

A
THESIS
entitled

APPLICATION OF SPECTROGRAPHY TO THE STUDY OF SECONDARY
GEOCHEMICAL DISPERSION PATTERNS RELATED TO MINERAL DEPOSITS
IN AFRICA AND THE FAR EAST

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ABSTRACT.

Laboratory studies were made of geochemical dispersion patterns for several elements in different environments, based upon spectrographic analysis of samples collected by other investigators.

Related spectrographic investigations are briefly reviewed. The spectrographic techniques are described with particular reference to practical investigations into (a) analytical bias due to variations in the bulk composition of test samples, and improvements obtained by a buffer procedure; and (b) a spectrographic technique for determining the major elements.

Both published and the modified spectrographic techniques were applied to five separate geochemical investigations as follows:-

1. Distribution of minor (trace) elements in stream sediments derived from seven Malayan granites. The results indicated that stanniferous granite regions may be distinguished from probably barren areas by the Sn content of the stream sediments. A degree of positive correlation exists between the contents of Sn and Be. Moreover, the minor element contents of the sediments suggest that phase variations exist within the different granites.

2 & 3. Distribution of minor, and in some cases major elements in soil profiles over various rock types in the vicinity of Cu-Co mineralizations in the N. Rhodesian Copperbelt and Uganda. Variations in the content and/or the ratios of various elements were observed to be related to soil horizon, rock type, and the presence or absence of mineralization.

4. Minor element distribution in a soil profile over galena mineralization in the Transvaal. Some similarities were revealed in the patterns of distribution for Pb, Mn, Ba and Co, which supplement previous findings for Pb.

5. Secondary dispersion patterns in near-surface soils related to a beryl-pegmatite in S. Rhodesia. Positive anomalies for the elements Be, Rb, Li, Ba, Sr and Sn were observed. Several other elements show their maximum contents in soils over the country rocks.

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CHAPTER I. INTRODUCTION AND PREVIOUS WORK.

Historical Introduction.

Spectral methods of analysis (including first spectroscopic and later spectrographic methods) have been applied to materials of geological interest since the first practical realisation of the analytical possibilities of the spectroscope by Bunsen and Kirchhoff in 1859. Their discoveries in that year of the elements rubidium and cesium from the flame spectra of mineral waters stimulated the examination of natural materials, originally by purely qualitative methods. As a result, discoveries of the elements thallium, indium, solar and terrestrial helium, gallium and seven rare earths, were to follow in the period to 1907 (Harrison, Lord and Loufbourow, 1948).

W. N. Hartley employed his improved quartz spectrograph of 1872 (now preserved in the Science Museum, London) in many contributions to mineralogical spectrum analysis published from 1884 onwards. He introduced the method of quantitative analysis by the visual comparison of spectra of unknown minerals with those of known composition. De Gramont, publishing from 1895, was similarly active among many investigators of the rarer constituents of minerals; he employed a method of fusion of mineral powder samples with sodium or lithium carbonates prior to excitation, the forerunner of modern alkali buffer techniques.

By 1929-1930 all the basic modern techniques for producing spectra had been applied in some degree to geological materials, largely minerals, but also to rocks, natural waters and meteorites (Fitch, 1929-1930). Powders, briquettes, solutions and occluded gases had been excited by arc, spark, flame or discharge tube techniques, using both spectroscopes and prism or grating spectrographs. The analytical interpretation of spectra was mainly by visual comparison, a method which is still employed in most geochemical prospecting applications. The use of internal standards, introduced by Gerlach (1925), and the development of suitable densitometers, accelerated the application of spectrography as a quantitative analytical method. The most active work in this direction was in the metallurgical field, where accuracy was particularly important (Brode, 1943, Chap. V).

The decade beginning 1930 saw the rise of systematic investigations into the geochemistry of trace elements by spectrographic methods. This period was introduced by the application of spectrography as an analytical tool in Goldschmidt's classical researches, wherein previously he had used X-ray crystallography and X-ray spectrographic methods. At Gottingen in the period 1929-1936 he employed the cathode-layer arc techniques of Mannkopf and Peters (1931) with notable success in studying the fundamental geochemistry of the trace elements (Strock, 1936; Goldschmidt, 1954).

In the related fields of applied science, spectrography was used as early as 1935 in geochemical prospecting for tin in Khapcheranga, U.S.S.R. (Ozerov, 1957); while in Sweden the investigation of geochemical prospecting began in about 1936, using spectrographic analysis of plant samples (Brundin, 1939). Goldschmidt's observations on trace element variations in soils, published in 1937, stimulated considerable interest in the applications of spectrography in pedology and agriculture. This field of research expanded rapidly with the development of techniques appropriate to agricultural problems, such as the use of pre-concentration for the analysis of trace elements in soil extracts (Mitchell, 1948)

Modern Spectrographic Practice as Applied to Geochemical Problems.

The following brief review is concerned primarily with the main trends in spectrographic practice. Attention is first given to Russia and Scandinavia, where the pioneer work took place, and secondly to America and Britain, where notable interest in applied geochemistry has been mainly a post-war development.

Russia and Scandinavia.

By far the most extensive applications of spectrography in geochemical prospecting have been in the U.S.S.R. (Fersman, 1939; Ginzburg, 1957; Krasnikov, 1957). The reason for this probably lies in the success which attended the first field surveys carried out in that country.

The first systematic geochemical surveys in Russia were used in prospecting for tin by the spectrographic analysis of surface materials in areas indicated as being favourable by "panning" heavy mineral concentrates (Ozerov, 1937; Ratsbaum, 1938, 1939). A small portable spectrograph and auxiliary equipment was specially designed for use in the field area. The technique employed arc excitation of the powdered sample loaded directly in a small anode crater; metal concentrations were estimated as lying within coarse ranges of <0.05 , 0.05 , 0.1 , 0.3 , 0.5 , 1 , 3 , and 10% Sn, according to the presence or absence of particular tin lines. Sergeev (1941) records a total of eleven field investigations involving spectrographic methods in the years 1935-1939; four were concerned with Sn mineralization; three with Pb-Sn; and one each with Pb, Cr, W-Mo and Cu-Pb-Zn. Ore discoveries or vein extensions of economic size were revealed in three investigations for tin, and one for tungsten. The spectrographic method was much the same for all the elements, although not all employed the portable field spectrograph. Sensitivities were relatively poor; the best values, which differed with the instrument used, were 0.05% for W; 0.01% for Sn, Pb, Ni, As, and Sb; and 0.01% for Mo (Sergeev, 1941). These operations were the precursors of many spectrographic surveys which, as Ginzburg (1957) notes, now constitute the most popular geochemical method used in the Soviet Union.

The present-day co-ordinated mineral search programme in extensive areas of the U.S.S.R. has favoured the establishment of stationary spectrographic and chemical laboratories to serve field parties in a given area for several years. The routine prospecting methods continue to employ semi-quantitative visual readings and a simple arc technique. This is done in the interests of speed and comprehensive element coverage with an adequate average sensitivity, at the expense of high accuracy and maximum sensitivity for each element. The best sensitivities quoted by Ginzburg (1957) are the following:- 0.01% for Zn, W; 0.001% for Ni, Co, Pb; 0.0005% for Cu, Mo; and 0.0001% for Ag.

Recent mineral discoveries by spectrographic ("metallometric") methods include ores of Sn, Cu, Pb, Zn and Mo, in various areas. Investigations were especially extensive, and more successful in open terrain with bedrock outcropping or under only thin soil cover, as in Central Kazakhstan. The spectrographic surveys have been of several types depending on the geochemical problem.

Comprehensive spectrographic analysis is considered to be appropriate for general prospecting in new areas, to cover all types of ore occurrence. Multi-element data is also used in investigating individual polymetallic deposits. Il'in (1956) mapped the zoned aureoles of dispersion of the elements Mo, W, Sn, Pb and Zn, around a granite source of complex tin mineralization. Such investigations of geochemical

association between elements in particular geochemical environments have verified that, in suitable cases, an "indicator element" may be sought as characteristic of a larger element group.

Analyses for the ore element alone are appropriate for local investigations, and for prospecting in a particular ore province - the successful early Russian work was almost entirely of this kind. Recent examples include spectrographic analysis for Be and/or Li to detect anomalies related to mineralised pegmatites (Karaeva et al 1958). Zalashkova et al (1958) mapped Be anomalies in soil cover overlying beryl pegmatites by a very simple spectrographic technique: visual estimates of the Be line density were made in arbitrary units, dispensing with the usual estimates of concentration against standards. This illustrates the continued use in Russian prospecting of the simplest kind of semi-quantitative technique.

On the other hand, more specialised techniques including the air-blast A.C. arc (Rusanov et al, 1957, 1958) and the distillation method (Mandelstam, 1957) may have significant applications in future Russian prospecting. The distillation method offers increased sensitivity, by pre-concentration, for certain moderately volatile elements, while the air-blast arc method provides a rapid and cheap method of introducing powdered samples into the arc.

The following points relevant to the advantages and defects of spectrographic prospecting methods are noted by Ginzburg (1957), based upon Russian work in geochemical methods of all kinds.

The main advantages are (a) the possibility of simultaneous determination of many elements, (b) simplicity and rapidity of operations, (c) possibilities of high productivity, and (d) low cost. Minor operational defects are (a) the difficulty of transport of the apparatus and (b) the need for electric power and skilled personnel. Analytical defects are (a) there is insufficient accuracy for some elements in the rapid comprehensive method, (b) the accuracy of results may be affected by the standard materials employed, (c) the sensitivity is not adequate for all elements, although specific techniques may be used to overcome this in some cases, and (d) spectrography is unsuitable for water analysis without special adaptations. The fact that the spectrographic method detects an element regardless of its mineral or chemical form gives more certainty of detection than mineralogical prospecting methods, but on the other hand, the gross content of an element in a sample may sometimes give less geochemical information than a selective method.

In Scandinavia the use of spectrographic analysis of plant ash for prospecting was introduced in 1936, by Palmquist and Brundin among others (Hawkes, 1957). The analytical technique was the cathod-layer arc method,

previously employed by Goldschmidt for trace element studies in fundamental geochemistry. This prospecting method was used also in the first studies in Canada, noted by Lundberg (1941). Brundin (1939) was granted an American patent for this form of prospecting. The example given concerns work in the Swedish Blyberg mining field, where the spectrographic analysis of plant ash revealed anomalous concentrations of lead, related to and underlying lead-silver vein. Although the lead accumulated in the plants proved to be the best indicator element, zinc, copper, silver and gold were also determined.

Recent Scandinavian spectrographic research includes an investigation of the analytical bias caused by variation in the bulk composition of soils (Makitie and Lappi, 1958); while unpublished prospecting studies by Kvalheim and others in the State Institute, Trondheim have involved both a mobile spectrographic unit and a laboratory direct-reading instrument (Kvalheim pers. comm., 1960).

North America and Britain (including overseas territories).

The active development of geochemical prospecting in America and Britain dates from the post-war period (Hawkes, 1947, 1949; Webb and Millman, 1950, 1951; Webb, 1953, 1956; Hawkes, 1957). The generalisations in this brief survey are drawn mainly from the important reviews of Webb (1953, 1956) and Hawkes (1957). Although mainly chemical methods of analysis have been employed in work originating in these countries, spectrographic methods have had some important applications.

The most extensive of the published applications of spectrography in prospecting have come from the laboratories of the U.S. Geological Survey. Following the Russian precedent, a mobile spectrographic laboratory was planned by the Geochemical Prospecting Section of the U.S.G.S. about 1953 and described in detail by Canney et al (1957). The initial application was in search for Cu-Pb-Zn ore by the analysis of drill core on the site (Myers et al 1956). An anode arc method was applied to a mixture of the sample with graphite, and concentrations were estimated semi-quantitatively by visual reading. The method is similar to that employed by Myers (1954) to provide semi-quantitative data on thirty-one detectable elements, including the major constituents, in rocks of the Colorado Plateau uranium province. A recent interpretation of the latter geochemical data is provided by Garrels and Larsen (1959).

Oda et al (1958) describe a modification of the Myers technique by adding calcium carbonate to the sample mixture, to serve as a spectrographic buffer with the object of swamping any compositional variations between samples. This modification was used in the mobile laboratory; field projects have so far included trace elements in igneous rocks, prospecting for beryllium, and investigations in the Death Valley salt pan (Oda, pers. comm., 1960). Analytical productivity is thirty to thirty-five samples for thirty elements, estimated semi-quantitatively, per two-man day.

This productivity would, of course, be less if all the samples contained all the elements in detectable amounts. It is notable that very similar figures for a three-man, eight-hour operation are quoted by Ginzburg (1957) for Russian semi-quantitative spectrographic surveys.

Waring and Annel (1951, 1953) describe a semi-quantitative technique for the comprehensive analysis of geological samples, which is relevant to prospecting. Samples are mixed with graphite and excited in an anode arc; an unusual feature is that comparison standards, on the other hand, are arced from evaporated solutions of pure metal salts. The concentrations of both trace and major elements are estimated visually within coarse concentration ranges, originally a factor of ten - which is nevertheless adequate for sorting diverse radio-active ore samples. Subsequent experience allowed estimates within a factor of three, and provided semi-quantitative data for geochemical studies of radio-active deposits (Waring, 1954). In this connection, Flanagan (1957) discusses the extraction of geochemically useful data from semi-quantitative spectrographic analyses, from a statistical point of view.

The work of Webb and Millman (1951) and Millman (1953, 1957) is important among the few British publications directly concerned with spectrographic analysis in geochemical prospecting. The first publication, which did much to stimulate interest in geochemical prospecting in British

territories, described work in Nigeria on geochemical dispersions from lead-zinc ore deposits overlain by residual tropical soils. Anomalies were successfully detected by the collection and spectrographic analysis of plant ash samples, employing the cathode-layer arc method (Webb and Millman, 1951). Millman (1953, 1957) also obtained positive results in the analysis of the soils from the same region (in this case by an anode arc technique). A complementary study of both soil and plant samples over copper-tin mineralisation in S.W. England revealed positive anomalies in this environment also. The elements determined, in all, were Pb, Ag, Zn, Sn and Cu.

Active prospecting by mining groups themselves is probably the largest, and least published part of the field. Webb (1953) notes the occasional use of spectrography in prospecting by some American companies at that time, which has certainly expanded, and the writer is aware of at least three Central African prospecting organisations where spectrographic methods have been applied. Williams (1960) indicates the large scale of recent geochemical prospecting activities by the Anglo-American Corporation of South Africa.

Some fields not directly concerned with prospecting are relevant from the point of view of this Thesis as regards spectro-analytical technique. Important among these are certain fundamental studies of trace elements in rocks or minerals. A recent, brief review is provided by Ahrens (1957),

whose authoritative texts on spectrographic methods of analysis include further references in this field (Ahrens, 1950, 1954). Other important contributions are collected in the standard works on geochemistry by Goldschmidt (1954), Rankama and Sahama (1950) and Mason (1952). Among British work, may be mentioned spectrographic studies on trace element distribution in rocks of the Skaergaard intrusion (Wager and Mitchell, 1943, 1948, 1951), and other igneous rock series (Nockolds and Mitchell, 1948; Nockolds and Allen, 1953, 1954, 1956). Some fundamental geochemical investigations have a direct bearing on prospecting, for example, that of Ahrens and Liebenberg (1950), which indicated that the spectrographic determination of tin in the micas from pegmatites might be used in reconnaissance for areas of tin mineralization.

Agricultural applications of spectrography are of interest, not only in the trace element geochemistry of soils, but also as regards analytical techniques, particularly those which emphasise sensitivity and generality of element coverage. Mitchell (1948) and Vaneslow and Liebig (1948) detail the spectrographic procedures in two active British and American centres, with recent reviews by Mitchell (1957) and Vaneslow et al (1957). Relevant applications have included studies of trace element behaviour in American podzolic soils by Connor et al (1957) and in British soil profiles by Butler (1954); Mitchell, (1955) and, more recently Berrow (1958).

A final point must be re-emphasised in this introduction to a Thesis devoted to the application of spectrographic arc techniques in geochemical investigations; that this analytical discipline is but one of many chemical and physical methods which form the tools of the geochemist, just as geochemical prospecting methods themselves are only a part, but an increasingly important one, of the sum total of mineral exploration methods.

In summarizing the relation between the spectrographic and other techniques for geochemical prospecting, a quotation from the review of American prospecting by J. S. Webb (1953, p. 339) is perhaps the most valid assessment:-

"Simple chemical tests are generally preferable for prospecting, but although these exist for a number of common ore metals there still remain others ... for which no satisfactory wet procedure has yet been developed. Spectrography, or some other technique, would be necessary in prospecting for these recalcitrant elements. Moreover, the comprehensive permanently-recorded data obtained by spectrographic analysis are desirable in research work, orientation studies and special problems involving the determination of several elements in each sample".

The geochemical investigations in this Thesis fall mainly into the latter categories, consisting of small-scale investigations in five sampling areas, into the geochemical characteristics of soil profile development and of secondary dispersions of elements associated with mineralization. At the same time, the chapter dealing with some results in geochemical prospecting for Be illustrates the application of spectrography to determining traces of an ore metal for which, in the early stages of this investigation, no satisfactory chemical analytical procedure was available.

SECTION 1. ANALYTICAL TECHNIQUES.

Section I comprises three Chapters which concern the spectrographic arc methods of analysis which were applied in geochemical investigations in Section II.

Chapter 2 concerns the determination of the minor elements, and Chapter 3 the major elements, while Chapter 4 describes two accessories which were made to facilitate respectively the exposure and the quantitative measurement of soil spectra.

CHAPTER 2. ANALYTICAL TECHNIQUES FOR MINOR ELEMENTS.

The term minor elements is applied to those elements which were determined in the range from 0 to 10,000 ppm. The metals which are sought as trace constituents in soils and other surface materials in geochemical prospecting, are mainly involved. Simple arc procedures were used with semi-quantitative estimation by means of comparison with prepared "standard" spectra.

The established and modified methods which were used are first described, followed by some details of the analytical test work which are of some general interest in the application of spectrography to geochemical investigations.

Techniques for Minor Elements Analysis.

Table 1 summarises the methods employed for determining the minor elements. It would be noted that with the Hilger large quartz spectrograph* which was employed it is not

*Hilger Models E492 and E742 were used at different times, preparing standard plates individually for each instrument. Each has a focal length of 170 cms.

possible to record simultaneously the most sensitive lines of all the minor elements, since it accepts photographic plates no larger than 10" long, whereas the useful spectrum length is some 30". At least two exposures are required to cover the wavelength range between the most sensitive line for Be at a wavelength of 2348A, and for Li at 6707A. In practice, it was found more convenient and more economical, to use a single intermediate wavelength range covering the sensitive lines of the elements most frequently determined, and to analyse (a) the alkalis and (b) Be, at the optimum wavelength, only where these elements were specially required.

The different methods employed are designated:-

Technique	Elements determined	Procedure	Reference
A	Rb, Li, Ba, Sr, Na ₂ O,) K ₂ O.)	Anode arc excitation. carbon mixture	Ahrens, 1954; Nockolds and Allen, 1953.
B	Be)		
C ₁	Minor elements of general interest.	Cathode-layer excitation. Li ₂ CO ₃ -carbon mixture,	Mitchell, 1948. (modified).
C ₂	ditto	Cathode excitation, large crater; Li ₂ CO ₃ -carbon mixture.	

TABLE 1. Spectographic techniques for minor elements.

	Technique A	Technique B	Technique C ₁	Technique C ₂
Wavelength range A.	8700-3250	3190-2340	4600-2730	4450-2700
Emulsion	Ilford Long-Range Spectrum	Kodak B 10.	Ilford N 30	Ilford N 30
Sample electrode	3.2 mm. ($\frac{1}{8}$ ") int. dia. 5.0 mm. deep. 4.8 mm. ext. dia.	As in A.	0.8 mm. ($\frac{1}{32}$ ") 8.0 mm. 2.9 mm.	4.0 mm. ($\frac{5}{32}$ "). 5.0 mm. 5.4 mm. = full diam. of rod.
Sample polarity	Anode	Anode	Cathode	Cathode
Exposure time	90 secs. from full 9 amp arc.	To completion (2-2 $\frac{1}{2}$ mins.).	To completion (3-3 $\frac{1}{2}$ mins)	60 secs. from full 9 amp. arc.
Sample mixture	1+1 carbon	1+1 carbon	1+ $\frac{1}{2}$ carbon+ $\frac{1}{2}$ Li ₂ CO ₃	1+ $\frac{1}{2}$ carbon + $\frac{1}{2}$ Li ₂ CO ₃
Electrode spacing	10 mm.	10 mm.	10 mm.	10 mm.
Arc current	9 amps.	9 amps.	9 amps.	9 amps.
Element lines used, A (Limits of visual detection, ppm).	Sr 4607.33 (2) Ba 4934.08 (10) Li 6707.84 (1) Rb 7800.22 (100) Na 5889.9/5895.9 (.01% Na ₂ O) K 7664.90 (.04% K ₂ O)	Be 2348.61 (1)	Mn 2801.06 (2) Pb 2833.06 (30) Sn 2839.98 (20) Ga 2943.63 (3) Be 3131.07 (20) Be 2348, (3) Mo 3170.34 (5) V 3185.39 (5) Cu 3273.96 (2) Ti 3377.48 (c.50) Ag 3382.89 (2) Ni 3414.76 (7) Zr 3438.23 (20) Co 3453.50 (10) Cr 4254.34 (2) La 4333.73 (15) Bi 3067.71 (35) Zn 3345.02 (1000) As 2349.84 (1000) Sb 2877.91 (320).	Pb 2833.06 (2) (2839.98 (7) Sn (3175.01 (7) Ga 2943.63 (1) Mo 3170.34 (5) V 3185.39 (5) Cu 3273.96 (2) Zn 3345.02 (c.500) Ag 3382.89 (2) Ni 3414.76 (5) Co 3453.50 (5) Mn 4034.49 (3) Cr 4254.34 (1)

Technical details common to all the techniques.

<u>Spectrograph</u>	Hilger Large Quartz.
<u>Slit</u>	.0125 mm. width. Approximately 4.5 mm. high, using a 3-exposure sector.
<u>Optics</u>	Single lens, collimator focus. A mask at the collimator admits light from 4.0 mm. of the arc column adjacent to the sample electrode.
<u>Rotating step-sector</u> (ref. Chap. 4)	Two steps giving three exposure levels per spectrum, relative exposures being 1, $\frac{1}{4}$, $\frac{1}{16}$.
<u>Electrodes</u>	Prepared from Champion spectrographic carbon rods, nominal dia. 5 mm.
<u>Power supply</u>	300V. D.C. supply from a 3-phase transformer-rectifier. The arc current is controlled by adjustable resistors connected in parallel, in series with the arc gap.
<u>Plate processing</u>	Dish development in Kodak D19 b developer at 18°C for (a) 4 mins., E10 plates or (b) 5 mins., N30 and Long-range plates; followed by a water rinse, approximately 10 mins. fixing in Kodak acid fixer, and 30 mins. washing in running water.

Sample Treatment.

All samples are gently ignited at 500-550°C for 2 hrs. (or 450°C overnight), in order to remove water and volatile matter. A portion of the ignited sample is finely ground in agate before analysis.

Buffer mixtures.

Techniques A and B employ pure carbon powder recovered from preparing the carbon electrodes.

Techniques C_1 and C_2 employ a buffer mixture consisting of 50% carbon and 50% Li_2CO_3 (with small additions of compounds of Ge, Pd, In, Y used in test work as internal standards). The preparation of this mixture, which serves also as a stock for the "major element buffer", is described in Chapter 3.

Sample mixing.

Approximately 50 mg. of sample is accurately weighed on a torsion balance, 500 mg. capacity, and mixed with an equal weight of appropriate buffer mixture. Mixing is carried out either (a) by grinding by hand in an agate mortar for 3 to 5 mins. or (b) by mechanical shaking in a Wig-L-Bug mixer for 30 secs.

Standards and interpretation of spectra.

The techniques were mainly employed for visual semi-quantitative estimations in geochemical samples, using a Hilger projection spectrum comparator to compare line densities with spectra prepared from standard mixtures. In preparing the standards, a synthetic base mixture simulating the composition of an intermediate igneous rock was used consistently throughout the work. Appendix A2 lists the composition of the base and the two series of standards which were prepared, (a) for the alkali elements and (b) for all other minor elements. The alkali standards (a) employed a dilution interval of 3.16-fold ($\sqrt{10}$) (Mitchell, 1948).

In the general element standards (b) a dilution interval of 1.78-fold ($\sqrt[4]{10}$) was adopted, giving element standard concentrations of 0, 1, 1.8, 3.2, 5.6, 10, 18, etc. ... to 10,000 ppm. This simplified the visual estimation of unknown samples by interpolation between the standards.

Densitometer readings for the quantitative measurement of line intensities were confined to preliminary test work. The low speed of instrumental reading prevents its routine use in semi-quantitative analysis, for prospecting purposes, where visual methods have the advantages of (a) speed, (b) sufficient accuracy for most purposes and (c) enabling lines still to be read at the lowest limit of sensitivity. Where densitometer readings were necessary an A.R.L. instrument was used, with evaluation of the stepped-spectrum readings by the method described in Chapter 4.

Applications.

The slightly modified conventional carbon arc techniques, A and B, were used in the geochemical investigations for the appropriate elements (Table 1), and more generally in routine applications not included in this Thesis. The modified "buffer" techniques C_1 and C_2 were introduced at an early stage in the work, following investigations of the spectrographic matrix effect which are described below. Techniques C_1 & C_2 (in Chapter 9) were used throughout for the common minor elements, firstly to ensure analytical consistency,

and secondly to give an extended trial to these techniques.

Technique C₁ introduces a 50% Li₂CO₃-carbon mixture to replace pure carbon in the cathode-layer technique described by Mitchell (1948). Advantages are (a) the buffer method was shown to reduce the bias effect due to varying bulk composition in test samples, while retaining adequate reproducibility and sensitivity; (b) the buffer procedure for the minor elements forms a simple combination with that for major element analysis (Chapter 3).

Associated disadvantages are that (i) the buffer element Li cannot, of course, be determined, (ii) the cathode-layer burns are inherently rather slow, and (iii) have limited sensitivity for the volatile elements. Method C2 (Table 1) was introduced to improve sensitivity for some elements, using a wide crater and a one-minute arc burn.

Performance.

(a) The analytical reliabilities of the established and modified methods A, B, C1 and C2, were checked by replicate analysis to determine the relative deviation, and by the "statistical series" method of Craven (1954) which provides an exacting practical test of the same nature.

Results for the latter performance test (Table 2) indicate that the relative deviation for a single analysis, in terms of two standard deviations, varies from ± 18 to 80% with a mean of the order of $\pm 50\%$. The results are in line

Table 2. Analytical Reproducibility.*
[Visual reading methods]

Method [ref. Table 1]	Element	No. of *statistical tests.	Relative Deviation (%, 2σ)
A	Rb	1	37.2
	Li	1	57.4
	Ba	1	18.3
	Sr	1	31.7
B	Be	2	41.3
C ₁	Cu	9	38.0
	Sn	6	46.5
	Pb	4	64.7
	Be	3	37.3
	Ni	2	47.0
	Cr	1	57.3
	Co	1	70.1
C ₂	Cu	1	27.9
	Sn	1	82.8
	Pb	1	72.7
	Ni	1	35.1

*Determined by the statistical test of Craven (1954):
each test involving 12 sample determinations.

with reproducibilities generally achieved by semi-quantitative arc methods for silicates. This degree of scatter is adequate for most soil geochemical investigations, considering (a) inherent sampling variables and (b) that variations in the trace element content of several fold are usually sought. Nevertheless the possible analytical variations are of the order of a factor of two, and this limits the geochemical significance which can be extracted from the results. Precision was increased by the usual expedient of duplicate analyses in most of the small scale research investigations in this Thesis.

(b) Productivity. Daily productivity for two operators, determining a single element by the slowest burn technique, C_1 , could be maintained at 42 samples. In multi-element determinations productivity is naturally reduced, and the time spent in reading soon determined the output of results: about 1 min. per element determination should be allowed for careful visual interpolation.

Analytical Test Work, with Special
Reference to the Matrix Effect.*

*The enhancement or suppression of a minor element line, and hence the error in estimating concentrations, due to changes in the bulk composition and/or physical form of the sample materials.

The matrix effect is widely recognised as a serious inherent defect in spectrographic analysis, not least in arc methods. The limited number of systematic investigations into this effect in geochemical materials, (Scott, 1945; Makite and Lappi, 1958), and its practical importance in certain geochemical applications - such as regional reconnaissance where element contents are compared between samples from widely-separated areas - directed attention to this topic.

The matrix effect was mainly studied in synthetic test materials whose chemical composition could be easily controlled. A limited investigation on the effect of changes in the physical constitution of test samples was also carried out.

1. Matrix Effect Using Established Arc Procedures, in Synthetic Matrices Including Extreme Types.

The procedures employed are those described by Mitchell (1948) and Ahrens (1954), based upon cathode-layer and anode excitation respectively, of mixtures of sample material with an equal weight of carbon powder: the latter contained a fixed addition of Pd* which was later examined as an internal standard element (Ahrens, 1954). Electrodes of types A and C₁ were used (Table 1).

The matrix effect was assessed by preparing analytical curves from dilutions of a common mixture of minor element

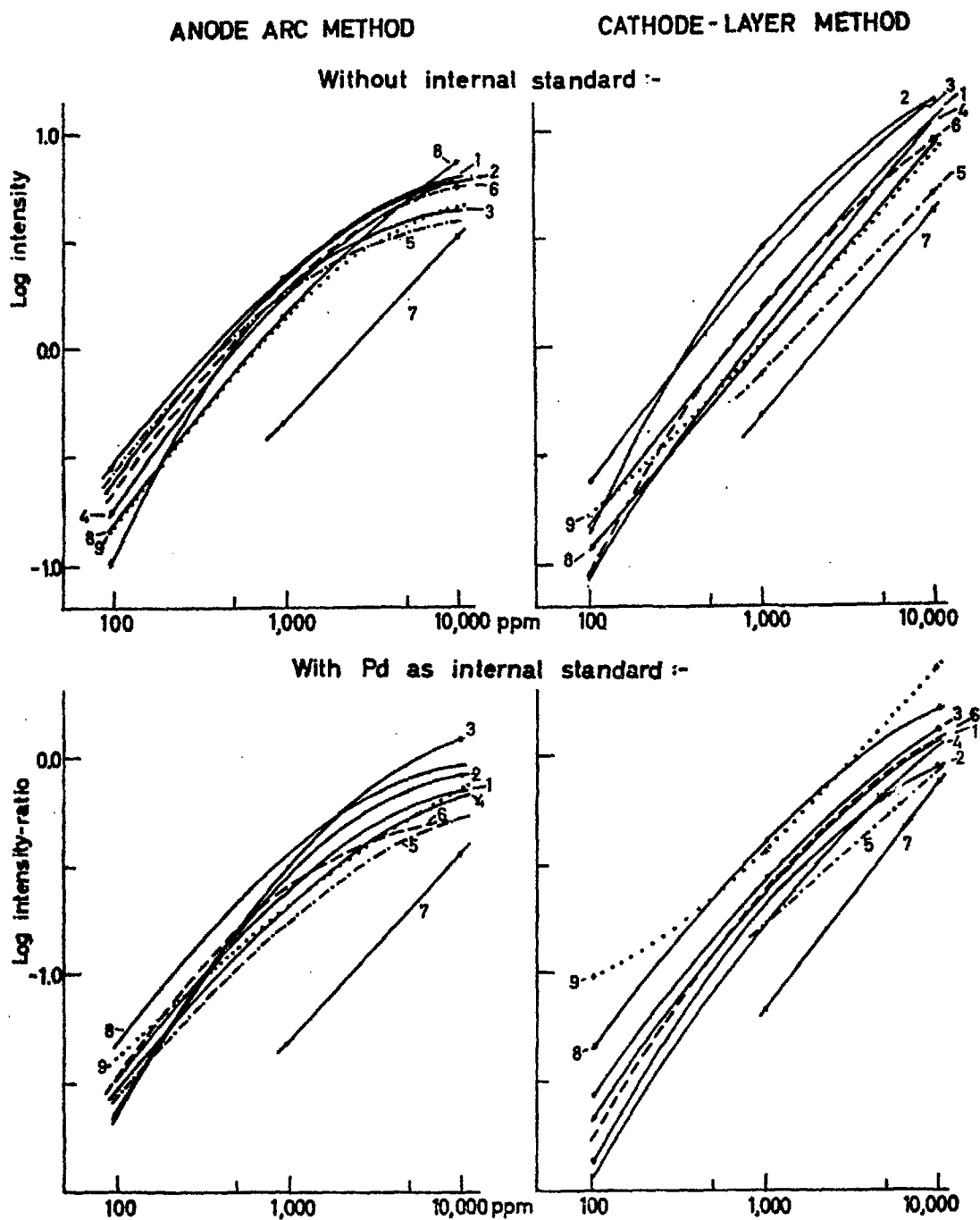
*Pd was present as tetramminepalladous nitrate, 0.1% mixture in carbon powder (R. Taylor, pers. comm.)

oxides into different "matrices" prepared from Specpure chemical materials. The dilutions contained nominally 10, 100, 1,000 and 10,000 ppm of each minor element. Since the same minor element content is present in each matrix series, a single analytical curve would result for a given element in the absence of any matrix effect; the displacement between the curves measures the extent of the matrix effect (Scott, 1945; Makite and Lappi, 1958).

The six minor elements, Cu, Pb, Sn, Ni, Cr and Mn were chosen for study since each is an important element in soil geochemical investigations, and they include a range of spectrographic behaviour types. The nine synthetic matrices investigated comprise five extreme components, namely, SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2CO_3 and Li_2CO_3 , and matrices simulating the composition of a granite, a diabase, an intermediate igneous rock, and a water evaporate (Appendix A₂).

The results of densitometer measurements of the line intensities, corrected for background, are presented in the analytical curves, Figures 1-6. Each Figure shows the curves for (a) anode arc- and (b) cathode-layer excitation, in each case both with and without Pd as the internal standard. Figure 7 shows the curve separations measured at a fixed arbitrary intensity level (unit relative intensity); this permits comparisons between relative element sensitivities in the different matrices, and in anode or cathode arc techniques.

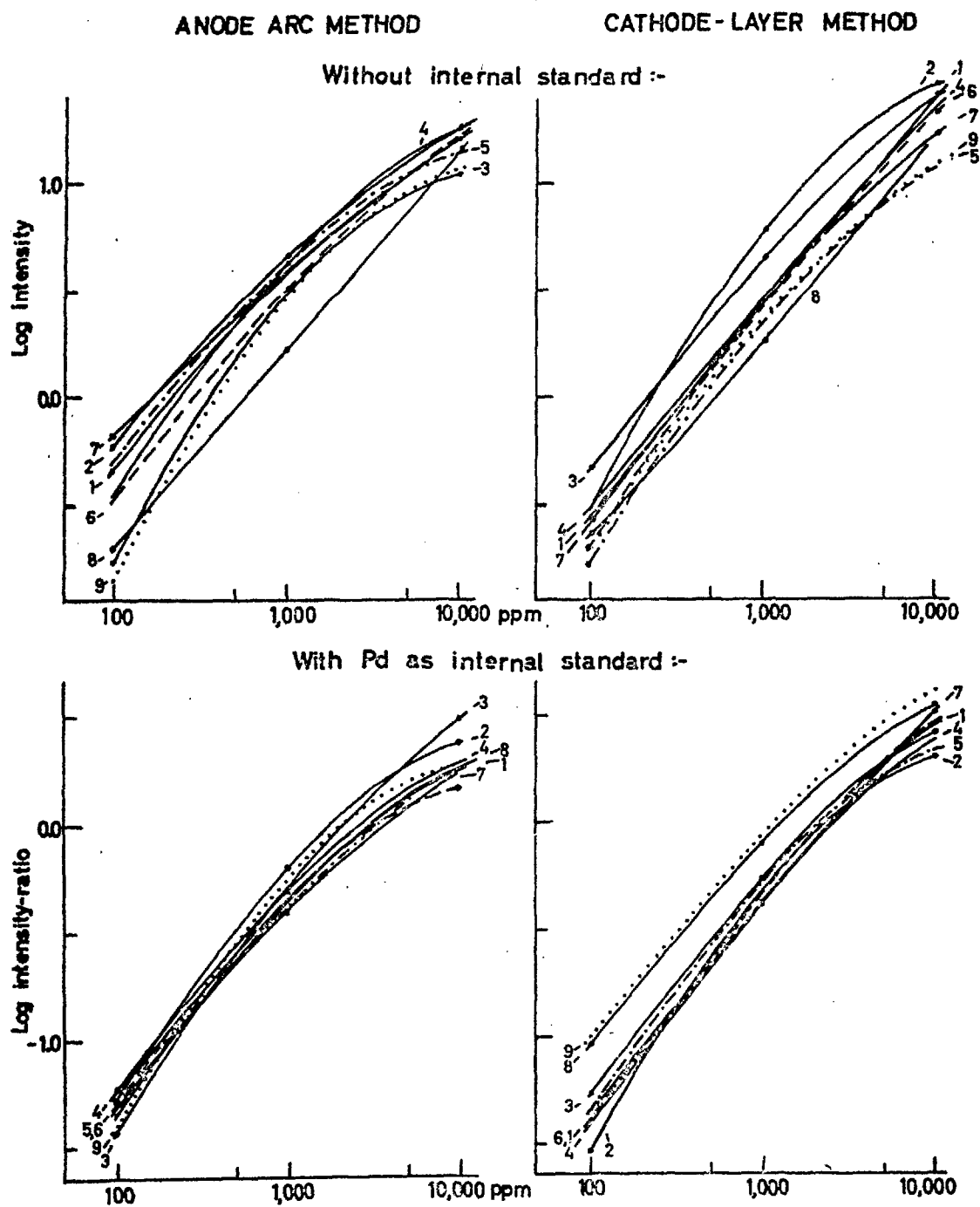
Fig.1. MATRIX EFFECT Analytical curves for Pb



MATRIX TYPES :-

- | | | |
|------------|----------------------------|-----------------------------|
| 1. Granite | 4. Average rock | 7. Fe_2O_3 |
| 2. Diabase | 5. SiO_2 | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 | 9. Li_2CO_3 |

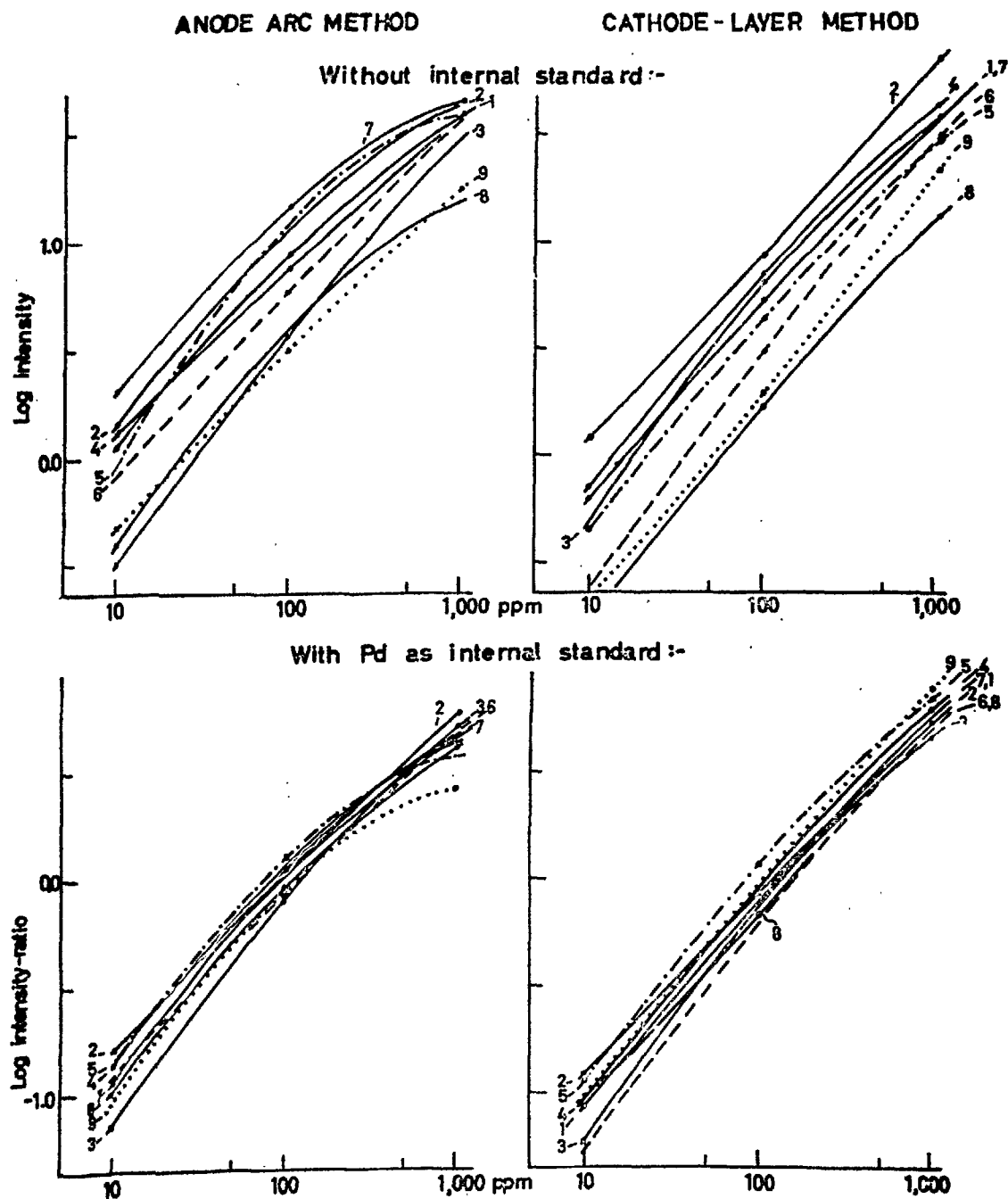
Fig. 2. MATRIX EFFECT Analytical curves for Sn



MATRIX TYPES :-

- | | | |
|------------|--------------------------------|-----------------------------------|
| 1. Granite | 4. Average rock | 7. Fe_2O_3 |
| 2. Diabase | 5. SiO_2 ——— | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 ——— | 9. Li_2CO_3 |

Fig.3. MATRIX EFFECT Analytical curves for Cu

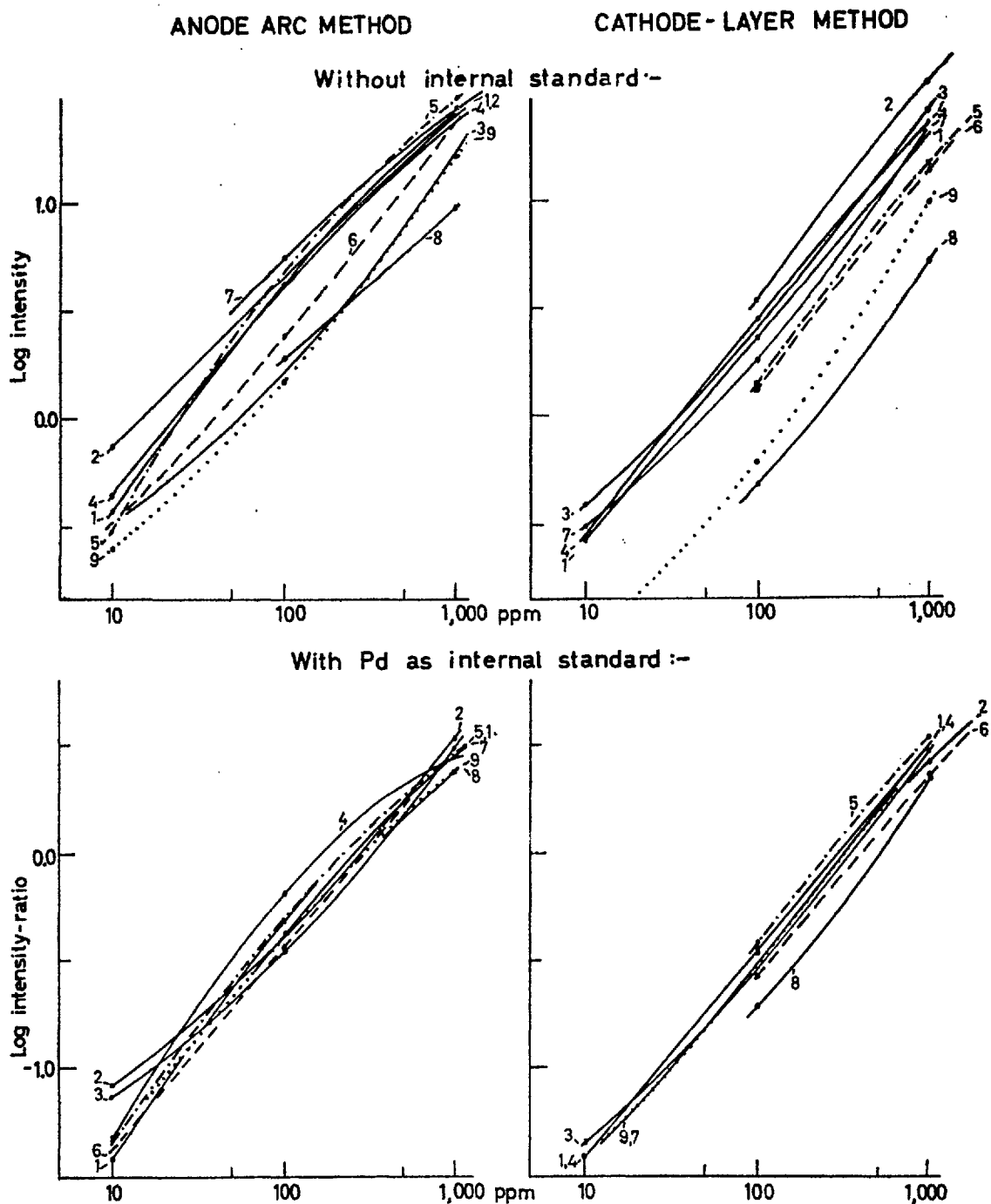


MATRIX TYPES:-

- | | | |
|------------|--------------------------------|-----------------------------------|
| 1. Granite | 4. Average rock | 7. Fe_2O_3 |
| 2. Diabase | 5. SiO_2 ——— | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 ——— | 9. Li_2CO_3 ····· |

Fig.4.

