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# ANALYTICAL, GEOCHEMICAL AND BIOGEOCHEMICAL STUDIES OF TUNGSTEN AND MOLYBDENUM

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philsophy at Massey University

> BERTRAM FRANCIS QUIN 1974

To Lyn

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#### ABSTRACT

Section I : Studies were carried out which significantly improved the sensitivity of the colorimetric method for the determination of tungsten in geochemical and plant samples with dithiol. Proton-induced x-ray fluorescence was also investigated to determine its suitability for the detection of nanogram quantities of tungsten. However although it showed considerable potential, the sensitivity of the method could not be developed sufficiently to compare favourably with colorimetry.

A rapid method for the determination of tungsten in ores and concentrates by atomic absorption spectrometry was developed which, through the use of an alkaline sample solution, was free of interference and instability problems.

Following a careful study of the parameters involved in the colorimetric method for the determination of molybdenum with dithiol, a simple procedure was developed which could be used for the analysis of a wide range of materials.

The use of the nitric/hvdrofluoric acid mixture for the digestion of soils and rocks was investigated. It was found that the tendency for calcium and magnesium to precipitate as their fluorides could be avoided by the addition of a small quantity of perchloric acid.

Section II : Scheelites from several localities in New Zealand were analysed for their trace element content. They were found to contain very low amounts of impurities. Their Sr/Ba ratio was found to be useful for distinguishing between lodes.

Section III : An investigation was carried out to compare the relative efficacy of geochemical and biogeochemical exploration for tungsten under a wide range of geological, vegetational, climatic and topographical conditions, It was found that, under most conditions, both soil and plant sampling could be used equally successfully to pinpoint scheelite bearing veins. In areas of high rainfall and rugged topography, soil sampling did not always reveal the presence of reefs and, in these cases, trunk-sampling of trees could provide additional information. Ιt was found that, for the purposes of biogeochemical prospecting, all tree species could be grouped together.

Following this investigation, a more intensive study was carried out at Barrytown to test the suitability of trend surface analysis of biogeochemical data for locating rich pockets of scheelite with veins, with promising results.

A brief comparison of geochemical and biogeochemical prospecting for molybdenum was carried out at Canaan, Nelson. It was found that plant sampling gave more information where the low soil pH prevented movement of molybdenum into the upper soil.

Section IV : Following the results of the biogeochemical exploration in Section IV, which showed the existence of differences in the distribution of tungsten between tree organs from Barrytown and Canaan, the affect of soil sodium and potassium was investigated and was found to be responsible for these differences.

(v)

As considerable areas containing scheelite mineralisation support pasture, an investigation was carried out to study the effects of applied tungsten on clover growth. Tungsten, applied as tungstate, was found to slightly decrease growth where fixation was the sole nitrogen source. In the presence of combined nitrogen, however, increases were recorded.

A comparison of the elemental composition of native tree species was carried out to investigate the effects of substrate composition. It was found that, whereas vegetation analysis can in general be used to indicate the presence of mineralisation within a rock type, it is not a reliable indicator of the composition of different rock types.

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GENERAL

INTRODUCTION

In respect to occurrence, metallurgy and properties, tungsten and molybdenum are remarkably similar. They both belong to Group 6b of the Periodic Table, with tungsten occurring in the third transition series and molybdenum above it in the second. Some of their physical and chemical properties are summarised in Table 0.1.

The chief uses of both metals are in the production of alloy steels ; even small amounts cause tremendous increases in hardness and strength. "High-speed" steels which are used to make cutting tools that remain hard even at red heat contain tungsten, molybdenum and chromium. Their high electrical efficiency makes them ideal for lamp filaments. Tungsten carbide is used for tipping cutting tools.

Despite their similarities however, tungsten and molybdenum show differences in various types of compounds that are difficult to explain, particularly in view of their similar ionic radii (Table 0.1). Both elements readily form stable oxy-salts known as tungstates and molybdates. Tungsten is found almost exclusively in the form of tungstates, chiefly scheelite(CaWO<sub>4</sub>) and wolframite ((Fe, Mn)WO<sub>4</sub>). However molybdenum, although found in small amounts as wulfenite (PbMoO<sub>4</sub>), occurs chiefly as molybdenite (MoS<sub>2</sub>), whereas  $WS_2$  is extremely rare. Moreover, their ores do not occur together as commonly as one might expect ; this is particularly true in New Zealand.

Another surprising difference between tungsten and molybdenum, particularly in view of their similar abundances (Table 0.1), and their similar properties in the soil, is that molybdenum is an essential Table 0.1

Physical and chemical properties of tungsten and molybdenum

Property	Tungsten	Molybdenum
Discovery	1781, Scheele	1783, Scheele
Atomic weight	183.86	95.95
Ionic radius, M <sup>6†</sup>	0.65 Å	0.62 Å
Melting point	3400 C	2600 C
Boiling point	5900 C	4800 C
Specific gravity	19.3	10.2
Valencies	2,4,5,6	2,3,4,5,6
Crustal abundance	1.5 ppm	1.5 ppm
Chief ores	scheelite, CaWO4 wolframite (Fe,Mn)WO4	molybden <b>ite</b> Mos <sub>2</sub> wolfenite, PbMoO <sub>4</sub>
Description of metal	very hard, brittle, steel grey colour	very hard, silver- white colour
Uses	alloy steels, tool steels, filaments, electric furnace wiring	alloy steels, tool steels, filaments
Solvents	nitric/hydrofluoric acid mixture, oxidising melts	hot con <b>c,</b> nitric or sulphuric acids, HF/HNO3, oxidising melts

element for plants (and animals), whereas tungsten is not. In fact, tungsten has been shown to act as a competitive inhibitor of molybdenum function in enzymes responsible for nitrogen fixation and the reduction of nitrate to nitrite (Takahashi and Nason, 1957; Hwang and Doi, 1965; Heimer <u>et al</u>, 1969).

Traditionally, tungsten and to a lesser extent molybdenum, have been amongst the more difficult elements to analyse. The two elements interfere with one another in colorimetric determinations because of their similar properties. Tungsten particularly is insensitive by emission spectrography, due to its high boiling point (Table 0.1), and both elements are relatively insensitive by atomic absorption spectrometry due to the formation of refractory oxides in the flame.

The writer's M.Sc. thesis (Quin, 1972) describes the development of a colorimetric method for the determination of tungsten in plants and soils with toluene -3, 4-dithiol (dithiol). The method, although accurate and free from molybdenum interference, lacked sufficient sensitivity for some applications, and an investigation was carried out to improve the sensitivity and, if possible, the productivity of the method. A relatively new nuclear method of analysis, proton-induced x-ray fluorescence, was also investigated to determine its potential for the detection of nanogram quantities of tungsten.

The determination of tungsten in ores and concentrates has long been a difficult task. Tungsten tends to precipitate out of the acid leach solution used in the colorimetric determination when present in large amounts ; matrix problems make 4

emission spectrographic analysis unreliable ; and although sensitivity is not a problem for tungsten rich samples, the wide range of polymeric and hetropolymeric tungsten species formed in acid solution make it impossible to obtain reliable results by atomic absorption spectrometry. An investigation was therefore carried out to see if the formation of these species could be avoided.

The colorimetric determination of molybdenum with dithiol has been in use for many years (Hamence, 1940; North, 1956; Stanton and Hardwick, 1967) and approximately 30 variants on the method have been published. This large number of procedures has arisen partly because of a tendency of individual workers to develop specialised techniques to fulfil their particular requirements, but largely because of insufficient study of the parameters involved. This thesis describes the development of a procedure which, by changing the method of sample dissolution as required, can be used for the determination of molybdenum in a wide range of materials.

Scheelite, one of the most abundant ores of tungsten, is widespread throughout the South Island of New Zealand, and the geology of the various deposits has been the subject of several articles (Finlayson, 1908; Williams, 1965; Mutch, 1969). However there is little chemical data on the ores available and, in view of the importance of impurities in controlling the value of the ore, it was considered that this aspect should be investigated. It was also hoped that chemical analysis could be used to distinguish between the various scheelite - bearing lodes of the complex Glenorchy area.

The demand for tungsten has been increasing in recent years and this has led to an accelerated search for it in many countries. Because of the deep soil cover and dense vegetation existing in many areas of New Zealand, outcrops are few, and soil and plant sampling are generally the most suitable methods for locating mineralised reefs. Following the promising results of the initial geochemical and biogeochemical exploration carried out by the writer at Barrytown (Quin, 1972; Quin and Brooks, 1972), it was decided to carry out an investigation to determine the relative efficacy of soil and plant sampling to locate scheelite mineralisation under a wide range of geological, vegetational, climatic and topographical conditions. The study areas selected were Glenorchy, Paradise, Macrae's Flat, Top Valley (Wairau Valley), Barrytown and Canaan ; their localities are shown in Fig. 0.1.

Following this investigation a more intensive study was carried out at Barrytown to test the suitability of trend surface analysis of biogeochemical data for locating rich pockets of scheelite within veins.

Considerably more geochemical and biogeochemical exploration has been carried out for molybdenum than tungsten, but previous work in New Zealand has been restricted to demonstrating the existence of geochemical and biogeochemical anomalies in the general area of mineralisation (Brooks and Lyon, 1966). Hence although molybdenum is of minor economic significance in New Zealand, it was of interest to determine whether plant or soil analysis could be used to locate buried mineralisation, and with this aim in mind a brief investigation was carried out at Canaan, Nelson.



Fig. 0.1. Map of South Island, New Zealand, showing schists of geosyncline and location of study areas.

The final section of this thesis describes three investigations which were prompted by the results of the exploration work. The results from Barrytown and Canaan showed differences in the uptake and distribution of tungsten by tree species, and pot trials were carried out with beech seedlings to determine the cause of the differences.

The second investigation was carried out to study the effects of tungsten on the growth of clover. Considerable areas of Otago, Westland and Nelson which are mineralised with scheelite have been developed into pasture, and the question arises to what extent growth is affected by the presence of tungsten, in view of literative references to the inhibitory effect of tungsten on molybdenum – dependent enzymes (Takahashi and Nason, 1957).

In the final study, the effect of substrate composition on the elemental composition of five native tree species was investigated for a wide range of major and trace elements.

In reporting elemental concentrations in plants, it was decided to adopt the generally recognised conventions of using an ash weight basis for the biogeochemical exploration, and a dry weight basis for all other work. For exploration studies, reporting of the data on an ash weight basis has the advantages that (i) it is intuitively more logical, as one is comparing the uptake of one or more metals relative to the other metals, which make up most of the ash content; (ii) metal concentrations in the ash are generally of the same order of magnitude as those in the soil, thus making comparison for exploration purposes more direct, and (iii) it has the practical advantage when dealing with large numbers of samples that the time-consuming drying to constant weight at 100 deg. C. For pot trials however, data are is not necessary. reported on a dry weight basis ; this is absolutely necessary when considering plant growth and physiology.

7

SECTION I

# DEVELOPMENT

OF

ANALYTICAL

METHODS

#### A. INTRODUCTION

The geochemical and biogeochemical studies described in this thesis were dependent on the development of suitable analytical methods for the determination of tungsten in plants, soils, rocks, ores and concentrates, the determination of molybdenum in plants, soils and rocks and the determination of a wide range of major and trace elements in plants and geochemical samples.

The analysis of tungsten in plants, soils and rocks necessitated the use of procedures that were more sensitive than atomic absorption spectrometry. Earlier work by the writer (Quin, 1972) included the development of a sensitive and accurate method for the colorimetric determination of tungsten in plants, soils and rocks with toluene -3, 4- dithiol (dithiol). This procedure was developed further to improve the limit of detectionin plants and productivity. An alternative method for determining small amounts of tungsten, <u>viz</u>. proton-induced X-ray fluorescence, was also investigated, but was found to have no advantages over the colorimetric method, at the present stage of development of the method.

For the analysis of tungsten ores and concentrates, the poor sensitivity of this element by atomic absorption spectrometry was not an important factor. Despite the suitability of the atomic absorption spectrophotometer for rapid analysis, there have been very few attempts to apply this instrument to the analysis of tungsten in its ores, or even in tungsten steels. This can be largely attributed to the tendency of tungsten to form a wide range of polymeric and hetropolymeric anions in acid solution. The types of tungsten species formed are dependent on the types of reagents used for dissolution of the sample, and on the presence or absence of other elements in the sample.

As the various anions produced in the dissolution procedure differ markedly in the ability with which they can be dissociated into free tungsten atoms, reliable results are very difficult to obtain. To surmount this problem, a method was developed which involved dissolution of the sample with a mixture of nitric and hydrofluoric acids, followed by evaporation to dryness. The acid - free residue was then redissolved in dilute alkali, in which tungsten exists Solely as the discrete tungstate anion, and the solution could then be analysed rapidly and accurately by atomic absorption.

For the determination of molybdenum in geochemical and plant samples, the dithiol colorimetric method was considered to be the best all round technique. Molybdenum, although more sensitive than tungsten by atomic absorption spectrometry, could only be determined in most types of sample, if solvent extraction was used in conjunction with at.omic absorption, thereby nullifying any speed advantage of atomic absorption over colorimetry. The dithiol method was considered to be superior to that using thiocyanate because the latter was less sensitive and more prone to interference. However a literative survey of published procedures for the determination of molybdenum with dithiol, showed that little attempt had been made to examine fully the parameters involved in this important method. Because of this, most procedures were very limited in their application, particularly with regard to sample types that could be analysed and

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to the presence of interfering elements. Because of the wide range of samples analysed for molybdenum in this thesis, it was felt that a thorough investigation of the dithiol procedure was warranted, and subsequently a procedure was developed which, by changing only the preliminary sample treatment, could be used for the determination of molybdenum in all types of geochemical and biological samples and even in steels.

Of the other elements determined in the investigations described in this thesis, aluminium, barium, bismuth, copper, iron, lead, magnesium, manganese, nickel, strontium, tin, titanium and zinc were determined by routine atomic absorption spectrometry and sodium and potasium by flame photometry, as described later in this section. Phosphorus and nitrogen analysis were carried out by Grasslands Division, DSIR, and a brief description of the methods used is given for the sake of completeness.

#### B. TUNGSTEN

## 1. Further development of colorimetric method

### (a) Introduction

The procedure developed in earlier work by the author (Quin, 1972) had a limit of detection of 1 ppm tungsten in plant ash and geochemical samples. Although the 1 ppm detection limit was adequate for the purposes of geochemical and biogeochemical prospecting, it became necessary to be able to determine low concentrations of this element in soils and particularly plants. The literature contains very few references to the background concentrations of tungsten in vegetation ; Brooks(1972) gives a figure of 0.5 ppm for plant ash, while Bowden (1960) found 0.02 to 0.15 ppm dry weight (approximately 0.4 to 3 ppm ash weight) in tomato seeds and tops, and 0.07 to 0.09 ppm dry weight (0.7 to 0.9 ash weight) in flax. However, because of the failure of the colorimetricmethod to detect tungsten in any vegetation samples from non-mineralised areas, it was considered that the normal concentrations of tungsten were probably lower than 0.5 ppm, ash weight especially in acid soils, where tungsten is rather immobile. An investigation was therefore carried out to determine to what extent the sensitivity of the method could be improved.

The other points that were considered to be worthwhile investigating were (i) whether fusion of soils with potnessing hydrogen sulphate prior to leaching with concentrated hydrochloric acid was necessary, and (ii) whether pre-ashing of the dried plant material was an essential step, or whether the tungsten could be leached directly from the dry matter with hydrochloric acid.

# (b) <u>Description of existing procedures</u>.(i) Equipment

Plant samples were ashed in a muffle - furnace at 500deg.C ; geochemical samples were fused at 550 deg. C. All sample weighings were carried out using a top-weighing Mettler Model P120 balance covering the range 0 - 120g. Borosilicate glassware was used throughout. A Bausch and Lomb Spectronic 20 Spectro-photometer was used for absorbance measurements.

# (ii) Solutions

Tin (**II**) chloride solutions. Prepare 20% and 10%(%/V) solutions of tin (II) chloride in 10M \_ hydrochloric acid.

Dithiol solution. Dissolve the contents of a  $5 \text{ cm}^3$  ampoule of toluene - 3, 4- dithiol in isoamyl acetate and make up to 500 cm<sup>3</sup>. Store in a refrigerator.

Standard tungsten solutions. Dissolve 90 mg of sodium tungstate in 104 hydrochloric acid and dilute to 500 cm<sup>3</sup> with this acid to give a solution containing 100  $\mu$ g tungsten per cm<sup>3</sup>. From this solution prepare solutions containing 10 $\mu$ g tungsten per cm<sup>3</sup> and 1  $\mu$ g tungsten per cm<sup>3</sup> in 10M hydrochloric acid.

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# (iii) Determination of tungsten in soils and rocks

Weigh 0.2 g of sample (minus 100 mesh) into a test tube, add 1 g of potasium hydrogen sulphate and mix. Fuse over a bunsen flame until a quescent melt is obtained and continue heating for a further two minutes. Alternatively, fuse in a muffle fornace at 550 deg. C. Leach in a hot water bath with 10 cm<sup>3</sup> of 10M hydrochloric acid until the melt can be broken up with a glass rod. Allow to settle, then transfer 5 cm<sup>3</sup> of the clear solution into a test-tube (150 x 12 mm), rimmed) containing 5cm<sup>3</sup> of a 20% solution tin (II) chloride in 10M HC1 and heat for 10 minutes at 85 deg.C.

Add 1 cm<sup>3</sup> of dithiol solution and continue heating for a minimum of six hours, or overnight. Remove the test tube from the water bath and add 5 cm<sup>3</sup> of isoamyl acetate or petroleum spirit to dissolve the globule containing the tungsten - dithiol complex. Measure the absorbance of the organic layer at 630 nm. If the absorbance is greater than that of the highest standard, repeat using a suitably smaller aliquot . from the remaining 5 cm<sup>3</sup> of sample solution, diluting this to 5 cm<sup>3</sup> with 10M hydrochloric acid and continuing from the addition of the tin(II) solution.

Standards. Make a series of standards representing 0 to 800 ppm, tungsten by adding 0 to 80.0  $\mu$ g of tungsten. Dilute to 10 cm<sup>3</sup> with 10% tin (II) chloride solution. Heat in a water bath for 10 minutes at 85 deg. C, add 1 cm<sup>3</sup> of the dithiol solution, and continue as above. (iv) Determination of tungsten in plant samples.

Dry the plant material to constant weight, weigh (if dry weight data is required), then char the samples on hot plates in a fume cupboard before ashing to completion in a muffle furnace at 500 deg. C. Cool, then weigh 0.1 g of plant ash into a test tube (150 x 12 mm, rimmed). Add 10 cm<sup>3</sup> of a 10% solution of tin (II) chloride in 10M HC1, heat in a water bath for 20 minutes at 85 deg. C, and continue as above.

Standards. As for soils.

# c. Further developments investigated

(ii) <u>Improvement of sensitivity</u> Use of smaller sample volume

Figure I.1 shows a calibration  $curv_{c}$  for the determination of tungsten. The 2 ppm standard gave an absorbance of  $0.005 \pm 0.001$ ; at 1 ppm the reading was  $0.003 \pm 0.001$  and this was considered to be the practical limit of detection of the original procedure. This sensitivity could be improved by adding 0.5 cm<sup>3</sup> of isoamyl acetate instead of 5 cm<sup>3</sup> to dissolve the minute globule (volume less than  $0.02 \text{ cm}^3$ ) containing the tungsten - dithiol complex and using 0.2 cm<sup>3</sup> capacity micro-cells. As these cells like the large cells, also have a 1 cm<sup>3</sup> path length, the sensitivity was increased ten-fold, that is, to 0.1 ppm. However because of the very small sample volume the technique was very susceptible to

turbidity, although isoamyl acetate gave less trouble in this respect than petroleum spirit ; hence its use as described above. The turbidity, caused by the presence of minute droplets of water in the organic solvent, could be removed by (i) filtering through filter paper soaked in isoamyl acetate or (ii) transferring the acetate to a warm dry vial immediately before transferring to the spectrophotometer cell. This causes the droplets of water to adhere to



Fig. I.1. Calibration curve for colorimetric determination of tungsten in geochemical samples and plant ash, using large cells.

the warm surface of the glass vial and hence they are not transferred to the cell.

Because of the small volume, filtering was difficult to perform quantitatively. The high volatility of the isoamyl acetate made it extremely difficult to ensure that the paper did not dry off slightly before addition of the sample. This would result in concentration of the sample solution, as the tungsten would now be contained in a smaller volume.

The second alternative was therefore preferred, although it was found in practice that 1 cm<sup>3</sup> was the minimum practical volume required to ensure that sufficient isoamyl acetate could be withdrawn, using a micro pipette, without risk of withdrawing some of the acid phase as well. Using this procedure, the detection limit was now 0.2 ppm, the absorbance reading for this standard being 0.003  $\pm$  0.001.

### Use of a larger sample of plant ash

Even with the improved detection limit, tungsten could still not be determined in many plant samples from non-mineralised areas, and hence it was decided to investigate the possibility of using a larger sample size. Increasing the sample size five-fold from 0.1 g. to 0.5 g. proved to be quite feasible, thereby improving the sensitivity to 0.04 ppm for an absorbance reading of 0.003  $\pm$  0.001. The only other modification to the procedure required was that it was now necessary to filter the sample solution ; after digestion of the sample with the 10% solution of tin (II) chloride in hydrochloric acid, before addition of the dithiol solution. Failure to do this often resulted in severe turbidity which could not be overcome. Fig. I.2 shows the standard curve for the revised procedures for the determination of tungsten in soils and plant ash.

Whilst investigation showed that the sensitivity could be improved still further by increasing the sample again, this had practical disadvantages. Most plant samples analysed were wood, and 1 g of wood ash represents up to 500 g. of dry material. Besides being difficult to completely ignite in a muffle furnace even with the pre-ashing stage, obtaining this amount of sample caused considerable damage to shrubs and small trees, and hence 0.5 g. of plant ash was set as the practical limit. In any case, virtually all plant samples analysed were found to contain more tungsten than the 0.04 ppm detection limit.

> (ii) Improvement of productivity Soils

Trial investigations showed that in the analysis of soils, containing small to moderate amounts of tungsten (less than 200 ppm) the preliminary fusion with potassium hydrogen sulphate was not necessary, the leaching with concentrated hydrochloric acid being sufficient to remove all the tungsten.

When the fusion step was omitted however, it was found to be necessary to ignite soil samples at 550 deg. C before leaching in order to remove any organic matter present in the soil. Failure to do this resulted in artificially high spectrophotometer readings, presumeably due to the extraction of minute particles of organic matter into the organic phase. The omission of the fusion step therefore only saved the weighing out of the potassium hydrogen sulphate, increasing the productivity from 150 to 175 samples per man day. The omission of the fusion step was therefore only considered to be worthwhile if all

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Fig. I.2. Calibration curve for the colorimetric determination of tungsten in geochemical samples and plant ash, using micro cells.
## Table I. 1

Analysis of soils for tunsten using fusion and ignition techniques

	Tungsten content (ppm)	
Sample no.	(i) Fused with KHSO <sub>4</sub> prior to leaching	(ii) Ignited at 550deg.C. prior to leaching
1	4.5	4.5
2	12	12
3	27	26
4	75	79
5	90	91
6	202	198
7	330	305
8	590	500
9	1210	850
10	1550	830

soils were known to contain less than 200 ppm. tungsten. Table I. 1 shows a comparison of results (i) using fusion and (ii) ignition only.

## Plant samples

An investigation was carried out to determine whether dry plant material could be leached directly with concentrated acid, omitting the dry ashing stage. In doing this, it was necessary to, firstly, digest the plant material with concentrated hydrochloric acid containing no tin (II) chloride, then transfer a 5  $cm^3$  aliquot to another test-tube containing  $5 \text{ cm}^3$  of a 20% solution of tin (II) chloride in concentrated hydrochloric acid. as in the analysis of soils. Failure to do this resulted in the formation of a dense red-brown precipitate, presumeably organic compounds of tin, which prevented extraction of the tungsten. Using the soil procedure however actually reduced the productivity, and in any case, complete extraction of tungsten could not be achieved (Table I.2). It was therefore concluded that dry ashing was an essential step for the determination of tungsten in plant material.

## (d) Conclusions

It was concluded that the practical limit of detection of the method had been improved to 0.2 ppm for soils, and 0.04 ppm. for plant ash, from the previous limits of 1 ppm in both cases.

Attempts to improve the productivity were successful for the analysis of soils, where it was found that fusion with potassium hydrogen sulphate was not necessary for samples containing less than 200 ppm. However dry ashing was found to be an essential in the analysis of plant material. Table I. 2

# Analysis of tungsten in vegetation with and without prior ashing

Sample	Number of determinations	Tungsten added (ppm)	Mean	Ashed Coeff. Va	Tungsten found Irn.(%) Mean	Not ashed Coeff. Varn.(
a	6	0	23.6	<u>+</u> 4.1	5.1	<u>+</u> 12
b	6	0	26.8	+ 3.8	4.6	<u>+</u> 25
а	6	50	72.9	+ 2.1	28.4	<u>+</u> 20
Ъ	6	50	77.5	+ 2.3	25.2	+ 30
С	4	0	0.25	+ 9.6	0.08	<u>+</u> 100
d	4	0	13.2	+ 4.8	3.8	+ 80
С	4	5	5.2	+ 2.8	2.8	<u>+</u> 90
d	4	5	18.4	+ 5.5	5.5	<u>+</u> 110
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## 2. Investigation into the use of proton induced X-ray fluorescence for the determination of nanogram quantities of tungsten.

(a) Introduction

During the same period that studies were being carried out to improve the sensitivity of the colorimetric method for the determination of tungsten, the opportunity arose for the author to investigate the suitability of

a new nuclear method; proton induced X-ray fluorescence, in this application.

Proton-induced X-ray fluorescence was first mooted by Johansson et al (1970) and Gordon and Kramer (1971). Other methods of excitation besides protons are possible, for example electrons, alpha particles, and X-rays. These have been commented on by Flocchini et al (1972) and Perry and Brady (1973). The use of protons for excitation has greater potential sensitivity than electrons (as used in the electron-probe) because of the lower background. Sensitivity is proportional to the mass of the exciting particle. Alpha particles, on the other hand, although heavier than protons, cannot be generated at a comparative rate, and hence sensitivity is very poor, the method being more suitable for the determination of major constituents (Franzgrote, 1972). Cookson et al (1972) used the method for the analysis of lake water, while Young et al (1973) used it to analyse sediments from aquious environments.

The measurements of X-rays (emitted as a result of excitation of electrons in the target by the bombarding protons) is more sensitive for heavy elements than is the measurement of  $\gamma$ -rays (emitted as a result of hits or near misses of the protons on the nuclei in the target). This is because the efficiency of  $\delta$ -ray excitation decreases rapidly as the atomic number of the element increases. The excitation of X-rays also becomes less efficient as the mass of the element increases, but the effect is not nearly as marked as for  $\gamma$ -rays. X-ray measurements therefore offered more potential for the determination of tungsten.

#### (b) Equipment

Measurements of X-ray fluorescence were carried out at the Institute of Nuclear Sciences, Department of Scientific and Industrial Research, Lower Hutt. The following description of the equipment used was kindly provided by Dr. N. E. Whitehead of the Institute.

The method employed protons generated by a 3.3 M c V Van de Graaff accelerator, the actual energy used being 2.5 M e V. The protons strike the sample containing tungsten in an evacuated target chamber which can contain up to 20 samples.

The targets are set at an angle of 45 deg. to the beam, and the X-rays emitted from the sample are detected by a Kevex Si (Li) X-ray detector. Scattered protons are prevented from reaching the detector by an absorber which is of sufficient thickness to absorb protons but not to significantly attenuate X-rays.

The pulses of the X-ray detector are fed into a preamplifier and main amplifier, then into a 4096 channel Pulse Height Analyser. The spectrum accumulated is either punched out on paper tape (if a plot of the spectrum is required), or fed into a Digital Equipment Corparation PDP 11 computer and stored on magnetic tape. The spectrum is then analysed by the computer using a programme which, given the description of two peaks, that is, the channel position and the atomic number of the element represented by the X-ray at the channel, searches until it finds peaks. A table of all X-rays and their energies is stored in the programme, and the computer checks to see whether any of the peaks found correspond to any of the X-rays in the table. A list of these is then printed out. The entire programme running takes a maximum of five minutes per spectrum.

The actual integration of the area under each peak is performed using a linear least-squares fit, until each is fitted as well as possible to the original spectrum.

