DISTRIBUTION OF PRECIOUS METALS AND GEOCHEMISTRY OF LATERITIC ORES

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

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ABSTRACT

Three lateritic profiles from different localities and of varying depth and degrees of development were analyzed for the precious metals, platinum, palladium, iridium and gold by radiochemical neutron-activation analysis. In addition, the distribution of major, minor and other trace constituents (iron, silicon, magnesium, nickel, cobalt, chromium, copper, manganese, zinc, uranium, sodium, chlorine and scandium) was determined. Instrumental activation analysis, radiochemical analysis and conventional chemical procedures were used. The mineralogy of the samples was studied using electron microscopy. Sufficient analytical data were obtained to justify the use of molecular proportions and net changes plots, and a coefficient correlation method, in order to elucidate the geochemical behaviour of the elements during the weathering processes.

CHAPTER 1

(LATERITE)

INTRODUCTION

Nickel is enriched in certain lateritic deposits which have originated by tropical weathering of basic rocks. Such deposits constitute a very important commercial source of the element. The ions Pd^{2+} and Pt^{2+} have similar radii, 0.86, 0.80 Å respectively which are fairly similar to the radius of Ni^{2+} (0.72). Moreover the second ionization potentials of Pt (18.56), Pd (19.42) and Ni (18.15) are of similar order. Such factors lead to the suggetion (Morris) that there might be a notable concentration of palladium and platinum in the lateritic nickel ores.

A review of the literature indicates that little is known about the geochemical distribution of platinum group metals during the weathering process (Wedepohl 1969); a situation that has arisen largely because of difficulties of chemical analysis.

A radiochemical method developed in this investigation permits a fairly rapid determination of palladium, platinum, gold and iridium. The procedure involves the irradiation of samples in a nuclear reactor, followed by radiochemical separation of the elements by a scheme based largely on liquid-liquid extractions. Extractions of platinum^{IV}, palladium^{II} and iridium^{IV} by di-n-heptyl sulphoxide in 1.1.2-trichloroethane were based on the distribution data of Lewis, et al.(1976), and precipitation procedures for Pt, Ir and Pd were similar to those described by Morris, Hill and smith (1963) and by Lloyd and Morris (1961).

Three profiles of varying depths and degrees of development were analyzed for precious metals as well as major, minor and other trace constituents. The mineralogy of the analyzed samples was studied using the electron microscope. Enough analytical data was obtained to justify the use of Molecular proportions and Net change plots.

Answers were sought to several questions. For example, are the major and minor changes which take place during the weathering and laterite formation recognizably different from those reported in previous studies? What factors appears to control depletion and enrichment of trace elements at different horizons of the profiles? Is there any correlation between distribution of the precious metals and other elements.

CHAPTER 1

LATERITE

The term "Laterite" was suggested by Buchnan in (1807) to denote certain reddish brown ferruginous residual rocks in S. India. Subsequently the term has been used widely for many red, ferruginous weathering products.

Reviews of laterite terminology and of laterization processes have been published in recent years by Mohr and Van Baren(1954), Tracey (1968), Hotz(1962), Maignen(1966) and Stephen and Norton(1973).

These studies permit the following generalization: Laterite is a product of tropical weathering formed by break down of parent rocks, by progressive removal of the more mobile constituents and by a complementary residual accumulation of insolublo weathering products. Goldich(1938) has emphasized the relative immobility of some constituents as an important factor in their concentration.

1.1 ORIGIN

The mechanisms of laterite formation have been the subject of numerous papers within last twenty years, including Eyles(1952), Wolfenden(1961), Harden and Bateson(1963), Maignen(1966), Grubb(1970) and Peterson(1971).

It is generally accepted that, in the origin of laterites, there are five independent variables (Jenny 1941) which effect the constitution and composition of any soil system. These are:

1. Climate
   - (i) Temperature
   - (ii) Precipitation
   - (iii) Vegetation
2. Topography

3. Parent Rocks

4. Weathering

A: Mechanical Weathering

B: Chemical Weathering

(i) Hydration

(ii) Hydrolysis

(iii) Oxidation

(iv) Carbonation

(v) Chelation

5. Time

1.2.1 Climate

Climate is one of the major factors involved in laterite genesis. The following features are important.

i- Temperature

ii- Precipitation (Intensity of rain-fall)

iii- Vegetation

These features have been discussed in detail by Mohr (1972), Dittler (1951) and Ollier (1975).

Field observations agree with the hypothesis that warmth favours laterite formation (Cady and Alexander 1962). Maignen (1958) suggested that a Sudan-Guinea climate with more than 80 inches rain-fall per year and with 2-4 months relatively dry is optimum for mobilization, accumulation and induration of iron and certain other elements in laterite.

Humbert (1948) concluded that a continuously wet condition does not favour laterite formation. The occurence of periods of drought, observed in many areas where laterite deposits occur, is thought by Maclaren (1966) to be requisite.

Tropical and sub-tropical climates are characterised by alternate wet and dry seasons, by hot weather and warm water throughout the year, and generally, by luxurient vegetation with corresponding abundant supply of bacterial life and organic compounds. Under these conditions, rock decay is carried further, leaching is more complete, and an enriched residual material is formed.

There is a tendency for the rate of chemical reactions to increase as temperature increases (Pickering 1951).

1.3.1 Parent Rocks

Laterite is found overlying a variety of rocks. It is more commonly over basic and ultrabasic rocks, although exeptionally it may be found on acid rocks, e.g, Fauta Djallan massive (Maignien).

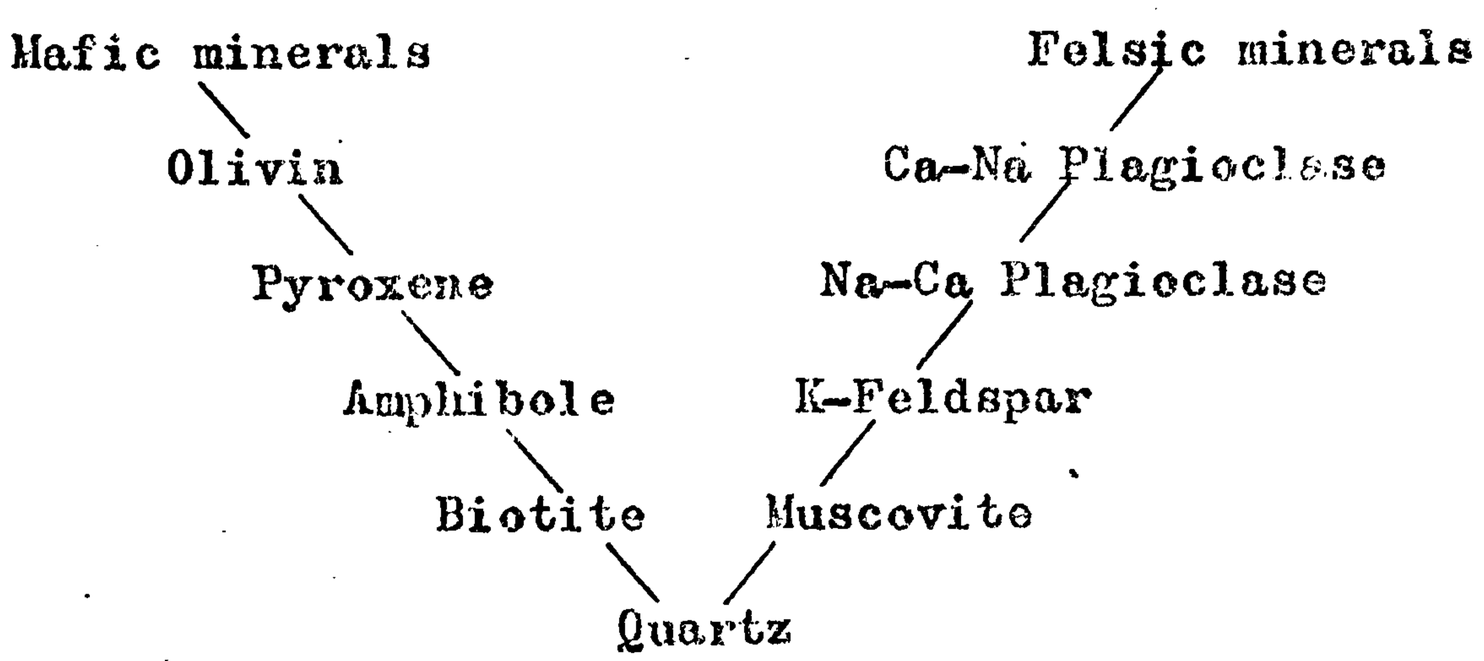
The economic importance of the occurrence of certain elements in laterites is clearly dependent upon the nature of the rock from which they originated, their chemical mode and the degree of natural concentration:

According to Vine(1949), similar soils are formed under quite different climatic conditions from a particular kind of parent rock. This is exemplified by the Serpentine soils of New Caledonia (Grange 1949) "they extended from near sea level on arid western coast (250 mm rain annually) up and over the central ranges (rain, 1900mm) and down to the east coast where there is a rain-fall of about 2500 mm, without the soil showing any significant changes in profile characteristics". On the other hand, difference in source rock composition leads to the formation of different soils in spite of similar climatic conditions.

Structure, as well as mineralogical and chemical composition, of the parent rock may have an important influence on soil formation.

Many scientists have drawn attention to the fact that minerals of basic rocks in general weather more readily than those of acidic rocks.(e.g., Goldich 1939)

On the basis of observation and experiment, the common minerals of igneous rocks can be arranged in two parallel series, according to rate of weathering:



The series show a striking resemblance to the order of crystalli-zation of minerals from igneous melts. The minerals that form at highest temperatures (olivine and calcic-plagioclse) being those susceptible to weathering.

1.4.1 Topography

Laterite has been generally associated with a level or gently sloping surface. This characteristic was emphasized at an early period by Oldham (1893) Holme (1914). They observed in Mozambique that laterites only occured on gently undulating plateau and never on steep slopes. Many laterites are associated with peneplains, as in Oregon (U.S.A).

Previous literature concludes that gentle-sloping surfaces are necessary to retain the accumulating residium, which would otherwise be washed away as soon as formed, and it also permits continual slow downward seep of rain water and a seasonal high water table.

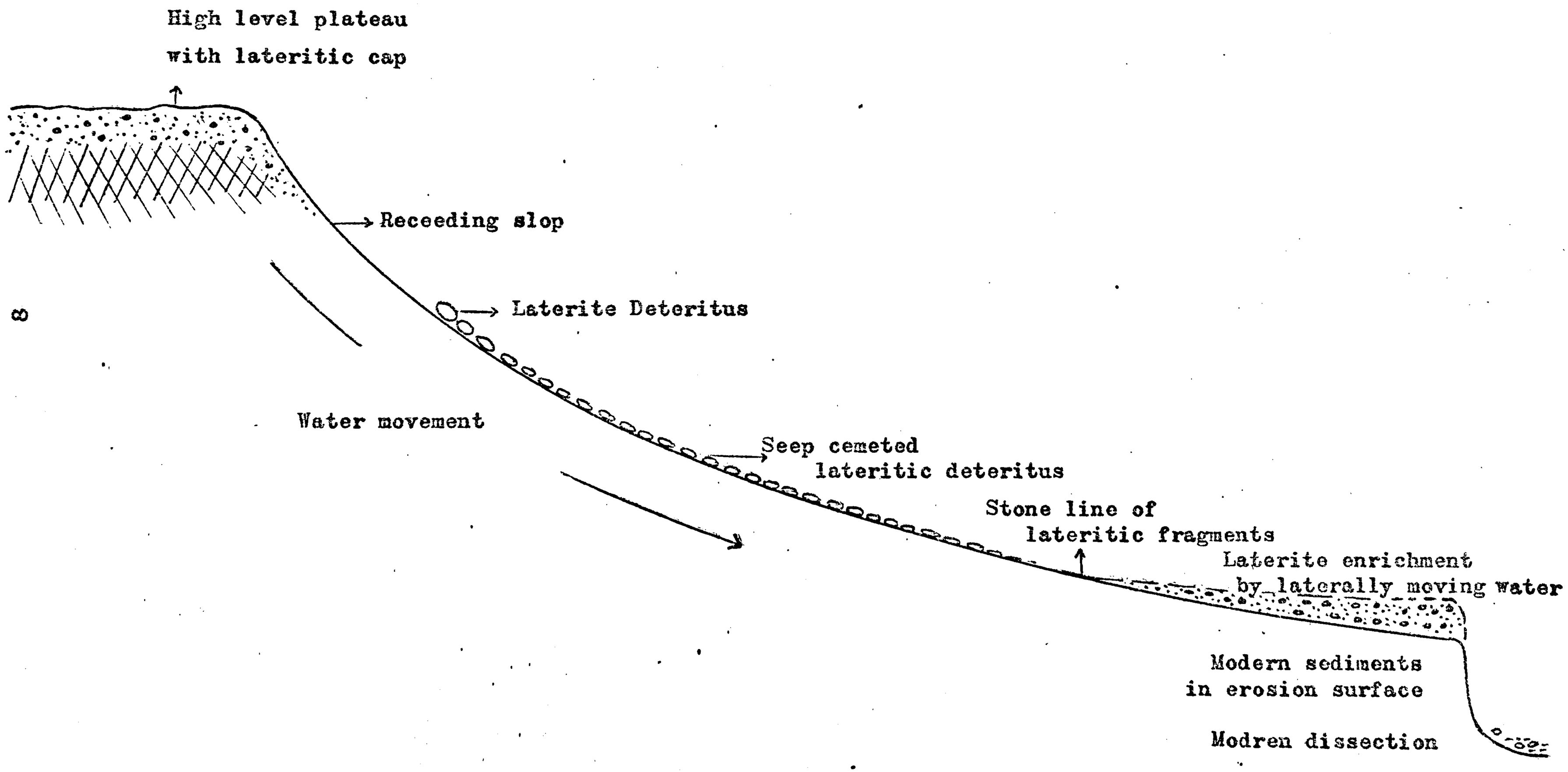
Lake (1890) classified the laterites according to topographic positions. He tried to suggest that topographic position has an effect on the origin and nature of the laterites.

Classification:

Group	Nature of laterite	Origin
Plateau	Vesicular	Non-detrial
Terrace	Partly Vesicular	Detrial & Non-detrial
Valley	Partly pellety	Detrial & Non detrial

A more elaborate scheme of classification has been presented by Moore(1955) and by Maignien(1958).

Fig. 1.1 Diagramatical illustration of topographic classification



Four Physiographically distinct landscapes with which laterite is commonly identified are:

1- High level peneplain remanents.

2- Colluvial foot steps.

3- Low-level plain having water tables or receiving water from high land.

4- Intermediate between upland and peneplain.

The first three are illustrated diagramatically in fig.1.1.

1.5.1 WEATHERING

Weathering reaction takes place primarily as a result of disequilibria between the lithosphere and hydrosphere, atmosphere, and biosphere (Keller 1954).

Rocks and minerals are responsive to their environment. They are stable under the conditions at which they were created but may become unstable with change of environment. Most of the rocks are formed under conditions of high temperature and pressure which do not pertain at the surface.

Weathering is much more important in the formation of economic-minerals than is generally realised (Bateman 1957).

Weathering is a complex operation that involves several distinct processes, such as disintegration, oxidation, hydration and hydrolysis. These processes may operate singly or jointly. Weathering generally subdivided into two catagories:

1- Mechanical weathering

2- Chemical weathering

1.5.2 Mechanical weathering

Mechanical action, although important in yielding valuable placer deposits, does not create the useful minerals; it merely frees and concentrates minerals already formed. However, it facilitates chemical weathering by reducing the size of the material, thus creating more specific surface available for chemical attack.

1.5.3 Chemical weathering

Chemical weathering involves reactions of rocks and minerals with the constituents of air and water at or near the Earths' surface. From different point of view, weathering means approach of a system involving rocks, air and water to equilibrium.

1.5.4 Rate of weathering

The rate of weathering of rocks is highly dependent upon numerous factors; these include :

i- Size of rock particles.

ii- Permeablility of the rock mass.

iii- Position of the ground water table.

vi- Temperature of the rock.

v- Composition of the rock.

iv- Amount of water active in weathering.

iiv- Oxygen and other gases in the system.

iiiv- Macro- and micro-flora and fauna present.

Because of the many variable factors, the rate of chemical weathering ranges widely from place to place.

Jenny(1941) quotes Hilger's (1897) experimental studies, where uniform rocks particles, 10-20 mm in diameter, were exposed to atmospheric influences for a period of 17 years. Limestone particles were very slightly reduced from original size, but 90% of the sandstone particles disintegrated, probably due to weathering of the cement.

Goldich calculated that the total amount of igneous rock weathered during the geological history of the earth, on the

assumption that all ^{40}Ar now found in the atmosphere and hydrosphere is a decay product of ^{40}K in the Earth's crust, and that all the ^{40}Ar has been released by weathering. He arrived at the figure 6462 Kg Cm^{-2} of rock having been weathered during $3.5x10^{9}$ years.

1.5.6 Chemical reactions

Rocks are weathered chemically by a large variety of reactions (Locus 1967). Those are followings:

1.5.7 Hydration

The simplest kind of weathering reactions involve dissolving of soluble minerals and the addition of water to form hydrates; e.g iron oxides absorb water and turn into hydrated iron oxides or iron hydroxides.

Stated as:

$$Fe_2O_3 + H_2O \rightleftharpoons 2FeOOH$$

Iron oxide + Water ——— Goethite

hydration is also important in the formation of clays. Frequently water may be incorporated as part of the crystal lattice in hydrated minerals (Keller 1961).

Hydration often involves a considerable volume change which may be important in physical weathering, exfoliation and granular disintegration (Ollier 1975).

Hydration, according to Ollier, actually prepares the minerals surfaces for further alteration by hydrolysis, oxidation and carbonation. It also enables the transfer of ions to take place with greater ease.

1.5.8 Hydrolysis

Hydrolysis in the weathering process refers to reaction between the H^+ and OH^- ions of water and the elements of rock or mineral. Water (even distilled and rain water) is not inert, it is a chemical reagent supplying H^+ and OH^- ions. These ions play an important role in controlling the reactions undergone in chemical weathering. Solubilities of many substances vary dramatically with the change of pH e.g; the solubility of iron is about 100,000 times greater at pH. 6 than at 8.5 (Ollier 1975).

Because most of the primary rock forming minerals are silicates, the hydrolysis and the weathering of silicates is of prime importance. Hydrolysis reactions of silicates are (Simplified formulae):

Olivine

$$Mg_2SiO_4 + 4H_2O \text{ ——— } 2Mg^{++} + 4OH^- + H_4SiO_4 \text{ (Silicic acid)}$$

K-Feldspar

$$4KAlSi_3O_8 + 22H_2O \text{ ——— } 4K^+ + 4OH^- + Al_4Si_4O_{10}(OH)_8 \text{ (Gibbsite)} + 8H_4SiO_4 \text{ (Silicic acid).}$$

1.5.9 Factors which promote hydrolysis

In order to continue this process the soluble product of hydrolysis must be removed from the active system. The product may be removed, wholly or in part, by several processes; these includes the following:

1- Repeated leaching by fresh rain water.

2- Introduction of H^+ ions.

3- Absorption of the product by colloidal substances.

Repeated leaching of rocks by fresh water performs at least two functions:

i- It carries away in solution the soluble substances.

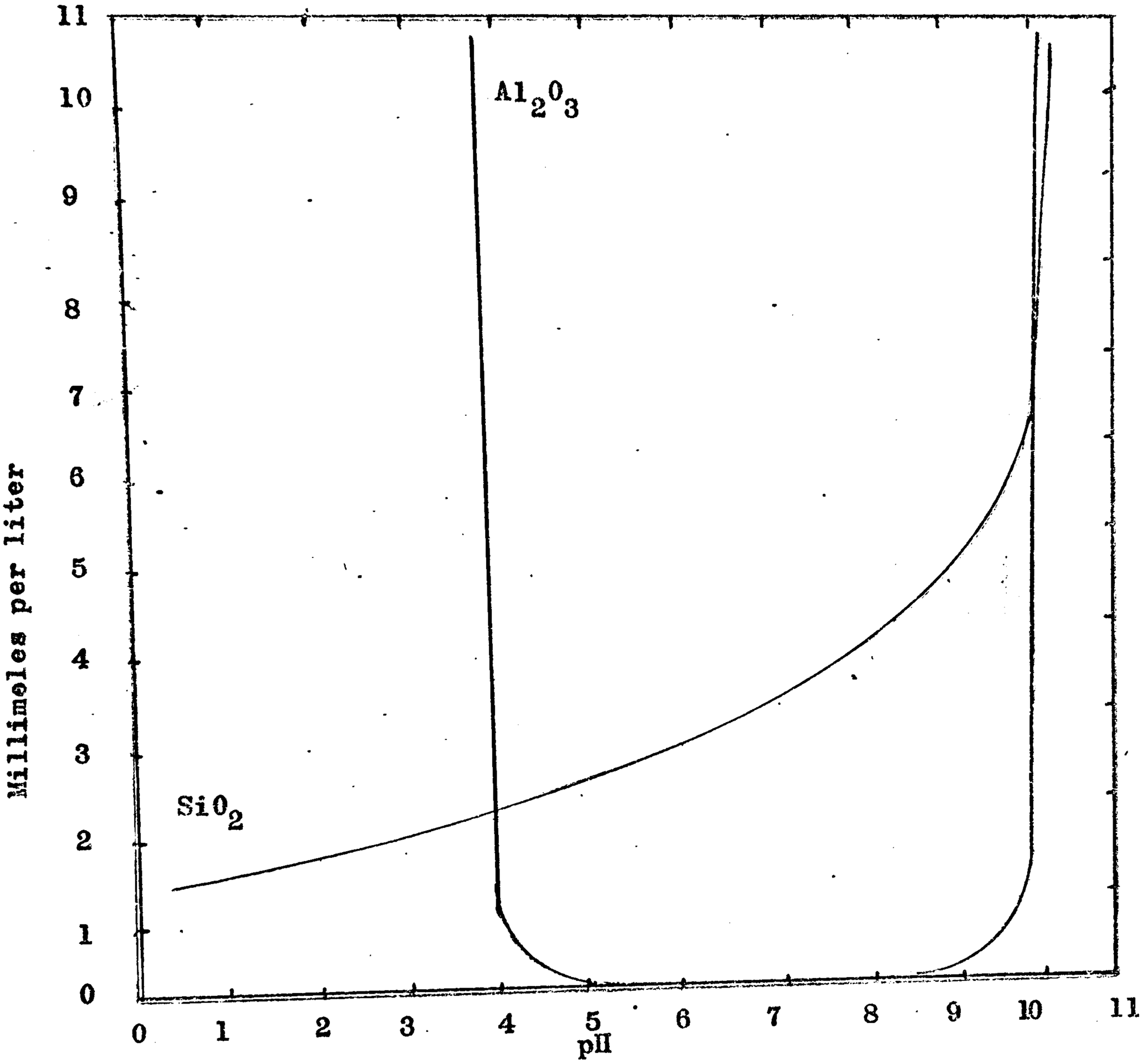
ii- It tend to determine the pH and oxidation potential in the weathering system. The pH value of the weathering system effects, inturn, the kind of products(e.g bauxite- laterite- koaline or other clay minerals). Rain water, is initially neutral (pH 7) or near so, but surface waters may be rendered acid or alkaline as a result of interaction in rock weathering system. Water may dissolve CO_2 and other acid forming gases from the air and soil system and organic acid from the soil, which render it acid in reaction.

Analogously it may pick up basic substances from certain soil, which make the water alkaline.

Keller(1957) concluded that the rate of rock weathering becomes important under conditions where the rocks are repeatedly leached with fresh water. The volume of water that is available for leaching tends to fix the pH of the weathering system and thereby influence the kind and amounts of the weathering products.

The effect of pH on Al_2O_3 and SiO_2 has been shown by Corren (1949) and Garrels (1956). At pH 10 and higher, both Al_2O_3 and SiO_2 are relatively soluble and therefore some amount of them may be released during hydrolysis. e.g., the Al_2O_3 and SiO_2 released from hydrolyzing nepheline and amphiboles(both have abrasion pH 10-11) are likely to be carried away, unless and untill their solution meet with the following conditions; either (i) reduction of pH, or (ii) evaporation of part of the water.

Fig. 1.2



The solubility of silica and alumina as a function of pH (from Mason, 1966).

Table 1.1 shows the pH of some common minerals when abraded in water.

Mineral	pH when abraded in water
Feldspars	
Albite	10
Oligoclase	9
Anorthoclase	8
Orthoclase	8
Microcline	8
Micas	
Biotite	8
Muscovite	7
Amphiboles	
Actinolite	11
Hornblende	10
Pyroxenes	
Augite	10
Hypersthene	8
Olivine	10
Nephline	11
Cabonates	
Calcite	8
Dolomite	9
Clay minerals	
Kaolinite	6
Montmorillonite	7
Quartz	7

Data simplified from Keller, 1957.

Let us assume that the pH of a solution derived from hydrolysis of Nephline is reduced from pH 10 to pH 8 (quite probable in nature), and observe the effect on solubility of Al_2O_3 and SiO_2. At pH 8 the solubility of Al_2O_3 is reduced to almost nil, but the solubility of SiO_2 is reduced to only a quarter of what it was at pH 10. It is expected, therefore, that at pH 8 hydrated Al_2O_3 will be precipitated probably as Gibbsite ($Al_2O_3.3H_2O$), or as Diaspore ($Al_2O_3.H_2O$), constituting Bauxite, whereas most or all of SiO_2 will remain in solution and be carried away.

1.5.10 Introduction of ions and their sources

i- Rain water and carbonic acid

Acidity of ground water is increased usually by the solution of CO_2 from the air and from the soil atmosphere in which the partial pressure of CO_2 may be as much as ten times that of the air. Carbonic acid (H_2CO_3) may effect weathering not only furnishing H ions, but also taking Ca, Mg, Fe and other ions out of the system in solution (perhaps as bicarbonates).

ii- Acid Clay

A very important acid in the weathering process is acid clay, a clay mineral which has a significantly high ratio of H ions in its cation exchange sites.

Clay can cover the surface of a primary silicates particles and attack it with maximum effectiveness by H ions, those always in intimate contact with the particle undergoing weathering (Ollier 1975).

iii- Living plants

Living plants provide a continuing source of H ions to the colloidal clay in contact with their roots and tends, therefore, to create an acid condition of the clay which, in turn, weathers the nearby rocks and minerals. Plant rootlets exchange H ions for Ca, Mg, K and other available cations which they take up as nutrients for the plant (Graham and Baker 1951).

1.5.11 Oxidation

. Oxidation of a substance occurs when it or one of its constituent atoms loses one or more electrons (e^-). Oxidation in the process of weathering usually occurs by the combination of elemental oxygen with the weathering substance, a reaction by which the oxidized substance loses electron to the oxygen.

Oxidation of minerals by gaseous oxygen essentially always occurs through the intermediate action of water in which the oxygen has first dissolved.

Oxidation takes place mostly in the aerated zone. Among the products of weathering, iron oxide are the most conspicuous because of their bright colours. They include two forms of anhydrous iron(III) oxide (the common mineral Hematite and less common Magnetic oxide) and at least two hydrated forms, Goethite ($Fe_2O_3.H_2O$) and lepidocrcite (FeOOH).

According to Keller(1961) and Reiche (1955), any ferrous compound on prolonged exposure to the air is oxidized, according to such reactions as:

$$Fe_2SiO_4 \text{ (Fayalite)} + \tfrac{1}{2}\ O_2 + 2H_2O \longrightarrow Fe_2O_3 + H_4SiO_4$$

$$2Ca\ Fe\ Si_2O_6 \text{ (Hedonbergite)} + \tfrac{1}{2}\ O_2 + 10\ H_2O + CO_2 \longrightarrow$$

$$\longrightarrow Fe_2O_3 + 4\ H_4SiO_4 + 4Ca^{++} + 4HCO_3^-$$

$$2FeCO_3 \text{ (Sedirite)} + \tfrac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 2H_2CO_3$$

Krauskopf (1967) states that almost certainly oxidation take place in steps. Details are not necessarily known, but it is very likely that the reaction involve progressive dissolving of the iron (II) compounds by H_2CO_3.

$$Fe_2SiO_4 + 4H_2CO_3 \longrightarrow 2Fe^{++} + 4\ HCO_3^- + H_4SiO_4$$

followed by oxidation of the Fe^{++}:

$$2Fe^{++} + 4\ HCO_3^- + \tfrac{1}{2}\ O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4\ H_2CO_3$$

1.5.12 Chelation

Chelation involves holding of an ion, usually a metal, within a ring structure of organic origin. Chelating agents can extract ions from otherwise insoluble solids, and enable the transfer of ions in a chemical environment where they would normally be precipitated.

Plants utilise chelating agents to extract ions (nutrients) from minerals, and thus enable mineral-weathering to take place at a much greater rate than would be indicated by simple ionic considerations.

The actual mechanism is not known in any detail(Ollier 1975). An instructive demonstration of chelation is described by Keller (1957). Powder calcite is stirred into an aqueous solution of the sodium salt of EDTA (Ethylene diamine tetra-acetic acid, a common chelating agent). No CO_2 is given off, the pH remains 10 to 11 (highly alkaline), and the Ca is taken up in solution by chelation and the carbonate ion remains in solution.

1.5.13 CARBONATION

The combination of cabonate CO_3^{--} or bicarbonate HCO_3^-, ions with a geological material is called carbonation. Ca, Mg, and iron bearing rocks are commonly weathered by carbonation ("iron bearing the least" Keller 1957).

Water dissolves or combine with CO_2 to form carbonic acid H_2CO_3:

$$3\ H_2O + 3CO_2 \longrightarrow H_2CO_3 + 3H^+ + CO_3^{--} + HCO_3^-$$

Rate of dissolution depends on

(i) Grain size of CO_3^{--}.

(ii)Duration.

CHAPTER 2

GEOCHEMISTRY

GEOCHEMISTRY

2.1.1 SOME COMMENTS ON THE GEOCHEMISTRY OF PLATINUM-METALS

The platinum metals are considered to be both siderophile and chalcophile. Their lithophile tendency is considered to be weak or negligible (Rankama and Sahama 1949, Wright and Fleischer 1965, Quiring 1962). As early as 1922 Goldschmit expressed the opinion that the scarcity of platinum metals in the lithosphere was due to their extremely siderophile nature and that this is the reason that they have not been concentrated in the silicate slag of the earth (upper crust), but rather in the core which probably consist of metallic iron with some nickel.

It has been deduced from the previous literature and data that platinum metals are more abundant in iron meteorites compared with stoney meteorites(chondrite),and this thing confirms the above view. In rocks, platinum metals are most generally associated with mafic and ultramafic series (Crocket1969). The high melting points and high densities of the metals are the properties which are usually cited to explain why the metals of this family are mainly associated with the early stages of magmatic differentiation.

It has been known from the previous literature that economically important deposits of platinum metals are preferentially connected with magmatic rock rich in magnesia and low in silica (Day 1970).

Platinum metals usually occur togather because of similarities in their chemical character(Table-1 after Fliescher 1965). Solid solution among the platinoids is extensive, because of similarity in their metallic radii. The metals also combine with or can be replaced in part by a significant amount of Fe(radius 1.27$\mathring{A}$), Ni (radius 1.24$\mathring{A}$) or Cu(radius 1.28$\mathring{A}$); (Goldschmidt 1954 and Fleischer 1965).

Table 2.1

	Pd	Ir	Pt
Metallic radius Å	1.37	1.35	1.38
Octahedral Covalent radius Å	1.31	1.32	1.31
Atomic No.	46	77	78
Atomic Weight	106.4	192.2	195.09

Data on the content of platinum metals in igneous rocks are scanty and scattered through a wide literature. Most of the results pertain to ultramafic rocks and related sulphides, because economically valuable deposits of platinum metals have been universally found associated with ultramafic rocks and base metals sulphides.

The content of platinum metals in igneous rocks has been summarized in table 2.2

Table 2.2 Platinum metals abundances in USGS standard rocks.

Rock Type	Pd (ppb)	Pt (ppb)	Ir (ppb
W-1 Diabase	18.5 (3)	16.2 (7)	0.25 (2)
G-1 Granite	2.5 (6)	8.2 (4)	0.07 (1)
PCC-1 Peridotite	3.0 (9)	5.1 (9)	2.5 (5)
DTS-1 Dunite	6.1 (9)	8.3 (9)	0.6 (8)
Serpentinite-Highly altered rocks, Oberfranken, Germany.	300 (6)	85 (6)	
Serpentinite-Less altered than above.	12 (6)	26 (6)	
Basalt-Kaisertuhl, Germany.	50 (6)	40 (6)	

Pd and Pt content of Bushveld Complex rocks, South Africa.
(After Hagen, 1954)

Rock Type	Pd (ppb)	Pt (ppb)
Granitic rocks	5	3
Gabboric rocks	31	21
Noritic rocks	15	38
Ultrabasic rocks (Pyroxenites)	59	48

Table Cont/...

Rock Type	Pd	Pt
Ultrabasic rocks (Peridotite)	12	17
Olivin (Bushveld dunite)	4	18
Norites (Sudbury)	6	11
Gabbros(Skaergaard)	18 (10)	18 (10)

References: 1. Baedecker, P., and W. Ehmann(1965). 2. Crocket,J., and Keays (1968). 3. Crocket,J., and G. Skippen(1966). 4. Das Sarma, B(1965). 5. Green, T.E.(1970). 6. Grimaldi,F., and M. Schnepfe(1967). 7. Haffty and Riley (1968). 8.Janasen, R (1971). 9. Nadkarni, R.A., and G.H. Morrison (1974). 10. Vincent, E., A. Smales(1956).

2.1.2 THE GEOCHEMISTRY OF PLATINUM METALS DURING WEATHERING

A review of literature shows that very little is known about the geochemistry of platinum metals in sediment(Wedepohl 1969). In the residual sediments, such as quartz conglomerates, platinum metals may occur, as does gold (Cousins 1971). Very little study has been carried out about possible chemical reactions which can occur during weathering and transportation. "Although the platinum metals are very resistant to chemical reaction, it must be remembered that they may be exposed to such attack through geological times of millions of years" Stumple (1970).

Alluvial platinoid grains (found in Good News Bay, Alaska.) are predominantly metallic alloys of platinum elements, generally considered as produced by erosion of the primary platinoid minerals disseminated in basic and ultrabasic rocks. (Mertei 1969).

According to Cousins(1975) alluvial concentration in South Africa indicates that differential leaching of platinum metals may take place. Amongst theplatinum metals the rough order of resistance to chemical attack appears to be:

Ir Os Ru Rh Pt Pd.

Cousins (1975) has demonstrated that Sodium Chloride is one of the most potent leaching agents for platinum metals under oxidizing conditions. Sodium chloride combines with platinum group metals to form soluble chloride complexes. Laboratory experiments indicate that the reaction is completed in a few hours when a 10% sodium chloride solution at 35^{o}C under a chlorine atmosphere, is used for this leach reaction.

Under natural conditions the reaction will be vastly slower, but the geological time element can be very long(Cousins 1975). Evidence in fav-our of this reaction is platinum, poor, Os+ Ir, rich, in alluvial deposits of Good News Bay (Meritei 1969).

According to Stumple (1974) platinum metals occur in solid solution in olivine, chrome-spinel, and sulphides. He also suggested that serpentinization may result in the release of nickel and platinum group elements from the olivine and spinel lattices. Uneconomic content of nickel in olivine might thus be transformed into potentially workable concentration, and the same applies to the platinum group elements. The Inaglinskily complex, Yokutia(U.S.S.R), is a good case in point.

Otteman and Augustithus(1967) suggested that the platinum nuggets (in W. Ethiopian laterite) are a derivative product of dunite, mainly formed by laterization. They suggested the following evidence for growth of platinum nuggets in lateritic soil:

(i) The angular shape and proturberances of the platinum nuggets (these shows no rounding due to erosion during transportation) can be taken as evidence the platinum nuggets growth in the lateritic soil.

(ii) The platinum nuggets enclose chromite grains identical to those of the ultrabasic rocks.

(iii) The presence of altered chromite grains as inclusions in the nuggets supports the view that the nuggets, growth has taken place in an environment of disintegration of ultrabasics. Iron oxide coating around the platinum could be formed during laterization.

Several other studies suggest that platinum may be mobile during weathering, and Cousins (1973) give evidence for mobility of palladium and platinum in forming placers. Evidence available so far points to $PtCl_6^{2-}$ as a transportable species. The most impressive (and best documented) placers are those of the Witwatersrand that contain Os + Ir. Wagner (1929) described the occurrence of supergene platinum and palladium minerals derived from the Merensky reef of Bushveld complex, South Africa, by leaching of the reef and redeposition of of platinoid in the anorthositicnorite foot wall. The area which was highly fractured had the largest amount of oxidation and redeposition of platinum metals and the ratio of Pt to Pd in the oxidised ore was found to be higher than in the primary ore; this provides further evidence that palladium is more readily leached than platinum.