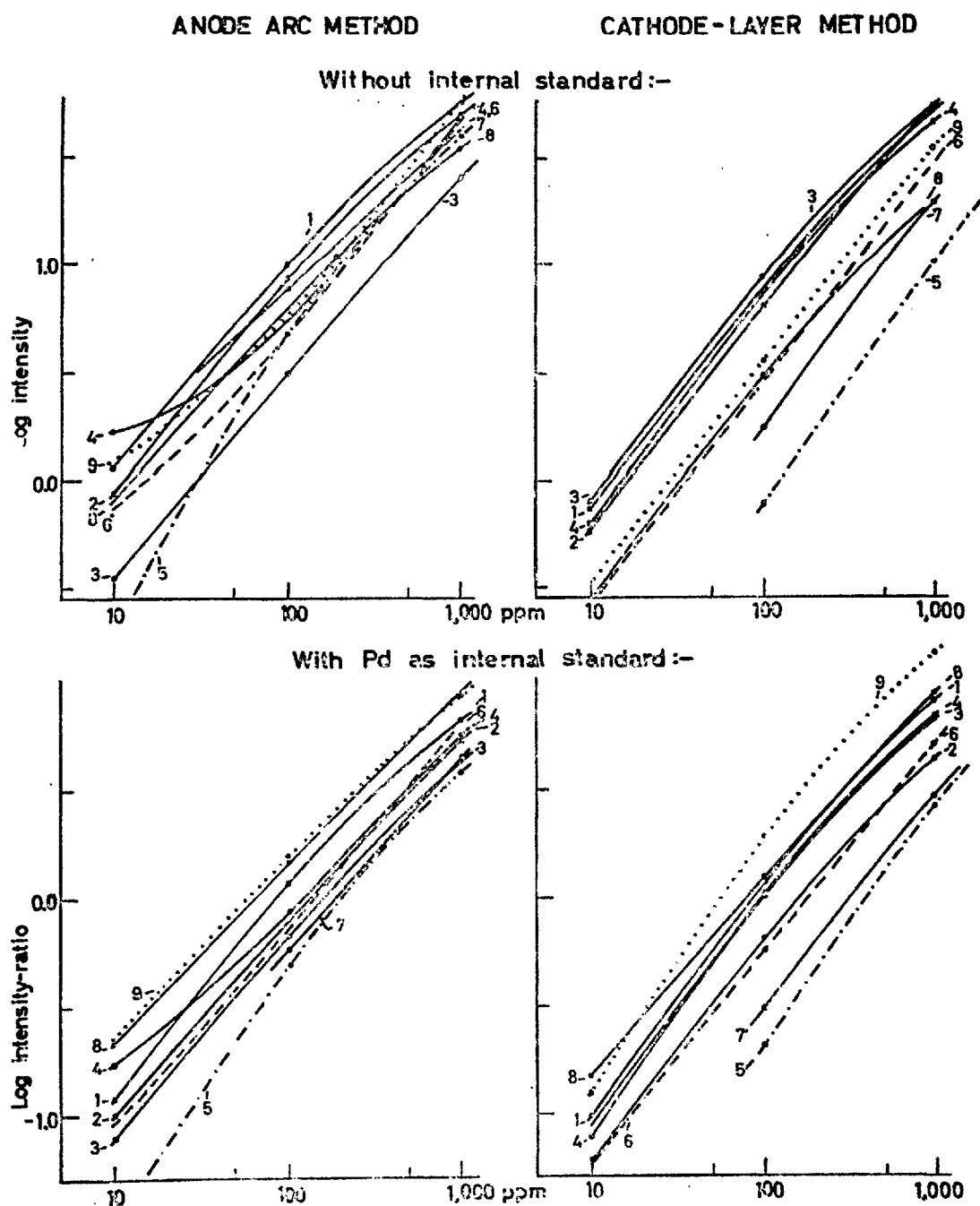
MATRIX EFFECT Analytical curves for Ni



MATRIX TYPES :-

- | | | |
|------------|--------------------------------|---------------------------------|
| 1. Granite | 4. Average rock | 7. Fe_2O_3 |
| 2. Diabase | 5. SiO_2 ——— | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 ——— | 9. Li_2CO_3 ——— |

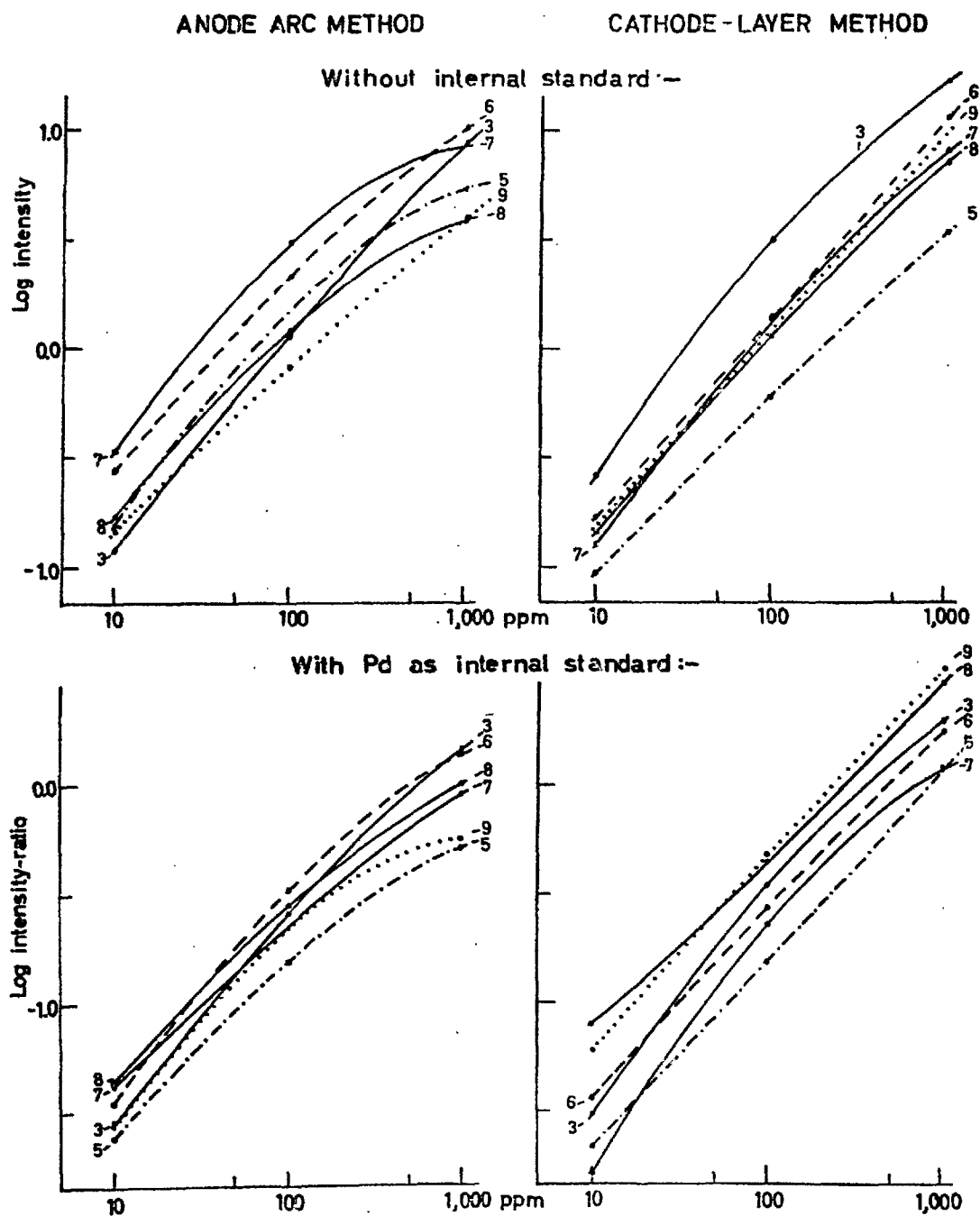
Fig. 5. MATRIX EFFECT. Analytical curves for Cr



MATRIX TYPES:-

- | | | |
|------------|----------------------------|-----------------------------|
| 1. Granite | 4. Average rock | 7. Fe_2O_3 |
| 2. Diabase | 5. SiO_2 | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 | 9. Li_2CO_3 |

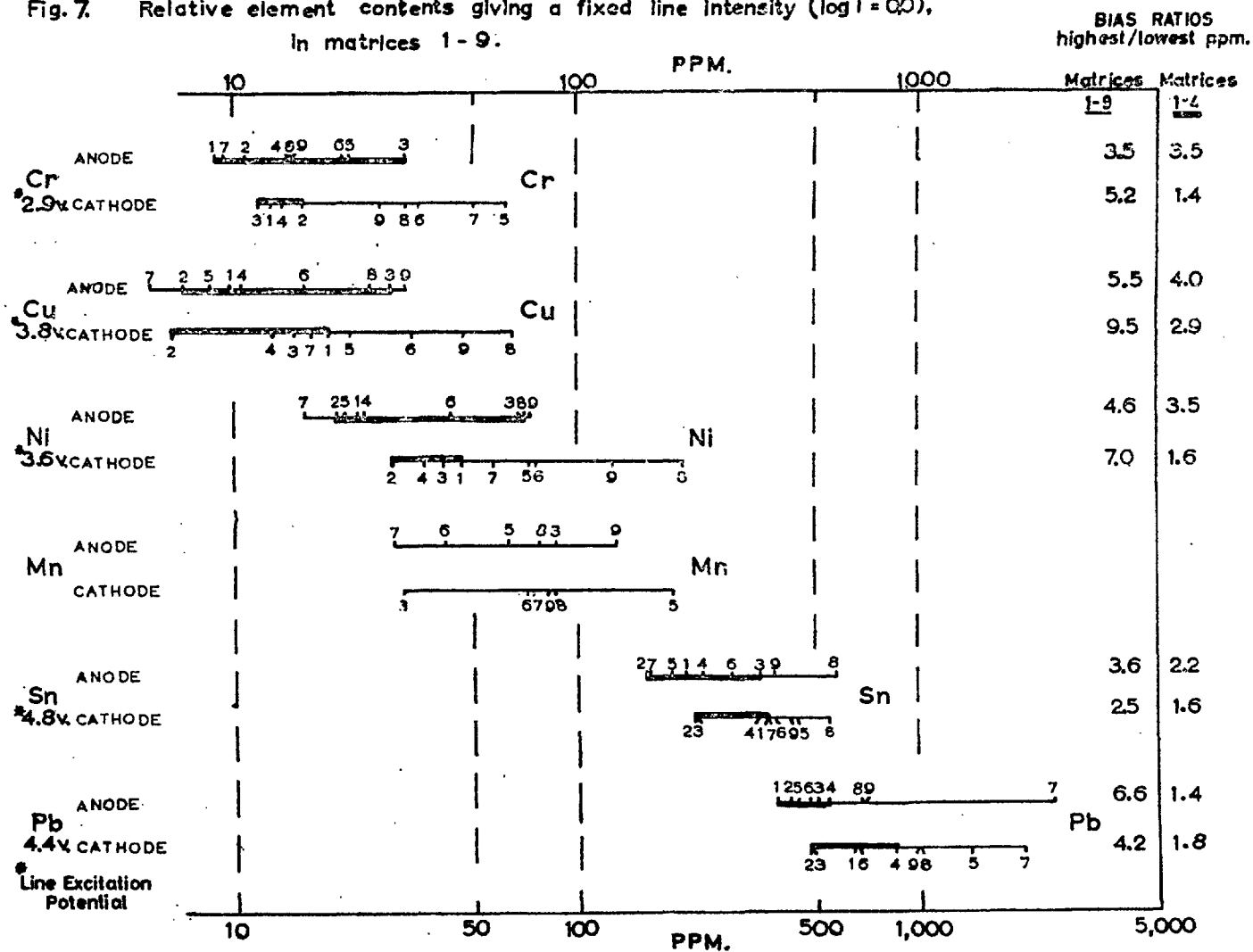
Fig. 6. MATRIX EFFECT Analytical curves for Mn



MATRIX TYPES :-

- | | | |
|--------------|--------------------------------|-----------------------------------|
| (1. Granite) | (4. Average rock) | 7. Fe_2O_3 |
| (2. Diabase) | 5. SiO_2 ——— | 8. Na_2CO_3 |
| 3. Water | 6. Al_2O_3 ——— | 9. Li_2CO_3 |

Fig. 7. Relative element contents giving a fixed line intensity ($\log I = 00$),
in matrices 1-9.



In discussing the results, (Figs. 1-7), indications of matrix effects are considered as not significant below a bias of some 20-40% (or a 1.3-fold factor), since this is the order of reproducibility for single arc burns using densitometer measurements (Table 3).

Matrix Effect on the Intensities of the
Minor Element Lines.

The bias effects encountered in many matrices considerably exceed the normal limits of reproducibility (Fig. 7).

(a) The bias ratios over all matrices for each element examined, vary from 3.5-6.6 fold by the anode arc method, and 2.5-9.5 fold by the cathode-layer technique.

(b) A reduced matrix effect is found on restricting the matrices to the simulated natural types. These comprise three "igneous rocks" and a calcareous "water evaporate"; it is noteworthy that the latter matrix (No. 3) does not always occur at the extreme bias position (Fig. 7). The moderate overall bias within the "natural" matrices is thought to be due to the relatively high content of calc-alkali oxides ($\geq 10\%$ total), which is common to each base (Appendix A₂).

The calc-alkali elements are efficient spectroscopic buffers (Ahrens, 1950) which means that even in small amounts they tend to control the arc environment and counter the effects of large variations in the contents of SiO_2 , Al_2O_3 and Fe_2O_3 .

Table 3.

Reproducibilities of (a) anode, (b) cathode-layer
carbon arc procedures (densitometer reading method).

Sample	No. of arcs.	Standard deviation, 2σ . Log Intensity units.							
		(a)				(b)			
		Cu	Cr	Ni	Co	Cu	Cr	Ni	Co
Soil 1	6	.164	.258	.144	.182	.056	.094	.088	.106
Soil 2	6	.126	.158	.094	.122	.078	.042	.058	.074
Synthetic silicate	9	-	-	-	-	.102	.146	.136	.122
Mean deviation (log I)		.145	.208	.119	.152	.079	.094	.091	.101
Relative deviation (2σ) (% of content)		± 40	61	32	42	± 20	24	23	26
		(Mean $\pm 44\%$)				(Mean $\pm 23\%$)			

(c) Pure SiO_2 and Fe_2O_3 matrices (Nos. 5 and 7) show some extreme bias trends. This justified the examination of simulated ferruginous and siliceous soils in subsequent tests (below).

(d) The different minor elements show highly individual responses to the matrix effect; both the magnitude of the matrix "spread", and the sequence of matrix sensitivities, differ from element to element (Fig. 7; of Makitie and Lappi, 1958).

(e) The conventional "depressant" effect of alkaline metal matrices (Nos. 8 and 9) is observed by both arc techniques, for Cu, Ni and Sn, but not for Cr and Pb. This shows (i) the inadvisability of generalisations and (ii) little correlation between depressant effect and the excitation potential of the lines (Fig. 7).

(f) Few regularities were observed between the excitation potential of the element line (Fig. 7), and the ionisation potential of the main matrix metal (Ahrens, 1950, p. 20), in attempting to explain the response of individual elements to different matrices. Similarly Scott (1945) found that observed changes in minor element intensities in various pure matrices could not be explained by the addition of easily-ionized atoms and consequent variations in the arc temperature. Brode and Timma (1949) found some regular variation with excitation potential and boiling point, in tests restricted

to mixtures of one test element and one matrix element in equal proportions. For mixtures of only moderate complexity, the matrix effect must be determined by experimentation, and can rarely be systematically explained: a conclusion supported by the present data.

Addendum: Effect of sample matrix on spectrum background intensity.

Table 4. Spectrum background intensity at different wavelengths, showing effect of matrix composition.

Matrix	Relative intensity of background* (Mean for three spectra)					
	Cathode-layer method			Anode arc method		
	2833 Å.	3274 Å.	3421 Å.	2833 Å.	3274 Å.	3421 Å.
1. Granite	4.2	4.2	7.1	3.0	3.2	4.9
2. Diabase	7.2	7.6	10.2	3.3	4.8	6.2
3. Water evaporate	4.6	8.3	12.6	1.8	3.3	4.3
4. Intermediate rock	4.8	6.5	7.9	3.5	4.4	5.4
5. SiO ₂	3.5	5.2	7.9	2.6	3.0	3.2
6. Al ₂ O ₃	2.3	3.9	5.4	1.3	2.6	3.2
7. Fe ₂ O ₃	10.0	7.9	12.8	7.6	5.2	10.0
8. Na ₂ CO ₃	0.95	2.0	2.6	.74	1.9	3.3
9. Li ₂ CO ₃	1.0 ^o	2.7	3.7	1.3	4.3	7.4

* taking that for Li₂CO₃ at 2833 Å., as

The data show that background at a given wavelength may vary up to 10-fold in different matrices (Table 4). The sequence of background intensity associated with each matrix is: Fe₂O₃ > water evaporate = Diabase = Intermediate rock = granite > SiO₂ > Al₂O₃ > Li₂CO₃ > Na₂CO₃.

While obviously less important than the variation of the element line intensity, the variation of background blackening with matrix composition, and especially the presence of a dense background, is an undesirable source of error in visual semiquantitative analysis. The relatively low spectrum background associated with the alkali carbonate matrices is a significant minor asset for employing them as spectrographic buffers.

Matrix Effect on the Line Intensity Ratios
to Pd as Internal Standard.

(a) The effect on the matrix spread of employing the ratio to Pd (Figs. 1-6, lower curves) compared to the curves without internal standardisation (Figs. 1-6, upper curves) is similar in both anode and cathode techniques. The five minor elements vary considerably in their behaviour.

(b) The use of Pd as internal standard gives a markedly reduced matrix bias for the elements Cu and Ni; moderate improvement for Sn, and less so for Mn. For Cr and Pb there is no improvement; for these elements the matrix effect seems more pronounced using Pd as internal standard than without such standardisation.

The effect of the internal standard method in compensating for matrix bias is rather different - even more exacting - than the question of compensating for between-burn variations. Nevertheless, the very limited success of Pd as a general

internal standard element is relevant to some observations by Oertel (1955). He stressed, in studying the trace element analysis of soil and plant ash, that effective internal standardisation depends upon close similarity in arc excitation properties between the analysis and standard element lines. An ideal line pair may not always be available, and in such cases improved reproducibility could more easily be achieved by replicates, without internal standardisation. Moreover, the internal standard method is time consuming.

The above observations led to the rejection of the internal standard method, and attention was turned to the simpler alternative of adding a buffer material to all samples as a means of swamping variations in matrix composition. In addition, a range of simulated natural soil types was examined. The cathode-layer method was employed in the required detailed investigation, mainly because in comparative tests, analytical reproducibility was rather better than in large-crater anode method. The corresponding mean relative deviations were 23% and 44% (Table 3).

II Matrix Effect in Synthetic Matrices Simulating Natural Soils.

The cathode-layer procedure was employed with (a) carbon mixtures of the samples and (b) various buffer admixtures.

The eight matrices investigated had the bulk composition shown in Table 5. To each matrix, a common minor element mixture was added, giving a known content of approximately 300 ppm. each of the elements V, Cr, Co, Ni, Cu, Mo, Ag, Sr and Pb. These eight mixtures were used to examine the matrix effect, by (a) arcing each in duplicate and (b) reading the "apparent ppm." content in each matrix, firstly visually against a single set of standards, and secondly confirming the results by densitometer readings against conventional "single-point" analytical curves (Ahrens 1954). Arbitrary reference standards in the synthetic "intermediate silicate rock" base were employed.

The divergence between the apparent ppm readings was the measure of the matrix effect, employing conventional carbon admixture of the test samples (Table 6, upper; Fig. 8).

The reproducibility for a single burn was established by densitometer readings from nine replicates of a synthetic standard mixture: the relative deviation averages $\pm 32\%$ for the different minor elements (Table p. 34).

Table 5. Synthetic Matrix Compositions

No.	Type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	% CaO (as CaCO ₃)	MgO	K ₂ O (as K ₂ CO ₃)	Na ₂ O (as Na ₂ CO ₃)	TiO ₂	MnO (as Mn ₃ O ₄)
10	Siliceous soil	94.6	2.7	0.9	0.44	0.07	0.07	0.11	0.73	0.01
11	Ferruginous laterite	8.9	16.5	71.2	0.49	0.31	0.06	0.06	0.82	1.18
12	Aluminous laterite	25.0	49.1	21.4	0.19	0.16	0.29	0.06	3.1	0.32
13	Average laterite	17.0	32.8	46.3	0.34	0.24	0.18	0.06	2.0	0.75
14	Calcareous soil	58.8	9.7	3.2	10.8	3.5	2.0	1.8	0.55	0.06
5	High alkalis soil	61.8	15.8	10.2	0.32	0.46	4.5	2.0	0.81	0.34
3	Water evaporate	13.4	1.1	1.1	33.9	4.9 (as MgSO ₄)	-	5.5 (as NaCl)	-	-
4	Intermediate rock	54.4	13.7	7.5	7.1	4.1	2.1	2.2	0.74	0.11

The following concentrations of minor elements were incorporated in each matrix mixture:-

Element	Pb	Sn	Mo	V	Cu	Ag	Ni	Co	Cr
ppm	317	316	282	314	314	317	313	270	310

Table 6. Matrix effect: (a) without and (b) with carbon - Li_2CO_3 buffer

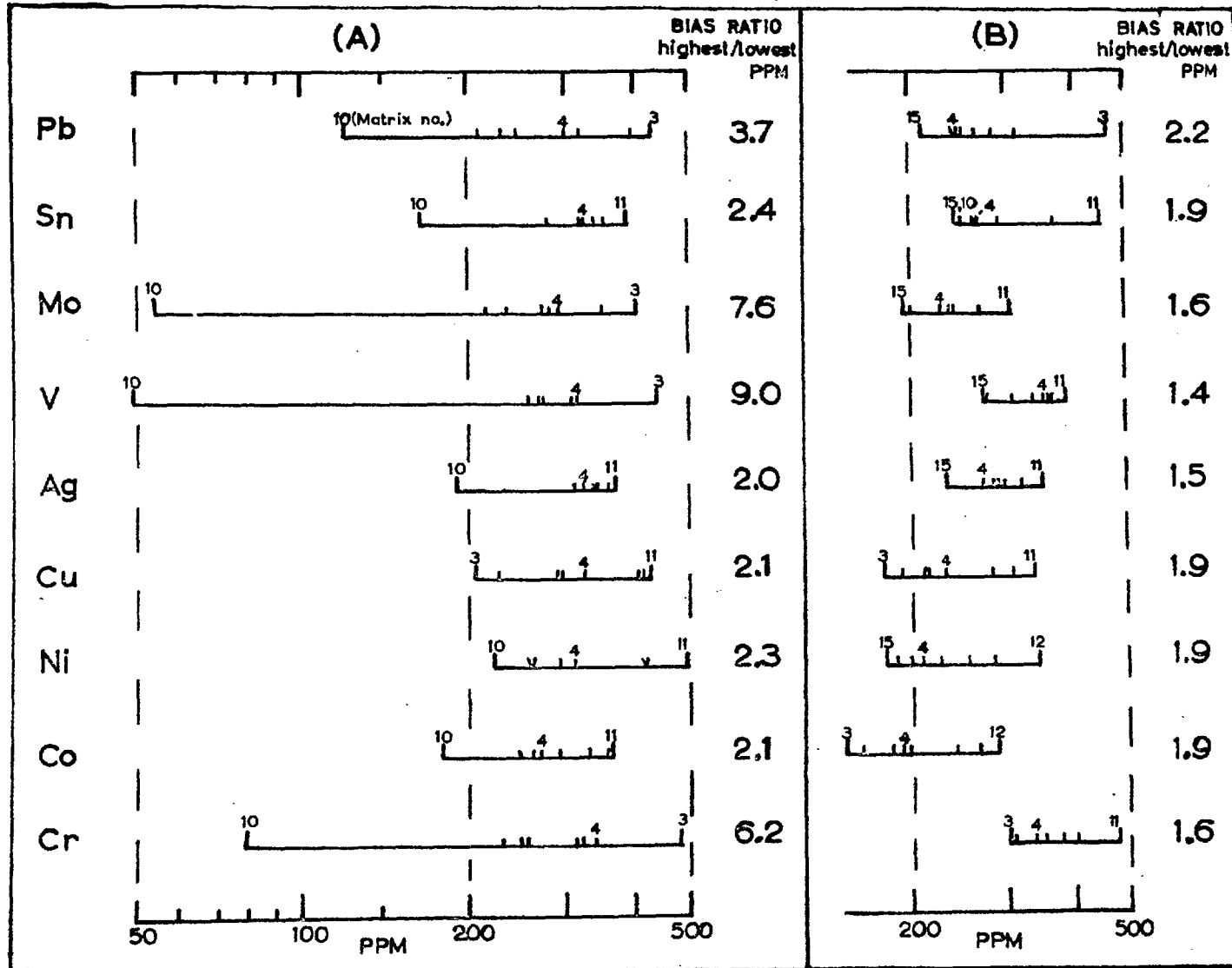
Sample Mixture	Element	Apparent ppm readings mean of duplicates								Actual ppm content
		MATRIX TYPE AND NUMBER								
		3 Water evaporate	4 Average rock	10 Siliceous soil	11 Ferruginous laterite	12 Aluminous laterite	13 Average laterite	14 Calcareous soil	15 High alkali soil	
(a)	Pb	420	294	115	208	240	227	386	323	317
50% sample	Sn	347	317	157	378	330	330	313	274	316
50% carbon	Mo	400	289	53	346	212	269	277	232	282
	V	440	310	49 ^b	255	270	266	305	310	314
	Ag	302	316	184	360	318	347	353	331	317
	Cu	203	320	223	425	403	410	290	295	314
	Ni	254	308	220	495 ^a	405	407	287	252	313
	Co	256	274	172	354	320	347	282	240	270
	Cr	480	325	77	245	250	228	318	310	310

Extreme bias ratio a:b = 10-fold

(b)	Pb	446	234	238	275	259	241	303	204	317
50% sample	Sn	258	260	238	438	285	358	243	234	316
25% carbon	Mo	290	228	235	307	200	247	238	194	282
25% Li_2CO_3	V	353	350	308	388	278	357	338	273	314
	Ag	312	265	280	341	273	280	288	228	317
	Cu	177	238	192	333	280	306	210	213	314
	Ni	187	207	197	257	340	284	225	178	313
	Co	150 ^b	190	196	275	285	238	182	162	270
	Cr	300	335	307	472 ^a	373	397	350	308	310

Extreme bias ratio a:b = 10-fold.

Fig.8. Matrix Effect (A)without and (B)with carbon-Li₂CO₃ buffer admixture.



Element Wavelength A.	Pb	Sn	Mo	V	Ag	Cu	Ni	Co	Cr
Single-burn reproducibil- ity (2σ)	32%	27%	30%	28%	34%	27%	38%	34%	40%

Observed results.

(a) The overall bias between the highest and the lowest matrix readings for all the elements is no less than 10-fold. This mainly reflects the extreme depression in the "siliceous soil" matrix of V, like Mo. These elements are more strongly depressed than Cr, which itself shows depression, as indicated in the preceding test on pure SiO_2 (Fig. 7).

(b) While the siliceous soil matrix is mainly depressant, lesser depression and enhancements affect some elements in the three "lateritic" matrices. The remaining "intermediate rock", "calcareous soil", "alkali soil" and "water evaporate" matrices give only moderate bias discrepancies. This confirms the previous indication that a significant proportion of calc-alkali elements, in almost any amount, helps to provide a common matrix environment. Moreover, the latter matrices have element sensitivities among the highest for all the matrices.

These observations suggested that the addition to all test samples of a fixed proportion of a suitable calc-alkali material might (a) serve as an effective spectrographic buffer and (b) enhance the low sensitivity for elements in siliceous

matrices in particular. This was investigated by replacing half the carbon used in the conventional sample/carbon admixture, with each of ten buffer substances. The buffers tested were (a) carbon alone, (b) Na_2CO_3 , (c) NaCl , (d) Na_2SO_4 , (e) NaHSO_4 , (f) KCl , (g) Li_2CO_3 , (h) CaCO_3 , (i) CaSO_4 , (j) MgSO_4 and (k) GeO_2 . In every case the operating conditions were those detailed for method C1, Table 1.

Initially, visual readings were made against an arbitrary set of standard spectra in the intermediate igneous rock base. These preliminary readings showed that each buffer in general altered the pattern of matrix effects encountered in the carbon-mixing method. The "apparent ppm" values for a given element in each matrix and buffer combination were then plotted on a logarithmic scale (cf Fig. 7). The ensuing "matrix spread" of the readings for a given element could then be measured. By treating all the elements in the same way, and measuring the overall spread for their superimposed plots, the overall matrix spread for a particular buffer was established. The results are shown in Table 7.

Table 7.

Buffer	Extreme "matrix spread" over all elements and matrices (visual readings).	
	mms, on log. scale	Bias factor Highest/lowest ppm.
Li_2CO_3	30	2.9
NaCl	43	3.6
CaCO_3	61	5.0
KCl	82	)))) 7.4
CaSO_4	83	
Na_2CO_3	84	
1 + 1C	103	
Na_2SO_4	127	15.8
GeO_2	133	)))) 18.7
NaHSO_4	136	
MgSO_4	137	

It should be noted that the conventional carbon-mixing technique with its overall matrix spread of 10-fold occurs half-way down the table. Four buffers actually give impaired matrix effects (some of these gave physically poor arc burns, despite many re-arcings), whilst a reduction in matrix bias is given by six of the calc-alkali buffers. Lithium carbonate, sodium chloride and calcium carbonate are clearly the most effective buffer materials on this overall basis. Lithium

carbonate was adopted as the buffer for routine semi-quantitative analysis, being marginally superior to sodium chloride in buffer effect, and with the advantage of being suitable as the buffer for major element analysis (Chap. 3). This permits a common stock of buffer mixture, and a simple two-stage sample dilution to be used for the comprehensive analysis of both minor and major elements.

Where lithium is required to be analysed as a minor element, sodium chloride or calcium carbonate (Oda et al., 1958) could be used; or potassium chloride, calcium sulphate (Harvey and Murray 1958) or sodium carbonate (Tongerlen; in Ahrens 1950, p. 155) with rather less advantage over carbon mixing only.

To confirm the results given by visual readings using the Li_2CO_3 -carbon buffer procedure, densitometer readings were made on duplicate spectra of the test mixtures. The results were expressed as "apparent ppm" by using the reference curves employed for investigating the carbon-mixing technique. The results showing the matrix effect by the two techniques (Table 6) can thus be directly compared. Figure 8 presents the same data in a graphical form.

The data (Fig. 8; Table 6) confirm that Li_2CO_3 is moderately effective in reducing the bias due to the matrix effect. For the Li_2CO_3 buffer procedure, the maximum apparent content of any element in any matrix is three times

that of the minimum apparent content of any element. This contrasts with the corresponding 10-fold factor encountered in the conventional carbon-mixing method. Although the "residual" matrix effect represents an undesirable bias, its magnitude is not much greater than possible reproducibility errors for visual semi-quantitative analysis (c.factor of 2.0) Moreover, the individual deviation from some central references standard (e.g. the intermediate rock base No. 4) is naturally less than the extreme bias factor. It may be noted that the former base occupies a fairly central position within the matrix bias charts (Fig. 8b), and is on that ground a suitable base for reference standards.

The reduced matrix effect in the Li_2CO_3 buffer method is due more than anything else to a general increase in trace element sensitivity in the siliceous soil matrix.

Conclusions.

(i) The Li_2CO_3 buffer method offers a significant advantage in reducing the magnitude of bias due to changes in chemical composition of the test samples, and actually enhances the element sensitivity otherwise obtained in the simulated silica-rich samples.

(ii) In common with other buffer methods for powdered samples, the method requires no lengthening of the analytical technique; a buffer mixture consisting of 50% Li_2CO_3 , 50% carbon is substituted for carbon in preparing the sample mixtures.

(iii) The analytical reproducibility found in routine practice, using visual readings (Table 2) is similar to that previously obtained in tests with the conventional carbon-mixing cathode-layer procedure.

Comparison with Other Studies of the Matrix Effect.

Makitie and Lappi (1958) made an intensive investigation, using a simple anode arc technique, mainly on natural soil and plant ash bases but also on some pure matrices. The data were mainly confined to the intensity ratios of each of ten common minor elements, to specific internal standard lines, namely, Ag for Cu, Pb, Sn; Pd for Co, Ni, V, Mo, Cr; Sr for Mn, and Cd for Zn. The analytical curves showed a serious bias effect for many elements, and although a quantitative comparison with the present results is not possible because of differences in technique and evaluation, the following similarities may be noted:-

i. Pb/Ag, V/Pd, Mo/Pd and Sn/Ag are particularly subject to matrix effect, with bias factors of the order of five-fold, rising to ten-fold in the case of Pb/Ag.

ii. Cr/Pd, Zn/Cd and Mn/Sr show ~~lower~~ but still significant errors.

iii. Cu/Ag, Co/Pd and Ni/Pd show little matrix effect.

In a separate study on simple matrices, of the intensities of the elements alone as distinct from intensity ratios, these

authors observed a strong depression of V in a matrix of silica compared with calcium oxide. Mo (which the present writer found similar to V in this respect) was not reported; the other elements, namely, Pb, Cu, Ag and Co, were less affected.

It is noteworthy that in matrices consisting only of SiO_2 and CaO in varying proportions, these authors observed that the intensities of the minor elements changed irregularly with matrix composition. Co for example, showed the same intensity in each extreme matrix component, but a marked enhancement otherwise, with a peak in the 1:1 material. Such inexplicable trends point to the importance of the experimental determination of the matrix effect in every problem. These authors note the success of certain buffers, especially CaCO_3 , in reducing the matrix effect, but recommend the method of grouping samples according to their compositional type, with appropriate sets of standard samples.

Scott (1945) found that the observed changes in intensities (and intensity ratios to iron) could be explained neither by the addition of easily ionized atoms nor by variation in the temperature of the source. In general, however, trace elements in the same periodic group are affected in the same manner. Thus Cu and Ag; Cr and Mo; Fe, Co and Ni; Zn and Cd behaved similarly towards silica and towards NaCl matrices, - Sn and Pb, on the other hand, did not

Again, elements which have generally similar physical properties, such as atomic weight, react in much the same manner, for example V and Cr; Mo and Zr; Fe, Co and Ni; Pb and Bi.

These general conclusions are very much in line with the trends revealed in the present matrix study.

The shift of analytical curves for Mo in granites, granodiorites and diorites, has been shown to depend on variations in the Ca and Mg contents (Vainshtein et al., 1956). Nedler (1955) in an investigation of errors in the spectrographic analysis of siliceous Pb ores, found that the intensity ratio of Pb/Bi was progressively enhanced by the additions of 10% Fe_2O_3 or 10% Na_2CO_3 to the sample. The effect could not entirely be accounted for by the lowering of the arc temperature, nor by changes in the degree of ionization: the remainder of the effect was attributed to a change in evaporation rate from the different mixtures.

III. Matrix Effect Due to the Physical Constitution of Samples.

The possibility of bias being introduced by differences in physical constitution between samples is recognised by spectrographic analysts, aside from the matrix effect due to chemical composition. Little systematic work has been published relevant to silicate materials, in contrast with the metallurgical field (Brode, 1945). Scattered investigations suggest, however, that significant bias effects can arise from purely physical differences between non-conducting samples. For example, Ricard et al (1955) observed an enhancement of the lines of Ti by igniting samples of clay at different temperatures; a similar effect occurred in pure TiO_2 , attributed to a slow transformation of its crystalline form. Evidence of this kind has led to the well-known recommendation that samples and the spectrographic standards should be closely similar to each other in both chemical and physical composition (Ahrens, 1950; 1954).

Experimental work.

A limited investigation of the "physical effect" was carried out, using the cathode-layer Li_2CO_3 buffer method (Technique C1, Table 1). The test involved measuring the line intensities of the minor elements Sn, Cu, Ni, and Cr, present in fixed amount in four types of mixtures; these were practically identical in chemical composition, but differed in the physical and chemical forms of (a) the minor elements

and (b) the major constituents.

A sample of the granite G-1 was employed as the "natural" matrix, and a "synthetic" counterpart, closely similar in chemical composition was prepared from a mixture of "Specpure" materials.

Composition of natural and synthetic granite

G-1 matrices.

	% oxide									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Total
Natural G-1 ^(a)	72.4	14.4	1.8	1.4	0.39	3.25	5.4	0.25	0.02	
Synthetic G-1 ^(b)	72.8	14.3	2.1	1.4	0.41	3.3	5.4	0.26	0.03	
(a) Analytical data after Ahrens (1954) and Mercy (1955). Sample ignited as per routine samples, 500-550°C for 2 hours. (b) Composition calculated from weighed additions of the pure components. The mixture sintered at 950-1,000°C for 2 hours.										

To each matrix, separate fixed additions were made of (a) a synthetic mixture of the "Specpure" compounds SnO₂, CuO, NiO, Cr₂O₃; and (b) separate additions of chemically analysed samples of cassiterite, malachite, oxidised Ni ore, and chromite.

A content of 316 ppm of each minor element was aimed for in each case, and dilutions were made in two stages to minimise errors. In the natural G-1 matrix, the existing element content was allowed for, using the values recommended

by Ahrens (1954, p. 27); Sn by Sandell (1957). It may be noted that these values, namely, 2 ppm Sn, 11 ppm Cu, 5 ppm Ni and 20 ppm Cr are small compared to the added amounts, so that the bulk of the minor element is in a known form in each test sample.

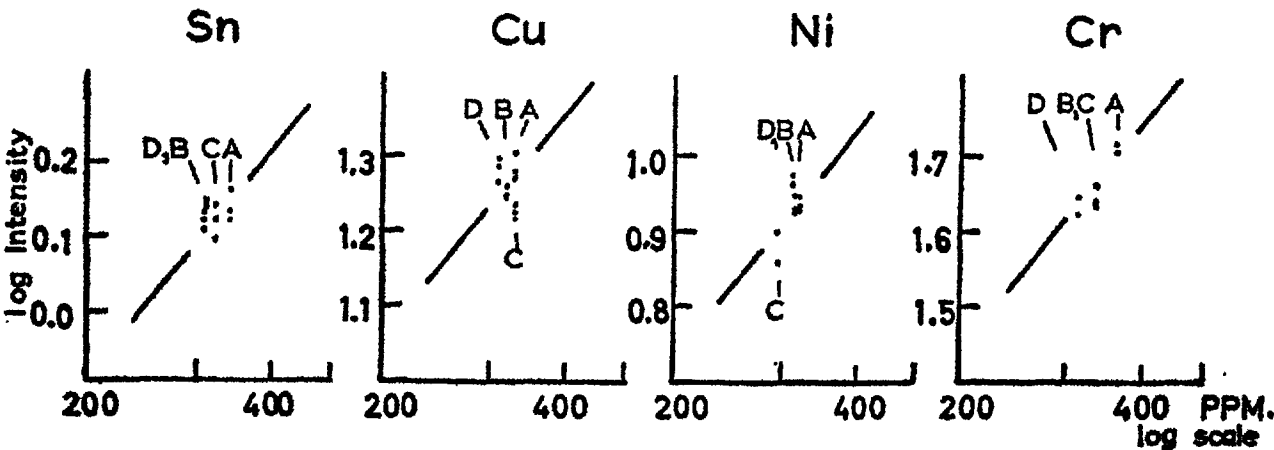
Table 8 shows the contents of the minor elements, together with the line intensities, corrected for background, from triplicate arcs for each test sample. The results plotted in the diagrams take into consideration the differences from exactly 516 ppm. in some test mixtures.

The data support a rather unexpected conclusion; namely, that no significant bias is imposed on the minor element intensities by the different constitutional forms either of (a) the minor elements themselves or (b) the bulk material of the samples. Quite close replicates were obtained in this investigation, the scatter being within $\pm 10\%$; so that even a bias of this low order due to the physical effect should be detectable, and its absence is noteworthy. An inference of practical importance is that in reference standards (of given chemical composition), both natural and synthetic materials should give the same line intensities and hence the same results in analysing unknowns.

While it would be inadvisable to generalise too far from the limited number of results, it may be noted that the test

TABLE 8. Element line intensities in mixtures of different physical form

Element Line A	A		B		C		D	
	Natural matrix + Natural minor elements		Natural matrix + Synthetic minor elements		Synthetic matrix + Natural minor elements		Synthetic matrix + Synthetic minor elements	
	Content ppm	Line † Intensity (log)	Content ppm	Line Intensity	Content ppm	Line Intensity	Content ppm	Line Intensity
Sr 2840	324 Sample A 971	.092 .120 .138	311 Sample A 1008	.102 .120 .130	344 Sample A 989	.120 .120 .160	312 Sample A 1006	.136 .136 .145
Cu 3274	333 Sample A 969	1.271 1.280 1.304	322 Sample A 1008	1.242 1.248 1.260	332 Sample A 987	1.216 1.221 1.232	312 Sample A 1006	1.264 1.285 1.295
Ni 3414	320 Sample A 973	.930 .935 .950	316 Sample A 1008	.923 .930 .950	294 Sample A 1004	- .860 .902	311 Sample A 1006	.967 .967 .978
Cr 4254	360 Sample A 967	1.702 1.715 1.715	334 Sample A 1008	1.635 1.635 1.660	334 Sample A 985	1.635 1.640 1.660	312 Sample A 1006	1.622 1.622 1.645

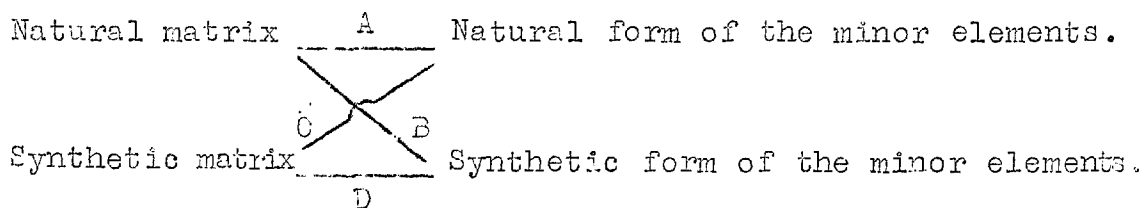


† Relative deviation ±10 %
on the same scales.

gives reasonable scope for detecting a 'physical' effect, if present:-

(i) The four selected minor elements, Sn, Cu, Ni and Cr, cover a range of arc volatility and sensitivity.

(ii) The samples cover all four possible combinations of physical form, represented by the pairs A, B, C, D below:-



The fact that none of these combinations imposed a significant bias on the line intensity of the minor elements examined, suggests that either (a) the physical effect is absent in the materials tested, or (b) that the effect is corrected by the buffer method. If the latter explanation is correct, it may probably be attributed to the fusion of the sample mixture during arcing, and the silicate fluxing properties of the lithium carbonate. Further work, such as a parallel test using alternative arc techniques, would be necessary to establish this point.

IV. Bias effect between two techniques for the alkali metals, using samples (a) alone and (b) admixed with carbon powder.

An investigation into conventional anode arc excitation procedures for the alkalis showed a result of some general interest, in that large analytical differences were observed between techniques which differ only in whether or not carbon is admixed with the samples (in equal proportions).

From numerous published methods for determining the alkalis spectrographically, attention was directed to those using cup electrodes and anode excitation, employing either the crushed samples only (Ahrens 1954; Deleon and Ahrens 1957), or with carbon admixture (Holyk and Ahrens 1953; Nockolds and Allen 1953; Shaw 1958).

Adopting an 1/8" diameter crater, and 9 amp anode excitation, tests showed that:- (a) in a series of synthetic standards (Appendix A₂) arced for 90 secs. without carbon mixing, the alkali elements dominated the spectrum as the contents of Na₂O and K₂O rose to above 2% each, and the less-volatile elements were depressed. This defect, clearly due to selective volatilisation, was much reduced in the presence of a 50% admixture of carbon.

(b) Analytical bias was present in the absence of carbon mixtures, in determining the alkalis in the granite G-1 against synthetic standards; when using a 50% carbon

Table 9.

Comparison of techniques for the alkali elements.

(a) Samples without carbon admixture.

(b) Samples with 1:1 carbon admixture.

Sample: Granite G 1.	ppm. visual readings (mean of five arcs).							
	(a)				(b)			
	Li	Rb	Ba	Sr	Li	Rb	Ba	Sr
Spectrographic analysis	275	3000	1600	1450	72	720	780	420
Recommended values (Ahrens, 1954).	22	570	1300	280	22	570	1300	280
Bias ratio	12.5	5.3	1.2	5.2	3.3	1.3	0.6	1.5

admixture, this defect, although not eliminated, was greatly reduced (Table 9). It was concluded that the methods employing carbon admixture offer higher accuracy for the alkalis than those without, at least in cases where natural standards closely resembling the samples are not available. This is no doubt due to the effect of carbon in suppressing fractional distillation and globule formation in non-conductors. This procedure was therefore adopted in routine alkali determinations (Method A, Table 1).

CHAPTER 3. ANALYTICAL TECHNIQUES FOR MAJOR ELEMENTS.

Introduction.

Some consideration was given to determining spectrographically the common major elements, namely, Si, Al, Fe, Ca, Mg, Na and K.

Although these elements rarely need to be determined on a routine basis in prospecting, major element analytical data can be of use:-

(i) in the study of weathering and dispersion processes, and (ii) to provide additional information on geochemical anomalies or concealed geology in cases of particular interest or difficulty revealed by the minor element data.

In addition, a readily available method for determining the major elements can be valuable in ad hoc analytical or geochemical problems involving geochemical materials.

Published spectrographic methods for major element analysis.

The majority of spectrographic methods for major element analysis of silicates have employed the D.C. arc and the generalisations incorporated in this brief summary are mostly drawn from the authoritative texts by Ahrens (1950, 1954).

A wide variety of major element methods have been proposed, illustrating the usual need for compromise between comprehensive coverage, precision, accuracy, and speed.

It is convenient to divide published techniques and their applications into three general categories:-

(a) Specialised quantitative methods, for specific analytical problems (relative deviation $\pm$ 3-10%).

(b) Quantitative methods for general purposes (relative deviation $\pm$ 5-15%).

(c) Semi-quantitative methods (relative deviation $\pm$ 15-30%).

The apparently coarse level adopted as quantitative, up to $\pm$ 10% relative deviation, is that taken by Ahrens (1954) as representative of internal standard arc methods, whether for major or minor elements.

Some of the most relevant published methods are listed in Table 10. Apart from being reproducible a method should of course be accurate, i.e. free from bias in the mean analytical result; precision and accuracy are distinguished in the Table where possible.

In the specialised quantitative methods two general approaches have been used. Firstly, within powder arc methods high accuracy can be obtained by using the arc and internal standard procedure best suited to particular analysis elements, and combining such methods into an analytical "scheme". The method of Kvalheim (1947) for example employs added Sr (as SrCO_3) as the buffer and internal standard for Al, Fe, Ca, Mg and Ti - and for Na and K in a separate arc burn - and Be (as BeO) as a buffer and internal standard for Si. Several workers have employed modifications of this method (Table 10).

Table 10. Spectrographic arc techniques for the major elements

Elements determined	Sample type ^a	Buffer ^b	Diluent ^c	Mixture ratio a.b.c.	Internal standard	Accuracy	Reference
(Al, Fe, Ca, Mg (Na, K (Si	Rocks, minerals " "	SrCO ₃ SrCO ₃ BeCO ₃ + NaCl, 1:3	carbon carbon carbon	1:1:4 1:1:4 1:1:10	Sr Sr Be	))) ± 10% approx.	Kvalheim, 1947 (modified: Dennen et al, 1950; Ahrens 1954). Leininger et al. 1954) Hawley et al 1956)
(Fe, Ca, Mg, Mn (Al, Ti	Silicates "	SrCO ₃ Y ₂ O ₃	carbon carbon	1:1:6 1:0.2:10	Sr Y	) precision) ± 4%	Rushton & Nichols, 1957.
(Al, Fe, Mg, Ti (Na, K	Cements, minerals " "	nil Li ₂ CO ₃	graphite nil	1:-:1 9:1:-	Ca Li	) precision) ± 7%	Hasler et al 1948 (modified Gillis et al 1949)
1. <u>Analytical schemes combining two or more individual methods.</u>							
2. <u>Chemical pre-treatment methods.</u>							
Al, Fe, Ca, Mg, K Ti	Soils, plants.	NaNO ₃ solution containing Mo dried on to the electrode			Mo	± 10%	¹ Shimp et al 1957.
3. <u>General purpose arc methods</u>							
Si, Al, Fe, Ca, Mg, Ti	Silicates	Ba(NO ₃) ₂ + NH ₄ Cl 1:1	nil	1:2:-	Ba	± 10%	Fitz & Murray 1945
Si, Al, Fe, Ca, Mg, Na, K, Tc.	Geological materials	nil	carbon or nil	1:-:1	Al, Fe	precision ± 5-14%	Dennen & Fowler 1955
Si, Al, Fe, Ca, Na & others	Silicates, non- conductors	Li ₂ CO ₃	graphite	1:4:20	Li and others	± 10% approx.	Bientema & Kroonen 1955 Bientema 1957
-do-	General powder samples	Li ₂ CO ₃	graphite	1:5:18	Li	precision 4-16%	Smith & Matarella 1957b
Si, Mg, Na, K & others	General powder samples	Li ₂ CO ₃ (& Co)	cellulose	1:3:16	Co	± 10% approx	² Noar 1955; Noar et al 1955

1. Employing an A.C. arc.

2. Employing mechanical introduction of the sample into the arc.

These schemes have good performance, but productivity is low if all the elements have to be determined, since two or more sample mixing or arc burn procedures are required.

In the second approach, chemical pre-treatment is employed to reduce the effect of chemical and physical variations between the samples. General sample coverage and good performance can be achieved in the final arc analysis, but over-all productivity and simplicity are impaired by needing a separate chemical stage. Thus Shimp et al (1957) have analysed soil and plant samples for Al, Fe, Ca, Mg and K by a procedure that involves solution and volatilization of silica, the addition of buffer and internal standard solution, and evaporation onto a carbon rod before arcing.

General-purpose methods (Table 10) usually sacrifice some performance compared with the foregoing specialised methods, but their relative simplicity is an advantage for geochemical applications. Thus Dennen and Fowler (1955) give analyses showing weathering in a granite and a sandstone, and variation of a shale with depth, to illustrate their general spectrographic method for the major elements. The powder sample is arced either directly or mixed with carbon powder, the aluminium (or iron) present in the sample serving as the variable internal standard. The method does not specially compensate for matrix variations, for example by high dilution or buffer admixtures, so that analytical calibration should be made using materials similar to the unknowns.

Other general purpose methods employ an added buffer material which may also serve as the internal standard. Examples include the use of barium nitrate as the internal standard and buffer in the analysis of small powdered samples (Fitz and Murray, 1945), while several workers have used lithium carbonate for the same purpose (Table 10). Thus Bientema and Kroonen, (1955) found that Li_2CO_3 has the effective buffer properties typical of alkali metal salts, and minimises the fractional distillation of elements of different volatilities, during the arcing of silicates and other non-conductors. These authors determined Si, Al, Fe, Ca and Na in limestone, dolomite, silicate glasses and refractories, to illustrate the wide range of element concentrations over which their method applies, with accuracies generally within $\pm 10\%$ of the chemical values.

Methods for major element analysis with only semi-quantitative accuracy have been applied to specific geochemical problems. Thus Waring and Annell (1951, 1953) used visual semi-quantitative estimates for major elements, by the same method as for the minor elements, to sort different radioactive minerals. Similar major element data for uranium ore and barren sandstone samples show that geochemically useful information is obtained in suitable cases, from visual estimates of concentrations within a factor of two (Gerrels and Larsen, 1959).

Experimental Investigation of Analytical Techniques
for the Major Elements.

The applied geochemical requirements for major element data limited the choice of techniques to straightforward powder arc methods of general applicability and modest accuracy. Methods based upon the addition of a buffer and internal standard were attractive since they offer some compensation for the matrix variations likely to be met in geochemical materials, with no manipulation other than mixing the powdered sample and buffer mixture in fixed proportions. Of several alternatives, the procedures of Bientema and Kroonen (1955), and Bientema (1957) were considered to offer the most promise for the following reasons:-

(i) The buffer is a Li_2CO_3 -graphite mixture (added to one twenty-fourth of its weight of sample) which gives an adequate buffering capacity without undue sensitivity loss.

(ii) Li alone may be used as the internal standard, or other elements can be incorporated in the buffer in order to give optimum internal standardization for any analysis element (Bientema 1957).

(iii) The method involves only a single-stage sample mixing and one arc procedure.

(iv) The method has been tried successfully on a variety of geological materials.

(i) Preliminary investigation.

Using the basic technique of Bientema and Kroonen (1955), duplicate arcs were made of six analysed samples comprising four rocks and two soils (Nos. 1-6, Table 11). Each sample was mixed with carbon-lithium carbonate buffer ($5C : 1Li_2CO_3$) in the proportions of one part of sample to twenty-four parts of buffer, and the arc details were the same for the final routine technique (Table 16) except for the following minor modifications:-

1. Wavelength range 4600 - 2730 Å.
2. Sample electrode 5 mm. deep. Sample mixture loaded to completely fill the crater.
3. Counter electrode: long thin form: 2.0 mm. diam. x 16 mm. long.
4. Rotating step sector of 6 steps, factor of 2.

Analytical curves were set up by (a) the original authors' method using a line of the Li buffer as the internal standard and (b) by a variable internal standard method employing a line of Si which, of course, is present in all the samples. These well-known alternative methods for analytical calibration can thus be compared.

The salient features of the test data are shown in the trial analytical curves (Figure 9) and in Table 12.

Table 11. Analysed samples for spectrographic major element calibrations

No.	Sample	Composition, per cent.								No. of Analyses	Analyst
		SiO ₂	Al ₂ O ₃	Tot. Fe as Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂		
1	Lateritic soil 1401	44.9	19.4	23.7	0.9	1.8	0.12	0.51	3.5	1	P. Curtis
2	Lateritic soil 1443	36.6	18.5	44.1	0.27	0.80	0.04	0.37	0.8	1	do.
3	Dolerite S587	45.6	12.0	20.3	9.8	5.7	2.6	0.5	3.7	6	D. Burns
4	Basalt-andesite G.194	54.0	12.8	14.5	7.3	3.4	3.6	1.3	2.6	8	I. Carmichael
5	Diorite T.13	55.9	18.4	6.3	5.5	3.4	4.6	2.7	1.0	6)	E.L.P. Mercy (1955)
6	Granite M.149	73.4	14.2	1.6	0.94	0.80	4.1	4.2	0.21	6)	
* Analyses by rapid chemical methods for silicates (Mercy 1955).											
7	Diabase W-1	52.3	15.1	11.30	11.0	6.6	2.00	0.63	1.1	)	Data after Ahrens, 1954; Mercy, 1955
8	2W ₁ + 1G ₁	59.0	14.87	8.1	7.80	4.53	2.42	2.22	0.82	)	
9	1W ₁ + 2G ₁	65.70	14.63	5.0	4.60	2.46	2.83	3.81	0.53	)	
10	Granite G-1	72.4	14.4	1.8	1.4	0.39	3.25	5.4	0.25	)	
11	Glass sand	(99.3)	0.265	0.0724	0.029	0.016	-	-	0.095	)	
12	Burnt refractory	32.38	59.39	0.90	0.26	0.50	0.06	2.11	2.93	)	U.S. Nat. Bureau of Standards.
13	Mesasi Fe-ore	2.16	-	96.49						)	
14	Argillaceous Limestone	14.11	-	1.63	41.32	2.19	0.39	0.71	0.16	)	
15	Dolomite	0.31	0.067	0.084	30.49	21.48	0.08	0.03	0.005	)	
16	Soda feldspar	68.92	19.13	0.067	0.36	0.053	10.77	0.41	0.017	)	
17	Bauxite	8.24	75.4	7.98	0.40	0.027	0.10	0.10	3.81	)	
18	Clay flint	47.53	42.98	1.09	0.11	0.29	0.08	0.60	2.64	)	
19	Clay plastic	62.45	26.98	2.17	0.22	0.76	0.27	3.35	1.51	)	

Table 12.

Agreement between duplicates using alternative internal standards.

		Mean differences between duplicate arcs. (log. intensity, with equivalent percentage variation)		
Element and line, A	No. samples (duplicate arcs)	(a) Without Int. standard.	(b) Li (3232.6 A) as Int. Std.	(c) Si (2881A) as Int. Std.
K 4044	3	0.092 (23.6%)	<u>0.032</u> (7.7%)	0.070 (17.5%)
Na 3302	5	0.080 (20.2%)	<u>0.011</u> (2.6%)	0.031 (7.4%)
Ca 3158.9	3	0.094 (24.2%)	<u>0.023</u> (5.4%)	<u>0.027</u> (6.4%)
Mg 2779.8	4	0.072 (18.0%)	<u>0.021</u> (5.0%)	0.040 (9.7%)
Fe 2929	5	0.083 (21.1%)	<u>0.019</u> (4.5%)	<u>0.023</u> (5.4%)
Al 3082	6	0.074 (18.6%)	<u>0.022</u> (5.2%)	<u>0.021</u> (5.0%)
Si 2881	6	0.082 (20.8%)	0.030 (7.2%)	<u>0.000</u> (0.0%)
The lowest differences, underlined, show the superior internal standard.				

Table 12 shows the mean differences between duplicate burns based on calculations of (a) the element line intensity alone, (b) the line intensity ratio to Li as internal standard, and (c) the ratio to Si as the internal standard. The agreement between duplicate arcs is improved when either internal standard ratio is employed. Differences between duplicates range from 18-24% for the various elements in readings without internal standards; these are reduced to $\leq 7.7\%$ for Li as the internal standard, and to $\leq 17.5\%$ for Si. Thus Li is superior to Si as a general internal standard, on the basis of replicates only, over all seven major elements. There are some individual exceptions for particular elements (cf. columns (b) and (c) with column (a), Table 12).