Fitted simultaneously with the peaks is a shape, known as the Bremstrahlung shape, which arises from the slowing down of electrons knocked out of orbit by protons, and results in a broad spectrum of X-rays. If the material has become charged, that is nonconducting, this spectrum is more intense. To avoid this, non-conducting samples are coated in carbon by standing them briefly in a carbon arc. The Bremstrahlung shape is sufficiently well known to enable an @x pression to be fed into the programme which generates this shape, and is fitted simultaneously with the peaks.

The peak areas can be considered as being counts generated by the previously recorded number of protons hitting the target. The areas can be compared with those in another spectrum by allowing, in a proportional manner, for the different proton dose, which is recorded by measuring the current flow it produces. This current flow is digitised and the pulses are counted. The electronics allow the accumulation of the spectrum until a pre-set figure, usually 80K, is reached, thus making direct comparison possible.

Figs. I.3 and I.4 show schematic diagrams of the X-ray spectrometer, and the system used for computer-assisted analysis of the gauna spectra, respectively. 24



Fig. I. 3. Proton-induced x-ray fluorescence.





Fig. I.4. Computer-assisted analysis of x-ray spectra.

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Table I. 3

X-ray peaks of tungsten

Peak	Energy (KeV)
WLa, WLa, WLa, WL B2 WL S	8.396 ) ) 8.333 ) 9.670 9.959 11.283

## (c) <u>Development work</u> (i) <u>Introduction</u>

The X-ray peaks of tungsten are given in Table I. 3. The two  $L_{\alpha}$  peaks are too close to be resolved, while the two  $L_{\beta}$  peaks are just resolvable. Fig. I.5 shows the spectra obtained from a sample of scheelite  $(caWO_{4})$ ; the iron and copper peaks are due to impurities in the sample. The sample was prepared by compressing finely ground scheelite into a 1 cm diameter disc with a hydraulic press set at a pressure of 20 tons.

At this point it will be explained why only the determination of tungsten by this method, and not molybdenum as well, was investigated.

There are different series of X-rays emitted, the K, L, and M series, which correspond to excitation of electrons in the K, L and M election shells respectively. The energies of these X-rays increase in the order

## M < L << K

For tungsten, the K X-rays are at 59 KeV. This energy is high enough such that the excitation efficiency is poor, and the penetrating power of the X-rays into the Si (Li) detector is quite good, there is a low counting efficiency. Hence, for tungsten, the L X-rays are used, these being in a suitable range of 8 - 11 KeV.

For molybdenum however, the  $K_{\alpha}$  X-ray is at a high 17.44 KeV, and hence would have a poor sensitivity. The  $L_{\alpha}$  X-ray has an energy of only 2.29 KeV, which is almost identical in energy to the sulphur peak at 2.30 KeV. These two peaks are far too close to be resolved and, in any sample, particularly plant samples, the concentration of sulphur is far higher than that of molybdenum. For these reasons, then, it was not considered worthwhile to investigate the determination of molybdenum by this method.



Fig. I.5. X-ray spectrum of scheelite (CaWO4).

In any case, the dithiol colormetric method for molybdenum developed later in this section is significantly more sensitive than that for tungsten, and furthermore, molybdenum, because it is an essential element for plants, tends to be present in greater amounts.

## (ii) Analysis of plant ash and soil samples

To examine the spectra obtained from plant ash and soil samples, one sample of each was prepared again using a hydraulic press to form a self-supporting disc of 1 cm diameter. The samples were from the area of tungsten mineralisation at Glenorchy and had previously been analysed colorimetrically and found to contain 35 and 40 ppm tungsten respectively. However, as shown in the spectra in Fig. I. 6, the two strongest tungsten peaks ( $WL_{\alpha}$ , and  $WL_{\alpha}$ ) are completely masked by strong copper and zinc peaks, whilst the weak  $\operatorname{WL}_{\mathsf{Y}}$  peak is obscured under the shoulder of a strong bromine peak in the plant ash spectrum (this is the reason for the asymmetry of the bromine peak) and is not observed in the soil spectrum (Fig. I. 6 because of the far higher background. The two WL<sub>B</sub> peaks are partly obsoured by another strong zinc peak. (The tantalum peaks were caused by scattered protons striking the tantalum target holder. This was subsequently changed to aluminium, the peaks for which are of very low energy (<1.5 KeV), and hence do not interfere with tungsten).

From the plots it was evident that the two  $WL_{\beta}$  peaks offered the most potential for the determination of tungsten. Computer analysis of the spectra, using the  $WL_{\beta}$  peak as a reference assignment, detected the presence of tungsten in the plant ash sample, but not in the soil sample, as the far higher background and lower peak heights of the latter made the fitting of peaks too indefinite.



Fig. I.6a. X-ray spectrum of plant ash from area of scheelite mineralisation.



Fig. I.6b. X-ray spectrum of soil from area of scheelite mineralisation.

It was evident then, that if the far lower levels of tungsten present in samples from nonmineralised areas were to be detected, some form of concentration, and/or purification (particularly to remove zinc), was going to be necessary.

> (iii) <u>Purification and concentration of tungsten</u> <u>using mion-exchange chromatography</u>

#### Introduction

Strelow and Bothma (1967) demonstrated that solutions of tungsten (VI) were strongly bound on to anion exchange resin when the acidity is between 0.01N and 4.0N. At higher concentrations the tungsten was less strongly absorbed, probably due to the tendency for tungsten (VI) to form polynuclear species in acid solution ; these polytungstate anions could be too large to be bound strongly to the resin. Experimental

A preliminary trial with Dowex 1-x8 40- mesh anion enchange resin in the chloride form confirmed the findings of Strelow and Bothma (1967), and the following procedure was adopted.

The plant ash and soil samples (0.5 g) were entracted with a small volume of 10M hydrochloric acid (approx. 5cm<sup>3</sup>). After centrifugation, the supernatant was diluted with dilute sodium hydroxide until the pH of the solution was 2.0. The solution was then diluted to  $50 \text{ cm}^3$  with deionised distilled water, then passed through a micro anion exchange column, made up with 0.5g of Dowex 1-x8 resin in chloride form, over a period of 10 minutes. The solution was recycled two more times, then the resin was mixed with half its weight of cellulose powder before being compressed into a self-supporting disc, 1 cm diameter and about 3 mm thick, using a hydraulic press set at a pressure of 10 tons.

Standards containing 50 and 500  $n_{\rm J}$  tungsten (corresponding to 0.1 and 1 ppm for an initial sample weight of 0.5 g) were made up using the same procedure. Because of the non-conductive nature of the resin/ cellulose mixture, samples and standards were coated lightly with carbon by standing them briefly in a carbon arc.

## Results and discussion

Disappointingly, tungsten was not detected in either of the samples or the two standards. As analysis of the filtrates for tungsten by colorimetry were negative, showing that all the tungsten present must have been absorbed onto the resin, it was realised that the poor sensitivity was due to a combination of (i) the large weight, and (ii) the large mesh size, of the resin used. Because of the very shallow penetration of the proton beam (20 - 40 nm, N.E. Whitehead, pers.comm.) only a small fraction, approximately

(	fractio	on d	f		fractio	ond	f		100	)	
(	sample	sur	face	х	sample	de	oth	х	1	)	=
(	struck	by	beam		struck	by	bea	m		)	

 $\left\{\begin{array}{ccc}\frac{1}{3} & x & \frac{30}{3000} & x & \frac{100}{1}\end{array}\right\} = 0.3 \%$ of the tungsten present was being hit.

In an attempt to improve the sensitivity, further trials were carried out using only 0.1 g of Dowex 1-x8 200-400 mesh resin. After drying, the resin was mixed with 0.05 g of cellulose powder. However, attempts to produce self-supporting discs from these mixtures failed. It was found that 2mm thick self-supporting discs could be formed by adding 0.2 g of potassium bromide to the resincellulose mixture, but the dilution resulting from the addition of the potasium bromide meant that little improvement in the sensitivity was obtained, a 5000 mg standard being the lowest that could be detected. Using the above formula, approximately

 $\left(\begin{array}{cccc} \frac{1}{3} & x & \frac{30}{2000} & x & \frac{100}{1} \end{array}\right) = 0.5 \%$ 

of the 5000 ng of tungsten present was being hit, and hence the theoretical detection limit of the method was of the order of

 $\left\{ 5000 \text{ x} \cdot \frac{0.5}{100} \right\} = 25 \text{ ng.}$ 

It was apparent then, that because of the depth of the sample discs, the anion exchange procedure was not a sufficiently sensitive method of purification.

(iv)	Pur	rificatio	on an	d co	onc	centration	ı of	tungst	en
	by	extracti	on i	nto	а	solution	of	dithiol	
	in	isoamyl	acet	ate.					

## Introduction

To surmount the lack of sensitivity caused by the shallow penetration of the proton beam, an investigation was carried out into the possibility of employing the extraction of tungsten into a solution of dithiol in isoamyl acetate, as used in the colorimetric method, and then evaporating this solution to dryness on to a flat non-absorbent surface.

A new thin plastic material (trade name "Kapton"), which was non absorbent, resistant to most chemicals and to the proton beam, had recently become available, and seemed ideal for the purpose.

#### Experimental

In the colorimetric method, tungsten can be extracted from either hot dilute hydrochloric acid, or hot concentrated hydrochloric acid containing 10% tin (II) chloride (Quin, 1972). The latter alternative was used in the colorimetric procedure developed, as the presence of tin (II) chloride was necessary to prevent interference from molybdenum, which also forms a green dithiol complex if not reduced. In this nuclear application however, molybdenum does not interfere with tungsten, and hence hot dilute acid was used. The procedure adopted as follows :

The plant ash or soil sample (0.5 g) was digested in a test tube, with 10 cm<sup>3</sup> of 1N hydrochloric acid for two hours at 80 deg. C. To this was added 1  $\mathrm{cm}^3$ of a 1% solution of dithiol in isoamyl-acetate, and the tungsten was extracted into this over a period of five hours heating at 80 deg. C, during which time the isoamyl acetate was reduced in volume to a small globule. The test tube was then removed from the water bath, and 0.5 cm<sup>3</sup> of isoamyl acetate was added to dissolve the globule. A micro-pipette was used to remove 100 µl of the sclvent which was then applied, drop by drop, to a 1 cm diameter disc of gapton attached to the sample holder. The sample holder was heated throughout the application of the solvent, to ensure that the Kapton dried completely between the addition of each drop.

Standards were prepared by extracting 200 ng of tungsten (as sodium tungstate) into a solution of dithiol in isoamyl acetate and diluting the subsequent globule formed to 2 cm<sup>3</sup> with isoamyl acetate. 10, 50, 100, 250, 500, and 100 ng standards were made by drying 10, 50, 100, 250, 500 and 1000  $\mu$ l respectively of the solution into Kapton.

Results and discussion

Fig. I. 7 shows the spectrum obtained from a typical sample, and is seen to be free from copper and zinc interference. The only remaining peaks are those for manganese and iron, probably due to the extraction of traces of these metals into the isoamyl acetate.



Fig. I.7. X-ray spectrum of plant ash extract dried onto Kapton film.

Complete elimination of interference had now been obtained, and because the tungsten was now contained in a thin film on Kapton, the fraction of tungsten present hit by protons was equal to the fraction of the sample disc covered by the beam.

Fig. I.8 shows the results obtained for a standard curve covering the range  $_{\bigcirc}$  - 1000 ng tungsten. The bars give a measure of the "noise" at each reading. As estimated before, the limit of detection is approximately 25 ng.

The severe curvature of the line was presumably due to the film of excess dried dithiol preventing the proton beam from reaching all the tungsten present once a certain limiting quantity of the solution of dithiol in isoamyl acetate had been applied. This occurred at the 50 ng standard (Fig. I.8), and this corresponded to 100  $\mu$ l of solution. To correct this, new standards were prepared separately, in each case dissolving the tungsten dithiol complex in 1cm<sup>3</sup> of isoamylacetate and transferring 100  $\mu$ l of this to the Kapton. The corrected graph, now linear, is also shown in Fig. I.8.

Table I.4 shows a comparison of the results of analysis of 3 samples of plant ash, from an area of tungsten mineralisation, by colorimetry and protoninduced X-ray fluorescence. Satisfactory agreement was obtained.

#### Sensitivity

Using the procedure described, and accepting a detection limit of 25 ng tungsten, a 0.5 g sample permitted a detection limit of 0.25 p.p.m. 32



Fig. I.8. Standard curves for tungsten by protoninduced x-ray fluorescence, showing effect of limited and unlimited sample depths.

#### Conclusions

The present detection limit of 0.25 ppm. does not compare favourably with the 0.04 p.p.m. limit obtainable by the colorimetric procedure, using a similar sample weight and micro-cells. Even reducing the final volume of isoamyl acetate to a bare minimum of 0.2 cm<sup>3</sup> instead of 0.5 cm<sup>3</sup> would only improve this to 0.10 p.p.m. This forced the conclusion that proton-induced X-ray fluorescence did not at present offer any advantage over colorimetry for the determination of small quantities of tungsten, and hence was not used for routine work. The method does however have enormous potential, and there is no doubt that future developments, particularly changes in beam energy and the use of low-background sample film will greatly increase sensitivity.

## Table I.4

Comparison of analysis of plant ash for tungsten by colorimetry and proton-induced X-ray fluorescence

	-		P. P.	m. tungs	ten	
	colorim	etr	y proton	-induced	X-ray fluoresc	enc
1	7.0	+	0.3	6.8	<u>+</u> 1.0	
2	35	<u>+</u>	2.2	30	<u>+</u> 5	
3	10.0	+	0.6	12	<u>+</u> 2	

3. Development of an atomic absorption spectrophotometric method for the analysis of tungsten in its ores and concentrates.

## (a) Introduction

The colorimetric method developed earlier by the author (Quin, 1972) and further developed as described in Section I.B.1 of this thesis, provided a rapid and sensitive method for the accurate analysis of tungsten in soils, stream and sediments, low grade ores and vegetation, and in the course of this work many hundreds of analyses were carried out.

The analysis of higher grade tungsten ores by this technique was, however, less satisfactory, as the analyses often had to be repeated several times using progressively smaller aliquots of the sample solution until the absorbance reading fcll on the range of the standard curve. Besides seriously reducing productivity, the large percentage volumetric error caused by the necessity to take very small aliquots (e.g.  $10 \ \mu$ l) decreased the reproducibility of the method.

A further problem encountered in the analysis of tungsten ores by the dithiol colorimetric procedure was the tendency for tungsten to precipitate out of the concentrated hydrochloric acid leach solution.

As the study of scheelite ores, described in Section II of this thesis, necessitated the analysis of many tungsten-rich samples, it was decided to investigate the suitability of atomic absorption spectrophotometry for the analysis of tungsten ores and concentrates.

## (b) Literature survey

Despite the suitability of atomic absorption for rapid analysis, there have been very few attempts to apply this technique to the analysis of tungsten. Although the poor sensitivity for tungsten, caused by the formation of the extremely stable tungsten trioxide in the flame, precluded its use for routine analysis in geochemical applications, this was not a serious handicap for the analysis of steels and ores. What did pose a far more serious problem was the tendency for tungsten to form a wide range of polymeric and heteropolymeric anionic species in acid solution. These species can differ markedly in their stability in the flame and hence in the ease with which they can be dissociated into tungsten atoms, and, because the proportions of the various species formed is dependent on the types of compounds used for sample dissolution and on the presence or absence of various elements in the flame, samples containing equal amounts of tungsten could give widely varying results depending on the sample composition.

In hydrochloric acid, the polymeric species  $HW_6O_{21}^{5-}$ ,  $W_{12}O_{41}^{-}$  and  $W_{12}O_{39}^{-}$  are formed, all of which are initially converted to tungsten trioxide in the flame. In the presence of phosphorus however, whether present in the sample or added as phosphoric acid, an equilibrium between tungsten trioxide and phosphotungstic acid,  $H_3(P(W_3O_{10})_4)$ , is set up in the flame. This acid decomposes more readily than  $WO_3$ , and hence enhances absorption. In the presence of fluorine, Scobbie (1973) claimed that unreactive fluoro-complexes are formed which volatilise still more readily. However, as investigations showed that addition of hydrofluoric acid to solutions of tungstate in water does not increase sensitivity, it

would seem that even if fluoro-tungsten species are formed in hydrofluoric acid, they are immediately converted to the oxide in the flame, rather than being directly decomposed into atoms. The presence of large amounts of iron leads to the formation of some iron tungstate species such as Fe  $W_{12}O_{40}^{5-}$  or Fe<sub>2</sub>  $W_{12}O_{42}^{6-}$ , which in the flame, give a mixed oxide even more stable than  $WO_3$ .

For the analysis of steels and alloys, the formation of the various polymeric and heteropolymeric species is not too serious a problem. This is because, provided a similar mixture of acids is used for the digestion of all samples, the composition of the sample solution will be relatively constant, provided the composition of the samples themselves does not vary greatly. Hence Knight and Pyzyna (1969), using a mixture of sulphuric, phosphoric and perchloric acids, and Welcher and Kriege (1969) and Husler (1971) both using nitric-hydrofluoric mixtures. obtained good agreement with other methods for the analysis of various steels and alloys containing 1.5 to 8% tungsten. However Rooney and Pratt (1972), the first authors who attempted to analyse a wide range of alloys and steels containing widely varying amounts of tungsten, found that reliable results could only be obtained by the method of standard additions. due to interference from metals such as Ni, Mo, Fe and Cr. Furthermore, they did not recommend their method to be used for samples containing greater than 10% tungsten.

This brings us to the reasons for the difficulties in analysing tungsten ores and concentrates. Not only may the concentration of tungsten vary from 0.1 to 80%, the sample composition can vary enormously with respect to other elements. For example, silicon can vary from a fraction of a percent to 47% if the sample if largely quartz; in the presence of large amounts of silicon in the sample solution, the highly stable silico-tungstic acid  $H_4(\operatorname{Si}(W_3O_{10})_4)$  is formed in the flame in preference to  $WO_3$ . Depending on the type of ore, the sample will be greatly enriched in either calcium or iron and mangamese. In addition, the composition of the country rock or gangue material will vary depending on the location of the deposit, and on the actual percentage of ore in the sample to be analysed.

Because of the insolubility of tungsten ores in most acids, previous procedures for their analysis incorporated the use of fusion to digest samples. Thomas et al (1969) used a potassium hydroxide fusion for the determination of tungsten in volframite concentrates. Hydrogen peroxide and phosphoric acid were added to minimise hydrolysis and to dissolve precipitated hydroxides, but the method was prone to anion interference and to the formation of heteropolymeric compounds in the flame (Scobbie, 1973). Keller and Parsons (1970) employed a lithium metaborate fusion in the determination of tungsten in silicate ores, followed by a controlled-pH dissolution of the melt with hydrochloric acid and These authors made virtually no study of ammonia. interference effects and the sample solution was very unstable, due to the tendency for tungsten to precipitate out of solution.

It was evident then, that to be able to reliably analyse tungsten ores, it would be essential to either (i) extract the tungsten from the sample solutions before atomic absorption determination, or (ii) prevent the formation of polymeric and heteropolymeric tungsten species. Of these two alternatives, the former seems on the surface to be far simpler and more feasible. However this was not the case. Rao (1970) tried this technique, extracting the tungsten, after fusion with lithium metaborate and dissolution with phosphoric acid, into a solution of methyl tricapryl ammonium chloride in di-isobutyl ketone. However, the maximum extraction he obtained was 91%, and the concentration of phosphoric acid was absolutely critical for obtaining reproducible results. As mentioned before, the presence of phosphorus, which is extracted as phosphate along with the tungstate, leads to the formation of phosphotungstic acid. As the composition of the sample will affect the concentration of the phosphoric acid, the position of the WO3- phosphotungstic acid equilibrium will vary from sample to sample, and largely for this reason the method was suitable only for the analysis of low grade ores, where the phosphate/tungstate ratio remained very high.

The second alternative was therefore chosen for investigation and, as it turned out, the solution was relatively simple.

# (c) <u>Development</u>

(i) <u>Digestion</u>

The tungsten ores, scheelite  $(CaWO_{A})$ , wolframite  $((f_{e}, M_{H})WO_{4})$  and tungstite  $(WO_{3})$  are not attacked by most acids, and hence all existing procedures for the analysis of tungsten ores incorporated fusion for sample decomposition. These ores however are all soluble in hydrofluoric acid, and, moreover, digestion with this acid results in complete dissolution of silica and decomposition of silicate lattices, and hence no tungsten remains trapped in any residue. Furthermore, digestion can be carried out in inexpensive polyprolylene beakers over a boiling water bath or hot plate. In the procedure adopted, a 0.2 g. sample was digested with 10cm<sup>3</sup> of a 1:1 mixture of concentrated hydrofluoric (40%, A.R.) and nitric (g.g.1.42, A.R.) acids. The solution was taken to dryness over a period of 2 - 3 hours, during which time the sample was suspended over a boiling water bath. Taking the solution to dryness ensures that virtually all the silicon present is volatilised as its volatile fluoride, while the presence of nitric acid ensures the oxidation of metals to their oxides. Hence tungsten is eventually

reprecipitated as yellow hydrated tungsten oxides,  $WO_3.H_2O$  or  $WO_2.2H_2O$ , irrespective of the original ore type, and no trace of acid remains.

The precipitate of tungsten oxide formed is readily ssoluble in potassium hydroxide on heating; and, what is vitally important, tungsten exists solely as the discrete tungstate anion. (Cotton and Wilkinson, 1967). This means that the complex equilibria set up in acid solution do not form, and, in any case, any metals that would form heteropoly species with tungsten acid solution are either volatilised during evaporation (silicon) or are insoluble in alkali. It was found that 10 cm<sup>3</sup> of 0.5M alkali was sufficient to ensure complete Initially a period of 15 minutes dissolution. heating was used, but it was found that this occasionally gave variable results, especially in samples containing large amounts of calcite. Analyses of somehigh-calcite samples showed that reproducile results could be obtained either by (i) carrying out a second extraction with more alkali, or (ii) heating the precipitate with the alkali for 30 minutes instead of the original period of 15 minutes (Table I.5). The use of more concentrated alkali accelerated the dissolution of the precipitate, but led to rapid clogging of the Conversely, solutions as weak as 0.2 m burner. could be used provided a larger period of heating was used, but a concentration of 0.5M was considered to offer the best compromise between speed and economy.

(ii) Flame conditions

Both sensitivity and more importantly, reproducibility, were found to be highly dependent on a number of factors, including flame stoichometry, the transverse position of the flame, the presence of air-drafts in the laboratory, and the air velocity in the fume exhaust.

#### Flame stiochiometry

The variation of absorbance with the fuel to oxidant (acetylene to nitrous oxide) ratio is given in Table I.6. The results show that the absorbance increases with increases in the ratio. For the low velocity burner systems employed in analytical atomic absorption, the reaction is widely accepted (Scobbie, 1973b ) as  $2N_{2}^{0} + C_{2}H_{2}$ products. In a fuel rich flame (Table I.6) the presence of reactive carbonaceous vapour species aids the reduction of the refractory tungstic oxide to tungsten However if the amount of excess fuel is atoms. increased beyond a certain point, solid carbon particles form as an agglomeration of soot, resulting in rapid clogging of the burner slit. The presence of these solid particles is shown by the yellow incandescence of the flame (Table I.6). The acetylene / nitrous oxido ratio chosen permitted the running of up to 50 samples before the build up of soot significantly altered the geometry of the flame, thereby necessitating recalibration of the standard curve.

Position of the flame

The high temperature (approximately 2900 deg.K.) of the nitrous oxide - acetylene flame as used in atomic absorption analysis is undoubtedly another major factor in enabling it to dissociate the tungsten oxide formed in the flame environment. In the nitrous oxideacetylene flame, the temperature in the intercenal zone is relatively constant (Scobbie, 1973b). Hence the height location of the burner is not very critical; an increase in height from 2 - 3 mm above the burner top (where maximum absorbance occured) to 10 mm was found to result in a decrease in absorbance of only 5%.

Table I.5

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Effect of time on extraction of tungsten from acid decomposition residue with potassium hydroxide

	Extraction time		Sample	
	15 minutes	<u> </u>	B	С
% WO3	from first extraction	56.4	23.2	1.96
% WO3	from second extraction	7.40	4.30	0.13
% WO3	in residue <sup>a</sup>	0.18	0.11	0.01
TOTAL	% WO <sub>3</sub>	64.0	27.6	2.10
	30 minutes	A	В	C
% WO3	from first extraction	63.9	27.4	2.08
% WO3	from second extraction	0.20	0.11	0.01
% WO3	in residue <sup>a</sup>	< 0.001	<0.001	<0.001
TOTAL	% WO <sub>3</sub>	64.1	27.5	2.08

<sup>a</sup> Determined colorimetrically

Table I.6

Effect of  $C_2H_2/N_2O$  ratio on tungsten absorbance

Flow rate acetylene	(1 min <sup>-1</sup> ) nitrous oxide	N <sub>2</sub> 0 7C <sub>2</sub> H <sub>2</sub>	Absorba 500 ppm	nce Height of W red cone (mm)	f Type of flame
7.0	14.0	2.0 *	0.02	2	lean
7.0	13.0	1.85	0.10	5-10)	
7.0	12.1	1.7	0.16	15 <b>-</b> 20 }	analyțical
7.0	11.2	1.6 **	• 0.22	20-25 )	range
7.0	10.5	1.5	0.24	25-30	rich
7.0	9.8	1.4	0.26	30-40	rich
7.0	9.1	1.3	0.26	luminescent	very rich
<u></u>					
*	toichiometric ra	atio			

metric ratio

Fuel-rich ratio used for analytical work \*\*

This transverse position of the flame is however critical in obtaining maximum absorbance and more importantly in obtaining as linear a standard curve as possible, and hence the flame must be located precisely by manipulation of both the transverse and rotational burner controls. The reason for the importance of the transverse position of the flame is exemplified by the absorption profiles for the absorbance from a 500 p.p.m. tungsten standard in fuel-rich and lean nitrous oxide-acetylene flames (Fig.I.9). The fuel-rich flame, although giving much higher absorbance, shows a much sharper decrease in absorbance with distance from the centre of the flame than did the lean flame. Chakrabarti et al (1970) obtained similar differences in absorption profiles between rich and lean flames for other elements. but did not comment on this important aspect.

#### Air draughts in the laboratory

The presence of air draughts in the laboratory significantly reduced the reproducibility of the method, no doubt due to their buffeting action on the flame. As seen in the previous section, displacement or distortion of the flame geometry would have a marked effect on absorbance.

## Air velocity in the fume exhaust

Calculations of the air velocity in the fume exhaust were made using a Dwyer Air Velocity Calculator. It was found that the normal air velocity was approximately 400 metres/minute, with normal minimum and maximum of 380 and 415 respectively. On very windy days however the air velocity could vary from 250 - 480 metres/minute over the space of a few minutes. Under these conditions, stability of the flame and hence of absorbance was very poor, and analyses could not be carried out under these conditions.



Fig. I.9. Absorption profiles for tungsten (0.1%) in rich and lean nitrous - oxide acetylene flames.
#### (iii) Calibration curve

Fig. I.10a shows the initial calibration curve obtained with no scale expansion for which standards containing up to 1% tungsten in solution (representing 50% W in the original sample) were used. Because of the severe non-linearity of the absorbance curve, high-grade samples could not be analysed with better than  $\pm$  10% accuracy. The curvature of the line is partly due to the fact that the absorbing line used, at 255.1 nm, is subject to spectral interference from another nearby tungsten line (255.0nm). The closeness of this non-absorbing line makes it difficult to isolate the 255.1 nm wave length, and hence the resultant tungsten absorbance is non-linear.

An additional cause of the non-linearity is broadening of the line source. When the lamp is operated at high current, as is necessary for tungsten, the width of the emitted line is greater. Ground state atoms sputtered at high current from the cathode will absorb light at the central wavelength just as they would in the flame. The result is a considerable change in the line profile, as is shown in Fig. I. 11. Absorption behaviour is not uniform over this width, and the area of intersection between emission and absorption profiles does not increase uniformly with concentration, but will curve towards the concentration asymptote.

Superior accuracy of high grade samples  $(\pm 0.2\%)$  was achieved, with the aid of  $\frac{1}{3}$  scale expansion, by using only standards covering the range 0 - 1000 ppm tungsten in solution, and diluting the sample solutions as required. Although the curvature is not reduced, the expansion of the readings makes it less noticeable and permits more accurate readings (Fig.I.10b).



Fig. I.10a. Standard curve for tungsten, no scale expansion.



