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SOME FIELD METHODS USED IN PROSPECTING FOR NICKEL

by

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SUMMARY

Some field methods which are recorded in the literature as applicable to the prospecting for nickel are described.

Detailed geological mapping is essential for nickel prospecting and knowledge of the distribution of nickel in ultrabasic rocks such as serpentine, peridotite, dunite and harzburgite is significant.

Lateritic deposits should be tested at or near the transition between the fresh bedrock and the base of weathering where the nickel content is highest. Variations in the colour of garnierite from light to dark green with a corresponding increase in nickel is significant.

Hydrothermal alteration is indicative in searching for epigenetic ores in new areas. The presence of major thrusts and shears may represent lines of weaknesses in which mineralizing fluids have migrated. Leached outcrops are useful guides as different types of boxworks form which vary according to the type of sulphide mass oxidized.

Aerial colour photographs will indicate zones of oxidation which may be sources of nickel.

Geophysical surveys using electromagnetic, magnetic, induced polarization and self potential methods are useful in the search for concealed sulphide bodies.

Orientation studies and establishment of sampling media and patterns are a necessary pre-requisite of geochemical prospecting.

Paper chromatographic methods are quick to perform, are highly sensitive, do not need skilled operators, and good results have been obtained under Australian field conditions. Precipitation chromatography takes longer to perform, sensitivity is lower and experienced personnel are needed to interpret the results. Colorimetric methods are quick to perform and are particularly suited for stream sediments.

Biogeochemical sampling is recommended in areas covered by thick or glacial sediments and heavily forested ground. This method of prospecting can be useful in indicating areas suitable for more detailed work.

Hydrochemical prospecting is suggested for highly dissected young mountain areas but there is no suitable field method for the determination of nickel in water and laboratory analysis is needed.

Geobotanical prospecting for nickel is of little use as no plant species have been discovered that grow only on ground covered by nickel ore.

Chemical methods of determining nickel in the field are useful but any large scale sampling programme requires the backing of spectrochemical laboratory analysis.

Maximum success in prospecting for nickel is attained by using all methods in an integrated effort.

INTRODUCTION

Native nickel does not occur in nature, and few nickel bearing minerals have been identified. The principal nickel minerals are:-

ARSENIDES	Niccolite (kupfer nickel) - Nickel arsenide, $NiAs$ (43.9% nickel, 56.1% arsenic) usually contains iron, cobalt, antimony and sulphur in small amounts.
	Chloanthite - Nickel arsenide, $NiAs_2$ (up to 28.2% nickel and 71.8% arsenic). Smaltite, $CoAs_2$ is always present.
ANTIMONIDE	Breithauptite - Nickel antimonide - $NiSb$
BLOOMS	Zaratite - Emerald nickel - $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ morenosite, nickel vitriol $NiSO_4 \cdot 7H_2O$
	Annabergite - Nickelbloom, $Ni_3 As_2O_8 \cdot 8H_2O$
SILICATES	Garnierite - Hydrated nickeliferous magnesium silicate, $(Ni, Mg) H_2SiO_4 \cdot nH_2O$
SULPHIDES	Pentlandite - An iron-nickel sulphide $(Fe, Ni)_{11}S_{10}$ (Fe: Ni ratio approximately 1:1)
	Millerite - NiS. (64.7% nickel, 35.3% sulphur)
	Polydymite - Nickel or nickel iron sulphide, Ni_4S_5 or Ni_3FeS_5
	Gersdorffite - Sulpharsenide of nickel $NiAsS$ (35.4% nickel, 45.2% arsenic, 19.3% sulphur)

Turekian and Carr (1960) used the combined methods of neutron-activation and emission spectrographic analyses to determine the abundances of nickel, chromium and cobalt in various units of the earth's crust. The figures (in parts per million) obtained for nickel are as follows:-

Ultramafics	2000
Basaltics	130
High-calcium granitics	14
Low-calcium granitics	0.4
Shales	71
Sandstones	1
Limestones	27
Deep-sea carbonate	30
Deep-sea clay	200
Schists	114

A knowledge of the principal nickel minerals, the abundance of nickel in the earth's crust and the presence of nickel in certain environments will aid in establishing a base on which a prospecting programme can be launched.

DISTRIBUTION OF NICKEL ORE BODIES IN ROCKS

Vogt (1923) showed that nickel content was highest in ultrabasic rocks and decreased progressively in acid rocks. He indicated that olivine contained the most nickel which decreased in content through enstatite, monoclinic pyroxene, amphibole to biotite, whilst none appeared in feldspars and feldspathoids.

Nickel ore bodies occur in three main forms:

(a) Segregations associated with basic and ultra basic rocks in which pentlandite, millerite, nickeliferous pyrrhotite and nickeliferous chalcopyrite are the principal minerals;

(b) Laterite deposits containing garnierite produced by the weathering of nickeliferous olivine rocks;

(c) Hydrothermal and pneumatolytic vein deposits containing niccollite, chloanthite and nickeliferous chalcopyrite.

(a) Nickel Sulphide Bodies

Economic nickel sulphide bodies are genetically associated with basic and ultrabasic rocks and according to Wilson (1953) occur within or very close to the parent intrusive and at or near the base. However the possibility that mobile sulphides may migrate to form deposits at considerable distance from their original source rocks should not be discounted. Rose (1966) has suggested that this factor may have important implications in the prospecting for further occurrences of ore in the Cobalt - Timagami - Sudbury area, Ontario. Thompson (1962) points to the almost constant association of nickel at approximately 0.2% with the magnesian olivine of large ultra mafic, fault-bounded provinces and the rare association of nickel sulphide minerals in ultra mafic rocks associated with circum-Pacific tectonics.

According to Wilson (1953) the most favourable primary structure for ore is a trough in the bottom of an intrusive, but secondary fault structures may serve to localise ore in the primary structure. Faults control the ore in the immediate vicinity of the lower contact of the intrusive and as the fault passes into the footwall the ore stops within a few hundred feet at most. Where the fault passes upwards into the basic intrusive rock away from the contact the ore terminates almost as abruptly as in the wallrocks and not only do the sulphides end as ore, they disappear completely from the fault. Nickel ore can be controlled by fault structure but the ore is not highly mobile at the time of formation and not transported far from the parent intrusive.

(b) Nickel in lateritic and silicate deposits

Peridotites with abundant magnesian olivine, dunite and harzburgite are important source rocks of nickel in lateritic and silicate deposits. These rocks are commonly found together in elongated masses aligned along major faults, particularly in the young orogenic zones between continents and oceans.

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Trace quantities of nickel are released from the crystal lattice of magnesian olivine when the latter breaks down chemically during weathering. A knowledge of the mechanics of this chemical weathering and the influence of groundwater may help in prospecting for nickel as the mineral is concentrated in different zones which may initially be determined by climate and topography. Laterite may form on flat or undulating country where erosion is slow and hydrated iron oxides aggregate into pisolites which eventually become cemented in a hard layer several feet thick. On steeper slopes erosion may continually remove the upper part of the iron rich zone of a weathering mantle as it develops and under such conditions laterite development is rare. A warm humid climate is necessary as it favours chemical weathering. Thompson (1962) states that in New Guinea rain forest areas, perpetual saturation of the entire soil profile inhibits the formation of laterite although a high concentration of iron oxides may be attained. Laterite has been seen at the surface of residual soils where forest cover is lacking and rainfall is low and seasonal. Under very dry conditions, or where surface run-off is high, thick residual soils do not form over ultramafic rocks, but infertile rubble containing magnesite, nodules accumulate, a type of weathering seen on Normanby Island.

The distribution of nickel through the weathering profile at Ocujal, Cuba, has been described by de Vletter (1955). He reports ore grade concentrations of nickel are rarely found in the top few feet of a lateritic nickel deposit, but are usually found in the lower half of the iron-rich zone and extend down to the base of weathering. Such deposits should be tested at or near the transition between the fresh bedrock and the base of weathering.

Molengraaff investigated the nickel and cobalt bearing laterite cover on the Waigeo Fields, West Irian and suggested the nickel bearing transition zone underneath the laterite cover which had been subjected to a long period of leaching is a possible ore reserve.

Structural controls can limit the extent of nickeliferous laterite deposits as Glaessner and Parkin (1958) have pointed out with regard to the nickel deposits of the Tomkinson Ranges, South Australia.

Parts of the complex of basic and ultrabasic rocks are overlain by nickeliferous laterites which are associated with shear zones in ultra-basic intrusives and therefore have not only the limited depth range common to lateritic deposits, but also have a restricted lateral extent.

Nickel magnesium silicate deposition represents the ultimate stage in the concentration of nickel derived from the weathering of nickeliferous magnesian olivine. Attainment of critical ionic concentrations of nickel, magnesium and silica for the deposition of nickel magnesium silicate possibly results from restricted groundwater movement or repeated evaporation or both. Small showings have been seen in Papua and New Guinea at or near the base of weathering in auger holes drilled through nickel-enriched clays. (Thompson 1962). The zone of silicate deposition in a weathering mantle would normally be beyond the limit of manual augering so that testing of nickel-enriched clays by this method can not be regarded as conclusive testing for nickel magnesium silicate deposits. The transition zone containing clay and residual boulders would have to be traversed to test for nickel silicate deposits which can only be done by hard rock drilling equipment or shaft sinking.

