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

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. R.R. Brooks, for his enthusiastic encouragement and assistance during the course of the work described in this thesis. I also thank my co-supervisor, Professor J.K. Syers, for his guidance during the absence of Dr. Brooks.

Particular thanks are due to the Mineral Resources Sub-Committee of the University Grants Committee for funds to support this project.

Thanks to Mr. J.H. Hogland of the Grasslands Division, D.S.I.R. for his assistance with the clover pot trials. Mr. P. Nes kindly carried out the nitrogen analyses.

To Dr. N.E. Whitehead of the Nuclear Sciences Institute, D.S.I.R. for his assistance during the investigation into the use of proton-induced X-ray fluorescence.

To Dr. C.R. Boswell of the Computer Science Department, Massey University, for carrying out the trend surface analysis of biogeochemical data.

To Dr. M.H. Timperley of Chemistry Division, D.S.I.R. for the use of his soil and plant data.

I am indebted to Carpentaria Exploration Ltd. for logistic support during the investigations at Barrytown, and in particular I would like to thank Mr. J.A.C. Painter of this company for his assistance. Alex Harvey Industries kindly provided accommodation at Glenorchy. I am very grateful to Mr. E.J. Sixtus of Motueka for his assistance during the investigations at Canaan.

Finally, I would like to thank the Ministry of Agriculture and Fisheries for permission to complete this thesis after my appointment.

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/hydrofluoric 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. It 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.

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.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES