THE DETERMINATION OF GOLD IN VEGETATION AND ITS APPLICATION TO SPECIFIC PROBLEMS IN BIOGEOCHEMISTRY

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ABSTRACT

Studies were carried out to devise a method for determining nanogram quantities of gold in vegetation.

The samples (0.5g) were digested with fuming nitric acid over a water bath. After addition of hydrochloric acid, the gold was extracted into a small volume (1 ml) of methylisobutyl ketone (MIBK). The organic layer was back-extracted with distilled water to remove iron interference and gold in the MIBK was determined by an electrothermal atomization technique with graphite furnace atomic absorption spectrometry.

The optimum instrumental conditions for drying, ashing and atomization of gold were as follows: drying, 4.5V, 20 secs; ashing 6V, 20 secs; atomization 8V, 4 secs. A furnace cooling time of 50 sec. was allowed to attain high precision of signal heights.

Tests on the efficiency of the method developed, showed high precision, good accuracy with the limit of detection of 1 ng/g. Recovery studies on the known amounts of gold added to vegetation, showed an average recovery of 99.4%. On the basis of these results, the method developed and outlined can be used on a routine basis for analysis of vegetation, soils and rocks.

Biogeochemical and geochemical studies were carried out at 4 areas having different geological, topographical and climatic conditions. These were: Waihi, New Zealand, Seruwila in Sri Lanka, the Serbomacedonian massif in Northern Greece, and Yathkyed Lake in Arctic Canada. At each of these study areas, different plant species were collected and analyzed together with the soil for biogeochemical studies.

Investigations were carried out to determine whether the concentration of gold in plants could be used to predict the concentration of this element in the soil and also whether any other elements present could be used as a pathfinder for gold.

The results of biogeochemistry showed good correlation existing between gold in plant and gold in soil provided the gold concentration in the substrate was sufficiently high. Arsenic was found to be a possible pathfinder element for gold, particularly when the latter is present with chalcophile elements.

The range of plant species analyzed in this study suggest that gold uptake is not restricted to any particular plant species or to plants with deep rooting system provided the substrate is auriferous.

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1.1 Introduction

The term biogeochemistry was first used in 1917 by the Russian scientist Vernadsky, who defined it broadly as the study of the relationship between living material and the geological environment. Biogeochemical prospecting, as known today, originated from this concept. It deals with prospecting for minerals by chemical analysis of plant samples collected from suspected areas of mineralization. The success of this technique relies on the assumption that an anomalous concentration of a metal in the substrate, presumably caused by the presence of the ore, will result in an anomalous concentration of that element in the vegetation growing upon it.

Pioneering work on biogeochemical prospecting began 50 years ago when Tkalich (1938) discovered that an arsenopyrite ore deposit in Siberia could be delineated by the iron content of the vegetation growing upon it. In 1939 Brundin showed that the abnormally high content of vanadium in the leaves of trees in a part of Sweden and tungsten in the leaves of some trees in Cornwall, England could be attributed to the high level of these metals in the soil. However, it was not until the late 1940's that Warren et al. (1947) initiated biogeochemical prospecting as a viable exploration technique.

Biogeochemical methods based on trace element levels in vegetation have received some attention, however their potential use in prospecting has not been fully investigated. The major reason for this is probably that analysis of soils and drainage sediments has proven so effective in prospecting that there has been very little incentive to develop other methods.

A recent survey showed that biogeochemical techniques using perennial plants with deep rooting systems are among the most economical methods of prospecting. A good example is the finding of juniper roots more than 60 m from the surface in the uranium mines in the Colorado Plateau. It is not only the root system but other factors such as the pH of the soil, drainage and perhaps also the region from which plants take up their moisture, which have to be taken into account.

It is difficult to assess the true effectiveness of biogeochemical prospecting because the method is seldom used by itself; nevertheless, there are documented cases where biogeochemistry has proved to be successful. Cannon (1960, 1964) used biogeochemistry to identify uranium deposits and more recently Dunn (1981) from the analysis of twigs of Picea mariane, identified uranium deposits in northern Saskatchewan beneath an overburden of 150 m of sandstone. Dunn found that the analysis of the soil did not accurately indicate the extent of the uranium deposit as the concentration of uranium in the soil was only between 1 to 3 µg/g compared with the concentration of 154 µg/g in the twigs of Picea mariane. Brooks (1983) provides a table detailing more examples of successful applications of biogeochemical prospecting.

1.2 Gold in Vegetation

Gold has long been known to be a microconstituent of many plants and animals including man. The Czechoslovakian alchemist, Paterson Hain James is said to have found gold in Hungarian grapes in the early Eighteenth century but it was not until much later that Lungwitz (1900) suggested that the gold content of vegetation might indicate mineralization in the substrate. Today there are several records of uptake of gold by vegetation dating back to Berg (1928) and Bertrand (1932) who were perhaps the two earliest workers on the accumulation of gold in vegetation and animals.

The plant, Equisetum species has been analyzed by a number of workers (Nemec et al. 1936, Warren and Delavault 1950, Razin and Rozhkov 1966, Cannon et al. 1968 and Brooks et al. 1981b). While Nemec et al. (1936) found an extraordinarily high value of 610 µg/g in the ash of Equisetum palustre, the results of the other workers only ranged from 0.17-0.40 µg/g of ash. Since then it has been shown that the method used by Nemec et al. was not specific for gold but had interference from arsenic giving Equisetum a much higher gold content.

A review of gold levels in about 100 different plant species as compiled by Jones (1970), shows that the maximum concentration is 36 ng/g with the mean of 7 ng/g. These results show that the gold concentration of vegetation is greater than the concentration in the earth's crust which is about 4 ng/g (Mason and Moore, 1982). More

recently Boyle (1979) presented a review on the biogeochemistry of gold and its deposits. Apart from Boyle, Brooks (1981b, 1982, and 1983) is the only other worker to have critically reviewed biogeochemical prospecting for gold. Erdman and Olson (1985) have compiled a comprehensive bibliography outlining fifty years of research into the use of plant analysis in prospecting for gold and other precious metals.

1.3 Biogeochemical Prospecting for Gold

The gold content of most plants normally ranges from 0.005 to 0.10 µg/g in the ash. When vegetation is to be used for prospecting for gold, the amount of gold in the plant material must be sufficiently high for analysis by the analytical procedure chosen. Unlike many other elements (such as nickel which plants can hyperaccumulate to the extent of 10 percent nickel in dry material - Jaffré et al., 1976) gold does not seem to be accumulated to any sufficient level by any plant species. Also because it is not known which plants can be used specifically to indicate gold deposits, emphasis has been placed on seasonal variations in the gold content of plants and its content in various organs of the plants. Schiller et al. (1973) noted marked seasonal variations in the gold content of plants, the maximum concentration being present during springtime. Dunn (1984) also found that maximum concentration of gold in alder twigs growing on the Southern La Range Belt, Saskatchewan was in spring (June).

With respect to the content of gold in the various organs of plants, Khotamov et al. (1966) state that the largest amounts of gold are concentrated in the above-ground portions of plants particularly the leaves. Warren and Barakso (1982) showed that young growth tends to have a higher gold content than old organs. Dunn (1984) concludes from a study in Saskatchewan, that the highest gold concentration occurs in the bark, followed by twigs, trunk and lastly needles.

The main obstacle to the use of biogeochemical methods for prospecting for gold lies with the analytical problems involved in determining this element at the very low concentrations (ng/g) normally found in vegetation. Unfortunately until recently, the only practical method of determining gold in vegetation was by the highly-expensive neutron activation analysis method. There is clearly a need

for an inexpensive, quick and a reliable method for analysis of gold, and the development of such a method is the main purpose of this thesis. A further aim was to determine whether biogeochemical prospecting could be used for detecting gold mineralization.

CHAPTER TWO

CHAPTER TWO

THE DEVELOPMENT OF AN ANALYTICAL TECHNIQUE

2.1 Introduction: Review of existing methods

Gold can be determined in geological and biological materials by a variety of methods, including fire assay, colorimetric analysis using mainly organic reagents, spectrography, atomic absorption spectrometry, neutron activation and panning. The analytical method employed to determine gold depends essentially on the type of geological or biological material to be analyzed and the level of gold present. The analysis of vegetation in prospecting is becoming popular as there is a growing awareness that the root system is in effect sampling several cubic metres of soil, rock or ground waters whereas only a relatively small volume is represented by soil or rock analysis. This is especially important for gold because it is concentrated in small localized areas.

One of the earlier attempts to determine gold in vegetation was by the gravimetric method. Nemec et al. (1936) analyzed Equisetum sp (swamp horsetails) as follows: samples were ashed and the ash was dissolved in aqua regia. After boiling until nitrous oxide fumes had disappeared, the samples were evaporated and then boiled with hydrochloric acid to precipitate silica which was filtered off. The dilute acid filtrate was then treated with hydrogen sulphide to precipitate acid-insoluble sulphides which were then assumed by the authors to represent entirely gold sulphide. The results obtained by this method were inaccurate as Brooks et al. (1981b) showed the precipitate to be basically sulphides of arsenic. Clearly this wet chemical method is not specific because it is difficult to isolate gold sulphide from the coprecipitated arsenic sulphide.

In 1948, the fire assay method was adopted on vegetation by Warren and Delavault (1950). The fire assay method basically involves taking a preweighed quantity of plant ash and melting it with a flux in a fire clay crucible in a hot furnace. During the chemical reactions occurring, gold is reduced by the flux to free metal beads. Reliable results can be obtained from the fire assay technique as actual gold beads are measured but for biogeochemical prospecting where

hundreds of samples have to be analyzed at low levels, this method will require the collection of some hundred grams of dry plant material per plant. Basically the fire assay method is slow and insensitive as the detection limit is only about 80-100 ng/g of ash (Warren and Barakso (1982).

Neutron activation analysis has been the method used most commonly for gold analysis since the 1970s. Here the vegetation is ashed, pelleted, irradiated with neutrons and counted after an appropriate cooling period. The concentration of the analyte is determined by comparing its radioactivity with that of the standards treated in exactly the same way as the analyte sample. Neutron activation is perhaps the most sensitive and reliable method of determining gold at trace levels but it has some disadvantages too. The first of these is its relative slowness. Assuming that the irradiation period is one hour and counting time is 15 minutes, then only 20-30 samples can be analyzed per day. This is not including the cooling time required, which for gold is between 5-7 days. By far the major disadvantage is the cost, typically about US$50 per sample. For gold there is also the interference problem from arsenic which in plant material has a concentration of at least a 1000 times higher than gold. The energy peak for As-76 at 559.1 keV is close to that of Au-198 at 411.8 keV.

There is an obvious need to develop a rapid, sensitive and inexpensive method for determining gold at the ng/g range. Flameless atomic absorption spectrometry using electrothermal atomization would appear to fulfil the above requirements very well. In the past very little work has been done using this method to determine gold in vegetation. However recently, Brooks et al. (1981a,1982) analyzed rock material and water using a modification of this suggested procedure. Baker (1983) using an analogous procedure to determine gold in vegetation reported a detection limit of 5 ng/g.

2.2 The Principle of Flameless Atomic Absorption Spectrometry

The general principle of atomization in a temperature-programmed furnace is discussed by Fuller (1977) and Price (1979). Briefly, the graphite tube is held between two electrodes. When a voltage is applied to the electrodes, the temperature of the atomizer is raised and by

simply varying the voltage across the electrodes, the temperature of the atomizer can be varied as required. While the atomizer is being heated, it is "sheathed" in a stream of inert gas (usually argon or nitrogen) which prevents oxidation of the atomizer and also removes vapor as it diffuses from the furnace. The generation of a population of free atoms whose atomic absorption is measured is achieved in 3 stages. These are the drying stage (solvent removal), ashing stage (organic matrix removal) and the atomization stage (atom production). In each stage of the thermal program, the temperature and the time may be selected according to the nature of the sample matrix and analyte element to be determined.

2.3 Experimental Details

2.3.1 Apparatus

Electrothermal atomization was achieved by replacing the burner assembly of the atomic absorption system (Model AA-5 Varian Techtron) with a pyrolytically-coated carbon rod atomizer (CRA) unit (Model 63, Varian Techtron). The spectrometer provided an automatic background correction by a deuterium lamp. Oxygen-free nitrogen was used as the sheathing gas. Sampling was accomplished with an Eppendorf 10 µl syringe with disposable polypropylene tips. Gold analyses were performed at the 242.8 nm resonance line with a slit width of 300 µm, corresponding to a spectral bandpass of 1 nm.

2.3.2 Preparation of Standards

All chemicals used were reagent grade. Water was deionized. Gold standards in the range 0-50 ng were made up in 2M hydrochloric acid from a BDH gold solution (1000 µg/g). The 2M hydrochloric acid was prepared from constant-boiling 6M hydrochloric acid. Methyl-isobutyl ketone (MIBK) was technical grade.

2.3.3 Preparation of Samples

(a) Rock and ore samples

These were ground in a rock grinder equipped with tungsten carbide concentric grinding rings, to pass -100 mesh.

(b) Soil Samples

These were air-dried and sieved to pass -100 mesh.

(c) Plant Samples

These were washed and dried at 100°C before being ground to a -50 mesh in a hammer mill.

2.3.4 Basic Principles of the Technique

The technique uses an oxidizing acid mixture to dissolve gold in vegetation followed by extraction as the chloro-complex, $HAuCl_4$, in MIBK and finally quantification of gold in the organic phase using electrothermal atomization combined with atomic absorption spectrometry.

2.3.5 Optimization of the Operating Conditions of the Flameless Atomic Absorption Spectrometer

The optimum voltage and time settings for the drying, ashing and atomization cycles of the spectrometer were determined experimentally as follows.

(a) Drying Cycle

This involved the selection of the voltage at which the solvent (MIBK) was completely removed. By keeping the other cycles (ashing and atomization) constant,the drying voltage was increased and the gold absorbance signal as atomization peak height was recorded. This is illustrated in Figure 2-1. It is obvious that 4.5 volts can dry MIBK.

The time required to dry the solvent at this optimum voltage is illustrated in Figure 2-2.

From these graphs, the optimum drying voltage and time were selected as 4.5 volts and 20 seconds respectively. Drying voltage and time are not so critical because solvent incompletely removed in the first stage of the programme will be vapourized in the ashing stage. However, when optimum conditions for drying are not used, sputtering of liquid occurs at the beginning of ashing cycle leading to loss of analyte; consequently a lower response is obtained.

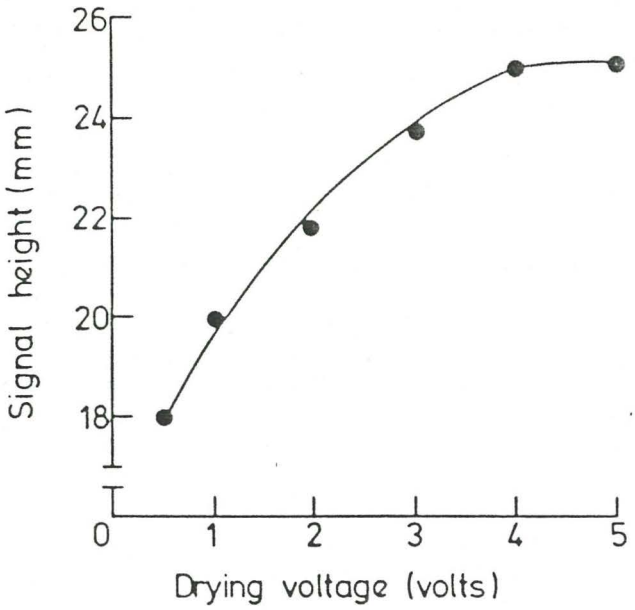

Figure 2-1 Effect of drying voltage on signal height

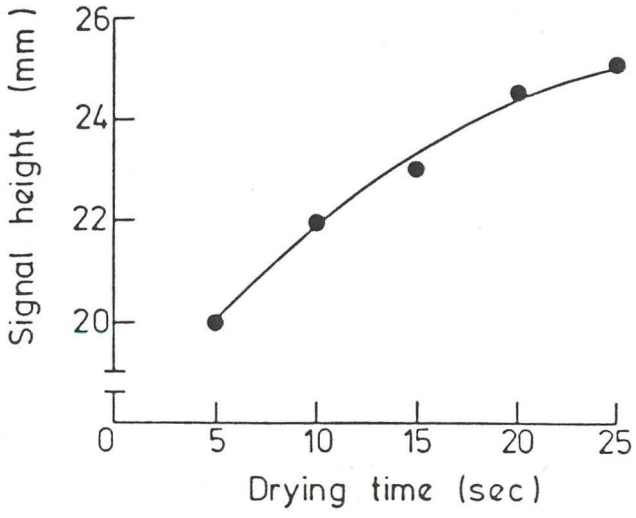

Figure 2-2 Effect of drying time on signal height

(b) Ashing Cycle

By gradually increasing the ashing voltage while keeping the drying parameters at the optimum settings and the atomization parameters constant, the changes in the signal height were measured. The results as illustrated in Figure 2-3 show that the optimum voltage for removing the organic matrix is 6 volts. The optimum ashing period of 25 seconds as illustrated in Figure 2-4 was obtained by gradually increasing the time and noting the effect on the absorbing signal. The selection of optimum ashing conditions are very critical because incomplete ashing leads to double peaks in atomization stage consequently the response is lower.

(c) Atomization Cycle

By varying atomization voltage and keeping the drying and ashing parameters at optimum, changes in peak height were recorded. Similarly the atomization period was selected. The effect of voltage and time can be seen in Figure 2-5 and Figure 2-6. The optimum atomization voltage and time were selected as 8 volts and 4 seconds. Figure 2-5 illustrates that selection of the optimum voltage is very critical.

2.3.6 Calibration of the Instrument

The temperature and time-controlling device on the atomizer were graduated in volts and seconds. To allow a comparison between the optimum conditions determined here and values already published in the literature, the voltages used in the drying, ashing and atomization cycles were correlated to a temperature scale as follows:

(a) Drying Cycle

A selection of pure organic solvents with boiling points between 50°C to 2000°C were used to calibrate the voltage scale over this temperature range. One drop (10 µl) of the solvent was placed in the atomizer and the voltage successively increased to the point where the liquid had evaporated totally. This voltage setting was then assigned the temperature relating to the boiling point of the solvent. The ashing and the atomization cycles were set at zero. Table 2-1 illustrates the relationship between drying voltage and temperature.

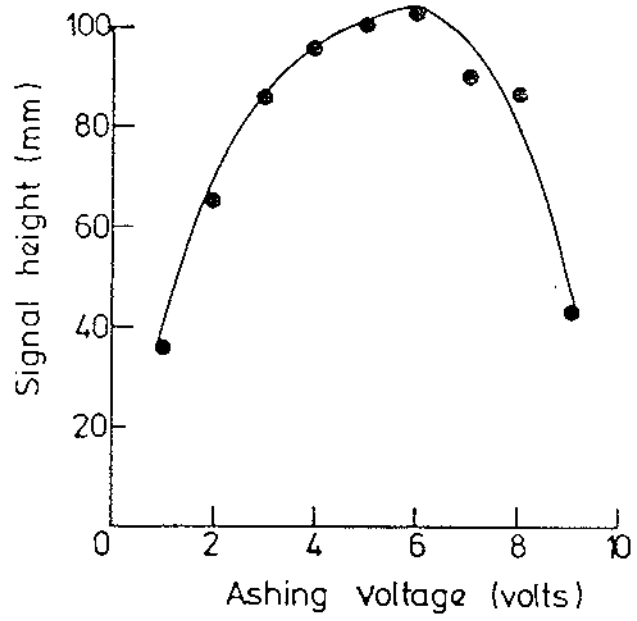

Figure 2-3 Effect of ashing voltage on signal height

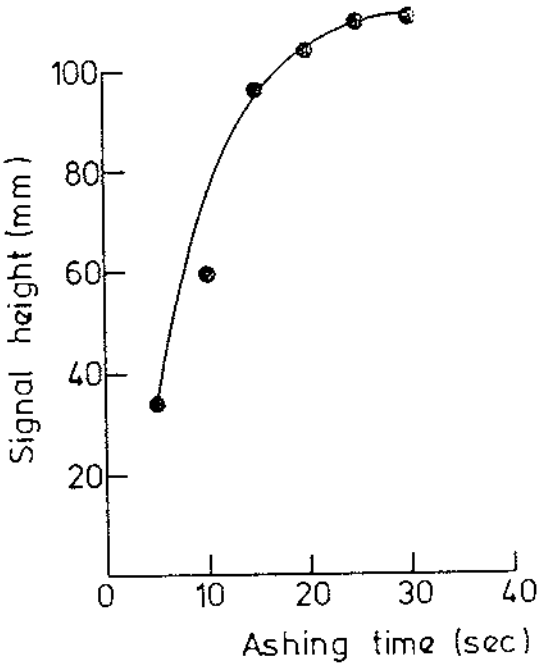

Figure 2-4 Effect of ashing time on signal height

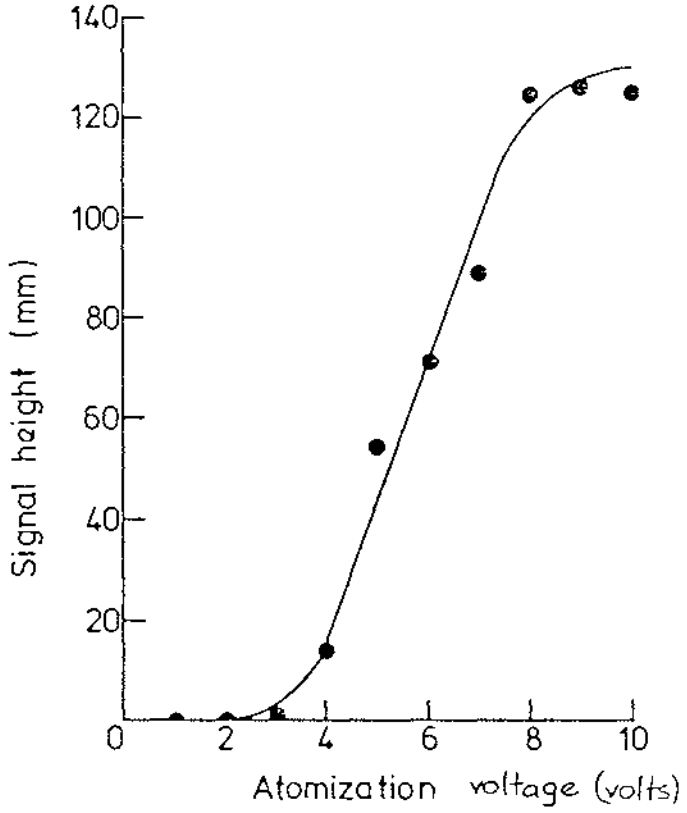

Figure 2-5 Effect of atomization voltage on signal height

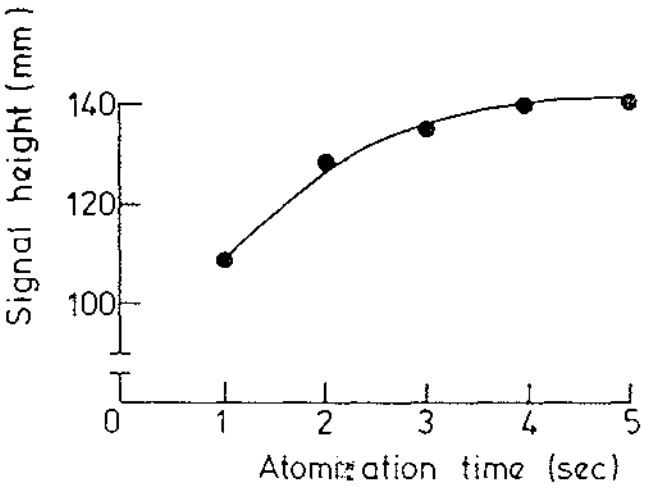

Figure 2-6 Effect of atomization time on signal height

Table 2-1 Relationship between voltage and temperature in drying cycle

Solvents used	Boiling Point ^{o}C	Voltage where solvent dried Volts
acetone	56	0.5
chloroform	61.7	1.0
carbontetrachloride	76.5	2.0
ethanol	78.0	2.5
cyclohexane	80.7	2.5
MIBK	116	5.0
acetic acid	118	5.5

The optimum drying voltage of 4.5 volts selected previously for MIBK, corresponds to a temperature of about 110^{o}C.

