 ppm molybdenum over an area of 7,000 square yards. Thus, it will be seen that both the extent and magnitude of this anomaly are considerably smaller than the Sende occurrence. The development of an extensive downslope dispersion pattern is limited by the close proximity of the River Wankatana.

The anomaly also terminates at an organic rich swamp. Mather attributes this to mobilisation of the element by the organic matter. This observation will be discussed more fully at a later stage when the influence of organic matter on the dispersion of molybdenum is considered.

In the soil profile developed over the Wankatana granite Mather reports an even distribution of molybdenum. However, compared with background areas, the residual soils over the mineralisation contain appreciably higher amounts of molybdenum, the bulk of which (70 percent) is in the minus82-mesh fractions. These differences in the molybdenum distributions in the Wankatana soils compared to those at Sende are considered to be due principally to the fact that no concretionary sesquioxide rich horizon is present in the latosol profile developed over the Wankatana granite.

The absence of an ironstone concretionary horizon in the granite soil profile and its presence in the amphibolite profile is not surprising when it is considered that the granite contains only

0.4 percent iron (Fe_2O_3+ FeO) compared to 11 percent iron (Fe_2O_3 + FeO) in the ferromagnesian rock (Mather 1959).

The stream bank soil in the vicinity of the mineralisation carries only very low concentrations of molybdenum fairly evenly distributed between the size fractions with only a slight tendency to concentration in the coarse and fine fractions (Figure 8). The limited extent of the residual soil anomaly has already been noted and it seems likely that the sample examined has been considerably diluted by barren material and it now exhibits a metal distribution similar to a local background sample.

III. Comparison of freely drained and waterlogged bank soils

It was considered that a different metal distribution might exist in the waterlogged bank soil below the stream water level as compared to the freely drained soil forming the upper part of the stream banks. Accordingly the stream banks were sampled both above and below the water level.

Only material from the Sende area is dealt with here since the molybdenum tenor of the Wankatana bank soils is uniformly low and no significant differences were apparent.

Complete size analysis of a local background soil from the Sende area indicates that the waterlogged material contains appreciably more molybdenum than the freely drained soil from the upper part of the same bank, (Table 29).

Table 29. Comparison of Molybdenum distribution in freely drained and waterlogged bank soil.

Site Number	Soil Type	-¼ +20	-20 +38	-38 +82	-82 +125	-125 +197	-197 +Silt	Silt	Clay	Size Fraction
35	Freely drained.	22	18	12	14	18	24	20	22	Mo ppm
Local Background	Water-logged.	34	34	26	32	22	18	46	72	Mo ppm

It is notable that, in contrast to the freely drained soil, the silt and clay fractions of the waterlogged soil carry relatively high molybdenum tenors compared with the other size fractions. This concentration of the metal in the most chemically active fractions of the waterlogged soil suggests that sorption of molybdenum from ground water entering the stream may be taking place.

Complete size analysis entails considerable expenditure of time per sample hence further investigation was confined to the plus and minus 82-mesh fractions of the bank soils. These results are compared with those for freely drained valley slope soils sampled about 100 ft. upslope from the stream bank (Figure 9).

i) Stream banks upstream from the mineralisation

At some distance from the mineralisation bank and slope soils have only very low molybdenum contents, usually less than 10 ppm. Nearer to mineralisation the tenor increases to as much as 40 ppm molybdenum and there is preferential concentration of the metal in the fine fractions of the waterlogged soil, relative to those of the freely drained soil. The coarse fraction always contains more molybdenum than the fines, a fact attributed to the abundant sesquioxide concretions in the former material.

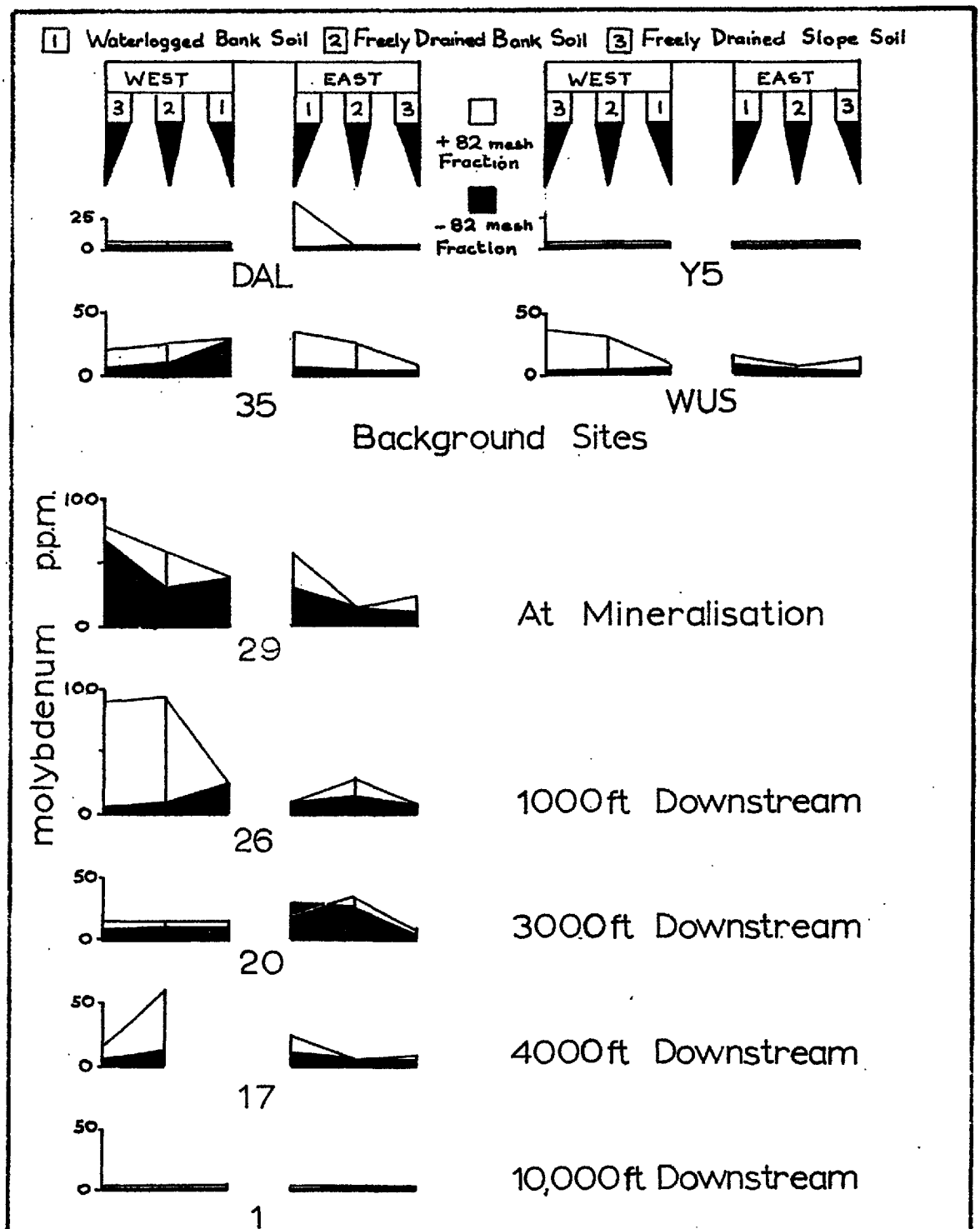


Figure 9. SENDE AREA. Molybdenum Content of Stream Bank and Valley Slope Soils

ii) Stream banks near mineralisation

Stream banks downslope from the mineralisation on the west bank of the River Sende, contain high tenors of molybdenum, particularly in the coarse concretion rich material. The fine fractions of the waterlogged bank soil again show a higher concentration of molybdenum than those of the freely drained soil.

iii) Bank soils downstream from the mineralisation

With increasing distance downstream from the mineralisation the molybdenum tenor of the bank soils decreases to background levels, the concentration of the element in the fines of the waterlogged soil as compared to those of the freely drained soil is less marked and the importance of the coarse material as the chief host of the metal diminishes.

The non-uniformity of derivation and structure of the stream banks examined leads to difficulty in interpreting the results obtained; this is particularly true in the Sende area where the banks have been disturbed by gold mining operations. Hence only a general explanation of the data presented above is possible.

The results suggest that, in the vicinity of mineralisation, fixation of molybdenum by the fine fraction of the bank soil below the water level may be taking place. Although the possible source of the molybdenum is groundwater draining deep levels of the mineralisation the flow of surface water through the unconsolidated banks parallel to the open channel cannot be entirely discounted.

Where the underlying rock type changes from amphibolite to granite about 3,000 ft. beyond the mineralisation the duricrust cover ends, and the metal content of the coarse fraction falls in relation to that of the fines as the iron rich molybdenum bearing material derived from the amphibolite is replaced by barren quartz and felspar derived from the granite.

A further problem presented by these data is the relationship of the slope soils to the bank soils. Away from the mineralisation, in almost every case, the freely drained bank soil contains more molybdenum than the soil upslope. The higher tenor of the bank soils may be due to eluvial concentration of the fine grained molybdenum bearing soil component during the movement of the soil downslope. No investigation of this possibility has been made hence its importance cannot be assessed. Alternatively, the high tenor of the bank soils may be due to molybdenum rich sediment deposited as alluvium in the stream banks. Molybdenum bearing alluvium may also be responsible for the higher tenor of the coarse fractions of the waterlogged soil compared with the freely drained material.

C. The Secondary Dispersion of Molybdenum in Active Stream Sediments

Although Mather's limited investigation of stream sediments was confined to the minus 82-mesh fraction, it has provided valuable orientation data for the present study.

The background molybdenum concentration in the minus 82-mesh fraction of stream sediments, as established by Mather for various rock types, are as follows: amphibolite, 4 - 6 ppm (average 5 ppm), talc schist 1 - 2 ppm, granite 2 - 4 ppm (average 3 ppm). Sediments collected during the present work over a 50 square mile area in the vicinity of Lake Sonfon confirmed, in general, the findings of Mather. In areas well away from mineralisation the molybdenum content of the minus 82-mesh fraction of the sediment of streams draining all rock types varied from 2 - 5 ppm molybdenum. This regional background concentration is somewhat lower than the molybdenum tenor in the vicinity of the Sende mineralisation where a local background of 5 - 10 ppm molybdenum was established for stream sediments.

Mather records the presence of a well marked anomalous molybdenum drainage dispersion train in the River Sende but only a feeble train in the River Wankatana sediments. This difference has been substantiated by the writer's investigations.

I. Distribution of molybdenum according to the particle size of the stream sediment

Sediment samples were collected in the streams at the sites indicated on the maps of the Sende and Wankatana areas, (Figures 5 and 6).

1. Mechanical Composition of the Stream Sediment

The mechanical composition of the stream sediment is closely related to the presence or absence of duricrust in the catchment and as duricrust is, in general, absent over granitic rocks, there is also a close correlation with bedrock lithology, (Table 30).

Table 30. Mechanical Composition of Stream Sediments of the Sende area

Bedrock lithology of catchment area.	Mechanical Composition. Weight percent.								
	Sample Site	-¼" +20	-20 +38	-38 +82	-82 +125	-125 +197	-197 +Silt	Silt	Clay
Late-kinematic Granite	BEI	31.7	50.0	9.4	2.1	1.1	2.0	1.3	2.7
	DAN	15.6	46.3	27.5	2.0	1.1	1.6	2.2	2.7
Late-kinematic Granite and Duricrusted Amphibolite	17	56.5	20.5	11.2	2.1	0.9	1.6	2.7	4.2
	1	60.5	16.5	16.8	1.7	0.6	0.8	0.9	2.1
Duricrusted Amphibolite	29	75.3	4.6	1.7	0.9	0.9	3.6	5.9	6.7
	F2	84.0	2.3	1.5	0.8	0.9	2.8	3.5	3.7
	35	92.4	2.5	0.4	0.2	0.2	0.8	0.3	2.2
	DAL	74.8	8.1	2.9	0.7	0.6	2.5	5.3	5.3
	WUS	81.5	7.4	1.8	0.5	0.4	1.3	3.0	4.4

Where duricrusted rocks form a considerable part of the adjacent catchment a high proportion of the stream sediment (70 - 90 percent) consists of very coarse material (greater than 20-mesh), most of which is composed of resistant duricrust fragments and ironstone concretions.

The coarse and medium fractions of sediments from granitic catchments, on the other hand, consist mainly of quartz and felspar grains and make up a smaller proportion of the whole sediment.

In contrast to the bank soils, the very fine fractions form only a minor component of the stream sediments. This is attributed to the relatively high velocity of the stream waters which prevents the accumulation of fines; the proportion of larger, heavier particles

is therefore increased in the sediment as compared to the soil due to the removal of the fine fractions downstream.

2. Distribution of Molybdenum in Sediments from Unmineralised Catchments

a) Duricrust well-developed in the catchment

In both the samples selected as typical background sediments the duricrust rich coarse fraction carries very little molybdenum, although it makes up the bulk of the sediment, (Figure 10).

The local background samples in the vicinity of the Sende mineralisation (DAL, WUS) present the same general aspect as the regional samples, but have higher tenors of molybdenum in all fractions. The distribution of molybdenum in the sample nearest mineralisation (WUS), is transitional between background and anomalous sediments in the increase in tenor of the coarse fraction relative to that of the fines.

In contrast to the bank soils, the most significant feature of the metal distribution in the sediments from barren areas is the very marked concentration of molybdenum in the silt size fraction. There is, in general, a progressive increase in molybdenum tenor with decrease in particle size with the notable and constant exception of the clay size material. The ratio of the molybdenum content of the clay to that of the silt in local background samples is lower than that of the regional background samples, perhaps because of the higher concentration of soluble molybdenum available for sorption in the vicinity of mineralisation. The low metal content of the clay fraction may indicate that the clay minerals, as such, play a relatively small part in removing molybdenum from stream waters.

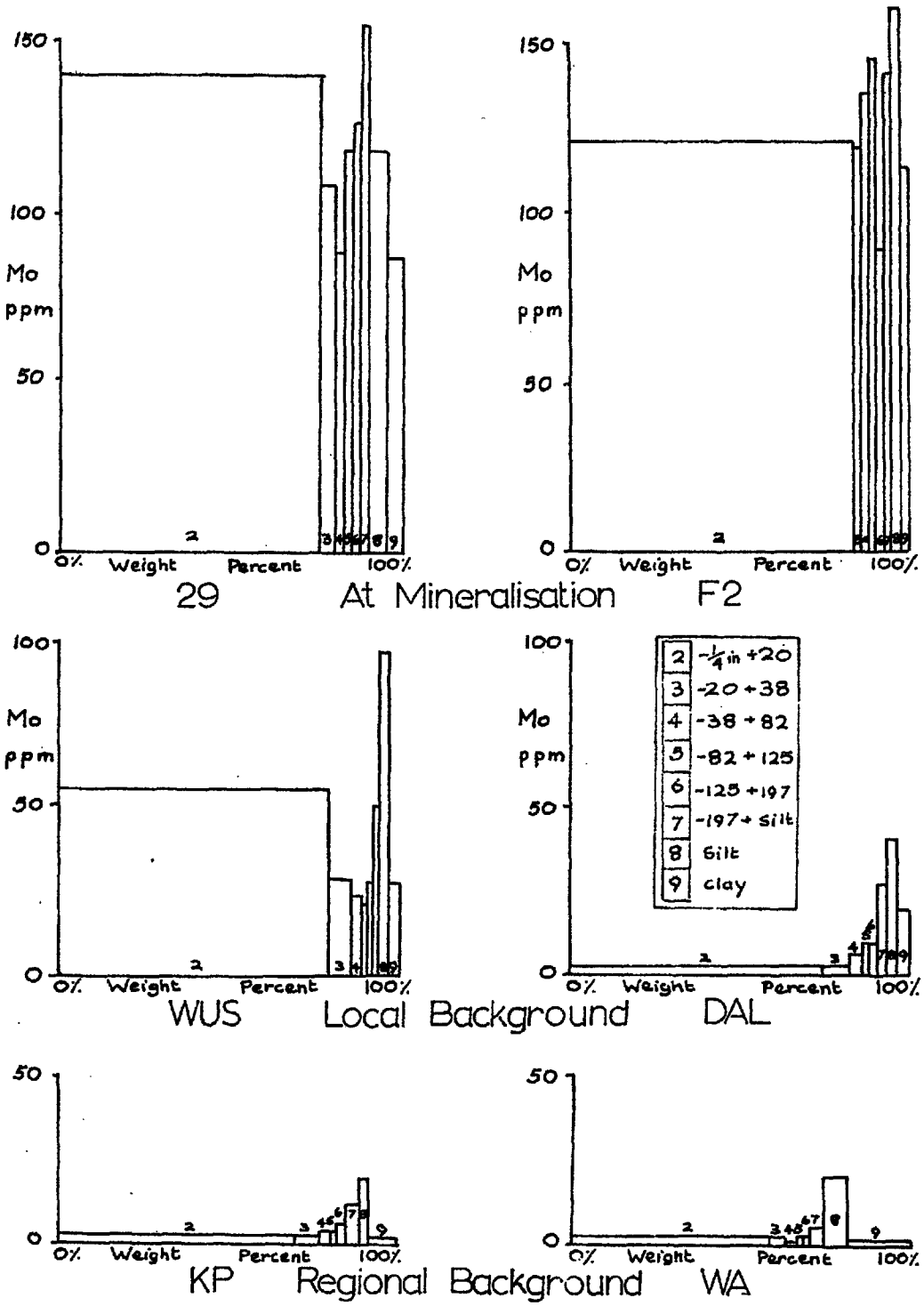


Figure 10. Distribution of Molybdenum in the Particle Size Fractions of Stream Sediment from the Duricrusted Area

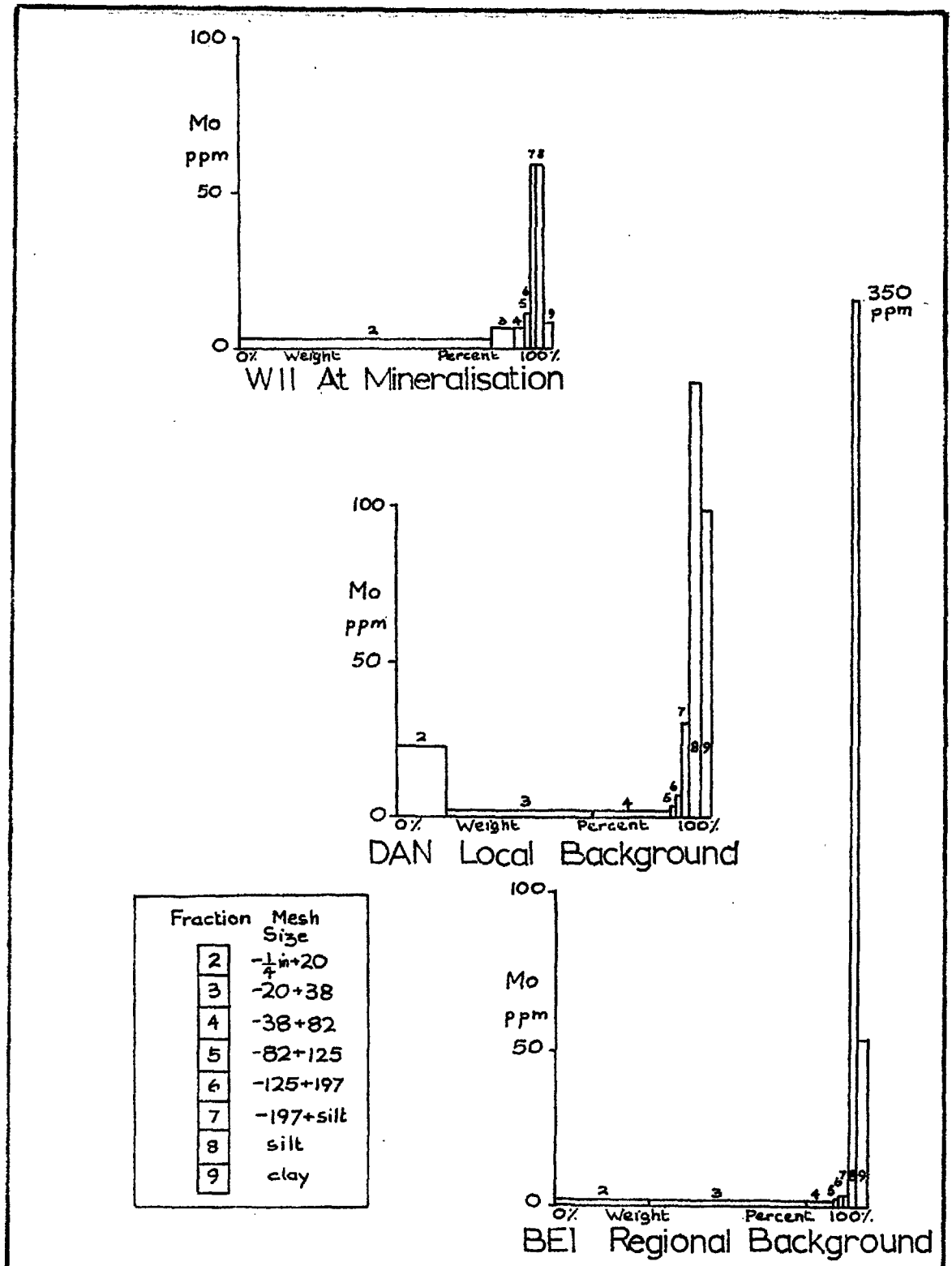


Figure 11. Distribution of Molybdenum in the Particle Size Fractions of Stream Sediment from the Non Duricrusted Area

The above data are taken to indicate chemical activity in the fine sediment fractions. Further examination of the sorption active components (clay minerals, sesquioxides, organic matter) of the fine sediment was therefore undertaken to clarify this point, (Section 4).

b) Duricrust absent or poorly-developed in the catchment

The molybdenum distribution in both regional and local background samples taken from streams draining late-kinematic granite resembles that of the duricrust group, in the general lack of molybdenum in the coarse fractions and maximum tenor in the silt, (Figure 11). However, the most remarkable feature of these samples is the extremely high tenor of the silt, far in excess of that of the silt fraction of sediment from the vicinity of mineralisation and of the bank soil silt from the same site.

This unexpected feature may be due to molybdenum-bearing particles of silt size or to the presence, within the silt fraction, of a component with a high sorption capacity for molybdenum. Further investigation of the distribution of the element within the sediment particles was undertaken and is discussed at a later stage in the thesis, (Section 4).

The local background sample also shows a high tenor of molybdenum in the plus 20-mesh material, as compared to the other fractions, which may be due to duricrust transported downslope from the edge of the depression in which this site is situated, (Figure 5). In this sample, the clay fraction also carries more molybdenum relative to the silt than in the regional background sample. This feature was also noted in the background samples from duricrusted areas and

is possibly due to an increase in the sorption activity of the clay fraction in the presence of higher concentrations of soluble molybdenum available near the mineralisation than in barren areas.

3. Distribution of Molybdenum in Sediments from Mineralised Areas

a) Duricrust well-developed in the catchment

Stream sediments in the vicinity of the River Sende mineralisation contain strongly anomalous concentrations of molybdenum in all the size fractions compared with the background sites, (Figure 10). The high molybdenum tenor of the very coarse fraction, which usually makes up over 75 percent of the sediment is not surprising, since the same fraction in the related bank soil also carried the highest metal concentration.

Although the other size groups are only of limited bulk their tenor may be higher than that of the coarse sand fraction (plus 20-mesh). It is this great increase in the molybdenum content of the fine fractions which contrasts strongly with the metal distribution in the soil. Suggestions have already been made as to the possible explanation of this phenomenon and it may be relevant to recall that the effect of waterlogging on bank soil was to increase the molybdenum content of the silt and clay fractions. This supports the idea that fixation of molybdenum from solution is, at least in part, responsible for the increased metal content of the fine sediment.

b) Duricrust poorly-developed or absent in the catchment

A sediment sample from immediately below the late-kinematic granite outcrop in the Wankatana river exhibits the molybdenum distribution features shown by the background samples in its lack of metal in the coarse fractions and relatively high tenor in the silt, (Figure 11).

The tenor of the silt fraction is, however, very much lower than that of the silt fraction of the background sample. That the sediment from the vicinity of mineralisation should have a lower tenor than that from background areas is unexpected. At a later stage in the thesis (Section II, 3) it will be shown that the sediment 5,000 ft. downstream from the Wankatana granite has a metal distribution similar to that of the regional background sample (BEI). The drainage on late-kinematic granite, upstream from the BEI sample site extends for over two miles hence the sediment at this site may have travelled a maximum of two miles in the drainage system. It appears therefore that transport in the drainage system of sediment derived from late-kinematic granite may give rise to a marked concentration of molybdenum in the silt fraction. In contrast with the regional background sediment and that 5,000 ft. downstream from the mineralisation the sediment near the mineralisation (Site W11) can only have travelled a maximum of 1,800 ft., the width of the granite outcrop. This may perhaps account for the incongruity of tenor of sediments from background and mineralised localities where late-kinematic granite occurs in the catchment.

The contrast of the high molybdenum content of the fine fraction of the sediment, compared to that of the corresponding fractions of the bank soil, which has been noted in other samples is also shown by the sample from the vicinity of mineralisation.

From the above data it is evident that the transition from bank soil to stream sediment brings about a considerable change in the metal distribution, particularly in the silt size fraction which becomes relatively rich in molybdenum. A closer examination of

the distribution of molybdenum within the sediment particles was therefore undertaken in the hope that it would lead to a better understanding of the changes referred to above.

4. Chemical Associations and Characteristics of Molybdenum in Stream Sediments

Molybdenum may be carried by the sediment particles in a number of forms, for example, in mineral lattices, as exchangeable anions, in association with a particular type of particle such as precipitated iron oxides, heavy mineral grains and organic matter, or as a discrete molybdenum mineral species like powellite $CaMoO_4$.

Furthermore, it was considered probable that the partition of molybdenum between these various forms would depend to a more or less marked degree on the form of the metal in the rock in particular whether it occurred as molybdenum minerals or within the lattices of the rock forming minerals.

a) The association of Molybdenum with Iron Oxides

The siderophilic nature of molybdenum is well known, thus it was of interest to investigate the relationship between molybdenum and the hydrated iron oxides of the stream sediment.

The work of White (1957) on the distribution of zinc in soils formed the basis of the method of study. The exhaustive survey of methods of removal and determination of the so-called free iron oxides of soil materials by Robichet (1957) supports the claim, by White, that the dithionite attack is specific for the removal of hydrated iron oxides and also concludes that it is the best method available to date. The original method (Galabutskaya and Govorova 1934) has been modified by several workers and in the present study the method of Aguilera and Jackson (1953) was followed,

with the omission of the versene which was found to be unnecessary. Full details of the procedure are given in the Appendix.

The molybdenum content of the dithionite extracts could not be determined directly because of gross interference from the iron in the colorimetric stage of the analysis. Hence, after removal of the free iron oxides the residue was analysed to determine the amount of lattice-held molybdenum. The molybdenum associated with the free iron oxides was then obtained by the difference between the total and lattice-held molybdenum content.

This is, however, a somewhat unsatisfactory procedure in view of the precision of the analytical method for molybdenum (± 40 percent at the 95 percent confidence level). Furthermore the molybdenum classified as associated with iron oxides will include any other forms of the element extractable by the dithionite attack. The extent to which exchangeable and other forms of molybdenum are taken into solution by this treatment has not been determined but in this connection, White notes that ammonium chloride exchangeable zinc is removed by the dithionite. It seems likely, therefore, that any loosely bonded molybdenum will be removed into the dithionite extract.

i) Distribution of molybdenum and free iron oxides between the sediment size fractions, (Figure 12).

In stream sediment samples from barren areas a relationship between molybdenum and the free iron oxide component is shown in the sample from a non-duricrusted catchment. The association is particularly marked in the fine sediment fractions due to the comparatively low iron and high, variable molybdenum tenor of the fractions. The duricrusted sample, on the other hand, contains so little, fairly evenly distributed, molybdenum that any correlation with the high iron oxide tenor is obscured.

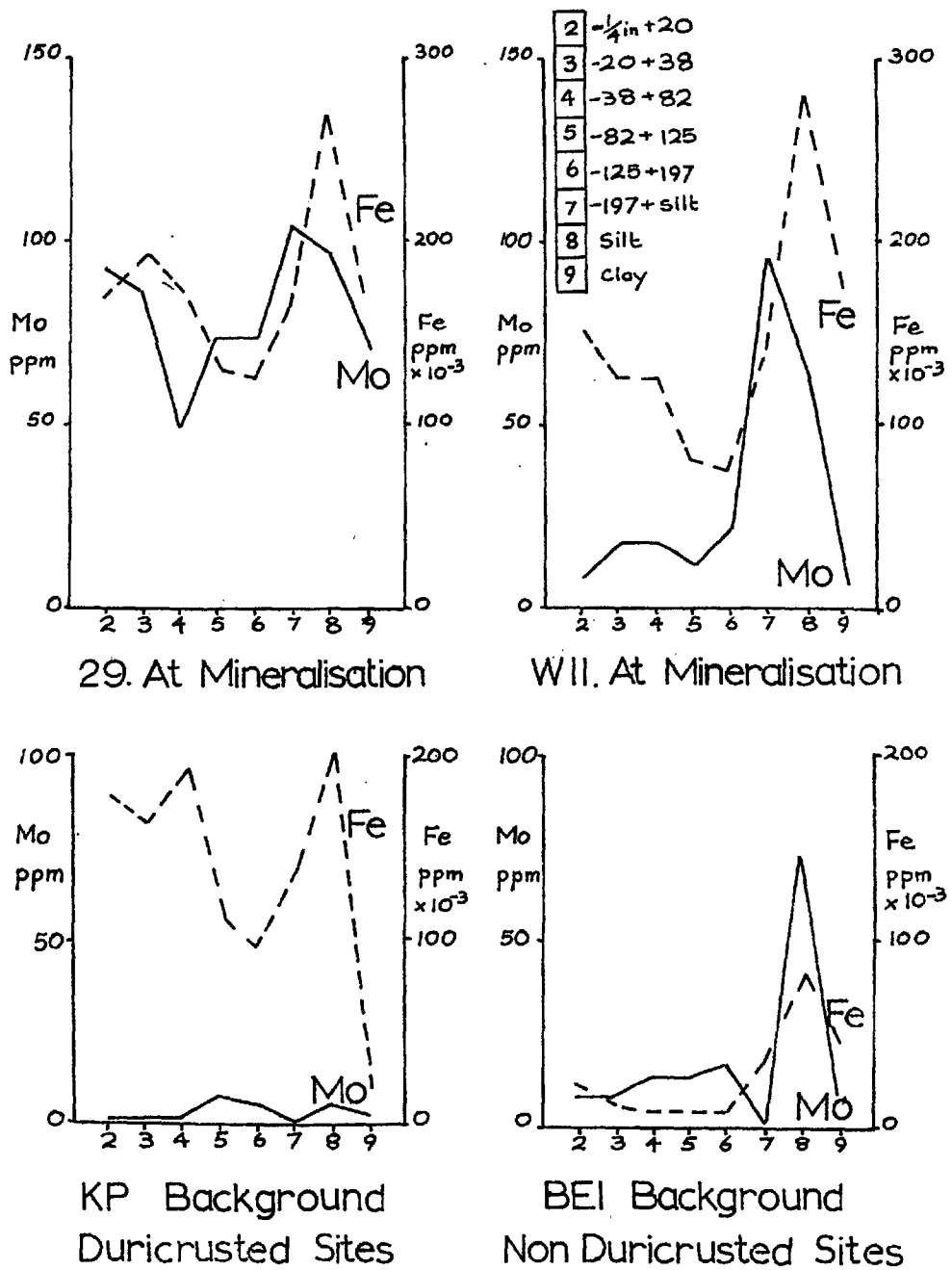


Figure 12 Association of Molybdenum and Iron in the Free Iron Oxide component of Stream Sediment

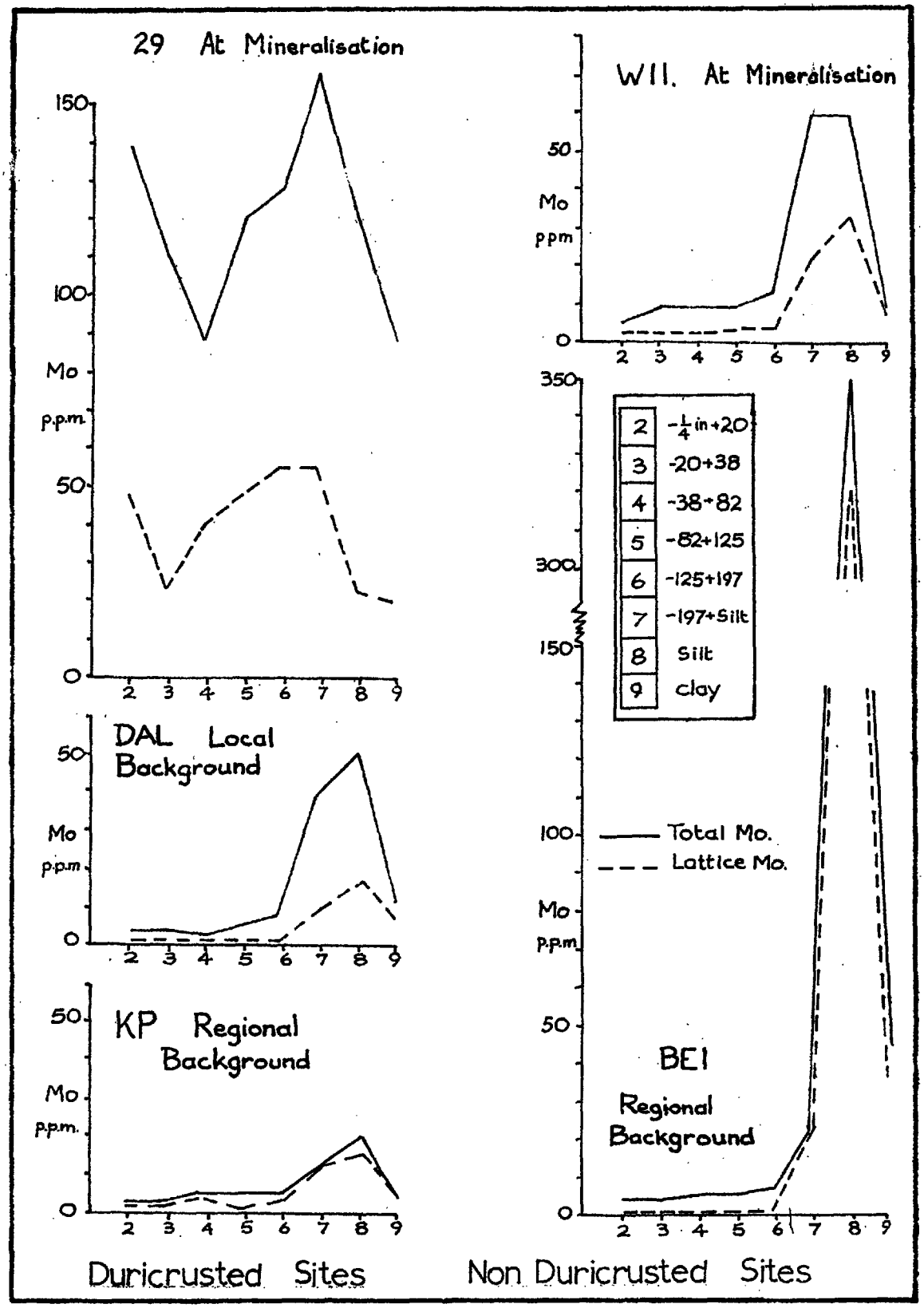


Figure 13 Distribution of Molybdenum between Mineral Lattices and Free Iron Oxides in Sediment Size Fractions

The similarity in distribution of molybdenum and free iron oxides within a given sample is more strongly marked in sediments from mineralised areas, particularly in the fine fractions. Despite a similar tenor and distribution of free iron oxides in the coarse fractions of sediments sampled near duricrusted and unduricrusted mineralisations, the molybdenum distribution in the duricrust rich sediment differs from that of sediment from an unduricrusted site. In the former case, molybdenum bearing duricrust particles, derived from the secondary dispersion pattern developed over the mineralisation, make up the coarse fractions of the sediment and a relationship between molybdenum and free iron oxides is therefore possible. In the latter instance, however, the iron bearing material is derived from the barren duricrusted area upstream from the mineralisation and the free iron oxides have no relationship with the mineralisation.

ii) Partition of molybdenum between free iron oxides and mineral lattices in the sediment size fractions, (Figure 13).

In regional background samples from both duricrusted and non-duricrusted catchments the bulk of the molybdenum is in the mineral lattices, particularly in the case of the fine fractions of the sediment. The very low proportion of lattice-held molybdenum in the coarse fractions of the sediment from the non-duricrusted catchment is probably due to the fact that this material is chiefly composed of barren quartz and felspar grains and duricrust fragments.

On approaching the duricrusted mineralisation, an increase is observed in the proportion of the total molybdenum associated with free iron oxides and in the sediment in the immediate vicinity of the mineralisation the greater part of the molybdenum is held by the free iron oxides.

Stream sediments in the immediate neighbourhood of the non-duricrusted mineralisation also exhibit an increased proportion of free iron oxide associated molybdenum compared with the background sediment. In contrast to the coarse fractions of the duricrusted sediment, those of the unduricrusted mineralisation carry only a low molybdenum tenor, presumably due to the presence of large amounts of quartz and felspar and only a small proportion of molybdenum bearing sesquioxide concretions.

The considerable decrease in molybdenum tenor in the clay fraction of most of the sediments compared to that of the silt can be largely attributed to the smaller quantity of free iron oxide held molybdenum in the clay fraction. However, in the case of the sample from the barren, unduricrusted catchment the difference in tenor of the silt and clay fractions is clearly due to the scarcity of the mineral carrying lattice-held molybdenum in the clay fraction.

The data presented above demonstrate a close relationship between molybdenum and free iron oxides in the stream sediments of the catchment areas examined.

As previously stated the proportion of the total molybdenum content of the stream sediment which is associated with the free iron oxides is greater in the vicinity of mineralisation than in barren areas. It seems likely that the non-exchangeable, lattice-held molybdenum of the sediment represents that molybdenum held in the lattices of silicate minerals present in the rocks of the catchment area, whilst the free iron oxide associated molybdenum is reprecipitated molybdenum originally derived from the ore minerals or rock forming minerals during weathering. This molybdenum may have been coprecipitated with iron oxides by sorption either from the ground water in the soil or from the surface water.

The effect of the host rock of the mineralisation on the distribution of molybdenum in the related stream sediments is notable. In particular the high proportion of free iron oxide held molybdenum present in sediments derived from the duricrusted amphibolite mineralisation is in marked contrast with the low tenor of this component in sediments associated with the disseminated mineralisation in the Wankatana granite.

b) The Association of Molybdenum with Manganese

In view of the efficiency with which manganese oxides can coprecipitate molybdenum from solutions (Tanaka 1958) an examination was made of the possible association of these two elements in the stream sediments.

Appreciable amounts of manganese were found to be present in the stream sediments, (Figure 14). In duricrust areas, manganese, like molybdenum, tends to be concentrated in the coarse particles of the stream sediment which consist chiefly of duricrust fragments and ironstone concretions, whilst the lack of manganese in these fractions of sediment from unduricrusted catchments, composed of quartz and felspar suggests some correlation between iron and manganese contents.

The relationship between the three elements iron, manganese and molybdenum in the coarse material remains obscure. Conditions favourable for the coprecipitation of molybdenum by manganese may have existed during the period of duricrust formation or alternatively, both molybdenum and manganese may have been coprecipitated by the hydrated iron oxides. The closer association of molybdenum with iron than with manganese may be due to the fact that, under most circumstances,

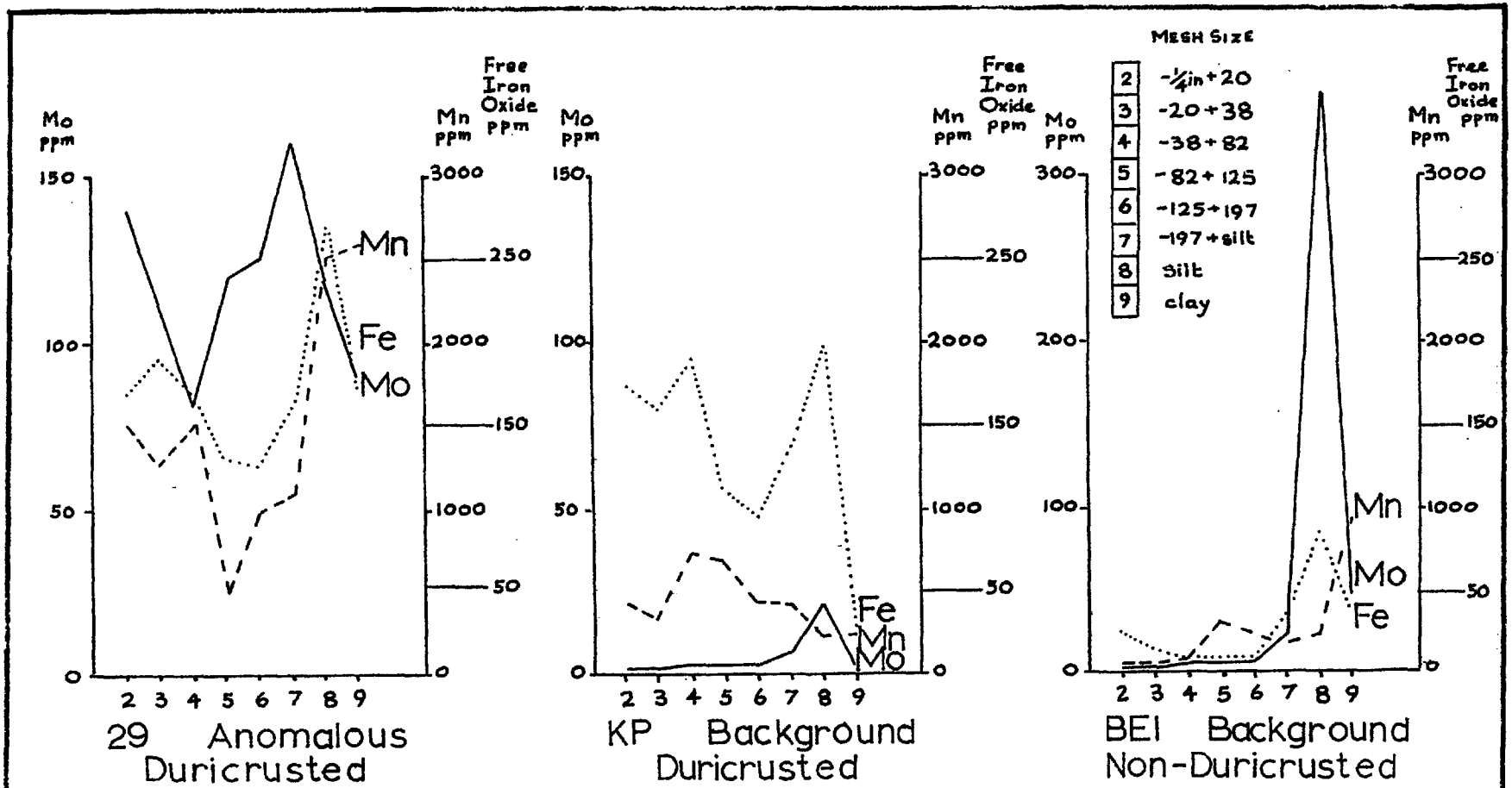


Figure 14. SENDE AREA. Distribution of Molybdenum, Iron and Manganese in Stream Sediment

hydrated oxides of iron would precipitate before those of manganese and thus may have removed most of the molybdenum from solution before the precipitation of the manganese commenced.