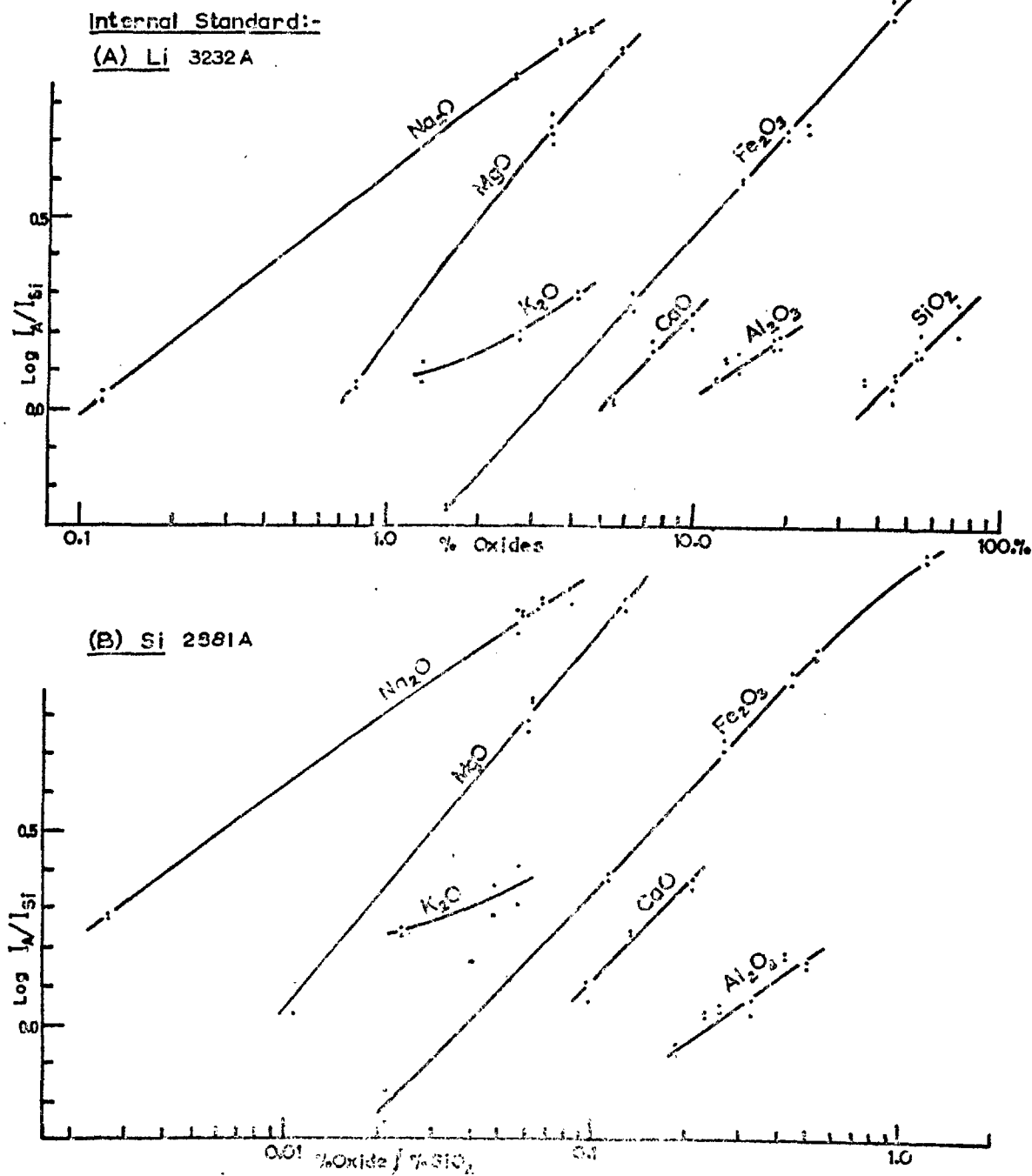
On the other hand, the trial analytical curves (Fig. 9) show that the alignment of sample points along the curve for a given element, as well as the scatter between duplicates, depends upon which internal standard is used. Thus, the slope and hence the analytical discrimination for K is better when Li is the internal standard; whereas for Fe, it is Si which gives the best alignment for all sample points.

In general, neither of the internal standards alone gave ideal test curves for all analysis elements, on the available test samples. Moreover, a combination of the two methods, each for the optimum elements, is inconvenient because of the difference between their methods of calculation. The Si variable internal standard method presents analytical curves, and results, as oxide ratios to SiO_2 , and requires a calculation of SiO_2 "by difference" - or by independent analysis - to give the individual oxide data. It is inconvenient to use this method for only one or two elements, with the Li internal standard method for the others.

(ii) Final technique investigation.

To obtain more satisfactory analytical curves than those by procedures (i), compounds of Ge, Cd, In and Y were tested as added internal standards having different volatilities from those of Li (and Si).

Fig.9. Trial Analytical Curves for Major Elements.



The addition of internal standard elements supplementary to Li was suggested independently by Bientema (1957) without specifying the elements to be used. Four possible internal standard elements were therefore selected from other relevant publications. Jaycox (1955) and Frisque (1957) employ Ge as a general internal standard for the major elements, while Ahrens (1954) uses Pd for minor elements of medium volatility and In for the volatiles. Ahrens later extended the use of Pd - as tetrammine palladous nitrate - as a comprehensive internal standard (R. Taylor pers. comm.). Y was employed by Rushton and Nichols (1957) as the internal standard for the other involatile oxides of Al and Ti, and Y_2O_3 completed the four compounds chosen for the present investigation.

Experimental work.

(i) Using the anode arc technique, visual readings of line densities were made to establish suitable concentrations for the internal standard compounds in the buffer mixture; the proportion of carbon to Li_2CO_3 was left unchanged at 5:1. A suitable mixture is easily prepared from the buffer employed for the minor elements. (Details are given at the end of this chapter).

(ii) A qualitative study was made of arc behaviour and line density in relation to electrode size and the addition of a layer of powdered carbon covering the sample mixture (Bientema and Kroonen, 1955; Bientema, 1957). A carbon

layer approximately 1.5 mm. deep was adopted to smooth the start of the arc burn; the crater depth was increased from 5 mm. to 6 mm. to compensate for the reduced weight of sample mixture under the cover.

(iii) The diameter of the upper or counter electrode was increased from 2.0 to 2.5 mm., enabling the length to be reduced from 16 mm. to 7-8 mm.; the flame-centering property of the thinner electrode was retained.

These minor modifications are described in the major element technique M (Table 16).

(iv) Thirteen analysed standard samples were obtained covering a wide range of concentrations (samples 7-19, Table 11). Each sample was treated by the mixing technique adopted for the major elements, and arced in triplicate (Technique M, Table 16).

Line intensities were measured with background correction, for a total of ten lines for the major elements and nine possible internal standard lines (Appendix A3). By testing (a) the effect of ratios to different internal standards on the line intensity variations between the triplicate arcs, and (b) plotting test analytical curves, the best analytical curves for the eight major elements were selected. These were obtained by using four separate internal standard lines, namely Ge for Mg, Fe and Si; Pd for Ca and Ti; In for Na and K, and a separate Ge line for Al.

Table 13 shows that the extreme difference between triplicate arcs averaged for all samples, ranges from 5.4 - 12.5% when using the chosen internal standards. The relative deviation for the mean, as normally calculated, would be less than the above value, based on the extreme deviation between triplicates. Burn variations without internal standard are themselves low in the present study, reflecting good repeatability between arc burns (Table 13).

The optimum line pairs give analytical curves (Fig. 10) with approximately linear plots close to the theoretical unit slope over wide ranges of concentration.

Precision and accuracy of the method.

The analytical precision was determined as shown in Table 14 by replicate arcings of two lateritic soils and one rock; the mixing procedure was checked by preparing two mixtures separately from each sample.

The results show:-

(i) Relative deviations (expressed as one standard deviation percent) range from ± 2 to 6% for all elements at all levels of concentration except the three lowest Na_2O and FeO contents, where relative deviations are $\pm 7.5\%$, 12% and 17% respectively; the variations in actual content are, however, negligibly small. The over-all average for the relative deviations is $\pm 5.2\%$.

TABLE 13. Major element standards. Effect of internal standards on the extreme intensity difference between the three replicate arc burns.

Standard Sample	Δ Log I = extreme difference between three replicate arcs															
	(a) Without internal standard								(b) With internal standard							
DIABASE W ₁	Si29876	Si29876 Ge3039	Al2652	Al2652 Ge2709	Fe2929	Fe2929 Ge3039	Ca3158	Ca3158 Pd3242	Mg2779	Mg2779 Ge3039	Na3302	Na3302 In3256	K4044	K4044 In3256	Th3355	Th3355 Pd3242
DIABASE W ₁	.032	.020	.025	.043	.047	.045	.020	.018	.022	.008	.035	.010	-	-	.035	.017
2W ₁ + 1G ₁	.058	.020	.050	.050	.040	.016	.055	.040	.062	.037	.027	.014	.072	.040	.032	.035
1W ₁ + 2G ₁	.030	.030	.060	.040	.021	.014	.095	.060	.010	.025	.030	.015	.090	.075	.083	.083
GRANITE G ₁	.033	.055	.010	.030	.018	.043	.057	.082	.007	.018	.020	.010	.050	.055	.080	.103
GLASS SAND	.048	.013	.017	.067	-	-	-	-	-	-	-	-	-	-	.018	.034
BURNT REFRACTORY	.085	.016	.035	.053	-	-	-	-	.055	.027	.110	.100	.046	.036	.025	.020
IRON ORE	-	-	-	-	.000	.018	-	-	-	-	-	-	-	-	-	-
ARGILLACEOUS LIMESTONE	.035	.010	-	-	.040	.028	.019	.025	.065	.041	.052	.017	.031	.025	.020	.004
DOLOMITE	-	-	-	-	-	-	.026	.009	.049	.010	-	-	-	-	.042	.025
Na FELSPAR	.015	.033	.010	.010	-	-	.050	.065	-	-	.015	.036	-	-	.133	.148
BAUXITE	.055	.022	.070	.055	.072	.020	.098	.103	-	-	-	-	-	-	.082	.047
CLAY FLINT	.012	.018	.036	.018	.020	.032	-	-	.023	.035	.075	.035	.050	.030	.005	.015
CLAY PLASTIC	.025	.020	.019	.029	.026	.016	-	-	.000	.010	.047	.005	.067	.025	.080	.085
MEAN	.039	.023	.033	.040	.032	.026	.053	.050	.033	.023	.046	.027	.058	.041	.053	.051
Equivalent percentage variation	(9.4%)	(5.4%)	(7.9%)	(9.7%)	(7.7%)	(6.2%)	(13.0%)	(12.2%)	(7.9%)	(5.4%)	(11.2%)	(6.4%)	(14.3%)	(9.9%)	(13.0%)	(12.5%)

Table 14. Precision of replicate spectographic analyses

Sample	Mixture No.	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO%	MgO%	Na ₂ O%	K ₂ O%	Total
Lateritic soil 1401	1	44.3	26.0	22.5	1.35	0.50	0.11	<0.5	94.76
		47.5	27.8	26.2	1.25	0.50	0.11	-	103.36
		46.3	24.6	24.4	1.24	0.46	0.13	-	97.13
		46.1	23.3	23.8	1.22	0.49	0.11	-	95.02
	Mean	46.05	25.4	24.2	1.27	0.49	0.12	-	
	2	47.5	24.6	22.5	1.32	0.50	0.15	-	96.57
		46.5	25.2	25.1	1.36	0.49	0.14	-	98.79
		49.5	25.7	24.1	1.26	0.50	0.12	-	101.18
		47.5	28.0	24.4	1.40	0.51	0.13	-	101.94
	Mean	47.75	25.9	24.0	1.34	0.50	0.13	-	
Grand Mean $\bar{x}$		46.90	25.7	24.1	1.30	0.49	0.13	-	98.62
Relative deviation % σ		± 1.50 $\pm 3.20\%$	± 1.61 $\pm 6.3\%$	± 1.24 $\pm 5.1\%$	$\pm .066$ $\pm 5.1\%$	$\pm .014$ $\pm 2.9\%$	$\pm .014$ $\pm 11.4\%$	-	
Lateritic soil 1443	1	37.5	19.7	44.1	<0.5	0.14	.048	<0.5	101.49
		40.0	18.2	46.7	-	0.14	.044	-	105.08
		37.5	17.7	44.1	-	0.14	.042	-	99.48
		36.8	18.1	46.0	-	0.15	.049	-	101.10
	Mean	38.0	18.4	45.2	-	0.14	.046	-	
	2	38.6	19.5	48.5	-	0.14	.038	-	106.78
		38.4	17.9	44.4	-	0.13	.040	-	106.58
		37.8	19.3	48.2	-	0.13	.032	-	105.46
		38.6	18.0	45.0	-	0.13	.030	-	101.76
	Mean	38.4	18.7	46.5	-	0.13	.035	-	
Grand Mean $\bar{x}$		38.2	18.6	45.9	-	0.14	.040	-	102.88
Relative deviation % σ		$\pm .98$ $\pm 2.6\%$	$\pm .81$ $\pm 4.4\%$	± 1.78 $\pm 3.9\%$	-	$\pm .010$ $\pm 7.3\%$	$\pm .007$ $\pm 17.3\%$	-	
Basalt andesite 4111 9194	1	54.6	12.7	14.9	8.60	3.85	2.70	1.43	98.67
		58.0	13.7	13.6	9.10	4.03	2.67	1.47	102.57
		55.0	13.9	13.9	9.50	4.03	2.78	1.39	100.50
		56.3	12.9	14.6	8.80	4.00	2.90	1.32	100.82
	Mean	56.0	13.3	14.3	9.00	3.98	2.76	1.40	
	2	56.7	13.5	14.1	9.78	3.87	2.76	1.24	101.95
		56.2	13.5	14.1	9.50	3.91	2.65	1.26	101.12
		55.7	14.0	14.5	9.27	3.91	2.60	1.32	101.30
		55.2	13.7	14.8	8.80	3.94	2.82	1.36	100.56
	Mean	56.0	13.7	14.4	9.34	3.91	2.71	1.30	
Grand Mean $\bar{x}$		56.0	13.5	14.3	9.17	3.94	2.74	1.35	101.00
Relative deviation % σ		± 1.09 $\pm 2.0\%$	$\pm .46$ $\pm 3.4\%$	$\pm .46$ $\pm 3.2\%$	$\pm .42$ $\pm 4.5\%$	$\pm .070$ $\pm 1.8\%$	$\pm .099$ $\pm 3.6\%$	$\pm .080$ $\pm 5.9\%$	

(ii) There is no significant difference between the duplicate mixtures for each sample.

(iii) Analytical totals are within two standard deviations of 100%.

Analytical accuracy is shown in Table 15, comparing spectrographic and chemical data on the eleven samples for which chemical analyses were available. The analysed standards used for preparing the analytical curves were not, of course, employed in this comparison. Spectrographic mean values are within 10% of the chemical means in thirty-nine out of sixty-five pairs of determinations, including eighteen of the twenty-six determinations in which the oxide content exceeds 10%. Approximately two-thirds of all determinations are thus within an accuracy limit of $\pm 10\%$.

Considering both precision and accuracy, the precision for a single estimate is of the same order, or better, than the mean accuracy obtained by comparison with chemical values. Thus replicate analyses are not justified, since replication can improve only the precision of the mean,* and not its accuracy. In routine analysis, samples were arced in duplicate, however, mainly to avoid the risk of chance erratic error.

*Standard deviation of the mean =

Standard deviation for a single determination

$\sqrt{\text{number of replicates}}$

Fig.10. Analytical Curves for Major Elements.

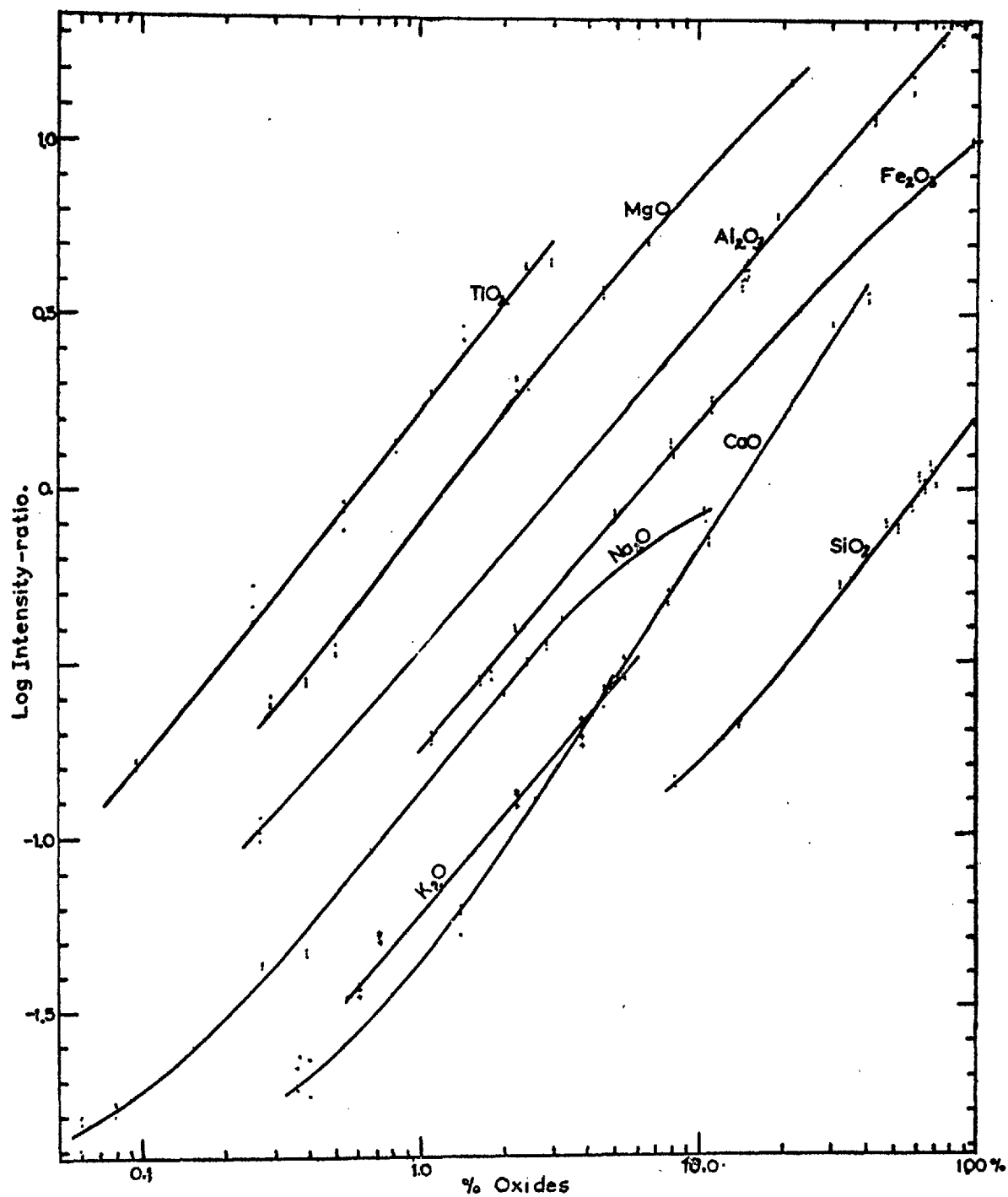


Table 15

Comparison of (a) spectrographic with (b) chemical analyses

Sample	No. of Analyses		% oven-dry basis						
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Diorite	3	a	54.1	17.1	5.7	5.8	3.0	3.9	3.4
T ₁₃	1	6	b	55.9	18.4	6.3	5.5	3.4*	4.6
Granite	3	a	64.7 ⁺	11.1	1.5	1.2	0.71	3.6	4.5
M149	1	6	b	73.4*	14.2*	1.6	0.94*	0.80*	4.1*
Dolerite	3	a	42.0	11.2	17.8	10.7	5.5	2.1	1.9
S587	2	6	b	45.6	12.0	20.3*	9.8	5.7	2.6*
Dolerite	3	a	45.0	11.1	18.3	11.8	7.0	2.1	<0.5
S588	2	2	b	46.0	11.2	19.9	10.3*	6.7	2.4*
Basalt-andesite	8	a	56.0	13.5	14.3	9.2	3.9	2.7	1.4
G194	3	8	b	54.0	12.8	14.5	7.3*	3.4*	3.6*
Tonalite	3	a	62.9	12.3	4.1	4.0	2.5	3.6	3.3
C9	4	6	b	64.7	15.4*	4.3	3.7	2.4	4.6*
Serpentinised trocolite	3	a	32.9	1.9	13.1	0.25	29.1	<0.1	<0.5
H6	4	6	b	35.0	2.6*	13.7	0.20	36.5*	0.07
Lateritic soil	8	a	46.9	25.7	24.1	1.3	0.5	0.13	<0.5
1401	4	1	b	44.9	19.4*	23.7	0.9*	1.8*	0.12
Lateritic soil	8	a	38.2	18.6	45.9	<0.5	0.14	0.04	<0.5
1443	4	1	b	36.6	18.5	44.1	0.27	0.80*	0.04
Limestone	3	a				45.0	0.61		
57/112	5	3	b			53.0*	0.47*		
Limestone	3	a				32.0	1.5		
57/100	5	3	b			39.0*	1.3		

Analysts: 1. Laboratory standard rocks, E.L.P. Mercy 1955.

2. D. Burns

3. I. Carmichael

4. P. Curtis

5. P. Bush

+ Biased by one low spectrographic result.

* Indicates difference between chemical and spectrographic means 10% of content.

Productivity.

If the sample mixture from the minor element analysis is available, as is the usual case, approximately six samples can be analysed for the major elements in one man-day.

Special geochemical limitations.

(a) Silica is normally the highest component and thus subject to the highest absolute error, which can seriously limit the usefulness of data for silica in geochemical studies. Providing the non-determined components such as carbonates, sulphides, etc. are known to be insignificant, equally useful or superior results can be given by reporting silica by difference - with an advantage in productivity. Silica was determined by difference in many geochemical samples, and determined directly mainly where the spectrum showed probably low silica, for example in highly ferruginous samples.

(b) In some tropical soils and sediments, the contents of Na_2O and K_2O are below the limit of determination by the major element method (approximately 0.1% and 0.5% respectively). These elements are therefore included in the minor element semi-quantitative procedure (Chapter 2). Similarly, titanium is also included for determination by either the minor or major element techniques. Low contents of other common elements, especially Ca and Mg in soils, might usefully be included in the minor element method.

For self-consistency, geochemical inferences for Na, K, Ti, were drawn only from data obtained by one analytical method in each case.

General conclusions on the applicability of the method.

The precision and accuracy of the major element technique are satisfactory in relation to other procedures of this simple type. Important features are (a) the generality of the method regarding sample types and element concentrations, (b) its minimum demands on equipment and analytical skill, and (c) its simple combination with the minor element buffer method into a comprehensive analytical scheme. The productivity of the method is satisfactory for small-scale experimental studies, but it is not well suited for large numbers of samples.

Taking these factors together, the method succeeds in meeting the main requirements for the geochemical applications which initiated the work, i.e. to provide useful major element data, (a) in studies of weathering and dispersion, and (b) in special geochemical problems raised by the minor element data, and (c) for the analysis of miscellaneous materials in ad hoc investigations.

Subject to the demand for data, productivity could be improved by suitable work organisation; maximum productivity could be attained by direct-reading spectrography, whereby Black (1956), for instance, achieved a rate of 20 minutes per sample using a conventional d.c. arc procedure.

Table 16 Spectrographic technique for major elements.

	Technique M
Wavelength range	4200 - 2640 Å.
Emulsion	Ilford N30.
Sample electrode	3.2 mm. ($\frac{1}{8}$ ") int. dia. 6.0 mm. deep; 4.1 mm. ext. dia.
Sample polarity	Anode. 7 amps.
Exposure time	To completion (2-2 $\frac{1}{2}$ mins.).
Sample mixture	1 part sample + 24 parts carbon-Li ₂ CO ₃ buffer containing internal standards.
Electrode spacing	6.0 mm. Central portion approx. 4 mm. accepted by the spectrograph optics.
Electrode loading	The electrode is loaded to within approx. 1.5 mm. of the top, and capped with carbon powder.
Analysis line	Internal standard line
Al 2652.48 Lower*	Ge 2709.62 --*bg. as for Al.
Mg 2779.83 Lower)	
Fe 2929.00 Higher)	Ge 3039.06 Lower.
Si 2987.64 Higher)	
Ca 3158.86 Higher)	Pd 3242.70 -- bg. as for Na.
Ti 3354.63 Lower)	
Na 3302.32 Lower)	In 3256.09 -- bg. as for Na.
K 4044.14 Lower)	
* Measuring point for background; "higher" or "lower" indicating the wavelength side of the line for reading the background.	

Spectrograph, optics, and plate processing are as described for the minor element techniques, Chapter 2.

1. Preparation of buffer mixtures.

Buffer Mixture 1. (Minor element analysis).

20 mg. each of tetrammine palladous nitrate, In_2O_3 and GeO_2 , and 40 mg. of V_2O_5 , are thoroughly mixed with 19.9 g. of carbon powder; a 10.0 g. portion is mixed thoroughly with 10.0 g. Li_2CO_3 , to give a stock buffer and internal standard mixture for minor element analysis (Method C¹, Table I¹).

Buffer Mixture 2. (Major element analysis).

For major element analysis, 10.0 g. of Mixture 1 is thoroughly mixed with 20.0 g. of carbon powder.

2. Sample mixing method.

Approximately 300 mg. of ignited minus 80-mesh sample is thoroughly ground and homogenised in an agate mortar.

A. For minor element analysis.

Equal weights of approximately 100 mg. of sample and Buffer Mixture 1 are thoroughly ground and homogenised for 5-7 mins. in an agate mortar.⁷ (Using a 500 mg. capacity torsion balance for samples; analytical balance for standards).

⁷ Or for 30 secs. in a plastic vial on a Wig-L-Bug mechanical shaker: these routine mixtures were re-homogenised by hand mix before preparing dilution "B" for the major elements.

B. For major element analysis.

About 30 mg. of mixture A is weighed on an analytical balance and transferred to an agate mortar. 11.5 times this weight of Buffer Mixture 2 is added and homogenised as above, for 10 mins.

CHAPTER 4. SPECTROGRAPHIC OPTICS AND EVALUATION.

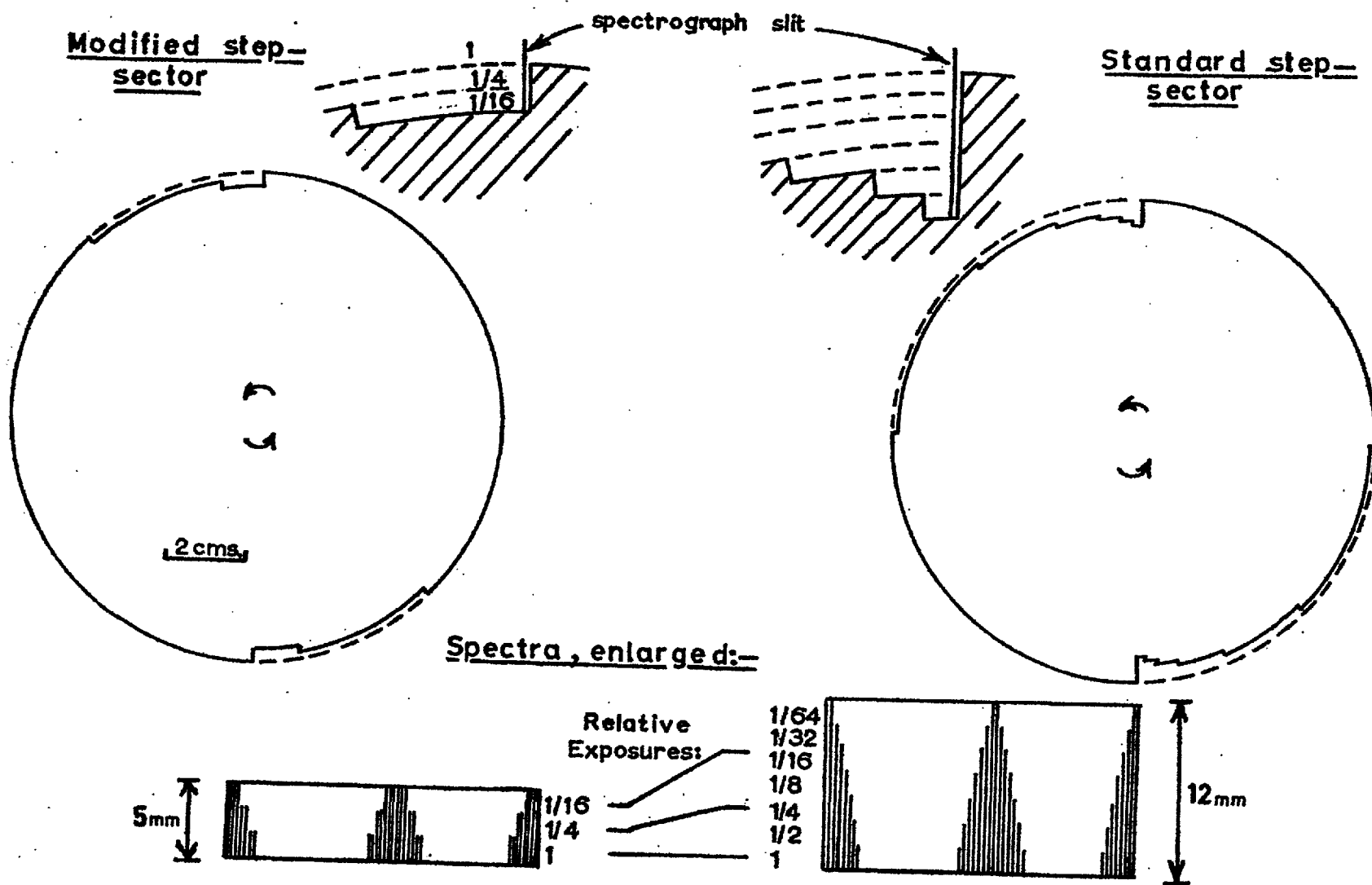
Introduction

In this section two pieces of equipment are described which were devised to meet the special requirements of soil spectrographic analysis. The first is a modified rotating step-sector designed to give an adequate range of exposure steps for each sample, combined with reasonable economy in the use of photographic plates. The second is a graphical evaluating board for rapidly converting densitometer readings into log relative intensity units.

Rotating Step-sector.

The sector, which is illustrated in Figure 11, has two steps giving $\frac{1}{2}$ and $\frac{1}{16}$ of the full exposure, the latter being accepted by the part of the slit not masked by the sector. Three intensity levels are thus obtained at the slit in the relative proportions $1:\frac{1}{4}:\frac{1}{16}$. In the resulting spectrum these three exposure steps, and thus the range of concentration which can be covered by a given element line, are the same as for the first, third and fifth steps of the standard six-step sector previously used. The smaller over-all height of the three-step spectrum allows fourteen spectra to be recorded on a four-inch plate, with an advantage in plate economy. Moreover, it is convenient in visual comparison readings that up to fourteen standard samples can be arced together.

Fig.11. Modified Step-Sector.



Future work.

While retaining the same exposure intervals, the step height could be cut down from 1.5 mm. to 1.0 mm. in order to give further plate economy and still permit densitometer readings of the lines where required. For purely visual semi-quantitative work, an independent Russian innovation might be copied, by reducing the step height to 0.2 to 0.4 mm. Kler(1957) describes such a sector for prospecting applications, using nine steps (exposure factor 2.15) which gives ten exposure levels from 1 to 1/1000, occupying only 3.1 mm.

Evaluating Board.

This term is applied to a drawing board which was adapted for rapidly evaluating spectrographic line intensities from densitometer readings. It should be stressed that it is only used in quantitative analytical methods which require plate reading by the densitometer: the main applications in the present study have been in determining the major elements.

Outline of established principles of photographic evaluation.

All quantitative spectro-analysis which employs photographic recording of the line intensities, is essentially a two-stage process.

Firstly, the densitometer reading which is related to the photographic blackening¹ of the spectrum line - or of a particular step in a step-sector exposure - must be converted into units expressing the relative intensity of the line in the arc source. Secondly, the analysis is completed by calculating the intensity ratio of the analysis line to the internal standard, and reading off the element concentration from the analytical working curve; the latter being established from samples of known composition treated in the same way as the unknowns.

This two-stage division enables the photometric factors such as (a) the change in blackening with line wavelength, (b) variations in photographic development, and (c) the presence of spectrum background, to be accounted for in the preliminary "evaluation" operation. The calculated relative intensity of the arc line is then independent of these photographic variables. If this were not so, the analytical curve itself would have to be laboriously re-established for every plate, in order to account for variations in the photographic factors.

¹ If the densitometer reading is designated d with the symbol d_0 for the clear plate reading and $d_\bullet$ for no light reading, the optical density, D , of the line is defined as:-

$$D = \log \frac{d_0 - d_\bullet}{d - d_\bullet}$$

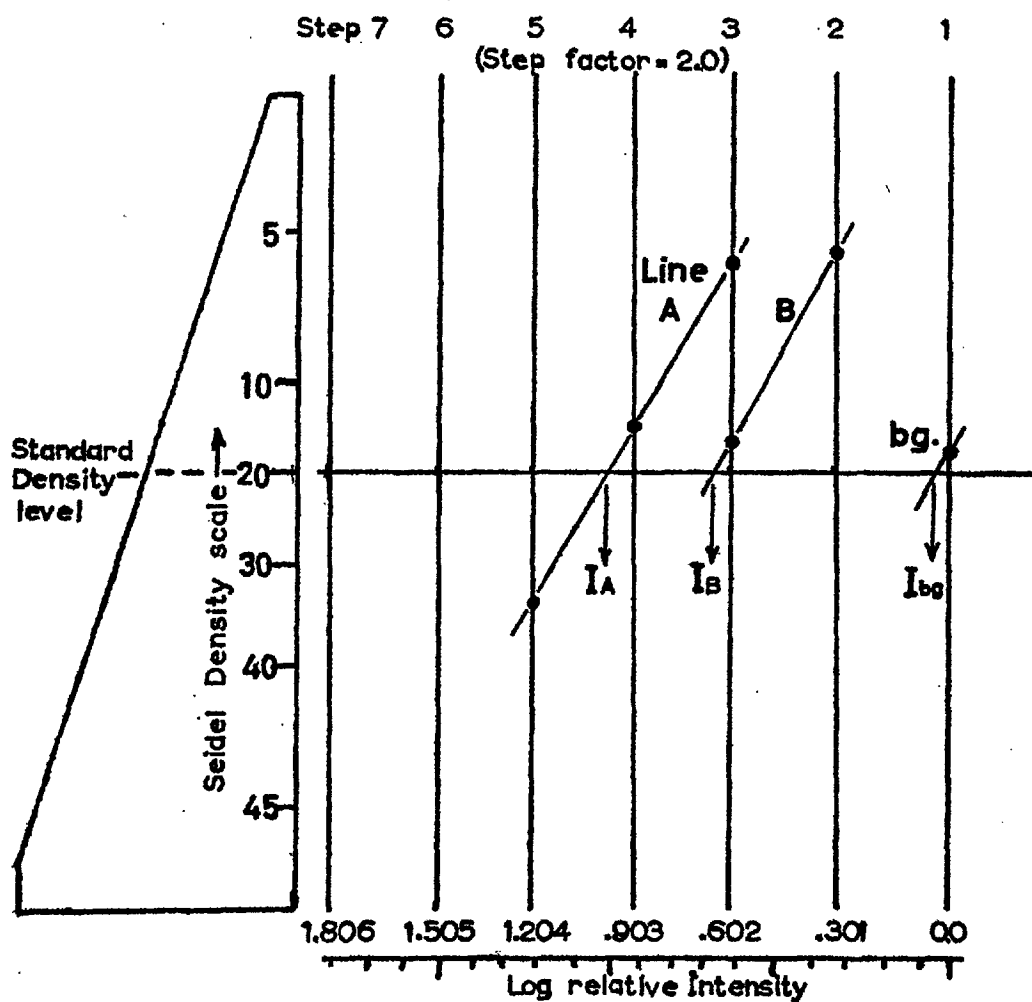
Usually d_0 is 0, and $d_\bullet$ is 100 in the A.R.L. densitometer used in this work, hence $D = \log \frac{100}{d}$.

The methods of photographic evaluation described by Black (1952) and Ahrens (1954) form the basis of the evaluating board. Both authors employ a graphical method - with minor differences in the plotting procedures - for evaluating relative line intensities at a standard density level. This method, known as the "self-calibration" or "blackening curve separation" method, offers high accuracy from a photographic viewpoint, and has been widely employed in soil and silicate analysis (Black; Ahrens (ibid.); Strock, 1936; Mitchell, 1948; Ahrens, 1950 p. 137; Philcox, 1957).

The method requires all the samples to be arced using a step-sector, and two or three steps (usually) to be measured in each line. By plotting the densitometer readings as ordinates on a suitable blackening scale, against the known relative exposures of the sector-steps, a short blackening curve is drawn for the spectrum line (Fig. 12). The relative intensity in the arc source is then obtained from the intercept of the blackening curve with a horizontal line drawn at some chosen standard density level. Where a line appears only in the full exposure step, as with weak lines and background, the required intensity intercept is given by parallel extrapolation.

Fig.12. Graphical Standard Density Method.

After Black, 1952.



For the vertical blackening scale both Black and Ahrens use the Seidel density² to replace the simple density¹ value. The object is to extend the straight line portion of the blackening curve, to reduce errors in drawing and in extrapolation.

In most quantitative spectrography it is necessary to subtract the intensity contributed by the spectrum background on which each line is superimposed. For this purpose a densitometer reading is made for the background itself and plotted in the same way as for the line-plus-background reading. From the two intensity intercepts, subtraction gives the required intensity of the line alone. The subtraction is made either by calculation or by an appropriate scale (Black, 1952).

Construction of the evaluating board.

The evaluating board differs in principle from the foregoing methods in two minor but important respects. Firstly a blackening scale³ slightly different from the Seidel density is used for plotting the densitometer readings, with the advantage of giving almost linear blackening curves for the particular emulsion employed. Secondly, and in consequence, a parallel motion ruler is added which simplifies and speeds the operations.

¹ Density $D = \log \frac{d_0}{d}$

² Seidel density $S = \log \left(\frac{d_0}{d} - 1.0 \right)$

³ Modified density transform $D_T = \log \left(\frac{d_0}{d} - 0.9 \right)$
ref. Addendum to this chapter.

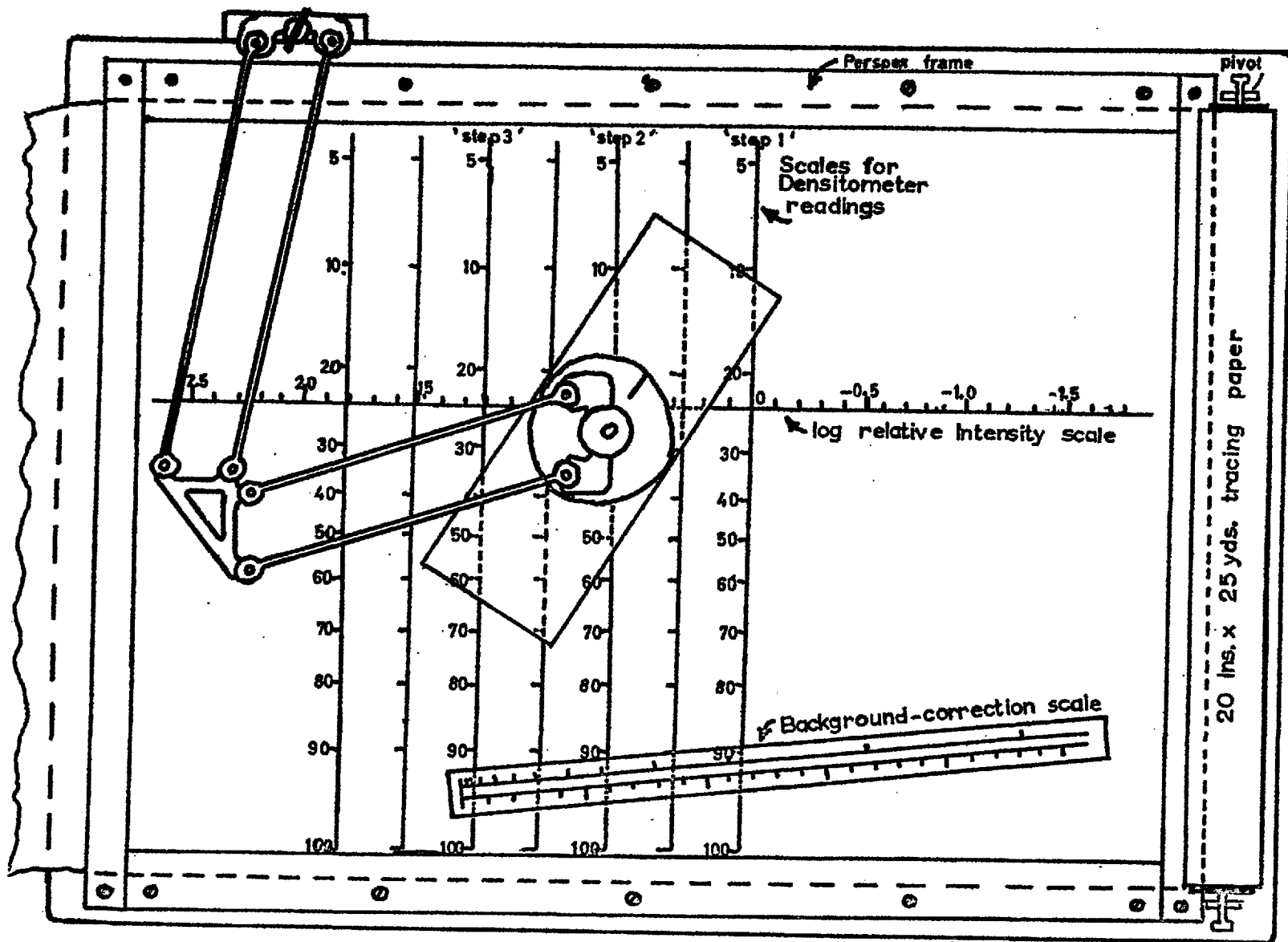


Fig.13 Evaluating Board

0 1 2 3 4 5 6
Scale - inches

A drawing board size 23" x 32" and a parallel motion ruler of adjustable angle are the main components of the board (Figure 13). For convenience, the plotting is done on a sheet of tracing paper overlying the calculating scales (S. R. Taylor, personal communication). The calculating scales (Appendix A4) consist of (a) six ordinates each marked directly in densitometer units but scaled according to the modified density transform, D_T ; (b) a horizontal scale of log relative intensity units, drawn through the "standard density" reading of 24.0 units - a value chosen to agree with the method already used in the laboratory. The horizontal is marked in log relative intensity values which correspond to the exposure factor between the sector steps: thus an interval of 0.602 log intensity units separates the verticals corresponding to steps '1' and '2' of the modified sector, which has a step factor of 4.0; (c) a background-correction scale is drawn separately on transparent plastic material, and used on top of the tracing paper.

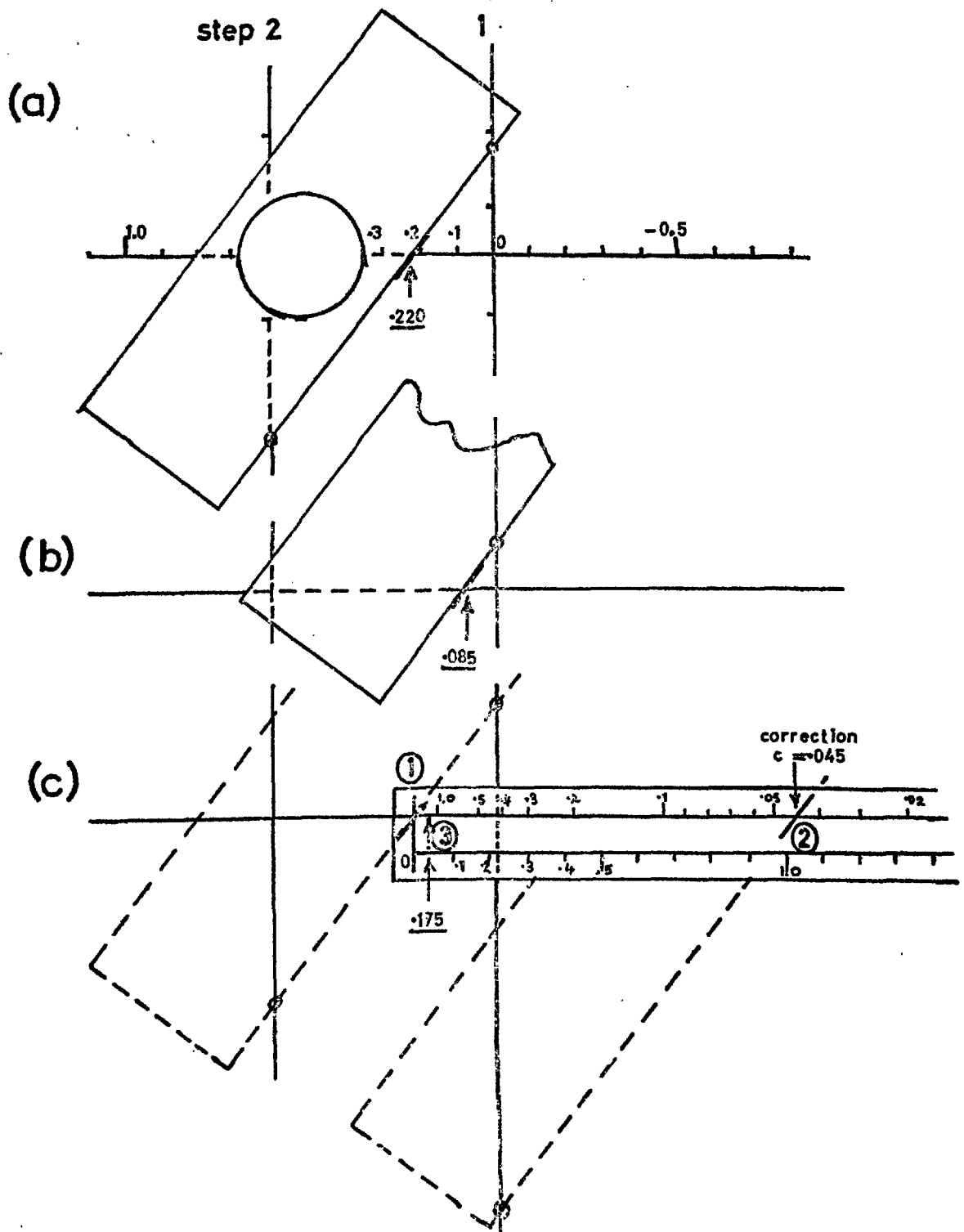
Operation of the Evaluating Board.

The practical operations are illustrated in Figure 14, and summarized below:-

(a) Intensity evaluation from densitometer readings of two spectrum steps.

Each step reading is plotted on the ordinate appropriate to the spectrum step, the parallel ruler is lined up and a

Fig.14 Operation of the Evaluating Board.



short line is drawn at the log I intensity intercept. If no background correction is required the log I value (line plus background) is read off (Figure 14a).

The slope of the ruler is now locked and used for plotting single step readings of other lines of the same or similar wavelength.

(b) Intensity evaluation from densitometer readings of single spectrum steps.

The single step reading is plotted on the ordinate appropriate to the spectrum step; the parallel ruler (which is locked at the blackening slope from a previous two-step reading) is lined up and a short line drawn at the log I intercept. If no background correction is required the log I value (line plus background) is read off (Fig. 14b).

(c) Background correction.

(i) The necessary single-step reading of the background near the line is plotted at the same time as the line (plus background) itself.

(ii) The transparent scale is laid over the two intensity intercepts with its origin at the line plus background intercept.

(iii) The required "correction", 'c' is read off along the upper scale opposite the background intercept.

(iv) The position of this 'c' value is noted on the lower scale and the evaluating board scale opposite this point gives the log intensity of the line free from background (Figure 14c).

(d) Conditions for selecting methods (a) or (b) for line reading and evaluation.

The practical significance of the standard density principle of evaluation is that the closer the step reading to the standard density level, the less is the intensity evaluation influenced by any inaccuracy the slope of the blackening curve. Where a step reading actually coincides with the standard density level, the line relative intensity is defined without any reference to the blackening curve, and the reading of a second step is superfluous. This principle is exploited in the evaluating board, and underlies the following simple rules for selecting the lines most appropriate for each reading method:-

Method (a)

Lines in which two steps straddle the standard density, neither being particularly close to it, are most suitable for reading both steps; the readings also serve to set the blackening slope for single step evaluations.

Method (b)

i. Lines in which one step reading is near the standard density level (e.g. 24 ± 5 divisions) are the most suitable for using the single step method, and the second step need not be read.

ii. Single step readings are necessarily made in weak lines, in background, and also in very intense lines.

Productivity.

A two step plot without background correction takes on average 20 seconds.

A single step evaluation with background correction - the usual routine case - takes from 5 to 20 seconds, depending on whether the background correction is known from a previous line or is individually determined.

Discussion.

Compared with related previous methods, the evaluating board offers the following advantages:-

(a) The linear blackening curve introduced by the modified density scale justifies the use of only two step readings to define the blackening curve for a line, and its correct relative intensity intercept.

(b) The parallel motion ruler facilitates (i) the plotting of single step readings of background etc., and (ii) the use of single-step routine line readings once the plate "slope" has been established by a two step reading in one spectrum.

Both (a) and (b) greatly reduce the number of multi-step readings, which are required in conventional methods for evaluating stepped spectra.

(c) A feature of the evaluating board is that the conventional method using two step readings in every line can be employed interchangeably with the faster, single step method.

Addendum: Density Transform Scale.

One of the new features of the evaluating board is the modified density transform which defines the blackening scales on which densitometer readings are plotted. In common with other density transforms, its purpose is to give essentially straight blackening curves by a mathematical manipulation of the densitometer readings.

The following graphical method was employed for determining the optimum linear transform N30 plates at the most-used wavelengths; the method is equally applicable to any emulsion or wavelength combination. Despite its simplicity it does not seem to be described in the literature.

Figure 15 illustrates the method for one particular wavelength. From a set of densitometer readings for a stepped spectrum line (or an alternative source of graded intensities for calibration purposes), the conventional Density and Seidel blackening curves are drawn. This is facilitated by using a logarithmic ordinate, on which the appropriate $\frac{100}{d}$ and $\frac{100}{d} - 1.0$ values for each step densitometer reading "d", are readily marked (Fig. 15).