(b) Ashing Cycle

Using pure metals, the voltage at which these metals melted was measured while the drying and the atomization cycles were kept at zero. Table 2-2 illustrates the temperature equivalence of the ashing voltage. The optimum ashing voltage of 6V corresponds to a temperature of about 420^{o}C.

Table 2-2 Relationship between ashing voltage and temperature

Metals	Temp. melting ^{o}C	Voltage-metals melted Volts
Sn	232	4.5
Cd	321	5.5
Pb	327	5.5
Zn	419	6.0
Mg	650	7.0
Al	660	7.0
As	817	7.5
Ag	961	8.5

(c) Atomization Cycle

Finally the atomization voltage was calibrated to the temperature scale by noting the voltage at which some selected metals melted. This is presented in Table 2-3.

Table 2-3 Relationship between atomization voltage and temperature

Metal	Melting temp. ^{o}C	Voltage-metals melted Volts
Sn	232	0.5
Cd	321	1.0
Zn	419	1.5
Mg	650	3.0
Al	660	3.0
As	817	4.0
Ag	961	4.5
Cu	1083	5.0
Mn	1250	5.5
Ni	1450	6.0
Fe	1540	6.5

The optimum atomization voltage of 8V selected for gold corresponds to a temperature of about 2200^{o}C by extrapolation of the graph of temperature against voltage (Fig. 2-7).

(d) Effect of Nitrogen Flow on Gold Signal

In flameless atomic absorption spectroscopy, the purpose of the inert gas flow is to provide an adequate sheathing of the carbon rod and to provide an inert atmosphere for atomization. The flow should not be so high that the gas removes the atomic vapour too quickly from the optical path.

By varying the flow of nitrogen gas and keeping all other parameters constant, the change in height of the gold signal was noted. Figure 2-8 shows that beyond a flow unit of 7, the atomic vapour passes too quickly, resulting in low responses. Although the flow units of 1-4 provide higher signal responses, the carbon rod is not fully sheathed, consequently oxidation occurs and results in a

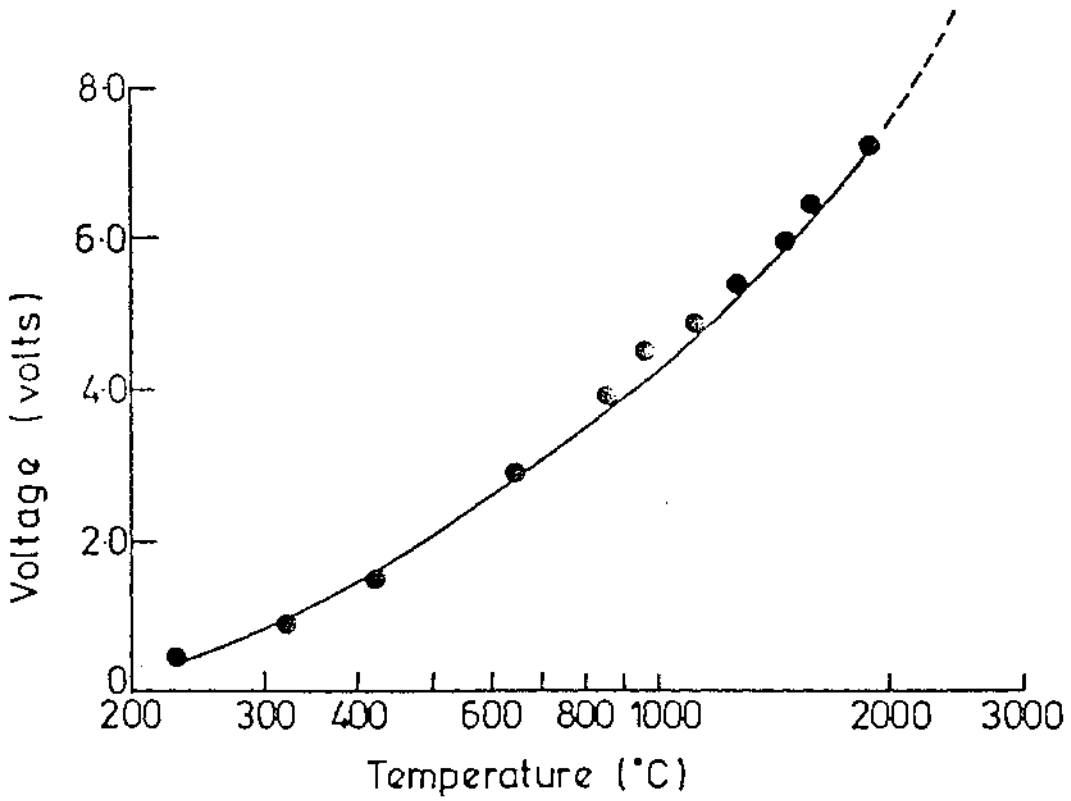

Figure 2-7 Relationship between atomization voltage and temperature

shortened life of the rod. The optimum gas flow rate for gold determination was selected as 5 units (approximately 3 litres per minute).

(e) Effect of Cooling Time of Atomizer on Gold Signal

As there is a steep temperature gradient along the carbon rod atomizer, any variations in the sample size, position or temperature of the rod will seriously alter the analytical signal. In this project the effect of rod cooling time on the gold signal was observed while other parameters were kept constant. Figure 2-9 shows that a cooling time of 50 seconds gives the best response with the optimum parameters selected for gold. When insufficient cooling time is allowed, the furnace is still hot, so drying and ashing are carried out at a higher temperature than intended, leading to substantial loss of analyte as seen in Figure 2-9.

After a preliminary investigation, the optimum operating conditions for the flameless atomic absorption spectrometer for gold analysis are presented in Table 2-4.

Table 2-4 The optimum instrumental parameters selected for analysis of gold

Varian Techtron Model AA-5 Spectrometer	
wavelength	242.8 nm
spectral slit width	300 μm
calibration mode	absorbance (peak height)
background correction	deuterium lamp
Varian Techtron Model 63 Carbon Rod Atomizer	
Drying	4.5 volts, 20 sec. (110°C)
Ashing	6 volts, 20 sec. (420°C)
Atomization	8 volts, 4 sec. (2200)
Sheathing gas	Oxy-free nitrogen
Sample volume	10 μl
Cooling time	50 sec.
Gas flow	5 units (3 litres / min)
Carbon rod used	pyrolytically coated

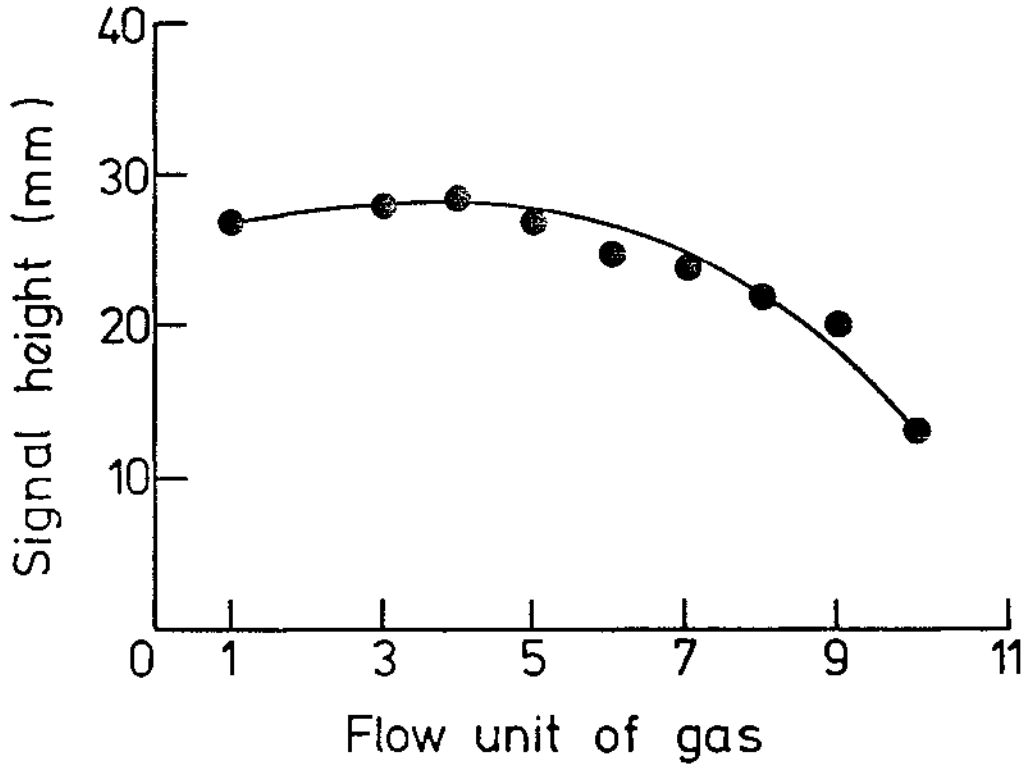

Figure 2-8 Effect of nitrogen flow on signal height

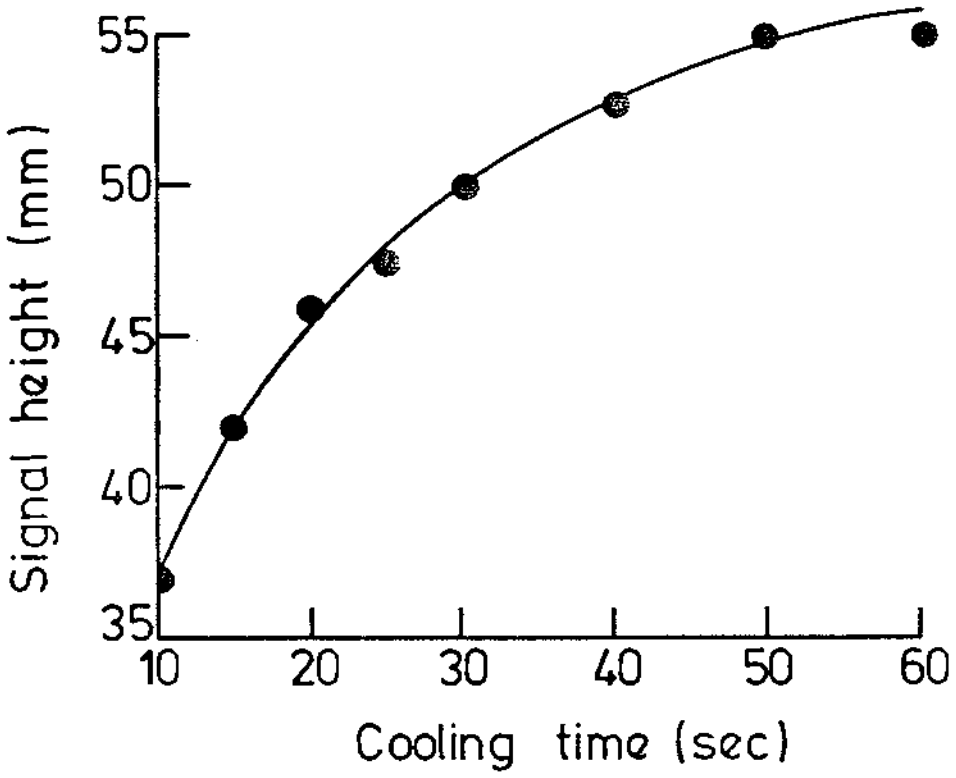

Figure 2-9 Effect of atomizer cooling time on signal height

2.4 Investigation of Some Parameters Affecting Sensitivity of the Method

2.4.1 The Solubility of MIBK in Hydrochloric Acid Solutions

When selecting the appropriate volume of MIBK to use to extract gold from solution, consideration must be made of the solubility of the organic solvent in different acid concentrations. The volume of MIBK selected must be sufficient to allow for its dissolution into the aqueous phase while still leaving sufficient for the extraction process to occur. Figure 2-10 shows the solubility of MIBK in various concentrations of hydrochloric acid. The values were obtained by shaking equal volumes of organic and aqueous phases together in a burette sealed at both ends. The final volumes were measured at equilibrium.

It was decided to use 2M hydrochloric acid as the aqueous medium in this investigation.

2.4.2 Sensitivity as a Function of Solvent Volume

Reducing the volume of MIBK added to 20 ml of hydrochloric acid (2M) containing nanogram quantities of gold has the effect of increasing the sensitivity of the method. This is seen in Table 2-5. This was done by extracting gold from different volumes of MIBK taking into consideration the solubility of MIBK in an aqueous medium.

Table 2-5 The effect of solvent volume on sensitivity and extraction of gold

Vol. MIBK added	Vol. remaining	Signal Ht. (mm)	% Extraction	% Increase sensitivity
1.00	0.70	15.0	98.0	1.0
0.90	0.60	17.0	97.5	1.1
0.80	0.50	24.5	97.0	1.6
0.70	0.40	27.5	96.0	1.8
0.60	0.30	41.0	95.0	2.7
0.50	0.20	68.0	93.0	4.5
0.40	0.10	302.0	87.0	20.1
0.30	0	-		

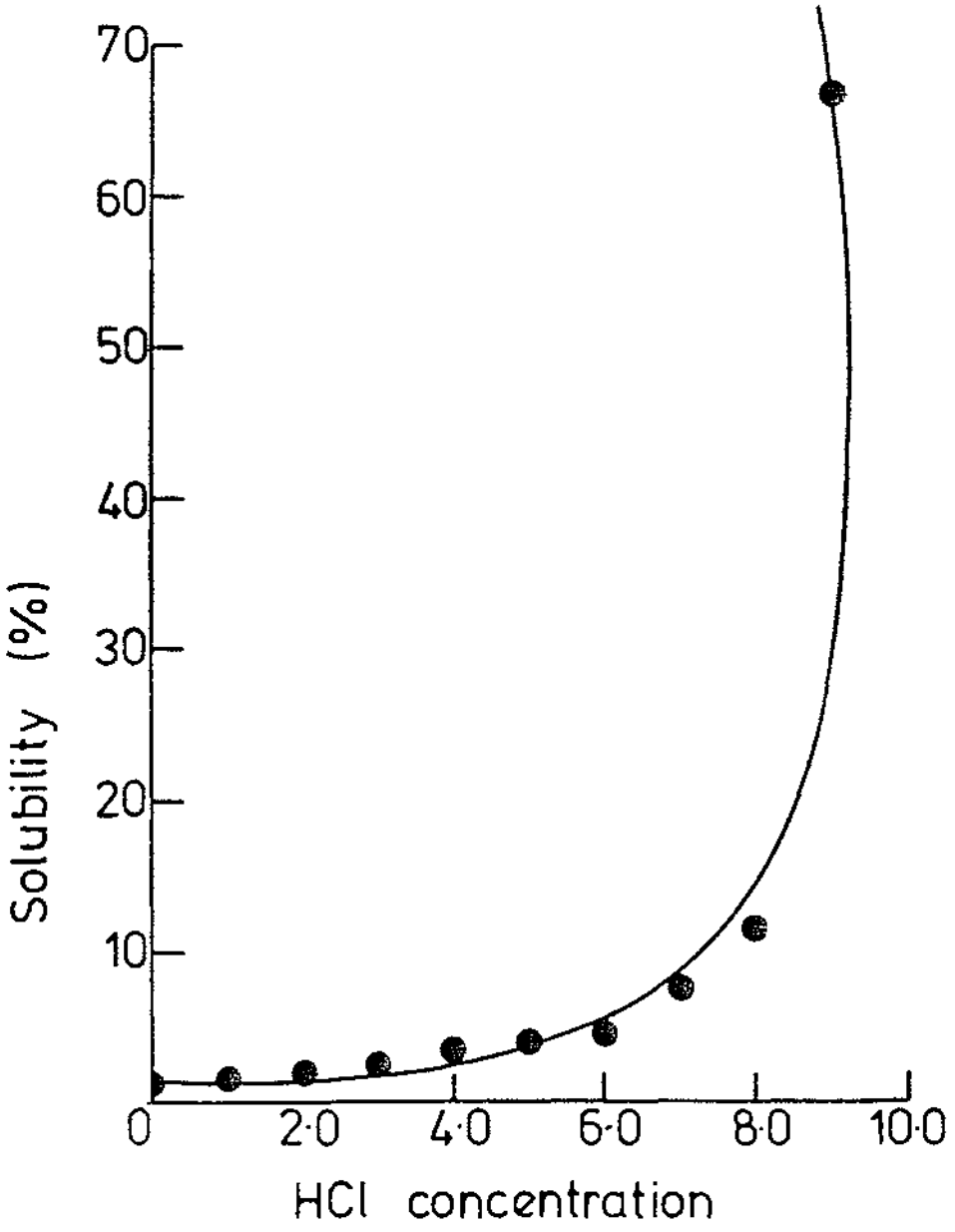

Figure 2-10 Solubility of MIBK in hydrochloric acid solutions

It has been shown by Brooks et al.(1981a) that gold has a distribution ratio of about 2000 between 2M hydrochloric acid and MIBK. Using this value, 98% of gold is extracted when 1.0 ml MIBK is added to 20 ml of aqueous phase. Because of 2% solubility of MIBK in 2M hydrochloric acid, the final volume of organic phase reduces to 0.7 ml. Although sensitivity is increased by a factor of 20 when 0.4 ml MIBK is used, the resultant volume remaining is so small (0.1ml) that there are problems of removing it to introduce it into the graphite furnace. The percentage of gold extracted is also low (87% only) as seen in Figure 2-11 and 2-12. In practice it was found that the addition of 1.0 ml of MIBK gave satisfactory results.

2.4.3 The Stability of the Gold Complex in MIBK

The stability of the $HAuCl_4$ complex in MIBK was tested by extracting 1 µg of gold from 150 ml of 2M hydrochloric acid into 10 ml of MIBK. The absorption signal was determined over a period of 17 days and showed that there was no detectable loss of gold from MIBK complex in this period. However, standard gold (111) chloride solution in 2M hydrochloric acid loses sensitivity probably by adsorption of gold onto the container walls and so has to be prepared fresh every few days.

2.4.4 The Volatility of Auric Chloride

Five ng of gold as auric chloride was absorbed on each of six 0.15g samples of silica. The samples were dried, then each was heated for one hour periods at different temperatures. Temperatures of 100, 200, 300, 400, 500 and 600^{o}C were used. The gold was then leached from the silica with aqua regia. The solutions were taken almost to dryness, then diluted with 2M hydrochloric acid. The gold was extracted into 1.0 ml of MIBK and was quantified as above. The results are shown in Figure 2-13 from which it can be seen that appreciable loss of gold occurred above 300^{o}C. This tells us that for decomposition of vegetation, the temperature cannot exceed 300^{o}C if hydrochloric acid mixture is present.

2.4.5 Interference Studies

A literature survey showed that determination of gold in rocks and ores by atomic absorption spectrometry based on extraction of gold as $HAuCl_4$ by MIBK, is susceptible to interference from Fe(III), Cr(VI),

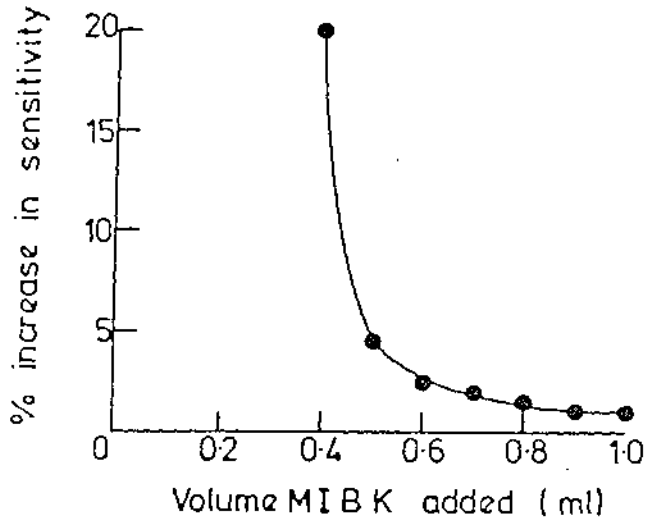

Figure 2-11 Relationship between volume of MIBK and sensitivity

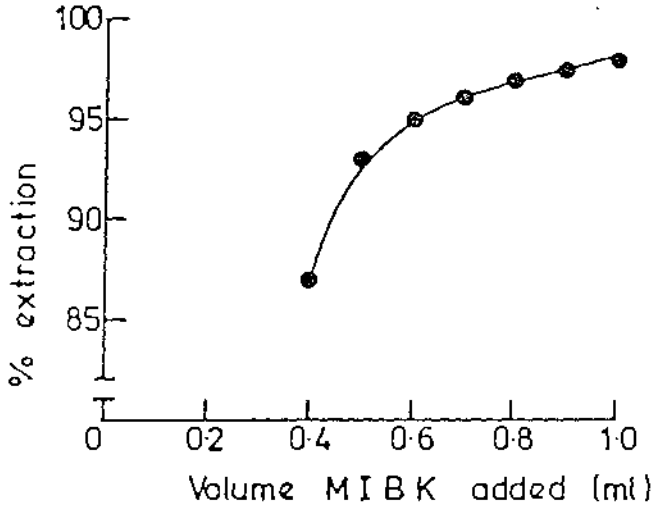

Figure 2-12 Relationship between volume of MIBK and percentage gold extraction

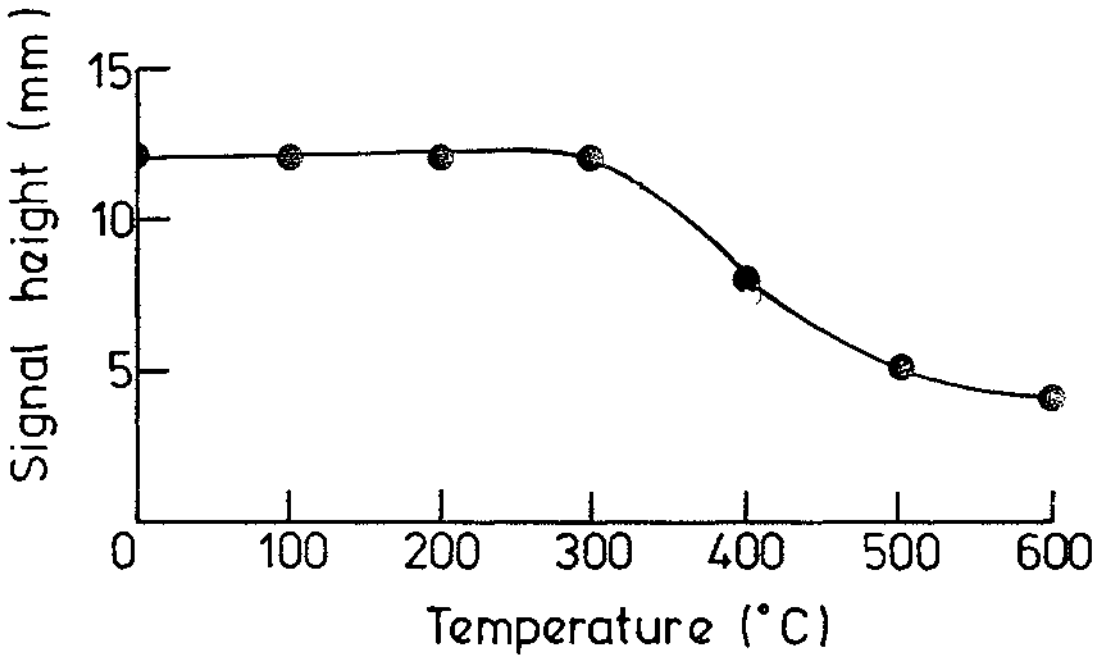

Figure 2-13 Effect of temperature on volatility of auric chloride

Te(IV), and As(III) as molecular absorption bands,(Morrison and Freiser (1957), Tindall (1965) and Hall (1979)). However in the graphite furnace atomization technique, the interference from arsenic should not be a problem because of its volatility. Arsenic should be lost during the atomization stage. Also the automatic background correction by the deuterium lamp, should eliminate most of the molecular absorption bands.

Nevertheless to investigate the effects of iron, chromium and tellurium, a hundred-fold mass excess of these ions was added to 50 ng gold standard and also to the solvent blank. Although iron, chromium and tellurium were coextracted with gold from 2M hydrochloric acid, neither the solvent blank nor the standard solution containing the 3 interfering ions showed any appreciable change in the absorption signal. Gold has a higher distribution ratio in MIBK than the interfering ions. This property can be utilized to remove the interfering ions. By back-washing the organic phase with 0.5M hydrochloric acid the ionic species are redistributed with the interfering species favouring the aqueous phase while most of the gold will remain in the organic layer.

2.5 Final Operating procedure

2.5.1 Dissolution of Gold from Vegetation Samples

By far the greatest problem in the determination of trace quantities (ng) of gold in vegetation lies in the destruction of the organic matter and subsequent dissolution of the gold without loss by volatilization.

With most oxidizing acid mixtures commonly employed for destroying organic matter, the acid has to be fumed off before gold can be taken up as auric chloride. At these higher temperatures gold is readily lost by volatilization, particularly when perchloric or sulphuric acid mixtures are used, hence the recoveries are incomplete (Table 2-8).

Decomposing samples in aqua regia only (HCl/HNO_3, 1:3) does not completely destroy all the vegetation. Samiullah (1983) has shown that gold at trace levels is readily adsorbed onto the filter paper. To eliminate this filtration process, a mixture of fuming nitric acid and aqua regia (the latter formed by adding hydrochloric to the nitric acid after oxidation is complete) was used and complete recovery of gold was

achieved. The decomposition has to be carried out in glassware heated over a water bath. It is noteworthy that polypropylene beakers gave a significant gold blank when used for decomposing samples. All glassware used was rinsed with aqua regia and then washed with deionized water.

2.5.2 Procedure

A 0.5g sample of finely ground vegetation(leaves, twigs, bark or wood) was digested with 5 ml of fuming nitric acid in a 50 ml borosilicate squat beaker heated over a water bath. After dissolution was virtually complete (c.a 5 min), 5 ml of concentrated hydrochloric acid and a little bromine vapor were added. The volume was reduced to 2-3 ml by heating, then transferred to a 20 ml graduated glass centrifuge tube. Constant-boiling 6M hydrochloric acid was added to bring the volume to 5 ml. The solution was further diluted to 15 ml with deionized water giving an acid strength of 2.0M. MIBK (1 ml) was added, the tubes stoppered and shaken vigorously on a test tube shaker for 5 minutes. The mixture was then centrifuged to separate the layers. A bulb pipette was used to remove all the aqueous layer except the last 4 mls. This was again diluted to 15 ml with deionized water giving an acid strength of 0.5M, stoppered, shaken and centrifuged.

After the equilibrations, the organic layer was reduced in volume from 1.0 to 0.55 ml of MIBK. Standards and blanks were treated in the same manner as the samples throughout the analytical procedure. Figure 2-14 shows a typical analytical work curve for gold as chlorocomplex in MIBK.

2.6 Testing of the Method

2.6.1 Reproducibility Tests

To minimize error from sample variability, 5g of sample was decomposed and made up to 50 ml using the method of decomposition previously explained. Aliquots of 15 ml were then pipetted into 10 tubes and each extracted for gold with 1 ml of MIBK. The solutions were back-extracted and analyzed for gold as seen in Table 2-6.

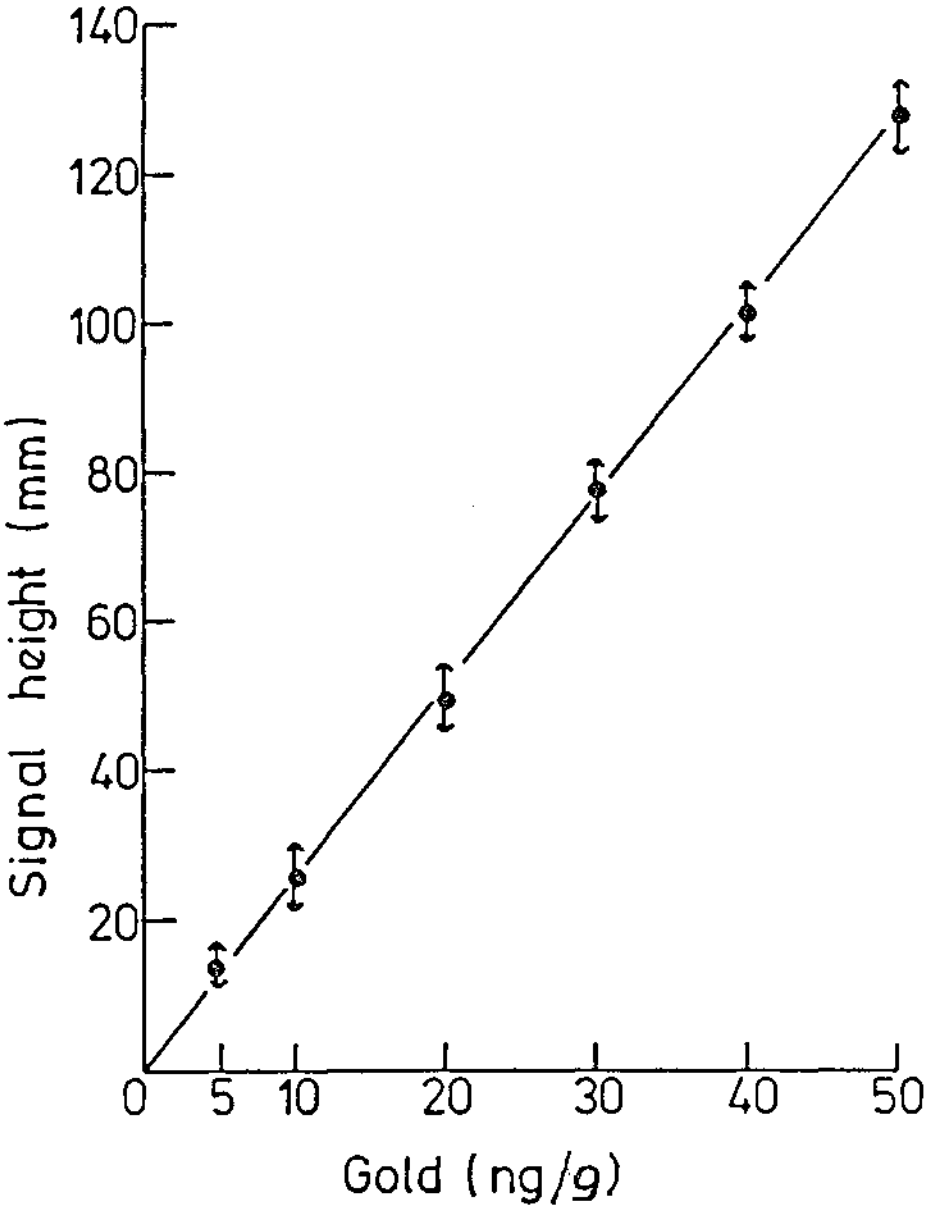

Figure 2-14 Calibration curve for gold as chlorocomplex in MIBK

Table 2-6 Reproducibility tests

sample	n	mean conc	RSD (%)
plant	10	170.0 ng/g	10.1

The relative standard deviation was 10% for a wood sample containing about 170.0 ng/g of gold. For lower concentrations a poorer precision would be expected, about 25% at the 5 ng/g level. However the RSD obtained is quite satisfactory considering the low concentrations involved.

2.6.2 Limit of Detection

The detection limit was defined as S/N = 2, where 'S' is the signal and 'N' is the root mean square noise determined from the background of the signal trace. The limit of detection was 1 ng for a 1.0 ml MIBK and about 0.2 ng for 0.5 ml of organic phase.

2.6.3 Recovery Studies

A recovery study shows that the method recovers gold at an average of 99.4%. Using plant and soil samples spiked with different amounts of gold prior to decomposition, recovery of gold ranged from 95.0-105%. This study indicated that very little or no gold was lost by using the method outlined here. The results as obtained are presented in Table 2-7.

Table 2-7 Recovery of known amounts of gold added to soil and plant samples

Sample	n	Gold present (ng)	Amount added (ng)	Gold found (ng)	Recovery %
soil	3	0	40.0	38.0	95.0
soil	3	0	20.0	19.5	97.5
plant	3	0	20.0	21.0	105.0
plant	3	0	10.0	10.0	100.0

Table 2-8 shows recovery of known amounts of gold that was added to plant samples decomposed by various other oxidizing acid mixtures. By using an average recovery of 99.4%, it can be said that errors up to 22% can be introduced when perchloric or sulphuric acid mixtures are used.

Table 2-8 Recovery of known amounts of gold added to plant samples decomposed by various other acid mixtures

Sample	Acid mixtures used	Gold present	Amount added ng	Gold found ng	Recovery %
plant	$HClO_4/HNO_3$ (1:4)	0	100.0	76.3	76.3
plant	H_2SO_4/HNO_3 (1:4)	0	100.0	82.0	82.0
plant	HNO_3	0	100.0	88.0	88.0
plant	HNO_3 fuming/HCl	0	100.0	98.5	98.5

2.6.4 Accuracy

Due to the almost complete absence of vegetation standards in which gold has been determined, the accuracy of this technique was difficult to evaluate. However Gladney (1980) using neutron activation analysis determined gold in the NBS standard orchard leaves. For 6 replicates of this material he obtained a value of 1.8 ng/g. Using the method explained in this work values of 4.0 and 4.5 ng/g were obtained for the same material. Considering the extremely low concentrations involved, agreement is reasonable. Sample, Ald-1, (Dunn, 1984) was also analyzed by this method. Dunn by neutron activation analysis obtained a range from 17 ng/g to 29.0 ng/g. Our result was 20.0 ng/g.

CHAPTER THREE

CHAPTER THREE

BIOGEOCHEMICAL STUDIES OF GOLD

3.1 General Introduction

Research on biogeochemical exploration for gold has been gaining interest since the development of the neutron activation method of analysis. Because there are no known indicator or hyperaccumulator plants for gold, most of the work has been concentrated on known gold mineralization areas to see how well the vegetation can reflect gold anomalies in the bedrock. The use of the so called pathfinder elements, particularly arsenic, has also been increasing.

Since 1950, Warren and his co-workers (eg Warren and Barakso 1950) have collected and analyzed plant materials for gold from areas where gold mineralization was known to occur. Using the hypothesis that samples consistently containing more than 10 ng/g are likely to occur only where gold is present in significant concentration, they tested their hypothesis on six mine localities in British Columbia. The results could not show any better illustration of the ability of vegetation to reflect anomalous gold in the vicinity of gold mineralization. Dunn (1984) in a study of vegetation from Saskatchewan, found gold enrichment at many localities some above known mineralization and others from areas where gold occurrences are unknown.

Baker (1983) analyzed some 900 plants from the Lisle gold field in northeast Tasmania and found about 60 to 600 times more gold in plants from mineralized areas as compared to plants from unmineralized areas. By analyzing Pseudotsuga menziesii (douglas-fir), Erdman and Leonard (1983) found two new distinct gold populations while the soil samples from the same area did not reveal anomalous gold. More recently, Warren et al. (1984) using some 608 samples comprising of 13 different species in Pinchi Fault, British Columbia found 20 areas with very high gold concentrations.

It is obvious from the above studies that when biogeochemical anomalies occur in several of the samples nearby, gold enrichment in the bedrock is possible. However, absence of gold enrichment in the vegetation does not necessarily indicate no mineralization. Several factors

such as pH of soil, drainage, and the type of mineralization may all play a significant role in the development of a biogeochemical anomaly. For example, gold disseminated in the bedrock or associated with pyrite may give a much better biogeochemical response than native gold that occurs as discrete grains in quartz veins. This is because gold in quartz veins are chemically inactive and so less accessible to plant roots. Poor correlation between gold in soil and in vegetation is often attributed to this phenomenon.

In this section of the thesis, the analytical method developed for gold was applied to 4 different areas. The aim of this investigation was to see whether gold concentration in plant species analyzed indicated the concentration of this element in the soil. Also to determine whether any other elements were associated with gold which might be indicative of the nature of substrate.

The criteria used for selection of a particular plant species for this investigation were as follows:

(a) that it be sufficiently widespread over the area being investigated

(b) that it be commonly found in areas of similar climate and ecological environment so that any conclusions made concerning its prospecting possibilities could be applied to these other areas.

3.2 Case Study I

Delineation of Auriferous Quartz Reefs by Analysis of the Bark of Pinus Radiata (Monterey Pine).

3.2.1 Introduction

Rocks and bark samples of Pinus Radiata from Union Hill, Waihi, New Zealand were analyzed for gold and other major elements to determine whether there was a significant different in elemental concentrations in quartz and in hydrothermally altered andesite.

The usual sampling medium is leaves, needles, or twigs but for very tall trees with fewer low branches, these sampling media are inappropriate. An alternative sampling media is bark and this has been

used by several workers including Nielsen et al. (1973) who used the bark of Eucalyptus lesouefii in Western Australia to determine the geological nature of the substrate.

3.2.2 The Geology of Union Hill, Waihi

Union Hill is located within the township of Waihi (Fig. 3-1) in North Island, New Zealand and is part of the Rosemount-Silverton Gold mining area (Williams, 1965) just to the southeast of the main ore bodies at Waihi. This work has been centred around the Mascotte, Amaranth and the Union reefs.

The area is underlain by a basement of Mesozoic greywackes and argillites (Morgan, 1924). These have been faulted and broadly folded generally along northwest-southeast trending axes. The rocks are overlain by a sequence of Tertiary (Miocene-Pliocene) intermediate to silicic terrestrial volcanics with minor contemporaceous sediments. The vulcanism has been divided into three main phases, andesite, rhyolitic and again andesitic. Extensive areas of hydrothermal alteration (propyhlisation) and quartz-calcite veining appear to post date very closely, the rhyolitic activity (5-6 million years ago). The country rock at Union Hill is andesitic suffering various degrees of alteration.

The two main reefs at Union Hill are the Union and Amaranth. The southwest extremeties of these reefs are well defined by old workings but their northeastern limits are poorly defined and are still uncertain.

The vegetation was cleared completely about 100 years ago and the original native cover has been replaced mainly by Pinus Radiata (Monterey Pine) and by Acacia mearnsii (black wattle).

3.2.3 Materials and Method

(a) Plant Organs Sampled

Outer bark samples were removed from specimens of Pinus Radiata. Two samples were taken at opposite sides of the trunk of each specimen in order to avoid bias due to different exposures. This is because root systems tend to translocate ions to aerial parts situated on the same side of the plant as themselves. Samples collected, weighed about 100g and these were then oven dried at 110°C before being ground to -50 mesh size in a hammer mill.

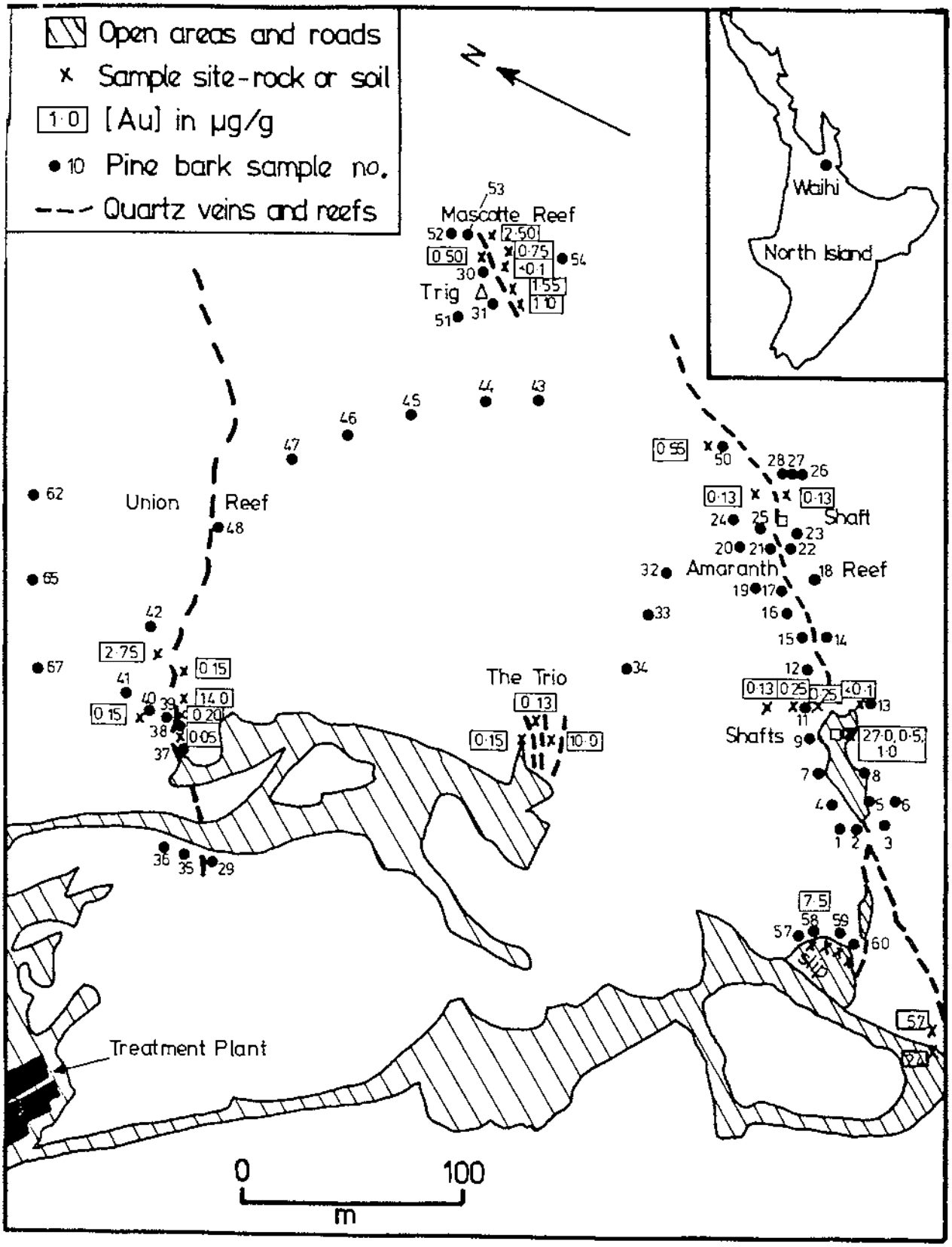

Figure 3-1 Map of the Union Hill area near Waihi showing sample location sites

(b) Soils

Soil samples were air dried and sieved to -100 mesh size.

(c) Rocks

Rock samples were ground in a rock grinder equipped with tungsten carbide concentric grinding rings to a -100 mesh size.

3.2.4 Analytical Method

(a) Gold in Rocks

For gold in rocks, samples (0.5g) were digested with three 10 ml portions of aqua regia ($HCl:HNO_3$, 3:1), evaporated to 3 ml, then diluted to 15 ml with deionized water. The gold was extracted into 2 ml of methylisobutyl ketone (MIBK).

(b) Gold in Vegetation

Gold in vegetation was analyzed by the method developed and outlined in Chapter 2 of this thesis.

(c) Other Elements

These were analyzed by Goff et al. (1985) as follows: soil and rock samples (0.5g) were digested with 10 ml of nitric and hydrofluoric acid (1:1) mixture. Digestion was carried out in polypropylene beakers suspended in a boiling water bath. The excess acid was evaporated off and the residue was redissolved in 10 ml of 2M hydrochloric acid prepared from redistilled reagent. The final volume was adjusted to 25 ml after filtering if necessary.

The bark samples (0.5g) were placed in borosilicate boiling tubes (50 ml) and heated in a heating block with 10 ml of a mixture of perchloric and nitric acid (1:4). Samples were heated to fuming, cooled and diluted with 2M hydrochloric acid to volume of 25 ml.

3.2.5 Analytical Techniques Used

(a) Gold was determined by graphite furnace technique (flameless AA) using the small volume organic phase extracts.

(b) Soil, rock and plant samples were analyzed for 20 other elements by inductively-coupled plasma emission spectrometry (ICP). These elements were Al, B, Ca, Co, Cr, Cu, K, Fe, Mg, Mn, Na, Ni, P, Pb, S, Sn, Si, Sr, and Zn.

(c) Silver was determined by flame atomic absorption spectrometry (AAS).

(d) Arsenic by flame atomic absorption spectrometry after isolating it from the samples as the hydrite.

Randomly chosen samples were analyzed for several elements by atomic absorption spectrometry to check the reliability of the ICP data. Agreement was in general very good.

3.2.6 Results and Discussion

Gold concentrations in the two rock types are summarized in Table 3-1.

Table 3-1 Gold concentrations (µg/g) in the two rock types from Union Hill

Quartz vein (µg/g)	Andesite µg/g
0.13	0.10
0.50	0.10
1.00	0.10
1.10	D.10
2.50	0.10
2.75	0.10
7.50	0.13
10.10	0.13
14.00	0.15
24.00	0.15
27.00	0.15
57.00	0.20
	0.50
	0.55
	0.75
n = 12	n = 15
$\bar{x}$ = 12.29	$\bar{x}$ = 0.22
σ = 16.81	σ = 0.205

t-Test = 2.83, $P < 0.01$, S^X

The data presented in Table 3-1 are lognormally distributed and all calculations were performed by converting data to base 10 logarithm. The t-Test on gold concentrations in quartz veins and in hydrothermally altered andesite showed significant difference ($P<0.01$) between the two means. In fact the quartz vein is about 55 times more enriched in gold than andesite. The other elemental concentrations in rock samples are included in Table 3-2. Other than gold, the quartz is also enriched in silver and perhaps cobalt and lead with respect to andesite. It is depleted in most other elements.