The most obvious difference in the distribution in the sediment of manganese and molybdenum is the preferential concentration of manganese in the clay fraction. It has already been noted that the clays contain considerably less iron than the silts, thus it would seem that conditions favourable for the chemical association of manganese with iron and molybdenum do not obtain in the present day drainage environment.

c) The Association of Molybdenum and Organic Matter

In the literature molybdenum has been reported to be associated with organic matter, for instance, in coal and petroleum. However, in the soils at Wankatana there is a negative correlation between the molybdenum tenor and the organic carbon content, (Mather 1959).

Marked accumulation of organic matter is not common in the drainage systems of the Sula Mountains but the very fine material in suspension just above the sediment surface may contain up to 16 percent of organic carbon. An examination has been made of the relationship between molybdenum and organic carbon in material of this type.

By gentle agitation of the water above the sediment, the fine grained material was dislodged and collected on glass fibre filter papers. This material was considerably darker in colour than that brought into suspension by more vigorous agitation of the water and which was collected on Whatman No. 542 cellulose filter papers. This is attributed to the presence of more organic matter in the finest

material and in every case where the 542 filter paper residue could be analysed without risk of contamination from the cellulose, it was found to contain much less organic carbon than the glass filter residue, (Table 31). By contrast the molybdenum content of the 542 filter paper residue is appreciably higher than that of the glass filter paper residue, (Table 32).

The reason for the low molybdenum content of the organic rich material may be related to the dominantly anionic character of humus (Larina et al 1957). Humus would therefore compete with molybdate ions for exchange positions in the sediment and it is significant that the removal of organic matter from stream sediment increased the molybdate sorption capacity, (Mather 1959).

Table 31. Organic Carbon and Iron Content of Suspended Sediment

Material		Site	1	20	W1	W7	W18
Iron ppm x 10^{-3}	542 suspension		22.0	20.0	8.0	14.0	10.3
	Glass filter paper suspension		16.5	14.0	4.0	5.0	5.0
Organic carbon percent	542 suspension		0.02	<0.02	0.31	<0.02	0.09
	Glass filter paper suspension		3.58	4.25	16.5	16.5	16.5

Table 32. Molybdenum Content of Suspended Sediment

Sample Site		1	17	20	26	29	35	F2	DAL	WUS	DAN	BEI
Mo ppm	542 suspension	26	20	18	32	36	2	16	2	4	8	2
	Glass filter paper suspension	15	8	14	14	14	9	14	3	3	4	3

From these data it would appear that there is in the stream sediment, as in the soil at Wankatana, a negative correlation between organic matter and molybdenum. It is possible that this is a significant correlation but it must be emphasised that the organic carbon-low 542 residue has a high iron content and considering the method of collection, probably a high silt content compared to the organic carbon-rich glass filter paper residue, (Table 31). Elsewhere it has been shown that high molybdenum tenors tend to be associated with iron and the silt fractions of the sediment, hence these components may be responsible for the differing molybdenum content of the suspended materials.

On the present data it is only possible to state that there is no marked association of molybdenum with the finely divided organic matter in the stream sediments.

d) Exchangeable molybdenum in stream sediments

It has been suggested in previous sections that sorption of molybdenum by the fine fractions of the sediment might be taking place and that the extent of this activity is related to the presence of free iron oxides.

The principal clay mineral present in the silt and clay fractions of the sediment, as determined by X-ray diffraction analysis, is kaolinite which has a low molybdate sorption capacity at the pH of the stream waters, pH 6.8 (Jones 1957). This is consistent with the low activity of the clay size fractions of the sediment which has already been noted.

However, despite the low sorption activity of the clay minerals present, it was found that a notable proportion (23 - 38 percent) of the total molybdenum content of the minus 82-mesh sediment is exchangeable with phosphate, (Table 33).

Table 33. Exchangeable Molybdenum content of minus 82-mesh Sediments of Sende area

Site	Distance from mineralisation feet	Total Mo ppm	Non-Exchangeable Mo ppm	Exchangeable Mo ppm	Exchangeable Mo percent
35	Background 2,000 upstream	13	10	3	23
F2	At mineralisation	100	72	28	28
29	At mineralisation	80	52	28	38
20	3,000 downstream	52	36	16	27
17	4,000 downstream	50	38	12	24
BEI	Background	2	2	≤ 2	none detected

Iron rich sediments were found to have a considerably higher anion exchange capacity than iron poor sediments, (Table 34), which tends to support the view that in the minus 82-mesh fractions of the stream sediments, iron compounds are chiefly responsible for the sorption effects observed.

Table 34. Anion Exchange Capacity of minus 82-mesh Sediment from Sende area

Site	Free Iron Oxides ppm x 10^{-3}	Exchangeable Molybdenum percent	Anion Exchange Capacity*
29	22.0	38	20.7
F2	16.8	28	19.7
BEI	3.25	None detected	4.7

*Millinols $(H_2PO_4)^-$ per 100 g sample at pH 6.8.

II. The Dispersion of Molybdenum in sediments downstream from Mineralisation

A further examination was made of the relationship between the molybdenum content of the bank soils and sediments downstream from the mineralisation to see if this would account for the observed characteristics of the dispersion train in the drainage system.

1. Duricrust well developed in the catchment area

a) Coarse sediment fraction (plus 82-mesh)

The local background molybdenum content of the coarse fraction of the stream sediment varies from 2 - 50 ppm molybdenum compared with 50 - 140 ppm molybdenum in sediment from streams draining the mineralisation.

Anomalous molybdenum values in the coarse fraction extend over a distance of approximately 5,500 ft. (Site 35 to Site 17, Figure 15a) and are coincident with high metal tenors in this fraction of both freely drained and waterlogged bank soils. The tenor of the sediment is, however, higher than that of the related bank soil. This may be due to the separation of rock fragments having a relatively low molybdenum content from dense molybdenum rich concretions through the elutriating action of the stream water. As a result of the above mechanism the metal rich concretions tend to remain in close proximity to their source whilst the rock fragments move further downstream giving rise to a relative increase in the metal tenor of the sediment as compared to the soil near mineralisation.

Alternatively, since molybdenite bearing dykes cross the stream channel between sample sites 26 and 29 (Wilson and Marmo 1959) soil carrying high metal tenors may occur between these sample sites and give rise to the peak molybdenum values in the sediment.

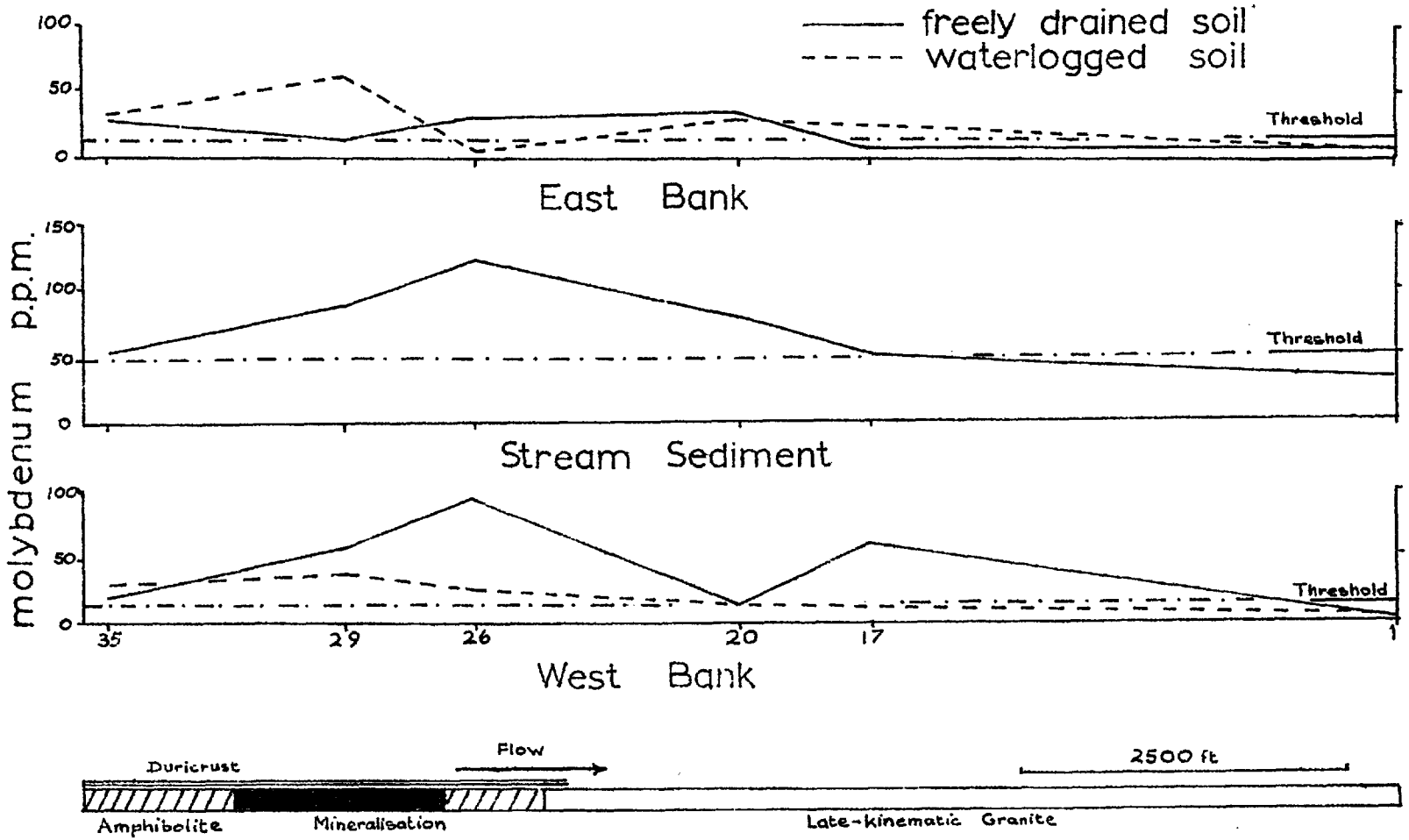


Figure 15a. Downstream Distribution of Molybdenum in the +82 mesh Fraction of River Sende Sediments and Bank Soils

The dispersion of the coarse sediment is of a mechanical nature. Downstream from the anomaly peak the tenor of the sediment falls to local background values over a distance of 10,000 ft. Over almost the whole of this distance the drainage bedrock is barren late-kinematic granite. The granite soils are unduricrusted and easily transported downslope by soil creep hence it might be expected that the metal rich sediment would be rapidly diluted by quartz and felspar fragments from the granite. That this is not so is evident from Figure (15a).

It has been suggested previously in the section on the distribution of molybdenum in bank soils that deposition of molybdenum rich alluvial material in the stream banks is taking place downstream from the mineralisation. This is considered to be the cause of the weakly anomalous tenor of the east bank of the stream for some distance below the mineralisation and for the isolated rise in the molybdenum content of the soil of the west bank 5,000 ft. below the mineralisation, (Site 17, Figure 15 a). The reworking of alluvial material may be largely responsible for the maintenance of a high metal content in the stream sediment below the mineralisation.

In addition, the resistance of the metal rich duricrust fragments to mechanical abrasion in the drainage system will also contribute to the persistence of anomalous coarse sediment for a considerable distance downstream from the mineralisation.

Tributary streams entering the Sende downstream from the mineralisation were nearly dry at the time of sampling, hence the movement of coarse material into the main drainage is at a minimum and dilution of the mineralised sediment in the main drainage from this source of barren material will therefore be negligible.

Furthermore, attention has been drawn to the disturbance of the banks of the Sende channel by gold mining operations. As a result of these workings banks of large boulders occur in certain stretches of the Sende channel which protect the stream banks against undercutting and thus inhibit bank collapse. In addition the movement of colluvial material into the drainage system is restricted by this material being trapped between the boulders. The nett result is that the mineralised sediment does not undergo the same degree of dilution by barren bank material as would be the case if the boulder banks were absent.

b) Fine sediment fraction (minus 82-mesh)

The local background for the minus 82-mesh fraction of the sediments is 2 - 15 ppm molybdenum, compared to 60 ppm at the anomaly peak.

Anomalous metal values (greater than 15 ppm) extend for over two miles downstream from the mineralisation and the strongest anomaly is coincident with the highest molybdenum tenors in the fine fraction of the bank soils, (Figure 15b).

Like the coarse sediment fraction, the molybdenum tenor of the fine sediment is notably higher than that of the bank soils.

The molybdenum in the fine sediment is considered to be derived from a number of sources. A large contribution is made by bank material entering the drainage through erosion of the banks by stream water. The molybdenum bearing material contributed by the banks may be of three principal types, a) alluvial material deposited by the stream to form its banks, b) colluvial soil derived from a mineralised area and containing anomalous amounts of molybdenum and

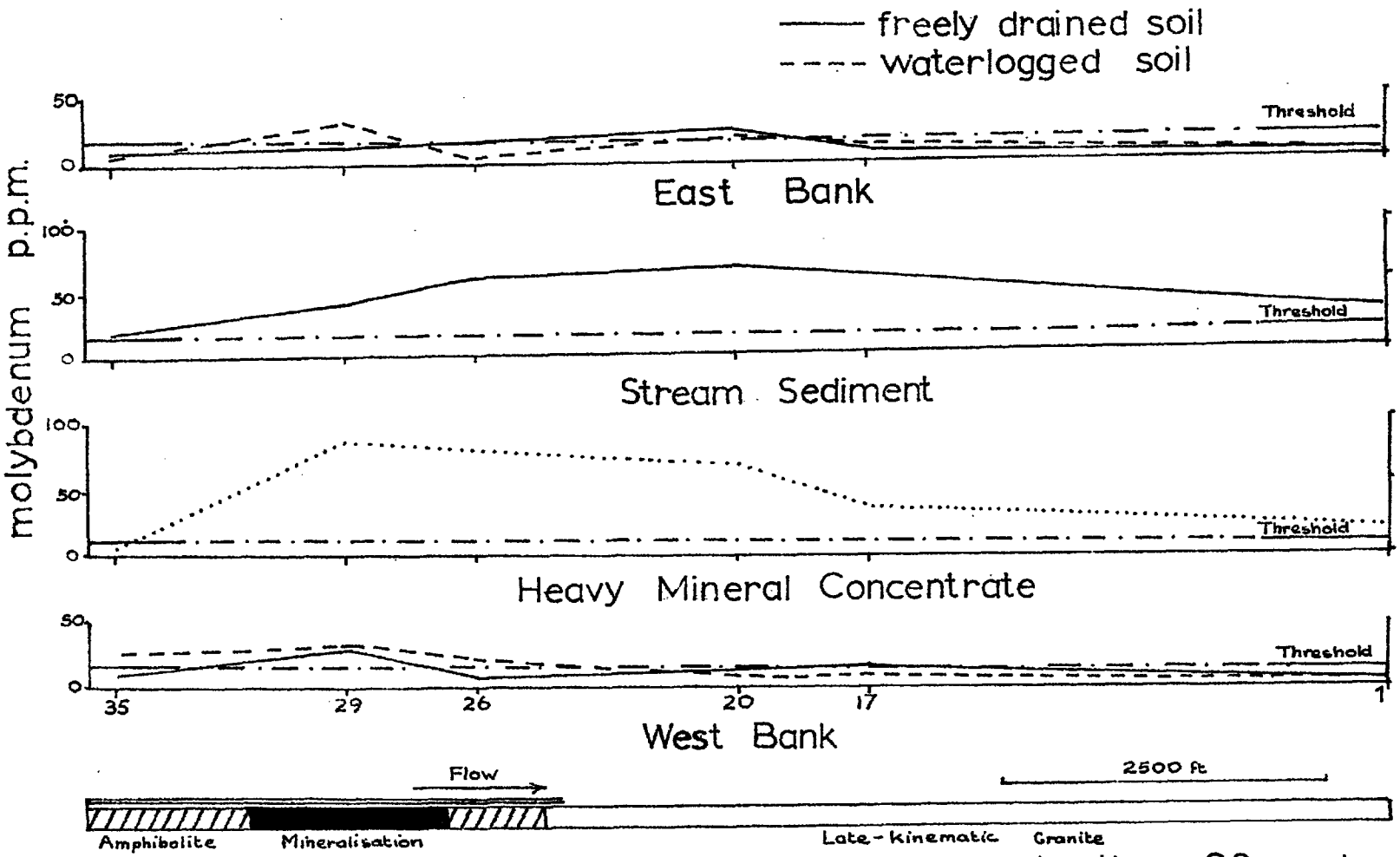


Figure 15b. Downstream Distribution of Molybdenum in the -82 mesh Fraction of River Sende Sediments and Bank Soils

c) the fine fractions of the waterlogged soil which contain molybdenum sorbed from groundwater solutions.

Consideration of Figure (15b) indicates that erosion of the bank soils alone cannot account for the high tenor of the fine sediment unless concentration of the molybdenum rich component of the material takes place in the drainage system. The heavy mineral component of the fine sediment has a high metal content hence the accumulation of this sediment component due to the removal of the lighter barren material by elutriation might possibly account for an increase in the tenor of the fine sediment as compared with the bank soil. However, insufficient data are available on the distribution of molybdenum in the mineral species present in the stream sediment to make any more definite statement on this possibility.

Alternatively, molybdenum may be entering the sediment from other sources in addition to the bank soils. It is suggested that groundwater entering the drainage system may not be completely stripped of its metal content by the waterlogged bank soils and that further reduction of the metal concentration in solution takes place in the drainage system, by precipitation and sorption reactions, as a result of which the molybdenum tenor of the fine sediment is increased.

The higher molybdenum content of the fine fractions of the sediment as compared to those of the waterlogged soil may reflect the greater sorption efficiency of the oxidised, freshly precipitated hydrated iron oxides in the drainage system as compared to the possibly partially reduced oxides in the fine fractions of the waterlogged soil.

The heavy mineral component of the fine sediment fraction contains a maximum of 80 ppm molybdenum compared with a background range of 2 - 15 ppm. The dispersion of this dense sediment component, which consists chiefly of magnetite, is largely mechanical, although it may possess some sorption activity by virtue of its fine particle size. Hence the dispersion train of this sediment component presents a similar aspect to the mechanically dispersed coarse sediment, but contrasts with that of the fine sediment as a whole. This is considered to support the suggestion that the dispersion of the fine sediment fraction as a whole is not entirely mechanical but is also controlled by sorption reactions.

2. Duricrust poorly developed or absent in the catchment

a) Coarse sediment fraction (plus 82-mesh)

The molybdenum content of the coarse fraction of the Wankatana sediment, in distinction to that of the Sende, gives virtually no indication of the presence of mineralisation, (Figure 16). The lack of molybdenum in the coarse fraction is considered to be due to this material being composed chiefly of barren quartz from the granite and duricrust fragments from the barren catchment area upstream.

b) Fine sediment fraction (minus 82-mesh)

The fine fraction of the Wankatana sediment exhibits a short lived low contrast anomaly in the immediate vicinity of the mineralised granite, compared with the extensive molybdenum dispersion train carried by this material in the Sende drainage system.

The heavy mineral fraction of the fine Wankatana sediment also contrasts with this fraction in the Sende sediments in carrying negligible amounts of molybdenum.

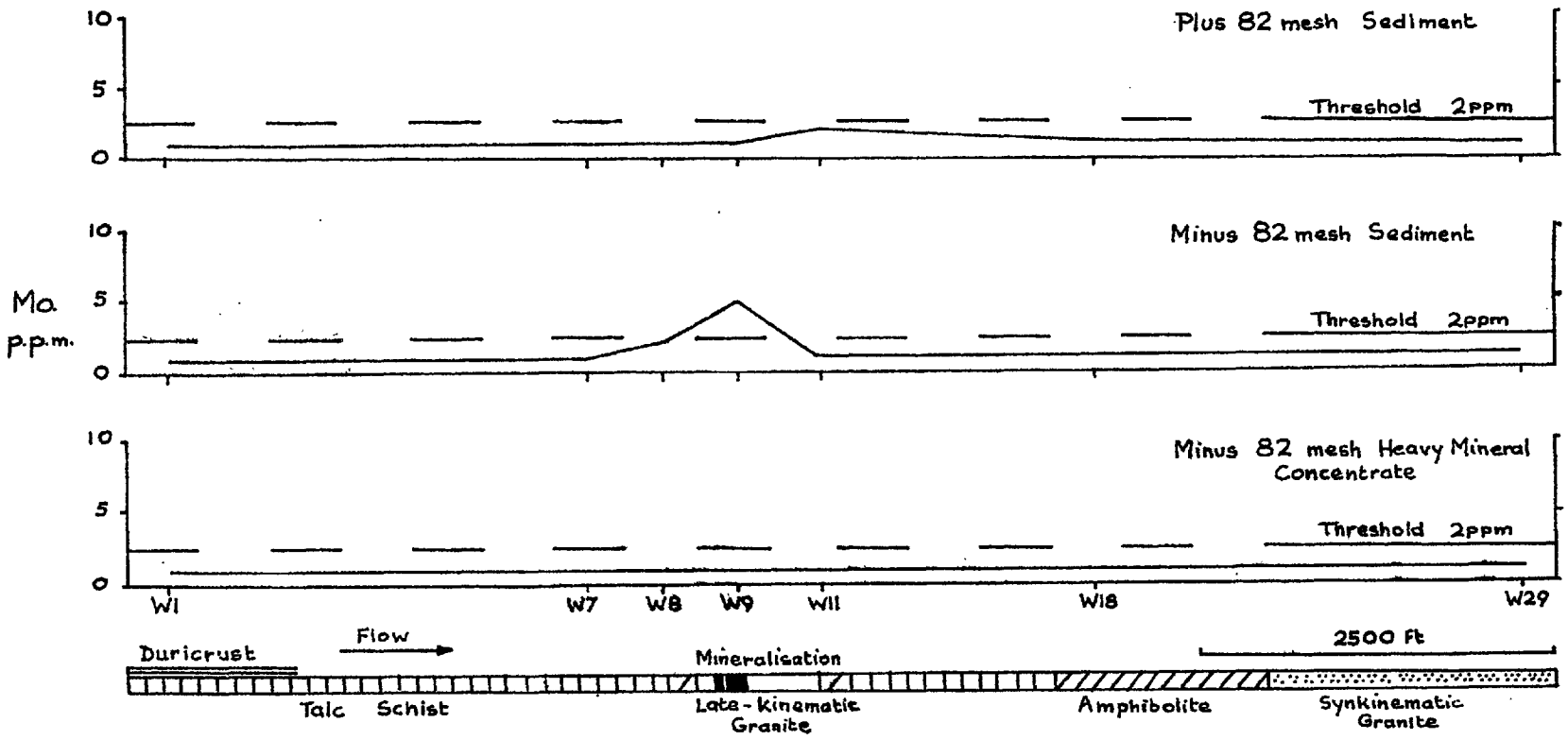


Figure 16. Downstream Dispersion of Molybdenum in River Wankatana Sediment

Owing to the rocky nature of the channel margins no extensive collection of bank soil material was possible and where this was obtained it carried only 2 - 3 ppm molybdenum.

The area of soil containing more than 50 ppm molybdenum is only about 7,000 square yards in extent as compared with 0.2 square miles of soil carrying over 50 ppm molybdenum overlying the Sende mineralisation. In addition, the ratio of the area of unduricrusted barren soil, i.e. potential diluent, in the catchment upstream from the Sende mineralisation to the area of anomalous soil is only 12 : 1 as compared to 3,500 : 1 at Wankatana.

The potential of the mineralised granite for supplying anomalous soil to the stream banks and drainage system is, therefore, somewhat limited and when such material does enter the drainage system it is rapidly diluted by the large volume of barren sediment carried by the Wankatana River. This is considered to be the chief reason for the lack of development of an extensive drainage train in the Wankatana sediment.

3. Variation in the Molybdenum Content of sediment size fractions downstream from mineralisation

In the previous section the variation in the molybdenum content of various sediment components downstream from the mineralisation was considered and it was suggested that, in the fine fractions of the sediment, the maintenance of molybdenum tenor may be due to sorption activity. A closer examination was made therefore of the variation of molybdenum distribution between the particle size fractions of the sediment downstream from mineralisation in an attempt to clarify this point. As a result of this study, further marked

differences in the metal dispersion behaviour in the Sende and Wankatana drainage systems have been revealed, (Figures 17a and 17b).

a) Duricrust well developed in the catchment

The general form of the molybdenum distribution in the sediment, as indicated by the plus and minus 82-mesh fractions discussed in the previous section, is confirmed by the more detailed work, (Figure 17a).

The predominance of the plus 20-mesh fraction as the principal host of the metal is emphasised and the gradual reduction in tenor and bulk of this fraction downstream is consistent with the factors already discussed, namely the reworking of alluvial banks, lack of dilution by barren soil and sediment downstream from the mineralisation and the resistance to comminution of the coarse duricrust particles.

In the fine sediment (minus 82-mesh) 10,000 ft. downstream from the mineralisation about 50 percent of the molybdenum is associated with free iron oxides, as compared with 60 - 80 percent at the mineralisation, (Site 29), hence it seems likely that sorption of metal from the stream waters may take place throughout the length of the anomaly.

b) Duricrust poorly developed or absent in the catchment

The very coarse fractions (plus 20-mesh) of the Wankatana sediment carry only very low tenors of molybdenum of the order of 2 ppm, rising to 5 ppm about 2,000 ft. downstream from the mineralised granite, (Figure 17b). This small rise in the molybdenum concentration in the vicinity of the mineralisation remains undetected when the plus 82-mesh fraction as a whole is analysed. The molybdenum in the very coarse material may occur in rock fragments or ironstone concretions which are sparsely distributed in the soil profile over the mineralisation.

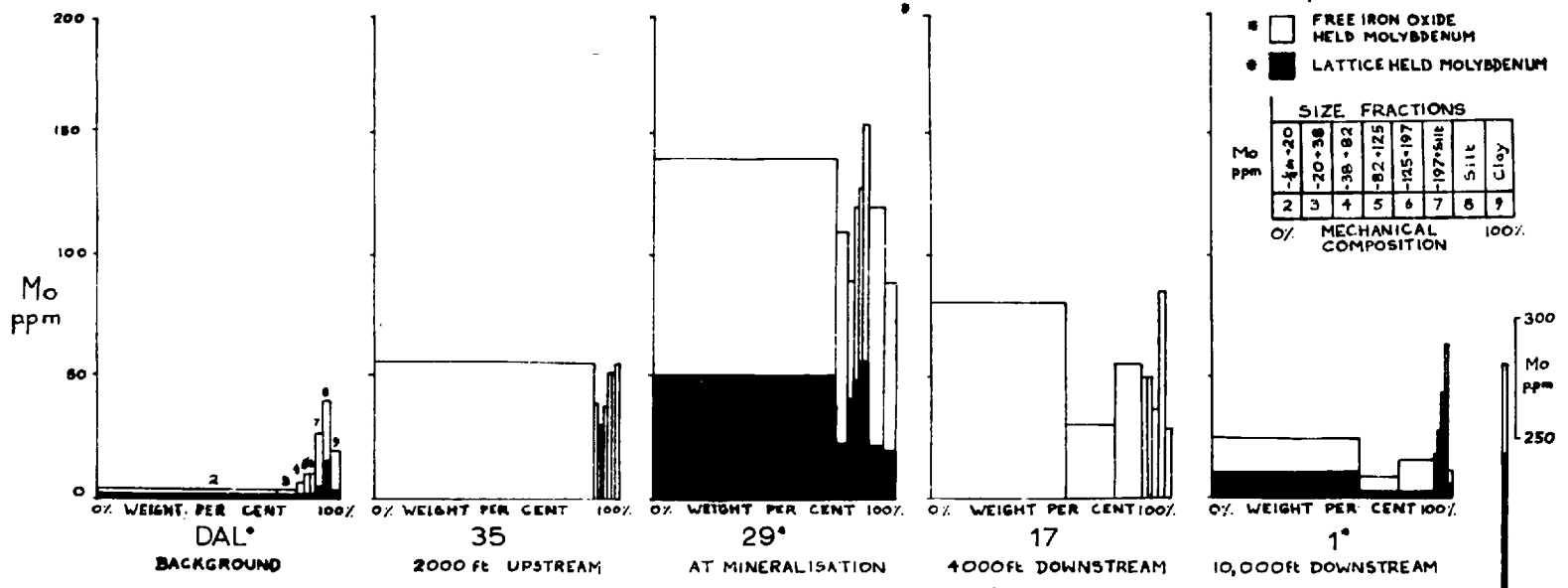


Figure 17a. Distribution of Molybdenum in River Sende Sediment Downstream from Mineralisation

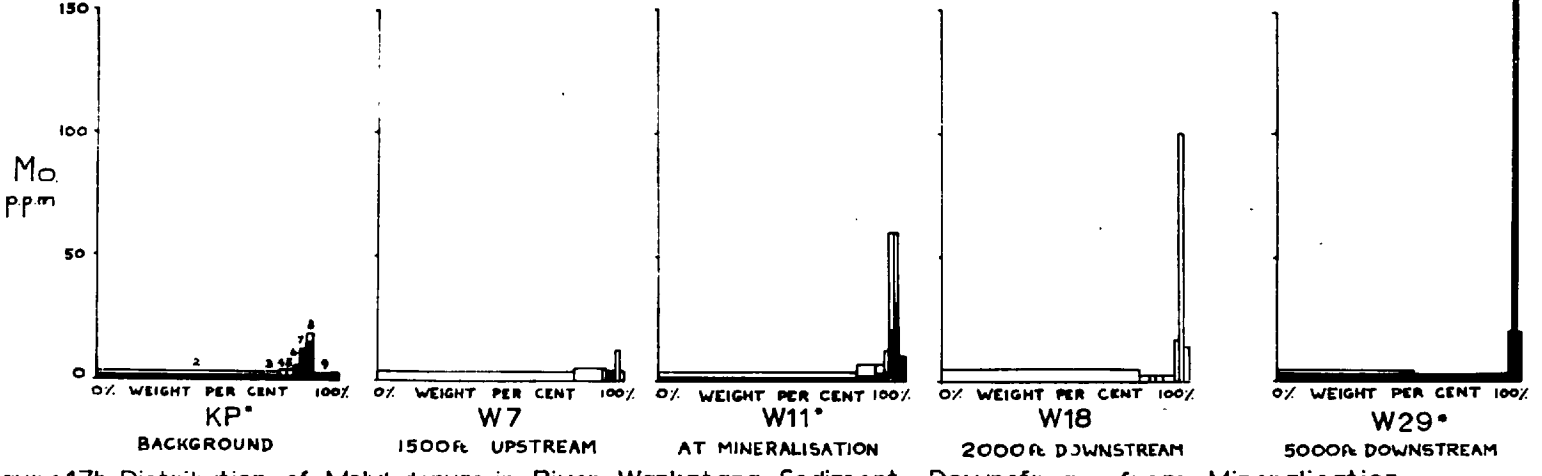


Figure 17b. Distribution of Molybdenum in River Wankatana Sediment Downstream from Mineralisation

In contrast to the metal distribution, as represented by the minus 82-mesh sediment as a whole, of virtually no departure from background tenors in the sediments downstream from the granite, the more detailed analyses reveal a rise in molybdenum tenor of the silt fraction to 280 ppm at a distance 5,000 ft. beyond the mineralisation, (Figure 17b).

The reason why analysis of the whole minus 82-mesh fraction did not indicate this very high molybdenum concentration in the silt is considered to be dilution of this fraction, which is of insignificant bulk, by the other comparatively barren components of the minus 82-mesh sediment fraction.

The rise in metal tenor downstream could be attributed to sorption of molybdenum by the active silt fraction, as may be the case in the Sende catchment, or to the presence of a silt sized molybdenum bearing mineral derived from the mineralised granite. Examination of the partition of the metal between silicate minerals and free iron oxides in the sediment 5,000 ft. below the mineralisation, supports the latter conclusion, since most of the molybdenum is held in mineral lattices in both silt and clay fractions, (Figure 17b).

In seeking to identify the possible mineral lattices in which the molybdenum may be held, it is of interest to note that the molybdenum-rich silt and the molybdenum-poor clay fractions have a similar mineralogical composition. X-ray diffraction analyses of these materials indicate that the former consists mainly of kaolinite, gibbsite and felspar and the latter of kaolinite, gibbsite and illite. It must be emphasised, however, that owing to the poor crystallinity of the material no reliable quantitative estimate of the relative

amounts of the mineralogical components is possible and that their identification is subject to considerable difficulty.

The possibility that felspar is the host of the molybdenum meets with some support from the literature. A notable proportion of molybdenum occurring in acidic rocks is contained in the felspar and Kuroda and Sandell (1954) go so far as to say that the element is almost certainly present in the structure of felspars, particularly in granites. This is supported by the data of Studenkova et al (1957) who found that 79 percent of the total molybdenum of a biotite granite in the Caucasus was held by the felspar.

However, in the absence of more evidence it is not possible to affirm that felspar is the mineral responsible for the high silt tenors and the identity of the host of the molybdenum remains uncertain.

The very high tenor of the silt fraction may be due to comminution of coarse molybdenum rich particles to silt size, below which no further reduction in size takes place by mechanical means owing to the cushioning effect of the water on the impact of the particles. It will be noted that at the mineralisation a considerable proportion of the total molybdenum content of the sediment is carried by the minus 38 plus clay size fractions, whereas 5,000 ft. downstream only the minus 197-mesh fractions carry any appreciable amount of metal and this is mainly in the silt, (Figure 17b). It is considered, therefore, that comminution of the molybdenum bearing sediment in the drainage system may be responsible for the accumulation of molybdenum in the silt size fraction. The distance travelled by the sediment in the drainage system will thus be important in controlling the amount of comminution of the sediment particles and the concentration of molybdenum in the silt fraction.

It may be recalled that a regional background sediment sample from a late-kinematic granite catchment (Site BEI in Figure 11) also carried an exceptionally high molybdenum content in the silt fraction compared with very low values in all the other fractions. This suggests that a high molybdenum content in the silt fraction of sediments may merely indicate the presence of late-kinematic granite in the catchment. Insofar as the late-kinematic granite appears to have a close association with molybdenum mineralisation, (the BEI granite is not known to be mineralised but is regarded by Wilson and Marmo (1959) as the possible source of the Sende mineralisation and a small molybdenite deposit at Mapoke is possibly related to an adjacent late-kinematic granite pegmatite), the discovery of high molybdenum tenors in silt sized sediment may indicate the presence of mineralisation associated with an acid intrusive.

D. The Dispersion of Molybdenum in the Stream Waters of the Sula Mountains

Soluble metals are leached from an orebody and its oxidising overburden by groundwater and percolating rainwater. Under suitable conditions, such metals may remain in solution for an appreciable time in the surface waters draining the deposit. Using ion exchange resins, Mather detected very small amounts of molybdenum in the waters of both the Sende and Wankatana Rivers but only in the immediate vicinity of mineralisation.

During the present work, further investigations have been carried out both in the areas studied by Mather and at greater distances from mineralisation. Using the more sensitive solvent extraction technique developed for the purpose, an extended

anomalous drainage train of soluble molybdenum has been detected in the waters downstream from the Sende mineralisation, whilst a less well defined anomaly is present in the Wankatana stream waters.

I. The Physical and Chemical Characteristics of the Field Area Waters

1. Temperature

Measurements of water temperature made in conjunction with pH and Eh observations gave values between 16°C and 26°C with an average of 22.5°C. As might be expected the water temperature varies according to the time of day and the amount of shade over the channel. The higher temperature range, compared with the waters of temperate regions, is important in its acceleration of chemical reactions and promotion of bacterial activity.

2. Redox Potential and Hydrogen Ion Concentration

Measurements were made of the redox potentials and hydrogen ion concentration of the stream waters since these are important in their control of the nature and the amount of dissolved ionic species which may be present.

Table 35. Molybdenum Study Areas. Water Quality Data.

Site	Rock Type	Distance from Mineralisation feet	pH	Eh +mv	HCO_3^- ppm	SO_4^{--} ppm	Oxine Mo ppb (Av.)	Oxine Fe ppb (Av.)
Regional Background Sites								
WA	A	15,000	-	290	36.5	0.40	0.07	82
Y5	A	5,000	6.4	290	9.8	0.06	0.06	-
BEI	LKG	5,000	6.9	270	7.9	0.04	0.04	137
HER	SKG	20,000	6.7	230	10.0	0.08	0.03	437
SKG	SKG	5,000	6.8	360	12.0	0.16	0.04	355
Sende Area. Local Background Sites								
DAL	AD	Tributary	6.7	270	17.5	0.28	0.03	48
WUS	AD	Tributary	6.9	300	3.6	0.04	0.07	143
F9	AD	Tributary	6.5	300	5.5	0.16	0.06	148
35	AD	2,000 upstream	6.7	300	8.9	0.04	0.04	124
Sende Area. Anomalous Sites.								
F2	AD	At mineralisation	6.8	270	6.9	0.08	0.10	117
29	AD	At mineralisation	6.9	250	7.8	0.05	0.06	193
26	AD	1,000 downstream	6.8	200	6.9	0.07	0.12	175
20	LKG D	4,000 downstream	7.0	290	8.2	0.08	0.13	293
17	LKG	5,000 downstream	6.7	250	8.8	0.07	0.10	259
DAN	LKG	Tributary	6.2	200	7.9	0.04	0.12	393
1	LKG	10,000 downstream	7.0	270	8.5	0.07	0.13	433
Wankatana Area. Local Background Sites								
W1	TS	5,000 upstream	6.9	300	12.2	0.24	0.08	176
W11	LKG	1,000 downstream	7.0	260	17.6	0.28	0.07	115
W29	SKG	5,000 downstream	7.5	270	19.3	0.08	0.04	193
Wankatana Area. Anomalous Sites								
KP	AD	15,000 upstream	-	270	12.7	0.28	0.11	190
W7	TS	1,000 upstream	7.4	270	18.5	0.16	0.10	196
W9	LKG	At mineralisation	6.6	270	18.5	0.28	0.11	192
W18	A	2,000 downstream	7.5	250	20.2	0.04	0.10	259

A - Amphibolite. D - Duricrust. LKG - Late-kinematic Granite

SKG - Synkinematic Granite. TS - Talc Schist.

The pH of the streams investigated varied from 6.2 - 7.5 with an average of 6.8 and the redox potentials from 0.2 - 0.3 volts, (Table 35). Under these conditions, molybdenum will be present in the waters as the molybdate anion, MoO_4^{--} (Krauskopf 1955). Very little soluble iron will be present, the stable iron species being solid ferric hydroxide, e.g. precipitated hydrated iron oxides, and no free carbonate ions will exist, all having been converted to bicarbonate. These theoretical conclusions have been substantiated by analyses of the waters for the ions mentioned.

No correlation could be established between Eh, pH and bedrock lithology or bicarbonate content.

3. Dissolved Solids Content

The values for the total dissolved solids content of the waters examined in the present study agree fairly well with Mather's data (Table 36), and are not atypical of surface waters from regions of high precipitation which may contain less than 50 ppm of dissolved salts, (Hem et al 1959). Moreover, since the samples were collected towards the end of the dry season, the concentration of dissolved salts may be expected to be at a minimum.

Table 36. Summary of Dissolved Solids Data for Sende and Wankatana Waters

	Mather's Data (Evaporation)	Elliott's Data	
Stream	Wankatana	Wankatana	Sende
Total dissolved solids ppm	38 42	Not determined	10, 20, 21, 22, 20, 30. Evaporation
Sulphate ppm	1.0 2.0	0.04 - 0.28. Av. 0.21 Ion Exchange	0.04 - 0.28. Av. 0.08 Ion Exchange
Bicarbonate ppm	10.4 7.8	12.0 - 20.2 Av. 18.6 Titration	3.6 - 17.2 Av. 8.0 Titration
Iron ppb	40 120	66 - 335 Av. 138 Solvent extraction	48 - 450 Av. 187 Solvent extraction 80 - 900 evaporation

a) Sulphate Content

The values obtained for the sulphate concentration in the stream waters examined by both field analysis and ion exchange methods are considerably less than 1 ppm (Table 35), despite the fact that the streams drain oxidising sulphide deposits. Furthermore, there is no systematic relationship of the sulphate values with mineralisation as has been noted in other parts of the world, (Belyakova 1958).