Fig. I.10b. Standard curve for tungsten, 40% scale expansion.



Fig. I. 11. Effect of emission line broadening and self-absorption on flame absorption. (d) Experimental

(i) Equipment

The digestions were carried out in  $50 \text{ cm}^3$  polypropylene beakers suspended over a boiling water bath.

Atomic absorption measurements were carried out with a Varian TechtronAA5 Atomic Absorption Spectrophotometer under the conditions listed below :

> Source : ASL hollow-cathode lamp at 20mA Mavelength : 255.1 n m Slit width : 0.15 nm Burner : Techhon AB50 Gas mixture : nitrous oxide, flow rate 7.5 scale units (20 p.s.<sup>i</sup>: tank) acetylene flow rate 8.0 scale units (10 p.s.i.at. tank), red cone 15 mm high. Scale expansion : approximately 40%. (ii) Standard tungsten solutions

Dissolve 6.30 g of tungsten trioxide(99.9%) in hot 0.5 M potassium hydroxide, and make up to 500 cm<sup>3</sup> with the alkali. This gives a solution containing 10,000 ppm tungsten in solution. From this prepare solutions containing 100, 250, 500, 750 and 1000 ppm by diluting with 0.5 M potassium hydroxide.

(iii) Digestion of the sample.

Digest 0.200 g. samples of ore or concentrate with 10 cm<sup>3</sup> of a 1 : 1 mixture ofhydrofluoric (40%, AR) and nitric (e.g. 1.42, AR) acids in polypropylene beakers over a boiling water bath. When samples have evaporated to dryness (2-3 hours), add  $10 \text{cm}^3$ of 0.5M potassium hydroxide and continue heating for 30 minutes at approx. 80 deg.C. Transfer solution and any residue into a  $10 \text{cm}^3$  graduated centrifuge tube, washing in with distilled water. Make up to  $10 \text{ cm}^3$  with distilled water, mix, and centrifuge for 2 minutes at 5000 p.m.

(iv.) Atomic absorption determination of tungsten

Set scale expansion so that the 500 ppm. standard gives an absorbance of 0.20-25, using 0.5M potassium hydroxide as blank (this will read 0.01 above distilled water). Check 500 ppm standard between each sample. For samples that are off the scale, dilute as necessary (up to 20 times) to get reading on curve.

### (e) Reproducibility and recovery tests

#### (i) Recovery of tungsten

Table I.7 shows the results of replicate analyses of a low-grade ore, to which known amounts of tungstentrioxide had been added. Recovery was complete within the precision of the method.

#### (ii) <u>Reproducibility</u> and accuracy

Table I.8 summarises analytical data for tungsten in synthetic samples and in selected samples of scheelite and wolframite ores. Table I.9 presents data for 20 separate analyses of the same sample done on 20 different days, and re-reading of the original sample solution on each of the 20 days. Finally, Table I.10 shows a comparison of results by this method and by the colorimetric method.

#### (f) Interferences

The use of potassium hydroxide as a matrix has several advantages : (i) The presence of a readily ionised element such as potassium enhances the tungsten absorption by acting as a ionisation suppressant (Thomas and Pickering, 1971; Scobbie, 1973)

Recovery	of WO3 added to 1	.ow-Grade ore sample
WO <sub>3</sub> added (mg)	WO <sub>3</sub> recovered <sup>a</sup> (mg)	Coefficient of variation (%)
0 50 100 150	1.0 50.9 100.8 150.2	+ 5.1 + 1.9 + 0.7 + 1.0

Table I.7

<sup>a</sup> Mean of 8 determinations

Table I.9

Analytical date for replicate determinations of tungsten in synthetic standards and ore samples

Sample <sup>a</sup>	Mean <sup>b</sup> % WO <sub>3</sub>	Coefficient of variation (%)
A (29.0% WO <sub>2</sub> )	29.2	+ 1.1
B (10.0% WO <sub>3</sub> )	10.1	<u>+</u> 2.5
$C (4.8\% WO_3)$	4.85	+ 2.3
$D (0.48\% WO_3)$	0.49	<u>+</u> 2.6
Scheelite ore, Westland	9.6	<u>+</u> 2.7
Scheelite ore, Marlborough	40.7	+ 2.2
Wolframite ore, Westland	27.6	<u>+</u> 1.2

- <sup>a</sup> Synthetic standards (A,B, C, D) by courtesy of Professor M. H. Buckenham, Otago University.
- <sup>b</sup> Mean of 8 determinations

and, because it is present in far greater concentrations than any other readily ionised elements, there is no need for the close matching of sample and standard solutions required in other method. (Rooney and Pratt, 1972); (ii) In alkali solution, tungsten exists solely as the monomeric tungstate anion (Cotton and Wilkinson, 1967) and hence the problems associated with the formation of various polyanions of varying stabilities when an acid matrix is used are not encountered ; (iii) the elements most likely to interfere if present in large concentrations are prejpitated. The digestion of the sample with hydrofluoric and nitric acid ensures that the metallic elements are converted to their oxides. Hence even the amphoteric elements iron and aluminium. many of whose salts are soluble in alkali, are present only in small amounts in the sample solutions because of the insoluble mixture of their oxides. Iron and aluminium were analysed in over 130 sample solutions prior to the determination of tungsten. The highest concentration of iron found was a mere 20 ppm, most values were less than 1 ppm. This is not surprising as FeO, Fe<sub>2</sub> O<sub>3</sub> and Fe (OH)<sub>2</sub> are all insoluble in 0.5 M alkali (Fe(OH), is soluble only in hot concentrated alkali). The concentrations of aluminium found varied from less than 5 ppm to 375 ppm, with a mean of 100 ppm, the higher concentrations of aluminium than iron being due to the more amphoteric nature of A1 (OH) 3. However investigation showed that concentrations of up to 2000 ppm aluminium had no effect on the absorbance by tungsten. The method therefore appears to be completely free of interferences.

## Table I.9

Analytical data for determination of tungsten in one sample on twenty consecutive days

Darr	% 1:	103	Dât	% WO3		
Day	Original sample Solution Reassay of same sample		Day	Original Sa Solution	nple Reassay of same sample	
1	23.4	24.3	11	23.6	23.7	
2	23.6	24.1	12	23.4	23.9	
3	23.6	24.0	13	23.0	23.8	
4	24.0	23.2	14	23.7	23.8	
5	23.8	23.5	15	23.5	23.6	
6	23.1	23.6	16	23.4	23.4	
7	23.0	22.9	17	23.9	24.4	
8	23.9	24.0	18	23.8	24.2	
9	23.5	23.4	19	23.8	23.6	
10	23.5	23.3	20	23.3	23.2	
No. Part and part of						

### (g) <u>Sensitivity</u>

Although the original requirement was only for a method capable of analysing samples containing more than 1%  $WO_3$ , the sensitivity of the method is much better than this and concentrations as low as 200 ppm in the original sample can be determined.

(h) Productivity

The inherent simplicity of the method lends itself to a high productivity, and a figure of 100 samples per man- day could be easily achieved.

#### (i) <u>Conclusion</u>

It is concluded that this investigation had resulted in the development of a rapid and accurate method for the determination of tungsten in ores and concentrates, and which, unlike previously published procedures, was not subject to complex solution equilibria and condensed phase interference effects.

# Table I.10

	% WO3				
Sample	Atomic Absorption	Colorimetry			
1	1.25	1.13			
2	0.075	0.07			
3	0.24	0.22			
4	1.30	1.56			
5	0.17	0.16			
6	0.19	0.18			
7	7.85	6.15			
8	1.19	1.09			
9	0.15	0.10			
10	0.22	0.19			
11	1.19	1.06			
12	3.70	3.01			
13	1.91	1.47			
14	0.88	0.92			
15	0.21	0.22			

# Comparison of atomic absorption and colorimetric analysis of tungsten ores

#### MOLYBDENUM

C.

#### 1. Literature survey

As mentioned earlier, the dithiol colorimetric method was considered to be the best all-round analytical technique available for the determination of molybdenum in geochemical and plant samples.

Atomic absorption spectrometry, although giving considerably better sensitivity for molybdenum than for tungsten (0.33 p.p.m. and 5.8 p.p.m. respectively for 1% absorption), is still insufficiently sensitive for the routine determination of molybdenum in most samples, as the dilution necessary to bring solid samples into solution takes the real sensitivity beyond the average abundance of molybdenum, 0.1 - 3plants, soils and rocks (Brooks, 1972). ppm in Van Loon (1972) found 3 p.p.m. molybdenum to be a practical limit of detection by conventional atomic Moreover, Dilli et al (1974) demonstrated absorption. that the acids present in the sample solution give rise to variable and unpredictable effects on the determination of molybdenum.

Henning and Jackson (1973) used a graphite furnace to determine molybdenum in plant tissue by flameless atomic absorption, obtaining a detection limit of approximately 0.1 ppm. However the determination of small amounts of molybdenum has more commonly been used by conventional atomic absorption in combination with solvent extraction. Various combinations of complexing agents and organic solvents have been used, including oxine and methyl n-amyl ketone (Butler and Mathews, 1966); oxine and methyl isobutyl ketone (Chan and Lum-Shue-Cham, 1969);

thiocyanate and butyl acetate (Grosz, 1970); methyl tricapryl ammonium chloride and methyl isobutyl ketone

(Rao, 1971); benzoin -oxime and chloroform (Hutchinson, 1972), and thiocyanate and methyl isobutyl ketone (Kim <u>et al</u>, 1974). Although these procedures achieved a satisfactory sensitivity, and circumvent the interference effects of the acids present in the sample solution, the various extraction steps nullified the speed advantage of the atomic absorption technique because they did not lend themselves to simultaneous treatment of large batches of samples.

Emission spectrography has been used extensively in geochemical and biogeochemical exploration for molybdenum (Brooks, 1972) but its sensitivity of 5 p.p.m. (Ahrens and Taylor, 1961) made it unsuitable for much of the work carried out in this thesis. Moreover, the method has a very low productivity (30 samples per man day, Quin, 1972) and hence emission spectrography was not considered further.

Of the various colorimetric methods in use for the determination of molybdenum (Elwell and Wood (1971) list approximately 80 reagents that have been used), only those employing thic & yanate and toluene-3, 4-dithiol have found wide application in the analysis of geochemical and plant samples. Studies of the literature convinced the author that the dithiol method was inherently more sensitive, reliable, and reproducible. The molybdenum thiocyanate complex has been widely criticised for its lack of stability and reproducibility, (Crouthamel and Johnson, 1954; Hobart and Hurley, 1962; Wilson and McFarland, 1964; Chan and Riley, 1966) and recent work by Greenland and Lillie (1974) and others has shown that the reaction mechanisms involved are far more complex than originally thought. Moreover, the lower extinction coefficient

of the thiocyanate method has meant that it does not have comparable sensitivity to the dithiol procedure ; the detection limits of even very recent procedures (Lillie and Greenland, 1974 ; Savaniar <u>et al</u> 1974) are no better than 0.1  $\mu$ g (representing 0.5 p.p.m. for the widely used 0.2 g sample weight).

2. Survey of existing dithiol procedures.

Since the introduction of the colorimetric method for the detection of molybdenum with toluene-3. 4-dithiol (dithiol) by Hamence (1940) and Miller (Miller and Lowe, 1940; Miller, 1941) the method has been applied to the determination of molybdenum in a wide range of materials. Basically the method consists of (i) sample decomposition, (ii) addition of dithiol solution to the acidified sample solution. and (iii) extraction of the green molybdenum dithiol complex into an organic solvent for colorimetric determination. Methods for the analysis of plants include those of Piper and Beckwith (1948), Bingley (1959), Gupta and Mackay (1965) and Ssekaalo (1971). All these methods except that of Gupta nnd Mackay (1965) utilised mixtures of nitric, sulphuric and perchloric acid to digest plant material ; the latter authors used a mixture of sulphuric acid and hydrogen peroxide. After digestion of the sample, Piper and Beckwith (1948) extracted copper with dithizone before extracting molybdenum with a solution of cupferron in chloroform. The cupferron was then destroyed and the molybdenumdithiol complex precipitated before being extracted into amyl acetate for colorimetric determination : Bingley (1959) found that the addition of iron to the sample digest prior to the extraction of the molybdenum dithiol complex was necessary to obtain full colour production.

Methods for the analysis of biological materials have been described by Bickford et al (1948), Allen and Hamilton (1952) and Bingley (1963). Bickford et al (1948) used a sulphuric and nitric acid digest. Citric acid was added to complex any tungsten present before extraction of molybdenum. Allen and Hamilton (1952) and Bingley (1963) used mixtures of nitric sulphuric and perchloric acids for sample decomposition. Allen and Hamilton (1952) then extracted copper with dithizone, after the method of Piperand Beckwith (1948), then precipitated and extracted the cupferrate complex of molybdenum, finally digesting the cufferrates before precipitating the dithiol complex and extracting it into petroleum ether. Bingley (1963) used thiourea to control copper interference. There have been many procedures published for the determination of molybdenum in geochemical samples.Clark and Axley (1955) used a sodium carbonate fusion for the analysis of soils and rocks. Interference by ferric iron was eliminated by reduction with potassium iodide and sodium thiosulphate. Jeffery (1956) used a sodium hydroxide fusion for the determination of molybdenum in silicate rocks. The metal was extracted from the sample solution into a solution of *x*-benzionoxime in ethanol and chloroform. After distilling off the organic solvent, sulphuric acid was added to destroy the organic matter present before the addition of the dithiol solution. North (1956) used a modified carbonate flux for the field determination of molybdenum in soils. Watkinson (1958) used anionexchange to separate molybdenum from tungsten in soils after digestion of the sample with hydrofluoric and hydrochloric acids. Baker (1965) found 5N hydrochloric acid to be sufficient to leach molybdenum from geochemical samples. Potassium iodide and sodium sulphate were

added to ensure complete reduction of iron (III) before addition of the dithiol solution and extraction into chloroform. Stanton and Hardwick (1967) used a potassium hydrogen sulphate fusion for the analysis of soils, sediments and rocks. Interference from iron (III) was prevented by reduction with ascorbic acid, while potassium iodide was added to reduce copper (II). Tungsten interference was suppressed by careful control of the time allowed for complex formation. Stubbs (1968) used sodium hypochlorite to leach molybdenum from geochemical samples in the field, prior to its qualitative detection by the addition of solid zinc dithiol. Finally Stanton (1970) modified his earlier procedure (Stanton and Hardwick, 1967) by replacing the acid fusion with perchloric acid digestion.

More specialised geochemical procedures included those of Jeffery (1956), who used a sodium hydroxide fusion for the analyses of molybdenum in tungsten ores. citric acid was used to help suppress formation of the tungsten dithiol complex, but, when the concentration of molybdenum was less than 500 p.p.m., correction for tungsten interference was necessary by measurement of the optical density of the organic extract at two wavelengths.Skewes (1959), in his method for the determination of molybdenum in copper ores, firstly extracted the molybdenum as its benzionoxime... complex into chloroform, then boiled off the chloroform before the addition of sulphuric acid and dithiol.

This large number of procedures has arisen partly as a result of individual workers developing specialised techniques which best seemed to fulfil their particular requirements, and partly as a result of insufficient investigation into the parameters involved, with the result that few if any of these procedures

could be easily modified to permit the analysis of other types of sample. Attempts at developing general - purpose procedures have been made by Marshall (1964) and Chan and Riley (1966). Marshall (1964) described procedures for the determination of molybdenum in soils, stream sediments, rocks and vegetation. Geochemical samples were leached with hydrochloric acid while plant material was dry ashed Iron interference before being dissolved in acid. is suppressed by reduction with ascorbic acid. and after the addition of dithiol, the molybdenum dithiol complex was extracted into chloroform. However this method necessitated the use of large sample sizes was subject to interference from tungsten and copper.

and plant samples particularly were susceptible to turbidity due to the dispersion of water droplets in the chloroform. The method of Chan and Riley (1966), for the analysis of silicate's and biological materials, although being relatively free of interferences, was not suitable for the routine analysis of large numbers of samples. The method utilised large sample weights (0.5 -1g of silicates and 10g of biological materials) and extremely large sample solutions (200 cm<sup>3</sup> for silicates and 500 cm<sup>3</sup> for biological samples). Moreover, a large number of steps were involved in the procedure (10 solution additions and volume adjustments).

The varied investigations carried out in this thesis necessitated the development of a rapid, accurate and sensitive method, which, with minimal alteration, could be used for the determination of molybdenum in a wide range of geochemical and plant samples. The method had to be suitable for the

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analysis of tungsten ores, and hence tungsten interference had to be completely eliminated. For geochemical exploration purposes, the method had to have a high tolerance to copper, due to the common association of these two elements in ore deposits. For biogeochemical exploration and especially plant study purposes, the method had to be extremely sensitive, to permit the use of small samples. This section describes the development of such a method.

3. Development of the method

In general terms, the three major points requiring investigation were (i) decomposition of samples, (ii) formation and extraction of the molybdenum-dithiol complex, and (iii) elimination of interferences.

### (a) Preliminary treatment of samples

(i) Ashing of botanical samples

Dry ashing at 500 deg. C. gave similar results to wet ashing with a mixture of nitric, sulphuric and perchloric acids, as used by Piper and Beckwith (1948), Allen and Hamilton (1952), Bingley (1959),Bingley (1963), and Ssekaalo (1971) (Table I.11). As no chemicals or surveillance is required in dry ashing, this method was adopted. The ashing of 2 g of plant material in 150 x 16 mm test tubes, for example, takes a maximum of 20 hours at 500 deg. C. If required, faster ashing could be achieved by the use of larger tubes or beakers.

#### (ii) Fusion of geochemical samples

Fusion with potassium hydrogen sulphate at 550 deg. C. may be carried out in borosilicate test tubes, which will last for 15 - 20 fusions before becoming very brittle. During the fusion, molybdenum is converted into soluble molybdate. Any organic matter is completely decomposed. Stanton and Hardwick (1967) had demonstrated that this fusion gives much more reproducible results than the low temperature sodium carbonate - sodium chloride - potassium nitrate fusion of North (1956), and gives similar results to digestion with perchloric acid (Stanton, 1970). Table I.12 shows a comparison of results by potassium hydrogen sulphate fusion and digestion with a mixture of nitric and hydrofluoric acid. Good agreement was achieved, and the fusion technique was chosen for its simplicity and more suitable application to large batches of samples.

(iii) Dissolution of steel samples

Although not of direct application in this work, it was of interest to determine whether the method developed was sufficiently versatile to permit the determination of molybdenum in steels. A 1:1 mixture of hydrochloric and nitric acids was used to dissolve steel samples in polypropylene beakers over a boiling water bath. After evaporation to dryness, the residue was treated with a further 2 cm<sup>3</sup> of nitric acid to ensure that all molybdenum present was oxidised to molybdenum (VI).

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Sample <sup>a</sup>	Molybdenum (p.	p.m. dry weight
	Dry ashing	Wet ashing
Ryegrass	3.4	3.4
Red clover	9.2	9.3
<u>Olearia rani</u>	33.0	32.5
Nothofagus fusca	0.75	0.62

Table I.11

Comparison of dry and wet ashing of plant material

<sup>a</sup> Average of five determinations

# Table I.12

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Comparison of KHSO<sub>4</sub> fusion and HF/HNO<sub>3</sub> digestion of geochemical samples

KHS04 Fusion	HF/HNO3 digestion
3.1	3.2
210	205
41	41
0.85	0.95
21	20
	3.1 210 41 0.85 21

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# (b) Parameters affecting the formation and extraction of the complex

(i) <u>The nature of the dithiol solvent</u>. The possible methods of adding the dithiol are (a) as solid zinc dithiol (Stubbs, 1968); (b) as a solution of dithiol in isoamyl acetate (Wells and Pemberton, 1941; North, 1956), so that formation and extraction of the molybdenum - dithiol complex take place simultaneously, and (c) as a slightly basic aqueous solution of dithiol or its zinc derivative (used in virtually all other procedures). In this case the complex is first formed as a slightly soluble suspension in the acid solution, then extracted into an organic solvent.

Method (a) is unsuitable because dithiol oxidises rapidly on exposure to air, and hence is more conveniently handled in solution.

Bowden (1964) has criticised the use of the solution of dithiol in isoamyl acetate as in method (b), claiming that the reagent was unstable in this form, developing a high yellow-green colour (caused by formation of oxidation products of dithiol) after only 3 days, even if kept in a refrigerator. However investigation showed that the reagent prepared in this way was at least as stable as the aqueous solution used in method (c), the solution being usable even after a year if stored in a refrigerator. This indicates that the dithiol used by Bowden must have been very impure.

A further criticism of method (b) was that extraction of molybdenum is very slow, being incomplete even after 15 minutes shaking (Piper and Beckwith, 1948). However investigation showed that complete extraction of 10  $\mu$ g of molybdenum into a 1% solution of dithiol in isoamyl acetate took only 4 minutes (Fig. I.12).



Fig. I.12. Rate of extraction of molybdenum into various solvents.

In method (c), thioglycollic acid is added to the reagent solution to slow the oxidation of dithiol, and the solution may be used for some months if stored in a refrigerator. The dithiol, which is readily soluble in aqueous sodium hydroxide, precipitates to form a white colloidal suspension when this solution is added to the acidic sample solution.

In contrast to dithiol, the molybdenum dithibl/complex is soluble in many organic solvents, and hence several, including petroleum spirit, butyl acetate, isoamyl acetate, carbon tetrachloride, and chloroform have been used for the extraction in method (c). These solvents were tested and all were found to completely extract the molybdenum, although the time for complete extraction varied considerably (Fig. I.12).

Isoamyl acetate was chosen for the proposed procedure because of the rapid extraction obtained and because sampling of the organic layer was cleaner than with the denser-than water carbon tetrachloride and chloroform. The rate of reaction is even faster at higher temperature (Gilbert, 1956), but this also favours the reaction of tungsten with dithiol (Bingley, 1959; Sandell, 1959).

(ii) Acidity of the sample solution.

Complete extraction of molybdenum (10  $\mu$ g) was obtained from hydrochloric acid over the range 0.5M to 8M. A final molarity of 2M was chosen because (i) the complexing of tungsten by citric acid is not complete above 2.5M (see later), (ii) the ability of ascorbic acid to reduce iron (III) is impaired in solutions greater than 4.5M and (iii) concentrations less than 2M had very low tolerance towards tin interference (see later).

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(c) Interferences from other elements

The elements found to interfere were tungsten, iron, copper and tin.

(i) <u>Tungsten</u>.

Tungsten forms a blue-green dithiol complex with an absorption maximum at 630 nm ( Bickford et al, 1948). However interference from tungsten is not a serious problem to overcome, as (i) tungsten (as tungstate) is only slightly soluble in acid, (ii) it reacts only very slowly with dithiol at room Sodium tungstate analysed by the temperature. proposed geochemical procedure but without citric acid (using 0.2g), gave a absorbance equivalent to only 8 ppm of molybdenum. However, it was considered desirable to remove tungsten interference altogether. so that the procedure could be used to determine molybdenum in tungsten ores. This was achieved by the addition of 20mg of citric acid which complexes tungsten, thus preventing the formation of tungsten dithiol. As shown in Table I.13, it was essential to keep the final acid concentration at 2M, as at higher acidities even greatly increased amounts of citric acid, as used by Marshall (1964) and Stanton (1970), does not achieve complete complexing of all the tungsten, and even  $50 \ \mu g$  of tungsten interfered after 10 minutes standing (Stanton and Hardwick, 1967). Citric and the similar tartaric acids have been used to complex tungsten at low acidities in several earlier procedures.

Sodium tungstate (AR) was used in testing interference from tungstate as this gave higher solubility of tungsten than, e.g., calcium tungstate (scheelite) or tungsten (VI) oxide. However as this contained 41 ppm molybdenum (Table I.14), it was

Table I.13

Effect	of	final	acid	l cond	centrati	Lon	on	complexing	of
		tung	sten	with	citric	aci	d		

Sample	Final	acid (14)	molarity	Citric (mo	acid y)	A680/ A630 Absention Ratic
40 ppm molybdenum standard		2		0		1.56
		2		20		1.56
		2		50		1.55
Sodium tungstate (AR)		3		0		0.74
		3		20		0.80
		3		50		0.83
		3		100		0.86
		2.5		0		0.92
		2.5		20		1.30
		2.5		50		1.35
		2.5		100		1.35
		2		0		1.12
		2		20		1.56
		2		50		1.56

necessary to determine how much of the absorption was due to molybdenum. This was done by measuring the A680/A630 ratio for pure molybdenum (1.56) and comparing this with the ratio achieved with sodium tungstate (Table I.13).

Interference from tungsten is seen to be completely eliminated with 20 mg of citric acid. "Specpure" tungsten (VI) oxide was analysed and gave no measurable absorbance (Table I.14).

(ii) <u>Iron</u>. Iron has been said to interfere in a number of ways :

(a) physically, the formation of an iron-dithiol complex (Clark, 1958);

(b) colorimetrically, by the interference of Fe
(III) extracted into the organic solvent (Clark
and Axley, 1955; Baker, 1965; Stanton and
Hardwick, 1967);

(c) by supression of the formation of the molybdenum-dithiol complex (Stanton and Hardwick, 1967);

(d) by enhancement of the absorption of the molybdenum-dithiol complex (Allen and Hamilton, 1952).

(a) Iron (III) forms a black dithiol complex slightly soluble in acid. Its formation is completely suppressed, provided the final acid concentration is less than 3M, by the presence of excess ascorbic acid, which reduces Fe (III) to Fe (II), without reducing Mo (VI). Fe (II) does not form a dithiol complex. Iron (III) if not reduced, may prevent complete formation of the molybdenum dithiol complex if present in sufficient concentration, by utilising all the available dithiol. The iron-dithiol complex is insoluble in isoamyl acetate and hence does not interfere colorimetrically.

Table	I.	14
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Analytical data for replicate determinations of molybdenum

Sample	Number of determinatio	Mean molyb ns conc. (ppm	odenum Range Coeff. ( 1) (ppm) varn. (?	of %)
Fish liver	5	2.4	2.3–2.6 <u>+</u> 6.1	
Clover	10	9.2	8.9-9.3 + 1.5	
Ryegrass	10	3.4	3.2-3.5 ± 3.6	
<u>Olearia</u> ran	i <sup>a</sup> 5	33.0	30.1-36.2 <u>+</u> 7.3	
Soil	10	0.95	0.91.0.97 + 2.1	
Soil <sup>a</sup>	10	10.4	10.1-10.7 + 1.7	
Scheelite c	ore <sup>b</sup> 5	6.5	6.3-6.6 + 2.1	
Copper-lead	ore <sup>C</sup> 5	7.5	6.9-8.2 <u>+</u> 6.8	
A.R. grade tungstate ( Mo)	Sodium 5 <100ppm	41	39-43. <u>+</u> 3.9	
B.S.C. No. Low Alloy S (0.14% Mo)	408 10 teel	1380	1310-1420 <u>+</u> 3.1	

- <sup>a</sup> From area of molybdenum mineralisation, Nelson, New Zealand.
- <sup>b</sup> From area of scheelite mineralisation, Otago, New Zealand.
- <sup>C</sup> From area of copper-lead mineralisation, Coromandel, New Zealand.

(b) Iron (III) will extract in small amounts into organic solvents including isoamyl acetate. Although all Fe (III) is reduced by ascorbic acid in the proposed procedure, some of the small amounts of Fe (II) that may also be extracted can be air-oxidised to Fe (III). However the absorption of the yellow Fe (III) species is negligible at 680 nm; reportedly strong absorption is probably an artifact resulting from the use of spectrophotometers with poor diffraction gratings. The strong Fe (III) absorption peak at 375 nm will show a peak at double this wavelength, viz. 750 nm, if a suitable filter is not used; this "peak" will result in significant absorption over the range 630-850 nm.

(c) Stanton and Hardwick (1967) reported that the presence of 2mg or more of iron reduced the formation of the molybdenum-dithiol complex by approximately 10%, and recommended the addition of iron to standards and samples for the sake of reproducibility. Investigations of this procedure showed that this suppression was due to incomplete reduction of Fe (III) due to the high acid concentration used.

Using the proposed procedure, complete recovery of an added 10 µg molybdenum was obtained from a 0.2g sample of "Specpure" Fe (III) oxide; the oxide alone gave no interference.