Kenneth (1971) suggested that platinum-nugget from Trinity county, California, was derived from ultrabasic rocks, mainly serpentine, and was formed at low temperature. The constituents of the nugget may have been transported and localised by fluid available during serpentization of host rock.

The above studies permit the following generalizations:

1- Platinoid metals are always associated with ultrabasic rocks and base metal-sulphides.

2- Evidence and experiments show that platinum metals may be mobile during weathering.

3- A likely mode of transportation of platinum elements in the weathering cycle is as chloro-complexes.

4- Another aspect is transportation and localization of these elements by fluid available during serpentization of host rock.

5- Residual concentration results in the accumulation of platinoid metals when other major constituents of ultramafic rocks are removed during weathering. The residues may continue to accumulate untill their volume make them of commercial importance.

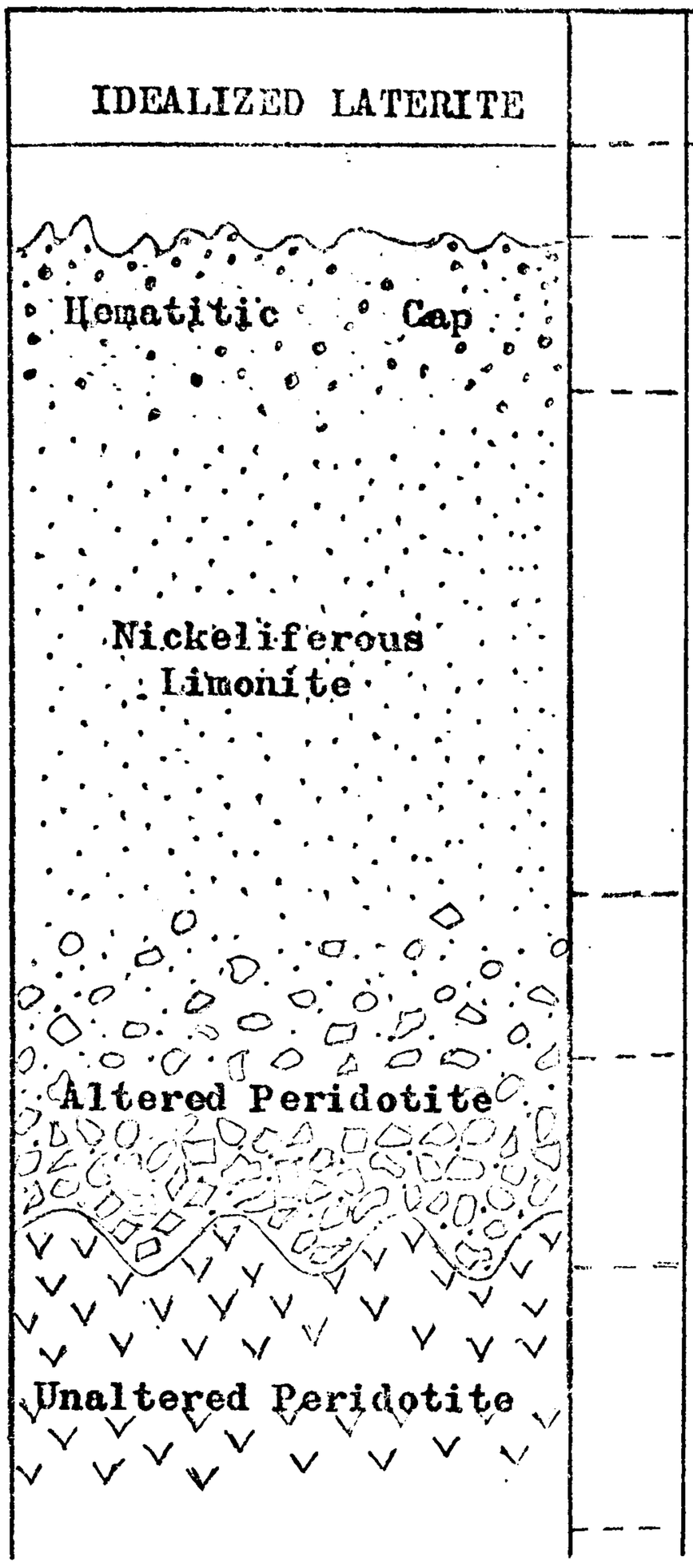
2.1.3 RELEVANT GEOCHEMISTRY OF MAJOR AND MINOR ELEMENTS

Several studies have dealt with the geochemistry of major and minor elements during weathering. Gordon and Muarata, 1952(Arkansas); Hotz, 1964 (Oregon); Santos Ynigo,1969(Philippine); and Harris,1966 (Oklohoma); and Zeissink, 1971(Australia).

The following generalisation appears valid on the basis of these previous studies. Ultramafic and mafic rocks, mainly peridotite and serpentine, contain on average, 0.2 percent Ni, 0.02 percent Co, 10 percent Fe and 0.2 percent Cr, with fresh and altered olivine as a main component (It is believed that olivine and pyroxene crystals contain the Ni and Co in their lattices). These rocks are progressively decomposed by carbon dioxide contained in surface water and by prolonged exposure to the atmosphere in humid , tropical and semi-tropical climates. As a result Si, Mg, Ca, K and Na are preferentially dissolved from the parent rock, leaving varying concentrations of Al, Fe, Cr, Co and Ni relative to fresh rock.

Roorda(1973) has shown an ideal section through a nickeliferous oxide deposit, broadly consisting of superficial nickeliferous limonite, altered peridtite and unaltered peridotite. The chemical and mineralogical variation through the depth of the shown profile (Fig.2.1) applies to many deposits in tropical and subtropical countries. There can be minor differences that may reflect variations in physiographical factors.

Mineralogically, the changes are from a mixture of olivine, pyroxene and serpentine to a final product composed predominantly of hydrated iron oxides and minor amount of clay mineral.



APPROXIMATE ANALYSIS - %				
Ni	Co	Fe	Cr_2O_3	MgO
0.8	0.1	50	1	0.5
0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5
1.5 to 1.8	0.02 to	25 to 40	1 to	5 to 15
1.8 to 3	0.1	10 to 25	2	15 to 35
0.25	0.01 to 0.02	5	0.2 to 1	35 to 45

Fig.2.1. Idealized section through a lateritic nickel orebody indicating composition as a function of depth.(From Rooda 1973)

The predominant mineral species resulting from weathering is goethite (FeOOH), it is characterised by a poor degree of crystalinity. According to Roorda(1973) in addition to some percentage of Ni, the goethite may contain Cr and Al. Hematite, Maghemite, chlorite, enstatite and chromite are accessory minerals commonly present in laterite.

CHAPTER 3

SAMPLES INVESTIGATED IN PRESENT WORK

GUATEMALAN PROFILE

3.1.1 GEOLOGY AND GEOGRAPHY

Nickel deposits of lateritic origin occur at La-Gloria in east Guatemala some 50 miles inland from Puerto Barrios on the Carribean coast. The nickel bearing material has been found over a large area in association with hills of partly serpentized peridotite on the sides of lake Izbal(Boldt 1967).

TOPOGRAPHY

The distribution pattern of the laterite at various elevations from the plain to gentle slopes and on ill-defined terraces, is probably due to block faulting.

CLIMATE AND VEGETATION

The climate is tropical. An average yearly precipitation is about 80-90" and average dayly temperature is about 30°C.

The vegetation developed on the ultramafic rock area is sparse compared to the dense growth on adjacent rocks.

3.1.2 PHYSICAL CHARACTERISTICS

The nomenclature used in this study to describe the various horizons observed in the profiles under investigation is as follows:

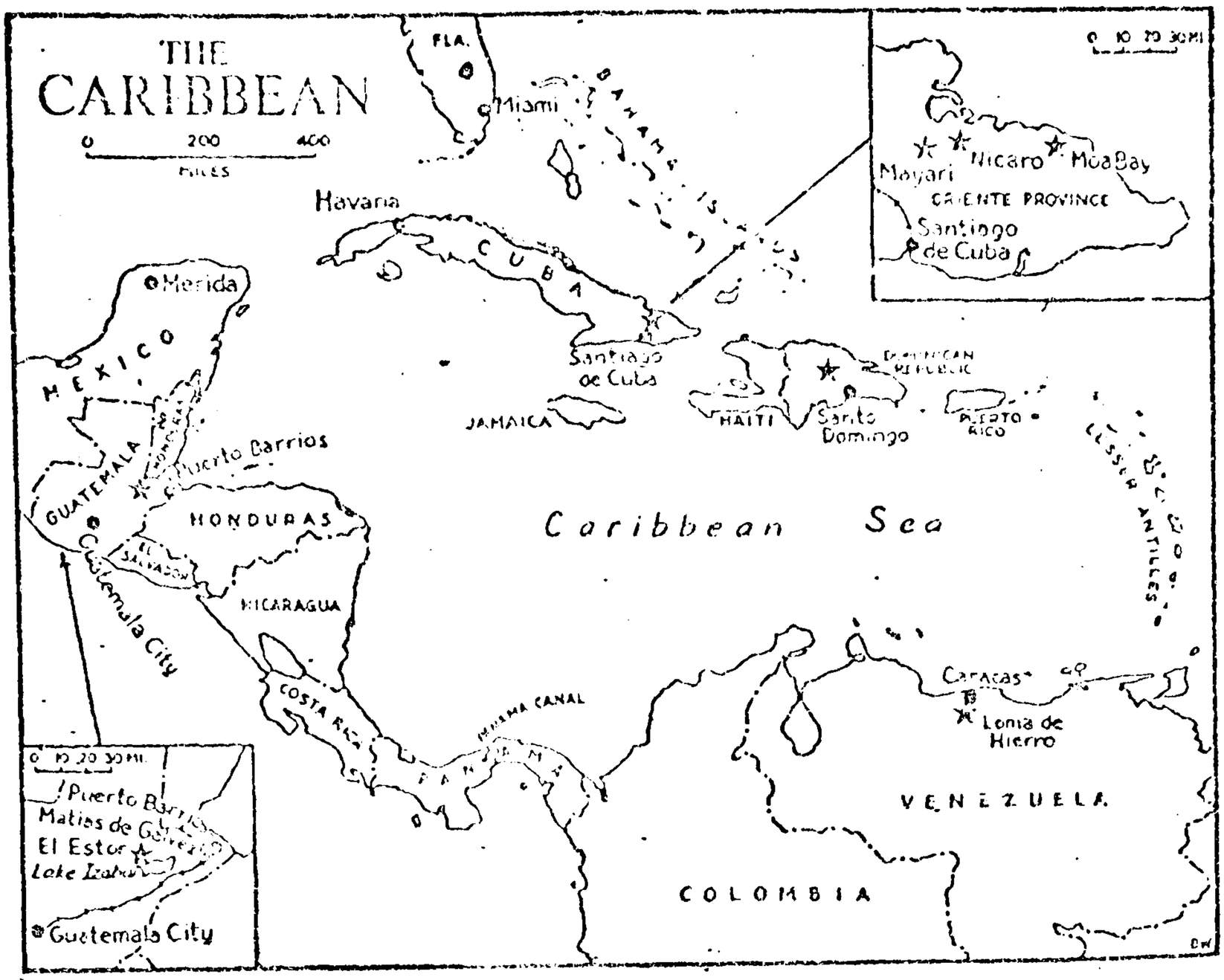
A-horizon: the eluviated(leached) top layers.

B-horizon: the illuviated(enriched) intermediate layers.

C-horizon: weathered parent material.

D-horizon: unaltered parent material.

The physical characteristics of the Guatemala profile is generally analogous to other nickeliferous laterites in tropical and sub-tropical countries. We have the following sequence as a function of depth.


THE CARIBBEAN
0 200 400
MILES
FLA.
Miami
BAHAMAS
Havana
CUBA
Santiago de Cuba
JAMAICA
HAITI
Santo Domingo
DOMINICAN REPUBLIC
PUERTO RICO
LESSER ANTILLES
0 10 20 30 MI
Nicaro
Moa Bay
Mayari
ORIENTE PROVINCE
Santiago de Cuba
Merida
MEXICO
GUATEMALA
Puerto Barrios
HONDURAS
EL SALVADOR
Guatemala City
NICARAGUA
COSTA RICA
PANAMA
PANAMA CANAL
Caribbean Sea
Caracas
Loma de Hierro
VENEZUELA
COLOMBIA
0 10 20 30 MI
Puerto Barrios
Matias de Galvez
El Estor
Lake Izabal
Guatemala City

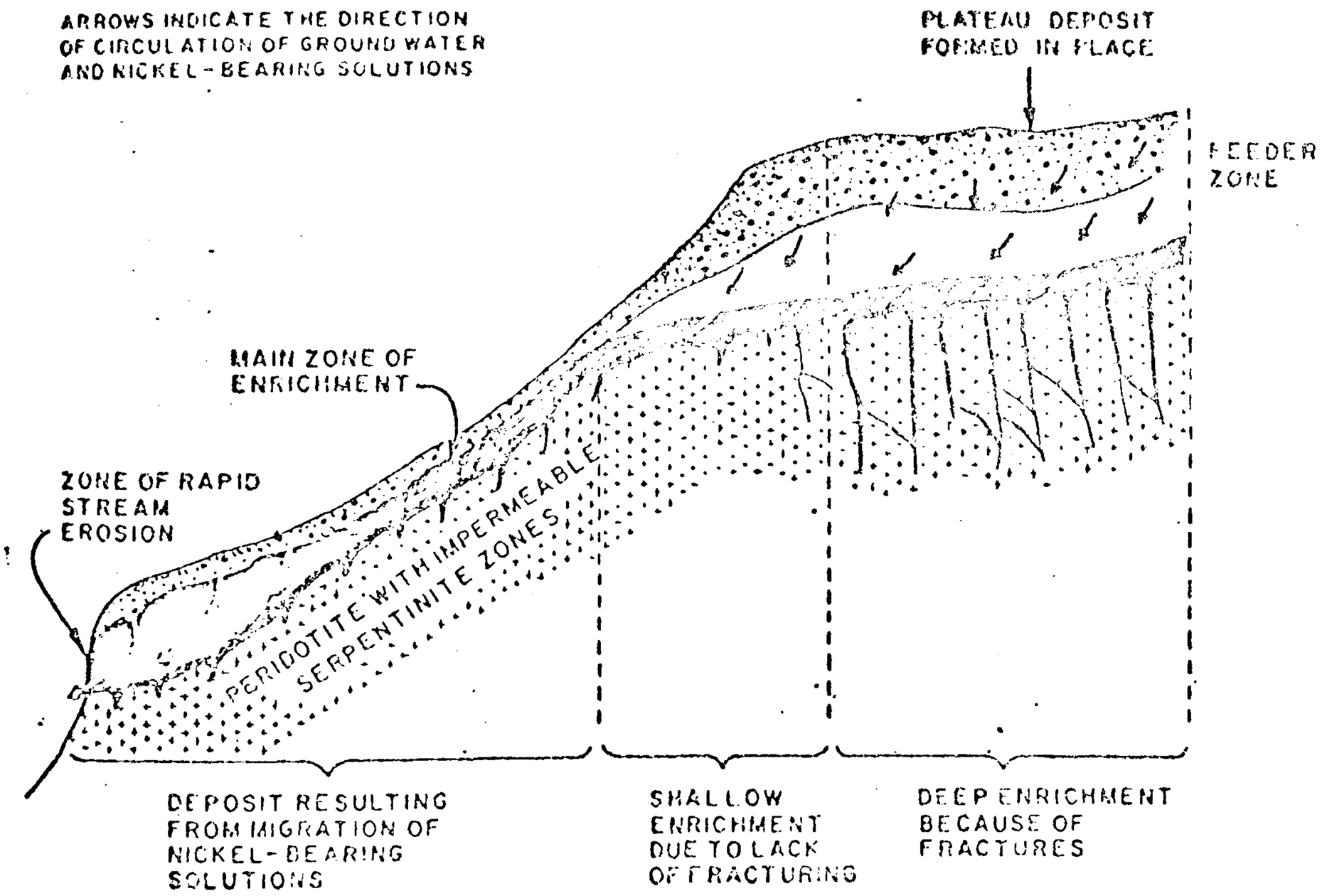

ARROWS INDICATE THE DIRECTION OF CIRCULATION OF GROUND WATER AND NICKEL-BEARING SOLUTIONS
PLATEAU DEPOSIT FORMED IN PLACE
FEEDER ZONE
MAIN ZONE OF ENRICHMENT
ZONE OF RAPID STREAM EROSION
PERIDOTITE WITH IMPERMEABLE SERPENTINITE ZONES
DEPOSIT RESULTING FROM MIGRATION OF NICKEL-BEARING SOLUTIONS
SHALLOW ENRICHMENT DUE TO LACK OF FRACTURING
DEEP ENRICHMENT BECAUSE OF FRACTURES

Fig. 3.1

LOCATION AND SAMPLE NO	DEPTH (M)	WEATHERING HORIZON	GRAIN SIZE INCHES	DESCRIPTION
L(1)	1.5-2.00	A	0-2	Reddish brown soil with organic matter and iron(III) oxide pellets. Slight amount of weathered serpentine.
L(2)	2.5-3.00	B_1	0-1	Highly weathered reddish brown soil of plastic iron oxides with some organic materiel. Fine earthy appearence.
L(3)	3.5-4.00	B_o	0-2	Yellow-orange soil with less iron oxide than L_2 and with saprolitic texture(with some fragments of soft peridotite).
L(4)	5.25-5.75	C_1	2-6	Yellow brown soil. Saprolitic texture with boulder of peridotite-serpentine.
L(5)Course	8.00-8.50	C_o	2-6	Slightly weathered rock(serpentine) fragments with fine grained soil with iron oxide. Gray-yellow colour.
L(6)Fine	8.00-8.50	C_o	0-2	
L(7)	10.25-10.75	D	+6	Slighly weathered peridotite-serpentine.

NEW CALEDONIAN PROFILE

3.2.1 GEOLOGY AND GEOGRAPHY

New Caledonia has one of the largest assemblages of ultramafic rocks. Nearly one third of the island about 2300 square miles out of the total area of about 7200 consists of peridotite or its alteration products. The peridotite is believed to have been introduced during tertiary period. There is a range of composition from dunite to peridotite (consisting of olivine, harzburgite and pyroxene).

TOPOGRAPHY

Topographic evolution has been an important factor in the development and localization of the nickel deposits. Lateritic weathering evidently took place on a peneplain or mature land-form that was being subjected to uplift and block faulting.During the laterization period valleys and canyons were eroded into the surface of the land due to stream activity. Flat and gently sloping surface favoured more effective action of ground water and at the same time were not subject to rapid erosion; wherever this erosion progressed at a faster rate than weathering, there was no opportunity for nickel deposits to accumulate.

3.2.2 PHYSICAL CHARACTERISTICS

The physical character of the New Caledonian profile shows general agreement with the other laterites found in tropical countries. The typical ore section consist of an upper layer of limonitic soil that graded downward into limonitic nickel ore, which in turn grades to serpentine ore that is in direct contact with the underlying parent rock.

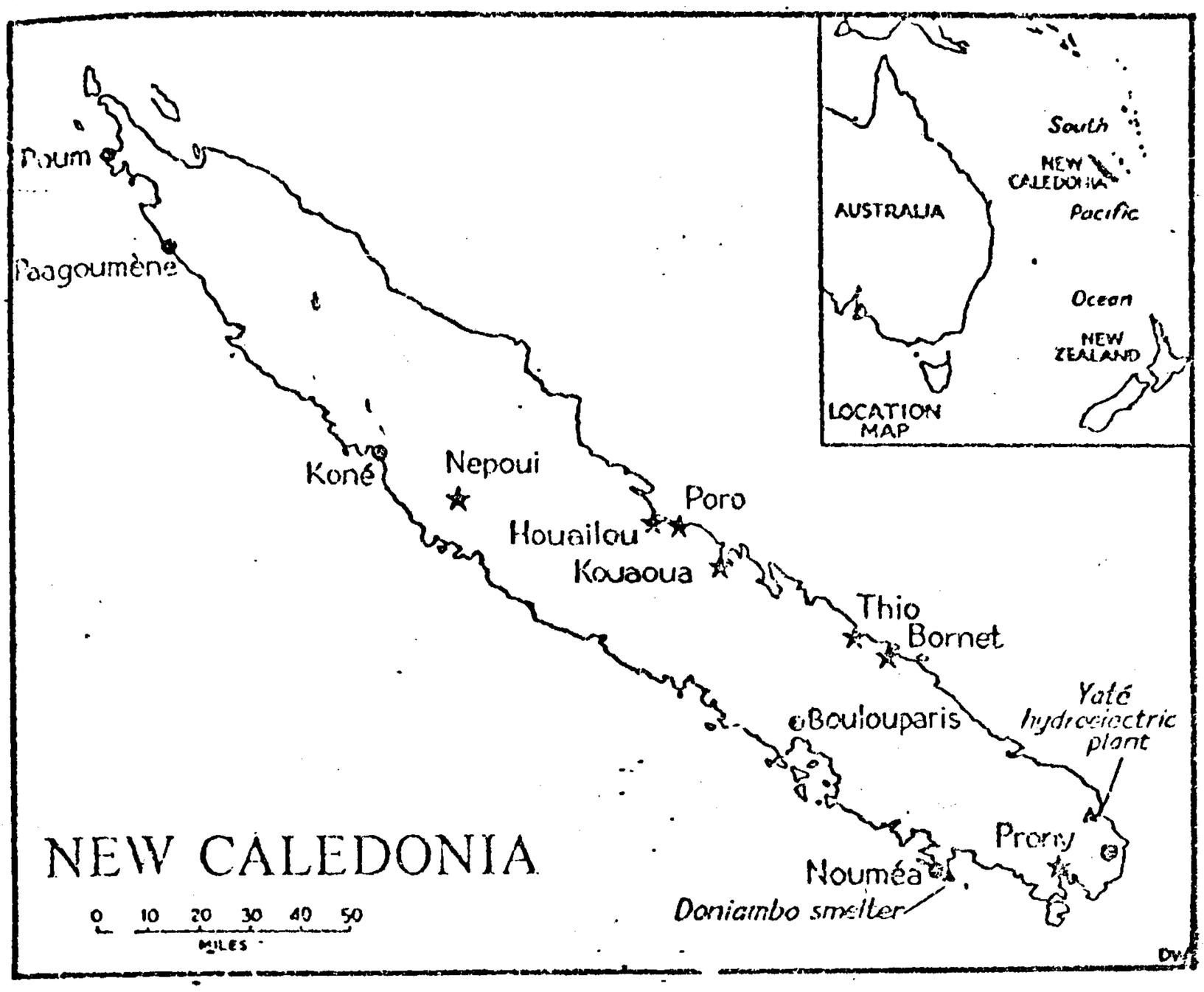


Fig. 3.2

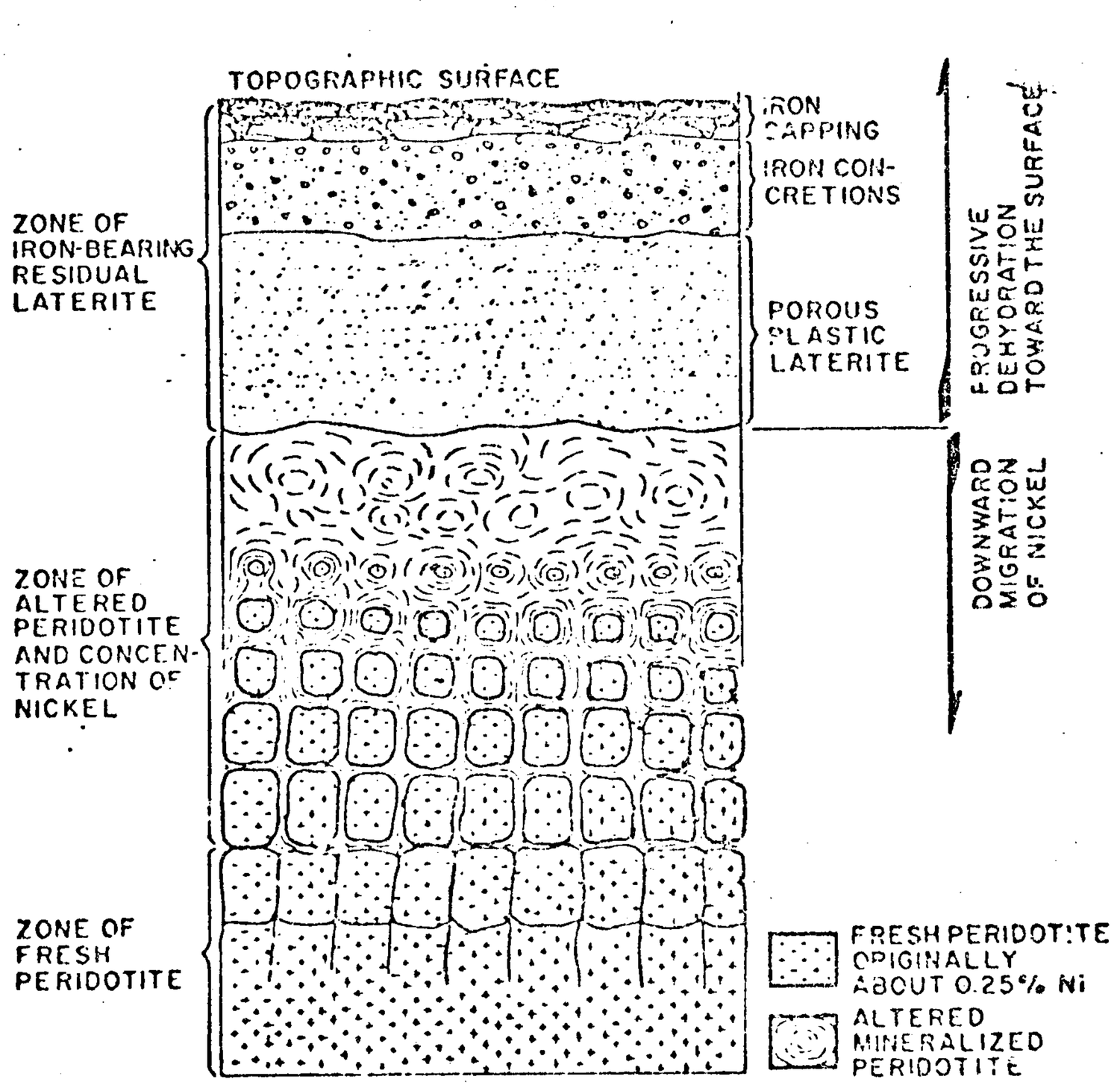


Fig. (After de Châtelat). Schematic ideal section showing the main zones of a complex lateritic deposit in New Caledonia.

Fig. 3.3

LOCATION AND SAMPLE NO	DEPTH (M)	WEATHERING HORIZON	DESCRIPTION
BNC 1	0–7	A	Ferricrete surficial soil consist mainly iron oxide (limonite). Reddish brown colour is due to iron oxides. Slight amount of organic matter with some serpentine fragments are present.
BNC 2	2–7	A	Yellow brown soil have the same sort of texture as BNC_1 with less organic matter.
BNC 3	7–11		
BNC 4	11–13		Textural resemblance begins to disappear in BNC_3 and BNC_4.
BNC 5	13–14	B	Highly weathered, dark red soil; rock completely disaggregated. Mostly contain iron oxide(limonite)with asbolite.
BNC 6	14–17	C	Yellow brown colour, mainly consist of saprolite and asbolite with less iron oxide. Some partly weathered serpentine rock fragments are also present in this horizon.
BNC 7	17–20	C	Gray-yellow colour, slightly weathered rock with saprolitic texture.

INDONESIAN PROFILE

3.3.1 GEOLOGY AND GEOGRAPHY

Large area of ultrabasic rocks in part overlain by nickel bearing laterites are found in the Islands of Indonesia.

The samples studied in this work are from Pomalea district lie within Lat. $4^{o}10^{'}$ s and Long. $121^{o}37^{'}$ E.

Relief is generally rugged with some plateau-like areas. Climate is tropical, heavy rainfall with dry intervals play an important role in laterite formation.

The vegetation on lateritic soil is sparse compared to the dense growth on adjacent areas.

3.3.2 PHYSICAL CHARACTERISTICS

Location and Sample No	Depth (M)	Weathering Horizon	Description
BIP1	11-13	A	Reddish brown colour with saprolite, limonite, enstatite and some grains of quartz.
BIP2	13-14 16-17	B	Dark red saprolite; with iron oxides enriched with base elements.
BIP3	17-20	C	Gray-yellow saprolite; serpentine peridotite with quartz boxwork.

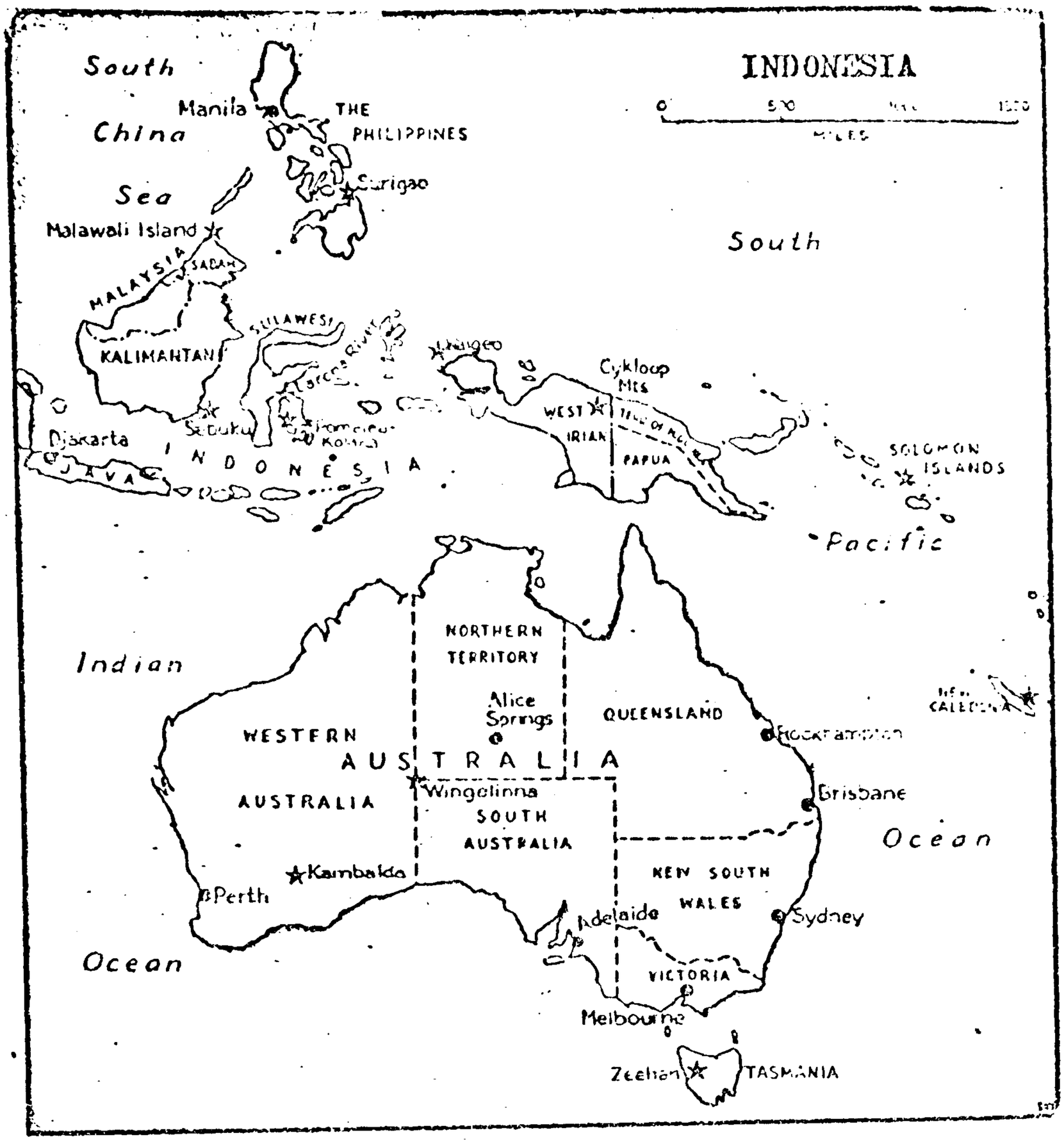

INDONESIA
South
China
Sea
Manila
THE PHILIPPINES
Surigao
Malawali Island
MALAYSIA
SABAH
SULAWESI
KALIMANTAN
Celebes Sea
Sandakan
Tarakan
Balikpapan
Ujung Pandang
Kaimana
Cyklop Mts
WEST IRIAN
PAPUA
Djakarta
JAVA
INDONESIA
SOLOMON ISLANDS
Pacific
Indian
Ocean
NORTHERN TERRITORY
Alice Springs
QUEENSLAND
WESTERN AUSTRALIA
AUSTRALIA
Wingellinna
SOUTH AUSTRALIA
Rockhampton
Brisbane
Kambalda
Perth
NEW SOUTH WALES
Adelaide
Sydney
VICTORIA
Melbourne
Zeehan
TASMANIA

Fig. 3.4

3.4.1 MINERALOGY

Mineralogical information obtained from preliminary micro--scopic examination of all chemically analyzed samples was inadequate due to the fact that samples were in very fine powder form. A further complication was the presence of iron oxide coating on most of the greins, which made identification difficult. Electron microscopic examination of the samples were preceded(grain were aggregate) by chemical treatment to remove the iron oxide coating.

The mineralogy of the Guatamala profile was found to be extremely uniform. Change in horizon corresponded to changes in the proportion of different minerals present rather than to abrupt appearance and disappearance of mineral phase.

The superficial reddish brown layer was found to consist mainly of a mixture of stongly magnetic iron oxides. Iron oxides, which are mainly responsible for the yellow, brown, and reddish colour of lateritic material, are mostly amorphous hydrates.

Goethite is microscopically recognisable as anisotropic flakes(Photo NO-), and the mineral is one of the main components formed during the alteration of serpentinite-peridotite.

Diffraction patterns corresponding to a mixture of a amorphous to poorly crystalline material (Limonite, Goethite and Hematite) were characteristics of the upper zone. Also present, but in very minor amount, were chlorite, residual grains of enstatite, and to a very small extent, olivine and quartz(the quartz is found to be of the chalcedonic type has no obvious crystal structure).

The proportion of iron oxides(including Goethite, Hematite and Limonite), which constitute the major part of the super-ficial zone, decreases with increasing depth.

Mineralogy of the B zone demonstrate a mixture of saprolite (highly weathered serpentine) with some iron oxides. Although Ni , Co, and Cr occur in all of the samples analysed, no specific mineral of these elements has been identified.

The mineralogy of the deepest or " least weathered zone" is mainly serpentized peridotite.

Mineralogy of New Caledonian profile is more or less same as of L profile. The superficial reddish brown layer mostly consist of poorly crystalline limonite with some chromite, enstatite and very rare grains of quartz.

The proportion of iron oxides(include limonite, goethite and hametite) which make the major part of the superficial zone decreases with increasing depth.

No specific mineral of Ni, Co and Cr has been identified.