The low concentration of sulphate ions is considered to be related to the fact that the samples were collected at the end of the dry season when the volume of groundwater in the zone of oxidising sulphides would be low, thus reducing the contribution of sulphate from the groundwater to the surface water. Moreover, in the absence of rain there is no contribution of sulphate to the drainage by water percolating through the soil in the zone of oxidation.

b) Bicarbonate Content

Like sulphate, the bicarbonate content of barren streams does not appear to differ regularly from that of waters draining mineralisation, (Table 35).

The bicarbonate content of the surface waters is closely related to the predominant rock type in the catchment area and to the presence or absence of duricrust, (Table 37).

Table 37. Relationship between Bicarbonate Content of Stream Water and Catchment Area Rock Type

Predominant Rock	Amphibolite	Talc Schist	Talc Schist	Granite
	Duricrusted	Partly Duricrusted	Little Duricrust	Not Duricrusted
Bicarbonate ppm	3.6 - 17.5	12.2 - 20.2	24.1 - 53.2	3.9 - 12.0
Average	8.2	14.3	39.3	8.5
No. of samples	10	7	9	5

The effect of duricrust in reducing the concentration of soluble ions such as bicarbonate and sulphate in the stream waters is ascribed to the relative impermeability of the indurated surface which minimises leaching by percolating rainwater and also the possibility that most of the soluble ions have already been removed from this mature latosol profile. Hence it is not surprising that the highest bicarbonate values are observed in the carbonate rich talc schist catchment where duricrust is absent.

c) Iron Content

No soluble iron could be detected in the stream waters examined at the sample site by a direct test with a sensitivity of 1 ppm iron. However, the iron contents of oxine extracts of the waters contain from 48 - 437 ppb iron (ppb = micrograms per litre), (Table 35).

It is considered that the oxine reagent will only extract ionic metals hence these data are taken to represent the ionic iron concentration of the waters.

The results for iron concentration obtained by evaporation range from 80 - 900 ppb and are considerably higher than the oxine extraction values, a fact which may reflect incomplete extraction of iron by oxine at pH 4.8 or that a large proportion of the soluble iron is in a form immune to extraction, e.g. non-ionic complexes.

No correlation is apparent between Eh, pH and oxine extractable iron values obtained for the waters.

d) Molybdenum Content

The oxine extractable molybdenum contents of barren stream water ranges from 0.03 - 0.07 ppb (8 samples) and on the basis of these data, molybdenum concentrations in excess of 0.08 ppb are considered to be anomalous, (Table 35). The anomalous values range from 0.08 - 0.13. Since the mean contrast between background and anomalous values is only of the order 2 : 1 and the reproducibility of the method ($\pm$ 100 percent at the 95 percent confidence level) is poor, anomalous concentrations of metal in the vicinity of mineralisation can only be distinguished with difficulty.

In comparison with the results for soluble molybdenum obtained by Mather, those of the writer are considerably lower, (Table 38). This may, in part, be explained by the fact that Mather used coarser filter paper (Whatman No. 40, pore size 2.1 - 2.8 μ) than the 542 filter paper (pore size 1.9 - 2.5 μ) used in the present work, which would allow more clay particles to pass into the water sample.

Table 38. Molybdenum Content (ppb) of Stream Waters in the Vicinity of Mineralisation

	Mather's Data		Elliott's Data	
River	Wankatana	Sende	Wankatana (W11)	Sende (29)
Evaporation	0.4, 0.3			0.01
Ion exchange		0.08, 0.16		0.01
Solvent extraction			0.07 (Lab extr.) 0.07 (Field extr.)	0.02 (Lab extr.) 0.06 (Field extr.)

A comparison of the molybdenum content of the stream waters of the field areas with that of waters from other parts of the world (Table 39), shows that the molybdenum concentrations encountered in the present study are considerably lower than those in both more temperate and more arid climates.

Location	Mine Water	Ground Water	Spring Water	Surface Water	Sea Water	Reference
Europe			130	21		Ter Meulen 1932
Japan			0.6	0.5	9.8-12.2	Sugawara et al 1959
Japan			70-160			Kuroda 1940
Japan	0-100					Hayashi and Yamata 1957
U.S.S.R. Central Kazakhstan	5-80			5 - 10		Belyakova 1958
U.S.S.R. Armenia	70-8000			1-1660		Dolukhanova 1956
U.S.S.R. Armenia			15-70	20		Malyuga 1958
U.S.S.R. Not known	300-700		0-270			Novokhatskii and Kalinin 1939
U.S.A. Nevada		6-200		60		Erickson and Marranzino 1960
U.S.A. General		0-270			0.1-0.5	Kehoe et al 1944

Table 39. Molybdenum content (ppb) of Natural Waters.

e) Organic Matter Content

No measurements have been made of the nature and amount of soluble organic matter present in the waters of the field areas.

II. The Dispersion of Soluble Molybdenum from Mineralised Areas.

1. Non-ionic Metal

Owing to the exceedingly low concentrations of molybdenum detected in the waters of the Sende and Wankatana drainage systems, no data were obtained on the amounts of soluble non-ionic molybdenum present. A suitable method for analysing directly this form of the metal has yet to be developed; most results for other metals in this form, e.g. copper, are obtained by the difference between "total" and "ionic metal" values. Even this method was inapplicable in the present study.

However, it seems reasonable to assume that some molybdenum, in the form of non-ionised complexes, may be present in the drainage system in view of the readiness with which molybdenum forms such compounds (Martell and Calvin 1953).

2. Ionised Metal

The presence of ionised molybdenum compounds in the waters of the Sula Mountains has been revealed by the results obtained by Mather and the writer using ion exchange and solvent extraction techniques.

The anomalous concentrations of soluble molybdenum detected in the stream waters are considered to be the result of metal bearing groundwaters entering the surface drainage system and also possibly to the solution of molybdenum from anomalous sediments.

The concentration of soluble metal carried by surface water depends on the capacity of the water to assimilate it. If, because of its pH, Eh and dissolved solids condition, the surface water is saturated with respect to the incoming metals, then precipitation of the metals takes place in the surface drainage system.

Alternatively, if the surface water is undersaturated with respect to the incoming metals, then they pass into the surface drainage in solution and cause a rise in the metal concentration of the stream waters. The extent of the rise in metal content is limited by a) the metal content of the inflowing water, b) the saturation capacity of the water for the metal involved, as defined in terms of its pH, Eh and dissolved solids condition and c) the sorption activity of the stream sediments and bank soils.

The concentrations of soluble molybdenum and iron detected in the Sende and Wankatana stream waters will be discussed in the light of the above factors.

a) River Sende

Anomalous molybdenum values (greater than 0.08 ppb) are found in the Sende river waters for over two miles downstream from the mineralisation, (Figure 18). Only one sample was collected at a greater distance, approximately four miles downstream, and the molybdenum content of this water was in the background range. The anomalous train of soluble molybdenum extends, therefore, between two and four miles beyond the mineralisation.

The highest oxine extractable metal values (i.e. soluble metal), are found about half a mile downstream from the outcrop of the mineralisation, (Figure 20), below which, after a fall in concentration, the tenor is maintained at an anomalous level for over a mile.

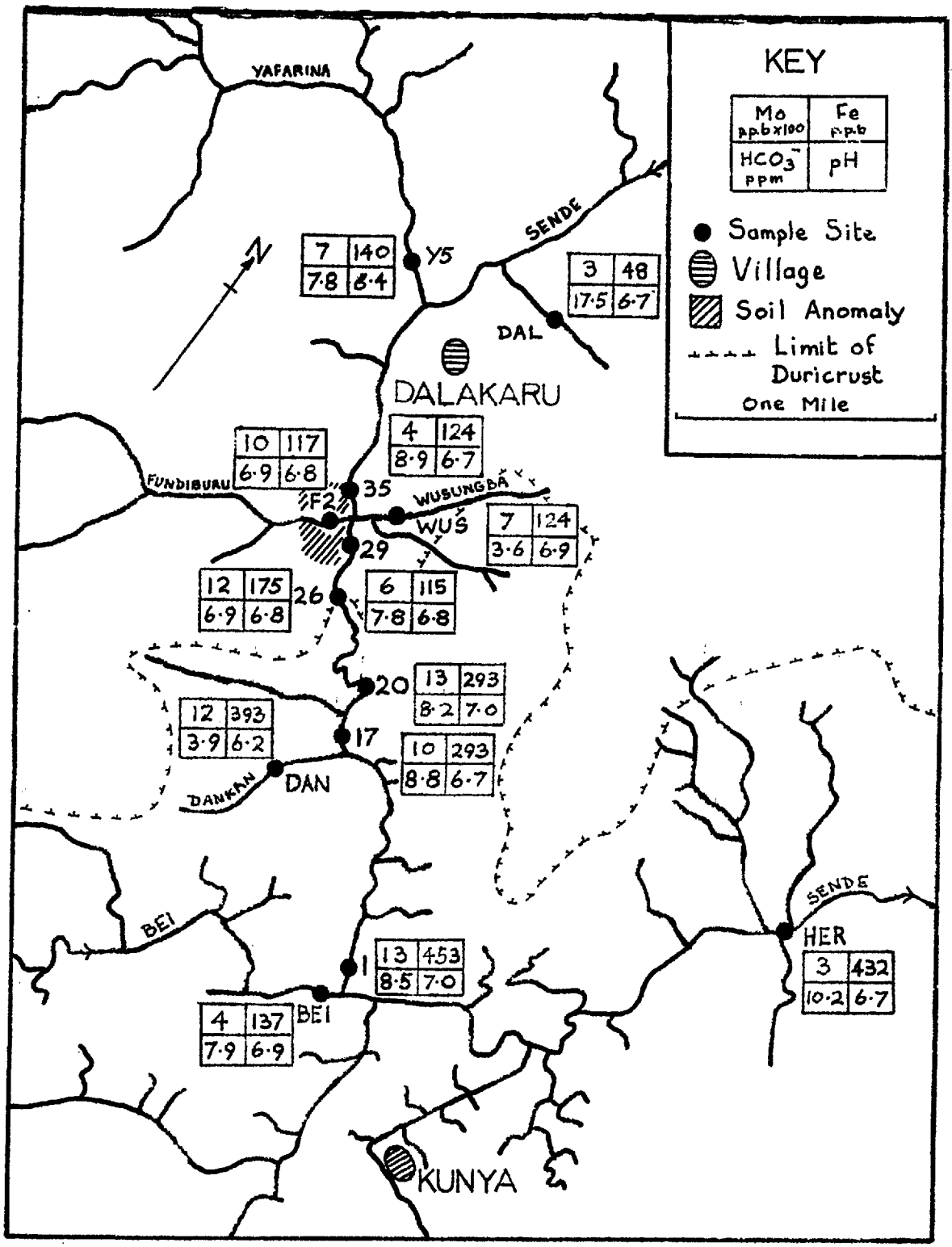


Figure 18. SENDE AREA Oxine Extractable Molybdenum and Iron in Stream Water

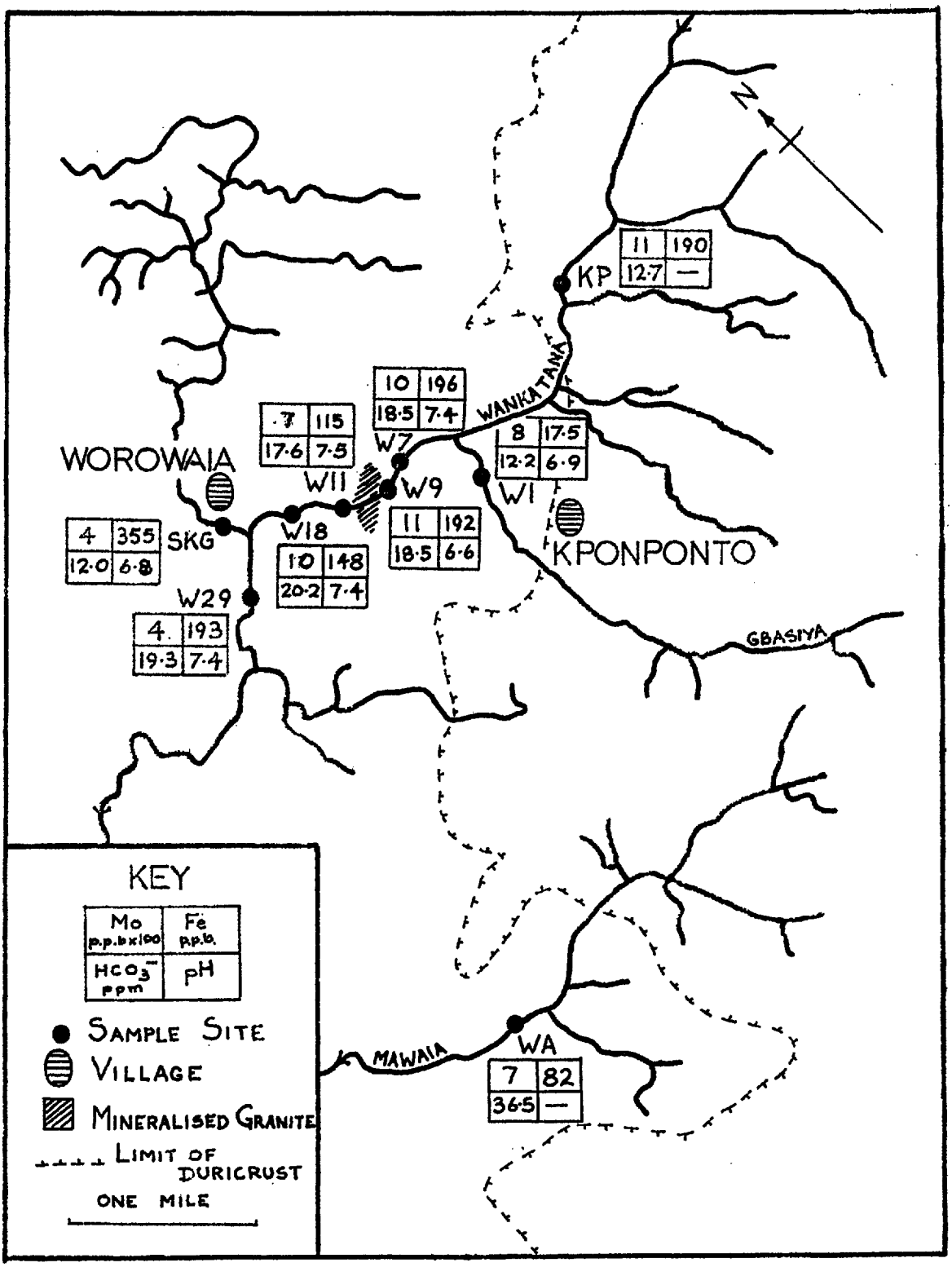


Figure 19. WANKATANA AREA Oxine Extractable Molybdenum and Iron in Stream Water

The coincidence of high molybdenum tenors in the fine fractions of the sediments and waterlogged bank soils with the zone of high soluble molybdenum values in the stream waters suggests than in the presence of a supply of soluble molybdenum, the element may be removed from solution by sorption reactions by fine sediment and soil particles, as proposed in the previous sections and that this mechanism may be limiting the concentration of soluble metal in the stream waters.

The metal tenor of the water downstream from the peak values falls abruptly. The reason for this is not known but may be due to analytical error, the general trend downstream being towards a rise in iron concentration and the maintenance of an anomalous molybdenum concentration. The lack of dilution of the anomalous water over such a considerable distance, nearly 10,000 ft. calls for further comment.

Since the granite bedrock of the stream in its lower reaches is not known to be mineralised, has a low iron content and leaching of the unconsolidated soil by rainwater was not taking place, the most likely source of the iron and molybdenum is considered to be the mineralised, iron rich amphibolite area upstream. The surface waters of this area carry a low soluble iron content, possibly due to precipitation and sorption reactions, hence the possibility of groundwater from the amphibolite area entering the drainage in the lower reaches must be considered.

Owing to the very slow accumulation of water in pits dug for the purpose of collecting groundwater, departure from groundwater characteristics takes place, due to oxidation and flocculation of colloidal particles. Hence no data directly related to the metal content of the groundwater were obtained.

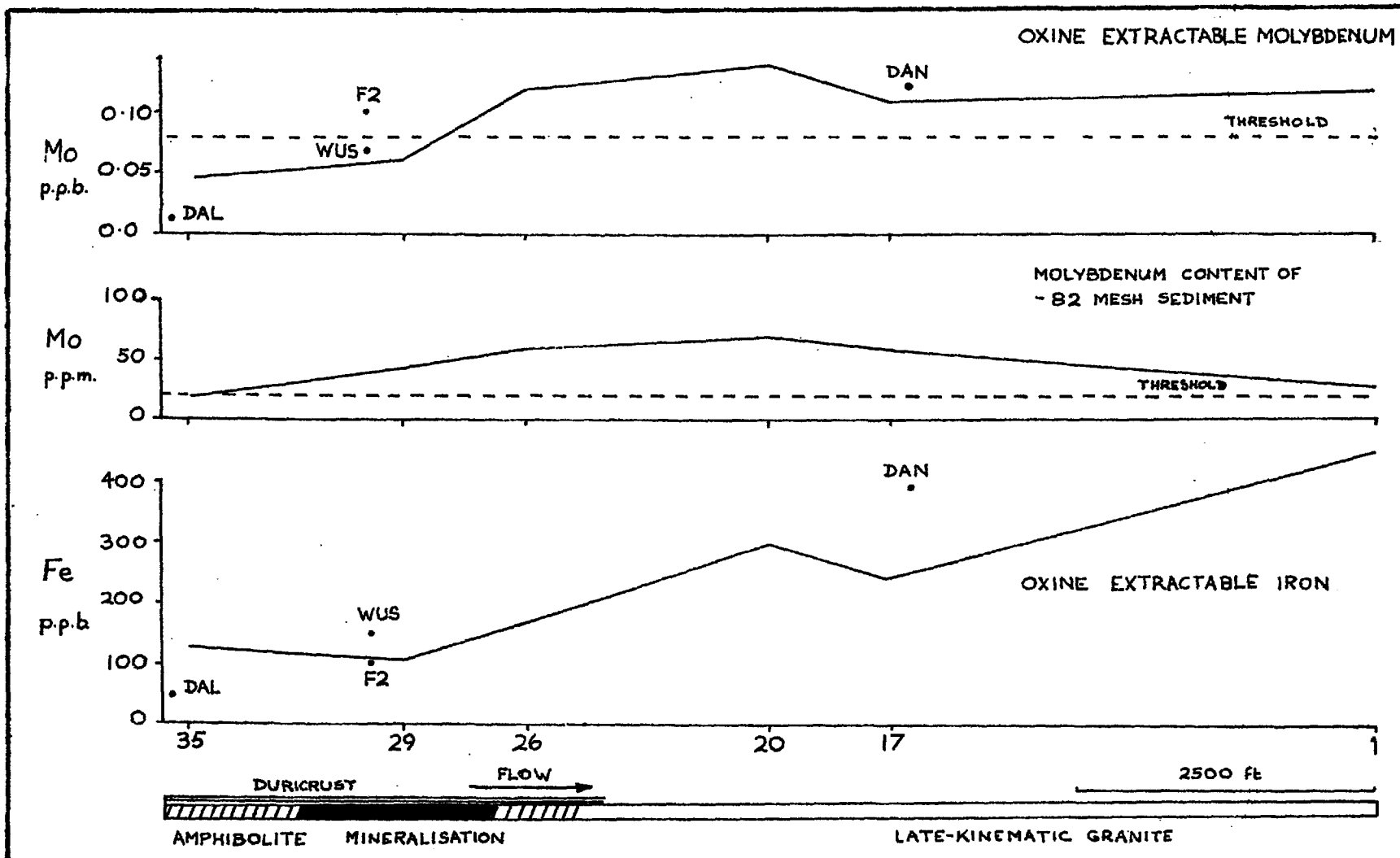


Figure 20. River Sende Downstream Dispersion of Oxine Extractable Molybdenum and Iron

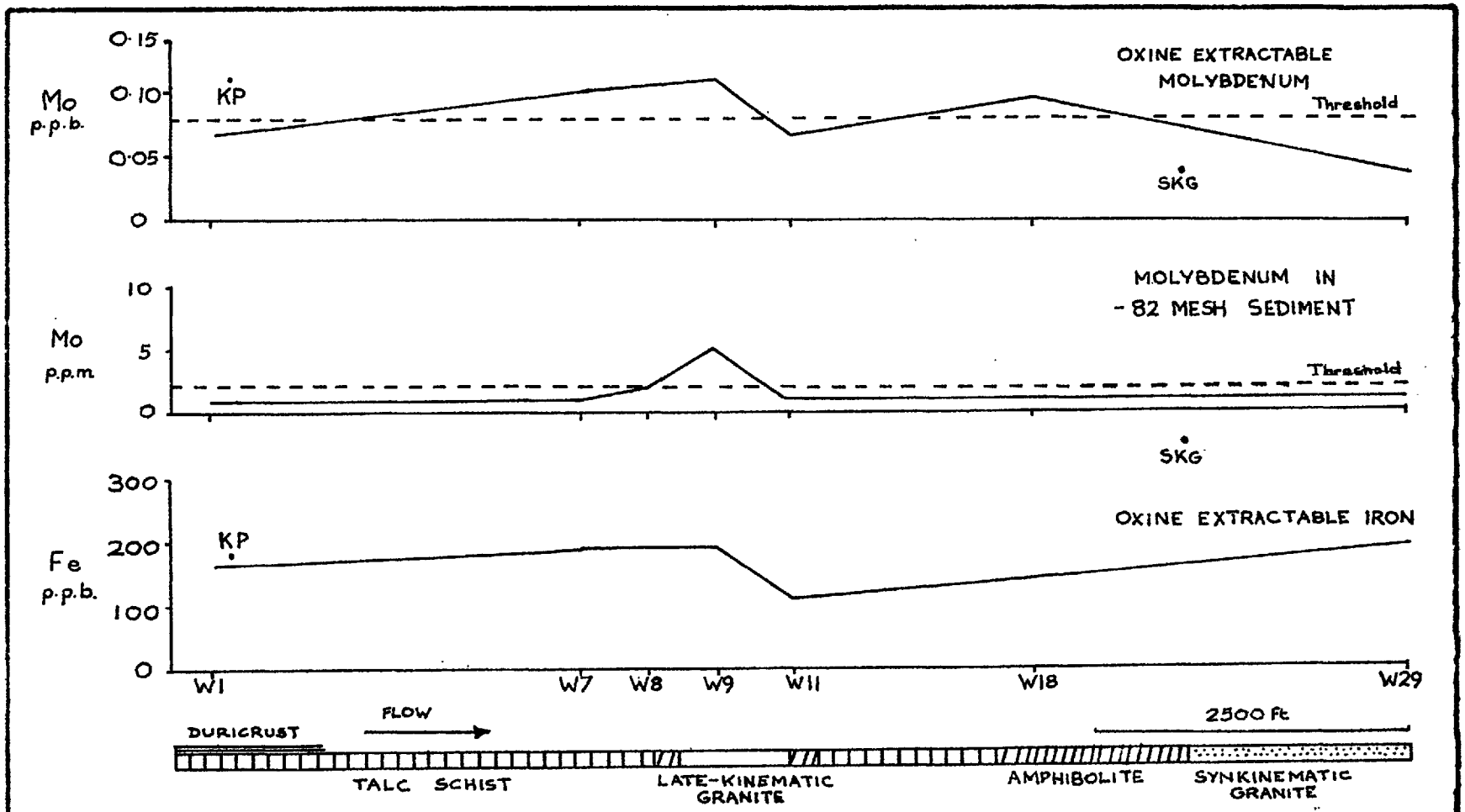


Figure 21. River Wankatana Downstream Dispersion of Oxine Extractable Molybdenum and Iron

However, indirect data are available from the Dankan, a tributary of the Sende, rising from a spring in the granite area, which dried up shortly after sampling, (Site DAN, Figure 18). In spite of the catchment bedrock of this stream being barren granite the water carries a high concentration of molybdenum and iron. It seems reasonable to assume, therefore, that the Dankan water is representative of groundwater entering the surface drainage in the granite area.

Thus, the molybdenum content of the main stream waters may be maintained and their iron content raised by the entry of groundwater similar in composition to that of the Dankan stream.

The groundwater having travelled for a considerable distance underground may be well buffered against changes in the chemical character of the environment and thus be slow to come into equilibrium with the surface waters with consequent persistence of anomalously high metal values in solution in the surface water.

Since all the other small tributaries of the Sende downstream from the duricrust boundary contained only small volumes of water compared with the main stream, straight volume dilution of the anomalous water will be at a minimum. This lack of dilution of the anomalous water may well be of more importance than the addition of metal bearing water in maintaining the saline dispersion train of molybdenum in the Sende. Although the Sende does not appreciably increase in size in the lower reaches it is apparent that an unknown volume of water is flowing through the gravelly river bed, hence changes in the volume of water and therefore in the dilution of anomalous water are difficult to estimate.

In addition the capacity of the surface water to carry iron and molybdenum in solution may be greater in the lower reaches of the catchment due to undetected changes in the composition of the water on passing from amphibolite to granite. Furthermore if such a change in the saturation capacity of the stream waters takes place, the stream sediment may release iron and molybdenum into solution to maintain the equilibrium conditions between the stream water and sediment.

No discussion of the ratio of soluble iron and molybdenum concentrations has been entered into since the precision of these data is poor (± 100 percent at the 95 percent confidence level), hence the error of the ratio will be considerable and the possibility of any meaningful relationship being discerned in these data is small.

b) River Wankatana

Both upstream and downstream from the mineralised granite the molybdenum content of the Wankatana water is higher than the threshold value established for the Sende waters (0.08 ppb). This may be related, in part, to the higher sulphate, bicarbonate and pH of the Wankatana waters producing conditions more favourable to the existence of soluble molybdenum, i.e. the Wankatana waters have a higher capacity to carry soluble molybdenum than those of the Sende, (Figure 19).

It is of interest that there is only a slight increase in soluble metal concentration in the vicinity of the mineralised granite. The Wankatana waters may be nearly saturated with regard to molybdenum and iron and the entry of metal bearing groundwaters near the mineralisation, would have little effect on the concentration of soluble metal in the stream waters and result in the precipitation of excess iron and molybdenum. It will be recalled that the fine sediment fractions increased in molybdenum tenor in the vicinity of the mineralisation, this may be in response to the above mechanism.

Immediately below the mineralisation both molybdenum and iron values fall abruptly and then rise again, (Figure 21). Whilst the similarity in behaviour of iron and molybdenum may be due to analytical error, a further explanation may lie in the observed rise in pH from 6.6 - 7.4, in this zone of the drainage system, as a result of which soluble iron may have been precipitated from solution carrying some molybdenum with it.

As the former conditions are re-established further downstream the concentration of soluble metal in the surface waters again rises but is once more depressed by the entry of the large tributary west of the village of Worowaia, (Figure 19). This stream is of comparable size to the Wankatana and carries background concentrations of molybdenum but a very high soluble iron content. As a result of dilution by this water the soluble molybdenum content of the Wankatana stream is reduced and its iron content increased.

Since, in these lower reaches of the Wankatana drainage, most of the molybdenum in the sediment is lattice held there appears to be little interaction between the sediment and stream waters; the paucity of free iron oxide rich sediment favours the persistence of molybdenum in solution.

The lower iron concentrations recorded in the Wankatana water compared with those of the Sende are possibly related to the higher bicarbonate level of the former, (Table 35), since Hem (1959) has noted an inverse relationship between soluble ionic iron and bicarbonate ions in natural waters. Furthermore, the higher pH levels in the Wankatana waters also favour a lower soluble iron content than those of the Sende.

E. Summary of observations and conclusions on the secondary dispersion of molybdenum in the drainage systems examined.

1. Two types of molybdenite mineralisation have been examined in this study of the drainage dispersion characteristics of molybdenum:

a) a vein mineralisation in amphibolite with duricrust overburden,

and b) a disseminated mineralisation in granite overlain by a non-indurated latosol.

2. Different drainage dispersion patterns arise from these mineralisations.

Bank Soils

3. Freely drained banks soils from barren schist and amphibolite catchments show little variation in molybdenum tenor between the various particle size fractions whilst those of late-kinematic granite catchments exhibit notable concentration of the element in the silt size fraction.

4. Near the amphibolite mineralisation distinct concentration of molybdenum is observed in the coarse fractions of bank soils and is attributed to the high molybdenum content of the duricrust component of these materials. In contrast, the coarse fractions of the granite soil, with no duricrust component, carry only very low tenors of molybdenum. The fine fractions of the soils from both mineralised areas show a tendency to concentrate molybdenum but this is not marked.

5. In the vicinity of mineralisation the fine fractions of waterlogged bank soil carry appreciable amounts of molybdenum, particularly in the silt and clay material, and in generally higher tenors than the related freely drained bank soil. This has been ascribed to the sorbtion of molybdenum by the active fractions of the

bank soils from groundwater entering the drainage near the mineralisation.

6. Downstream from the mineralisation, the deposition of molybdenum bearing sediment in the stream banks is also considered to be responsible, in part, for the high molybdenum tenors of the bank.

Stream Sediments

7. The transition from soil to sediment brings about a reduction in the proportion of fines as compared to the coarse fractions due to elutriation of the sediment by the rapidly flowing stream water.

8. Background sediments carry from 0 - 5 ppm molybdenum in the minus 82-mesh fraction, rising to 10 ppm in the vicinity of mineralisation.

The coarse fractions of the sediment, like those of the soil, are the chief hosts of the molybdenum and the contrast in tenor between amphibolite and late-kinematic granite soil is maintained in the sediment. The fine background sediment fractions, particularly the silt fraction exhibit a considerable increase in molybdenum tenor, compared with the soil, in both Sende and Wankatana areas. In the Sende area this is ascribed to an increase in the sorption capacity of these fractions whilst in the Wankatana sediment it is due to the presence of a molybdenum bearing mineral in the silt fraction. It is notable that in all cases the clay fraction of the stream sediment carries comparatively little metal. This is attributed to the low molybdate sorption capacity of the clay and also to the low free iron oxide content of this material.

9. Sediments from mineralised areas exhibit a similar molybdenum distribution to the background samples, with accumulation of molybdenum in the coarse fractions of the duricrust bearing sediment, but not in that derived from the unduricrusted mineralisation, and distinct concentration of the element in the silt fraction.

10. Whilst in the stream sediment from the area of duricrusted mineralisation the overall tenor of the size fractions is higher than in the background sediment, the reverse is the case with the sediment derived from mineralised granite. This difference is related to the different mode of occurrence of the molybdenum in the duricrust-rich and duricrust-poor sediment types.

11. Molybdenum is closely associated with hydrated iron oxides in the drainage systems examined, particularly in the Sende sediments, where the distribution of the element can be largely interpreted in terms of this relationship. In contrast, the bulk of the molybdenum in the Wankatana sediments is held in mineral lattices and the sediment dispersion train produced is consistent with this mode of occurrence.

12. Molybdenum derived from molybdenite is associated with the hydrated iron oxides in the sediment whilst the molybdenum held in crystal lattices in the host rock of the mineralisation tends to persist in this form in the drainage system.

13. Hydrated iron oxides are chiefly responsible for the appreciable tenor of exchangeable molybdenum in the fine fractions of the stream sediment from the duricrusted area. Very little of the molybdenum held in the sediments of the unduricrusted area is exchangeable, consistent with its mode of occurrence.

14. The molybdenum carried in the stream sediments exhibits no direct association with manganese or organic carbon.

15. Downstream from the Sende mineralisation a well defined extended dispersion train of molybdenum bearing sediment is produced in contrast to the almost complete absence of an anomalous train in the Wankatana sediment.

16. The dispersion of molybdenum in the stream sediments examined is chiefly of a mechanical nature.

17. In the Wankatana sediments the coarse material, consisting mainly of quartz and barren duricrust fragments, has a very low molybdenum content, hence the molybdenum drainage train in this fraction goes undetected unless detailed size analyses are carried out. In contrast, the molybdenum rich duricrust component of the coarse sediment fraction in the Sende sediment produces an anomalous dispersion train extending approximately one mile below the mineralisation.

18. The difference in the extent of development of the molybdenum drainage train in the Sende sediments as compared to those of the Wankatana, is principally related to the smaller area of potential diluent material upstream from the mineralisation and the larger area of anomalous soil in the former drainage system. In addition, the length of the Sende sediment dispersion train is probably being enhanced by the re-working of molybdenum-bearing alluvium and, in the fines, by the sorption of molybdenum from groundwater solutions. Furthermore, the inhibition of dilution of the anomalous sediment by barren material downstream from the mineralisation, due to the disturbance of the stream banks by mining operations, tends to maintain the sediment anomaly in the Sende drainage.

19. More detailed size analyses of the fine sediment reveal the concentration of molybdenum in the silt fraction of both drainage systems.

20. In the case of the Sende sediment, this is attributed, in part, to the sorption activity referred to above whilst in the Wankatana sediment it is due to the presence of a molybdenum-rich mineral in the silt fraction. The accumulation of this mineral in the silt may be due to the mechanical comminution of coarse molybdenum-rich sediment particles during transport in the drainage system. The identity of the mineral is not known.

21. The discovery of high molybdenum tenors in the silt fraction of a stream sediment may indicate the presence of late-kinematic granite in the catchment with which molybdenum mineralisation could be associated.

Water

22. Both the Sende and Wankatana streams carry very low concentrations of soluble molybdenum (less than 0.2 micrograms/litre) as determined by the solvent extraction technique used in this work.

23. The dispersion train of soluble molybdenum detected in the Sende waters may be maintained by the influx of metal-bearing groundwater in the lower reaches of the drainage system, the lack of dilution by barren tributaries and the equilibrium between the water and the metal rich sediment.

24. In comparison with the Sende, the Wankatana water carries a higher concentration of molybdenum which is possibly related to the lower tenor of the element associated with free iron oxides in the sediment. Furthermore, the chemical character of the Wankatana water differs from that of the Sende and may promote molybdenum and iron solubility.

PART FOUR. FACTORS INFLUENCING THE SECONDARY DISPERSION OF MOLYBDENUM IN THE DRAINAGE SYSTEMS OF THE SULA MOUNTAINS.

The factors influencing the extent of dispersion of molybdenum from the mineralisations studied may be considered under three broad headings: geological, chemical and biological, the first controlling to a large extent the last two.

In the immediate environment of the mineralisation the geological factors are of paramount importance in regulating the supply of mobile molybdenum to the soil, whilst during the transition from the soil into the drainage system, chemical influences become increasingly important, until they predominate in their control of the saline dispersion of the element in the stream water.

Biological factors make their most significant contribution to the dispersion of molybdenum in the soil and water phases of the dispersion system.

I. Geological Factors Influencing the Dispersion of Molybdenum

Some of the more important geological factors which appear to exert an influence on the extent of molybdenum dispersion from mineralisations under the field area conditions have emerged from the present study.

The release of molybdenum from the mineralisations is dependent on the form of the mineralisation itself and the nature of the host rock of the mineralisation, the latter having far-reaching influence as a result of its control of the type of soil profile developed and the secondary minerals produced.

The importance in this study of the pedology, resulting from the interaction of rock type, climate, topography and vegetation, all of

which influence the dispersion of molybdenum, lies in the fact that the soils are the chief source of the stream sediments.

1. The Form of the Mineralisation

The molybdenite occurrences studied were of two types: that at Dalakaru consisting of molybdenite bearing calcite veins in a massive amphibolite, whilst at Worowaia, the molybdenite is disseminated in late-kinematic granite.

In the disseminated form, the ore mineral is enclosed by relatively stable silicates such as quartz and felspar, whereas in the veins the gangue minerals are calcite and ankeritic carbonate. In addition, the common occurrence of pyrite in the veins provides a ready source of acid solutions which will assist in the breakdown of both the ore and gangue minerals. Furthermore, the veins, occupying structural breaks, will tend to provide channelways for groundwater solutions thus assisting in the general decomposition of the host rock.

From the above consideration it would seem that the conditions obtaining in the River Sende mineralisation favour the solution of molybdenum bearing minerals whilst in the case of the Wankatana occurrence the disseminated nature of the molybdenite tends to inhibit its solution.

The distribution of molybdenum in individual minerals of the rocks concerned has not been examined, but in this connection Kuroda and Sandell (1954) have noted that molybdenum^{IV} (ionic radius 0.68A) can occur in most mineral species because it may substitute for iron^{III} (0.67A), titanium^{IV} (0.64A), magnesium^{II} (0.78A) and iron^{II} (0.83A) in crystal lattices and that the element is almost certainly present in the structure of felspars, particularly in granites. This

statement is of particular interest in the present study in the case of the contrast in molybdenum distribution in the Sende and Wankatana sediments; the latter carrying a high proportion of the molybdenum in mineral lattices whilst the former do not. This is consistent with the possible genetic relationship between the sulphide phase molybdenite and the silicate phase molybdenum in the Wankatana granite and the lack of such a relationship between the sulphide molybdenum in the veins and the barren amphibolite country rock of the Sende mineralisation.

The occurrence of lattice held molybdenum in the stream sediment is possibly only indicative of an abnormal molybdenum concentration in the silicate rock which may or may not be mineralised. Furthermore, in view of the similar distribution observed in barren, late-kinematic granite catchment sediments, high tenors of lattice held molybdenum in the silt may be a normal expression of this type of catchment bedrock.

2. The Nature of the Host Rock of the Mineralisation

The nature of the host rock of the mineralisation is considered to be of prime importance in controlling the secondary dispersion behaviour of molybdenum. Upon it depend

i) the type of latosol developed,

ii) the secondary minerals produced by the weathering process,

and iii) the chemical character of the drainage water

all of which influence the extent of molybdenum dispersion from mineralisations.

a) Latosol Development

The Sende mineralisation occurs in a ferromagnesian rock with an iron content (Fe_2O_3 + FeO) of more than 11 percent whilst the late-kinematic granite host of the Wankatana mineralisation carries

only 0.4 percent iron (Fe_2O_3 + FeO). It is not, therefore, surprising that the dense cuirass of cemented iron oxides typically developed over the amphibolites and talc schists is almost always absent from the granite.

In the preceding sections, emphasis has been placed on the presence or absence of an indurated latosol horizon in the soil profile since this would seem to be a major factor controlling the mode and extent of molybdenum dispersion from the mineralisations studied.

To recapitulate the findings of the present study; in areas where mineralisation is absent, molybdenum is fairly evenly distributed throughout the various fractions of the soil whilst in the presence of a source of molybdenum, i.e. mineralisation, the element has a bi-modal distribution.

Soil

a) Plus 82-mesh fractions. Accumulation of molybdenum in these fractions and particularly in the plus 20-mesh material is most marked in the presence of an indurated latosol horizon over the mineralisation. Mather demonstrated that the tenor of molybdenum increases appreciably in the soil horizon characterised by ironstone concretions. This concretionary material is the chief constituent of the coarse fractions of the bank soils in duricrusted areas and is therefore, largely responsible for the high metal tenors in these fractions in the vicinity of mineralisation.

On the other hand, the coarse fractions of granitic bank soils and slope soils consist largely of quartz and felspar grains which contain comparatively little molybdenum.

b) The silt and clay fractions. The silt and clay fractions of bank soils from mineralised areas carry a high proportion of the total metal content of the soil due to the large bulk of these fine particle size fractions. The fine fractions of waterlogged soils carry higher tenors of metal than those of the related freely drained soil which is attributed to the removal of molybdenum from groundwater through the sorption activity of the silt and clay particles of the waterlogged soil. Since molybdenum bearing solutions are absent or only of limited occurrence as soil pore water, in the freely drained soil the sorption activity of this material will be limited. Unfortunately, no data are available for the partition of molybdenum between mineral lattices and iron oxides in the soil, but more information is available for the stream sediments derived from these soils.

Sediment

a) Plus 82-mesh fraction. As in the soils the very coarse fraction (plus 20-mesh) carries the highest tenors of molybdenum. This is consistent with direct mechanical derivation of the sediment from the soils.

b) The silt and clay fractions. In contrast to the soils the fines exhibit a considerable rise in molybdenum tenor and decrease in bulk on entering the drainage system. The latter effect is attributed to the high water velocity which elutriates the fines from the coarse sediment. The change in the molybdenum tenor may be due to the sorption of molybdenum by precipitated hydrated oxides in the oxidised aqueous environment of the drainage system. The sorption effect is more marked in the sediment than in the waterlogged bank soils possibly because the content of active free iron oxides is lower in the anaerobic

environment of the waterlogged banks than in the surface drainage. It is found that sediments derived from an iron rich rock such as the Sende amphibolite contain more iron oxide associated molybdenum, i.e. sorbed metal, than those from the iron poor Wankatana granite, whilst the granitic sediments carry a greater proportion of their molybdenum in mineral lattices. Thus the type of latosol also influences the partition of molybdenum in the sediments.

b) Topography

Insofar as both the Sende and the Wankatana drainage systems originate on the duricrust plateau, flow torrentially down the scarp and the rejuvenated section of the valleys and then more gently in their unduricrusted lower reaches, the stream profiles are very similar, hence the development of different dispersion patterns cannot be attributed to any marked difference in water velocity in the two drainage systems.

The supply of soil to the drainage system depends on the topography produced by the interaction of the climate and the catchment area rock, and in this case upon the presence of duricrust.

In the presence of duricrust, the high plateau with low hills and few streams occupying very large catchment areas contrasts with the dissected topography of unduricrusted areas where the stream density is doubled, catchment areas are smaller in size and the relief is more varied. As a result, the potential of each type of area for supplying soil, both barren and mineralised, to the drainage system is markedly different. Mather has calculated the area of potential diluent soil in the unduricrusted part of the Wankatana catchment upstream from the mineralisation, compared to the area of

mineralised soil to be in the ratio of 3,500 : 1, whilst in the Sende catchment the same ratio is only 12 : 1. In view of this great contrast, the suppression of development of an extensive sediment drainage train from the Wankatana mineralisation is not surprising.