(d) Several earlier procedures have stated that the presence of small amounts of iron is essential to obtain complete formation of the molybdenum-dithiol complex (Allen and Hamilton, 1952; Bingley, 1959; Bingley, 1963) and/or that it increases the extinction coefficient of the complex (Piper and Beckwith, 1948; Allen and Hamilton, 1952). However investigation showed that the presence of 2mg Fe(II) did not significantly increase the rate of extraction or formation of the molybdenum-dithiol complex at room temperature, whether the dithiol was added as an aqueous solution or as a solution in isoamyl acetate. It seems probable, therefore, that any affect of iron in earlier procedures was probably of a catalytic nature, as has been proposed by Gilbert (1956).

As stated earlier, then, the proposed procedure is completely free from iron interference of any type.

#### (iii) Copper

Copper (II) interferes with the formation of the molybdenum-dithiol complex by rapidly forming a very stable purplish-black dithiol complex (Clark, 1958), and can therefore, if sufficient copper is present, utilise all the dithiol added. As with the iron (III) dithiol complex, the copper complex is insoluble in isoamyl acetate and hence does not interfere colorimetrically. Simply adding more lithiol does not cure the problem however, as the suspension of copper dithiol at the acid-ester interface can prevent complete formation and extraction of the molybdenumdithiol.

The addition of potassium iodide suppresses copper interference by reducing any Cu (II) not reduced by ascorbic acid to Cu (I), and precipitating it as copper (I) iodide. This method of reducing copper interference has been employed by Stanton and Hardwick (1967) whilst Clark and Axley (1955) and Baker (1965) have employed it instead of ascorbic acid to reduce iron (III). Stanton's method has a toleration of 2mg copper; although it is stated that more can be tolerated by the addition of more potassium iodide (Stanton and Hardwick, 1967), investigation of this procedure showed that this was not the case, due to either the tendency of the ascorbic acid to reduce the iodine formed by reduction of copper (II), back to iodide or the tendency for large amounts of iodide to reduce molybdate to the green MoOCl<sub>5</sub><sup>2-</sup> species (MoV) in strong acid (Jorgenson, 1962). The former case would permit more copper-dithiol to form; the latter would suppress the formation of molybdenum-dithiol.

The proposed procedure permits the complete extraction of molybdenum in the presence of up to 5mg copper (representing 0.5%, 5% and 100% in biological, geochemical and steel samples respectively). For practical purposes then, the procedure may be assumed to be free from copper interference as, if in any of the former cases the limit is exceeded, as for example in copper ores, it is only necessary to reduce the sample size. This is far more convenient than having to extract the copper first, using reagents such as dithizone (Bickford et al, 1948; Piper and Beckwith, 1948) or extracting molybdenum as the benzoinoxime (Jeffery, 1956; Skewes, 1959) or cupferron (Piper and Beckwith, 1948; Allen and Hamilton, 1952) complex before converting it to the dithiol complex.

The proposed procedure, then, has a greater tolerance to copper than earlier procedures, permitting the determination of molybdenum in high-copper samples without prior separation. Some iodine is extracted into the isoamyl acetate, but its absorption at 680 nm is negligible. The absorption should be measured within 2 hours of adding the isoamyl acetate however, as the dithiol is gradually oxidatively decomposed as more iodine is extracted. (iv) <u>Tin</u>.

Like copper, tin interferes by forming a dithiol complex, (Clark, 1958), red in colour, which although insoluble in isoamyl acetate, can prevent the formation of the molybdenum complex by utilising the dithiol, or the extraction by settling at the acid-ester interface. The proposed procedure will permit the complete extraction of molybdenum in the presence of up to 1 mg tin. Although greater tolerance can be achieved by adding more dithiol, (the tin complex is far less stable than that of copper), it is preferable to reanalyse high-tin samples by replacing the 3 cm<sup>3</sup> of potassium iodide solution in the procedure by an equal volume of 8M hydrochloric acid. When this is done, even tin compounds may be analysed for molybdenum, and added molybdenum is completely extracted (Table I.15). Although the red tin-dithiol complex forms after the addition of the dithiol, it decomposes on shaking with isoamyl acetate as the dithiol alone is extracted into the ester; the dithiol is then free to complex the molybdenum.

Other elements that were tested for interference and found to have no effect were As, Sb and Se. \*

4. Experimental

(a) Equipment

A Bausch and Lomb Spectronic 20 spectrophotometer fitted with a red filter and an accessory phototube was used.

A muffle furnace was used for the fusion of geochemical samples and for the ashing of botanical and biological samples. Borosilicate glassware was used throughout. (b) Reagents

Analytical - reagent grade chemicals were used, except for dithiol and isoamyl acetate.

Reducing Solution. Prepare a solution containing 15% (w/V) of ascorbic acid and 2% citric acid in distilled water.

Potassium iodide solution. Prepare a 100% (w/v) solution of potassium iodide in distilled water. Add 0.5% (w/v) ascorbic acid.

<u>Dithiol solution</u>. Add 6 ml of ethanol to 1g of zinc dithiol followed by 10 cm<sup>3</sup> of water, 4g of sodium hydroxide, and 2 cm<sup>3</sup> of thioglycollic acid. Mix well, and dilute to  $300 \text{ cm}^3$  with distilled water. Store in a refrigerator.

Isoamyl acetate. Boiling range 125-142 deg. C.

Standard molybdenum solution. Dissolve 0.1261g of sodium molybdate dihydrate in 4M hydrochloric acid and dilute to 500 cm<sup>3</sup> with this acid to give a solution containing 100  $\mu$ g of molybdenum per ml. From this solution prepare solutions containing 10  $\mu$ g and 1  $\mu$ g of molybdenum per cm<sup>3</sup> in 4M hydrochloric acid.

5. Procedures.

(a) Determination of molybdenum in botanical and biological samples

Weigh 2g of dried material into a test tube (e.g. 150 x 16mm) and ash to completion at 550 deg. C. Allow to cool, weigh (if ash percentage data are required), add 10 cm<sup>3</sup> of 4M hydrochloric acid and heat in a water bath at 80 deg. C. for 15 min. Allow to cool to room temperature ( < 30deg.C) and settle, then transfer 5 cm<sup>3</sup> of the clear solution to a test tube (150 x 16mm). Add 1 cm<sup>3</sup> of reducing solution, mix and allow to stand for 5 min. Add  $3 \text{ cm}^3$  of potassium iodide solution and, mixing after each addition, 1 cm<sup>3</sup> of dithiol solution and allow to stand for 1 min. Add 5 cm<sup>3</sup> of isoamyl acetate, shake vigorously for 60 sec on a vortex mixer, then measure the absorbance of the organic layer at 680 nm within 2hr. If the absorbance is greater that that of the highest standard, repeat using a suitably smaller aliquot from the remaining sample solution, diluting this to 5 cm<sup>3</sup> with 4M hydrochloric acid and continuing from the addition of the ascorbic acid solution.

Standards. Make a series of standards representing 0, 0.2, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 ppm Mo by adding respectively to 10 test-tubes 0, 0.2, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 µg Mo. Dilute to 5 cm<sup>3</sup> with 4M hydrochloric acid and continue from the addition of the ascorbic acid solution.

# (b) Determination of molybdenum in geochemical samples

Weigh 0.2g of sample (-100 mesh) into a test tube, add 1g of potassium hydrogensulphate and mix. Fuse at 500 deg. C. for 10 min., or alternatively fuse over a Bunsen flame until a quiescent melt is obtained and continue heating for a further 2 min. Leach in a water bath with 10 cm<sup>3</sup> of 4M hydrochloric acid at 80deg.C. until the melt can be broken up with a glass rod. Allow to cool to room temperature ( < 30deg.C) and settle. Transfer 5cm<sup>3</sup> of the clear solution to a test tube (150 x 16 mm), and continue as above from the addition of the ascorbic acid solution. Standards. Make a series of standard representing 0, 2, 5, 10, 25, 50, 75, 100, 150 and 200 ppm Mo by adding respectively to 10 test tubes 0, 0.2, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 150.0 and 20.0 µg Mo. Dilute to 5 cm<sup>3</sup> with 4M hydrochloric acid and continue from the addition of the ascorbic acid solution.

(c) Determination of molybdenum in steels

Dissolve 0.2g of sample in 5 cm<sup>3</sup> of a 1:1 mixture of concentrated hydrochloric and nitric acids, taking to dryness over a boiling water bath. Add 2 cm<sup>3</sup> of nitric acid and again take to dryness. Heat the residue with 10 cm<sup>3</sup> of 4M hydrochloric acid for 10 min at 80deg.C., then cool, make up to 10 cm<sup>3</sup> with distilled water, and centrifugate. Transfer 0.25 cm<sup>3</sup> of the clear solution to a test tube (150 x 16 mm), add 4.5 cm<sup>3</sup> of 4M hydrochloric acid, and continue as above from the addition of the ascorbic acid solution.

#### Standards.

Make a series of standards representing 0, 40, 100, 500, 1000, 1500, 2000, 3000 and 4000 ppm Mo by adding respectivity to 10 test-tubes 0, 0.2, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 15.0 and 20.0 µg Mo. Dilute to 5 cm<sup>3</sup> with 4M hydrochloric acid and continue from the addition of the ascorbic acid solution.

6. Testing of method.

(a) Reproducibility and recovery tests

Table I.14 shows the results of replicate analyses of various samples by the proposed procedure.

Recovery of molybdenum added to all types of samples was complete within the precision of the method (Table I.15).

The U.S. Geological Survey standard sample G--1 and W-1 were analysed by the proposed procedure with
Sample	Mo present (µg)	Mo added (µg)	Mo found (µg)	Coeff. of varn. (%)
Clover	9.2 <sup>a</sup>	10.0	19.2	+ 0.8
Ryegrass	3.4 <sup>a</sup>	10.0	113.3	+ 1.0
Soil	0.09 <sup>a</sup>	10.0	10.1	+ 2.0
Granite	0.13 <sup>b</sup>	10.0	10.1	+ 1.5
Scheelite ore	0.65 <sup>b</sup>	10.0	10.7	<u>+</u> 1.3
"Specpure" WO3	0.00 <sup>b</sup>	10.0	10.0	<u>+</u> 0.5
A.R. grade tin (II) chloride	0.00 <sup>b</sup>	10.0	9.9	<u>+</u> 1.9
B.C.S. No. 408 Low alloy steel	69 <sup>a</sup>	10.0	78.5	+ 2.3

# Table I.15

Molybdenum recovered from various samples

<sup>a</sup> Mean of 10 determinations

<sup>b</sup> Mean of 5 determinations.

mean values of 6.2 and 1.3 ppm respectively being obtained. These values are in satisfactory agreement with the neutron activation results of Hamaguchi et al. (1962), who reported 7.0 ppm for G-1 and 1.3 ppm for W-1.

### (b) Sensitivity

The proposed procedure allows for the determination of 0.05, 0.5 and 10 ppm in botanical, geochemical and steel samples respectively. Sensitivity may be increased 10-fold if required by using only 0.5  $\rm{cm}^3$ of isoamyl acetate in conjunction with micro-cells. Beer's law is obeyed over the range used. Α standard curve is shown in Fig. I.12. 1-13

(c) Productivity

If fusions are done in a furnace, up to 150 geochemical samples can be analysed per man day. while ashed biological and botanical samples may also be analysed at this rate. The procedure described for ashing and dried vegetation involves a minimum of labour and enables large numbers of samples to be treated simultaneously.

### 7 Conclusions

It is concluded that, in terms of rapidity, recovery, and particularly versatility, the procedure developed represents a significant improvement over existing colorimetric methods for the determination of molvbdenum.

Tolerance to interference has also been markedly improved.



Fig. I.13. Standard curve for colorimetric determination of molybdenum.

### C. OTHER ELEMENTS

#### 1. Introduction

Of the other elements analysed by the writer in the following investigations, potassium and sodium were determined by flame photometry, using a Gallenkamp Model FH 500, while aluminium, barium, bismuth, calcium, chromium, copper, iron, lead, manganese, magnesium, strontium, tin, titanium and zinc were determined by atomic absorption spectrometry, using a Varian Techtron Model AA5.

Although once the sample is in solution the determination of all these elements is largely routine, the dissolution of both geochemical and plant samples required some investigation.

2. Treatment of geochemical samples

(a) Preliminary treatment

Samples collected in the field were stored in sealed plastic bags for transportation. Soils were partially air-dried in the laboratory, lightly crushed to separate aggregated particles, then sieved through a 20 mesh nylon sieve. The coarse fraction was discarded, and the remainder dried completely. Total soil analyses were performed on this fraction after complete grinding by hand to - 100 mesh, again using a nylon sieve, while - 100 mesh fraction analyses were performed after removal of this fraction.

Rock samples were hard ground to -100 mesh for analysis.

(b) Dissolution procedure

There has been much discussion over recent years on the methods for dissolving soils and rocks. Ahrens <u>et al</u> (1963) described a detailed procedure based on ion -exchange and emission spectrographic techniques for the analysis of silicate rocks. This scheme used a hydrofluoric / aqua regia / sulphuric acid attack and gave complete dissolution although successive treatment was necessary for some samples.

Suhr and Ingamells (1966) described a solid fusion technique for the dissolution of silicate rocks using lithium tetraborate followed by dilute nitric acid. Solid fusion methods, however, are not readily applicable to the preparation of samples to be analysed for trace metals by atomic absorption spectrophotometry due to the high salt content arising from the fusion mixture.

Probably the most efficient method is a high temperature attack using concentrated hydrofluoric acid in a Teflon lined bomb (Langmhyr and Paus, 1968). While this method gives complete dissolution it is impractical for large numbers of samples. On the other hand, the most common acid mixture used by mining companies for soils and rocks is that of concentrated perchloric and nitric acids. This does not, in general, give complete dissolution, but if the extent of the attack is the same for all samples, the results will be reasonably reliable.

In our laboratory, a modification of the procedure described by Brooks (1960) has been used for several years (Cohen, 1969; Lyon, 1969; Whitehead, 1970; Timperley, 1971; Quin, 1972; Severne, 1972). Soil and rock samples are treated with 1:1 concentrated hydrofluoric and nitric acids in polypropylene beakers suspended in boiling water. The flow chart for the complete analysis by this technique is shown in Fig. I.14. The procedure results in virtually complete dissolution of soils, with the remaining metals in the residue (analysed by emission spectrography) being traces of titanium and iron



Fig. I.14. Flow sheet for dissolution and analysis of geochemical and plant samples.

(presumably from magnetite and/or titanomagnetite), and chromium (probably from chromite which is virtually insoluble under these acid conditions).

A far more serious problem was posed by the periodic presence of calcium and magnesium in the residue. The was not due to incomplete dissolution of the sample but rather to precipitation of the metals as their very insoluble fluorides as the last of the acid was evaporated. Investigation showed that this problem could be circumvented by the addition of a small amount  $(0.25 \text{ cm}^3)$  of the high boiling point perchloric acid to the digestion mixture. This had the effect of preventing the residue from coming completely to dryness, and hence all the fluoride was evaporated. The small volume of perchloric acid used did not cause any interference during atomic absorption determinations.

3. Treatment of plant samples

(a) Preliminary treatment

On arrival at the laboratory, plant samples were removed from their plastic bag containers and dried for 24 hours at 95 deg. C.

Although soil contamination is a possible source of error in plant analysis (Mitchell, 1960) this was assumed to be of very minor importance in the areas surveyed since there was little exposed soil, except at Glenorchy. For this reason, plants were not washed before drying except where circumstances made this necessary.

(b) Ashing techniques

There are two main methods for the dissolution of plant material :

(i) dry ashing at 450 - 600 deg. C. in a muffle furnace followed by dissolution of the ash in dilute hydrochloric or nitric acids, and (ii) wet ashing with mixtures of nitric and perchloric acids at approximately 100 deg. C.

If volatile metals such as arsenic, selenium or mercury are to be determined, it is necessary to use the wet method since these metals are all vaporised to varying extents even at 450 deg. C. Other less volatile metals such as lead, zinc and cadmium can also be lost during dry ashing (Mitchell, 1964), but this is very dependent on the sample (Macuta etal, 1970). For example, the presence of large amounts of chloride increases the losses of many metals by the formation of volatile chlorides, while the presence of phosphate reduces losses. However Giron (1973) found that dry ashing at 550 deg. C. gave more reproducible results than wet ashing for calcium, copper, iron, manganese, magnesium, potassium, sodium and zinc in plants.

If low levels of metals in plants are to be determined, then wet ashing has the disadvantage that the concentrated acids must be of exceptional purity to avoid excessive contamination of the sample. Acid blanks can only be used to successfully correct for this contamination if the sample contains appreciably more of the element than the blank.

Furthermore, the large amounts of perchloric or nitric acids remaining in the solution after wet ashing may cause interference during the atomic absorption determinations, (Govindaraju, 1970; Maruta <u>et al</u>, 1970). With dry ashing however, the ash is usually dissolved in dilute hydrochloric acid which results in negligible contamination of the sample.

For these reasons, dry ashing at 500 deg. C. was used in preference to wet ashing. A flow sheet for the plant analysis procedure as shown in Fig. I.14. This method resulted in approximately 98% dissolution (assuming all carbonaceous material had been removed by ashing), and the remaining 2% was shown to be composed almost entirely of silica (emission spectrographic analysis).

### 4. Interferences

## (a) Chemical interferences

Few serious chemical interferences were found ; the chief problems arose in the measurement of calcium, magnesium, potassium and sodium (Ramakrishna, et al, 1966; Govindaraju, 1970). In plant samples most of the interference with the determination of these elements is caused by phosphate, while in soil solutions the interference arises mainly from aluminium, iron and phosphate. Organic complexing reagents have been used to counteract this problem (Wallace, 1963; Govindaraju. 1970) but most of the interference can be reduced to an acceptable level by adding excess strontium nitrate to the solution (En'well and Gidley, 1967). In the present work, a solution of 0.8% strontium nitrate (0.33% Sr) was used. Alkali metals can also cause interferences in the determination of calcium and magnesium due to ionisation effects (David, 1959) but these were largely overcome by using mixed standards of the metals.

(b) Scattering and non-atomic absorption

The reflection by solid particles in the flame of incident radiation from the lamp away from the slit, thus causing an apparerent absorption, is called "scattering". This and non-atomic absorption, the absorption of incident radiation by molecules in the flame, were both corrected for by rerunning samples with the hydrogen lamp, and subtracting this from the total absorption. As this problem is greatest at short wavelengths, only elements with absorption lines below 2700 A needed to be redone this way.

# 5. Conditions used in atomic absorption determinations

Table I.16 lists the conditions employed for the elements determined by atomic absorption spectrophotometry.

# 6. Accuracy and reproducibility of the dissolution and analytical methods

To evaluate the accuracy and reproducibility of the methods used, five standards of the standard diabase W-1 were interplaced at random in a batch of 30 rock samples. This procedure led to a Croce estimate of the precision actually obtained during a normal dissolution and analytical sequence. The results are shown in Table I.17.

For all elements, accuracy and reproducibility was good and adequate for this project. Similar reproducibility was obtained for plant samples.

### 7. D.S.I.R. analyses

Total nitrogen and nitrate - nitrogen analyses of plant material were carried out by Grasslands Division, D.S.I.R., Palmerston North. Nitrogen was determined colorimetrically with phenol, after Kjeldahl digestion, on a Technicon Auto-Analyser. Nitrate nitrogen was determined colorimetrically by reaction with sulphanilamide and naphthyl - ethylene diamine after hydrazine reduction.

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Element	Wavelength nm	Flame	Strontium present	Hydrogen lamp correction used	Notes
aluminium	309.3	N20-C2H2	no	no	
barium	553.5	air-C2H2	no	no	atomic emission
bismuth	223.1	air-C <sub>2</sub> H <sub>2</sub>	no	yes	determination
calcium	422.7	air-C <sub>2</sub> H <sub>2</sub>	yes	no	
chromium	357.9	air-C <sub>2</sub> H <sub>2</sub>	no	no	fuel-rich
copper	324.7	air-C <sub>2</sub> H <sub>2</sub>	no	no	flame used
iron	248.3	air-C <sub>2</sub> H <sub>2</sub>	no	yes	
lead	217.0	air-C <sub>2</sub> H <sub>2</sub>	no	yes	
manganese	279.5	air-C <sub>2</sub> H <sub>2</sub>	no	no	
magnesium	285.2	air-C <sub>2</sub> H <sub>2</sub>	yes	no	
strontium	460.7	air-C2H2	no	no	
tin	235.5	air-H <sub>2</sub>	no	yes	
titanium	364.3	N <sub>2</sub> 0-C <sub>2</sub> H <sub>2</sub>	no	no	
zinc	213.9	air-C2H2	no	yes	

Table I.16Details of conditions for atomic absorption spectrometry

Analysis of standard diabase W-1

Element Average (p.p.m.)		Coeff. varn. (%)	Accepted value (p.p.m.) <sup>a</sup>		
aluminium	84,800	<u>+</u> 4.5	78,600		
barium	190	<u>+</u> 5.1	180		
bismuth	<10	-	0.2		
calcium	76 500	+ 2.7	75,000		
chromium	128	+ 3.0	120		
copper	115	<u>+</u> 1.6	110		
iron	80,100	+ 2.1	79,100		
lead	8.7	<u>+</u> 6.0	8		
magnesium	39,100	+ 3.1	38,800		
manganese	1450	+ 3.9	1 320		
potassium	- 5150	<u>+</u> 1.9	5230		
sodium	15,800	+ 1.2	15,400		
strontium	180	+ 4.2	180		
tin	3.5	<u>+</u> 6.7	3		
titanium	7200	+ 5.5	6400		
zinc	93	<u>+</u> 1.9	82		

<sup>a</sup> From Fleischer (1970)

THE TRACE ELEMENT COMPOSITION OF NEW ZEALAND SCHEELITES

SECTION II

### A. INTRODUCTION

The three most important areas for scheelite production in New Zealand have been at Glenorchy and Macrae's Flat in Otago, and the area to the north of the Wairau Valley in Marlborough. In the Otago area. scheelite is found in quartz lodes associated with minor amounts of sulphide, calcite, and a little The mineralogy of the Marlborough veins is gold. similar to that of the Otago veins and in both areas the country rock is a low grade regionally metamorphosed schist of the chlorite grade. Α summary of the data on the chemistry, mineralogy and genesis of these scheelite occurrences was given by Williams (1965). This summary reveals the almost complete lack of chemical data on the scheelite. Barraclough and Reay (1970) analysed scheelites from these areas for strontium magnesium and iron by atomic absorption spectrometry. Attempts to detect cobalt, chromium, lead, manganese, molybdenum, nickel and tellurium were unsuccessful due to the insensitive procedures used.

There are even less data available on the scheelite from the smaller deposits at Canaan in Nelson and at Barrytown on the West Coast. At Canaan, the scheelite occurs at a granite-marble contact, while at Barrytown, granite and greywacke form the country rock.

This study was undertaken to help remedy this lack of information, with the main aim of detecting the presence of any undesirable concentrations of impurities. Returns for ore are proportionally greater for the richer and purer the concentrates. Buyers of ore generally specify the levels of impurities at which they impose penalties, and the

levels at which they reject the ore. A typical Japanese specification is shown in Table II.1.

The second aim of this study was to determine whether chemical analysis would be of use in the correlation of scheelite lodes in the complex Glenorchy area.

B. ANALYSIS OF SCHEELITE

Analysis of scheelite

 (a) Purification

Scheelite was separated from quartz gangue by hand picking under ultra-violet light, followed by grinding to -100 mesh and centrifuging in pure bromoform. The quartz was then decanted off with the bromoform, and the scheelite residue taken to dryness.

### (b) Chemical analysis

To test the purity of the concentrates, tungsten was determined on all samples by atomic absorption spectrometry using the method described in Section I.A1. Samples were concentrated to 80% MO<sub>3</sub>. Molybdenum was determined colorimetrically using the method described in Section I.B. Of the other metals, potassium and sodium were determined by flame photometry, and all others by atomic absorption spectrometry, using the conditions described in Section I.C.

### C. RESULTS AND DISCUSSION

1. Levels of impurities in scheelites

The scheelites varied in colour from light cream to pale brown. However the fluorescence colour of all samples was a blue white, probably due to the low manganese and molybdenum contents (Greenwood, 1943).

Table II.2 shows the levels of penalisable, and other, metal impurities in the scheelites. The extremely high purity of the ores is immediately

# Typical Japanese tungsten ore specification

Constituent	Levels of some individual constituents at which penalties begin (%)	Levels which result in rejection of ore (%)
Bi	0.1	0.5
Cu	0.04	0.2
Fe	1.0	3.0
Mn	0.7	-
Mo	0.02	0.07
Sn	1.5	1.6

Average concentrations of penalisable and other metallic impurities in scheelites (p.p.m.)

Location	Number of		Penalisable impurities				Other impurities						
	samples	Bi	Cu	Fe	Mn	Мо	Sn	A1	Cr	Pb	Mg	Ti	Zn
Glenorchy	16	< 10	45	280	65	7.2	21	390	<1	13	80	5	35
Bendigo	3	< 10	30	3	3	5.2	12	410	×1	7	17	6	15
Macrae's Flat	4	~10	35	1150	30	4.5	12	490	<1	26	660	80	95
Wairau Valley	3	~10	1.5	1	1	6.0	55	80	< 1	10	15	< 5	23
Barrytown	4	-10	35	50	20	5.2	12	4	<1	30	16	< 5	10
Canaan	4	:10	35	400	5	6.4	11	120	<1	135	750	11	10

apparent. An early paper by Finlayson (1908) had a detrimental effect on scheelite exploration because he reported the presence of "distinct traces of molybdenum in varying quantities up to one per cent". The presence of molybdenum causes difficulties in the refining of the tungsten and hence reduces the price of the concentrate. However Barraclough and Reay (1970) could not detect molybdenum in scheelites from Glenorchy, Macrae's Flat, and Marlborough (detection limit 100 ppm) and the data in Table II.2 show that all New Zealand scheelites are virtually free of molybdenum. There is therefore no basis whatsoever for Finlayson's statement.

As with molybdenum, the concentrations of bismuth, copper, iron, manganese and tin are well below the penalisable levels in all samples. Furthermore, most of the small amount of iron is probably present as iron sulphide, rather than as a constituent of the scheelite lattice.

2. Correlations between lodes

(a) Introduction

The high strontium content of some New Zealand scheelites has been noted by Barraclough and Reay (1970), who discovered the possibility of dividing them into groups on the basis of their strontium content. These groupings coincided with the geographic groupings of the scheelite areas and reflected the metamorphic zones in which the scheelite occurs. However they found the strontium content to be too variable to distinguish between lodes within the Glenorchy field. However in the course of this investigation it was found that the scheelites also contained considerable amounts of of barium, and that the Sr/Ba ratio could be more reliably used to distinguish lodes.

Calcium and strontium diadochy in natural scheelites, although uncommon, does occur elsewhere. Vermaas (1952) reported the presence of 0.38% Sr in a South African scheelite, and the larger radius of the Sr  $^{2+}$  (1.13Å compared to 0.99Å for ca $^{2+}$ ) was presumed by Barraclough and Reay (1970) to be responsible for the increased lattice parameter.

However the results of the investigation have demonstrated that Ba can also substitute for Ca in scheelite at equivalent concentrations to that of Sr, and hence the much larger Ba  $^{2+}$  ion (radius 1.35Å) Would have considerably more effect on the lattice parameters than would Sr  $^{2+}$ . That this is so for artificial compounds has been demonstrated for in an early paper by Sullen and Nylander (1943).

(b) Results and discussion

Strontium and barium contents of some New Zealand scheelites are shown in Table II.3. A number of features of the analyses are worthy of comment. The granite areas of Barrytown and Canaan are notable for their low strontium content. The Wairau Valley (Marlborough) scheelite, although occuring in low grade regionally metamorphosed schist similar to that at Glenorchy and Macrae's Flat, is markedly lower in both strontium and barium.

Of more direct interest are the Sr/Ba ratios for two of the main Glenorchy lodes, namely the state and Sunshine lodes. The former is slightly lower in strontium and higher in barium, although the differences are barely significant. The Sr/Ba ratios

· · · · · · however, are significant, and it is concluded that, with more intensive sampling this ratio could be used to determine what mine localities belong to what lodes, a question which, because of the structural complexity and lack of marker horizons, has never been satisfactorily answered.