Pecora et al., (1949) have described variations in garnierite near Riddle, Oregon which may be of help in prospecting for nickel silicate deposits. They report on three types of garnierite which vary in colour, depending upon their origin. A light coloured garnierite was found to be an alteration of an olivine-rich rock, a bright green garnierite was formed by continual chemical reaction of groundwater on earlier formed garnierite, and a dark green garnierite was deposited from groundwater solutions. In general it was found that the garnierite specimens rich in nickel were darker green than those poor in nickel. Hotz (1964) came to a similar conclusion regarding the garnierite deposit at Nickel Mountain, Oregon; the garnierite ranging from pale greenish yellow through yellowish green to brillian green with an increasing nickel content in the same direction.

(c) Hydrothermal Alteration

Hydrothermal alteration of rocks is a favourable sign in searching for epigenetic ores in new areas. Wilson (1953) maintains that wallrock alteration, common in most hydrothermal deposits is not consistent in nickel-copper-sulphide bodies, for in many mines fresh unaltered hypersthene in norite acts as gangue of disseminated sulphide blebs. Uralitization is common in places and in the Sudbury area silica is abundant along some of the faults. Nickel may occur in montmorillonite, chlorite and talc, where it substitutes for magnesium to a limited extent. In exploration wallrock alteration does not necessarily extend a great distance beyond an orebody, but when of sufficient width is a useful guide to ore search. Major thrusts, shears and transcurrent faults are guides for ore search as in many cases they represent lines of weaknesses up which mineralizing fluids have migrated. Recognition of hydrothermal alteration can play an important part in the discovery of ore, but there is always the need for supporting evidence of structural guides, geophysical and geochemical anomalies.

(d) Native Nickel Iron

Native nickel iron as waruite, souesite and josephinite occurs in serpentinized peridotites belonging to Alpine orogeny. Krishnarao (1964) suggests the mineral group may have originated by reduction of the nickel-bearing silicates or sulphides during serpentinization of the peridotites. When nickel-iron occurs in quantity as in Poschiavo (Switzerland) it appears as a silver white metallic dust on serpentine and is strongly magnetic. It usually occurs in such small quantity that microscopic examination is needed to identify it.

The native nickel iron from Oregon is reniform or botryoidal and from Poschiavo is granular and pseudomorphic after cubic minerals such as magnetite and pentlandite. At Poschiavo, Philadelphia, and Elba Virginia talc is associated with the native nickel iron ≡≡≡≡≡≡≡≡≡≡≡ which always occurs in the intergranular spaces or in veins of serpentine. Pyrrhotite always exhibits an early paragenetic relationship when associated with native nickel iron and pentlandite; chromite - magnetite - hematite are other associations.

(e) Leached Outcrops as a Guide to Nickel Ore

When a sulphide mass is oxidised, solutions enter fractures and cracks between crystals, and deposit limonite, forming a boxwork pattern which remains in the outcrop after the sulphide minerals have been removed. Limonite derived from a particular material is usually different from that derived from other materials, therefore the boxworks will differ and recognition of different types of boxworks will aid the prospector. Whitten (1965) has described different types of boxworks which are summarised in TABLE 1. Pyrrhotite for example, yields a coarse cellular spongy mass with more or less uniform cell size, it's colour is brick red and empty cells help to distinguish it from the coarsely cellular products of other sulphides.

The gossan of nickeliferous pyrrhotite deposits is essentially limonite and if arsenic is present nickel forms with it annabergite or "nickel bloom" a moderately stable salt, green in colour, and often found at the surface which may be indicative of a nickeliferous deposit below. Gossans, while usually indicating the morphology of the underlying deposit may differ in size. Bateman (1950) suggests that where laterally transported exotic limonite is present, mushrooming exaggerates the size of a deposit, for example, a number of small parallel veins may give the appearance of an economic lode. Blanchard (1939) however stated that leached outcrops are only one-quarter or even one-half the width of the sulphide mass below.

Field evaluation of leached outcrops is a preliminary step in the evaluation of a metalliferous prospect, and its main function is to assist in the recognition of the mineral content of the primary ore. False gossans may be distinguished from true gossans (the former lacks indigenous limonite and type of voids differ). Indigenous limonite derived from ore minerals may be distinguished from transported limonite derived from pyrite. Recognition of the features of leached outcrops during early field work may guide mapping, help to determine priorities and pave the way for an efficient exploration programme.

THE USE OF AERIAL PHOTOGRAPHS IN NICKEL EXPLORATION

The most important use of photo-geology is as a preliminary guide to the reconnaissance and regional mapping of large areas. Base maps may be produced from the aerial photographs which can be used for the plotting of subsequent field data. Rock type, faults, fissures, joints and folds may all influence the localisation of nickel ore, and such features are depicted on aerial photographs. Nickel is associated with ultra basic rocks, and recognition of such types is important as they indicate a possible source of the mineral. In the Mount Davies Range, for example, peridotite and harzburgite layers are conspicuous on black and white aerial photographs because they support a thick mallee growth which contrasts sharply on the photographs with the light coloured norite slopes, covered with thick spinifex growths.

The use of colour aerial photography has been discussed by Hartman (1965) who outlines its advantages in its application to mineral exploration. He states that evidence of primary and supergene mineralization at the surface of an area is more evident and can clearly be established by using colour photographs.

TABLE 1

LEACHED DERIVATIVES FROM ORE AND GANGUE MINERALS (From Whitten 1965)

Derivative	Character	Colour	Type[1]	Voids[2]	Derivative	Reference
Cellular Sponge	Small uniform rounded cells, thick walls	Brick red	T	E	Pyrite	Blanchard (1939)
Columnar	Columnar or stalactitic	Brick red to black	Ex	M	Pyrite	
Botryoidal	Botryoidal crusts; acid solutions; strong neutraliser	Black	T	M	Pyrite	
Dense Jasper	Black; little cellularity; Shrinkage cracks	Black	T	M	Pyrite	
Siliceous sinter	White, silica boxwork; inert gangue	White	I	E	Pyrite	
Crystal Cavities	Negative crystal surrounded by a bleached zone or partly filled by limonite crusts	Brown	T	E-0	Pyrite	
Cellular sponge	Coarse spongy mass	Brick red	I	E	Pyrrhotite	
Coarse Cellular	Angular, thin, wide rigid walls; broken web work	Ochreous	I	0	Chalcopyrite	Blanchard & Boswell (1925)
Fine Cellular	Thin, small friable walls	Yellow-orange	I	0	Chalcopyrite	Blanchard (1939)
Pitch or Varnish	Thin superimposed films in a compact mass	Dark brown to brown black	I	0	Chalcopyrite	
Arborescent	Clinkery mass of branching clusters of subresinous granules	Yellow to brown black	I	-	Arsenopyrite & Pyrite	Blanchard (1942)

[1] I = indigenous, T = transported, Ex = exotic

[2] 0 = occupied, E = empty M = massive or semi-massive

Gossan, alteration haloes, and oxidation zones are features in which colour is the primary recognition aspect; hence the advantage of the aerial colour photograph. Hartman describes an aerial colour photograph of a western area in the U.S.A., where an Agfa Colour Aerial CN-17 complementary colour film was used, exposed through a six inch lens from ten thousand feet. Brownish red oxidation zones were recognised as target areas for follow up exploration, but these zones did not show on black and white photographs printed from the colour negative. Fitzpatrick and Wilson (1965) point out that the Nairne and other pyritic beds in the Kanmantoo Group of the eastern Mt. Lofty Ranges (S.A.) develop surface gossans with typical reddish soils, a feature easily traceable on colour photographs. They also suggest that colour photography is useful in delineating basic and ultrabasic bands of differing composition in layered basic igneous complexes such as occur in Mt. Davies Range in South Australia and adjacent parts of Western Australia.

THE ROLE OF GEOPHYSICS IN PROSPECTING FOR NICKEL

There is no geophysical method which will lead directly to the discovery of nickel ore but geophysical methods can be used to locate sulphide ore bodies which may contain nickel minerals. W.R. Bergey et. al., successfully used a variety of geophysical methods to locate the copper-nickel ore bodies at the Temagami Mine, Ontario. An aeromagnetic survey was carried out over the prospecting area which outlined major structural features. This work was followed by geophysical ground surveys using electromagnetic, self-potential and resistivity methods. The result of these geophysical surveys was the locating of a sulphide body containing nickel.

Electromagnetic methods are useful in the search for concealed sulphide ores such as pyrites pyrrhotite and chalcopyrite. Horvath (1957) gives an account of the successful application of the electromagnetic and self-potential methods in the Zeehan field, Tasmania in 1952-53.

There is little difference in conductivity between pyritic ores carrying useful metals e.g. nickel, and pyritic ores without a metal of economic interest. Any conducting body such as graphitic schist can give rise to an anomaly so for reliable results it is advisable to apply as many geophysical methods as possible.

Much of Australia's mineral area is weathered to a depth of 400 ft., the groundwater is usually highly saline and the contrast in the conductivity of lode and country rock is reduced, thus decreasing the effectiveness of the electromagnetic survey. Forwood and Roberts (1965) have described applications of the electrical method of induced polarization which shows anomalies over known areas of mineralization, but does not indicate anomalous results over saline overburden or weathered rock. The method seems likely to prove useful in locating sulphide orebodies.