Because of the high stream density, mineralisation in unduricrusted areas is more likely to be near a drainage system than those in duricrusted areas. There is therefore a greater possibility of formation of sediment drainage trains in unduricrusted areas. Whereas the duricrust topography is typified by deeply incised, steep sloped valleys those of the unduricrusted areas are more open with less steep slopes. However, the lower slopes of both valley types carry unconsolidated soil brought down by soil creep and sheet wash, supporting a similar density of vegetation. Thus, whilst transport downslope of soil may be somewhat easier in the Sende area due to the steeper slopes this is offset by the shorter slope, compared with the unduricrusted valleys, which limits the amount of material available for transport. This is further emphasised by the very sparse covering of unconsolidated surface soil on the duricrusted hilltops compared with the complete coverage of unconsolidated soil on the unduricrusted hills. A greater amount of material will tend, therefore, to be moving into the drainage system in the Wankatana catchment than in the Sende system.

A further difference in the two drainage systems lies in the disturbance of the Sende banks by gold workings which are absent in the Wankatana. In the latter case therefore, the soil moves unimpeded into the drainage further facilitating dilution of anomalous sediment, whilst in the Sende catchment soil is deposited

in the pits and banks of boulders left by the mining operations and is thus prevented from entering the drainage. The boulders protect the stream banks from undercutting and also trap metal bearing alluvium, the reworking of which tends to maintain high metal tenors in the active sediment. On the other hand, in certain stretches of the drainage system, the workings may have facilitated the erosion of the banks through the destruction of the soil profile. The molybdenum dispersion train in the Sende sediments is, therefore, probably longer than would be the case if the banks had not been disturbed by mining operations.

c) Climate

Apart from the influence which the climate has on the pedology produced in the regions studied, it is, with gravity, the chief agent responsible for the movement of molybdenum bearing soil into the drainage system.

Molybdenum in the soil is mobilised through the effects of rain in three spheres of action, a) sheet wash, b) leaching and c) ground water. The efficiency of the first two agencies is closely related to the presence of duricrust in the catchment area and thus also to the nature of the host rock of the mineralisation.

In both duricrusted and unduricrusted areas sheet wash during the torrential rains is a major factor in the transport of soil down the steep valley slopes. However, the effects are greater in the unduricrusted catchment because the area of unconsolidated soil is greater than in the duricrusted areas. In addition, the duricrust surface is relatively impermeable, except for structural breaks, as a result of which the time of contact of the rainwater and the soil

is less than in the unconsolidated soil of the unduricrusted catchment and therefore the amount of leaching which takes place is much less.

From the above, it will be apparent that the overall effect of the duricrust is to reduce the amount of soil and also soluble molybdenum supplied to the drainage by the action of the heavy rains.

Accordingly, the type of latosol developed in the mineralised catchment area, which is closely related to the bedrock lithology, is largely responsible for the extent of development of the sediment drainage train through its effects on the distribution of molybdenum in the soil, the type of topography produced and the amount of surface run-off. Thus, conditions directly attributable to the presence of duricrust favour the inhibition of molybdenum dispersion in the Sende catchment, whilst dispersion of the element is promoted by the absence of duricrust in the Wankatana area.

3. The Nature of the Secondary Minerals produced during Weathering

A further influence exerted by the host rock of the mineralisation lies in its control of the species of secondary mineral formed during the process of weathering.

a) Molybdenum minerals

Molybdenite undergoes oxidation in the zone of weathering to form oxides, e.g. Molybdite MoO_3, Ilsemannite, $Mo_3O_8nH_2O$ and molybdates e.g. Wulfenite $PbMoO_4$, Powellite $CaMoO_4$ and Ferrimolybdite $Fe_2O_3 3MoO_3 8H_2O$. Aluminium molybdate may also be formed (Jones and Milne 1956). According to Khitarov and Ivanov (1937) molybdenite forms an intermediate compound MoO_3SO_4 in the oxidising zone before reacting with any available cations to form molybdates.

Molybdite may be formed in the immediate vicinity of the oxidising molybdenite but probably has only a brief existence before reacting with a cation to form a molybdate. The mineral ilsemannite is of very rare occurrence and it does not seem likely that it will occur in important amounts in the field areas, although it has been reported from the Wankatana district.

The occurrence of molybdenite and galena together at Dalakaru favours the formation of wulfenite in the course of weathering, and this mineral, in very limited amounts, has been reported by officers of the Sierra Leone Geological Survey. The low calcium content of the latosols of the Sula Mountains and their highly oxidised condition do not favour the production of powellite.

Ferrimolybdite is a not uncommon product of the alteration of molybdenite in the presence of oxidised iron compounds. Although it has not been identified in samples from the field area, since its ochreous nature and yellow-brown colour make it difficult to distinguish from limonite, it would seem that ferrimolybdite is likely to be the most common secondary molybdenum mineral produced during the formation of the Sula Mountains latosols.

b) Hydrated oxides of Iron and Aluminium

From their study of the weathering products of silicate rocks Fields and Swindale (1954) conclude that a mature soil developed over basic rocks will contain crystalline oxides of iron, aluminium and titanium plus some kaolin; less mature soils contain a higher proportion of amorphous hydrated oxides whilst acidic rocks with a low iron content produce hydrated oxides of aluminium and silica accompanied by kaolin.

These findings are consistent with X-ray diffraction patterns obtained from the silt and clay fractions of stream sediments which indicate the presence of kaolinite $Al_4Si_4O_{10}(OH)_8$, gibbsite $Al_2O_3 3H_2O$, geothite $Fe_2O_3H_2O$ and haematite Fe_2O_3. Quantitative estimations of the mineral composition of these materials are difficult but the iron oxides tend to be concentrated in the silt rather than the clay, a fact in line with chemical analyses of these sediment materials.

c) Clay minerals

According to Merwe and Heystek(1952) the freely drained latosols of the humid tropics contain kaolinite as their dominant and characteristic clay mineral. X-ray diffraction analyses of the silt and clay fractions of soil and sediment from the field area confirm that kaolinite is the principal clay mineral present.

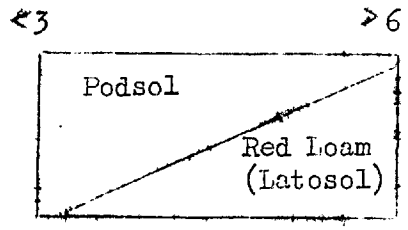
II. Chemical Factors influencing the Secondary Dispersion of Molybdenum

The geology of the catchment area is important in its control of the chemical composition of the underground and surface water.

1. Temperature

The chief influence of the high ambient temperature (80°F air temperature and 18° - 26°C surface water temperature (cf 30° - 70°F air temperature and 15° - 20°C water temperature in the U.K.) is the acceleration of the rate of chemical reaction. In simple chemical systems a rise of 10°C approximately doubles the rate of reaction. Hence, in the tropics, chemical reactions will proceed with greater rapidity than in temperate regions, resulting in rapid weathering of fresh rock and decomposition of dead vegetation.

The rate of chemical weathering and rock type have been related to the air temperature index of Szymkiewicz (1947) by Stephens (1949).



$T = 2.5^{t}/10$ where t = air temperature in °C.

Mather has calculated the air temperature index in the Sula Mountains to be 16. Thus all the field area soils fall into the latosol division.

Jenny et al (1949) in a comparative study of decomposition rates of organic matter in temperate and tropical regions found that in the tropics (Columbia, South America) the amount of organic matter produced is between two and ten times that in the temperate region studied (Sierra Nevada, California) and that equilibrium was reached on tropical forest floors in less than ten years compared with 60 - 300 years in the temperate region. In addition, the air and water temperature range of the field area favours the active growth of micro-organisms. Similarly, both pH and Eh increase with rise in temperature. Thus considerable differences in the dispersion behaviour of elements may arise in tropical regions as compared to temperate areas merely due to the higher ambient temperatures.

2. Oxidation Potential and Hydrogen Ion Concentration

The oxidation potential (Eh) and the hydrogen ion concentration (pH) are valuable parameters in defining the chemical character of the natural environment, since most chemical reactions are controlled, to a greater or lesser degree, by these two factors.

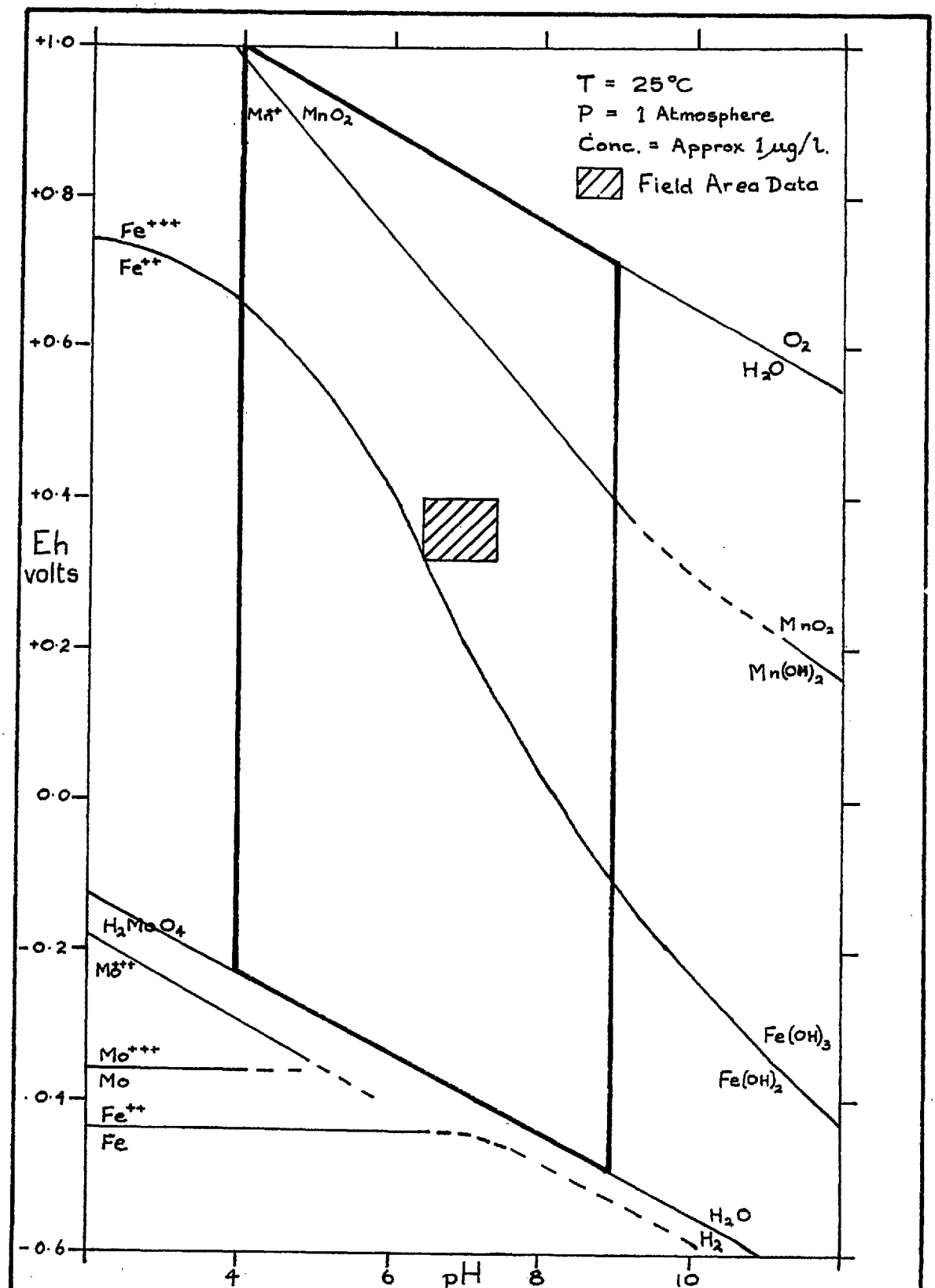


Fig22 Stability Fields of Ionic Species of Mo, Fe, Mn.
(after Krauskopf 1955)

Chemical reactions taking place in nature are generally limited to the pH range 4 to 9 and the Eh range -0.4 to +0.8 volts, (Krauskopf 1955). The oxidation potential of the environment varies with pH, temperature and the partial pressure of oxygen.

In his study of the soils of the field area, Mather recorded a pH range of 5.9 to 7.0, and in river water a range of 6.8 - 7.0. These values were confirmed in the present study; Eh values for river waters lie between +0.3 and +0.4 volts. The limits of the field areas in terms of Eh and pH can thus be related to other published data (Figure 22) and the ionic species existing under these conditions can be predicted.

Molybdenum

It will be seen from Figure (22) that under the neutral, oxidising conditions of the drainage systems studied, molybdenum is in the Mo^{VI} state in the form of the molybdate anion $(MoO_4)^{--}$. This is in contrast to its presence in the Mo^{IV} state in the environment of the mineralisation where, in molybdenite, it is in the cationic form Mo^{++}. Thus, on oxidation this element undergoes a considerable change of character which has a marked influence on the solubility of the compounds involved. This will be further referred to in the following section on solubility.

From the foregoing data it seems reasonable to assume that in the drainage systems studied the predominant form of molybdenum will be the molybdate anion, probably in combination with the ferric cation in the compound ferrimolybdite.

Iron

The predominant, stable form of iron present in the drainage systems investigated will, according to Figure (22) be solid ferric hydroxide $Fe(OH)_3$, e.g. the precipitated, hydrated iron oxides referred to in the previous sections.

Very little iron can remain in solution between pH 5 and pH 8 and Eh +0.3 to +0.5 volts according to Hem et al (1959) who give a theoretical limit of 10 µg/litre Fe^{III}. However, oxine extractable (soluble ionic) iron concentrations of 40 - 400 µg/litre were recorded in the present study. The difference between theoretical and practical values may be due to the fact that the former were obtained from relatively simple synthetic solutions whilst natural waters are more complex and the presence of other ions not considered by Hem and Cropper may be enhancing the iron solubility.

Furthermore, the proximity of observed pH and Eh values to the stability field of ferrous iron (Figure 22) suggests that, under the field area conditions, the ferrous-ferric equilibrium may be operating at a higher Eh level than is indicated by the diagram. Hem et al (1959) note that at pH 6 a fall of only 0.14 volts in Eh can raise the soluble iron concentration from below the limit of detection to 100 µg/litre. The presence of soluble iron in amounts up to a few hundred µg/litre in the stream waters might thus be accounted for.

A further possibility, which has already been referred to, is that the surface water contains some groundwater which has not attained equilibrium with the surface environment. The oxidation potential and hydrogen ion concentration of many groundwaters are favourable for the presence of considerable amounts of ferrous iron

in solution. That such favourable conditions may obtain in the ground waters of the field area is inferred from the observation of abundant precipitation of orange, ferric hydroxides, at seepages along the river banks, indicating an abrupt adjustment of the concentration of soluble iron on entering the surface environment. If the adjustment is incomplete anomalous amounts of soluble iron will be found in the surface waters.

Manganese

According to Figure (22), manganese under the field area conditions will be present as the manganous cation Mn^{II} and not as the hydrated oxide. This may explain why there is no close association of manganese and molybdenum in the stream sediment since precipitation of the manganese salt is not taking place. It is also possible that the concentration of manganese in the clay is due to sorption of the manganous cation by the clay minerals.

The dissociation of carbonic acid H_2CO_3 is generally the most important source of hydrogen ions in natural waters and controls the pH levels attained. Natural waters are usually well buffered by the system.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$$

This system is modified in the presence of salts, e.g.

$$R^{++}CO_3 + H^+ + 1\tfrac{1}{2}H_2O \rightleftharpoons HCO_3^- + R^{++} + 1\tfrac{1}{2}H_2O \rightleftharpoons R(OH)_2 + CO_2 + H_2O$$

Thus in the groundwater environment, where the partial pressure of CO_2 is relatively high (soil air may contain 0.1 - 1.5 percent CO_2 by volume) the equilibrium is displaced to the left and a low pH is established, whilst on entering the surface environment, the partial pressure of CO_2 falls (atmospheric CO_2 is only 0.03 percent by volume)

and the equilibrium moves to the right with a resultant increase in pH. The metal hydroxide, e.g. $Fe(OH)_3$ remains in solution in the groundwater until its solubility product is exceeded as the pH rises on entering the surface drainage.

3. Solubility of minerals

The solubility of the secondary minerals produced by the weathering process is closely related to pH and Eh conditions and in the case of molybdenum the pattern of solubility of molybdenite differs from that of soil molybdenum compounds, (Table 40).

Table 40. Solubility of Molybdenum Compounds (ppm) in various reagents (after Barshad 1951)

Compound	Soil Molybdenum 1	2	3	Molybdenite MoS_2	Ferrimolybdite $Fe_2O_3 3MoO_3 8H_2O$
Total Mo ppm	9.7	5.8	4.0		
Reagent	Molybdenum ppm				
Water	4.8	3.9	3.1	0.05	5.4
0.1N NaOH	4.7	2.6	1.2	0.44	88.0
0.1N HCl	0.2	0.5	0.2	2.84	168.0

Molybdenum minerals are most soluble in acid solution whereas soil molybdenum compounds dissolve most readily in alkalies. This difference is possibly directly related to the change of state undergone by molybdenum from cation to anion which was noted in the previous section. Barshad (1951) suggests that the difference in behaviour of the minerals and the soil compounds is due to molybdenum being present in the soil, not as a distinct mineral, but as soluble molybdate, sorbed molybdate and as a component of soil organic matter.

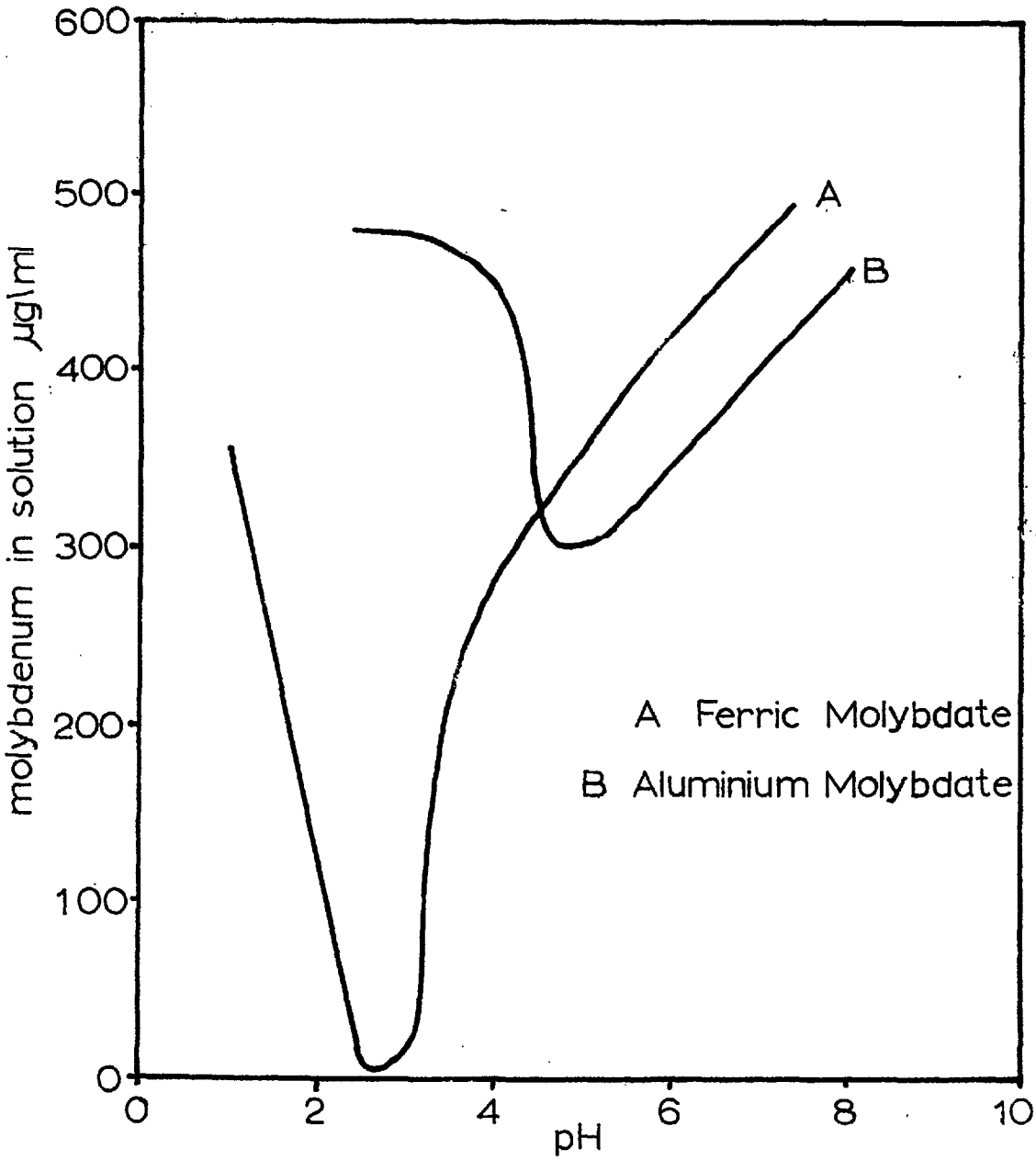


Figure 23 Solubility of Molybdates precipitated with either $FeCl_3$ or $AlCl_3$
(after Jones 1957)

A detailed investigation of the solubility of ferric and aluminium molybdates in synthetic solutions was made by Jones (1957). The molybdates were precipitated with either ferric or aluminium chloride at various pH levels (Figure 23). Both compounds exhibit a distinct minimum solubility over a narrow pH range, with minima at pH 2.7 and 4.8 for ferric and aluminium molybdate respectively. From Jones' data it seems likely that under the pH conditions obtaining in the field area waters (pH 6.5 - 7.4) both ferric and aluminium molybdates may be appreciably soluble.

The presence of other inorganic ions may affect the solubility of molybdates. According to Belyakova (1958), the presence of calcium bicarbonate in waters in amounts greater than 10 percent of the dry residue results in the precipitation of calcium molybdate. The presence of sulphate ions tends to maintain the solubility of molybdates since this ion is a strong competitor for exchange sites in the sediment and will displace sorbed molybdate. Dolukhanova (1956) reports that in the Armenian waters examined, high molybdenum concentrations occurred in waters having a high sulphate content.

In the present study no relationship could be discerned between the molybdenum, bicarbonate and sulphate contents of the stream waters examined. This is not surprising in view of the low concentration of ions involved and the crude analytical methods employed.

Hem et al (1959) have shown that the solubility of iron is inversely related to the bicarbonate content of the solution and owing to the close control over the solubility of molybdenum exerted by iron, the bicarbonate concentration may indirectly influence molybdenum solubility.

4. Sorption Activity

The term sorption is used to denote a variety of mechanisms which, by the attraction of ions to solid surfaces in the solution effectively remove ions from the solution. The strength of the attraction varies from extremely weak forces (Van der Waal's or physical attraction), through stronger ones, due to differing electrostatic charges on ions and solid, to the formation of definite chemical bonds (chemisorption).

Many coprecipitation reactions operate by a sorption mechanism in which the highly active precipitate surface strongly attracts free ions from the solution.

Ions are adsorbed to some extent on any solid surface, the amount of sorption increasing with the area of active surface available. Thus the naturally occurring colloidal materials, clays and precipitated hydrated oxides, will be effective sorption agents.

The sorption capacity of kaolin type minerals for molybdenum in synthetic solutions has been investigated by Jones (1957), (Figure 24). The maximum sorption capacity of kaolin for molybdenum occurs over the narrow pH range 3.0 to 5.5 at a molybdenum concentration of 0.8 µg/litre and decreases at lower concentrations. The sorption activity of kaolin will thus be negligible under the field area conditions (pH 7 and molybdenum concentration less than 0.2 µg/litre). This is consistent with the observations that in the drainage systems studied the clay fraction carries conspicuously low amounts of molybdenum.

Furthermore, the low molybdenum content of the clay fraction is related to a low content of free iron oxides. Several workers have concluded that anion adsorption by clays is due to the associated iron oxides (Coleman 1944, Perkins and King 1944, Chattergee and Datta 1951).

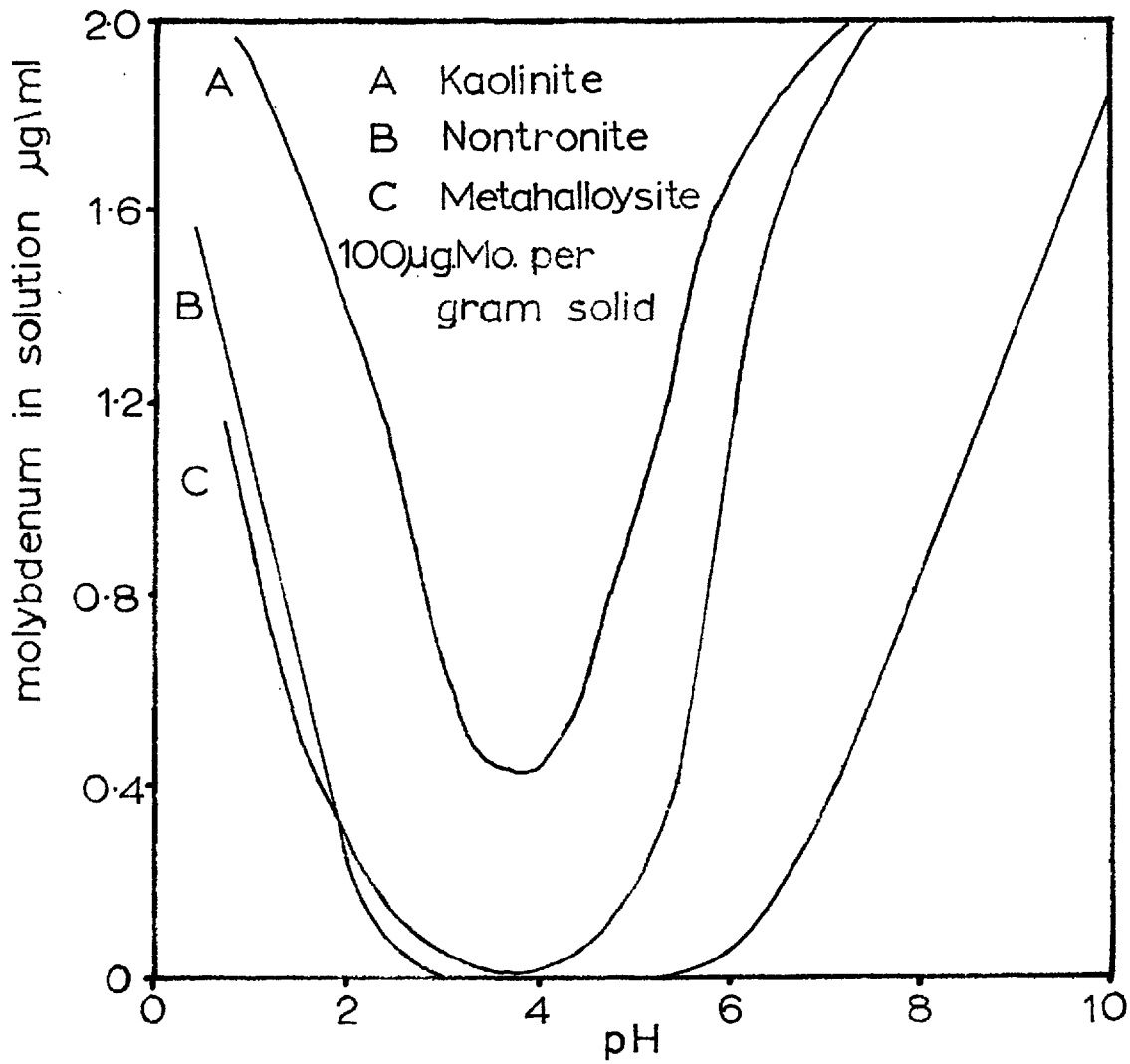


Figure 24. Effect of pH on the sorption of molybdate by Kaolin group minerals

(after Jones 1957)

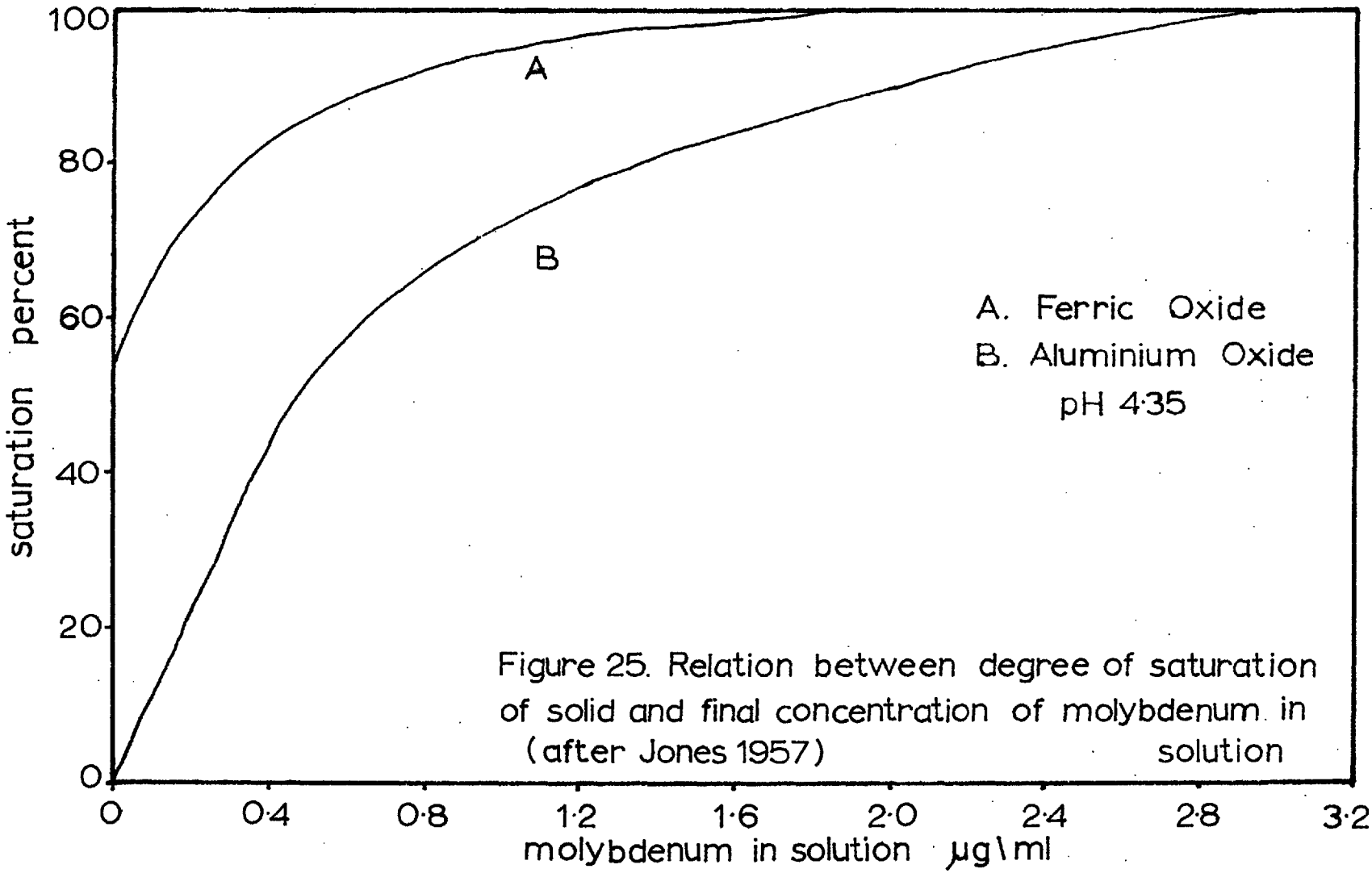


Figure 25. Relation between degree of saturation of solid and final concentration of molybdenum in solution (after Jones 1957)

This is supported by data published by Wells (1956) who showed that when the iron oxides were removed from a soil consisting of 60% clay, 15% iron and 6% organic carbon, its ability to sorb molybdenum was substantially reduced.

In the present work it has been shown that the anion exchange capacity of soil material poor in iron is very much less than that rich in iron.

The activity of iron and aluminium oxides in removing molybdenum from synthetic solutions has also been investigated by Jones (1957). It can be seen from Figure (25) that at pH 4.3 the affinity of these compounds for molybdenum decreases at lower molybdenum concentrations until below a concentration of 0.2 µg/ml (ppm)mmolybdenum only ferric oxide sorbs appreciable amounts of molybdenum from solution. Further data given by Jones indicate that at a molybdenum concentration of 8 µg/litre the ferric oxide is 42 percent saturated and contains 31,000 ppm molybdenum whilst the aluminium oxide contains only 146 ppm molybdenum (0.36 percent saturated).

Ferric oxide is thus shown to be considerably more efficient in removing molybdenum from solution than aluminium oxide.

Jones' results were obtained under laboratory conditions and must be applied with caution to the soil solutions and natural waters of the field areas having a pH of 7 and considerably lower molybdenum concentrations. In previous experiments, Jones has shown that ferric oxide shaken with sodium molybdate solutions completely scavenged molybdenum from the solutions in the pH range 4 - 6 whilst at pH 7, 98 percent was recovered (Jones 1956).

The charge, however, carried by colloidal precipitated material is modified by the pH of the solution. Thus colloidal ferric hydroxide is positively charged in acid solution but at higher pH levels the charge is neutralised and eventually reverses to become negative. The pH at which the charge on ferric hydroxide becomes zero lies between pH 5 and 6, (Krause 1928, Hem and Skougstad 1959).

Hence, while below pH 5 - 6 the positively charged ferric hydroxide may be expected to adsorb the negatively charged molybdate ion, above this pH level, little sorption may take place. On theoretical grounds, therefore, at the pH levels prevailing in the stream waters investigated, little sorption of molybdate by ferric iron, by this mechanism, would be expected.

The close relationship between free iron oxides and molybdenum observed in the present study, however, suggests that sorption does take place. This incongruity may be ascribed to -

a) the nature of the sorption may be more physical than chemical, i.e. by occlusion rather than by chemisorption, and in this connection it is of interest to note that natural ferrimolybdites examined by Jones and Milne (1956) were non-stoichimetric in composition. This may be explained by formation by occlusion giving rise to a variable chemical composition, rather than by a more chemical reaction which would produce a compound of constant composition.

b) that the positive ferric hydrosol is stabilised by other colloids and is still active at the field area pH level.

c) that again, theoretical limits should be applied with caution to natural solutions. Hem has noted that the particle size of natural ferric hydroxide is usually smaller than that produced in synthetic solutions and it will, therefore, be more active.

In the absence of more precise data on the nature of the sorption process, all that can be said is that sorption of molybdenum from soil solutions and natural waters by free iron oxides undoubtedly takes place but the sorption mechanism remains unknown.

III. Biological Factors affecting the Dispersion of Molybdenum

1. Vegetation

The concentration of molybdenum effected by plants may be considerable. For instance, the water plant Azolla growing in canal water containing only 0.021 ppm molybdenum contained 1.13 ppm molybdenum (Ter Meulen 1932).

Very few plant samples have been analysed from the Sula Mountains but the molybdenum content of twig samples of Parkia filacoides gave only a poor correlation with that of the surface duricrust (Mather 1959). However, as Mather points out, a closer relationship probably exists between the plant molybdenum and the molybdenum content of the water available to the plant roots. Furthermore, Mather's data apply to only one species of plant.

No vegetation samples were collected during the present study.

The vigorous plant growth, stimulated by the climatic conditions of the field area, leads to the production of much vegetation debris which contains the molybdenum accumulated by the plants during growth. This debris is rapidly broken down through the action of micro-organisms and may cause molybdenum to be released into a soluble form and so be effectively dispersed into the soil.

The practice of burning large areas of vegetation may also contribute to the dispersion of the molybdenum accumulated in plants first by the molybdenum rich ash being dispersed by the wind immediately after burning and secondly by the ash being leached by the rains which follow shortly after the period of farm-making.

2. Fungi

That certain fungi have important associations with molybdenum has been shown by Swaby and Passey (1953) who demonstrated that Aspergillus niger can release appreciable amounts of molybdenum from soils and rocks.

Water samples transported to London from Sierra Leone in sealed containers and acidified to pH 1.5 contained precipitated material when opened for analysis, which consisted of orange iron oxides in close association with fungal hyphae and contained an appreciable amount of molybdenum (between 14 and 83 percent of the total molybdenum content of the sample, Table 24).

Whether the molybdenum was held by the fungus or by the iron oxides is not known, but the fungus may have been instrumental in causing the precipitation of the oxides because the iron was required in its metabolism. This is in line with the suggestion of Harder (1919) that iron bacteria remove iron, held as organic complexes, from solution in order to utilise the organic radicle whilst the iron is oxidised and precipitated as the hydroxide.

3. Micro-organisms

The climatic conditions in the field area are near the optimum for the growth and activity of micro-organisms such as bacteria. The bacteria Azobacter and Anoboena, which are important in the fixation of nitrogen in the soil, need molybdenum to carry out this function and on their death molybdenum is released into the soil (Mulder 1948).

An indirect influence on the dispersion of molybdenum lies in the property of certain bacteria, e.g. Escheria colli of reducing and rendering soluble ferric iron thus possibly releasing fixed molybdenum.

However, probably the most important part played by bacteria in promoting the dispersion of molybdenum is their continuous rapid destruction of decaying vegetable matter, releasing the accumulated trace elements.

4. Organic matter

Reference has already been made in the section on temperature to the amount and high rate of production of organic matter in the tropics and the activity of micro-organisms rendering any appreciable accumulation of organic matter unli ely under the freely drained conditions of the field area.

The association of molybdenum and organic matter has been suggested by Barshad (1951), and Goldschmidt (1954) notes the accumulation of molybdenum in coal ash and petroleum products, whilst Grigg (1953) found that the molybdenum extracted by 2 percent NaOH solution from soils was related to the loss in weight on ignition by the factor 0.78. In the present work, however, no strong evidence of an association between molybdenum and organic carbon in the soil could be found.

According to Demolon and Barbier (1939) humus forms definite compounds with clay, the presence of which reduces the sorption capacity of the clay. This has been demonstrated experimentally by Barbier et al (1946). Mather found that removal of organic matter from alluvium and sediment samples from the Sula Mountains region resulted in a marked increase in the molybdate sorption capacity of the sample and concluded that the anionic humus compounds were occupying exchange sites, thereby making them unavailable to molybdate anions. Furthermore the lower molybdenum content of the organic

rich surface soils compared with that of the underlying horizons may also be due to the above mechanism.

The decomposition of organic matter produces active compounds possessing the ability to form highly stable co-ordination complexes (chelates) with inorganic ions. Such chelate compounds are believed to be responsible to a large extent for the translocation of metals within the soil profile (Lovering 1934, Fieldes and Swindale 1954 and Barshad 1955).

Ng Siew Kee and Bloomfield (1960) reported the solution of a number of trace elements by decomposing plant materials under anaerobic conditions. The presence of micro-organisms is not essential since sterile aqueous extracts of plant material also induced solution of the trace elements, but to a lesser extent. Molybdenum, in the form of hydrated ferric molybdate, was mobilised after six days' incubation but on aeration of the solution was coprecipitated by the ferric hydroxide formed. During incubation the pH of the solution rose and it was suggested that this may be the cause of the molybdenum mobilisation. It is of interest that molybdenum in the form of calcium molybdate was not mobilised by a similar treatment.

In further experiments (Ng Siew Kee and Bloomfield 1962) the mobilisation of soil molybdenum compounds was demonstrated in a similar set of experiments, (Figure 26). The pH of the solutions remained practically constant throughout the experiments indicating that the solution of the molybdenum was not merely the effect of pH change, whilst on aerating the solution an appreciable amount of the molybdenum remained in solution even though iron was precipitated, suggesting the inhibition of the coprecipitating mechanism by compounds

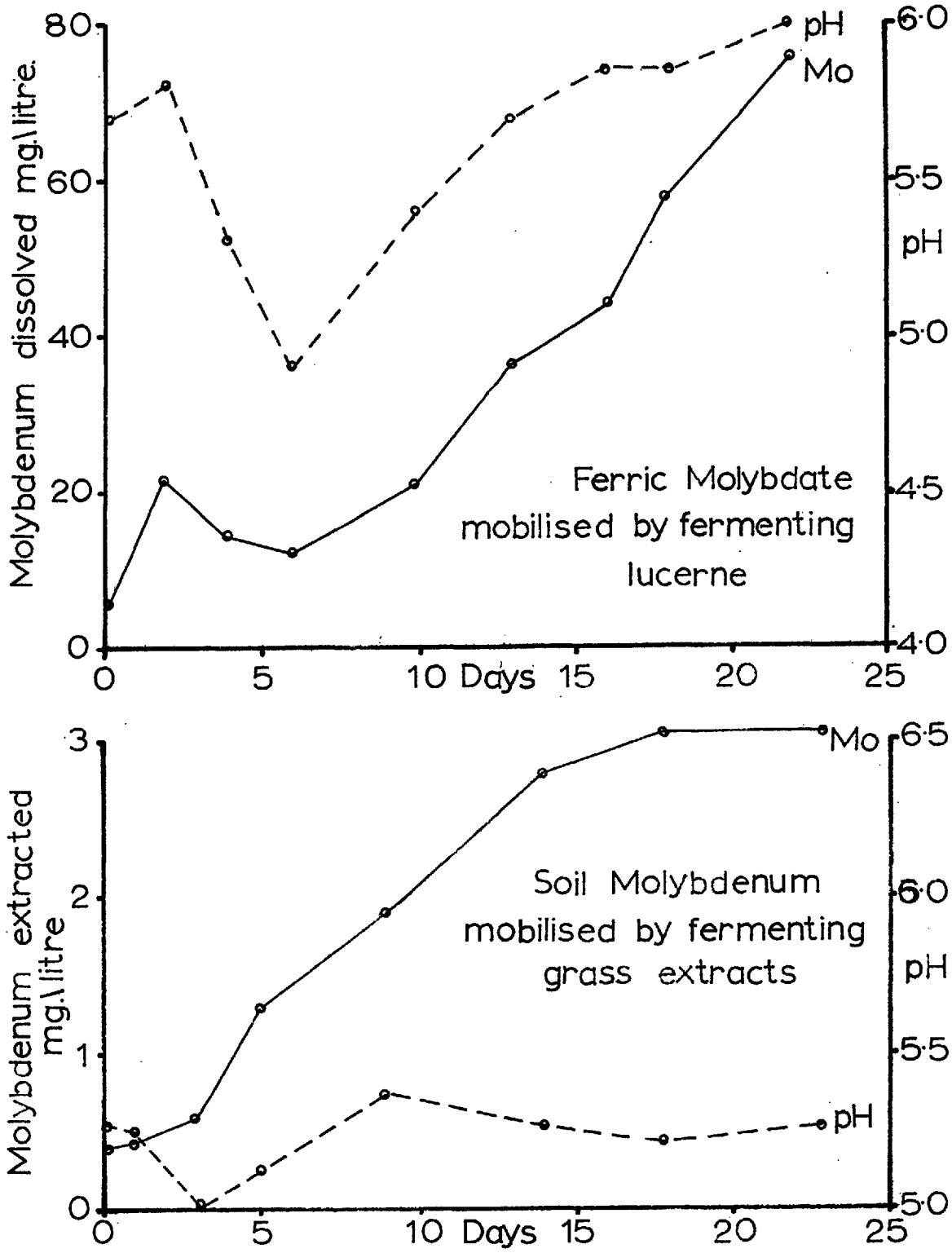


Figure 26 The Mobilisation of Molybdenum by fermenting Plant Materials

(after Siew Kee and Bloomfield 1960,1962)

produced from the organic matter.