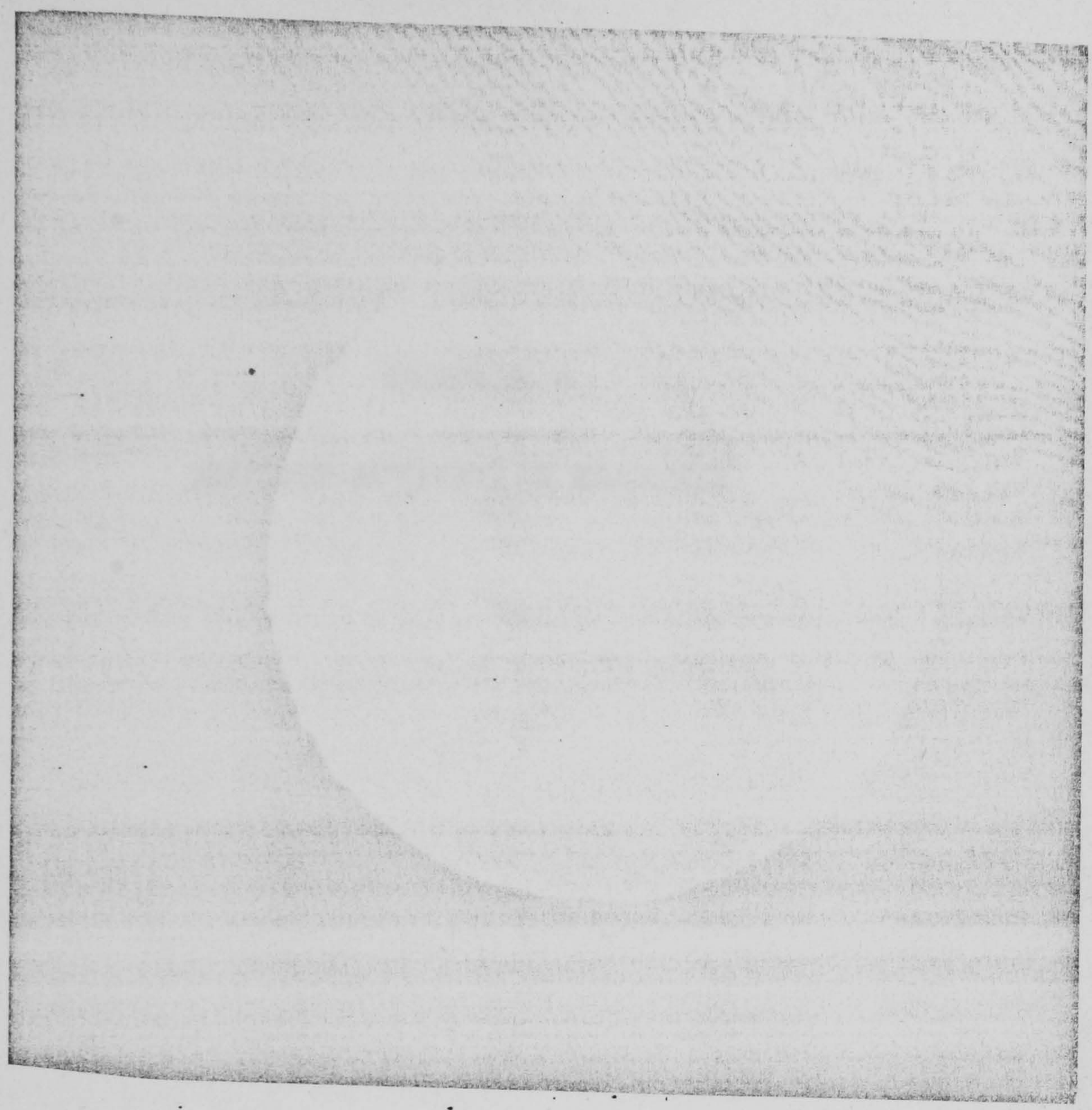


Photo No-L Electronmicrograph x 3.4 x 10^4 Aggregate of goethite needles.

CHAPTER 4

NEUTRON ACTIVATION ANALYSIS

CHAPTER 4

NEUTRON ACTIVATION ANALYSIS

A reactor neutron activation technique was developed and used to determine the submicrogram quantities of gold, platinum, iridium and palladium in the lateritic ores. The study involved liquid-liquid extraction for chemical separation of these elements. Subsequently nondestructive activation technique was used to determine the minor and major elements.

A brief account of basic activation theory and its application to the present work, is presented here.

4.1.1 BASIC THEORY

Neutron activation is an elemental analysis technique based on the principle that when stable isotopes are irradiated with neutrons they may give rise to radioactive products as a result of nuclear reaction. The unique characterstics, such as the half life and radiation spectrum, of the radionuclide. The amount of induced activity is proportional to the mass of isotope present in the original material.

The disintegration rate "A" induced at the end of irradiation time "t_i" and measured at a subsequent time "t_d" after the end of irradiation is given by the equation.

$$A = N\sigma\phi\,(1 - e^{-0.693x\, t_i/T_{\frac{1}{2}}})\, e^{-0.693x t_d/T_{\frac{1}{2}}} \quad \text{------(4.1)}$$

where ϕ is the neutron flux ($n\ cm^{-2}\ s^{-1}$)

σ is the activation cross-section of the target element

N is the number of atoms of the target element undergoing the nuclear reaction and is given by

$$N = \frac{N_a \times w \times f}{A}$$

where N_a is the Avogadro's constant(6.023×10^{23} atoms/mol)

w is the weight of the target element (g)

f is the fractional abundance of a particular isotope of the target element giving rise to the particular nuclear reaction.

As already mentioned, the activity induced is proportional to the quantity of element present in the sample. Therefore, from equation(4.1), when other terms and constants are known, N and ultimately w can be determined. This method is known as the absolute method. On the face of it procedure appears fairly straightforward and simple, but it has its serious drawbacks such as: (i) magnitude of σ are not sufficiently accurately known (ii) the flux ϕ may vary during the irradiation period (iii) a self-shielding correction must be worked out or be experimentally determined or else some procedure must be adopted to render self-shielding effects negligible (iv) the efficiency of the detector must be known.

In view of the difficulties presented by these factors, a comparative method is preferred to the absolute method. The comparative method involves activating a standard or comparator,

containing a known amount (W_s) of the element of interest, under the same conditions as the sample containing an unknown amount (W_x) of the element. The ratio of the activities induced in the sample and in the standard is proportional to the ratio of the amount of element present in the sample and the standard, i.e.,

$$\frac{W_x}{W_s} = \frac{A_x}{A_s} \qquad \text{---------- (4.2)}$$

where A_s and A_x are the induced activities in the standard and in the sample normalised for decay, etc. As A_s, A_x and W_s are measurable quantities, W_x can be assessed from equation (4.2).

4.2.1 Measurement Of Induced Activity

The type of activity measuring device depends upon the nature and energy of the radiation being detected. The determination of activity by beta-counting is, usually, made by different types of Geiger Muller counters. The G.M. tubes with an end-window are generally used when the sample is in the form of precipitate which is mounted on a planchette. In construction , the G.M. counter is among the simplest of all radiation detectors. It consists of an earthed metallic cylinder with an insulated central wire which made the anode. The tube is filled with a gas, which is ionized by the incoming radiation. It operates in the region where an applied high voltage **versus** count rate curve for a sample of fixed disintegration rate yields a plateau. The plateau of a good G.M. tube is generally 300 volts long, and increase in count rate with applied voltage is generally less than 3% per 100 volts.

One of the disadvantages of the G.M. counter is the relatively long recovery time before the counter can distinguish a successive event. One can minimize this error by counting the samples with count rate less than 10,000 Cts per minute. Generally an external fixed dead time, which is greater than the natural dead time of the tube, is imposed on the counter system by electronic means. Under these conditions the observed counting rate is related to the true counting rate by the relation:-

$$N_{true} = \frac{N_o}{1 - N_o \tau}$$

where τ is the electronically imposed dead time and N_o is the observed count rate.

Self-absorption of β-radiation

Another error introduced in beta counting is due to the absorption and scatter of particles in the sample itself. If there was no self absorption the count rate should increase linearly with the increasing thickness but after a certain thickness this linearity is not maintained and the curve flatens out for very thick samples. To eliminate this effect one may use very thin samples or else the correction factor should be determined experimentally by measuring the count rate of different amounts of precipitates maintaining in each case the same sample geometry. A curve of this type was constructed for ^{109}Pd by adding palladium precipitate to a counting tray with fixed circular area(see fig. 4.1). An end-window type G.M. counter in conjunction with a PANAX scaling system was used for this purpose. In the comparative

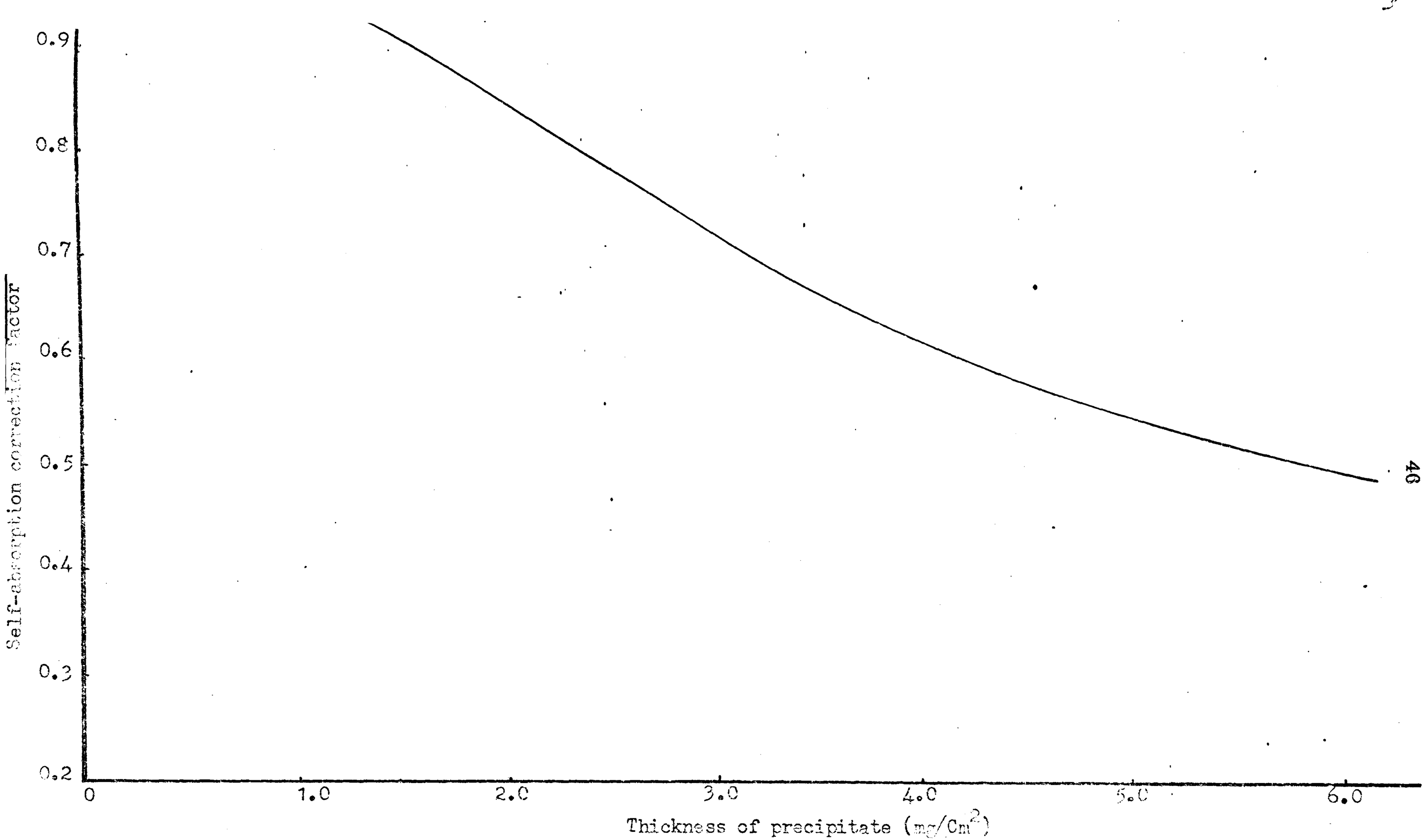


Fig.4.1 — β-self-absorption curve for palladium complex (Palladium-109)

method one can avoid the self-absorption correction by insuring that the final precipitate from the standard and the sample are of essentially the same thickness and geometry.

4.2.2 Gamma ray spectrometry

Gamma ray measurement by means of a scintillation detector is preferred to beta counting, because a number of corrections such as self-absorption and dead time can be avoided. Also with suitable equipment, such as a single channel or multichannel analyser one can determine the count rate for gamma rays of selected energy in the presence of radiation of different energy.

Scintillation detector

NaI(Tl) crystals are the most commonly used scintillation detectors. In these detectors the quantity of light emitted by a NaI(Tl) crystal is prportional to the amount of energy dissipated by the gamma ray in its interaction with the crystal. A photo-multiplier tube is used to convert the emitted light into an electrical pulse which remains proportional to the gamma ray energy transfered in the crystal. The pulses from PM tube are amplified and measured using a pulse height analyser.

Sodium iodide crystals are available in various sizes and geometries. A well-type crystal is particularly suitable when the sample is contained in a plastic or polyethylene counting tube. Cylindrical crystals are useful for any sample geometry. A precipitate can be conveniently counted by placing the planchette under

the cylindrical crystal. The distance between the source and detector can be varied to suit count rate.

Equipment used for activity measurements

A 2" well-type NaI detector coupled with PANAX single channel analyser, and a PAKARD 2" x 2" cylindrical detector coupled with 800 channel(PAKARD) analyser, was used in the present work.

Single channel analyser

From a PANAX single channel analyser, used for part of this work, a high voltage between 200 and 2000 volts can be applied to the PM tube. The amplifier gain suitable for the measurement can be adjusted for amplification factor of 8, 16, 32 and 64 so that gamma ray spectrum from a particular isotope falls within 100 mv on the pulse height dial. The window covers the portion of the spectrum between the lower and upper discriminators. This system allows one to determine gamma ray energies for qualitative analysis. Preset time, preset counts and scanning facilities are also provided in this system. An energy calibration curve for this analyser was constructed using standard radioactive sources(see fig. 4.2).

Multichannel analyser

The multichannel analyser used in this work was a Pakard 'Spectrazoom' with 800 channels, together with a visual display system and an integrator. The integrated counts in a peak can be determined by setting the channel numbers on the lower and upper

dails of the integrator. The analyser possesses a timing system which permits counting in either of two modes: in the live time, the timer operates only during the time when ADC(analog to digital converter) is accepting counts, with automatic compensation for analyser dead time; in the clock time mode, the timer indicates elapsed clock time during operation.

Semiconductor(Ge Li) Detector

Semiconductor detectors are presently the most exiting alternatives to scintillation detectors. Their most striking feature is the resolution , typically at least ten times higher than for NaI (Tl), and thus allowing a much more detailed study of complex spectra. A futher advantage is the fast pulse rise time(about one nano second, Adams 1970). The main short-coming is presently the small size of sensitive volume, resulting in a low intrinsic efficiency for gamma photons of intermediate and high energy. The principle of operation of such detectors is basically the collection of the electric changes released in a solid by the absorption of photons or charged particles.

Resolution of the detection system

The resolution of a spectrometer is usually expressed in percentage, using the ratio of the full width at half height (FWHM) in the energy units of the photopeak corresponding to energy E.

$$R = \frac{FWHM \times 100}{E} \quad \%$$

Normally the resolution for a detection system is quoted for the 662 Kev photopeak of Cesium-137 and it varies with the gamma ray energy.

For a detector the resolution for the ^{137}Cs photopeak should be 10%. The resolution of our 2" well-type NaI detector coupled with single channel analyser and that of 2" x 2" NaI cylindrical detector coupled with multichannel analyser were found to be 12% and 8%, respectively. Resolution of Ge Li detector used is better than 2.5 Kev (FWHM) for the 1.332 Mev peak of ^{60}Co.

4.2.3 Photopeak Evaluation

Covell's method was used for the evaluation of photopeak area. According to this method the number of counts in the channels are represented graphically as rectangular areas. In fig. 4.2 the channel with highest counts C_o is represented as n_o. The succeeding channels on the low energy side of the peak have counts C_{ℓ_1}, C_{ℓ_2} C_{ℓ_3} .....C_{ℓ_m}, and down the high energy side they are represented by C_{h_1}, C_{h_2} .....C_{h_m}. The summation of counts in all these channels shown graphically as total area under the peak, (say) equal to A. If this area A is divided by a line connecting the coordinate values of C and C , the area above the line is A_1 and area below this line is represented by A_2. From fig.

$$A = C_o + \sum_{i=1}^{n} C_{\ell_i} + \sum_{i=1}^{n} C_{h_i}$$

and

$$A_2 = A - A_1 = \frac{(2n-1)(C_{\ell_m} + C_{h_m})}{2} + (C_{\ell_m} + C_{h_m})$$

$$= (n + \frac{1}{2})(C_{\ell_m} + C_{h_m})$$

By substitution

$$A_1 = C_o + \sum_{i=1}^{n} C_{\ell_m} + \sum_{i=1}^{n} C_{h_i} - (n + \frac{1}{2})(C_{\ell_m} + C_{h_m})$$

The standard deviation of this value is given by

$$\sigma(A_1) = \left[A_1 + (n - \frac{1}{2})(n + \frac{1}{2})(C_{\ell_m} + C_{h_m})\right]^{1/2}$$

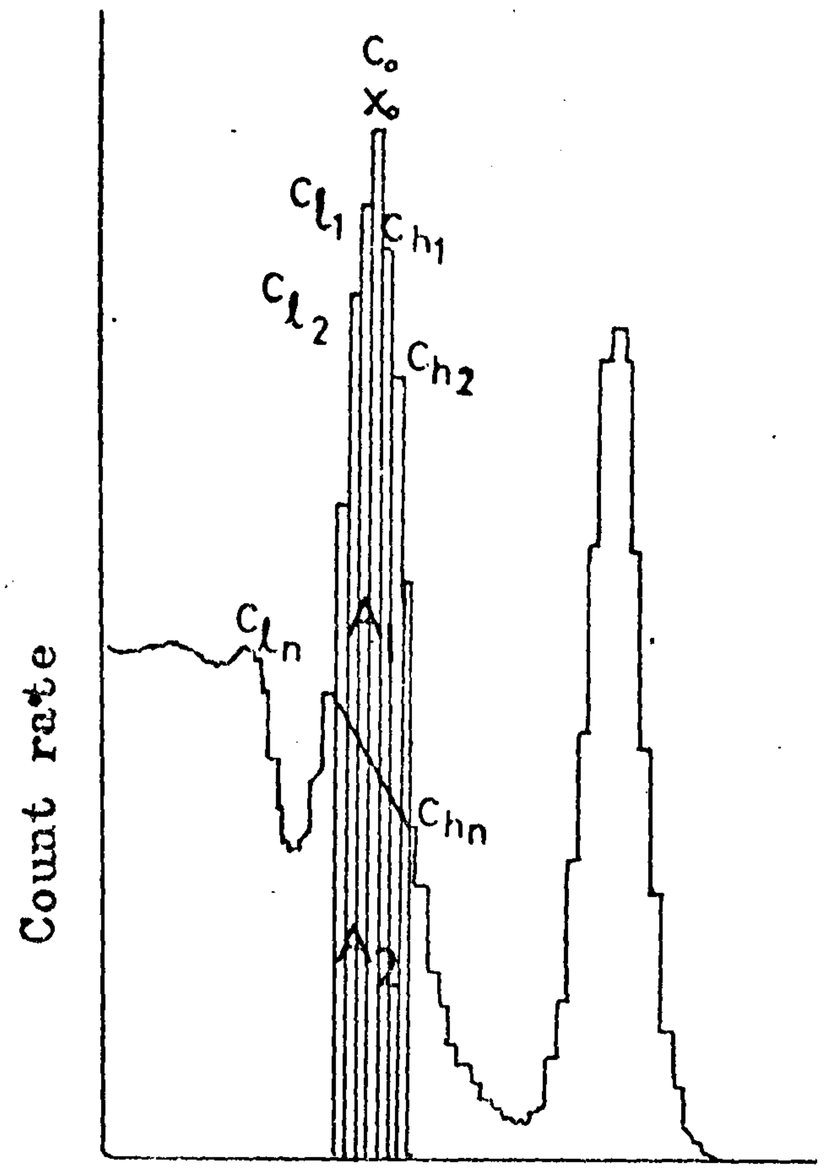


Fig.4.2 — Evaluation of a photopeak by Covell's method.

ERRORS ASSOCIATED WITH PRODUCTION AND MEASUREMENT OF ACTIVITY

A number of factors were considered to minimize the errors in activation analysis as described below.

4.3.1 Neutron self-shielding

When samples of finite thickness are irradiated the neutron flux becomes progressively smaller towards the centre because of the absorption of neutrons in the outer layers. If the selfshielding is negligible or occurs to a different degree in the standard as compared to the sample, then different specific activities will result and the error in the analysis will be dependent upon the difference in two selfshielding effects.

In this work the composition of the standards(for nondestruct-ive analysis) was made approximately the same as that of samples; therefore, any flux perturbation within the sample or standard should essentially apply equally to both. Hence, it was concluded that the selfshielding effect would not introduce any significant error in the analyses.

4.3.2 Sample self-absorption

The self-absorption of gamma rays in the sample material counted should not present any serious error, because this effect would be of the same degree in both the standard and the sample, for their composition was virtually identical.

4.3.3 Timing errors

It is not possible to count the sample and the standard with the same detector simultaneously, so a decay correction is necessary. However, as samples and comparators were counted in succession, such error are very small.

4.3.4 Geometrical considerations

It is obviously essential that samples and comparators should be counted at the same constant geometry. This was achieved by placing the samples and standards in a fixed position on a perspex plate holder.

ERRORS ASSOCIATED WITH COUNTING DATA

4.4.1 Background correction

For a fixed setting on an analyser the back-ground count rate was recorded before and after the sample counting. The means of these counts were subtracted from the sample count rate. In case of multichannel analyser, the automatic background subtraction facility was used. A typical background spectrum obtained by using a 2" x 2" NaI detector with the multichannel analyser is shown in fig. 4.3.

4.4.2 Photopeak shift

Because of the inherent nature of electronic counting system, the position of a photopeak in a gamma ray spectrum of of a radionuclide may drift slightly.

This phenomenon is observed particularly at higher count rates. Consequently, the energy corresponding to a particular channel number will vary. In such a situation if two samples have widely different count rates the integration of counts between two fixed channels will not correspond to a fixed energy range basis. To minimize such potential error the integration for a given spectrum was performed over a constant number of channels, the integration range starting from a point located at a fixed number of channels from that with the maximum count rate. Also, the integration range was chosen at a width to include the entire photopeak of interest.

4.4.3 Dead time correction

The measurement of activity was performed using the live-time mode of the pulse-height analyser; this permits automatic correction of the count rate for dead time losses.

4.4.4 Counting statistics

Due to the random nature of the radioactive decay process, the relative statistical standard error, σ , for the accumulated counts, N, is given by the equation

$$\sigma = \frac{\sqrt{N}}{N}$$

CHAPTER 5

RADIOCHEMICAL ACTIVATION ANALYSIS

CHAPTER 5

RADIOCHEMICAL ACTIVATION ANALYSIS

Nondestructive activation analysis is perhaps the ideal method if interference from radionuclides induced in the sample matrix can be avoided. However, in the analysis of complex ore samples the activities produced from major constituents is likely to preclude the direct measurement of activities arising from elements present in the sample in submicrogram quantities. Therefore, a chemical separation becomes necessary. In such a case, the sample is dissolved after being irradiated and then various constituents are separated by precipitation, ion exchange, solvent extraction or by some other appropriate chemical method. The isolation of the radionuclides of the desired elements, is commonly made using isotopic carriers. The carrier method involves the addition of a known amount of inactive stable element to the solution of irradiated material to serve as a carrier of the radionuclide throughout the subsequent separation steps. The use of carriers permits ordinary analytical manipulations on a milligram scale. Moreover, after the addition of the carrier, the chemical separation need not be quantitative. The weight of the final isolated carrier can be obtained by gravimetrically. or by colorimetry, titrimetry etc.

The chemical yield of the separation is determined by comparing the weight of the element obtained after the chemical separation to the weight of the carrier element added. Clearly separation methods giving 100 % yield are preferable. However, in most cases this cannot

Table 5.1 Nuclear data for precious metals.

Target nuclide	Natural abundance (%)	Thermal neutron activation cross-section (barns)	Product nuclide	Half life of product	Major radiations emitted (Mev)
^{197}Au	100	98.8	^{198}Au	84.8 h	β^- 0.962 max γ 0.412 (95%)
^{191}Ir	38.5	750	^{192}Ir	74.2 d	β^- 0.67 max γ 0.296 (29%), 0.308 (30%), 0.317 (81%), 0.468 (49%) (Others)
^{193}Ir	61.5	110	^{194}Ir	18.0 h	β^- 2.24 max γ 0.328 (10%) (Others)
^{107}Ag	51.35	35	^{108}Ag	2.4 m	β^- 1.64 max β^+ 0.90 max γ 0.632 (1.7%)
^{109}Ag	48.65	89	^{110}Ag	24.4 s	β^- 2.87 max γ 0.658 (4.5%)
^{103}Rh	100	144	^{104}Rh	43.0 s	β^- 2.44 max γ 0.56 (2%)
		11	$^{104}Rh^m$	4.43 m	β^- 0.50 max γ 0.051 (47%) (Others)
^{190}Pt	0.0127	150	^{191}Pt	3.0 d	γ Several with low percentage
^{192}Pt	0.78	14	^{193}Pt	500 y	
		2	$^{193}Pt^m$	3.5 d	γ 0.099 (11%) (Others)
^{196}Pt	25.2	0.9	^{197}Pt	20.0 h	β^- 0.67 max γ 0.077 (20%)
		0.05	$^{197}Pt^m$	85.0 m	β^- 0.737 max γ 0.346 (13%) (Others)
^{198}Pt	7.19	4.0	^{199}Pt	30 m	β^- 1.69 max γ Several
		0.03	$^{199}Pt^m$	14.1 s	γ 0.393 (90%)

continue on next page

^{102}Pd	0.96	4.8	^{103}Pd	17.5 d	Very weak γ-rays of 0.297, 0.362 0.498 Mev.
^{106}Pd	27.3	0.29	$^{107}Pd^{m}$	21.3 s	Pd X-rays, *o.2!*
^{108}Pd	26.7	12.0	^{109}Pd	13.5 h	β^- 1.028 max γ Ag X-rays, 0.088(5% with $^{109}Ag^{m}$)
		0.2	$^{109}Pd^{m}$	4.7 m	γ Pd X-rays 0.138(58%)
^{110}Pd	11.8	0.2	^{111}Pd	22 m	β^- 2.2 max γ Several weak gamma rays
		0.04	$^{111}Pd^{m}$	5.5 h	β^- 2.0 max γ Weak gamma-rays

be achieved, because of the numerous separation steps and the necessity of speed where short lived radionuclides are concerned.

The effect of chemical yield incorporated in equation(4.2) gives

$$\frac{W_x}{W_s} = \frac{A_x \cdot Y_s}{A_s \cdot Y_x} \qquad \text{———————(5.1)}$$

where Y_s and Y_x are the chemical yields of the element from the comparator and the sample, respectively.

5.1.1 Neutron activation analysis of trace quantities of gold, platinum, iridium and palladium.

The purpose of this part of the project was to develop an accurate and rapid radioactivation method to determine trace quantities of gold, platinum,iridium and palladium in geological samples. The samples used for this purpose were Nickeliferous Laterite ores.

The feasibility of neutron activation analysis for these elements in a given sample can be ascertained from a consideration of their nuclear properties. A list of the stable nuclides of the elements of interest and of the radionuclides produced through (n,γ) reaction is given in table 5.1. From the nuclear data given in the table it can be deduced that the radionuclides most appropriate for the analyses are ^{198}Au, ^{197}Pt, ^{194}Ir, ^{192}Ir, and ^{109}Pd. The use of short lived radioisotopes can be ruled out due to the time required for radiochemical separations and from the fact that the radiochemistry was performed at a considerable distance from the nuclear reactor.

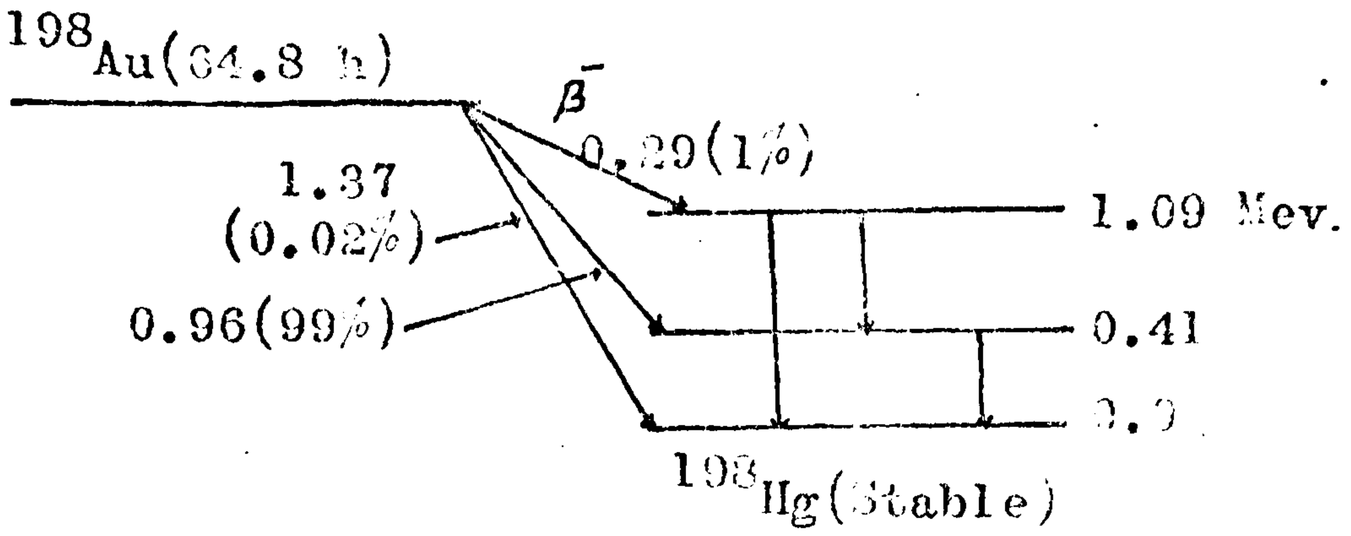
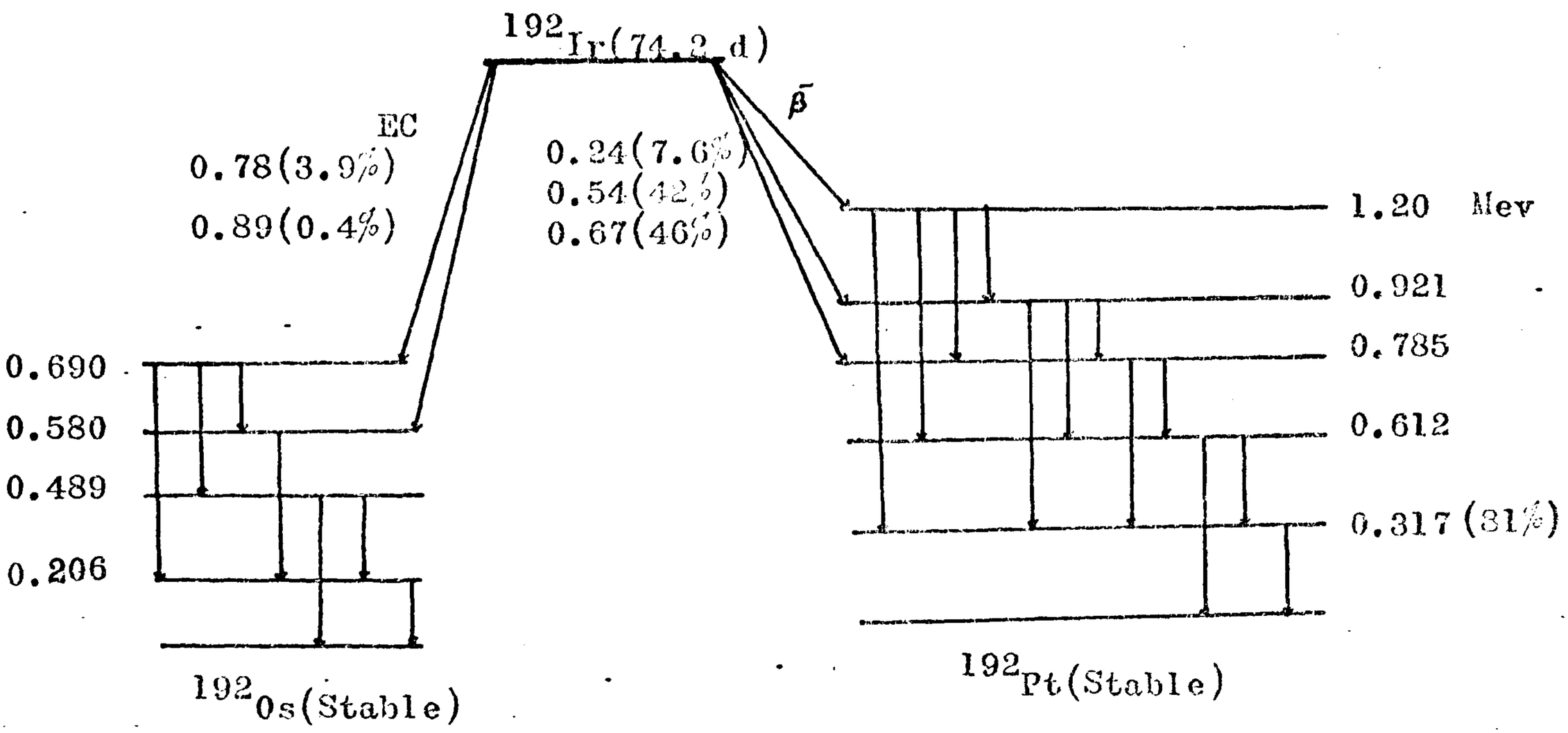


Fig. 5.1 The decay scheme of ^{198}Au



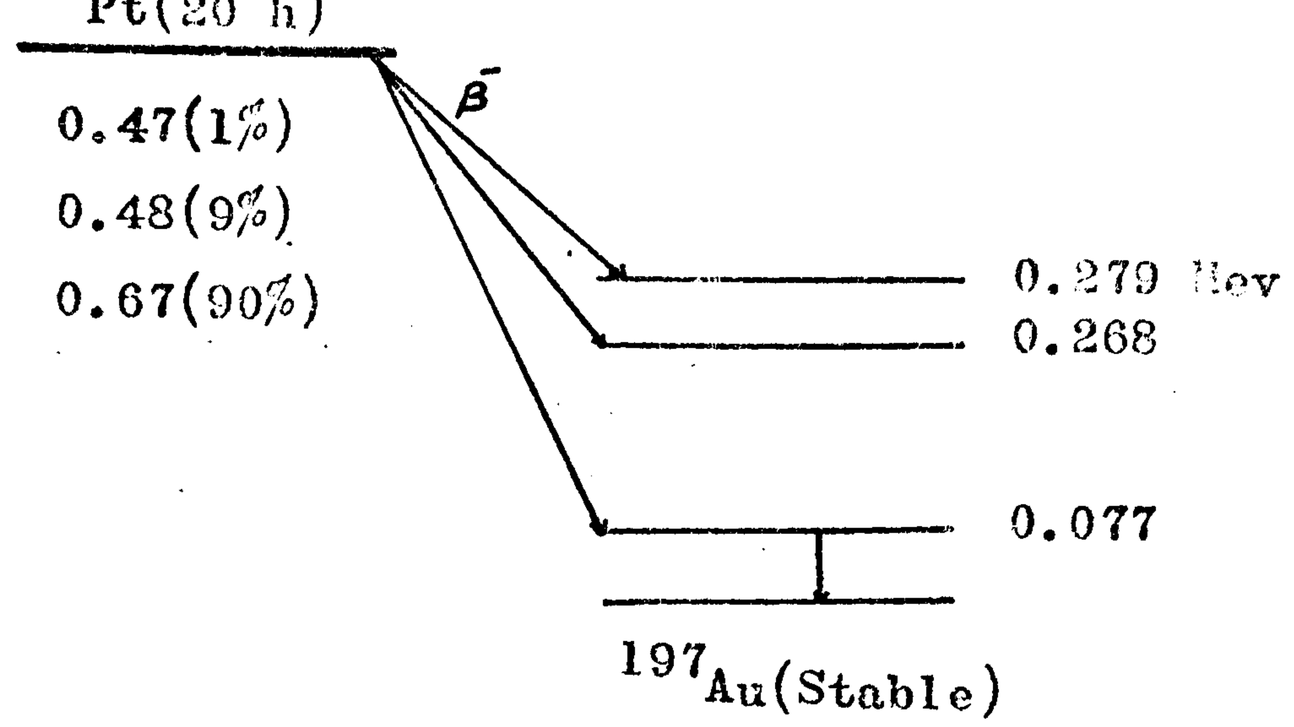


Fig. 5.3 The decay scheme of ^{197}Pt

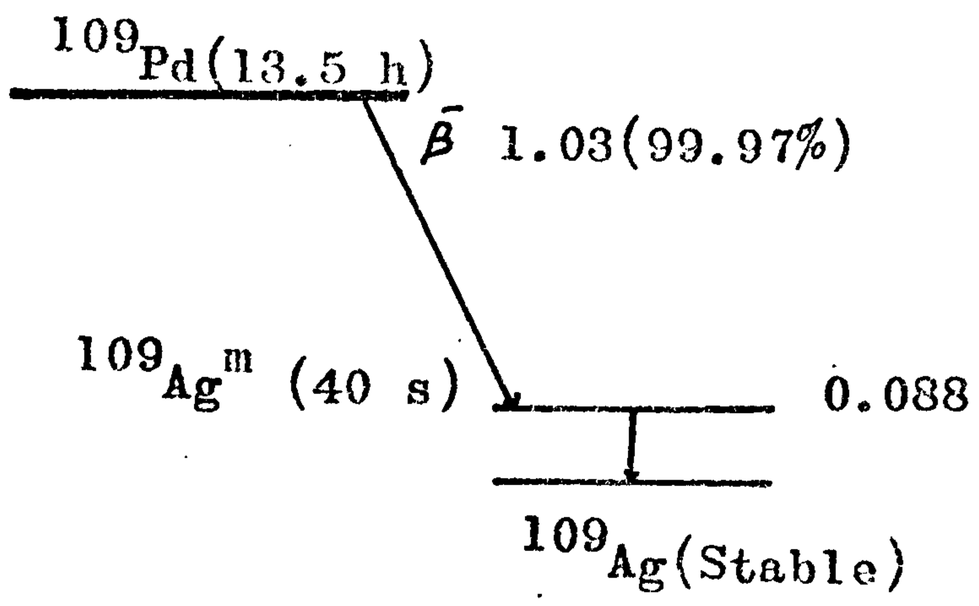


Fig. 5.4 The decay scheme of ^{109}Pd

5.2.1 Measurement of radioactivity

The decay scheme of Platinum-197 is shown in figure 5.3. This isotope decays by β^- emission to stable gold-197. The maximum β-ray energy is 670 Kev, so a G.M. counter can be used conveniently provided that radiochemical purity is achieved. The gamma ray spectrum of ^{197}Pt is largely determined by low energy radiation, namely gamma rays of 77 Kev and 191 Kev and Au X-rays. In the present work gamma spectrometry could not be used because of the low activity from samples and the high background in this energy region. Thus an attempt was made to achieve high purity of platinum and use a G.M. counter.