Table 3-2 Mean elemental concentrations (μg/g) in the rocks from Union Hill

Elements	Quartz vein (12) mean(A)	s.d*	Host Andesite (15) mean(B)	s.d*	B/A	Enrichment	t-Test	
Al	7400,	3090-17800	93000,	44700-195000	12.6	And	P=0.0000,	S^{XX}
Ag	20,	3-154	2,	1-3	0.1	Quartz	P=0.0011,	S^{XX}
As	13,	8-21	46,	19-107	3.5	And	P=0.000,	S^{XX}
Au	12.3,	0.7-204	0.22,	0.05-1.02	0.02	Q	P=0.0000,	S^{XX}
B	26,	18-37	104,	40-275	4.0	And	P=0.0000,	S^{XX}
Ca	812,	398-1660	7250,	3980-13200	8.9	And	P=0.0000,	S^{XX}
Co	44,	27-72	9,	5-17	0.2	Q	P=0.0000,	S^{XX}
Cr	2.2,	0.7-6.7	45,	32-61	20.4	And	P=0.0000,	S^{XX}
Cu	4.5,	1.2-17.8	8,	3-22	1.8	And	P=0.24,	NS
Fe	1550,	389-6200	21400,	12300-37200	13.8	And	P=0.0000,	S^{XX}
K	562,	229-1380	6460,	3020-13800	11.5	And	P=0.0000,	S^{XX}
Mg	162,	93-281	955,	269-3470	5.9	And	P=0.0000,	S^{XX}
Mn	64,	14-295	64,	13-316	1.0	-	P=1.0,	NS
Na	707,	245-1620	11700,	6310-21900	16.6	And	P=0.0000,	S^{XX}
Ni	1.2,	0.7-2.0	1.5,	0.9-2.8	1.2	And	P=0.24,	NS
P	30,	20-46	30,	15-61	1.0	-	P=0.98,	NS
Pb	10,	3-31	5,	4-7	0.5	-	P=0.13,	NS
S	234,	83-660	977,	173-5500	4.2	And	P=0.013,	S^{X}
Sr	9,	5-20	16,	11-23	1.8	And	P=0.0063,	S^{X}
Zn	20,	6-72	41,	11-154	2.1	And	P=0.16,	NS

*s.d. shown as a range because distributions were lognormal

S^{XX} = $P<0.001$, (very highly significant)

S^{X} = $0.01 > P \geq 0.001$, (highly significant)

S = $0.05 > P \geq 0.01$, (significant)

NS = $P>0.05$, (not significant)

A t-Test was also carried out on the other elements and showed that in fact a very significant ($P<0.001$) difference existed in the means of most elemental concentrations in the two rock types.

The difference in the elemental concentrations were so great that similar patterns were expected to be also reflected in the bark samples of Pinus Radiata growing over the two rock types. If significant differences in elemental concentrations in the bark were also obtained, then the bark could be used effectively for predicting the nature of the substrate.

To test the above hypothesis, all sample sites for which bark samples were available were divided into two populations (quartz or andesite) on the basis of field observations. This gave 25 samples as growing on quartz and 42 samples on andesite. The gold concentrations in the bark of Pinus Radiata are summarized in Table 3-3.

Table 3-3 Gold concentration (ng/g dry mass) in Pinus Radiata

Growing on Quartz (ng/g)		Growing on Andesite (ng/g)		
0.10	8.0	0.5	1.0	8.0
0.10	9.0	1.0	1.0	8.0
1.0	13.0	1.0	1.5	12.0
1.0	14.0	1.0	2.0	19.0
1.0	14.0	1.0	2.0	20.0
1.0	16.0	1.0	2.0	23.0
1.0	21.0	1.0	2.8	25.0
1.0	23.0	1.0	3.0	28.0
1.0	24.0	1.0	3.0	30.0
4.0	34.0	1.0	4.0	32.0
5.0	197.0	1.0	5.0	49.0
5.0		1.0	5.0	50.0
6.0		1.0	6.0	72.0
6.0		1.0	6.0	79.0
$n = 25$		$n = 42$		
$\bar{x} = 16.88$, s.d. = 0.43-660.7*		$\bar{x} = 12.21$, s.d. = 0.65-234.4*		

t-Test $P>0.5$ = N.S. (not significant)
*s.d., shown as a range because distributions were lognormal.

The t-Test on gold concentrations in Pinus Radiata growing on the two rock types showed the means to be not significantly different. This suggests that the gold in P. Radiata cannot distinguish between the two different rock types. However, when all the other elemental concentrations were considered, the t-Test showed that only two elements had concentrations that were significantly different from each other: sodium, $P = 0.014$ and nickel, $P = 0.033$. Both chromium ($P = 0.09$) and copper ($P = 0.09$) had possibly significant difference as summarized in Table 3-4.

As there was no certainty about the nature of the substrate from the results of bark analysis, it was decided to divide the samples into two discrete populations to some extent arbitrary. The two populations were classified on the basis of the gold content of the bark (ie ≤ 10 ng/g) or >10 ng/g) and a t-Test was carried out for all the elements using these two populations. Once again the calculations were performed on logarithmically-converted data. The results as summarized in Table 3-5 show that only iron and arsenic are correlated with gold indicating the presence of an auriferous substrate. The association of gold-arsenic-iron indicates the presence of arsenopyrite in the substrate.

A correlation analysis for intra-elemental relationships within the bark was carried out and the results are shown in Table 3-6.

A feature of Table 3-6 is the large number of very highly significant relationships ($P<0.001$) for a number of elements. Because this analysis was not performed on bark samples based on rock types, not much can be said about the inter-elemental effects on different rocks. However, gold was correlated positively only with arsenic and sulphur and possibly with copper showing the predominantly chalcophile role of gold in this environment.

Finally bark samples were reassigned to two populations based on site maps rather than field observations giving 40 samples on andesite and 27 on quartz reef as seen in Table 3-7.

The results were essentially the same ie, nickel and sodium showed significant difference with probabilities of $P = 0.017$ and $P = 0.042$ respectively. Chromium and copper also showed significant difference between the two rock types with P values of $P = 0.05$ for chromium and $P = 0.01$ for copper. The latter value for copper was

Table 3-4 Mean elemental concentrations in bark of Pinus Radiata growing on different rock types

Elements	Growing on Quartz		Growing on Andesite		t-Test	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	P	Significance
Al	721	407-933	615	525-1000	0.80	-
As	0.033	0.005-0.22	0.023	0.004-0.13	0.19	-
B	9.2	5.8-14.6	10.9	7.2-16.5	0.32	-
Ca	1028	678-1556	891	566-1390	0.87	-
Cr	0.31	0.16-0.60	0.45	0.18-1.11	0.09	PS
Cu	1.3	0.61-2.82	2.33	0.78-7.0	0.09	PS
Fe	132	60-288	124.7	65-236	0.80	-
K	111	68-182	117	68-200	0.41	-
Mg	199	141-282	185	126.6-277	0.73	-
Na	224	163-307	267	183-390	0.014	S
Ni	0.24	0.14-0.41	0.38	0.13-1.11	0.033	S
P	68	50.6-91	63.4	42-95	0.79	-
Pb	1.56	0.8-3.0	1.8	0.8-3.95	0.92	-
S	103	66-160	123	52.7-288	0.68	-
Si	148	87-253	118.6	59-236	0.96	-
Sr	7.4	5.3-10.3	6.7	4.7-9.6	0.68	-
Zn	8.3	3.8-18	8.7	5-15	0.18	-
Au	0.017	0.001-0.66	0.012	0.001.0.23	0.65	-

S^{XX} = $P<0.001$ (very highly significant)

S^{X} = $0.01>P\geq0.001$ (highly significant)

S = $0.05>P\geq0.01$ (significant)

PS = $0.1>P\geq0.05$ (possibly significant)

\- = $P>0.1$ (not significant)

Table 3-5 Mean elemental concentrations (µg/g dry mass) in bark of Pinus Radiata from the two populations

Elements	Conc when Au≤10 ng/g		Conc when Au>10 ng/g		t-Test	
	$\bar{x}$	s.d	$\bar{x}$	s.d	P	Sig
Al	645.0	442-942	677.0	451-1019	0.64	-
As	0.02	0.004-0.10	0.05	0.01-0.40	0.073	PS
Au	0.002	0.001-0.005	0.029	0.015-0.057	0.0000	S^{XX}
B	10.1	6.4-16.0	10.5	7-15.8	0.68	-
Ca	937.0	618-1422	955.0	583-1563	0.89	-
Cr	0.36	0.16-0.83	0.45	0.2-1.03	0.32	-
Cu	1.6	0.70-3.8	2.5	0.71-8.8	0.16	-
Fe	114.0	58-225	164.0	83-324	0.050	PS
K	120.0	70-205.6	104.5	67.8-166	0.29	-
Mg	192.0	130-284	186.6	129-270	0.76	-
Mn	17.0	9.9-29.5	16.6	10.2-27.2	0.84	-
Na	244.0	165-361	262.0	196-349	0.40	-
Ni	0.30	0.13-0.72	0.35	0.12-0.98	0.59	-
P	65.0	46-93	64.0	43-96	0.87	-
Pb	1.51	0.76-3.1	2.1	0.92-4.6	0.17	-
S	106.2	55.7-202	136.0	59-316	0.23	-
Si	126.5	67.6-237	136.8	70-268	0.66	-
Sr	6.9	4.8-9.9	7.2	5.3-9.8	0.59	-
Zn	8.3	4.2-16.4	9.1	5.1-16	0.56	-

S^{XX} = $P<0.001$ (very highly significant)
S^{X} = $0.01>P\geq0.001$ (highly significant
S = $0.05>P\geq0.01$ (significant)
PS = $0.1>P\geq0.05$ (possibly significant)
- = $P>0.1$ (not significant)

Table 3-6 Matrix of correlations between elemental concentrations in bark of Pinus Radiata

	Al	As	Au	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Sr
Ag	-															
Au	-	S														
B	-	-	-													
Ca	S^{XX}	-	-	-												
Cr	S^{XX}	-	-	S^{XX}												
Cu	-S	S^{XX}	PS	-	-	-										
Fe	S^{XX}	S^{X}	-	S^{XX}	S	S^{XX}	S^{XX}									
K	S^{XX}	-	-S	S	S^{XX}	S^{XX}	-	S^{XX}								
Mg	S^{XX}	-	-	-	S^{XX}	S^{XX}	-	S^{X}	S^{XX}							
Mn	S^{X}	S	-	-	S^{XX}	S^{XX}	-	S^{XX}	S^{XX}	S^{XX}						
Na	S^{X}	S	-	-	S^{X}	S^{XX}	S^{X}	S^{XX}	S^{XX}	S^{XX}	S^{X}					
Ni	-	-	-	-	-	S^{XX}	S^{X}	S^{XX}	S^{XX}	-	S^{X}	S^{XX}				
P	S^{XX}	-	-	-	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	-	S^{XX}	S^{XX}	S^{X}			
S	$-S^{X}$	S^{XX}	S	-	-	-	S^{XX}	S^{XX}	-	-	-	-	-	-		
Sr	S^{XX}	-	-	-	S^{XX}	S^{X}	-	S	S^{X}	S^{XX}	S^{X}	S	-	S^{XX}	-	
Zn	S	-	-	S^{XX}	S^{XX}	S^{XX}	S^{X}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{X}	S^{XX}	-	S

S^{XX} = $P<0.01$ (very highly significant)

S^{X} = $0.01>P\geq0.001$ (highly significant)

S = $0.05>P\geq0.01$ (significant)

PS = $0.1>P\geq0.05$ (possibly significant)

\- = $P>0.1$ (not significant)

Table 3-7 Mean elemental concentrationsin bark of Pinus Radiata based on field observations

Elements	Bark from Quartz (27)		Bark from Andesite (40)		t-Test	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.	P	Sig
Al	698.2	484-1007	626.6	422.7-930	0.085	PS
As	0.04	0.004-0.09	0.02	0.005-0.33	0.43	-
Au	0.006	0.001-0.027	0.004	0.009-0.016	0.22	-
B	9.2	5.9-14.5	11.0	7.2-16.7	0.13	-
Ca	1009	664-1534.6	895.4	571.5-1403	0.17	-
Cr	0.31	0.16-0.59	0.46	0.19-1.13	0.051	S
Cu	1.5	0.54-4.1	2.2	0.80-5.8	0.013	S
Fe	131.8	61-284	126	66-240	0.75	-
K	110	67.8-180	118	69-203	0.71	-
Mg	195	135.5-281	187.5	126-279	0.42	-
Mn	18.3	10.3-32.3	16.0	9.8-26.2	0.37	-
Na	226.5	165-310	266.7	182-391	0.042	S
Ni	0.24	0.14-0.4	0.39	0.13-1.14	0.017	S
P	65.8	47-92	64.6	43.7-95.3	0.42	-
Pb	1.65	0.80-3.43	1.72	0.80-3.71	0.45	-
S	112	60-211	116	53.4-253.5	0.27	-
Si	139.6	75.5-258	123	64-237	0.14	-
Sr	7.3	5.3-10.2	6.8	4.7-9.7	0.23	-
Zn	8.4	3.9-18.2	8.6	4.9-14.8	0.79	-

S^{XX} = $P<0.001$ (very highly significant)

S^{X} = $0.01>P\geq0.001$ (highly significant)

S = $0.05>P>0.01$ (significant)

PS = $0.1>P\geq0.05$ (possibly significant)

\- = $P>01$ (not significant)

largely influenced by a highly anomalous copper value in a sample suspected to have been contaminated. When this value was removed, the copper relationship was no longer significant.

3.2.7 Conclusions

There are three elemental concentrations in the ash of Pinus Radiata from Union Hill which are highly indicative of the nature of the substrate: namely chromium, nickel and sodium. From Table 3-2, it will be noted that sodium and chromium are the two elements with the highest degree of enrichment in andesite relative to quartz. Nickel shows very little enrichment in andesite.

Although gold levels in the two rocks are significantly different, gold in the bark of Pinus Radiata did not show any significant difference between the two rock types.

3.2.8 Acknowledgement

I am grateful to Goff et al. (1985) for permission to use their ICP data.

3.3 Case Study II

Biogeochemical Exploration Studies for Gold at the Seruwila Copper-Magnetite Prospect in Sri Lanka

3.3.1 Introduction

In 1971, a large copper-magnetite ore body was discovered in Sri Lanka by the Sri Lankan Geological Survey. The prospect is situated in the Seruwila area (Fig. 3-2) some 20 km southeast of the town of Trincomalee and has been the subject of assessment by the French organisation BRGM and by the Sri Lankan Geological Survey. It is the first base metal deposit to be discovered in Sri Lanka. The geology and ore mineralogy have been investigated by Jayawardena, (1985). Wijesekera (1984) has shown with the aid of drilling programme that the copper concentration is between 1-1.5 percent and iron is about 30 percent. Brooks et al. (1985) have recently carried out geochemical and biological exploration studies over the Seruwila deposit at its northeastern extremity at Kollan Kulam. In this part of the prospect, the terrain is relatively undisturbed and is marked by a prominent gossanous outcrop of the ore body.

Gold biogeochemical studies were carried out on the soil and plant samples collected by Brooks et al. (1985) over the 180 m transect across the ore body. The aim of this work was to analyze the soil and

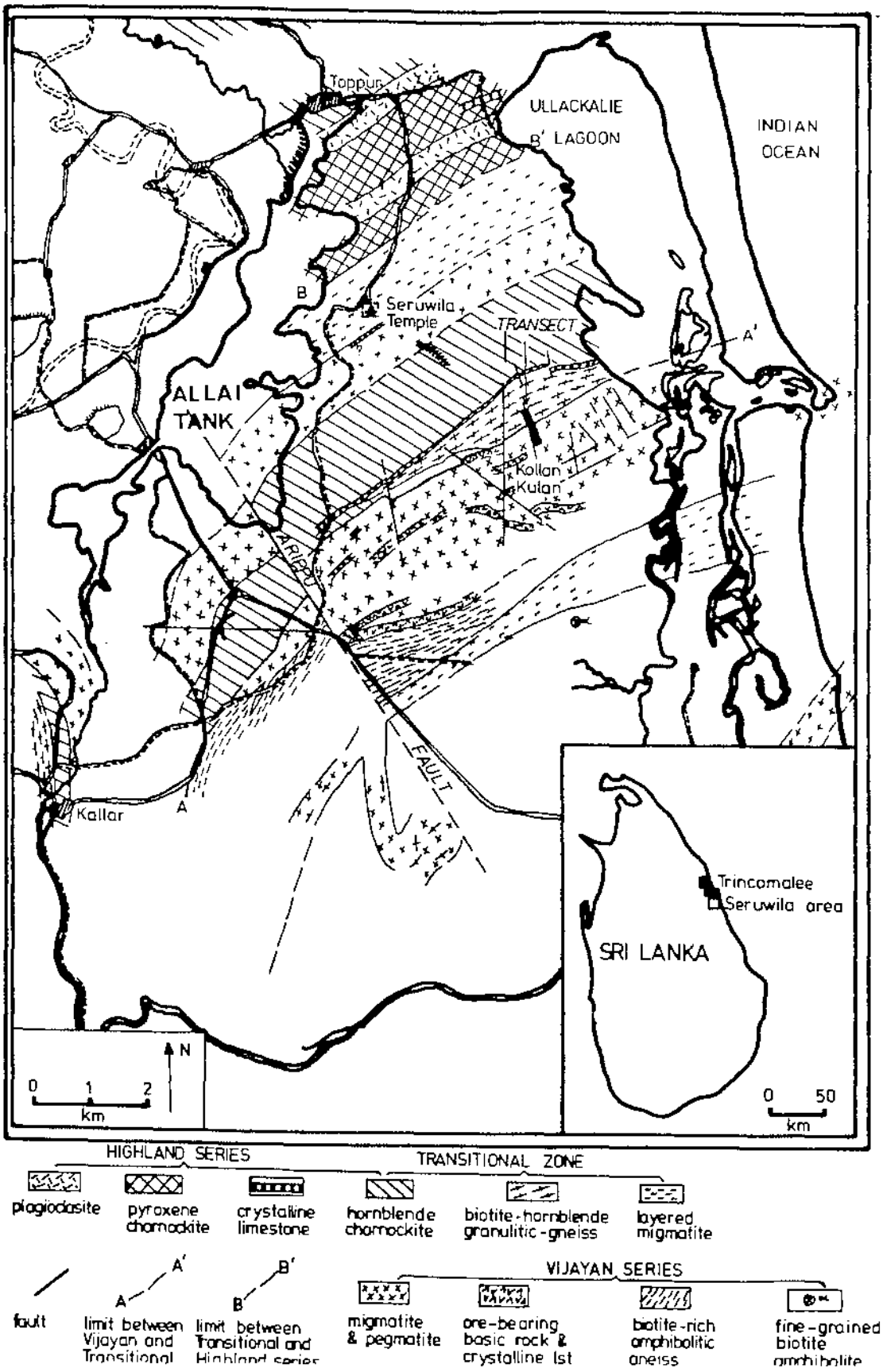

Figure 3-2 Map of the Seruwila Copper-Magnetite Prospect.
By courtesy, Sri Lankan Geological Survey

plant samples for gold (using the developed method) and find out if gold is indicative of the position of the ore body as determined by the drilling programme of 1984.

3.3.2 The Geology and Mineralogy of the Seruwila Copper-Magnetite Prospect

According to Jayawardena (1984), the Seruwila copper-magnetite mineralized area as seen in Figure 3-2 is underlain by a Precambrian metamorphic basement covered by recent Quaternary sands and alluvium. The Seruwila deposit is located immediately to the southeast of the contact between the Vijayan and Highland Series rocks. The Vijayan Series is composed of granites, granitic gneisses, migmatites and hornblende biotite gneisses and has reached the amphibolite facies of metamorphism. The Highland Series is composed of charnockites and associated metasediments which have undergone repeated cycles of metamorphism.

The general strike of foliation in the northeast of the prospect varies from N 35^{o} E to 85^{o} E, the average being N 55^{o} E. In the southwest (Alioluwa and Mottamalai areas), the strike of the foliation is highly variable. The regional dip is towards the northwest and is more than 50^{o} to subvertical. In the Kollan Kulam and Panichchan Kulam area a few gossanous outcrops with very steep southeastern dips have been observed.

The main types of ore mineralization (Jayawardena, 1984) are as follows:

(1) Thin lenticular pods of magnetite. This ore consists only of large grains of magnetite intergrown with other gangue minerals.

(2) Mixed ore of magnetite and sulphides. This ore shows numerous yellow sulphide patches distributed more or less uniformly. This category of the ore is rich in sulphides with grades reaching 2-3 percent copper.

(3) Scattered types of ore with predominant sulphides. This type is poor in magnitude and due to the scattered nature of the sulphides, gives low metal content.

The ore body at Kollan Kulam is of the second type as described above and like the other areas of the prospect, contains an appreciable amount of apatite. An analysis of the gossan at Kollan Kulam gave 6.53 percent copper, 46.62 percent iron and 2.06 percent phosphorus. There were also anomalous concentrations of siderophile cobalt, manganese and nickel as well as of chalcophile zinc.

3.3.3 Climate and Vegetation of the Seruwila Area

Seruwila is located within a moister part of the "Dry Zone" of Sri Lanka and experiences pronounced summer (July) drought as well as the influence of the Northeast Monsoon (December to February). For nearby Trincomalee, mean annual precipitation is 1667 mm and the mean temperature is 27.0°C with little monthly variation.

The climax vegetation of the area is generally regarded as dry mixed evergreen scrub/forest Mueller-Dombois, 1968). This forest rarely exceeds 20 m in height and is stratified into emergent trees, a subcanopy with a dense understorey of tall shrubs and lianes. it is classified within the Chloroxylon-Berrya-Citex-Schleichera series recognized by Gaussen et al. (1964). Common trees in the Seruwila area the emergents Manilkara hexandra and Alseodaphne semicarpifolia and the low or subcanopy species Drypetes seplaria, Lepisanthes tetraphylla, Cassia fistula and Dimorphocalyx glabellus. Frequent associated understoney shrubs are Polyalthia Korinti, Glycosmis mauritiana, Plerospermum canescens and Memecylon umbellatum.

3.3.4 Materials and Methods

3.3.4.1 Soil Geochemistry

Surface soil samples were collected at 10 m intervals across a northwest-southeast 180 m transect of the ore body at Kollan Kulam. This transect extended to background at each side of a prominent gossanous outcrop of composition described previously. Soil samples were sieved to -100 mesh size in a nylon sieve and stored in labelled bottles.

(a) Analysis for Gold

Soil samples (0.5g) were digested on water bath with 10 ml of fuming nitric acid. The contents were heated to dryness and then 10 ml of aqua regia (HCl / HNO_3, (3:1)) were added and taken to dryness again. The residues were redissolved in 6M hydrochloric acid and heated until 3 ml was left. The procedure from here onwards was the same as that outlined in Chapter 2.

(b) Analysis of Other Elements by ICP

Soil samples (0.5g) were digested in polypropylene beakers with a 1:1 mixture of hydrofluoric and nitric acids. The contents were heated to dryness in a water bath and the residues were redissolved in 2M hydrochloric acid. The samples were then analyzed for 18 elements by plasma emission spectrometry (ICP) using an ARL 34000 instrument with a polychromator for simultaneous analysis of all elements.

3.3.4.2 Geobotany

The 180 m transect passed through an area of dense shrubby vegetation. The area was largely undisturbed apart from the path cleared by the Sri Lankan Geological Survey team in 1980. This area was rapidly being covered by trees and shrubs. The numbers of different plant species appearing within a band of 1.5 m on each side of a tape laid along the transect were recorded. There were a total of 14 species present but only two, Glycosmis mauritiana (A) and Pterospermum canescens (B) were sufficiently abundant. A species list was also prepared for the gossaneous outcrop. Species recorded from the Gossan were coded from G1 to G12 as seen in Table 3-8.