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GEOCHEMICAL PROSPECTING

Emplacement of a mineral deposit leads to an anomalous dispersion of some indicator material in the environs of the deposit either during or after emplacement, a factor which is the basis of geochemical prospecting. In the search for any mineral there are preliminary requisites which should be dealt with before commencing the prospecting programme. These are; theories of ore occurrence, geological and geochemical data of known mineral occurrences in the area to be prospected, the geochemical behaviour of different elements in the superficial environment under the particular geologic, topographic, climatological and biological conditions pertaining, and techniques of chemical analysis. Such knowledge allows a suitable choice of indicators, media to be tested, sampling and analytical techniques, and a sound basis for the interpretation of any anomalies found.

(a) Orientation Stage

For the field programme to be effective the methods of prospecting should be subjected to preliminary tests in both laboratory and the field. Equipment and procedures for routine sampling should be determined at the cheapest cost per sample consistent with positive results. The methods chosen must be capable of detecting any geochemical anomaly that is significant in relation to the occurrence of ore. It is necessary to decide the lowest level of concentration that may be significant with respect to ore occurrence, the figure being called threshold, which is a cut off value expressed as multiples of background or some absolute figure such as parts per million of metal content. Threshold is the cut off value between that which constitutes normal background variation, and that of anomalous geochemical values which may be significant in relation to ore. To determine a threshold value for nickel, samples should be collected and analysed from the vicinity of known ore deposits where there is little surface disturbance by artificial agents. Such ore bodies are rare in Australia, as contamination by mining upsets the geochemical equilibrium. (Rattigan, 1965). So threshold is an arbitrary working figure often related to mineralized zones rather than ore bodies. In virgin areas it is often an arbitrary figure chosen from an assessment of plotted metallometric data, compared with that of actual mining fields.

By the end of orientation work a field testing kit with sampling devices, analytical equipment and reagents should have been designed for use in the field.

(b) Sampling media

Secondary dispersions offer the most direct guide to buried nickel ore through the many media available for testing. These media include: weathered bedrock, leached outcrops, residual soils, river silts, river sands and gravels, glacial deposits, mineralized zones, stream and underground water.

Solid media are less liable to marked fluctuation in the quantity of dispersed trace elements in space and time, and so offer the best scope for quantitative determinations essential in outlining anomalies.

Stream waters suffer from rapid fluctuations in the soluble and insoluble mineral concentration carried due to variation in rainfall and surface run-off. Their use is restricted in Australia which is predominantly arid or semi-arid. In dissected areas a rapid coverage of large areas can be made by "beheading" the headwaters and upper catchment of river systems by testing stream silts, or waters at sample points near the confluence of tributaries with major streams. Any anomalous indications can then be traced to their source by progressive testing upstream. Mather (1965) has stated that the length of a detectable train of anomalous values downstream from a significant deposit is usually found between one thousand feet and five miles, and maximum area of the catchment basin in which such an anomaly may be detectable is between five and twenty square miles. He suggests that sediment should be collected from the upper ten square miles of a drainage basin, and downstream from here sampling should be restricted to valley slope soils and small streams leading to the main ore.

Alluvial deposits carry absorbed metallic salts and fragments of resistates deposited by stream waters. These deposits remain when there is no surface flow and do not suffer as much from rapid fluctuations of indicated content as do stream waters. Silts and clays deposited in beds or lenses are most useful trace prospecting media for most base metals as they are less subject to leaching and may hold greater quantities of absorbed metallic salts than coarser deposits. (Rattigan 1965).

In the lower parts of minor drainage basins and valleys bordering major streams colluvial soil samples should be collected from the lower parts of the valley slopes. (Mather 1965). These samples although not representing such a large part of the drainage basin as stream sediments could pick up metal values from dispersion fans radiating from mineralization upslope. Samples should be collected from above stream flood level and material from old river terraces should be avoided.

Residual soils are a well used sampling media in Australia as their distribution is wide. They have constant local characteristics and are easily sampled. Mather suggests soil profiles down to weathered rock should be sampled in detail and at close intervals. This data will provide a picture of the vertical and lateral distribution of nickel in the soil profile, and possibly reflect the secondary dispersion pattern.

Underground waters are constantly migrating and are influenced by the incidence and frequency of rainfall, and are not conveniently sampled in systematic fashion.

Moraine deposits can be sampled rapidly but few areas in Australia are covered by surficial glacial deposits.

Trace-analysis techniques have been applied to plants, but it should be noted that the metal content of plants may vary according to the age of the plant, the part tested, the season, and the trace element content of soils and waters in which the plant is growing.

In detailed metallometric surveying of an anomalous area, the area should be topographically contoured and the chosen grid spacing should be so closely spaced as to allow the pattern of the anomaly to be outlined clearly in metallometric contours. This is necessary to obtain maximum data for inferring the locus

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of ore and thereby a proper siting of a first exploratory drill hole.

The orientation stage, sampling media, collection of samples, correct plotting of metallometric contours, and a sound knowledge of geochemical principles are important factors in any programme of geochemical prospecting and their correct interpretation and operation are vital to the success of any prospecting project.

(c) Use and Methods of Chromatography in the Detection of Nickel

Gordon et. al (1943) defined chromatography as "the technical procedure of analysis by percolation of a fluid through a body of comminuted or porous rigid material, irrespective of the nature of the physico-chemical processes that may lead to the separation of substances in the apparatus."

In the field-detection of nickel, techniques using paper chromatography and precipitation chromatography have been developed. (See Appendices 1 to 6 for description of chromatographic field methods, reagents and equipment used).

1. Paper Chromatography

There are four essentials of paper chromatography which are: dissolution of a small part of the mineral to obtain its metal ions in about 1 ml of solution, chromatographing a drop of the solution on paper by ascending solvents that have been selected to separate the ions by elevating them to different levels on the paper, identification of the position of the ions on the paper by reagents that produce either coloured or fluorescent compounds, and identification of the ions by colour, fluorescence and relative position on the paper.

The use of sodium peroxide fusion in zirconium crucibles provides a method for the dissolution of minerals (Belcher 1963). However pyrrhotite is soluble in hydrochloric acid whilst millerite, niccolite and pentlandite dissolve in nitric acid. To about 0.05g of finely ground mineral in a small test tube add 10 drops of HCl (1ode) 1 or 2 drops of HNO_3 (1ode). Heat and the ore minerals go into solution.

2. Precipitation Chromatography

Spain, Ludeman and Snelgrove (1962) use precipitation chromatography to identify metal ions in minerals. The stationary phase is ammonium sulphide (the precipitant) in agar gel; the mobile phase being an acid solution of the mineral. When this solution is introduced into the column the metal constituents of the solution are precipitated as sulphides in an order following the published solubilites. See Table 2. The metals are identified by the colour of their sulphides, transparency and relative positions on the column. Since the distribution involved is based on the solubility product equilibrium the bands develop in a fairly predictable fashion.

TABLE 2

COLOUR BANDS ON AGAR GEL COLUMNS IN ORDER OF APPEARANCE

Part of table by Spain et al, (1962)

Metal and Solubility of Sulphide	Metal in agar gel in descending order	Effects in solution above gel meniscus	Major sulphide band in gel
Te^{4+} insol.	Te^{4+}	Colourless solution	Opaque, sharp moderate brown TeS_2
Co^{2+} 0.0038	Co^{2+}	Pink solution	Transparent brownish-black with grey CoS Liesegang
Ni^{2+} 0.0036	Ni^{2+}	Slightly greenish solution	Brownish black transparent NiS

(d) Colorimetric Methods

This method of analysis depends upon the conversion of an element to a more or less strongly coloured compound in solution, or sometimes in colloidal suspension. Successful field methods for the determination of nickel have been evolved. (Bloom 1962) (See Appendices 7 and 8 for description of colorimetric methods, reagents and equipment used).

Paper and precipitation chromatographic methods and colorimetric methods for the determination of nickel in the field are simple to perform, equipment and apparatus are moderately priced, and easily portable, the methods are as effective in the field as at base camp and in the case of paper chromatography semi-skilled personnel can be easily trained to perform the experiment. Results of the experiments may vary with variations in temperature and humidity: if a large dilution factor is involved sensitivity is reduced and by precipitation chromatography a 24 hour period is necessary for the complete development of a chromatogram before nickel is detected.

(e) Biogeochemical Prospecting for Nickel

This method of prospecting is based on the analysis of plant ash and of the ash from different parts of the plant for metal content. The basis of the method is the ability of plants to absorb, and to be affected by high concentrations of metals from deposits at considerable depth or from a mineralized halo surrounding the ore.

Rankama (1940) used the biogeochemical method in Finland where areas were covered by Quaternary glacial deposits where it became possible to outline the underlying nickel ore body by means of the isograds based on the determinations of nickel in plant ash. The average nickel content of plants (Betula) examined by Rankama was 0.15% as against 0.001 - 0.006% in areas outside the nickel mineralization. Reichen (1950) has described a geochemical field method for the determination of nickel in plants. See Appendix 11.