Palladium-109, with a half life of 13.5 h, decay by β^- emission (see fig. 5.4) to a metastable state $^{109}Ag^m$. The latter de-excites by IT with a half life of 40 seconds to stable ^{109}Ag with the emission of 88 Kev gamma rays. Since the half life of the parent is much greater than that of the daughter nuclide, secular equilibrium is established in the system, the effective half life being that of the parent, 13.5 h ^{109}Pd. For the measurement of activity β^--counting was considered to be most suitable because the activity of Palladium-109 induced in the samples was too low for the measurement of 88 Kev gamma rays (silver-109m) in the presence of high background in this low energy region.

Natural gold is monoisotopic and by (n,γ) reaction it give rise to 64.8 h ^{198}Au. The decay scheme of gold-198 is quite simple (see fig. 5.1) and it can be seen that the gamma spectrum shows essentially only one photopeak, corresponding to a γ-energy of 412 Kev.

The gamma spectra produced on activation of the sample (L) shows the 412 Kev photopeak distinctively. These spectra were obtained with the NaI ($2''$) well type detector coupled to a PANAX single channel analyser and a $2'' \times 2''$ detector coupled to a multichannel analyser(fig. 5.5 ___), respectively. Interference with measurement of the intensity of the peak can arise from other activities induced in the sample matrix. From the nuclear data for Pt, it can be inferred that activities produced from this element are very minute under the irradiation conditions employed; none of the Pt radioistopes emit gamma rays of energy close to 412 Kev except ^{199}Pt and $^{199}Pt^{m}$ which have half lives of 30 minutes and 14.1 seconds, respectively. The activity, due to these isotopes, can be allowed to decay away before counting the Gold-198 activity. In any case the activities induced are negligible, because of the small cross-section, low isotopic abundance and low gamma ray abundances. Interference from the reaction sequence $^{196}Pt(n, \gamma)$ $^{197}Pt \xrightarrow{\beta^-}$ $^{197}Au(n, \gamma)$ ^{198}Au is negligible as the amount of Platinum-197 produced from Platinum-196 is very small because the cross-section(0.9 b) for this reaction is small.

From a consideration of the data in table (5.1) it appears that ^{192}Ir and ^{194}Ir should be the suitable radionuclides for the determination of iridium. It would have been convenient if the shorter lived ^{194}Ir isotope could have been used for analysis, but its gamma abundance is low. A waiting period of a few days is required to allow the ^{194}Ir to decay away before a measurement of ^{192}Ir activity. Iridium-192 has its photopeaks at 317 and 468 Kev.

5.3.1 Interfering nuclear reactions

For the activation analysis of trace elements, a high sensitivity can be attained by using large neutron fluxes and long irradiation times. However, the irradiation in a high neutron flux presents inherent problems. Under high neutron flux conditions some second order nuclear reactions can cause significant interference in the analysis of trace elements because they can yield the measured nuclide from elements other than that of interest. Second order interference could arise through processes of the type

$$ {}^{A}_{Z}X(n,\gamma)\ {}^{A+1}_{Z}X \xrightarrow{\beta^-} {}^{A+1}_{Z+1}X\ (n,\gamma)\ {}^{A+2}_{Z+1}X $$

$$ \xrightarrow{\beta^+,EC} {}^{A+1}_{Z-1}X\ (n,\gamma)\ {}^{A+2}_{Z-1}X $$

Thus, if an element ${}_{Z+1}X$ or ${}_{Z-1}X$ is to be determined in a sample matrix containing a large amount of ${}_{Z}X$, the above kind of reaction may add significantly to the amount of radionuclide actually formed from the element being determined. Ricci and Dyer (1964) calculated the interference for 23 cases as a function of irradiation time. A compilation of second order interference is also given by Op de Beek(1970).

Another problem that may arise with high neutron flux irradiations is the possible occurrence of threshold reactions induced by fast neutrons. This is particularly important where irradiation is done in a reactor position of low cadmium ratio.

The threshold reactions can produce $^{A}_{Z-1}X$ and $^{A}_{Z-2}X$ from a $^{A}_{Z}X$ parent by (n,p) and (n,α) reactions which might cause serious interference in the activation analysis. As such reactions usually have very low cross-section, they may frequently be neglected when the flux has a high thermal: fast ratio.

It appears from the composition of the samples that none of the major elements in these rocks, is adjacent to the elements of interest in the periodic table; thus second order interferences are not of significance in this work. Calculations show that threshold reactions are also unimportant particularly as the samples were irradiated in a well thermalized region of the reactor.

5.4.1 Detection sensitivities

The minimum detectable amount D_ℓ of an element can be calculated by the relation:

$$D_\ell = \frac{A_\ell}{\Sigma_{gm} S D \phi \varepsilon f} \qquad (5.2)$$

where A_ℓ is the minimum detectable amount of radioactivity which is related to the background of counting equipment, the confidence level required and the counting time, Σ_{gm} is the macroscopic activation cross-section per gram of the element, S is the saturation factor given by $1- \exp\left(-\frac{0.693 \times ti}{T_{1/2}}\right)$, D is the decay factor, ε is the over-all counting efficiency of the detector, f is the

absolute abundance of the radiation measured and ϕ is the thermal neutron flux.

Now if a_1 is the total counting rate(source plus background) and a_2 is the background counting rate, the net count rate of the source is given by :

$$C = a_1 - a_2$$

If a_1 has been measured during time t_1 and a_2 during t_2 , the statistical error in the evaluation of net activity is given by

$$\sigma = k \sqrt{\frac{a_1}{t_1} + \frac{a_2}{t_2}} \qquad \text{.....(5.3)}$$

where k is the confidence level required.

The activity from the radioactive source will be detected if the net counting rate is higher than the statistical error given by the equation(7.3) which is then equal to the minimum detectable activity, i.e.,

$$A_l = k \sqrt{\frac{a_1}{t_1} + \frac{a_2}{t_2}} \qquad \text{.....(5.4)}$$

At the limit of detection $a_1 \approx a_2$ and t_1 can be taken equal to t_2 or $t_1 = t_2 = t$.

therefore, relation(7.4) becomes

$$A_l = k \sqrt{\frac{2\,a_2}{t}}$$

and equation(7.2) can be written in the form

$$D_l = \frac{k \sqrt{2a_2/t}}{\Sigma_{gm} S D \phi \epsilon f} \qquad \text{.....(5.5)}$$

which gives the minimum amount of element that can be detected

under a certain set of conditions.

The detection sensitivities of the elements of interest were calculated using the nuclear data listed in table 5.1. Irradiation period of 14 hours at a thermal flux of 2.5×10^{12} n s^{-1} cm^{-2} was assumed and a decay period of 20 hours before counting. The counting efficiencies of 10 % for a gamma counter and 10 % for a beta detector was assumed. The counting time was taken arbitrarily equal to 10 minutes and constant k was taken equal to 3 (99.7 % confidence level). The background of gamma spectrometer in our laboratory is shown in fig. 5.5. The background counting rate in the energy interval for the 412 Kev photopeak of Gold-198 was about 40 cpm and for the 317 Kev photopeak of iridium-192 was ~ 50 cpm. For the beta counter, the background was taken equal to 20 counts per minute. The results of the calculations are shown in table 5.2. It must be emphasized that the minimum detectable amount of elements shown are theoretically derived values and are merely indicative of the relative detection limits of the elements involved. The actual experimental sensitivities depend mainly on the chemical separation and activity measurements associated with the analysis.

Table 5.2

Detection sensitivies of trace elements. (These results are calculated assuming 100 % yield and no neutron self-shielding and no sample self-absorption)

Stable isotope	Product nuclide	Half life	Radiation detected and its energy (kev)	Saturation factor(14 hrs irradiation)	Decay factor (20 hrs decay)	Sensitivity of the element. (microgram)
^{197}Au(100%)	^{198}Au	64.8 h	γ 412(95%)	0.1391	0.8074	1.8×10^{-5}
^{191}Ir (38.5%)	^{192}Ir	74.2 d	γ317(81%)	0.0055	0.9922	4.2×10^{-4}
^{193}Ir (61.5%)	^{194}Ir	18.0 h	γ328(10%)	0.4167	0.4630	2.5×10^{-4}
^{196}Pt (25.2%)	^{197}Pt	20.0 h	β^-	0.3844	0.5000	3.0×10^{-3}
^{108}Pd (26.7%)	^{109}Pd	13.5 h	β^-	0.5126	0.3063	4.4×10^{-4}

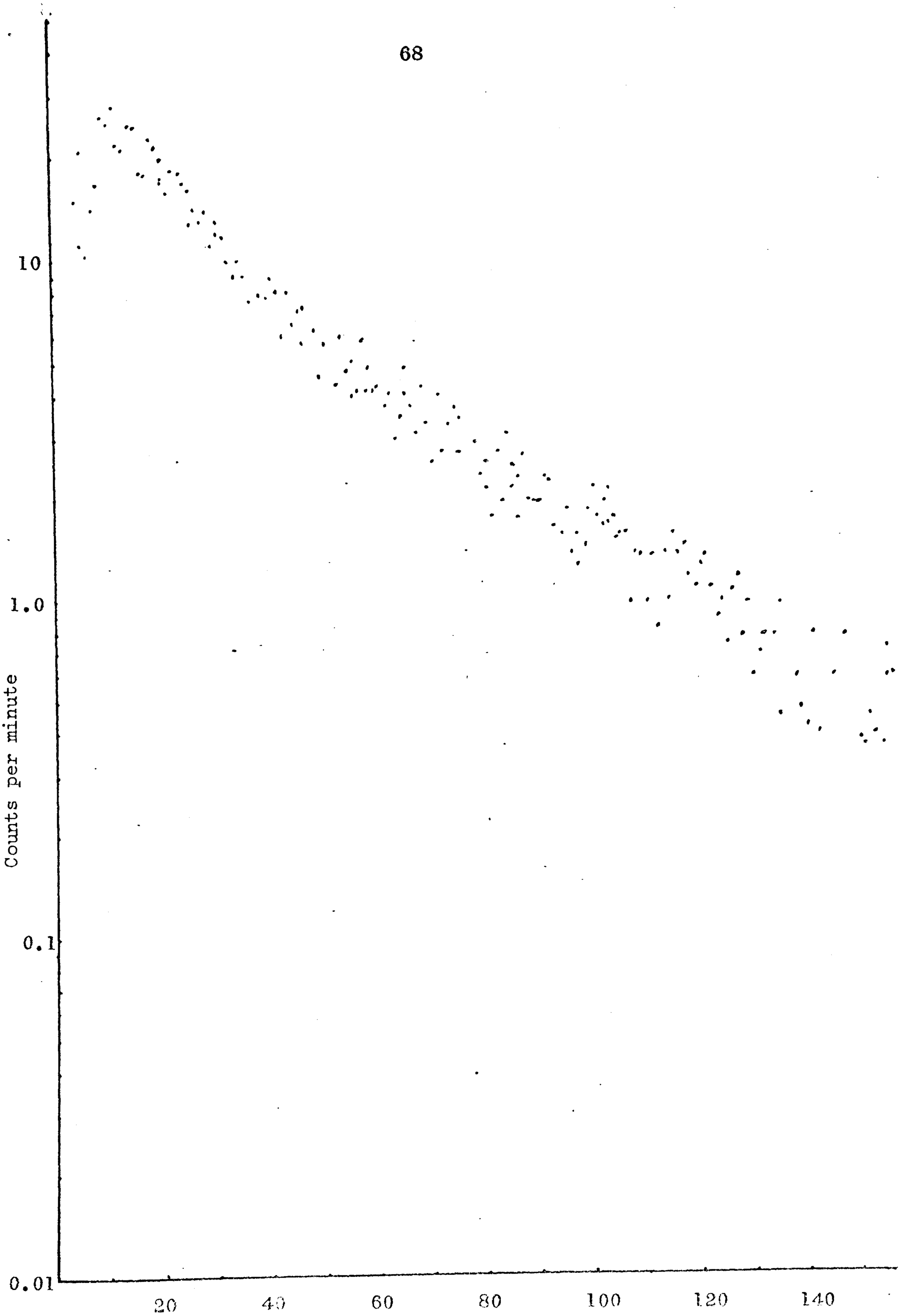


Fig. 5.5 — Background spectra for 2″ x 2″ NaI detector with 200 channel analyser. EHT = 450 x 2 v, Gain = 28.25

EXPERIMENTAL

5.5.1 Preparation of samples and standards for irradiation

The samples analyzed in this work were in the form of fine powder. About 0.4g - samples of material were accurately weighed into silica irradiation tubes of 4mm internal diameter and fitted with pure aluminium caps.

A comparator was prepared by weighing out 0.1cm^3- aliquots of freshly diluted standard solutions of the individual noble metals into a silica ampoule of 4mm-internal diameter. The ampoule was sealed with a burner, the lower part being kept cool.

The samples and comparators were packed togather with silica wool in a standard scew-top aluminium isotope cans: four samples of lateritic -ore and two composite standards were the usual content.

5.6.1 Irradiation

The samples analysed in this investigation were irradiated in the research reactor 'HERALD' at the Atomic Weapons Research Establishment, Aldermaston, and they were usually with a flux of 2.5×10^{12} thermal neutrons cm^{-2} s^{-1}. After irradiation for ten hours, the samples were allowed to decay overnight before delivery to our laboratory for radiochemical processing.

Radiation level at 1 meter from the surface of the irradiated can was usually 2.5 to 3.5 mR.

5.7.1 ANALYTICAL PROCEDURE

Outline

The radiochemical procedure is summarized in the flow diagram shown in fig. 5.6. It involved heating with Na_2O_2 to attack the rock samples. Isotopic carriers and holdback carriers were employed. Subsequent separations giving radiochemical purity of the elements of interest were based primarily on liquid-liquid extractions and precipitations.

REAGENTS

Au carrier : 10 mg/cm^3 in conc. HCl

Pt carrier : 10 mg/cm^3 in conc. HCl

Ir carrier : 10 mg/cm^3 in conc. HCl

Pd carrier : 10 mg/cm^3 in conc. HCl

Ag carrier : 20 mg/cm^3 as $AgNO_3$

HCl : conc.

HCl : 6M

HCl : 4M

HCl : 2.9M

HCl : 1.4M

HCl : 0.5M

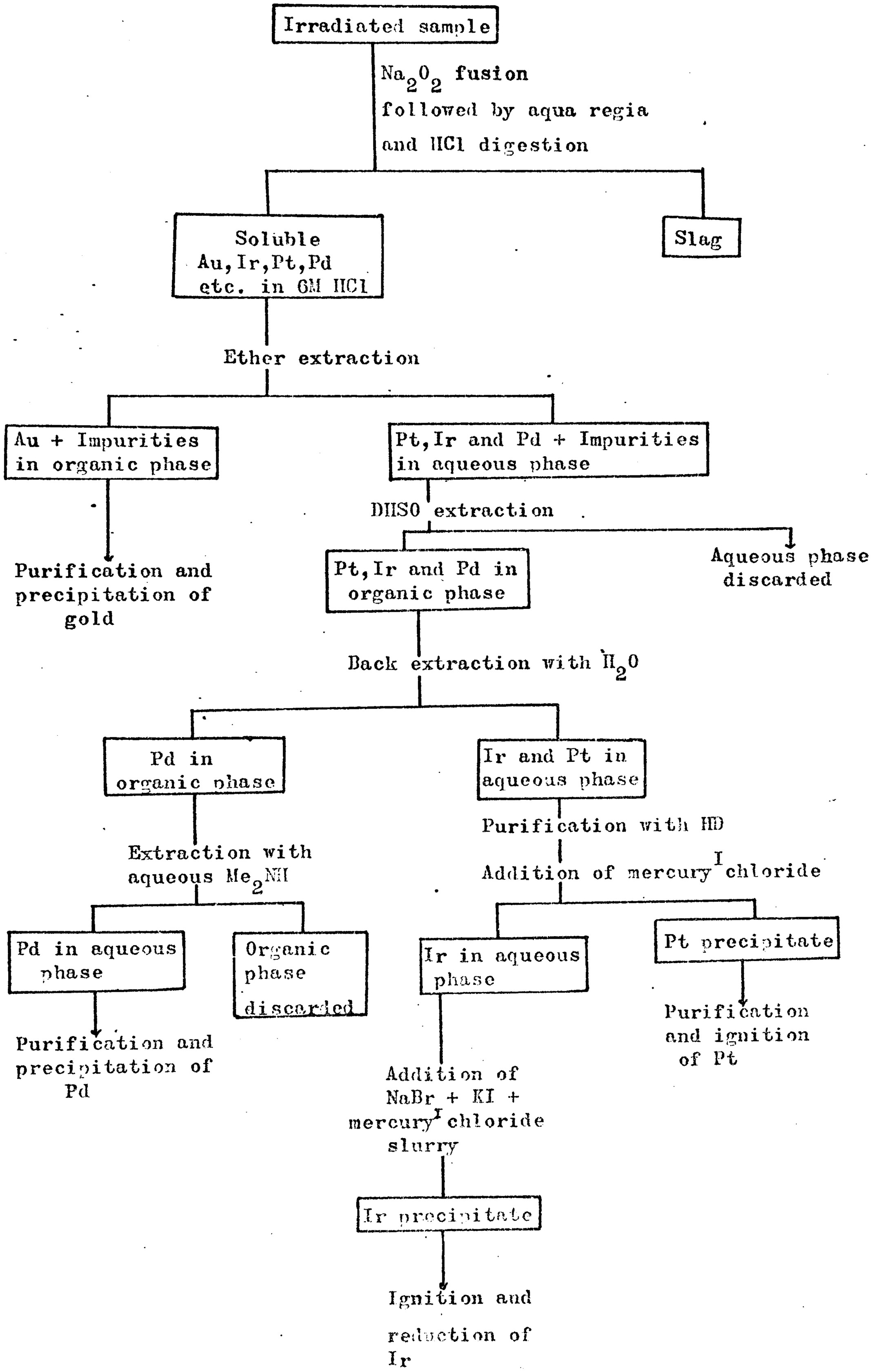
HNO_3 : conc.

Oxalic acid : 5%

H D : 0.5M in heptane

Diethylether : saturated with 6M HCl

Fig. 5.6


Irradiated sample
Na_2O_2 fusion
followed by aqua regia
and HCl digestion
Soluble
Au, Ir, Pt, Pd
etc. in 6M HCl
Slag
Ether extraction
Au + Impurities
in organic phase
Pt, Ir and Pd + Impurities
in aqueous phase
Purification and
precipitation of
gold
DIISO extraction
Pt, Ir and Pd in
organic phase
Aqueous phase
discarded
Back extraction with H_2O
Pd in
organic phase
Ir and Pt in
aqueous phase
Extraction with
aqueous Me_2NH
Purification with HD
Addition of mercury I chloride
Pd in aqueous
phase
Organic
phase
discarded
Ir in aqueous
phase
Pt precipitate
Purification and
precipitation of
Pd
Purification
and ignition
of Pt
Addition of
NaBr + KI +
mercury I chloride
slurry
Ir precipitate
Ignition and
reduction of
Ir

Dimethylamine(Me_2NH) : 10 %

Dimethylglyoxime : 1 % in ethanol

Na_2O_2 : powder

Mercurous nitrate : solid

NaBr : solid

KI : solid

Br_2 in conc. HCl

Trichloroethane (TCE)

Di-n-heptyl sulphoxide(DHSO) : 1M in TCE (the sulphoxide was synthesised by the method of Morris and Lewis[68]).

Procedures for preparation and standardization of carrier solutions

5.8.1 Gold

Dissolve one gram of pure gold in aqua regia and evaporate almost to dryness. Add three 5 cm^3 portions of conc. HCl and evaporate each time to low bulk. Transfer to a 100 cm^3 volumetric flask and fill up to the mark with conc. HCl to make a solution with a concentration of ca. 10 mg of gold per cm^3.

For standardization pipette 1 cm^3 of the carrier solution into a 100 cm^3 beaker and make it to 50 cm^3 with .6M HCl. Extract the gold three times with 10 cm^3 portions of diethylether(previously saturated with 6M HCl). Evaporate the organic phase with 15 cm^3 of 5 % oxalic acid solution by heating on a steam bath at 70 ---80 °C for 10 minutes. Filter the gold precipitate onto an ashless filter paper. Wash the precipitate with 4M HCl, then with H_2O and

then with ethanol. Ignite it in a weighed silica crucible at 850°C.

5.8.2 Platinum(IV)

To prepare platinum carrier solution, dissolve 1 g of pure platinum metal in aqua regia, remove nitrate ions by repeated evaporation to dryness with conc. HCl. Take up the final residue in conc. HCl and make it to 100 cm^3 in a volumetric flask to yield a solution containing 10 mg of platinum per cm^3.

Pipette 1 cm^3 of carrier solution into a 250 cm^3 beaker, reduce the solution to low bulk and take up in 2.9M HCl to a total of ca. 50 cm^3. Add freshly prepared mercury^{I}chloride slurry[67] and boil the solution for 10 minutes. Collect the precipitate on an ashless filter paper and wash with 2 % HCl. Place the precipitate in a weighed silica crucible and ignite in a muffle furnace for 1.5 hours. Cool the crucible to room temperature in a desiccator and weigh.

5.8.3 Iridium(IV)

Dissolve 2.296 g of $(NH_4)_2$ Ir Cl_6 in conc. HCl and evaporate to low bulk. Take up in conc. HCl and transfer to a 100 cm^3 volumetric flask. Make the solution upto the 100 cm^3 mark with conc. HCl to give a solution containing 10 mg of iridium per cm^3.

Pipette 1 cm^3 of carrier solution into a 250 cm^3 beaker. Reduce the solution to low bulk and make it to 100 cm^3 with 2.9M HCl. Add 10 g of NaBr and 5 g of KI. Boil the solution and add an excess of mercury^{I}chloride slurry. Boil until the colour changes from brown to black. Allow the precipitate to settle, filter it onto an ashless filter paper. Ignite at 800 °C and reduce in a

hydrogen atmosphere at 800°C in a weighed silica crucible. Cool the crucible in a desiccator and weigh.

5.8.4 Palladium(II)

The procedure for preparing the palladium carrier solution is exactly similar to that for gold and platinum.

Standardization can be accomplished by precipitation of Pd with dimethylglyoxime. Dilute 1 cm^3 of palladium carrier solution to 100 cm^3 in a 250 cm^3 beaker and cool in a ice-bath. Add 1% dimethylglyoxime solution(in ethanol) dropwise. The suspension of palladium dimethylglyxomate, $Pd(C_4H_7N_2O_2)_2$, is obtained. Allow it to stand for 20 minutes and then filter it in a weighed sintered glass crucible. Wash the precipitate with water and then with 95 % alcohol. Dry the precipitate to a constant weight at 110 °C in an oven, cool to room temperature in a desiccator and weigh.

5.9.1 Sequence of radio-chemical analysis

As the 13.5 hours ^{109}Pd and 20 hours ^{197}Pt have much shorter half lives than the Gold-198 and Iridium-192, the separation of palladium and platinum from the irradiated samples was performed first. The next separation was that of gold. The isolation of ^{192}Ir was left to the last because of the long half life.

RADIOCHEMICAL PROCEDURE

5.10.1 Sample dissolution and carrier addition

Remove the aluminium cap from the irradiation tube and transfer the activated rock sample into a nickel crucible. Add 2.5 g of Na_2O_2 powder and mix thoroughly. Cover the mixture with a thin layer of sodium peroxide powder. Place the lid on the crucible and heat at 480 ---500 ^{o}C in a muffle furnace for ~12 minutes. Remove the crucible from the furnace and cool it by immersing the outside walls in a beaker of water. Detach the cooled sintered cake from the crucible and transfer it to a 250 cm^3 beaker containing 1 cm^3 Pd, 2 cm^3 each of Au, Pt, Ir and 1 cm^3 of silver carrier solutions; cover the beaker immediately with a watch glass. Add ca. 5 cm^3 of conc. HCl to the crucible and loosen any adhering material by scraping with a glass rod. Heat it for a few minutes and transfer the acidic solution to the beaker containing the sintered cake and carrier solutions. Rinse the crucible with a small amount of water and add this to the contents in the beaker. Evaporate to low bulk. Add ca. 15 cm^3 of aqua regia and evaporate almost to dryness on a hot plate. Add 10 cm^3 portions of conc. HCl and reduce to small bulk. Take up the residue in 10 cm^3 of 6M HCl and filter off silica. Reject the silica to active waste.

5.10.2 Radiochemical separations

(1) From the final solution obtained by above procedure extract

gold three times successively with 10 cm^3 portions of diethylether (previously saturated with 6M HCl). Combine and retain the organic layers for gold purification.

(2) Extract platinum, iridium and palladium from the aqueous phase with three 10 cm^3 portions of 1M di-n-heptylsulphoxide in TCE solution. The shaking process should not last more than one minute.

(3) . Extract back platinum and iridium into aqueous solution with four successive 10 cm^3 portions of H_2O. The palladium(with impurities) is left in the organic phase.

(4) To remove the base metals from the aqueous phase, extract with two successive 10 cm^3 portions of 0.5M HD in heptane(shake it gently). Retain the aqueous phase for platinum and iridium purifications.

Palladium

In step(3), palladium is left in the DHSO-phase. Strip this organic phase three times with 10 cm^3 10 % Me_2NH. Discard the organic layer. Acidify the aqueous solution with HCl and add 1 cm^3 of silver carrier solution(20 mg of Ag cm^{-3}). Filter and discard the precipitate of AgCl. To the filtrate add dropwise 1 % DMG in ethanol to precipitate palladium. Centrifuge and discard the supernatant. Dissolve Pd-glyoximate with 1 cm^3 of aqua regia and evaporate to dryness. Add 2 cm^3 of conc. HCl and reduce to low bulk. Repeat HCl addition and evaporation. Add 1 cm^3 of Au-carrier solution and warm to reduce to low bulk. Take up in 10 cm^3 of 6M HCl and extract gold three times with 10 cm^3 portions of diethyl -ether(previously saturated with 6M HCl). Discard the organic phase. Evaporate the aqueous phase to low bulk and take up in

50 cm^3 of 0.5M HCl. Add 1 % DMG in ethanol dropwise to reprecipitate palladium. Centrifuge and discard the supernatant liquid. Wash the precipitate twice with small portions of water and then twice with 95 % ethanol. Slurry the precipitate with 95 % ethanol on to a weighed aluminium counting tray by using a transfer pipette. Make sure that the distribution of the precipitate on the counting tray is uniform. Dry under an infra-red lamp at 110 ^{o}C, cool and weigh to obtain the chemical yield.

Platinum

Reduce the solution, from step(4), to a low bulk and add 2.9M HCl to make the volume ca. 50 cm^3. Add 1 cm^3 Ag-carrier. Filter and discard the precipitate of AgCl. Boil the solution and add freshly prepared mercury^{I} chloride slurry.* Boil the solution for 10 minutes and collect the precipitate on a filter paper. Dissolve the precipitate with hot brominated conc. HCl into a clean beaker. Evaporate the resulting solution to ca. 2 cm^3 and dilute to 50 cm^3 with 2.9M HCl. Reprecipitate platinum with further freshly prepared mercury^{I} chloride slurry. Filter the precipitate on an ashless Whatman No.

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* The slurry of mercury^{I} chloride can be prepared by the addition of dilute HCl to a hot solution of mercury^{I} nitrate in dil. nitric acid; wash the precipitate of mercury^{I} chloride by decantation with distilled water until free from acid. It should be used with a little water as semi-fluid mixture.

541 filter paper and wash with hot 2 % HCl. Heat the precipitate in a porcelain crucible in a fume cupboard to burn off the filter paper and volatilize mercury. Then ignite it at 900 ^{o}C in an electric muffle furnace. Transfer the platinum metal to a weighed aluminium counting tray and determine the chemical yield.

Gold

Gold was extracted with diethylether in step 1. Wash the organic phase three times with 10 cm^3 portions of 1.4M HCl and discard the washes. To the organic phase add 20 cm^3 of 5 % oxalic acid solution and heat on a water bath at 70 ---80^{o}C till the whole of the organic layer has evaporated. Filter the gold precipitate using an ashless filter paper. Wash it with 4M HCl and then with H_2O and ethanol. Ignite in a weighed silica crucible at 800^{o}C. Cool and transfer the gold metal to a weighed aluminium tray for activity measurements; determine the yield by weighing.

Iridium

After the precipitation of platinum, iridium is left in the solution. Reduce the solution to low bulk and make to 100 cm^3 with 2.9M HCl. Add 10 g of NaBr and 5 g of KI. Boil the solution and add excess of freshly prepared mercury^{I} chloride slurry. Boil it until the colour changes from brown to black. Allow the precipitate to settle and filter it on a Whatman No. 541 ashless filter paper. Ignite in a silica crucible in a muffle furnace at 800^{o}C and then reduce in a hydrogen atmosphere at 800^{o}C. Transfer the iridium

metal to a weighed counting tray for measurement of activity and chemical yield.

5.10.3 Procedure for irradiated comparators

Break the ampoule containing irradiated standards and trans--fer the contents to a 250 $\cdot$ cm^3 beaker containing carrier solutions. Rinse out the ampoule several times with water and transfer to the same beaker. Reduce the solution to low bulk and take up in 10 cm^3 of 6M HCl. Extract gold with diethylether and evaporate with 5 % oxalic acid to give a gold precipitate.

The procedure for the extraction and purification of platinum, iridium and palladium standards is exactly the same as for samples except that the HD treatment in step(4) is not needed

ERROR CONSIDERATIONS

Various errors associated with neutron activation analysis have been discussed by Smale(1957), Plumb and Lewis(1955) and Morris(1962). Some of these errors, especially those concerning with the radiochemical activation analysis, were not discussed in chapter4 and are considered below.

(1) Flux inhomogeneities

The unperturbed flux in a reactor may be expected to be fairly constant under irradiation conditions although a spatial flux gradient may exist in the vicinity of an irradiation position. This flux gradient can be quite large particularly near the reflector. Thus a sample and a comparator activated simultaneously in adjacent positions may be exposed to fluxes of different magnitudes, resulting in an error when a comparison of induced activities is made. To avoid such an error, in this investigation, the samples and comparators were packed closely together to minimize the gap between them to less than one cm.

(2) Neutron selfshielding

Neutron selfshielding effects are unimportant in the application of the activation method to the analysis of an "average rock" (Morris 1964). Furthermore, the comparators used were in microgram quantities, the neutron attenuation of such dilute samples would certainly be negligible.

(3) Sample weights

The 0.4 g samples of lateritic ore were weighed to an accuracy of 0.01 mg. Since the concentration levels of trace elements calculated from the analysis were rounded off to two significant figures due to other error considerations, the uncertainty in the weight of sample did not have any considerable influence on the experimental results.

(4) Interfering nuclear reactions

The effect of different interfering reactions has already been discussed in section 5.3.1 and also in connection with the results.

(5) Determination of chemical yield

In the gravimetric determination of chemical yield factors for gold, platinum and iridium, the precipitates weighed generally more than 15 mg. An error of less than 0.6% due to the weighing was observed. The palladium dimethylglyoximate precipitates weighed generally ca. 20 mg. An error of less than 0.4 % was accepted.

(6) Gamma ray spectrometry

Comparative measurements made by comparing the areas of corresponding photopeaks in the two gamma ray energy spectra are also liable to uncertainties, particularly when the peak or peaks of interest are located in the region of the spectrum having a

Compton and Bremsstrahlung continuum. Although the Compton and Bremsstahlung background can be subtracted from the peak area by creating a base line across the minima on either side of the peak, the method still may have its uncertainties. Even with computer techniques, it is generally accepted that gamma ray spectrometry gives an inherent error of ≥ 5 % (Kruger, 1971).

In the light of above considerations of error it is apparent that the uncertainties in the results of this activation analysis are caused mainly by unavoidable factors inherent in the method. Whereas the errors due to the chemical manipulations, like sample weighing, aliquot sampling, etc., were never more than 0.6 %. The error contribution of activity measurements alone, varied between 1 and 5 %. In the particular case of determination of platinum, the statistical error of counting contributed significantly to the overall errors of the results.

Precision and accuracy of results

Often the precision is estimated from the counting statistics but it is also suggested that a more realistic way of determining the precision of a technique is to analyse replicate samples and compute the precision directly from the results thus obtained. This procedure presupposes the existance of a homogeneous sample to be analysed in replicate, since the precision thus obtained includes errors due to the sampling in addition to the errors inherent in the analytical method. In this work the standard deviations were determined from analysis of at least four replicates.

