DEPARTMENT OF
MINERALS AND ENERGY

501271

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

Record 1974/188

BUREAU OF MINERAL RESOURCES
LIBRARY
copy
3
CANBERRA, A.C.T.

SAMPLING AND ANALYTICAL PROCEDURES USED FOR THE 1973 GEOCHEMICAL EXPLORATION PROGRAM

by

A.G. ROSSITER, B.I. CRUIKSHANK and J.G. PYKE

The information contained in this report has been obtained by the Department of Minerals and Energy as part of the policy of the Australian Government to assist in the exploration and development of mineral resources. It may not be published in any form or used in a company prospectus or statement without the permission in writing of the Director, Bureau of Mineral Resources, Geology and Geophysics.

BMR
Record
1974/188
c.3

501271

Record 1974/188

SAMPLING AND ANALYTICAL PROCEDURES USED FOR
THE 1973
GEOCHEMICAL EXPLORATION PROGRAM

by

A.G. ROSSITER, B.I. CRUIKSHANK and J.G. PYKE

CONTENTS

SUMMARY

During 1973 soil, stream sediment, and heavy-mineral samples were collected as part of the Bureau of Mineral Resources' geochemical exploration program. The soils and stream sediments were analyzed for Ag, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, and Zn by atomic absorption spectrophotometry and for As, Ba, Ce, Ni, Pb, Rb, S, Sn, Th, U, and W using X-ray fluorescence spectrometry. Heavy-mineral concentrates were examined optically and analyzed for Ag, Bi, Ce, Co, Cr, Cu, La, Mo, Nb, Ni, Pb, Sn, Ta, W, Y, Zn, and Zr using D.C. arc optical emission spectrography. Stream sediment and heavy-mineral samples were checked for anomalous radioactivity by gamma-ray spectrometry. The techniques used in the collection of the samples and their subsequent analysis by these various methods are described.

INTRODUCTION

During 1973 the Bureau of Mineral Resources (BMR) undertook geochemical exploration work in the Georgetown (Qld) and Westmoreland (Qld - NT) districts. Details of the field methods employed to collect samples and the laboratory procedures used in their examination and analysis are outlined here. The results and conclusions of the two surveys will be presented initially as BMR Records.

SAMPLING METHODS

Soils, sieved stream sediments, and heavy-mineral concentrates were sampled.

Soil samples were collected with a conventional 7.6 cm (3-inch) hand auger. The use of this device was slow and laborious but as few samples had to be taken from depths of greater than 30 cm, a more elaborate procedure was not justified. At each locality about 500 g of material was collected and details of the sampling depth, the nature of soil profile, colour and texture of the A and B horizons, underlying lithology, land use, and any evidence for leaching, contamination, or transport were recorded on field sheets.

Sieving of stream sediments to minus 180 micron (85 mesh BSS) was carried out on site using plastic sieves fitted with nylon bolting cloth. More than 50 g of sieved material was collected; in many cases it was necessary to sift as much as 10 kg of sediment to recover the desired amount of sample. Field data noted included stream width, whether the stream was flowing or dry, sediment texture, the position in the creek bed from which the sample was collected, bank type, presence of stain or possible contamination, lithology of nearby outcrop, and land use.

Heavy-mineral concentrates were obtained by panning in 45 cm (18-inch) gold prospector's dishes. As the streams of both areas were dry during the field season 5-10 kg samples for panning had to be transported back to base camp in large plastic bags. The heavy material was only roughly concentrated (until 10-50 g remained) in the field, further separation was carried out after the samples were returned to the laboratory (Page 4).

It is hoped to reduce the tedium associated with sieving and panning during future surveys by employing a mechanical sieve shaker and a small mineral jig, both electrically driven. An ultrasonic cleaner and a small compressor unit will facilitate cleaning of the 20 cm (8-inch) stainless steel sieves to be used.