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Table	II	• 3

Strontium	and	barium	contents	10	New	Zealand	scheelites

Locality	No. of samples	Sr(%)	Ba (%)	Sr/Ba
	*******			na ana amin'ny kaodim-paositra dia mampika mpikambana amin'ny fisiana amin'ny fisiana amin'ny fisiana amin'ny f
Glenorchy				
state lode	6	0.11 <u>+</u> .02	0.16 <u>+</u> .03	0.69 <u>+</u> 0.10
Sunshine lode	6	0.13 + .02	0.13 <u>+</u> .02	1.00 <u>+</u> 0.07
Overall	16	0.12 + .05	0.15 <u>+</u> .06	0.8C <u>+</u> 0.25
Bendigo	3	0.17	0.15	1.13
Macrae's Flat	4	0.17	0.15	1.13
Wairau Valley	3	0.01	0.02	0.50
Barrytown	4	0.005	0.16	0.03
Canaan	4	0.029	0.09	0.22

### SECTION III

GEOCHEMICAL AND BIOGEOCHEMICAL EXPLORATION FOR TUNGSTEN AND MOLYBDENUM

### A. INTRODUCTION

1. Tungsten

There is little published work in existence dealing with geochemical, and particularly biogeochemical, exploration for tungsten. Most papers on exploration have dealt solely with the use of soil and stream sediment sampling to locate general areas of mineralisation (e.g. Hosking, 1970; Varlamoff, 1970); there have been few attempts to actually locate deposits using soil and/or plant analysis. The first recorded biogeochemical exploration was carried out in the late 1930's by Palmquist and Brundin. They discovered that trees and shrubs growing on high tungsten soils in Cornwall, England contained anomalous amounts of this element. Little of their work was published, apart from a procedure describing the sampling and analytical technique used (Brundin, 1939). In later years, several Russian works referred to the possibility of using biogeochemical exploration for tungsten (Vinogradov, 1954; Malyuga, 1964; Kabiashvili, 1964), but to the authors knowledge it was not until 1966 that an investigation was carried out (Kovalevsky, 1966) to determine if plant analysis could be used to locate individual deposits. Kovalevsky found that, although W concentrations in the plants did not correlate well with those in the soil (he assumed this to be caused by the irregular dissolution of tungsten in the soil profile), the highest concentrations of tungsten in the woody parts of Pinus sibirica were found in trees growing over tungsten - bearing veins and veinlets. He concluded that branches and trunks rather than leaves should be sampled, and that sampling points should be no more than 5-10m apart to avoid missing individual veins. Unfortunately, he

did not give any indication of the relative success of soil sampling for locating veins.

The results of Kovalevsky , work indicated the potential of using vegetation analyses as a means of prospecting for tungsten, and earlier work by the writer confirmed this. Pot trials with silver beech (Quin. 1972; Quin. Brooks and Reay. 1972) showed that the concentration of tungsten in the plant organs does give a reasonable prediction of that in the soil. provided that soil properties (eg pH) are constant and that the tungsten is evenly distributed throughout In field work at Barrytown, (Quin, 1972; the soil. Quin and Brooks, 1972) it was found that, whilst the concentration of tungsten in tree fern leaves correlated closely with the concentrations in the soil, this was not the case with trees. Investigation showed that this was caused largely by the uneven distribution of tungsten in the soil. Tree ferns because of their shallow and restricted root system. would derive minerals from a small area and from depths approximating those of soil sampling. The root systems of trees, however, encompasses a large volume of soil ; a single soil sample taken from the vicinity of the tree is therefore not always representative of the soil "sampled" by the tree roots. Finally, the feasibility of using trunk sampling to locate tungsten bearing veins under soil cover was briefly investigated, with promising results (Quin, 1972).

In this work, further investigations were carried out firstly, to compare the relative efficacy of soil and plant sampling for locating tungsten deposits in areas with differing geological, vegetational, climatic and topographical environments, and secondly, to investigate the feasibility of

of using trend surface analysis of tungsten concentrations in tree trunks to locate extensions of known scheelite - bearing reefs. The results of these investigations are described in this section.

### 2. Molybdenum

In contrast to tungsten the literative contains a great number of papers dealing with geochemical and biogeochemical exploration for molybdenum. Geochemical exploration has also been extensively discussed in several books (Hawkes, 1957; b@inzburg, 1957; Vinogradov, 1959; Hawkes and Webb, 1962; Brooks, 1972) and reviews (Bloom, 1966; Davy, 1973), while biogeochemistry has also been discussed in review papers/books (Carlisle and Cleveland, 1958; Cannon, 1960; Malyuga, 1964; Chikishev, 1965; Fortescue, 1970; Cannon, 1971; Davy, 1973 ) and books (Ginzburg, 1960; Hawkes and Webb, 1962; Brooks, 1972).

The following points appear to have been widely accepted. Stream sediment or soil sampling are the most applicable methods where molybdenum ore is exposed or near the surface. Biogeochemical prospecting will be most appropriate when molybdenum ore is shallowly based. Oxidising and alkaline conditions also favor the use of biogeochemical exploration, as molybdenum is then present as soluble molybdate, which is readily taken up by plants.

In New Zealand, soil and plant sampling were shown to delineate similar anomalous areas at an area of molybdenum mineralisation at Takaka, Nelson (Brooks and Lyon, 1966; Lyon and Brooks, 1969). However no New Zealand work has been published dealing with the suitability of using biogeochemical prospecting

where deep soil cover and other factors such as leaching preclude the use of soil sampling. Because of this, a brief investigation was carried out at an area of molybdenum mineralisation at Canaan, Nelson. The results of the work are described in this section.

#### B. TUNGSTEN

 The detection of scheelite-bearing orebodies by the analysis of plants and soils

(a) Introduction

Previous work by the writer (Quin, 1972) had been confined to a single area of tungsten mineralisation at Barrytown, on the west coast of the South Island. However, tungsten, as scheelite, is spread widely throughout the South Island in areas differing widely in their geological, vegetational,climatic and topographical environments. The South Island therefore offered an ideal opportunity to test the suitability of plant and soil sampling for locating tungsten deposits under a wide range of conditions.

### (b) Description of test areas

Investigations were carried out at the following areas : Glenorchy (West Otago), Paradise (West Otago), Macrae's Flat (East Otago), Top Valley (Marlborough), Barrytown (Westland) and Canaan (Nelson). The test areas can be divided into two broad groups on the basis of their lithology. Fig. 0.1 shows the general location of the test areas while Fig. III.1 shows each of them in some detail.

# (i) Glenorchy, Paradise, Macrae's Flat and Top Valley

The areas of this group are all underlain by the mica-schists of the New Zealand geosyncline (Fig.O.1) which probably had its beginnings in the carboniferous or early Permian. The soils have been formed largely in situ from this schist and belong chiefly to the "brown-grey" classification. The vegetation at the Macrae's Flat area is mainly native indigenous tussock

## Fig. III.1 Detailed maps of test areas

a Glenorchy (after Williams, 1965)
 b Paradise (provided by A.R. Mutch)
 c Macrae's Flat (after Williamson, 1939)
 d Wairau Valley (provided by R.G. Whitehead)
 e Barrytown
 f Canaan (after Williams, 1959)



grass species (chiefly <u>Festuca novae</u> - <u>zelandiae</u> and <u>Chionochloa rubra</u>). These and several introduced grass species were present at Glenorchy, as well as some manuka (<u>Leptospernum scoparium</u>). Bracken (<u>Pteridium aquilinum</u>) is dominant at the Top Valley and Paradise test areas, although mixed grass species and manuka are also common at the latter area.

Although plant growth is dow in the above areas, due to low rainfall (Table III.1), there is also little loss of nutrients from the soils, which are generally quite fertile, and have an average pH of 6 (Table III.1). The top 15 cm has a characteristic browngrey colour and contains an abundance of organic matter. The topography of these areas is relatively gentle at Macrae's Flat and Paradise, whereas the terrain at Glenorchy, Top Valley is somewhat more hilly.

### Description of mineralisation

The scheelite mineralisation in these areas generally occurs sporadically in lodes of least several hundred metres length, with minor associated mineralisation such as gold, sulphides and calcite being present.

All four areas have been mined sporadically during the past century, generally on a small scale.

The Glenorchy lode was discovered in the 1880s by the tracing of alluvial scheelite in the Buckler Burn to its source (Fig. III.1a). Mining at Glenorchy has persisted longer than anywhere else in New Zealand. The scheelite workings are mainly in rocks of the chlorite-3 subzone as described by Hutton (1940). The material within the lodes comprises lode schist containing ubiquitous pyrite and arsenopyrite crystals, and quartz lenses with flattened scheelite ore shoots.

Locality	Average annual	Sc	oil pH
	rainfall (cm)	average	range
Glenorchy	110	6.0	5.1 - 6.7
Paradise	110	5.9	5.3 - 6.6
Macrae's Flat	60	6.1	5.8 - 6.4
Top Valley	100	5.0	4.8 - 5.4
Barrytown	270	4.6	4.3 - 4.9
Canaan	190	5.0	4.1 - 5.5

# Table III.1

Rainfall and soil pH data for the test areas

In many places the quartz is lacking and the scheelite then occurs peppered throughout bands of crushed schist (Mutch, 1969).

The Paradise lode was discovered in 1915, and represents a very strong structure containing two reefs which merge at depth (Williams, 1965), Fig. III.1b. The lode channel is filled with masses of broken and crushed schist containing lenses and veins of quartz, which carry scheelite, calcite and sulphides (Henderson, 1937).

Mining at Macrae's Flat (Fig. III.1c) probably commenced prior to 1875 (Williams, 1965). The quartz averages 0.6 m in width and mullock makes up perhaps 60 per cent of the filling. There is some calcite gangue, pyrite and arsenopyrite are common and chalcopyrite occurs sparingly. Some gold is associated with the sulphides and with the brecciated schist within the lode walls, and some is free in the quartz. Scheelite occurs as veinlets running through the quartz (Williams, 1965).

The Jubilee gold-scheelite lode in the Top Valley of the Wairau Valley (Fig.III.1d) was discovered in 1889 (Williams, 1965). Downey (1928) recorded six separate lodes in the basin of Top Valley stream. After an interval of fifty years, work has recently recommenced in the area.

(ii) Barrytown and Canaan

These areas of this group are both underlain by predominantly granitic (possibly Precambian) material. The soils derived from this slow-weathering substrate have a low pH (Table III.1) and are relatively infertile, particularly near the ridges and spurs at Barrytown, presumably as a result of the leaching of nutrients by the high rainfall (Table III.1) The topography of these areas is rugged, particularly at Barrytown, where the altitude increases from approximately 30 m to 500 m over a distance of 2 km (Fig. III.1e).

The vegetation of these high-rainfall areas is predominantly New Zealand beech (Nothofagus spp). Kamahi (<u>Weimannia racemosa</u>) is also very common at Barrytown. Chief understory species are <u>Quintinia</u> <u>acutifolia</u> and <u>Myrsine salicina</u> at Barrytown, and <u>Griselinia littoralis</u>, <u>Macropiper excelsum</u> and <u>Cordyline australis</u> at Canaan (Fig. III.1f). In both areas, the forestfloor is covered in a rich growth of ferns such as the ubiquitous crown fern (<u>Blechnum discolor</u>).

### Description of mineralisation

The mineralisation at these areas occurs in and associated with discontinuous quartz reefs. The tungsten mineralisation at Barrytown was discovered in 1970, and consists mainly of scheelite with a little wolframite existing in a series of quartz veins containing discrete crystals, and as scheelite disseminated in greisen veins and veinlets. The quartz veins appear to have a strike length of 30 - 70 m, with a maximum width of 0.7 m, and tend to occur in swarms containing 10-40 veins over a width of 2-3 m (Quin, 1972). Associated mineralisation is confined mainly to arsenopyrites.

The scheelite-bearing reefs at Canaan were discovered in 1956 by Mr. E.J. Sixtus, and represent the first discovery of this mineral at or near the granite-marble contacts in Nelson. The mineral occurs mainly in discontinuous quartz reefs in both granite and diorite (Williams, 1959). Within the quartz,

scheelite normally forms irregular nodules and streaks, and occasionally crystals enclose calcite. It is commonly accompanied by abundant fine-grained white mica.

### (c) Field work

Field work was all carried out in the late summers (February/March) of 1972 and 1973 in order to avoid seasonal variations in plant composition. In any case, seasonal variation was not expected to be significant in the low rainfall areas of the first group, and the nutrient composition of the beech species, which in New Zealand are evergreen, has been shown to be fairly constant particularly in the late summer, autumn, and winter (Miller, 1963; Timperley, 1971).

At each area, the positions of the chosen reefs were located from outcrops and a soil and plant-sampling transect was carried out across each reef at some distance (>20 m) from the nearest outcrop. The assumed position of the reef was designated with a zero coordinate; sampling was continued, at 5-10 m intervals, 50 m on either side of the reef in a direction perpendicular to the strike.

The transect at Glenorchy was carried out down a slope of approximately 20deg. and began above the Kelly lode and continued across the State lode some 100 metres below it. At Paradise, two transects were made across the western lode, both were on gently undulating ground. The transect across the Deepdell lode at Macrae's Flat sloped at a gentle 5deg, whilst that at Top Valley was at 25 deg. The Barrytown and Canaan areas provided additional problems in that the presence of tree species meant that (i) it needed to be decided whether it would be best to sample trunk wood, leaves or twigs, and (ii) whether the many species present could be grouped together for exploration purposes.

To solve these problems, samples of trunk wood, leaves and twigs were collected from the commonest species present at randomly selected sites. The results (Table III.2) show that firstly, trunk wood almost invariably contained the highest concentrations of tungsten, especially at Barrytown, thereby making it the most useful organ for sampling. Secondly, the Biological Absorption Coefficient, or BAC (Brooks. 1973), defined as the concentration of an element in the plant ash divided by that in the soil was remarkably constant for different species; different species at one area showed less variation in the BAC for tungsten than did the same species at different Hence it was concluded that, for the purposes areas. of biogeochemical exploration, the different tree species present at a particular area could be grouped This finding is of considerable together. importance, as much previous biogeochemical exploration has been severely restricted because of an (unnecessary)

insistence on sampling only a small number of species, which in many cases would not be present at the area to be investigated.

Following this preliminary investigation, two transects were carried out at Barrytown across the suspected position of a mineralised reef, both transects being carried out across a hillside. Tungsten samples were collected without regard to species type. Wood was taken from the outer trunk after removal of the bark.

Table	III.	2
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Tungsten BAC values for trees from Barrytown and Canaan

		and the second se				
Location	n Species	Number of		BAC value		
		samples	trunk	leaves	twigs	
Barrytown	Nothofagus menziesii	27	0.16	0.03	0.03	
,	N. truncata	53	0.13	0.03	0.02	
	N. fusca	15	0.12	0.03	0.02	
	Veinmannia racemosa	53	0.12	0.03	0.03	
	Quintinia acutifolia	30	0.14	0.02	0.03	
	Myrsine salicina	42	0.15	0.04	0.02	
Canaan	Nothofagus menziesii	15	0.25	0.20	0.22	
	N.truncata	20	0.31	0.20	0.24	
	N. fusca	8	0.28	0.19	0.24	
	Weinmannia racemosa	28	0.25	0.24	0.28	
	Pseudowintera colora	ta 15	0.18	0.20	0.27	
	Coprosma rugosa	15	0.26	0.26	0.27	
	Dracophyllum townson	ii 12	0.32	0.26	0.25	
Three separate reefs were worked on at Canaan, the transects across these were at 20deg, level and 45deg respectively. Trunk wood samples are collected, again without regard to species type, as well as leaves from the fem <u>Blechnum nigrum</u>. At all areas, soil samples (500g) were taken from the upper B horizon at each plant sampling site.

(d) Chemical analysis

Tungsten in soils and plant ash was determined colorimetrically with dithiol (Quin, 1972).

(e) <u>Results</u>

(i) Glenorchy

Because of problems of identification of the many species of native and introduced grass present, a composite sample of all species growing at each site was collected. As seen in Fig. III.2a, the tungsten levels in both the soil and composite grass samples accurately indicated the presence of the Glenorchy State lode and the smaller Kelly lode. At the former lode, the anomaly as indicated by the grass was considerably greater than the anomaly in the soil.

(ii) <u>Paradise</u>

At Paradise, the grass (again composite samples) and soils both located the lode with some precision in both transects (Fig. III.2b). Tungsten levels in bracken and manuka however were either too low or too variable to be of much use.

(iii) Macrae's Flat

The vegetation here was much less diverse being made up almost entirely of two species of native tussock grass (Festuca novae-zelandiae and Chionochloa rubra). A sample of each was therefore taken at each site and analysed separately. Although the species



Fig. III.2. Transect data for tungsten in soils and vegetation. (a) Glenorchy, (b) Paradise, (c) Macrae's Flat (d) Wairau Valley.

differed in their ability to take up tungsten, <u>F</u>. <u>novae-zelandiae</u> having a higher plant/soil ratio for this element (Table III.3) than <u>C</u>. <u>rubra</u>, it was found that the plant anomaly which most accurately located the lode was obtained by averaging the data for the two species, this giving a peak at +5 m (Fig. III.2c).

The soil data was less effective in locating the position of the lode because three similar anomalous peaks (-10, 0, and +10 m) were obtained (Fig. III.2c). In addition, the soil anomaly showed a spread of at least 70 m compared to 40 m for the vegetation.

#### (iv) Top Valley

At Top Valley, the bracken was found to be rather unsuccessful for locating the Jubilee lode, the concentrations of tungsten in this plant being very low (Table III.2). The tungsten level in the soil, however, located the lode more successfully although, as at Macrae's Flat, a rather wide spread (60 m) was obtained (Fig. III.2d).

(v) Barrytown

In the upper transect (Fig. III.3a) besides accurately pinpointing the ven the tree trunk analyses have indicated the presence of an offshoot of the main vein at +15m, thereby providing more information than soil sampling alone. In order to be certain of locating the reefs and their extensions, however, many trees have to be sampled at each site because of the possibility of the roots of smaller trees not penetrating the vein. Hence each point in the diagram represents the average of three trees. An interesting relationship discussed earlier (Quin, 1972), and confirmed after more detailed sampling was that the tungsten concentrations were highest in the side of the tree nearest the vein.





#### (vi) <u>Canaan</u>

Although trunk analysis accurately located the reefs in each case (Fig. III.3b), in no instance was plant sampling superior to soil sampling, as in every case the soil also accurately located the reefs. This finding is in marked contrast to that of Williams (1959) who concluded that soil sampling was suitable for revealing scheelite-bearing areas at Canaan but not individual reefs. This erroneous conclusion was no doubt largely due to the wide sampling pattern used (100 m) and partly because of the inadequacies of the analytical field test used ( Lakin <u>et al</u>, 1952).

In this study, it was found that soil sampling could even be used successfully down a 45 deg. slope (reef 3, Fig. III.3b). A pronounced "tail" was apparent in the downslope position. The results for the soils and tree trunks from reefs 2 and 3 indicate the presence of offshoots of the main reefs at  $\pm 10 \text{ m}$  (reef 2).

(f) Discussion

(i) <u>Glenorchy</u>, <u>Paradise</u>, <u>Macrae's</u> Flat and Top Valley

These test areas are similar in that they have a common lithology, relatively gentle topography, similar climates and a predominantly, but not entirely, shallow rooted vegetation. The soils may be considered to reflect the composition of the bedrock. The vegetation may therefore also be expected to reflect the soil composition and it is therefore unlikely that plant sampling in these areas will give any additional information not provided by soil sampling. However in every case, with the possible exception of Top Valley, the vegetation was successful in locating the lodes, and moreover had the distinct advantage of

### Table III.3

Summary of data for concentrations of tungsten in soils and plant ash from transects across mineralised reefs

Locality	Samples	Tungsten concentrations (ppm)	Average plant ash/soil tungsten ratio for anomalous values (&Ac)
Clanamelar	Coil	4.80	
Glenorchy	Soll	4-82	-
	Grass (composite	1-180	1.2
Paradise	Soil	3-35	-
	Grass (composite	e) 1 <b>-</b> 40	1.1
	Pteridium aquili	num <1-20	0.5
	Leptospermum sco	parium	
	na particular particular particular a conference de la confe	<1–11	0.4
Macrae's Fla	t Soil	2-53	-
	Festuca novae-ze	elandiae 1-78	1.1
	Chionochloa rubr	ra < 1-44	0.7
Top Valley	Soil	1-130	-
	Pteridium aquili	num <1-12	0.1

being much faster than soil sampling.

A striking feature of the results for Top Valley, is the anomalously low value for the plant/ soil tungsten ratio (Table III.3). A likely reason for this low uptake of tungsten is the low pH of the soil (Table III.1). Romney and Rhoads (1966) have shown that the solubility and therefore availability of tungsten, as the WO<sub>4</sub>-ion, decreases with decrease in pH.

(ii) Barrytown and Canaan

These areas are similar in that both are underlain by predominantly granitic material, have rugged topography (particularly at Barrytown) high rainfall (again more so at Barrytown) and have a vegetation comprising a tall forest tree canopy, a shrub understory and a dense covering of ferns over the forest floor. As in the previous areas. the concentrations of tungsten in the leaves of the shallow-rooting species (for example, ferns) will reflect the concentrations of tungsten in the soils. However the levels of this element in the soils are liable to be controlled to some extent by leaching and soil creep as well as by tungsten concentrations in the bedrock. The levels of tungsten in the tree species however, because of the possibility that their root systems may penetrate the bedrock, may indicate the presence of deep-seated reefs not manifested by tungsten anomalies in the soil (see upper transect across reef at Barrytown, Fig. III.3a).

At Canaan, the ability of soils to indicate successfully the location of all the reefs and their offshoots is possibly partly due to a shallower soil cover and partly due to higher levels of leached

tungsten in the soil. The Barrytown soils have even lower pH values than the Canaan soils ('Table III.1) and this probably explains why the BAC values for Barrytown trees are considerably lower than those at Canaan, (Table III.2). Top Valley, where the soil pH is also about 5 has similar BAC values (Table III.3). Another striking difference between the results for Barrytown and Canaan however is the different distribution of tungsten between the organs of trees from the two areas (Table III.2). At Canaan, tungsten in the trunks, leaves and twigs are similar. The data for the Barrytown however, show that the concentration of tungsten in the tree trunks is far higher than that in the leaves or twigs. A possible explanation for this is that there is insufficient soluble Na- and K-ion in the Barrytown soils (because of leaching), to ensure transportion of the negative  $WO_A$ -ion up the xylem to the leaves and twigs. Tungsten may therefore be deposited in the roots and trunk. perhaps as the rather insoluble calcium tungstate.

This possibility was investigated in pot trials the results of which are described in the next section.

(g) Conclusions

The main conclusions of this investigation may be summarised as follows :

Soil sampling is under most conditions a very effective tool for locating scheelite mineralisation, provided sampling distances are sufficiently close (5-10 m) and that accurate methods of analyses are used.

Shallow rooting vegetation such as tussock grass (using composte samples) and ferns can also be used to locate scheelite in areas of lower rainfall and gentle topography, but the anomalies are in some cases less pronounced than those provided by soils. However the faster nature of plant sampling, and the fact that sharper anomalies are usually obtained, tend to more than balance this disadvantage.

In areas of high rainfall and rugged topography, soil sampling may not always reveal the presence of reefs or extensions of known reefs. In these cases, trunk sampling of deep rooted tree species often provides additional information.

Finally, the biological absorption coefficient (BAC) for tungsten is remarkably constant for the common tree species present at a particular area; in fact there was less variation in BAC values between different species at one area than between the same species at different areas. This important finding means that, for the purposes of biogeochemical exploration, the different tree species present at a particular area may be grouped together.

## 2. <u>Trend-surface analysis of tungsten</u> <u>concentrations in tree trunks at Barrytown</u>. (a) Introduction

Following the results of the previous investigation, in particular with regard to the use of tree trunk analysis to locate scheelite bearing veins, it was decided to carry out a further investigation at Barrytown to determine just how much information could be obtained by this method compared to soil sampling in areas subject to landsliding and leaching. The need for this further study was prompted by the particular difficulty in tracing scheelite-bearing veins between outcrops in these conditions. It was decided therefore to carry out concentrated sampling over a small area of suspected mineralisation, and apply trend-surface analysis to the data.

#### (b) Trend-surface analysis

The purpose of this technique is to separate observed map data into various components, each of which may be more easily interpreted than the raw data. It involves the fitting of surfaces - of best - fit by regression analysis procedures to the observed data. These surfaces are given by a regression equation from which an estimate of the value of the variable measured (called the "dependent" variable) may be made for each point on the area sampled. These estimated values lie on the surface of - best - fit. The regression equation has the form :

 $T = K + K_1 L_1 + \cdots + Kn Ln + \cdots$ where T is the estimated value of the variable at point (X, Y) on the sampling area, K is the regression constant,  $K_1$  to Kn are regression coefficients and  $L_1$ to Ln are terms in the coordinates X and Y. These terms are the "independent" variables and may be polynomial or non-polynomial.

To obtain the components of the date set, the behaviour (trend) of the environmental or regional processes which act over the area are assumed to be given by the surface - of - best - fit, and the deviations of the observed data from this surface contain the error component of the date. Thus, in theory, the method enables the behavious of the regional processes to be examined free of experimental error. In practice the surface can be influenced by other effects which will be explained below with reference to geochemical data. The application of trend analysis to geological and geochemical map data has been discussed and illustrated by a number of workers over the last two decades (Krumbein, 1956; 1959; Connor and Miesch, 1964; Agterberg, 1964; Krumbein, 1966; Cameron, 1968; Meisch and Connor, 1968; Nichol <u>et al</u> 1969). In the case of geochemical data, the results may be considered as having three main components :

(a) Regional trends due to large-scale geological processes such as changes in the nature of the bedrock which affect the major part of the sampling area ;

(b) Local deviations from the regional trend ; these extend over more than one sample site and generally arise from small-scale geological anomalies such as mineralisation ;

(c) Random variation over the sampling area, usually called "moise" which is caused by sampling and analytical error.

To obtain these three components from a trend analysis procedure, the surface - of - best - fit is considered to be the regional component. The local and noise components are contained in thedeviations of the observed lata from the regional trend. These deviations are usually called "residuals" and the latter two components may be separated by observing the sign of adjacent residuals. In this case positive residuals reflect regions of anomalous local influence. If the dependent variable is a metal concentration in the soil, then these anomalous features may be mineralised zones. Residuals of negative sign contain the noise component of the data.

Although in most prospecting applications, it is the positive residuals which are of most interest,

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the actual trend surface may also be useful to indicate the regular behaviour of the data over the area concerned.

The method of trend analysis used was developed for the writer by Dr. C. R. Boswell, Computer Department, Massey University, from the method of Miesch and Connor (1968), and used polynomials to the fourth degree.

(c) Field work

The location of the study area is shown in Fig. 0.1 and in more detail in Fig. III.4. Two belt-transects (A and B) measuring 10 x 24 m were measured out across a steep hillside (slope 40 deg.) at positions believed to be underlain by a vein containing scheelite mineralisation. All large trees (trunk diameter > 15 cm) within the transects, irrespective of species, were sampled and labelled according to their X and Y coordinates. Approximately 40 trees were included in each transect.

(d) Results

Fig. III.5 shows the results for the two transects, the data showing the tungsten concentration in the trunk of the tree at those coordinates. Fig. III.6 shows the results after computer analysis, and includes isoconcentration contours (Fig. III.6a) trend surfaces (Fig. III.6b), and "residuals" (Fig. III.6c).

In the upper transect, Transect A, the "residuals" show a high positive anomaly at Y = 6m(also shown in the isoconcentration contours), indicating the presence of a scheelite - bearing vein, while the X-coordinate indicates this vein has a rich pocket at X = 4 m. The smaller anomaly at Y = 14 mpossibly indicates the presence of an offshoot of the main vein. As well as delineating these rich pockets,



Fig. III.4. Map of Barrytown study area showing site of Transects.





Fig. III.5. Original tungsten - tree data for Transects A and B.

the trend analysis was very useful in demonstrating that the anomalous area at Y = 22 m in the isoconcentration contour was not due to mineralisation ; after subtracting the trend surface plot, the residuals (Fig. III.6c) show no trace of an anomaly here, indicating that the high values were probably caused by transported tungsten in the soil.

In the lower transect, Transect B, "the residuals" show positive anomalies at Y = 11 m and Y = 12 m. Only the latter is indicated on the isoconcentration contours of the original date (Fig. III.6c). Moreover, the "residuals" plot has indicated the richest pockets - to be located t X = 2 m and X = 8 m.