Fig. 5.7

^{198}Au gamma spectrum after separating gold from rock L-1
(2" x 2" NaI detector with multichannel analyser)

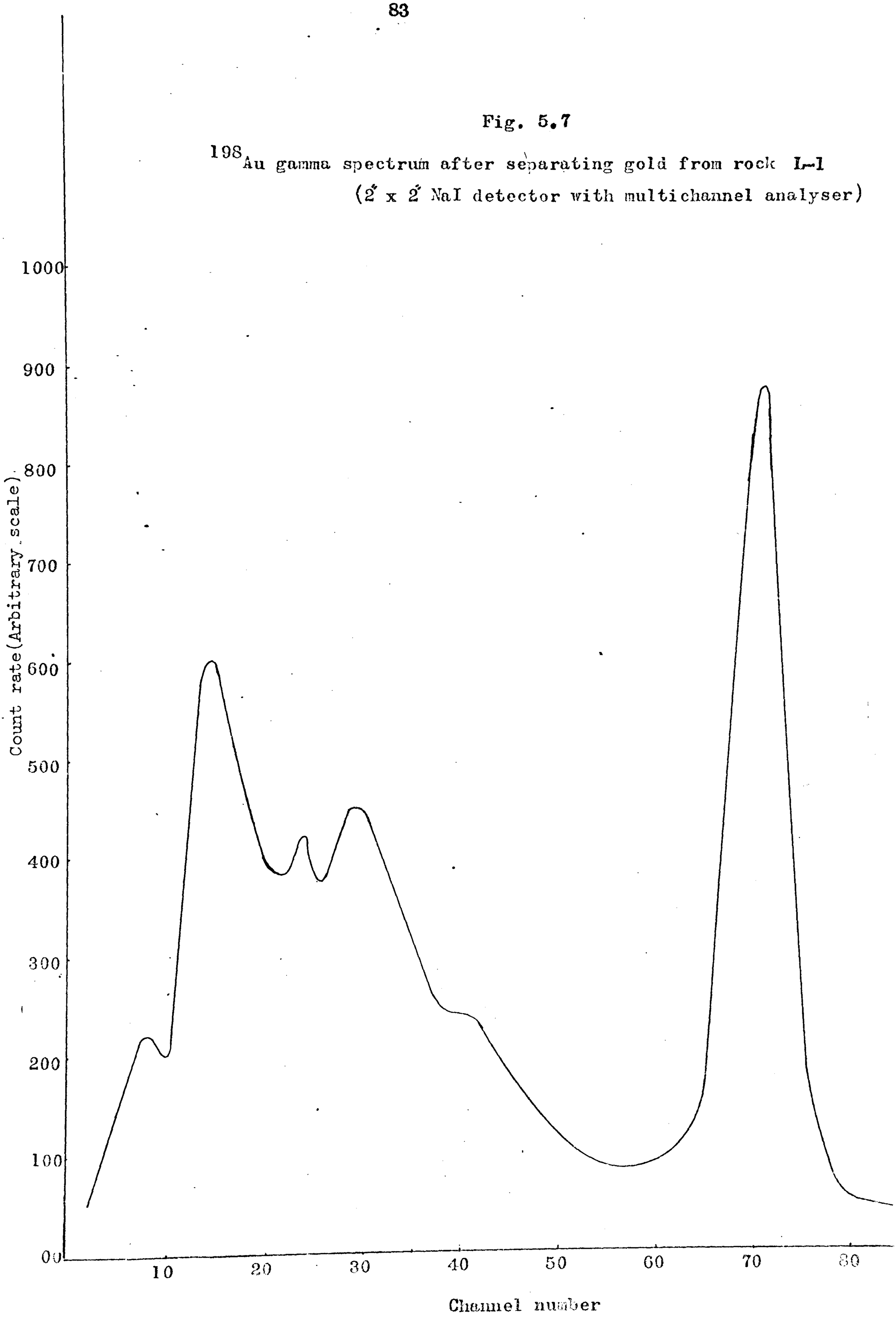
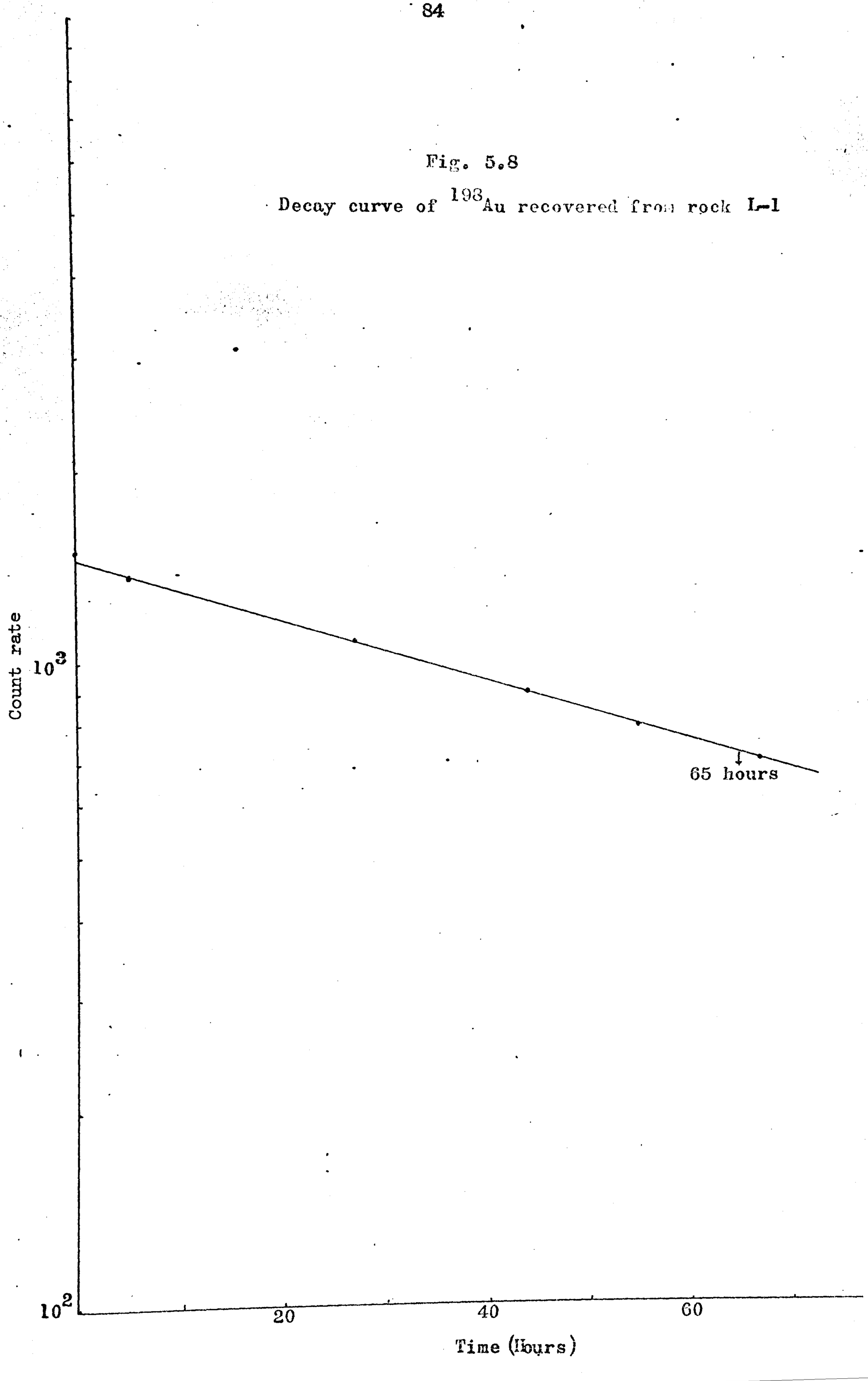


Fig. 5.8

Decay curve of ^{198}Au recovered from rock L-1



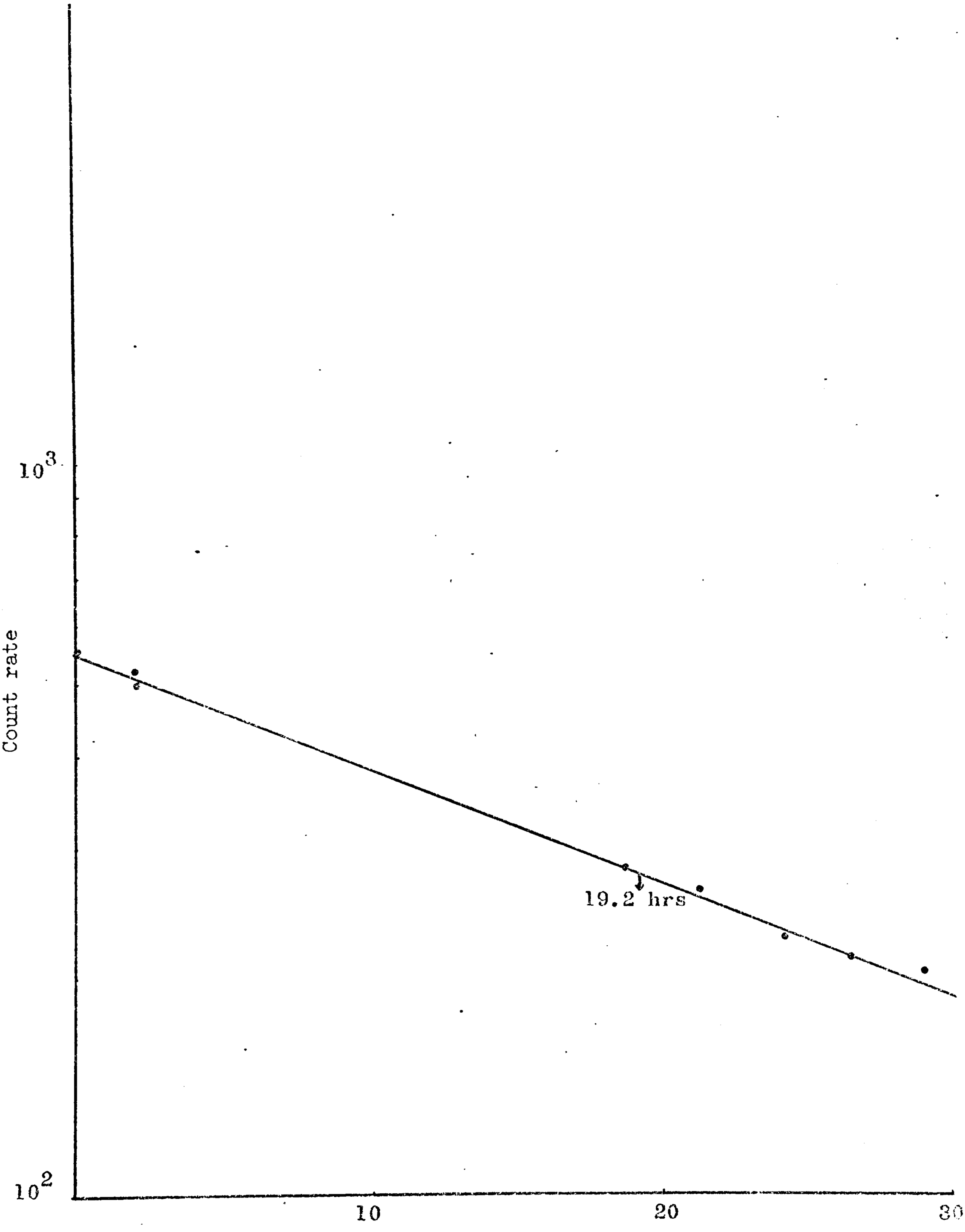


Fig. 5.9 — Decay curve for ^{197}Pt extracted from rock L -3

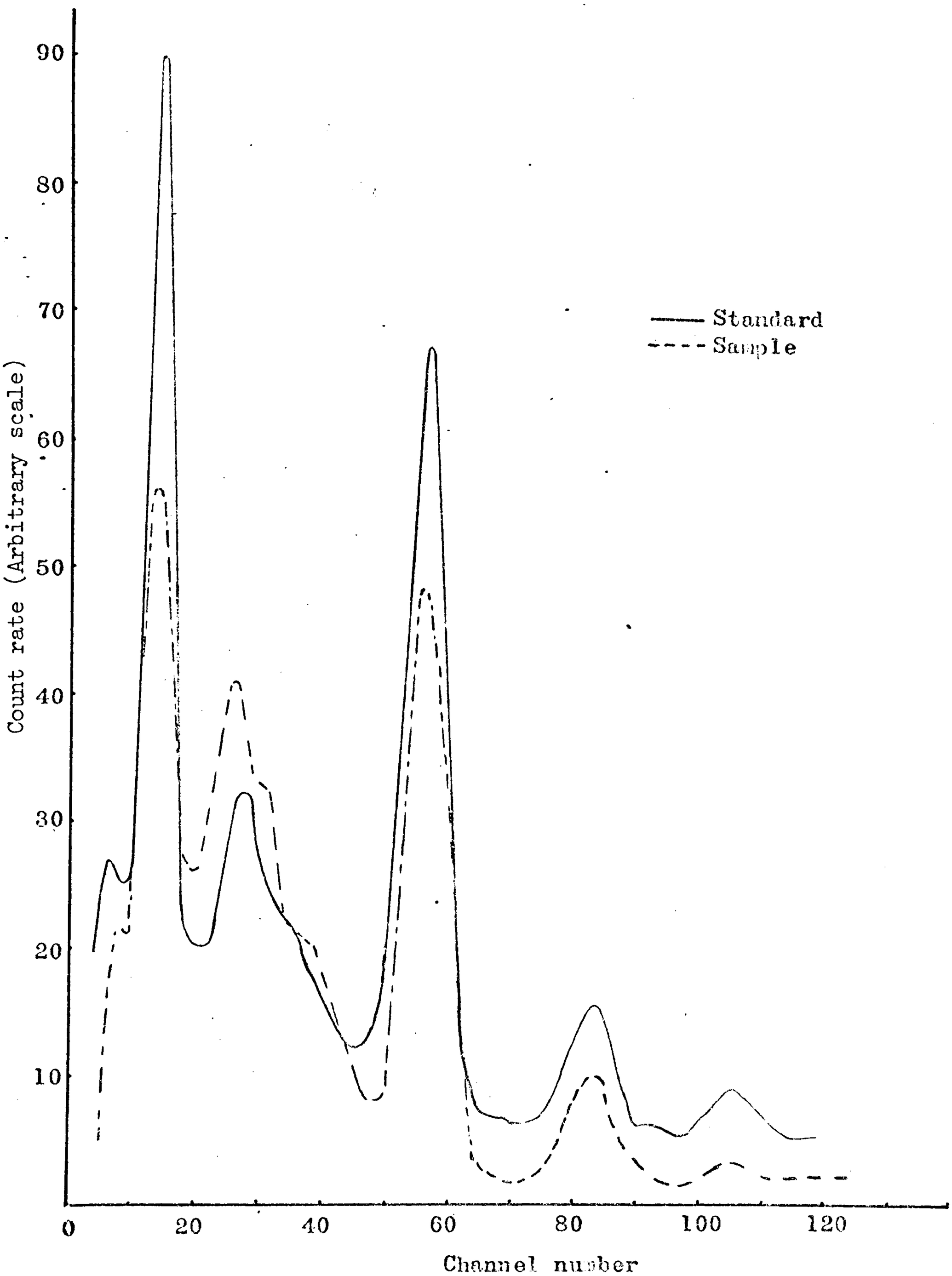


Fig. 5.10 -- Spectra of Iridium-192 extracted from rock L-3 and a comparator. Detector used was 2" x 2" NaI crystal.

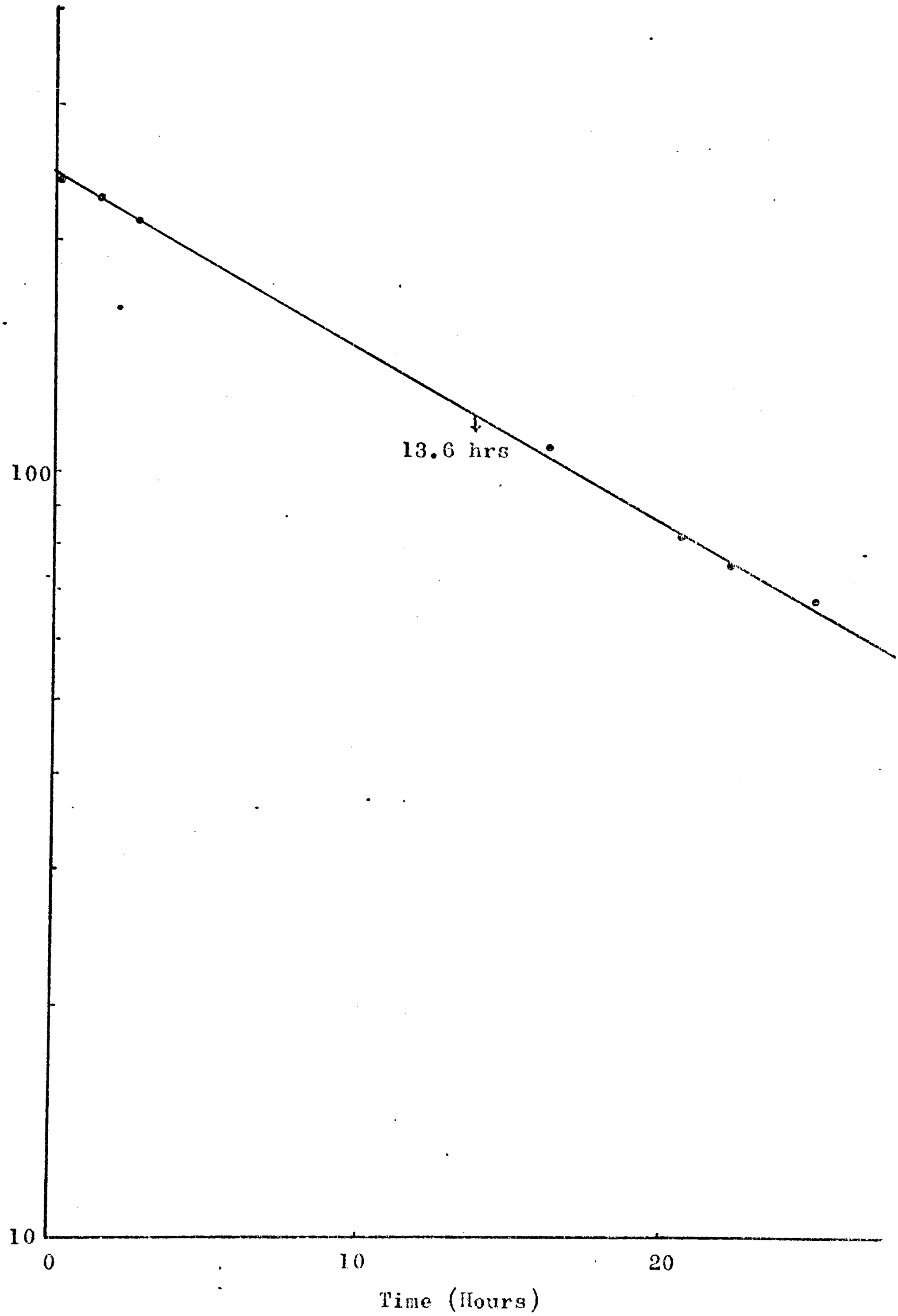


Fig. 5.11— Decay curve of ^{109}Pd extracted from Sample L - 1

RESULT AND DISCUSSION

The results obtained from activation analyses of gold, platinum, iridium and palladium in Lateritic Nickel-Ore samples are given in tables 5.3-5.12 . These tables shows the results of individual analyses, together with the average value and standard deviation of the mean.

Analysis for gold

Fig.5.7 shows a γ-spectrum of ^{198}Au extracted from sample(L1). The prominent 412 Kev photopeak was used in the measurements of gold content. The decay curve shown in fig.5.8 demonstrates the high radiochemical purity attained by this procedure. Chemical yields obtained for gold were generally better than 80 % (varying between 75 and 90 %).

Analysis for Platinum

Platinum-197 activity was determined by β-counting because the count rate was low and it was difficult to measure 77 Kev gamma peak in the presence of the higher background. The decay curve shown in fig.5.9 gives half life of 19.2 hours and indicates that a fairly good radiochemical purity has been achieved. The average chemical yield obtained by the procedure was approximately 80 percent.

Analysis for iridium

A gamma spectrum of iridium from sample is compared with that of an iridium standard in fig. 5.10 To construct the decay curve of iridium, sample counting, using the 317 Kev peak of ^{192}Ir was done every two hours on the first day of separation,

then every day up to a week and afterwards once a week over a period of $2\frac{1}{2}$ months. The average chemical yield for iridium, obtained by the procedure, amounts to ca. 84 %, and varied between 87 and 92 %.

Analysis for palladium

Beta activity of ^{109}Pd was measured with an end-window G.M. counter and decay curves were taken (see fig. 5.11). The curves demonstrated the absence of any significant contamination. No interference from 22 min ^{111}Pd was expected, since the time spent in radiochemical separations ensured the complete decay of ^{111}Pd to 7.5 d ^{111}Ag. Silver-111 was removed by the addition of Ag-carrier and subsequent precipitation of AgCl. Moreover, as could be inferred from the nuclear properties in table 5.1, the induced activity of ^{111}Pd was much less than the ^{109}Pd activity.

Crocket and Skippen have shown that the interference due to the reaction ^{235}U(n,f) ^{112}Pd, ^{109}Pd is ca. 5.53×10^{-3} % when 1 µg of Pd and U are present. Thus, a contribution arising from fission can be neglected in the determination of palladium in these samples. (because the U contents in most of the samples are less than 15 ppb. The average chemical yield obtained in the Pd separation was ca. 65%. It was possible to achieve a much higher yield; however, the activity gained in this way would have been offset by the increased self-absorption. Therefore, no attempt was made to separate the palladium quantitatively.

Table 5.3 Distribution of Platinum as a Function of Depth through a Guatemalan Lateritic- Ore deposit

Sample	Depth (metres)	Description	Pt(ppb) (NAA Method)	Average
L1	1.50-2.00	Surficial Laterite	135.6	
			141.5	
			138.0	
			144.6	140 ± 4
L2	2.5-3.00	Plastic Laterite	145.5	
			145.2	
			147.3	
			144.7	145 ± 1
L3	3.50-4.00	Saprolite	166.2	
			164.7	
			181.3	
			179.7	173 ± 9
L4	5.25-5.75	Boulders in saprolite zone	135.7	
			134.2	135 ± 1
L6	8.00-8.50	Fines of weathered rock	102.3	
			101.7	
			98.6	
			103.4	101 ± 1
L5	8.00-8.50	Weathered rock	96.1	
			97.1	
			96.3	
			97.8	97 ± 1
L7	10.25-10.75	Rock	66.2	
			68.7	
			67.1	
			69.6	68 ± 2

TABLE 5.4 Distribution of Palladium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Pd(ppb) (NAA Method)	Average
L1	1.50–2.00	Surficial Laterite	87.1	
			85.0	
			83.5	
			80.7	84 ± 3
L2	2.50–3.00	Plastic Laterite	82.0	
			81.6	
			76.5	
			75.2	79 ± 4
L3	3.50–4.00	Saprolite	56.0	
			57.1	57 ± 1
L4	5.25–5.75	Boulders in saprolie zone	92.7	
			91.7	
			94.7	
			93.9	93 ± 3
L6	8.00–8.50	Fines of weathered rock	51.3	
			50.2	
			49.8	
			51.5	50 ± 1
L5	8.00–8.50	Weathered rock	47.7	
			45.1	46 ± 2
L7	10.25–10.75	Rock	37.6	
			36.4	
			37.9	
			36.6	37 ± 1

TABLE 5.5 Distribution of Iridium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Ir(ppb) (NAA Method)	Average
L1	1.50–2.00	Surficial Laterite	8.15	
			8.24	8.2 ± 0.1
L2	2.5–3.00	Plastic Laterite	14.30	
			13.92	
			13.84	
			13.47	13.9 ± 0.4
L3	3.50–4.00	Saprolite	15.62	
			15.65	
			14.90	15.2 ± 0.5
L4	5.25–5.75	Boulders in saprolite zone	10.40	
			10.39	
			12.03	
			12.02	13.2 ± 2.2
L6	8.00–8.50	Fines of weathered rock	7.35	
			7.43	
			7.65	
			7.40	7.4 ± 0.1
L5	8.00–8.50	Weathered rock	6.13	
			6.72	
			7.02	
			6.93	6.7 ± 0.4
L7	10.25–10.75	Rock	4.61	
			5.50	
			4.38	
			5.45	5.0 ± 0.6

TABLE 5.6 Distribution of Noble Metals as a Function of Depth through a Guatemalan Lateritic-Ore deposit

Gold contents.

Sample	Depth (metres)	Description	Au (ppb) (NAA Method)	Average
L1	1.5-2.00	Surficial Laterite	11.56	
			10.97	
			12.60	
			12.18	11.8 ± 0.8
L2	2.5-3.00	Plastic Laterite	14.54	
			14.02	
			13,47	
			13.01	13.8 ± 0.7
L3	3.5-4.00	Saprolite	8.90	
			9.02	8.9 ± 0.1
L4	5.25-5.75	Boulders in saprolite zone	5.92	
			6.30	
			5.41	
			6.12	5.9 ± 0.4
L6	8.00-8.50	Fines of weathered rock	4.96	
			5.65	
			5.83	
			5.45	5.6 ± 0.6
L5	8.00-8.50	Weathered rock	4.84	
			4.91	
			4.74	
			4.80	4.8 ± 0.1
L7	10.25-10.75	Rock	3.44	
			3.27	
			3.14	
			2.98	3.2 ± 0.2

TABLE 5.7 Distribution of Platinum as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Pt(ppb) (NAA Method)	Average
BNC1	0 - 2	ferricrete	107.0	
			102.0	
			103.0	
			123.0	108 ± 9
BNC2	2 - 7	Limonite	166.0	
			161.0	
			167.0	
			162.0	164 ± 3
BNC3	7 - 11	limonite	154.5	
			154.8	
			149.3	
			145.3	151 ± 5
BNC4	11 - 13	Limonite	196.5	
			195.3	
			189.7	
			186.5	190 ± 5
BNC5	13 - 14	Limonite and Asbolite	128.8	
			122.0	
			121.5	
			151.6	131 ± 14
BNC6	14 - 17	Limonite and Asbolite	105.3	
			111.0	
			110.0	
			112.0	110 ± 3
BNC7	17 - 20	Saprolite	82.8	
			85.0	
			80.1	
			82.0	83 ± 2

TABLE 5.8 Distribution of Palladium as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Pd(ppb) (NAA Method)	Average
BNC1	0 - 2	Ferricrete	78.0	
			80.0	
			79.0	
			83.0	80.0 ± 2.1
BNC2	2 - 7	Limonite	50.0	
			49.0	
			57.1	
			54.8	52.5 ± 3.8
BNC3	7 - 11	Limonite	80.8	
			81.7	
			78.8	
			79.7	80.2 ± 1.2
BNC4	11 - 13	Limonite	26.5	
			28.6	
			28.5	
			26.2	27.5 ± 1.3
BNC5	13 - 14	Limonite and Asbolite	25.8	
			24.5	
			24.7	
			23.4	24.6 ± 1.0
BNC6	14 - 17	Limonite and Asbolite	21.0	
			21.6	
			21.7	
			22.0	21.5 ± 0.5
BNC7	17 - 20	Saprolite	21.8	
			21.1	
			21.3	
			21.7	21.0 ± 0.5

TABLE 5.9 Distribution of Gold as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Au(ppb) (NAA Method)	Average
BNC1	0 - 2	Ferricrete	34.40	
			32.50	
			28.10	
			26.50	30.4 ± 3.7
BNC2	2 - 7	Limonite	31.00	
			29.00	
			34.00	
			33.00	31.7 ± 2.2
BNC3	7 - 11	Limonite	41.05	
			40.14	40.5 ± 0.6
BNC4	11 - 13	Limonite	11.40	
			12.90	
			8.13	
			12.80	11.3 ± 0.3
BNC5	13 - 14	Limonite and Asbolite	7.01	
			9.83	
			7.01	
			8.28	8.0 ± 1.3
BNC6	14 - 17	Limonite and Asbolite	8.90	
			10.0	
			9.40	
			9.70	9.5 ± 0.5
BNC7	17 - 20	Saprolite	6.59	
			6.61	
			7.09	
			6.84	6.3 ± 0.3

TABLE 5.10 Distribution of Iridium as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Ir(ppb) (NAA Method)	Average
BNC1	0 - 2	Ferricrete	8.5	
			7.4	
			8.5	
			7.1	7.8 ± 0.7
BNC2	2 - 7	Limonite	5.9	
			5.4	
			5.5	
			5.1	5.4 ± 0.4
BNC3	7 - 11	Limonite	5.2	
			5.8	
			5.1	
			4.5	5.2 ± 0.5
BNC4	11 - 13	Limonite	6.4	
			6.3	
			5.1	
			5.0	5.7 ± 0.7
BNC5	13 - 14	Limonite and Asbolite	6.7	
			5.1	
			7.6	
			5.8	6.5 ± 0.6
BNC6	14 - 17	Limonite and Asbolite	5.2	
			4.9	
			5.6	
			4.8	5.1 ± 0.4
BNC7	17 - 20	Saprolite	4.4	
			5.0	
			5.1	
			4.9	4.8 ± 0.3

TABLE 5.11 Distribution of Noble Metals as a Function of Depth through an Indonesian Lateritic Nickel-Ore Deposit

Sample	Depth (metres)	Description	Pd(ppb) (NAA Method)	Average
BIP1	11-13	Limonite & Asbolite	52	
			54	
			51	
			53	52±2
BIP2	13-17	Saprolite	42.3	
			41.8	
			46.1	
			45.9	44±2.3
BIP3	18-19	Saprolite & Quartz boxwork	27.5	
			27.3	
			28.0	
			28.4	27.8
			Ir(ppb)	
BIP1	11-13	Limonite & Asbolite	16	
			17	
			15.8	
			15.4	16±1.3
BIP2	13-17	Saprolite	7.2	
			7.8	
			6.9	
			6.3	7.05±0.6
BIP3	18-19	Saprolite & Quartz boxwork	4.7	
			5.2	
			5.4	
			5.9	5.3±1.2

TABLE 5.12 Distribution of Noble Metals as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Sample	Depth (metres)	Description	Au(ppb) (NAA Method)	Average
BIP1	11-13	Limonite & Asbolite	14.1	
			15.4	
			14.4	
			15.7	14 ± 1.9
BIP2	13-17	Saprolite	8.3	
			8.1	
			9.2	
			9.1	8.5 ± 1.5
BIP3	18-19	Saprolite & Quartz boxwork	6.9	
			6.8	
			6.4	
			6.2	6.2 ± 1.9
			Pt(ppb)	
BIP1	11-13	Limonite & Asbolite	64.5	
			64.4	
			70.4	
			69.7	67.25 ± 3.2
BIP2	13-17	Saprolite	42.8	
			41.9	
			43.3	
			44.4	43.1 ± 1
BIP3	18-19	Saprolite & Quartz boxwork	17.3	
			15.5	
			19.3	
			20.1	18.05 ± 3.3

CHAPTER 6

NONDESTRUCTIVE ACTIVATION ANALYSIS

CHAPTER 6

NONDESTRUCTIVE ACTIVATION ANALYSIS

The published literature shows that nondestructive activation analysis has proved to be a powerful method for the fast and accurate determination of several major and minor elements in geological samples.

Since chemical and radiochemical processes are often time-consuming, especially for multielemental analysis, there is a definite advantage with purely instrumental technique using gamma ray spectrometery. Gamma ray specrometery, particularly with high resolution semiconductor Ge-Li detectors has proved invaluable for this mode of activation analysis. Extensive reviews of this subject has been presented by Adams and Hoste(1971) and by Gijbels(1973).

A list of stable nuclides and radionuclides involved in the present work is given in table 6.1.

6.1.1 Irradiation And Cooling Time

The choice of proper irradiation and cooling time is most important in instrumental activation analysis, and is made so as to maximise as for as possible the activities of radionuclides of interest in comparision with those of others. For elements which produced short lived isotopes on neutron activation it is desirable to use short irradiation and cooling times, whilst on the other hand for long-lived nuclides it is best to use a long cooling time and correspondingly a long irradiation time may be required to achieve adequate sensitivity. As a result of such factors, it is desirable to calculate the best compromise.

6.1.2 Preparation of Standard

Initially consideration was given to using the U.S.G.S standard rock PCC-1 as a comparator. However, available literature values for the contents of certain elements in this rock vary over the range 50-150 %. Moreover, the Fe, Ni, and Cr concentrations in this rock are lower than in the laterites, while on the other hand the concentration of Mg and Si is higher. Hence, it was decided to prepare an artificial standard by mixing known amounts of the elements, as pure oxide or chloride, in the proportions to correspond to the composition of a typical laterite matrix. The components were uniformly admixed by mechanical shaking for two hours. The homogeneity of the standard powder was tested by irradiating duplicate portions and determining the specific activities of constituents. Both batches gave almost identical specific activities, thus confirming that the reproducibility of the standard prepartion could be trusted. The composition was also tested by cross checking with PCC-1. Composition of standard is given in table 6.2.

6.1.3 Preparation of Sample and Standard for Irradiation

About 0.4g samples of powdered lateritic ore and similar weights of the standard were accurately weighed into polythene irradiation tubes(4 mm internal diameter). These containers of sample and standard were packed together tightly with silica wool in a standard 1 inch dia.x3 inch long polythene tube.

6.1.4 Irradiation

Irradiations were made in the research reactor 'HERALD' at A.W.R.E., Aldermaston, and most often were of 2 hours duration.

The thermal flux at the irradiation position was 2.5×10^{12} n s^{-1} $cm.^{-2}$ The irradiations usually involved 4–6 samples of laterites, togather with two portions of stndard. The activated samples were generally made available for analysis 11–14 hours after the end of irradiation. In the case of determination of chlorine, however; irradiations of 30 min duration were made and counting was performed about 2–3 hours after the end of the activation period.

Table 6.1

Element	n, γ Nuclide measured	Cross Section σ	γ-Ray used(Kev)	Interfering γ-rays (Kev)
Na	15.0h-^{24}Na	0.53	1369	-
Sc	83.9d-^{46}Sc	22.0	889 1120	-
Cr	27.8d-^{51}Cr	16.0	320	(319 ^{147}Nd)
Mn	2.56h-^{56}Mn	13.3	847	(845 ^{27}Mg)
Fe	45.6d-^{59}Fe	0.0034	1095 1292	-
Co	5.26y-^{60}Co	37.0	1333 1173	(1326 ^{124}Sb)
Cu	12.8h-^{64}Cu	4.5	511 1226	-
Zn	13.8h-^{69m}Zn	0.075	439	-
Cl	37.3m-^{38}Cl	0.4	1600	-
Ni	2.55h-^{65}Ni	1.5	1480 1115	-

TABLE 6.2

Composition of Artificial Standard

Elements (Oxides and Chlorides)	Weight (Grams)
Fe_2O_3	4.490
SiO_2	3.000
MgO	1.700
Al_2O_3	0.070
NiO	0.300
CoO	0.020
CuO	0.005
Cr_2O_3	0.250
MnO	0.150
Zn O	0.010
Sc_2O_3	0.001
	10.00 g

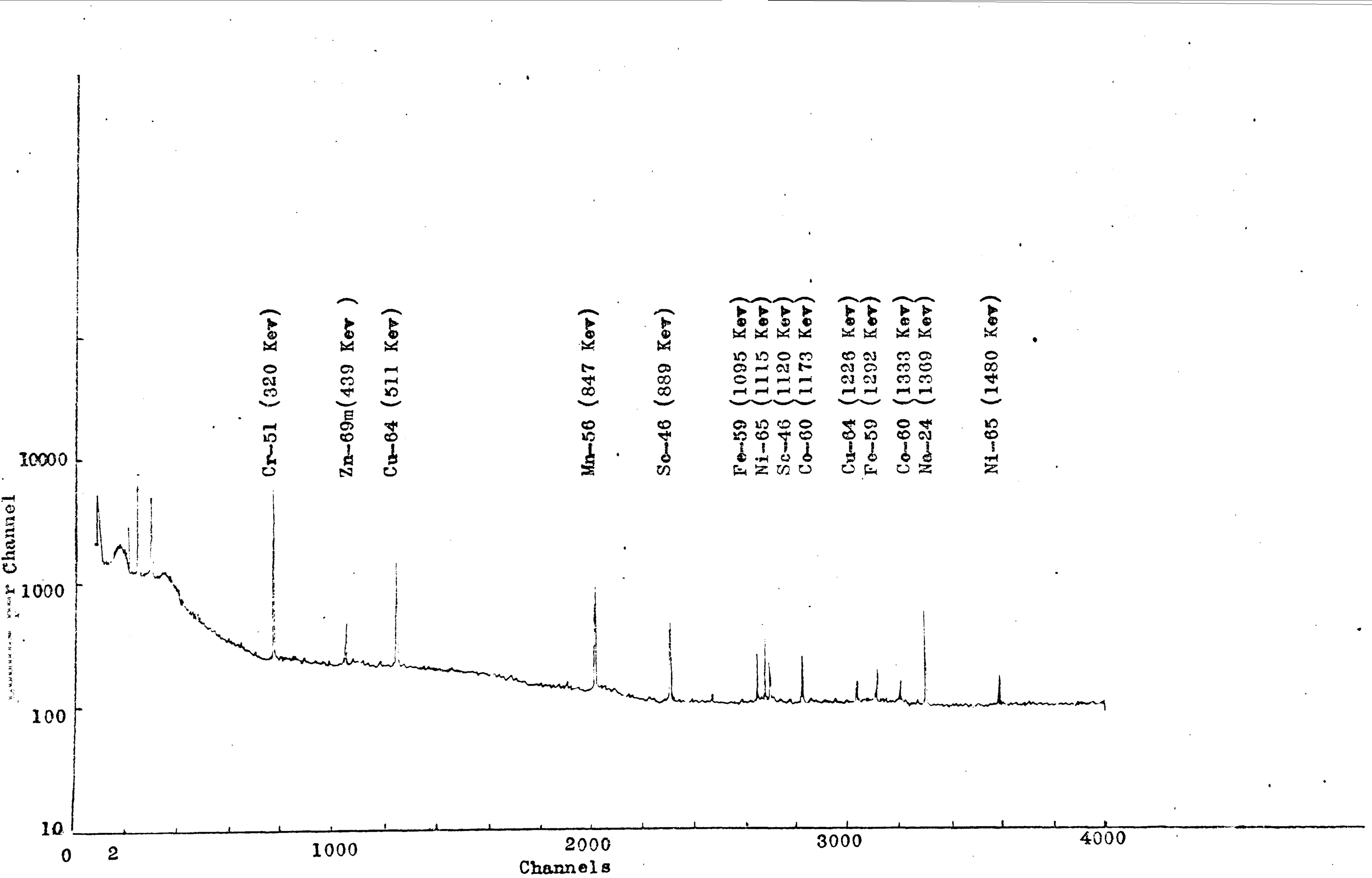


Fig.1. Gamma spectrum obtained from a thermal neutron irradiated sample(L) with a 42.5mm Ge(Li)

CHAPTER 7

ANALYTICAL METHODS FOR MAJOR AND MINOR ELEMENTS

ANALYTICAL METHODS FOR MAJOR AND MINOR ELEMENTS

The elements Mg, Si, Ni, Fe, and Cr were determined using gravimetric and titrimetric methods. The techniques have been described in text books (Vogel 1970 and Maxwell 1968). Supplemental facets were obtained from other publications. Cu and Co were determined by a spectrometric method described by Sandell(1959) and Morrison(1966).

Replicate analyses were run in each case. Good agreement was generally achieved between nondestructive activation analyses and the chemical analyses.

Chemical analyses of 17 samples are listed in table 7.1-7.36 together with corresponding nondestructive activation results.