Most of the sampling was done during the 1973 field season using ground crews equipped with 4-wheel-drive vehicles. A short time, however, was devoted to assessing the usefulness of a helicopter for regional geochemical sampling. The exercise was carried out in the Georgetown area with a Bell 206A Jetranger and no difficulty was encountered in landing close to predetermined sample points. At each site the helicopter remained on the ground for 2-5 min while one or two 10 kg stream-sediment samples were collected. After 20 samples had been taken the helicopter returned to the base camp where the samples were sieved and panned. Four such loops could be completed in a day giving a total of 80 samples. This compares with 10 samples per day averaged by a 2-man ground crew. The helicopter technique was most successful and will be used extensively during future BMR geochemical sampling programs.

ATOMIC ABSORPTION ANALYSIS OF SOILS AND STREAM SEDIMENTS

Sample preparation

Stream sediments were sieved to minus 180 micron in the field and needed no further sample preparation. Soil samples were invariably moist and were dried in an air oven at 60°C for 24 hours. The dry material was sieved to minus 500 micron (30 mesh BSS), then transferred to plastic vials.

Sample digestion

A comparison between a 'total' digestion using a mixture of hydrofluoric and perchloric acids, and an 'aqua regia' digestion (hydrochloric and nitric acids) was made. The results (Table 1) indicate that the 'aqua regia' method gives rather incomplete decomposition of the sample; Cu and Li are the only two elements for which the results obtained using the two types of digestion are comparable. Consequently, it was decided to use the more laborious 'total' method, thereby sacrificing speed for greater precision of results, as detailed below:

1. Material for analysis was accurately weighed (1.000 ± 0.003 g) and transferred to a platinum basin.
2. Perchloric acid (6 ml; 1:1) and hydrofluoric acid (10 ml, 40%) were added and the mixture heated on a waterbath until fuming.
3. Fuming on a hotplate was continued until a 'dry' cake formed.
4. Hydrochloric acid (5 ml; 1:1) was then added and the cake dissolved by gentle heating.
5. After cooling, the contents of the basin were transferred to a 25 ml volumetric flask and made up to volume.

The samples were digested and analyzed in batches of 20. A reagent blank was prepared with each batch.

Analysis

The samples were analyzed for Ag, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, and Zn using a Varian AA-4 spectrophotometer linked to a Kelvin Servoscribe chart recorder, recording in the percent transmission mode. The instrumental conditions employed and detection limits obtained are shown in Table 2.

Calculation of results

Non-atomic absorption (NAA) corrections were made for low concentrations of Cd, Co, Ni, Pb, and Zn, using nearby non-resonance lines of the element involved (Co and Zn) or non-resonance lines of another element (Sn 224.6 and 233.5 nm for Cd, Ni, and Pb). Calibration curves plotted on log/linear graph paper were prepared for each batch of samples from instrument responses for standard solutions. All subsequent calculations were done manually.

TABLE 1. Comparison of results using 'total' and 'aqua regia' digestion before atomic absorption analysis. The first figure in each case is 'total'. All results are in parts per million.

Sample No.	Ag	Be	Cd	Co	Cr	Cu	Li	Mn	Ni	Pb	Zn
73301001	2/1	2.0/0.8	ND/ND*	16/7	58/24	26/24	10/9	1130/443	20/13	326/282	220/206
73301003	2/1	1.3/0.3	ND/ND	16/13	96/34	47/43	10/9	1360/738	38/22	25/18	85/51
73301004	2/1	1.5/0.3	ND/ND	25/13	93/34	48/48	11/10	1350/795	38/25	22/18	85/51
73301006	2/1	1.3/0.3	ND/ND	30/17	95/33	45/44	11/9	1280/615	38/23	20/10	90/44

* ND = not detected

TABLE 2. Instrumental conditions employed for atomic absorption analysis.

Element	Line (nm)	Slit width (micron)	Lamp current (mA)	Flame type *	Flame stoichiometry	NAA correction	Detection limit (ppm) **
Ag	328.1	100	4	A/A	Oxidising		1
Be	234.9	100	8	NO/A	Reducing		0.3
Cd	228.8	200	3	A/A	Oxidising	Sn 224.6	1
Co	240.7	150	5	A/A	Oxidising	Co 238.8	2
Cr	357.9	100	5	NO/A	Reducing		4
Cu	324.8	50	3	A/A	Oxidising		2
Li	670.8	100	6	A/A	Oxidising		1
Mn	279.5	100	5	A/A	Oxidising		1
Ni	232.0	50	8	A/A	Oxidising	Sn 233.5	2
Pb	217.0	150	6	A/A	Oxidising	Sn 224.6	4
Zn	213.9	100	6	A/A	Oxidising	Zn 210.0	0.5