Sampling techniques have been described by Warren, et al., 1952, who suggest comparisons should be made only between the same plant parts of the same age of the same species and from the same height on the plant. They advocate the suitability of second-year twigs to give more reproducible results than first-year twigs, and that anomalies may be more pronounced when results are expressed in terms of ash rather than dry weight. Table 3 shows the average metal content in the ash of nickel in five types of vegetation growing in unmineralized ground. Most systematic sampling programmes consist of sampling at 100 to 200 foot intervals after plants have been samples over barren and mineralized ground to establish which species are useful, and the cutoff above which values should be considered anomalous. Webb and Millman (1950) consider a safe maximum interval of sampling to lie between one half and two thirds the minimum dimensions of the detectable dispersion halo. Values obtained may be plotted to outline mineralized ground.

The time when the sample is taken, the weather, pH of the soil, and density of the ground are significant factors. For example, Leutwin and Pfeiffer (1954) state that the ash of small branches of birch contained 0.025% nickel in March but only 0.001% nickel in September. This was from an area of metamorphosed ultramafic rocks in a humid climate in the Frieberg Deposit, Saxony, showing that it is not possible to draw conclusions regarding nickel in subsoil horizons on the basis of nickel content of the plants. The relative nickel content of plants collected over extensive areas and in the same season is important in outlining boundaries of nickel-bearing rocks.

Marmo (1953) investigated the Nokia District, Finland, an area of phyllites and schists with uneconomic content of pyrrhotite, chalcopyrite and sphalerite, and examined cranberry leaves for nickel, copper and zinc. Nickel was found in the ash of plants growing on strong magnetic anomalies, but was absent in the ash of plants from areas where such anomalies were not apparent. As a result of these investigations Marmo concluded that geophysical methods were important when prospecting for economic deposits, the biogeochemical methods playing a supplementary role.

Biogeochemical methods of prospecting are useful in areas covered by a thick mantle of loose material, by glacial sediments, in heavily forested areas and waterlogged ground, and semi-deserts, but there are disadvantages. The depth to which prospecting by plants is effective depends on the root penetration, although Vinogradov (1955) assigns 30m to nickel ores as the maximum depth to which they are detectable by biogeochemical means, but Ginzburg suggests that this figure may be unreliable. However depth of penetration of plant roots may permit sampling of a deep horizon inaccessible by surface soil sampling, and if its roots reach the groundwater table it has an additional advantage. Interference from transported surface soils is eliminated by plant sampling and permits prospecting in areas where residual soil is nonexistent or varied.

The biogeochemical method of prospecting is useful in delineating areas suitable for more detailed investigation.

TABLE 3

Average nickel content in the ash of five types of vegetation growing in unmineralized ground in parts per million. (After Cannon 1960).

	Ni content
Grasses (above ground)	54
Other herbs (above ground)	33
Shrubs (leaves)	91
Deciduous trees (leaves)	87
Conifers (needles)	57

(f) Hydro - Geochemical Prospecting for Nickel

Hydro-geochemical prospecting can be a valuable tool in prospecting for various metals including nickel and is particularly suited to certain environments. In highly dissected young mountainous areas the method may be very effective as waters have an easier access both to the exposed and blind ore bodies, and the water table may be at the surface in many places. The metal content of the circulating waters is lowered by dilution with atmospheric waters in the rainy season and during melting of snows; factors which should be noted by the prospector. Water samples collected in the dry season when the ground water-table is stabilised below the oxidized zone may contain no metal, but may do so when the ground water rises to the boundaries of the oxidized zone. The method is recommended for highly dissected forested areas covered by thick sediments.

Surface drainage and shallow underground waters in non-mineralized areas contain nickel in 1 x 10^{-6} - 1 x 10^{-5} g/l. magnitudes and in mineralized areas 1 x 10^{-5} - 1 x 10^{-3}. (Ginzburg 1960). The presence of nickel in waters is determined entirely by their pH, and nickel is precipitated at pH 6.8 as hydrated silicates and to a lesser extent as nickel hydroxides, and is not detectable at a more alkaline pH. The nickel content of water in serpentinite bodies varies from 0.025 - 0.06 ml. and may be as high as 0.1 - 0.2 mg/l. If nickel is present as a sulfate it may be as high as 13.3 mg/l. In dry residues of waters from polymetallic deposits the nickel content varies from 0.001 to 0.006 - 0.009%, whilst the pH of waters containing minute amounts of nickel may be as alkaline as 8 to 8.85.

GEOBOTANY AND NICKEL PROSPECTING

Cannon (1960) has discussed the merits of botanical prospecting for ore deposits. This technique requires a systematic study of the species of plant growing over known ore deposits in the area to be prospected as compared to the species of a topographically similar area of non-mineralized ground, a process requiring personnel with botanical training. Table 4 shows the results of plant sampling in different localities and correlation of the results with the presence of nickel. Not one plant species has been found that grows only on ground covering a nickel deposit and if one did some botanical training would be necessary if the prospector were to depict it. It is concluded that Cannon's suggestions have little or no practical value to the nickel prospector.

TABLE 4

PROSPECTING FOR NICKEL BY PLANT ANALYSIS
(After Cannon 1960)

Locality	Plant Sampled	Results
British Columbia	Fir, cedar	Good correlation
Cuba	Vegetation	Good correlation
Finland	Birch	Good correlation
Germany	Birch, spruce, pine	Good correlation
U.S.S.R.	Grasses, herbs	Good correlation

CHEMICAL VERSUS SPECTROCHEMICAL METHODS OF MINERAL DETERMINATION

The results of the measurements, the precision, and the reliability of the geochemical survey depends on the sensitivity and exactitude of the methods employed. A comparison of the merits and otherwise of field chemical methods and laboratory spectrochemical methods have been discussed by Ginzburg (1960) and Howard and Baker (1963).

Spectrochemical methods have the advantage that the ground sample is taken directly for analysis thus eliminating the sampling digestion stage, and reducing risk of contamination. Operations are simple and rapid, 32 elements or more can be determined at one time, identification is positive and up to tens and hundreds of thousands of determinations per year per instrument can be made. There is of course the high initial cost of equipment, the need for an electric current, skilled personnel and the fact that samples must be sent to the spectrograph. Carney et al., (1957) have described a truck-mounted spectrographic laboratory which was successfully used in the field. However, a large Quartz spectrograph is a difficult and sensitive instrument to move and the more complex direct reading spectrographs cannot be moved. Suitable roads also have to be available and if the idea of the mobile spectrographic laboratory is discounted, samples should be sent to the laboratory at headquarters.

Chemical methods for the field determination that have been described have for the most part been characterized by speed, simplicity sensitivity; the precipitation chromatographic method being the exception as far as speed is concerned. The number of analyses can not compare with the spectrograph, and difficulty may be encountered in the preparation of concentrated buffer solutions free from trace metal impurities. But chemical methods can be made more sensitive by virtue of the relatively greater weight of sample that can be taken for analysis, also on the spot tests can be made. An oft-quoted disadvantage of the chemical method is its inability to analyse more than one element at a time, but this becomes an advantage if only one element such as nickel is being sought.

Chemical methods for field determination of minerals are useful for on the spot analysis but all sampling on a large scale should have the backing of laboratory facilities for spectrochemical analysis.

CONCLUSIONS

The locating of a nickel ore body or any mineral of economic value may be achieved by a combination of geological, geophysical and geochemical investigations. Photogeologic and geophysical methods will not lead directly to a nickel deposit, but colour aerial photographs will indicate a zone of oxidation and electromagnetic and induced polarization methods are useful in the search for concealed sulphide bodies. Leached outcrops and hydrothermal alteration zones may be indicative of an economic deposit. The importance of orientation studies is stressed before a geochemical prospecting programme is put into practice. On-the-spot tests using chromatographic and colorimetric methods are useful with biogeochemical and hydrogeochemical testing recommended for areas covered with dense vegetation. However, all sampling on a large scale requires the backing of laboratory facilities for spectrochemical analysis. A combination of geological, geophysical and geochemical surveys will yield data on which a reasonably accurate assessment of the possibilities of finding an ore body can be made, but an integrated effort is needed to ensure maximum success.

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APPENDIX I

SOLVENT MIXTURES USED IN PAPER CHROMATOGRAPHY

Solvent Mixtures are necessary to separate a small number of metal ions from each other. Four solvent mixtures are used and as two of the mixtures contain hydrofluoric acid, vessels and apparatus should be of polythene, which is also durable under field conditions. The solvent mixtures are placed in wide-mouthed jars of about 6 litres capacity with screw-top or clamp-on polythene lids.

Solvent 1 (after Ritchie 1964)

Development time: 6 hours
Effective life if well sealed: 4 or 5 days
Butanol 50ml, 10NHCl 25 ml, 40% HF 1 ml and water 24 ml

Solvent 2

Development time: 6 hours
Effective life if well sealed: 4 or 5 days
Add to separating funnel - butanol 50 ml, water 50 ml and 40% hydro bromic acid 5 ml. Shake well for one or two minutes and allow the phases to separate. Run off and discard the lower (aqueous) layer. To the butanol fraction add 40% HBr (20 ml).

Solvent 3

Development time: 3 hours
Effective life if well sealed: 3 or 4 days
Ethanol 30 ml, methanol 30ml and 2 N HCl 40 ml.

Solvent 4

Development time: 1 hour
Effective life if well sealed: 1 or 2 days
Acetone 90ml, 10 N HCl 5 ml, 40% HF ml and water 4 ml.