TABLE 7.1 Distribution of Iron as a Function of Depth through a Guatemalan Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Fe % (Chemical Method)	Fe % (INAA Method)
L1	1.50–2.00	Surficial Laterite	43.82	42.37
L2	2.50–3.00	Plastic Laterite	32.21	31.51
L3	3.50–4.00	Saprolite	25.21	24.93
L4	5.25–5.75	Boulders in Saprolite Zone	9.15	9.10
L6	8.00–8.50	Fine of Weathered Rock	22.56	22.15
L5	8.00–8.50	Weathered Rock	10.53	10.08
L7	10.25–10.75	Rock	7.95	7.88

TABLE 7.2 Distribution of Nickel as a Function of Depth through a Guatemalan Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Ni % (Chemical Method)	Ni % (NAA Method)
L1	1.50–2.00	Surficial Laterite	1.71	1.71
L2	2.50–3.00	Plastic Laterite	1.92	1.91
L3	3.50–4.00	Saprolite	2.13	1.98
L4	5.25–5.75	Boulders in Saprolite Zone	1.91	1.85
L6	8.00–8.50	Fine of Weathered Rock	1.68	1.45
L5	8.00–8.50	Weathered Rock	1.18	1.15
L7	10.25–10.75	Rock	0.65	0.62

TABLE 7.3 Distribution of Silica as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	SiO_2 % (Chemical Method)
L1	1.50-2.00	Superficial Laterite	3.25
L2	2.50-3.00	Plastic Laterite	7.25
L3	3.50-4.00	Saprolite	20.35
L4	5.25-5.75	Boulders in Saprolite	32.75
L6	8.00-8.50	Fine of Weathered Rock	10.25
L5	8.00-8.50	Weathered Rock	21.50
L7	10.25-10.75	Rock	34.25

TABLE 7.4 Distribution of Magnesium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mg % (Chemical Method)
L1	1.50-2.00	Superficial Laterite	4.28
L2	2.50-3.00	Plastic Laterite	8.95
L3	3.50-4.00	Saprolite	12.84
L4	5.25-5.75	Boulders in Saprolite	10.35
L6	8.00-8.50	Fine of Weathered Rock	5.23
L5	8.00-8.50	Weathered Rock	8.34
L7	10.25-10.75	Rock	16.55

TABLE 7.5 Distribution of Chromium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cr % (Chemical Method)	Cr % (NAA Method)
L1	1.50-2.00	Superficial Laterite	0.087	0.083
L2	2.50-3.00	Plastic Laterite	0.086	0.081
L3	3.50-4.00	Saprolite	1.343	1.252
L4	5.25-5.75	Boulders in Saprolite	1.287	1.213
L6	8.00-8.50	Fine of Weathered Rock	1.300	1.005
L5	8.00-8.50	Weathered Rock	0.780	0.680
L7	10.25-10.75	Rock	0.655	0.651

TABLE 7.6 Distribution of Manganese as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mn % (Chemical Method)	Mn % (NAA Method)
L1	1.50-2.00	Superficial Laterite	0.283	0.260
L2	2.50-3.00	Plastic Laterite	0.310	0.313
L3	3.50-4.00	Saprolite	0.261	0.251
L4	5.25-5.75	Boulders in Saprolite	0.219	0.219
L6	8.00-8.50	Fine of Weathered Rock	0.198	0.195
L5	8.00-8.50	Weathered Rock	0.123	0.123
L7	10.25-10.75	Rock	0.098	0.098

TABLE 7.7 Distribution of Cobalt as a Function of Depth through a Guatemalan Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Co % (Chemical Method)	Co % (NAA Method)
L1	1.50–2.00	Superficial Laterite	0.125	0.115
L2	2.50–3.00	Plastic Laterite	0.150	0.135
L3	3.50–4.00	Saprolite	0.293	0.260
L4	5.25–5.75	Boulders in Saprolite Zone	0.156	0.145
L6	8.00–8.50	Fine of Weathered Rock	0.213	0.195
L5	8.00–8.50	Weathered Rock	0.125	0.115
L7	10.25–10.75	Rock	0.81	0.073

TABLE 7.8 Distribution of Copper as a Function of Depth through a Guatemalan Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cu % (Chemical Method)	Cu % (NAA Method)
L1	1.50–2.00	Superficial Laterite	0.132	0.131
L2	2.50–3.00	Plastic Laterite	0.143	0.138
L3	3.50–4.00	Saprolite	0.129	0.123
L4	5.25–5.75	Boulders in Saprolite	0.127	0.127
L6	8.00–8.50	Fine of Weathered Rock	0.117	0.116
L5	8.00–8.50	Weathered Rock	0.114	0.113
L7	10.25–10.75	Rock	0.0163	0.0161

TABLE 7.9 Distribution of Scandium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Sc (ppm) (NAA Method)
L1	1.50-2.00	Superficial Laterite	128
L2	2.50-3.00	Plastic Laterite	80.5
L3	3.50-4.00	Saprolite	60.8
L4	5.25-5.75	Boulders in Saprolite	22.18
L6	8.00-8.50	Fine of Weathered Rock	55.00
L5	8.00-8.50	Weathered Rock	23.8
L7	10.25-10.75	Rock	21.4

TABLE 7.10 Distribution of Zinc as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Zn % (NAA Method)
L1	1.50-2.00	Superficial Laterite	0.0142
L2	2.50-3.00	Plastic Laterite	0.0124
L3	3.50-4.00	Saprolite	0.0065
L4	5.25-5.75	Boulders in Saprolite	0.0026
L6	8.00-8.50	Fine of Weathered Rock	0.0057
L5	8.00-8.50	Weathered Rock	0.0037
L7	10.25-10.75	Rock	0.0024

TABLE 7.11 Distribution of Sodium as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Na % (NAA Method)
L1	1.5-2.00	Superficial Laterite	0.0075
L2	2.50-3.00	Plastic Laterite	0.0231
L3	3.50-4.00	Saprolite	0.0245
L4	5.25-5.75	Boulders in Saprolite	0.0240
L6	8.00-8.50	Fine of Weathered Rock	0.0175
L5	8.00-8.50	Weathered Rock	0.0233
L7	10.25-10.75	Rock	0.0262

TABLE 7.12 Distribution of Chlorine as a Function of Depth through a Guatemalan Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cl % (NAA Method)
L1	1.50-2.00	Superficial Laterite	0.0531
L2	2.50-3.00	Plastic Laterite	0.0435
L3	3.50-4.00	Saprolite	0.0600
L4	5.25-5.75	Boulders in Saprolite	0.0220
L6	8.00-8.50	Fine of Weathered Rock	0.0576
L5	8.00-8.50	Weathered Rock	0.0193
L6	10.25-10.75	Rock	0.0221

TABLE 7.13 Distribution of Cobalt as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Co % (Chemical Method)	Co % (NAA Method)
BNC1	0 - 2	Ferricrete	0.062	0.057
BNC2	2 - 7	Limonite	0.081	0.079
BNC3	7 - 11	Limonite	0.106	0.093
BNC4	11 - 13	Limonite	0.151	0.150
BNC5	13 - 14	Limonite & Asbolite	0.256	0.251
BNC6	14 - 17	Limonite & Asbolite	0.157	0.135
BNC7	17 - 20	Saprolite	0.089	0.080

TABLE 7.14 Distribution of Copper as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cu % (Chemical Method)	Cu % (NAA Method)
BNC1	0 - 2	Ferricrete	0.133	0.118
BNC2	2 - 7	Limonite	0.150	0.129
BNC3	7 - 11	Limonite	0.173	0.156
BNC4	11 - 13	Limonite	0.254	0.235
BNC5	13 - 14	Limonite & Asbolite	0.270	0.230
BNC6	14 - 17	Limonite & Asbolite	0.221	0.210
BNC7	17 - 20	Saprolite	0.156	0.134

TABLE 7.15 Distribution of Nickel as a function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Ni % (Chemical Method)	Ni % (NAA Method)
BNC1	0 - 2	Ferricrete	0.73	0.71
BNC2	2 - 7	Limonite	1.52	1.47
BNC3	7 - 11	Limonite	1.65	1.59
BNC4	11 - 13	Limonite	1.41	1.35
BNC5	13 - 14	Limonite & Asbolite	1.75	1.71
BNC6	14 - 17	Limonite & Asbolite	3.21	3.10
BNC7	17 - 20	Saprolite	1.61	1.56

TABLE 7.16 Distribution of Iron as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Fe % (Chemical Method)	Fe % (NAA Method)
BNC1	0 - 2	Ferricrete	47.0	46.7
BNC2	2 - 7	Limonite	49.5	48.5
BNC3	7 - 11	Limonite	51.0	49.1
BNC4	11 - 13	Limonite	49.5	49.3
BNC5	13 - 14	Limonite & Asbolite	52.3	52.0
BNC6	14 - 17	Limonite & Asbolite	38.1	38.8
BNC7	17 - 20	Saprolite	12.5	11.3

TABLE 7.17 Distribution of Chromium as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cr % (Chemical Method)	Cr % (NAA Method)
BNC1	0 - 2	Ferricrete	0.314	0.350
BNC2	2 - 7	Limonite	0.340	0.338
BNC3	7 - 11	Limonite	0.830	0.689
BNC4	11 - 13	Limonite	1.504	1.471
BNC5	13 - 14	Limonite & Asbolite	1.754	1.652
BNC6	14 - 17	Limonite & Asbolite	2.154	2.035
BNC7	17 - 20	Saprolite	1.051	1.010

TABLE 7.18 Distribution of Manganese as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mn % (Chemical Method)	Mn % (NAA Method)
BNC1	0 - 2	Ferricrete	0.127	0.142
BNC2	2 - 7	Limonite	0.209	0.210
BNC3	7 - 11	Limonite	0.195	0.200
BNC4	11 - 13	Limonite	0.253	0.254
BNC5	13 - 14	Limonite & Asbolite	1.803	1.800
BNC6	14 - 17	Limonite & Asbolite	1.716	1.685
BNC7	17 - 20	Saprolite	0.673	0.715

TABLE 7.19 Distribution of Silica as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	SiO_2 % (Chemical Method)
BNC1	0 - 2	Ferricrete	3.85
BNC2	2 - 7	Limonite	2.65
BNC3	7 - 11	Limonite	4.15
BNC4	11 - 13	Limonite	4.75
BNC5	13 - 14	Limonite & Asbolite	4.25
BNC6	14 - 17	Limonite & Asbolite	14.08
BNC7	17 - 20	Saprolite	26.32

TABLE 7.20 Distribution of Magnesium as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mg % (Chemical Method)
BNC1	0 - 2	Ferricrete	Less than 0.2
BNC2	2 - 7	Limonite	"
BNC3	7 - 11	Limonite	"
BNC4	11 - 13	Limonite	0.2
BNC5	13 - 14	Limonite & Asbolite	0.8
BNC6	14 - 17	Limonite & Asbolite	1.4
BNC7	17 - 20	Saprolite	11.2

TABLE 7.21 Distribution of Scandium as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Sc (ppm) (NAA Method)
BNC1	0 - 2	Ferricrete	98
BNC2	2 - 7	Limonite	108
BNC3	7 - 11	Limonite	110
BNC4	11 - 13	Limonite	84
BNC5	13 - 14	Limonite & Asbolite	122
BNC6	14 - 17	Limonite & Asbolite	96
BNC7	17 - 20	Saprolite	55

TABLE 7.22 Distribution of Zinc as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Zn % (NAA Method)
BNC1	0 - 2	Ferricrete	0.68
BNC2	2 - 7	Limonite	0.63
BNC3	7 - 11	Limonite	0.65
BNC4	11 - 13	Limonite	0.64
BNC5	13 - 14	Limonite & Asbolite	0.94
BNC6	14 - 17	Limonite & Asbolite	0.91
BNC7	17 - 20	Saprolite	0.07

TABLE 7.23 Distribution of Sodium as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample	Depth (m)	Description	Na % (NAA Method)
BNC1	0 - 2	Ferricrete	-
BNC2	2 - 7	Limonite	-
BNC3	7 - 11	Limonite	0.026
BNC4	11 - 13	Limonite	0.012
BNC5	13 - 14	Limonite & Asbolite	0.043
BNC6	14 - 17	Limonite & Asbolite	0.066
BNC7	17 - 20	Saprolite	0.127

TABLE 7.24 Distribution of Chlorine as a Function of Depth through a New Caledonian Lateritic-Ore Deposit

Location & Sample	Depth (m)	Description	Cl % (NAA Method)
BNC1	0 - 2	Ferricrete	0.027
BNC2	2 - 7	Limonite	0.017
BNC3	7 - 11	Limonite	0.038
BNC4	11 - 13	Limonite	0.043
BNC5	13 - 14	Limonite & Asbolite	0.271
BNC6	14 - 17	Limonite & Asbolite	0.315
BNC	17 - 20	Saprolite	0.260

TABLE 7.25 Distribution of Iron as a Function of Depth through a Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Fe % (Chemical Method)	Fe % (NAA Method)
BIP1	11-13	Limonite & Asbolite	49.13	49.05
BIP2	13-17	Saprolite	20.81	19.10
BIP3	18-19	Saprolite & Quartz boxwork	10.15	9.13

TABLE 7.26 Distribution of Nickel as a Function of Depth through a Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Ni % (Chemical Method)	Ni % (NAA Method)
BIP1	11-13	Limonite & Asbolite	1.46	1.40
BIP2	13-17	Saprolite	2.83	2.71
BIP3	18-19	Saprolite & Quartz boxwork	2.41	2.35

TABLE 7.27 Distribution of Cobalt as a Function of Depth through a Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Co % (Chemical Method)	Co % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.123	0.116
BIP2	13-17	Saprolite	0.064	0.059
BIP3	18-19	Saprolite & Quartz boxwork	0.031	0.022

TABLE 7.28 Distribution of Copper as a Function of Depth through a Indonesian Lateritic-Ore Deposit

Location & Sample	Depth (m)	Description	Cu % (Chemical Method)	Cu % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.075	0.070
BIP2	13-17	Saprolite	0.115	0.113
BIP3	18-19	Saprolite & Quartz boxwork	0.051	0.048

TABLE 7.29 Distribution of Magnesium as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mg % (Chemical Method)	Mg % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.261	-
BIP2	13-17	Saprolite	8.284	-
BIP3	18-19	Saprolite & Quartz boxwork	10.442	-

TABLE 7.30 Distribution of Silica as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	SiO_2 % (Chemical Method)
BIP1	11-13	Limonite & Asbolite	4.34
BIP2	13-17	Saprolite	22.04
BIP3	18-19	Saprolite & Quartz boxwork	27.60

TABLE 7.31 Distribution of Sodium as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Na % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.0021
BIP2	13-17	Saprolite	0.0027
BIP3	18-19	Saprolite & Quartz boxwork	0.0011

TABLE 7.32 Distribution of Chlorine as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cl % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.074
BIP2	13-17	Saprolite	0.033
BIP3	18-19	Saprolite & Quartz boxwork	0.020

TABLE 7.33 Distribution of Scandium as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Sc (ppm) (NAA Method)
BIP1	11-13	Limonite & Asbolite	90
BIP2	13-17	Saprolite	56
BIP3	18-19	Saprolite & Quartz boxwork	18

TABLE 7.34 Distribution of Zinc as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Zn % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.0110
BIP2	13-17	Saprolite	0.0066
BIP3	18-19	Saprolite & Quartz boxwork	0.0019

TABLE 7.35 Distribution of Chromium as a Function of Depth through a Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Cr % (Chemical Method)	Cr % (NAA Method)
BIP1	11-13	Limonite & Asbolite	1.35	1.21
BIP2	13-17	Saprolite	1.05	0.98
BIP3	18-19	Saprolite & Quartz boxwork	0.37	0.35

TABLE 7.36 Distribution of Manganese as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location & Sample No.	Depth (m)	Description	Mn % (Chemical Method)	Mn % (NAA Method)
BIP1	11-13	Limonite & Asbolite	0.819	0.812
BIP2	13-17	Saprolite	0.638	0.680
BIP3	18-19	Saprolite & Quartz boxwork	0.267	0.260

RADIOCHEMICAL DETERMINATION OF URANIUM

Uranium was determined using a modification of the radiochemical method developed by Baltakmens(1975).

Reagents

Yttrium^{III} carrier 5 mg/cm^3

Uranium(natural istopic ratio)

Standard solution: 2.5 µg / cm^3

HCl : conc.

HCl : 8N

HCl : 0.5N

HNO_3: conc.

H_2SO_4: 2N

H_2SO_4:0.1N

Procedure

Weigh 3 grams of the powdered sample and transfer it to a 250 cm^3 beaker. Add ca 15 cm^3 of aqua regia and evaporate almost to dryness on a hot plate. Dissolve the residue by boiling gently for a few minutes with 8M hydrochloric acid. Let the solution cool and filter off the silica. Pass the filterate through an anion exchange column (1cm-diam.) con--taining 8cm^3 of FF IP SRA 66, 52-100 mesh (or equivalent) resin, which has been pretreated with 15cm^3 of 8M HCl, allow a flow rate of about 1-1.5cm^3 min^{-1}. Wash the column with 15cm^3 of 8M HCl, followed by 25cm^3 of 0.5N HCl. Natural radioactive elements present in the sample, (U, Pa, Bi, Po) are sorbed on the column ; Th, Ra, Ac, Pb are not and pass through the column. Of the major stable elements, only Fe(III) is sorbed, e.g.,Al, Ca, Mg are not (Baltakmens 1975).

Elution with 0.5M HCl removes U, Pa, and Fe(III); Bi and Po remain on the column.

Evaporate the 0.5M HCl eluate to dryness over low heat, then dissolve the residue by warming with $5cm^3$ of 2N sulphuric acid. Cool the solution, dilute to $100cm^3$ with demineralized water and pass through an identical column, to that used previously but this time pretreated with $15cm^3$ of 0.1M H_2SO_4. Uranium and Pa are sorbed on this second column, together with a small amount of Fe. Washing with $50cm^3$ of 0.1M H_2SO_4 removes most of the sorbed Fe. Fifty cm^3 of 0.5M HCl are than passed through the column , and the first $15cm^3$ of eluate are discarded this may contain traces of Fe and the subsequent eluate is collected. This 15--$50cm^3$ fraction contains the Uranium. One cm^3 of yttrium^{III} carrier solution(equivalent to 5mg of yttrium) is added, the solution boiled, and the uranium is co-precipitated on $Y(OH)_3$ by addition of carbonate-free ammonium hydroxide. After cooling the precipitate is filtered on a weighed 1 inch diameter sintered glass disc. Uranium can be found by counting the $Y(OH)_3$ source after a suitable interval(1 day).

The procedure for comparators is exactly the same as used for the sample.

Uranium content was calculated from the equation:

$$\text{Weight of U in sample} = \frac{Ys}{Ystd} \times \text{Weight of U in std.}$$

Data on analyzed samples is given in tables 7.37-7.39.

TABLE 7.37 Distribution of Uranium as a Function of Depth through a Guatemalan Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	U (ppb) (Radiochemical Method)
L1	1.5-2.00	Surficial Laterite	6.33
L2	2.50-3.00	Plastic Laterite	8.45
L3	3.50-4.00	Saprolite	16.90
L4	5.25-5.75	Boulders in Saprolite	12.67
L6	8.00-8.50	Fine of Weathered Rock	12.50
L5	8.00-8.50	Weathered Rock	10.78
L7	10.25-10.75	Rock	7.56

TABLE 7.38 Distribution of Uranium as a Function of Depth through a New Caledonian Lateritic Nickel-Ore Deposit

Location & Sample No.	Depth (m)	Description	U (ppb) (Radiochemical Method)
BNC1	0 - 2	Ferricrete	4.00
BNC2	2 - 7	Limonite	4.22
BNC3	7 - 11	Limonite	6.35
BNC4	11 - 13	Limonite	12.50
BNC5	13 - 14	Limonite & Asbolite	10.56
BNC6	14 - 17	"	33.80
BNC7	17 - 20	Saprolite	17.46

Table 7.39 Distribution of Uranium as a Function of Depth through an Indonesian Lateritic-Ore Deposit

Location Sample No.	Depth (m)	Description	U (ppb) (Radiochemical Method)
BIP1	11-13	Limonite & Asbolite	16.90
BIP2	13-17	Saprolite	42.22
BIP3	18-19	Saprolite & Quartz boxwork	12.69

pH DETERMINATION

pH measurements were made in order to gain information on possible effects of acidity on the distribution of the elements in the lateritic samples.

Determinations were made by adding 50 cm^3 of distilled water (pH 6.5–6.8) to 1 gram of disaggregated sample in a polythene tube. The tube was agitated for 2 hours. After 12 hours the pH of the solution was measured with a Beckmann G-type labortary pH-meter at ca. 20°C. All operations were carried out in an atmosphere of nitrogen (the specially designed vessel used for this experiment is shown in Fig. 7.1). Results are given in tables 7.40.

The pH measurements reported here should be considered as only approximating to the natural waters, because they were made under labortary conditions rather than field conditions. However, the actual values and the trends from sample to sample are similar to those that might be expected to be typical of lateritic soils. On the other hand, there are considerable differences between the three profiles studied. Some overall interpretations can be made in a very general way.

1- The pH values of all three profiles increase with the depth (pH 5–9).

2- Top surficial horizons are acidic in BNC and BIP. In the case of the L profile pH measurements in A-horizon is 7.05(slightly basic) and the high Mg content in this A-horizon suggests that there is some basic rock content left.

3- An important feature in all three profiles is the correlation between depth of distribution of elements and pH at which precipitation of their hydroxides commences.

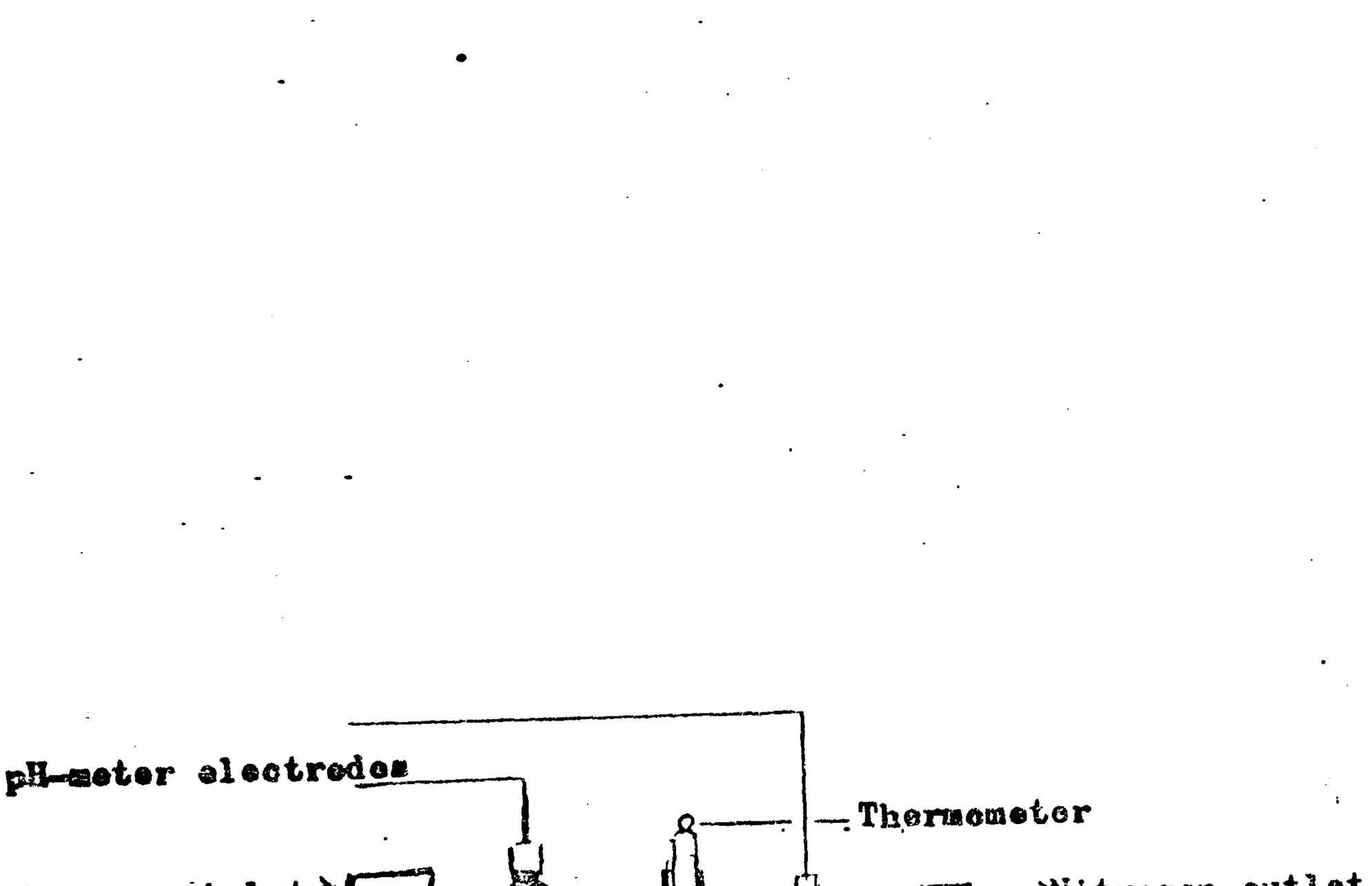


Fig. 7.1 Vessel used for pH measurements

TABLE 7.40 pH as a function of depth in all three profile.

Location & Sample No.	Depth (M)	Description	pH values
L1	1.50–2.00	Surficial Laterite	7.05
L2	2.5–3.00	Plastic Laterite	7.2
L3	3.50–4.00	Saprolite	7.5
L4	5.25–5.75	Boulders in Saprolite	8.3
L6	8.00–8.50	Fine of Weathered Rock	7.5
L5	8.00–8.50	Weathered Rock	8.2
L7	10.25–10.75	Rock	9.2
BNC–Profile			
BNC1	0 - 2	Ferricrete	6.5
BNC2	2 - 7	Limonite	6.2
BNC3	7 - 11	Limonite	5.9
BNC4	11 - 13	Limonite	5.8
BNC5	13 - 14	Limonite & Asbolite	6.3
BNC6	14 - 17	"	7.3–7.8
BNC7	17 - 20	Saprolite	8.25–9.00
BIP–Profile			
BIP1	11 - 13	Limonite & Asbolite	6.8–7.00
BIP2	13 - 17	Saprolite	7.0–7.3
BIP3	18 - 19	Saprolite & Quartz boxwork	7.8–8.3

SOLUBLE CHLORIDE DETERMINATION

A water leaching experiment was also performed to determine the soluble chloride content of the samples. One gram samples were leached with 25cm^3 of pure distilled water. The soaked samples were agitated for two hours on a shaker. After 24 hours the supernate was filtered through a No. 450 Whatman filter paper into a 20 cm^3 volumeteric flask and made up to the mark with conductivity water. A 0.5 cm^3 aliquot was weighed into a small polythene tube. Standards were prepared from 0.01M HCl solution.

Samples and comparators were packed togather in a 1 inch wide X 4inches long polythene container and sent for irradiation in the nuclear reactor HERALD. A thermal flux of 2.5x 10^{12} n cm^{-2} s^{-1} was used. After irradiation for 1/2 hour the samples were immediatly returned to our laboratory for counting. A Ge-Li detector was used for the the activity measurement. Results are given in table 7.4l.

It may be commented here that photopeaks of radionuclides formed by activation of cobalt and manganese were noted in the spectra: this suggest that at least some of these two elements may be present in the lateritic samples in a water-soluble chemical form, e.g. as chloride.

TABLE 7.41

Location & Sample No.	Depth (M)	Description	Cl % (INNA)
L1	1.5–2.00	Surficial Laterite	0.0013
L2	2.5–3.00	Plastic Laterite	0.0012
L3	3.5–4.00	Saprolite	0.0057
L4	5.25–5.75	Boulders in Saprolite	0.0051
L5	8.00–8.50	Fine of Weathered Rock	0.0054
L5	8.00–8.50	Weathered Rock	0.0031
L7	10.25–10.75	Rock	0.0012
BNC-Profile			
BNC1	0 – 2	Ferricrete	0.0070
BNC2	2 – 7	Limonite	0.0067
BNC3	7 – 11	Limonite	0.0193
BNC4	11 – 13	Limonite	0.0198
BNC5	13 – 14	Limonite & Asbolite	0.1925
BNC6	14 – 17	"	0.0962
BNC7	17 – 20	Saprolite	0.1231
BIP- Profile			
BIP1	11 – 13	Limonite & Asbolite	0.059
BIP2	13 – 17	Saprolite	0.022
BIP3	18 – 19	Saprolite & Quartz boxwork	0.014

DETERMINATION OF MOISTURE CONTENT

Weigh 1 gram of the sample, and transfer it to a clean, weighed 30 ml platinum crucible. Weigh the covered crucible and sample ; the difference in weight of the sample should not exceed o.1 mg. Place the uncovered crucible in an oven, cover it with a 7 cm diameter filter paper, and heat it at 105–110 ^{o}C for 1 hour. Transfer the crucible to a desiccator, cover and allow it to cool for 30 min before weighing.

Heating, cooling and weighing was sometime repeated until constant weight is obtained. Loss in weight will be moisture content of the sample.

TABLE 7.42 Moisture content in the samples as a function of depth

Location & Sample No.	Depth (M)	Description	Moisture Content %
L1	1.5–2.00	Surficial Laterite	4.9
L2	2.5–3.00	Plastic Laterite	5.6
L3	3.5–4.00	Saprolite	5.7
L4	5.25–5.75	Boulders in Saprolite	5.7
L6	8.00–8.50	Fines of Weathered Rock	8.1
L5	8.00–8.50	Weathered Rock	8.0
L7	10.25–10.75	Rock	3.4
BNC-Profile			
BNC1	0 - 2	Ferricrete	4.5
BNC2	2 - 7	Limonite	6.3
BNC3	7 - 11	Limonite	4.6
BNC4	11 - 13	Limonite	2.5
BNC5	13 - 14	Limonite & Asbolite	2.7
BNC6	14 - 17	"	2.6
BNC7	17 - 20	Saprolite	1.2
BIP-Profile			
BIP1	11 - 13	Limonite & Asbolite	1.72
BIP2	13 - 17	Saprolite	2.00
BIP3	18 - 19	Saprolite & Quartz boxwork	2.50

CHAPTER 8

INTERPRETIVE TECHNIQUES

MOLECULAR PROPORTION PLOTS

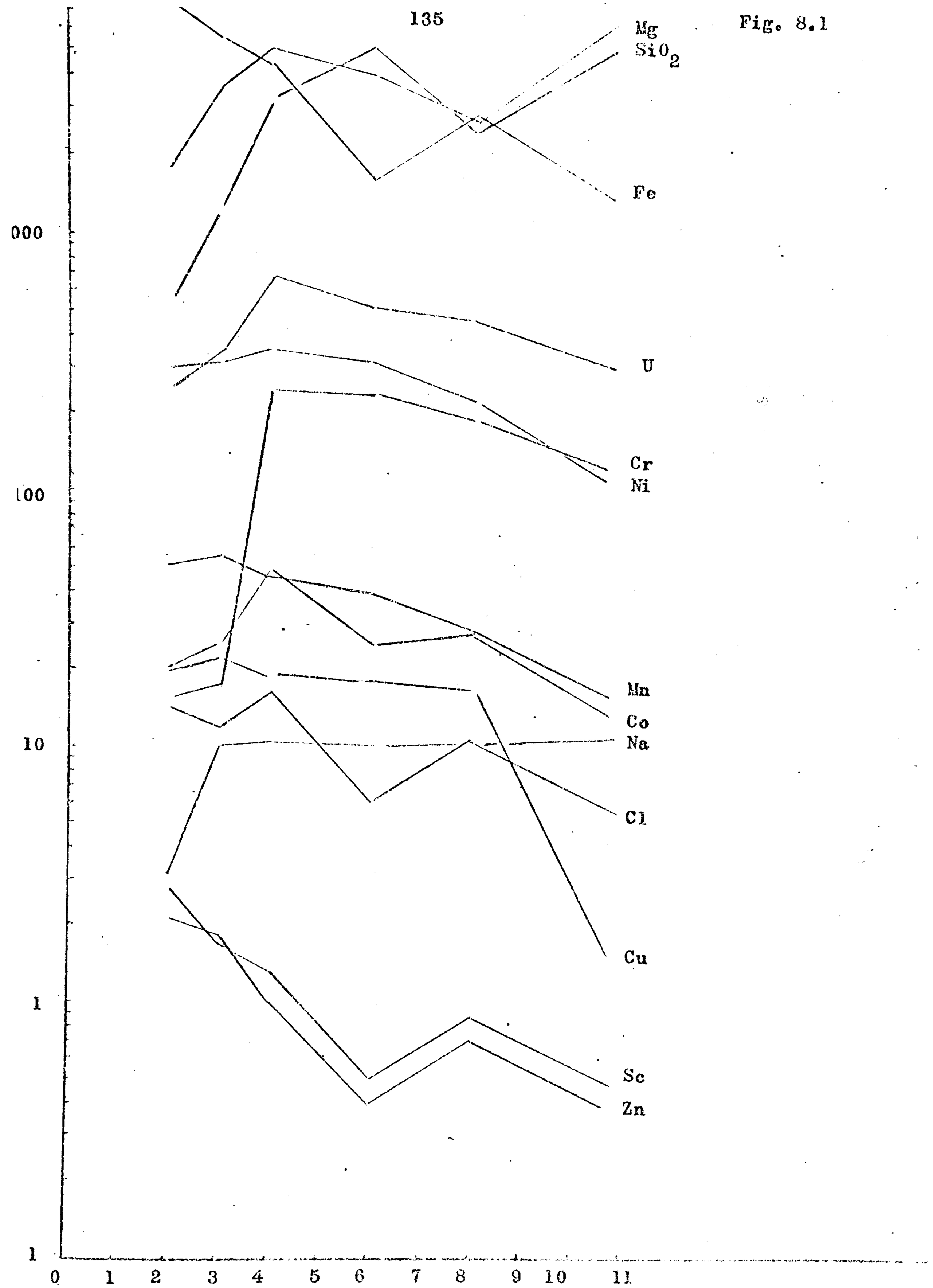
The purpose of the molecular proportion plots (Reiche, 1950) is to show the changes in the chemistry of individual profile with depth. Molecular proportions were used rather than weight percent because chemical changes are a function of the number of molecules rather than the weight of reactant. A logarithmic scale was used for the molecular proportion to allow all the components to be plotted on the same diagram without resorting to different scales for major and minor elements.

Figures 1-6 contains the molecular proportion plots for each profile studied.

The obvious trends shown by the plots are the decrease of Mg, Si and Na from bed rock into soil, and the apparent increase in all other components, although the extent of the relative changes and the depth at which maximum enrichment or depletion occurs varies from profile to profile.

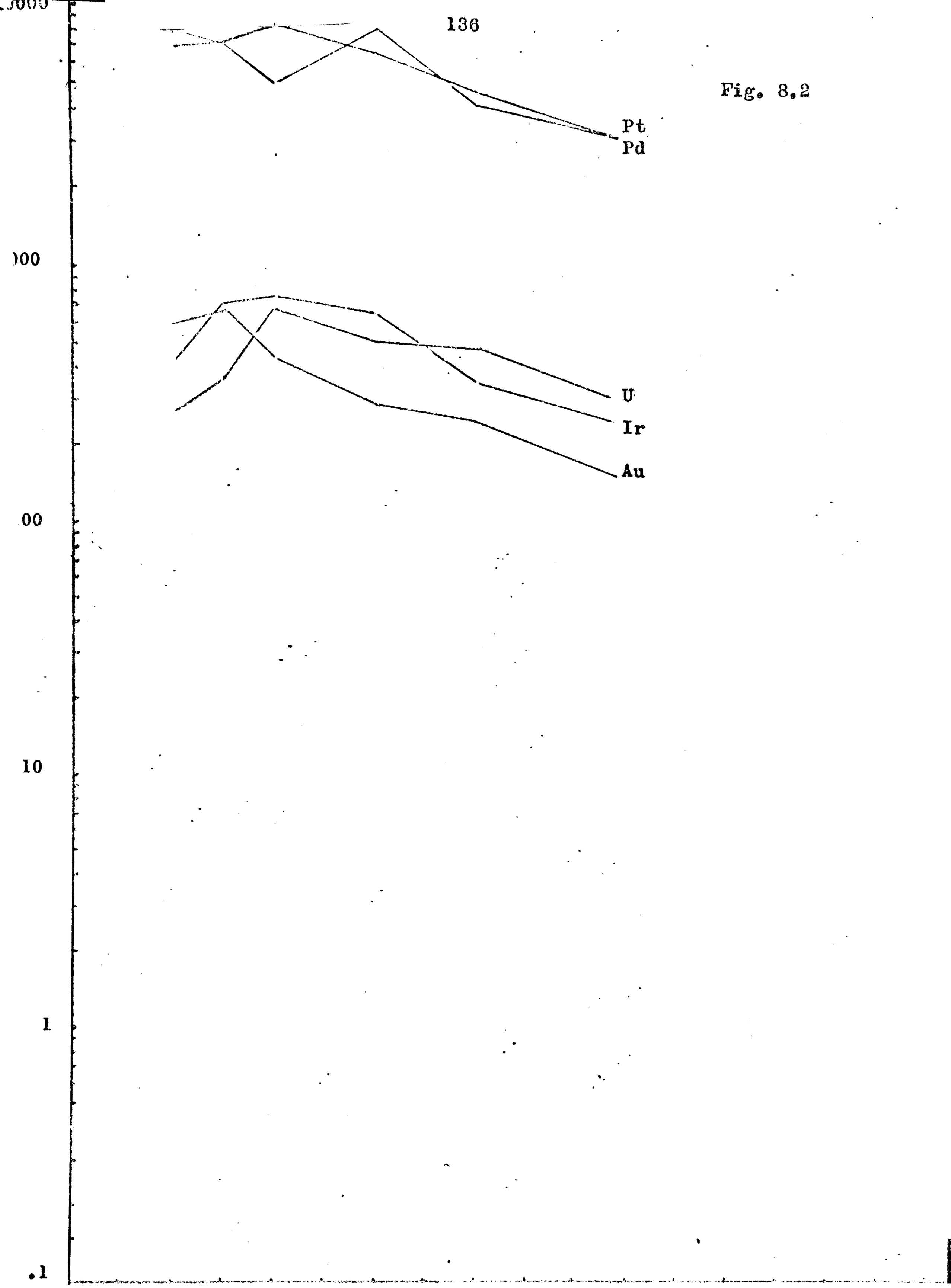
The major elements distribution shown by these plots is similar to variation generally recognised in the weathering of basic and ultrabasic rock. The variation will be discussed in detail in a later section.