* A/A - air/acetylene; NO/A - nitrous oxide/ acetylene; NAA - non-atomic absorption

** Detection limit defined as 1% absorption; ppm in solid (1 g of sample in 25 ml of solution)

X-RAY FLUORESCENCE ANALYSIS OF SOILS AND STREAM SEDIMENTS

Sample preparation

All samples were ground for 90 s in a Siebtechnik vibratory mill (agate vessel). Before grinding the soils had been dried and sieved as outlined on page 2. Powder pellets with a boric acid backing were then prepared.

Analysis

The samples were analyzed for As, Ba, Ce, Ni, Pb, Rb, S, Sn, Th, U, and W using a Philips PW 1210 X-ray spectrometer fitted with a Torrens TE 108 automatic sample changer. The operating conditions employed and the detection limits obtained are shown in Table 3. Synthetically prepared standards were used throughout and were checked against USGS rock standards.

Calculation of results

The method outlined by Norrish & Chappell (1967) was used for converting count-rates to element concentrations. Dead-time corrections were carried out automatically by the spectrometer. Empirical interfering element corrections were applied to U (corrected for Rb interference), W (Ni), Ba (Ce), and As (Pb) count-rates. Mass absorption coefficient measurements (for Fe, Zn, and Rb, Kα wavelengths) were made on 50 samples selected at random from the sample range and average values calculated. Non-linear background corrections were made using 'spec' pure Al_2O_3 and SiO_2.

IDENTIFICATION OF MINERALS PRESENT IN HEAVY-MINERAL CONCENTRATES

The roughly panned concentrates were forwarded to the laboratory in Canberra where they were passed through bromoform (S.G. 2.89) and the quartz and feldspar removed. A hand magnet was used to extract magnetite which often formed a considerable proportion of each concentrate. Frequently these procedures left less than 1 g of heavy minerals from an original sample (before panning) of 5-10 kg.

TABLE 3. Operating conditions employed during X-ray fluorescence analysis. Counting time for peaks was 100 seconds. For all elements except sulphur, 40-second background counts were made on each side of the peak, one 100-second background measurement was carried out for sulphur determinations. The gas used in the flow counter was a 10% solution of methane in argon.

Element	Line	Peak 2θ	Background 2θ's	Tube	Tube voltage (kV)	Tube current (mA)	Vacuum	Primary collimator	Crystal	Counter	Theoretical detection limit (ppm)
As	Kα	48.82°	±0.32°	Mo	95	20	No	Fine	LiF 220	Scint.	4
Ba	Lβ	128.67°	±2.30°	Au	50	40	Yes	Coarse	LiF 220	Flow	3
Ce	Lβ	78.97°	±0.95°	Au	60	32	Yes	Fine	LiF 200	Flow + Scint.	2
Ni	Kα	71.26°	±0.80°	Au	60	32	Yes	Fine	LiF 220	Flow	1
Pb	Lβ	28.22°	±0.25°	Mo	95	20	No	Fine	LiF 200	Scint.	3
Rb	Kα	26.62°	±0.27°	Mo	95	20	No	Fine	LiF 200	Scint.	1
S	Kα	75.67°	-2.50°	W	60	24	Yes	Coarse	PE	Flow	19
Sn	Kα	19.90°	+0.65°	W	95	20	No	Fine	LiF 220	Scint.	2
Th	Lα	27.46°	±0.20°	Mo	95	20	No	Fine	LiF 200	Scint.	2
U	Lα	37.31°	±0.25°	Mo	95	20	No	Fine	LiF 220	Scint.	2
W	Lα	62.43°	±0.75°	Au	60	32	Yes	Fine	LiF 220	Flow	3

Polished thin-section grain mounts were prepared for a representative selection of the concentrates. Microscopic examination of the sections in both transmitted and reflected light gave a general picture of the heavy-mineral assemblages present in the samples. This basic information formed a guide when the remainder of the concentrates were examined under a zoom stereoscopic microscope - the mineral grains being simply spread loosely on a glass slide.