A fan of blackening curves may be visualised between and beyond the Density and Seidel curves, all related by being plots of $\frac{100}{d} - "a"$ on the logarithmic scale. The common formula for this "family" of density functions is $\log \left(\frac{100}{d} - a \right)$, "a" being a small positive number, and any

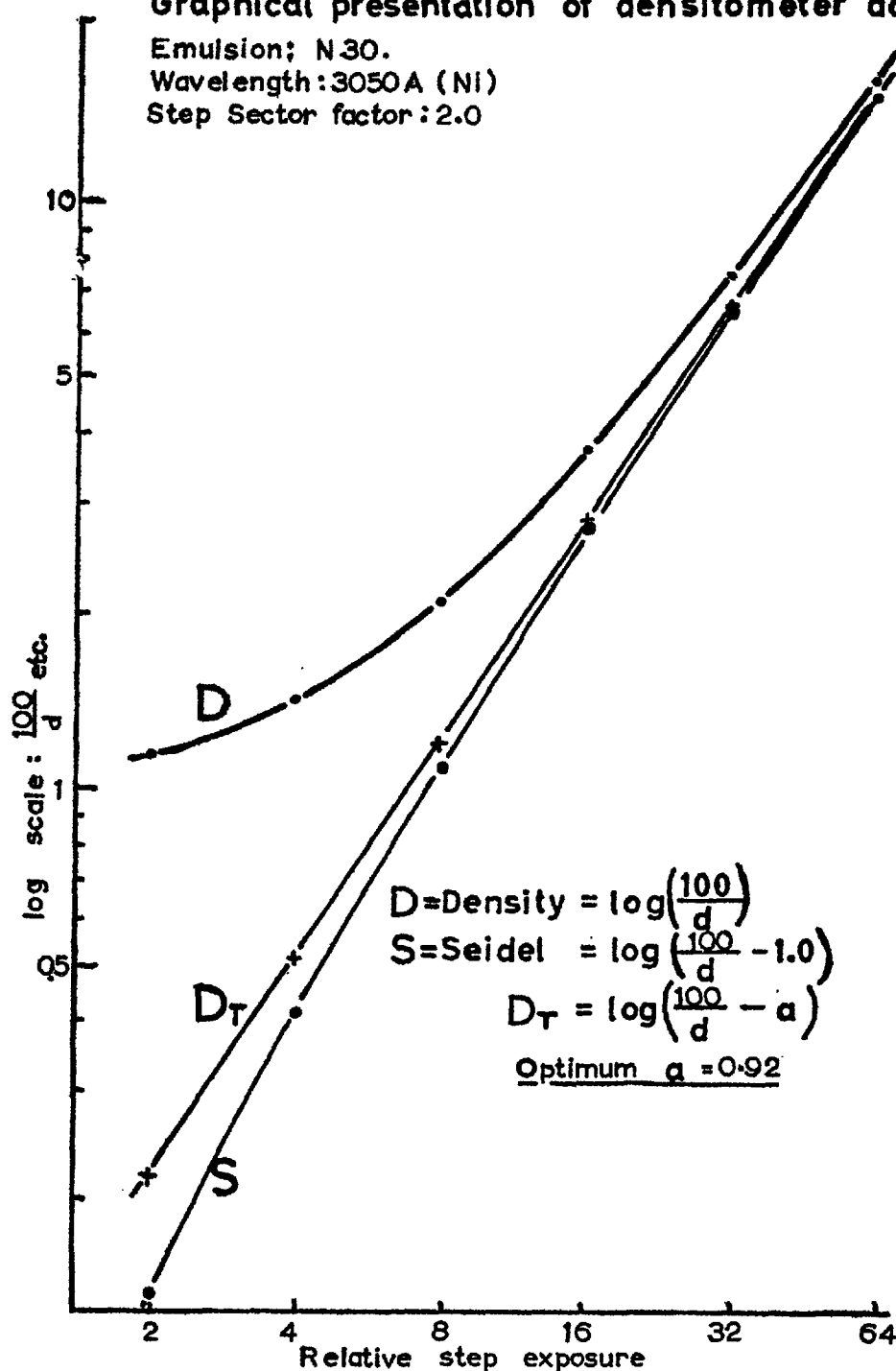
Fig.15 Density Transforms.

Graphical presentation of densitometer data.

Emulsion; N30.

Wavelength: 3050 Å (NI)

Step Sector factor: 2.0



Densitometer readings: d ($d_0 = 100$)

87.75

70.5

48.0

26.5

13.5

6.25

one function is defined by a particular value of this parameter "a".

The method for determining the most linear function for a given set of densitometer readings is now obvious. After drawing the Density and Seidel curves, a transparent ruler is adjusted between them to select the particular value of "a", equal for each step point, which best fits a straight line. For the example shown in Figure 15, the value of "a" was 0.92.

This procedure was followed for twelve lines in the most-used range of wavelengths (2741-4030A), the mean value for "a" being 0.9. The optimum density transform for the routine plates is therefore defined as $D_T = \log \left(\frac{100}{d} - 0.9 \right)$. The values of this function are tabulated in Appendix A4.

Discussion.

The relationships between the present D_T function (in its generalised form) and four alternative density transforms are shown in the following Table.

Density Transforms.

Name or reference	Formula
1. Optical Density	$\log \left(\frac{1}{T} \right)$
2. Seidel density (Kaiser, 1941)	$\log \left(\frac{1}{T} - 1.0 \right) = \log \left(\frac{1-T}{T} \right)$
3. D_T (present author)	$\log \left(\frac{1}{T} - a \right) = \log \left(\frac{1-aT}{T} \right)$
4. Crosswhite and Deike, 1953.	$\log \left(\frac{a'-T}{T} \right)$
5. Kaiser, 1947.	$a'' \log \left(\frac{1}{T} - 1.0 \right) + (1-a'') \log \left(\frac{1}{T} \right) = \log \left(\frac{1-T}{T} \right)^{a''}$

In each case, $T = d/d_0$ represents the densitometer reading, and "a" is the variable parameter for those functions which represent a comprehensive family rather than a single blackening expression.

The comprehensive functions (3, 4, 5, above) differ mainly, from the practical viewpoint, in the method of selecting the value of the parameter giving the most linear function for a particular photographic emulsion.

The parameter in (5) is determined either by calculation or by selecting the best fit from many previously-drawn scales (the Respectra calculator, Kaiser, 1951; Anderson, 1956). The transform family (4) is designed for the easy application of "a" as a variable in the electrical circuit of a modified densitometer. On the other hand, in the writer's transform (3), the parameter is determined graphically without needing special equipment.

SECTION II. GEOCHEMICAL INVESTIGATIONS.

The following five Chapters concern the application of the spectrographic techniques described in section 1, to geochemical investigations of samples from five different field areas. The topics for investigation were suggested by Dr. J. S. Webb, from previous field studies in the Geochemical Prospecting Research Centre, in cases where (a) the multi-element data furnished by spectrography could make a useful addition to previous results based mainly upon single element data (Chapters 6, 7, 8), and (b) in the preliminary examination of samples from new field areas for geochemical reconnaissance or orientation purposes (Chapters 5 and 9).

CHAPTER 5. MALAYA.

Introduction.

The study of field samples from Malaya concerned geochemical reconnaissance for granite areas favourable for tin mineralization, based upon the spectrographic analysis of stream sediment samples. The work formed part of a preliminary geochemical investigation in the region, undertaken in 1957-8 by Dr. J. S. Webb in co-operation with members of the Geological Survey Department, Federation of Malaya. As a result of this preliminary work, a more detailed study on geochemical prospecting for Sn is being pursued by S. Kaewbaidhoon (1961, in preparation).

More generally, the present study was an extension to new terrain of geochemical drainage reconnaissance by means of sampling and analysis of stream sediments, which has been successfully applied in Central Africa by Webb, Tooms and others. Webb and Tooms (1959) describe such reconnaissance

for Cu in N. Rhodesia, with reference to related investigations in Rhodesia (Tooms 1955; Govett, 1958) and Uganda (Holman, 1956); while Jay (1959) and Watts (1960) have investigated the stream sediment dispersions of Co and Nb respectively, also in Rhodesia. These investigations have shown that in favourable cases, anomalous contents of traces of the ore metal may be detected up to several miles downstream from sub-outcropping mineralization.

Applications of spectrography in prospecting for Sn were pioneered by Russian work from 1935 onwards, referred to in Chapter 1 (Ozerov, 1937; Ratsbaum, 1938; Fersman, 1939; Ginzburg, 1957). These applications mainly concern the delineation of mineral occurrences by soil analysis, although in some cases the preliminary selection of areas for detailed examination was made by "panning" for heavy minerals in alluvium. In Sn prospecting studies in Nigeria also, spectrographic analysis of soil and plant materials have been successfully employed (Webb and Millman, 1951; Millman, 1953). The spectrographic determination of Sn in pegmatitic micas was proposed as a method of reconnaissance for favourable Sn areas by Ahrens and Liebenberg (1950), while among other studies of primary geological materials, Jedwab (1955, 1956, 1957) employed the spectrographic determination of Sn and other elements in biotites as a means of distinguishing stanniferous from non-stanniferous

granites of the French Central Massif.

The objective in the present study was to characterise Malayan granites from seven widely separated localities as probably mineralized or non-mineralized, from the composition of the sediments of streams draining the granite hills. Only two to six stream sites were sampled (in duplicate), in each area, in order to test the effectiveness of geochemical reconnaissance on the most economical scale of sampling.

From this limited and economical pattern of sampling, the geochemical data obtained by spectrographic analysis showed (a) a distinction between stanniferous and non-stanniferous granite areas on the basis of the Sn content of the sediments, (b) a sympathetic correlation between Sn and Be, and (c) distinctions in lithology between the different granites based upon the minor element assemblage in the sediments.

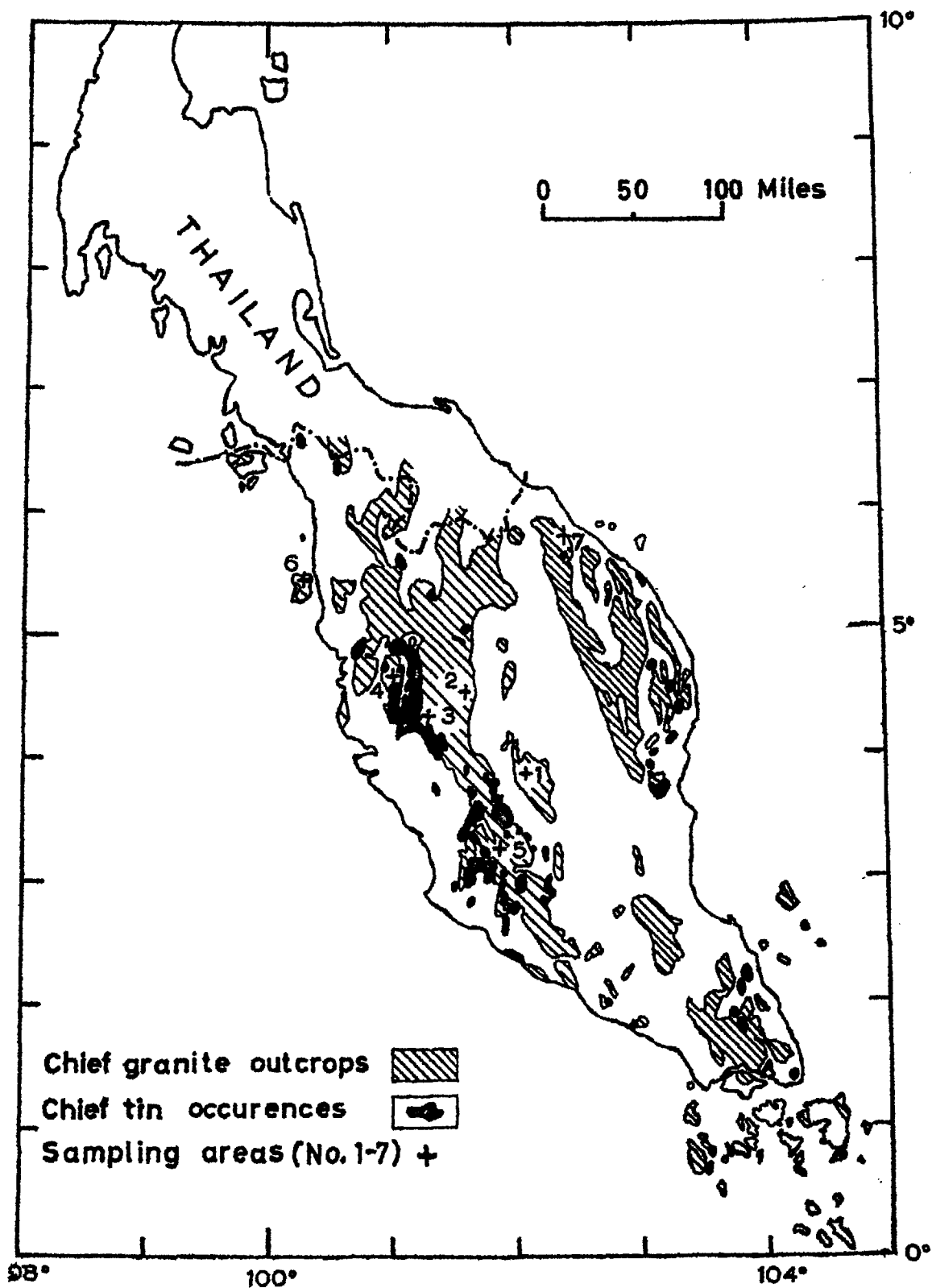
General Description of the Study Area.

The following outline is mainly drawn from authoritative descriptions of the geology of Malaya by Paton (1958), and of geography by Dobby (1958).

Location.

Figure 16 shows the location of the seven sampling areas, the major outcrops of granite, and the chief known Sn deposits.

Fig.16 MALAYA Showing location of sampling areas
for geochemical reconnaissance.



Topography and climate.

Malaya lies near the centre of the Sunda platform, a stable land area until the inundation of the peneplain, which now underlies the shallow seas around the Malay Peninsula. The country thus presents an ancient land surface, and the prevailing tropical climate has led to a combined mantle of weathering products and of jungle, which accentuate the maturity of the landscape forms.

Two main topographic features can be distinguished - wide alluvial plains (with some low undulating country), and relatively high mountain chains, with steep but rounded profiles. The latter in general form parallel ridges with a NNW-SSE trend, parallel to the main fold structures of the Late Mesozoic orogeny, with which the granite is associated. The granite cores of the folds now form the major mountain ranges, following the erosion of the older but softer sedimentary rocks, which remain mostly beneath the valley floors.

The most important mountain chain, the Main Range, lies towards the western side of the country and extends for some 240 miles, rarely below 3000 feet and with peaks approaching 7000 feet; west of the Main Range there are some parallel though lower ranges. A second mountain region lies to the eastern side of the country, also composed mainly of granites, but less extensive and generally lower than the Main Range.

The coastal alluvial plains are widest on the western seaboard, extending up to 12 miles from the coast.

The climate is tropical, hot and humid all the year round. There are monsoon periods in July and November, the latter bringing heavy rain from the northeast, but most of the annual rainfall occurs as heavy showers with little seasonal variation. The annual rainfall is between 75 and 125 inches in the study areas, and average monthly temperatures are within ten degrees of 80° F at all seasons. There is virtually complete cover of thick jungle over the whole country except for man-made paddy-fields, mine clearings, and settlements.

Geology.

The geology of Malaya is not very diverse in character. Until recently only five main rock series were believed to be present, described as follows, in order of increasing probable age:-

1. The granites (Cretaceous).
2. The younger arenaceous series - Quartzite, mudstone, shale, and conglomerate (Triassic).
3. The calcareous series - Limestone, calcareous shale, and shale (Carboniferous-Permian).
4. The Pahang volcanic rocks - Pyroclastic and extrusive rocks, tuffs and lavas, compositions varying from rhyolite-andesite-basalt. Age mainly permian, also Carboniferous and Triassic.
5. The older arenaceous series - Quartzite, conglomerate, shales and chert (Carboniferous).

The correlation of Malayan sedimentary rocks has been based mainly on lithology, since fossils are rare; an improved classification will result when the implications of fossil discoveries which extend the stratigraphical range downwards to the Upper Cambrian, have been worked out (Paton 1958).

The granites, which principally concern the present study, occur abundantly in all States of the Federation. There is little evidence of major compositional variation among the various granite masses. The Table below shows some typical analyses for the Main Range granites (after Roe, 1951).

Analyses of Main Range granites (percent).

Sample No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O
1.	71.64	14.09	0.52	2.26	1.92	0.04	3.83	4.68
2.	74.80	14.71	0.46	1.26	1.16	0.54	2.76	3.67
3.	70.24	17.43	0.33	2.11	2.08	0.99	2.10	3.39
4.	73.10	13.44	0.31	2.03	2.10	0.80	2.89	4.37
5.	74.00	13.86	0.30	1.16	0.58	0.59	0.62	8.39

1. Porphyritic granite from Gap, Ulu Selangor.
2. Fed microgranite, near Tapah, Perak.
3. Granite rich in biotite Cameron Highlands, Perak.
4. Porphyritic biotite granite, Raub District, Pahang.
5. Porphyritic biotite-microcline granite, as above.

Biotite is invariably present in the granite; in some areas this is distinguished by large felspar phenocrysts, elsewhere by the presence of hornblende or tourmaline - particularly on the granite margins. The granites commonly

have more basic margins especially in the eastern parts of the country, where the variation goes as far as quartz-diorite.

Weathering. This usually persists to great depths under the tropical conditions existing in Malaya; in one case a boring penetrated 500 ft. of decomposed material before reaching the solid granite bedrock. The weathering process in granite first breaks down the felspar to kaolin, leading to a mixture of fine clay and coarse sand which may be 50 ft. thick. Blocks of fissured granite disintegrate into rounded boulders within the clay-sand mass; all these products eventually being transported down the stream beds. High precipitation aids the removal of weathered material especially from steep slopes, and indeed it is only in hilly areas with active streams that good rock exposures occur in Malaya.

Soil formation is predominantly one of laterisation, though there are considerable areas of podzolisation. Impeded drainage in the subsoil is common in many areas, with water-logged soils and swamps occurring both on the coastal plains and in valleys inland.

Economic geology.

Malaya is the world's main producer of tin ore, with an annual output of some 62,000 tons of concentrates in 1956. With the exception of the lode tin worked underground near

the southern edge of the east coast granites, and some lodes worked opencast in other areas, the majority of Malayan tin occurs in alluvial deposits, which are worked opencast by either dredging or gravel-pump methods. The same extraction method applies in the limited number of cases where the loose deposits are eluvial, i.e. weathered in situ from the mineralized bedrock.

In general the tin producing areas form two belts, one along the west side of the Main Range granite and its subsidiary ranges, and the other, of much less importance, on the flanks of the east coast granite (Figure 16). Two main zones of production in the western area - the Kinta Valley to the north and around Kuala Lumpur to the south - produce about three-quarters of Malaya's tin. The richest deposits occur in the Kinta Valley west of the Main Range granites, where cassiterite-bearing alluvium lies deeply over the valley floor of eroded pinnacled limestone.

The primary tin lodes are mainly developed in sedimentary rocks into which the granites are intrusive, suggesting expulsion of Sn during the batholithic emplacement; Sn veins also occur, often with quartz and hydrothermal minerals, in the granites themselves.

A general association is apparent between the tin ore and certain granites, and there is little doubt that it originated from the granite itself; the irregular distribution of

individual Sn occurrences is less easy to explain. Although there is some correlation between the occurrence of ore and the existence of limestone in contact with the granite, and the presence of zones of folding and fracture may have favoured accumulation of Sn in some localities (e.g. the Kinta Valley), these correlations with lithology and structure are absent in other parts of the country. It is inferred that some granite masses are less stanniferous than others, and it was to this question that the present geochemical study was indirectly applied.

Field Sampling and Geochemical Investigation.

The seven individual sampling areas (Nos. 1-7, Fig. 16) are described in numerical order. The sequence is chosen arbitrarily by arranging the geochemical results in order to decreasing contents of Cr and V; these elements have fairly homogeneous and distinctive values for each sampling area. The following details of field sampling and spectrographic analysis apply to each area.

Field sampling.

This was carried out between January and March 1958 by members of the Geological Survey Department, Federation of Malaya, in a co-operative geochemical investigation planned by Dr. J. S. Webb.

The writer is indebted to the following geologists who collected samples and provided field geological data from the respective sampling areas:

- | | | |
|---------|----------------------------------|----------------------|
| Area 1. | Gunong Benom, Pahang. | D. Rishworth. |
| 2. | Cameron Highlands, Pahang.) | |
| 3. | Bujang Melaka, Perak. |) E. F. Bradford and |
| 4. | Menglembu, Perak. |) Dr. J. S. Webb. |
| 5. | Ginting Sempak, Pahang-Selangor. | S. MacDonald. |
| 6. | Penang Island. | A. Renwick. |
| 7. | Bukit Yong, Kelantan-Trengganu. | D. Slater. |

Field sampling sites were chosen where road bridges crossed suitable streams draining the granites. Samples were collected from the active sediment in the middle of each stream, taking duplicate samples at every site, usually some yards apart along the stream course. The granites typically form elevated areas which the roads tend to skirt thereby cutting across the radial drainage pattern, and favouring this simple and economical system for collecting samples.

Details of the field samples and spectrographic results are listed in Appendix B₅.

Spectrographic analysis.

The minus 80-mesh fractions sieved from the dried samples were received by the writer for analysis. These samples were ignited at 500°C before analysis by some or all of the following spectrographic techniques, which have previously been described in detail.

Elements determined.	Procedure	Technique (Chapter)
Rb, Li, Ba, Sr, Na ₂ O, K ₂ O .	Anode arc, carbon mixing	A)
Other minor elements	Cathod-layer arc, Li ₂ CO ₃ -carbon buffer method.	) Chap. 2. C ₁)
Major elements	Anode arc, buffer method.	M. Chap. 3.

Sampling Area - 1. Gunong Benom, Pahang.

Gunong Benom mountain (6918 ft.) lies near the centre of a granite complex, roughly circular in outline with a radius of 7 - 12 miles, which forms rugged hill country with some twenty peaks above 5000 ft. This granite complex is isolated from the Main Range granites, which lie to the west.

There has been little organised prospecting within the complex, which is not a tin producing area. Gold occurs in restricted areas outside the granite margins especially to the west near Raub, where an important mine is located. Recent interest has centered on the eastern margins where

magnetite and haematite deposits occur and isolated occurrences of gold, cassiterite and galena have been reported. A boring within the eastern granite area showed high concentrations of ilmenite, iron oxides and pyrite, and traces of allanite, thorite, cassiterite and barites. The margins of the granite area, especially to the west include so-called hybrid and basic igneous rocks (gabbros, syenites and monzonites) which are post-Triassic and have been intruded by the granites. Sedimentary rocks adjacent to the complex comprise argillaceous and calcareous formations lying mainly to the west with sandstones and tuffs to the north.

Field sampling and analytical data.

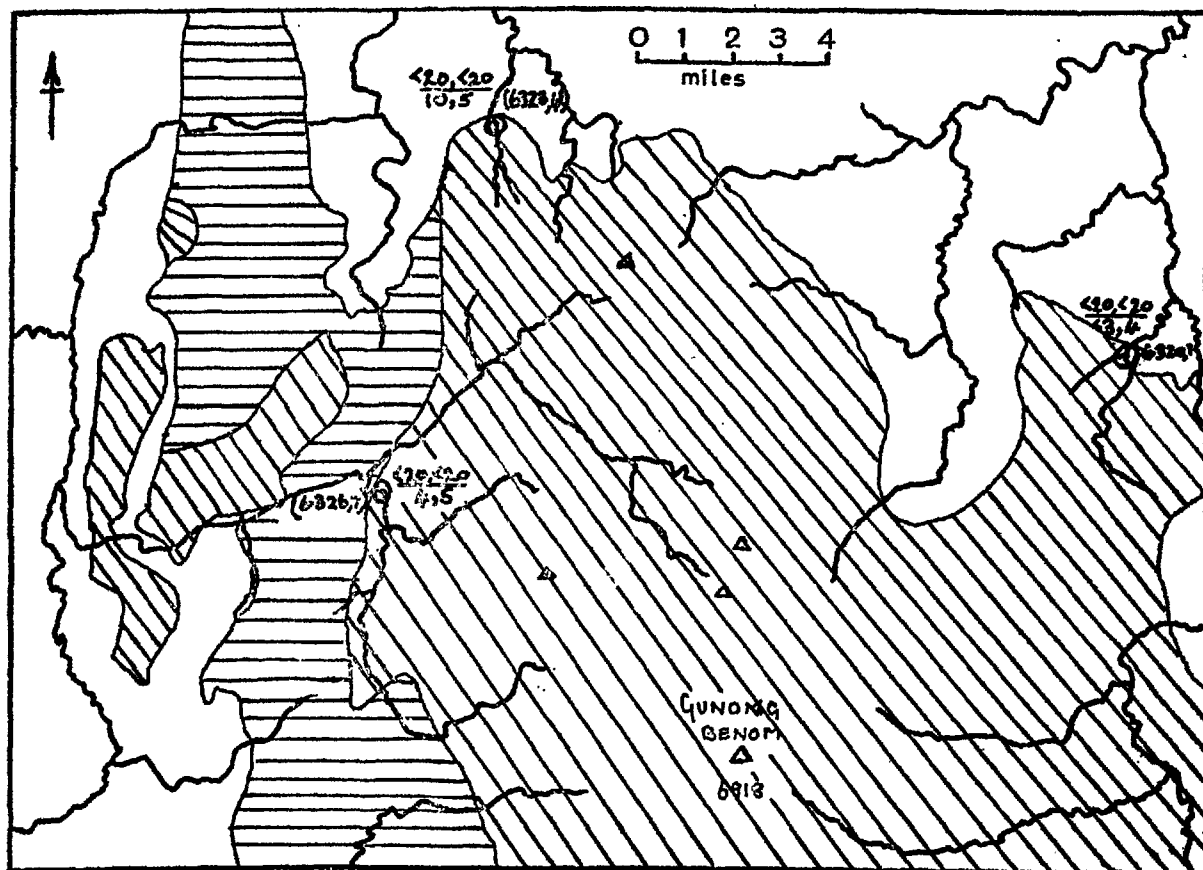
Two sediment samples were collected from each of three streams draining the periphery of the granite area to the northwest, north and northeast. Figure 17 shows their location and the known geology of the area with the spectrographic results for Sn and Be.

The descriptions and complete spectrographic analyses of the six sediment samples are shown in Appendix B₅. The data for the elements of main interest are summarised in Table 17, with the results from other sampling areas for comparison.

Geochemical results.

The data show the following main points of geochemical

Fig.17 Area 1: Gunong Benom, Pahang.



KEY to Figs. J7-22:-

○ sampling site

$\frac{420,420}{4,5}$	Sn ppm
	Be ppm

(6324,7) Sample nos.

 Granite

 hybrid & basic igneous rocks

☐ Sedimentary rocks.

⚒ Tin occurrence.

importance:-

(i) Mineralization. Sn is below the limit of detection (20 ppm.) at all three stream sites. Be, which is associated with Sn in other sampling areas, is also relatively low, rising to 10 ppm. in only one sample, and 5 ppm. or less in the others. Sn and Be values of this order might be expected in normal, non-mineralized granites and, to a first approximation, in the stream sediments derived from them.

The sample results, although limited in number, are consistent in suggesting that the parent granite is non-stanniferous.

(ii) Lithology. The stream sediments in this area are distinguished geochemically from all the others by the relatively high contents of V, Cr, Sr, and Ba. Ni and Co are enhanced to a slight extent. The CaO and MgO contents are also rather higher than in other areas, based upon a single sample analysed for the major elements in each case (Table 17). On the other hand, the major element composition is similar in other respects to samples from other areas, and apart from Fe, the sediment approximates the range of composition for Malayan granites (ref. Introduction). Moreover, the contents of Cu, Pb, Rb and Li are similar to those found in the sediments from other areas, and consistent with the order encountered in acid igneous rocks and derived soils (Mitchell 1955).

In crystalline rocks, V and Cr are typically associated with iron oxides, and also with amphiboles, pyroxenes and micas; Sr with Ca-bearing minerals; and Ba with biotite and potash feldspar, especially in the earliest generations (Lason, 1952). Insofar as the derived sediments reflect the composition of the parent rock in each area (which depends upon the absence of local differences in weathering effects), the Gunong Benom granite may be characterised as relatively the most basic of the seven which were investigated.

Despite the known occurrence of basic igneous rocks outside the drainage area, the sediments probably reflect the geochemical composition of the granite, rather than local drainage from basic igneous rocks, as shown by the relatively low Cu, Ni and Co values. The distinctively high values of V, Cr and Ba in the Gunong Benom sediments are especially interesting in view of the reported occurrence of high concentrations of iron oxides and minor barites in the boring from the granite.

(iii) General. The limited geochemical data suggest that the Gunong Benom sediments, and probably the parent granite, differ in lithology and mineralization from samples taken from other granite areas, as well as being geographically separated from them. The geochemical prospecting evidence is negative as regards tin mineralization - qualified by the preliminary nature of the reconnaissance and the need for more detailed sampling.

Table 17. Spectrographic data, showing mean and range of results (ppm).

SAMPLING AREAS																									
	1.GUNONG BENOM			2.CAMERON HIGHLANDS			STANNIFEROUS GRANITE AREAS									7. BUKIT YONG									
							3. BUJANG MELAKA			4.MENGLEMBU			5. GINTING SEMPAK			6. PENANG ISLAND									
Elements related to tin mineralization:-																									
Sn	<20	<20	<20	20	24	37	35	83	240	140	346	5000	20	200	850	32	56	130	<20	16	27 *				
Be	<3	5	10	4	6	10	4	14	35	20	29	35	<3	15	40 ²	4	15	30	<3	3	4				
													<3	9	25 ²										
Other elements																									
V	55	89	140	25	45	70	25	42	65	20	36	55	7	16	35	7	13	17	5	8	17				
Cr	40	72	100	15	41	70	15	24	40	15	24	32	2	10	30	3	7	10	3	5	12				
Ni	14	37	60	5	21	45	5	11	20	15	25	40	5	16	30	5	10	25	<5	6	15				
Sr	180	253	400	35	49	65	40	46	60	18	22	+25	40	50	60	3	14	+25	3	15	25				
Ba	700	1017	1500	170	245	300	130	189	250	45	48	+50	130	186	240	35	59	+80	60	116	160				
Co	<7	8	15	<7	7	15		<7			<7		<7	4	12		<7			<7					
Cu	5	6	8	2	3	7	3	6	10		2		2	5	30	2	4	10	2	2	3				
Pb	20	62	100	50	71	100	40	57	70	60	77	90	40	56	90	40	92	300	30	40	60				
Li	18	24	35	40	57	80	35	69	120	18	20	+22	20	78	120	40	68	+90	20	37	55				
Rb	350	800	1300	600	790	1000	200	665	1200	350	425	+500	1000	1440	2200	300	558	+1100	150	400	900				
No. of samples	6			10			8			4 +2			24			10 +8			8						
Major components determined in single samples (%):-																									
Al ₂ O ₃	13.8			17.3			22.9			23.1			13.3			17.8			17.4			9.1		6.5	
Fe ₂ O ₃	4.8			2.0			6.0			3.6			1.3			3.3			2.0			0.83		0.5	
CaO	1.6			<0.3			<0.3			<0.3			<0.3			<0.3			<0.3			<0.3		<0.3	
MgO	1.4			0.4			0.8			0.15			0.15			0.8			0.11			<0.1		<0.1	
Na ₂ O	0.55			0.69			0.64			0.11			1.0			0.98			0.77			0.39		0.14	
K ₂ O	6.0			8.0			4.3			1.9			8.1			5.2			5.2			2.8		2.0	
Sample No.	6323			6243			6234			6229			6271			6284			6260			6310		6318	

* Low value, mean, and high value, are shown in each case. Samples below the limit of detection were assumed one half of the limit.

² Selected samples remote from tin workings.

Sampling Areas - 2. Cameron Highlands, Pahang,
and - 3. Bujang Melaka, Perak.

These sampling areas are described together since they are adjacent (Fig. 16). Figure 18 shows the outline geology and the sampling sites in both areas.

Geology of the Cameron Highlands area.

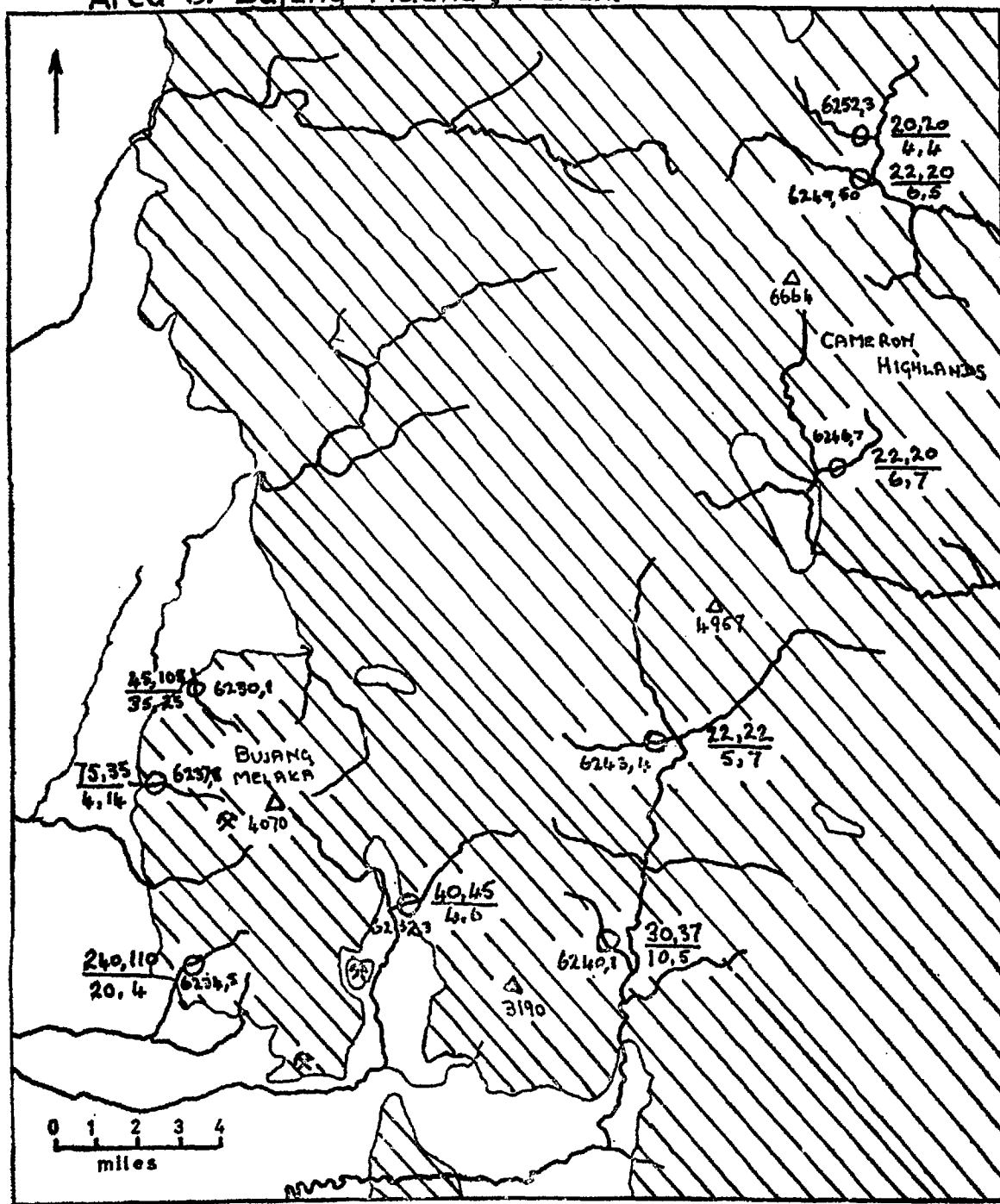
This area forms part of the Main Range granite and is, so far as is known, non-stanniferous in this vicinity. In contrast, large alluvial tin deposits occur in the Kinta valley only some 16 miles to the west, part of which are undoubtedly derived from other portions of the Main Range granite. The rocks in the Cameron Highlands are predominantly biotite granite, but a number of sedimentary roof pendants remain.

Sampling. Two samples of sediment were taken from each of five stream sites spaced over some 20 miles; four of these streams drain granites to the west, and one to the east, of the roughly N-S main road along which they were collected (Fig. 18).

Geology of Bujang Melaka area.

The Bujang Melaka granite forms a dome-shaped boss roughly elliptical in outline, and approximately 10 miles by 5 miles along each axis. It forms a distinct topographical feature although it is no more than an offshoot of the Main Range granite. Coarsely porphyritic, grey, medium-grained

Fig.18 Area 2. Cameron Highlands, Pahang.
Area 3. Bujang Melaka, Perak.



biotite granite predominates, with some marginal micro-granites and aplites, especially tourmaline aplites. The area is stanniferous: mineralized pegmatites occur in three distinct areas, in which the minerals cassiterite, wolframite, galena, chalcopyrite, beryl, pyrite, arsenopyrite, fluorine minerals and rare molybdenite have been reported. Two of the pegmatite areas have been mined and one is still a small producer of tin. Bujang Melaka lies, however, on the eastern edge of a major alluvial mining district.

Sampling. Two sediment samples were taken from each of four streams, three draining radially from the Bujang Melaka dome, and the fourth draining from the Main Range granite to the east (Fig. 18).

Analytical data for Cameron Highlands and Bujang Melaka.

Spectrographic analyses for the ten sediments from the Cameron Highlands and the six from Bujang Melaka are tabulated in Appendix B5; Table 17 summarizes the data for the elements of main interest.

Geochemical results.

(i) Mineralization. Higher mean values for Sn and Be distinguish sediments derived from the mineralized Bujang Melaka granite from the barren Cameron Highlands area, and from two other areas which are probably non-stanniferous (Areas 1 and 7, Table 17).

Referring to Table 17, it may be noted that threshold values of 48 ppm Sn, and 12 ppm Be are obtained by doubling

the mean values from areas believed to be unmineralized. These threshold values are essentially gauged by inspection; the 2-fold factor ensures their significance compared with the order of error of $\pm 50\%$ in the spectrographic results. The estimates may be rather high, since no single background sample exceeds the threshold values. Four probably stanniferous areas are clearly distinguished, by mean values of both Sn and Be above the respective threshold values. These comprise areas 3, 4, 5 and 6 (Table 17), three of which are known to be mineralized, and a single Sn occurrence has been reported in the fourth area, independently of the geochemical results.

In comparing the Sn and Be data for Bujang Melaka and the Cameron Highlands, the geochemical distinction based upon the mean data is emphasised by considering the individual sampling points (Fig. 18). Although the number of samples is limited and confirmatory work is required, the data suggest that three granite areas can be distinguished from the sediment analyses:- (a) a barren area drained by four streams lying north and south of the Cameron Highlands proper; (b) the mineralized Bujang Melaka area, represented by three radial stream sites, and (c) a transition area, consisting of a single granite hill lying between areas (a) and (b), and drained by two streams. The sediments

from streams draining each area show the following values:-

	No. of stream sites	Range in ppm.	
		Sn	Be
(a) Barren area (Cameron Highlands)	4	20-22	4-7
(c) Transation area	2	30-45	4-10
(b) Mineralized area (Bujang Melaka)	3	35-240	4-35

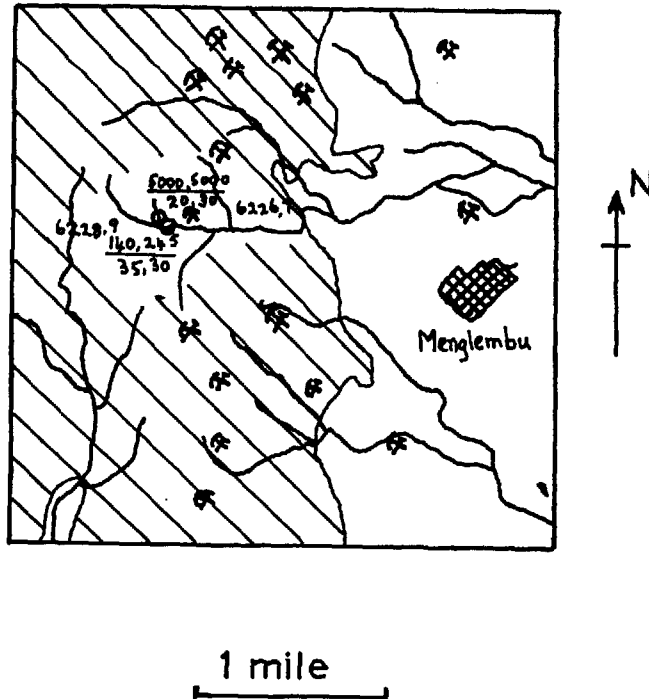
(ii) Lithology. The contents of minor elements other than Sn and Be show broad similarities between the Cameron Highlands and Bujang Melaka areas. The low Cr and V content suggest that the parent granites are less basic than that of Gunong Benom (Area 1), and not much different from the Menglembu area (Area 4) which also lies within the boundaries of the Main Range granite (Table 17, Fig. 16).

Sampling Area - 4. Menglembu, Perak.

This area lies on the western edge of the Kinta valley tin producing area. Lode tin occurs in the Menglembu granite, and the risk of contamination from previous mining activity made the area unsuitable for systematic reconnaissance sampling. However, two test samples were taken in duplicate from a small stream and its tributary (Fig. 19).

The Menglembu granite forms an outlier close to the western edge of the Main Range granite, and probably connected with it beneath the intervening sedimentary deposits, mainly of limestone.

Fig.19 Area 4. Menglembu, Perak.



The analytical data are shown, as before, in Appendix B5 and in summary in Table 17.

The four samples show the following main points of geochemical importance:-

(i) Mineralization. The mean Sn and Be values are higher than in any other area, and the individual samples all show values of Sn and Be above the threshold levels calculated from non-mineralized areas (Table 17). The difference in Sn values (approximately 190 and 5,000 ppm) between the two individual streams may reflect only different degrees of contamination, although it may be significant that the higher value occurs in the faster stream, where residual concentration of cassiterite could be expected. The Be values do not vary sympathetically with Sn in individual samples.

(ii) Lithology. Sediments from the two streams have similar values for most elements other than Sn; the data, (Table 17) show a geochemical pattern for the ferrides not greatly different from the Main Range granite areas of Bujang Melaka (stanniferous) and Cameron Highlands (non-stanniferous). Both the major and minor alkali elements are however relatively low in the individual samples which were analysed; the lack of correlation between Sn on the one hand and K_2O , Li and Rb on the other is noteworthy, although in secondary materials leaching could produce this result independently of a possible primary association.

Sampling Area - 5. Ginting Sempak,
Pahang - Selangor Border.

This rugged area comprises part of the Main Range granite lying some 90 miles to the south of the preceding areas, Nos. 2, 3 and 4 (Fig. 16). The region contains several old workings for both lode and alluvial tin, and the valleys bordering the granite uplands are important present-day alluvial producers.

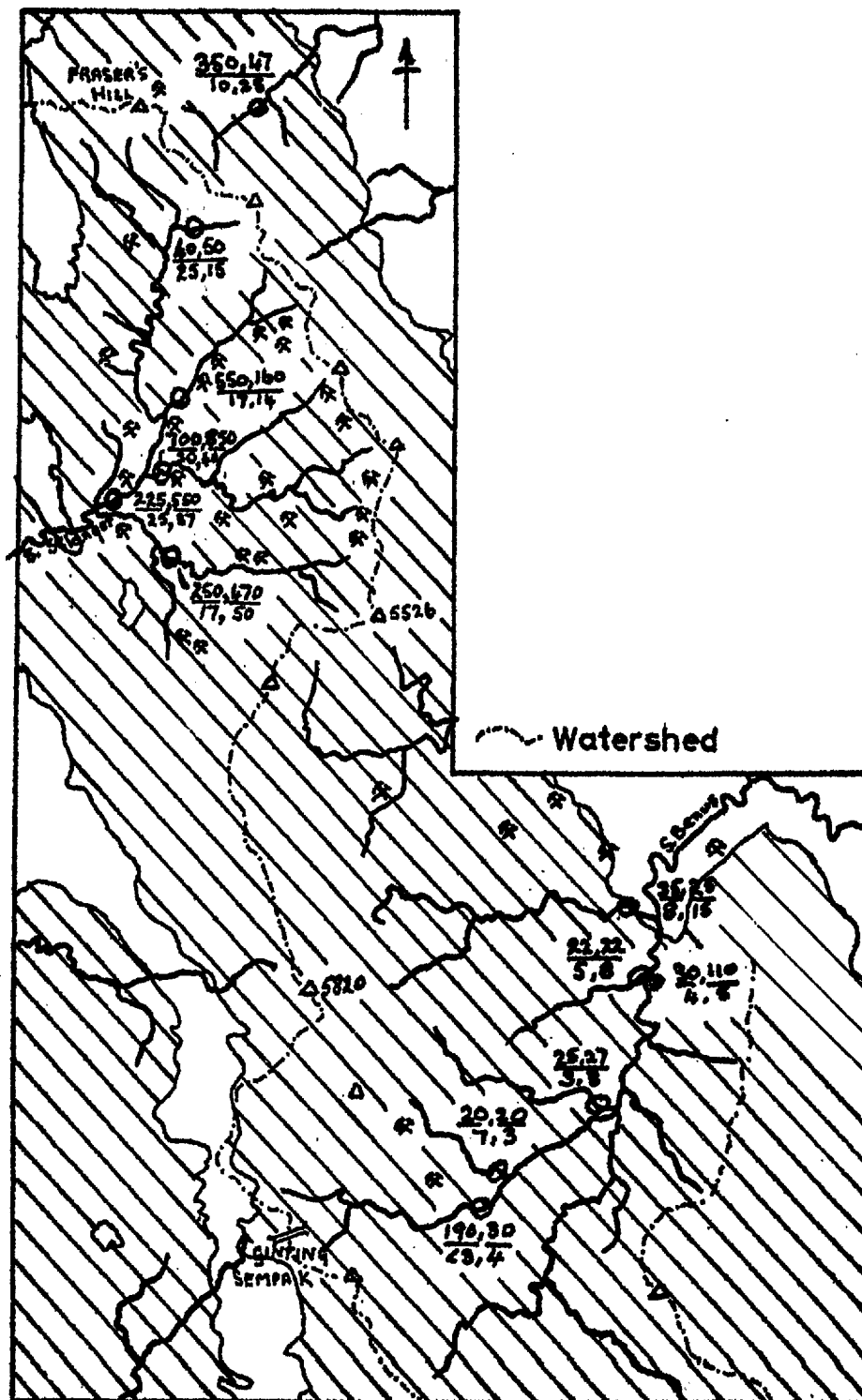
The granite is predominantly a medium grained biotite granite with local development of granite-porphry and micro-granite, and intrusions of aplite and pegmatite. In mineralized areas, cassiterite occurs associated with pneumatolytic minerals including tourmaline, mica, fluorite and topaz. Tin ore is usually located in fracture zones in the granite in thin quartz-tourmaline stringers. Few veins are rich enough to support underground mining methods and the prohibition, in 1933, of mining by sluicing eluvium from the weathered granite slopes, led to the abandonment of most tin workings in the area (Roe, 1950).

Figure 20 shows the twelve stream sampling sites, at each of which duplicate sediment samples were collected, the analytical results for Sn and Be, and the local geology.

Analytical data.

The spectrographic analyses for the twelve sediment samples are given in Appendix B5, with the results for the

Fig.20. Area 5. Ginting Sempak, Pahang - Selangor.



elements of main interest summarised in Table 17.

Geochemical results.

There is a considerable scatter of values between the sampling sites, and in some cases between duplicate samples at a given site, especially for Sn itself. This probably reflects (a) the erratic distribution of individual grains of cassiterite in samples; or (b) possible contamination from old mine workings. A significant geochemical pattern emerges, however, by comparing both the mean and the range of Sn contents with those for other sampling areas (Table 17).

(i) Mineralization. The average and the peak values for Sn and Be clearly reflect the mineralized nature of the Ginting Sempak granite, when compared with threshold values calculated for non-mineralized sampling areas. Even when all the samples noted as being possibly contaminated (field data Appendix B5) are omitted from the results, the anomalous regional content for Sn still reflects the mineralized nature of the Ginting Sempak granites (Table 17).

(ii) Lithology. The geochemical data for many elements other than Sn and Be show some similarities with sediments from areas 2 and 3, north of Ginting Sempak, which also lie within the Main Range granites. The fact that V and Cr are relatively lower may reflect the low iron content in some of the samples met in this area.

Sampling Area - 6. Penang Island.

Penang Island lies off the West coast of Malaya, some 180 miles northwards from the preceding sampling area (Fig. 16). Peaks in the northern half of the island, where sampling took place, rise to some 2,500 feet. The entire island consists of granite bedrock. The only report of mineralization is from one locality on the northern coast, said to contain alluvial cassitierite and associated niobium-tantalum minerals.

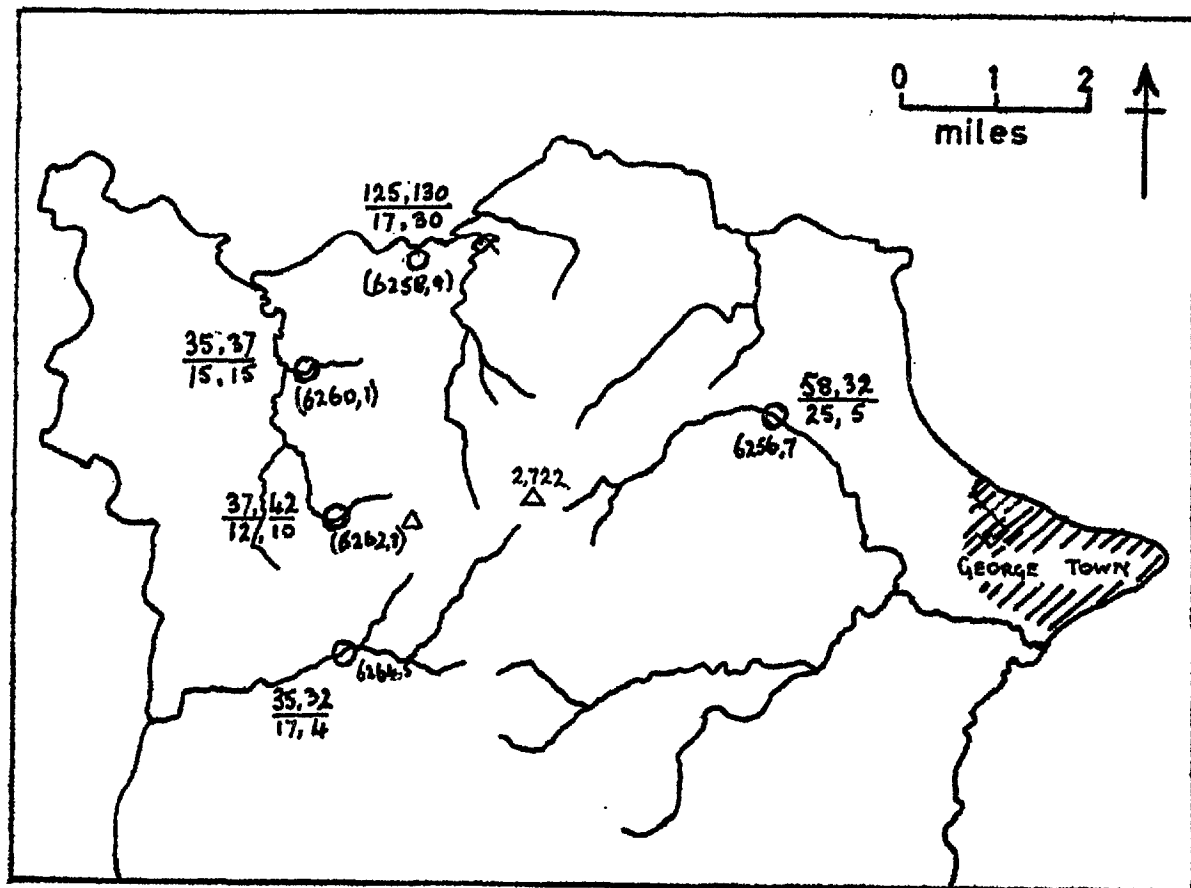
Figure 21 shows the location of the five stream sampling sites, at each of which two sediment samples were collected.

The spectrographic results are tabled as before in Appendix B5 and in Table 17.

The pair of samples taken at each site (Fig. 21) show generally good agreement, probably reflecting the absence of (a) coarse SnO_2 and (b) mining contamination in this area.

(i) Mineralization. Both Sn and Be are detected in all samples, and the mean values compared with un-mineralized sampling areas suggest that the Penang granite is probably stanniferous, despite the discovery so far of only one concentration in the area (Table 17). It is noteworthy that the highest Sn and Be values occur at the site draining northwards from the hills, as does the one reported occurrence of alluvial tin.

Fig.21 Area 6. Penang Island.



Values for Sn and Be in the Penang sediments are little lower than those for the Bujang Melaka area, which is known to be stanniferous. The similar number of samples taken, and the similar disposition of sites sampling the radial drainage, justify comparing the two areas directly (Table 17). The similar mean contents of Sn and Be suggest that the two granites may have similar potential for mineralization, although this need not, of course, imply the occurrence of similar economic concentrations in the two areas.

Further prospecting of the Penang area should be undertaken.

(ii) Lithology. Elements other than Sn and Be in the sediments, show rather lower contents of V, Cr and Ni than in previous areas, but relatively high values for Pb, Li, Rb and K_2O . These suggest the retention of resistant micas from the parent granites, along with quartz, in these mainly light coloured sediments (see also Bukit Yong area, below).

Sampling Area - 7. Bukit Yong,
Kelantan-Trengganu Borders.