3.3.4.3 Biogeochemistry

Leaf material of the dominant shrubs G. mauritiana (A) and P. canescens (B) were sampled where possible at 10 m intervals along the 180 m transect. This resulted in 19 specimens of A and 14 specimens of B. In addition, 12 other species growing exclusively on the copper-magnetite gossan were sampled. The plant specimens collected were washed and dried at 100°C before being stored in labelled packets.

(a) Method for Gold

Gold in vegetation was determined using the method outlined in Chapter 2.

(b) Method for Other Elements

The samples for analysis by ICP were ashed at 500°C for 4 hours. The weighed plant ash was dissolved in 2M hydrochloric acid.

3.3.5 Results and Discussion

(a) Soil Geochemistry

The mean elemental concentrations for 19 elements in the soil and in the ore are shown in Table 3-8. The elemental concentrations of these 19 elements at each sampling point along the transect are presented in Appendix I. Figure 3-3 shows a plot of values for seven elements (Ca, Cu, Co, Fe, Mo, Ni and P) at each sampling point along the transect. These elements were chosen because they revealed maximum contrast between sites near the gossan and at background. It is evident from this Figure that both copper and iron in soils are primary indicators of mineralizat ion; however several other elements (Au, Ca, Co, Mo, Ni and P) are good pathfinders for the ore body in this area.

Correlation analysis for intra-elemental concentrations in the soils were performed and a matrix of correlation for selected elements are shown in Table 3-9. Only highly significant relationships ($P<0.01$) are shown.

It is seen that iron and copper are well correlated with virtually all of the other elements listed in this Table. In fact iron correlated well with fourteen elements while copper correlated with twelve elements. Surprisingly, gold correlated well with thirteen elements. Although gold did not correlate with arsenic, other correlat-ions suggest gold to be present with sulphide minerals like pyrite and chalcopyrite in this substrate. From Jayawardena's paper (1984), Brooks et al. (1985) deduced that sources of some of the elements listed in Table 3-10 are as follows (sources in parentheses): calcium (calcite, siderite and malachite); cobalt, carrollite and magnetite); chromium (magnetite); copper (bornite, azurite, chalcopyrite and malachite); iron magnetite, spinel, hercynite, ilmenite, hematite, limonite and goethite); magnesium (silicates); manganese (magnetite); molybdenum (magnetite);

Table 3-8 Mean elemental concentrations (µg/g except where otherwise stated) in the dry matter of plant foliage, soils and ore from the Kollan Kulam area of the Seruwila copper-magnetite deposit at Kollan Kulam, Sri Lanka

Material	n	Al	As	B	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	S	Sr	Zn	Au
		(%)		(%)					(%)	(%)	(%)	(%)		(%)		(%)				(ng/g)
Soils	19	8.03	100	0.30	1.49	52	46	675	4.83	1.69	0.17	0.53	7	4.15	58	0.13	0.19	586	150	6.0
Ore	1	2.28	<40	1.17	7.51	194	50	65300	46.62	0.37	0.28	0.64	36	3.00	440	2.06	0.01	234	428	8.0
		(µg/g)		(µg/g)					(µg/g)			(µg/g)		(µg/g)						
Plant A	19	67	<4	39	n.d.	1.6	1.0	5	107	1.42	0.29	47	<1	174	4.4	0.13	0.11	119	125	4.06
Plant B	14	250	<4	37	n.d.	1.9	1.1	17	287	0.74	0.33	262	<1	214	4.8	0.16	0.05	131	119	n.d.
Plant G1	1	47	<4	37	n.d.	3.5	0.4	15	60	1.82	0.59	66	<1	251	3.4	0.19	0.03	400	112	n.d.
Plant G2	1	49	<4	15	n.d.	0.3	0.2	11	83	1.21	0.27	35	<1	149	1.2	0.17	0.05	189	37	1.0
Plant G3	1	36	<4	46	n.d.	0.2	0.2	9	56	1.39	0.18	16	<1	138	1.5	0.17	0.04	199	63	1.0
Plant G4	1	53	<4	55	n.d.	0.3	0.4	15	59	0.81	0.33	43	<1	180	4.1	0.09	0.04	396	183	n.d.
Plant G5	1	35	<4	52	n.d.	0.2	0.1	14	43	1.27	0.28	48	<1	239	3.9	0.13	0.01	173	58	1.0
Plant G6	1	34	<4	42	n.d.	0.1	0.2	6	56	1.10	0.19	15	<1	233	2.1	0.09	0.13	144	43	1.0
Plant G7	1	33	<4	37	n.d.	0.2	0.1	6	59	1.02	0.39	14	<1	233	3.5	0.10	0.03	265	45	n.d.
Plant G8	1	76	<4	51	n.d.	0.7	0.5	21	89	1.81	1.29	23	<1	428	3.0	0.18	0.30	945	270	n.d.
Plant G9	1	61	<4	35	n.d.	0.3	0.2	11	73	0.93	1.07	58	<1	613	2.4	0.10	0.10	398	74	n.d.
Plant G10	1	96	<4	49	n.d.	0.5	0.5	20	107	1.56	0.67	44	<1	384	2.1	0.23	0.12	800	62	n.d.
Plant G11	1	105	<4	58	n.d.	0.7	0.5	9	97	0.89	0.55	61	<1	163	4.0	0.24	0.10	1058	79	n.d.
Plant G12	1	48	<4	26	n.d.	0.5	0.2	8	64	1.15	0.46	29	<1	182	1.4	0.21	0.17	387	72	n.d.

A - Glucosmis mauritiana Tanaka (Rutaceae)
B - Pterospermum canescens Roxb. (Sterculiaceae)
G1 - Dimorphocalyx glabellus Thw. (Euphorbiaceae)
G2 - Cassia fistula L. (leguminosae)
G3 - Tiliacora acuminata (Lam.) Miers (Menispermaceae)
G4 - Atalantia monophylla DC. (Rutaceae)
G5 - Lepisanthes tetraphylla (Vahl.) Radlk. (Sapindaceae)
G6 - Manilkara hexandra (Roxb.) Dubard (Sapotaceae)
G7 - Ficus arnottiana (Miq.) Miq. (Moraceae)
G8 - Ecbolium viride (Forsk.) Alston (Acanthaceae)
G9 - Canthium sp. Lam. (Rubiaceae)
G10 - Grewia polugama Roxb. (Tiliaceae)
G11 - Zizuphus oenoplia (L.) Mill. (Rhamnaceae)
G12 - Allophulus cobbe (L.) Bl. (Sapindaceae)

Notes:
1. n.d. not determined
2. Mean values shown either as arithmetic or geometric means depending on the statistical distribution of the data.

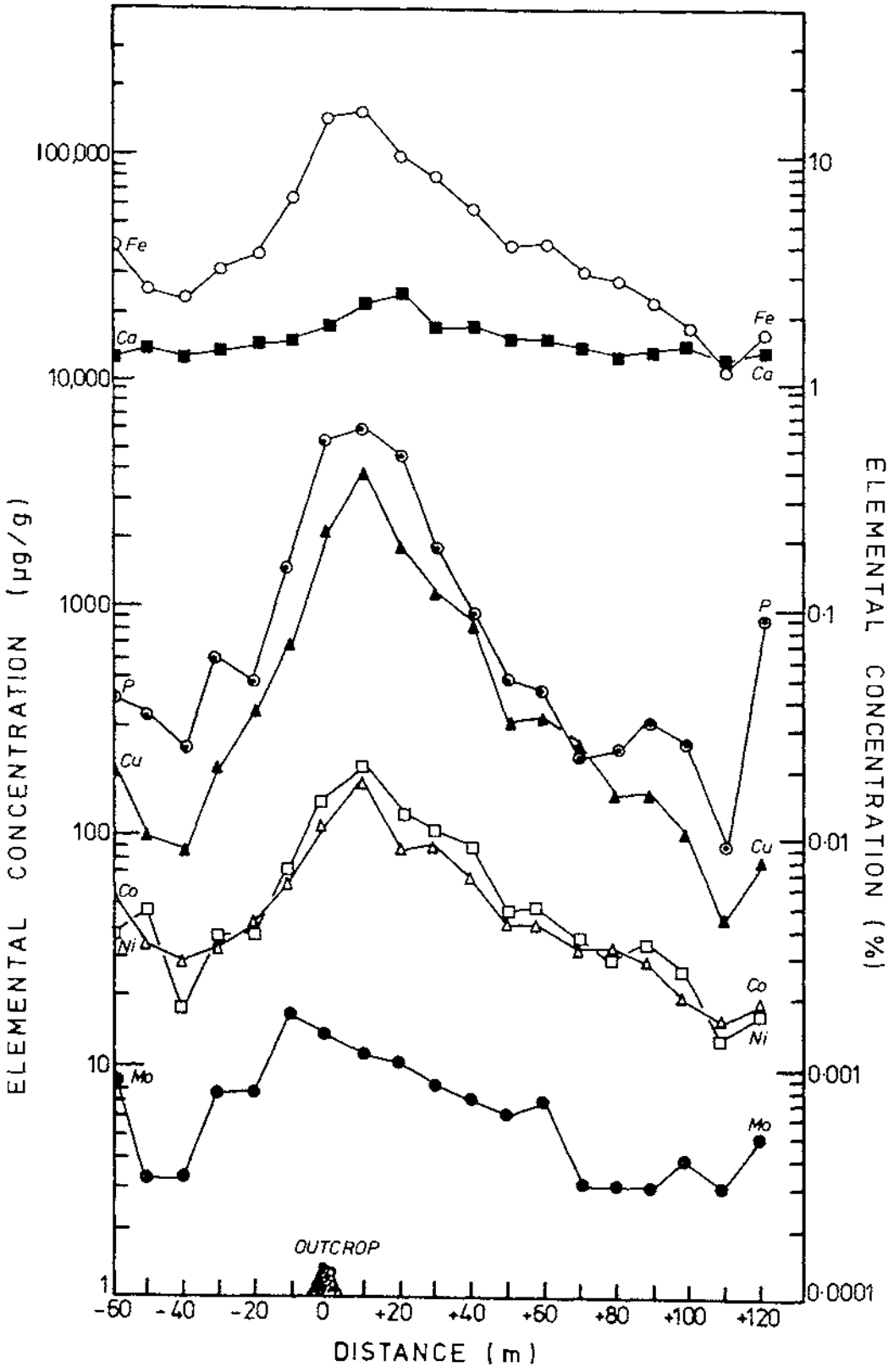

Figure 3-3 Concentrations of ore-indicating elements in soils along a transect of the Seruwila copper-magnetite prospect

Table 3-9 Matrix of correlation for elemental concentrations in soils overlying the Seruwila copper-magnetite prospect

	Al	As	B	Ca	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	P	Sr	Zn
As	-														
B	-	-													
Ca	-	-	S^{XX}												
Co	-	S^{X}	S^{XX}	S^{XX}											
Cr	-	-	S^{XX}	-	S^{XX}										
Cu	-	-	S^{XX}	S^{XX}	S^{XX}	S^{X}									
Fe	-	S^{X}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}								
Mg	-	-	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}							
Mn	S^{X}	S^{XX}	-	-	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{X}						
Mo	-	-	-	-	S^{X}	S^{XX}	-	S^{XX}	S^{X}	S^{XX}					
Ni	-	S^{X}	S^{XX}	S^{XX}	S^{XX}	-	S^{XX}	S^{XX}	S^{X}	S^{XX}	S^{X}				
P	-	-	S^{XX}	S^{XX}	S^{XX}	S^{X}	S^{XX}	S^{XX}	S^{X}	S^{X}	S^{X}	S^{XX}			
Sr	-	-	S^{X}	S^{X}	S^{X}	-	S^{X}	S^{X}	S^{X}	-	-	S^{XX}	S^{X}		
Zn	-	S^{XX}	-	-	S^{XX}	-	S^{X}	S^{XX}	-	S^{XX}	-	S^{XX}	-	-	
Au	-	-	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	S^{XX}	

S^{XX} = $P<0.001$ (very highly significant)

S^{X} = $0.01>P\geq0.001$ (highly significant)

\- = $P>0.01$ (not significant)

nickel (pentlandite); phosphorus (apatite); strontium (calcite); zinc (sphalerite).

(b) Biogeochemistry

Only two taxa (Glycosmis mauritiana - A and Pterospermum canescens - B) had a wide enough distribution in the test area to be seriously considered for biogeochemical prospecting. Gold was determined only in Glycosmis mauritiana (A) as there were not enough samples of taxa B. Elemental concentrations for some selected elements in Glycosmis mauritiana are presented in Appendix II.

Correlation analysis for plant leaf versus soil elemental concentrations was carried out on the data and the findings are shown in Table 3-10.

Table 3-10 Matrix of correlation for elemental concentrations in soils and plant material

Plant (A)	Al	Au	B	Co	Cr	Cu	Fe	K	Mg	Mn	Ni	P	S	Sr	Zn
Al	-	-	-	-	-S	-	-	-	-	-S	-	-	-	-	-
Au	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	-	-	-	-	-	-	-	-	-	-	-	-	-	-S	-
Co	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-S	-
Cu	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	S^X	-S	-S	$-S^X$	$-S^{XX}$	-S	$-S^X$	-S	-S	$-S^{XX}$	-S	-S	S	-S*	-S
K	-		S	S	S	S	S*	-	-	S*	S	S	S	S**	-
Mg	-	-	-	-S	-	-	-	-	-	-S	-	-	-	-	-
Mn	S*	-	-	-	-	-	-	-	-	-S	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P	-	-	-	S*	S	S*	S*	-	-	S*	S	S*	-	-	-
S	-	-	-	-	-	-	-S	-	-	-	-	-	-	-S*	-
Sr	S**	-	-	-	-S	-	-	-S*	-	-S	-	-	-	-S	-S
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

S^{XX} = $P<0.001$ (very highly significant)

S^X = $0.01>P\geq0.001$ (highly significant)

S = $0.05>P\geq0.01$ (significant)

\- = $P>0.05$ (not significant)

There is no correlation between the copper content of the soil and the concentration of this element in the plant leaves. But this is in agreement with the findings of Timperley et al. (1970) that biogeochemical prospecting is seldom successful when relying on elements such as copper and zinc which are plant micro-nutrients. Over certain ranges of soil concentration, the abundances of these elements in the plant tissue are internally controlled so that plants tend to have constant concentrations of these elements irrespective of the levels of these metals in the soil.

Gold in the soil was also not correlated to gold in plant. This poor correlation could perhaps be due to the very low level of gold present in this area. The maximum concentration of gold in soil was only 21.0 ng/g. Nevertheless gold in soil was highly indicative of the position of ore body and this is illustrated in Figure 3-4 together with the concentration of gold in the plant at these sites along the transect.

The important feature of the data in Table 3-10 is the highly significant relationship ($P<0.01$) between phosphorus in species A and the content of this element in the soil. Clearly the phosphorus content of Glycosmis mauritiana is highly indicative of iron and copper mineralization in the soil.

Table 3-10 also shows that iron uptake by Glycosmis mauritiana is affected by presence of elements like B, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, S, Sr, Zn and Au in the soil. This would normally indicate that the vegetation be chlorotic in highly-mineralized substrates. The field observations did not however indicate chlorosis and it would seem that although iron uptake is reduced in relative terms, the absolute amounts are not low enough to produce chlorosis because of the very high iron content of the substrate.

3.3.6 General Conclusions

The data obtained show that in the soils, the concentrations of the ore elements, copper and iron, and of the pathfinders calcium, cobalt, manganese, magnesium, molybdenum, nickel, phosphorus and gold were highly indicative of the position of the ore body as determined by the drilling programme.

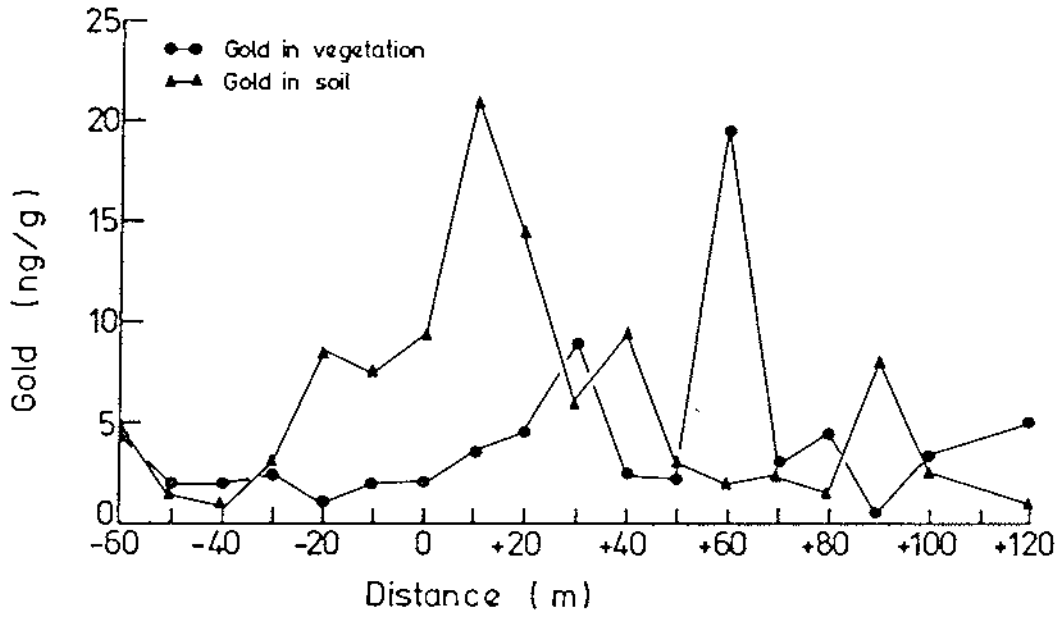

Figure 3-4 Concentration of gold in plant and gold in soil along the transect of the Seruwila copper-magnetite prospect

The plant species, Glycosmis mauritiana appears to have the potential for biogeochemical prospecting on the basis of its ubiquity and ability to reflect mineralization in the substrate. This latter ability is centred around use of the pathfinder phosphorus (and to a lesser extent potassium). The plant Glycosmis mauritiana) cannot be used for biogeochemical prospecting for gold in this area.

3.3.7 Acknowledgement

I am grateful to Brooks et al. (1985) for permission to use their ICP data.

3.4 Case Study III

The Arsenic content of Rumex acetosella L. and Minuartia Verna (L.) Hiern as a guide to Gold Mineralization in the Serbomacedonian massif, Northern Greece

3.4.1 Introduction

It has been known for many years that the presence of certain elements in plant species or in soil samples can indicate the existence of mineralization in the substrate. These elements are known as indicator or pathfinder elements.

Arsenic is a recognised pathfinder element for many precious and base metal deposits particularly those containing sulphides and sulpho-salts. It is a common associate of Cu, Ag, Au, Zn, Cd, Hg, U, Sn, Pb, P, Sb, Bi, S, Se, Te, Mo, W, Fe, Ni, Co and Pt metals.

Most of the early geochemical investigations, using arsenic as a pathfinder were primarily concerned with soil sampling. The arsenic content of vegetation has been investigated extensively as an alternative sampling medium since 1964 when Warren et al. (1964, 1968) found that Douglas fir (Pseudotsuga menziesii) tended to accumulate arsenic in the mineralized zones of the Western Cordillera in Canada and in USA. Talipov et al. (1968) noted a direct correlation between the arsenic content of the ashes of plant and gold content of arseniferous soils in Russia.

Recently, Kelepertsis et al. (1984) have analyzed Rumex acetosella and Minuartia verna from the Serbomacedonian massif in Northern Greece for base metals and arsenic. Their results show the ability of

these two plant species not only to tolerate and indicate base metals, Cu, Zn, Pb and Fe but also arsenic. Most of the ore occurrences in the Serbomacedonian massif are auriferous and it was decided to analyze these plants and the corresponding soil samples for gold to determine the degree to which the arsenic content of these plants can delineate gold mineralization in Northern Greece.

3.4.2 The Geology of the Serbomacedonian Massif, Northern Greece

Plant and soil samples were taken from eleven mineralized areas in the region of Serbomacedonian massif as illustrated in Figure 3-5. These are:

(1) The Doirani Lake Volcanic stock district (DO-IR) which is situated within metamorphic rock (gneiss, schists). According to Panagos et al. (1978) the volcanic rock is a K_2O-rich trachyte with hydrothermal alteration zones and traces of disseminated copper mineralization.

(2) The Gerakario-Mylochori district (MG-IR, MG-2R, MG-3R, MG-3AM) has volcanic stock of rhyolitic composition intruding and overlies metamorphosed and tectonised rocks.

(3) The Askamnies, Laodikino-Kilkis area (AS-IR, AS-IAM). Here mica gneisses and mica schists prevail. Also present is quartz vein with calcopyrite and pyrite minerals.

(4) The Tatidi farm area (Ta-IR). Here mixed sulphide mineralization occurs in the form of quartz vein with gneisses and mica schists as host bedrocks.

(5) The Laodikino (borehole F6) area (F6-IR) consists of metamorphics (gneisses and schists). The mineralization occurs in the form of copper-quartz vein.

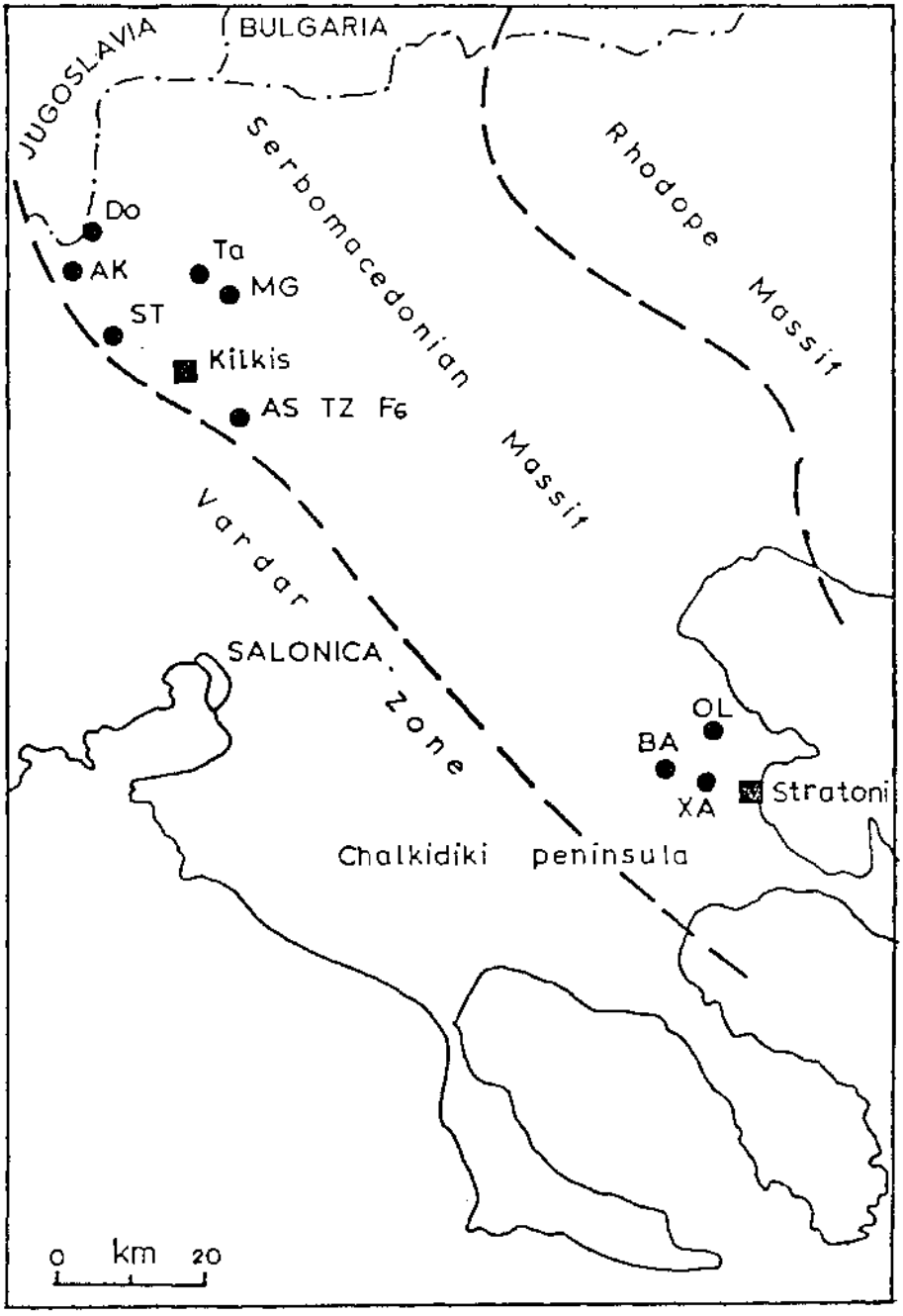

Figure 3-5 Map of northern Greece showing sample location sites

(6) The Tsoumas Laodikino area (Tz-IAM) also consists of metamorphics (gneisses and schists). The mineralization occurs as copper-quartz veins.