It is possible that the high molybdenum content of the Dankan stream water, (Figure 18) may be due to the inhibition by organic matter, present in the headwater swamp, of coprecipitation from the groundwater. Ng Siew Kee and Bloomfield (1962) also suggest that molybdenum may retain its anionic character even when complexed, hence the oxine extractable molybdenum data may include some molybdenum present in complexed but ionic form in the stream waters.

IV. Summary of Factors influencing the Secondary Dispersion of Molybdenum

A number of factors, of a geological, chemical and biological nature, have been examined with regard to their influence on the dispersion of molybdenum in the drainage system. They are summarised below, not necessarily in order of their importance.

1. The Sende vein mineralisation, having gangue minerals unstable under the weathering conditions of the field area, releases molybdenum into the soil more readily than the Wankatana mineralisation, where the disseminated molybdenite is enclosed by relatively stable silicate minerals.

2. The formation of an indurated latosol horizon over the Sende amphibolite and its almost complete absence from the Wankatana granite is largely due to the difference in the iron content of these rocks.

3. The presence or absence of a duricrust overburden to the mineralisation has an important influence on the drainage dispersion pattern produced. In the presence of duricrust much of the molybdenum released from the mineralisation is accumulated in this highly resistant material and is mechanically dispersed in the coarse fractions of the stream sediment for a considerable distance, whilst

in its absence no such accumulation takes place and only a minor dispersion train is formed by the coarse fraction of the stream sediment.

4. Sediments derived from the mineralised Sende duricrusted amphibolite contain more free iron oxide associated molybdenum, i.e. sorbed metal, than those from the iron poor Wankatana granite which carry the bulk of their molybdenum in mineral lattices.

5. The presence of duricrust produces a plateau of low relief and low stream density as compared to the dissected topography with high relief and high stream density developed in its absence. The dilution of mineralised sediment is, therefore, potentially greater in the unduricrusted area.

The mineralisation in an unduricrusted area will probably be nearer to a stream due to the high drainage density and hence the metal bearing soils will have a greater chance of being dispersed in the drainage system than in a duricrusted area.

6. The disturbed banks of the Sende river tend to enhance the length of the sediment drainage train by inhibiting bank erosion and the entry of barren colluvial material into the drainage and also by trapping metal bearing sediment, the reworking of which maintains the tenor of the sediments. The Wankatana has undisturbed banks and the entry of bank soil into the drainage is unimpeded.

7. The effects of rainfall are modified by the presence of duricrust, where, in the near absence of surface soil the rain runs off the almost impermeable surface with minimal leaching action. By contrast, in the absence of duricrust the unconsolidated surface soils are leached and transported into the drainage by rainwash. The overall effect of

the duricrust is, therefore, to reduce the amount of soil and soluble molybdenum supplied to the drainage system by the heavy rains.

The presence of duricrust gives rise to conditions which inhibit the dispersion of molybdenum in the Sende area whilst dispersion of the element is promoted by the absence of duricrust in the Wankatana area.

9. The most common secondary molybdenum mineral likely to be produced by the weathering of the two types of mineralisation is ferrimolybdite.

10. Hydrated iron and aluminium oxides, possessing appreciable molybdate sorption capacity, are produced by both the amphibolite and the granite host rocks but in greater quantities by the former.

11. Kaolinite, the chief clay mineral resulting from the weathering of both rock types, has only a low molybdate sorption capacity under the field area pH, Eh and molybdenum concentration conditions.

12. The temperature of both the stream water and the air in the field areas promotes chemical reaction and organic growth with the consequent facilitation of molybdenum dispersion.

13. The most important chemical factors influencing the dispersion of molybdenum in the soils and drainage systems are their redox potential and hydrogen ion concentration. From a consideration of these parameters, the chemical species present in the field area environment, which are of particular importance in this study, are molybdenum, in the form of the molybdate ion, iron, as solid ferric hydroxide and manganese in the soluble manganous state. No carbonate ions will be present in the drainage system. These theoretical considerations are, in general, confirmed by field observations.

14. The solubility and sorption behaviour of the secondary minerals is largely a function of pH.

Molybdenite is most soluble in acid solutions whilst ferrimolybdite is more soluble at higher pH levels. Ferric molybdate is least soluble at pH 2.7, hence, under the practically neutral conditions of the field area waters, ferrimolybdite may have an appreciable solubility. However, much of it is removed from solution by coprecipitation or sorption on hydrated iron oxides in the soil and drainage system. The sorption mechanism is not fully understood.

15. The presence of other soluble ions affects the solubility of ferric molybdate, but, in view of the low total dissolved solids content of the field area waters this effect may be of minor importance. However, it seems possible that the difference in chemical composition of the Wankatana water from that of the Sende may explain the higher soluble molybdenum content of the former stream.

16. Molybdenum is essential to the healthy growth of plants and may be accumulated in plant tissue and subsequently released when plants are destroyed by burning or during the natural decomposition of dead vegetation.

17. Micro-organisms are chiefly responsible for the destruction of organic materials to form humus, a source of chelating agents which promote the dispersion of molybdenum.

18. Organic matter does not accumulate to any great extent in the soils and drainage systems of the field areas due to the activity of micro-organisms. It is the source of the chelating agents referred to above, which, in addition to complexing molybdenum, may also form similar compounds with hydrated iron oxides with the subsequent release of the associated trace elements such as molybdenum.

PART FIVE. OBSERVATIONS ON THE SECONDARY DISPERSION OF ARSENIC IN THE SOIL, STREAM SEDIMENT AND NATURAL WATERS OF THE SULA MOUNTAINS.

A. Description of the River Yirisen Field Area.

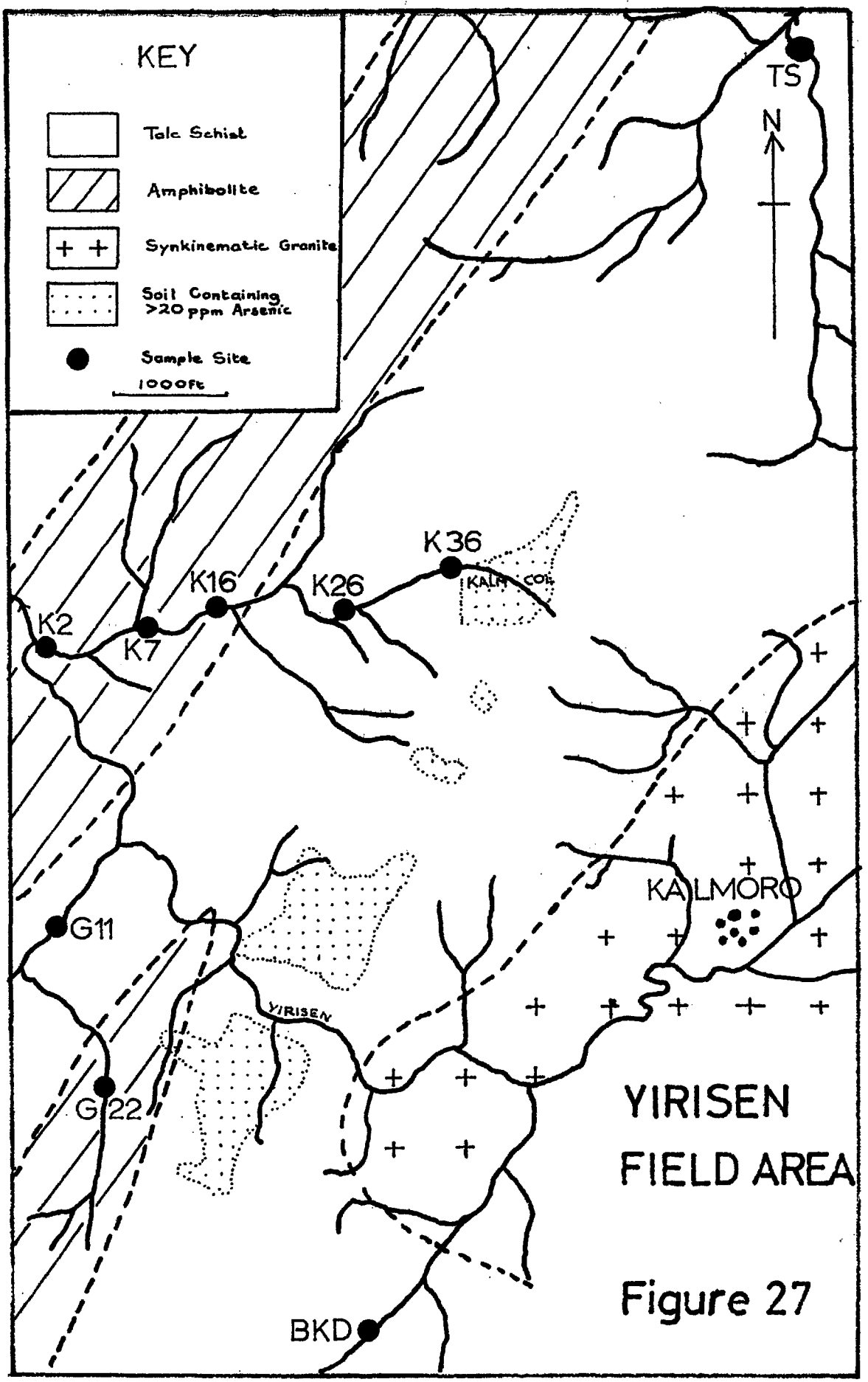
About two miles east of Masumbiri, the River Yirisen exposes sulphide bearing rock in its bed. Several lodes carrying sulphides, including arsenopyrite, chalcopyrite, galena, zincblende and boulangerite and meneghinite (two sulphoantimonates of lead), have been discovered by officers of the Sierra Leone Geological Survey. Samples from the mineralisation also assay about 12 dwt gold per ton, (Wilson and Marmo 1959). The gangue minerals are sericitic quartz, tourmaline, chlorite and fuchsite (chrome mica). A little further upstream gold bearing aplitic quartz veins cross the river channel.

The mineralisation has been worked and near an adit the river bed is full of mineralised spoil.

The talc carbonate schist country rock has an almost vertical dip and is deeply dissected into many hill ranges by a multitude of small streams. A cupola of metasomatised synkinematic granite occurs about 1,300 ft. to the east of the mineralisation.

The main Yirisen River flows in an incised valley, cut in the bottom of an older, deeply weathered, mature valley. The riverdescends 700 ft. in about two miles with several high waterfalls along its course.

A tributary, known as Kalm Col, cuts the strike extension of the mineralisation about one mile before joining the main river. This stream is uncontaminated by mine workings and was the principal site of the arsenic investigation, (Figure 27).


KEY
Talc Schist
Amphibolite
Synkinematic Granite
Soil Containing >20 ppm Arsenic
Sample Site
1000ft
TS
N
K36
K16
K26
K2
K7
G11
G22
BKD
KALMORO
YIRISEN
YIRISEN FIELD AREA
Figure 27

The Kalm Col stream rises in a swampy depression, from which it takes its name, and on reaching the lip of the Col, flows in a precipitous course to the Yirisen River. In the middle section of its course the gradient flattens and some marshy tracts of stream bed are encountered. Along the whole stream the valley sides are extremely steep.

Only the tops of the highest hills, the last vestiges of the 2,000 ft. erosion surface, and the bottom of the old valley floor are duricrusted. Elsewhere a thin immature soil is being formed.

The stream valley slopes are intensively farmed and when cleared of vegetation may contribute appreciable amounts of soil to the drainage system, whilst in the fallow period the slopes are covered with dense secondary bush. High forest occurs only along the margins of the main river.

B. The Secondary Dispersion of Arsenic in the Soil

I. Previous Work

The secondary dispersion of arsenic in the residual soils of the Yirisen area was studied in detail by Mather (1959). The following paragraphs summarise his principal conclusions.

1. Background Areas

Analyses of minus 82-mesh soil collected from a depth of 18 - 24 ins. at distances greater than 2,000 ft. from the mineralisation contain only 1 ppm of the element, whilst within 1,000 - 2,000 ft. of the mineralisation, soil overlying talc schist and amphibolite carries between 5 and 10 ppm arsenic. The arsenic content of synkinematic granite soils is erratic and ranges from 1 - 20 ppm. The patchy distribution of the arsenic in soils derived from this latter rock

is attributed to uneven metasomatism of the granite. For the purpose of delineating the anomalous zone, Mather established the threshold value of arsenic in soils at 10 ppm.

Analysis of the particle size fractions obtained by dry sieving the soil samples revealed an even distribution of arsenic between all the fractions and no concentrations of the element were observed in any particular sub-horizon of the soil profiles examined.

2. Mineralised Areas

A linear zone of arsenic rich soil 600 ft. long and 100 - 200 ft. wide carrying between 100 and 1,100 ppm arsenic was found by Mather in the vicinity of the Yirisen mineralisation.

A tendency for the arsenic to be associated with the coarse (plus 82-mesh) fractions rather than the fines (minus 82-mesh) was noted and was more marked in a pit 250 ft. from the mineralisation than in those nearer to it. The arsenic was found to be evenly distributed between the sub-horizons of the soil profiles examined, except in the pit at some distance from the mineralisation, referred to above, where higher concentrations of arsenic were found in the upper soil horizons. This was taken to indicate lateral dispersion of arsenic away from the mineralisation in the upper illuvial horizons of the soil profile.

In the indurated, concretionary latosols on the hill crests the arsenic content of the concretionary horizon was found to correspond closely with that of the underlying weathered rock.

II. The Distribution of Arsenic in Stream Bank Soils

A limited investigation of the arsenic distribution in the soils found at the stream margins was undertaken in the present work. These

soils consist largely of colluvial and residual material with, in places, some alluvium.

1. Background Areas

In the particle size fractions of freely drained and waterlogged bank soils from unmineralised areas, arsenic is preferentially concentrated in the plus 82-mesh fractions, particularly the plus 20-mesh material, and to a lesser extent in the clay. No significant difference is apparent in arsenic distribution in freely drained and waterlogged soils, (Figure 28).

2. Mineralised Areas

Near the mineralisation in the Kalm Col stream, the waterlogged bank soil exhibits a similar arsenic distribution to that of the background samples but the overall arsenic tenor is increased and the preferential concentration of the element in the plus 82-mesh fractions and the clay material is enhanced, (Figure 28). In contrast, the freely drained soil contains high concentrations of arsenic evenly distributed between all the size fractions.

The distribution of arsenic between the various size fractions is considered to reflect the form of occurrence of the element. The high concentration of arsenic in the coarse fractions is probably due to arsenic held in duricrust fragments. The low arsenic content of the intermediate fractions of the waterlogged soil as compared to those of their freely drained counterpart is probably due to lack of sorption-active sesquioxides, which would be soluble under the anaerobic conditions obtaining in the waterlogged soils.

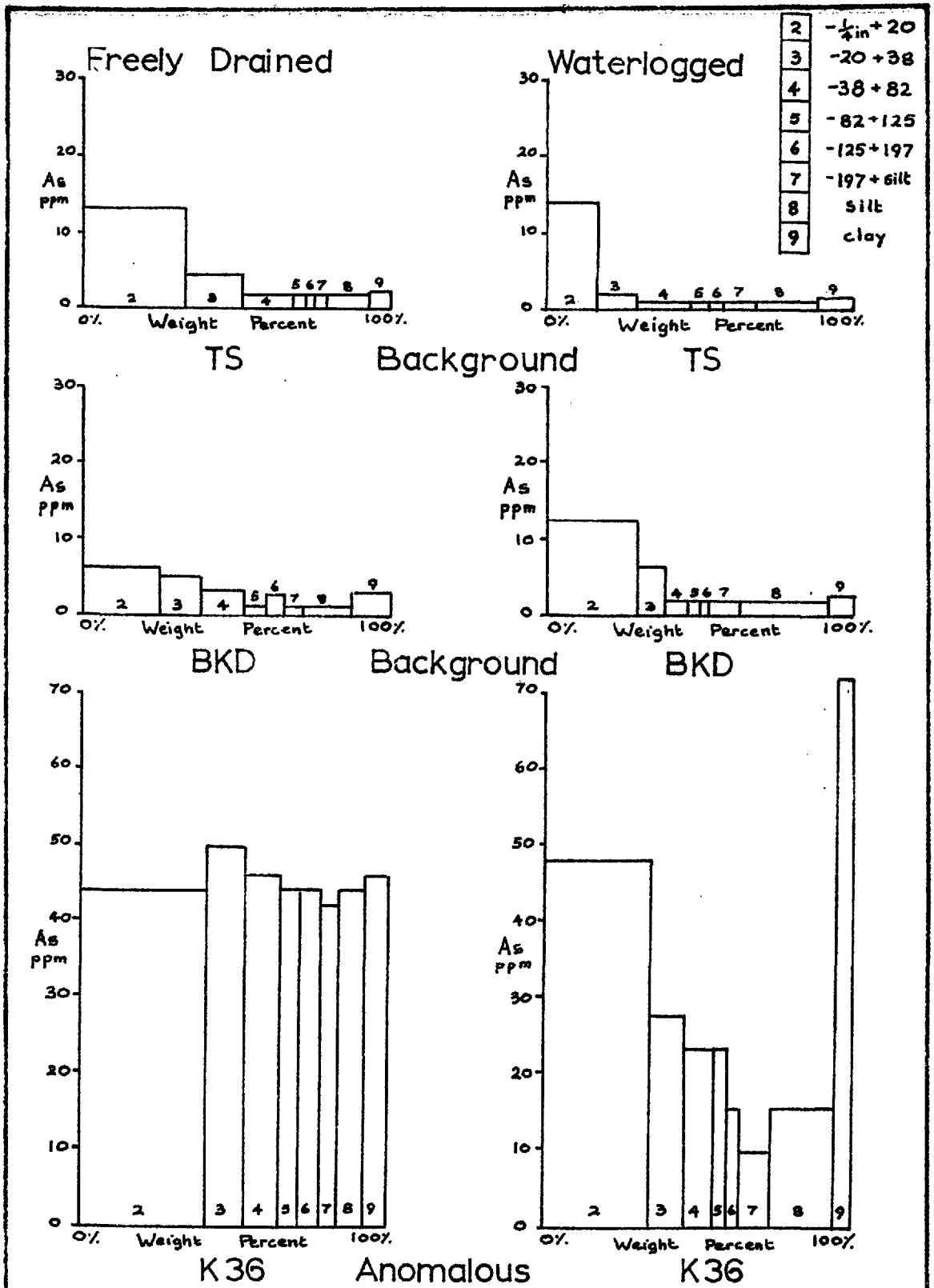


Figure 28. Distribution of Arsenic in Bank Soils

It is of interest to note that, when waterlogged, the clay fraction has a higher tenor than when freely drained. A similar observation was made on the waterlogged Sende River bank soils (molybdenum area) in the vicinity of the mineralisation and hence is not confined to a particular element. The higher metal tenor of the clay fraction of waterlogged soils as compared to freely drained soils may well be due to sorption of metal from groundwater entering the surface drainage.

III. Forms of Arsenic present in the Soil

Soil samples from the vicinity of mineralisation (Site K36) were used to examine the effect of waterlogging on the various forms of arsenic present in the soil. The forms investigated were (i) water-soluble arsenic, (ii) arsenic soluble in neutral, normal ammonium acetate solution, i.e. exchangeable arsenic, and (iii) arsenic soluble in neutral normal ammonium citrate solution, i.e. complexable arsenic.

The anomalous soil samples were collected from the freely drained valley slope and the waterlogged swampy Col. The swamp material was divided into two portions on collection, one part being kept in a sealed polythene bag to retain its moisture until analysed 12 months later in London, and the other being dried in the sun at the sample site.

Table 41. Solubility of Soil Arsenic in Various Extractants

	Wet Swamp Soil	Dried Swamp Soil	Freely Drained Soil
Total arsenic content ppm	75	60	45
Total iron ppm x 10^{-3}	17	18	16
Extractant	As ppm	As ppm	As ppm
Water			
1st Extract	<0.25	<0.25	<0.25
2nd Extract	0.25	<0.25	<0.25
Total	>0.25 <0.5	<0.5	<0.5
Neutral N Ammonium Acetate			
1st Extract	<0.25	0.5	<0.25
2nd Extract	<0.25	0.5	<0.25
Total	<0.5	1.0	<0.5
Neutral N Ammonium Citrate			
1st Extract	1.75	<0.25	1.25
2nd Extract	7.65	2.25	4.75
Total	9.40	2.25	6.0

Separate samples (2 g of the minus 82-mesh material) of these soils were agitated on an automatic shaker with 10 ml of each of the extractants for 15 minutes. After centrifuging, the liquor was decanted and analysed for arsenic. The procedure was then repeated with a fresh aliquot of the same extractant and this too was analysed for arsenic.

Two treatments were thought to be sufficient but this proved not to be the case. It is evident that further treatment would possibly extract additional amounts of arsenic, however, insufficient time was available for further experiments along these lines.

1. Water-soluble arsenic

Both the poorly drained swamp soil and the freely drained slope soil contain little water-soluble arsenic whilst 0.36 percent of the total arsenic content of the wet swamp soil is water-soluble (Table 41). It seems likely, therefore, that some of the arsenic is fixed against leaching by water during the drying process. Alternatively, the moist anaerobic storage conditions of the wet swamp soil may have promoted bacterial action resulting in an increase in the water-soluble arsenic content of this soil.

2. Acetate-soluble arsenic

The poorly drained swamp soil carries more arsenate ions, exchangeable by acetate ions, than the well drained valley slope soil. Comparison of the wet and dry swamp soils indicates that the amount of exchangeable arsenic increases on drying. The reason for this is not known but it seems possible that the drying process may convert some ferrous iron to ferric with a resultant increase in the number of exchange sites in the soil. The increase in exchangeable ions is not due to a change in the iron concentration in the soil since analysis indicates that the iron content of all the soils examined is very similar.

3. Citrate-soluble arsenic

The difference in the amounts of citrate soluble arsenic held by the dried poorly drained and well drained soils is considerable, being 3.6 and 13 percent of the total arsenic content respectively. The

undried swamp soil contained a similar proportion of citrate-soluble arsenic (12.6 percent) to that of the well drained soil. It would, therefore, appear that this form of arsenic is made less available if the poorly drained soil sample is dried before analysis. However, the remarks made above, concerning the possibility of bacterial action during storage of the sample, also apply to the citrate-soluble fraction of the wet swamp soil.

The relatively high concentration of citrate-soluble arsenic released from all the samples as compared to the other forms suggests that organic complexing compounds may well be important in solubilising and transporting arsenic in the soil.

From the present, very inadequate data it would appear that, in regions such as the field area having well defined wet and dry seasons, the drying out of the inundated latosol profile will influence the mobility of the various forms of arsenic in the soil to a different extent, the overall effect being to reduce the mobility of the element by promoting its fixation in the soil during the dry season. During the onset of the wet season, mobilisation of arsenic held by sesquioxides may be accelerated if on passing through the organic rich surface soil, the rain water takes into solution organic compounds capable of forming soluble complexes with the arsenic and the sesquioxides.

C. The Secondary Dispersion of Arsenic in Stream Sediments

Mather's limited investigation of the Kalm Col sediments revealed an anomalous zone 1,000 ft. long where the minus 82-mesh sediment contained between 100 and 200 ppm arsenic. This arsenic concentration diminished erratically from 100 to 20 ppm over a distance of 1,800 ft.

downstream and eventually reached the background concentration of 5 - 10 ppm, 3,500 - 4,000 ft. below the mineralisation. The principal source of the arsenic rich sediment was considered by Mather to be an area of soil on the flanks of the Kalm Col swamp 20,000 square yards in extent and carrying between 20 and 750 ppm arsenic.

In the present work a more detailed examination has been made of the distribution of arsenic in the drainage of the Yirisen area and in particular that of the Kalm Col stream.

I. Distribution of Arsenic according to the particle size of the Stream Sediment

1. Mechanical Composition of the Sediments

All the sediments examined exhibit a similar mechanical composition which closely resembles that of the Sende and Wankatana sediments, (Table 42). The bulk of the sediment is composed of plus 20-mesh material consisting mainly of tabular fragments of weathered schist and amphibolite with some duricrust concretions. The smaller particle sizes are very poorly represented, making up only 5 - 10 percent of the sediment and, as was noted in the Sende and Wankatana drainage systems, form a smaller proportion of the sediment than of the soil due to elutriation by the fast current of the streams.

Table 42. Mechanical Analyses and Arsenic Content of Yirisen Sediment

Description	Site and Sample No.	Size Fraction	-¼" +20	-20 +38	-38 +82	-82 +125	-125 +197	-197 +Silt	Silt	Clay
Regional Background	TS 220901	Weight %	70.7	11.4	4.4	1.1	0.9	2.5	6.2	2.5
		As ppm	50	10	10	10	10	10	10	190
Regional Background	BKD 220238	Weight %	82.5	4.4	2.6	0.26	0.32	0.92	1.85	1.85
		As ppm	44	48	14	14	14	12	18	24
Local Background	G11 220154	Weight %	70.0	6.5	3.1	3.1	1.4	4.9	6.9	3.7
		As ppm	14	12	6	6	4	4	8	14
Local Background	G22 220178	Weight %	75.9	8.9	3.0	0.8	0.9	3.0	4.9	2.2
		As ppm	44	18	16	14	10	10	12	12
3,500 ft. Downstream	K2 220228	Weight %	62.1	17.8	6.2	1.7	1.4	3.8	4.3	3.0
		As ppm	80	70	70	70	20	20	20	60
2,900 ft. Downstream	K7 220216	Weight %	73.0	11.0	4.9	1.9	1.5	2.3	2.8	2.1
		As ppm	140	130	90	90	70	70	170	190
2,000 ft. Downstream	K16 220920	Weight %	70.3	13.6	3.9	1.0	1.0	2.6	5.4	2.9
		As ppm	230	140	140	120	110	80	190	150
1,000 ft. Downstream	K26 220201	Weight %	64.4	14.5	3.9	1.0	0.8	2.5	5.6	3.2
		As ppm	190	140	60	70	70	60	80	30
At mineralisation	K36 220190	Weight %	70.9	12.7	6.2	1.0	1.3	2.1	3.1	2.4
		As ppm	180	260	140	140	140	220	260	330

2. The distribution of Arsenic in Sediments from Barren Areas

In background sediments arsenic resides chiefly in the plus 20-mesh fraction with values ranging from 15 - 50 ppm, (Table 42). The intermediate size fractions (minus20 plus 197-mesh) generally carry only a minor proportion of the total arsenic content of the sediment by virtue of their small bulk. Distinct concentrations of the element are found in the silt and clay fractions, particularly the latter, (Figure 29).

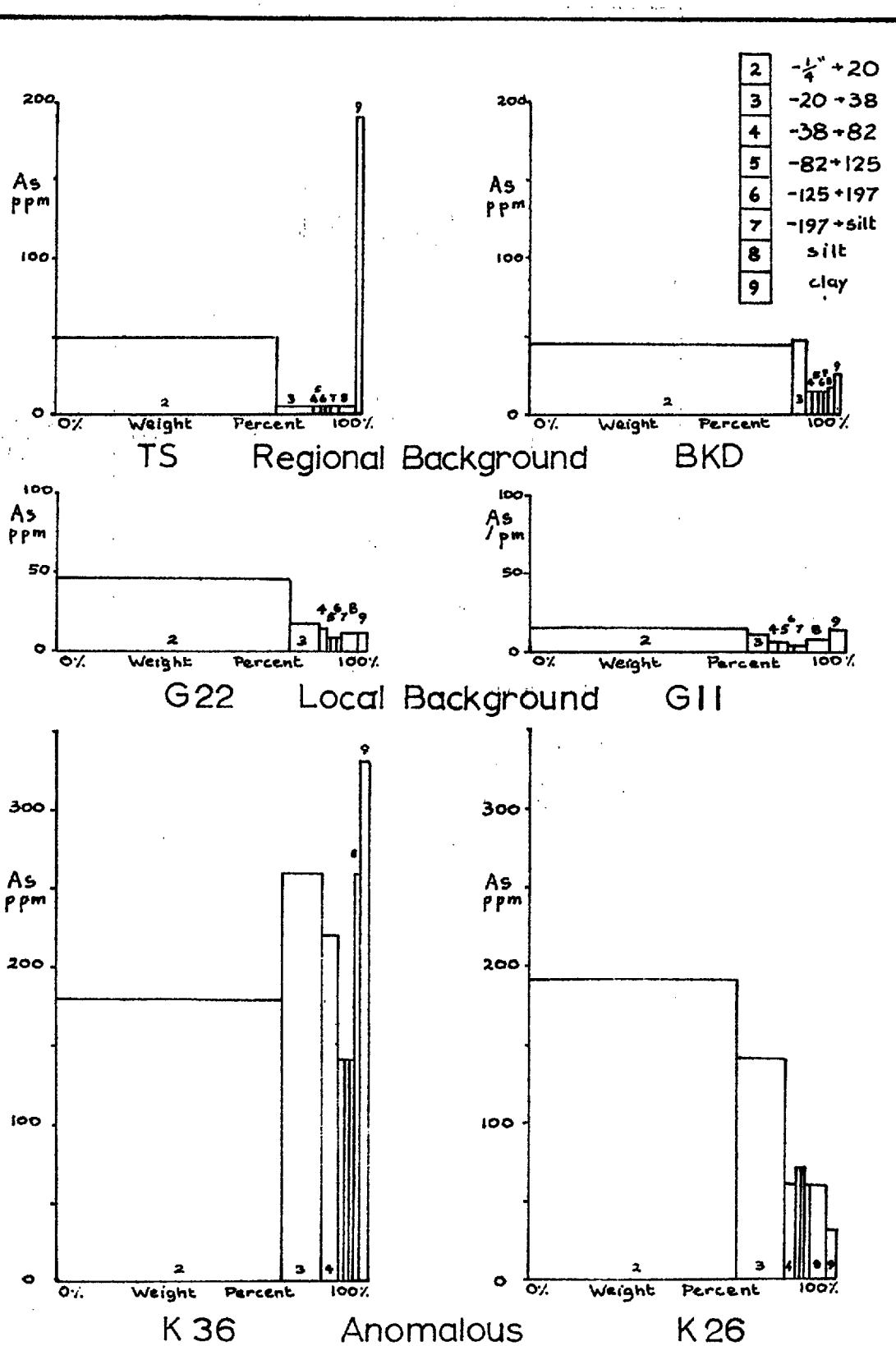


Figure29Distribution of Arsenic in Stream Sediment

By contrast with the bank soils the sediments of background streams carry appreciably higher tenors of arsenic whilst maintaining the same metal distribution between the particle size fractions. It may be recalled that a similar relationship between the tenor of stream sediments and bank soils was noted in the drainage systems examined in the section on molybdenum. Hence similar explanations to those suggested for the Sende and Wankatana drainage systems may also apply to the Kalm Col stream.

Whilst in the fine fractions of the sediment the increased tenor compared with the bank soils may be due to sorption activity this will not apply to the coarse material. That duricrust material is the chief host of arsenic in the coarse fractions of the sediment is indicated by analyses of the plus 20-mesh material of a background sediment, (Site TS, Figure 27) which show that the duricrust carries 18 times more arsenic than the talc schist. Similarly in the same fraction of sediment from a mineralised site (K36, Figure 27) the duricrust component carries 2.5 times more arsenic than the talc schist. Hence in the coarse sediment fractions the increased tenor as compared to the bank soils is considered to be due to the separation of the almost barren tabular talc schist flakes from the dense angular arsenic rich duricrust fragments by elutriation in the drainage system.

3. The Distribution of Arsenic in Sediments from Mineralised Areas

As in the background sediments, the sediment in the immediate vicinity of the mineralisation carries the bulk of its arsenic content in the plus 82-mesh fractions, particularly the plus 20-mesh material and exhibits distinct concentration of the element in the silt and clay fractions. This bimodal distribution of arsenic which is

present in both soil and sediment is taken to indicate two modes of dispersion of the element: mechanical dispersion of arsenic in the duricrust and rock fragment components and chemical dispersion in the sorption active components such as clay minerals and free iron oxides.

The tenor of the mineralised sediment is, again like that of the background sediment, higher than that of the bank soils, possible reasons for which have been suggested above.

In the sediment 1,000 ft. downstream from the mineralisation, (Site K26, Figure 29), although a concentration of arsenic is present in the coarse material only small amounts of arsenic are present in any of the minus 82-mesh fractions and the clay is conspicuously low in arsenic. The cause of this will be suggested in the following section (Section II).

II. Chemical Associations and Characteristics of Arsenic in Stream Sediments

In order to gain a better understanding of the distribution of arsenic in the stream sediments described above, a more intensive examination was made of the association of the element with other sediment components.

1. The association of arsenic with hydrated iron oxides

Selected samples from anomalous and background areas were treated in a manner similar to that described in the section on molybdenum to remove the hydrated iron oxides. It should be borne in mind that the free iron oxide associated arsenic will also include any loosely bonded arsenic removed by the dithionite treatment.

The proportion of the total arsenic which is associated with the free iron oxides is higher in the vicinity of mineralisation than in background areas. This is most marked in the minus 82-mesh fractions and is perhaps attributable to the exchange activity of this material, (Figure 30).

Most of the arsenic in background samples is lattice-held and even in mineralised samples an appreciable amount of the arsenic carried by the sediment resides in mineral lattices. This may be due to the incomplete weathering of the rock fragments before they enter the drainage system thus preserving any minor concentrations of disseminated sulphides and arsenic present in the rock forming minerals.

It is considered that lattice-held arsenic represents that form of the element present in the lattices of rock forming minerals in contrast to the free iron oxide associated arsenic which may be derived from the breakdown during weathering of both ore and host rock minerals.

A close relationship is apparent between the amount of free iron oxides present in the sediment and the concentration of arsenic in the very fine fractions in particular, (Figure 31a). This may possibly be ascribed to the activity of free iron oxides in sorbing arsenic from solution. The similarity in distribution of the free iron oxides and arsenic in the coarse fraction of the sediment is considered to indicate that arsenic may have been coprecipitated with the hydrated iron oxides during the formation of the duricrust, fragments of which are chiefly responsible for the high arsenic tenor of the coarse material.

The lack of arsenic in the clay fraction at the anomalous site 1,000 ft. beyond the mineralisation (Site K26), which was referred to earlier, may be attributed, in part, to the paucity of free iron oxides in this material.

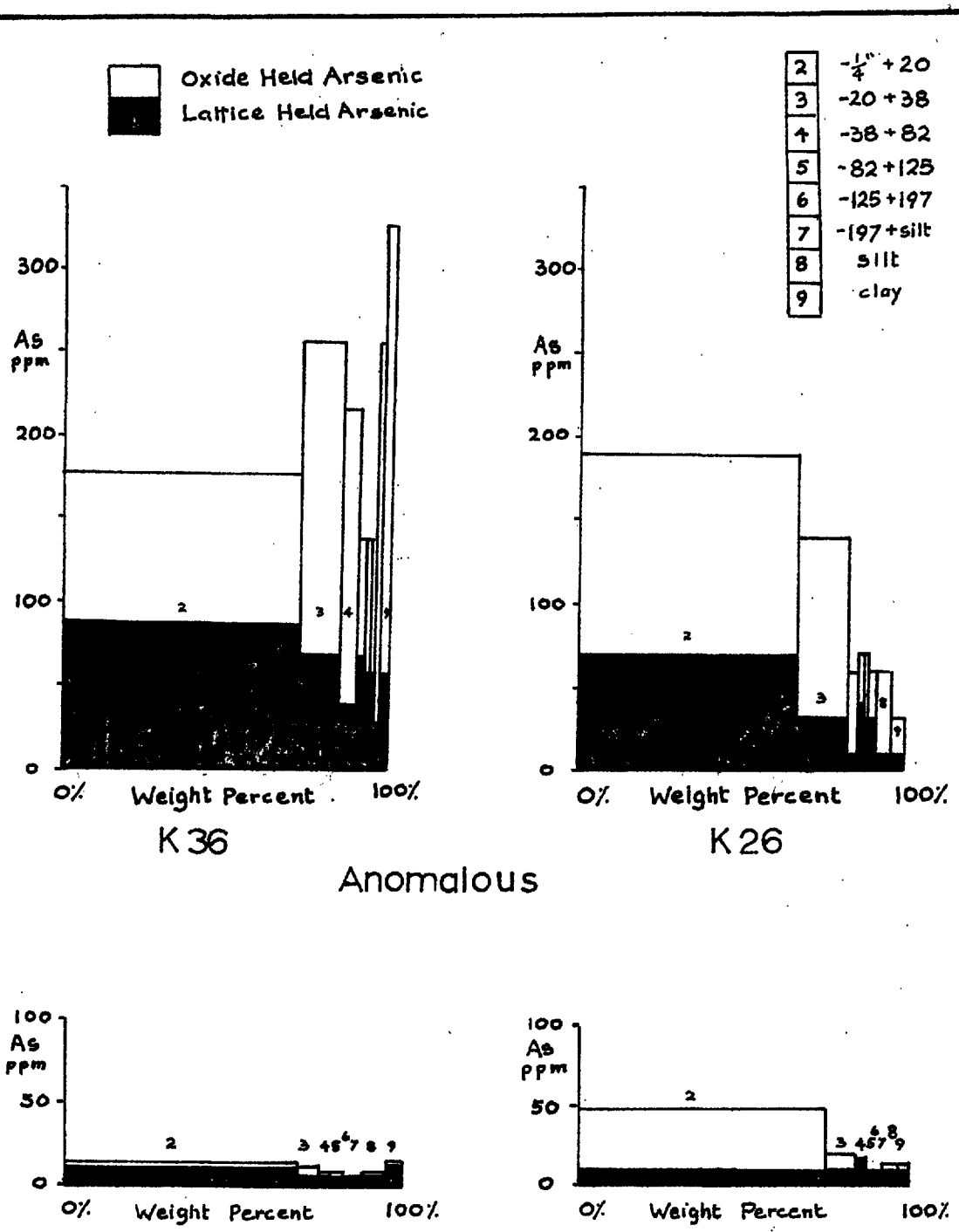


Figure30Distribution of Arsenic between Mineral Lattices and Hydrated Iron Oxides in Stream Sediment

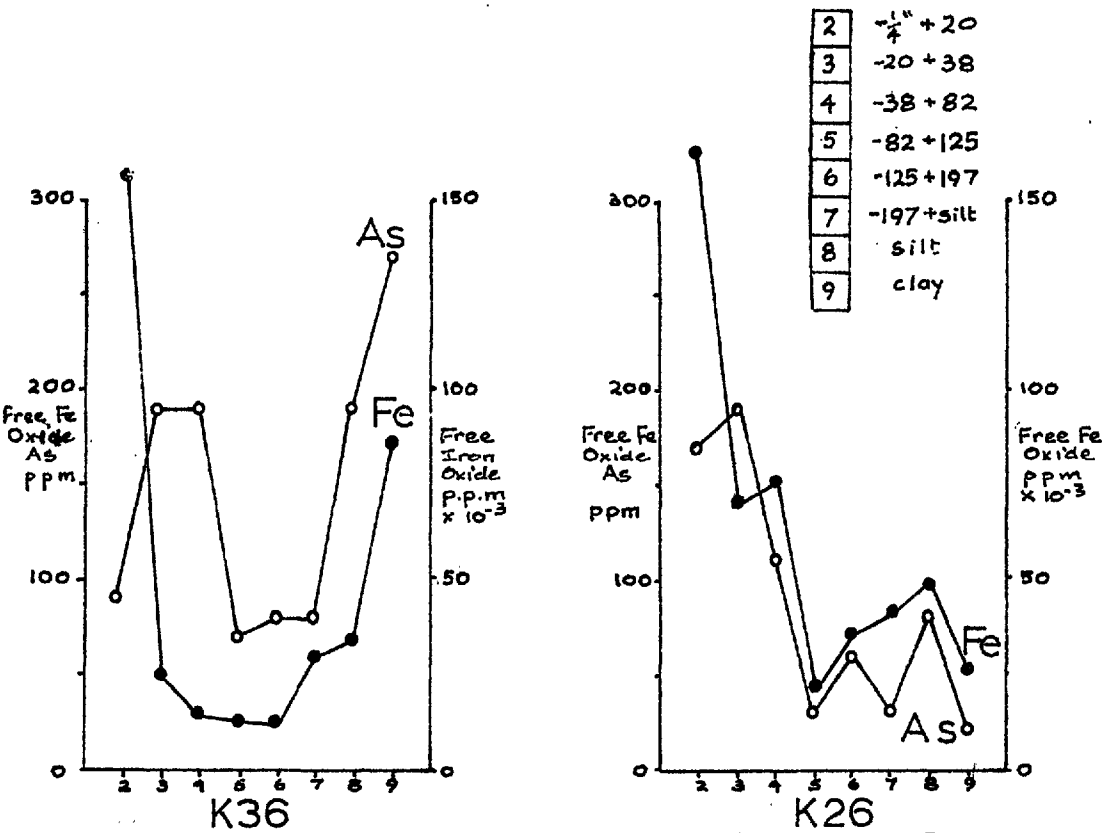


Fig 31 a. Association of Arsenic and Free Iron Oxides in Stream Sediment

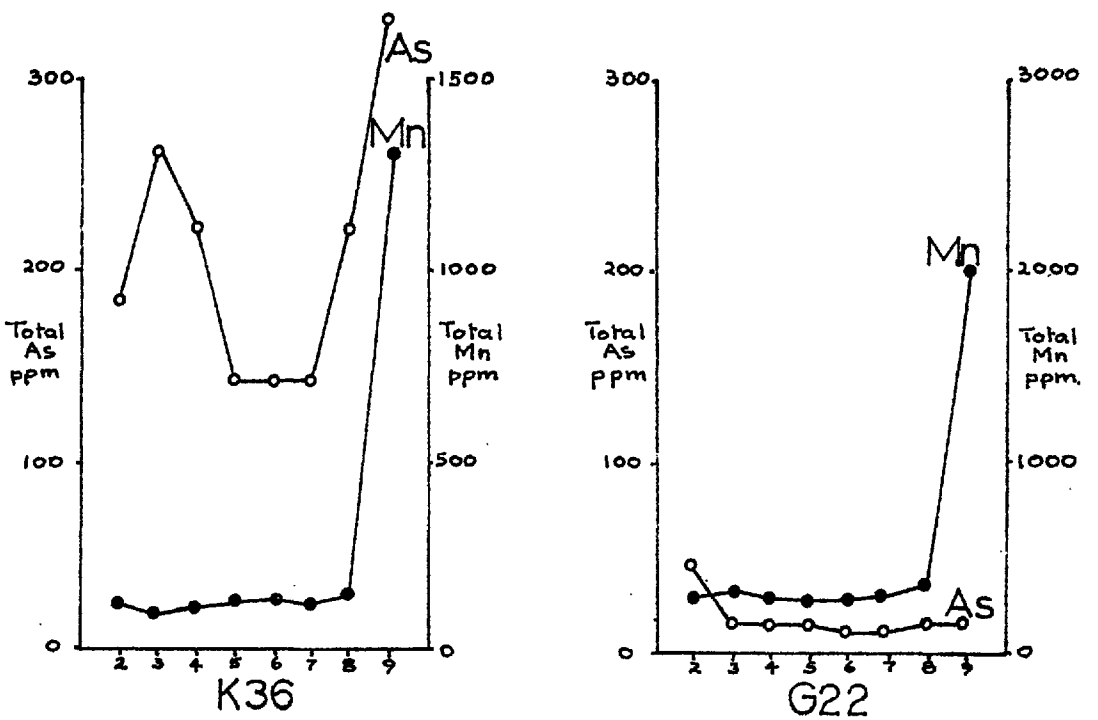


Fig 31 b. Association of Arsenic and Manganese in Stream Sediment

2. The association of arsenic and manganese

The efficiency of hydrated manganese oxide as a scavenger of arsenic from solution (Sugawara et al 1956) suggested the possibility that this may take place either in the soils or the streams examined.