To determine whether these anomalies corresponded with the position of the bedrock mineralisation, trenches were dug across the centre of both transects and samples were taken from the highly weathered upper bedrock. B-horizon soil samples were taken at corresponding points. The position of the trenches are shown by the line CD in Transect A and by EF in Transect B (Fig. III.6c). The rock and soil data are plotted in Fig. III.6d. In both line transects, the position of the highest value for the rock samples coincided exactly with the Y - coordinate of the plant anomalies in the "residuals" plots. The soil values, however, pinpointed the highest bedrock values in transect B only.

The high concentration of tungsten in the soil relative to that in the rock suggests that the scheelite may be fairly readily leached from the weathering bedrock and precipitated in the soil downslope.

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# Fig. III.6 Trend surface analysis of data for Transects A and B.

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- (a) isoconcentration contours ;
- (b) trend surfaces ;
- (c) "residuals",
- (d) Soil and rack data for line transacts () and EF.

TRANSECT A

TRANSECT B



#### (e) Discussion and conclusion

The plant data, in addition to enabling the Y-coordinate of the mineralisation to be pinpointed more accurately than the soil data, have also indicated the positions of the richest mineralisations in the veins. The 40 - odd trunk samples collected in each transect were collected in a similar time (2 men, 2 hours) required to collect the dozen or so soil samples, due to the thick layer of humus and tree roots whose presence impedes the rate of soil sampling. Hence the two methods as used are directly comparable in terms of information obtained for comparable effort ; this applies to sample analysis as well, as, although there are more plant samples, they require only dry ashing before extraction of the tungsten, whereas soils have tobe dried, sieved, fused and leached before extraction.

In conclusion, it is considered that the use of trend surface analysis of date from belt - transect sampling of tree trunks, although hardly applicable to widespread regional reconnaisance because of the high sampling density involved, shows considerable potential for delineating extensions of known mineralisation, and locating rich pockets in known veins.

C. MOLYBDENUM

1. Biogeochemical exploration for molybdenum at Canaan, Nelson.

(a) Introduction

Molybdenum mineralisation, in the form of molybdenite, was discovered at Canaan, Nelson in 1956 by Mr. E. J. Sixtus. This deposit has not previously been mentioned in the literature ; a rather exhaustive study of minerals in the region (Williams, 1959) did not refer to its presence. The location of the deposit is shown in Fig. 0.1 and in more detail in Fig. III.7. The molybdenite occurs in a leanly mineralised quartz reef, approximately 5 meters in width and striking roughly north-south, which outcrops about 0.5 kilometers north-west of the old homestead (Fig.III.7). Minor lead, copper and iron sulphide mineralisation are also present, scattered throughout the vein, whereas the molybdenite occurs only in the outer portions of the vein. A yellow secondary mineral was present as a stain on the quartz, this may be wulfenite.

Although the vein is far too leanly mineralised with molybdenum to be of economic significance, it was ideal for the purposes of prospecting as, apart from this one outcrop, there was very little visual sign of the reef which is said to be possibly as long as 10 kilometers, (E. J. Sixtus, pers. comm.). It was therefore of considerable interest to determine whether the vein could be located by soil and / or plant sampling.

(b) Field work

The area surrounding the outcrop had been burnt off recently, and the only vegetation available for sampling were dead tree trunks. The strike of the vein was followed north for 40m, B - horizon soil samples and dead trees being sampled every 10m. At this point a small stream crossed the strike of the vein, which does not however outcrop in the stream. Dense vegetation was present north of the stream (50m from outcrop) and trunk wood, leaves and twigs were collected from each tree species present.



Fig. III.7. Map showing location of molybdenum mineralisation Canaan, Nelson.

#### (c) Chemical analysis

Molybdenum in stream sediments, soils and vegetation was determined by the colorimetric procedure developed and described in Section I.b of this thesis.

#### (d) Results and discussion

Table III.4 gives the results for the soil, stream sediment and dead wood sampling along the strike of the vein. The rapid drop in soil molybdenum down to background levels (3ppm) in only 40 m indicates that there is little leaching of molybdenite from the vein. The pH of the soil was found to average a low 5.1, and it is well known (Davy, 1973) that the mobility of molybdenum is very low under these said conditions, due to the formation of molybdic acid. In very acidic conditions (pH<4), the mobility starts to increase again due to the formation of soluble polymeric molybdate anions; mobility is at a minimum in the pH range4.5 - 6.

The results for the live trees sampled north of the vein (Table III.5) show that molybdenum is taken up in large amounts despite the very low molybdenum content of the soil. Background concentrations would be only 0.5-1 ppm. This indicates that the tree roots are penetrating the vein through the soil cover, as, in the immediate vicinity of the vein, the pH is considerably higher (e.g. 6.7 at the outcrop) and hence molybdenum is available for uptake. Within a few cm of the vein however, the pH drops to around 5. This explains both (i) why the molybdenum content of the B-horizon soil is very low, and (ii) why a high concentration of molybdenum in the trees must mean that their roots are in close proximity to a vein, as high concentrations of transported molybdenum in a low pH soil do not result in such high concentrations. That this is so was checked by ...

Distance from vein	Molybdenum	(ppm)
(m)	soil	dead wood
0	37	16
10	21	20
20	7	22
30	3.6	12
40	5.5	28

(9)

# Table III.4

Molybdenum concentrations in soils and dead wood

sampling at an area 3 km south of the vein, where molybdenum leached from molybdenite - bearing quartz stringers in a high pH environment have resulted in soil values as high as 300 ppm (M. Zuckermann, pers. comm.). The results for this area are shown in Table III.6. The distribution of molybdenum in trees (Table III.5) shows an interesting contrast with that of tungsten. With the notable exception of Myrsine divaricata and the Nothofagus species, the concentration of molybdenum is higher in the leaves than twigs or sapwood ; tungsten is almost invariably highest in the trunk wood (Table III.2). This finding is probably related to the fact that, unlike tungsten, molybdenum is an essential element for plants, and hence is more likely to be transported into the aerial organs.

(e) Conclusions

This brief investigation has yielded some very valuable information concerning prospecting for molybdenum is New Zealand. Firstly, the results have demonstrated that biogeochemical prospecting can be used to locate molybdenum - bearing reefs in acid conditions, as the higher  $_{\rm PH}$  in the immediate vicinity of the reefs results in the formation of soluble molybdate which is readily absorbed by tree roots.

Secondly, the results have demonstrated the superiority of tree sampling over soil sampling in these conditions where the low pH of the soil does not permit molybdenum to be transported through the soil profile. Molybdenum concentrations in tree samples collected above inferred position of reef 50m from outcrop

Species	No. of samples	Ave. molybo Leaves	lenum <sup>*</sup> (ppm as Twigs	sh weight) Outer wood	
Griselina lucida	2	140	16	120	
Myrsine divaricata	3	16	40	65	
Libocedrus bidwillii	1	13	12	10	
Cyathoides fasciculata	2	14	8	12	
Phyllocladus alpinus	2	24	13	14	
Podocarpus totara	5	24	11	11	
Coprosma rugosa	4	43	30	11	
Nothofagus fusea	4	6	13	22	
N. menziesii	3	8	10	15	
Pseudowintera colorat	a 6	18	7	13	
Dracophyllum townsoni	<u>i</u> 3	20	16	15	

\* Ave. soil concentration 4.6 ppm.

Molybdenum concentrations in trees and soils in an area of transported molybdenum

Site	Sample	Molybdenum	in soil	(ppm)	Molybdenı	um in tr (p	ee organs pm ash wt)	
					Leaves	twigs	outer wood	
1	soil (pł	H 4.7)	140					
	Nothofagus sola	andri			4.3	2.1	2.6	
	N. truncata				3.7	2.3	2.4	
2	Soil (pr <u>N. truncata</u>	I 5.4)	70		6.3	3.1	3.9	

Thirdly, high concentrations of molybdenum precipitated in a low pH soil after transportation from a high pH environment will not result in high concentrations of molybdenum in trees, and hence the results of tree analysis should be capable of distinguishing between the presence of mineralised reefs and merely transported molybdenum.

Fourthly, where a molybdenum – bearing reef is overlain by a high soil, soil and tree sampling should be equally successful in delineating anomalies.

Finally, the results have indicated that, as with tungsten, virtually all tree species should be suitable for biogeochemical prospecting. However, although too few samples of each species were collected to reliably determine their average BAC values, the great variance in molybdenum concentrations in general, and in particular the manner of distribution between the organs, indicates that biogeochemical prospecting for molybdenum would require rather more elaborate orientation surveys than does tungsten.

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SECTION IV

BIOGEOCHEMICAL

STUDIES

#### A. INTRODUCTION

This Section describes three investigations carried out to attempt to answer questions raised by the results of the biogeochemical exploration survey.

The first investigation was prompted by the differences found in the uptake and distribution of tungsten by tree - species from the Barrytown and Canaan areas. An investigation was carried out to determine whether differences in the levels of soluble sodium and potassium in the soil at the two areas could be responsible for these findings.

The second investigation was carried out to study the effects of soil tungstate on the growth of clover. Considerable areas of scheelite mineralisation in Otago, Westland and Nelson have by now been developed into pasture, and the question arises to what extent growth is affected by the presence of tungsten. There are several references in the literature concerning the inhibitory effect of tungstate on plant enzymes which require molybdenum ; other workers have suggested that tungsten can substitute for molybdenum in these enzymes and actually increase growth.

The final investigation was carried out to determine the effect of substrate composition on the composition of native trees for a wide range of major and trace elements. The author was fortunate to be able to carry out investigations at two areas which, while being totally different geologically, had virtually identical vegetation cover. This provided an unique opportunity to study the variations which could occur in the composition of some of New Zealand's commonest native tree species, and the implications of this for large scale prospecting.

# B. THE EFFECT OF SODIUM AND POTASSIUM IN THE SOIL ON THE UPTAKE OF TUNGSTEN BY NOTHOFAGUS FUSCA. 1. Introduction

The results of the biogeochemical exploration for tungsten described in Section III showed the existence of some interesting differences between the Barrytown and Canaan areas. Firstly, the total uptake of tungsten was lower at Barrytown, and secondly, the distribution of tungsten between the organs of tree species was different ; at Barrytown tungsten was invariably higher in the trunk wood than in the leaves or twigs, while at Canaan tungsten was evenly distributed on a concentration basis. Table IV.1 shows the distribution of tungsten within the organs of two tree species common to both areas.

The first difference, the lower total uptake of tungsten (see BAC values in Table III.2) is probably largely due to the lower average soil pH at Barrytown (Table III.1); the uptake of tungsten has been demonstrated to decrease with decrease in pH (Romney and Rhoads, 1966). Once the tungsten is taken up however, other factors must determine how it is distributed within the tree. Investigation showed that the levels of ammonium-acetate-soluble sodium and potassium in the soil, and the concentrations of these elements in tree organs, were lower at Barrytown than at Canaan. As the presence of a mobile cation would be essential for the transportation of the tungstate anion up the xylem to the leaves of a plant, it was decided to carry out pot trials to determine the effect of added sodium and potassium on the uptake and distribution of tungsten.

Average concentrations of tungsten in organs of two trees species common to Barrytown and Canaan

		(ppm as	sh weight)
Species	Organ	Barrytown	Canaan
			na a standard an
Nothofagus menziesii	trunk	30.4	8.8
	leaves	9.3	10.7
	twigs	8.1	13.7
Weinmannia racemosa	trunk	21.6	34.2
	leaves	10.5	30.1
	twids	6.8	22.5

#### 2. Preliminary field work

Initial measurements of soluble sodium and potassium in the soil were made using the water soluble content of the -100 mesh fraction. as this fraction was used for exploration work. These gave average values of 375 and 350 ppm sodium, and 45 and 55 ppm potassium, for Barrytown and Canaan respectively. However it was later considered that more reliable estimates of the available sodium and potassium would be obtained by measuring the ammonium acetate - soluble levels in the total soils, as used in agricultural tests for soil fertility. This method gave average values of 130 and 220 ppm sodium, and 50 and 90 ppm potassium for Barrytown and Canaan respectively; that is, the Barrytown soils had considerably lower levels of both elements. Leaves. twigs and trunk wood were taken from two species of trees common to both areas (Nothofagus menziesii and Weinmannia racemosa) and analysed for sodium and The results (Table IV.2) show that the potassium. Barrytown trees contained lower concentrations of both elements.

#### 3. Setting-up of pot trial

Approximately 20 soil samples (500 g) were collected at randomly selected sites from each area. After air-drying, the soils were lightly ground to separate aggregated particles, and the +20 mesh fraction was removed by sieving and discarded. The -20 mesh fractions were then mixed to produce a representative soil sample from the two areas.

It was hoped to use seedlings of <u>Nothofagus</u> <u>menziesii</u> (silver beech) for the pot trial, as this was the most abundant species common to both areas, and had been used in a earlier pot trial, (Quin, 1972). Average concentrations of sodium and potassium (% ash wt) in two tree species from Barrytown and Canaan

Species	Organ	<u>Barrytown</u> Na K	<u>Canaan</u> Na K
Nothofagus menziesii	trunk	0.37 2.9	0.52 3.8
	leaves	0.68 4.9	0.75 6.1
	twigs	0.40 3.1	0.56 4.0
Meinmannia racemosa	trunk	0.25 1.9	0.39 2.7
	leaves	0.40 2.7	0.56 4.1
	twigs	0.26 2.3	0.39 3.0

However lack of availability forced the use of <u>N.</u> fusca (red beech). This species was also present at both areas, but was less common than <u>N. menziesii</u>, particularly at Barrytown.

The seedlings, which were one - year - old specimens grown from seed in potting mix, were transplanted to the Barrytown and Canaan soils, after the roots had been carefully washed, at a density of three seedlings per pot. The pots, which were plastic and held approximately 300 g of soil (dry weight), were placed in plastic dishes so that any drainage could be reabsorbed by the contents of the pot.

After 20 days, addition of the treatment solutions was commenced. The two soils were each split into four categories (a) control, (b) tungsten added, (c) tungsten and sodium added, (d) tungsten and potassium added. Sufficient tungsten (as  $Na_2 WO_4 \cdot 2H_2O$ ), sodium and potassium (as their chlorides) were added to give additional concentrations of 200, 1000 and 1000 ppm respectively. The treatment solutions were made up to 500 cm<sub>3</sub> and added at a rate of 35 cm<sup>3</sup> per day for 14 days.

At Day 15 or 1 day after the cessation of the addition of the treatment solutions, soil samples were taken from the pots and analysed for total tungsten and ammonium acetate - soluble sodium and potassium. The results are given in Table IV.3. Note the higher concentration of sodium in the soils to which tungsten had been added as sodium tungstate.

At the same time, leaf samples were collected and analysed for tungsten, sodium and potassium. Further leaf analyses were carried out at Day 85, and at Day 300 the plants were harvested. Soil was

# Soil data for pot trial

		Concentra	tions (ppm)
		Barrytown	Canaan
Total tungsten			
Ū	control pots	26	12
	tungsten pots	220	230
Soluble sodium			
	control pots	1 30	220
	+ tungsten pots	200	290
	+ tungsten, sodium pots	1150	1200
Soluble potass	ium		
	Control pots	50	90
	+ tungsten,potassium pots	800	850

shaken from the roots which were then thoroughly washed in running water. The seedlings were divided into roots, stems and leaves for analysis.

4. Analytical methods

Tungsten in soils and plant ash was determined colorimetrically (Quin, 1972) using improvements described in Section I of this thesis. Sodium and potassium were determined by flame photometry.

5. Results and discussion

The Day 15 data (Table IV.4) show that. although the original concentration of tungsten in the Barrytown soil was more than twice that in the Canaan soil, the uptake of tungsten was only slightly greater, probably as a result of the lower pH of the Barrytown soil (4.6 compared to 5.0). After the completion of the addition of the treatment solutions (Day 15 data) the concentration of tungsten in the leaves had increased dramatically. The influence of soil sodium and potassium on the uptake of tungsten was shown conclusively by the results for the sodium and potassium pots, as in both cases the tungsten concentration was greatly increased. The results for the Canaan samples were invariably higher than those for Barrytown.

The Day 85 data showed an interesting reversal. The tungsten concentrations had decreased in all treatments, but most markedly for the sodium and potassium pots, where the concentrations had decreased to well below those for the tungsten - only and control pots. A possible explanation for this is as follows. The huge initial uptake of tungsten is associated with an increased uptake of potassium and particularly sodium (Table IV.4). The presence of the excess sodium and potassium in the plants could quite easily Plant data for pot trial

Day	Soil	Concentrations (ppm dry weight)							nt)		
		Control pots		+tungsten po		pots +	ots +tungsten sodium pots			+tungsten, potassium pots	
		Na	K	Na	K	N	Ia	K	Na	K	
15	Barrytown	620	4000	1600	4000	650	00	3800	600	5700	
	Canaan	670	5500	1900	5400	660	00	5200	670	8700	
		V		P			$\mathbb{W}$		W		
0	Barrytown	2.	3	2.	2		2.	0	2.	4	
	Canaan	1.	9	1.	8		1.	8	2.	0	
15	Barrytown	2.	5	13.	0		37		31		
	Canaan	1.	8	20.	0	1	140		73		
85	Barrytown	2.	5	3.	0		Ο.	9	0.	01	
	Canaan	2.	0	4.	9		1.	7	0.	3	
300	Barrytown	2.	6	4.	5	1	0.5	5	7.	5	
	Canaan	1.	9	6.	2	1	6.0	)	9.	5	
prevent the tungsten from being immobilised, for example by precipitation as CaWO<sub>4</sub> or incorporated in macromolecules, and the data indicate that this mobile tungstate can be readily removed from the plant. In the absence of the additional sodium and potassium, the majority of the tungsten taken up is probably immobilised, as is indicated by the stable tungsten concentrations in the control pots.

By Day 300, the tungsten levels had built up again for the sodium and potassium treatments, and stayed relatively constant for the tungsten - only treatment. These results suggest that, although the presence of excess sodium and potassium prevents rapid immobilisation of the tungsten in the plant, as time goes on the tungsten is slowly immobilised, thereby permitting more to be taken up.

Distribution of tungsten in plants, Day 300

In the final stage of this experiment, the plants were harvested and split into roots, stems and leaves to investigate the pattern of distribution of tungsten in the plants from the two areas. The results (Table IV.5) show that the proportion of tungsten in the leaves and stems is far higher for the potassium and particularly sodium treatments. For all treatments, the leaves / roots and stems / roots ratios are higher for Canaan than for Barrytown.

As had been found in an earlier pot trial (Quin, 1972; Quin, Brooks and Reay, 1973), the distribution of tungsten in the control pots is much more uniform, the concentration of tungsten in the roots being roughly the same as that in the leaves. In the presence of applied tungsten, the high relative concentration of tungsten in the roots, particularly in the tungsten only treatment, indicates that the

#### Locality Tungsten concentrations (ppm) Ratios Treatment leaves/roots stems/roots leaves roots stems Control 28 0.82 0.50 23 14 Barrytown + 17 25 12 280 0.09 0.04 0.16 + W, Na 105 50 310 0.33 + W, K 55 35 290 0.19 0.12 22 0.86 0.55 Control 12 19 + W 0.17 0.09 Canaan 52 27 310 300 0.53 0.23 + W, Na 160 70 + W, K 95 50 330 0.29 0.15

# Distribution of tungsten in seedlings, Day 300

plants can somehow suppress the transport of tungsten into the aerial parts of the plant. This effect was also found to exist for clover, as shown in the next investigation.

#### 6. Conclusions

The  $r_{e}$ sults of this investigation have demonstrated the effects of soil sodium and potassium on the uptake and distribution of tungsten by beech seedlings. The addition of sodium and / or potassium slightly increases the overall uptake of tungsten ; concentrations of tungsten in the roots are unaffected, but more is transported to the leaves and twigs. C. THE EFFECTS OF TUNGSTATE AND NITROGEN SOURCE ON THE DRY WEIGHT AND NITROGEN YIELDS, AND MOLYBDENUM AND TUNGSTEN CONTENT, OF WHITE CLOVER (TRIFOLIUM REPENS).

#### 1. Introduction

Molybdenum is known to be an essential element for plants, and Nicholas and Nason (1955) identified it as being the metal constituent of the enzyme nitrate reductase, which reduces nitrate to nitrite, the first step necessary in the conversion of absorbed nitrate into amino acids. Molybdenum is also an essential constituent of the enzyme nitrogenase (Krylova, 1963), which is responsible for the reduction of molecular nitrogen to ammonium by legume Rhizobia nodules.

Tungsten, added as tungstate, has been shown to function as a competitive inhibitor of molybdate uptake and utilisation in Azotobacter vinelandii, (Keeler and Varner, 1957), and reduces the growth of these bacteria both when nitrogen is the sole nitrogen source, and when nitrogen as added as nitrate (Keeler and Varner, 1957; Takahashi and Nason, 1957). Tungstate has also been found to act as a competitive inhibitor of molybdate utilisation in the fungus Aspergillus niger, when nitrate is the sole nitrogen source, (Higgins et al, 1956). In all these examples, high tungsten to molybdenum ratios (approximately 100:1) were necessary to produce inhibition of growth or molybdenum utilisation, and it was found that decreasing the ratio to approximately . unity by the addition of more molybdenum invariably reversed the tungsten inhibition. Tungsten has also been found to suppress the utilisation of molybdenum in nitrogen fixation in several other bacteria strains (Krylova, 1963; Hwang and Doi, 1965) apparently in the same fashion is in nitrate reduction.

More recently, Heimer et al (1960) studied the effect of tungstate on nitrate assimilation in higher Tungstate was found to prevent the plants. development of nitrate reductase activity in barley shoots and cell cultures of tobacco, and higher tungstate concentrations had the additional effects of preventing root and shoot development in barley. Again, decreasing the tungstate to molybdate ratio to unity was found to reverse tungstate inhibition. It was concluded that tungstate probably acts by inhibiting the incorporation of molybdenum into nitrate reductase, rather than by inhibiting the formation of the apoenzyme. Furthermore, they demonstrated that tungstate does not inhibit nitrate uptake by tobacco cells or barley seedlings, in contrast to the bacterial work of Keeler and Varner (1957).

In apparent contrast to the results of these physiological experiments, the results of field tests carried out by Davies and Stockdill (1956) showed that, in the presence of added molybdate, the addition of tungstate did not adversely affect the growth of the legume white clover, and, in the absence of additional molybdate actually resulted in an increase in growth, although this increase was less than that produced by an equivalent amount of molybdate. They concluded that tungsten was probably acting as a substitute for molybdenum in its role in nitrogen fixation (that is, in the enzyme nitrogenase), although less effectively.

As there are widespread areas of tungsten (predominantly scheelite) mineralisation in the Otago and Southland areas of New Zealand (Williams, 1965) parts of which support pasture and native tussock, it was decided to investigate the effect of anomalous concentrations of tungsten in the soil on pasture growth. Biogeochemical exploration in these areas had demonstrated the existence of tungsten concentrations as high as 80ppm in soils and 20ppm dry weight in tussock and pasture (see Section III of this thesis) compared to normal levels of 0.05 -2ppm in soils and 0.02 - 0.6ppm in pasture.

It was decided that the greatest amount of information would be obtained by carrying out pot trials to study the effect of nitrogen source, and tungstate level, on the growth, of white clover (<u>Trifolium repens</u>) one of New Zealand's most commonly used pasture species.

# 2. Methods

Plants were grown from seed, the seeds being planted after germination. at a density of 16 per pot in greywacke sand in a glasshouse. The pots were plastic and measured 15 x 15 x 15cm and, when filled with sand, had a water holding capacity of approximately 1000cm<sup>3</sup>. The pots were covered for 4 days with wet paper to reduce evaporation after which the paper was removed and the addition of nutrient solutions was commenced. Details of the basal nutrients solution are given in Table IV.6. Treatment solutions consisted of three different nitrogen sources (fixation, nitrate and ammonium), and three different tungsten concentrations (0, 5 and 50ppm). Tungsten was added as the soluble sodium tungstate; the control solution to which no tungsten had been added, the 5ppm solution to simulate likely levels of this element in soils containing tungsten transported from scheelite bearing ore - bodies, and the 50ppm solution to simulate likely concentrations near in situ mineralisation. These concentrations were designated WO, W1 and W2 respectively (Table IV.6).

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The first nutrient application was made using quarter - strength solutions, the second using half strength, the third three - quarter strength, and the fourth and subsequent application with full-strength solutions.

The solutions were applied at a rate of 200cm<sup>3</sup> three times a week, this being sufficient to induce drainage and hence prevent accumulation of ions. Four replicates of each treatment were used.

The plants were harvested after 10 weeks growth, then washed thoroughly in water before they were subdivided into roots and shoots. The samples were oven-dried at 100 deg.C for 24 hours.

The total nitrogen content of the dried plant material was determined with a Technicon Auto-Analyser, after Kjeldahl digestion. Nitrate was determined colorimetrically by reaction with sulphanilamide and napthyl - ethylenediamine after hydrazine reduction. Molybdenum and tungsten were determined colorimetrically by the methods described in Section I of this thesis. Nitrogenase activity in plants receiving combined nitrogen was determined by acetylene reduction assay.

3. Results

(a) Dry weight and nitrogen yields

There was a significant ( $P_40.05$ ) effect of tungstate level on both dry weight and nitrogen yields, and an interaction ( $P_40.10$ ) with nitrogen source.

Tungstate had the least effect on yields in the absence of combined nitrogen (Figs. IV.1a and 2a). The trend is similar for roots and shoots and indicates that tungstate is slightly inhibiting growth and nitrogen yields (Table IV.7).

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	Common to all	treatments*	
Ele	ements and compounds	mM	total ppm element
Na	(Na <sub>2</sub> CO <sub>3</sub> )	0.7	16.1
K	(K <sub>2</sub> \$04)	0.6	23.5
Мg	(MgSO <sub>4</sub> ,7H <sub>2</sub> O)	0.2	4.9
Ca	(CaC1 <sub>2</sub> )	0.7	28.0
Έ	(NaH2P04,2H20)	0.1	3.1
S	(K <sub>2</sub> SO4)	0.5	16.0
C1	(CaC1 <sub>2</sub> )	1.4	99.3
С	(Na <sub>2</sub> CO <sub>3</sub> )	0.3	3.6
Tra	ace elements and compounds	MM	ppm element
Fe	(Fe-EDTA)	7	0.390
В	(H <sub>3</sub> BO <sub>3</sub> )	15	0.162
Mn	$(MnSO_4, 4H_2O)$	2.5	0.137
Cu	(CuSO <sub>4</sub> SH <sub>2</sub> O)	0.5	0.032
Zn	$(ZnSO_4, 7H_2O)$	1.0	0.065
Со	(CoSO <sub>4</sub> ,7H <sub>2</sub> O)	0.25	0.015
Мо	(Na2MOO4.2H20)	0.25	0.024
	Other add:	itives	
Ele	ement and compounds	mM	ppm element
Ν	(as NaNO <sub>3</sub> )	3.6	50
Ν	(as NH4C1)	3.6	50
1.10	level (Na <sub>2</sub> WO <sub>4</sub> ,2H <sub>2</sub> O)	0	0
W1	level "	0.037	5
₩2	level "	0.368	50

\*pH adjusted to 6.8 with dilute HC1

Where nitrate and ammonium were the nitrogen source, the yields show a marked increase for the W1 treatment (Figs. IV.1b and 2b, 1c and 2c) particularly for the shoots. The yields decrease for the W2 treatment, but are still higher than those for the W0 treatment.

Acetylene reduction assay of clover plants receiving nitrogen as nitrate and ammonium showed that, at the time of harvest, some fixation was occurring. The rates were 17 and 7 µmoles ethylene/pot/hour for nitrate and ammonium plants respectively with significant effect of tungstate.

Tungstate also had no significant effect on the nitrate content where fixation was the only source of nitrogen, the nitrate content was very low (less than 5ppm). Nitrate - treated plants contained approximately 0.1% nitrate; those treated with ammonium contained an unexpectedly high 0.05% nitrate.

#### (b) Molybdenum contents

There was a significant interaction  $(P_{<}0.01)$  of tungstate level of molybdenum content.

Where fixation was the only source of nitrogen, the presence of tungstate enhanced the uptake of molybdate, both on a mass and concentration basis (Fig. IV.3a and Table IV.8) even though the dry weight and nitrogen yields slightly decreased (Fig. IV.1a).

For nitrate - treated plants, the molybdenum content of the shoots showed a marked increase at the W1 tungstate level, and a smaller increase at the W2 level (Fig.IV.3b). However these trends closely follow the yield trends (Figs. IV.1b and 2b), and the concentration of molybdenum does not appear to have increased (Table IV.8).



Figs. IV. 1 and 2.

 Growth and nitrogen yield responses of white clover to tungstate when growing on different nitrogen sources.
(a) fixation; (b) nitrate; (c) ammonium.