(7) The Olympiada district (Chalkidiki) (OL-IR) is a well known source of Cu-Pb-Zn ore. The bedrock consists of metamorphics (biotite, plagioclase, microcline gneisses) and volcanic porphyritic rocks.

(8) The "Black rock" area at Akritas (Ak-IR, Ak-2R) is silicified rock of rhyolitic composition associated with pyrite, magnetic and chalcopyrite mineralization.

(9) The Stavrochori district (ST-IR), northwest of Kilkis consists of metamorphics (gneisses). There are no signs of sulphide mineralization.

(10) The Varvaro district, Chalkidiki peninsula (BA-IR). Here manganese mineralization occurs in metamorphic rocks (biotite gneiss).

(11) The Hander district, Chalkidiki peninsula (XA-IR, XA-IAM). The manganese mine is in metamorphic rock consisting of gneisses and amphibolites. The mine is associated with the Stratoni mine which is characterized by Cu-Pb-Zn-Ag-Au mineralization.

3.4.3 Materials and Method

Samples of the two plants and the corresponding soil samples were collected during the summer of 1983 from different mineralized areas by Kelepertsis et al. (1985). A summary of sample localities with the description of mineralized rocks is presented in Table 3-11. The plant samples were first washed and then dried at 100°C while the soil samples were air dried and then ground to a -100 mesh size.

Table 3-11 Sample localities and mineral paragenesis for sites used in this investigation

Sample	Mineral paragenesis	Location	Plant species present
DO-1R	pyrite (FeS_2) magnetite (Fe_3O_4) chalcopyrite ($Cu_2SFe_2S_3$)	Doirani Lake	Rumex (R)
MG-1R MG-2R MG-3R MG-3A	pyrite magnetite chalcopyrite	Gerakario- Mylochori	R
AS-1R AS-1A	pyrite chalcopyrite arsenopyrite	Askamnies Laodikino	R Minuartia (M)
XA-1R XA-IA	Mn oxides (pyrolusite) Mn carbonates Sphalerite (minor) Galena (PbS) Arsenopyrite ($FeAsS_2$)	Hander Stratoniki	R M
Ta-1R	pyrite chalcopyrite Sphalerite Galena Arsenopyrite	Tatidi farm	R
F6-1R F6-1A	pyrite chalcopyrite arsenopyrite	Borehole F6 Laodikino	R M
TZ-1R TZ-1A	pyrite chalcopyrite arsenopyrite	Tzoumas Laodikino	R M

Sample	Mineral paragenesis	Location	Plant species present
OL-1	pyrite sphalerite galena minor chalcopyrite arsenopyrite	Olympiada Chalkidiki	R
Ak-1	pyrite magnetite Chalcopyrite Sphalerite Galena	Akritas Doirani	R
ST-1	unknown	Stavrochori Kilkis	R
BA-1	Mn oxides	Varvara Chalkidiki	R

3.4.4 Analytical Methods Used:

(a) Gold in plants: were determined by the method developed and outlined in Chapter 2.

(b) Gold in soils: Soil samples (0.5g) were heated with 10 ml of fuming nitric acid until dryness over a steam bath. Then 10 ml portions of aqua regia were added and taken to dryness until only white siliceous material remained. The residues were dissolved in 6M hydrochloric acid and the procedure from here onwards was same as for the plants.

(c) Other major elements

The soil samples (0.10-0.15g) were decomposed with fuming nitric acid, taken to dryness and finally made to 10 ml with 2M hydrochloric acid. The plant samples (0.10-0.15g) were ashed at 500^{o}C and the ash redissolved in 10 ml of 2M hydrochloric acid. These solutions were then analyzed for major and trace elements by ICP.

3.4.5 Results and Discussion

Table 3-11 shows the sample localities and the description of the mineral rocks present in this study area. It is obvious from the Table that species Rumex (R) is more widespread than Minuartia (M). In fact Minuartia was found in only five of the fourteen sites.

Elemental concentrations in the soil and plant species are presented in Appendix III and IV respectively.

(a) Elements in the Soil

Correlation analysis between ten selected elements in the soils overlying the Serbomacedonian massif is presented in Table 3-12.

It will be noted that gold gave a highly significant positive correlation ($P<0.01$) with arsenic in soil and this is illustrated in Figure 3-6. High arsenic in the soil reflects high gold in the substrate suggesting the substrate to be perhaps arsenopyrite. Gold also correlated well with both manganese ($P<0.01$) and nickel ($P<0.05$).

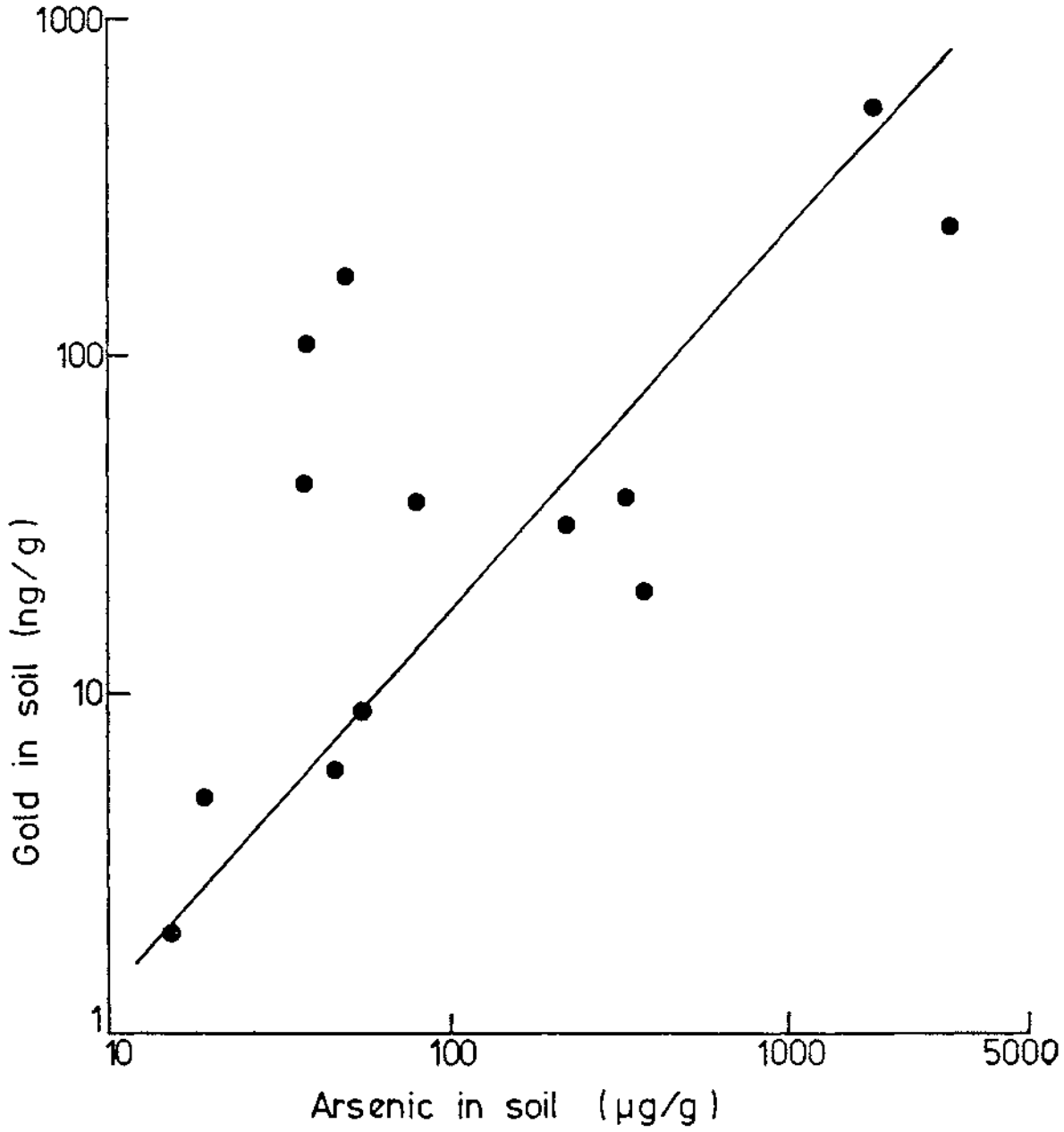

Figure 3-6 Relationship between gold and arsenic levels in soils from Northern Greece

Table 3-12 Matrix of correlation for elemental concentrations in the soil

	As	Au	Cd	Co	Cu	Fe	Mn	Ni	Pb
Au	S^X								
Cd	-	-							
Co	-	-	S						
Cu	-	-	-	-					
Fe	-	-	-	-	S				
Mn	S^X	S^X	-	S^X	-	-			
Ni	S	S	S^X	S	-	-	S^{XX}		
Pb	-	-	S^{XX}	-	-	-	S^X	S^X	
Zn	-	-	S^X	S^{XX}	-	S^X	S	S	S^{XX}

S^{XX} = $P<0.001$ (very highly significant)
S^X = $0.01>P\geq0.001$ (highly significant)
S = $0.05>P\geq0.01$ (significant)
- = $P>0.05$ (not significant)

Other positive significant relationships were arsenic correlating with both manganese ($P<0.01$) and nickel (0.05) in manner similar to gold. This could perhaps mean that both manganese and nickel are present as gangue minerals in arsenopyrite.

Some highly significant correlations between the major base metals were Fe-Zn, Zn-Pb, Mn-Ni, Mn-Pb, and Fe-Cu. These relationships were somewhat expected because of the mineral occurrences in this area. The trace elements like Cd, Co and nickel all correlated well with zinc and lead suggesting that they are present in the massif in the form of impurities in zinc and lead minerals.

(b) Elements in the Plant

Intra-plant correlation analysis for gold and arsenic with other elements is presented in Table 3-13.

Table 3-13 Matrix of correlation for gold and arsenic with other selected elements

Plants	Au	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
As	S^X	S^X	-	-	S^X	-	-	-	-
Au		S	-	-	S^X	-	-	S^{XX}	-

S^{XX} = P<0.001 (very highly significant)

S^X = 0.01>P>0.001 (highly significant)

S = 0.05>P>0.01 (significant)

\- = P>0.05 (not significant)

Correlation analysis of the data showed that gold in plants was related to the level of As, Cd, Fe and Pb.

Clearly the arsenic and iron correlation with gold suggests probable association of gold with arsenopyrite.

(c) Plant-Soil Relationship

The gold content of soil and plant samples are summarized in Table 3-14.

Table 3-14 Gold concentration (ng/g) in soil and plant samples of Rumex(R) and Minuartia (M)

Location	Species	Gold soil (ng/g)	Gold plant (ng/g)
DO-IR	R	9.0	1.5
MG-IR	R	5.0	2.0
MG-2R	R	6.0	1.0
MG-3R	R	107.0	4.0
MG-3AM	M	107.0	3.0
AS-IR	R	32.0	4.5
AS-IAM	M	32.0	11.0
XA-IR	R	564.0	6.5
XA-IAM	M	564.0	14.0
Ta-IR	R	38.0	4.0
F6-IR	R	20.0	9.0
F6-IAM	M	20.0	4.0
TX-IR	R	37.0	4.0
TZ-IAM	M	37.0	2.5
OL-IR	R	249.0	29.0
AK-IR	R	42.0	8.5
AK-2R	R	178.0	10.0
ST-1R	R	2.0	2.0

Values of gold in soil show strong anomalies at sites XA-1, OL-1, MG-3 and AK-2. These high values are also reflected in the plant samples except in MG-3. Sites DO-1, MG-2 and ST-1 had very low gold values in soil and in the plant species as well.

A correlation analysis between gold in soil and gold in both species of plants showed a significant positive relationship ($P<0.05$) as illustrated in Figure 3-7. Although both Rumex and Minuartia are basically shallow-rooted plants, they can reflect anomalous gold when corresponding gold values in the soil are high.

The correlation analysis for soil-plant data is presented in Table 3-15.

Table 3-15 Matrix of correlation for selected elemental concentrations in soils and plant material from the Serbomacedonian massif, Northern Greece

Plant	Soils									
	As	Au	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Au	S^{XX}	S	-	S^{XX}	-	-	S^{X}	S	-	-
As	S^{XX}	S	-	S^{XX}	-	-	S^{X}	S	-	-
Cd	-	-	-	-	-	-	-	S	-	-
Co	-	-	-	-	-	-	-	S	-	-
Cu	-	-	-	-	S^{XX}	-	-	-	-	-
Fe	S	S^{X}	-	-	-	-	-	-	-	-
Mn	S^{XX}	S^{XX}	-	-	-	-	S	S^{X}	-	-
Ni	-	-	-	-	-	-	-	S^{XX}	-	-
Pb	-	-	-	-	-	-	-	S	S^{XX}	-
Zn	-	-	-	-	-	-	-	S^{XX}	-	S^{XX}

S^{XX} = $P<0.001$ (very highly significant)

S^{X} = $0.01>P\geq0.001$ (highly significant)

S = $0.05>P\geq0.01$ (significant)

\- = $P>0.05$ (not significant)

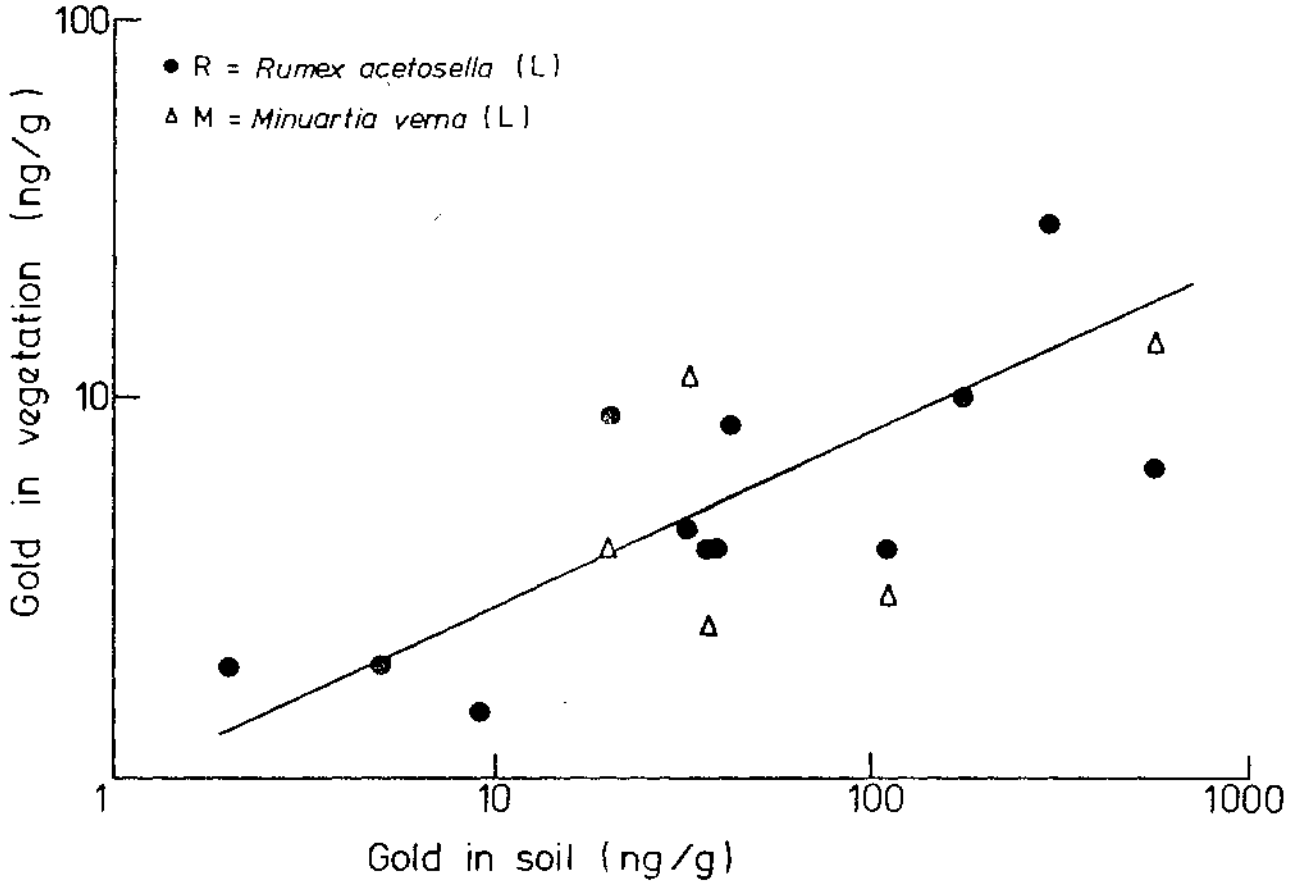

Figure 3-7 Relationship between plant and soil gold levels in Rumex (R) Minuartia (M)

Gold in soil was also related significantly to arsenic, iron and manganese. Other than gold in plant any one of these elements could be used for biogeochemical prospecting for gold in this area. Once again the association of gold with arsenic and iron suggests arsenopyrite is most likely to be the host mineral for gold.

The gold content of Rumex and Minuartia is not only associated significantly with gold in soil but also with other elements like arsenic, cobalt, manganese and nickel. This again shows the possibility of both manganese and nickel being present as gangue minerals in arsenopyrite.

With regard to the other elements, copper, nickel, lead, zinc and arsenic are the only elements which showed highly significant ($P<0.001$) relationship between the levels in plants and in the soils.

3.4.6 General Conclusion

The main conclusion emerging from this investigation is that arsenic is a good pathfinder element for gold particularly when the substrate is arsenopyrite.

The elements gold, arsenic, manganese and iron content of Rumex and Minuartia can all be used for biogeochemical prospecting for gold in the Serbomacedonian massif. The plants, Rumex and Minuartia not only appear to tolerate and reflect base metal levels in soil but also arsenic and gold.

3.4.7 Acknowledgement

I am grateful to Kelepertsis et al. (1985) for permission to use their ICP data.

3.5 Case Study IV

Biogeochemical Prospecting for Gold in Arctic Canada.

3.5.1 Introduction

Canada is a major producer of gold. Its annual output ranks just behind South Africa and the United States.

Gold and other minerals are found mainly in the rocks of the Canadian Shield (Fig. 3-8). These Precambrian rocks occupy about 4,500,000 square kilometres and include granites, gneisses, schists, quartzites and many other crystalline rocks. The rocks contain many useful ores which yield gold, silver, platinum, copper, nickel, cobalt, iron, lead and zinc.

Because the rocks are very old, they have become worn down and invaded by the sea. The lowest part of the Canadian Shield now forms Hudson Bay.

Canada was completely glaciated 10,000 years ago during the Ice ages and as a result, the soils are juvenile and composed mainly of glacial till.

In the areas of Northern Canada north of the tree line (approximately $60^{o}N$) the soils of the tundra are underlain by permafrost so that they are waterlogged and often do not reflect bedrock because they have been transported by glacial activities.

Gold is found throughout Canada and the main areas are:

(i) The Timmins and Kirkland Lakes areas of Ontario
(ii) Noranda and Vald'Or in Quebec
(iii) The Yukon
(iv) British Columbia
(v) North West Territories

Gold was first discovered in Northwest Territories at Yellowknife at the Western edge of the Canadian Shield and has been mined there since 1937. The northeast section of the Shield has been virtually unexplored.

Recently gold was discovered in the eastern part of the Territories by Ken Reading who was working for Aberford Resources Ltd,

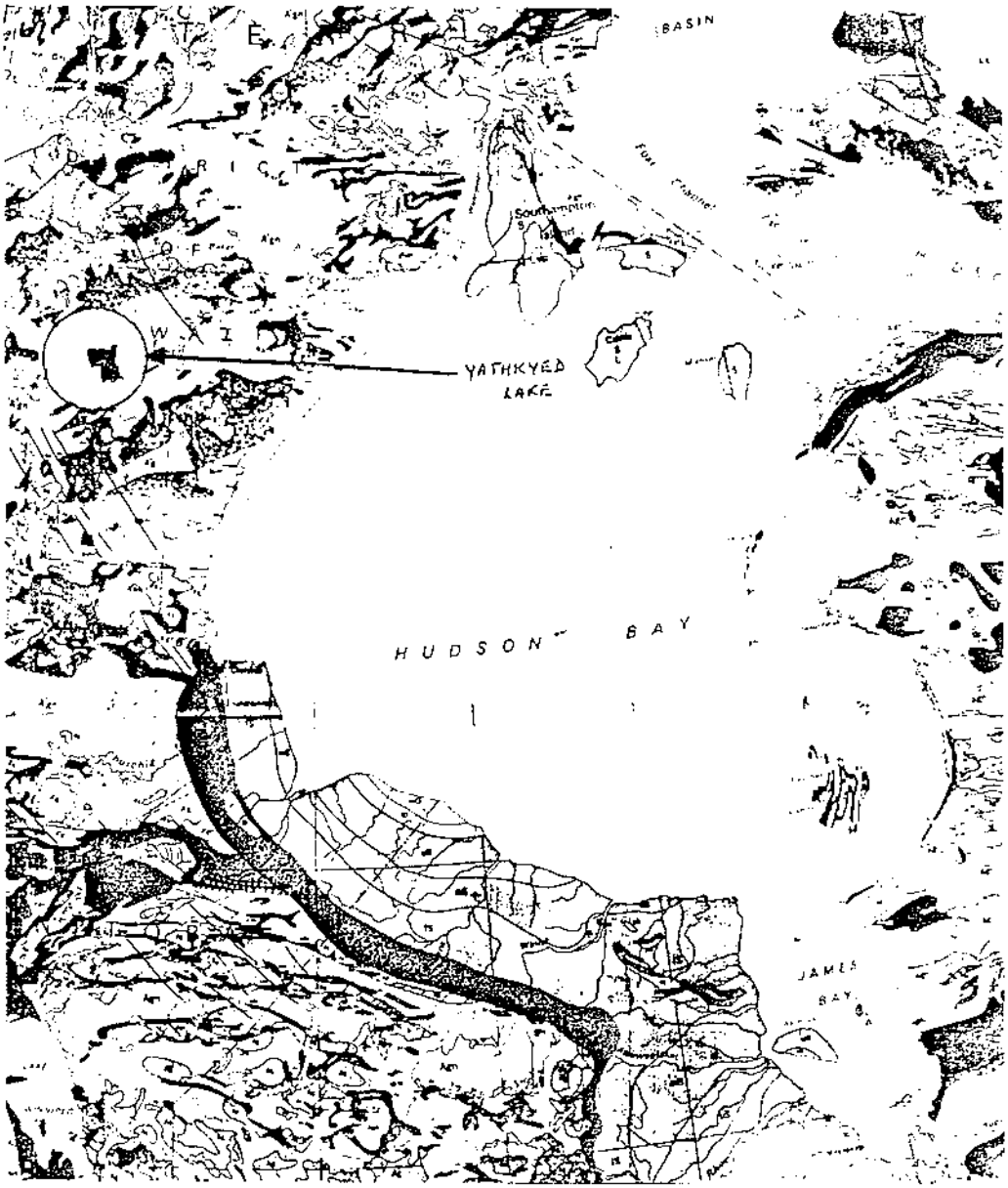

Figure 3-8 Map of Arctic Canada showing the sample location site, near Yathkyed Lake

an exploration company based in Calgary, Alberta. The gold was found in frost boils situated northwest of Yathkyed Lake some 250 metres inland from the northwestern shore of Hudson Bay. Frost boils are areas where the bedrock is sometimes exposed due to frost action (frost heave).