If large numbers of determinations needed, double the quantities.

APPENDIX 2

REAGENTS AND EQUIPMENT USED IN PAPER CHROMATOGRAPHY

Reagents

Butanol
Ethanol
Methanol
Hydrochloric acid
Hydrobromic acid
Hydrofluoric acid
Glacial acetic acid
Acetone

Ammonium polysulfide
Ammonium hydroxide
8 - hydroxyquinoline
Stannous chloride
Rosolic acid, 1g
Sodium acetate. 10g
Sodium tartrate, 10g

A few grams each of the soluble salts of common metals can be included (avoid nitrates, sulfates, phosphates if possible).

Equipment and Materials

4 polythene jars about 6 litre capacity with wide mouths and lids.
1 polythene measuring cylinder 0-5 ml.
1 polythene measuring cylinder 0-100 ml.
12 polythene microbeakers 10 ml.
4 polythene trays (16 cm x 12 cm x 3 cm)
2 vaporizers (rubber bulb with glass top, or nasal vaporizers are satisfactory)
1 portable U.V. lamp
1 small double thickness black cloth tent or hood
Chromatography paper
Absorbent paper (newspaper, printed or not will do)
Soft glass tubing (for capillary tubes)
Portable burner
1 500 ml glass beaker

APPENDIX 3.

PREPARATION OF CHROMATOGRAMS AND DETECTION OF IONS ON CHROMATOGRAMS
SEPARATION AND ESTIMATION OF NICKEL

Preparation of Chromatograms

A large selection of chromatography paper is available. (See Lederer and Lederer, 1957) Whatman No. 1 chromatography paper at 21° c ± 1°c can be used for determination of nickel ions, but in humid tropical conditions papers with greater wet strength could be used e.g. Macherey - Nagel 263.

Rectanges (30cm x 25 cm) upon which parallel chromatograms may be run are effective. The test solution is applied to the paper from a thin glass capillary tube in the form of a half-inch smear. Applications are allowed to dry. The narrow strips 3cm x 25cm, are suspended from hooks in the lid, or the large rectangles are converted to slightly gaping cylinders with a paper clip at the top. Jar is sealed and covered by a second larger vessel to minimise unequal heat or air currents. In the search for unknown metal content the detection tests require that four chromatograms of each test solution be prepared in each solvent. Parallel chromatograms using known solutions of metals alongside the unknown, often eliminate further search for the identity of the metals in the sample solution. Inspection by opening the jar is possible but should be avoided.

Detection of Ions on Chromatograms

1. Coloured Spots on the Chromatograms

Many ions form coloured complexes with the solvents without the aid of the reagents. The spots which may be fleeting, should be marked on the chromatograms as soon as possible after they are taken out of the solvent, the visibility of the spots being controlled by the concentration of the ion in the test solution. But the absence of a spot on the chromatogram at this stage does not prove the absence of the ion, reagents being more positive in this respect. But detection of an ion in this way can save the use of a reagent. SEE TABLE 5a.

2. Detection by Ammonium Polysulfide Solution

Coloured sulphides are detected on one chromatogram from each solvent by holding it over a concentrated solution of ammonium polysulphide or by dipping it into a dilute aqueous solution. SEE TABLE 5b. It is seen that nickel and cobalt give the same colour.

3. Detection by 8-Hydroxyquinoline solution

Most metals form either coloured or fluorescent hydroxyquinolates, the optimum precipitation or fluorescence for each metal ion being controlled by the pH of the hydroxyquinoline solution.

A solution is prepared thus: Dissolve about 2g of 8-hydroxyquinoline in some ethanol (20ml) leaving a slight excess of the solute. Add a few drops of a saturated sodium acetate solution (about 10g in 10ml of water) and then glacial acetic acid slowly until the solution becomes clear and yellow. At this stage the pH is usually about 5, but may range from 2 - 6. This solution is effective only for about twenty minutes.

After being dipped in the solution the chromatograms are placed on absorbent paper and any coloured spots marked with pencil, then they are viewed under ultra-violet light to observe fluorescence. SEE TABLE 5c.

4. Specific Detecting Reagents for Nickel (After Ritchie 1964)

The reagents and colours in visible light are:-

Ammonium polysulphide	Brown-black
Oxine	Green-black
Dithizone	Green
Diphenylcarbanzone	Violet

Identification of Metal Ions

The metal ions are identified primarily by their RF values or chromatographic profiles.

$$RF = \frac{\text{distance moved by the ion}}{\text{distance moved by the solvent front}}$$

RF VALUES OF METAL IONS

ION	SOLVENT 1	SOLVENT 2	SOLVENT 3	SOLVENT 4
Cu^{2+}	0.53	1.0 and 0.54	0.65	0.56
Co^{2+}	0.45	0.30 - 0.38	0.70	0.45-0.55
Ni^{2+}	0.52	0.32	0.63 - 0.67	0.03

Distances are measured from the point of application to the solvent front or the centre of the spot. Some ions produce a tail that merges from below in to the spot; if so calculate RF values to the top of a spot.

The chromatographic profile of an ion is obtained by plotting and joining its RF values in the solvents on 4 adjacent columns. The C.P. for each ion is characteristic and permits identification of the ion.

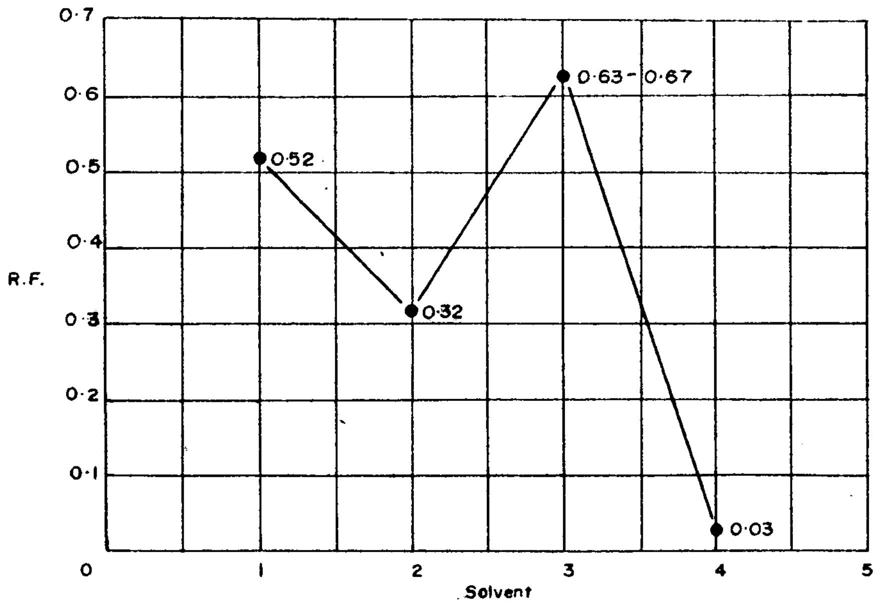

Fig. I

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CHROMATOGRAPHIC PROFILE OF NICKEL

TABLE 5a

COLOUR OF SPOTS ON CHROMATOGRAMS AS TAKEN FROM SOLVENTS

ION	SOLVENT 1	SOLVENT 2	SOLVENT 3	SOLVENT 4
Ni^{2+}	Green	Yellow	Yellow-green	Green

TABLE 5b.

DETECTION BY $(NH_4)_2S$ SOLUTION

ION	COLOUR OF SPOT
Ni^{2+}	Brownish-black
Co^{2+}	Brownish-black

TABLE 5c

DETECTION BY 8-HYDROXYQUINOLINE SOLUTION
(pH2-6)

ION	COLOURED SPOT	FLUORESCENCE
Ni^{2+}	Green-brown	
Co^{2+}	Brown-yellow	

Under field conditions RF values vary with temperature and humidity. Humidity is a problem as the ascents of the solvents by capillarity is almost stopped when the paper becomes moist. Inconsistent results may be obtained when the vessels are exposed to wind or direct sunlight, hence their covering of a box which overcomes the problem. Ritchie ((1963) has shown that hot dry conditions are conducive to higher RF values, hot-wet conditions produce values slightly lower than the hot-dry, and cold-wet conditions produce lower RF values than the hot conditions. Identification of ions cannot be made by reference to the published RF values obtained under laboratory conditions. This may be overcome by running parallel chromatograms in such a way that known and unknown ions may be compared. SEE TABLE 6.

An air-tight container kept dry by silica gel should overcome the moisture problem.

Nickel	Solvents	1	2	3	4
		0.52	0.32	0.63-0.67	0.03

Colour of sulphides : Brownish-black

Colour of hydroxyquinolate: Green-brown

Fluorescence: Absent

Hunt and Wells (1954) North and Wells 1959 have developed paper chromatographic methods for determination of copper, cobalt, nickel etc. in soils which represent a significant advance in geochemical prospecting.