Figs. IV. 3 and 4.

Molybdenum and tungsten responses of white clover to tungstate when growing on different nitrogen sources. (a) fixation; (b) nitrate; (c) ammonium.

# Table IV.7

Percentage change from WO treatment, in shoot dry weight and nitrogen yields, with variation in applied tungstate

N Source	Tungstate level	Percentage change				
		Dry weight	yield N yield			
Fixation	W1	- 9.4	-20.1			
	1:12	-21.4	-12.9			
Nitrate	7/7	+61.1	+40.2			
	1/2	+41.2	+39.5			
Ammonium	<i>V</i> /1	+106.5	+89.3			
	W2	+69.3	+45.2			

Where nitrogen was supplied as ammonium, there is very much lower molybdenum content for all tungstate treatments (Fig. IV.3c). However, the W2 treatment resulted in a marked increase of molybdenum over the WO and W1 treatments in the shoots and roots, both on a mass and concentration basis (Table IV.8).

(c) Tungsten contents

In all three nitrogen treatments, the tungsten contents shows significant increases with increases in applied tungsten (Fig.W.a-c). Interestingly, whereas molybdenum was higher in the shoots than in the roots for all treatments, on a mass basis, tungsten was invariably concentrated in the roots, both on mass and concentration bases. This was particularly noticeable at the higher level of applied tungstate (W2). This finding is in agreement with earlier studies involving silver beech seedlings (Quin, <u>et al</u>, 1972) and with the work of Romney and Rhoads (1966) on bush beans.

As is the case with molybdenum, the tungsten content is lowest where ammonium was the supplied nitrogen source (Fig.IV.c. but the difference was far less pronounced.

#### 4. Discussion

The existence of nitrogen - fixing activity in the combined nitrogen fed plants indicates that there is a molybdenum requirement for nitrogenase in all treatments, although this requirement is presumably reduced in the presence of combined nitrogen. The presence of considerable amounts of nitrate in ammonium fed plants indicates that some of the ammonium supplied was being converted to nitrate by bacteria in the sand culture, so that these plants were taking up both ammonium and nitrate.

Experimental data expressed in concentrations (dry weight)

N source	Tungstate	N (	%)	Mo (נקק	n)	W (ppm)		
	level	Shoots	Roots	Shoots	Roots	Shoots	Roots	
Fixation	WO	2.86 <u>+</u> 0.24	2.75 <u>+</u> 0.17	10.5 <u>+</u> 2.9	18.7 <u>+</u> 1.6	0.9 <u>+</u> 0.4	1.4 <u>+</u> 0.5	
	<i>\:</i> /1	2.51 <u>+</u> 0.38	2.79 <u>+</u> 0.46	17.3 <u>+</u> 4.5	16.3 <u>+</u> 1.5	2.3 <u>+</u> 1.3	2.3 <u>+</u> 8	
	1:12	3.14 <u>+</u> 0.28	2.91 + 0.32	24.1 <u>+</u> 3.5	24.5 <u>+</u> 3.0	6.6 <u>+</u> 2.5	124 <u>+</u> 15	
Nitrate	1.70	3.52 <u>+</u> 0.27	3.50 <u>+</u> 0.20	9.2 + 1.2	13.4 <u>+</u> 1.5	1.3 <u>+</u> 0.4	1.4 <u>+</u> 0.6	
	1/1	3.01 <u>+</u> 0.15	2.83 + 0.38	11.7 <u>+</u> 1.4	10.4 <u>+</u> 1.1	2.5 <u>+</u> 1.3	1.3 <u>+</u> 3	
	1/2	3.49 <u>+</u> 0.34	3.47 <u>+</u> 0.22	10.1 + 0.8	13.1 <u>+</u> 2.3	8.6 <u>+</u> 3.2	52 🛓 19	
Ammonium	1.10	3.63 <u>+</u> 0.41	3.58 <u>+</u> 0.42	1.0 <u>+</u> 0.1	2.6 <u>+</u> 0.9	0.7 <u>+</u> 0.3	1.4 <u>+</u> 0.3	
	191	3.50 <u>+</u> 0.19	3.40 <u>+</u> 0.17	0.9 <u>+</u> 0.1	1.9 <u>+</u> 0.4	0.7 <u>+</u> 0.3	4.6 <u>+</u> 1.6	
	1:72	3.66 + 0.36	3.43 <u>+</u> 0.25	2.5 <u>+</u> 0.4	3.3 <u>+</u> 1.1	3.8 <u>+</u> 1.1	58 <u>+</u> 22	

In this discussion therefore, combined nitrogen-fed plants will be considered to have a minor molybdenum requirement for nitrogenase, and ammonium fed plants a molybdenum requirement for nitrate reductase.

The reduction in dry weight and nitrogen yields when fixation was the only nitrogen source indicates that tungsten may be slightly inhibiting the utilisation of molybdenum by nitrogenase. The increased uptake of molybdenum in the presence of tungstate, as illustrated by the mass and concentration data (Fig.IV.3a and Table IV.8) probably counteracts to some extent the inhibitory effect of the tungstate on nitrogen fixation.

In the same way, the increased uptake of molybdenum obtained in the presence of tungstate when combined nitrogen is supplied (Fig.IV.3b and 3c), probably counteracts the inhibitory effect of tungstate on nitrate reduction.

In other words, it is proposed that the uptake of molybdenum is demand-regulated, for, although a yield of only 40 µg molybdenum per pot was obtained for nitrogen - fixing and nitrate-fed plants in the absence of applied tungstate, this figure is capable of being almost doubled in the presence of high concentrations of applied tungstate (Fig.IV.3).

The increases in yields obtained for the combined-nitrogen fed plants in the presence of tungstate are unlikely to be due to either firstly, the ability of tungsten to replace molybdenum in its metabolic role as proposed by Davies and Stockdill (1956), because all physiological experiments (Higgins <u>et al</u>, 1956; Keeler and Varner, 1957; Takahashi and Nason, 1957; Krylova, 1963; Hwang and Doi, 1965; Heimer <u>et al</u>, 1968) have led to the conclusion that tungstate reduces molybdenum dependent enzyme activity and secondly, purely as a result of the increased uptake of molybdenum, because the concentration of this element should not be limiting, especially in ammonium fed plants. A more likely explanation for the increased yields is that the tungstate may release some of the applied phosphate that has become bound to the sand; all sands bind phosphate to some extent, and the relatively low phosphorus concentrations in the plants (0.16 - 0.27% dry weight) indicate that the phosphorus concentration may have been limiting. The results do imply however that tungsten has less effect on nitrate reductase than on nitrogenase.

The releasing action of applied tungstate could also explain the results of the field tests of Davies and Stockdill, (1956) who found that amounts of sodium tungstate of up to 230 g/acre gave significant increases in clover yield. The tungstate may have merely been releasing molybdate held in an unavailable form, and, once the free molybdate concentration ceased to be limiting, yields would level off. This would also explain the fact that, in the presence of additional molybdate, the addition of tungstate had no effect.

The relatively low molybdenum content of the ammonium fed plants is further evidence for a demandregulated uptake of this element, as in this case there is reduced requirement for nitrogenase and nitrate reductase. It is possible that, as suggested by Williams and Thornton (1972), the presence of the ammonium ion itself somehow reduces the uptake of molybdate.

The high concentration of tungsten in the pots relative to the shoots indicates that clover can to some extent preferentially differentiate

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between molybdate and tungstate at some stage in the root tissue.

Finally this experiment has shown that clover can tolerate tungstate to molybdate ratios of 1000:1, and it is therefore highly unlikely that the presence of tungsten mineralisation will seriously affect pasture growth. It is worth noting that the highest concentrations of tungsten found in clover shoots in this experiment (17 ppm) were similar to the highest concentrations found in field samples (20ppm).

# D. A COMPARISON OF METAL CONCENTRATIONS IN THE LEAVES OF FIVE NEW ZEALAND NATIVE TREE SPECIES GROWING ON ACIDIC AND BASIC SUBSTRATES 1. Introduction

Despite the large amount of ecological and biogeochemical research that has been carried out  $\boldsymbol{a}$ n New Zealand's native tree species. (in particular. see Miller (1963) and Brooks (1972) respectively), no comparative studies on the effect of substrate composition on the concentrations of a range of major and trace elements in specific tree species have been undertaken. In order to study this effect. an investigation was carried out in two areas in the South Island of New Zealand. The areas were selected because, whilst they were very different geologically, they had similar vegetation cover. Leaves from the five chief species present at both areas, together with their associated soils, were analysed for ten elements by atomic absorption spectrophotometry.

# 2. The study areas

Area A (Fig. IV.5), situated near Barrytown, on the west coast of the South Island, is a granite mass, approximately 2 km<sup>2</sup>, which is surrounded to the north, south and east by greywacke and to the west by recent alluvium. Area B, situated in north-west Nelson, consists of a narrow belt of basic and ultrabasic rocks, 60 km in length, which have intruded the surrounding sediments. Pyroxenite, with minor gabbro, is the most extensive rock type of the complex.

The soils of the two areas, while differing markedly in chemical composition, show a certain physical similarity; both show the presence of a



Fig. IV. 5. Map of New Zealand showing sites chosen for vegetation composition comparison.

dark red-brown humus-rich A horizon, and a lighter coloured B horizon containing many rock fragments. The pH values for the soils from the two areas are also very similar, both having a mean value of approximately 4.5.

Both areas have high annual rainfalls (270 cm for area A and 230 for area B), and rugged topographies (altitude ranges 30-- 600 m at area A and 450 - 800 m at area B). The vegetation is dominated at both areas by the beech species; mainly Nothofagus truncata (hard beech) giving way to N. menziesii (silver beech) at higher altitudes (greater than 500-550 m). At both areas, small stands of N. fusca (red beech) were found dotted amongst the more evenly distributed N. truncata and N. menziesii. By far the most numerous non-beech species at both areas was Weinmannia racemosa (kamahi), while the understorey was dominated numerically by Quintinia acutifolia. These species are all evergreen. Plate IV.1 shows the leaves of these fine species which were chosen for investigation.

In addition, the less common species <u>Podocarpus ferrugineus</u> (miro), <u>Metrosideros</u> <u>umbellata</u> (rata) are found at both areas, as are the secondary species <u>Pseudopanax crassifolium</u>, the shrubs <u>Pseudowintera colorata</u> (koropito) and <u>Coprosma</u> <u>foetidissima</u> (kupiro) and the ubiquitous fern <u>Blechnum</u> <u>discolor</u> (crown fern). The remarkable similarity of the vegetation present made the two areas ideal for comparison. Species found only at area A included <u>Myrsine salicina</u>, <u>Podocarpus specatus</u> (matai) and other podocarps; those found only at area B included <u>Grisilinia littoralis and Podocarpus hallii</u>.



PLATE IV - 1 Leaves from the trees sampled.

- A. Nothofagus truncata
- B. N. fusca
- C. <u>N. menziesii</u>
- D. Weinmannia racemosa
- E. Quintinia acutifolia

#### 3. Sampling and analysis

Field work was carried out during late summer (February). The same sampling procedures were employed at both areas. Samples of leaves (50 g) were taken from thirty trees of each of the five chief species present at randomly selected sites within the two areas, care being taken to sample trees of a wide range of size and age, and to collect new and old leaves from various points around the tree to ensure that the samples were as representative as possible. Samples of upper B-horizon soil (250 g) were taken near each tree sampled. Soil and plant samples were stored in plastic bags until arrival at the laboratory, then analysed by the procedures described in Section I of this thesis.

#### 4. Results and discussion

Table IV.9 shows the results of the analyses, giving the range and median for each element in the soil and tree samples from the two areas, while Fig. IV.6 shows the results in histogram form.

#### (a) Potassium

The median concentration of potassium is 2.4% in the acid soils of area A compared to only 1.1% in the basic soils of area B (Table IV.9). In spite of this, this, the concentration of this element were, in all the tree species, about twice as high on average in the samples from area B. In an effort to explain this, studies were made of the ammonium acetate-soluble levels of potassium in the two types of soil. It was found that the concentrations of soluble potassium were actually considerably lower in the acid soils (40 ppm compared to 160 ppm for the basic soils). While it is difficult to say how well the ammonium acetate-soluble potassium levels correspond

		Potassium	Calcium	Magnesium	Iron	Manganese	Zinc	Copper	Cobalt	Chromium	Nickel
Soils	A										
(total)	в				L					_	alle.
	РРМ	25000	40000	40000	40000	1000	65	100	50	650	200
Nothofagus	А		L								L
menziesii	в		1				1.	<b>.</b>			
N truncata	A										
ru. ir uncata	в					(has					la de
	A				£		_				1
N. fusca	В	L							da		
Weinmannia	A				Jh_	Ballan .					
racemosa	В			L	<u>k</u>		<b>b</b>	<b>.</b>	J.	Las.	Jan.
Quintinia	A					Ju.		k.			
acutifolia	В			Jr.	Jp.						Jan.
	РРМ	4000	10000	5000	50	650	30	5	0.65	10	6.5

Fig. IV. 6. Histograms of elemental concentrations in soils and plants from acidic (A) and basic (B) areas.

			Potassium	Calcium	Magnesium	Iron	Manganese	Zinc	Copper	Cobalt	Chromium	Nickel
A total		r	1100-31000 24000	200-4000 1400	700 <b>-</b> 5600 2900	1000 <b>-</b> 31000 24000	40-460 90	10-125 52	5 <b>-</b> 150 27	7-25 20	50 <b>-</b> 120 82	4-30 14
A soluble*		r	15-200 40	6-74 19	10 <b>-</b> 200 65	0.7-30 4	0.1-4.5 0.8	0.05 <b>-0</b> .9 0.45	0.2-1.0 0.4	n.d.	0.5-1.5 1.0	n.d.
Soil B total		r	6100-42000 11000	13000-83000 49000	13000-75000 50000	33000-69000 43000	550-1870 1080	57 <b>-</b> 130 88	7 <b>-</b> 200 57	34-89 61	125 <b>-13</b> 00 660	60 <b>-3</b> 90 208
B soluble*		r m	50-250 160	25 <b>-</b> 1500 240	90-250 145	0.1-6.0 1.5	0.4-20 2.5	0.1-1.2 0.6	0.2-1.3	n.d.	0.5-4 1.25	n.d.
N sersiegii	A	r	1280-2240 1710	2500 <b>-</b> 4800 3290	352-640 544	30-106 57	144 <b>-</b> 720 210	25-57 36	2.2 <b>-</b> 6.2 4.1	0.62-1.0 0.80	0.23-1.3 0.55	1.1-4.8 2.1
N. BOUSIOSII	В	r	1576 <b>-</b> 5254 2480	1745-8463 7000	1074-2737 1853	55 <b>-</b> 112 79	111 <b>-</b> 832 580	12.1-40 19	3.0-7.4 4.7	0.36-0.80 0.64	0.22-1.4 0.56	3.3-16.1 2.9
N. truncate	A	r	880-2300 1220	3640-7280 5460	572 <b>-</b> 884 770	27-41 35	145 <b>-</b> 280 195	11 <b>-3</b> 1 20.5	1.7-3.7 2.6	0.71-1.3	0.20-0.63 0.41	0.61-2.0 0.82
No trancata	В	r m	3238-10308 4700	7760 <b>-</b> 16456 9650	16 <b>49-2579</b> 2400	42-100 63	550 <b>-</b> 1242 630	9.8-19.9 14.2	2.7-7.4 3.7	0.46-1.0 0.66	0.31-0.98 0.53	2 <b>.3-</b> 12.5 5.4
N fusce	A	r	1450-4680 2900	6812-10769 8720	545 <b>-</b> 730 654	23-68 39	130-310 200	19-31 20.6	3.7-5.6 5.1	0.11-1.4 0.60	0.31-0.72 0.41	1.3-3.8 1.8
Nº TUBCE	в	r	3237-10308 4630	2335-15108 9750	1755 <b>-</b> 3440 2330	41-105 68	161–958 800	10.2 <b>-</b> 23.7 13.1	4.0-6.7 5.1	0.51-1.4 0.96	0.23 <b>-</b> 0.81 0.51	2.5-12.3 7.6
W. 7868068	A	r	770-2415 1300	1014-17670 10450	3304-10025 4900	31-81 47	226 <b>-</b> 1285 450	8.4-34.1 12.9	3.2-10.0 5.1	0.24-1.0 0.78	0.32-1.2 0.64	1.1-7.4 2.7
	В	r	464-7812 3120	1137-161 <sup>0</sup> 0 9670	2520-7560 4450	19–101 29	144-111 565	5.2 <b>-</b> 22.8 9.4	1.9-6.3 2.9	0.25-1.3 0.64	0.52-17.8 3.8	2.5-19.9 5.3
	A	r	1348~5130 3880	9162-17108 12600	3259-8745 5240	37-83 53	207-1303 550	9.8-20.6 12.8	2.3-6.0 3.4	0.81-1.3 1.0	0.38-2.2 0.72	2.7-5.4 3.6
A. GOMONIOITO	В	r	5242 <b>-</b> 14536 8620	6848-16197 10610	1863-7486 4005	28-102 43	453 <b>-</b> 1380 1024	7.2-16.1 10.2	2.3-6.0 3.4	0.64-1.1	0.50-5.3 0.87	2.5-8.1 4.5

A, area A; B, area B; r, range; m, median; n.d., not determined; \*, soluble in 1N ammonium acetate.

Table IV.9. Analytical data for soils and tree leaves from acidic (A) and basic (B) areas.

to what is actually available to the trees, these results do indicate that potassium is rather less mobile in the acid soils, probably due to the differing cation-fixing potential of the chief clay minerals present in the two types of soil, as the soils are similar in other respects, e.g. organic matter and pH.

It is, however, more difficult to explain why the plants from area B should contain higher, rather than similar, concentrations of potassium, even if the availability of this element is higher. One may conclude that, in this situation, trees will take up far more potassium than they metabolically require.

#### (b) <u>Calcium</u>

The soils of area A contain extraordinarily low concentrations of calcium, even for an acidic soil. However, despite the fact that the basic soils of area B contain 35 times as much total calcium, or 13 times as much ammonium acetate-soluble calcium (Table IV.9), there is a marked difference in the concentrations of this element in only one of the five tree species studies, namely <u>N. menziesii</u>. This would seem to indicate that the levels of calcium in the soil necessary for normal tree growth are far lower than that normally present and, unlike potassium, the uptake of calcium can be controlled more rigorously by many tree species growing in calcium rich soils.

#### (c) <u>Magnesium</u>

As is the case for calcium, the basic soils of area B are higher in magnesium, in this case by a factor of 17 for total magnesium, although only by a factor of 2 for ammonium acetate-soluble magnesium. (Table IV.9). It is interesting to note, however, that unlike as is the case for calcium, the three beech species all respond to this increased concentration of magnesium in the soil by increasing the concentration of this element in their leaves, by a factor of 3. The other two species studies however, actually show slightly decreased concentrations on the high-magnesium basic soil. This suggests that these two species are able to suppress the uptake of this element in magnesiumrich soils; this may indicate that excess magnesium can adversely affect certain species.

### (d) Iron

The results for this element are identical in pattern to those for calcium. The concentration of this element, which is twice as high in the basic soils on a total basis, and three times as high in soluble iron (Table IV.9), results in definite increases in the concentrations of iron in the three beech species, but <u>decreases</u> in the other two species (Table IV.9). Presumably then, the same explanations as put forward for magnesium may apply.

# (e) Manganese

The acidic soils have very low concentrations of this element, having only a twelfth of the concentration of manganese in the basic soils on

a total basis or a third on a soluble basis (Table IV.9). Unlike the case for magnesium and iron however, the concentrations of manganese are higher in all five species from the basic area, by a factor of about 3 for the beech species, 2 for <u>Q. acutifolia</u> and 1.2 for <u>W. racemosa</u>. These results again indicate that the beech species exhibit less restriction in their control of metal concentrations in their leaves. The results for manganese show an interesting contrast to those for calcium, the concentrations of which are far more rigorously controlled.

# (f) Zinc

The results for this element are in complete contrast to those for manganese. Whilst the soils of area B have on average a zinc concentration 1.7 times that in the area A soils, on a total basis, and 1.3 times as high on a soluble basis (Table IV.9), all five species have higher concentrations of zinc when growing in the lower zinc soils of area A.

# (g) Copper

Although the soils of area B are higher in copper than those from area A on a total and soluble basis (Table IV.9), the concentration of this element in the trees studies is quite similar for the two areas, only <u>W. racemosa</u> showing a significant difference (Table IV.9). This species actually contains more copper when growing on the lower-copper soils of area A. These results indicate that the concentration of copper in trees is relatively rigidly controlled, in agreement with the findings of Timperley, Brooks and Petersen (1973).

# (h) Cobalt

The results for this element are similar to those for copper, the threefold increase in the total cobalt concentration of the area B soils over those of area A having little effect on the cobalt concentration in any of the tree species.

#### (i) Chromium

Unlike the previous eight elements studied chromium is not an essential element for plant growth. Although its total concentration differs greatly in the two soil types, the basic soils of area B having a median value eight times that for the acidic soils of area A, (Table IV.9), the ammonium acetate soluble level is only 1.25 times as high. This probably explains the similar concentrations of this element in the trees. A notable exception is <u>W. racemosa</u>, which contains six times the concentration of chromium on the basic area as on the acidic area.

# (j) <u>Nickel</u>

The concentration of nickel, the second non-essential studied in this investigation, again shows a great difference in the two soil types, the basic soils being higher in their total concentration of this element by a factor of 15 (Table IV.9). This increase has resulted in significant increases in plant concentrations for all the tree species, particularly the three beech species.

It is interesting to note from the histograms (Fig.IV.1b) that the concentrations of nickel in the soils and trees from area B indicate the presence of two distributions. This is particularly obvious for the beech species. This is probably a result of the presence of small amounts of nickel mineralisation in this area; the first distribution could indicate the normal nickel distribution in basic soils and their associated trees, while the second distribution probably represents samples of soil and their associated trees from mineralised sites.

#### 5. Conclusions

The results of this investigation have shown that the concentrations of both major and trace metals in the same tree-species growing on different substrates can differ greatly, and that different species of the same genus will not necessarily react in the same way to changes in the sutstrate. Furthermore, it cannot be assumed that a higher total concentration of a particular element in a particular soil type will necessarily result in an increase in the concentration of this element in the tree. Tn fact the reverse may be true, as is the case for potassium in all species, and magnesium and iron in Q. acutifolia and W. racemosa, indicating that factors such as availability and tolerance of plants towards metals, as well as the total metal concentration in the soils, is important in controlling their concentration in the plant.

Furthermore, the fact that the three beech species have higher concentrations of magnesium and iron when growing in substrates containing more of these elements, whereas <u>Q. acutifolia</u> and <u>W. racemosa</u> have lower concentrations, shows that different tree species can differ greatly in their response to variations of concentrations of some elements in the soil. In other cases, especially essential trace elements such as copper and cobalt, increased concentrations of metals in the soil have virtually no affect on the concentration of these elements in the plants.

These findings have important implications in the field of biogeochemical exploration, particularly in large scale investigations where tree analysis may be used to identify rock types rather than small-scale investigations used to locate small ore veins. For example, of the five species investigated, only <u>W. racemosa</u> could be reliably used to indicate an increase of total chromium in the substrate by analysing for this element alone. None of the species analysed could be used to locate high-copper rock types, and the analysis of zinc in trees could actually lead to erroneous conclusions about the concentration of this element in the substrate.

Although the analysis of trees for several elements would no doubt increase the possibility of using plant analysis to distinguish between rock types, especially in conjunction with the use of discriminant analysis, as has been carried out by Nielsen et al (1973) in Western Australia, the difficulties mentioned above probably at least partly explain the relatively poor results obtained These same authors achieved for by this method. better results with geobotanical techniques, i.e. However the fact that in New plant mapping. Zealand, two rock types of very different chemical composition have been found to have very similar vegetation cover indicates that, in countries similar to New Zealand. with relatively mild climate and a rainfall which is generally sufficient for year-round plant growth, plant mapping techniques are unlikely to be of any more use than chemical analysis in distinguishing between rock types.

It is concluded then, that in New Zealand and countries of similar climate, biogeochemistry is likely to be of use only in small scale investigations, for example in locating small orebodies, where the local concentration of one or more metals may be very anomalous. That the

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method can be used on this scale in New Zealand has been shown to be the case for elements such as molybdenum (Brooks and Lyon, 1966), lead and zinc (Nicolas and Brooks, 1969), uranium (Whitehead and Brooks, 1969), nickel (Timperley, Brooks and Petersen, 1970; Timperley, Brooks and Petersen, 1972), tungsten, and silver (Quin et al, 1973). SUM IARY

AND

GENERAL CONCLUSIONS

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The aims of this thesis, which were described more fully in the General Introduction, were as follows :

(1) To improve the sensitivity and productivity of the colorimetric method for the determination of tungsten in geochemical and plant samples described in the writer's M.Sc. thesis;

(2) To investigate the suitability of protoninduced x-ray fluorescence for the detection of manogram quantities of tungsten in plant samples;

(3) To develop an interference-free method for the determination of tungsten in ores and concentrates by atomic absorption spectrometry;

(4) To investigate fully the parameters involved in the colorimetric determination of molybdenum with dithiol, and thereby develop a general-purpose procedure;

(5) To study the effectiveness of the method used for the routine analysis of geochemical and plant samples by flame photometry and atomic absorption spectrometry;

(6) To study the trace element content of New Zealand scheelites, to determine (i) the presence of any penalisable impurities, and (ii) whether chemical analysis could be used to distinguish between lodes;

(7) To compare the relative efficacy of geochemical and biogeochemical exploration for locating scheelite-bearing veins in a wide range of geological, vegetational, climatic and topographical conditions;

(8) To investigate the suitability of trend surface analysis of biogeochemical data for locating rich pockets of mineralisation within reefs; (9) To carry out a brief comparison of geochemical and biogeochemical prospecting for molybdenum at Canaan, Nelson;

(10) To study the effects of soil sodium and potassium on the uptake and distribution of tungsten by beech seedlings;

(11) To study the effects of tungsten and nitrogen source on the growth of white clover;

(1.2) To investigate the effects of substrate composition on the elemental composition of five native tree species for a wide range of major and trace elements.

The results presented in Sections I to IV of this thesis show that these aims have largely been achieved.

The development of the Analytical methods described in Section I are considered by the writer to be of prime importance in this work, as analytical chemistry holds the key to the understanding and interpretation of geochemical and biogeochemical phenomena. Blind acceptance of suspect analytical results has led to many erroneous conclusions in these fields in the past.

By the use of a smaller volume of organic solvent and micro spectrophotometer cells, the detection limit of the dithiol colorimetric method for the determination of tungsten was improved from 1 ppm to 0.2 ppm for geochemical samples, and from 1 ppm to 0.04 ppm for plant ash. It was found that the productivity for the analysis of soils could be increased slightly by omission of the fusion step, but an attempt to improve the productivity of the plant analysis by omission of the dry ashing stage was unsuccessful. The use of proton-induced x-ray fluorescence for the determination of tungsten was investigated, but although being of great interest, the sensitivity of the method could not be improved sufficiently to compare favourably with colorimetry. The method does however show considerable potential for the routine detection of nanogram quantities of many elements.

A rapid, accurate and reproducible method for the determination of tungsten in ores and concentrates by atomic absorption sp<sub>GCtro</sub>photometry was developed. The use of an alkaline sample solution meant that the method was free of the condensed phase interference and instability problems associated with earlier procedures.

By a careful study of the parameters involved in the determination of molybdenum with dithiol, a simple procedure was developed which, by merely altering the digestion to suit the sample, could be used for the analysis of biological, botanical and geochemical samples and even steel.

The use of the nitric/hydrofluoric acid mixture for the digestion of soils and rocks prior to flame photometric or atomic absorption analysis was investigated and it was found that the tendency for calcium and magnesium to form insoluble fluorides could be avoided by the addition of a small quantity of perchloric acid.

New Zealand scheelites were found to contain very low amounts of impurities, these invariably being well below the permissible levels. It was found that the ratio of strontium to barium in scheelites could be used to distinguish between lodes at the complex Glenorchy area.