This, the final area investigated, is situated in the north-eastern corner of Malaya, some distance from the granite areas previously described (Fig. 16).

Bukit Yong mountain is composed entirely of granite, and lies towards the northern end of the east coast granite range.

Although important lode and alluvial tin deposits occur at the southern end of this range, the main mass is apparently barren. No tin is produced in the Bukit Yong area although cassiterite has been reported as a minor accessory mineral disseminated in the granite.

Four radial streams were sampled in duplicate (Fig. 22).

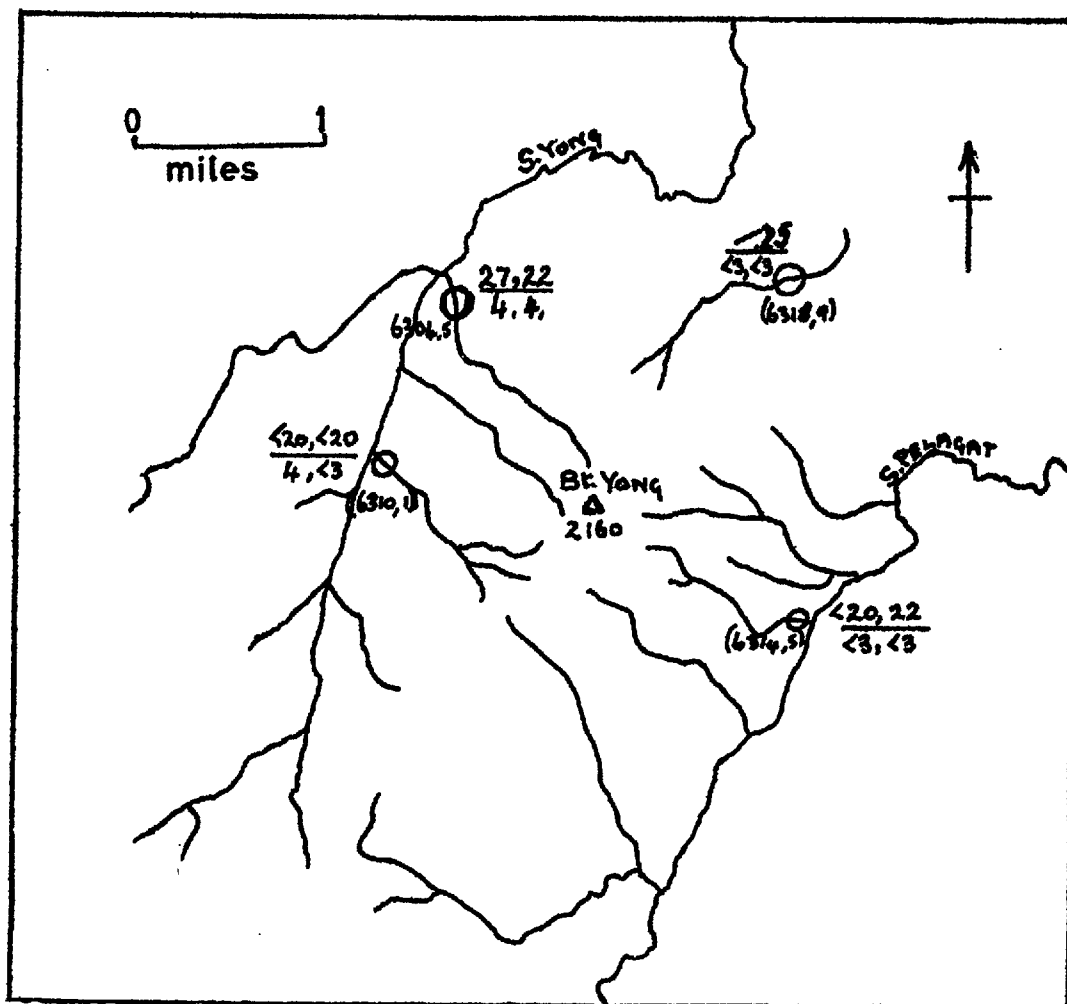
The spectrographic results tabulated in Appendix B5 and summarized in Table 17, show the following features:-

The pairs of samples taken at each site agree well, with the exception of a single high value for tin (320 ppm) which was not confirmed by a chemical method, and was therefore omitted from consideration in the results.

(i) Mineralization. Disregarding the single erratic high value for Sn, all other Sn and Be results are distinctly low compared with sediments from other sampling areas (Table 17). The limited data suggest that the Bukit Yong granite is probably not significantly stanniferous.

(ii) Lithology. Data for elements other than Sn and Be in the Bukit Yong sediments show some broad similarities with samples from Penang Island (Table 17). The Bukit Yong samples have the lowest contents of Cr, V, Fe_2O_3 and Al_2O_3 of the sediments examined. This is reflected in the pale colours in the samples.

Fig. 22 Area 7. Bukit Yong, Kelantan.



General Discussion.

Taking the results from the seven sampling areas together, the following main points emerge from this preliminary geochemical reconnaissance.

(1) Sampling and interpretation of results.

The sampling pattern was notable for its economy - both in the small number of samples representing each area, the use of stream sites close to the motor roads, and the collection of sediments simply as grab samples from the stream courses. All the sediments collected were analysed, and the results compared without segregating samples according to their appearance in the field, nor by the colour and bulk composition of the analytical samples. In view of this, some degree of scatter in the sample results within each area is to be expected. Jay (1959) for example, observed in work in Rhodesia that Co values varied up to ten-fold between sandy and clayey sediments collected within a few yards of each other in a single stream. In general the scatter is relatively low for many elements in the present study areas except for Sn and to a lesser extent Be. This is probably due to the fact that these elements are likely to occur as discrete mineral grains, while most other elements are liable to trace constituents of common minerals. The validity of using stream sediments as a method for areal sampling is best shown in Gunong Benom, where three sites, 8 and 14 miles apart,

show less than a 3-fold range of content for most elements (Table 17).

Providing the mean analytical results are considered, significant chemical distinctions can be made between the different areas, from this limited and economical pattern of samples.

(ii) Tin mineralization. A distinction between stanniferous and non-stanniferous areas can be made on the basis of (a) the mean Sn content and (b) the mean Be content of the sediments. The approximate threshold values distinguishing mineralized from non-mineralized areas are 48 ppm Sn and 12 ppm Be.

The data suggest an indirect association of Be with Sn mineralization. Individual samples do not show a detailed correlation between the two elements, but the mean values for sediments from each sampling area show a high regional content for Be in stanniferous areas, and vice versa (Table 17). It is probable that the two elements occur in separate minerals but have a common origin associated with the granite: Sn and Be are often associated in late pegmatitic solutions, and cassiterite and beryl occur together in some Malayan pegmatites.

Time did not permit an investigation of the mineralogical form of Be and Sn in the sediments, which would be an interesting topic for future work. The separation and

analysis of heavy and light mineral fractions would be one appropriate method.

(iii) Lithology. Apart from mineralization, lithological distinctions between the different granites can be inferred from the minor element assemblage in the sediments. The results are necessarily tentative in view of (a) the absence of hard rock samples, (b) the probable variations in leaching and weathering effects and (c) the limited number of samples. Nevertheless, the Gunong Benom area stands apart from the rest by the characteristic "basic" facies of the stream sediments; while the other areas can be arranged in order of the decreasing content of the ferride elements, which have fairly homogeneous values within each area.

(iv) Summary. Geochemical reconnaissance is aimed at selecting areas more favourable than others for further, more detailed prospecting examination. The present investigation showed that significant reconnaissance information can be obtained from spectrographic analyses of a small number of easily-collected samples. Moreover, the multi-element spectrographic data provide (a) coverage for possible complex mineralizations, in this case Be as well as Sn, and (b) indications of variation between samples from different areas, related to changes in lithology.

Further work along these lines in Malaya has confirmed these preliminary results. Two separate reconnaissance investigations in N. Rhodesia, one in a niobiferous carbonate area and the other in the Copperbelt, have shown marked differences in a number of elements in the sediments, indicating the presence of at least two distinct geochemical provinces.

CHAPTER 6. THE COPPERBELT OF NORTHERN RHODESIA.

In contrast to the application of spectrography to geochemical reconnaissance in Malaya, the study of samples from the Copperbelt mainly concerned the effects of weathering and soil-forming processes on the vertical distribution of the ore metals Cu and Co, and several other elements. For this purpose, samples from six soil profiles were examined. In addition, a limited investigation was made of lateral geochemical dispersion in near-surface materials.

The study was suggested by Drs. J. S. Webb and J. Tooms, and based upon field samples mainly provided by them; it forms a continuation of previous work in the Copperbelt by these and other members of the Geochemical Prospecting Research Centre. This includes investigations by Tooms (1955) and Govett (1958), concerning mainly Cu and to some extent Co in soils and stream sediments; by Webb and Tooms (1959) on geochemical reconnaissance by the analysis of Cu and Co in the drainage system; and by Jay (1959) concerning the geochemical dispersion of Co and U. The previous workers generously made available certain of their field samples, on which the present work is based. In addition to the foregoing fundamental studies, the mining groups in the area - without whose co-operation the former and present work would have been impossible - have been engaged for some time in applied geochemical prospecting. Published reference to these

activities are made by Garlick (1953, 1959) and Williams (1960).

For the present study, six profiles of freely-drained soils were examined, each developed upon different rock-types characteristic of the region. These profiles were studied in some detail in order to determine and compare the dispersion patterns for particular minor and major elements under the soil-forming conditions which apply within each profile.

A second, smaller, group of samples selected from near-surface traverses were analysed, in order to compare the surface contents of Cu, Co, and other elements developed over the sub-outcrop of mineralization in two different environments, namely, freely-drained soils compared with poorly-drained soils extending into a stream-sediment train.

The objective of the study was to add the multi-element data furnished by spectrographic analysis to that obtained in previous work on the geochemical dispersion of Cu and Co. At the same time, inter-element associations which might be of value in prospecting, were sought between the main ore-metals and others not so intensively studied in this area.

While the new data reveal no elements other than Cu and Co as effective indicators of mineralization, useful observations were made on the effect of soil-forming processes in the Copperbelt environment, upon distribution of the ore-metals and other elements.

General Description of the Study Area.

Anton Gray (1929), Davidson (1931) and Jackson (1932) provide accounts of the geology of the Copperbelt which have been drawn upon by the writer. More recent geological data and discussions are contributed by Garlick and Brummer (1951), Garlick (1953) and Darnley (1958, 1960), while Dixey (1943, 1944) has investigated the geomorphology of the region in detail.

Descriptions of the geology in the field areas of the present study are provided by Govett (1958), Tooms and Webb (1959) and Jay (1959) and are quoted in part in the following summary.

Location and topography.

The location of the study areas within the Copperbelt are shown in Figures 23 and 24.

Broadly, the present-day land surface is an elevated peneplain situated at an altitude of about 4,000 - 4,500 feet; the most widespread surface within the Copperbelt represents a peneplanation of late-Tertiary age. The terrain is dominantly flat or gently undulating with slopes rarely exceeding 1-2° except near the streams and rivers, where gradients increase as a result of local erosion following rejuvenation of the drainage system.

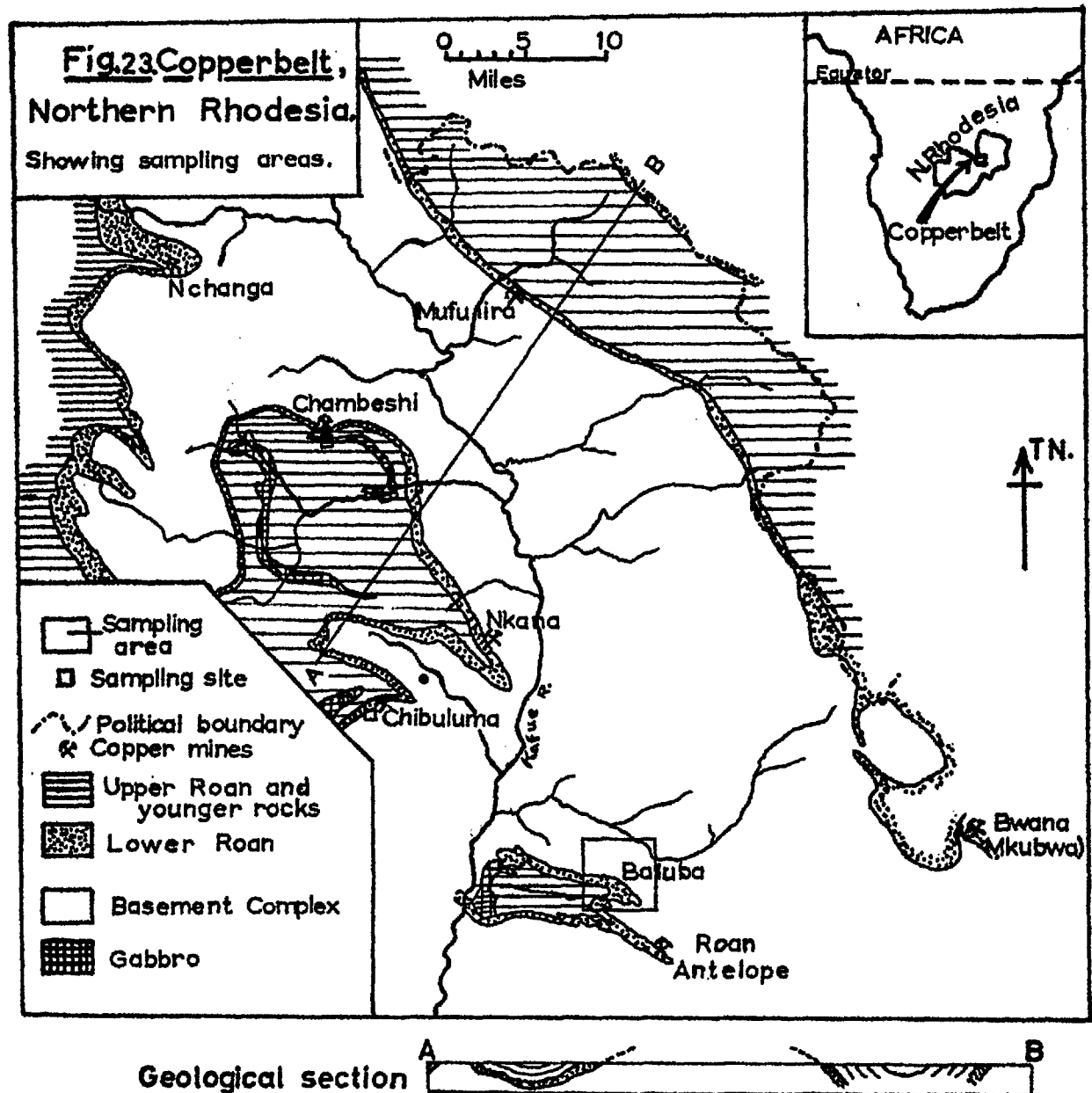
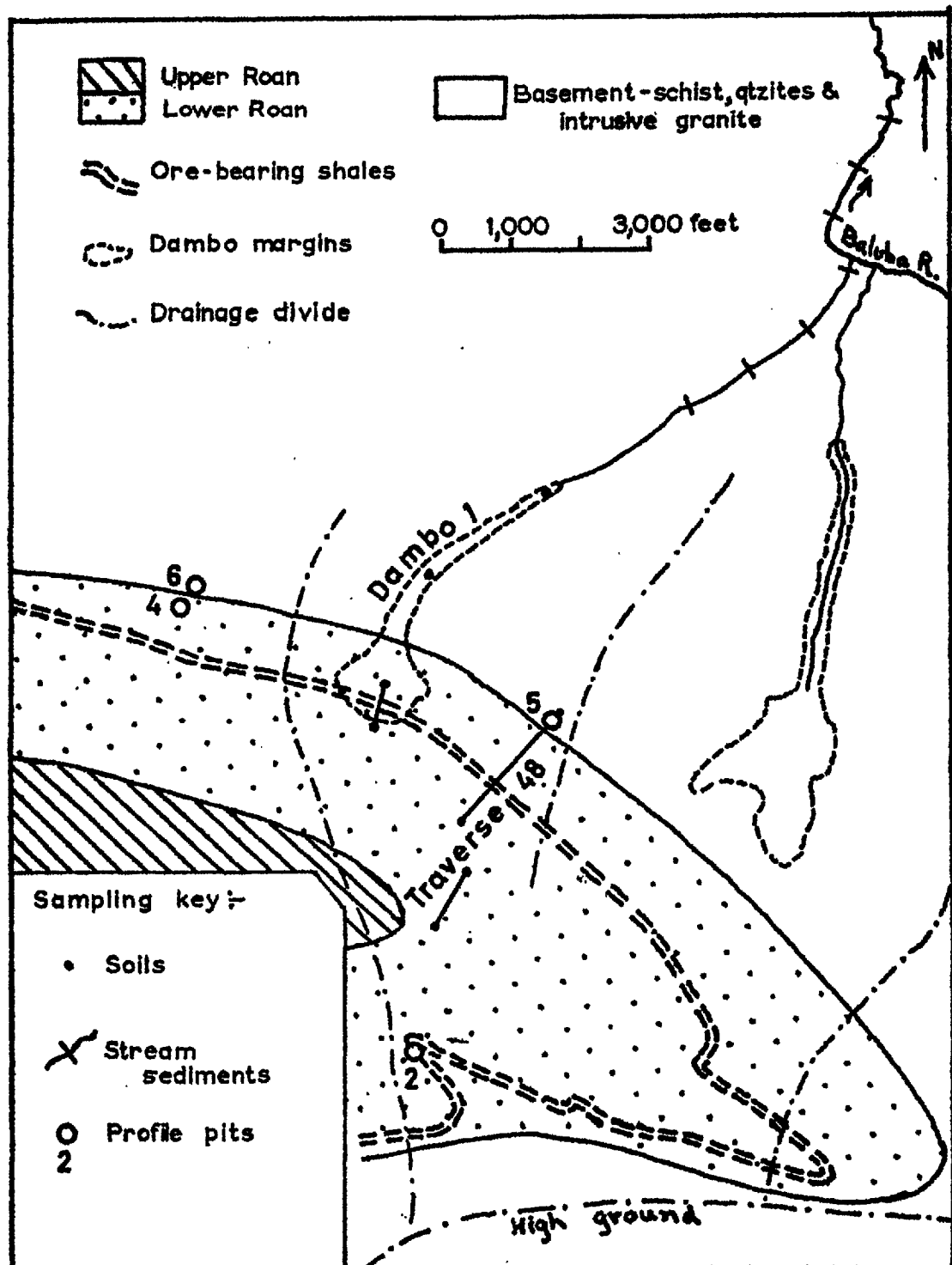


Fig.24 Baluba area , showing sampling sites.



Climate and vegetation.

The Copperbelt enjoys a sub-tropical climate, since the relatively high altitude reduces the temperatures and humidity which would otherwise prevail at this latitude. The climate is markedly seasonal, with dry, temperate winters and warm, wet summers. Almost all the total annual rainfall of 45-50 inches, falls between November and May, mainly as heavy thunder showers. The mean daily maximum temperatures are about 87° and 57° in October, falling to some 77° and 42° in July.

The vegetation consists of open forest ^a savannah which covers the region. Almost the only natural clearings are the small scattered grassy areas of swampy ground, often seasonal swamps, known locally as dambos. These shallow depressions often form the "headwater dambos" of streams, although a second type of dambo occurs along the downstream courses. In total they occupy only 10% of the land area.

Weathering and soil formation.

Prolonged tropical weathering coupled with low surface relief ensure that weathering is far in advance of erosional transport, so that deeply-weathered residual soils, some 20 or even 60 feet thick, are characteristic of the region. A detailed soil classification is beyond the scope of the present investigation, and it is sufficient to distinguish the two extreme soil types which occur under freely-drained

and dambo (impeded drainage) conditions, respectively.

The first group are included in the "Plateau Soils" of the Rhodesias, which are apparently related to the ferruginous lateritic soils of the Transvaal (Wellington 1955, p. 331). These soils are characterised by a pronounced iron nodule horizon, and will be referred to as latosols, as recommended by Kellog (1948). The following idealised profile description is taken from Jay (1959), based upon measurements of several freely-drained profiles on different rock types.

Idealised freely-drained soil profile.

Horizon	Thickness	Description
A ₁	1 in.-3 ins.	Light to dark brown sandy loam.
A ₂	2 ft.-10 ft.	Buff to reddish brown clay or sandy clay.
Stone Line	1 in.-6 ins.	Quartz or other rock fragments in clay.
B	2 ft.-6 ft.	Red-brown ferruginous clay with or without ferruginous concretions.
C ₁	4 ft.-10 ft.	Off-white and reddish brown mottled clay.
C ₂	4 ft. +	Very pale clay. Decomposed bedrock at base.

The soils developed under the conditions of poor drainage and seasonal flooding in the dambos, can be described as gley soils, being characteristically bleached and clayey below some 12-18 inches. The surface and sub-surface horizons are black to grey due to the high content of organic matter.

Also in contrast with the freely-drained soils, nodule accumulations are normally absent. It is probable that the dambo soils, at least in the "headwater dambos" are mainly residual in origin (Tooms 1955).

The stream sediments in the area, a few samples of which were involved in the present study, consist mainly of re-distributed dambo and bank soil materials.

Geology.

Beneath the mantle of residual weathering products, the geological formations of the Copperbelt form an essentially simple succession.

A simplified stratigraphic column for the Copperbelt-Katanga region is shown in Table 18, and an outline geological map in Figure 23.

The Basement Complex, comprising Archaean schists, gneisses, quartzites and conglomerates, with intrusive granites, outcrops extensively within the Copperbelt. A major unconformity separates the Basement from the sediments of the Katanga System, whose lowest group, the Lower Roan, contains all the known Copperbelt ore bodies. Folding, followed by erosion, has left only the synclinal remnants of the Katanga System, and the enclosed bedded mineral deposits, within the margins of the Copperbelt. Metamorphism is evident throughout the Copperbelt-Katanga region, and metasomatism of various types can be recognised in rocks

Table 18. Simplified stratigraphic column (after Garlick, 1953).

System	Series	Group	Formation
KATANGA SYSTEM	Kundelungu Series	Upper Kundelungu	Sandstones
			Shales
			"Calcaire Rose"
			Small Tillite
		Lower Kundelungu	Sandstones
			Shales
			"Serie Recurrant"
			Kakontwe Lime-stone.
	Mine Series	Mwashia	Big Tillite
			Carbonaceous Shales
			Quartzite
			Argillite
		Conglomerate	
		Upper Roan	Dolomites and Shales
Lower Roan	Quartzites		
	Argillites		
Conglomerates			
-----Unconformity-----			
BASEMENT COMPLEX:-			Quartzite,
MUVA SYSTEM			Schist and
			Conglomerate
LUFUBU SYSTEM			Schist, Gneiss
<u>Intrusives:</u> Granites have to date been found intrusive only into the Lufubu System.			
Gabbro and minor granophyre intrusions occur in the Upper Roan, Mwashia, and Kakontwe Limestone.			

ranging from the Basement granites through almost every formation of the Katanga System (Darnley 1960). Nevertheless, field evidence of post-Basement igneous activity is not very widespread within the Copperbelt.

Granitic intrusives have to date been found only within the Basement complex (Garlick and Brummer 1951). Basic igneous rocks mainly comprise gabbroic sills occurring within the Upper Roan, Mwashia and Kakontwe Limestone (Garlick 1953).

Economic geology.

The Copperbelt ores consist of disseminated Cu, Co and Fe sulphides in varying proportions, confined within beds of the Lower Roan sediments. Two main host rocks can be distinguished, namely ores in argillite and in ortho-quartzite; either type may be more or less calcareous. The ore horizon rarely exceeds 50 feet in thickness, but may be of great lateral extent. Minor U occurs in association with some of the Cu-Co deposits, usually in a partly separated zone, and is at present recovered mainly at Nkana.

The sulphides often show a zonal arrangement, vertically and/or horizontally within the ore horizon; the average mine grade is some 2 to 5% Cu, while Co varies from a trace to some 0.5%. Fe is also variable, and is often low. Massive sulphides occur as local segregations in drag-folds, or in minor veinlets and are considered to result from

localised redistribution under metamorphic conditions.

Secondary sulphide enrichment has affected some, but not all, of the Copperbelt ore-bodies, usually occurring at a depth of some 300 feet below the surface. The ore-bodies are almost completely oxidised above this level. The primary Cu sulphides are chalcopyrite, bornite and chalcocite, and the Co sulphide is linnaeite, while the secondary minerals include chalcocite, malachite, azurite, cuprite, native Cu and chrysocolla (Bateman 1930).

Other Copperbelt minerals, which are of geological but not of economic interest, comprise the widespread occurrence of tourmaline, local concentration of fluorite mainly in the Kakontwe Limestone, of scheelite in folds within the Roan ore-shale, and elsewhere of traces of Mo and V in association with the Cu-Co-U deposits. Ni is reported as a minor separate phase only at Nkana (Davidson 1953), and is strikingly low within the Cu-Co deposits of the Copperbelt as a whole. Traces of Ni are present in pyritic disseminations (Garlick 1953). Like Ni, both Pb and Zn are rare within the Copperbelt, apart from isolated minor occurrences (Darnley, 1958). It should also be noted that whereas economic concentrations of Cu-Co sulphides are confined to the Lower Roan, minor disseminations occur at several horizons within the sediments, notably in the Mwashia shales, in several Upper Roan calcareous horizons, and occasionally within the

rocks of the Basement Complex (Garlick 1953 ; Darnley 1960).

Field Sampling and Geochemical Investigation.

The field samples were collected and generously made available by Drs. Webb, Tooms and Jay.

Soil profiles.

The six soil profiles studied in detail are described in Table 19, from the field notes of Drs. Tooms and Jay, published in part in Tooms (1955) and Jay (1959). The location of the pit profile sites are shown in Figures 23 and 24.

The six profiles are typical of the freely-drained residual latosols which occur in the region over the varied bedrock types. These comprise a mineralized shale, a mineralized feldspathic quartzite, and un-mineralized granite, schist, feldspathic quartzite, and gabbro.

Analytical methods.

The minus 80-mesh fraction sieved from the samples were taken for analysis. This fraction, which includes the clay silt, and fine sand grades, has previously been shown to be both convenient, and the optimum as regards Cu and Co, for geochemical prospecting investigations in the Copperbelt (Tooms, Govett, Jay *ibid*).

The sieved samples were ignited at 500°C prior to analysis by some or all of the following spectrographic techniques. The procedures have been described in detail

Table 19. Field descriptions of Soil profiles.

Profile No. Bedrock type & Location.	Sample No.	Depth	Soil horizon and description
1. Mineralized felspathic quartzite, Chibuluma. Over sub-outcrop of ore horizon.	NR: 631	0-1'	A ₁ Very sandy, yellow-brown soil.
	632-4	1'-10'6	A ₂ Very sandy, red-yellow-brown soil.
	635	10'6-13'6	B Nodular ferralite, stained qtz. at base: some black nodules.
	636	13'6-15'6	B Nodular ferralite.
	(do do		separated nodules)
	637-9	15'6-24'6	C ₁ Very sandy soil, mottled red-brown to off-white; some black specks; some blue-grey clay at depth.
	641-45	24'6-34'	C ₁ Mainly blue-grey sandy clay, with some red bands & Fe nodules externally white; occasional black specks; quartz veins at base. -C ₂
2. Mineralized shale, Baluba. Over sub-outcrop of ore horizon (Figure 24).	NRT: 108	0-3"	A ₁ Sandy clay soil, slightly orange to brown.
	109-11	3"-1'0	A ₁ ditto
	112-14	1'0-3'0	A ₂ ditto
	115-19	3'0-8'0	A ₂ As above but with abundant black spots, less at the top.
	120	8'0-9'0	A ₂ ditto
	121	9'0-9'6	B Lateritic clay with black wad.
	122-7	9'6-12'6	B Laterite nodular; brown to yellow with black mottle and wad; some quartz fragments.
	(122	9'6-10'0	Separated nodules).
	128-32	12'6-17'6	C ₁ Mottled clay after shale with black wad; ferruginous clay at top.
	(129	13'6-14'6	Separated black Mn wad).
	133-37	17'6-22'6	C ₁ Mottled clay after shale, with black wad.

Profile No. Bedrock type & Location	Sample No.	Depth	Soil horizon and description
3. Gabbro Chambishi Over gabbro intrusive into dolomite, some distance down-slope from ore.	14: 2946	0-6"	A ₁ Dark brown loam.
	2947	6"-1'0	A ₁ Red-brown clay.
	2948-53	1'0-6'0	A ₂ Rather redder brown clay
	2954-5	6'0-8'0	A ₂ As above with quartz fragments.
	2956-9	8'0-12'0	B Red-brown to brown clay with nodules, some indurated.
	2960-7	12'0-20'0	C ₁ Brown & yellowish clay, moist below 14'.
	2968-74	20'0-27'0	C ₁ White decomposed gabbro. Mottled brown in upper 3'.
	2975-77	27'0-30'0	C ₂ White decomposed gabbro, last foot below water.
4. Felspathic quartzite. Baluba Over Lower Roan quartzite, near Basement schist contact; 700 ft up-slope from ore. (Figure 24)	NRT: 50	0-3"	A ₁ Pale mid-brown, Sandy clay soil with grass roots.
	51-53	3"-1'0	A ₁ Pale red-brown sandy clay soil, fewer roots with depth.
	54-56	1'0-15'3	A ₂ As above, becoming redder towards base.
	57	15'3-16'3	B Nodular laterite, with some quartz rubble.
	(57	do.	Separated nodules).
	58-9	16'3-20'3	B Nodular laterite, red-brown matrix becoming paler at base.
	60-62	20'3-36'3	C ₁ White decomposed felspathic quartzite, mottled in part with some pale neutral brown clay.
5. Granite, Baluba Over granite intrusive into Basement schist, near Lower Roan contact; 1400 ft from ore. (Fig 24).	NRT: 94	0'3"	A ₁ Greyish buff sandy soil.
	95-7	3"-1'0	A ₁ ditto
	98-100	1'0-6'0	A ₂ Buff sandy clay.
	101	6'0-7'9	B Nodular laterite.
	(101	do.	Separated nodules).
	102	7'9-10'3	B Nodular laterite.
	103-5	10'3-16'3	B Laterite & lateritic clay passing to C ₁ into red stained granite with quartz veins.
	106-7	16'3-21'3	C ₂ Kaolinized granite.
6. Basement schist, Baluba. Over Basement schist near contact with Lower Roan; 1100 ft. upslope from ore (Figure 24)	NRT: 63	0'3"	A ₁ Pale grey-buff sandy clay soil.
	64-66	3"-1'0	A ₂ Pale red-brown sandy soil.
	67-68	1'0-4'3	A ₂ ditto.
	69	4'3-4'9	B Narrow laterite zone with schist inclusions.
	(69	do.	B Separate nodules).
	70-71	4'9-13'3	C ₁ -C ₂ Sericite schist passing below into quartz sericite schist.

in the sections indicated. The ferruginous nodules and Mn segregations picked out by hand from certain of the profile samples, were crushed separately, ignited, and treated by the same analytical procedures.

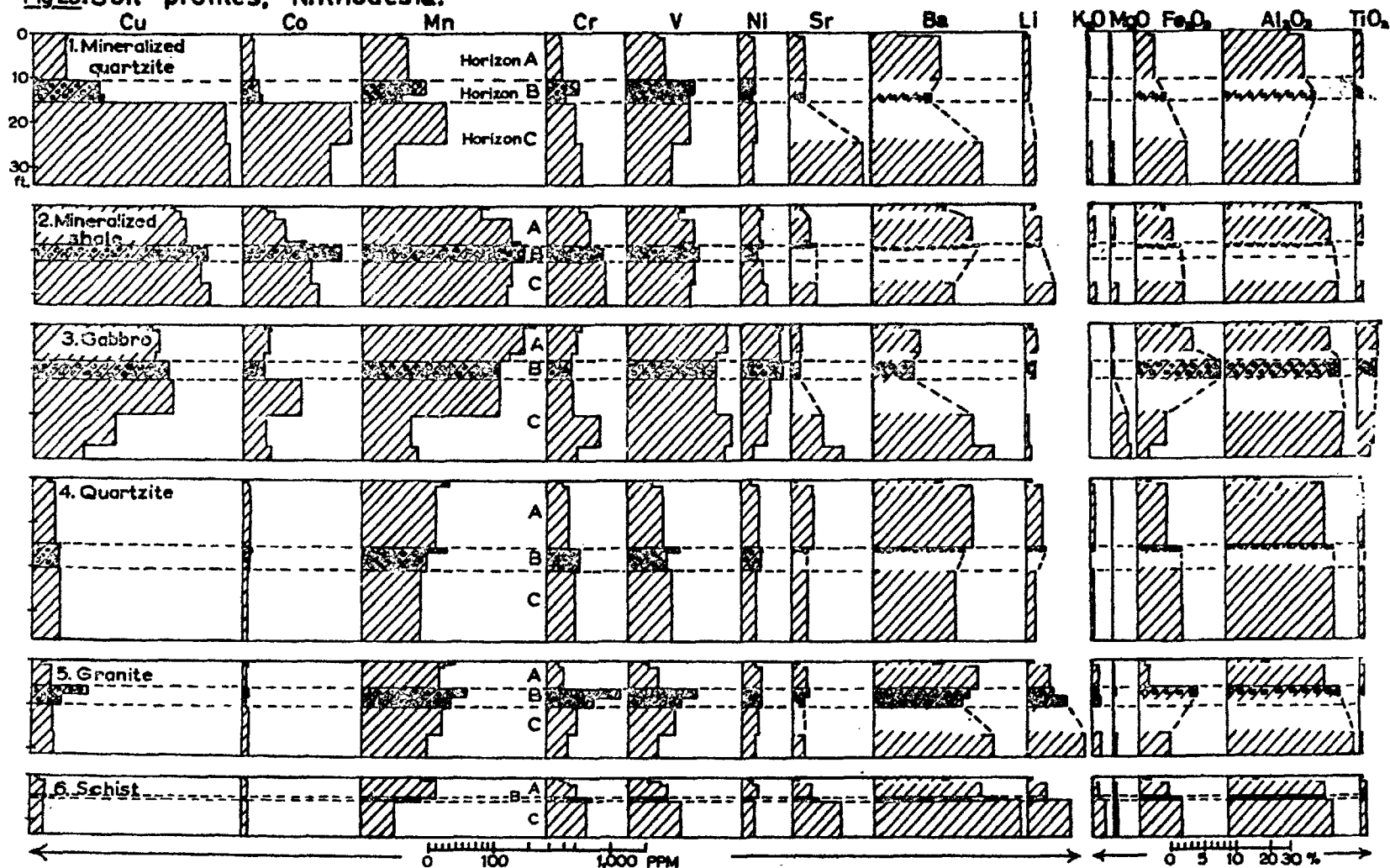
Elements Determined.	Procedure.	Technique (Chapter No.)
Be	Anode arc, carbon mixing	B(Chap. 2)
Rb, Li, Ba, Sr, Na ₂ O, K ₂ O	Anode arc, carbon mixing	A(Chap. 2)
Other minor elements	Cathod-layer arc, Li ₂ CO ₃ - carbon buffer method	C ₁ (Chap. 2)
Major elements	Anode arc, buffer method	M(Chap. 3)

The analytical results are tabulated in full in Appendix B6.

Observed Distribution of the Analysed Elements
in the Soil Profiles.

The profile distributions for the elements which show the most significant geochemical variations are shown in Figure 25, with the main soil horizons indicated as A, B, and C. For easy comparison of elements within each profile, and between different profiles, a common ppm scale applies to all the minor elements, and similarly a common scale of % for the major element oxides. It should be noted that the scale is linear from 0 to 100 ppm (or 0 to 10% major oxides); above 100 ppm or 10% the scale is logarithmic, for convenience in plotting (Fig. 25).

Fig 25. Soil profiles, N. Rhodesia.



It should be borne in mind that the data, based upon minus 80-mesh samples, primarily concern the friable secondary products of weathering in the fine sand and clay fractions at different levels within the soil profile. The coarser fractions, mostly representing resistant or partially weathered minerals and rock fragments, are excluded. The amount of this material varies considerably with depth, and with bedrock; for example, the gabbro is thoroughly decomposed even at the lowest sampling depth, whereas fragments of the more resistant, siliceous rock types may persist into the A horizons. The elimination of this variable amount of primary material from the samples enables the effects of weathering to be more directly investigated. In the B horizon, however, some of the secondary material, usually a small proportion of the whole, occurs as more or less indurated concretions which are excluded from the samples; the minus 80-mesh fraction naturally contains much of this illuvial material in disseminated form. Since the ferruginous nodules probably represent the end-product of accumulation in the B horizon, some were picked out by hand and analysed separately (Table 23).

The main features of the distribution of the major and minor elements within each profile may be summarized from the data as follows:-

Profile 1. Mineralized quartzite.

The profile is characterised by strong leaching of the moderately soluble elements from the upper horizons. Cu, Co and Fe are especially affected, conforming to previous geochemical observations showing that only weak Cu-Co anomalies may be developed over mineralization in quartzites (Tooms, 1955; Webb, 1956).

- (a) Strong leaching from the upper horizons relative to lower horizons affects Cu, Co, Sr, Fe, (Ba, Cr, K, Li, Mg).*
- (b) Concentration or partial retention in the B horizon, especially in the nodules, is shown by Fe, V, Cr, Cu, Mn, Mo, (Al).
- (c) Elements showing little change are Ni, (Al).
- (d) Elements which decrease in content^{down-profile} are Si, Ti, (Mn).
- (e) Elements showing accumulation at the immediate surface, or a relatively small decrease are Si, Cu, Co, Cr, Ti, Mn.

Profile 2. Mineralized shale.

The profile is characterised by much less pronounced leaching than profile 1.

- (a) The following elements are moderately leached, Co being the most affected: Co, Li, Fe, Cr, (Sr, V, Al)

*Symbols in brackets refer to elements showing the relevant trend less markedly.

(b) The B horizon and the Fe nodules are enriched in Co, Cu, Fe, Mn, Ba, V, Mo, (Al).

Manganese segregations from the upper C horizon show specific concentrations of Co, Mn, Cu, Ni, Ba, Pb, Mo, V, Fe, Al.

(c) Ni, Ti, (K, V, Mn, Ba) are relatively constant.

(d) Si increases towards the surface.

(e) Si, Mn, V show some relative accumulation in the immediate surface horizon.

Profile 4. Unmineralized quartzite.

The profile is characterised by very small variations with depth.

(a) No element is strongly leached, ignoring the decrease at surface for elements probably incorporated in clay material. Slight leaching affects Fe, Cr, Al, Cu.

(b) In the B horizon, only the iron nodules show significant accumulation effects, which involve the elements Fe, Cu, Cr, V, (Mo, Mn, Co).

(c) Most elements are constant, namely, Ni, Ti, K, Co; or approximately so:- Cu, Cr, V, Sr, Ba, Li, (Al).

(d) Elements which decrease with depth are:- Si, Mn, (Ba, Li, K).

(e) Local accumulation in the surface horizon is shown by Si and Mn

Profile 5. Basement granite. (Kaolinised).

This profile shows quite marked accumulations in the B horizon of Fe_2O_3 and some associated elements: the B horizon material has roughly the same composition as the separated iron nodules. Moreover, leaching or eluviation of Fe, Al, Li from the upper horizon is quite pronounced.

- (a) Leaching from the upper horizons affects Fe, Li, Al, Ba, Mg.
- (b) Elements concentrated or partly retained in the B horizon, including the nodules, are:- Fe, Cr, V, Cu, (Mn, Mo, Al).
- (c) Ni, Sr, (K, Co, Cu) are relatively constant.
- (d) Si, Ti, Mn (Ni) decrease with depth.
- (e) Si and Mn show local accumulation in the surface horizon.

Profile 6. Basement schist.

This shallow profile differs from the granite profile mainly in lacking strong accumulation in the B horizon; even the ferruginous nodules are enriched in few elements but Fe.

- (a) Leaching from the upper horizons affects Fe, Ba, Sr, Li, V, Cr and Al.
- (b) Accumulation in the B horizon is not pronounced. Fe, Cr, (Li, Cu) are moderately enriched in the iron nodules.

- (c) Ni, Co, Ti and Cu remain relatively constant.
- (d) Si and Mn increase towards the surface, but only Si shows a maximum in the immediate surface layer.

Profile 3. Gabbro.

This profile stands apart from the others, which are all characterised by some degree of leaching from the upper horizons, of Fe_2O_3 . Cu and Co in particular. In the gabbro profile, however, these elements have distinctly high contents in the upper horizons, and Mn, Cr and V show persistence or accumulation to the actual surface. Moreover, Fe, Mn, Cu and Ni decrease sharply in content at depth (Fig. 25).

- (a) Overall leaching from the upper horizons strongly affects Ca, Mg, Na, Ba and Sr.
- (b) Accumulation or relative retention in the B horizon is shown by Fe, (Cu, Al, Ni), while Co and Cu peaks occur in the upper C horizon.
- (c) No element is really constant although Cr, V and Al show lesser variations than other elements.
- (d) A general increase in content towards the surface is shown by Cu, Mn, Fe, Cr, Ni, Ti, Si, and Li. Fe is almost certainly enriched in the upper profile horizons relative to the unaltered gabbro rock (cf. data for Chibuluma gabbro). Fe is strikingly enriched compared with the present basal material of the profile, where leaching of iron in the reduced form has probably occurred.

(e) Accumulation in the immediate surface horizon is shown by Si, Ti, Mn, Cr, V, Ni.

Magnitude and Distribution of Individual Constituents in the Soil Profiles Related to (a) Mineralization and (b) Lithology.

Major Elements.

The main features of the major element data (Table 20, Fig. 25) are as follows:-

(i) SiO₂.

SiO₂ exceeds 55% in the minus 80-mesh fraction of every soil horizon examined. The surface horizon, especially in soils developed from granitic and arenaceous rocks, is often much more siliceous than immediately underlying materials.

As noted in describing the individual profiles, Si shows a general tendency to increase towards the surface, as other elements, notably Fe and Al, are removed. This is probably due to the selective elutriation of the fine clay and silt fractions, leaving a high proportion of quartz sand in the surface horizons.

(ii) Al₂O₃ and Fe₂O₃.

Alumina is the second largest component in all the profile samples, and considerably exceeds Fe₂O₃. Like Fe₂O₃, its content is only moderate in the Copperbelt profiles compared with many tropical soils (cf. Tables 20, 21).

Table 20 Major constituents and certain minor elements in the soil profiles

Sample depth	Horizon	% Oxides(ignited sample basis)												Ratios				
		Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂	Mn	ppm			Cu:Co	Co:Ni	Co:Fe ₂ O ₃	Cu:Fe ₂ O ₃	Cu:Fe ₂ O ₃
		*		*		*	*	*	+						ppm	%	(nodules)	
Profile 1. Mineralized quartzite																		
0-12"	A ₁	.04	.06	<.2	<.6	2.2	10.4	0.86	86	60	53	15	17	3.5	0.88	6.8	24.1	
1'10'6"	A ₂	.08	.23	.25	"	2.9	13.8	1.08	82	70	50	18	25	2.8	0.72	6.2	17.2	
13'6"-15'6"	B	.05	.28	.24	"	4.5	17.0	1.02	77	60	120	30	20	4.0	1.5	6.7	26.7	11.9
24'6"-34'0"	C	.06	.50	.51	"	7.8	12.2	0.53	78	50	1350	160	21	8.4	7.6	20.5	173.2	
Profile 2. Mineralized shale.																		
0"-3"	A ₁	.02	.35	.35	.6	3.9	13.5	0.83	81	350	380	32	27	11.8	1.19	8.2	97.4	
3'-8'	A ₂	.05	1.0	.49	"	5.7	22.8	1.06	69	550	550	65	30	8.5	2.17	11.4	96.5	
9'6"-10'0"	B	.06	1.1	.45	"	6.8	23.7	1.00	67	550	600	100	30	6.0	3.3	14.7	88.2	+ (75.3
17'6"-22'6"	C	.10	1.5	.94	"	7.2	26.7	1.06	60	500	900	130	40	6.9	3.3	18.1	125.0	(433.
Profile 3. Gabbro																		
0'-6"	A ₁	.01	.05	0.2	<.6	6.3	13.4	3.8	76	900	250	35	55	7.2	0.64	5.6	39.6	
1'-6'	A ₂	.02	.12	0.22	"	8.4	22.8	3.1	65	700	320	40	60	8.0	0.67	4.8	38.1	
8'-12'	B	.01	.07	0.29	"	14.5	27.1	3.0	55	430	380	34	65	11.2	0.52	2.3	26.2	
20'-27'	C ₁	.12	.04	2.24	0.88	4.1	29.2	2.6	60	75	130	35	40	3.7	0.88	8.5	31.7	
27'-30'	C ₂	1.2	.05	2.70	1.81	1.6	28.0	1.9	62	85	75	43	19	1.7	2.27	26.9	46.9	
Chibuluma gabbro rock (drill hole).																		
		2.0	5.7	7.5	2.44	7.1	18.5	0.72	56	50	5	14	43	0.44	0.33	1.97	0.7	
Profile 4. Quartzite.																		
0"-3"	A ₁	.01	.15	<.2	<.6	2.1	5.5	0.50	92	140	30	<7	14	>4	<0.50	<3.3	14.3	
1'-15'3"	A ₂	.05	.65	"	"	4.5	19.8	0.83	72	120	35	11	27	3.0	0.41	2.4	7.7	
15'3"-16'3"	B	.05	.55	"	"	6.6	23.5	0.89	68	150	42	14	32	3.0	0.44	2.1	6.4	20.8
20'3"-36'3"	C	.03	.45	"	"	6.6	23.3	0.85	69	90	43	9	23	4.8	0.39	1.36	6.5	
Profile 5. Basement granite.																		
0"-3"	A ₁	.02	.22	<.2	<.6	0.95	6.4	0.44	92	170	22	<7	18	>3	0.40	<7.35	23.2	
1'-6'	A ₂	.05	1.0	.28	"	2.6	19.0	0.79	76	130	30	7	30	4.3	0.23	2.69	11.5	
6'-7'9"	B	.06	1.0	.35	"	9.0	26.1	0.78	63	210	85	12	28	7.1	0.43	1.3	9.4	7.2
16'3"-21'3"	C	.10	1.5	.55	"	4.9	34.3	0.56	57	100	35	10	20	3.5	0.50	2.0	7.1	
Profile 6. schist.																		
0"-3"	A ₁	.03	.30	<.2	<.6	1.7	4.7	0.39	93	90	7	<7	10	>1	<0.70	<4.1	4.1	
1'4'3"	A ₂	.12	1.1	.39	"	4.3	18.8	0.92	72	130	22	10	25	2.2	0.40	2.3	5.1	
4'3"-4'9"	B	.14	1.3	.40	"	6.3	18.5	1.00	67	90	25	8	17	3.1	0.47	1.27	4.0	1.6
4'9"-13'3"	C	.45	2.0	.54	"	6.3	22.1	0.95	63	50	20	10	20	2.0	0.50	1.59	3.20	

Spectrographic technique and probable reliability (mean of duplicate determinations):-

* Major element photometric technique, probably accurate to $\pm 10\%$ of content.

+ In iron and manganese nodules, respectively.

Na₂O, K₂O: Visual semiquantitative method for alkalis, self-consistent within a reproducibility of some $\pm 50\%$.

+ Values calculated by difference from 100%.

Table 21. Composition of some lateritic soils

Sample depth	Analysis %							
	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
Laterite, Cuba ¹								
0-26"	.49	.06	.33	.12	63.0	18.5	.80	3.3
Aluminous laterite, Costa Rica ²								
0-10"	.23	.14	.50	.25	15.6	37.1	2.02	19.8
25-40"	trace	.20	.15	.19	17.0	38.5	2.44	19.7
Laterite clay, Transvaal ²								
0-9"	.17	.74	1.40	.11	20.8	27.3	2.11	25.0
9-24"	.17	.75	1.16	.10	20.4	28.0	3.21	26.4
Lateritic podzol, South Africa ³								
B ₃ horizon	1.88	4.62	.50	.28	10.7	16.4	.85	65.0

1. From 'Pedology' J.S.Joffe, 1949 p.473.

2. From Lawton, K. in 'Chemistry of the soil' Bear, Ed.1955 p.67.

3. From 'Tropical soils' Mohr & van Baren, 1954. p.403.

Changes in Al content related to the different bedrocks are rather small, but broadly conform to the lithology. Thus, in the lower C horizons, the kaolinized granite has the highest alumina content, the gabbro second, closely followed by the shale.

The vertical distribution of Al_2O_3 shows in general little variation other than a slight decrease towards the surface with a sharp decrease in the actual surface horizons, particularly in the more sandy profiles (3, 4, 5, Figure 25).

The small accumulation of Al_2O_3 in the B horizons, compared to Fe_2O_3 (Figure 25), is emphasised again when considering the composition of the iron nodules.

Despite the ferruginous red colour of the soils, the iron oxide content in the Copperbelt profiles shows rather low values, which exceed 10% in only one sample. The data of Jay (1959) for Fe in a number of Copperbelt soils confirm this observation.

The highest iron contents occur in the Chambishi gabbro profile, reflecting the high content of iron minerals in this rock type. It may be noted that values of 8-14% Fe_2O_3 in the A_2 and B horizons of the gabbro profile, are comparable with those found throughout the latosol profile over norite in the Transvaal (Chapter 8). The mineralized shale is second to the gabbro in the iron content of the near-surface Copperbelt soils (likewise Al_2O_3).

Particularly in profiles over siliceous bedrocks, the iron probably occurs largely as an oxide coating on the sand and clay grains, especially in samples from the upper horizons. This is shown by the paler colour produced by crushing such samples in an agate mortar.

The content of iron varies considerably with depth, as described in the individual profiles. Only in the profile over the gabbro does the iron content of the A horizon exceed that of the C horizon; coupled with the general tendency of iron to accumulate in the B horizon (typically in the iron nodules), this indicates that five of the six profiles are podzolic in character as far as Fe is concerned.

From the practical viewpoint the limited data suggest that (a) it is unlikely that the analysis of near-surface samples for Si, Al or Fe would improve the indications of bedrock lithology based upon soil colour and texture, except for high iron contents indicating the gabbro; (b) there is no evidence of significant variations in the major element content related only to mineralization (cf. mineralized and unmineralized quartzites); nor would such variation be expected on geological grounds, with the possible exception of Fe over ferruginous Cu-Co orebodies.

(iii) TiO₂, K₂O, Na₂O, CaO, MgO.

Contents of these elements are much lower than for SiO₂,

Al_2O_3 and Fe_2O_3 . The main variations down-profile have been noted as general leaching of calc-alkalies from the A and B horizons, and the tendency for the TiO_2 content to decrease with depth. None of these elements shows a significant preference for the B horizon, nor its nodules.

The calc-alkali elements show some variations with lithology, mainly reflected in data from the C horizon. Thus, K_2O is relatively high at depth in the shale, granite and schist profiles, and probably by incorporation in micas and clay minerals, has partly resisted leaching in the upper horizons (Fig. 25). On the other hand, high Na_2O , CaO and MgO values distinguish the gabbro profile at depth (Table 20), but these values do not persist into the upper horizons. The leaching of these calc-alkali elements shows the predominance of tropical weathering mechanisms over the bedrock composition in deciding the contents of mobile elements in the surface soil.

With the important exception of the gabbro, the Ti content varies little with bedrock type. The high TiO_2 content in the C horizon of the gabbro profile is distinctive, and it increases to double this value at the surface. Mineralogical or chemical determination of the resistant titanium minerals has often been suggested as an index of removal by weathering of more soluble rock constituents

(Reiche, 1950). On this basis, the 2-fold increase for TiO_2 suggests that weathering and leaching of major soluble constituents has been more extensive for the gabbro than other profiles.

Major elements: summary.

From the practical viewpoint of soil analysis as a guide to lithology, it appears from the limited data that:-

(a) Apart from the gabbro profile, the major element contents in surface soils do not vary by large factors with the bedrock type. Soil colour and texture are probably superior to major element analyses as guides to bedrock lithology; rapid (chemical) determination of Fe and Ti might, however, be investigated for the positive recognition of soils developed from gabbroic rocks.

(b) There is no suggestion of direct correlation between the major element composition of soils and underlying mineralization, in the single comparative case, namely between mineralized and non-mineralized quartzites.