Samples of till and vegetation were collected by Ken Reading during the 1984 season and were analyzed at Massey University as part of this research programme.

Biogeochemical prospecting for gold has not been done in the tundra to any extent in the past and certainly not in the eastern part of the Canadian Shield. Biogeochemical prospecting has an obvious advantage in this part of the world since the till is very difficult to sample beneath the thick layer of organic material which covers it and moreover has often been transported from a long distance.

The results of the biogeochemical project are presented in section 3.5.3.

3.5.2 Materials and Methods

Samples of Arctic plants and till from near Yathkyed Lake were oven dried at 105°C overnight and the till was ground and sieved to -80 mesh size. The plant material was ground in a hammer mill to -40 mesh size.

The plant species sampled were:

A = Salix lanata
B = Betula glandulosa
C = Empetrum nigrum
D = Arctostaphylos alpina
E = Vaccinium uliginosum
F = Ledum decumbens

These plant species are shown in Figure 3-9. The sites from where the till and plant materials were collected are shown in Figure 3-10. These were spaced at intervals averaging 1 m. At each site, vegetation (aerial part) and till were sampled.

Samples of plant material (0.5g) were digested with 5 ml of fuming nitric acid until decomposition was complete. Then 10 ml of concentrated hydrochloric acid was added and the solutions were evaporated to 3 ml on water bath. The solutions were transferred to

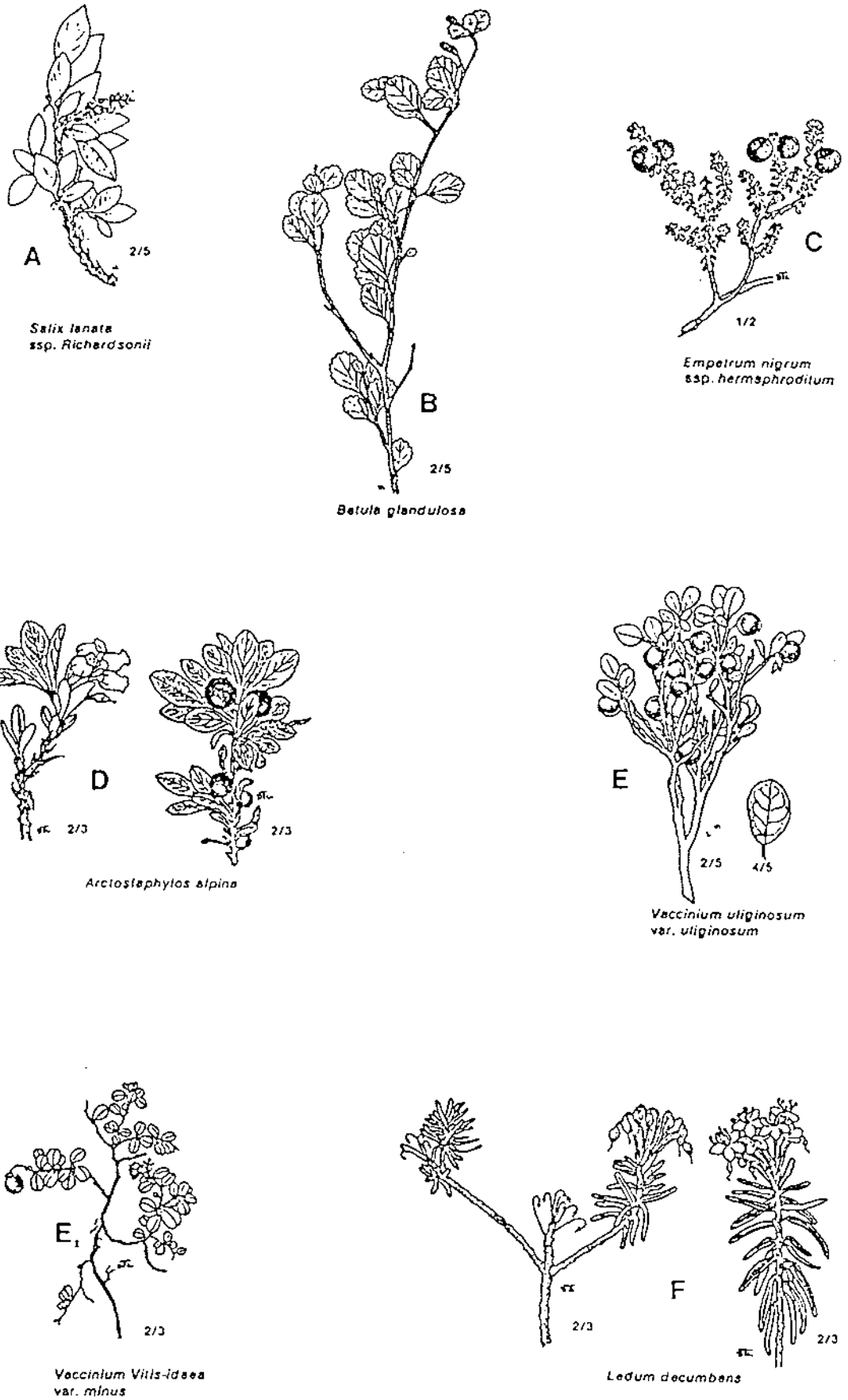

Figure 3-9 Drawings of the 6 plant species sampled near Yathkyed Lake

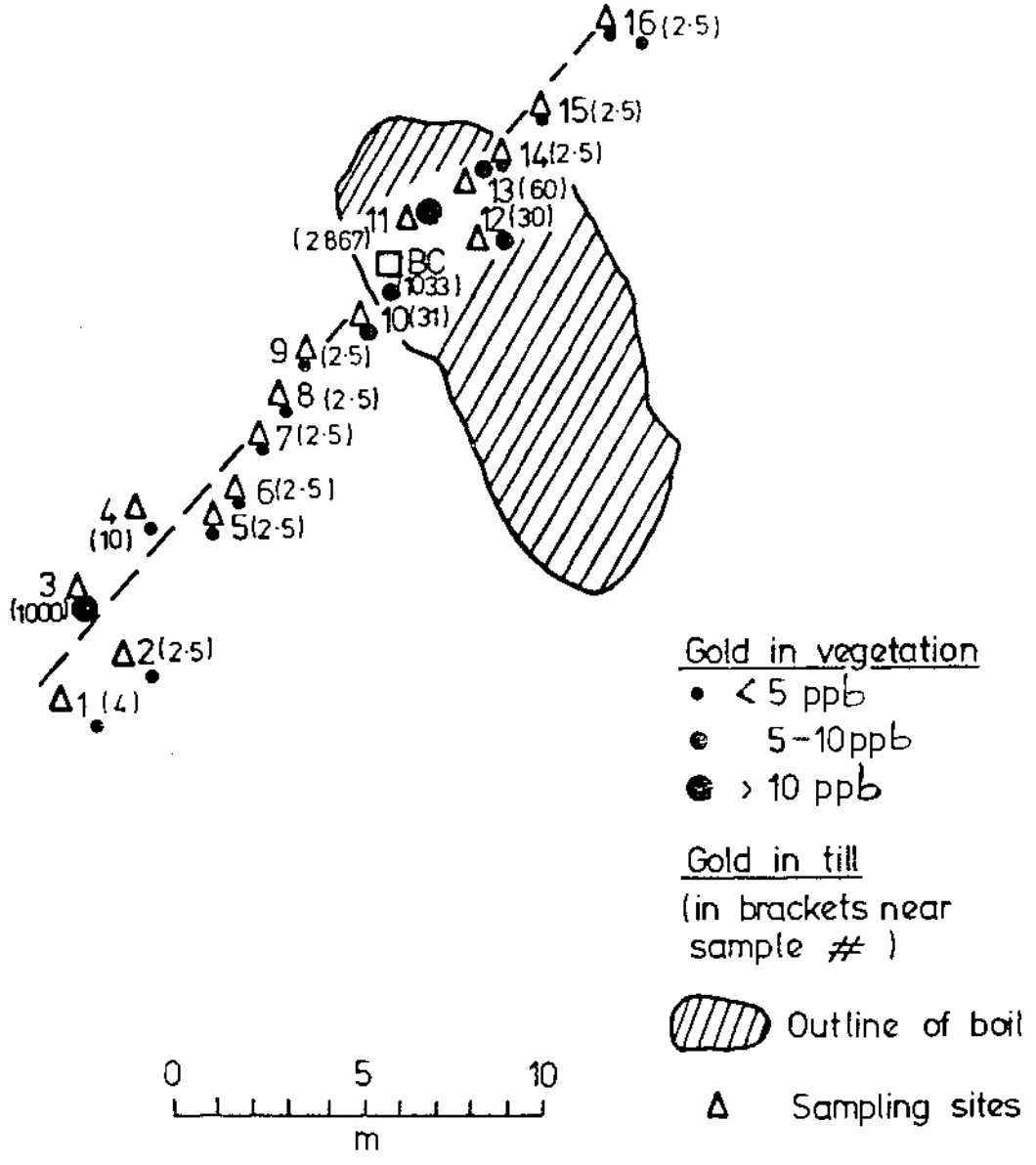

Figure 3-10 Map of the auriferous boil showing sample location sites along the transect near Yathkyed Lake

centrifuge tubes and the volumes were adjusted to 15 ml with distilled water to give an acid concentration of almost 2M hydrochloric acid. Five ml was kept for plasma emission analysis (ICP) and the remaining 10 ml solutions were shaken with 1 ml of methylisobutyl ketone (MIBK). After centrifuging, most of the lower aqueous phase was removed with a pipette and diluted with distilled water to give an acid concentration of about 0.5M. Equilibrium was again achieved by shaking during which the iron was back-extracted into the aqueous layer. The MIBK layer was analyzed for gold by flameless atomic absorption spectrometry. Samples of soil (0.5g) were evaporated with five mls of fuming nitric acid and then 10 ml portions of aqua regia were added and evaporated until only white siliceous material remained. After the decomposition stage, the procedure was the same as for plant analysis.

The remaining separate acidic solutions (5 ml) were analyzed by ICP for the elements Al, As, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr and Zn.

3.5.3 Results and Discussion

(a) Elements in Till

The elemental levels in the till samples are shown in Table 3-16.

The valuesfor gold show very strong anomalies at sites 3 and at sites 10-13 forming part of an anomaly discovered in a previous survey. Visual inspection of this Table shows an obvious association between gold and a number of elements such as As, B, Fe, and S. These and other associations were determined statistically by correlation analysis using logarithmically-transformed data because the original data were lognormally distributed.

The gold-arsenic relationship ($P<0.001$) is shown in Figure 3-11. There is clearly a good relationship at the sites anomalous with respect to gold.

A matrix of correlation is shown in Table 3-17. They show strong correlations between gold and the following elements: As, Cu, Fe, Na and S.

Table 3-16 Elemental levels in till samples (µg/g except where otherwise stated)

Site No.	Al	As	B	Ca	Cr	Cu	Fe (%)	K	Mn	Na	Mg	Ni	P	S	Sr	Zn	Au ng/g
1	3900	25	3	3500	30	12	1.26	615	140	640	2500	17	795	900	35	444	3.8
2	5450	45	4	1650	34	16	1.25	985	90	605	2750	17	385	1100	19	385	2.5
3	2200	4650	30	1900	15	65	11.13	950	130	2695	950	38	720	11150	25	415	1000
4	4900	155	3	2100	32	16	2.45	660	85	565	2750	16	655	1300	22	365	10
5	8200	35	3	2200	41	23	1.66	1295	130	675	3850	25	545	1200	26	415	2.5
6	4350	30	3	1000	25	12	1.09	595	50	625	1450	16	400	1250	13	365	2.5
7	9750	475	53	4125	34	70	3.18	1163	88	1013	2500	31	925	2500	35	425	2.5
8	6850	60	3	1500	35	25	1.82	830	85	630	2700	19	360	1200	17	370	2.5
9	3700	85	3	1000	31	24	1.46	545	55	655	1850	13	310	1200	13	380	2.5
10	3500	1288	8	1125	26	23	4.51	613	88	613	2250	11	513	3625	13	350	31
11	4125	3250	19	1375	28	30	4.99	1688	88	1013	2500	15	613	4375	29	388	2867
12	5625	338	15	2000	36	25	2.85	1200	138	863	3500	21	575	1500	23	400	30
13	4625	1175	24	1500	33	24	3.44	1100	100	838	2875	19	600	2625	19	388	60
14	3550	15	180	3200	28	21	1.10	665	185	855	2450	17	770	950	43	465	2.5
15	3750	5	3	2850	29	11	1.05	730	130	585	2650	16	775	850	34	400	2.5
16	10350	20	3	5150	50	21	2.08	2050	360	685	6350	29	650	1050	47	435	2.5
B.C.	5325	2100	45	1425	45	50	6.76	2123	98	1838	2700	195	728	5850	30	503	1033

B.C. = Boil centre

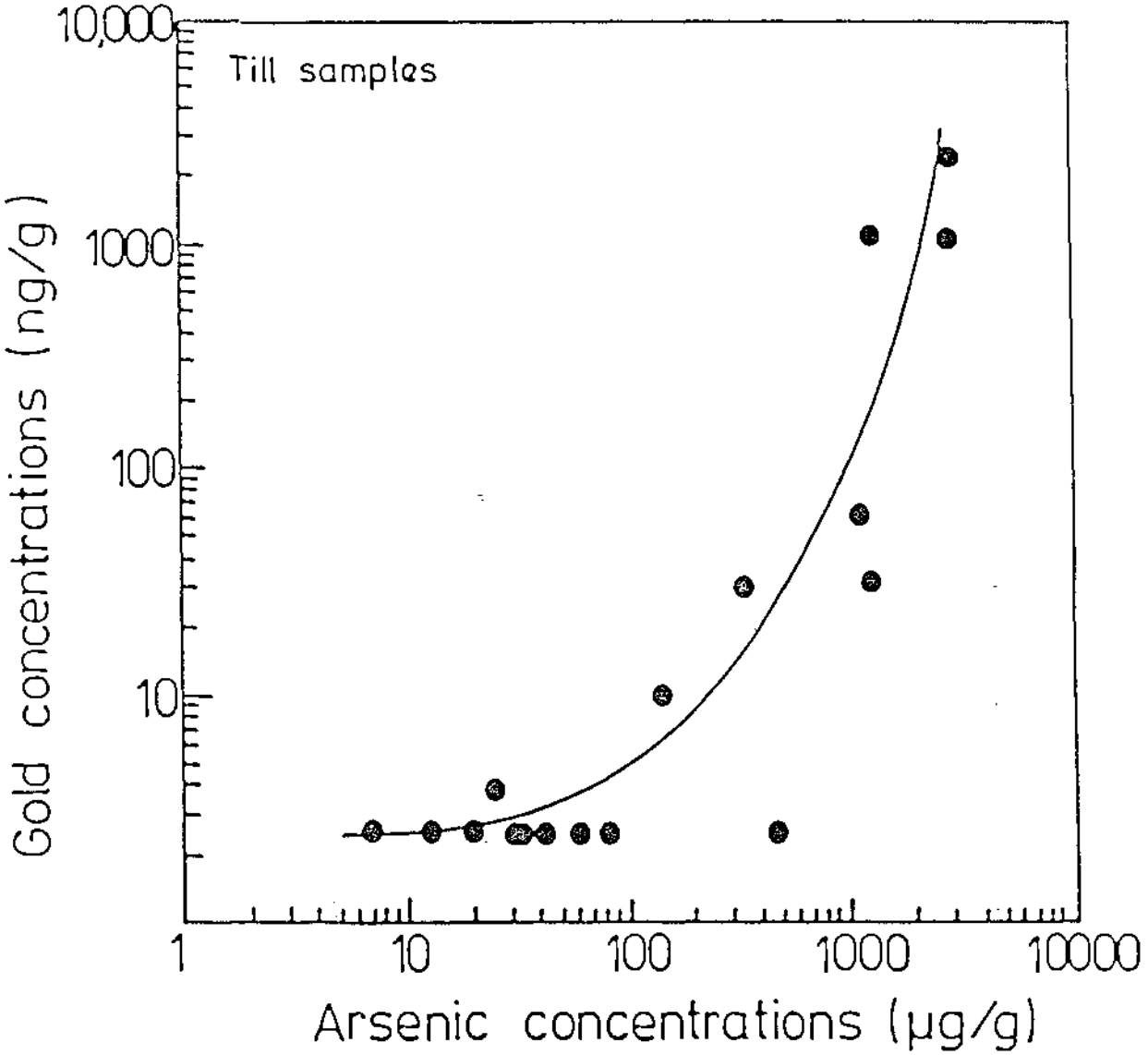

Figure3-11 Relationship between gold and arsenic levels in till samples from Arctic Canada

Table 3-17 Elemental correlation coefficient in till samples

	Al	As	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Sr	Zn
As	-															
B	-	S														
Ca	-	-	-													
Cr	S^{XX}	-	-													
Cu	-	S^{XX}	S^{X}	-												
Fe	-	S^{XX}	-	-	-	S^{XX}										
K	S	-	-	-	S	S	S	-								
Mg	S^{XX}	-	-	S	S^{XX}	-	-	S								
Mn	-	-	-	S^{XX}	-	-	-	-	S							
Na	-	S^{X}	S^{X}	-	-	S^{XX}	S^{XX}	-	-	-						
Ni	-	-	-	-	-	S	S	S^{X}	-	-	S^{X}					
P	-	-	S	S^{X}	-	-	-	-	-	S	-	-				
S	-	S^{XX}	S	-	-	S^{XX}	S^{XX}	-	-	-	S^{XX}	-	-			
Sr	-	-	-	S^{XX}	-	-	-	S	-	S^{XX}	-	-	S^{XX}	-		
Zn	-	-	S	S	-	-	-	S	-	S	S	S^{XX}	S^{X}	-	S^{XX}	
Au	-	S^{XX}	-	-	-	S	S^{XX}	-	-	-	S^{XX}	-	-	S^{XX}	-	-

S^{XX} = P<0.001 (very highly significant)
S^{X} = 0.01>P≥0.001 (highly significant)
S = 0.05>P≥0.01 (significant)
- = P>0.05 (not significant)

The correlations with As and Fe indicate a probable association with arsenopyrite, a common host mineral for gold in the Canadian Shield. It is noteworthy that correlations also exist for other chalcophiles such as Cu and S. The correlation with Na is very difficult to explain and deserves a more thorough geochemical investigation.

(b) Elements in Plants

Elemental levels in plant material are shown in Table 3-18. The code for the samples is as follows: The numeral is the site number and letters refer to the plant species.

Table 3-18 Elemental levels in plants from Yathkyed Lake (µg/g except for gold which is ng/g = ppb)

Site	Species	Al	As	Au	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Sr	Zn
1	A	146	8	0.5	11	8460	7	5	378	8640	2220	450	420	9	2400	2190	94	309
	B	153	9	0.5	12	3090	9	9	552	5280	1530	390	450	10	2460	1290	30	384
	C	224	13	0.5	13	5490	22	6	924	4230	1770	540	420	11	1140	1590	23	222
	D	315	7	0.5	11	9082	8	6	680	8094	1672	228	494	5	2356	1254	61	334
	E	326	5	0.5	17	6450	10	7	505	5750	1550	1350	650	9	2000	2150	26	400
	F	214	11	1.0	15	4590	7	4	579	4920	1200	1110	360	5	1050	1140	16	210
2	C	339	18	0.5	21	5400	8	5	1020	3330	1410	690	360	8	750	1230	16	198
	E	275	6	0.5	21	5940	14	13	570	5400	1260	1200	480	11	1020	1860	17	276
3	E	430	136	33.0	19	6480	10	7	6540	3720	1620	540	480	7	720	1800	13	246
4	A	214	8	1.0	27	10440	7	6	534	10320	1080	600	480	10	2040	2580	47	348
	B	154	9	1.5	16	4260	5	6	576	4680	1320	480	360	5	1920	1080	23	324
	C	413	16	1.5	21	5160	63	7	3348	4080	960	360	420	11	780	1260	13	228
	F	261	8	3.0	24	5100	7	5	936	5940	1080	1020	540	5	960	1260	10	26
5	B	674	32	0.5	21	3900	20	8	1905	6450	2100	600	1050	15	2250	2250	27	795
	D	580	27	1.0	13	6120	97	13	12108	6240	1020	120	420	14	1440	7500	16	264
6	C	369	22	1.0	19	4920	16	5	1482	4680	1320	360	420	11	840	1680	11	234
	E	436	10	1.0	17	6020	13	5	1092	1462	1290	1462	516	8	946	2064	18	318
7	F	437	20	1.8	22	5580	20	8	1644	5040	1380	1020	480	9	960	1440	13	264
8	D	397	98	0.8	18	7200	9	6	2142	4560	960	300	480	6	1020	1320	17	312
	E	453	85	1.2	25	6900	15	11	2040	4400	1400	900	800	11	1100	2600	16	450
9	F	295	62	1.0	26	6600	16	8	1230	6420	1500	480	480	14	1200	1680	16	282
10	F	822	708	32.0	19	4080	16	17	7278	6060	960	240	480	7	1080	2040	14	258
11	F	5161	182	20.0	14	3196	22	12	17340	4828	1904	340	408	7	748	1564	10	204
12	B	576	194	14.0	13	4560	17	12	4440	4710	1200	270	450	10	1650	1860	38	453
	F	864	225	99.0	15	3750	47	13	5820	5070	990	540	450	8	960	1710	15	267
13	B	263	55	3.8	12	2700	6	6	1644	6630	1590	510	420	5	2640	1410	15	333
	D	652	75	2.5	15	10000	17	11	2800	4400	2300	200	1300	12	1300	2400	32	860
	F	318	86	5.3	17	4650	8	7	1830	6210	1080	1080	450	6	1110	1470	11	258
14	A	195	11	3.0	10	6210	13	6	840	19680	1800	300	480	8	1380	4260	53	324
	B	250	74	4.5	18	3450	5	6	1650	6780	2010	1020	480	5	2820	1530	22	369
	E	416	64	3.8	22	4950	16	12	1550	4400	1600	1250	800	10	1100	2400	21	505
	F	230	23	3.8	47	4410	8	5	780	4800	1269	1290	660	5	1290	1410	13	249
15	B	287	6	3.8	15	5070	9	8	1680	4920	1980	450	510	9	1740	1410	46	537
	E	250	9	2.0	34	4770	14	11	840	3960	1080	1230	450	10	1080	1680	33	318
16	B	143	14	2.0	20	5430	5	7	420	4140	1530	360	540	5	1470	1230	55	570
	E	242	18	3.8	13	5820	19	9	1200	4350	1770	930	420	7	1110	1890	31	303

It is apparent from Table 3-18 that the gold in plant closely follows the arsenic levels. Correlation analysis of the data (Table 3-19) showed that gold in plants was related to the levels of Al, As, Cu, and Fe but inversely to Ca. Clearly the arsenic and iron content in vegetation as a pathfinder for gold was first suggested by Warren and Delavault (1964). Our work confirms the value of arsenic for this purpose. The negative correlation of gold with calcium is not unexpected as calcium uptake by plants is usually decreased by excessive uptake of heavy metals such as iron. Uptake of gold is not sufficient to cause this physiological effect, but uptake of iron certainly is. The relationship between gold and arsenic for Ledum sp. is shown in Figure 3-12.

