ANALYTICAL AND BIOGEOCHEMICAL
STUDIES OF TUNGSTEN

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"Knowing is not enough
We must apply
Willing is not enough
We must do"

Goethe

ABSTRACT

Section I: Studies were carried out to determine the optimum conditions for the determination of tungsten with a large quartz emission spectrograph. By making use of silver chloride as a carrier, large electrodes and the 2947 A analysis line, soils and rocks containing as low as 10 ppm tungsten could be analysed with reasonable reproducibility. Reliable results were not achieved for plant samples however, and the productivity of the method was very low.

In view of these shortcomings, the use of the dithiol colorimetric reagent for the analysis of tungsten was investigated, and a reliable procedure with a detection limit of 0.1 ppm and very high productivity was developed for the analysis of soils, rocks and vegetation.

Section II: Pot trials were carried out to investigate the uptake of tungsten by young plants of *Nothofagus menziesii* (silver beech). It was found that, although most of the tungsten taken up from the soil remained in the roots, the concentrations of this element in the leaves, stems and roots of the plants were all related to the tungsten concentration in the soil.

Section III: Biogeochemical and geochemical investigations were carried out in an area of tungsten mineralisation at Barrytown, Westland. The results of preliminary investigations showed that the levels of manganese, tin and lead in the soil were associated with the tungsten level, and may therefore be of possible use as pathfinders for tungsten.

An investigation was carried out to determine whether the concentration of tungsten in plants could be used to predict the concentrations of this element in the soil. It was found that while shallow-rooting species such as tree-ferns could be successfully used to detect soil anomalies, the relationship between the levels of tungsten in soils and tree species was rather less distinct. Detailed study of trunk and soil samples indicated that this was caused largely by variation in soil properties, particularly pH, which was found to affect the solubility of tungsten.

Despite the unsuitability of trees for indicating concentrations of tungsten in the soil, it was found that tree-trunk analysis could be successfully used to locate tungsten-bearing veins, without restriction in the number and types of species used.

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GENERAL

INTRODUCTION

The term biogeochemistry was first used in 1922 by the Russian scientist Vernadsky, who defined it broadly as the study of the relationships between life, in all its forms, and the geological environment. Biogeochemical prospecting is the application of this concept to prospecting for minerals, by the chemical analysis of plant samples collected from suspected areas of mineralisation, and is based on the general presumption that an anomalous concentration of a metal in the substrate, hopefully caused by the presence of a valuable ore body, will result in an anomalous concentration of that element in the vegetation growing thereon.

The first recorded use of biogeochemical prospecting was in 1936, when trial plant surveys carried out by Palmquist and Brundin of the Swedish Prospecting Company indicated the presence of abnormally high contents of tin and tungsten in Cornwall, and lead and zinc in Wales, in the leaves of trees and shrubs growing in soils containing large amounts of these metals. Unfortunately, apart from a patent covering the technique used (Brundin, 1939) very little of their work was published.

In the years following this early work, there has been a great deal of biogeochemical research carried out, particularly in Russia, where understanding of the factors affecting the success of biogeochemical prospecting has progressed to the stage where all prospecting teams now have at least one biogeochemist included.

Unfortunately, the same is not generally true of Western countries, largely due to a lack of close liaison between mining companies and university research groups. Much excellent biogeochemical research has failed to be applied to prospecting because of a lack of appreciation of, or interest in, the practical requirements of a prospecting method on the part of the scientist. On the other hand, many mining companies, for example in Australia, have tried biogeochemical prospecting for themselves, but because of insufficient study of the factors which can affect the success of the method, obtained poor results and rejected this type of mineral exploration. If biogeochemical prospecting is to develop further, this situation must be rectified.

In New Zealand, most biogeochemical prospecting research has been based on the assumption that the soil indicates what is in the bedrock, and argues that if plant analysis can be used to indicate what is in the soil, then plant sampling is to be preferred to soil sampling, because the samples are lighter and collection is faster, particularly in areas where the presence of thick layers of forest litter, humus - rich soil and tree roots render soil sampling extremely slow (Brooks and Lyon, 1966). However time has proven that these advantages do not sufficiently outweigh the disadvantages such as the necessity for skilled samplers and the fact that, in many cases, before the concentration of a metal in the soil can be even approximately predicted from its concentration in the plant, several factors such as the soil pH and drainage must be taken into account. Although computerised mathematical techniques incorporating these factors, for example multiple regression analysis, can be used to improve the prediction of soil anomalies from plant data (Timperley, Brooks and Petersen, 1971), this puts biogeochemical prospecting out of the reach of small companies, requires still more skilled personnel, and severely reduces its speed advantages.