(c) The main geochemical application of major element soil analyses lies in indicating the trends of leaching and accumulation in the various soil horizons. For this purpose, the moderately-quantitative data provided by spectrography are a useful supplement to inferences drawn from field observations and/or from data for the minor elements.

Minor Elements

Contents of the minor elements as a whole.

The mean values and range of element content encountered in all the profile horizons and nodule samples examined, are shown in Table 22, compared with values for the world's soils tabulated by Swaine (1955).

A cursory survey of the combined data from the six soil profiles suggests that:-

(a) The calculated "average" soil profile sample is enriched in Cu and Co relative to the geochemical abundance of these elements, and to their normal contents in soils. This observation naturally reflects the inclusion of mineralized Copperbelt soil profiles. It is, however, significant that this enrichment is virtually confined to Cu and Co among all the elements determined.

(b) Thus, the small range of Ni content, and its relatively low content even in the mineralized samples, indicates that it is not strongly associated with Cu and Co.

(c) Mo and Pb, from very incomplete data, may possibly be enriched above their abundance in the lithosphere: even their maximum contents, in separated nodules are, however, quantitatively insignificant compared to Cu and Co.

(d) The most abundant of the minor elements in the "average" soil profile sample are, in order of content:-

$Mn \approx Cu > Ba > Co > V > Cr > Ni = Sr \approx Li$ (Table 22).

Table 22.

Mean and ranges of constituents in the soil profiles and separated nodules for 6 N. Rhodesian soils.

Northern Rhodesia soil profile samples (total 49 samples).			World soils (after Swaine, 1955).			
Element	Content		Very Low	Common Range	Very High	Abundance in Lithosphere ppm
	Mean	Range				
SiO_2 %	64	(40) 55-93				
Al_2O_3	20.2	4.7-34				
Fe_2O_3	8.0	1.6-14.5(41)				
TiO_2	1.1	0.39-3.8				
K ₂ O	0.71	0.04-2.0				
MgO	0.45	0.20-2.7				
Na_2O	0.11	0.01-1.2				
Mn ppm	405	50-900 (5000)	20	200-4000	X%	1000
Cu	362	7-1350 (3250)	0.4	3-100	8000	70
Ba	189	40-500 (600)	10	100-4000	X%	430
Co	127	<7-240 (4000)	<0.1	1-70	300	40
V	106	25-200 (380)	1	20-700	1000	150
Cr	74	15-120 (700)	0.5	7-1000	>1%	200
Ni	31	10-65 (115)	0.7	8-700	8000	100
Sr	31	10-120	10	60-1000	4000	150
Li	28	4-90 (100)	1	7-200	2000	65
La	26	<20-105	<0.1	3-90	700	18.3
Ga	20	4-33	8	10-80	200	15
Pb	-	<30-30 (90)	0.2	3-200	8000	16
Mo	-	<5-7 (13)	<0.1	0.2-7	200	2.3

X Where the extreme values occur in separated nodules, these are bracketed ().

Content and Vertical Distribution
of Individual Minor Elements.

(i) Cu.

The adjacent table shows that (a) the Cu content at depth clearly distinguishes the two mineralized profiles from all the others, but that (b) in the more accessible upper horizons, which are normally sampled for geochemical prospecting purposes, some irregularities occur in the Cu values.

Cu content of the main soil horizons (ppm).

Soil Horizon	Mineralized Profiles		Un-mineralized profiles			
	1. Quartzite	2. Shale	3. Gabbro	4. Quartz- ite	5. Granite	6. Schist
A ₁	53	380	250	30	22	7
A ₂	50	550	320	35	50	22
B	120	600	380	42	85	25
Lower C	1350	900	75	43	35	20

Thus, the upper horizons of the mineralized quartzite are so depleted in Cu that a value of only 50 ppm represents underlying mineralization, against a "background" content of 30 ppm over the barren quartzite. Leaching is facilitated by the porosity of the Chibuluma quartzite and its derived sandy soils. The surface soil over the mineralized shale is much less strongly leached, probably due to the greater

content of the primary and secondary clay minerals, and the effect of their adsorption and base-exchange properties in retaining ions of otherwise soluble elements, including Cu.

Finally, (c), the Cu content of both A and B soil horizons over the gabbro exceeds that of any other profile except the mineralized shale (likewise Co). The ferruginous gabbro soil retains Cu, Mn and Ni, although these elements are apparently leached at depth. It is not impossible that lateral migration down-slope has introduced some of the Cu and Co from the sub-outcrop of mineralization at Chambishi (Jay 1959), but anomalous contents of Cu and Co are generally found in soils developed over the Copperbelt gabbros.

(ii) Co.

Most of the remarks made for Cu regarding the surface geochemical anomalies apply in general to Co. Thus reference to the adjoining table shows that in the A2 soil horizons, the content of Co over the mineralized quartzite is only twice that of the barren quartzite, granite and schist: Co in the gabbro soil exceeds this feeble anomaly over mineralized quartzite and is only moderately surpassed by the value of 65 ppm Co which distinguishes the mineralized shale.

Co content of the main soil horizons (ppm).

Soil Horizon:	Mineralized profiles		Un-mineralized profiles			
	1. Quartzite	2. Shale	3. Gabbro	4. Quartz- ite	5. Granite	6. Schist
A ₁	15	32	35	<7	<7	<7
A ₂	18	65	40	11	7	10
B	30	100	34	14	12	8
Lower C	160	130	43	9	10	10

Two characteristic problems in geochemical prospecting are thus illustrated in the profile data, namely, (a) the development over weathered gabbro rocks of relatively high Cu and Co contents unrelated to economic mineralization, and (b) the development over mineralizations of similar grade but in different host rocks, of quite dissimilar surface anomalies - in the case of the Chibuluma quartzite the anomaly is little above the background level for the unmineralized bedrock. Tooms and Webb have drawn attention to these difficulties, and to possible practical methods for resolving them (Tooms, 1955; Webb, 1956). The recommended approaches are (a) the field identification of areas underlain by each bedrock type, and the use of appropriate local background and threshold values, as indicated by the geochemical orientation

survey. (b) The chemical determination of readily-extractable Cu rather than total Cu may, in favourable cases, increase the contrast between anomalies of low total Cu content related to mineralization and the background. This method is successfully applied to stream sediment samples (Webb and Tooms, 1958), but may be less effective in the leached and dessicated samples of freely-drained soils. The practical solution of taking geochemical prospecting samples from the B horizon, to overcome the effects of leaching from upper horizons, is impracticable and un-economic in the Copperbelt because in the deep, mature soil profiles, the B horizon often lies over 10 feet beneath the surface.

(c) The chemical determination of Ni in addition to Cu and Co enables non-significant anomalies related to the gabbro bedrock to be identified by the relatively low Co:Ni ratio.

Discussion of the spectrographic results.

The present data confirm that the gabbro soils are relatively high in Ni content, giving a Co: Ni ratio lower than the ratio in mineralized soils, which is of the order of unity or greater (see Table below, and Table 20).

The following table summarizes the contents and ratios of certain elements in the A₂ soil horizons:

Profile	Cu ppm	Co ppm	Cu:Fe ₂ O ₃ ppm: %	Co:Fe ₂ O ₃ ppm: %	Co:Ni ppm:ppm
Mineralized quartzite	50	18	17.2	6.2	0.72
Mineralized shale	550	65	96.5	11.4	2.17
Gabbro	320	40	38.1	4.8	0.67
Quartzite	35	11	7.7	2.4	0.41
Basement granite	30	7	11.5	2.7	0.23
Basement schist	32	10	5.1	2.3	0.40

In addition, relatively high contents of Fe and Ti distinguish the gabbro surface soils, amongst this limited number of profiles. Consequently, the Co:Fe ratio is also of value in distinguishing the non-significant Co anomaly over the gabbro from anomalies related to mineralization. The low Co:Fe ratio gives a slightly greater distinction between the gabbro and the mineralized quartzite than does the Co:Ni ratio. Analytical error must be borne in mind in considering the significance of these ratios; an advantage of the Co:Fe ratio is that only the minor element is determined semi-quantitatively.

In the problem of detecting the weak Cu anomaly developed over mineralization in quartzite, contrast with the "background" profile (2:1) is slightly improved (to 2½:1) by using the Cu:Fe ratio. A similar finding

applies to the Co anomaly and the Co:Fe ratio. No other elements determined, or their ratios, offered a significant advantage in distinguishing near-surface soil anomalies related to mineralization.

These observations are based upon data for only one profile over each bedrock type, in some cases from widely separated localities. Variations, for example in iron content, in samples from different areas would affect the general applicability of the observations, which clearly require testing on a wider sampling basis. If this work is pursued, a rapid chemical method for determining iron, such as the one described by Jay (1959) would be more economical than spectrography for determining this single major element.

Minor Elements, other than Cu and Co.

(iii) Mn, Ni, V, Cr.

The adjacent tables and Fig. 25 show some features relating the contents of these elements with mineralization and/or lithology.

Element contents in the main soil horizons (ppm):-

Mn

Soil Horizon:	Mineralized profiles		Un-mineralized profiles			
	1. Quartzite	2. Shale	3. Gabbro	4. Quartz-ite	5. Granite	6. Schist
A ₁	60	350	900	140	170	90
A ₂	70	550	700	120	130	130
B	60	550	430	150	210	90
Lower C	50	500	85	90	100	50

Ni

A ₁	17	27	55	14	18	10
A ₂	25	30	60	27	30	25
B	20	30	65	32	28	17
Lower C	21	40	19	23	20	20

V

A ₁	50	80	200	32	25	30
A ₂	60	110	200	55	45	60
B	100	110	160	80	110	60
Lower C	70	100	190	68	45	80

Cr

A ₁	22	50	55	20	15	20
A ₂	25	65	45	35	25	45
B	30	65	38	50	120	70
Lower C	55	90	45	43	32	60

(i) Relatively high total Mn contents in the A₂ horizons of the gabbro and shale profiles, distinguish these from profiles over more siliceous bedrocks. The gabbro soil also shows higher contents of Ni and V than any other, no doubt in association with the high Fe which has already been noted.

(ii) In addition to Mn, the A₂ horizon of the shale shows moderately high contents of Ni, V and Fe (second only to the gabbro) and actually the highest Cr of all profiles at this horizon. The contrast in Ni, V and Cr contents between corresponding horizons of the shale and other profiles is not large however, rarely exceeding 2-fold (Tables above; Fig. 25). In this connection, data for a single soil traverse over the mineralized shale at Baluba show a similar moderate increase for Ni and Cr immediately over the shale horizon (Fig. 26). The association of the minor ferrides with Fe in the argillite and the derived soils may be due entirely to normal sedimentary processes. The alternative possibility that these elements are directly related to the Cu-Co mineralization in the shale must remain open, since samples from a non-mineralized shale profile were not available for examination. In comparing the mineralized and barren quartzite profiles, however, there is no indication that the Ni, Cr, V, Mn or Fe contents of the soils are increased over Cu-Co mineralization (Fig. 25).

(iii) It has already been noted that although the near-surface horizons of the gabbro soils have a relatively high Co content, this is exceeded by Ni. Thus the low Co:Ni ratio distinguishes the Co anomaly over the gabbro from that over the mineralized shale, where the Co:Ni ratio exceeds 1.0. Jay, (1959 p. 69) has previously established this distinction between soils over the Chambishi gabbro and over Cu-Co mineralization, both in argillaceous host rocks, at Baluba and Chambishi. The present data show that Ni also predominates over Co in the A₂ horizons of the siliceous background profiles (Nos. 4, 5, 6), and over the mineralized quartzite in which Cu and Co are leached, but not Ni (Fig. 25). Thus, rather than the low Co:Ni ratio alone, a high magnitude of Ni (approx. 40 ppm) should be present for characterising a soil developed over a gabbro.

(iv) The vertical distribution of Mn in the profiles (Fig. 25) shows the following main features:- (a) a minor accumulation in the surface horizons, probably in association with organic matter, (b) local accumulation in the B or upper C horizons, and (c) a general lack of direct relationship of Mn content with Fe or other predominant elements. The nodule data (discussed below) provide some detailed comparisons and contrasts between the accumulation of Fe and Mn.

(v) The Ni content varies little with depth, except in the gabbro profile, where the content decreases with depth, paralleling to some extent Fe, Cu and Ti. Ni shows little tendency to accumulate with Fe, Cu or other elements in the B horizon, nor in the iron nodules. The relative immobility of Ni may be due to formation of stable Ni silicates (Rankama and Sahama, 1950, p. 684), but since its content is low in any of the profiles, it may well be present as a minor accessory incorporated in resistant primary iron oxides, or residual in secondary iron oxides derived from the weathering of ferromagnesian minerals or iron sulphides.

(vi) V and Cr show some contrasts with Ni and Mn, by tending to parallel the distribution of Fe in the un-mineralized siliceous profiles, Nos. 3, 4, 5 (Fig. 25). Moreover, the iron nodule data also suggest that V and Cr follow Fe rather closely in the process of accumulation in the illuvial B horizon.

(iv) Sr, Ba, Li.

Sr, Ba and Li were determined in selected samples representing only the main profile horizons (Fig. 25).

(i) Li shows some association with K_2O , probably retained within mica and clay minerals. Slightly higher Li contents distinguish C-horizon samples over the granite (90 ppm), schist (65 ppm) and shale (45 ppm) from the other decomposed

bedrocks, the lowest being the gabbro with 8 ppm Li.

Leaching of Li (likewise Sr), suppresses the surface expression of these variations with lithology (Fig. 25).

(ii) For Sr, the only noteworthy variation with lithology is the higher Sr content in the C horizon over the mineralized quartzite as compared to the barren quartzite. Since there is a similar relationship for Mg, this probably reflects the persistent but variable content of carbonates in the Roan sediments (Davidson, 1954 p. 245), rather than a direct relationship with mineralization. As with Li, leaching of Sr prevents the expression in the accessible A_2 horizons, of variations in Sr content, related to the bedrock type (Fig. 25).

(iii) Ba is more abundant than Li or Sr, but in the profiles examined, it shows relatively small variations in content at depth, which cannot be positively related with the bedrock type or with mineralization. Moreover, the effects of leaching towards the surface again obscure the surface expression of the content of Ba at depth. The gabbro profile shows a greater degree of leaching for Ba and Sr than do other profiles, corresponding to the thorough leaching from upper horizons of Ca and Mg, which are relatively high at depth.

Distribution of the Major and Minor Elements in
Iron Nodules and Manganese Segregations.

The composition of iron nodules separated from the B horizon of five profiles, and of manganese segregations from the upper C horizon of the mineralized shale, provide some information on some aspects of accumulation in the illuvial zone which is typical of most Copperbelt soils. The analytical data of main geochemical interest for the separated nodules and the surrounding minus 80-mesh material ("the matrix") are shown in Table 23.

Iron nodules.

1. The iron oxide content of the separated nodules, and the factor of concentration relative to the adjacent matrix material, varies considerably for the five samples examined. The Fe content varies from 11 to 41% Fe_2O_3 , and the factor of concentration from 2:1 to 6.6:1. Considerable variations may be expected also between different nodules, from the same profile. Thus, in discussing the present data, the variable factor of iron concentration must be taken into account; the ratio of the content of a particular minor element in the nodules to its content in the matrix (its factor of concentration) is used as an index of its tendency to accumulate with Fe.

Table 23. Composition of (a) nodules separated from soil horizons compared with (b) sieved minus 80-mesh material at the same depth.

	PPM												% Oxides										Ratios					
	Cu	Co	Mn	Cr	V	Ni	Sr	Ba	Li	Ga	Mo	Pb	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂	Cu:Co	Co:Ni	Co:Fe ₂ O ₃ ppm	Co:Fe ₂ O ₃ %	Cu:Fe ₂ O ₃ ppm	Cu:Fe ₂ O ₃ %	Fe ₂ O ₃ conc _{factor}	
Profile 1. Mineralized quartzite																												
Ferruginous nodules separated from nodular laterite (B horizon) at 13'6"-15'6" depths.																												
(a) Fe nodules	350	22	200	210	190	21	10	120	13	20	6	<30	.03	.68	.28	tr	29.5	19.9	.94	49	15.9	1.0	.0.75	11.9	66:1			
(b)-80-mesh material	120	30	60	30	100	20	23	90	8	10	<5	<30	.05	.28	.24	tr	4.5	17.0	1.02	77	4.0	1.50	6.7	26.7				
	●		●	●	●		○		(●)	●	(●)		(○)	●			●	●		○								
Profile 2. Mineralized shale																												
Ferruginous nodules separated from nodular laterite, brown-yellow with black mottle (B horizon) at 9'6"-10'0" depth																												
(a) Fe nodules	1000	120	2000	250	180	35	38	210	23	30	8	30	.06	1.0	.46	tr	13.3	25.5	1.03	58	8.3	3.43	9.0	75.3	2:1			
(b)-80-mesh material	600	110	550	65	110	30	40	230	25	20	<5	<30	.06	1.1	.45	tr	6.8	23.7	1.00	67	5.5	3.34	16.2	88.2				
	●		●	●	●					●	●						●	●		○								
Black manganese wad (spots) separated from mottled, partly ferruginous clay, after shale at 13'6"-14'6" depth (C ₁ horizon)																												
(a) Mn wad	3250	4000	5000	65	160	115	43	600	100	25	13	90	.05	1.0	.45	tr	7.5	29.0	.81	60	0.81	34.8	533.4	433	1.4:1			
(b)-80-mesh material	550	75	300	70	90	25	50	200	35	20	<5	<30	.05	1.1	.58	tr	5.3	22.7	1.05	68	7.3	3.0	14.1	104				
	●	●	●		●	●		●	●	●	●	●					●	●		○								
Profile 4. Felspathic quartzite																												
Ferruginous nodules separated from nodular laterite at 15'3"-16'3" depth																												
(a) Fe nodules	850	48	350	700	380	39	10	110	15	32	11	<30	.03	.43	<.2	tr	40.8	17.8	.66	40	17.7	1.23	1.2	20.8	6.2:1			
(b)-80-mesh material	42	14	150	50	80	32	25	170	30	20	<5	<30	.05	.55	<.2	tr	6.6	23.5	.89	68	3.0	0.44	2.12	6.4				
	●	●	●	●	●			○	(○)	○	●		(○)				●	○		○								
Profile 5. Basement granite																												
Ferruginous nodules separated from nodular laterite at 6'0"-7'9" depth (B horizon)																												
(a) Fe nodules	80	11	220	120	130	30	17	145	36	26	7	<30	.07	.9	.33	tr	11.2	28.1	.84	59	7.3	0.37	0.98	7.2	4.3:1			
(b)-80-mesh material	85	12	210	120	110	28	25	180	40	29	5	<30	.06	1.0	.35	tr	9.0	26.1	.78	63	7.1	0.43	1.33	9.4				
do. overlying A ₂ horizon	30	7	130	25	45	30	22	220	35	20	<5	-	.05	1.0	.28	tr	2.6	19.0	.79	76	4.3	0.23	2.7	11.5				
	●	(●)	(●)	●	●			(○)	(●)	●							●	●		○								
Profile 6. Basement schist																												
Ferruginous nodules separated from narrow laterite zone at 4'3"-4'9" depth (B horizon).																												
(a) Fe nodules	32	7	85	120	65	14	38	330	48	16	<5	<30	.31	1.8	.53	tr	19.5	26.9	.93	46	4.6	0.5	0.36	1.6	3.1:1			
(b)-80-mesh material	25	8	90	70	60	17	40	320	30	15	<5	<30	.14	1.3	.40	tr	6.3	18.5	1.0	67	3.1	0.47	1.27	4.0				
	(●)			●					●				●				●	●		○								

- Elements showing concentration in nodules: factor approx 2-fold (or analytically significant for major elements)
- " " " " " : factor of 5-fold or over.
- Elements showing concentration in minus 80-mesh material = factor of 0.2-fold.
- () Indicates factors below X2-fold but probably analytically significant.

2. Of the major elements, only Fe itself is strongly concentrated in the nodules: the contents of the other major constituents remain essentially the same as in the matrix. Increased contents of Al_2O_3 are, however, found in three of the five nodule samples, and some calc-alkali elements are slightly enriched in certain iron nodules relative to the A and B (not C) horizons; alkali leaching is not observed.

3. Cr is the element most closely associated with the iron nodules. It is unique among the elements analysed in concentrating in all five iron nodules by a factor of the same order or greater than the factor for Fe_2O_3 .

4. Cu is also enhanced in all the nodules, but in only one case (the barren quartzite) is its factor of concentration higher than that of Fe_2O_3 . In other words, the Cu:Fe ratio is in most cases reduced in the nodules compared to the bulk of the B horizon. (Table 20). From the very limited number of samples, neither the Cu content nor Cu:Fe ratio in the nodules correlate in detail with mineralization. Four samples do so, but an important exception is that nodules from barren quartzite are higher in Cu (and Cu:Fe ratio), than nodules from the mineralized quartzite: the same applies to Co.

5. V increases in all five nodule samples, but the factor of concentration is mostly less than that for Cu.

6. Mn is strongly concentrated in the iron nodules in only two profiles, the mineralized shale and the mineralized quartzite. In the three un-mineralized profiles, Mn is only slightly enriched in the nodules (Table 23).

7. Mo and Pb are concentrated above their limits of detection in certain iron nodules, and may be associated fairly directly with Fe, as are Cr, V and Cu. The highest Mo content is 11 ppm, in iron nodules from the barren quartzite; the mineralized shale, granite, and mineralized quartzite being next in order. Thus, no consistent relation with mineralization is shown by the present limited data.

8. In contrast with Cu, Co is not closely associated with the iron nodules. The content of Co increases slightly in three of the five iron nodules, by up to 1.5-fold. The increase is insignificant compared to the factor for Fe_2O_3 , up to 6.0 fold, so that the Cu:Fe ratio is distinctly lower in all five iron nodules than in the matrix material.

9. Ni accumulates in only the most ferruginous sample, by a 2-fold factor from 20 to 39 ppm Ni. Like Co, Ni is not directly associated with iron accumulation in the nodules.

Discussion.

The distribution of iron and other elements in the ferruginous nodules may be briefly related to the general distribution of iron in the Copperbelt profiles examined.

It has been shown that in the upper soil horizons, the iron content exceeds 10% Fe_2O_3 only over the gabbro bedrock. Moreover, in all but the gabbro profile, iron is leached from the A horizon relative to the C. Accumulation occurs in the B horizon relative to the A in all profiles, but the iron content does not always exceed the C, at least as regards the sieved soil fractions. Some allowance must be made for the exclusion of the ferruginous nodules, although Jay (1959) notes that their proportion to the whole B horizon is not usually great, and coarse material containing less than the average amount of iron has also been excluded from the sieved samples. The iron nodules examined rise to 30 and 40% Fe_2O_3 in the two highest samples; even here, the predominance of sesquioxides over silica is quite small. The limited data points to the introduction by illuvial processes, of Fe with associated minor elements, and relatively little alumina. Thus there are similarities in five of the profiles, excluding the gabbro, to the characteristics of red podzolic soils (Robinson, 1949).

Manganese segregations.

The manganese segregations from the upper C horizon of the mineralized shale profile show some important differences from the iron nodules in their element associations (Table 23). This is to be expected from the different

patterns which Fe and Mn show in the cycle of weathering. These elements tend to be more or less separated in the products of weathering, despite their close association in many primary rock minerals (Mason, 1952 p. 147).

1. Co is strongly concentrated with Mn in the segregations examined; the content of each metal is approximately 0.5%, and the Co:Mn ratio is in fact greater than in the matrix material.

2. Other elements appreciably concentrated in the segregations are Cu, Ni, Ba, Pb, Li, Mo and V, in that order of concentration in the segregations relative to the matrix. While Cu shows a 6-fold concentration this is relatively insignificant compared to the 53-fold factor for Co; Co in fact exceeds Cu in these segregations, thus reversing their normal abundance in Copperbelt soils.

3. Cr is not accumulated, and Fe and Al increase by only small factors.

Geochemical mechanisms applying in iron nodules and manganese segregations.

Within the iron nodules, preferential accumulation with iron is shown only by the minor elements Cr, Cu, V, Mo, Mn and Pb. Co is only an incidental component of the nodules, and not significantly concentrated in them. The data confirm observations by Tooms (quoted in Jay, 1959) and also Jay's own findings, that Co associates to a lesser extent with Fe than with Mn in freely-drained profiles.

Anion adsorption on the iron hydroxide colloid of vanadate, molybdate, arsenate, selenate and phosphate ions is the mechanism usually thought to explain the occurrence of Cr, V, Mo, As, P in sedimentary iron ores (Mason, 1952 p.154). While this may explain the accumulation of Cr, V and Mo in the iron nodules, adsorption onto a positively-charged iron hydroxide colloid cannot explain the association of Cu with the nodules. If prominence is to be given to soil colloidal processes, negatively-charged colloids such as argillaceous clays or colloidal silica would have to be involved to adsorb the polarized Cu^{++} ion (Perelman, 1957). Since negative colloids also include organic substances, several possibilities exist for Cu to be incorporated in such colloids and then flocculated in the illuvial B horizon.

On the other hand, it may be assumed the co-precipitation of Cu (inter alia) from solution, accompanies the precipitation of iron in the illuvial horizon (Tooms, 1955; Govett, 1958), analogous to the chemical "scavenging" action of precipitated Fe and Mn hydroxides. The soil pH and Eh conditions are then important factors. The role of bacterial agencies in the precipitation of Fe and Mn should not be overlooked, although these processes are incompletely understood (Rankama and Sahama, 1950 p. 674; Berrow, 1958). It is very probable that two or more different mechanisms are

involved in the accumulation in iron nodules of such varied elements as V, Mo, Mn, Pb and Cu, coupled with the exclusion of Co and Ni.

Whatever the detailed mechanism, the work of Webb, Tooms (1955) and Jay (1959) among others in the Copperbelt shows that Cu is quite strongly associated with Fe in freely-drained soils, and the accumulation of Cu with Fe and Al in the B horizon of temperate podzols is well established (Perelman, 1957).

The pronounced accumulation of Co together with Cu, Pb, Ba, Ni and other elements in the manganese segregations may be explained by the adsorption and co-precipitation properties of manganic hydroxide.

Manganic hydroxide gel, in contrast to that of iron, is negatively charged and consequently has a high affinity for adsorption of positive metal ions, the attraction being greatest for ions of large size and high charge. Consequently, oxidate sediments rich in manganese often contain notable amounts of Li, K, Ca, Ba, B, Ti, Co, Ni, Cu, Zn, Pb and other elements, while manganese wad may contain up to 2.8% NiO, 8.3% CoO, 9.5% BaO and 14% CuO (Rankama and Sahama, 1950 p.650).
Relevance of iron nodules and manganese segregations to geochemical prospecting.

The foregoing results based upon a very limited number of samples, suggest that the analysis of the above materials offers little promise for geochemical prospecting purposes.

Firstly, there are obvious practical and economic drawbacks in sampling from the zone of nodular accumulation, which often lies at depths exceeding 10 ft. in the Copperbelt. Secondly, only specific elements are concentrated in the iron nodules, and this concentration probably varies with (a) the concentration of Fe itself and (b) the quantity of the minor element mobilized in solution, rather than its total content. Thus erratic variations in the minor element content may occur which are not only related to mineralization or lithology: this is illustrated by the abnormally high content of Cu, Co, Mo and some other elements in the highly ferruginous nodules from the un-mineralized quartzite profile.

Nevertheless, significant concentration effects are observed in the nodules, notably for Cu, Mo and Pb, among elements which may be related to Cu-Co mineralization, on geological grounds. Their analysis in nodule samples might serve as a guide to ore, mainly on a qualitative basis.

Similar considerations probably apply to the analysis of separated Mn segregations, based upon data from only one sample. Qualitative indications of Cu-Co mineralization is already implied in the presence of Mn segregations in reasonable amount. Thus, Anton Gray (1929 p. 31) notes that limonite present in most oxidised outcrops over Copperbelt orebodies is often accompanied by manganese and copper oxides, and that black sooty oxides "which contain Fe, Mn and

sometimes Cu^{II} are common in the oxidised ore zones. Davidson (1931) refers to the black oxide of Cu, Co, Mn and Fe occurring in and laterally transported from the oxidised outcrop at Chambishi, while Jay (1959 p. 141) states that except in the immediate vicinity of mineralization (at Daluba) the concretionary patches of manganese oxides are absent from the freely-drained soil profiles.

Conclusions.

Multi-element spectrographic data for the profile and nodule samples, although limited in number, give some practical indication of the effects of weathering in the six profiles examined.

From the prospecting viewpoint, no indicator elements were revealed as alternatives to Cu and Co, the principal ore metals. Mo, Pb and Ni were detected locally concentrated in certain iron and manganese segregations, but their values in these selected samples do not correlate with mineralization. Further investigation of these elements, on a wider sampling basis might usefully be pursued.

It is suggested that the ratios of Co:Fe and Cu:Fe merit further investigation as possible aids in (a) detecting Cu and Co anomalies in highly leached environments and (b) distinguishing non-significant Cu and Co anomalies related to gabbro bedrocks.

The investigation indicates the scope for spectrographic methods, simple enough to be used in a routine prospecting laboratory, in investigating weathering and soil-forming processes related to geochemical prospecting problems. The methods employed are suitable for similar investigations in other areas where:-

(a) the geochemical variations sought are large compared with the modest accuracy of the analytical methods;
and (b) the multi-element coverage offered by the spectrograph can be used with advantage.

Traverse Samples.

Figs. 26 and 27 present the geological and spectrographic data relating to near-surface samples collected by Drs. Tooms and Webb for the traverses shown in Fig. 24. Each traverse crosses the sub-outcrop of Cu-Co mineralization in shale at Daluba, but the samples comprise soils from the A₂ horizon of freely-drained profiles on the one hand (Fig. 26), and dambo soils extending into a stream sediment train, on the other (Fig. 27).

The data for Cu and Co generally conform to the distribution for these metals established by the extensive work by Tooms, (1955); Govett, (1958); Webb and Tooms, (1959) and Jay, (1959). Thus, while both Cu and Co show significant anomalies in freely-drained soils, with an

Fig.26. Traverse : Line 48, Baluba.

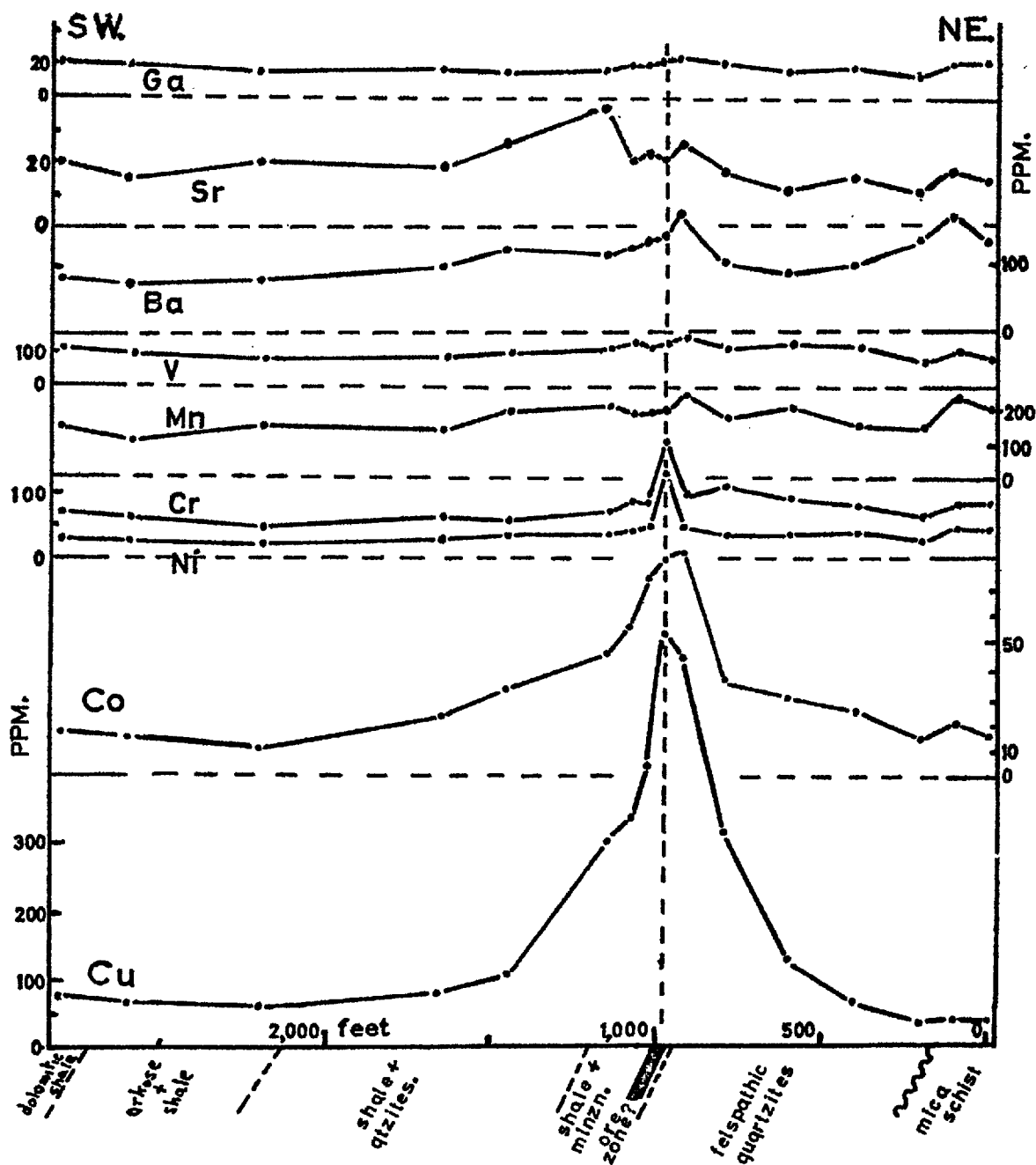
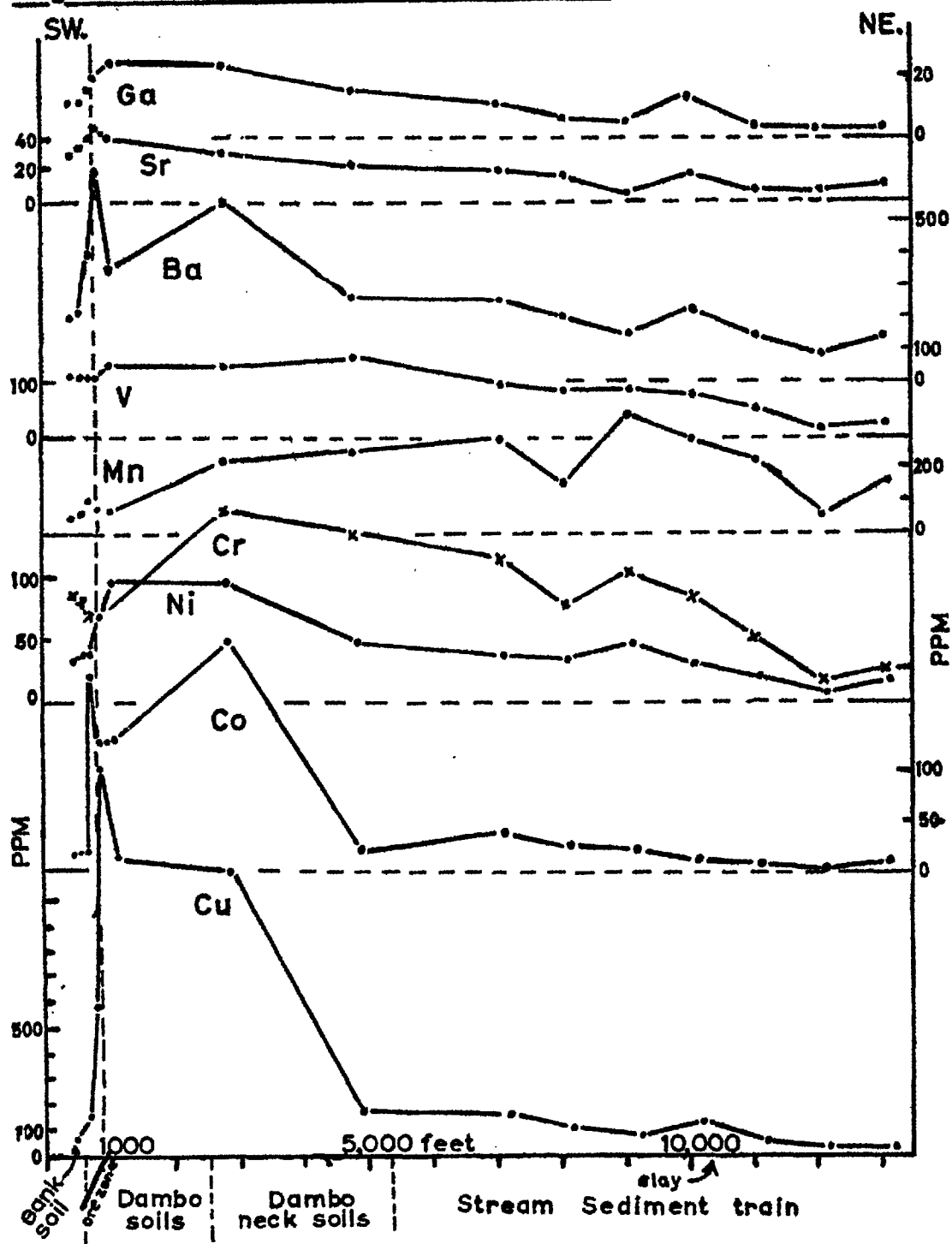


Fig.27. Traverse: Dambo 1, Baluba.



anomaly width of some 1200 ft., higher anomaly peaks occur in the dambo soils and the anomaly width is very much greater. Anomalous Cu and Co contents extend down-drainage into soils of the dambo neck and to the stream sediment train.

The spectrographic data show the following features relevant to geochemical prospecting for elements other than Cu and Co:-

(a) In the freely-drained soil traverse (Fig. 26) the main feature of the data is the moderate increase in the content of both Ni and Cr immediately over the shale horizon; this has previously been noted and discussed. The geochemical contrast with the contents of Ni and Cr remote from mineralization is some 2-3-fold. Thus these elements are less effective indicators of mineralization than are Cu and Co, on the grounds of (i) lower geochemical contrast and (ii) limited lateral dispersion. If Ni and Cr are related to Cu-Co mineralization in the shale, as distinct from lithology, their limited lateral dispersion would make them suitable for the precise location of mineralization within the broader anomalies developed for Cu and Co.

No other element determined* shows a significant anomaly related only to the position of the ore shale. However, Ba shows a minor peak in that vicinity, with a second peak over

*Mn, Ga, V, Rb, Li, Ba, Sr, Na, K, Pb, Sn, Mo, Ag.

the mica schist. Sr shows a slight anomaly, probably analytically significant, but not clearly related to mineralization.

(b) Referring to the second traverse (Fig. 27), the distribution of Ni shows a superficial resemblance, at a much lower content, to the pattern for Cu and Co. The Ni peak samples, however, lie a little down-drainage of the sub-outcrop of mineralization, and the "anomaly" value of 100 ppm is no greater than that in the freely-drained soils. These features contrast in detail with the behaviour of Cu and Co, but on the limited data from both traverses, it is at least possible that the Ni anomalies are related to mineralization.

A geochemical anomaly exists for Cr in the dambo and drainage samples, but the values are too erratic to suggest a correlation with Cu-Co mineralization.

An unexpected feature of the data is that the calc-alkali elements Ba, Li and K show the closest correlation with the dispersion pattern of the ore metals, Cu and Co. Fig. 27 shows the distribution for Ba, while the adjacent Table indicates that Li and K also parallel Cu to different degrees, whereas Sr shows less correlation, and Na almost none.

Traverse Distance (ft.)	Cu ppm	K ₂ O %	Li ppm	Ba ppm	Sr ppm	Na ₂ O %
500	63	.8	35	200	30	.03
700	165	.8	45	200	35	.05
775	575	1.2	120	400	40	.11
900	1500	1.3	80	650	45	.07
1100	1150	1.0	90	350	40	.08
2900	1000	.6	70	550	30	.05
4900	165	.6	60	260	21	.10
7200	150	.5	48	250	18	.09
8200	100	.2	40	200	15	.08
9200	63	.15	20	140	4	.08
10200	125	.5	45	220	18	.12
11200	48	.1	15	140	5	.05
12200	12	.06	6	85	8	.03
13200	17	.1	8	125	12	.06

K predominates among the associated elements, and the roughly similar dispersions of K, Cu, Co, Ba and Li might suggest that they are contained together within resistant micas or in clay minerals derived from the mineralized shale. Other considerations, however, suggest that these elements have probably been introduced, partly separately, into the dambo soils from groundwaters draining (inter alia) mineralized ground, and fixed by precipitation or adsorption in the organic-rich dambo soils. The erosion of these soils and their incorporation in stream sediment would explain the approximate parallel between the different elements in

their distribution downstream. Webb and Tooms, (1959) have suggested that this mechanism applies, in part, to the development of drainage dispersion trans for Cu and Co.

Several important features of the present data are consistent with the foregoing mechanism. Firstly, precipitation from the groundwater into the dambo soils would explain the facts that (a) the five elements mainly associated in the drainage dispersion, Cu, Co, Ba, Li and K, show higher anomalous contents than they do in freely-drained soils; and (b) while Cu and Co are clearly related to mineralization, K, Li and Ba are probably not, from the limited soil profile data: the data suggest that leaching from the weathered schist or granite is the probable source of K, Li and Ba (Fig. 25).

Secondly, erosion and physical transport of the dambo soil material would account for the similar drainage dispersion patterns for elements which differ in their chemical properties in solution (Cu, Co, Ba, Li and K).

Further work is clearly necessary before drawing firm conclusions from the preliminary spectrographic data. The most promising investigation from the practical viewpoint, would be to establish whether or not Ni and Cr are generally related to Cu-Co mineralization, by the examination of samples from suitable mineralized and un-mineralized areas.

Secondly, drainage dispersion trains in both mineralized and background areas should be examined for the calc-alkali and ore elements, in order to establish whether the two groups of elements are related directly or indirectly in the drainage system, as a guide to the mechanisms of drainage dispersion.

CHAPTER 7. BUKANGAMA RIDGE, UGANDA.

Introduction.

The samples examined from this area comprised six soil profiles collected and previously investigated by J. D. Jacobson (1956), as part of a detailed geochemical prospecting programme near the Kilembe Cu-Co mine, Uganda. This programme was commenced in 1954 by Dr. J. S. Webb, at the invitation of the Uganda Geological Survey. Encouraging preliminary results were obtained, and the study of geochemical prospecting for Cu and Co in this hilly tropical terrain was continued, mainly by chemical analyses for Cu, (a) in the soils, by Jacobson (1956), and (b) in the drainage system, by Holman (1956). Some results of investigations of Cu and Co at Kilembe, contrasted with geochemical prospecting studies in the Rhodesian Copperbelt, are summarized by Webb (1956). Research work under Dr. Webb's direction has been continued at Kilembe by D. R. Clews (in preparation), and in the present ancillary study.

Previous work had shown that the steep topography of Bukangama Ridge permits surface erosion to compete with chemical weathering, so that relatively shallow and immature profiles are developed, in contrast with the mature and senile soils of the Copperbelt peneplain. Thus, leaching of Cu from the upper horizons, under comparable geological

conditions is less pronounced at Kilembe than in the Copperbelt. Moreover, the upper B horizon, wherein Cu and Co anomalies are well developed, lies on average, only 15" below the surface at Kilembe (Jacobson, 1956). Geochemical prospecting by analysis of soil samples for Cu is relatively straightforward, the principal problem being the discrimination of Cu anomalies related to mineralization on the one hand and dolerite dykes, on the other. The present study was made, therefore, primarily with the view to studying the profiles distribution of the common minor elements as a result of soil formation, and to examine geochemical distinctions between the bedrock types.

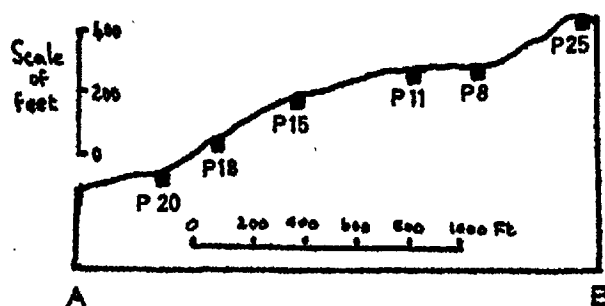
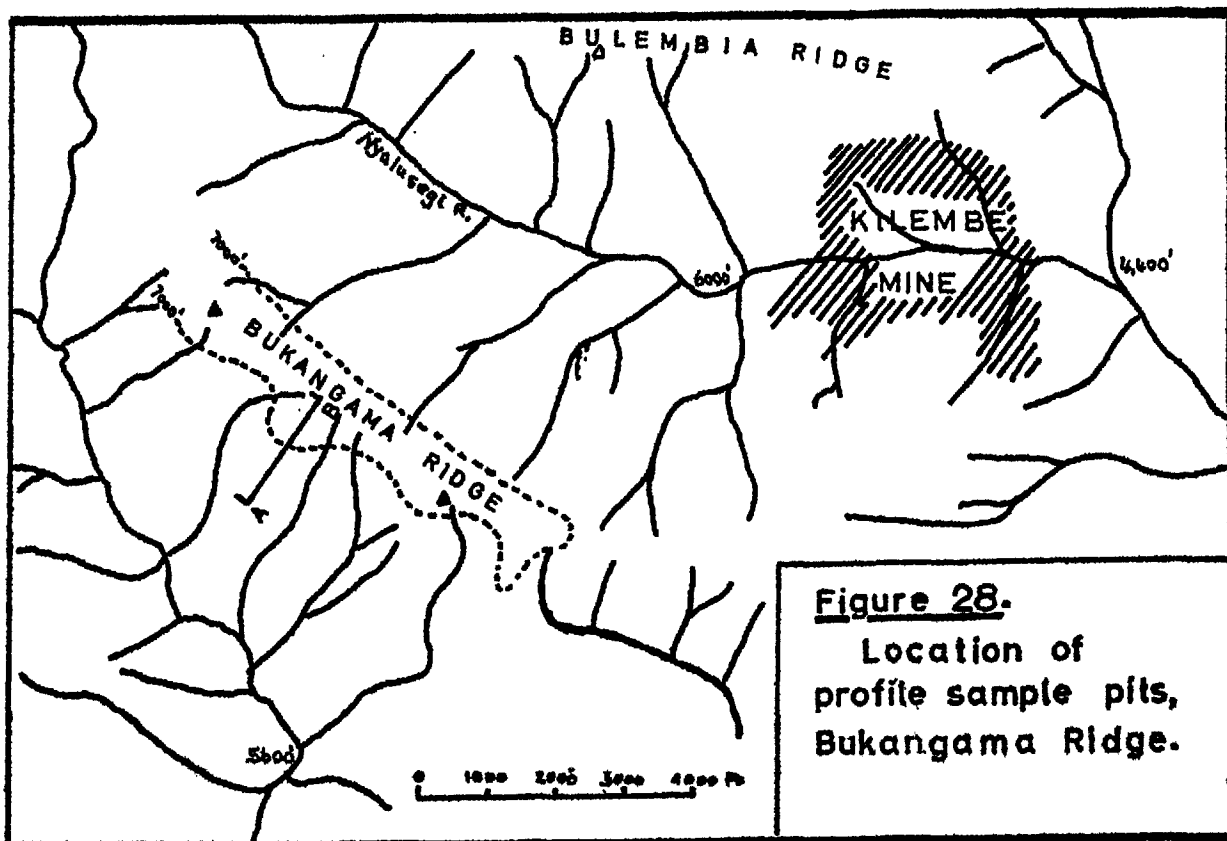
General Description of the Sampling Area.

The following outline is based on detailed descriptions of the Kilembe area from the geochemical prospecting viewpoint by Jacobson (1956) and Holman (1956). Their sources of information in addition to field observations, were obtained from the work of the Uganda Geological Survey and the staff of Kilembe Mines Ltd.

Location and topography.

Figure 28 shows the location of Bukangama Ridge and the profile sampling sites on its south-western slope.

The Cu-Co mine at Kilembe lies in the Nyalusegi river valley, in the south-eastern foothills of the Ruwenzori



Topographic section.

After Jacobson, 1958.

mountain range. Bukangama Ridge forms the south-western side of the valley, and the topography displays the vigorous relief with steep, straight slopes, typical of the active erosion which has succeeded the uplift of the Ruwenzori range in Recent geological times.

Many valleys near the centre of the Ruwenzori show evidence of past or present glaciation, but no glacial effects have been seen below 8000 ft. in the southern part of the range, and the soils on Bukangama Ridge may therefore be regarded as free from glacial transportation. Moreover, although gradients vary between 20° and 50°, there is no evidence of widespread slipping or terracing of the soil material.

Drainage.

The topography and surface drainage of Bukangama Ridge appears to be independent of any geological control. The country rocks strike across the axis of the ridge, and although some dolerites trend parallel to the ridge crest, they are not large enough to have influenced the topography.

Brooks generally rise in water-logged areas at or just below the gully head, though sometimes there may be a well-defined headwater spring. On Bukangama Ridge, running water appears at surface some 600-800 ft. below the Ridge

crest. Holman and Jacobson suggest that because of the steep topography, the water-table lies at a considerable depth below surface, at least on the upper slopes, even during the wet season. Drainage of the soils probably occurs mainly by lateral movement in the porous upper horizons of the soils; there is little surface sheet-wash even during tropical rains.

Climate and vegetation.

Although the area lies close to the equator, the climate in the elevated foot-hills may be described as temperate. The average rainfall at Kilembe is about 40-50 inches, falling mostly in two periods, with drier intervals in January and June. The daily temperature variation shows little change from 60 and 80°F throughout the year.

Bukangama is situated in the forest belt, but as a result of native agriculture, the predominant vegetation is now elephant grass and bracken. This secondary growth provides a thick and continuous vegetal cover.

Soils.

Features observed in the soils of Bukangama Ridge by previous workers show that:-

(a) the persistent soil cover is dominantly residual and freely-drained, though appreciable thicknesses of colluvium may develop towards the base of slopes.

(b) active soil creep is a general feature, but land slipping is not widespread.

(c) the profiles are relatively shallow, rarely exceeding 5-7 ft. in depth (cf Rhodesian Copperbelt, Chap. 6). The soil horizons are not sharply differentiated. Jacobson notes that the visual identification of the major A, B and C horizons is difficult in most cases, since there is often little change in the appearance of the soil below the top few inches. Concretions are not usually present in the B horizon, while soil fragments can co-exist with secondary products in many different horizons. The soil profiles are relatively immature.

(d) Beneath the black top soil, the profiles are predominantly red in colour. Jacobson (1956) describes them as ferrallitic soils, after Robinson (1949), indicating that the red colour derives from retention of iron oxides in the soil.

The generalized soil profile is described below after Jacobson (1956).

Geology.

The Ruwenzori Mountains form an uplifted block of Precambrian formations, consisting mainly of migmatite gneisses, schists, quartzites and plagioclase amphibolites, the latter probably of volcanic origin. The Kilembe Series

Generalized soil profile from Bukangama Ridge

(from Jacobson 1956).

Horizon	Range in ins.	Approx. Ave. Thick- ness	Colour	Comments
A ₀₀₊₀			-	Rotted Vegetation matting noticeably thicker on ridge tops.
A ₁	0-12	3	Dark grey (dry) Black (wet)	Fine sandy loam, porous and loose when dry, fibrous, very thin in cultivated areas. Boundary clear or gradational.
A ₃	2-18	12	Dark red-brown to chocolate brown	Clay loam, massive but friable. Boundary clear or gradational.
B	6-96	37	Yellow to red, paler colour over granite rock.	Sticky sandy clay. Parent material fragments increase downwards. Stone line sometimes present near top of horizon. Boundary diffuse.
C	6-?	-	-	Defined as being reached when the amount of fragmental parent material is judged to be in excess of the matrix.

which carries the Cu and Co sulphide deposits, occurs as a relatively small inlier, in-folded in the gneisses of the S.W. foothills (McConnell, 1956). The Series consists mainly of a group of albite-quartz granulites, derived by metamorphism of sedimentary rocks; bands of plagioclase amphibolite; and intrusions of alaskite-pegmatite and dolerite.