From Figure (3b) it will be seen that, whilst manganese exhibits a strong affinity for the clay sized sediment, a tendency already noted in the Sende sediments, arsenic is only strongly associated with the clay material in the vicinity of mineralisation, (Site K36). Furthermore, manganese, in contrast to arsenic, shows no tendency to be concentrated in the coarse duricrust bearing sediment. It is evident, therefore, that there is no direct association of arsenic and manganese in the sediments examined.

3. The association of arsenic and organic carbon

The very fine grained sediment collected on Whatman No. 542 filter papers and glass fibre filter papers were examined for a relationship between the arsenic and organic carbon contents.

Table 43. Arsenic and Organic Carbon Content of fine grained suspended Sediment

Site	K36	K26	K16	K7	K2	BKD	TS	G22
Distance from mineralisation, ft.	0	1000	2000	2900	3500	Background		
			Arsenic	ppm				
542 suspension	260	200	120	80	60	10	10	<10
Glass filter suspension	320	230	220	60	50	40	40	20
			Organic Carbon	Percent				
Glass filter suspension	5.7	7.1	18.7	7.0	5.9	7.7	26.9	2.5

It is clear that no direct relationship exists between the amount of organic carbon and the arsenic content of the glass fibre filter residue (Table 43). The higher arsenic content of the finer glass fibre filter residue as compared to the 542 residue is possibly due to the inclusion of a higher proportion of arsenic bearing clay in the former material.

III. The Dispersion of Arsenic in Stream Sediment downstream from the Mineralisation

1. Distribution of arsenic in selected components of the stream sediment

Various components of the stream sediment, e.g plus and minus 82-mesh fractions and fine grained bottom sediment, downstream from the Kalm Col mineralisation were examined in order to discover the extent of the dispersion of arsenic in the drainage and the factors contributing to the development of such a drainage dispersion train.

a) Coarse sediment fraction (plus 82-mesh material)

Near the bedrock source, (Site K36), the coarse stream sediment carries an arsenic tenor which is consistent with its derivation from the related bank soils, (Figure 32). However, 1,000 ft. downstream, (Site K26) whilst the sediment tenor has risen to nearly 200 ppm arsenic that of the bank soils is close to the background range, (10 ppm). This site (K26) is located on marshy ground at the base of the precipitous descent from the Col. It is concluded, therefore, that the high tenor of the coarse sediment is due to deposition of coarse particles derived from the mineralisation in the Col, in response to the sudden change in the stream gradient. The sorting of talc schist flakes from metal bearing duricrust fragments, previously referred to, may possibly account for the increase in arsenic tenor at this point as compared to that of the sediment in the Col.

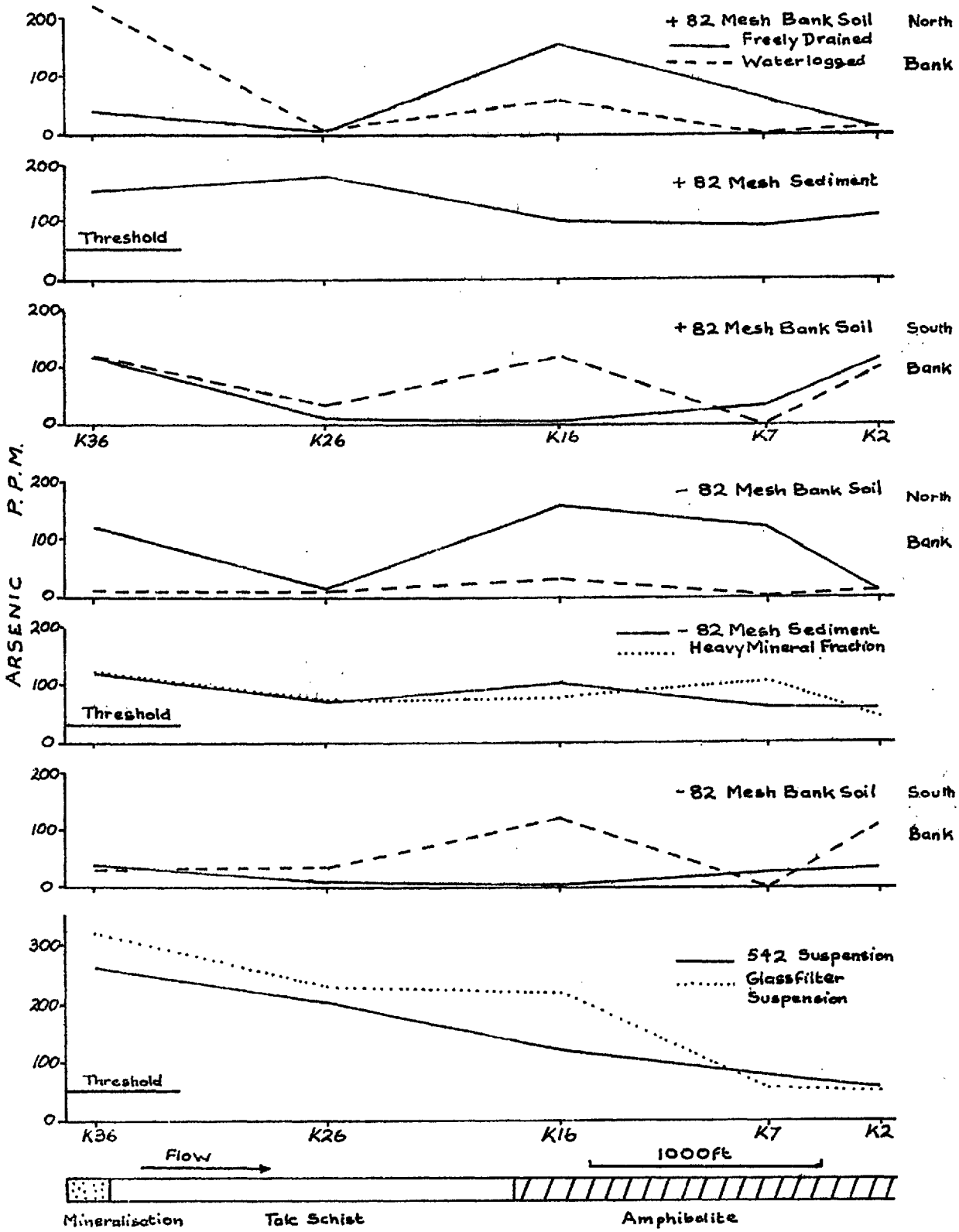


Figure 32 Distribution of Arsenic in Stream Bank Soils and Sediments Downstream from Kalm Col.

About 2,000 ft. downstream from the mineralisation (Site K16), the arsenic tenor of the sediment has fallen to 100 ppm, through dilution by the almost barren bank soils, at which level it remains until the main River Yirisen is reached. In the region of this site, (K16), the bank soils on each side of the stream differ markedly in arsenic tenor and character.

The freely drained soil of the north bank carries a high arsenic tenor and overlies waterlogged soil with a much lower metal content; on the south bank the reverse is the case, with almost barren freely drained soil overlying a metal rich waterlogged horizon. This difference in metal distribution is considered to reflect a dissimilar structure of the two stream banks. It will be noted from Figure (32) that the fine fraction (minus 82-mesh) of the bank soils has essentially the same metal distribution as those of the coarse fractions. The origin of the metal distribution is therefore probably common to both size fractions, i.e. mechanical and not due to sorption effects, which would only be exhibited by the fines.

The site K16 is well removed from mineralisation (2,000 ft.) and the adjacent slope soils carry only background tenors of arsenic (5 - 20 ppm). It may be expected therefore that residual and colluvial bank material will have arsenic tenors of this order. On the other hand the stream sediment at this point carries 100 ppm arsenic. It is concluded therefore that the arsenic rich sections of the banks are composed of alluvium whilst the arsenic poor sections consist of colluvial or residual material.

Thus the structure of the north bank is interpreted as being of alluvium deposited on a residual bank and that of the south bank as colluvium overlying alluvium.

Furthermore, near the confluence with the River Yirisen (Site K2) an alluvial terrace on the south bank of the Kalm Col stream contains 75 ppm arsenic rising to 125 ppm in the stream bank itself.

The entry of material from these banks by soil creep and bank erosion may account for the maintenance of the anomalous tenor of the coarse sediment over the last 1,500 ft. of drainage.

No data are available for the waterlogged horizon of the banks of the Kalm Col stream at Site K7, 3,500 ft. below the mineralisation since the stream flows in a solid rock channel at this point.

At several points along its course the Kalm Col stream is joined by tributaries, of which those entering 1,000 ft and 2,000 ft. (Sites K26 and K16) downstream from the mineralisation are of particular interest since their headwaters may be draining the area of anomalous soil delineated by Mather. The contribution of arsenic bearing sediment to the Kalm Col stream by these tributaries cannot be discounted. Unfortunately, no data for the arsenic content of the coarse fractions of these tributary sediments at their point of entry were obtained. However, since the fine sediment fraction (minus 82-mesh) carries less than 10 ppm arsenic in both cases, it is considered that the contribution of arsenic to the Kalm Col drainage by the coarse fractions of the tributary sediments will also be low.

It is concluded, therefore, that the dispersion of arsenic in the coarse fraction of the Kalm Col sediment is of a mechanical nature and is not inconsistent with the sediment being derived from bank materials by erosion and soil creep.

b) Fine sediment fraction (minus 82-mesh material)

The arsenic carried by the fine sediment fractions may be derived from the stream bank soils by erosion or by sorption from surface and ground waters.

Near the mineralisation (Site K36) the arsenic content of the fine sediment is consistent with its derivation from the freely drained bank soils, but not from the waterlogged horizons of the swamp soil which contain comparatively little arsenic, (Figure 32). It would appear, therefore, that material enters the drainage dominantly by soil creep and sheet wash rather than by bank erosion which would contribute material with a lower arsenic content than that of the sediment. However it was concluded above that bank erosion is, in part, responsible for bringing coarse bank material into the drainage; this must also apply to the fines. Hence it seems likely that fine bank material enters the drainage both by erosion and soil creep. Furthermore, there is also the possibility that the waterlogged soil on entering the more oxidised conditions of the surface drainage, is capable of sorbing arsenic from solution due to the presence of freshly precipitated hydrated iron oxides.

The metal tenor of the fine sediment is only gradually reduced with increasing distance from the mineralisation. Examination of the stream banks about 2,000 ft. downstream (Site K16) suggests that the tenor of the sediment may be enhanced by arsenic rich bank material entering the drainage. The distribution of arsenic in the fine fraction of the bank soils at this point closely resembles that of the coarse material referred to in the previous section. It is concluded that both fractions have the same origin and that the high arsenic tenor

in the waterlogged horizon as compared to the freely drained soil is not due to sorption of arsenic from ground water but is of alluvial origin.

As previously mentioned, the fine fractions of the tributary sediments at their confluence with the Kalm Col stream carry only background amounts of arsenic and hence are considered to have little influence on the arsenic dispersion train in the main stream.

It is concluded, therefore, that dispersion of arsenic in the fine fraction of the Kalm Col sediments, like that of the coarse material, is predominantly mechanical and that the chief source of the sediment is the stream bank material. This conclusion is further supported by the close similarity in behaviour of the unreactive heavy mineral component of the fine sediment fraction, with the fine fraction as a whole.

c) Fine grained bottom sediment

Examination of the fine grained bottom sediment collected by filtration on to Whatman No. 542 papers and glass fibre filters indicates that these materials carry very high tenors of arsenic, perhaps due to the high silt and clay content of these fractions.

The arsenic content in both types of material falls gradually to background levels consistent with steady dilution with barren material. It is considered, therefore, that the arsenic carried by this type of material is also predominantly mechanically dispersed.

2. Variation in the distribution of arsenic in the particle size fractions of the sediment downstream from mineralisation.

More detailed analyses of the particle size fractions of the sediment along the length of the Kalm Col stream generally confirm the conclusions drawn in the previous section.

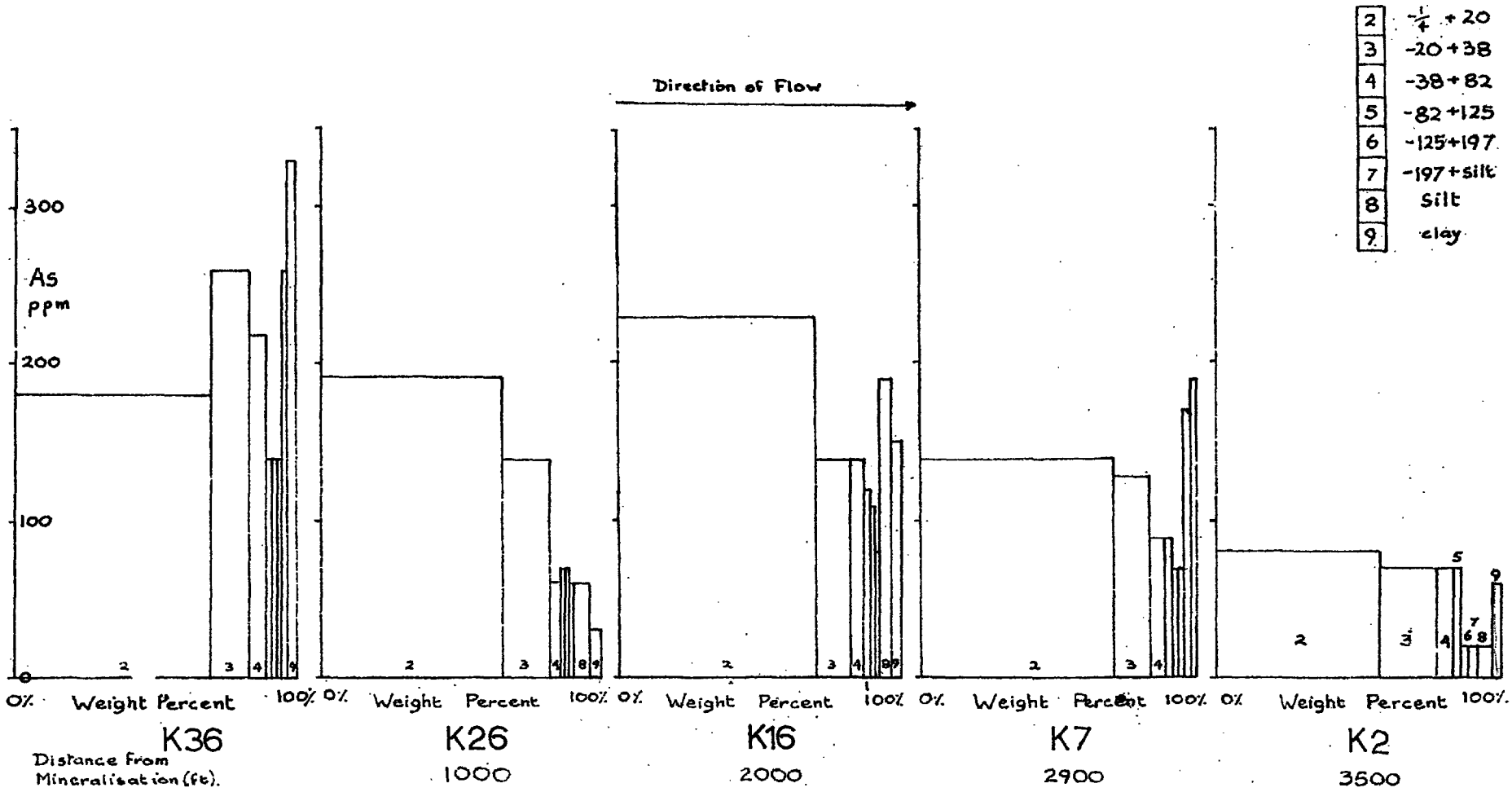


Figure 33. Downstream Distribution of Arsenic in Sediment Size Fractions

The bulk of the arsenic in the sediment is carried by the very coarse fraction (plus 20-mesh), whilst the high tenor of the silt and clay fractions is consistent with the high arsenic content of the very fine grained bottom sediments as previously suggested, (Figure 33).

It is considered therefore, that the chief source of the anomalous sediment is the Kalm Col mineralisation and that arsenic rich material is mechanically dispersed downstream, its tenor being protected from dilution by barren material by the re-working of alluvium deposited in the banks. There is little evidence of any extensive sorption activity except in the swampy Col near the bedrock source of the arsenic.

D. The Secondary Dispersion of Arsenic in Stream Waters.

Very few data concerning arsenic in the waters of the Yirisen area were obtained by Mather because of the inadequacy of the analytical methods available at that time.

Using the coprecipitation technique developed in the present study soluble ionic arsenic was detected in the waters of the streams studied by Mather although the procedure is still far from satisfactory and the waters of the mineralised area cannot be distinguished from those of barren streams with any degree of certainty.

I. The Physical and Chemical Characteristics of Yirisen Stream Waters.

The analytical data obtained for the Yirisen stream waters are summarised in Table (44).

1. Temperature

The temperature of the stream waters examined ranged from 22.5 - 27.0°C, average 23°C in February and from 26.0 - 30.0°C, average 28°C in April. These are slightly higher values than those given by the Sende and Wankatana waters, due no doubt to the fact that the Yirisen streams are smaller in volume and have less vegetation cover.

Table 44. Analytical Data for Yirisen Stream Waters

Site No.	Distance from mineralisation feet	Temperature		Bicarbonate ppm		pH		Eh volts		SO_4^{--} ppm	Fe ppm	As ppb
		Feb.	April	Feb.	April	Feb.	April	Feb.	April	Feb.	Feb.	Feb.
K36	At mineraln.	22.5	27.5	26.9	27.6	7.2	7.3	0.34	0.32	<2.5	<1.0	0.21
K26	1,000 Downstream	27.0	30.0	52.2	38.8	7.2	6.9	0.28	0.32	<2.5	<1.0	0.21
K16	2,000 Downstream	-	26.0	-	53.2	-	7.2	-	0.39	-	-	0.17
K7	2,900 Downstream	22.5	-	46.2	51.2	7.4	7.4	0.31	0.34	<2.5	<1.0	0.17
K2	3,500 Downstream	24.0	-	41.5	44.5	7.4	7.6	0.32	0.33	<2.5	<1.0	0.17
G11	Background	22.5	-	36.4	-	6.9	-	0.31	-	<2.5	<1.0	0.13
G22	Background	22.5	-	26.8	24.1	6.9	6.8	0.34	0.36	<2.5	<1.0	0.22
TS	Background	-	30.0	-	39.2	-	7.3	-	0.33	<2.5	<1.0	0.23
PKD	Background	21.0	30.0	50.6	39.2	7.2	7.2	0.29	0.36	<2.5	<1.0	0.14

2. Redox Potential and Hydrogen Ion Concentration

The oxidation potentials of the Yirisen waters range from 0.28v to 0.39 v (Table 44). The values are plotted in Figure (34) where it will be seen that they all lie within the arsenate stability field, and in the field of solid ferric hydroxide.

The pH values encountered ranged from 6.9 to 7.4. It is not surprising that these values are higher than those of the waters draining the mainly duricrusted amphibolite or granite of the molybdenum study areas, since the principal rock type in the Yirisen area is unduricrusted talc schist. Thus not only are carbonates available in the rock but, in the absence of duricrust, they are easily leached from the rock and unconsolidated soil.

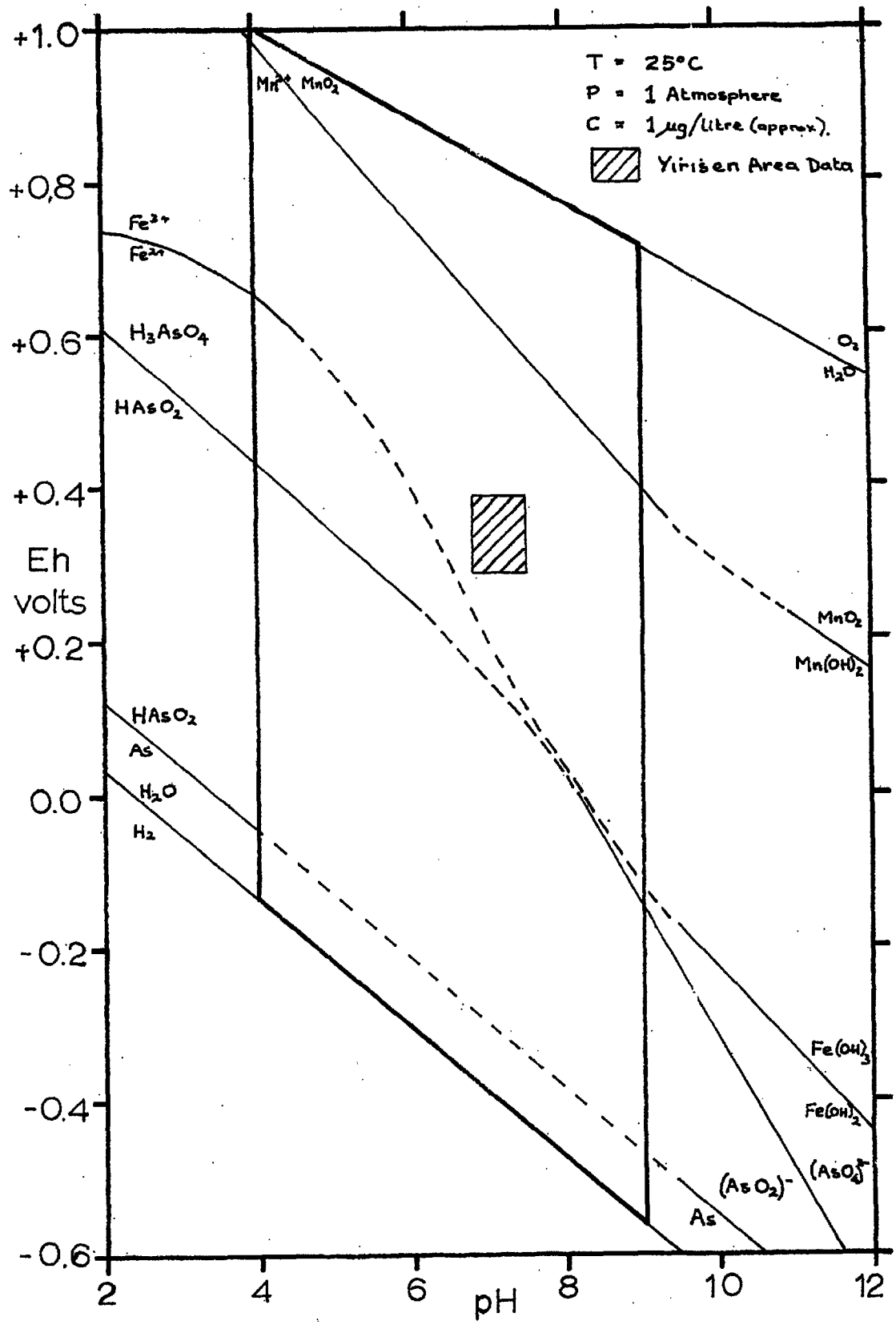


Figure 34. Stability Fields of Ionic Species of As, Fe, and Mn.
(after Krauskopf 1955)

3. Dissolved Solids Content

No data are available on the total dissolved solids content of these waters owing to difficulties encountered during evaporation.

a) Sulphate content

Analyses carried out at the sample site for sulphate failed to detect this ion. It is concluded therefore, that the sulphate content of the stream water is less than 2.5 ppm (mg/litre).

b) Bicarbonate content

Sample site analyses indicate a range of bicarbonate concentration in the waters examined of 24 - 53 mg/litre. These relatively high values are consistent with the occurrence of an actively weathering carbonate bearing rock in the catchment area. No carbonate ions are present in the waters since the pH values are less than 8.35, below which level carbonate ions are converted to bicarbonate ions.

c) Iron content

The analytical procedure used at the sample site proved to be inadequate to detect the very low iron concentrations encountered. Owing to the low affinity of the Dowex resins for iron, a factor not known at the time of the investigations, no additional data could be obtained by ion exchange concentration. It is assumed therefore, that the iron concentration in the stream waters is less than 1.0 mg/litre; the limit of sensitivity of the field test.

d) Arsenic content

The arsenic concentrations observed in the Yirisen stream water obtained by the coprecipitation method are given in Table (45). The average arsenic concentration (determinations were made in triplicate) ranged from 0.13 - 0.23 ppb (micrograms per litre). Confirmation

of these values by analyses of the Dowex resin eluates was invalidated due to contamination during the analytical procedure.

Table 45. Arsenic Content of Yirisen Stream Waters by Coprecipitation Technique

Precipitate Site	K36	K26	K16	K7	K2	G11	G22	BKD	TS
Distance from mineralisation ft.	0	1000	2000	2900	3500	2000	1000	2000	5000
(1) As ppb	0.20	0.25	0.24	0.15	0.24	0.15	0.30	0.18	0.25
(2) As ppb	0.20	0.24	0.23	0.18	0.15	0.12	0.18	0.18	0.23
(3) As ppb	0.24	0.15	0.12	0.20	0.12	0.12	0.18	0.12	0.22
Av. As ppb	0.21	0.21	0.17	0.17	0.17	0.13	0.22	0.14	0.23

Water samples of 5 litres volume from a background site (G11) and a mineralised site (K36), acidified with hydrochloric acid in the field and shipped to London for analysis were evaporated down to a volume of one litre. This volume (1 litre) is greater than that at which an azeotropic mixture of water and hydrochloric acid would form which would result in the loss of arsenic as a chloride.

After neutralisation with ammonia solution, the samples were treated with the coprecipitation reagents and the precipitates obtained were analysed for arsenic. The background sample (G11) was found to contain 0.12 ppb arsenic as compared with 0.13 ppb arsenic obtained in the field, whilst the anomalous sample (K36) contained 0.9 ppb arsenic compared with an average of 0.21 ppb in the field precipitates.

The lack of agreement between the field and laboratory determinations on the anomalous sample underlines the poor precision of the coprecipitation procedure. It is of interest to note that whilst in the field precipitation was spontaneous, in some of the laboratory trials precipitation had to be initiated by scratching the vessel with a file.

It is clear, therefore, that no definite statement can be made concerning the arsenic content of the Yirisen area stream waters, except that it appears to be very low, in the region of 1 ppb.

The arsenic content of waters from other parts of the world is shown in Table (46). Even allowing for the poor extraction given by the coprecipitation technique, the arsenic content of the surface waters of the field area is notably low.

Table 46. Arsenic content (ppb) of Natural Waters

Location	Ground Water	Springs	Mine Water	Surface Water	Sea Water	Reference
New Zealand		Trace - 26,000				Grimmett & McIntosh 1939
Brazil				1 - 3		Bastos & Salum 1958
Ghana			150-750			Maker 1958
Sierra Leone			1 - 160			Mather 1959
Austria			3400 - 5200			Hayek & Weirer 1951
Germany				4.5-13.4 22		Heide & Moenke 1956
Germany				2 - 3		von Bulow & Otto 1931
U.S.A. Colorado			8×10^6			Clarke 1924
U.S.A.	0-8500			0 - 8	1 - 8	Kehoe et al 1944
U.S.A. S. Dak.		500				Miller & Byers 1935
Japan		0.4			1.1	Sugawara et al 1956
Japan					3.6	Ishibashi et al 1951
Atlantic Ocean					12-16	Black & Mitchell 1952
U.S.S.R. S. Urals			100-200			Herman 1958

E. Summary of Observations and Conclusions on the Secondary Dispersion of Arsenic in the Kalm Col Drainage System.

1. Arsenopyrite bearing quartz veins occur in the Yirisen river valley in Sierra Leone. The veins, some of which carry gold, conform to the strike of the enclosing talc schists.

2. On the higher slopes and hill tops the mineralised zone is overlain by a mature indurated latosol whilst on the steep rejuvenated valley slopes, a thin, unconsolidated, immature soil is being developed. Both the unconsolidated soil and the concretionary latosol contribute barren and arsenic bearing material to the drainage system by soil creep and sheet wash.

3. Arsenic is concentrated in the plus 20-mesh fraction of the background bank soils, which consist chiefly of ironstone concretions and talc schist fragments. There is no significant difference in arsenic distribution in freely drained and waterlogged bank soil in background areas.

4. The linear mineralised zone passes through a swampy Col (Kalm Col) in which the drainage system investigated originates. The soil overlying the mineralisation contains up to 200 ppm arsenic compared to 5 - 15 ppm in background bank soils. The arsenic is evenly distributed between the particle size fractions of freely drained anomalous soil whilst, in waterlogged anomalous soil, distinct concentration of the element is observed in the clay size material. Intermediate size fractions of the anomalous waterlogged soil have lower tenors than those of freely drained soils. This is attributed to the solubilisation of sesquioxides at deeper, more anaerobic levels in the swamp soils.

5. Soils which have been dried out in the sun before analysis released less watersoluble but more acetate-soluble arsenic after 30 minutes treatment than samples kept in their original moist condition until analysed. It would appear, therefore, that fixation of certain forms of arsenic takes place on drying the sample. This may be due to the water-soluble components being fixed by sesquioxides during the drying process and the sesquioxide-held arsenic being, in part, exchangeable by acetate ions.

6. A solution, containing citrate ions capable of forming soluble complexes with iron, released considerably more arsenic from both swamp and slope soils than either water or an acetate solution. This is considered to indicate the importance of complexing ions in promoting the dispersion of arsenic in the soil and drainage system.

Dried swamp soil released less citrate-soluble arsenic than moist swamp soil indicating that the drying process also causes fixation of complexable arsenic.

However, the possibility of bacterial action solubilising some of the arsenic in the sealed moist soil during storage must also be considered.

7. The stream sediments consist mainly of coarse material, arsenic rich latosol concretions and nearly barren talc schist fragments, with only a small proportion of minus 82-mesh particles.

8. In background sediments the bulk of the arsenic is carried in the plus 20-mesh fraction in amounts up to 50 ppm. This is consistent with its derivation from the stream bank soils. Some sorption activity is shown by the clay size particles but this is not generally very significant.

9. Mineralised sediments also carry the bulk of their arsenic in the coarse fractions, particularly the plus 20-mesh material. The arsenic content of the minus 82-mesh stream sediment from mineralised sites, ranges from 30 - 100 ppm compared to 5 - 30 ppm in background sediments. The silt and clay fractions, although of insignificant bulk, may have the highest arsenic tenors. The bimodal distribution of arsenic is taken to indicate two forms of occurrence of the element in the bank soils and stream sediments

a) in duricrust and rock fragments

and b) sorbed on the surface of active particles such as clays and hydrated iron oxides.

10. In background sediments most of the arsenic is held in mineral lattices whilst in the vicinity of mineralisation a considerable proportion of the total arsenic content of the sediment is associated with free iron oxides.

11. It is considered that the lattice-held arsenic represents that present in the lattices of rock forming minerals whilst the arsenic associated with the free iron oxides is derived from the breakdown of both ore and host rock minerals.

12. The appreciable proportion of the total arsenic carried in the mineral lattices of the stream sediment is attributed to the incomplete weathering of rock fragments before they enter the drainage system.

13. There is no direct association of arsenic with either manganese or organic carbon in the sediments examined.

14. The distribution of arsenic in the sediments downstream from the Kalm Col mineralisation may be largely interpreted in terms of their derivation from the related bank soils. The contribution of tributary sediments to the arsenic dispersion train in the Kalm Col drainage is negligible.

15. There is little evidence of the sorption of arsenic from surface or groundwater elsewhere than in the immediate vicinity of the mineralisation.

16. Very fine grained bottom sediments carry notably high tenors of arsenic possibly due to a high content of arsenic rich clay material.

17. It is concluded that arsenic held in the Kalm Col sediments is mainly being mechanically dispersed downstream from the mineralisation.

18. The stream waters of the Yirisen area contain only very low concentrations of soluble arsenic.

PART SIX. FACTORS INFLUENCING THE SECONDARY DISPERSION OF ARSENIC IN THE KALM COL DRAINAGE SYSTEM

Most data regarding the behaviour of arsenic in the zone of weathering are concerned with soil arsenic. No previous study of the behaviour of arsenic in drainage systems appears to have been made prior to the work of Mather (1959). The basic chemical principles governing the dispersion of this element in the soil apply to stream sediments, but are modified by the increased proportion of water in the drainage system as compared with the soil.

The geological, chemical and biological character of the Yirisen area exert a combined influence on the extent of secondary dispersion undergone by arsenic. The results of the present study will be examined in the light of data on some of the more significant factors which appear to control the mobility of arsenic in the zone of weathering.

I. Geological Factors

1. The Form of the Mineralisation

The mineralisation exposed by the Yirisen river carries arsenopyrite in fine grained, sericitic quartz veins, running parallel to the schistosity of the surrounding talc-chlorite-carbonate schist.

Mather's work suggests that the primary dispersion of arsenic, in concentrations greater than 50 ppm, is limited to within 120 ft. of the veins. The mobility of arsenic is thus likely to be restricted by the resistance to weathering of its quartz host and the element will only slowly be released into the soil.

Pyrite, which occurs in the veins and disseminated within the schist may be a further source of arsenic since this mineral often carries the element as an impurity in its lattice, and the inclusion

of arsenic in the lattices of other minerals such as quartz and plagioclose felspar is not to be discounted.

The nature of the mineralisation at Kalm Col is not known, but since the Col is on the northern extension of the strike of the Yirisen veins, a similar character is assumed.

2. The Nature of the Host Rock of the Mineralisation

The chief influence of the country rock on the dispersion of arsenic from the mineralisation lies in its control of the type of latosol and secondary mineral species produced by the weathering process. The topography and vegetation of the area are also within its sphere of influence.

i) Latosol Formation

The talc-chlorite-carbonate schist is, by nature, soft and its resistance to weathering is further reduced by the nearly vertical dip of the foliation which facilitates the entry of rainwater.

Owing to the rejuvenation of the Yirisen drainage system, the mineralised zone is overlain by both indurated and non-indurated latosols. The wide, old valley floor is deeply weathered, its slopes and the tops of flanking hills are overlain by mature concretionary latosols. The hill cappings are of the same origin as the extensive areas of duricrust described in the molybdenum field areas further north. The formation of a concretionary latosol over this ferromagnesian rock is not surprising in view of its iron content of 7.24 percent (Fe_2O_3 + FeO).

During the formation of the indurated latosol, secondary dispersion of arsenic took place from the weathering mineralisation. This dispersion aureole of arsenic rich soil has been dissected by subsequent weathering to leave only outliers of anomalous soil on the spurs of

the old valley where the mineralisation occurs. Mather suggests that this may be the explanation for the high arsenic content of isolated duricrusted areas which are surrounded by nearly barren freshly weathering talc schist.

The Yirisen River has cut through the old valley floor to a depth of over 100 ft. to expose solid rock in the stream channel. On the steep, new valley slopes a thin, rubbly, immature soil is forming. Arsenic in these unconsolidated soils will be more mobile than that in the indurated latosols since they are easily leached by the rain and support a prolific vegetation, which may promote the solubilisation of arsenic by supplying organic debris, the source of chelating agents capable of suppressing the sorption of the element by iron oxides.

The coarse fractions of the stream sediment consist mainly of duricrust fragments and flakes of talc schist, samples of which from mineralised and background areas gave values of 2.4 : 1 and 18 : 1, respectively, for the ratio of the arsenic content of the concretionary material to that of the schist fragments. This is considered to support the idea of concentration of arsenic in the concretionary latosols during their formation. Arsenic thus held in the iron oxides of the concretions is being mechanically dispersed in the coarse fractions of the sediment. Incomplete weathering of the talc schist fragments before entering the drainage is considered to be responsible for the high proportion of arsenic held in the mineral lattices of the sediment.

Topography

The rejuvenation of the drainage system and easily weathered rock of the catchment area, combine to produce dissected ridges of high ground separated by deeply eroded river valleys with gentle upper slopes and steep lower slopes down to the channel edge.

The gradient of the stream is very variable from sheer waterfalls to placid braided courses. Where the stream velocity falls in response to a change in gradient, sediment may be deposited as alluvium. The re-working of metal bearing alluvium tends to maintain the tenor of the sediment and thus to enhance the length of the sediment dispersion train. The character of the streams is controlled, to some extent, by the bedrock as, for example, waterfalls are almost entirely confined to areas of amphibolite.

The steep slopes of the rejuvenated valley contribute considerable quantities of soil to the drainage by soil creep and by sheetwash during the wet season. The erosion of the overburden has been accelerated by the removal of vegetation from the slopes during farm making. Hence, a plentiful supply of soil material is available for the formation of a drainage anomaly in the Kalm Col sediments.

ii) Secondary minerals produced during weathering

a) Arsenic minerals

The principal arsenic bearing mineral in the Yirisen area is arsenopyrite, which under the oxidising conditions in the zone of weathering is converted to limonite $Fe_2O_3nH_2O$ and scorodite $FeAsO_4 2H_2O$. This latter mineral is relatively stable in the oxidising zone but, eventually, it too forms limonite with the release of the arsenic. Blanchard (1942) has observed that as much as 50 percent of the original arsenic was retained by freshly oxidised arsenopyrite; strongly leached and weathered material retained 25 percent and in no instance he examined was the arsenic wholly lost.

Although the pH and Eh conditions in the Kalm Col swamp soil are favourable for the formation of arsenites, it seems certain that on

entering the oxidising environment of the surface drainage system arsenates will be the chief species, principally in combination with iron.

b) Hydrated oxides of iron and aluminium

Under freely drained conditions the weathering of the talc schist produces abundant hydrated oxides of iron and aluminium. The swampy conditions encountered in Kalm Col may promote the formation of ferrous iron compounds, however, on becoming aerated at the surface of the swamp, the water containing soluble ferrous iron will precipitate iron as ferric hydroxide. The presence of ferrous iron in the swamp soil may be inferred from the many instances of ferric hydroxide gels coating the mud and stagnant pools of the swamp.

The efficiency of sesquioxides in fixing arsenates is well known, hence the abundant production of these materials in the soil and drainage systems of the field area is important in its restriction of the mobility of arsenic.

c) Clay minerals

No X-ray diffraction data are available for the composition of the Yirisen area clays. Whilst, no doubt the chief clay minerals present in the freely drained soils of the Yirisen area will be kaolin types, the possibility that the waterlogged conditions in the Kalm Col swamp may give rise to other species of clay mineral must be considered.