Separation and Estimation of Nickel (also applicable to Copper and Cobalt)

The soil sample is ground and passed through an 80 mesh sieve. A weighed sample (0.5g) is mixed with 1g of powdered potasium bisulphate in an 18 x 150 m.m. hard glass test tube. Fuse gently for 1 minute. Cool and then add 2ml of acid mixture (prepared by mixing 50ml HCl cs.g.1-18), 5ml HNo_3 (s.g. 1.42) and water to make up 100ml. Immerse the lower inch of the tube in boiling water for 10 minutes, with occasional shaking. Allow to cool whereupon silica settles out. Take 0.01ml of the clear supernatant liquor as the chromatographic sample and apply it to one strip of the slotted paper. Nine similar samples can be applied to the same sheet. The sheet is rolled into a cylindrical shape and held with a paper clip. Stand the cylinder in a 600ml beaker floating in a boiling water bath, (to dry the sample solution added). After three minutes transfer the paper cylinder to another 600ml beaker, to which 10 minutes previously, 20ml of the following solvent has been added: ethyl methyl ketone (pure and dry) 15ml, hydrochloric acid (s.g. 1.18) 3ml, water 2ml. Cover beaker with a petri dish. Develop until the solvent front just reaches the top of the strip. Remove chromatogram and allow to dry. Neutralise paper by exposure to ammonia vapour for two minutes. Spray both sides of paper with 0.1% solution of rubeanic acid (0.1g rubeanic acid dissolved in 60ml of warm ethanol, filtered and made up to 100ml with water). Allow to dry and estimate metal content by comparison with standard chromatograms. Copper, cobalt and nickel form bands at positions corresponding to RF values respectively 0.68, 0.5, 0.27.

Agrinier, H(1957) has reported a specific method for the qualitative and/or quantitative determination of nickel in ores. (The method is also applicable to cobalt and copper).

Agrinier suggests vessels 25cm x 9cm and Whatman No. 1 paper. The ore is crushed and sorted under a low power stereomicroscope to avoid incorporation of extraneous material in the sample.

Grind the sorted ore finely and place 10mg of it in a silica micro beaker. Add 10 N HNO_3 (3 drops) and evaporate dryness. Dissolve the residue in 15% HCl (2 drops). The solvent mixture is prepared as follows: acetone 87 ml, 12 NHCl 8 ml, water 5 ml. The chromatogram is developed until an ascent of 10cm is achieved and is then dried in a current of cold air. The chromatogram is then exposed to ammonia fumes for five minutes. Spray both sides of the chromatogram with rubeanic acid (1% solution in ethanol). Wait several minutes for spots to appear. Identification is based on the following data.

	RF	Colour
Ni^{2+}	0.05	Blue Spot
Co^{2+}	0.5	Brownish yellow spot
Cu^{2+}	0.65	Olive green spot

Estimations are made by comparison with prepared standard chromatograms.

Prepare standard solutions as follows: Weigh 1g Co_2CO_3, 1g CuO, 0.91g NiO and place in a 50ml beaker and add 12 NHCl (20 ml). Dry carefully without spitting. Take up the residue in 15% HCl (71ml). This solution contains 1% of each metal per ml. Make the following dilutions: 0.8, 0.6, 0.5, 0.4, 0.3, 0.2, 0.15, 0.10, and 0.01%. Apply 0.01 ml of each solution at suitable positions on the paper. All developments are achieved under humid conditions by placing 100 ml of water in the vessel. Thirty minutes before the separation the solvent is added to a dish which rests on the floor of the vessel. The paper as a cylinder is allowed to stand in the solvent in the dish. An ascent of 10cm is sufficient. After development the chromatogram is treated with reagent as above. The percentage content of the particular metal in the ore is obtained by multiplying the value obtained by comparison by one hundred.

TABLE 6

R.F. VALUES OF METAL IONS UNDER AUSTRALIAN FIELD CONDITIONS
(After Ritchie 1963)

Metal Ion	Solvent 1				Solvent 2				Solvent 3				Solvent 4			
		40°	35°	12°		40°	35°	12°		40°	35°	12°				
	Published	Humid 10% Hot-Dry	H.80 % Hot-wet	H.80% Cold-wet	Published	H.10% Hot-Dry	H.80% Hot-wet	H.80% Cold-wet	Published	H.10% Hot-Dry	H.80% Hot-wet	H.80% Cold-wet	Published	H.10% Hot-Dry	H.80% Hot-wet	H.80% Cold-wet
Cu^{2+}	0.53	0.34-0.92	0.34-067	0.45	0.54-1.0	.92	C-0.58	0.32	0.65	0.77	0.72	0.73	0.56	0.87	0.80	0.45
Co^{2+}	0.45	0.28	0.40-0.80	0.42	0.30-0.38	0.28	0.20	0.24	0.70	0.74	0.72	0.66	0.45-0.55	0.58	0.42	0.26
Ni^{2+}	0.52	0.27	0.61	0.40	0.32	0.27		0.24	Up to 0.67	0.77	0.65	0.58	0.03	0.02	0.02	0.25

Solvent 1 = Butanol-conc. HCL-conc. H.F-water (100:50:2:48)
2 = Butanol fraction of butanol-conc. HBr-water (100:10:90) + conc. HBr (40)
3 = Ethanol-methanol - 2N HCL (60:60:80)
4 = Acetone-conc. HCL-conc. HF-water (180:10:2:8)

APPENDIX 4

ADVANTAGES, DISADVANTAGES AND RESULTS OF THE DESCRIBED PAPER CHROMATOGRAPHIC METHODS

Advantages

a. The processes and manipulations by the operator are very simple

b. Equipment and materials are moderately priced.

c. Method is as effective in the field (at a base camp) as in the laboratory.

d. While the total time for analysis might be 6 or 7 hours, the equipment can be left unattended for 5/6ths of this time.

e. Very small quantities of the mineral are needed and so pure samples are easier to obtain.

f. Semi-skilled personnel can be easily trained to perform the experiment.

Disadvantages

a. Variation of RF values with variation in temperature and humidity.

b. If a large dilution factor is involved sensitivity is reduced.

Results

The paper chromatographic method is very sensitive, and usually unobserved impurities show up on the chromatograms, and so great care must be taken when taking the 0.05g mineral sample, that foreign material is not included. In general if a metal constitutes 10% of a mineral it will show up on the chromatogram. If the concentration of the mineral is increased the presence of metal constituents may be revealed and high concentration of the major constituents may create difficulties with large dense spots. The use of a sensitive specific reagent will eliminate or diminish the effect of some major constituents, and will facilitate the detection of the minor constituent required.

APPENDIX 5

THE CHROMATOBOX

This consists of a polythene box (7.5cm x 7.5cm x 4.5cm) containing a small compartment which takes from 5-8ml of solvent. This compartment leads over a weir to a larger compartment which accommodates a strip of chromatography paper (40cm x 6cm) which is rolled with a band of Teflon of similar length. The surface of the Teflon is raised thus separating the layers of the paper from each other and also allowing uniform flow of the solvent along the paper. The roll is held secure by an open polythene ring. The paper is rolled so that one end of it protrudes to such an extent that it can be led over the weir into the solvent. Here it is held between two small glass plates, which are held together by a glass rod pressing against them. A tightly fitting polythene lid is provided. The test solution is applied to the paper in the usual way on the horizontal surface near the weit. After the sample dries, the solvent is added and development is carried out in the closed chromatobox. The same methods of detection and identification of ions as apply to ordinary paper chromatography are used here.

For field and laboratory use, the chromatobox is a simple and efficient method of paper chromatography. It was introduced by Barrollier of Schering, A.G., West Berlin. (See Ritchie, 1964).

APPENDIX 6

PRECIPITATION CHROMATOGRAPHY. PREPARATION OF GEL COLUMNS AND SAMPLES FOR ANALYSIS, ADVANTAGES AND DISADVANTAGES

Preparation of gel columns

Soft glass tubing (6mm bore) is cut into 24 cm lengths, constricted by drawing out at the centre and then cut into halves. The wide ends are fire polished. It is convenient to make up batches of 100 at a time. The gel columns, if stored in an atmosphere of propane or natural gas last up to six days.

Place 4g agar agar (shredded) in a 1,000ml beaker and add enough water to cover it. Stand for about an hour until the shreds are swollen and the soluble pigment is leached away. Pour off excess water. Add the gel to another beaker containing a boiling solution of sodium acetate trihydrate, N.F. grade, (54g in 200ml water). Keep boiling for about 5 minutes or until only occasional shreds of agar remain undissolved. Filter while hot through a glass wool pad into a storage flask. The batch is enough for about 120 columns and will keep indefinitely in a stoppered flask. The glass tubes are filled as follows: Place the hot stock solution (rewarmed if necessary) into a test tube (22 x 100mm), add 3 drops ammonium sulphide (A.R. grade) and stir. Place the glass tube (constricted end downwards) into the gel and wait until it rises about two-thirds of the tube. The tube is then withdrawn (with a finger pressed tightly over the wide end) and cooled in ice or cold water until the gel sets. If bubbles form at the top of the gel in the tube, and cannot be dislodged by tapping, the tubes should be discarded. The filled tubes will not keep even 24 hours unless stored in an atmosphere of propane or natural gas.