It seems, therefore, that if biogeochemical prospecting is to be considered by Australasian mining companies as a worthwhile tool in the search for minerals, it must be demonstrated that in certain geological, topographical and climatic environments, it can give more information than soil sampling. For example, the presence of deep soil or an unmineralised overburden, or the effect of leaching or soil creep, can all prevent the presence of mineralisation from being manifested in the upper soil (from where soil samples are taken), or may produce a soil anomaly at some distance from the actual source. The extensive root systems of some tree species can reach and therefore "sample" deep soil and even bedrock thus pinpointing the exact position of ore bodies.

Some work of this nature has been carried out in North America, and recently in Australia (Severne, 1972). For example, Keith (1968) by analysing the covering vegetation in the upper Mississippi valley district, successfully detected lead and zinc mineralisation under an overburden of loess where no soil anomalies were obvious. However, where loess was absent, he found that soil analysis gave better results than plant analysis. Another example is provided by the work of Kleinhampl and Koteff (1966) who found that conifer samples indicated uranium deposits at depths as great as 70 feet. There is, however, very little published work dealing with the success of plant sampling in areas where, because of factors such as high rainfall and rugged topography, leaching, soil creep and landsliding obscure the soil-bedrock relationship.

The application of biogeochemical prospecting has also been hindered by the lack of suitable rapid methods of analysis for some metals. This has been particularly true for tungsten. Although previous workers have studied the tungsten content of plants in relation to biogeochemical prospecting (Palmquist and Brundin, /unpublished/ Kovalevsky 1966), the success of their investigations were severely limited by their method of analysis, namely the emission spectiograph. This instrument, besides being relatively slow in operation, is somewhat imprecise and has a poor limit of detection for tungsten, particularly in samples of high alkali-metal content such as plant ash (Mitchell, 1964).

Although the faster and more sensitive colorimetric methods for the determination of tungsten in soils and rocks, using either thiocyanate or toluene - 3,4 - dithiol (dithiol) have been in use for some years (Ward, 1951; North, 1956), they had not been successfully applied to the analysis of vegetation. The thiocyanate method of Aull and Kinard (1940) was too insensitive for the determination of natural tungsten in vegetation, and the dithiol method of Allen and Hamilton (1952) was too slow and insensitive to be suitable for biogeochemical prospecting. There therefore existed a real need for a rapid, sensitive, and reproducible method for the determination of tungsten in vegetation.

This need became apparent to me some months after the discovery in 1970 of tungsten at Barrytown, Westland, by Carpentaria Exploration, when, with the kind permission and extensive assistance of that company, I began an investigation into the feasibility of biogeochemical prospecting for tungsten in the area.

The area involved in the study is shown in Fig. 0.1, and consists of a granite mass of approximately a square mile in area, which rises from an altitude of approximately 100' at its western extremity to about 1500' in the east, and is surrounded to the north, south and east by hornsfels and greywacke, and to the west by recent surficial deposits. The tungsten mineralisation [a], approximately 98-99% scheelite and 1-2% wolframite, exists in a series of quartz veins containing discreet crystals up to ¼" size and as scheelite disseminated in griesen veins and veinlets up to 2-3mm in thickness. The dimensions of the quartz veins are generally obscured, but appear to have a strike length of 100-200' with a maximum vein size of 0.7m, and tend to occur in swarms containing 10-40 veins over a width of 2-3m.

The annual rainfall of the area is high, approximately 110", with maximum and minimum monthly averages of 14" and 4" in October and December respectively, and the leaching resulting from this, in combination with the granite parent rock, has produced a soil poor in nutrients and of low pH. The soil consists of a dark-brown humus-rich A horizon approximately 0.3m in depth, and lighter brown B horizon of extremely variable thickness and lower organic content. Both horizons contain many rock fragments. The vegetation is predominantly *Nothofagus truncata* (hard beech) and *Weimannia racemosa* (kamahi), with increasing

[a]Description of mineralisation provided by Mr J.A.C. Painter, Party Leader, Hokitika, Carpentaria Exploration Co. Pty Ltd.