Of the two main alternative clay mineral types, illite and montmorillonite, the presence of the former is not favoured since potassium is required for its formation and this element is notably lacking in the talc schists, according to the analysis of Wilson and Marmo (1959).

The formation of montmorillonite requires a supply of bases, e.g. Mg, Ca and of silica rather than alumina. Although the supply of bases from the talc schist would appear to be adequate (these rocks contain 25 - 35 percent MgO), the pH conditions in the swamp in the region of pH 6, favour the retention of alumina and the solution of silica, hence silica will tend to be leached from the clay minerals, a condition unfavourable to the formation of montmorillonite having a silica : alumina ratio of 2 : 1.

It is concluded, therefore, that the clay mineral most likely to be present in the Kalm Col swamp is kaolinite, the typical clay mineral of the humid tropical environment.

II. Chemical Factors

1. Temperature

The general effects of temperature in influencing the dispersion of elements in the field areas by the promotion of chemical and biological activity has already been noted in the section of molybdenum.

2. Redox Potential and Hydrogen Ion Concentration

The redox potentials and hydrogen ion concentration values for the surface waters of the Yirisen area have been plotted on a Krauskopf type diagram in Figure (34). Although a departure from the stability fields obtained in synthetic solutions is to be expected under natural conditions, the diagram gives a useful indication of ionic species likely to be present in the natural waters.

The data for the Yirisen waters all lie in the arsenate stability field, which was expected from the highly oxidising nature of the environment. Insoluble ferric oxide will be the most common stable form of iron and this is also apparent from observations in the field. Manganese, if present in the Yirisen waters, is likely to occur as the manganous ion.

The only data for ground water are for the Kalm Col swamp, where the depth to the bedrock was only four feet and the water seeped in very slowly since the pit was only just below the water table. The seepage water accumulated over a period of four days before the measurements were made, hence the Eh and pH values recorded are probably higher than those of the true groundwater. Under the conditions measured (pH 6.5 and Eh 0.11 v, as compared with pH 7.3 and Eh 0.33 v in the surface water) considerably more iron could be held in solution in the groundwater than in the surface water, but on being exposed to the atmosphere, the excess will be precipitated as ferric hydroxide in the surface swamp water and in the upper horizons of the swamp soil. Other ions such as arsenite or arsenate may be occluded in these precipitates.

3. Solubility of secondary arsenic minerals

The solubility of ferric and aluminium arsenates, the most likely common forms of arsenic in the drainage system has been investigated by Wiklander and Alvelid (1950). Both compounds exhibit a similar variation in solubility with pH, having distinct minima at pH 2.3 and 4.1 respectively, but the iron arsenate is less soluble at the minimum (Figure 35). Under the pH conditions extant in the Yirisen surface waters (pH6.8-7.5), both ferric and aluminium arsenate would be expected to be appreciably soluble. The present study, however, suggests that the solubility of these compounds is limited due to the activity of hydrated ferric oxides and clay minerals in sorbing arsenic from solution.

Wiklander and Alvelid also examined the effects of other ions on the solubility of the arsenates, (Figure 36a). Whilst the addition of KCl had little effect on the aluminium system, a marked broadening

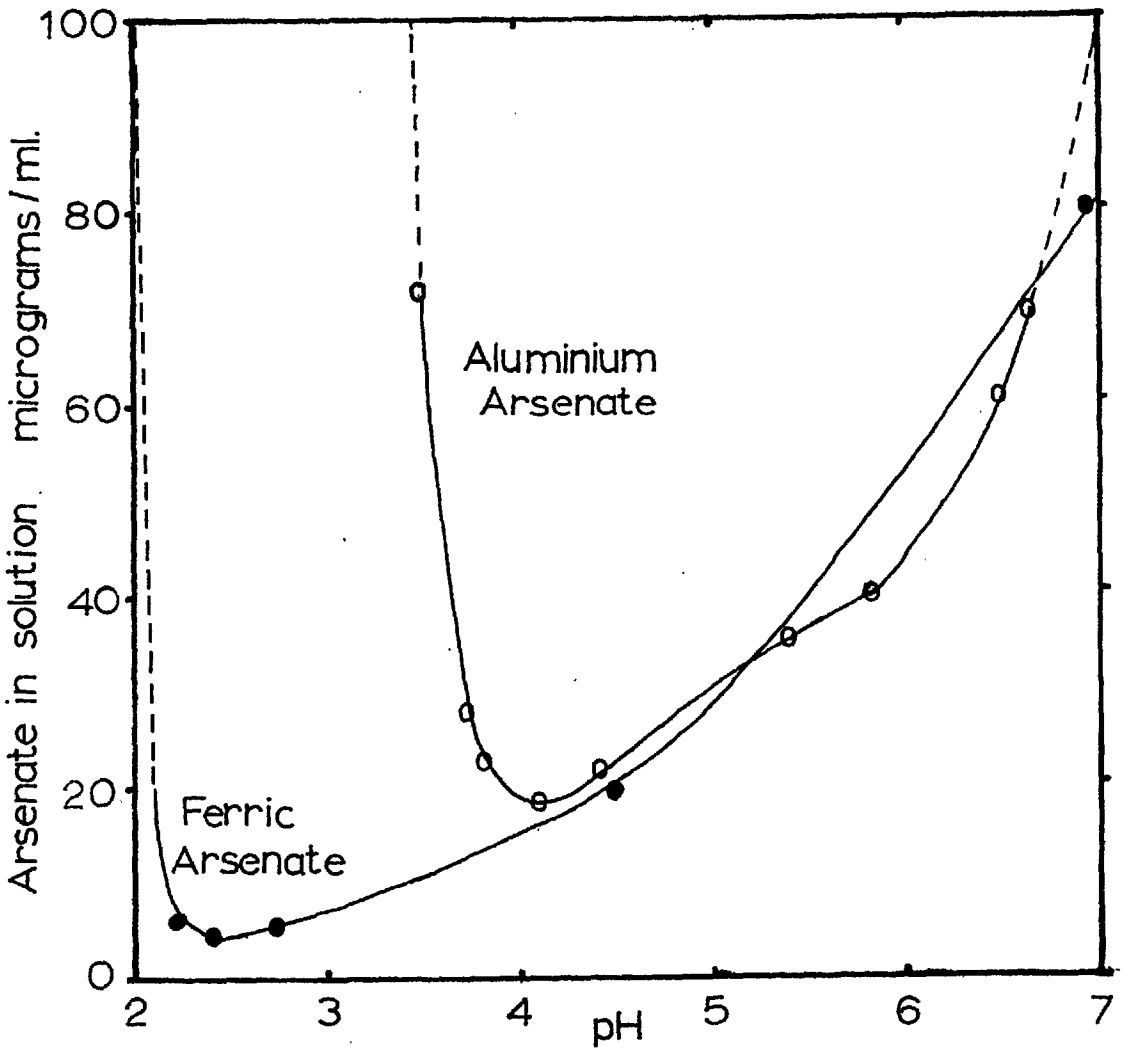
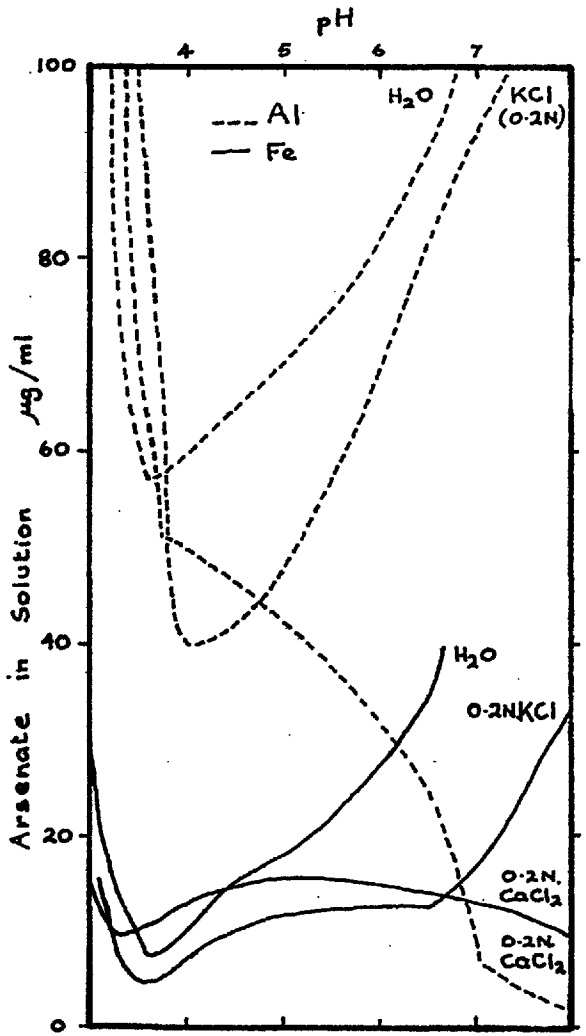


Figure 35. Solubility of Arsenates precipitated with $AlCl_3$ or $FeCl_3$

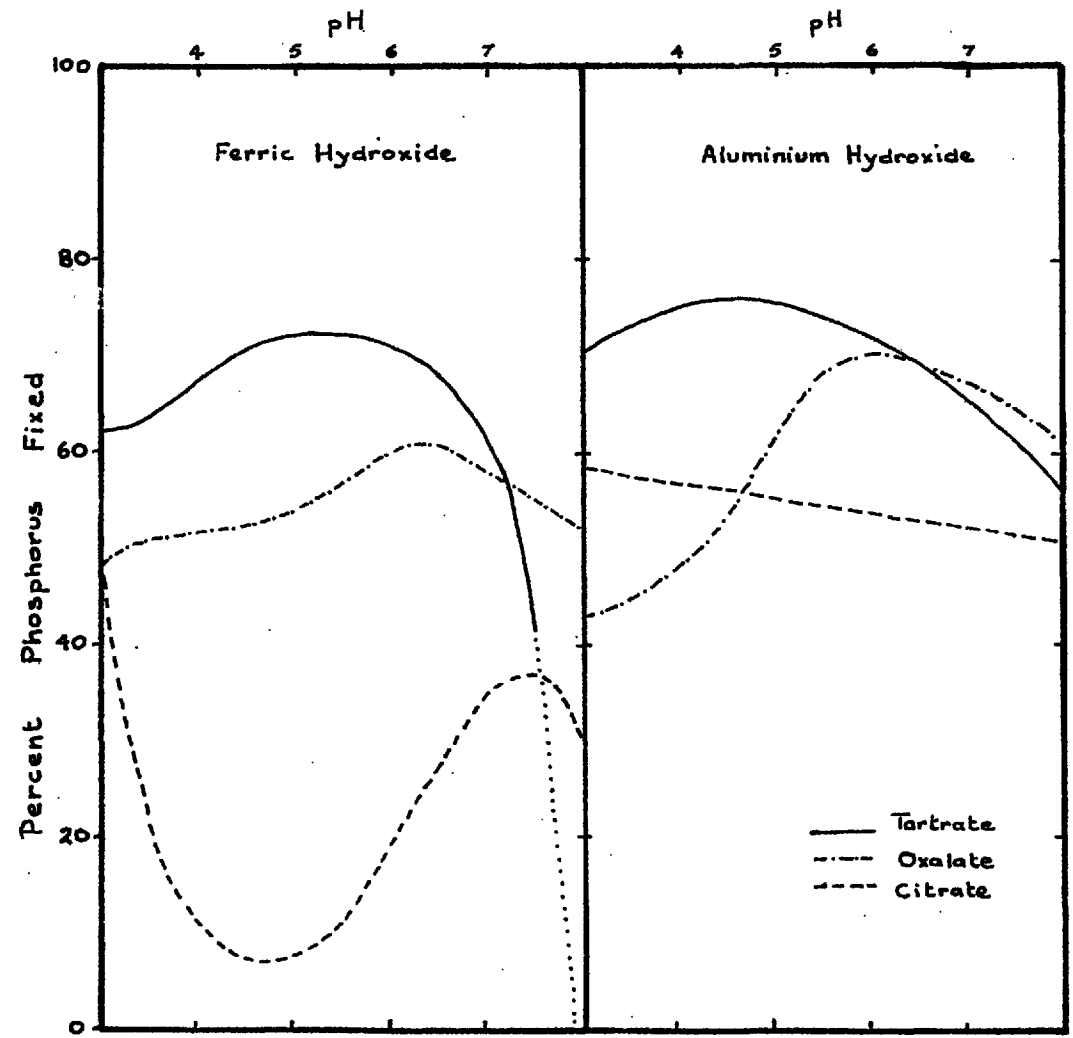
(after Wiklander and Alvelid 1950)

Figure 36a



Solubility of Aluminium and Iron Arsenates in the presence of Phosphate as affected by pH and the presence of other Ions
(after Wiklander and Alvelid 1950)

Figure 36b



The Influence of pH on the Efficiency of Organic Ions in Preventing Phosphorus fixation by Sesquioxides
(after Struthers and Sieling 1950)

in the range of low solubility was produced in the iron compound. Calcium ions caused notable reduction in the solubility of both arsenates at higher pH levels due to the formation of insoluble calcium arsenate. The low tenor of calcium in the Yirisen soils (450 ppm) precludes the formation of this compound in significant quantities.

When the experiments were repeated using soils instead of synthetic hydroxides, the solubility of the arsenates was found to be considerably reduced by the addition of KNO_3, K_2SO_4, KCl, NaCl and $CaCl_2$, but increased by phosphate, which caused rapid desorption of arsenate ions because of its greater affinity for the exchange sites. Thus, in considering the solubility of arsenates in the Yirisen waters the presence of other salts needs to be taken into account. These data are lacking. It is inferred, however, that the salt content will be low, by analogy with the molybdenum bearing waters, and that at this dilution the effect of other salts will be minimised.

Mather examined the solubility of fresh and weathered arsenopyrite and found that appreciable quantities of soluble arsenic were released after shaking 0.5 g of material with 60 ml of water for one hour. Between 6 and 96 micrograms per litre arsenic (0.3 - 5.0% of the total arsenic content) were dissolved, the quantity released from the weathered material being 3 - 10 times that from the fresh mineral. It seems reasonable to assume that such arsenic released in the soil would become fixed by sesquioxides and clay minerals. Weathered rock and swamp soil, treated in the same way as the minerals, released only 1 - 3 percent of their arsenic, producing a solution with a concentration of 6 micrograms per litre.

In the present work, freely drained slope soil and dried out swamp soil, leached for 30 minutes, released no detectable water-soluble arsenic whilst moist swamp soil released 0.36 percent of arsenic soluble in water. This difference may be due to fixation of arsenic during the drying process or, alternatively, to the solubilisation of the element in the moist soil, by bacteria, during storage. When the leach water contained an organic complexing agent (citrate) appreciable amounts of arsenic were released from all the soils, indicating the influence of such ions in mobilising arsenic.

The very low solubility of arsenic in the field area soils and sediments is indicated by the sub-microgram quantities detected in the surface waters. Notwithstanding the large error of the analytical method, this indicates the strong tendency to immobilisation of the element by hydrated oxides and clay minerals.

4. Sorption Activity

Reference has already been made to the process of sorption in the section on molybdenum. Arsenic, in the form of the arsenate and arsenite anions, may be sorbed from solution by colloidal particles such as clay minerals and hydrated iron oxides.

As stated previously the identity of the clay minerals in the Yirisen area soils and sediments is unknown but it is considered that kaolinite is the clay mineral most likely to be present.

Kaolin showed little affinity for arsenate ions unless it had been activated by ball milling or treatment with hot NaOH. In concentrated solutions kaolin sorbed more arsenate than phosphate, but similar amounts of both ions in dilute solutions. The amount of both anions sorbed increased with decreasing pH of the solutions

in the range pH 3 - 7, (Sieling 1946). Thus, in the Yirisen stream waters with an arsenate concentration of less than one microgram per litre and a pH of 6.8 - 7.4 very little sorption by kaolin type clays would be expected. However, it is apparent from the present study that the clay mineral present possesses an appreciable sorption capacity. Whilst in the oxidising environment of the drainage system this may be due to the associated iron oxides, in the waterlogged swamp soils it is considered to be a property of the clay mineral itself. It is concluded, therefore, that under the circumstances extant in the deeper levels of the swamp soil kaolinite may have an appreciable sorption capacity for arsenic, which is probably in the form of arsenite ions.

That iron and aluminium compounds associated with the clay minerals are responsible to a greater or lesser degree for the sorption capacity of the clay fraction of the soil is the opinion of most workers on this topic, (Dratschew 1933, Coleman 1944, Wiklander 1946). In the present work a close association has been shown between the amounts of hydrated iron oxides and arsenic present in the stream sediment size fractions.

James (1957) in a study of arsenic dispersion in the latosols of Southern Rhodesia, notes the fixation of the element in iron rich soils in contrast to its leaching out of iron deficient soils and suggests that the formation of insoluble iron and aluminium compounds is responsible.

Studies by Wilander and Fredrickson (1946) showed that both arsenite and arsenate in synthetic solutions were adsorbed by hydrated iron and aluminium oxides, particularly by the iron compound which achieved practically 100 percent sorption. Similarly, soils rapidly removed arsenate ions from solution but arsenite ions, although sorped rapidly at first, were not completely removed after 30 days. The sorption efficiency of different soils varied, depending on several factors, including the amount of iron oxides and clay minerals present and the presence of other inorganic ions.

The concentrations of ions used in the above experiments (100 - 6,000 µg/l) were considerably higher than those encountered in the present study (less than 1 µg/l), and it has already been noted that sorption efficiency decreases at low concentrations. The fixation of arsenate ions by ferric and aluminium coompounds is therefore, expected to be less effective at the arsenate concentration observed in the waters of the field area.

The sorption of anions by sesquioxides is inhibited by various substances produced in the soil by the action of bacteria on organic matter. The experiments of Swenson, Cole and Sieling (1949) with phosphates indicate that the most effective organic ions were those which formed complexes with iron and aluminium, such as citrate and oxalate. The structure of the organic ion and the pH of operation were found to be important factors in controlling the extent of sorption inhibition (Figure 36b), (Struthers and Sieling 1950). Further experiments with humus and lignin indicated that these substances possessed in a lesser degree the inhibitory qualities exhibited by the simple carboxylic acids.

That sorption of arsenic is taking place is indicated by the concentration of the element in the sediment size fractions containing most active sesquioxides, i.e. the silt and clay fractions. In the section on the sorption of molybdates by sesquioxides, attention was drawn to the possibility that the charge on the colloidal ferric hydroxide at the pH levels of the surface waters examined may be negative and that the molybdate anion would not be chemically bonded to the precipitated sesquioxide but may be held in the precipitate surface by physical bonds. Similar considerations apply to the arsenate anion and a similar sorption mechanism may account for the association of arsenic and free iron oxides in the sediments.

III. Biological Factors

1. Vegetation

Unlike molybdenum, arsenic is not essential to plant growth and is not normally accumulated in the tissues of living plants. However, when growing on arsenic rich soil, grasses may take up arsenic in amounts toxic to grazing cattle (Grimmet and MacIntosh 1939). Similarly, the use of arsenical insecticides also results in anomalous amounts of arsenic being present in plant tissue (Weber 1957).

Mather noted arsenic in amounts ranging from 0.2 - 5.0 ppm and 0.1 - 2.0 ppm in the leaves and twigs respectively of the plant Ricinodendron africanus growing on soil with an arsenic content of 9 - 1,140 ppm. There will thus be little possibility of transformation of inorganic soil arsenic into soluble organic arsenic through the agency of the plant metabolism in the case of this species. How far this may take place in other plants is not known.

2. Micro-organisms

The function of micro-organisms in the production of chelating substances from organic matter has been discussed in the molybdenum section.

Certain bacteria have been observed to have the specific function of oxidising arsenite to arsenate in the soil, (Quastel and Scholefield 1953). Turner (1949) isolated 15 strains of bacteria from sheep dip fluids which can oxidise arsenites, all belonging to the genus Pseudomonas. Under optimum conditions these bacteria oxidised up to 90 mg of arsenite per hour per mg dry weight of bacteria at pH 7, but reaction was completely inhibited outside the pH range 3 - 11.

Furthermore, according to Olivier and LePeintre (1955), under anaerobic conditions bacteria may cause the reduction of ferric iron to ferrous and release any associated arsenic into the soil. Thus, under the conditions of restricted drainage encountered in Kalm Col the action of bacteria may be of considerable importance in promoting the mobilisation of arsenic.

3. Organic matter

The importance of organic matter as a nutrient for bacteria and a source of chelate compounds has been dealt with in the section on molybdenum. The overall effect of the decomposition of organic matter appears to be beneficial to the solution and mobilisation of arsenic bound to sesquioxides.

Struthers and Sieling (1950) have shown that chelating agents which release arsenic from sesquioxides have a characteristic optimum pH reaction range which varies according to their structure. At low pH levels fairly simple compounds, e.g. citrates, are most effective, but with increasing alkalinity, more complex molecules, e.g. amino acids,

predominate. Thus, the original composition and the stage of decomposition of the organic matter are important in the mobilisation of elements in the soil.

The enrichment of arsenic in organic rich materials has been noted by Goldschmidt (1954) and summarised by Krauskopf (1955). In black shales the element is concentrated up to 15 - 45 times its average crustal abundance. Coal ash is enriched by a factor of 100 whilst petroleum ash and asphalt may carry up to 4,000 times the crustal average. In the present work, however, no association of arsenic and organic matter in stream sediments could be observed in the few data available.

IV. Summary of factors influencing the Secondary Dispersion of Arsenic in the Yirisen area

The factors summarised below all appear to influence, to a greater or lesser degree, the extent of secondary dispersion of arsenic in the drainage systems studied. The order of their presentation is not necessarily the order of their importance.

1. The form of the mineralisation.

Arsenopyrite bearing quartz veins in talc schist host rock release arsenic only slowly into the soil hence the supply of the element from this source is limited. In addition, arsenic may be derived from the weathering of veins and disseminations of pyrite occurring in the talc schist.

2. The nature of the host rock of the mineralisation.

The nature of the country rock controls the type of latosol and secondary mineral species formed during weathering, both of which have significant influence over the dispersion of arsenic.

3. Latosol formation.

The talc-carbonate schist country rock carries sufficient iron to form duricrust but over most of the mineralised zone this has been removed as a result of the rejuvenation of the drainage system and a new immature soil profile is being developed on the valley slopes.

The thin, unconsolidated soil now being formed over the lower valley slopes is easily leached and transported into the drainage system by soil creep and sheet wash. Duricrust is found only on the old valley slopes and hill tops as a remnant of an old platform surface and is also being eroded. An old secondary dispersion pattern formed in the duricrust overburden of the mineralisation supplies arsenic rich duricrust fragments to the stream bank soils and to the drainage system where they are mechanically dispersed in the coarse fractions of the sediment.

4. Topography.

The highly dissected topography of the field area with steep slopes and high stream density facilitates the movement of soil into the drainage system and thus promotes the formation of drainage dispersion trains. Re-working of metal bearing alluvium tends to enhance the length of the sediment dispersion train.

5. Secondary minerals produced during weathering.

Scorodite, ferric arsenate seems likely to be the most common secondary arsenic mineral in the zone of weathering. The dispersion of arsenic is limited by the stability of this mineral. The hydrated iron oxides capable of sorbing soluble arsenic compounds, which are produced in abundance by weathering of the talc schist also limit the mobility of arsenic in the zone of weathering. Whilst kaolinite,

the principle clay mineral produced under the weathering conditions of the field area, has a low arsenate sorption capacity in synthetic arsenic solutions, under the field area conditions it exhibits an appreciable affinity for arsenic.

6. Temperature.

The air and water temperature of the field areas promotes chemical reaction and micro-organism growth and thus assists, e.g. in the production of chelates by micro-organisms, and retards, e.g. in the production of free iron oxides, the dispersion of arsenic.

7. Redox potential and hydrogen ion concentration.

Under the Eh and pH conditions recorded in the surface water of the field area arsenic will be present as the arsenate anion, iron as insoluble ferric hydroxide and manganese as a soluble manganous ion, whilst in the ground water of the Kalm Col swamp ferrous iron and arsenites may be present.

8. Solubility of arsenic minerals.

On theoretical grounds ferric and aluminium arsenates would be expected to be appreciably soluble under the pH and Eh conditions of the field area waters. The present work indicates that this is not the case. It is considered that sorption reactions are, in part, responsible for the lack of soluble arsenic in the drainage system.

9. Sorption activity.

The arsenic sorption activity of kaolinite and hydrated iron oxides in the field areas is contrary to predictions based on laboratory studies using synthetic solutions. The sorption activity of kaolinite may be enhanced by hydrated iron oxides, but is itself appreciable particularly in waterlogged bank soils where arsenites may be present. Like molybdates, arsenates may be sorbed on hydrated iron oxides by physical rather than chemical bonds.

10. Vegetation.

Arsenic is not essential to plant growth and is not normally accumulated in plant tissue. Vegetation, therefore, probably plays little part in the dispersion of arsenic, apart from being the source of organic debris from which chelate compounds are derived.

11. Micro-organisms.

Certain micro-organisms promote the dispersion of arsenic by oxidising arsenites to arsenates and by releasing arsenic from iron compounds.

12. Organic matter.

Organic matter when broken down by micro-organisms is a source of powerful complexing agents capable of mobilising arsenic in soils and stream waters.

PART SEVEN. GENERAL COMPARISON OF THE DISPERSION BEHAVIOUR OF MOLYBDENUM AND ARSENIC

The dispersion characteristics of an element are determined by its intrinsic chemical properties and the nature of the dispersion environment.

Molybdenum is a metal element which exhibits valencies of 2, 3, 4, 5 and 6, of which the Mo^{IV} and Mo^{VI} oxidation states are most common. Arsenic occurs in two oxidation states, As^{III} and As^{V} and, because it has both metallic and non-metallic properties, is referred to as a metalloid.

The ionic radii of the two elements, in their chief valency states are of the same order and substitution of these elements in mineral lattices for such ions as Fe^{III} and Si^{IV} may be explained by the similarity of the ionic radii of the elements concerned, (Table 47).

Table 47. Ionic radii of elements for which arsenic and molybdenum may substitute in mineral lattices

Ion	Si^{IV}	As^{V}	Al^{III}	As^{III}	Mo^{VI}	Ti^{IV}	Fe^{III}	Mo^{IV}	Fe^{II}
Ionic Radius Å	0.43	0.46	0.57	0.58	0.62	0.64	0.67	0.70	0.83

The distribution of arsenic and molybdenum in rocks and minerals has been summarised by Onishi and Sandell (1955) who note that, except for quartz, in which arsenic may occur in notable concentrations whilst molybdenum is generally absent, the two elements tend to vary similarly in distribution from one mineral to another but the variation is greater for molybdenum. When whole rocks are compared no relationship can be found between the distribution of arsenic and molybdenum.

Goldschmidt first drew attention to the significance of the factor z/r, the ionic potential of the element, where z is the charge on the ion and r is the radius of the ion, as a measure of the geochemical behaviour of an ion in an aqueous environment. Elements having an

ionic potential less than 3 tend to form soluble cations in solution, elements of intermediate ionic potential (3 - 11) tend to be precipitated from solution by hydrolysis, their ions being associated with hydroxide groups, whilst high ionic potential (greater than 11) elements tend to form soluble anions.

Molybdenum and arsenic have intermediate to high ionic potentials, (Table 48). The association of these elements with precipitated hydrated oxides observed in the present study is in line with theoretical data.

Table 48. Ionic potential of arsenic, molybdenum and related elements

Ion	Fe^{III}	As^{III}	Al^{III}	Mo^{IV}	Ti^{IV}	Mn^{IV}	Mo^{VI}	Si^{IV}	As^{V}
Ionic Potential	4.5	5.0	5.3	5.7	6.3	7.7	9.7	10	11

The existence of ions in the natural environment is largely controlled by redox conditions and hydrogen ion concentration. The oxidation potentials encountered in nature range from minus 0.41 v to plus 0.82 v, the approximate stability range of water at pH 7, and pH levels from pH 4 - 8, (Mason 1952). Several workers have calculated the limits of the stability fields of metal ions under natural Eh and pH conditions (Krauskopf 1955, Garrels 1959) and these studies are the basis of the Krauskopf type diagrams presented earlier.

Molybdates are stable under natural conditions whilst molybdites are only formed in very acid, reducing environments. Arsenic, on the other hand, may be present in soils and natural waters as arsenate or arsenite ions or even, under very reducing conditions, as native arsenic. In the oxidising, neutral conditions obtaining in the drainage systems of the Sula Mountains the predominant forms of the elements will be molybdates and arsenates, two very similar anions.

Table 49. Comparison of dispersion data for molybdenum and arsenic

Item	Molybdenum	Arsenic	Source
Atomic Number	42	33	P
Atomic Weight	95.95	74.91	P
Oxidation States	2,3, 4, 5, 6	3, 5	P
Ionic Radius Å	0.70, 0.62	0.58, 0.46	K
Ionic Potential	5.70, 9.70	5.0, 11.0	M
Possible substituents in lattices	Fe^3, Ti^4, Si^4, Al^3	Si^4, Al^3	KS OS
Ore Mineral	Molybdenite MoS_2	Arsenopyrite FeAsS	WM
Secondary Minerals	Molybdates e.g. Ferrimolybdite $Fe_2O_3 3MoO_3 8H_2O$	Arsenates e.g. Scorodite $FeAsO_4 2H_2O$	
Minimun solubility of ferric salt ppm	< 10 ppm (pH 2.7)	~ 10 ppm (pH 2.4)	J WA
Solubility of ferric salt at pH 7 ppm	~ 450	~ 80	J . WA
Abundance in lithosphene ppm	1	2	KS OS
" " granite Av. ppm	1.1	1.7	OS
" " basalt "	1.1	1.9	OS
" " ultra-basics "	0.4	2.8	OS
" " siliceous sediment "	1	-	
" " calcareous sediment "	< 0.5	< 0.5	OS
" " organic sediment "	1 - 100	5 - 15	OS
" " soil "	2	5	S
" " coal ash "	100 - 200	100 - 500	K
" " asphalt & petroleum ash "	50 - 1500	1500	K
" " plants	0.5	< 2	H
" " fresh water Av.ppb		0 - 80	K et al
" " sea water "	0.2 - 3.0	3 - 24	M

P - Partington (1950): K - Krauskopf (1955): M - Mason (1951):
H - Hawkes (1957): KS - Kuroda & Sandell (1954):
OS - Onishi & Sandell (1955): WM - Wilson & Marmo (1959):
J - Jones (1957): WA - Wiklander & Alvelid (1950): K et al - Kehoe et al (1944).

The mobility of arsenic and molybdenum in the zone of weathering will depend largely on the solubility of the above anions in the presence of abundant sesquioxides. The variation in solubility of ferric arsenate and molybdate with pH is remarkably similar in aspect hence a similar dispersion behaviour would be expected of the two anions. It is concluded in the present work that, although on theoretical grounds the molybdate and arsenate salts of ferric iron are appreciably soluble at the pH and Eh levels of the surface waters of the field areas, their solubility is, in fact, very low due to physical sorption reactions.

Hawkes (1957) has observed that "the mobility of arsenic is dominated by the extreme stability and insolubility of the iron arsenates that form as secondary minerals". This observation is supported by the present work and a similar statement could be made about molybdenum under the conditions of the field areas.

Both molybdenum and arsenic form insoluble calcium compounds, the extent of secondary dispersion of the two elements in a calcareous environment would, therefore, be expected to be limited. This supposition is supported by the low average content of these elements occurring in calcareous sediments, (Table 49).

Organic compounds derived from the decomposition of plant material are able to mobilise molybdenum in the form of soluble complexes, Siew Kee and Bloomfield (1962). It is considered that arsenic may be similarly affected since both elements show a similar tendency to concentration in organic rich material, e.g. coal and oil, (Table 49).

Perhaps the major difference between the behaviour of the two elements in the zone of weathering is the essential nature of molybdenum to the healthy growth of organisms, a characteristic not shared by arsenic. The biological cycle of molybdenum may be an important factor in translocating the element in the upper soil horizons through the action of micro-organisms and plants.

In summary, the chemical similarity between arsenic and molybdenum is expressed in the general similarity of their dispersion behaviour in the environment of the Sula Mountains.

PART EIGHT. APPLICATION OF THE PRESENT DATA TO PROSPECTING FOR MOLYBDENUM AND ARSENIC

One of the aims of the present investigation was the development of more efficient reconnaissance prospecting techniques for molybdenum and arsenic, under conditions similar to those encountered in the Sula Mountains, on the basis of additional information on the dispersion mechanism of these two elements. It should be emphasised that the following discussion and conclusions are applicable only to the Sula Mountains of Sierra Leone and to other areas of similar physical conditions.

From a prospecting viewpoint one of the most important discoveries of the present study is that under the conditions encountered, molybdenum is present in the surface waters of both barren and mineralised areas in only very minor quantities and that the contrast between the anomalous and barren waters is small. This is in complete contrast to results obtained in North America and the U.S.S.R. where water sampling is extensively used in prospecting both for molybdenum deposits and for other mineral deposits containing molybdenum as an accessory element. Accordingly, even though highly sensitive, but not very precise, methods of detecting arsenic and molybdenum have been developed by the writer, water analysis cannot be considered a practical prospecting tool in areas like the Sula Mountains. This conclusion will only be altered if highly sensitive, high precision, analytical techniques of water analysis are developed to replace the slow, imprecise techniques employed by the writer, when detection of the apparently long anomalous saline drainage train from molybdenum deposits might well prove the most effective primary prospecting method.

Of the solid components of the drainage, i.e. the various types of sediment and the stream banks, the longest arsenic and molybdenum drainage trains were detected in the sediment fines (minus 82-mesh). Furthermore, this size fraction is more representative than the coarse material and can be separated from the remainder of the sediment by a single sieving operation as compared to the two sievings required for the other fractions.

Collection of fines will, therefore, enable anomalies to be detected with the minimum number of samples per unit area. The actual sample interval to be employed will depend on the grade and tonnage of the deposit being sought and on the degree of certainty with which it is desired to eliminate ground. In the summary given later in this section, recommendations on the sample interval have been based on the detection with a fair degree of certainty of the great majority of marginal and economic deposits.

In analysing the fines it is desirable, if maximum contrast is to be obtained between background and anomaly, to estimate only the easily extractable metal and, in particular, the iron oxide held arsenic and molybdenum. Furthermore, where a deposit is at some distance from a stream, no anomalous material may be entering the drainage mechanically and that entering in solution will be dominantly held by the iron oxides. Under these conditions no anomaly may be detectable with a total attack although a significant anomaly is present in the iron oxide component of the sediment.

Collection of minus 200-mesh sediment and its analysis by both partial and total attacks may be useful in distinguishing sediment having a high tenor of lattice-held molybdenum in the silt size fraction, which appears to be a characteristic of granites associated with molybdenum mineralisation.

Although the longest drainage trains are found in the fines, maximum contrast in duricrusted areas is found in the coarse fraction. It is, therefore, recommended that in following up anomalies in duricrusted areas the coarse fractions of the sediment be analysed to determine with maximum precision the point of entry of anomalous material. Additional confirmation of this data could be obtained from the heavy mineral fractions of the fines and in non-duricrusted areas this is recommended as a normal procedure.

No particular advantage will be obtained by analysing the coarse fractions in duricrusted areas with a partial attack in preference to a more rigorous attack but for the purposes of standardisation of laboratory procedures, a partial attack will normally be most convenient. However, in analysing heavy mineral fractions the most rigorous attack possible should be employed consistent with the requirements of productivity. A strong alkaline fusion attack is, therefore, recommended.

Summary of Proposed Reconnaissance Prospecting Procedure for Molybdenum and Arsenic Deposits

1. Reconnaissance Survey

a) Samples of the minus 82-mesh stream sediment should be collected from streams comparable with the Sende at 2,500 ft. intervals in duricrusted terrains and at 500 ft. intervals in unduricrusted areas. Analysis should be by both fusion and rapid methods until sufficient data are available to assess the value of the rapid method of analysis in the areas concerned.

b) The main streams should be sampled above and below the confluence of tributaries and the tributaries themselves at some distance upstream from the confluence beyond the effects of backwash from the main stream.

Tributaries over 2,500 ft. in length should be sampled at the same intervals as in the main stream.

2. Follow-up Survey

a) Anomalous tracts of the catchment revealed by the reconnaissance survey should be sampled at shorter intervals in both duricrusted and unduricrusted areas so that the point of entry of anomalous material can be determined. Collection should be made of minus 82-mesh sediment, the heavy minerals component of this fraction and duricrust concretions (minus $\frac{1}{4}$ in. plus 20-mesh), where these are present. These materials should be analysed by the standard analytical method, i.e. fusion attack although the rapid attack may be of use in analysing the crushed duricrust concretions.

b) Both upstream and downstream from the point of entry of anomalous material, stream banks should be sampled at 500 ft. intervals. Attention should be paid to the structure of the banks and where possible both residual and colluvial material should be sampled, only the minus 82-mesh fractions of these soils need be analysed.

3. Soil Survey

a) An orientation survey of the metal content of soils from barren and mineralised areas to establish background and threshold values for soils will be necessary before interpretation of anomalous soil values is possible.

b) Having traced the source of the sediment anomaly to particular sections of the stream banks, the valley slope soils sampled on a grid pattern with a traverse interval selected on the basis of the results of orientation survey.

c) After the above preliminary soil survey a detailed soil sampling programme and extensive pitting will be necessary to locate the bedrock source of the soil anomaly.

PART NINE. RECOMMENDATIONS FOR FUTURE RESEARCH

The present work has suggested a number of problems of both a general and specific nature which are considered to merit further investigation. These are listed briefly below.

1. Problems specific to molybdenum and arsenic

i) The application of solvent extraction and ion exchange techniques to the detection of molybdenum and arsenic in natural waters, with a view to improving the precision of the present methods.

ii) The solubility and stability limits of naturally occurring arsenic and molybdenum compounds.

iii) Extension of the present type of investigation into other types of natural environment, in particular, calcareous areas and those of low oxidation potential, e.g. swamps.

iv) Further comparison of the dispersion behaviour of these two elements in duricrusted and unduricrusted terrains.

v) The eluvial dispersion of molybdenum and arsenic.

vi) The dispersion of molybdenum and arsenic in ground water.

vii) The nature of the association of molybdenum and arsenic with hydrated iron oxides in soils and stream sediments.

viii) The extent of formation of chelate or complex compounds by these elements.

ix) The nature of the dispersion mechanism of molybdenum from unduricrusted disseminated mineralisations such as that at Wankatana.

x) The association of molybdenum and arsenic anomalies in soils and stream sediments with gold and base metal deposits.

2. General Problems

i) Ion exchange procedures need to be investigated with a view to selecting a particular form of resin and operating procedure for the pre-concentration of a specific metal or group of metals in natural waters.

ii) Methods of pre-treatment for water samples to prevent the precipitation of metals during storage by other ions and natural organisms.

iii) The effects on metal distribution and availability of long periods of storage, and drying and re-wetting, of soil and sediment samples.

iv) A closer study of redox potential, hydrogen ion concentration and dissolved solids data in relation to the trace element content of natural waters to aid the prediction of element behaviour in an aqueous environment, e.g. in river estuary and off-shore studies.

v) A study of the possible advantages arising from the dispersion of samples by ultrasonic means and the subsequent separation of the clay and silt fractions using a cyclone apparatus, with a view to eliminating the need for a chemical dispersant.

vi) A study of the anion exchange capacity of clay minerals and other naturally occurring exchange active materials, e.g. iron oxides, organic matter, with particular reference to the anions of those elements of economic significance such as molybdates, arsenates, zincates, plumbates and vanadates.

vii) Little is known of the biological control of trace element dispersion in nature. This problem would repay examination, e.g. with regard to the association of particular trace elements with specific components of organic materials.

PART TEN. LIST OF REFERENCES

Aguilera, H.L. and Jackson, N.L. 1953 — Iron oxide removal from soils and clays. Soil Sci. Soc. Amer. Proc. 17, 359 - 364.

Almond, Hy. 1953 — A field method for the determination of manganese in soils. U.S. Geological Survey Open File Report

Ditto 1953 — Field method for the determination of traces of arsenic in soils. Anal. Chem. 25, 1766 - 1767.

Arden, T.V. 1961 — Ion exchange processes in the atomic industry. Australasian Inst. Min. & Met. Proc. No. 198, p. 180.

Aubert, H.V. 1950 — Observations sur la degredation des sols et la formation de la cuirasse lateritique dans le Nord Ouest du Dahomey (A.O.F.). Trans. 4th Int. Cong. Soil Sci. 3, 127 (F).

Baker, C.O. 1955 — Unpublished report of Sierra Leone Geological Survey, quoted in Wilson and Marmo 1959.

Barbier, G. Chabannes, J. and Maillet, P. 1946 — Absorption des ions phosphorique a la surface des colloides argileux par intermediane des alkaline terreux. Ann. Agron. 16, 7. (F).

Barshad, I. 1951 — Factors affecting the molybdenum content of pasture plants. Soil Sci. 71, 297 - 313, 387 - 398.

Ditto 1955 — Soil development in "Chemistry of the Soil" Ed. F.E. Bear. Reinhold Pub. Co. N.Y.

Bastos, H.L. and Salum, R.A. 1958 — Identification of arsenic in water by coprecipitation. Rev. Brasil Farm. 39, 109 - 116.

Belyakova, E.E. 1958 — Migration of elements in underground and surface waters of Central Kazakhstan. Geochemistry 2, 176.

Black, W.A.P. and Mitchell, R.L. 1952 — Trace elements in algae and sea water. J. Marine Biol. Assoc. 30, 575.

Blanchard, R.
1942
Leached derivatives of arsenopyrite and chromite.
Econ. Geol. 37, 596.

Boltz, D.F.
1958
Colorimetric determination of non-metals. Ed. Boltz, D.F.
Interscience Inc. N.Y.

Chattergee, B.
and Datta, S.
1951
Phosphate fixation by the clay minerals montmorillonite and kaolinite.
J. Soil Sci. 2, II, 224 - 233.