Fig. 8.1



GUATEMALAN PROFILE

Fig. 8.2



GUATEMALAN PROFILE

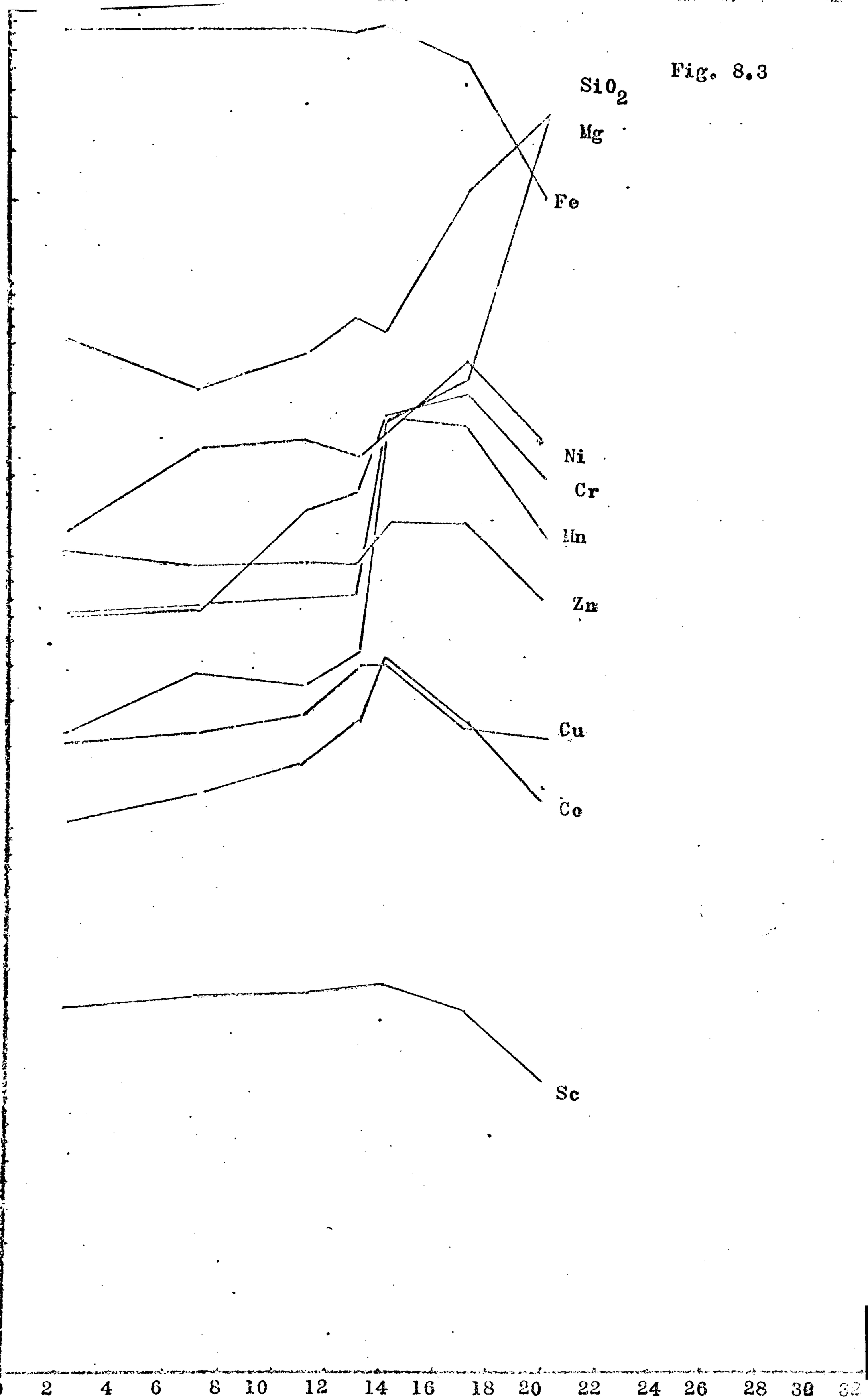


Fig. 8.3

NEW CALEDONIAN PROFILE

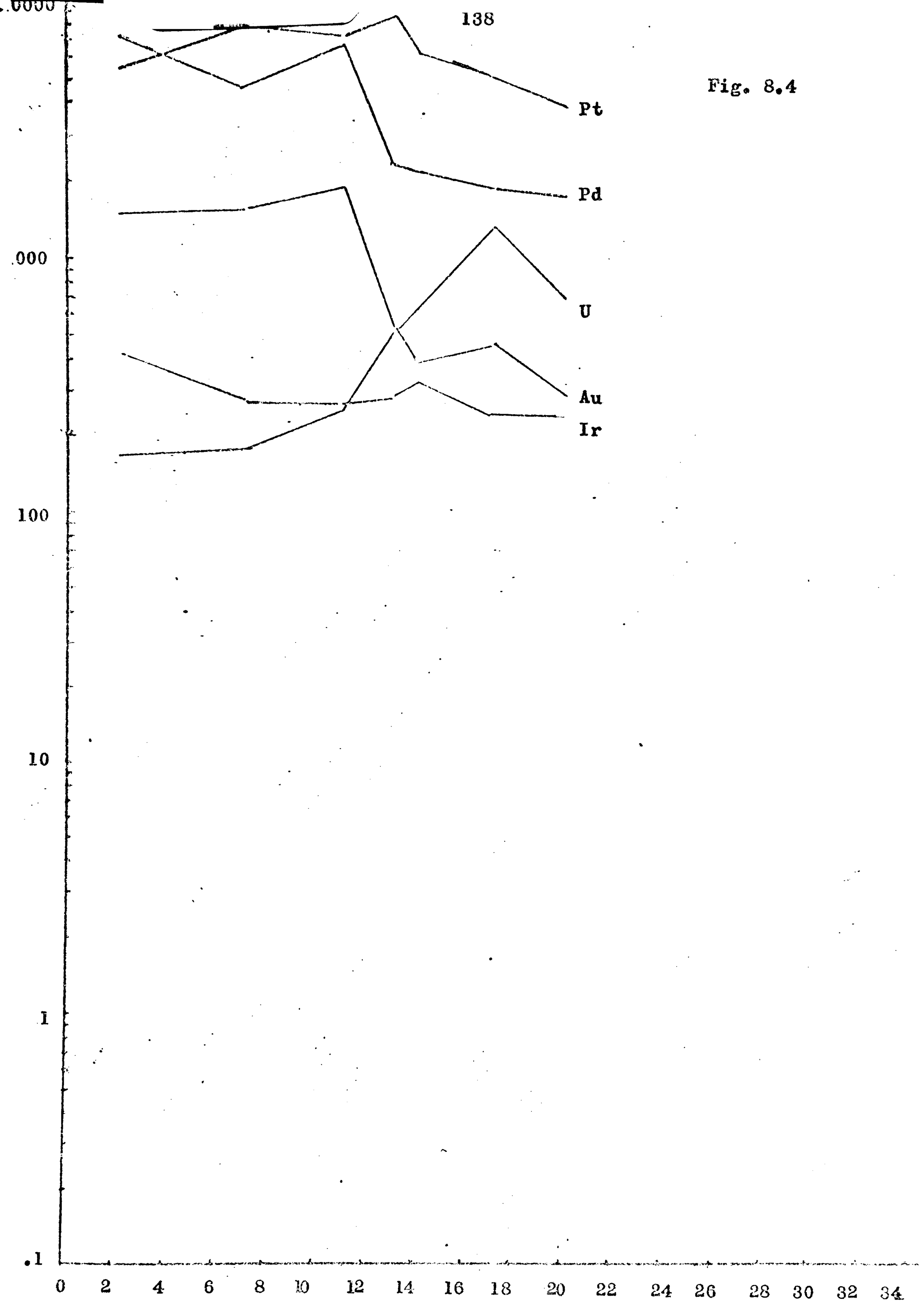


Fig. 8.4

NEW CALEDONIAN PROFILE

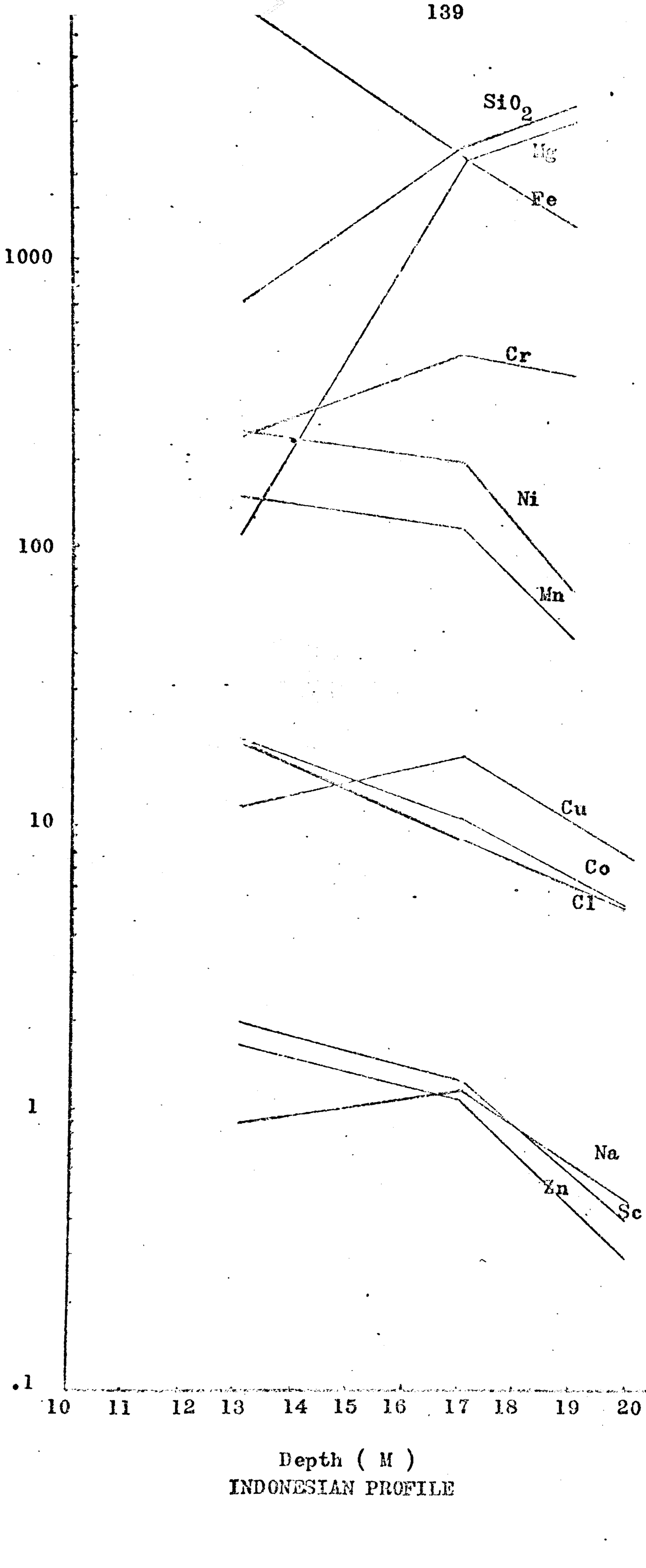


Fig. 8.5

INDONESIAN PROFILE

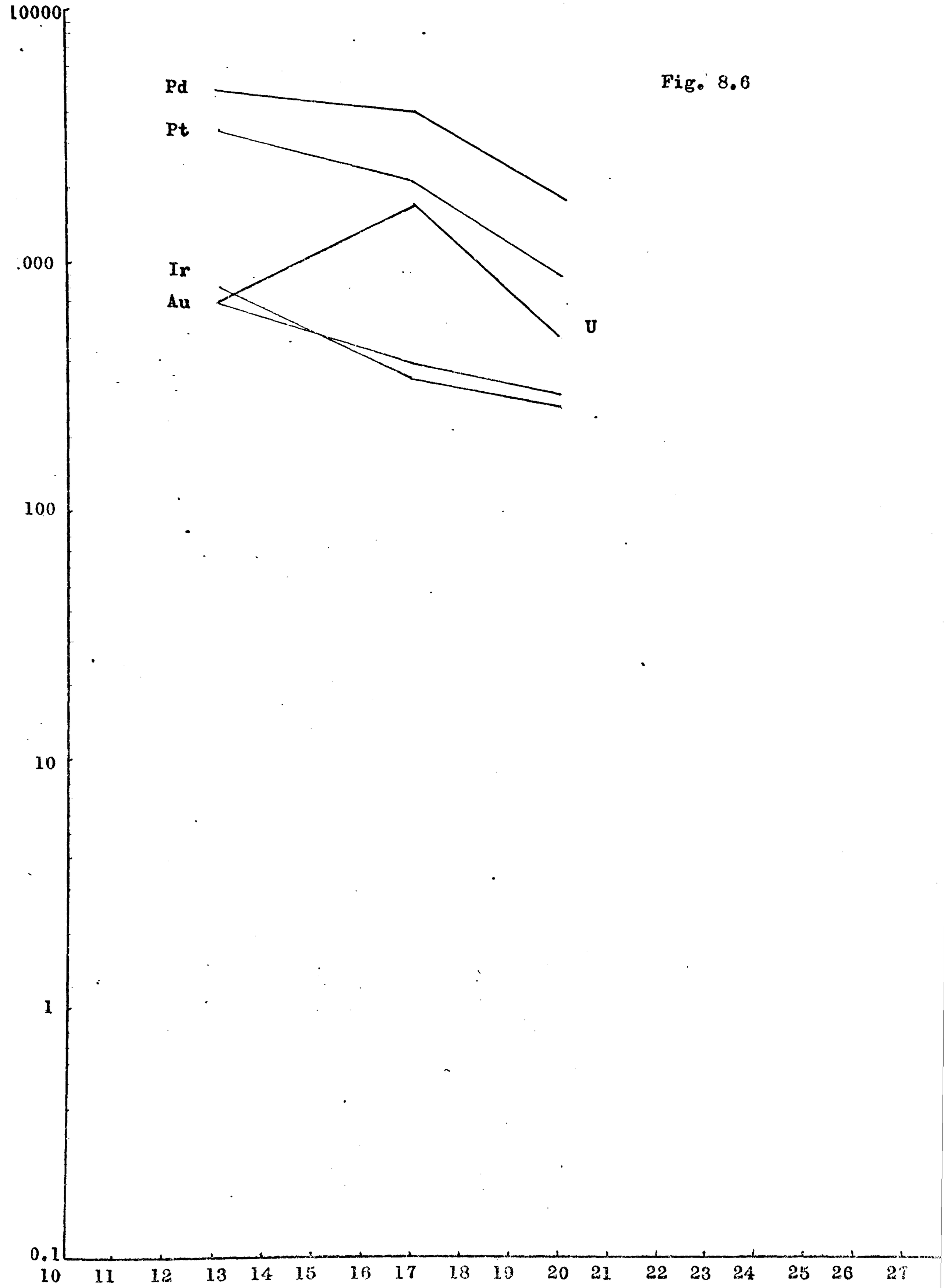


Fig. 8.6

INDONESIAN PROFILE

NET CHANGE PLOTS

The molecular proportion plots show the absolute amount of each element present in different levels of profiles but do not give any information about gains and losses relative to fresh rock. For example, an apparent incease in Fe may be due to depletion of Fe at a slower rate than other elements.

The following expression was used to calculate actual gains and losses:

$$= \frac{\text{Weight (percentage) in weathered rock(laterite)}}{\text{Weight (percentage) in Fresh rock}}$$

As might be expected from the molecular proportion plots, Mg and Si are the most consistent in trend. They are depleted in all three profiles, the extent of depletion increasing toward the surface in every profile. The ranges covered vary from profile to profile, but in general, depletion is more pronounced in the BNC profile than in the less mature profile L.

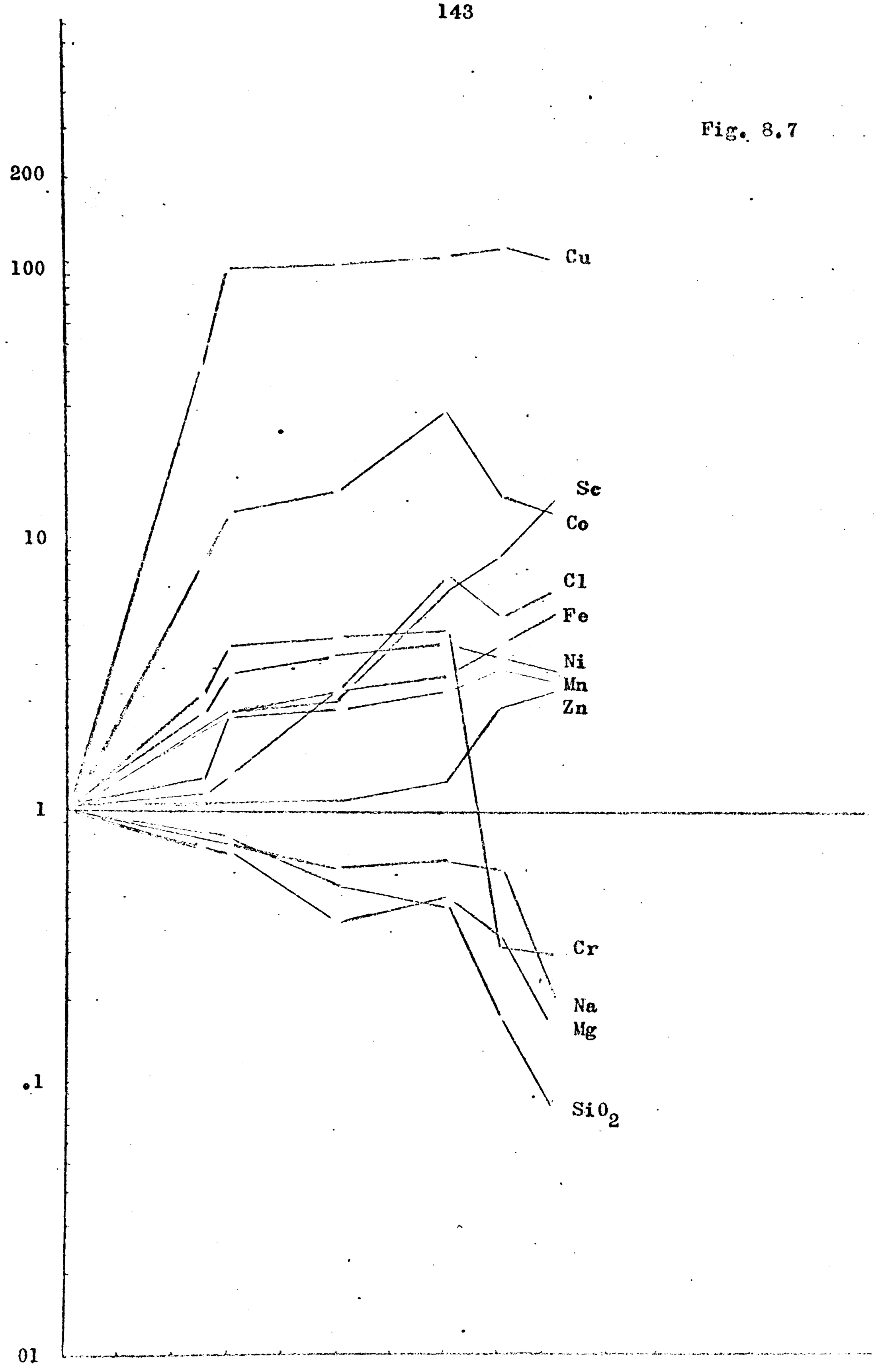
Iron shows absolute gains in all the profiles examined, and Ni, Co, Cr and Mn are also enriched. For each of these elements the zone of maximum enrichment is not necessarily the same for every profile. The BNC profile fig.8.10 shows a distinct tendency for these elements to be enriched at a depth just above the bed rock, whilst, on the other hand in the L profile fig.8.7 they are enriched just below the surface (top layer+intermediate layer).

Zn, Cu and Sc are enriched to some extent in the profiles, but the levels of enrichment do not necessarily coincide for each of these elements.

Na and Cl are depleted in all three profiles, the extent of depletion increasing towards the surface in each case. Cl is slightly enriched at depth relative to fresh rock.

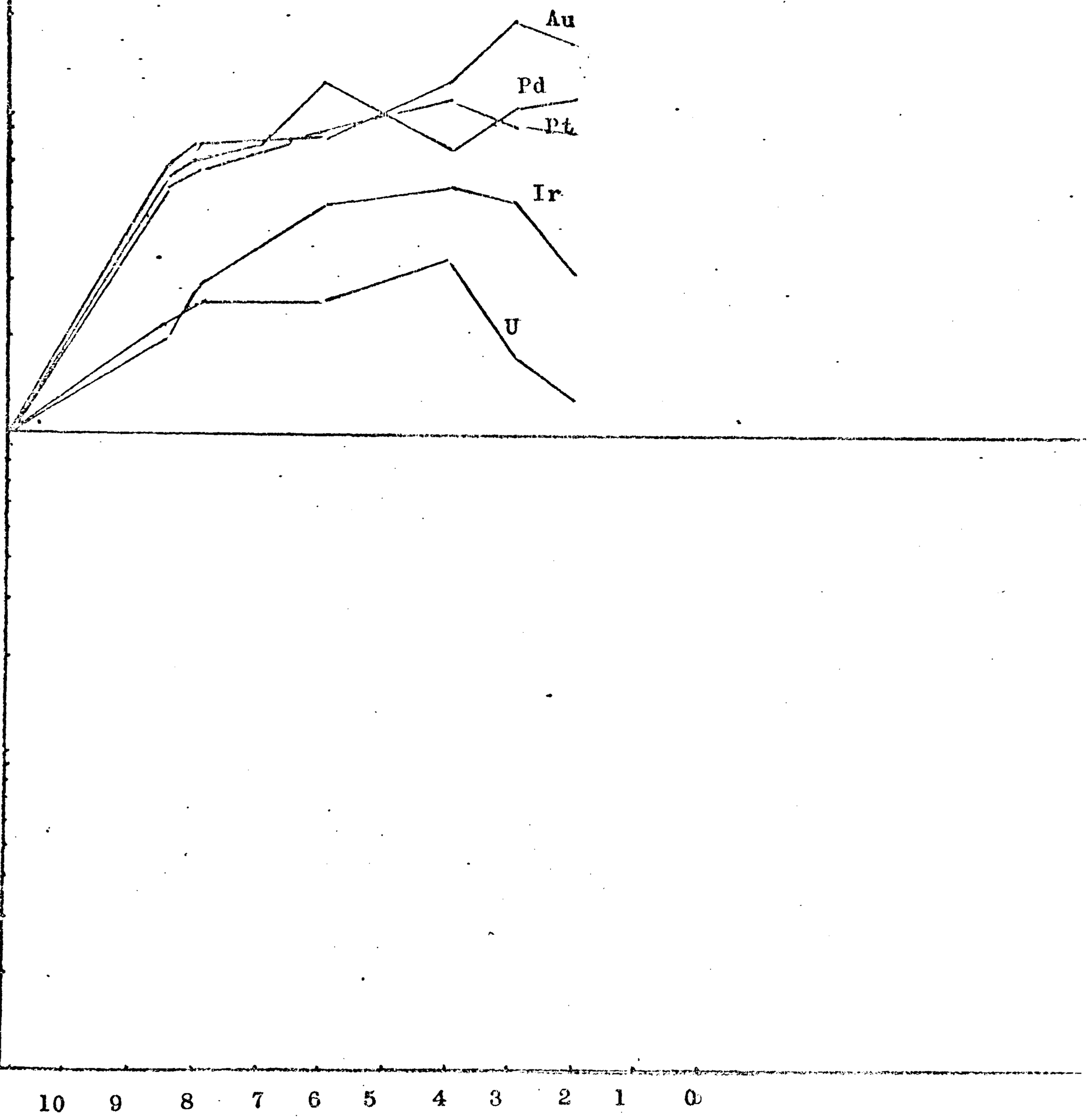
Platinum group metals are enriched in the intermediate zone in the profiles. Concentration in the B horizon indicate the possibility of migration of Pt metals.

Fig. 8.7



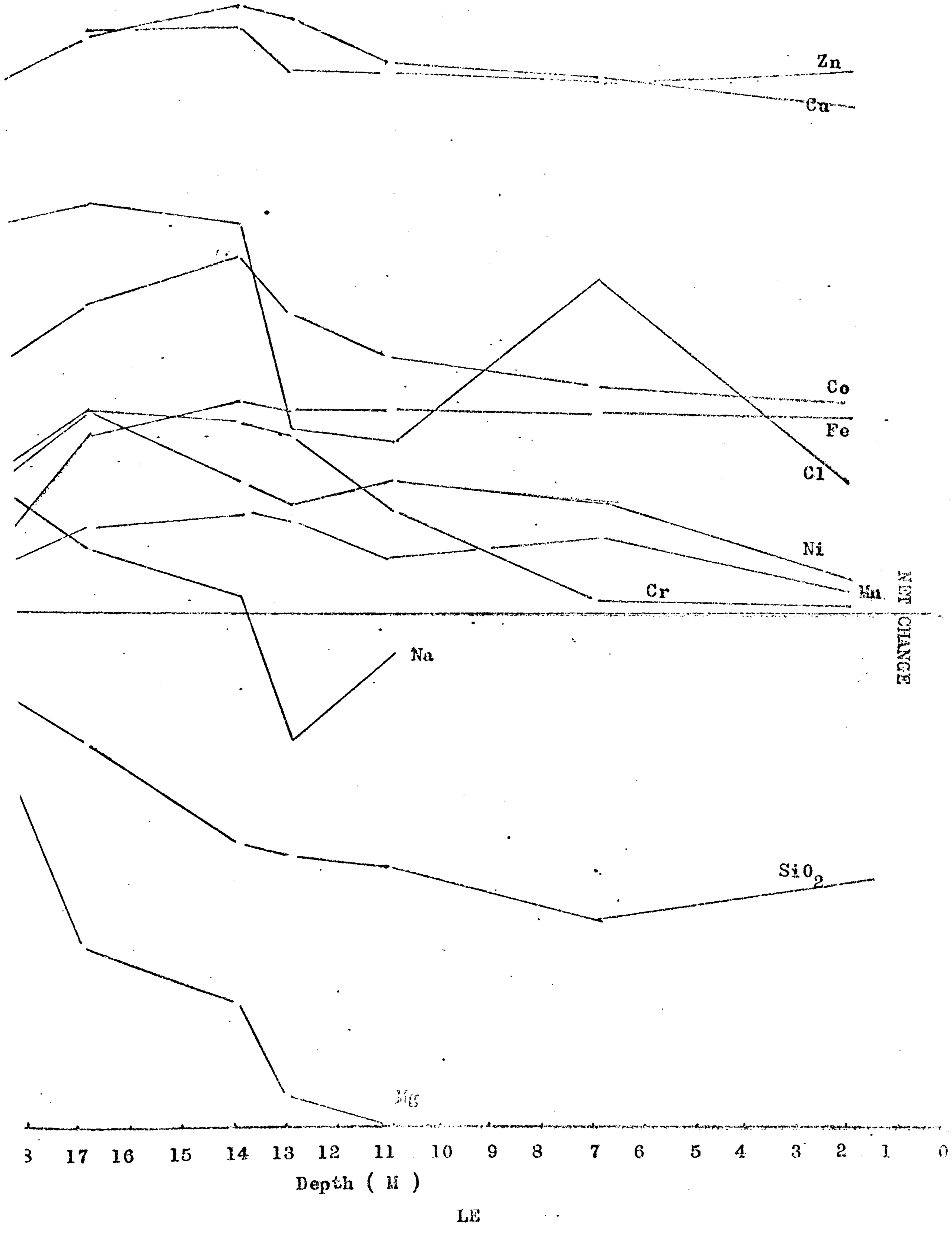
GUATEMALAN PROFILE

Fig. 8.8



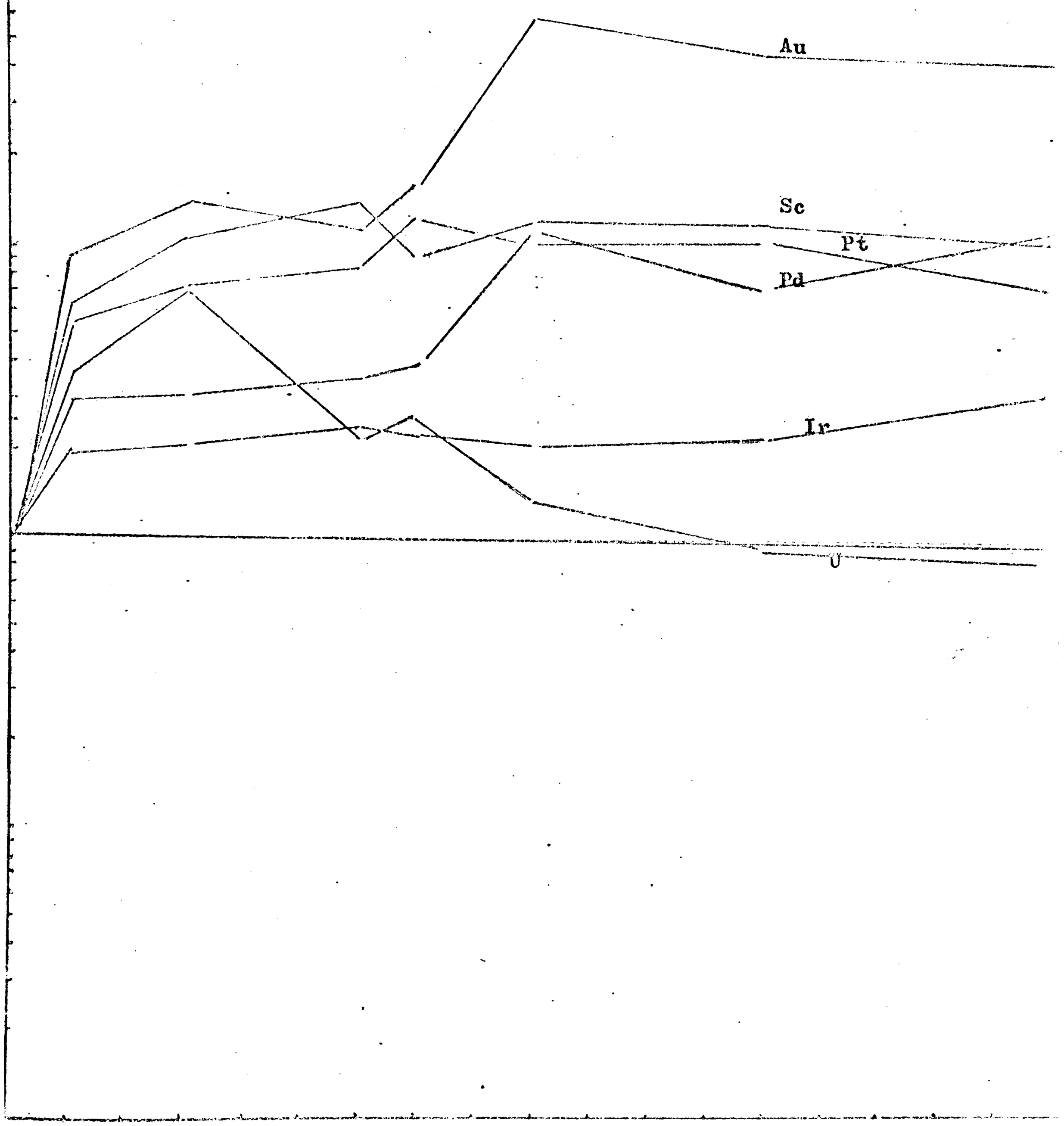
GUATEMALAN PROFILE

Fig. 8.9


Zn
Cu
Co
Fe
Cl
Ni
Mn
Cr
Na
SiO_2
Mg
CHANGE
3 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Depth (M)