A large-scale geochemical and biogeochemical exploration survey showed that, under most conditions, both soil and plant sampling could be used equally successfully to pinpoint buried scheelite-bearing veins, provided sampling distances were sufficiently close (5-10m). Although plant anomalies were in some cases less pronounced than those provided by soils, the facts that sampling is faster with plants and sharper anomalies were often obtained tended to balance this disadvantage. In areas of high rainfall and rugged topography, soil sampling did not always reveal the presence of reefs, or extensions of known In these cases, trunk-sampling of deepreefs. rooted tree species, regardless of species, could provide additional information, but the high sampling density required makes this method more suitable in locating extensions of known veins rather than as a general reconnaissance tool.

The finding that all tree species could be grouped together for the purposes of biogeochemical prospecting for tungsten was of considerable importance; it may well be that this is also the case for other non-essential elements.

Trend surface analysis was found to be a useful technique for locating rich pockets of mineralisation within reefs.

Biogeochemical prospecting was demonstrated to be superior to geochemical prospecting for molybdenum where low soil pH prevented movement of molybdenum into the upper soil. 171
The levels of ammonium acetate - soluble sodium and potassium in the soil were found to increase the transport of tungsten into the aerial organs of beech seedlings.

Tungsten, applied as tungstate, slightly decreased the growth of clover where fixation was the sole nitrogen source, indicating the presence of a slight inhibitory effect of tungsten on the molybdenum - dependent enzyme nitrogenase. In the presence of combined nitrogen however, increases in growth were recorded.

A comparison of the elemental composition of five native tree species growing on acidic and basic substrates showed that, whereas vegetation analysis can in general be used to indicate the presence of mineralisation within a rock type, it is not a reliable indicator of the composition of different rock types.

In conclusion, this thesis has ranged over many disciplines, including analytical chemistry, geochemistry, geochemical and biogeochemical exploration, plant physiology and ecology. It is felt by the writer that the results of this thesis have indicated how study in one field can lead to important questions in, and provide answers to, investigations in other fields.

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REFERENCES

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Agterberg, F. P. (1967), Earth Sci. Rev. <u>3</u> 47-77, Computer techniques in geology.

- Ahrens, L. H., Edge, R. A. and Brooks, R. R. (1963), Analytica Chim. Ack. <u>30</u> 551-573, Investigations on the development of a scheme of silicate analysis based principally on spectrographic and ion exchange techniques.
- Ahrens, L. M., and Taylor, S. R. (1961), Spectrochemical analysis. Addison-Wesley, Reading.
- Allen, S. H., and Hamilton, M. B. (1952), Anal. Chim. Acta <u>7</u> 483-493, The estimation of molybdenum and of tungsten dithiol.
- Baker, W. E. (1965), Australas. Inst. Mining Metall. No. 214. 125-134, rapid colorimetric procedures in geochemical prospecting for molybdenum.
- Barraclough, D. and Reay, A. (1970), Proc. Aust. Inst. Min. Metall. No. 236 17-20, Analyses of some New Zealand scheelites.
- Bickford, C. F., Jones, W. S., and Keene, J. S. (1948), J. Am. Pharm. Ass. <u>37</u> 255-261, Micro-determination of molybdenum and tungsten in organic materials.
- Bingley, J. B. (1959), J. Agric. Food Chem. <u>7</u> 269-270, Simplified determination of molybdenum in plant material by 4 - methyl-1,2 - dimercapto-benzene (dithiol).
- Bingley, J. B. (1963), J. Agric. Food Chem. <u>11</u> 130-131, Determination of molybdenum in biological materials with dithiol. Control of copper interference.
- Bloom, H. (1966), Geochemical exploration as applied to copper-molybdenum deposits. biology of parphyry copper deposits, South-west North America. Univ. of Arizona Press, 111-119.
- Bowden, P. (1964), Analyst <u>89</u> 771-774, A geochemical field method for determining tungsten in soils and stream sediments.
- Bowen, H. J. M. (1960), Biochem. J. **77** 79-82, The determination of tungsten in biological material by activation analysis.
- Bowen, H. J. M. (1966), Trace elements in biochemistry. Academic Press, London.
- Brooks, R. R. (1960), Nature <u>185</u> 837, Dissolution of silicate rocks.

- Brooks, R. R. (1972), Geobotany and biogeochemistry in mineral exploration. Harper and Row, New York.
- Brooks, R. R. (1973), J. Appl. Ecol. 10 825-836, Biogeochemical parameters and their significance in mineral exploration.
- Brooks, R. R. and Lyon, G. L. (1966), N.Z. Jl. Sci. <u>9</u> 706-718, Biogeochemical prospecting for molybdenum in New Zealand.
- Brundin, N. (1939), U.S. Pat. 2158980, Method of locating metals and minerals in the ground.
- Butler, L. R. P., and Mathews, P. M. (1966), Analytica Chim Acta <u>36</u> 319-327, The determination of trace amounts of molybdenum by atomic absorption spectroscopy.
- Cameron, E. M. (1968), Can. Jl. Earth Sci. <u>5</u> 287-309, A geochemical profile of the Swan Hills Reef.
- Cannon, H. (1960), Science N.Y. 132 591, Botanical prospecting for ore deposits.
- Cannon, H. (1971), Taxon <u>20</u> 227-256, Use of plant indicators in groundwater surveys, geologic mapping and mineral prospecting.
- Carlisle, D. and Cleveland, G. B. (1958), State of California, Divn of Mines, Special report 50, Plants as a guide to mineralisation.
- Chakrabarti, C. L., Katyal, M. and Villis, D. E. (1970), Spectrochimica Acta <u>25B</u> 629-645, Absorption profiles of flames used in atomic absorption spectroscopy.
- Chan, K. M., and Riley, J. P. (1966), Analytica Chim. Acta <u>36</u> 220-229, The determination of molybdenum in natural waters, silicates and biological materials.
- Chau, Y. K. and Lum-Shue-Chan, K. (1969), Analytica Chim. Acta <u>4B</u> 205-212, Atomic absorption determination of microgram quantities of molybdenum in lake waters.
- Chikishev, A. G. (1965), Plant indicators of soils, rocks and subsurface waters. Consultants Bureau, New York.
- Clark, L. J. and Axley, J. H. (1955), Anal. Chem. <u>27</u> 2000-2003, Molybdenum determination in soils and rocks with dithiol.

- Clark, R. E. D. (1958), Analyst <u>83</u> 396-402, o-Dithiols in analysis Part VII. Toluene -3, 4-dithiol as a general analytical reagent in qualitative analysis.
- Cornor, J. J. and Miesch, A. T. (1964), Stanford Univ. Publs., Geol. Sci. <u>9</u> 110-125, Application of trend analysis to geochemical prospecting data from Beaver County, Utah.
- Cohen, N. E. (1969), Studies on the analytical geochemistry of uranium and associated elements in the Hawks Crag Breccia of New Zealand. Ph.D. Thesis, Massey Univ. New Zealand.
- Cookson, J. A., Ivanovich, M., and Pilling, F. D. (1972), Analysis using proton-induced x-rays, UKAEA Report AERE-PR/NP/18.
- Cotton, F. A., and Wilkinson, G. (1967), Advanced Inorganic Chemistry, Interscience, New York.
- Crowthamel, C. E., and Johnson, C. E. (1954), Anal. Chem. <u>26</u> 1284-1291, Thiocyanate spectro-photometric determination of molybdenum and tungsten.
- David, D. J. (1959), Analyst 84 536-545, Determination of calcium in plant material by atomic absorption spectrophotometry.
- Davies, E. B. and Stockdill, S. M. J. (1956), Nature <u>178</u> 866, A pasture response to sodium tungstate on a New Zealand soil.
- Davy, R. (1973), Amdel Bulletin No. 15, 1-36, Geochemical prospecting for molybdenum.
- Dilli, S., Gawne, K. M., and Ocago, G. V. (1974), Analytica Chim. Acta <u>69</u> 287-294, Interference by acids in the determination of molybdenum by atomic absorption spectrometry.
- Downey, J. F. (1928), Quartz reefs of the West Coast Mining District, New Zealand. Govt. Printer, Wellington.
- Elwell, W. T. and Gidley, J. A. F. (1967), Atomic absorption spectrophotometry. Pergamon Press, Oxford.
- Finlayson, A. M. (1908), Trans. New Zealand Inst. <u>40</u> 110-122, The scheelite of Otago.
- Fleischer, M. (1965), Geochim. Cosmochim. Acta <u>29</u> 1263-1284, Summary of new data on rock samples G-1 and M-1, 1962-1965.

- Flocchini, R. G., Feeney, P. J., Sommerville, R. J., and Cahill, T. A. (1972), Nucl. Inst. Methods 100 397-402, Sensitivity versus target backings for elemental analysis by alpha-excited x-ray emission.
- Fortescue, J. A. C. (1970), Taxon 19 695-704, Research approach to the use of vegetation for the location of mineral deposits in Canada.
- Franzgrote, E. J. (1972), Advances in x-ray analysis <u>15</u> 388-406, Use of a solid-state detector for the analysis of x-rays excited in silicate rocks by alpha particle bombardment.
- Gilbert, T. M., Jr. (1956), The reaction between molybdenum and toluene-3, 4-dithiol. Ph.D. Thesis, University of Minnesota, Minnesota.
- Ginzburg, I. I. (1960), Principles of geochemical prospecting. Pergamon Press, Oxford.
- Giron, H. C. (1973), Atomic Absorption Newsletter <u>12</u> 28-29, Comparison between dry ashing and wet digestion in the preparation of plant material for atomic absorption analysis.
- Gordon, B. M., and Kramer, H. W. (1971), On the development of a system for trace element analysis in the environment by charged particle x-ray fluorescence, U.S.A.E.C. Report BNL 16182.
- Govindaraju, K. (1970), Appl. Spectros. <u>24</u> 81-85, Use of complexing agents as solvents for atomic absorption determination of calcium and magnesium in silicates.
- Greenland, L. P., and Lillie, E. G. (1974), Analytica Chim. Acta 69 335-346, A solvent extraction study of molybdenum chloride and molybdenum thiocyanate complexes.
- Greenwood, R. (1943), Econ. Geol. <u>38</u> 56-64, Effect of chemical impurities on scheelite fluorescence.
- Grooz, F. A. (1970), Some studies involving the determination of molybdenum by atomic absorption spectroscopy, Ph. D. Thesis, University of South Dakota.
- Gupta, U. C. and MacKay, D. C. (1965), Soil Science <u>99</u> 414-415, Determination of molybdenum in plant materials using 4-methyl, 1,2-dimercaptopbenzene (dithiol).

- Hamaguchi, H., Kuroda, R., Chimuzu, T., Isukahara, I., and Yakamoto, R. (1962), Geochem. Cosmochim Acta 26 503-505, Values for trace elements in G-1 and W-1 with neutron activation analysis. II Molybdenum, tin, tantalum and tungsten.
- Hamence, J. H. (1940), Analyst <u>65</u> 152-154, A new test for the detection of molybdenum and tungsten.
- Handbook of Chemistry and Physica, R. C. Weast Editor, The Chemical Rubber Co., Cleveland, Ohio, 52nd Edition.
- Hawkes, H. E. (1957), Bull. U.S. geo. Sun. 1000-F, 225-355, Principles of geochemical prospecting.
- Hawkes, H. E. and Webb, J. S. (1962), Geochemistry in mineral exploration. Harper and Row, New York.
- Heimer, Y. M., Wray, J. L. and Filner, P. (1969), Plant Physiol, 44 1197-1199, The effect of tungstate on nitrate assimilation in higher plant tissues.
- Henderson, J. (1937), Ann. Rep. N.Z. Geol. Sun. <u>31</u> 16-22, Glenorchy district.
- Henning, S., and Jackson, T. L. (1973) Atomic Absorption Newsletter 12 100-101, Determination of molybdenum in plant tissue using flameless atomic absorption.
- Higgins, E. S., Richert, D. A. and Westerfield, W. W. (1956), Proc. Soc. Exptl. Biol. Med. <u>92</u> 509-511, Tungstate antagonism of molybdate in <u>Aspergillus</u> <u>niger</u>.
- Hobart, E. W., and Hurley, E. P. (1962), Analytica Chim. Acta <u>27</u> 144-152, Spectrophotometric determination of molybdenum and tungsten in niobium with dithiol.
- Hosking, K. F. G. (1970), Problems associated with the application of geochemical methods of exploration in Cornwall, England. Geochemical Exploration, Proceedings of the 3rd International Geochemical Exploration symposium, Toronto, 176-189.
- Husler, J. (1971), Atomic Absorption Newsletter 10 60-62, Determination of Cr, Mn, Mo W and V in tool and alloy steels by atomic absorption spectrometry.
- Hutchinson, D. (1972), Analyst <u>97</u> 118-123, The determination of molybdenum in geological materials by combined solvent extraction - atomic absorption procedure.

- Hutton, C. O. (1940), N.Z. Geo. Sun. Mem. <u>5</u> Metamorphism in the Lake Wakatipu region, Western Otago, New Zealand.
- Hwang, J. C. and Doi, S. (1965), Hakko Kogaku Zasshi 41 474-480, Nitrogen fixing organisms III Effects of scme metals on the growth of nitrogen fixing organisms.
- Jeffery, P. G. (1956), Analyst 81 104-109, The simultaneous photometric determination of molybdenum and tungsten in silicate rocks.
- Jeffery, P. G. (1957), Analyst <u>82</u> 558-563, hotometric determination of molybdenum in tungsten ores.
- Johansson, R., Akselsson, R., and Jonansson, S. A. E. (1970), Nuclear Instruments and Methods <u>84</u> 141-143, x-ray analysis; Elemental trace analysis at the 10<sup>-12</sup> level.
- Jorgensen, C. K. (1962), Absorption spectra and chemical bondings in complexes. Pergamon Press, Oxford.
- Kabiashvili, V. A. (1964), Soobshch. Akad. Nauk Georgian SSSR <u>35</u> 83-86, Biogeochemical significance of dispersed tungsten.
- Keeler, R. F. and Varner, J. E. (1957), Arch. Biochem. Biophym. <u>70</u> 585-590, Tungstate as an antagonist of molybdate in <u>Azotobacter</u> vinelandii.
- Keller, E., and Parsons, M. L. (1970), Atomic Absorption Newsletter 9 92-93, Determination of tungsten in silicate ores.
- Kim C. H., Owens C. M. and Smythe, L. E. (1974) Talanta (impress) The determination of traces of molybdenum in soils and geological materials by atomic absorption spectrometry using solvent extraction of the molybdenum - thiodyanate complex.
- Knight, D. M., and Pyzyna, M. K. (1969) Atomic Absorption Newsletter 3 120-130, Determination of C., Cr, Co, In, No, Ni, Simmer V in tool steels by atomic absorption systematry.
- Kovalevsky, A. L. (1966), Geokhimiya No. 6 737-744, Biogeochemistry of tungsten in plants.
- Krumbein, W. C. (1956), Am. Ass. Petrol Geo. Bull. 40 2163-2194, Regional and local components in facies maps.

- Krumbein, M. C. (1959), Jl. Geophys. Res. 64 823-834, Trend surface analysis of contour - type maps with irregular control-point spacings.
- Krumbein, W. C. (1966), Off. Nav. Res., Geogr. Brch. Tech. Rep. No. 2, ONR Task No. 388-078, A comparison of polynonial and Fourier models in map analysis.
- Krylova, N. B. (1963), Dokl. Mosk. Sel'skohcz. Akad. No 89 314-319, Tungsten and nitrogen fixation.
- Lakin, H. W., Almond, H. and Ward, F. N. (1952), U.S. Geol. Surv. Circ. 161, Compilation of field methods used in prospecting by the U.S. Geological Survey.
- Langmyhr, F. J. and Paus, P. E. (1968), Analytica Chim. Acta 43 397-408, Analysis of i.organic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique.
- Lillie, E. G. and Greenland, L. P. (1974), Analytica Chim. Acta <u>69</u> 313-320, Spectrophotometric determination of molybdenum in rocks with thiocyanate.
- Lyon, G. L. (1969), Trace elements in New Zealand plants. Ph. D. Thesis, Massey Univ. New Zealand.
- Lyon, G. L. and Brooks, R. R. (1969), N.Z. Jl. Sci. <u>12</u> 200-206, The trace element content of <u>Olearia</u> rani and its application to biogeochemical prospecting.
- Malyuga, D. P. (1964), Biogeochemical methods of prospecting. Authorised translation from the Russian. Consultants Bureau, N. Y.
- Marshall, N. J. (1964), Econ. Geol. <u>59</u> 142-148, Rapid determination of molybdenum in geochemical samples using dithiol.
- Maruta, T., Suzuki, M. and Takeuchi, T. (1970), Analytica Chim. Acta. <u>51</u> 381-385, Interference of acids in atomic absorption spectrophotometry.
- Miesch, A. T. and Connor, J. J. (1968), Kansas Geol. Sun., Comp. Contr.27, Stepwise regression and non-polynomial models in trend analysis.
- Miller, C. C. (1941), J. Chem. Soc. 92, Preliminary observations on the behaviour of rhenium and molybdenum with toluene-3, 4-dithiol.
- Miller, C. C., and Lowe, A. J. (1940), J. Chem. Soc. (1940), 1258-1263, Qualitative semimicro-analysis with reference to Noyes and Bray's system : the tantalum and the tungsten group.

- Miller, R. B. (1963), N.Z. Jl. Sci. <u>6</u> 364-413, Plant nutrients in hard beech.
- Mitchell, R. L. (1960), Jl. Sci. Fd. Agric. No. 11 553-560, Contamination problems in soil and plant analysis.
- Mitchell, R. L. (1964), Tech. Comm. Commow. Bur. Soil Sci. No. 44A, The spectrochemical analysis of soils, plants and related materials.

Mutch, A. R. (196), N.Z. Geol. Sulv.Rep. N.Z.G.S.40, The scheelite resources of the Glenorchy district, West Otago.

- Nichol, I., Garrett, R. G. and Webb, J. S. (1969), Econ. Geol. 64 204-220, The role of some statistical and mathematical methods in the interpretation of regional geochemical data.
- Nicholas, D. and Brooks, R. R. (1969), Proc. Australas. Inst. Min. Metall. No. 231 59-66, Biogeochemical prospecting for zinc and lead in the Te Aroha region of New Zealand.
- Nicholas, D. J. D. and Nason, A. (1955), Plant Physiol. <u>30</u> 135-138, Role of molybdenum as a constituent of nitrate redulase from soybean leaves.
- Nielsen, J. S., Brooks, R. R., Bos ell, C. R. and Marshall, N. J. (1973), J. Appl. Ecol. 10 251-258, Statistical evaluation of geobotanical and biogeochemical data by discriminant analysis.
- North, A. A. (1956), Analyst 81 660-668, Geochemical field methods for the determination of tungsten and molybdenum in soils.
- Perry, S. K., and Brady, F. P. (1973), Nucl Instr. Methods 108 389-396, A comparative study of alpha particles and x-ray induced x-ray emission for elemental analysis.
- Piper, C. S., and Beckwith, R. S. (1948), J. Soc. Chem. Ind. <u>67</u> 374-379, A new method for the determination of small amounts of molybdenum in plants.
- Quin, B. F. (1972), Analytical and biogeochemical studies of tungsten. MSC thesis, Massey University, New Zealand.
- Quin, B. F., Brooks, R. R., Boswell, C. R. and Hoggins, F. E. (1973), N.Z. Jl. Sci. <u>16</u> 737-746, Plant and soil indicators of quartz reefs in the Maratoto Valley, New Zealand.

- Quin, B. F., Brooks, R. R. and Reay, P. F. (1972), Plant and Soil <u>36</u> 699-703, The accumulation of tungsten by <u>Nothofagus</u> <u>menziesii</u>.
- Ramakrishna, T. V., Robinson, J. V. and West, P. V. (1966), Analytica Chim. Acta. <u>36</u> 57-64, The determination of calcium and magnesium by atomic absorption spectroscopy.
- Rao, P. D. (1970), Atomic Absorption Newsletter <u>9</u> 131-132. Solvent extraction procedure for the determination of tungsten in ores.
- Rao, P. D. (1971), Atomic Absorption Newsletter 10 118-119, Determination of molybdenum in geological materials.
- Romney, E. M. and Rhoads, W. A. (1966), Soil Sci. Soc.Amer. Proc. <u>3</u> 770-773, Neutron activation products from Project Sedan in plants and soils.
- Rooney, R. C., and Pratt, C. G. (1972), Analyst <u>97</u> 400-404, The determination of tungsten and silicon in highly alloyed materials by atomic absorption spectroscopy.
- Rowe, C. J. (1973), Varian Techtron Technical Topics, March, 1973, Why do curves curve?
- Sandell, E. B. (1959), Colorimetric determination of traces of metals. Interscience, New York.
- Savaniar, C. P., Arunachalam, M. K., and Hariharan, T. R. (1974), Analytica Chim Acta <u>69</u> 305-311, Spectrophotometric determination of molybdenum (VI) with 2-mercapto benzo- thiopyrone and ammonium thiocycanate.
- Scobbie, R. (1973), Varian Techtron Technical Topics, April, 1973, The determination of boron, silicon and tungsten by atomic absorption spectroscopy.
- Scobbie, R. (1973), Varian Techton Technical Topics, September, 1973, Tharacterstics of the nitrous oxide - acetylene flame.
- Severne, B. C. (1972), Botanical methods of mineral exploration in Vestern Australia. Ph.D. thesis, Massey Univ. New Zealand.
- Skewes, H. R. (1959), Aust. J. Appl. Sci. <u>10</u> 464-469, The determination of molybdenum and its application in the hydrometallurgy of copper.
- Ssekaalo, H. (1971), Analyst <u>96</u> 346-348, A rapid and accurate method for the determination of molybdenum in plant materials with toluene -3, 4-dithiol.

- Stanton, R. E. (1970), Australas. Inst. Mining Metall. No. 235 101-102, The colorimetric determination of molybdenum in soils, sediments, and rocks by zinc dithiol.
- Stanton, R. E. (1970), Proc. Australas. Inst. Min. Metall. No. 236 59-60, The colorimetric determination of tungsten in soils, sediments and ores by zinc dithiol.
- Stanton, R. E., and Hardwick, A. J. (1967), Analyst <u>92</u> 387-390, The colorimetric determination of molybdenum in soils and sediments by zinc dithiol.
- Strelow, F. W. E., and Bothma, C. J. C. (1967), Anal. Chem. 39 595-599, Anion exchange and a selectivity scale for elements in sulphuric acid media with a strongly basic resin.
- Stubbs, M. F. (1968), Analyst <u>93</u> 59-60, Modification of dithiol tests for the field determination of molybdenum.
- Suggate, R. P. (1961), N.Z. Jl. Geol. Geophys. <u>4</u> 392-399, Rock-stratigraphic names for the South Island schists and undifferentiated sediments of the New Zealand Geosyncline.
- Suhr, N. H. and Ingamells, C. O. (1966), Anal. Chem. <u>38</u> 730-734, Solution techniques for analysis of silicates.
- Sullen, L. G. and Nylander, A. L. (1943), Arkiv. Kemi, Mineralogi Geologi <u>17A</u> 1-27, On the oxygen position in tungstates and molybdates with the scheelite structure.
- Takahashi, H. and Nason, A. (1957), Biochem. Biophys. Acta. 23 433-474, Tungstate is a competitive inhibitor of molybdate in nitrate assimilation and in nitrogen fixation by Azotobacter.
- Thomas, P. E., and Pickering, W. F. (1971), Talanta <u>18</u> 127-137, Role of solution equilibria in atomic absorption spectroscopy.
- Thomas, P. E., Sanders, J. B., and Chumnong, H. (1969) Resonance lines 1 5-10, The determination of tungsten in wolframite concentrates.
- Timperley, M. H. (1971), Biogeochemical studies of nickel and copper in New Zealand. Ph. D. Thesis, Massey Univ. New Zealand.

- Timperley, M. H., Brooks, R. R. and Petersen, P. J. (1970), Econ. Geol. <u>65</u> 505-510, Prospecting for copper and nickel in New Zealand by statistical analysis of biogeochemical data.
- Timperley, M. H., Brooks, R. D. and Peterson, P.J. (1972), Prox. Australas.Inst. Min. Metall. No 242 25-36, The improved detection of geochemical soil anomalies by multiple regression analysis of biogeochemical data.
- Van Loon, J. C. (1972), Atomic Absorption Newsletter, 11 60-62, The determination of small amounts of molybdenum in soils by atomic absorption spectrometry for geochemical exploration purposes.
- Varlamoff, N. (1970), Behaviour of tungsten minerals and ores in the weathering zone under equatorial and tropical conditions - possibilities of geochemical exploration and prospecting. Geochemical Exploration, Proceedings of the 3rd International Geochemical Exploration Symposium, Toronto, 279.
- Vermaas, F. H. S. (1952), Amer. Min. 37 719-736, South African scheelites and an x-ray method for determining members of the scheelitepowellite series.
- Vinogradov, A. P. (1954), Trudy Biogeokhim Lab. Akad. Nauk SSSR 10 3-27, Search for ore deposits by means of plants and soils.
- Vinogradov, A. P. (1959), The geochemistry of rare and dispersed chemical elements in soils. Conniltant Bureau, New York.
- Wallace, F. J. (1963), Analyst, <u>88</u> 259-265. The determination of magnesium in aluminium alloys by atomic absorption spectroscopy.
- Ward, F. N. (1951), U.S. Geol. Surv. Circ. No. 119, Determination of tungsten - geochemical samples.
- Watkinson, J. H., (1958), New Zealand J. Sci. 1 201-219, The spectrophotometric determination of molybdenum, tungsten and vanadium in soils and plants. Part 1 - in soils.
- Welcher, G. G., and Kriege, H. (1969), Atomic Absorption Newsletter '8 91-101, The determination of major alloying elements in high-temperature nickel-base alloy<sub>5</sub> by atomic absorption spectrometry.

- Wells, J. E., and Pemberton, R. (1947), Analyst <u>72</u> 185-188, The microchemical determination of molybdenum in steel.
- Whitehead, N. E. (1970), Aspects of radiobiogeochemistry. Ph. D. Thesis, Massey Univ., New Zealand.
- Whitehead, N. E. and Brooks, R. R. (1958), Econ. Geol. <u>64</u> 50-56, A comparative evaluation of scintillometric, geochemical and biogeochemical methods of prospecting for uranium.
- Williams, C. and Thornton, I. (1972), Plant and Soil <u>36</u> 395-406, The effect of soil additives on the uptake of molybdenum and selenium from soils from different environments.
- Williams, G. J. (1959), Proc. Min. Conf. Otago Univ. 6 Paper 140, Economic minerals at Canaan, North-West Nelson.
- Williams, G. J. (1965), Economic geology of New Zealand. Eighth Commonwealth Mining and Metallurgical Congress, Australia and New Zealand. Australas. Inst. Min. Metall. Melbourne.
- Williamson, J. H. (1939), N.Z. Geol. Surv. Bull. 39, The geology of the Naseby Subdivision, Central Otago.
- Wilson, A. M., and McFarland, O.K. (1964), Anal. Chem. <u>36</u> 2488-2493, Quantitative conversion of molybdate to Mo(V) by the stannous chlorideperchlorate reaction and spectrophotometric determination as tricaprylyl-methylaminonium oxytetrathiocyenatomolybdate (V).
- Young, F. C., Roush, M. L. and Berman, P. G. (1973), Int. Jl. Appl. Radiation and Isotopes 24 153-163, Trace element analysis by protoninduced x-ray excitation.

## PUBLICATIONS ARISING FROM THIS THESIS

- Quin, B.F. and Brooks, R.R. (1973), Analytica Chim. Acta <u>65</u> 206-209, The rapid determination of tungsten in ores and concentrates by atomic absorption spectrophotometry.
- Quin, B.F., Brooks, R.R., Boswell, C.R. and Painter, J.A.C. (1974), Jl. Geochem. Expl. <u>3</u> 43-51, Biogeochemical exploration for tungsten at Barrytown, New Zealand.
- Quin, E.F. and Brooks, R.R. (1974) Plant and Soil <u>41</u> 177-185, Tungsten concentrations in plants and soils as a means of detecting scheelite-bearing ore-bodies in New Zealand.
- Quin, B.F. and Brooks, R.R. (1974), Analytica Chim. Acta <u>in press</u>, The rapid colorimetric determination of molybdenum with dithiol in biological, geochemical and steel samples.
- Quin, B.F. and Hoglund, J.H. (1975), to be submitted to Plant and Soil, The effects of tungstate and nitrogen source on the dry weight and nitrogen yields, and tungsten and molybdenum content, of white clover (<u>Trifolium repens</u>).
- Quin, B.F. and Brooks, R.R. (1975), <u>In preparation</u>, Biogeochemistry as an aid for the detection of unexposed molybdenum mineralisation.