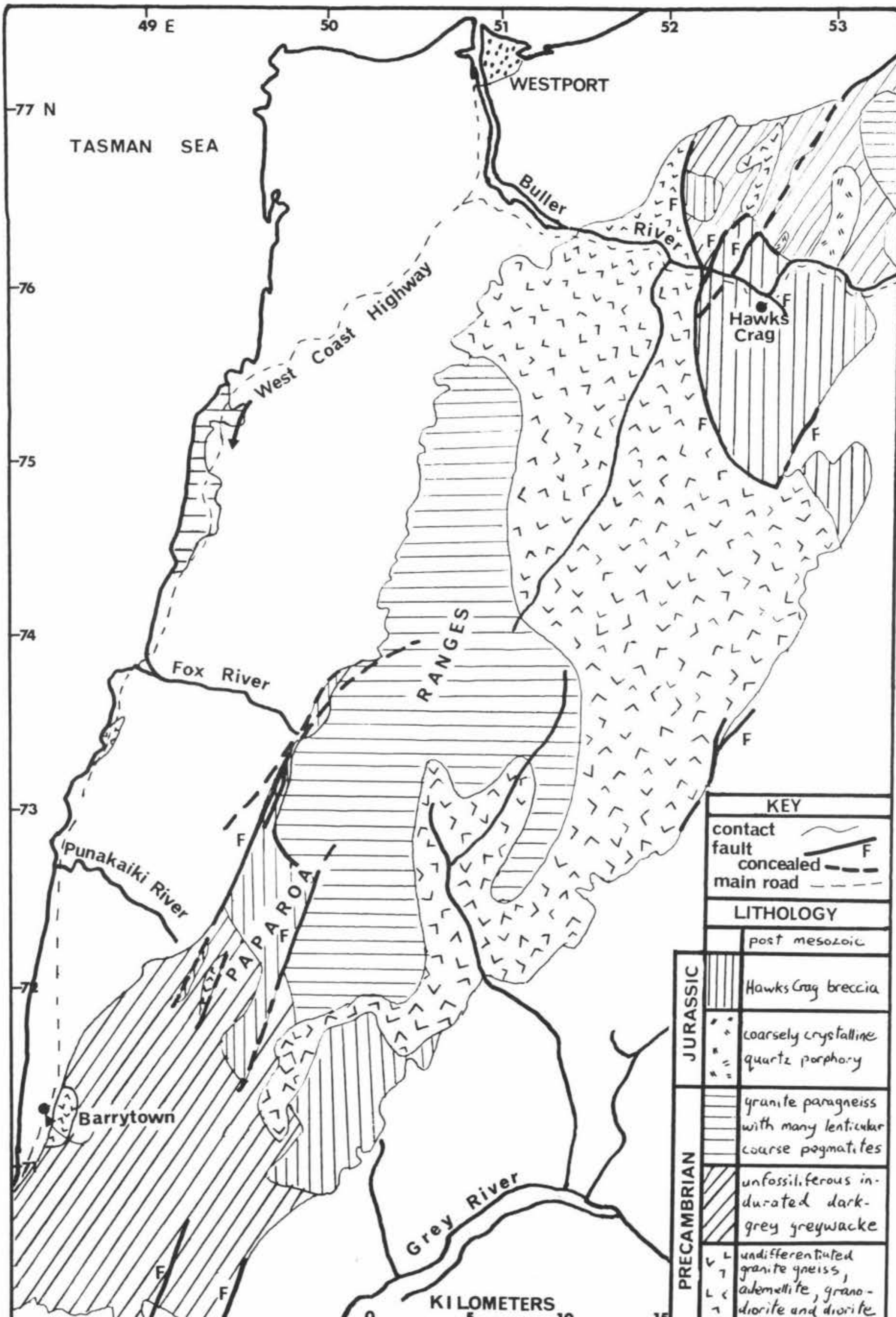

Fig. 0.1. Map showing geology of Paparoa Range.
After Bowen (1964).

dominance of *Nothofagus menziesii* (silver beech) at higher altitudes. The pale-grey leached A_2 soil horizon, characteristic of the mor- producing beech species, was observed in many flatter areas. Chief secondary species include *Quintinia acutifolia* and *Myrsine salicina*, and much of the forest floor is covered in a dense growth of ferns such as the ubiquitous *Blechnum discolor* (crown fern). The tree ferns *Cyathea medullaris* (king fern) and *Dicksonia squarrosa* (wheki) are common on stream banks, as were many smaller ferns such as the *Blechnum* species.

To conclude this general introduction, the aims of this project may be summarised broadly as follows:

1. To develop rapid, sensitive and reproducible procedures for the determination of tungsten in vegetation, soils and rocks, in any concentration, on a routine basis.

2. To determine whether biogeochemical prospecting has any useful role to play in the detection and pinpointing of tungsten ore bodies, and to compare its success with that of soil sampling, particularly in areas subject to leaching, soil creep and landsliding.

3. To investigate some of the factors which obscure the plant-substrate relationship with respect to tungsten, to assist in the interpretation of future field work.