Rock types which occur at Kilembe Mine and on Bukangama Ridge are described by Holman (1956) as follows:-

The granulites are dark-coloured rocks of fine to medium grain size, containing quartz, albite, and pyroxene, with sericite, biotite, epidote, iron ore and tourmaline. The Cu-Co sulphide ore at Kilembe occurs mainly in the granulites, enclosed between a quartz-felspar amphibolite below and a second amphibolite above.

The amphibolites are distributed irregularly as bands of varying thickness in the granulites. The rock may consist largely of dark green amphibole, becoming lighter as the amount of quartz and felspar increases. The grain size is also variable. Scattered grains of chalcopyrite and pyrite occur in the rock, even well away from mineralization.

The pegmatitic rocks are known locally as alaskites. They commonly contain quartz, albite, orthoclase, anorthoclase and microcline. Grains of pyrite and chalcopyrite may be scattered through the rock, more frequently at the margins.

The shape of the pegmatites is often irregular; usually they follow the bedding or cut it at a small angle, and may be up to 60 feet thick. Contacts with the host rock may be sharp, or gradual over several feet. The country rocks appear to have suffered very little alteration or disturbance during emplacement of the pegmatites.

The dolerites are fine to coarse grained, containing labradorite, pyroxene, biotite and micro-pegmatite. Grains of chalcopyrite are common, as in many other dolerites in Uganda which are independent of economic mineralization.

Mineralization.

Chalcopyrite, pyrite, linnaeite, magnetite, and pyrrhotite are the minerals commonly occurring in the Kilembe ore, either disseminated in the granulites or as massive bands. The mineralization follows the folded structure imposed upon the beds, but the ore boundaries are indistinct. The tenor of the ore varies approximately between 1-5% Cu : and 0.1-0.6% Co.

A zone of oxidation extends to about 60 feet below the surface, with very little secondary enrichment. This contrasts with oxidation to five times this depth in the Copperbelt. The host rock is intensively weathered at the surface, with bands of gossan which may retain small blebs of sulphides within the iron oxides.

Field Samples and Geochemical Investigation
at Bukangama Ridge.

Unlike the ore occurrence at Kilembe, the greater part of the sulphide mineralization on Bukangama Ridge was found by Jacobson (1956) to occur within the amphibolites.

Figure 29 summarises Jacobson's description of the bedrock geology revealed by his pitting and geochemical results, for the traverse which includes the profiles for the present study.

Briefly, the Ridge crest at this point is intersected by a mineralized amphibolite, which becomes barren down-slope. The surface Cu anomaly indicates two parallel zones of mineralization, some 200 ft. apart. Further downslope, biotite schist and granulite horizons are succeeded by injection gneiss, and intrusions of alaskite and dolerite also occur within the sampling area (Fig. 29).

The six pit profiles collected by Jacobson, and selected for spectrographic analysis, are listed in the adjacent tables, with descriptions of (a) the original bulk samples and (b) the sieved minus 80-mesh fraction which was taken for analysis.

Analytical techniques.

The sieved minus 80-mesh samples were gently ignited at 500°C for two hours, prior to analysis by the following spectrographic techniques:-

Elements determined	Procedure	Technique (Chap.)
Alkalis:- Na_2O , K_2O , Li, Rb, Ba, Sr.	Anode arc, carbon mixing.	A (Chap. 2)
Cu, Co, Ni, Cr, Mn, Mo, Pb, Sn, Ag.	Cathode-layer arc, Li_2CO_3 -carbon buffer method.	C_1 (Chap. 2)

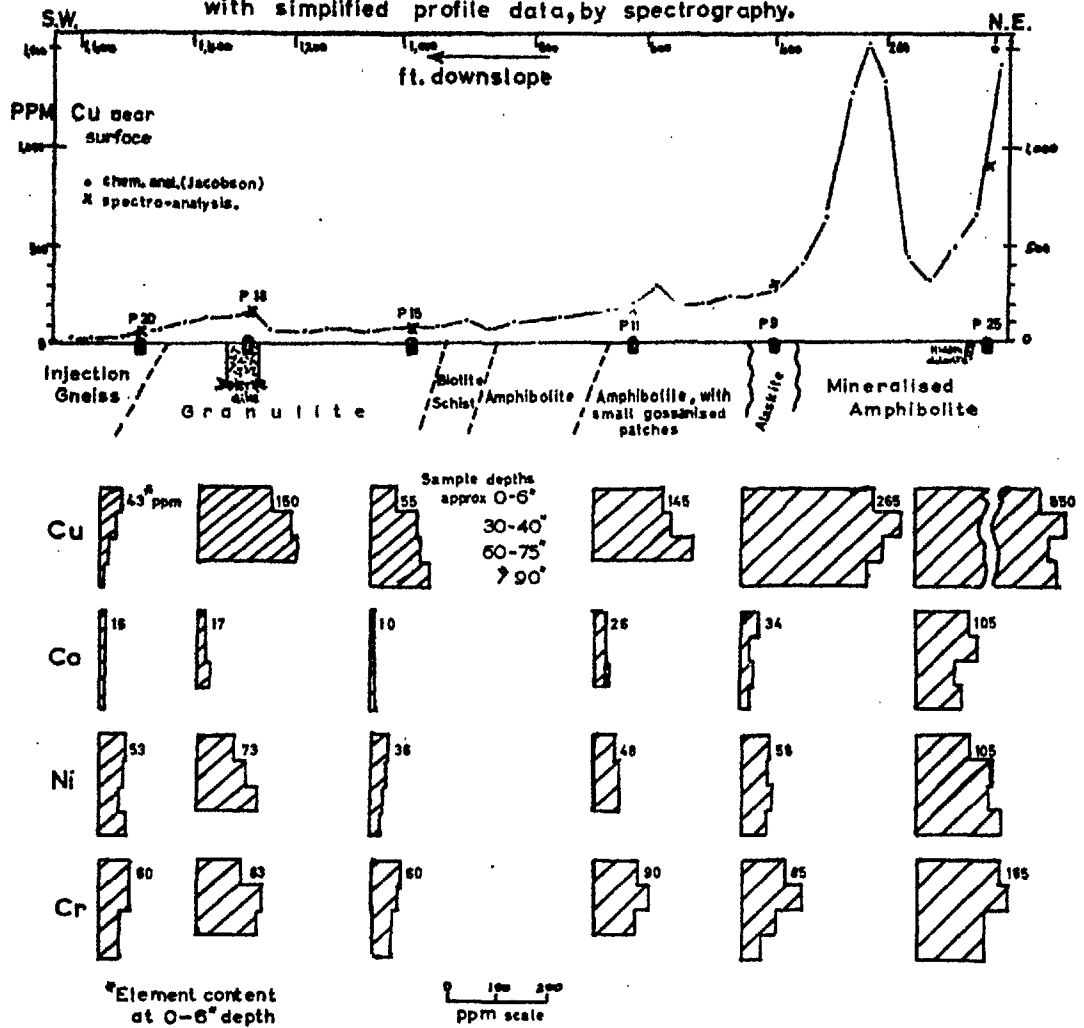
The results are tabulated in Appendix B7, and Figures 29 and 30 show the profile distribution for the elements of main interest from the geological viewpoint.

Observed Distribution of the Analysed Elements in the Soil Profiles.

Fig. 29 shows the simplified profile distribution for the elements Cu, Co, Ni and Cr, compared with the near-surface Cu contents, determined chemically by Jacobson (1956). Figure 30 shows the histograms in more detail, on the scale employed for the preceding Copperbelt data, to facilitate comparison between the two areas.

The main features of geochemical interest in the sample descriptions and in the observed distributions of the elements are as follows:-

Fig. 29. Bukangama Ridge: Geology & surface Cu content after Jacobson (1956), with simplified profile data, by spectrography.



1. General features common to the six soil profiles.

(a) There is a generally high content of the ferrides Mn, Ni, Cr, and (qualitatively) Fe, even over bedrocks which are not themselves high in ferromagnesian minerals, namely, the granulite, gneiss and alaskite profiles (Fig. 30). The highest Ni and Cr values occur together in the ferruginous clay soils over the dolerite and mineralized amphibolite. Almost all samples after ignition show a generally high content of red-brown ferruginous clays, even including the surface layers.

(b) Calc-alkalies Li and Na_2O show low values and little change with bedrock or with depth, suggesting relatively complete leaching. K_2O on the other hand, increases in the micaceous soil profiles, namely over the gneiss and granulite.

(c) Leaching from the upper horizons is only generally seen for Cu, as noted by Jacobson, and is not very pronounced. In particular, no element shows any tendency to decrease sharply in the immediate surface horizon.

(d) Changes in concentration down-profile are gradational rather than sharp, conforming to the field description of the profiles. In particular, there is little evidence of strong accumulation of any element in the B horizon, with the significant exception of mineralized amphibolite. Here, accumulation in the B horizon affects Cu, Co, Mn, Ni and

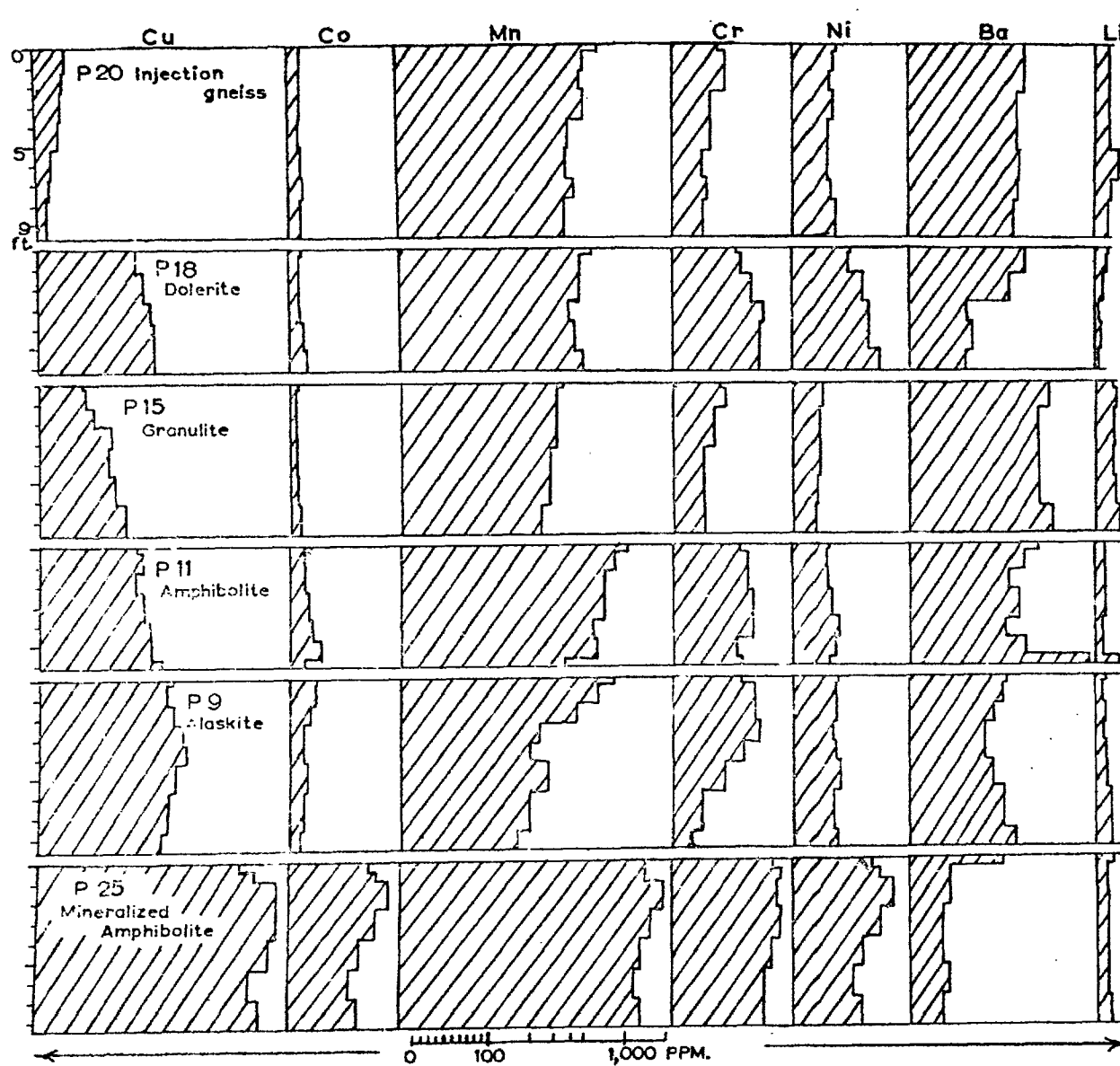


Fig. 30.
Soil Profiles,
Bukangama
Ridge.

(qualitatively) Fe. This may reflect initial mobilisation by oxidation of the sulphides. Jacobson (1956) notes in this connection that black stains of manganese occur along with gossany oxides in the subsoil of this profile.

(e) The sample descriptions often show co-existence of brown ferruginous clays and decomposed or even fresh rock fragments, at several horizons. This dis-equilibrium emphasises the immature nature of the soil profiles.

(f) All the surface samples show a loss on ignition of over 20%, of which 9-10% may be due to organic matter, in addition to the loss of 10% related to residual moisture which is common to all the samples down-profile.

2. Indications of bedrock lithology and mineralization.

The combination of soil data for several elements (Figures 29 and 30) provides a more detailed index of lithology than was possible by Jacobson's work based mainly on Cu and partly upon Ni and Co.

At the six profile sites, the surface contents of the ore-metals Cu and Co decrease downslope, away from mineralization, except for a significant minor Cu peak over the dolerite. This conforms to Jacobson's findings (1956). From the limited data, it may be noted that if Jacobson's threshold value of 100 ppm for Cu is adopted and a Co threshold of 20 ppm assigned by inspection of the data, then

the contents of Cu and Co at surface are anomalous up to 400 feet from the anomaly peak (Fig. 29). Only Cu, however, is anomalous over the dolerite, and to this extent Co appears more attractive as the (single) ore indicator element. Further work would be necessary before generalizing from this limited number of samples. Moreover, depending upon the analytical technique, the higher content of Cu might make this element preferable for prospecting purposes, at least in the initial detection of anomalies.

The Cu anomaly over the dolerite reflects the minor chalcopyrite commonly associated with such basic intrusives. Providing multi-element analyses are available, the ratio of Co to Ni clearly distinguishes the Cu-anomalous soil over this bedrock from that over the mineralized amphibolite (Fig. 29), as noted by Jacobson (1956). This observation follows work by Holman (1956) showing that the ratio of Co to Ni in tropical soils can reflect the low ratios which characterise basic igneous bedrocks.

At the same time, the contents of Ni and Cr are actually greater over the mineralized amphibolite than the dolerite (Fig. 29), although it is not possible from the limited data to decide whether Ni and Cr are related directly to the Cu-Co mineralization. The high Ni and Cr in the mineralized amphibolite soils may be either an original characteristic of the amphibolite, or they may have been introduced along

with the mineralization. In comparing the mineralized and barren amphibolite profiles (Figs. 29, 30) it appears that Ni and Cr, while higher in the former, do not increase in proportion to Co. The possibility that Ni and Cr are introduced with mineralization might deserve further investigation, which should include hard rock samples. Jacobson has shown that, whereas Ni occurs as a trace constituent of the Kilembe ore, it is also found in soils on Dukangama Ridge independently of both Cu-Co mineralization and of dolerites; he suggests a separate introduction of Ni.

In addition to the high Ni and Cr contents, other similarities between the dolerite and mineralized amphibolite soils are: (i) the sieved samples from both profiles show a high proportion of yellow-brown ferruginous clays, (ii) Ba, K_2O and Na_2O are comparable and low in both profiles (Fig. 30; Appendix B7). While this limited data is not diagnostic, it suggests that apart from the ore metals Cu and Co, there are several similarities in composition between soils derived from the two bedrocks. Mineralogical similarities between amphibolites and dolerites, especially with regard to the ferromagnesian components, could easily lead to rather similar iron-rich soils. The important distinction for geochemical prospecting purposes remains the high content of Co, and high Co to Ni ratio (approx. 1.0) associated with mineralization.

The mineralized amphibolite profile differs from the un-mineralized amphibolite, whose soils are lower in Cu, Co and Ni, higher in K_2O , Ba, and Li at depth, and have a more sandy texture. The soils of the granulite show the characteristics of a less basic facies. The iron oxide colour is little paler than the amphibolite (P. 11), but the minor ferrides, Mn, Ni and Cr are lower than in any other profile. Moreover, the granulite has micaceous soils, like the gneiss, reflected in similar and relatively high contents of K_2O , Rb and Li (Fig. 30; Appendix B7). The gneiss gives rise to the palest soils, and to the lowest Cu content, especially at depth. The proximity upslope of granulite enclosing a dolerite dyke, may explain why Co and Ni are higher in soils over the gneiss than over the granulite. Soil movement downslope is suggested by the increase of Cu, Mn and Cr towards the surface in the gneiss profile; the lower horizons are probably more representative of the gneiss bedrock.

The remaining profile, over alaskite-pegmatite, shows a physical resemblance to the gneiss profile in that both possess a pale clay rich C horizon. The upper horizons are, however, much more ferruginous than the gneiss, in addition to the anomalous contents of Cu and Co. Coupled with the increase towards surface of Mn and Cr, the high content of ferrides is probably due to transport by soil creep, or in

solution, from the iron-rich soils of the amphibolite upslope (Figs. 29, 30). The anomalous surface contents of Cu and Co may likewise be due to transport downslope, and not directly reflect the composition of the alaskite bedrock itself. On the other hand, the relatively high Cu values over the alaskite persist at depth, and the possibility that Co, with Fe, Mn and Cr, have been removed by leaching at depth, should not be overlooked.

Further work is clearly required on hard rock samples, to follow up the foregoing indications of bedrock lithology from the soil data. This is especially necessary since lateral transport of soil components is probably an important effect in this terrain.

3. Comparison of geochemical characteristics of Bukangama and Copperbelt soils.

The contrast in topography and the rate of erosion, between the ridge at Bukangama and the peneplain of the Copperbelt have been noted by Webb (1956), in connection with geochemical prospecting for Cu and Co mineralization in each area. The most significant differences concern the relative immaturity of the Bukangama soils compared with the mature or senile soils of the Copperbelt. Thus (a) over comparable geological materials, leaching of the ore elements Cu and Co is much less pronounced at Bukangama; (b) profile differentiation is less complete, and (c) the depth of soil

development is also less at Bukangama; the B horizon is accessible at a depth of some 15-18", compared with over 10 feet in many Copperbelt profiles. These are in general assets in prospecting for Cu and Co at Bukangama. On the other hand, (a) the steep slopes at Kilembe promote soil creep, which may complicate the interpretation of surface geochemical anomalies, and obscure others under colluvial cover at the foot of slopes. Moreover, (b) soil anomalies do not persist for such large distances as in the Copperbelt.

The present limited data (a) confirm the characteristic features of the vertical distributions of Cu and Co in each area, and (b) add new elements which bring out the following features (cf. Figs. 25 and 30):..

(i) At Bukangama, there is little leaching from the immediate surface layer, even of moderately soluble elements. This contrasts with the sharp decrease in Fe, Cu, Co, Cr, Ba and Li at the surface in several Copperbelt profiles.

(ii) Accumulation of the minor ferrides in the B horizon is almost absent in the Bukangama profiles, except in the mineralized amphibolite, for Mn, Ni, Co and Cu. Significantly, segregations of manganese oxides are noted by Jacobson in this profile. Accumulation of ferrides in the B horizon is, in contrast, a common feature of the Copperbelt profiles, related with the occurrence of actual iron oxide concretions.

(iii) The tenor of the minor ferrides, especially Mn and Ni is generally higher in the Bukangama profiles than in the Copperbelt, reflecting (a) the more ferruginous nature of the clays associated with basic rocks such as dolerite and amphibolite. These soils broadly compare with the surface soils over the Copperbelt gabbro. (b) The re-distribution of the abundant ferruginous clays (physically or in solution) probably accounts for the moderately high contents of ferrides over other rock types at Bukangama. There is insufficient data to infer regional enrichment in the ferride elements.

(iv) The mobile elements, such as Li, Na_2O , are leached from the Bukangama profiles even at depth, reflecting (a) their inherently rapid leaching even from relatively youthful tropical soil profiles and (b) the relative shallowness of the profiles. This brings all horizons above the water-table, below which the calc-alkali elements are relatively retained, as seen at considerable depth over appropriate bedrocks in the Copperbelt.

CHAPTER 8. ARGENT, TRANSVAAL.

Introduction.

The geochemical investigation in this area concerns the distribution of minor elements in a soil profile developed over lead mineralization, compared with a second profile developed over unmineralized norite bedrock. The profiles were sampled by Dr. J. S. Webb, who had previously investigated the distributions of Pb and Zn from the geochemical prospecting viewpoint (Webb, 1956), and who proposed the present multi-element study.

The spectrographic data reveal associations between certain elements in particular soil horizons, and the results are discussed with reference to the geochemical mechanisms which may be responsible for the observed element distribution.

Location and Geology.

The Argent lead mine is situated in the Transvaal. Mineralization consists of galena in a steeply-dipping quartz vein system, within a basic igneous country rock - the Bushveld norite.

The deposit is one of several types of metallic lodes which appear to be connected genetically with the Bushveld complex: these include, elsewhere in the Transvaal, auriferous quartz veins; silver ore containing chalcopyrite and tetrahedrite; galena with zinc blende, and cobalt deposits (Du Toit, 1939 p. 123).

Sampling.

The following Table describes the two profiles which were investigated.

Argent soil profiles (description by Dr. J. S. Webb).

Bedrock.	Sample No.	Sample depth (ins.)	Description.
Norite background.	48	0- 6	Roots, which occur throughout profile.
	49	8-16	Concretionary zone.
	50	18-20	Base of rubble zone; concretions.
Ore profile; ten feet east of Argent Main Vein.	51	0- 4	Blackish-brown; many roots.
	52	4-12	Red-brown sandy loam, gravelly; some roots.
	53	12-24	Red-brown loam; some roots; slight Mn segretations.
	54	24-36	Red-brown clays with ferruginous concretions. Ferrocrete rubble base; Mn segretations; with many roots.
	55	36-48	Red-brown loam grading into soft, weathered norite; occasional Mn segretations.

Laterisation, which is the predominant soil-forming process in the area, is reflected qualitatively in (a) the ferruginous red-brown colour of the inorganic (ignited)

samples, and (b) by the occurrence of concretions and ferrocrete rubble zones in the profiles. Segregations of manganese oxides occur both within and below the ferrocrete zone of the mineralized profile.

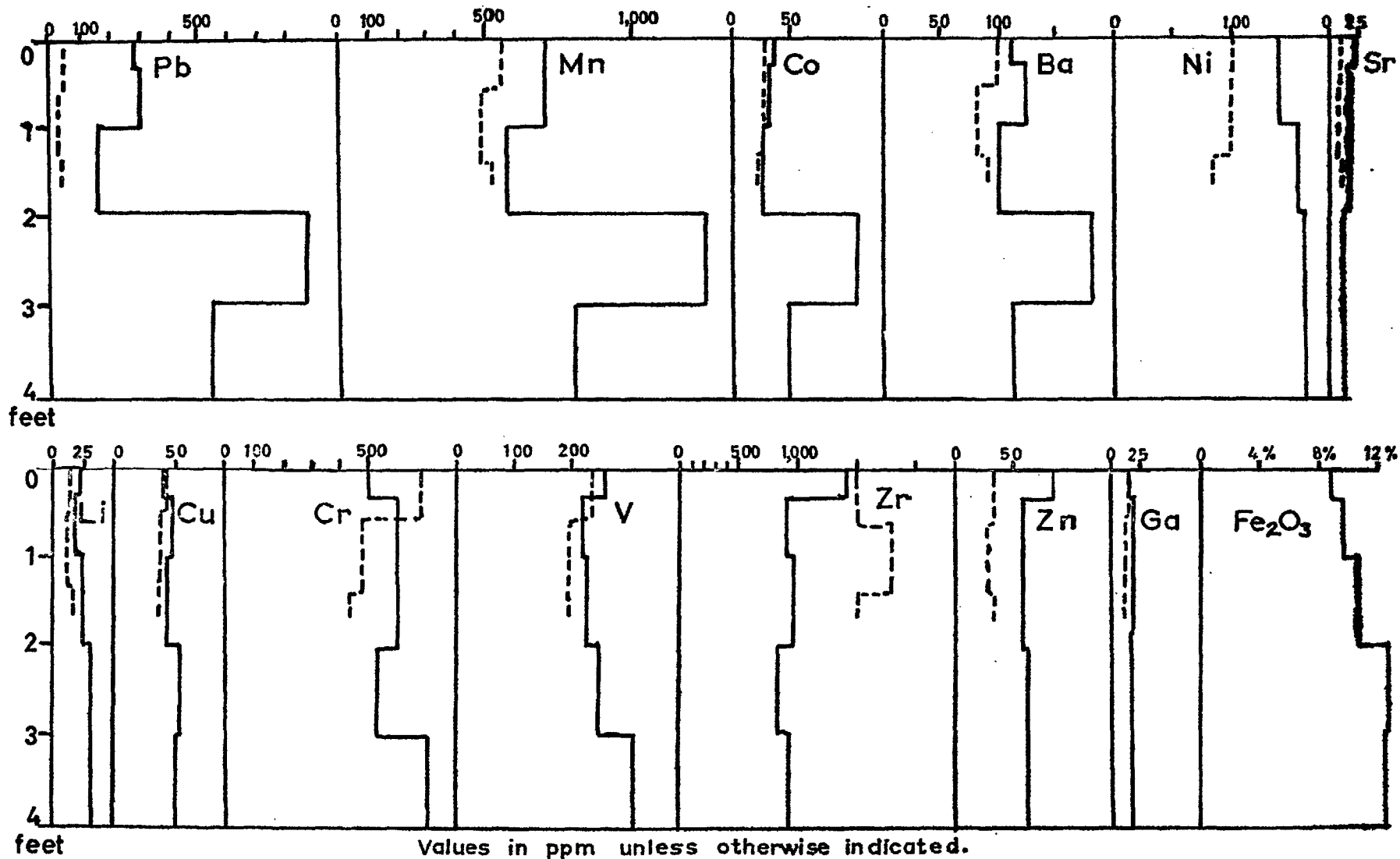
Spectrographic analysis.

The minus 80-mesh fractions sieved from the lightly crushed samples were ignited at 500°C prior to spectrographic analysis. The minor elements were determined by the following procedures which have previously been described in detail; in addition, zinc and Fe were determined by other analysts, using colorimetric chemical procedures.

Elements determined.	Procedure.	Technique.
Be	Anode arc, carbon mixture	B (Chap. 2)
Li, R, B, Sr	Anode arc, carbon mixture	A (Chap. 2)
Other minor elements	Cathod-layer arc, Li_2CO_3 -carbon buffer mixture	C_1 (Chap. 2)
Zn	Visual colorimetric analysis by dithizone	Chemical analysis
Fe	Colorimetric analysis	Chemical analysis

The analytical data are tabulated in Appendix B₈, while Fig. 31 shows the profile distribution for the elements of main interest from the viewpoints of geochemical prospecting and soil-forming processes.

Fig.31. Vertical Soil Profiles: near Pb mineralization
over un-mineralized norite



Geochemical Results.

Comparison of Element Contents between the Mineralized and Un-mineralized Profiles.

(a) Minor elements related to mineralization:

Pb shows a distinct anomalous content at or near the surface (0-1 ft.) in the mineralized profile, compared with the norite background (285 ppm versus 40 ppm Pb). Of the other elements determined, only Zn shows values in the near-surface soils which suggest a relationship to the mineralization; the Zn contents over ore and background are 85 and 35 ppm Zn, giving a contrast factor of only 2-fold compared with 7-fold for Pb. Pb is by far the best indicator element.

As Webb, (1956) previously found, Pb shows local accumulation in two separate horizons over mineralization, namely, in the organic-rich surface soil, and in the concretionary zone 2-3 ft. below the surface (Fig. 31). Pb values of 875 versus 25 ppm occur in the concretionary horizon in the mineralized and background profiles respectively, more than doubling the anomalous content and contrast obtained from near-surface samples.

The limited data suggest that prospecting samples in this area should be taken from the concretionary zone, in order to improve the detectability of geochemical anomalies related to Pb mineralization. A similar recommendation is made by Perel'man (1957) for general spectrographic

prospecting in Russian podzolic soils, which typically show pronounced leaching of trace elements from the upper horizons, and relative accumulation in the illuvial horizon. Nevertheless, further investigations on an areal sampling basis would be required at Argent, to relate the optimum sampling depth with the effective width as well as the intensity of the Pb anomalies.

(b) Minor elements probably unrelated to mineralization.

The elements Co, Ba, Sr, Li, Cu, Cr, V, Ga, Zr and Sn, Mo, Ag (Appendix B₈), show no significant increase in content in the near-surface soil over mineralization compared with the background norite, and Mn and Ni increase by only small factors (about 1.5-fold). It is probable that all these elements are derived entirely from the bedrock, and are unrelated to the Pb mineralization. They are non-significant for practical geochemical prospecting purposes. Nevertheless, it may be significant from the viewpoint of the minor accessory minerals of the ore zone, that in the sample from the greatest depth over the mineralization, the elements Co, Ni and Li are slightly enriched by approximately two-fold, compared with the barren profile.

The relatively high values for Ni (130 ppm), Cr (500 ppm) and Co (30 ppm) in the near-surface soils are consistent with the levels encountered in soils derived from basic igneous bedrocks (Mitchell, 1955). Moreover, the Co:Ni ratio is

less than unity, a typical situation in basic igneous rocks which is often reflected in the composition of residual tropical soils derived from them (Holman, 1956; Webb, 1956).

Vertical Distribution of Elements in the Profiles,
Related to Geochemical Processes.

The data for variations with depth of Fe and certain minor elements can be related to geochemical mechanisms which may be involved in developing the soil profile.

(a) The field description suggests that the soil matrix material changes only gradationally in colour and texture, despite the sharply defined zone of rubble and iron concretions. This gradational change in colour is reflected by the fairly small change in Fe content in the minus 80-mesh samples (Fig. 31).

The gradational increase in Fe content with depth is approximately paralleled by the ferrides Ni, Cr, V, and to some extent by Cu. It is probable that Fe, Ni, Cr, V, and Cu are retained together in the iron oxide minerals, of either primary or secondary origin. Data from the Copperbelt profiles also, has suggested a fairly close association for Fe, Cr, V and Cu in freely-drained soils.

(b) The variations with depth of Mn, Pb, Ba and Co are in sharp contrast with the gradational changes for Fe in particular, and for Cr, V, Ni and Cu. Although parallel

distributions between two or more elements need not imply a common process of geochemical dispersion, a single mechanism may possibly be involved in this case, in the co-precipitation or adsorption of Pb, Ba and Co with precipitated manganese oxides. Not only are manganese segregations observed in the field samples, but data for Mn segregations from the Copperbelt shale profile, have shown a significant association between (inter alia) Mn, Co, Ba and Pb. (Cu is not co-accumulated with these elements in the Argent profile, probably because it is much less abundant and less mobile than in the mineralized profile from the Copperbelt).

(c) Other mechanisms than precipitation of manganese segregations may, however, have contributed to the accumulation of Mn, Pb, Ba and Co in the concretionary horizon. Although Fe does not closely parallel Mn, Pb, Ba and Co as regards the histograms for their total contents, Fe_2O_3 increases down-profile by some 3% in the sieved samples from the Argent profile. This increase is quantitatively very large compared with the increases for Mn, Pb, Ba and Co, and these elements may well have been co-precipitated or otherwise fixed by iron oxides in the concretionary zone.

(d) Since Ba and Pb form insoluble sulphates (especially Ba), and since Pb and other sulphates are produced in the weathering of galena deposits, a mechanism involving the

sulphate ion may be involved in the related distribution of these elements (Fig. 31). Sulphate ion might usefully be determined in future investigations.

(e) The important surface accumulation shown by Pb, and to a lesser extent by Mn, Ba and Co, is no doubt related with organic matter in the surface horizons. Surface enrichment of Pb, first described by Goldschmit, is also well-known in soils of temperate climates, either independently of mineralization (Mitchell, 1955) or in soils over lead mineralization (Webb, 1958).

(f) Turning to relatively constant elements in the profile (Fig. 31), the data shows that whereas Co tends to accumulate in the concretionary zone, Ni does not. This distinction suggests that either (a) Ni has suffered less mobilization in solution than Co, thus being less available for retention in the illuvial horizon, or (b) that selective precipitation has caused the specific retention of Co, perhaps by oxidation and precipitation with MnO_2 . Separation by adsorption processes is unlikely because of the similar size and valence of the two ions (Co^{++} , 0.72A radius; Ni^{++} , 0.69A).

(g) The data for Sr, which is not accumulated in the concretionary zone, shows contrasting behaviour to Ba. Sr is more mobile than Ba in the zone of weathering, and once in ionic solution, tends to be removed from the soil; not only

are Ba compounds generally less soluble than those of Sr, but the larger radius of Ba^{++} makes it more strongly adsorbed by clays and other colloids, analagous to the behaviour of K^+ compared with the smaller Na^+ ion (Rankama and Sahama, 1950 p. 483).

Summary.

The investigation illustrates the value of multi-element spectrographic data in studying the distribution of the minor elements, including ore metals, in the products of weathering and soil formation.

From the geochemical prospecting viewpoint, data from the very limited number of samples reveals no effective indicator element other than the main ore metal, Pb. The profile distribution of Pb confirms previous observations of its tendency to accumulate in both the organic-rich surface horizon and in the concretionary zone of the soil profile (Webb, 1956). Subject to the need to determine the effective widths of Pb anomalies in the two enriched horizons, the data suggest that prospecting samples should be taken from the concretionary zone in order to increase the effective content and contrast of the anomalies, and thereby improve their detectability in geochemical prospecting.

CHAPTER 9, DEPE NO. 2 CLAIMS, S. RHODESIA.

Introduction.

The application of spectrography in this, the final geochemical investigation in this report, concerns the geochemical dispersion patterns developed in residual tropical soils over a beryl-pegmatite dyke.

The work formed part of an intensive study of geochemical prospecting for Be in Rhodesia and Uganda, commenced in 1958 under the direction of Dr. J. S. Webb at Imperial College (Debnam and Webb, 1960; Debnam, 1960, in preparation). The present study was part of the first phase of the programme, in which spectrographic analysis was particularly appropriate because (a) no simple chemical or other test for Be was then available and (b) multi-element data were appropriate in the preliminary survey. Subsequent detailed investigations have been carried out (a) by rapid chemical tests for Be (Debnam and Webb, *ibid*; Hunt *et al* 1960), and (b) by the "beryllometer", a portable instrument for determining Be in the field by neutron activation analysis (Bowie *et al* 1960).

The samples examined in the present report were collected, and proposed for investigation, by Dr. J. S. Webb and A. H. Debnam; they comprise soils from a single traverse across the beryl pegmatite and the enclosing schist country

rocks. The objective was to determine the distribution of several minor elements including Be, to complement the foregoing investigations of this element alone. The spectrographic results show distinctive geochemical dispersion patterns in the soils which reflect (a) mineralization and (b) composition of the country rocks. Be, Li, Rb, Ba, Sr and Sn show positive anomalies related to the pegmatites, and Li and Rb in addition to Be appear to be effective indicator elements for prospecting purposes. On the other hand, the ferrides Ni, Co, Cr and V, and likewise Cu, show "negative" anomalies or troughs over the dyke; the higher values on either side almost certainly are related to the basic nature of the schist country rock.

Previous Work.

The foregoing publications by Debnam and Webb refer in detail to the limited amount of previous work concerned with geochemical prospecting for Be. A detailed review is therefore not appropriate in the present limited study, but the following relevant spectrographic studies may be noted.

In prospecting for beryl pegmatites in the U.S.S.R., Zalashkova et al (1958) detected Be anomalies in plants and residual soils; for detecting the soil anomalies, Be concentrations were assessed in arbitrary units by visual estimates of line blackening. Karaeva et al (1958) used

conventional comparison standards, and the air-blast A.C. arc, in similar studies in residual soil cover up to 4-12 feet thick, and found both Li and Be to be positive indicator elements for mineralized pegmatites. The fundamental geochemistry of Be in rocks of the U.S.S.R. has been studied in detail by Beus (1956); (Beus and Sazhina 1956).

In New England, Stoll (1945) detected a limited primary dispersion of Be in wall rocks of mineralized pegmatites, while prospecting for Be by the spectrographic analysis of pegmatite rock samples suggested that mineralization was absent in another area (Perry and Cooke 1946).

Studies of mineral associations for particular elements in pegmatites which have a bearing on the present study, have shown Rb to be incorporated in beryl (Borovik et al 1958) and in alkali feldspars (Heier et al 1959); Li was low in the latter feldspars, and this element usually concentrates in biotite and muscovite micas (Siroonian et al 1959). Jedwab (1956) also notes the association of high Li, Be and Sn in biotites separated from beryl granulites. Data in the present Thesis (Chapter 5) has shown a degree of correlation between Be and Sn in stream sediments derived from stanniferous granites in Malaya, where the nature of the Be source is not yet known.

General Description and Geochemical Investigation at Bepe No. 2.

Detailed geological descriptions and general information on the area, and the field samples, were provided by Dr. J. S. Webb and A. H. Debnam.

The Bepe No. 2 pegmatite is situated in south eastern Southern Rhodesia, in generally flat terrain, where the vegetation consists of thin sub-tropical forest savannah. In contrast with the deep soil cover developed on the peneplain of Northern Rhodesia, the residual overburden at Bepe varies from only a few inches to 8 feet thick, and is a degraded latosol.

The pegmatite dyke is up to 250 ft. wide over a length of 700 ft. and occurs in tremolite schist country rock; it forms a very low ridge feature (Fig. 32). Economic mineralization in the complex quartz-felspar-mica pegmatite consists mainly of beryl, which shows a zonal arrangement, apparently associated with quartz bands. Beryl crystals reach 12 inches in diameter, and the mineral is worked by opencasting at the western end of the pegmatite. Near-surface soil samples examined in the present study were collected by A. H. Debnam from a traverse across the pegmatite at its eastern end, where the ground is essentially undisturbed by mining activity.

Spectrographic Analysis.

The minus 80-mesh fractions sieved from the soils were received by the writer, and ignited for 2 hrs. at 500°C prior to analysis by the following spectrographic techniques, which are described in detail in Chapter 2.

Elements determined	Procedure	Technique (ref. Chap. 2)
Rb, Li, Ba, Sr	Anode arc, carbon mixing	A
Be	Anode arc, carbon mixing	B
Other minor elements	Cathode arc, large crater, Li ₂ CO ₃ -carbon buffer method.	C ₂

The technique for the common minor elements is a development of the cathode-layer method which was employed for all other investigations in this Thesis, introducing a large crater for maximum sensitivity for the volatile elements (method C₂. Chap. 2.). Because of the possibility of bias between two different semiquantitative arc methods, it is not intended to compare the absolute values of results between areas in which different methods were employed. A limited comparative test on the standard granite G-1, however, showed that only Cr was appreciably subject to bias (enhancement) in the modified technique C₂.

Geochemical Results.

The geochemical traverses are illustrated in Figs. 32, 33. The first shows the dispersion patterns for elements which give positive soil anomalies related to the pegmatite, namely, Be, Li, Rb, Ba, Sr and Sn. The data for chemical determinations of Be, which are shown for comparison purposes, were obtained by Debnam using a rapid test based upon the colorimetric reagent Beryllon II (Debnam and Webb 1960). It will be noted that there is reasonably close agreement between the spectrographic and the chemical data, except towards the northern end of the traverse where the chemical values are slightly but persistently lower than the spectrographic results. The reason for this significant detail discrepancy remains to be discovered.

Fig. 32. Soil Traverse ; Bepe, S.Rhodesia.

(A) Be, Rb, Li, Sr, Ba, Sn.

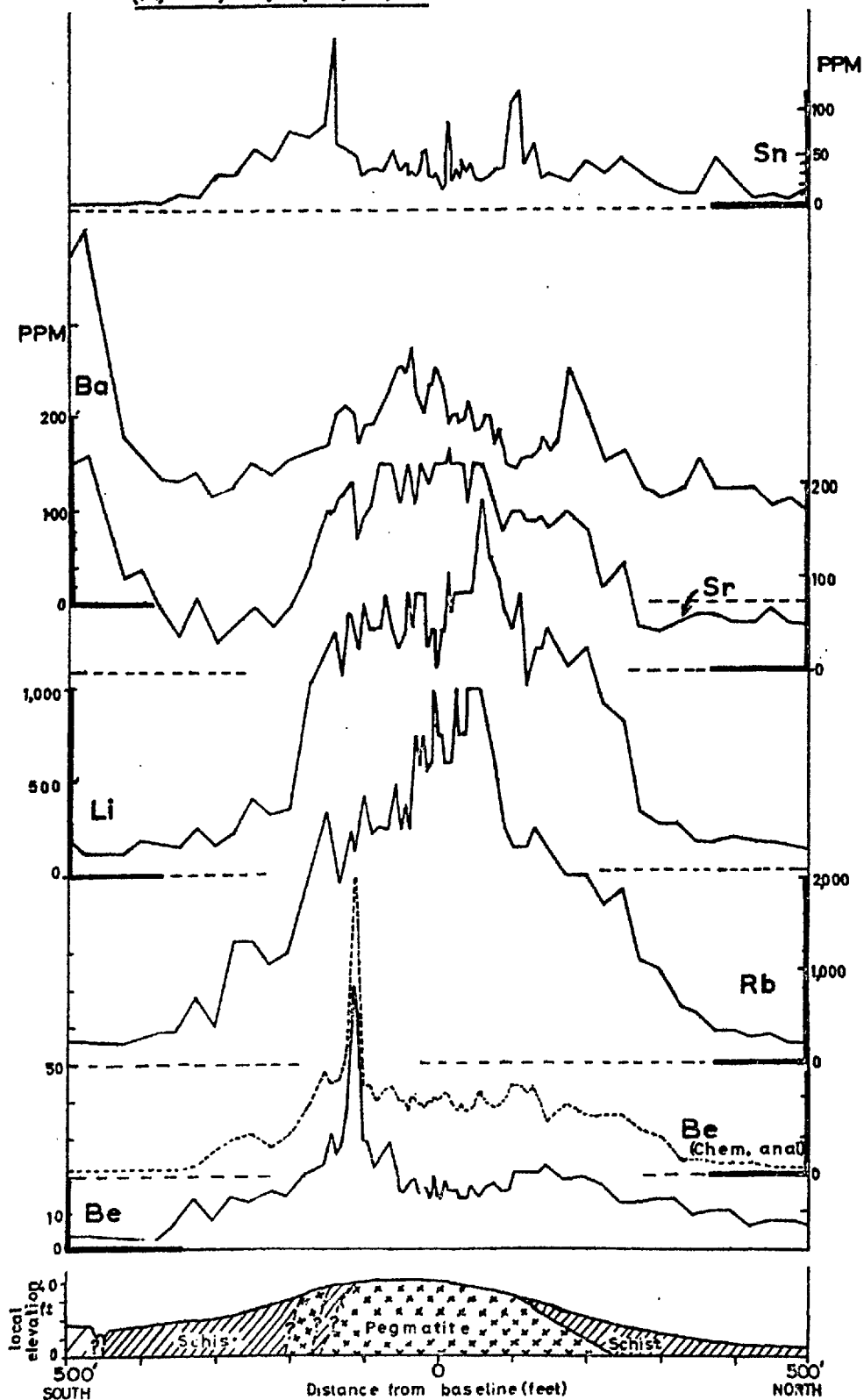


Fig. 33. Soil Traverse; Bepe, S. Rhodesia.

(B) Co, Ni, Cr, V, Cu, Mn, Pb, Ga.

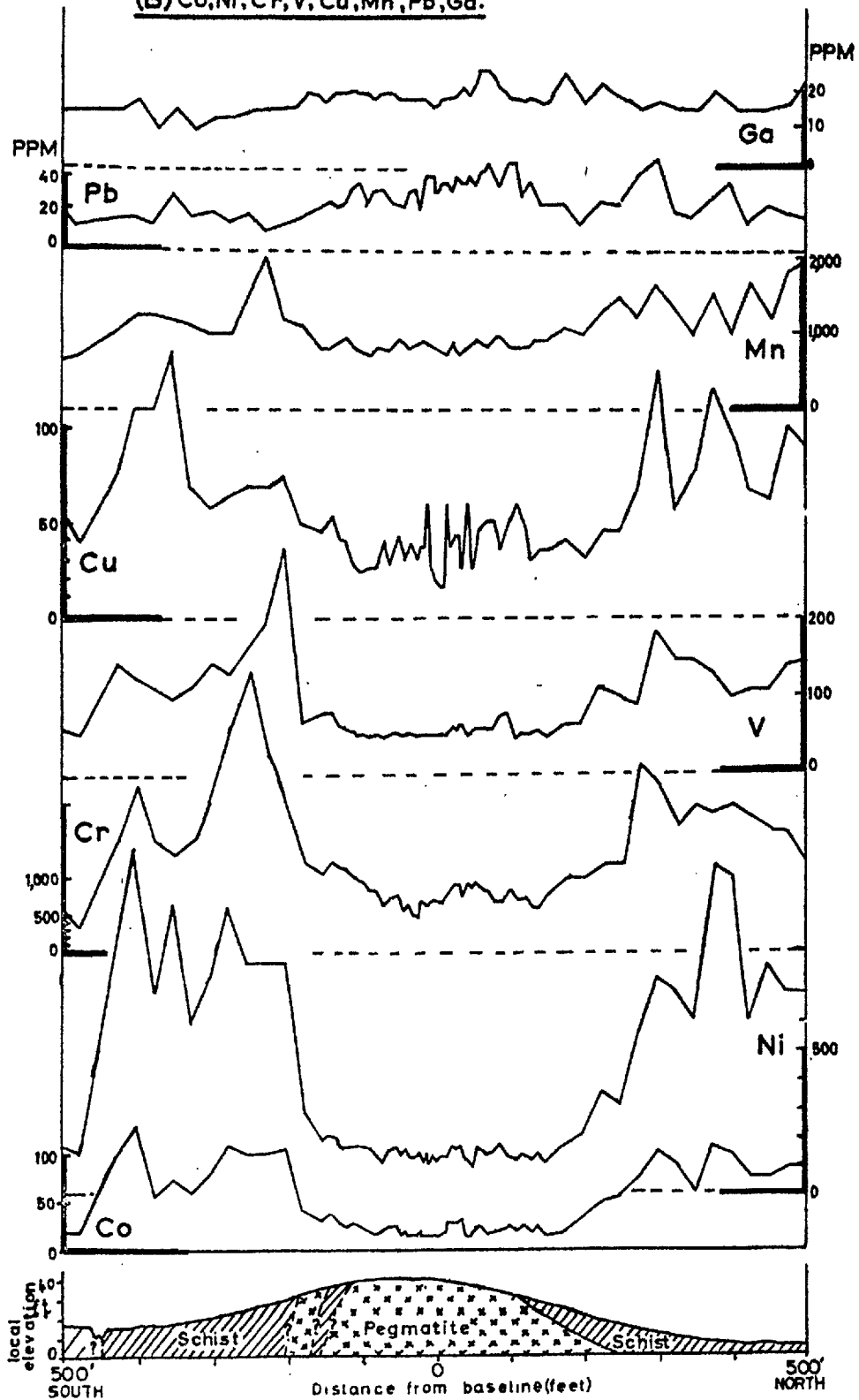


Fig. 33 shows the geochemical traverses for the elements which give negative anomalies or troughs over the dyke (Ni, Co, Cr, V, Cu), and for those which show little significant variation (Mn, Pb, Ga).

The principal features of the analytical results from the practical point of view are as follows:-

(a) Be, Li, Rb, Ba, Sr and Sn show positive anomalies related to the pegmatite. The local variations for individual elements within the broad anomaly, however, do not show a close sympathetic correlation. Be, Ba and particularly Sn tend to show rather erratic distributions across the anomaly; there is some slight evidence of antipathy between the location of the peak value for Be compared with Rb and Li (Fig. 32). These local variations may be related to (i) primary zoning in the pegmatite ~~or~~ (ii) partial segregation in the products of weathering.

(b) Ni, Co, Cr, V and Cu show negative anomalies, or troughs over the dyke. The higher values on either side are almost certainly related to the basic nature of the schist country rock.

(c) Mn, Pb and Ga show little tendency to vary in a manner that can be related to the geology, although there is, perhaps, slight evidence that Mn decreases over the dyke, as might be expected.

(d) For the most part, both positive and negative anomalies have a comparable width of the order of 150 ft. on either side measured from the contacts of the dyke. The anomaly width is approximately 550 ft., the sub-outcrop of the dyke being some 250 ft. across. The discrepancy between the spectrographic and chemical results for beryllium on a few samples from the north side of the dyke has already been mentioned. If the spectrographic data prove to be the more reliable, which is by no means certain, then it is possible that there may be an appreciably wider anomaly for Be than for the other elements.

The findings of Debnam and Webb (1960) based upon chemical determinations of Be may be quoted with reference to the spectrographic data (Fig. 32). These authors found that the peak value of 80 ppm Be rising from a broader anomaly, reflects the main beryl zone. The observed lateral dispersion of Be for some 150 ft. on either side of the dyke is undoubtedly derived by secondary dispersion from the dyke, since samples of the bedrock collected not more than 5 ft. from the contact gave only background Be values. Away from the main beryl zone, the Be content in the minus 80-mesh soil fraction is fairly uniform and appears to be unaffected by the presence of scattered large fragments of Be. In contrast, the beryllometer gives both erratic and much higher results, reflecting the average bulk composition of the near-surface soil (Debnam and Webb, 1960; Bowie et al 1960).

Further work by Debnam (1960, in preparation) may determine to what extent the homogeneity of the Be values is due (a) to Be derived from weathering of associated pegmatite minerals and (b) to chemical or biochemical dispersion of beryl. Beus is of the opinion that 25-50% of the total Be in pegmatites may be incorporated in feldspar and in mica; moreover, he considers that high Be contents in these minerals need not indicate the beryl content of the pegmatite - an important consideration for interpreting geochemical soil survey data (Debnam and Webb 1960). Similarly, published observations of the association between particular elements and pegmatite minerals suggest that feldspars and micas may contribute to the bulk of Rb and Li respectively, in soils derived from pegmatites, rather than beryl itself. Such considerations are important in considering the individual anomaly peaks for different elements in the present data (Fig. 32), in relation to mineral zoning. There is clearly scope for detailed investigations of trace element associations with particular minerals, both in the primary pegmatite minerals and in their products of weathering.

(e) In terms of the contrast with the local background, Li and Be give comparable anomalies. The contrast for Rb is rather greater, while that for Ba, Sr and Sn is distinctly less. The strength and homogeneity of the Li and Rb anomalies are such that further attention should be given to

the possible value of these elements as geochemical indicators of mineralized dykes, in addition to Be. (cf Karaeva et al 1958).

(f) At the southern end of the traverse beyond the stream, Ba and Sr show a marked rise and Cr, V, Cu, Co and Ni decrease. The fact that Li, Rb, Be and Sn tend to remain at the same local background level suggests that the other variations in composition may well be related to a change in the lithology of the country rock, and not to the presence of a second mineralized pegmatite. Although this observation is based on only two samples taken beyond the stream at the end of the traverse, Debnam (pers. comm.) states that the decomposed schist changes in appearance in this vicinity.

(g) The samples examined included a limited number of soils collected over apparently un-mineralized bedrock at some distance from known pegmatite dykes. The bedrocks comprised schists from two localities and a granite; the spectrographic results for the overlying background soils are shown in table 24. The data are in accordance with the acid and basic nature of the two bedrock types.

Comparison of the background values over the granite with the results along the pegmatite traverse (Fig. 32), indicate that the anomalies would have either been suppressed to varying degrees, or actually eliminated in the case of Sr and Ba, had the pegmatite occurred in granite country rock. Nevertheless,

Table 24

Mean analysis of soils over un-mineralized rocks.