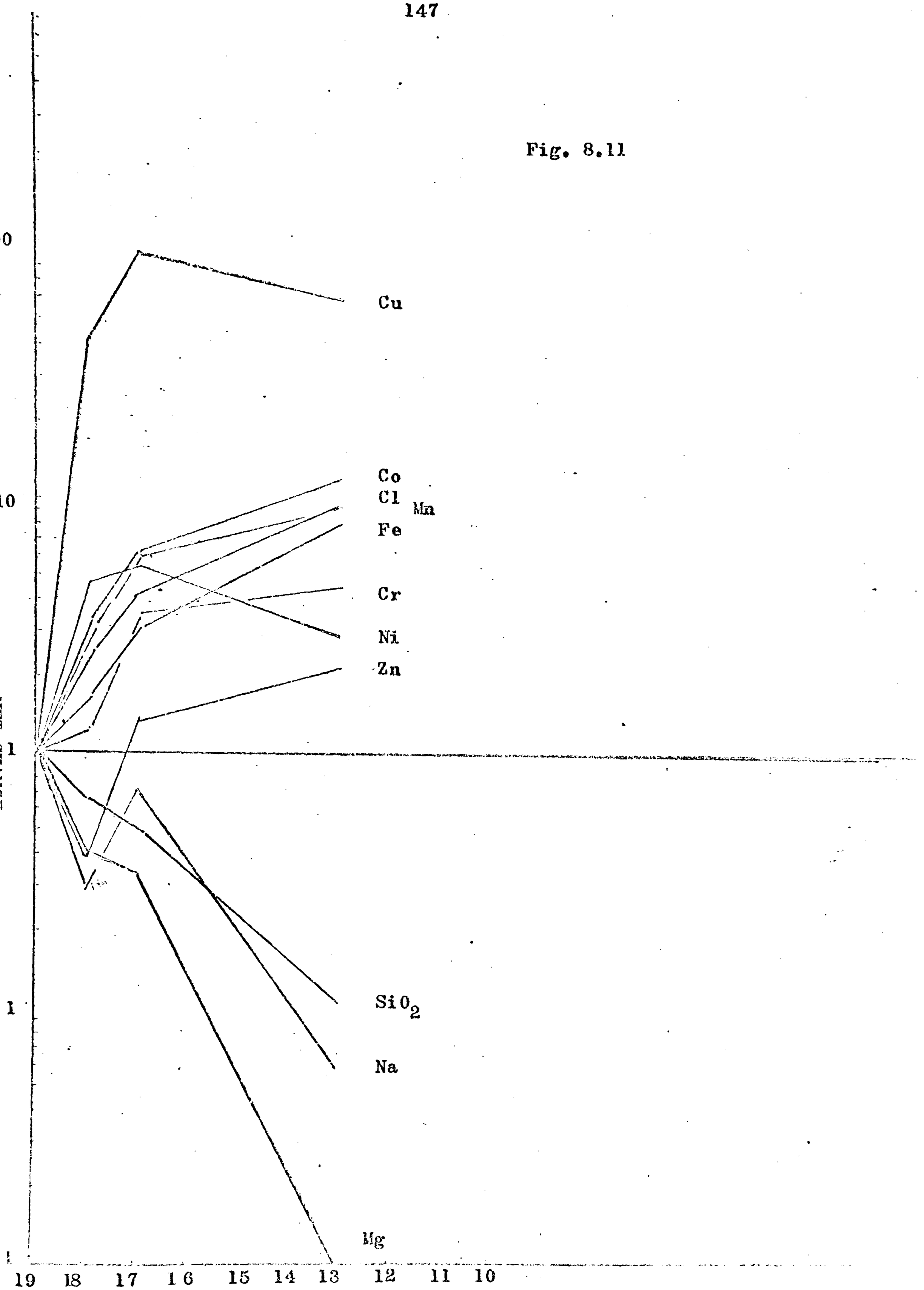
LE

Fig. 8.10



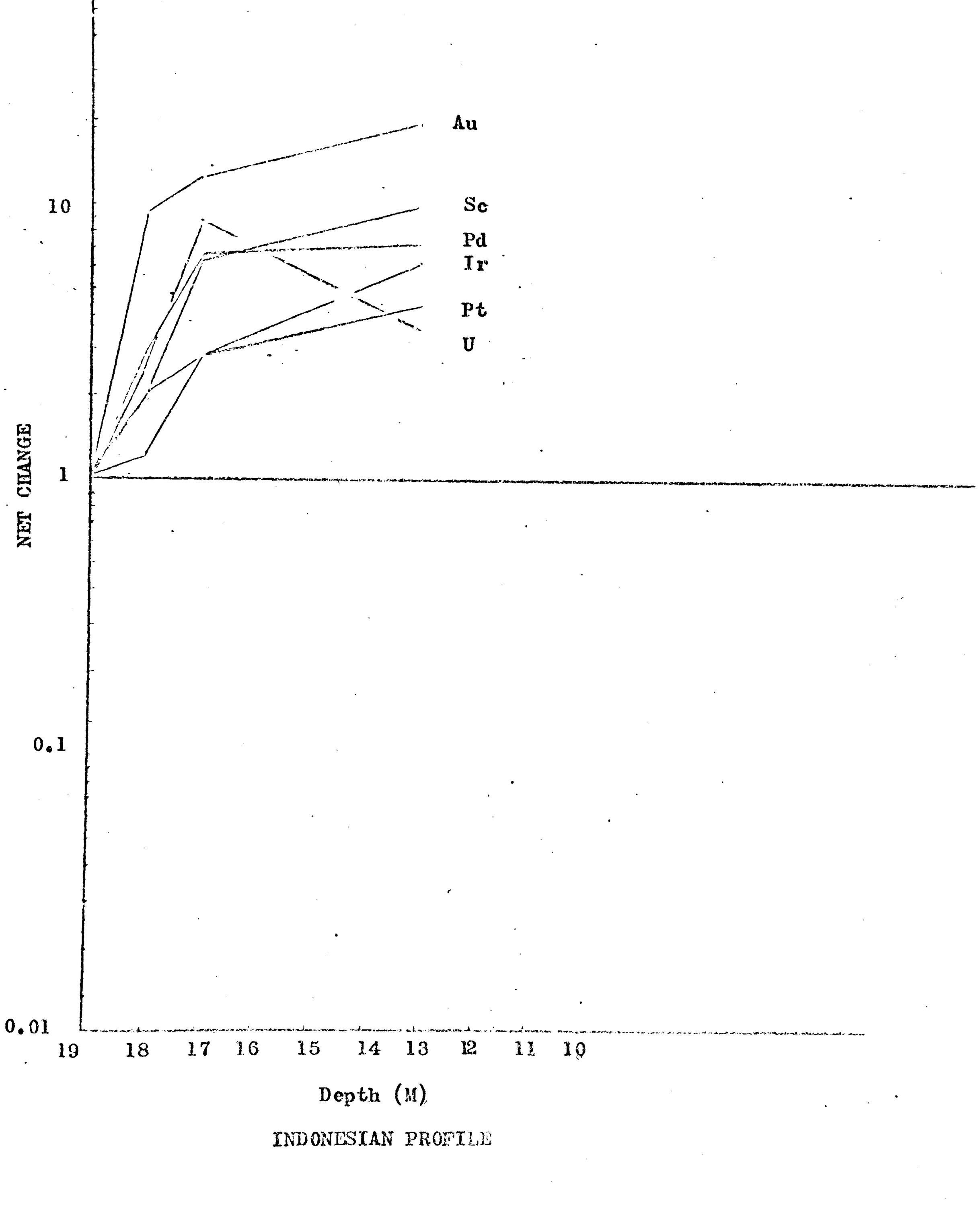
NEW CALEDONIAN PROFILE

Fig. 8.11



INDONESIAN PROFILE

Fig. 8.12



INDONESIAN PROFILE

CORRELATION COEFFICIENTS

The purpose of computing correlation coefficient is to see if two variables, in this case two elements or oxides, are closely associated, and to obtain a quantitative measure of their similarity. In this study a product moment correlation coefficient was computed for all possible pairs of elements, using the following formula:

$$r = \frac{1/N \sum_{i=1}^{n} x_i y_i - \bar{x}\,\bar{y}}{S_x S_y}$$

r= correlation coefficient for variables x and y

N= total number of samples

x_i= values of variable x for the ith sample

y_i= values of variable y for the ith sample

$\bar{x}$= arithmetic mean of N_x values

$\bar{y}$= arithmetic mean of N_y values

S_x= standard deviation of N_x values

S_y= standard deviation of N_y values

The product moment correlation coefficient is a measure of the degree of linearity of points on an X-Y plot. For example, we could take analyzed values for Ni and Co for different samples and plot as points, the value for Co being the x coordinate and the value for Ni the y coordinate. If the 14 points all lie on a striaght line and an incease in Ni corresponds to an increase in Co, we could say that a perfect direct relationship exists between Ni and Co. The product moment correlation coefficient

in such a case would be equal to +1. Conversely if all the points lay on a straight line, and an increase in Ni resulted in a decrease in Co, a perfect inverse relationship exists between the two variables and the correlation coefficient in this case would be -1. On the other hand, if our plotted points were sca-ttered randomly, we would say that no correlation existed and this would give us a correlation coefficient of about zero. We could also obtain a correlation coefficient of 0 even though the points fell on a straight line in two special cases, where this line was either vertical or horizontal. It is easy to see that this condition is indicative of no correlation as one variable changes with no effect on the other. Values of the correlation coefficient can range between 0 and +1 or -1; intermediate values would mean that there is a possibility that correlation exists, values close to 0 would mean that essentially no correlation can be shown, whereas values close to 1 would mean that the variables correlate well.

On the basis of the present data we can not establish any factual trend which would exist in nature overall, and inter-pretations must be made with caution.

Mg, Si and Na form the leached group in all the profiles studied.

Fe, Mn, Zn and Sc are closely associated in all three assemblages indicating that they are probably all present in iron oxides.

Cu appears to be associated with Mn in the deposit L. Perhapes they are fixed by organic matter which is plentiful in the surface horizons of the L profile. Im the BNC profile the lack of such a fixing agent may result in downward migration and fixing of Cu within the iron oxides.

Table 8.13.

Sc	−.87												
Cl	−.21	+.71											
Zn	−.71	+1.0	+.59										
SiO_2	+.73	+.10	−.71	−.88									
Mg	+.89	−.62	−.40	−.33	+.88								
Mn	−.43	+.81	+.64	+.80	−.70	−.42							
Cr	+.38	−.57	+.06	−.71	+.49	+.23	−.26						
Cu	−.38	+.49	+.46	+.54	−.62	−.68	+.80	−.29					
Co	+.06	+.12	+.71	+.04	−.19	−.07	+.43	+.61	+.50				
Ni	−.23	+.44	+.62	+.44	−.45	−.42	+.84	+.19	+.88	+.72			
Fe	−.07	+.96	−.76	+.96	−.90	−.60	+.81	−.56	+.55	+.21	+.62		
U	+.46	−.43	+.07	−.45	+.34	+.19	+.00	+.76	+.34	+.80	+.50	−.30	
Pd	−.40	+.46	+.11	+.49	−.27	−.40	+.74	−.24	+.66	+.02	+.68	+.44	−.07
Pt	−.18	+.51	+.57	+.52	−.38	−.20	+.86	+.02	+.77	+.66	+.93	+.57	+.44
	Na	Sc	Cl	Zn	SiO_2	Mg	Mn	Cr	Cu	Co	Ni	Fe	U

Correlation Coefficient Matrices (L Profile)

Table 8.14

Zn	+.38												
Na	-.67	+.53											
Cl	-.19	+.97	+.67										
SiO_2	-.85	-.50	+.98	+.65									
Mg	-.81	-.83	+.92	+.29	+.93								
Mn	+.30	+.98	+.21	+.89	+.26	-.30							
Cu	+.26	+.58	-.60	+.42	-.15	-.93	+.62						
Cr	-.00	+.54	-.11	+.76	+.27	-.75	+.81	+.84					
Co	+.42	+.69	-.37	+.57	-.14	-.71	+.79	+.92	-.63				
Ni	+.03	+.64	-.18	+.88	+.34	-.22	+.72	+.40	+.77	+.40			
Fe	+.90	+.30	-.95	-.94	-.99	-.96	-.10	+.30	-.08	+.30	+.18		
U	-.33	+.64	+.40	+.78	+.60	+.00	+.63	+.35	+.80	+.30	+.88	-.46	
Pd	+.36	-.63	-.43	-.74	-.53	-.60	-.66	-.63	-.76	-.58	-.55	+.44	-.67
Pt	+.39	-.59	-.92	-.62	-.70	-.73	-.36	+.36	-.05	+.14	-.17	+.71	-.38	+.12
	Sc	Zn	Na	Cl	SiO_2	Mg	Mn	Cu	Cr	Co	Ni	Fe	U	Pd

Correlation Coefficient Matrices (BNC Profile)

Table 8.15

	Sc	Zn	Na	Cl	SiO_2	Mg	Mn	Cu	Cr	Co	Ni	Fe	U	Pd
Zn	+.99													
Na	+.64	-.63												
Cl	+.96	+.92	+.89											
SiO_2	-.94	-.95	-.86	-.90										
Mg	-.98	-.94	-.88	-.99	+.99									
Mn	+.98	+.98	+.75	+.89	-.88	-.88								
Cu	+.40	+.38	-.95	+.1	-.08	-.05	+.50							
Cr	+.98	+.97	+.77	+.87	-.87	-.85	+.99	+.58						
Co	+.99	+.98	+.88	+.99	-.99	-.98	+.94	+.21	+.92					
Ni	-.66	-.61	-.14	-.86	+.88	+.89	-.53	+.41	-.51	-.80				
Fe	+.94	+.94	-.30	+.99	-.99	-.99	+.88	+.07	+.86	+.99	-.80			
U	+.15	+.14	+.84	-.15	+.16	+.19	+.31	+.39	+.33	-.03	+.62	-.17		
Pd	+.96	+.95	+.82	+.83	-.82	-.80	+.99	+.66	+.99	+.89	-.43	+.81	+.42	
Pt	+.99	+.99	+.62	-.95	-.94	-.95	+.98	+.38	+.97	+.98	+.67	+.95	+.13	+.63

Correlation Coefficient Matrices (BIP Profile)

DISCUSSION

In this section, the results of 17 analyzed samples has been used in conjuction with other interpretive techniques (Molecular proportion plots, Gains and losses plots and correlation coefficient) in order to explain the distribution and behaviour of individual elements during the laterite formation.

MAJOR ELEMENTS

SILICA

Behaviour of SiO_2 in the profiles investigated generally conforms with the trends reported previously for laterites developed on ultramafic rocks. Silica is depleted in all samples, the extent of depletion increasing toward the surface in each profile. This shows that SiO_2 content is decreased with increased weathering, regardless of variations in chemical and physiographical conditions (Harris 1966). It has been shown that the solubility of SiO_2 depends on pH value and temperature (Mason 1954, Corren 1949 and Krauskopf 1959).

It is quite obvious from the molecular proportion and net change plots that the silica content decreases sharply going from fresh rock to laterite, but some times it increases again slowly towards the top of a profile. Such an effect is illustrated in case of BNC profile and probably arises from residual concentration of difficultly soluble silicates. Thus mineralogical examination of the upper part of this laterite revealed minute particles of quartz and chlorite.

According to Krauskopf transport of SiO_2 apparently takes place mainly in the colloidal state and to a lesser extent as ionised silicic acid in true solution.

MAGNESIUM

The tendency for a depletion of magnesium during the transformation of rock to laterite was noted in each of the profiles investigated. This trend has also been reported by Harris(1966), Krauskopf(1959), Wedepohl(1969) and Zessink(1969). It is gener--ally accepted that rain water containing carbonic acid, attacks olivine (which may contain 25% Mg. Goldschmidt,1954) and leaches out the Mg as bicarbonate. It is evident from analytical data, molecular proportion and net change plots that magnesium is very consistent in trend. The element is depleted in all the studied profiles, the extent of depletion, increases toward the surface in each profile, just like SiO_2. As already mentioned in the comments on net change plots, in the case of the BNC profile Mg depletion is pronounced (or more complete), which corresponds to the fact that the BNC profile has been exposed to weathering for a longer period than profile L .

IRON

Iron shows absolute gains in all profiles examined. There is a definite trend which can be made out for enrichment relative to fresh rock. An apparent increase in Fe may be due to depletion of Fe at a slower rate than other elements rather than actual enrichment(Krauskopf1954). Lateritic ore changes from gray-yellow brown at the bottom to dark red at the top corresponding to the distribution of the iron minerals.

Iron occurs in the higher levels of the profiles, mostly as hydroxides; goethite, hematite and limonite. In the BNC profile, iron is dissolved in the upper most layers and is redeposited a few metres below the surface.

The likely mode of transportation of FeIII may be as bicarbonate(Corren 1949).

NICKEL

Nickel is quite enriched in the studied profiles relative to the fresh rock(which contain 0.5% Ni).

In the L profile, the major amount of nickel is concentrated in the shallow horizon. Turner (1968) pointed out the relation-ship between goethite and nickel and showed that high nickel values are associated with zoned goethite concentration. Zeissink (1969) suggested that amounts of Ni in the upper ferruginous horizon are held in the lattice of the goethite and of aluminium hydroxide. In the profiles BNC and BIP nickel is concentrated at deeper horizons. Perhaps the Ni is initially sorbed on the iron^{III} hydroxide, but in the more mature profiles (like BNC and BIP) leaching may be more thorough so that the quite loosely held Ni migrates downward until it is fixed, e.g.,in serpentine. The nickel may be redeposited in small cracks and interstices in serpentine (Goldschmidt 1954. Corren 1949).

CHROMIUM

The usual amount of Cr in fresh serpentine is 0.31 % (De Wall 1971). Chromium in primary rock occurs as accessary chromite, and is incorporated in very minor quantities in olivine and chlorite.

The laterite samples contain negligible amounts of chromite and olivine. However, some of the chromium in the profiles might be associated with chlorite. The Net changes indicate that considerable Cr is lost in the shallow horizon and stongly concentrated in deeper levels of the BNC profile. Chromium (III) form a very insoluble hydroxide, but under strong oxidizing conditions a soluble chromate (VI) may be formed which may migrate downward until it is fixed as iron (III)chromate, Krauskopf (1959), Santos-Yingo(1960) and Wolfendon(1965). Santos uses this argument to explain the tendency for Cr in Phillipine and Cuban laterites to be concentrated near the base of the Fe-rich zone.

MANGANESE

Manganese shows enrichment in the fractions high in poorly crystalline iron oxide. Mn^{+2} probably substitutes for Fe^{+2} in ultramafic rock. During weathering it may be oxidized to +4 state and precipitated as hydroxide(Rankama Sahama 1966). If present in the form of colliodal MnO_2(negatively charged sol.), it might be expected to be associated with colloidal iron hydroxide(positively charged sol.) Krauskopf (1954) . This could explain the close correlation between Fe and Mn, which is very apparent in the L profile. According to Rankama Sahama(1966) during the weathering, Mn may dissolve mainly as bicarbonate and behaves rather like iron. In the zone of weathering the carbonate is directly converted into manganitic oxide and hydroxide.

COBALT

Cobalt is tremendously enriched relative to the fresh rock and its distribution trend is apparently similar to Ni. It is believed that the olivine and pyroxene crystals contain Ni and Co substituted in their crystal lattices. Co and Ni have approximately the same ionic radii and may be expected to behave similarly However, it has been suggested by Zeissink(1971) that Ni has the greater mobility.

Both Ni and Co, reflect similar behaviour in all the profiles studied. It is possible that the same mechanism is responsible for concentration of both these elements.

COPPER

Concentration of Cu in fresh rock is about 0.0012% Flanagan (1969). Like manganese the element shows a definite enrichment in upper and intermediate levels of the lateritic profiles. One would expect copper to be depleted during weathering, due to its high solubility, however, enrichment up to many fold takes place. The higher copper values in the upper part of the profile could suggest that the element is associated here partly with organic material. Krauskopf(1954) suggested that copper may be fixed near the surface either as an insoluble hydroxide or hydroxy-carbonate or absorbed on iron(III) hydroxide. It is evident from the profiles that Cu is enriched in horizons where iron is enriched.

Adsorption of Cu from aqueous solution has been studied experimentally by Corren(1924) and by Krauskopf(1956).

The difference in adsorption capacity between different types of adsorbents can be easily derived from data of experiments published by Krauskopf(1956). At pH 7.7 to 8.2 in a set of experiments close to natural conditions, they used solutions containing about 500 ppb Cu and suspensions of 1.5% to 30ppm adsobent and obtained the following rate of removal by adsorption. Montmorillonite= 99.4%; freshly precipitated $Fe_2O_3nH_2O$= 98, freshly precipitated MnO_2nH_2O = 96%; dead plankton 42 %; peat = 98% ; ligonite = 66%.

Zeissink (1971) has described the absolute and relative increase of Cu in two lateritic profiles of serpentinite. The maximum absolute concentration, occuring in an upper ferruginous zone(30% Fe_2O_3 is 200 ppm Cu).

CHLORINE

Chlorine is surprisingly enriched overall in intermediate and deeper zones. According to Rankama (1966) chlorine goes readily into solution during weathering as chloride. When the chloride solution comes in contact with heavy metals, particularly Hg and Ag, in a surficial part of an ore body sparingly soluble chlorides of the metals may be precipitated. Rucklidge(1972) suggested that a high % of chlorine may be a significant component of serpentine in altered ultramafic rocks. A high chlorine concentration is unusual, but evidence suggests that chlorine may play a significant role in the alteration of olivine and in the redistribution of metal-cations (Rucklidge 1972, Wedepohl 1971).

URANIUM

The average abundance of uranium in ultrabasic rocks is 4–5 ppb, Flanagan(1969). Our studied profiles show a very slight increase in concentration in the deeper part, relative to fresh rock concentration. During weathering, the U minerals presumably yield hydrated oxide, having been previously brought into solution as uranyl complexes(UO_2^{2+}) Goldschmidt, 1954. The soluble uranium compounds are readily absorbed on hydroxide gels of iron, aluminium and silica; therefore, U may become enriched in hydrolyzate and oxidate. It is assumed that U has been leached out from the shallow horizon and absorbed at deeper horizons.

ZINC

The upper levels of the profiles contain concentrations of Zn up to ten times those in the original value. The concentration of this element is somewhat unexpected as it is usually depleted during weathering. This behaviour can be explained as due to Zn being absorbed in goethite(iron hydroxide).

Zeissink(1971) suggested the Zn enrichment in ferrugineous zone, probably because of adsorption on ferric iron oxides and on montmorillonite. Due to the low mobility of Zn and its adsorption on ferric iron oxide, clay minerals and organic residues, Zn is often slightly higher in soils than in the related undecomposed rocks.

Adsorption of Zn has been experimentlly demonstrated by Krauskopf (1956).

SCANDIUM

Molecular proportions and Net change plots showed that scandium is quite enriched in surficial and in shallow horizons. The Sc^{3+}—(Fe^{3+},Al) diadochy explains the concentration of Sc in the profiles where Fe^{3+} and Al are strongly concentrated, and upon further weathering the element probably becomes associated with goethite. Scandium concentration in basic laterites has been observed by Zeissink(1971), Welfendon(1966) and Hotz(1955).

The Sc^{3+} ion is found experimentally to be adsorbed from artificial sea water by hydrous ferric oxides and clay, reaching 90–100% at pH 7–8 (Yushimura). The adsorption by ferric hydroxide starts at pH 4 and reaches a maximum in the range where hydrolysis of Sc^{3+} begins (Wedepohl 1969).

Correlation coefficient data show a striking association of Sc^{III} and $iron^{III}$.

GOLD

The unaltered rocks studied contain 3–6 ppb; the data for the laterite profiles (maximum 40 ppb), suggest that the element becomes slightly concentrated during weathering, particularly in the more mature New Caledonian profile. Because gold is chemically inert (Sahama 1955) and its compounds are readily reduced to metal, it remains largely in the native state and becomes concentrated in the resistates; owing to its high specific gravity, gold often concentrates in placer deposits. However, gold is readily dissolved and transported, possibily largely in colloidal solution (Wedepohl 1969).

Gold enrichment has been reported by Tenykov (1970) in Bauxites, including samples from 40 localities, mostly in U.S.S.R. It was found that 20 deposits formed from igneous rocks(mafic and ultramafic rocks) averaged 8.4 ppb. An.

Such observations suggest that the gold content in laterite is related to that of the parent rock. Gold may be dissolved in the weathering process, and adsorption on iron or aluminium hydroxide or clay minerals may effectively inhibit its prolonged leaching by ground water.

IRIDIUM

Hardly there is any literature available on geochemical behaviour of iridium. Iridium is chemically inert and is very resistive toward any reaction in nature. Slightly higher values relative to fresh rock in the profiles is due to decrease in total volume of parent rock.

PLATINUM AND PALLADIUM

The studied profiles indicate enrichment of platinum and palladium relative to the parent rocks. The profile (L) shows that Pd is concentrated in the deep B horizon relative to A and C horizons. The depletion of Pd remains large even after correction for the dilution effect of organic matter and hydration. Organic dilution was tested by determining weight loss by roasting the sample to drive off organic material and moisture. On the other hand, in the case of the BNC profile, Pd is enriched in A and deep B.

The composite profiles indicate that Pt contents are enhanced in the horizons where iron hydroxide or oxide concentration is high. This behaviour may suggest that Pt may have been sorbed on iron hydroxide or oxide.

Razin (1965) suggested that the Pt metals are released from decomposed minerals and absorbed on the newly formed hydrous iron hydroxides. He also demonstrated in laboratory the capacity of the hydrous iron hydroxides to absorb Pt- metals. In a series of experiments, pieces of natural hydrous iron oxides were placed in solution of salts of different Pt-metals. After a few days, these pieces were taken out of the solutions, dried, brushed with a stiff brush(to exclude the effect of surface coating on the analytical results), powdered, and analyzed Pt-metals absorbed from the solution were always present in the hydrous iron oxides.

Platinum group metals, particularly Pd, might well have been transported as chloride complexes (Otteman 1967, Cousins 1973).

The critical assumptions concerning this suggestion are: (i) the concentration of Pd needed in solution to achieve appreciable tranport and (ii) that the chloride concentration is high enough. Fuchs(1973) has suggested that in area containing aqueous media the higher the chloride, the more mobile are the Pt and Pd. Palladium becomes readily soluble as a chloro-complex, so although chloride content may not necessarily be essential for Pt metals-mobility, it can certainly promote it. Cousins's (1975) laboratory experiment indicated that the reaction is completed in a few hours when a 10 % NaCl solution at 35°C is used under an atmosphere of chlorine. Under natural conditions the reaction will be much slower, but the geological time element can be correspondingly long. Evidence in favour of this kind of process comes from the observation that Pt is poor, and Os+Ir are rich in alluvial deposits of Good News Bay (Mertei 1969). It was assumed that transportation of Pd in solution as $PdCl_4^{2-}$ arose in relatively acidic condition, such as those found in a tropical forested environment. Furthermore, at chloride concentration of0.2%, Pd(II) may be dissolved and a relative mobility of Pd may be achieved.

The existence of stable, but presently unrecognised, Pd-organic complexes is possible and these could serve to enlarge the field of mobility. Fuchs(1974) reported the Pd content of a tree sample and suggested a possible Pd mobility in an organic cycle.

COMPARISON WITH OTHER LOCALITIES

The studied profiles from Guatemala (L), New Caledonia (BNC) and Indonesia (BIP) are not only geochemically similar but they also show great similarities with other lateritic profiles formed by weathering of serpentine and peridotite, such as those in Australia (Ziessink 1971), Cuba (Corren 1954), Phillipines (Santos 1966) and Oregon, U.S.A. (Hotz 1954).

Analyses of the profiles are given in Table 9.1–9.7, together with the analyses of laterites from other localities. Comparison of analyses emphasizes the similarity in chemical compositions of all the profiles, but it also reveals some differences that may reflect differences in climatic environment and physiochemical factors under which weathering took place.

Laterites formed from peridotite and serpentine by weathering under tropical climatic conditions have a notably lower content of SiO_2 and Mg, and higher content of Fe than the laterite of South west Oregon developed under humid climate. Distribution of Ni and Co are essentially the same in each case, however. The higher rainfall in tropical regions may be responsible for the lower SiO_2 and Mg relative to Fe and Al.

Pickering 1951 has demonstrated the importance of temperature on the rate of weathering.

Other factors have been discussed previously, in chapter -1.

Table 9.1

COMPOSITION OF (L) PROFILE AS A FUNCTION OF DEPTH

	L1	L2	L3	L4	L5	L6	L7
Depth(m)	1.5–2.00	2.5–3.00	3.5–4.00	5.25–5.75	8.00–8.50	8.00–8.50	10.25–10.75
Fe% Chem	43.82	32.21	25.21	9.15	10.53	22.56	7.95
INAA	42.37	31.51	24.93	9.09	10.10	22.15	7.88
Ni% Chem	1.73	1.86	2.13	1.91	1.18	1.60	0.65
INAA	1.69	1.91	1.98	1.85	1.21	1.45	0.52
Co% Chem	0.12	0.15	0.29	0.15	0.12	0.21	0.08
INAA	0.11	0.13	0.26	0.14	0.11	0.19	0.07
Cu% Chem	0.13	0.14	0.12	0.12	0.11	0.11	0.01
INAA	0.13	0.13	0.12	0.12	0.11	0.11	0.01
Cr% Chem	0.08	0.09	1.34	1.28	0.78	1.30	0.65
INAA	0.08	0.08	1.25	1.21	0.68	1.10	0.65
Mn% Chem	0.28	0.31	0.26	0.22	0.12	0.20	0.09
INAA	0.26	0.31	0.25	0.22	0.12	0.20	0.09
Mg% Chem	4.28	8.95	12.84	10.35	8.24	5.23	16.55
SiO_2 Chem	3.25	7.35	20.25	32.75	21.50	10.35	34.25
Zn% INAA	0.014	0.012	0.0065	0.0026	0.0037	0.0056	0.0024
Cl% INAA	0.053	0.043	0.060	0.0220	0.0193	0.0576	0.0221
Na% INAA	0.0075	0.0231	0.0245	0.0231	0.0285	0.0175	0.0262
Sc(ppm)"	128.0	80.0	60.0	22.0	23.0	55.0	21.0
Au(ppb) NAA	11.8	13.8	8.9	5.85	4.7	5.6	3.3
Pt "	140	145	173	135	97	101	68
Pd "	84	79	57	93	46	50	37
Ir "	8.2	13.9	15.2	13.2	6.7	7.4	5.0

Table 9.2

COMPOSITION OF BNC PROFILE AS A FUNCTION OF DEPTH

	BNC1	BNC2	BNC3	BNC4	BNC5	BNC6	BNC7
Depth(m)	0–2	2–7	7–11	11–13	13–14	14–17	17–20
Fe% Chem	47.0	49.5	51.0	49.5	52.3	38.1	12.5
INAA	45.7	48.5	49.1	49.3	52.0	38.8	11.3
Ni% Chem	0.73	1.52	1.65	1.41	1.75	3.21	1.61
INAA	0.71	1.47	1.59	1.42	1.71	3.20	1.56
Co% Chem	0.082	0.081	0.106	0.151	0.256	0.157	0.08
INAA	0.051	0.077	0.093	0.150	0.271	0.159	0.08
Cr% Chem	0.314	0.340	0.830	1.5o4	1.754	2.153	1.05
INAA	0.350	0.338	0.689	1.471	1.652	2.035	1.09
Cu% Chem	0.138	0.150	0.173	0.254	0.270	0.221	0.156
INAA	0.118	0.129	0.156	0.235	0.230	0.210	0.134
Mn% Chem	0.127	0.209	0.195	0.253	1.803	1.716	0.673
INAA	0.142	0.210	0.200	0.254	1.800	1.685	0.715
Mg% Chem	-	-	-	0.2	0.8	1.4	11.2
SiO_2 Chem	3.8	2.6	4.1	4.7	4.2	14.0	26.3
Cl% INAA	0.027	0.17	0.038	0.043	0.271	0.315	0.260
Na% INAA	-	-	0.026	0.012	0.043	0.066	0.127
Zn% INAA	0.680	0.630	0.650	0.640	0.940	0.910	-
Sc(ppm) "	98	108	110	84	122	96	55
Au(ppb) NAA	30.4	31.7	40.5	11.3	8.00	9.50	6.3
Pt "	108	164	151	190	131	110	83
Pd "	80.0	52.2	80.2	27.5	24.6	21.5	21.0
Ir "	8.0	5.4	5.2	5.7	6.5	5.1	4.2

Table 9.3

COMPOSITION OF (BIP) PROFILE AS A FUNCTION OF DEPTH

	BIP1	BIP2	BIP3
Depth(m)	11-13	13-17	18-19
Fe% Chem	49.13	19.10	1o.15
INAA	49.05	20.81	9.13
Ni% Chem	1.46	2.83	2.43
INAA	1.40	2.71	2.35
Co% Chem	0.123	0.064	0.031
INAA	0.116	0.059	0.022
Cr% Chem	1.350	1.050	0,370
INAA	1.213	0.901	0.353
Cu% Chem	0.075	0.115	0.051
INAA	0.070	0.102	0.048
Mn% Chem	0.819	0.638	0.267
INAA	0.812	0.690	0.269
Mg% Chem	0.261	8.284	10.442
SiO_2% Chem	4.34	22.04	27.60
Cl% INAA	0.074	0.033	0.020
Na% INAA	0.0021	0.0027	0.0011
Zn% INAA	0.0110	0.0066	0.0019
Sc(ppm) INAA	90	56	18
Au(ppb)	14.0	8.5	6.2
Pt " NAA	67.0	43.1	18.4
Pd "	52.0	45.3	20.5
Ir "	16.0	7.0	5.3

Table 9.4

COMPOSITION OF OREGON PROFILE AS A FUNCTION OF DEPTH

Depth (feet)	(0-1)	(1-2.8)	(2.8-5.5)	(5.5-8.2)	(8.2-10.8)	(10.8-17.8)	(17.8
SiO_2	21.2	18.5	15.6	21.4	35.1	32.0	43
Fe_2O_3	47.3	52.0	56.1	49.1	38.6	32.1	8.1
MgO	4.1	1.7	2.1	3.3	4.7	14.1	43.1
Na_2O	0.1	0.07	0.06	0.004	0.04	0.05	0.02
MnO	0.28	0.25	0.25	0.44	0.46	0.27	0.14
CoO	0.07	0.13	0.14	0.14	0.07	0.04	0.02
Cr_2O_3	2.0	2.1	1.8	2.4	1.2	1.1	0.56
Ni	1.4	2.0	1.8	2.0	2.0	2.05	0.37

Table 9.5

COMPOSITION OF NEW CALEDONIAN PROFILE AS A FUNCTION OF DEPTH

Depth (M)	0 ——							below 28.5
SiO_2	0.1	1.49	1.65	24.16	37.04	36.47	35.53	34.9
Fe_2O_3	73.2	69.2	70.5	36.19	12.71	11.1	12.48	8.34
MgO	-	0.07	4.15	19.53	33.78	31.92	33.68	42.63
Cr_2O_3	5.54	5.39	2.69	0.39	0.55	0.21	0.55	0.31
MnO_2	0.52	6.5	1.23	0.54	0.2	0.21	0.23	0.14
NiO	0.17	0.31	1.54	3.11	2.54	2.41	2.36	0.44
CoO	0.01	0.022	0.088	0.095	0.072	0.067	0.84	0.03

Table 9.6

COMPOSITION OF CUBAN*PROFILE AS A FUNCTION OF DEPTH

Depth(feet)	(0-2.1)	(2.1-3.3)	(3.3-12.7)	(12.2-15.7)	(15.7)
SiO_2	3.28	2.25	1.83	1.55	41.93
Fe_2O_3	63.04	69.56	71.12	68.10	7.84
MgO	0.33	0.48	0.64	0.6	34.02
Na_2O	0.47	0.3	0.48	0.39	0.36
Mn	0.42	0.28	0.38	0.47	0.12

Table 9.7

COMPOSITION OF AUSTRALIAN PROFILE AS A FUNCTION OF DEPTH

Depth (F)	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–40	40–45	45–50	50–55	55–60	F.S
Fe_2O_3	60.65	64.39	44.26	31.57	47.24	32.14	25.38	20.02	13.95	12.81	10.52	9.25	8.55
SiO_2	11.32	9.44	29.62	49.56	19.96	31.24	36.52	43.66	41.92	41.0	40.98	40.50	43.56
MgO	0.52	0.9	2.72	1.91	7.12	13.21	18.8	19.3	22.56	23.51	23.52	27.79	28.30
Cr_2O_3	1.74	1.56	2.21	1.41	1.85	1.59	0.91	0.80	0.57	0.52	0.50	0.43	0.37
NiO	2.27	2.3	2.53	1.52	2.87	2.53	2.12	1.21	0.73	0.64	0.54	0.46	0.42
MnO	1.14	1.18	0.61	0.44	0.61	0.32	0.30	0.29	0.13	0.11	0.09	0.07	0.06
Co ppm	4290	4620	4620	1540	3860	2750	1432	900	340	290	240	170	140
Cu "	200	180	88	90	55	43	39	46	13	12	10	9	7
Sc "	80	72	46	31	45	25	22	18	22	10	13	9	5
Zn "	270	268	321	276	303	427	349	123	77	80	68	49	31
Pt ppb	80	60	40	110	80	90	100	110	80	23	60	40	52
Pd "	42	40	40	40	80	42	42	50	120	30	48	110	78

SUMMARY

A radioactivation method developed in this investigation has proved useful for the determination of precious metals at sub-micro level in geological samples.

Coefficient correlation, molecular proportion and net change plots prove very valuable aids in studying the behaviour of the elements during weathering.

The ore zone, in BNC is situated in the lower part of the section. On the other hand, in L profile ore zone is located in the higher level of the section.

Magnesium, Silicon and Sodium form a group of easily leached elements. Magnesium shows a tendency to be perefertially removed with respect to SiO_2. All other major and minor elements are enriched in studied profiles. The extent of the relative changes and depth at which maximum enrichment or depletion occur varies from profile to profile.

Analyses and interprative techniques have revealed that in the L profile the maximum concentrations of Co, Mn, Zn, Sc, Ni and Cr occur in the upper layers, with the Fe_2O_3. Some of these elements are probably held in the lattices of goethite. Copper tends to concentrate near the surface, probably in chemical combination with organic matter.

In the New Caledonian profile Sc and Cu occur in the upper zone. However, the maximum concentrations of Ni, Zn, Mn, and cobalt occur not in the upper zone, but in the deeper zone. The removal of Zn, Mn, Ni and Co from upper horizon of the BNC deposits, and their concentration at greater depth, tend to

suggest that BNC is a more mature profile. This could have been caused by a variety of factors, such as higher rain fall and differences in topography and may involve a longer period of exposure to weathering.

Perhaps the elements were initially sorbed on the iron hydroxide, but subsequent leaching forced the loosely held elements to migrate downwards until they are fixed, e.g in serpentine or with another precipitate (when pH value becomes higher near the basic rocks).

It is very evident that dissolution of elements, migration and redeposition occur continuously.

Platinum group metals are enriched in the intermediate zone in the profiles. Concentration in the B horizon indicate the possibility of migration of Pt metals. Platinum metals, particularly Pd, may have migrated as chloride complexes.

Gold and Iridium are very resistive toward any chemical reaction in nature. They always stayed in the residual concentrates. Slightly higher values relative to parent rock in the profiles is due to decrease in total volume of parent rock.

CONCLUSION

The radiochemical method developed in this investigation permits a fairly rapid determination of Pt, Pd, Au and Ir. Specificity is achieved and the procedure demonstrates the practical advantage of using liquid-liquid extractions for separation of these elements. The method is useful for studying a great number of geochemical problems.

Physical characteristics, Mineralogy and Elemental changes which characterized the weathering of the ultramafic rocks in the areas studied are closely similar to changes reported for other deposits in tropical areas.

Changes in trace elements and precious metals can not be closely compared to other literature references because of their paucity of data; however, the elements (Pt metals) are concentrated, which suggest mobility of these elements.

Molecular proportion plots, Net change plots and Coefficient correlation proved useful in this study and should be valuable tools in the interpretation of similar problems.

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