Preparation of Samples for Analysis

Place the finely ground minerals (0.5 - 1.0g) in a 20ml porcelain casserole and add concentrated HCl (5 drops), and concentrated HNO_3 (5 drops). Evaporate to dryness and then add 6 M HCl (1ml). Transfer to a test tube. The quantity of sample necessary is determined by trial. Take 2 drops of the mineral solution and add 6 M HCl (8 drops). Place 3 drops of this solution on top of the gel column. To avoid the formation of bubbles, place the tip of an eye-dropper near the top of the gel at the curve and apply the solution drop by drop. Bubbles may be removed by tapping, or be drawn out by the tip of the eye-dropper. Stand the column upright for 48 hours in the same test tube to which the sample solutions were transferred. Allow diffusion of some of the sample solution upwards from the bottom of the column. Then the colour bands and other characteristics are observed and interpreted. These are transparency, sharpness of boundaries, the presence of precipitate above the meniscus of the gel, the relative positions of the precipitates on the column, and presence of Liesegang banding. See Table 2.

Liesegang bands are useful in distinguishing between colbalt and nickel, both minerals forming bands of the same colour, but nickel is without Liesegang bands.

Banding is not complete until 48 hours, but most ions can be identified within 24 hours.

Advantages of Precipitation Chromatography

(a) Cheap and portable equipment

(b) All metals that produce insoluble sulfides may be identified in mixtures by a single simple precedure.

(c) Concentration may be estimated roughly by density of precipitate.

Disadvantages

(a) Considerable experience is necessary to interpret the results.

(b) 48 hour period is necessary for the complete development of a chromatogram - 24 for nickel.

(c) Considerably lower sensitivity than other colorimetric or spectrographic methods.

(d) Instability of the agar gel columns.

APPENDIX 7

COLORIMETRIC METHOD. DETERMINATION OF TOTAL AND AVAILABLE NICKEL USING DIMETHYLGLYOXIME

Field Determination of Nickel Using Dimethylglyoxime

Bloom (1962) has described methods of determination involving total nickel and available nickel.

Total nickel is the amount of metal extracted from the sample by hot (1:3) nitric acid after digestion for one hour. Available nickel is defined as that which is extracted by ammonium citrate at ambient temperature.

Determination of Total Nickel

Weigh 0.2g sample, minus 80 mesh fraction, into a culture tube and add 3ml (1:3) nitric acid. Digest sample for about 1 hour at low heat on a hot plate. As the solution evaporates add water. Dilute with water to 10-ml mark and mix. Transfer a 2-ml aliquot to a tube containing 5-ml buffer solution B. See Appendix 2. Scoop about 25mg of hydroxylamine-hydrochloride into tube, add ½-ml dimenthylglyoxime solution, and mix. Solution should be blue; if not add dilute ammonium hydroxide until blue. Add 1ml xylene and shake vigorously for about 20 seconds. Let phases separate for 5 minutes and read colours. Compare with standards. If nickel content of aliquot used is greater than the end standard, repeat using a smaller aliquot.

Preparation of Standards

To eight tubes, add 0,2,4,6,9,12,15 and 20 micrograms of nickel, respectively. Add 5ml of buffer solution B. Add ½-ml dimethylglyoxime solution and mix. Add 1ml xylene and shake vigorously for 20 seconds. Let phases separate for 5 minutes and use. These standards are usually good for 48 hours. As the precipitate settles out after about ½ hour, shake tube gently from side to side for a second or two before using.

To calculate parts per million:

Micrograms in standard x 10/ml aliquot x5 = p.p.m.

Advantages

(a) This method is cheap and the equipment is readily available from chemical supply houses.

(b) More than 70 determinations can be made per man day.

(c) Wide range of standards allows from 25 to 10,000 ppm to be determined, higher values being obtained by making appropriate dilutions.

Determination of Available - Nickel

Scoop about 0.5 or 1g of minus 80 mesh sample into a calibrated tube. Add 5ml of buffer solution A (see Appendix 2) followed by ½-ml dimethylglyoxime solution. Add 1 ml xylene and shake vigorously for about 20 seconds. Rotate the tube horizontally for about a minute. Hold upright and look for orange or pink in the upper layer. If a 0.5g sample does not yield orange, double the sample size.

Semi-quantitative estimations are made as follows: Add 1-or 2-ml increments of xylene and shake vigorously for about 3 seconds between additions and continue until the orange or pink is discharged. Record the volume of xylene used. This volume is converted to parts per million thus:

of	0.5-g sample used	ml of xylene x 7
	1.0-g " "	ml of xylene x 3.5

Advantages

(a) Equipment is easily portable allowing immediate semi-quantitative determinations at the sample site.

(b) Non breakable polyethylene wash bottles are suitable containers for the solutions. (Place sample in a calibrated culture tube, add appropriate amounts of reagents by squeezing the polyethylene reagent bottles, shake tube and intensities of resulting colour are estimated).

(c) About 2 minutes are required for a determination.

(d) Method suited for the analysis of stream sediments.

Hawks and Bloom (1956) report that variations in sediment sizes have a pronounced effect upon available metal values and that more metal is carried in the finer fractions.

Both these field methods for the determination of nickel are rapid, inexpensive and simple to perform.

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APPENDIX 8

REAGENTS AND APPARATUS FOR DETERMINATION OF AVAILABLE AND TOTAL NICKEL (Colorimetric Method)

Standard Nickel Solution, 0.01 per cent. Dissolve 0.0448g of $NiSO_4 \cdot 6H_2O$ in water and dilute to 100 ml with water. One ml contains 100 micrograms of nickel. Make dilutions of 10 micrograms per ml from this solution.

Water. All reference to "water" refer to metal-free water usually purified by passing it through a resin demineralizer.

Dimethylglyoxime 1 per cent. Dissolve 1 g dimethylglyoxime in 100 ml of ethyl alcohol.

Aquet 50 per cent solution in water. Add 1 part of Aquet to 1 part water and mix. Aquet is 25 per cent solution of non-ionic butyl phenoxy polyoxethylene ethanol and is sold as a detergent by the Emil Greiner Co., 20 N. Moore St., New York 13, N.Y.

Thymol Blue. 0.04 per cent solution

Hydroxylamine-hydrochloride. Grind coarse crystals down to about minus 2mm to obtain rapid solution.

Nitric Acid (1+3). Mix 25ml of concentrated nitric acid with 75ml water.

Xylene. ACS GRADE.

Buffer Solution A (for use with "available-nickel" test).

Dissolve 25g of ammonium citrate, 4g hydroxylamine-hydrochloride in about 300ml of water and add 5ml of thymol blue. Add concentrated ammonium hydroxide until a strong blue colour is obtained (pH 8.5). Remove heavy metals by extracting with 15-ml portions of 0.01 percent dithizone in carbon tetrachloride, until dithizone is green. Remove the dithizone with several washing of chloroform until the latter is colourless. Dilute to 500ml with water and add 3ml of Aquet and mix. If resulting solution is not blue, add more ammonium hydroxide. (It may be unnecessary to extract the buffer if reagents are nickel-free and not too high in copper and cobalt. Determine this by running a blank).

Buffer Solution B (for use with "total nickel" test)

Proceed as with the preparation of Buffer Solution A, above, but omit the addition of hydroxylamine-hydrochloride.

APPENDIX 8 (Cont.)

2 100-ml-volumetric flasks, glass stoppered.

50 culture tubes, borosilicate, 18 x 150 mm, marked at 10-ml volume.

10 culture tubes, borosilicate, 18 x 150 mm, (for use with "available-nickel" test). Calibrate as follows: Mark $5\frac{1}{2}$ ml volume with a zero. Graduate rest of tube at 2ml intervals; mark at 2,4,6,...14ml.

4 Test-tube racks to hold about 20 tubes each.

2 dropping bottles, 125-ml capacity, stoppered.

6 Polyethylene wash bottles, 8-oz capacity.

2 Pipettes 1 ml capacity, 0.1-ml graduations.

2 Pipettes 10ml capacity, 0.5-ml graduations.

50 corks to fit culture tubes (polyethylene stoppers are available from the Dynalab Corp., Rochester, N.Y. Catalogue No. 1274 size 2).

APPENDIX 9

A FIELD METHOD FOR THE DETERMINATION OF NICKEL IN SOIL

Stanton and Cooper (1958) describe a field method for determination of small amounts of nickel in soils and rocks.

Procedure

Weigh 0.2g of sieved sample into a borosilicate test tube. Mix with 1g of potassium bisulphate (fused, powder). Fuse until frothing has ceased and heat for a further 2 minutes. A primus stove fitted with an improvised "coronet" attachment to support 6 tubes in the flame is adequate. Allow the melt to cool, and then add 5 ml of N hydrochloric acid. Digest on a sand tray until the melt has disintegrated. Pipette an aliquot of 2ml into a test tube containing 5ml of buffer solution. Operate with a batch of 10 samples from this stage. Use tubes 10 x 180mm if high values are expected. Calibrate the tubes at 5ml and the buffer solution added from a polythene wash-bottle. Add 1 ml of a furildioxime solution. Cork the tube and shake vigorously for 2 minutes. Compare the intensity of yellow in the solvent phase with a set of standards. If the unknown has a greater intensity than the highest standard, dilute with a known volume of benzene until it is within the range of the standards.

Nickel content in parts per million

$$= \frac{b \times v \times d}{w \times a}$$

b = matching standard (g)
v = volume of solvent phase (ml)
d = volume of leach solution (ml)
w = weight of sample (g)
a = aliquot taken (ml)

Preparation of Standards

To 10 test tubes each containing 5ml of buffer solution, add respectively 0,0.05,0.1,0.2,0.3,0.4,0.5,0.6,0.7, and 0.8ml of a standard solution containing 5 u g of nickel per ml. Add 1 ml of α furildioxime solution. Cork the tubes and shake vigorously for 2 minutes.