Rock type	No. of Samples	ppm.													
		Be	Li	Rb	Sr	Ba	Sn	Co	Ni	Cr	V	Cu	Mn	Pb	Ga
SCHIST	3	2.5	25	ND <200	15	75	ND <7	210	1500	c.4500	120	370	2200	20	17
SCHIST	4	<1	25	ND <200	25	65	ND <7	100	250	1300	140	150	1400	20	25
GRANITE	2	7	300	1300	210	370	8	6	25	170	45	17	650	55	20

Elements sought but not detected (with detection limit, ppm):-

Mo (<5)
Ag (<2)

Be, Li, Rb and Sn would still have shown positive anomalies indicating the mineralized pegmatite.

Summary.

The following conclusions may tentatively be drawn from the results of this small scale investigation.

(a) Determining the overall trace element assemblage in residual soils may provide a useful geochemical indication in mapping concealed geology. Two sharply contrasted rock types, coupled with relatively thin soil cover, provided a particularly clear illustration in the present study.

(b) From the prospecting viewpoint, the elements Li and Rb in particular deserve further investigation as possible indicator elements for mineralized pegmatite dykes. Karaeva et al (1958) employed a visual spectroscope for determining Li in prospecting for pegmatites, and this approach might be investigated in other areas, including the present one. In view of the relative mobility of Li and Rb, an investigation of their dispersion in the drainage system might be carried out as a possible aid in geochemical reconnaissance for pegmatites.

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Appendix A₂

Composition of Minor Element Standard Mixtures.

Series (a) General Minor Element Standards.

- (i) Base. Synthetic "intermediate igneous rock" composition. Prepared from Specpure oxides and carbonates, sintered at 1,000°C, and having the following calculated composition (%):-

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
59.8	15.1	8.3	7.7	4.5	2.4	2.2

- (ii) Minor element standards. These were prepared by step-wise dilution with the base, of a common mixture of 25 minor element compounds. The standards contained nominally the following amounts (ppm.) of each minor element:-

10,000, 5623, 3162, 1780, 1000, 562, 316, 178,
100, 56, 32, 18, 10, 5.6, 3.2, 1.8 ppm.

The minor elements comprise: Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ce, La, W, Pb, Bi, Th, U.

Series (b) Alkali Element Standards.

- (i) Base. Synthetic intermediate igneous rock composition, but omitting Na₂O and K₂O:-

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
	62.7	15.8	8.7	8.1	4.7

(ii) Alkali element standards. These were prepared stepwise from a common mixture of seven alkali metal compounds. The highest standard contained 10,000 ppm. each of Li, Rb, Sr, Cs, Ba, and 50,000 ppm each of Na_2O and K_2O . The standard series contained 10,000, 3162, 1000, 316, 100, 32, 10, 3.2, 1 ppm each of the minor alkalis, and five times this amount of the oxides Na_2O , K_2O .

Base No.	Composition type	Composition %								
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO (as CaCO ₃)	MgO	Na ₂ O (as Na ₂ CO ₃)	K ₂ O	TiO ₂	MnO (as Mn ₃ O ₄)
1	"Granite"	68.6	13.6	1.9	1.3	0.37	3.1	5.1	0.24	0.028
2	"Diabase"	47.3	13.7	10.2	9.9	6.0	1.8	0.57	0.99	0.15
3	"Water Evaporate"	13.4	1.1	1.1	33.9	4.9 (as MgSO ₄)	5.5 (as NaCl)	-	-	-
4	"Intermediate igneous rock"	54.4	13.7	7.5	7.1	4.1	2.2	2.1	0.74	0.11
5	SiO ₂)	pure materials.								
6	Al ₂ O ₃)									
7	Fe ₂ O ₃)									
8	Na ₂ CO ₃)									
9	Li ₂ CO ₃)									
"Specpure" materials were used for all nine bases.										

APPENDIX A3.

Intensity data for major element standards

(including all the analysis and internal standard lines investigated).

Sample	ANALYSIS ELEMENTS										POTENTIAL INTERNAL STANDARDS (* = ADOPTED)									
	Al	Mg	Si	Fe	Si	Ca	Na	Ti	Ca	K	Ge	Ge*	Li	Ge*	Pd*	In*	Y	Pd	Pd	
	2652	2779	2881	2929	2987	3158	3302	3354	3644	4044	2651	2709	2741	3039	3242	3256	3327	3421	3634	
W - 1	.730	1.060		.602	.225	.590	.730	1.005	1.280		.445	.105	1.255	.344	.732	1.315	.633	.694	1.053	
	.725	1.038		.574	.205	.592	.695	1.030	1.250		.428	.072	1.230	.330	.750	1.290	.668	.690	1.030	
	.705	1.055		.555	.237	.572	.705	.995	1.222		.450	.095	1.230	.342	.732	1.290	.650	.700	1.038	
2W-1+G-1	.740	.948		.480	.340	.460	.790	.900	1.105	.419	.454	.140	1.235	.390	.795	1.295	.610	.745	1.082	
	.690	.886		.450	.282	.405	.763	.868	1.048	.347	.415	.065	1.220	.344	.732	1.260	.675	.695	1.028	
	.720	.926		.440	.305	.460	.774	.895	1.125	.392	.415	.070	1.220	.347	.755	1.265	.685	.710	1.040	
1W-1+2G-1	.690	.615		.245	.330	.200	.800	.733	.833	.520	.395	.050	1.215	.310	.770	1.260	.730	.730	1.057	
	.710	.625		.266	.345	.190	.830	.650	.850	.610	.430	.085	1.215	.345	.770	1.275	.665	.734	1.040	
	.650	.625		.252	.315	.105	.810	.670	.800	.546	.415	.050	1.215	.325	.735	1.265	.585	.700	1.045	
G - 1	.600	-.255		-.246	.310	-.527	.875	.375	.163	.700	.395	.035	1.195	.305	.755	1.245	.585	.728	1.045	
	.610	-.262		-.232	.307	-.470	.862	.395	.165	.750	.385	.030	1.210	.295	.730	1.240	.580	.718	1.035	
	.610	-.262		-.228	.340	-.490	.855	.455	.175	.700	.385	.015	1.200	.280	.732	1.235	.675	.700	1.030	
GLASS SAND	-.860				.603			.030				.152		.420	.805	1.280				
	-.843				.621			.025				.140		.425	.834	1.285				
	-.855				.573			.012				.090		.389	.793	1.260				
BURNT REFRACTORY	1.220	.105			0.085		-.555	1.420		.218		.080		.369	.780	1.245				
	1.235	.095			.110		-.555	1.445		.215		.100		.378	.800	1.270				
	1.200	.150			.025		-.665	1.435		.172		.012		.297	.775	1.235				
IRON ORE			.835	1.372								.102		.385						
			.780	1.372								.102		.378						
			.825	1.372								.080		.367						
ARGILL LIMESTONE		.625		-.230	-.380	1.323	-.095	.343		-.054		.045		.310	.784	1.230				
		.560		-.270	-.400	1.342	-.147	.340		-.085		-.010		.286	.784	1.195				
		.625		-.253	-.365	1.338	-.113	.360		-.085		.022		.315	.805	1.220				
DOLOMITE		1.495	-.125			1.230		-.690				.052		.330	.765	1.240				
		1.510	-.100			1.215		-.707				.060		.335	.753	1.240				
		1.544	0.000			1.241		-.665				.110		.375	.770	1.290				
Na FELSPAR	.890				.450	(.920)	1.185	-.415				.100		.380	.810	1.278				
	.885				.435	.905	1.200	-.500				.100		.355	.810	1.262				
	.880				.435	.870	1.200	-.367				.100		.388	.795	1.257				
BAUXITE	1.430		1.325	.532	-.455	(.830)		1.685				.100		.400	.860	1.262				
	1.360		1.255	.460	-.510	.920		1.625				.070		.340	.830	1.215				
	1.385		1.315	.498	-.475	.822		1.603				.110		.358	.825	1.231				
CLAY FLINT	1.136	-.278		-.382	.235		-.535	1.400		-.210		.070		.345	.764	1.231				
	1.136	-.295		-.400	.240		-.560	1.400		-.260		.070		.332	.770	1.205				
	1.100	-.272		-.380	.228		-.610	1.405		-.245		.052		.320	.760	1.190				
CLAY PLASTIC	1.000	.154		-.094	.350		-.187	1.182		.293		.052		.305	.758	1.175				
	.985	.154		-.110	.325		-.145	1.202		.335		.030		.300	.735	1.220				
	.981	.154		-.084	.345		-.140	1.122		.360		.055		.310	.740	1.220				

APPENDIX A4.

Transformed Density Function for N_{30} plates

Table of $D_T = \log_{10} \frac{100}{d} - 0.90$

Where d = galvanometer deflection in cms; and $d_0 = 100.0$ cms.

d cms	.00	.25	.50	.75
5	1.281	1.259	1.238	1.217
6	1.198	1.179	1.161	1.143
7	1.127	1.110	1.094	1.079
8	1.064	1.050	1.036	1.022
9	1.009	0.996	0.984	0.971
10	0.959	0.947	0.936	0.924
11	0.913	0.903	0.892	0.881
12	0.817	0.861	0.851	0.842
13	0.832	0.823	0.813	0.804
14	0.795	0.787	0.778	0.769
15	0.761	0.753	0.744	0.736
16	0.728	0.720	0.713	0.705
17	0.697	0.690	0.683	0.675
18	0.668	0.661	0.653	0.647
19	0.640	0.633	0.626	0.619
20	0.613	0.606	0.600	0.593
21	0.587	0.580	0.574	0.568
22	0.562	0.556	0.550	0.544
23	0.538	0.532	0.526	0.520
24	0.514	0.508	0.503	0.497
25	0.491	0.486	0.480	0.475
26	0.469	0.464	0.459	0.453
27	0.448	0.442	0.437	0.432
28	0.427	0.422	0.416	0.411
29	0.406	0.401	0.396	0.391
30	0.386	0.381	0.376	0.371
31	0.367	0.362	0.357	0.352
32	0.347	0.343	0.338	0.333
33	0.328	0.324	0.319	0.315
34	0.310	0.305	0.301	0.296
35	0.292	0.287	0.283	0.278
36	0.274	0.269	0.265	0.260
37	0.256	0.252	0.247	0.243
38	0.239	0.234	0.230	0.226
39	0.221	0.217	0.213	0.208

d cms	.00	.25	.50	.75
40	0.204	0.200	0.196	0.191
41	0.187	0.183	0.179	0.175
42	0.171	0.166	0.162	0.158
43	0.154	0.150	0.146	0.142
44	0.138	0.134	0.129	0.125
45	0.121	0.117	0.113	0.109
46	0.105	0.101	0.097	0.093
47	0.089	0.085	0.081	0.077
48	0.073	0.069	0.065	0.061
49	0.057	0.053	0.049	0.045
50	0.041	0.037	0.033	0.029
51	0.026	0.022	0.018	0.014
52	0.010	0.006	0.002	1.998
53	1.994	1.990	1.986	1.982
54	1.978	1.975	1.971	1.967
55	1.963	1.959	1.955	1.951
56	1.947	1.943	1.939	1.936
57	1.932	1.928	1.924	1.920
58	1.916	1.912	1.908	1.904
59	1.900	1.896	1.892	1.889
60	1.885	1.881	1.877	1.873
61	1.869	1.865	1.861	1.857
62	1.853	1.849	1.845	1.841
63	1.837	1.833	1.829	1.825
64	1.821	1.817	1.813	1.809
65	1.805	1.801	1.797	1.793
66	1.789	1.785	1.781	1.777
67	1.773	1.769	1.765	1.760
69	1.740	1.736	1.731	1.727
70	1.723	1.719	1.715	1.710
71	1.706	1.702	1.698	1.693
72	1.689	1.685	1.681	1.676
73	1.672	1.668	1.663	1.659
74	1.655	1.650	1.646	1.641

d cms	.00	.25	.50	.75
75	1.637	1.632	1.627	1.623
76	1.619	1.614	1.610	1.605
77	1.601	1.596	1.591	1.587
78	1.582	1.577	1.573	1.568
79	1.563	1.559	1.554	1.549
80	1.544	1.539	1.534	1.529
81	1.524	1.519	1.515	1.510
82	1.505	1.499	1.494	1.489
83	1.484	1.479	1.474	1.468
84	1.463	1.458	1.452	1.447
85	1.442	1.436	1.431	1.425
86	1.420	1.414	1.408	1.403
87	1.397	1.391	1.385	1.380
88	1.374	1.368	1.362	1.356
89	1.349	1.343	1.337	1.331
90	1.324	1.318	1.312	1.305
91	1.299	1.292	1.285	1.279
92	1.272	1.265	1.258	1.251
93	1.244	1.237	1.229	1.222
94	1.215	1.207	1.199	1.191
95	1.184	1.176	1.168	1.160
96	1.151	1.143	1.134	1.126
97	1.117	1.108	1.099	1.090
98	1.081	1.071	1.061	1.052
99	1.042	1.032	1.021	1.011
100	1.000			

Appendix A₄.

Preparation of Scales for the Evaluating Board.

The scales were drawn on "Permatrace" drawing material 0.003" thick.

(a) Horizontal scale - log relative intensity. (log I)

A linear scale, 15.0 cms. = 1.00 log I unit. The range, from right to left is -1.8 to +2.6 log I, enabling all densitometer readings to be covered in any spectrum step.

Seven verticals are set up at intervals of 0.301 log I, starting at 0.00 (unit intensity) for step number 1.

(b) Vertical scales - densitometer readings (d).

Values of d were marked at intervals corresponding to the values of $D_T = \log \left(\frac{100}{d} - 0.90 \right)$ as tabulated above.

The scale is 20.0 cms. = 1.00 D_T unit.

Markings were begun from the standard density level, $d = 24.0$ through which passes the horizontal scale. The two end verticals were scaled directly, and the others marked from them.

(c) Background-correction scale.

This is a separate scale marked on a strip of "Permatrace" 17" x $1\frac{1}{2}$ " x .003". Two scales are marked, $\frac{1}{2}$ " apart. The lower scale carries log I units from 0.0 to 2.7 (left to right), scaled as in (a). When the scale is in use, these log I values correspond to the separation between the

intensities of the line plus background and the background respectively. From tables of subtraction logarithms* "correction values" are marked on the upper scale, opposite corresponding log I separations on the lower scale.

*Mitchell, Scott and Farmer. Logarithmic tables for use in quantitative spectrographic analysis, II. Macaulay Inst. for Soil Research Ann. Report 1943-4.

(Results in ppm. unless otherwise stated).

Lab. No.	Field No.	Ti	Zr	Ni	Co	Cr	Be	Mn	Pb	Sn	Sb	Ga	Pi	As	V	Cu	Ag	% * Loss	Rb	Li	Ba	Sr	s.q. only Na ₂ O K ₂ O % %	
* MENGLEMBU																								
6226	WM/1a	> 1%	7000	40	N.D.	17	20	450	90	5000	N.D.	32	N.D.	N.D.	20	2	N.D.	4.29%	500	22	50	25	.08	1.5
6227	WM/1b	> 1%	3500	25	"	15	30	480	90	5000	"	20	"	"	20	2	"	3.08%	350	18	45	18	.10	1.5
6228	WM/2a	> 1%	1200	17	"	32	"	150	60	140	"	45	"	"	55	2	"	9.77%	-	-	-	-	-	-
6229	WM/2b	> 1%	1000	15	"	30	30	180	70	215	"	45	"	"	50	2	"	10.3%	-	-	-	-	-	-
PUJANG MELAKA																								
6230	WM/3a	> 1%	450	5	"	15	35	450	40	45	"	25	"	"	25	3	"	4.77%	450	35	130	40	.15	2.5
6231	WM/3b	> 1%	650	7	"	17	25	520	50	105	"	25	"	"	30	5	"	4.43%	450	40	150	40	.15	2.0
6232	WM/4a	7000	500	12	"	40	4	520	60	40	"	15	"	"	45	4	"	3.77%	200	30	180	40	.07	1.5
6233	WM/4b	5000	350	10	"	40	6	400	70	45	"	15	"	"	50	4	"	5.35%	320	35	200	50	.10	1.5
6234	WM/5a	> 1%	3000	20	"	20	20	1000	70	240	"	35	"	"	45	8	"	5.47%	800	100	170	60	.70	4.0
6235	WM/5b	> 1%	3000	20	"	30	4	600	60	110	"	30	"	"	65	10	"	6.88%	1200	120	200	50	.50	4.0
6237	BM/M1	6000	650	10	"	15	4	340	60	75	"	35	"	"	30	7	"	4.30%	1000	100	230	50	.60	5.0
6238	BM/M2	5000	550	7	"	15	14	400	50	35	"	20	"	"	25	6	"	3.79%	800	90	250	40	.50	4.0
CAMERON HIGHLANDS																								
6240	CH/A1	4000	350	7	"	25	10	400	50	30	"	15	"	"	25	2	"	3.85%	600	80	250	35	.40	3.0
6241	CH/A2	3500	400	15	"	25	5	350	70	37	"	25	"	"	35	2	"	4.76%	1000	80	250	45	.70	4.0
6243	CH/C1	8000	400	7	"	18	5	400	100	22	"	30	"	"	25	2	"	4.05%	800	70	300	50	.5	4.0
6244	CH/C2	7000	350	5	"	15	7	270	90	22	"	25	"	"	25	2	"	4.64%	1000	60	280	50	.5	4.0
6246	CH/E1	1%	450	15	7	40	6	400	90	22	"	25	"	"	45	7	"	5.15%	800	50	280	65	.5	4.0
6247	CH/M2	> 1%	600	20	10	50	7	550	70	20	"	25	"	"	50	7	"	5.74%	1000	60	250	50	.5	3.0
6249	CH/G1	> 1%	750	30	10	70	6	500	80	22	"	25	"	"	70	3	"	5.05%	700	40	250	50	1.0	3.0
6250	CH/G2	> 1%	1500	30	10	50	5	500	50	20	"	25	"	"	70	3	"	6.11%	600	40	200	45	.8	3.0
6252	CH/J1	> 1%	2000	45	15	70	4	400	60	20	"	20	"	"	60	3	"	5.57%	800	45	170	50	.6	2.0
6253	CH/J2	> 1%	3000	40	7	60	4	300	50	20	"	20	"	"	50	4	"	4.76%	600	40	220	45	.6	2.0

Lab. No.	Field No.	Ti	Zr	Ni	Co	Cr	Be	Mn	Pb	Sn	Sb	Ga	Bi	Mo	V	Cu	Ag	% Loss	Rb	Li	Ba	Sr	Calq. only Na2O % K2O %
PENANG ISLAND																							
6256	PG/2	>1%	3500	25	N.D.	10	25	600	50	58	N.D.	25	N.D.	N.D.	17	8	N.D.	5.28%	350	40	80	15	.13 1.3
6257	PG/3	3000	2000	10	"	4	5	350	50	32	"	25	"	"	10	5	"	3.74%	450	50	80	18	.15 1.5
6258	PG/4	8000	600	10	"	3	17	1300	160	125	"	40	"	"	10	3	"	8.42%	320	70	35	3	.10 1.0
6259	PG/5	3000	500	5	"	3	30	2000	300	130	"	50	"	"	7	10	"	9.40%	350	80	35	3	.13 1.2
6260	PG/6	2000	500	15	"	3	15	450	50	35	"	30	"	"	12	2	"	6.59%	1100	80	60	20	.4 3.0
6261	PG/7	2000	300	5	"	4	15	500	40	37	"	30	"	"	12	2	"	8.00%	1000	90	70	15	.5 3.0
6262	PG/8	3500	200	7	"	10	12	450	60	37	"	40	"	"	15	2	"	6.30%	300	70	80	14	.3 1.3
6263	PG/9	3500	300	5	"	10	10	250	75	42	"	40	"	"	15	2	"	8.80%	600	60	50	15	.3 1.5
6264	PG/10	4000	400	7	"	10	17	400	50	35	"	30	"	"	17	2	"	5.37%	-	-	-	-	- -
6265	PG/11	4000	500	15	"	10	4	450	80	32	"	30	"	"	17	2	"	8.39%	-	-	-	-	- -
GAP GINTING																							
6269	SS1	>1%	800	17	"	22	N.D.	650	40	190	"	15	"	"	35	3	"	2.46%	1000	45	240	60	.4 3.0
6270	SS1a	>1%	1200	20	"	15	4	475	55	30	"	15	"	"	25	3	"	2.04%	1200	40	240	60	.5 4.0
6271	SS2	>1%	500	7	"	5	7	300	50	20	"	18	"	"	15	2	"	1.83%	1200	30	170	60	.5 4.0
6272	SS2a	>1%	700	12	"	2	3	160	50	20	"	15	"	"	7	2	"	1.13%	1300	20	150	45	.6 4.0
6273	SS3	>1%	2000	25	"	3	3	400	50	25	"	18	"	"	10	2	"	2.55%	1100	60	200	50	.8 6.0
6274	SS3a	3000	500	17	"	2	3	350	90	27	"	12	"	"	7	3	"	1.84%	1100	70	200	50	.8 4.0
6275	SS4	4000	500	12	"	7	5	350	60	22	"	12	"	"	12	2	"	2.25%	1300	60	240	60	.8 6.0
6276	SS4a	>1%	4000	25	"	5	8	1300	45	22	"	10	"	"	12	3	"	2.96%	1000	60	180	50	.6 3.0
6277	SS5	>1%	4000	30	"	12	4	1000	50	30	"	7	"	"	20	5	"	1.63%	1100	45	220	60	.7 5.0
6278	SS5a	5000	600	10	"	15	5	350	60	110	"	10	"	"	15	2	"	2.10%	1100	60	240	50	.6 5.0
6279	SS6	2000	400	10	"	10	8	200	80	35	"	30	"	"	7	2	"	3.30%	1400	100	200	50	.9 6.0
6280	SS6a	6000	3000	25	"	5	15	300	60	25	"	25	"	"	10	2	"	4.29%	1300	70	160	45	.9 4.0
6281	SS7	3000	2000	20	"	7	10	600	70	350	"	25	"	"	7	7	"	3.24%	1100	90	180	50	.6 3.0
6282	SS7a	4000	450	10	"	15	25	400	50	47	"	20	"	"	25	5	"	4.62%	1200	100	180	50	.6 4.0
6283	SS8	6000	375	17	11	30	17	450	65	250	"	25	"	"	25	8	"	4.97%	1600	120	220	50	.8 4.0
6284	SS8a	5000	400	17	12	30	30	500	45	470	"	25	"	"	35	8	"	5.55%	1600	90	220	50	.7 4.0
6285	SS9	3000	400	15	N.D.	10	30	400	90	700	"	25	"	"	15	10	"	4.52%	1600	80	140	40	.5 4.0
6286	SS9a	4000	600	15	"	10	40	450	60	850	"	27	"	"	18	30	"	5.65%	1600	90	130	40	.4 3.0
6288	SS10a	>1%	2000	25	"	20	17	700	70	550	"	25	"	"	20	4	"	4.93%	2200	120	170	50	.7 7.0
6287	SS10	3000	2000	25	"	12	14	900	60	160	"	25	"	"	25	3	"	4.85%	1800	110	150	50	.6 7.0
6289	SS11	7000	600	7	"	4	25	400	40	40	"	25	"	"	15	2	"	4.25%	2000	110	150	50	1.0 7.0
6290	SS11a	4000	600	10	"	3	15	300	60	50	"	20	"	"	10	4	"	4.80%	2200	130	180	50	1.0 7.0
6291	SS12	6000	400	7	"	5	25	350	40	225	"	20	"	"	10	4	"	4.93%	1800	100	140	40	.7 6.0
6292	SS12a	1200	350	5	"	3	37	250	60	550	"	25	"	"	7	4	"	4.01%	1800	90	160	40	.7 5.0

Lab. No.	Field No.	Ti	Zr	Ni	Co	Cr	Be	Mn	Pb	Sn	Sb	Ga	Bi	Mo	V	Cu	Ag	% Loss	Rb	Li	Ba	Sr	s.q. only		
																							Na ₂ O	K ₂ O	
																							%	%	
BUKIT YONG																									
6304	BY/1	600	250	5	N.D.	3	4	350	60	27	N.D.	20	N.D.	N.D.	7	3	N.D.	7.20%	900	55	160	22	.4	3.0	
6305	BY/2	600	250	15	"	3	4	300	50	22	"	20	"	"	5	2	"	6.68%	600	45	120	25	.4	3.0	
6310	BY/7	500	220	5	"	4	4	150	30	N.D.	"	15	"	"	7	2	"	4.30%	180	25	130	14	.12	1.0	
6311	BY/8	600	200	N.D.	"	4	N.D.	120	30	"	"	7	"	"	17	2	"	3.49%	150	20	140	12	.10	0.8	
6314	BY/11	500	200	"	"	3	"	180	40	"	"	7	"	"	5	2	"	4.75%	600	50	120	20	.2	2.0	
6315	BY/12	500	220	5	"	5	"	150	45	22	"	10	"	"	5	3	"	5.23%	450	50	120	18	.3	1.6	
6318	BY/15	1700	1700	12	"	12	"	70	35	320	"	7	"	"	10	2	"	4.26%	150	25	80	3	.05	0.7	
6319	BY/16	1000	300	5	"	7	"	30	30	25	"	5	"	"	12	2	"	2.59%	180	25	60	3	.06	0.8	
GUNONG BENOM																									
6320	GB/1	>1%	400	14	"	40	"	450	20	N.D.	"	5	"	"	55	5	"	3.81%	350	18	900	220	1.3	2.0	
6321	GB/2	>1%		30	10	70	4	450	30	"	"	7	"	"	100	5	"	3.60%	350	25	800	200	1.3	2.0	
6323	GB/4	>1%	350	25	15	80	10	500	100	"	"	10	"	"	80	8	"	2.66%	1300	35	1500	320	.7	6.0	
6324	GB/5	>1%	5000	45	10	100	5	350	70	"	"	7	"	"	140	5	"	1.73%	1000	20	1500	400	.9	7.0	
6326	GB/7	4000	5000	50	N.D.	70	4	400	80	"	"	7	"	"	60	8	"	1.64%	1000	25	700	180	1.3	6.0	
6327	GB/8	6000	4000	60	"	70	5	450	70	"	"	7	"	"	100	7	"	2.28%	800	22	700	200	1.2	6.0	
Sensitivity limits:				5		7	-	3	-	-	20	320	-	35	5	-	-	1		-	-	-	-	-	-

* N.D. = Not detected.

* % Loss = % loss on ignition (2 hrs. at 500°C).

MALAYA Sample data

Sampling Area	Sample No.	Field description	Stream data			Colour (-80 mesh ignited sample)
			Width ft.	Depth ins.	Flow	
1. Gunong Benom.	6320	Coarse sand	5	6-9	2ft/sec.	mid-brown do.
	6321	Do. 30 yd downstream				
	6323	Coarse sand	3-6	6-12	1ft/sec.	mid-brown do.
	6324	Do. 60 yd downstream				
	6326	Sandy gravel	20	12-18	2ft/sec.	neutral-grey
	6327	do.				
2. Cameron Highlands	6240	- - - - -	15	12	medium	off-wht
	6241	- - - - -				lt-grey
	6243	- - - - -	12	18	do.	off-wht
	6244	- - - - -				do.
	6246	- - - - -	10	12	fairly fast	lt-brown
	6247	- - - - -				do.
	6249	- - - - -	25	12	medium	do.
	6250	- - - - -				do.
3. Bujang Melaka	6230	- - - - -	10	24	medium	red-brown
	6231	- - - - -				do.
	6232	- - - - -	15	4	fast	pale buff
	6233	- - - - -				
	6234	- - - - -	10	6	medium	mid-brown
	6235	- - - - -				do.
	6237	- - - - -	4	12	slow	mid-brown
	6238	- - - - -				do.
4. Menglembu	6226	Stream draining near	4	6	fast	re-buff
	6227	old lode mines				do.
	6228	do. tributary of	2	3	slow	ochre
	6229	above stream.				do.

Sampling Area.	Sample No.	Field description	Stream data			Colour (-80 mesh ignited sample)
			Width ft.	Depth ins	Flow	
5. Ginting Sempak	6269	Sand. Numerous	20	24	fast	lt-brown do.
	6270	do. boulders				
	6271	Sand. Near foot of fall	10	12	medium	v pale grey
	6272	Mine in catchment area				
	6273	Sand	10-15	30	fast	do. do.
	6274	do.				
	6275	Sand with little silt	6-10	15	slow	v lt-brown
	6276	do.				
	6277	Sand and sandy silt	30	36	medium	do. do.
	6278	do.				
	6279	Sand among boulders	15-20	36	fast	do. do.
	6280	Possible mine contam.				
	6281	Sand among boulders	10-15	24	fast	do. do.
	6282	do.				
	6283	Sand with little silt	20	30	fast	do. do.
	6284	Old mines upstream				
	6285	Fine sand; old mines	22	24	quite fast	do. do.
	6286	upstream				
	6287	Grade sand; old mines	17	12	quite fast	do. do.
	6288	upstream				
	6289	Grand sand	10	12	fast	do. do.
	6290	do.				
	6291	Sand with little silt	25-30	15	fast	do. do.
	6292	Old mines upstream				

MALAYA Sample data continued.

Sampling Area	Sample No.	Field Description	Stream data			Colour (-80 mesh ignited sample)
			Width ft.	Depth ins.	Flow	
6. Penang Island	6256	-----	8	10-15	fast	lt-brown
	6257	20 ft downstream				do.
	6258	-----	10	12	fast	do.
	6259	30 ft upstream				do.
	6260	-----	12	12-24	very slow	lt-grey
	6261	20 ft upstream				lt-brown
	6262	Rocky stream bed	12	15-30	very fast	lt-brown
	6263	30 ft upstream				do.
7. Bukit Yong	6264	Rock pools	20	12-36	very fast	do.
	6265	10 ft downstream				do.
	6304	Among boulders	6-8	24	slow	pale-buff
	6305	30 yd upstream				
	6310	Among boulders	20	24-38	slow	do.
	6311	30 yd upstream				do.
	6314	Among boulders	20	24-36	slow	lt-buff
	6315	70 yd upstream, at 6 ins depth				buff
	6318	At 12 ins depth	8	12-24	very slow	off-wht
	6319	50 yd upstream				lt-buff

APPENDIX B.6. Soil Profiles, N. Rhodesia - Spectrographic Analyses (mean).

			PPM (IGNITED SAMPLE BASIS)																% OXIDES										
Sample No.	Depth	Ignition % loss	Cu	Mn	Cr	V	Co	Ni	Ga	Mo	Sr	Ba	Li	Rb	Be	La	Pb	Na ₂ O	K ₂ O	* Fe ₂ O ₃	* Al ₂ O ₃	* TiO ₂	* MgO	* CaO	+ SiO ₂	* SiO ₂			
NR- 631 632,3,4 635 36(NODULES) 36(MATRIX) 37,8,9 41,2,3,5	0"-12" 12"-10'6" 10'6"-13'6" 13'6"-15'6" 15'6"-24'6" 24'6"-34'0"	3.9 4.4 5.5 9.6 5.1 4.7 3.3	53 50 100 350 120 1250 1350	60 70 100 200 60 150 50	22 25 50 210 30 45 55	50 60 110 190 100 100 70	15 18 25 22 30 240 160	17 25 25 21 20 26 21	8 12 12 20 10 15 18	PROFILE 1 MINERALIZED QUARTZITE, CHIBULUMA								30 30 22 25 8 30 105	30 30 30 30 30 30 30	.04 .08 .08 0.3 .05 .06 .06	.06 .23 .23 .68 .28 .50 .50	2.2 2.9 2.9 29.5 4.5 7.8 7.8	10.4 13.8 13.8 19.9 17.0 12.2 12.2	0.86 1.08 1.08 0.94 1.02 0.53 0.51	0.2 0.6 0.6 0.6 0.6 0.6 0.6	86.4 81.6 48.6 76.9 78.2 78.2 78.2			
NRT 108 109,10,11 112,3,4 115-119 120 121 122(NODULES) 122(MATRIX) 122-7 128-32 129(Mn Spots) 129(MATRIX) 133-7	0"-3" 3"-12" 12"-3'0" 3'0"-8'0" 8'0"-9'0" 9'0"-9'6" 9'6"-10'0" 9'6"-12'6" 12'6"-17'6" 13'6"-14'6" 17'6"-22'6"	5.9 5.9 6.0 6.2 6.7 7.2 7.9 7.5 8.2 6.0 9.1 6.5 5.3	380 450 500 550 500 600 1000 600 850 750 3250 550 900	350 300 300 550 650 600 2000 550 700 550 5000 300 500	50 50 60 65 65 50 250 65 85 90 65 160 70 90	80 90 80 110 90 80 180 110 120 110 4000 90 130	32 37 50 65 100 90 120 30 28 35 115 25 75 40	27 30 35 30 35 35 35 30 28 35 25 25 43 50 40	18 20 20 20 22 20 30 20 23 23 25 100 200 140	PROFILE 2 MINERALIZED SHALE, BALUBA								13 18 5 32 5 5 8 40 25 7 600 200 45	20 27 22 27 35 25 35 27 25 25 230 200 230	20 30 30 30 30 30 30 30 30 30 90 30 30	.022 .035 .05 .05 .05 .06 .06 .05 .05 .05 .10	.35 .50 1.0 1.0 1.0 1.0 1.0 1.1 1.1 1.1 1.5	3.9 4.6 5.7 5.7 5.7 6.8 6.8 7.5 5.3 7.2	13.5 15.3 22.8 22.8 22.8 23.7 23.7 29.0 22.7 26.7	0.83 0.83 1.06 1.06 1.06 1.00 1.00 0.81 1.05 1.06	0.35 0.33 0.49 0.49 0.49 0.45 0.45 0.45 0.58 0.94	0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6	80.9 78.3 68.8 68.8 68.8 66.7 66.7 59.8 67.5 60.1	

Sample No.	Depth	Ignition % loss	ppm (IGNITED SAMPLE BASIS)																% Oxides								
			Cu	Mn	Cr	V	Co	Ni	Ga	Mo	Sr	Ba	Li	Rb	Be	La	Pb	Na ₂ O	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	MgO	CaO	SiO ₂	SiO ₂	
PROFILE 3. "GABBRO" CHAMBISHI																											
14- 2946	0"-6"	7.2	250	900	55	200	35	55	20	<5	17	45	12	<200		25	<30	.013	.05	6.3	13.4	3.8	<0.2	<0.6	76.1		
2947	6"-12"	7.9	280	700	55	200	45	65	25	<5						30	<30										
2948-53	12"-6'0"	7.8	320	700	45	200	40	60	25	<5	18	70	18	<200	<1	30	<30	.015	.12	8.4	22.8	3.1	0.22	<0.6	65.0		
2954,5	6'0"-8'0"	8.7	290	530	38	160	33	60	25	<5						28	<30										
2956-59	8'0"-12'0"	9.2	380	430	38	160	34	65	27	<5	12	60	15	<200	2.5	30	<30	0.11	.065	14.5	27.1	3.0	0.29	<0.6	54.8	54	
2960-67	12'0"-20'0"	10.6	420	430	40	160	90	45	33	<5						32	<30										
2968-74	20'0"-27'0"	14.0	130	75	80	220	35	40	30	<5	50	200	4	<200		45	<30	.12	<.04	4.1	29.2	2.6	2.24	0.88	60.4	52	
2975,6,7	27'0"-30'0"	12.6	75	85	45	190	43	19	25	<5	80	230	8	<200	1.5	25	<30	1.2	.05	1.6	28.0	1.9	2.70	1.81	61.6	61	
PROFILE 4 FELSPATHIC QUARTZITE, BALUBA																											
NRT- 50	0"-3"	4.3	30	140	20	32	<7	14	5	<5	10	110	10	<200		<20	<30	.01	.15	2.1	5.5	0.50	<0.2	<0.6	91.6		
51,2,3	3"-12"	3.8	22	160	25	40	8	16	<7	<5						<20	<30										
54,5,6	12"-15'3"	6.1	35	120	35	55	11	27	14	<5	35	280	25	<200		20	<30	.05	.65	4.5	19.8	0.83	<0.2	<0.6	72.1		
57(NODULES)	15'3"-16'3"	7.8	850	350	700	380	48	39	32	11	10	110	15	<200		<20	<30	.03	.43	40.8	17.8	0.66	<0.2	<0.6	39.8	30	
57(MATRIX)		7.4	42	150	50	80	14	32	20	<5	25	170	30			20	<30	.05	.55	6.6	23.5	0.89	<0.2	<0.6	67.8		
58,59	16'3"-20'3"	7.0	40	100	50	60	12	30	18	<5						20	<30										
60, 1,2	20'3"-36'3"	6.6	43	90	43	68	9	23	17	<5	25	140	15	<200		25	<30	.03	.45	6.6	23.3	0.85	<0.2	<0.6	68.7		
PROFILE 5 BASEMENT GRANITE, BALUBA																											
NRT- 94	0"-3"	2.3	22	170	15	25	<7	18	8	<5	10	110	10	<200		<20	<30	.015	.22	0.95	6.4	0.44	<0.2	<0.6	92.0		
95,6,7	3"-12"	2.6	15	140	18	30	10	20	10	<5						30	<30										
98,9,100	12"-6'0"	5.4	30	130	25	45	7	30	20	<5	22	220	35	200	<1	25	<30	.050	1.0	2.6	19.0	0.79	0.28	<0.6	76.2		
101(NODULES)	6'0"-7'9"	8.5	80	220	120	130	11	30	26	7	17	145	36	200		23	<30	.065	.9	11.2	28.1	0.84	0.33	<0.6	58.5		
101(MATRIX)		8.3	85	210	120	110	12	28	29	5	25	180	40	300		38	<30	.06	1.0	9.0	26.1	0.78	0.35	<0.6	62.6		
102	7'9"-10'3"	8.3	45	160	70	80	7	30	22	6	17	160	60	200	<1	20	<30	.060	1.2								
103,4,5	10'3"-16'3"	7.6	32	130	45	70	10	25	20	<5						20	<30										
106,7	16'3"-21'3"	8.2	35	100	32	45	10	20	25	<5	17	300	90	300	<1	30	<30	.10	1.5	4.9	34.3	0.36	0.55	<0.6	56.9		

Sample No.	Depth	Ignition % Loss	ppm (fused sample basis)														% Oxides										
			Cu	Mn	Cr	V	Co	Ni	Ga	Mo	Sr	Ba	Li	Rb	Be	La	Pb	Na ₂ O	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	MgO	CaO	SiO ₂	SiO ₂ *	
PROFILE 6 SCHIST BALUBA																											
NRT-63	0"-3"	1.6	7	90	20	30	<7	10	4	<5	10	120	8	<200		<20	<30	.025	.30	1.7	4.7	0.39	0.2	<0.6	92.8		
64,5,6	3"-12"	2.8	14	130	35	50	10	17	10	<5						25	<30										
67,68	12"-4'3"	4.0	22	130	45	60	10	25	14	<5	30	230	30	300		20	<30	.12	1.1	4.3	18.8	0.92	0.39	<0.6	71.7		
69(NODULES)	4'3"-4'9"	4.2	32	85	120	65	7	14	16	<5	38	330	48	350		<20	<30	.31	1.8	19.5	26.9	0.93	0.53	<0.6	46.2	42	
69(MATRIX)		3.5	25	90	70	60	8	17	15	<5	40	320	30	300		25	<30	.14	1.3	6.3	18.5	1.0	0.40	<0.6	67.4		
70,71	4'9"-13'3"	1.2	20	50	60	80	10	20	15	<5	75	500	65	400		28	<30	.45	2.0	6.3	22.1	0.95	0.54	<0.6	63.0		
DRILL-CORE SAMPLES, VICINITY OF CHIBULUMA "GABBRO"																											
A. Carbonate rich specimen		0.49	4	410	33	50	19	38	9	<5	33	33	150	380		<20	<30	0.8	2.8								
B. Biotite rich specimen 50' beyond A		1.24	5	50	58	90	14	43	18	<5	230	170	360	1000		25	<30	2.0	5.7	7.1	18.5	0.72	7.52	.44	55.9	52	
C. "Gabbro"(biotite rich)		.58	5	160	150	210	70	90	16	5	90	130	210	420		22	<30	c4.0	c4.0								
D. 11' beyond C		.59	5	140	150	220	63	80	19	5	180	150	190	450		110	<30	c4.0	c4.8								

Elements sought, but below the limit of detection in all samples: Sr (<20 ppm), Ag (<2 ppm).

* determined by spectrographic technique for major elements.

+ calculated by difference from 100%

Sample descriptions. Soil profiles Uganda

Pit No. bedrock (and T.C.No.)	Sample depth	Description	+ Horizon	Ignit- ion loss %	Remarks on ignited, minus 80 mesh samples
1. Injection gneiss (P20)	0-3"	Near black organic soil + mica flakes	A ₁	20.6	) The palest of the profiles;) light red brown at surface,) very pale in C horizon.) Clayey rather than gritty,) especially in surface) samples.
	3"-1'3"	Grey-brown soil, some roots + mica flakes	A ₃	13.4	
	1'3"-2'3"	(Neutral brown, friable clay lumps,)		9.6	
	2'3"-3'9"	(few roots + mica.)		8.3	
	3'9"-5'3"	Neutral brown, much clay; rock)		8.0	
		fragments below.)	B	7.2	
	5'3"-6'9"	ditto.)		5.1	
	6'9"-7'9"	Pale-brown clay + pallid rotted rock)	C	4.0	
2. Dolerite dike (P18)	0-3"	Dark-brown organic soil, some roots	A ₁	19.3	) Middle red-brown through-) out the profile, very) clayey (?Fe.Al clays).)))
	3"-1'3"	Brown clay soil; few small rock fragments.)	A ₃	14.6	
	1'3"-2'9"	ditto.)		13.5	
	2'9"-3'9"	Partly rotted rock fragments, with yellow-)	B	13.5	
		brown clays.)		13.7	
	3'9"-5'3"	Yellow-brown clay + yellow-brown rotted)		13.1	
3. Granulite (P15)	0-3"	Near blk. organic soil + mica flakes.	A ₁	22.8	) Middle red-brown, very) similar to P11, below;) mica visible in all) samples.)
	3"-1'3"	Brown clay soil.	A ₃	11.4	
	1'3"-2'3"	Brown clay soil; soft micaceous rock)		10.8	
		fragments (iron stained).)	B	10.1	
	2'3"-3'3"	ditto.)		9.7	
	3'3"-4'9"	ditto.)		9.0	
	4'9"-6'3"	Brown clay; mottled brown-white rotted rock.)	C	6.8	
	6'3"-7'9"	Brown clay; yellow-white rotted rock.			

Sample descriptions. Soil profiles Uganda

Pit No. bedrock (and T.C.No.)	Sample depth	Description	Horizon	Ignition loss %	Remarks on ignited, minus 80 mesh samples.
4 Amphibolite (Gossany) (P11)	0-3"	Grey-brown clay soil, roots + rock fragments.	A ₁	20.6	Middle red-brown, slightly paler towards surface where samples are moderately gritty.
	3"-1'3"	Angular rock rubble + yellow-brown clay.	A ₃	12.5	
	1'3"-2'3"	Brown-yellow clay + small rounded rubble.	) -----) B	10.7	
	2'3"-3'9"	ditto.		11.2	
	3'9"-4'9"	Brown-yellow clay + mottled white rotted rock.	----	10.4	
	4'9"-5'9"	ditto.	C	9.4	
	5'9"-6'3"	Pale brown clay + pallid rotted rock.		6.1	
5. Alaskite (P 9)	0-3"	Dark brown organic sandy soil.	A ₁	23.2	Colour changes from middle red- brown in the B horizon, slightly paler A. very pale C horizon. Moderately gritty except C horizon clays.
	3"-1'3"	ditto. over yellow- brown clay-soil.	) A ₃) -----	14.4	
	1'3"-2'3"	Yellow-brown clay + iron-stained angular rock fragments.		10.4	
	2'3"-3'3"	ditto.	) B	11.1	
	3'3"-4'3"	Yellow-brown clay + many small mottled rotted rock fragments.		8.9	
	4'3"-5'9"	ditto, white rotted rock fragments.	) -----) C	8.2	
	5'9"-7'9"	Mainly mottled white rotted rock fragments		8.8	
	7'9"-8'9"	mottled white-brown clays.		9.4	
6. Mineralized Amphibolite (P 25)	0'-6"	Near blk. organic soil + roots		24.5	Middle red-brown, slightly darker (chocolate) in B horizon, very clayey. Similar to P18.
	6"-1'0"	Red-brown clay soil + angular rock fragments		13.3	
	1'0"-2'6"	Red-brown clay + angular rock fragments.		11.8	
	2'6"-4'0"	Red-brown clay, small white rock fragments.		11.2	
	4'0"-5'6"	Yellow-brown clay, small rotted rock fragments.		11.2	
	5'6"-7'0"	ditto, mottled white rotted rock.		10.1	
	7'0"-8'6"	ditto, some very pallid rotted rock.		9.9	

No nodular concretions were observed in any of the samples.

Horizons designated by Jacobson (56).

Pit No. & bedrock	Sample depth	ppm, ignited sample basis										% oxides		Qualitative Analyses				
		Mn	Mo	Cu	Ni	Co	Cr	La	Rb	Li	Ba	K ₂ O	Na ₂ O	Fe	AL	Ti	Ca	Mg
Injection Gneiss (P20)	0"-3"	850	<5	43	53	16	60	22	250	20	200	1.1	.06	mod.	mod.	mod.		low
	3'-1'3"	650	<5	40	50	14	70	20	300	20	200	1.1	.09		low	high	low	"
	1'3"-2'3"	600	<5	35	45	13	70	20	300	20	200	1.2	.06	↑				"
	2'3"-3'9"	650	<5	32	50	14	50	22	350	20	170	1.2	.08		↓	↑	↑	"
	3'9"-5'3"	500	<5	30	40	11	50	22	200	20	170	1.3	.06					"
	5'3"-6'9"	450	<5	20	40	13	40	22	250	30	180	1.2	.05					"
	6'9"-7'9"	550	<5	15	45	17	45	22	250	20	170	1.1	.05			mod	very	"
	7'9"-9'9"	420	<5	10	55	14	40	22	200	17	160	1.0	.05	low	high	low	low	"
Dolerite dike (P18)	0"-3"	750	5	150	73	17	83	23	120	15	200	0.8	.05	mod	mod	mod		low
	3'-1'3"	600	5	150	70	15	90	20	100	12	200	1.0	.07	high	low	high	low	"
	1'3"-2'9"	600	<5	170	90	16	110	20	180	10	150	0.4	.02	↓	↓	"	↑	"
	2'9"-3'9"	500	5	190	100	15	130	20	<100	2	70	0.5	<.01	↓		"	↑	"
	3'9"-5'3"	550	5	200	100	20	120	20	<100	7	80	0.2	.01	mod		"	very	"
	5'3"-6'3"	650	<5	200	120	22	120	20	<100	5	70	0.1	.02	high		"	low	"
Granulite (P15)	0"-3"	450	5	55	36	10	60	21	400	20	300	1.7	.13	mod	mod	mod		low
	3"-1'3"	400	5	60	37	8	68	20	500	25	300	1.7	.12	high	low	high	low	"
	1'3"-2'3"	400	<5	70	32	7	55	20	400	20	250	1.5	.08		↓	"	↑	"
	2'3"-3'3"	400	<6	95	31	8	55	23	400	22	250	1.5	.08	↓		"	↑	"
	3'3"-4'9"	350	5	90	32	8	40	22	400	20	250	1.5	.06			"		"
	4'9"-6'3"	350	5	100	27	10	40	<20	500	25	250	1.8	.06	mod		"	very	"
	6'3"-7'9"	300	5	120	25	12	40	<20	600	30	320	2.5	.08	high		"	low	"
Amphibolite (Gossany) (P11)	0"-3"	1350	6	145	48	26	90	24	120	12	250	0.7	.08	mod	mod	mod	low	low
	3"-1'3"	1100	6	160	45	20	100	25	120	12	200	0.7	.08	high	low	high	mod	"
	1'3"-2'3"	900	6	140	45	18	100	25	100	12	150	0.6	.06			"	↑	"
	2'3"-3'9"	900	6	160	50	25	110	25	100	12	180	0.6	.05	↓	↓	"	↑	"
	3'9"-4'9"	750	6	180	60	30	110	20	100	8	140	0.6	.03			"		"
	4'9"-5'9"	800	6	180	55	40	80	20	100	8	200	0.8	.03	slightly		"	very	"
	5'9"-6'3"	450	6	220	45	18	90	<20	300	30	600	2.0	.06	higher		"	low	"

APPENDIX B.7. Soil profiles. Uganda

Pit No. & bedrock	Sample depth	ppm, ignited sample basis										% oxides		Qualitative Analyses *				
		Mn	Mo	Cu	Ni	Co	Cr	La	Rb	Li	Ba	K ₂ O	Na ₂ O	Fe	AL	Ti	Ca	Mg
Alaskite (P9)	0"-3"	1050	5	265	58	34	85	20	100	12	150	0.5	.05	mod	mod	mod	high	low
	3"-1'3"	800	5	240	55	32	110	22	100	10	140	0.6	.05	high	low	high	low	low
	1'3"-2'3"	550	5	270	55	25	110	ND 20	100	12	120	0.6	.04	↑	↓	↑	↑	"
	2'3"-3'3"	300	6	320	50	16	120	<20	<100	10	100	0.5	.03	↑	↓	↑	↑	"
	3'3"-4'3"	250	5	340	55	15	90	20	<100	12	100	0.6	.03	↑	↓	↑	↑	"
	4'3"-5'9"	350	5	280	60	22	65	22	100	14	120	0.6	.03	mod	↓	mod	very	"
	5'9"-7'9"	250	<5	250	50	16	35	22	150	25	140	1.2	.04	low	↓	mod	very	"
	7'9"-8'9"	200	<5	220	55	12	20	40	100	25	170	1.2	.05	low	high	low	low	"
Mineralized Amphibolite (P25)	0"-6"	1800	6	850	105	105	165	26	<100	20	130	0.5	.06	mod	mod	mod	mod	mod
	6"-1'0"	1800	7	1100	110	120	180	35	<100	12	50	0.3	.03	high	low	high	low	low
	1'0"-2'6"	2500	5	1600	130	150	170	35	<100	14	50	0.2	.02	"	↓	"	↓	↓
	2'6"-4'0"	2000	5	1600	150	120	180	27	100	14	40	0.2	.02	"	↓	"	↓	↓
	4'0"-5'6"	1700	<5	1400	160	90	150	30	100	14	40	0.3	.02	"	↓	"	↓	↓
	5'6"-7'0"	1500	<5	1000	140	75	130	25	130	14	50	0.4	.02	"	mod	"	mod	mod
	7'0"-8'6"	1700	<5	1200	170	90	130	25	130	16	40	0.4	.06	"	high	"	low	"

Elements sought but not detected in all samples (with limits of detection, ppm):

Pb (<30), Sr (<20), Ag (<2).

* arrows show trends of increasing content.

APPENDIX B. 8. Analytical data for Argent Soil Profiles.

Profile No.	Sample No.	% * Loss	P.P.M. (ignited sample basis) Mean of duplicate determinators															Ratio Co:NO.	% Fe ₂ O ₃ +
			Mn	Pb	Ga	V	Cu	Ni	Co	Cr	Ti	Zr	Be	Li	Ba	Sr	Zn +		
1 (Norite)	48	5.4	550	40	13	235	43	100	28	675	>1%	1550	1.5	14	100	11	35	0.28	
	49	4.8	475	20	11	200	38	100	24	475	"	1800	1.5	12	80	9	30	0.24	
	50	5.0	525	25	11	200	35	85	23	435	"	1500	1.5	17	90	11	35	0.27	
2 (over ore)	51	8.1	700	285	15	260	38	140	35	500	"	1400	1.5	19	110	19	85	0.25	8.8
	52	7.4	700	300	16	220	45	140	30	600	"	900	1.5	17	120	14	60	0.21	9.7
	53	8.0	575	170	16	225	43	155	25	600	"	950	1.5	25	100	15	60	0.16	10.7
	54	8.5	1450	875	17	240	53	160	105	525	c.1%	800	2.0	30	180	11	65	0.66	12.7
	55	7.8	800	550	18	300	50	160	45	700	c.1%	900	2.0	30	110	12	65	0.28	12.6

Other elements sought, but below the limit of detection on all samples:-

S_n (< 20 ppm)

Mo (< 5 ")

Ag (< 2 ")

Rb (< 200 ")

+ Chemical analyses by Misses A.J. MacDonald and R. Thomas.

* % Loss on ignition for 2 hrs. at 500°C.