Table 3-19 Matrix of correlations between elemental concentrations in plants

Elements	Al	As	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Sr	Zn
As	S^{XX}															
B	-	-														
Ca	-	-	-													
Cr	S^{XX}	-	-	-												
Cu	S^{XX}	S^{X}	-	-	S^{XX}											
Fe	S^{XX}	S^{XX}	-	-	S^{XX}	S^{XX}										
K	-	-	-	-	-	-	-									
Mg	-	-	-S	-	-	-	-	-								
Mn	-	-	S^{X}	-	$-S^{X}$	-	$-S^{X}$	-	-							
Na	-	-	-	-	-	-	-	-	S	-						
Ni	-	-	-	-	S^{XX}	S^{X}	-	-	-	-	S					
P	-S	-	-S	-	-S	-	-S	S^{X}	S	-	-	-				
S	-	-	-	S	S^{X}	S	-	S	-	-	-	S^{XX}	-			
Sr	$-S^{X}$	-S	$-S^{X}$	S	-	-	$-S^{X}$	S	S^{X}	-	-	-	S^{XX}	-		
Zn	-	-	-	-	-	-	-	-	S^{XX}	-	S^{XX}	-	S^{XX}	-	S^{XX}	
Au	S^{X}	S^{XX}	-	-S	-	S^{X}	S^{XX}	-	-	-	-	-	-	-	-	-

S^{XX} = P<0.001 (very highly significant)

S^{X} = 0.01>P≥0.001 (highly significant)

S = 0.05>P≥0.01 (significant)

\- = P>0.05 (not significant)

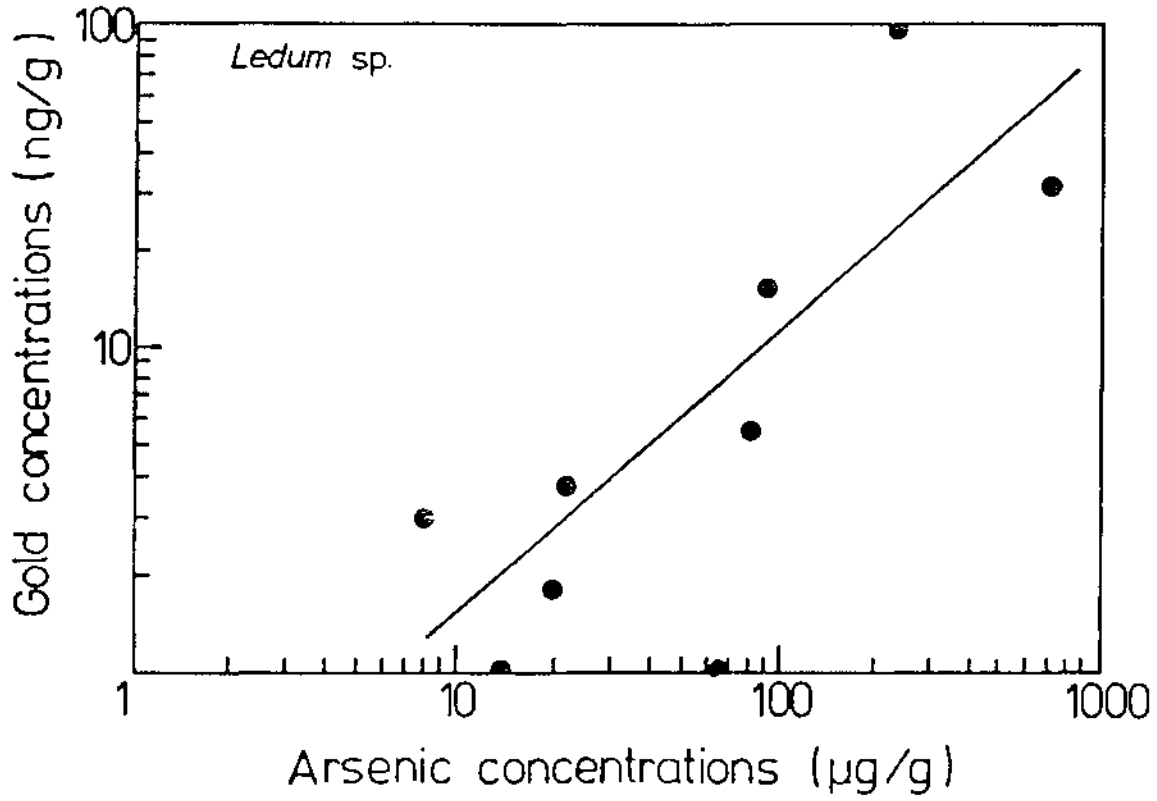

Figure 3-12 Relationship between gold and arsenic levels in Ledum decumbens

It is apparent from Table 3-19 that only plant species, Ledum decumbens, was sufficiently abundant to provide enough samples for statistical analysis (9 specimens).

(c) Plant-Soil Relationships

The ultimate justification of the biogeochemical method lies in the significant plant-soil relationships. The correlation analysis of plant-soil data for Ledum decumbens is shown in Table 3-20.

Table 3-20 Matrix of correlation between elemental concentrations in plants and till samples of Ledum decumbens

	Plant																
Soil	Al	As	B	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	S	Sr	Zn	Au
Al	S	PS	-PS	-	-	S	S^X	-	-	-PS	-	-	-PS	-	-	-	-
As	S	PS	-PS	-	-	S	S^X	-	-	-PS	-	-	-PS	-	-	-	-
B	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	-	-S	-	-	-	-S	-	-S	-	S	-	-	-	-S	-	-	-
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	S	PS	-PS	-	-	S	S^X	-	-	-PS	-	-	-S	-	-	-	PS
K	S	-	-	-	-	-	S	-	-	-	-	-	-S	-	-	-	-
Mg	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-S	-	-	-	-S	-	-	-	-	-
Na	-	-	-	-	-	-	-	-S	-	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-	-	PS	-	-	-	-	-	-	-
P	-	-	-	-	-	-	-	-S	-	PS	-	-PS	-	-PS	-	-	-
S	S	PS	-	-	-	S	S^X	-	-	-PS	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	$-S^X$	-	PS	-	-	-	-PS	-	-	-
Zn	-	-	-	-	-	-	-	-S	-	S	-	-	-	-	-	-	-
Au	S^X	-	-PS	-S	-	-	S^X	-	-	-	-	-	-S	-	-PS	-	PS

S^{XX} = P<0.001 (very highly significant)

S^X = 0.01>P≥0.001 (highly significant)

S = 0.05>P≥0.01 (significant)

PS = 0.10>P≥0.05 (possibly significant)

\- = P>0.10 (not significant)

Gold in plants was related to iron and gold in till. These relationships were only possibly significant probably because the number of samples was low. If more samples had been used the relationship would have been more significant.

Inverse soil-plant relationships for gold in soil with boron, calcium, phosphorus and strontium are probably because of the restricted uptake of these elements (particularly calcium) by the Ledum sp. due to the antagonistic effect of excessive iron and gold uptake. The excessive iron uptake is further indicated by the significant iron in plant correlation with iron in the till ($P<0.01$).

The relationship between gold in soil and gold in all species of plant is shown in Figure 3-13. Although this relationship is only possibly significant ($0.05>P\geq0.10$) for Ledum species, it is strongly significant ($P<0.01$) when all species of plants from 18 statistically significant data points are considered together.

The results of this plant-till gold correlation analysis suggest that any of the six plant species analyzed could be used for biogeochemical exploration for gold in this area provided they are sufficiently abundant. Possible pathfinder element for gold could be iron.

3.5.4 Conclusions

It is concluded that the work has demonstrated the efficiency of biogeochemical prospecting for gold in the Arctic tundra of Canada. If larger-scale tests confirm these findings, a useful and potentially very rapid technique of exploration for gold will have been developed. Vegetation sampling is potentially 5 or 6 times faster than till sampling and could be of economic benefit for mineral exploration programme in this part of the world, particularly if the ground is frozen when the speed advantage is even greater.

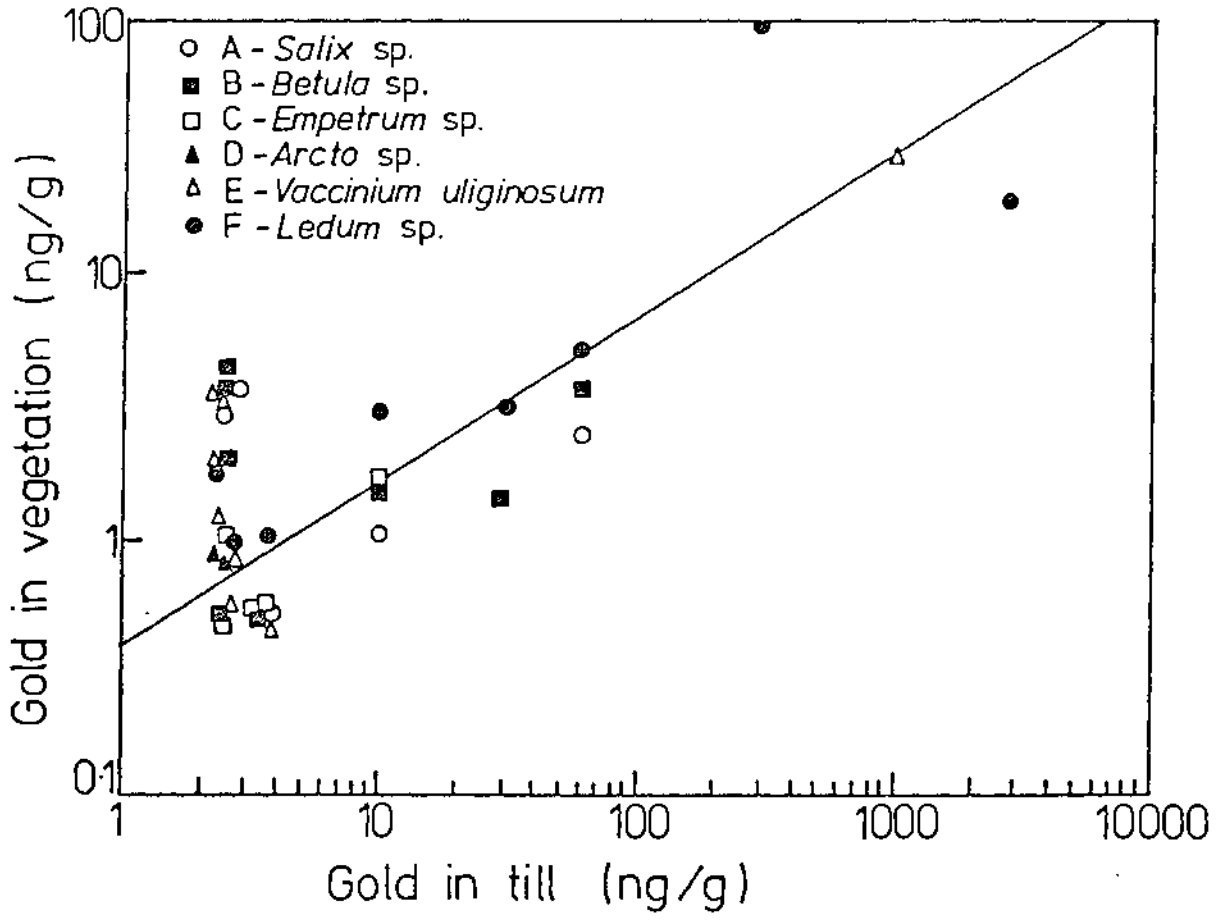

Figure 3-13 Relationship between plant and till gold levels in all species of plants from Arctic Canada

SUMMARY AND GENERAL CONCLUSIONS

SUMMARY AND GENERAL CONCLUSIONS

The analytical section of this thesis showed that by careful selection of the instrumental parameters, low concentrations of gold in vegetation as well as in soils and rocks could be determined by the electrothermal atomization technique using an atomic absorption spectrometer equipped with a graphite furnace unit.

Gold in vegetation was dissolved by using a mixture of fuming nitric acid and aqua regia solutions, over a water bath, extracted (as the chloro-complex) into MIBK and then analyzed. This method was found to be reliable and accurate with a limit of detection of 1 ng/g.

Using this technique, gold was determined in vegetation, rocks and soil from 4 vastly different climatic, topographical and geological areas. Correlation analyses was conducted between gold concentrations in the vegetation and gold concentrations in the soils. These relationships were then used to test the efficiency of biogeochemical methods of prospecting for gold.

The study revealed a strong correlation between gold concentrations in vegetation and gold in soil thus demonstrating the usefulness of vegetation as an exploration aid for gold. This study also confirmed the use of arsenic as a pathfinder for gold particularly when the latter is present with chalcophile elements.

By using the biogeochemical data from the Yathkyed Lake in Canada (case study IV), a gold anomaly was discovered at site number 3, an area where mineralization was not suspected because of the rugged topography. This finding was subsequently confirmed by the geologists using geophysical methods. This clearly demonstrates the importance of biogeochemical method of prospecting particularly on areas susceptible to landslides, glacial drifts and on steep slopes where soil geochemistry is ineffective.

The main findings of this work were as follows:

(i) The development of a method for analysis of gold in vegetation which is not only reliable, accurate and sensitive but also cheap and rapid.

(ii) The demonstration:

(a) that concentration of gold in vegetation is closely related to the gold levels in the soil

(b) of the usefulness of arsenic as a pathfinder element for gold particularly when the latter is present with chalcophile elements

(c) that gold uptake by plants is not restricted to anyone particular plant species over auriferous soils

(d) that depth of plant rooting system is not particularly important for gold uptake by plants growing over arsenopyrite substrates.

Further work in areas of gold mineralization should be carried out with the following aims:

(i) To substantiate further the validity of using arsenic as a pathfinder for gold in different types of substrate.

(ii) To test the reliability of deep rooted and shallow rooted plants for biogeochemical exploration in different types of substrate.

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APPENDICES

Appendix I Elemental concentrations (µg/g unless otherwise stated) in the soil samples from Seruwila

Location	Al	As	B	Ca (%)	Co	Cr	Cu	Fe (%)	K (%)	Mg	Mn	Mo	Na (%)	Ni	P	S	Sr	Zn	Au (ng/g)
-60	10.82	112	2775	1.17	51	58	196	3.61	1.82	1512	1067	8	3.52	34	393	1808	545	211	4.5
-50	9.3	98	2481	1.29	32	29	92	2.42	1.40	1167	477	3	3.88	44	316	1662	653	145	1.5
-40	8.29	93	2363	1.21	26	26	80	2.18	1.97	823	305	3	4.11	17	228	1842	612	118	1.0
-30	10.42	25	4349	1.32	32	59	198	2.93	2.72	1250	407	7	4.08	31	578	1925	646	53	3.0
-20	10.19	106	2877	1.37	39	58	336	3.35	2.31	1475	528	7	4.18	38	432	1840	596	172	8.5
-10	8.25	120	2935	1.43	60	90	665	5.99	2.09	1935	746	16	3.86	64	1390	1975	537	179	7.5
0	7.55	155	3526	1.68	104	76	2069	13.61	2.36	2010	861	13	3.45	130	5050	1917	714	226	9.5
+10	7.65	156	3726	2.10	172	75	3960	14.32	1.28	3621	1040	11	3.18	200	5880	2036	764	271	21.0
+20	8.84	25	5769	2.29	87	71	1810	9.39	1.62	3971	708	10	4.68	120	4375	2128	679	125	14.5
+30	9.35	152	3687	1.66	93	50	1165	7.69	1.76	2637	871	8	4.67	97	1749	2067	552	223	6.0
+40	10.00	149	3363	1.73	62	50	818	5.65	1.84	2230	619	7	5.24	86	851	2317	631	192	9.5
+50	6.84	107	2594	1.45	40	33	306	3.92	1.40	1290	405	6	4.34	45	482	1848	502	165	3.5
+60	7.52	124	2524	1.50	41	35	335	3.97	1.50	1369	390	7	4.55	48	432	1801	550	161	2.0
+70	8.48	85	2434	1.42	33	30	250	2.98	1.43	1080	373	3	4.41	35	226	1850	556	125	2.5
+80	7.19	91	2155	1.25	33	28	153	2.91	1.31	950	446	3	3.95	29	243	1805	490	107	1.5
+90	7.61	101	2308	1.38	29	28	156	2.27	1.42	1171	368	3	4.25	34	318	2066	515	143	8.5
+100	5.50	101	2443	1.50	20	28	104	1.72	1.95	1382	236	4	5.20	25	311	1832	657	112	2.5
+110	3.12	25	3073	1.36	19	31	80	1.67	0.98	1402	213	5	3.98	18	923	1487	488	36	1.0

Appendix II Elemental concentrations (µg/g unless otherwise stated in Glycosmis mauritiana from Seruwila

Location	Al	B	Co	Cr	Cu	Fe	K (%)	Mg (%)	Mn	Ni	P	S	Sr	Zn	Au (ng/g)
-60	51	41	1	1	4	73	1.45	0.25	21	1	1422	1056	6	122	4.5
-50	55	34	1	1	4	73	1.54	0.18	19	1	1470	961	15	120	2.0
-40	75	35	1	1	4	119	1.53	0.21	37	1	1356	896	15	104	2.0
-30	52	28	1	1	4	72	1.60	0.26	26	1	1549	1121	26	131	2.5
-20	46	42	1	1	5	67	1.45	0.24	20	1	1386	980	24	81	1.0
-10	55	42	1	1	7	66	1.23	0.27	33	2	1183	1024	63	126	1.8
0	37	28	1	1	7	48	1.68	0.18	22	4	1589	388	68	95	2.0
+10	31	29	1	1	3	43	1.50	0.16	16	5	1594	517	55	95	3.3
+20	38	39	1	1	4	54	1.44	0.27	18	4	1213	1250	87	128	4.3
+30	54	32	1	1	5	88	1.69	0.27	22	3	1697	1063	118	135	9.0
+40	59	41	1	1	5	103	1.94	0.28	21	9	1650	1598	182	180	2.5
+50	142	46	1	1	10	165	0.77	0.32	109	5	789	791	102	98	2.3
+60	52	44	1	1	3	118	1.15	0.25	22	4	1035	1039	121	108	19.5
+70	70	30	1	1	4	168	1.52	0.23	20	10	1149	978	128	105	3.0
+80	65	54	1	1	4	113	1.38	0.40	66	9	821	1385	170	130	4.5
+90	93	39	1	1	5	136	1.34	0.33	54	10	1123	1287	199	141	0.5
+100	128	44	12	1	9	168	1.53	0.60	231	6	1490	452	215	138	3.5
+110	82	39	1	1	5	186	1.29	0.32	76	3	1383	1326	249	142	5.0

Appendix III Elemental concentrations (µg/g) in the soil samples from Northern Greece

Sample	Au	As	Mn	Cd	Cu	Co	Zn	Pb	Fe(%)	Ni
DO-1	0.009	55	318	10	63	7	40	47	2.26	105
MG-1	0.005	19	1000	8	32	22	124	70	4.77	129
MG-2	0.006	46	245	8	79	11	70	299	3.76	194
MG-3	0.107	38	391	10	683	10	55	313	2.57	150
AS-1	0.032	220	294	7	1160	17	65	25	3.00	131
XA-1	0.564	1730	10600	<5	48	16	877	776	2.79	358
Ta-1	0.038	332	6920	97	258	55	10400	6350	6.69	386
F6-1	0.020	370	386	9	1350	21	72	49	3.28	148
TZ-1	0.037	80	536	11	1180	16	57	35	6.34	134
OL-1	0.249	2900	9820	40	98	110	4770	932	4.72	324
AK-1	0.042	37	5380	11	2660	40	9190	1320	15.20	177
Ak-2	0.178	50	318	9	3050	15	843	658	5.80	141
ST-1	0.002	<15	226	9	21	10	45	21	1.29	201

Appendix IV Elemental concentrations (µg/g except for gold which is ng/g) in plant species *Rumex* (R) and *Minuartia* (M) from Northern Greece

Sample sites	Species	Au (ng/g)	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
DO-1	R	1.5	<5	<0.7	2.5	0.5	11	157	699	0.4	2	<2	31
MG-1	R	2.0	<5	<0.8	<0.9	0.6	3	56	443	1.4	4.5	<2	36
MG-2	R	1.0	<5	<0.7	1.9	0.6	12	290	256	1.1	3.8	4	34
MG-3	R	4.0	<5	<0.7	<0.7	0.5	18	92	86	0.3	5.2	<2	55
MG-3AM	M	3.0	<7	1.6	1.0	1.6	41	448	108	1.0	4.3	10	63
AS-1	R	4.5	<5	<0.7	4.1	0.7	13	153	172	1.1	5.0	3	42
AS-1AM	M	11.0	<5	1.2	1.1	1.4	36	694	120	0.9	6.6	6	66
XA-1	R	6.5	24	<0.7	0.8	2.2	7	878	1770	2.2	6.3	23	128
XA-1AM	M	14.0	102	1.1	1.4	5.9	14	2070	4070	3.1	21.0	42	523
Ta-1	R	4.0	<5	2.4	<0.7	2.2	9	243	116	0.7	27.4	16	1390
F6-1	R	9.0	<5	<0.8	<0.8	<0.5	26	202	103	0.6	2.2	<2	47
F6-1AM	M	4.0	21	0.7	<0.7	2.0	60	1770	270	<0.3	4.1	<2	54
TZ-1	R	4.0	<5	<0.7	1.1	0.8	18	121	181	1.3	4.7	<2	51
TZ-1AM	M	2.5	<5	1.9	<0.7	0.8	52	536	140	<0.3	2.8	3	42
OL-1	R	29.0	196	2.8	<0.8	2.4	13	1580	604	3.8	3.3	156	546
AK-1	R	8.5	<5	0.9	<0.8	0.5	54	512	247	<0.3	1.6	16	633
AK-2	R	10.0	<5	0.7	1.3	0.9	186	2020	107	3.0	1.9	35	116
ST-1	R	2.0	<5	<0.8	1.6	<0.6	4	199	902	1.3	4.5	3	20
BA-1	R	1.0	<5	<0.7	0.9	8.2	6	860	117	1.2	14.8	7	45