Preparation of Reagents

1. N hydrochloric acid

Mix 40ml of the concentrated acid (sp. gr. 1.18) with 400 ml of water.

2. Buffer Solution

Dissolve 200g of tri-ammonium citrate in 500ml of water, treat with 0.01% dithizone in carbon tetrachloride to remove copper, and extract the excess dithizone with carbon tetrachloride. This minimizes interference from copper but may be omitted if the combined copper content of the samples and reagent is less than 300 p.p.m. Dilute 50ml of the stock citrate solution and 130ml of ammonia solution (sp.gr 0.880) to 1 litre.

The resulting solution will have a pH value of 10.3 (the optimum pH range for the extraction of nickel furildioxime by benzene from a citrate solution is 9.0 - 10.3). If the ammonia solution has a specific gravity greater than 0.880, a proportionately larger volume must be taken.

3. α furildioxime solution

Dissolve 0.3g in 10ml of ethyl alcohol (absolute) and mix with 90ml of benzene. A yellow colour may develop on standing but will not interfere with the test providing the solution is not kept for more than 7 days.

4. Standard nickel solution

Dissolve 50mg of nickel powder in 10ml of 25% nitric acid and dilute to 500ml with water. Dilute 5ml of this stock solution to 100ml with water to give a solution containing 5 μg of nickel per ml. Fresh dilute solution should be prepared from the stock solution each day.

Copper imparts a brownish colour to the solvent phase which may affect visual comparison with standard solutions, but this is not usual provided the copper to nickel ratio does not exceed 30.1

Advantages of the Method

(a) A mean accuracy of ± 25% is easily achieved by a relatively unskilled operator.

(b) 80-100 samples can be analysed per 8-hour man day.

(c) Nickel is detected at 1 p.p.m.

Field tests were satisfactorily carried out in Tanganyika and Bechuanaland when over 3000 soil samples were analysed. Nickel content of soil as determined by the above test can be related to the underlying bedrock e.g. high Ni values from picrite and olivine norite, low over acid gneiss, norite and anorthosite.

APPENDIX 10

EQUIPMENT AND REAGENTS FOR DETERMINATION OF NICKEL IN SOIL

(After Stanton & Coope, 1958)

BASIC EQUIPMENT REQUIRED

1 Torsion balance, 500-mg capacity

2 Rough balance, 250-g capacity, for weighing reagents.

3 Mixed bed ion exchange unit for preparing metal-free water. A simple unit may be constructed from 2 ft. of polythene tubing (approximately 1-in. internal diameter) filled with ion exchange resin. 1lb of resin is normally adequate for one field season.

4 2 racks, each to hold 10 test tubes.

5 2 racks, each to hold 50 test tubes.

6 Glass-writing diamond

7 Perspex scoop
Made from perspex bar (3 in. x $\frac{1}{2}$ in. x $\frac{1}{2}$ in.) with a cavity drilled out to measure 1g of powdered potassium bisulphate.

8 Primus stove, No. 5 silent burner.

9 Improvised steel "coronet" attachment to hold six tubes in the primus flame.

10 Hot plate, or another primus stove, with a sand tray containing a layer of sand $\frac{1}{2}$-$\frac{3}{4}$ in. deep.

11 Multi-tube rack to support test tubes while digesting on the sand tray.

12 Automatic dispenser, 5 ml.

13 Pyrex reagent bottle, 500ml.

14 Cork borers

15 Pipette, pyrex 2 ml.

16 Pipette, pyrex, graduated, 10ml x 0.1 ml.

17 Pipette, pyrex, graduated, 1ml x 0.01 ml.

18 Automatic pipette, 2ml

19 Pyrex measuring cylinder, 1 litre.

20 Pyrex measuring cylinder, 100ml.

21 2 Pyrex measuring cylinders, stoppered, 100ml.

22 Pyrex volumetric flask, 500ml.

23 Pyrex beaker, squat, 50ml.

24 Pyrex beaker, squat, 1 litre.

25 Pyrex separating funnel, squib type, 1 litre

26 2 Polythene wash bottles, 500 ml.

27 2 Polythene reagent bottles, 1 litre

28 Polythene reagent bottle, 4.5 litres.

Additional Equipment Required per 1000 Determinations

1. 1 gross pyrex test tubes, rimless 16 x 150mm.
2. 3 dozen pyrex test tubes, rimless, 18 x 180 mm or 19 x 150 mm
3. 4 dozen corks to fit tubes in item 2
4. 6 corks, 1-in diameter at narrow end.

Reagents Required per 1000 Determinations

1. 2 litres hydrochloric acid, sp. gr. 1.18, Analar
2. 200g tri-ammonium citrate
3. 2 litres ammonium solution, sp.gr. 0.880, Analar.
4. 4g α furildioxime
5. 6 litres benzene, crystallizable
6. 150ml ethyl alcohol, absolute
7. 50mg nickel powder
8. 10ml nitric acid, sp.gr. 1.42, Analar
9. 1.5kg potassium bisulphate, fused, powder
10. 0.1g dithizone, Analar
11. 500ml carbon tetrachloride

Items 10 and 11 will not be needed if it is found unnecessary to treat the citrate for the removal of copper impurities.

APPENDIX 11

GEOCHEMICAL FIELD METHOD FOR DETERMINATION OF NICKEL IN PLANTS

(After Reichen 1951)

PROCEDURE

The fresh plant material is placed in a platinum dish and ashed directly over the flame of the Coleman stove. The material should be stirred occasionally during the ashing to facilitate burning. After glowing ceases, it should be removed from the burner and the ash allowed to cool. The ash is pulverized and mixed thoroughly with a glass rod flattened on the end.

Ten milligrams of ash are placed in a calibrated test tube, and 0.5ml hydrochloric acid is added and the mixutre is heated in a boiling water bath for 20 mins. The test tube is transferred to a rack and 0.2 ml molybdate solution, 0.5 ml sodium citrate solution, and 1 drop thymol blue are added. The mixture should be shaken thoroughly and ammonium hydroxide added until the solution turns yellow. Then the freshly prepared 1 to 1 ammonium hydroxide is added carefully, one drop at a time, to just a true blue. If the flakes of carbon remaining from the ashing cause confusion in seeing the colour of the solution the carbon should be allowed to settle out before adding more ammonium hydroxide. The volume is made up to 2 ml with purified water, shaken thoroughly and let stand for about 15 minutes to allow most of the calcium citrate to precipitate before filtering. To filter, the air is squeezed out of a rubber bulb which is placed over the open end of a filter stick, and the stick is inserted into the test tube. The vacuum draws the liquid into the filter stick rather rapidly.

A confined spot with 0.2ml of the solution is made on dimethylglyoxime reagent paper in the chromagraph. When the spots are dry they are compared with the standard series to determine the amount of nickel in the sample of plant ash.

APPARATUS AND REAGENTS

Apparatus

A burner such as a Coleman GI pocket stove to ash the samples.
A balance such as Roller-Smith, Model C, 0 to 75mg., to measure the sample. A metal free (lucite) scoop, previously calibrated by weighing a measured amount of pulverized plant ash, can also be used.

Test Tubes, 13 x 100 mm. calibrated at 2 ml.

Filter Sticks, as those listed in Scientific Glass Co. catalogue, Catalogue No. M-2480C.

Micropipet, 0.5 ml. calibrated in tenths.

Rubber bulbs of the type used on large pipets or syringes such as listed by Eimer and Amend, Catalogue No. 14-070.

APPENDIX 11 (cont)

Reagents.

Hydrochloric acid, constant boiling or 1 to 1.
Sodium citrate. Dissolve 50 grams of sodium citrate in 100 ml water.
Ammonium hydroxide, concentrated and 1 to 1, freshly prepared.
Thymol blue indicator solution, 0.1%.
Molybdate solution. Dissolve 1 gram of molybdic acid in a few milliliters of dilute sodium hydroxide and dilute with water to 100ml.
Water, distilled in an all-borosilicate glass still or passed through a resin demineralizer such as the Bantam manufactured by Barnstead Still and Sterilizer Co.
Standard nickel solution, 0.01%.
Dimethylglyoxime reagent paper. Dip sheets of Whatman No. 50 Filter paper into a saturated solution (approx. 2%) of dimethylglyoxime in acetone. Insert the paper at a rapid, constant rate, as pauses in the immersion produce an uneven coating. When the paper is dry, it should be dipped again. The standard series and the tests should be made on the same batch of paper. Cut the reagent paper into strips 7/16 inch wide. The edges which have been handled should be discarded.
Standard series of nickel dimethylglyoxime spots. A series of standard nickel dimethylglyoxime spots were prepared from 0.2ml. portions of solutions containing 0.5, 1.25, 2.5, 3.75, 5.0, 7.5, and 10 micrograms of nickel per ml. (corresponding to 0.010, 0.025, 0.050, 0.075, 0.10, 0.15, and 0.20%, respectively, of nickel in the ash for a 10-mg sample), each standard solution containing 0.2 ml molybdate solution, 0.5 ml sodium citrate, and 1 drop thymol blue in 2 ml., and each adjusted to pH 8.8.

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