Clark, G.I.
1957
Encyclopaedia of Chemistry.
Reinhold Pub. Co., N.Y.

Clarke, F.W.
1924
Data of geochemistry.
U.S.G.S. Bull 770, p. 644.

Coleman, R.
1944
Phosphorus fixation by the coarse and fine clay fractions of kaolinitic and montmorillonitic clays.
Soil Sci. 58, II, 71 - 78.

Demolon, A.
and Barbier, G.
1939
Condition de formation et constitution du complex orgelo-humique des sols.
Compte Rendu, 188, 656 (F).

Dolukhanova, N.I.
1956.
Hydrogeochemical methods of prospecting for Cu-Mo deposits, in "Geochemical Prospecting for ore deposits in U.S.S.R." Ed. Krasnikov, 1957.

Dratschew, S.M.
1933
The adsorption of arsenite ions by soil.
Zeit. Pflanz. Dung, 30A, 156 - 167.

Erickson, R.L.
and Marranzino, A.P.
1961.
Hydrogeochemical anomalies Fourmile Canyon Eureka Co., Nev., U.S.A.
U.S.G.S. Prof. Paper 424 - B.

Fieldes, M.
and Swindale, L.D.
1954.
The chemical weathering of silicates in soil formation.
N.Z. J. Sci. Technol. 36B, 140 - 154.

Galabutskaya, E.
and Govorova, R.
1934
Min. Suir, 9, 27. Qu. in Robichet, O. (1957).

Ginsburg, I.I.
1959.
Principles of geochemical prospecting.
Pergammon Press, Oxford.

Goldschmidt, V.M.
1954
Geochemistry.
Clarendon Press, Oxford.

Gorsuch, T.T.
1959
Radiochemical investigations on the recovery for analysis of trace elements in organic and biological material.
Analyst, 84, 135 - 173.

Grigg, L.J.
1953
Determination of available Mo of soils.
N.Z. J. Sci. Technol. 34A, 405 - 411.

Grimmet, R.E.R.
and MacIntosh, I.G.
1939
The occurrence of arsenic in soils and waters in the Waiotapu Valley.
N.Z. J. Sci. Technol. 21A, 137.

Harder, E.C.
1919
U.S.G.S. Professional Paper 113.

Hawkes, H.E.
1957
Principles of geochemical prospecting.
U.S.G.S. Bull. 1000 - F.

Hayashi, H.
and Yawata, S.
1957.
Molybdenum poisoning in cattle III.
Bull. Chugoku Agric. Expt. Stat. 3, 556 - 562 (J). (C.B.S. Abstract).

Hayek, E.
and Wierer, H.
1951
Arsenic content of mine waters in the vicinity of Badgestein.
Tscherm. Miner. Petrog. Mitt. 2, 290 - 1.
C.A. 46, 6296 - 7, 1952.

Heide, F.
and Moenke, H.
1956
Arsenic content of the River Saale
Naturwissenschaften, 43, 80 - 81.
Water Pollution Abs. 669, 1956.

Hem, J.D. et al
1959
A survey of chemical equilibria and redox potentials.
U.S.G.S. Water Supply Paper 1459 A - E.

Herman, L.D.
1958
Geochemical zonation in the Blyava deposit, S. Urals.
Geochemistry, 4, 430 - 451.

Ishibashi, M.
1951
Determination of arsenic in sea water.
Bull. Inst. Chem. Res., Kyoto, 24, 68.
C.A. 1951, 45, 443.

James, C.H.
1957
Applied geochemical studies in S. Rhodesia.
Imperial College Geochem. Prospecting Research Centre, Tech. Comm. 12.

Jenny, H.
Gessel, S.P.
and Bingham, F.T.
1949
Comparative study of decomposition rates of organic matter in temperate and tropical regions.
Soil Sci. 68, 419 - 432.

Jones, L.H.P.
1956
Interaction of Fe and Mo in soils.
Science, 123, 1116.

Jones, L.H.P.
1957
Solubility of Mo in simplified systems.
J. Soil Sci. 8, 313.

Ditto
and Milne, A.A.
1954
Ferrimolybdite.
Australian J. of Sci. 17, 100 - 102.

Ditto
and Milne, A.A.
1957
Aluminium molybdate and its formation in clay minerals.
Nature, 178, 1115.

Kehoe, R.A. et al
1944
The concentration of certain trace metals in drinking water.
J. Amer. Water Wks. Assoc. 36, 637.

Kellog, C.E.
1949
Preliminary suggestions for the classification and nomenclature of the great soil groups in tropical and equatorial regions.
Comm. Bur. Soil Sci. Tech. Comm. 46, 76.

Khitarov, N.I.
and Ivanov, L.A.
1937
Geochemistry in environments of the oxidised zone.
Mat-Tsentr. N.I. Geol. Razv. Inst. Geokhim. Sb 1. In Maluga (1958).

Kolthoff, I.M.
and Carr, C.W.
1943
Accumulation of traces of arsenate by coprecipitation with $MgNH_4PO_4$.
Anal. Chem. 20, 728.

Krainov, S.R.
1958
L'utilisation des cours d'eau alimentes par des eux souterraines pour la prospection hydrochimique des gites mineraux.
Ann. Serv. Inf. Geol. BRGM No. 31, 42 - 46 (Rf).

Krause, A.
1928
Transformation of o-ferric oxide hydrate into m-ferric oxide hydrate.
Zeit. Anorg. u Allg. Chemie, 176, 398 - 402.

Krauskopf, K.B.
1955
Sedimentary deposits of rare metals.
Econ. Geol. 1955, Ann. Vol. I, 411.

Kuroda, K.
1940
Molybdenum content of hot springs and their seasonal variation.
Japan Chem. Soc. Bull. 15, 65.

Kuroda, P.A.
and Sandell, E.B.
1954
The geochemistry of molybdenum.
Geochem. et Geocos. Acta, 6, 35 - 63.

Krasnikov, V.I.
1957
Editor Geochemical Prospecting for ore deposits in the U.S.S.R.
Science Translation Service, University of Alabama, 1959.

Larina, N.K. and Kasatochkin, V.I. 1957
Ionic exchange and structure of humic acids. Pochvovedenie, 9, 28.

Lovering, T.S. 1934
Geology and ore deposits of the Breckenridge mining district, Colo. U.S.G.S. Prof. Paper 176.

Maker, D.L. 1958
Konongo water supply. P.W.D. Report, Accra, Ghana.

Malyuga, D.P. 1958.
An experiment in biogeochemical prospecting for molybdenum in Armenia. Geochemistry, 3, 314.

Martell, A.E. and Calvin, M. 1953
Chemistry of the metal chelate compounds. Prentice Hall, N.Y.

Mason, B. 1952
Principles of geochemistry. Wiley, N.Y.

Mather, A.L. 1959
Geochemical Prospecting studies in Sierra Leone. Ph.D. Thesis, University of London.

Merwe, Van de and Heystek 1952
Clay minerals of South African soil groups. I. Laterites and related soils. Soil Sci. 74.

Meulen, H. Ter 1932
Accumulation of molybdenum in some aquatic plants. Rec. trav. chim. 51, 549 - 550.

Miller, J.T. and Byers, H.G. 1935
A selenium spring. Ind. Eng. Chem. News, 13, 456.

Morrison and Freiser 1959
Solvent extraction in analytical chemistry.

Mulder, E.C. 1948
Importance of molybdenum in the nitrogen metabolism of micro-organisms and higher plants. Plant and Soil, 1, 94 - 119.

Ng Siew Kee and Bloomfield, C. 1960
The solution of some minor element oxides by decomposing plant materials. Geochem et Geocos. Acta 24, 206 - 255.

Ditto 1962
The effect of flooding and aeration on the mobility of certain trace elements in soils. Plant and Soil 16, 108.

North, A.A.
1955
Geochemical field methods for the determination of tungsten and molybdenum in soil.
Scientific Report CRL/AE 127, D.S.I.R., Teddington, Middlesex.

Novokhatskii, P.
and Kalinin, S.K.
1939
Molybdenum in mine, mineral and surface waters.
Comptes Rend. Akad. Sci. U.R.S.S. 24, 278 (C.A. 1940, 34, 1106).

Olivier, H.R.
and Le Peintre, M.
1955
Solubilisation by biochemical means of arsenic bound to iron in the soil.
Ann. Inst. Pasteur, 88, 668.

Onishi, H.
and Sandell, E.B.
1955
Geochemistry of arsenic.
Geochem. et Geocos. Acta 7, 1 - 33.

Partington, J.R.
1950
Textbook of inorganic chemistry.
Macmillan, London.

Perkins, A.T.
and King, H.H.
1944
Phosphate fixation by soil minerals.
II Fixation by Fe, Si, Ti oxides.
Soil Sci. 58, II, 243 - 250.

Piper, C.S.
1950
Soil and lant analysis.
Interscience, N.Y.

Pollett, J.D.
1952
The geology and mineral resources of Sierra Leone.
Col. Geol. and Min. Res. 2, 3.

Popova, T.P.
1957
Modern methods of field determination of micro elements in natural waters during hydrogeochemical prospecting in Krasnikov. (1957).

Quastel, J.H.
and Scholefield, P.G.
1953
Arsenite oxidation in soil.
Soil Sci. 75, 279 - 287.

Rankama, K.
and Sahama, T.G.
1950
Geochemistry.
University of Chicago Press

Robichet, O.
1947
Methodes due dosage du fer.
Ann. Agron. 3, 257 - 324.

Rubins, E.J.
and Dean, L.A.
1947
Anion exchange in soils.
Soil Sci. 63, 377, 389.

Samuelson, O.
1953
Ion exchange in analytical chemistry.
Wiley, N.Y.

Sandell, E.B.
1950
Colorimetric determination of traces of metals.
2nd Ed. Interscience, N.Y.

Ditto
1959
Ditto 3rd Edition.

Scaetta, H.
1940
Observations sur l'origine et al constitution des sols de l'Afrique Occidentale Francaise.
Ann. Agron. 10, 101 (F).

Schollenberger, C.J.
1927
A rapid approximate method of determining soil organic matter.
Soil Sci. 24, 44.

Scott, W.W.
1950
Standard methods of chemical analysis.
Ed. N.H. Furman. Van Nostrand, N.Y.

Sieling, D.H.
1946
The role of kaolin in anion sorption and exchange.
Soil Sci. Amer. Proc. 11, 161.

Small, J.
1954
Modern aspects of pH.
Bailliere, Tindall, Cox, London.

Stanton, R.E.
and Gilbert, M.
1956
Analytical procedures employed at Geochemical Prospecting Research Centre.
Imperial College, London. Tech. Comm. 1 - 10.

Stephens, G.G.
1949
Comparative morphology and genetic relationships of certain Australian Soils.
Soil Sci. 1, 123.

Struthers, P.H.
and Sieling, D.H.
1950.
Effect of organic anions on phosphate precipitation by iron and aluminium as influenced by pH.
Soil Sci. 69, 205.

Sugawara K.
Tanaka, M.
and Kanamori, S.
1956
Spectrophotometric determination of arsenic in natural water and its application to silicate and biological materials.
Bull. Chem. Soc. Jap. 29, 670 - 673.

Sugawara, K.
Tanaka M.
and Okabe, S.
1959
Separation and determination of microgram quantities of molybdenum in natural waters.
Bull. Chem. Soc. Jap. 32, 221 - 222.

Studenkova et al
1957
Geochemistry 2, 113.
(Quoted by Malyuga, A.P. 1958)

Swaby R.J. and Passey, B.I. 1953
Availability of trace elements from rocks and minerals.
Aust. J. Agric. Res. 4, 292.

Swenson, Cole and Sieling 1949
Fixation of phosphate by iron and aluminium and its replacement by organic and inorganic ions.
Soil Sci. 67, 3 - 22.

Szymkiewicz D. 1947
Etudes climatologique.
Acta Soc. Botan. Poloni, 18, 1. (F).

Tanaka, N. 1958
Methode due precipitation a pH constant des oxides hydrates.
Mikrochemica Acta 2, 177 (F).

Ter Meulen 1932
The accumulation of molybdenum in some aquatic plants.
Rec. Trav. Chim. 51, 549 - 50.

Tikhomirov N.I. and Miller, S.D. 1946
On a physico-chemical method of prospecting for molybdenum in the semi-desert climate of the N. Lake Balkhash area.
Razvedkanedre 12, II 34 - 39. Quoted in Hawkes (1957).

Tooms, J.S. 1955
Geochemical dispersions related to copper mineralisation in N. Rhodesia.
Ph.D. Thesis. University of London.

Turner 1949
Bacterial oxidation of arsenite.
Nature 164, 76 - 77.

Wadelin and Mellor 1952
Extraction of molybdoarsenic acid by n-butyl alcohol.
Analyst, 77, 708.

Weber, J.H. 1957
Arsenic in cigarette tobacco.
J. Sci. Food Agric. 8, 490.

Wells, N. 1953
The spectrographic determination of molybdenum in plants and soils.
N.Z. Soil News 3, 40.

Ditto 1956
Molybdate ion fixation in New Zealand soils.
N.Z. J. Sci. Technol. 37, 482.

White, M.L. 1957
The occurrence of zinc in soil.
Econ. Geol. 52, 645.

Wiklander L. 1950
Kinetics of phosphate exchange in soils.
Kungl. Lantbr. Hogs. Ann. 17, 407 - 440.

Wiklander, L. and Alvelid, S. 1950
The solubility of arsenate in synthetic systems and soils.
Kungl. Lantbr. Hogs. Ann. 17, 342.

Wiklander, L. and Fredrickson 1946
Studies on the sorption of sodium arsenate and arsenate by soils and synthetic iron and aluminium oxides.
Acta Agric. Svecana 1, 345 - 376.

Wilson, N.W. and Marmo V. 1959
The geology, geomorphology and mineral resources of the Sula Mountains.
Sierra Leone Geological Survey Bull. 1.

APPENDIX. Methods of Analysis

The water used in the following chemical analytical procedures was demineralised before use by passage through an ion exchange column. All reagents used were of Analar quality and where possible a check was made on their suitability for the tests by running reagent blank analyses.

A. The analysis of Soils and Stream Sediments

a) Total molybdenum

The method is based on that of Bagshawe and Truman (1947) modified by North (1955).

Reagents

1. Fusion Mixture. A mixture by weight of 5 parts sodium carbonate, anhydrous. 4 parts sodium chloride and 1 part potassium nitrate; all ground to pass through a minus 80-mesh sieve and thoroughly mixed.
2. Hydrochloric acid, sp. gr. 1.18.
3. Hydroxylamine hydrochloride, 2.5% solution. Dissolve 25 g hydroxylamine hydrochloride in 900 ml conc. HCl and dilute to 1 litre with water.
4. Amyl acetate.
5. Zinc dithiol, 1% solution. Weigh 0.25 g zinc dithiol into a 25 ml stoppered cylinder. Add 1 ml HCl conc. and shake. Dilute to 25 ml with amyl acetate. Mix well and store in a refrigerator.
6. Sodium molybdate, dihydrate.
7. Standard molybdenum solution, 100 µg/ml. Dissolve 250 mg sodium molybdate dihydrate in 1 litre of water.

Procedure

1. Weigh 0.25 g of sieved sample (minus 80-mesh) into a 15 ml nickel crucible containing 1.25 g fusion mixture.
2. Mix sample and flux. Fuse until frothing ceases.
3. Allow melt to cool. Add 2 ml water. Leave on hot plate overnight at low heat.
4. Transfer the contents of the crucible to test tube calibrated at 5 ml. Adjust volume to the mark with washings from the crucible.
5. Boil the contents of the tube to break up the melt.
6. Mix thoroughly and allow to cool and settle.
7. Pipette a 2 ml aliquot of the clear solution into 2 ml of 2.5% hydroxylamine hydrochloride solution contained in a 16 x 150 mm test tube calibrated at 2 ml and 4 ml.
8. Shake the tube to liberate the carbon dioxide and cool below 30°C.
9. Add 0.5 ml 1% zinc dithiol solution. Shake gently at frequent intervals over a period of 20 minutes.
10. Compare with standards. Mo ppm = 10 x rating of standard.

Standards

To 12 test tubes each containing 2 ml hydroxylamine hydrochloride solution, add 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 5.0, 7.0 and 10.0 µg of molybdenum in solution. Dilute to 4 ml with water. Add 0.5 ml dithiol solution. Shake gently over a period of 20 minutes. Keep in dark when not in use.

Notes

Tungsten interferes if the temperature of solvent extraction is above 30°C. Copper and gelatinous silicic acid also interfere but both can be removed by scrubbing the solvent phase with conc. HCl. The solvent phase is reduced in volume by this procedure due to hydrolysis of the amyl acetate.

Iron interference is eliminated by the use of an alkaline fusion.

The precision of the method is ± 40%.

b) NaOH soluble molybdenum (Rapid Method)

For the derivation of this method see the Analytical Development Section (Part Two).

Reagents

1. Sodium hydroxide, 10% solution. Dissolve 10 g of pellets in 100 ml water.
2. Hydroxylamine hydrochloride, 2.5% solution. Dissolve 2.5 g of hydroxylamine hydrochloride crystals in 100 ml conc. HCl.
3. Zinc dithiol, 1% solution. Dissolve 0.25 g of the powder in 1 ml conc. HCl and dilute to 25 ml with amyl acetate.

Procedure

1. Weigh 0.25 g of the sieved sample (minus 82-mesh) into a silica crucible (3.5 cm).
2. Heat until all the organic matter has burnt off.
3. When cool, transfer to a 16 x 150 mm test tube.
4. Add 5 ml 10% NaOH solution. Boil vigorously for 1 minute.
5. Allow to settle.

6. Transfer a 2 ml aliquot of the liquor to a 16 x 150 mm test tube.

7. Add 2 ml 2.5% hydroxylamine hydrochloride solution, shake to mix.

8. Add 0.5 ml 1% zinc dithiol solution and shake gently over a period of 20 minutes.

9. Match with standards.

Standards

See Total Molybdenum Method.

The precision of the method is better than ± 25%.

c) Total Arsenic

Originally the method of Almond (1953), the arsenic method has been modified by Stanton and Gilbert (1956). Further modifications, made during the course of the present work are:

i. The use of sodium arsenate as the standard reagent in place of arsenic trioxide - the arsenate is more easily soluble and arsenic is added to the standards in the principal form in which it occurs in the samples, As^{V}.

ii. An addition of potassium iodide to the sample solution before the addition of stannous chloride solution results in the reduction of As^{V} to As^{III}, being practically instantaneous. Previously, erratic results were obtained due to the variable reduction time allowed to the samples by the operator's technique.

Reagents

1. Potassium hydroxide, pellets.

2. Zinc metal pellets activated with copper.

3. Hydrochloric acid, concentrated, sp. gr. 1.18.

4. Potassium iodide solution, 2.5%. Dissolve 10 g of crystals in 400 ml water.

5. Stannous chloride solution, 10%. Dissolve 25 g of the dihydrate in 250 ml conc. HCl.

6. Stannous chloride solution, 0.75%. Mix 75 ml of the 10% solution with 375 ml conc. HCl and 550 ml water. Do not keep this solution longer than two days.

7. Mercuric chloride papers. Manufactured by Johnsons of Hendon Ltd.

8. Lead acetate solution, 15%. Dissolve 15 g of the trihydrate in 100 ml water containing 1 ml glacial acetic acid.

9. Lead acetate wool. Saturate glass wool with the lead acetate solution and allow to dry. Pack a loose plug of this wool into each Gutzeit tube and replenish when it is discoloured along half its length.

10. Standard arsenic solution, 100 µg/ml. Dissolve 42 mg sodium arsenate ($Na_2HAsO_4 7H_2O$) in water, add 0.1 ml conc. HCl and dilute to 100 ml with water.

Procedure

1. Weigh 0.1 g of sieved sample into a 15 ml nickel crucible.
2. Moisten with a few drops of water and add 0.5 g KOH pellets.
3. Heat gently until dry and then fuse keeping at red heat for 2 minutes.
4. Allow the melt to cool and add 3 ml water.
5. Loosen the melt by scraping with a nickel spatula and transfer the contents of the crucible to a 16 x 150mm test tube calibrated at 10 ml.
6. Rinse the crucible with 3 ml conc. HCl and transfer to the test tube.

7. Adjust the volume in the test tube to 10 ml with washings from the crucible.

8. Mix well and allow to settle.

9. Pipette a 2 ml aliquot into a 19 x 180 mm test tube calibrated at 2 ml and 5 ml and containing 2 ml of potassium iodide solution.

10. Dilute to 10 ml with 0.75% stannous chloride solution.

11. Add 2 - 4 g zinc pellets and connect a Gutzeit head to the test tube without delay, having previously placed a mercuric chloride paper in the head of the Gutzeit tube.

12. Leave for 1 hour, remove the mercuric chloride paper and compare with artificial standards. As ppm = 50 x rating of standard.

Standards

Pipette four aliquots each of 0.0, 0.1, 0.2, 0.4, 0.6 and 1.0 ml of a 5 µg/ml standard arsenate solution into 2 ml of KI solution in a 19 x 180 mm test tube calibrated at 2 ml and 10 ml. Treat as described in 10 - 11 above. After 1 hour remove the mercuric chloride papers and select the average spot for each quantity of arsenic. Prepare artificial standards by matching these with filter papers painted with water colours.

The precision of the method is ± 25%.

d) Total Iron

The method is based on the standard thioglycollic acid procedure (Scott 1950).

Reagents

1. Reagent solution. Dissolve 40 g tartaric acid in approximately 200 ml water; add 50 g (40 ml) thioglycollic acid and 200 ml ammonia (sp.gr. 0.880). Dilute to 1 litre with water.

2. Standard iron solution, 100 µg/ml. Dissolve 432 mg of ferric ammonium sulphate crystals in approximately 50 ml water. Add 5 ml conc. HCl and dilute to 500 ml with water.

3. Hydrochloric acid, sp. gr. 1.18.

4. Nitric acid, sp. gr. 1.42.

5. Perchloric acid, 60%.

Procedure

1. Weigh 0.1 g sample into a small beaker (30 or 50 ml).

2. Add 0.5 ml conc. HNO_3. If vigorous reaction occurs add further small quantities of acid while heating on a hot plate until frothing ceases.

3. Add 5 ml perchloric acid and heat to fuming. The residue must be pure white.

4. When cold transfer the residue to a calibrated test tube diluting to 10 ml with washings from the beaker.

5. Pipette a 1 ml aliquot into a 16 x 150 mm test tube calibrated at 5 ml and 10 ml and containing 5 ml reagent solution.

6. Dilute to 10 ml with water and shake to mix.

7. Compare with standards. If the colour is more intense than that of the 200 µg standard repeat from 5 with a smaller aliquot.

Standards

To 12 test tubes each containing 5 ml reagent solution add respectively 0.0, 5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 150 and 200 µg of iron. Dilute to 10 ml with water and mix. Keep in dark when not in use.

The precision of the method is ± 25%.

e) Total Manganese

The method is essentially that of Almond (1953).

Reagents

1. Potassium bisulphate, fused powder.
2. Sulphuric acid, 0.5N. Add 14 ml conc. sulphuric acid sp. gr. 1.84 to about 500 ml water, dilute to 1 litre.
3. Acid mixture. Add 125 ml conc. sulphuric acid to about 500 ml water, mix well and cool. Add 62.5 ml conc. nitric acid sp. gr. 1.42 and 62.5 ml ortho-phosphoric acid sp. gr. 1.75. Mix well and dilute to 1 litre.
4. Potassium periodate Analoid pellets.
5. Standard manganese solution, 100 µg/ml. Dissolve 203 mg of manganese sulphate crystals in about 100 ml of water; add 100 ml 0.5N sulphuric acid and dilute 500 ml with water.

Procedure

1. Weigh 0.1 g of the sieved sample into a 16 x 150 mm test tube.
2. Mix with 0.5 g potassium bisulphate and fuse.
3. Leach with 5 ml 0.5N sulphuric acid.
4. Pipette a 1 ml aliquot into an 18 x 180 mm test tube calibrated at 5 and 10 ml and containing 5 ml acid mixture.
5. Add 0.2 g (1 Analoid pellet) of potassium periodate and bring to the boil.
6. Boil for 30 seconds and then heat in a boiling water bath for 10 minutes.
7. Dilute to 10 ml with water and compare with standards.

Standards

To 19 test tubes each containing 5 ml acid mixture add respectively 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 30, 40, 50, 60, 80, 100, 150, and 200 µg of manganese. Add 0.2 g potassium periodate and bring to the boil. Continue boiling for 30 seconds and then heat in a boiling water bath for a further 10 minutes. Make up to 10 ml with water. Keep in dark when not in use.

Precision of method: ± 25%.

f) Organic Carbon

The method was derived from the wet combustion procedure of Schollenburger (1927).

Reagents

1. Sulphuric acid, conc. sp. gr. 1.84.
2. Potassium dichromate, 0.4N solution. Dissolve 19.61 g of the crystals in 1 litre of water.
3. Ferrous ammonium sulphate, approximately 0.2N. Dissolve 78.6 g of the salt in 1 litre of water containing 20 ml conc. sulphuric acid.
4. Diphenylamine indicator. Dissolve 0.5 g diphenylamine in 100 ml conc. sulphuric acid. Pour into 20 ml cold water. Keep in the dark.
5. Sodium fluoride, powder.

Procedure

1. Weigh 0.3 g of sample into a 250 ml conical flask. Add 10 ml potassium dichromate solution and 10 ml conc. sulphuric acid.
2. Heat over a low flame for about 25 seconds, taking care to keep the temperature below 175°C.

3. Allow to cool thoroughly. Add 100 ml water and about 5 g sodium fluoride.

4. Titrate with 0.2N ferrous ammonium sulphate solution using 3 drops of diphenylamine as indicator. The initial colour is dark green which changes to inky blue and then to light indigo. Titration can be carried out rapidly to this point, then proceed carefully dropwise to the green end point.

5. Do a blank solution in the same manner.

Calculation

The percentage of organic carbon in the sample is calculated by the following formula:

$$\frac{B - U}{B} \times D \times N \times A \times 100 \times F = \% \text{ organic carbon.}$$

Where B is ml ferrous solution used for the blank

U is ml ferrous solution used for the sample

N is the normality of the dichromate solution (0.4)

D is ml of dichromate solution used

A is the milliequivalent weight of carbon (0.003)

W is the weight of the sample

F is the recovery factor (1.2) a correction to give comparable results with dry combustion methods.

The precision of the method is $\pm$ 15%.

g) Removal of Free Iron Oxides

The procedure follows that of Aguilera and Jackson (1953) with the omission of the versene from the citrate reagent.

Reagents

1. Citrate reagent. Dissolve 75 g trisodium citrate in 900 ml water. Adjust the pH of the solution to 7.3 by the addition of saturated citric acid. Dilute to 1 litre.

2. Dithionite reagent. Dissolve 20 g sodium dithionite in 100 ml water. Adjust the pH of the solution to 7.3 by addition of 10% NaOH solution. Prepare this reagent fresh for each batch of samples.

3. Sodium chloride, saturated solution.

Procedure

1. Weigh 1 g of sample into 100 ml Pyrex centrifuge tube.

2. Add 40 ml citrate reagent and raise the temperature to 80° - 90°C on water bath.

3. Add 5 ml dithionite reagent and stir constantly for 5 minutes and then occasionally for a further 10 minutes.

4. Add 10 ml saturated sodium chloride solution and digest for 5 minutes.

5. Centrifuge 5 minutes at 2,500 rpm and decant supernatant liquor.

6. Repeat the whole procedure on the residue and combine the first and second extracts.

7. Wash the residue once with citrate reagent and add the washings to the liquor previously obtained. Make up this liquor to a known volume and determine the iron on an aliquot by the thioglycollic acid procedure.

8. Dry the residue. Determine the arsenic or molybdenum content by the standard procedure. Subtraction of the result of

this analysis from the total metal content gives the metal associated with the free iron oxides.

Note

Using the analytical method previously described molybdenum cannot be determined directly on the extract because of interference from iron.

Arsenic cannot be determined on the extract by the Gutzeit method because of interference from H_2S liberated in the decomposition of the dithionite by the Gutzeit reagents.

h) Exchangeable Molybdenum

The method used is a modification of that of Rubins and Dean (1947). The preliminary treatment with sodium acetate solution was ommitted because of the possible displacement of some of the exchangeable molybdenum by the reagent. Rubins and Dean used this reagent to bring all their soils to the same pH before treatment. The pH used in the present experiments was 6.8, this being the average pH recorded by Mather for the soils of the field areas. Rubins and Dean worked at pH 5.7 because their solutions buffered at this pH. Decolorisation of the phosphate extracts with charcoal was not carried out because of the possibility of removal of trace elements by this treatment. Test indicated that the dark colour of the extract did not interfere with the colorimetry at the dilutions used in the present work.

Reagents

1. Sodium dihydrogen phosphate, 0.44M Dissolve 69 g of the salt in 1 litre of water. Adjust to pH 6.8 by the addition of 10% NaOH solution.

Procedure

1. To 2.5 g of air dried sample contained in a Pyrex centrifuge tube add 25 ml phosphate solution.
2. Heat the sample in a boiling water bath for 1 hour.
3. Centrifuge for 5 minutes at 2,500 rpm and decant the liquor into a beaker.
4. Repeat the above extraction twice more, making a total of three extractions.
5. Wash the residue with 25 ml 50% ethanol in water and then with 95% ethanol. Discard the washings.
6. Dry the residue and determine the molybdenum content by the usual method. Subtraction of the molybdenum content of the residue from the initial value gives the exchangeable molybdenum content of the sample. Molybdenum could not be determined on the extract, as the evaporated residue was found to be infusible with the present procedure.

i) Anion Exchange Capacity

This is essentially the method of Rubins and Dean (1947).

Reagents

1. Phosphate reagent. Dissolve 1.25 g ammonium meta-vanadate in 400 ml conc. sulphuric acid. Dissolve 50 g ammonium molybdate in 400 ml water. Mix the two solutions.
2. Sodium hydroxide, 0.125N solution. Dissolve 5 g of the pellets in 1 litre of water.
3. Standard phosphate solution, 0.04 mg P_2O_5 per ml. Dissolve 6.1335 g of potassium dihydrogen phosphate in water. Dilute to two litres. Dilute 50 ml of this solution to 2 litres.

Procedure

1. 1 g of the residue from the exchangeable molybdenum determination is treated with 25 ml 0.125N NaOH solution in the same manner as described in the exchangeable molybdenum procedure.
2. Filter the extract liquor and make up to a known volume.
3. Take a 5 ml aliquot of this solution and add 20 ml water and 50 ml phosphate reagent. Make up to 50 ml with water.
4. Zero Unicam using a blank solution of 10 ml phosphate solution made up to 50 ml with water.
5. Read absorbance of the samples at 530 mu.

Calculation of exchange capacity

The anion exchange capacity of the sample with respect to $(H_2PO_4)^-$ at pH 6.8 is calculated as follows:

Standard solution containing 0.2 mg P_2O_5 gives a Unicam reading of A units.

Sample solution gives a Unicam reading of B units.

P_2O_5 content of the sample is $\frac{B \times 0.2}{A}$ mg

Dilution factor is F, hence the total P_2O_5 content of the extract is $\frac{0.2\ BF}{A}$ mg.

Divide by the millimolecular weight of P_2O_5 to bring into millimols.

$\frac{0.2 \times B \times F}{A \times 142}$ is the total amount of P_2O_5 absorbed per gram of sample.

P_2O_5 is equivalent to $2(H_2PO_4)^-$ hence the exchange capacity with respect to $(H_2PO_4)^-$ is $\frac{2 \times 0.2 \times B \times F}{A \times 142}$ per gram of sample.

Hence the anion exchange capacity of the sample is $\frac{100 \times 2 \times 0.2 \times B \times F}{A \times 142}$ millimols $(H_2PO_4)^-$ per 100 g at pH 6.8.

B. Natural Waters

a) Bicarbonate determination

Reagents

1. 0.001N Hydrochloric acid. Prepare 1N acid by mixing 40 ml of the concentrated acid with 400 ml of water. Dilute 1 ml of this solution to 1 litre with water. Standardise the solution by titrating with 0.01N sodium carbonate solution, using methyl red as indicator.

2. 0.01N Na_2CO_3. Dissolve 530 mg of the anhydrous salt in water and dilute to 1 litre.

3. Phenolphthalein solution. Dissolve 50 mg of the powder in 100 ml 95% ethanol.

4. Screened indicator solution. Dissolve 125 mg methyl red and 83 mg methylene blue in 100 ml 95% ethanol.

Procedure

1. Add one or two drops of phenolphthalein solution to 200 ml of water sample.

2. Titrate with 0.001N acid until colourless. Note amount of acid used.

3. Add one or two drops screened indicator and titrate to the grey end point.

4. Note amount of acid used.

Calculation of bicarbonate content

Titre with phenolphthalein a ml.

Titre with screened indicator b ml.

Sample volume V ml. Normality of acid N.

$$\text{Then } Na_2CO_3 = \frac{2a \times 53 \times N \times 1000}{V} \text{ mg/l.}$$

$$NaHCO_3 = \frac{b \times 84 \times N \times 1000}{V} \text{ mg/l.}$$

Note. The above determination should be made immediately after the sample has been taken.

If the water has a pH less than 8.35 there will be no pink colour with phenolphthalein and carbonate is absent.

b) Determination of Sulphate in Water

Reagents

1. Acid salt solution. Dissolve 240 mg of sodium chloride in 900 ml of water, add 20 ml HCl conc. and dilute to 1 litre with water.
2. Barium chloride dihydrate crystals.
3. Gum Acacia solution. Dissolve 10 g in 100 ml boiling water, filter through Whatman No. 41 paper when cold.
4. Standard sulphate solution, 0.5 mg/ml. Dissolve 907 mg of potassium sulphate in water, and dilute to 1 litre.

Procedure

1. Place 20 ml filtered water in 18 x 180 mm test tube calibrated at 20 and 25 ml.
2. Add 5 ml acid salt solution.
3. Add approximately 250 mg barium chloride crystals by scoop.

4. Shake for 30 seconds to dissolve the crystals.

5. Compare the turbidity against standards using a dark background.

6. Sulphate in mg/l = 50 x matching standard.

Standards

To 12 test tubes calibrated at 20 and 25 ml add respectively 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 mg of sulphate. Add 1 ml gum acacia solution and dilute to 20 ml with water. Add 5 ml acid salt solution followed by 250 mg barium chloride crystals. Cork the tubes and shake for 30 seconds.

c) Determination of Molybdenum by Solvent Extraction

For derivation see Analytical Development Section.

Reagents

1. Buffer solution. Dissolve 136 g of sodium acetate in 1 litre of water containing 58 ml glacial acetic acid.

2. Chloroform.

3. Oxine solution, 5%. Dissolve 5 g of 8-hydroxyquinoline powder in 100 ml ethanol.

4. Nitric acid, conc. sp. gr. 1.42.

5. Perchloric acid, 60%.

6. Hydroxylamine hydrochloride, 2.5%. Dissolve 2.5 g hydroxylamine hydrochloride in 100 ml conc. HCl.

7. Thioglycollic acid.

8. Zinc dithiol, 1%. Dissolve 1 g zinc dithiol in 1 ml conc. HCl and dilute to 100 ml with amyl acetate.

Procedure

1. Filter the water sample through Whatman No.542 paper[a].
2. To a 1.5 litre sample, contained in a 2 litre Squibbs-type separating funnel[b], add 50 ml buffer solution and 10 ml oxine solution.
3. Invert the funnel once or twice to mix the solutions.
4. Add 20 ml chloroform and shake vigorously for 1 minute[c].
5. Allow the phases to separate. Run off the lower chloroform layer into a beaker or dish.
6. Add 10 ml of chloroform to the sample and invert the funnel once or twice to mix. There is no need to shake at this stage.
7. Allow the phases to separate. Run off the chloroform into the same vessel as before.
8. Repeat the chloroform washings until the organic phase is colourless.
9. Evaporate the chloroform extract to dryness on a sand bath.
10. Fume the residue with 0.5 ml portions of conc. nitric acid until the residue is red-brown or yellow. All carbonaceous matter must be oxidised[d].
11. Fume the residue with 0.5 ml portions of perchloric acid until the residue is light brown or yellow.
12. Take up the residue in 2 ml hydroxylamine hydrochloride solution[e] and transfer the leach to a test tube calibrated at 4 ml.
13. Wash out the vessel with less than 2 ml water and add the washings to the test tube. Make up to the 4 ml mark with water.
14. Add 0.1 ml thioglycollic acid and shake to mix[f].

15. Add 0.5 ml zinc dithiol solution and shake gently at intervals over a period of 30 - 45 minutes.

16. Match against standards after 45 - 60 minutes.

Standards

To 12 test tubes add 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 µg Molybdenum. Make up to 2 ml volume with water. Add 0.1 ml thioglycollic acid and 2 ml hydroxylamine hydrochloride solution. Shake to mix. Add 0.5 ml zinc dithiol solution and shake gently, periodically, over a period of 30 - 45 minutes. Full colour develops in about 1 hour.

Notes

a) Coarser grades of filter paper may allow fine suspended particles to pass into the sample.

b) Oxine reacts with molybdenum^{VI} between pH 3.6 - 7.3 and with iron between pH 2.8 and 11.3. At the pH of the buffer, 4.6 - 4.8, 100% extraction of the molybdenum oxinate into chloroform can be achieved.

c) Most oxinates are shades of yellow. Vanadium is, however, magenta-black and iron forms a green-black oxinate. In the presence of iron the solution becomes green. The intensity of this colour serves as an indication of the amount of iron present in the sample. The chloroform extract is black in the presence of iron.

d) All organic matter must be removed before fuming with perchloric acid or detonation may occur.

e) If the determination of iron is not required the residue can be leached with 2 ml cold N-sodium carbonate solution thus rendering the iron insoluble and eliminating its interference in the molybdenum determination.

f) Thioglycollic acid has been used to prevent the formation of a blue discolouration in the amyl acetate solvent phase, believed to be due to residual oxidation products of the fuming operation. Addition of thioglycollic acid delays full colour formation by 30 - 45 minutes.

g) If the solvent phase is dirty or discoloured yellow, transfer to a test tube containing 6N HCl and shake. This often clears the solvent phase.

h) Iron may be determined on the aqueous phase of the leach by taking a suitable aliquot, making up to 5 ml with water in a test tube and adding 5 ml iron reagent. (See Total Iron Determination).

d) Determination of Arsenate by Coprecipitation

For the derivation of the method see Analytical Development Section.

Reagents

1. Ammonium chloride solution. Dissolve 165 g of the salt in water and dilute to 1 litre.
2. Ammonia solution, sp. gr. 0.880.
3. Sodium phosphate solution. Dissolve 126 g of trisodium phosphate duodecahydrate crystals in 1 litre of water.
4. Magnesium sulphate solution. Dissolve 82 g of magnesium sulphate heptahydrate in 1 litre of water.

5. Hydrochloric acid, 6N. Mix 240 ml of the concentrated acid with 200 ml water or use the constant boiling mixture (6.11N).

6. Potassium iodide solution, 2.5%. Dissolve 10 g of the crystals in 400 ml water.

7. Stannous chloride solution, 10%. Dissolve 25 g of the dihydrate in 250 ml conc. HCl.

8. Zinc metal. Pellets activated with copper.

9. Mercuric chloride papers. Manufactured by Johnsons of Hendon Ltd.

10. Standard arsenic solution, 100 µg/ml. Dissolve 42 mg of sodium arsenate heptahydrate in 100 ml water containing 0.1 ml conc. HCl.

Procedure

1. Filter the water sample through Whatman No. 542 paper.

2. To a 1 litre sample contained in a conical Squibbs-type separating funnel add 10 ml ammonium chloride solution and mix.

3. Add 25 ml ammonia solution and mix.

4. Add 5 ml sodium phosphate solution and mix.

5. Add 5 ml magnesium sulphate solution and mix.

6. After setting aside for at least 1 hour, run off the white precipitate into a conical flask (250 ml).

7. Rinse the walls of the separating funnel with 5 ml 6N HCl and add to the flask.

8. Add 2 ml potassium iodide solution and mix, then add 1 ml stannous chloride solution.

9. Add 2 - 4 g zinc pellets and connect immediately to a Gutzeit head containing a mercuric chloride paper.

10. Leave for 1 hour. Remove the mercuric chloride paper and compare the spot with standards at once.

Alternatively from stage 6 if it is inconvenient to proceed immediately with the determination.

6a Run the precipitate into a Whatman No. 542 filter paper (11 cm) instead of the flask and transfer the paper to a suitable container for storage. A screw-topped plastic specimen tube of 15 ml capacity was found convenient.

7a Dissolve the precipitate through the paper by dropwise addition of 5 ml of 6N HCl from an automatic pipette and proceed as from stage 8.

e) Extraction of elements from stream waters using Ion Exchange Resins

Reagents

1. Resin. Dowex A1, H^+ form; Dowex 21K, Cl^-form.
2. Anion elutriant; a buffered salt solution consisting of 20 g sodium chloride plus 2 g disodium hydrogen phosphate and 2 g trisodium phosphate. This solution should have a pH of 9.
3. Cation elutriant, 10% hydrochloric acid.

Procedure

1. Filter 10 litres of water through Whatman No. 542 paper.
2. Store in 5 litre capacity cubitainers closed with a sliding clip.
3. Using the cubitainer as a reservoir pass the water through a resin column (16 cm x 1.5 cm) at a rate of 1 litre per hour.
4. Remove the resin from the column into a plastic funnel, the end of which is closed by 82-mesh silk gauze.

5. Elutrate the resin with 25 ml anion elutriant. Wash the resin with 15 ml water. Collect the eluate in a 100 ml conical flask.

6. Set the eluate aside and take aliquots for the appropriate anion analyses.

7. Repeat the elutriation with the cation elutriant using 25 ml volume followed by a wash with 15 ml water.

8. Analyse this eluate for cations.