Some minerals could be recognized by virtue of their optical properties alone but additional tests were often necessary. The tests used were as follows:

1. Samples were checked for the presence of fluorescent minerals under a Hanovia ultra-violet lamp. Some uranium minerals were found to fluoresce but generally the technique was of little use.
2. Tentative identifications of cassiterite were checked by placing a few grains of the mineral on a zinc plate and adding a drop of dilute hydrochloric acid. Under these conditions cassiterite grains developed a grey coating of metallic tin.
3. In cases where it was suspected that monazite was present the samples was checked for radioactivity on a gamma-ray spectrometer (p. 7). A small percentage of monazite in a concentrate was found sufficient to produce a measurable increase in radioactivity above the background level.
4. Uranium minerals were generally present in amounts too small for their radioactivity to be detected with the gamma-ray spectrometer, and optical determinations of such minerals were confirmed by chemical means. The grains of contention were fused in a $NaHSO_4/NaF/Na_2CO_3/K_2CO_3$* flux. On irradiation with

---

* By weight $NaHSO_4$ (2%), NaF (5%), remainder equal amounts of Na_2CO_3 and K_2CO_3.

UV light uranium minerals could be easily recognized by the fluorescent haloes that they produced in the flux.

Sometimes minerals could not be definitely identified using the above techniques and there was no alternative but magnetic separation and hand-picking followed by X-ray diffraction. Spectrographic analysis was also employed on occasions as an aid to identification.

EMISSION SPECTROGRAPHIC ANALYSIS OF HEAVY-MINERAL CONCENTRATES

After optical examination, the heavy-mineral concentrates were halved using a riffle splitter and one portion ground in an agate mortar and pestle before spectrographic analysis. Initially a semiquantitative scan was carried out on a Hilger and Watts large quartz spectrograph. The samples (weighing approx 50 mg each) were loaded into graphite electrodes and arced to completion at 7 amps D.C.; the resultant spectra were compared with standard photographic plates. Interference produced by Ti lines from the abundant ilmenite in the concentrates was a problem initially. The difficulty was overcome by decreasing the arcing time to 90 s. There was sufficient excitation for most of the elements of interest to volatilize without interference from the involatile element Ti. Mixing the samples with quartz prevented sample loss during arcing.

The next step was more accurate emission spectrographic analysis using a Hilger and Watts direct-reading 3-metre Polychromator. First, the samples were ignited for 4 hours at 1000°C to drive off volatiles. Then one part of sample (50 mg) was mixed with two parts of graphite, and the mix was loaded into a graphite electrode and arced at 8 amps D.C. for 130 s. Duplicate analyses were made of each sample. An internal standard (Pd) and the USGS rock standards were used for the construction of calibration curves used in the calculation of results.

Elements determined using one or both optical emission techniques were Ag, Bi, Ce, Co, Cr, Cu, La, Mo, Nb, Ni, Pb, Sn, Ta, W, Y, Zn, and Zr. Detection limits were low (10 ppm or less) for those underlined; the method was less sensitve for the others, and detection limits ranged up to several hundred parts per million in the case of Ce and Zn.

GAMMA-RAY SPECTROMETRIC ANALYSIS OF STREAM SEDIMENTS AND HEAVY-MINERAL CONCENTRATES

Stream sediment and heavy-mineral samples were checked for anaomalous radioactivity using a Philips automatic digital single-channel gamma-ray spectrometer. Total radiation from each sample was measured for 4 min, and the result compared with the average background values calculated at regular intervals during the work.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of K. Armstrong, A. Hoey, and H. Pelz during the field work; C. Robison, G. Sparksman, and G. Willcocks with the atomic absorption analysis; Dr J. Sheraton, J. Weekes, and B. West with the XRF work; and T. Slezak and J. Weekes with the emission spectrographic analysis.

REFERENCES

Norrish, K., & Chappell, B., (1967) - X-ray fluorescence spectrography. In J. Zussman (Ed.) PHYSICAL METHODS IN DETERMINATIVE MINERALOGY, 161-214. London & N.Y., Academic Press.